Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Development of isotope-enriched phosphatidylinositol-4- and 5-phosphate cellular mass spectrometry probes

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Abstract: Synthetic phosphatidylinositol phosphate ($PtdInsP_n$) derivatives play a pivotal role in broadening our understanding of $PtdInsP_n$ metabolism. However, the development of such tools is reliant on efficient enantioselective and regioselective synthetic strategies. Here we report the development of a divergent synthetic route applicable to the synthesis of deuterated PtdIns4P and PtdIns5P derivatives. The synthetic strategy developed involves a key enzymatic desymmetrisation step using Lipozyme TL-IM®. In addition, we optimised the large-scale synthesis of deuterated myo-inositol, allowing for the preparation of a series of saturated and unsaturated deuterated PtdIns4P and PtdIns5P derivatives. Experiments in MCF7 cells demonstrate that these deuterated probes enable quantification of the corresponding endogenous phospholipids in a cellular setting. Overall, these deuterated probes will be powerful tools to help improve our understanding of the role played by $PtdInsP_n$ in physiology and disease.

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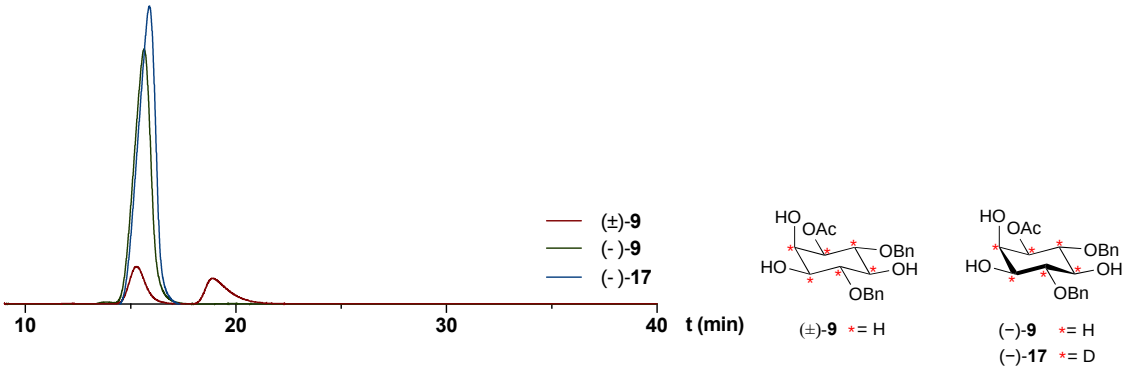


Figure S1. Chiral HPLC traces (ChiralPak® AD-H column, heptane/IPA 85:15, 1.0 ml.min^{-1}, 254 nm) of the single enantiomers (−)-**9** (green) and D_6-(−)-**17** (blue), obtained through enzymatic desymmetrisation, overlaid with the chiral HPLC trace for the racemic protonated derivative (±)-**9**. Bn = benzyl, Ac = acetate.

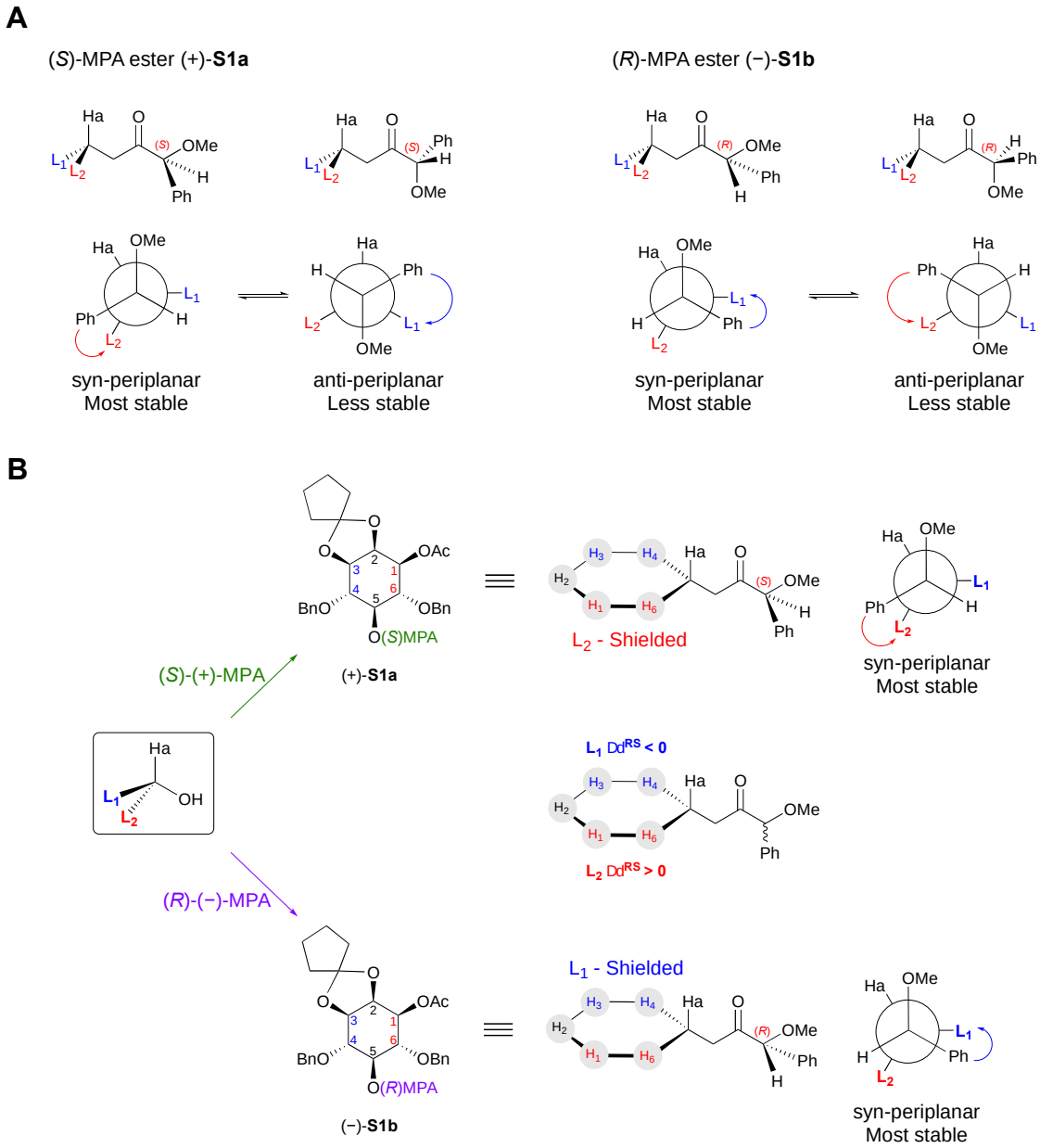


Figure S2. Conformational model. (A) Amongst the two main conformations of the (*R*)- and (*S*)-MPA esters, the *syn*-periplanar conformer has been shown to be the most stable. (B) Conformational model for MPA esters. Me = methyl; Ph = phenyl; Ac = acetate; Bn = benzyl; MPA = α-methoxy-phenylacetic acid.

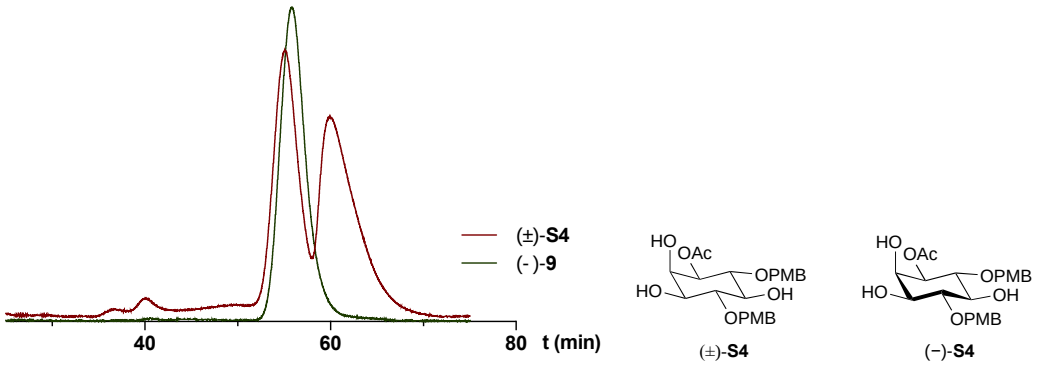


Figure S3. Chiral HPLC traces (ChiralPak® AD-H column, heptane/IPA 85:15, 1.0 ml.min^{-1}, 254 nm) of the single enantiomers (−)-**S4** (green) obtained through enzymatic desymmetrisation, overlaid with the chiral HPLC trace for the racemic derivative (±)-**S4**. PMB = 4-methoxybenzyl; Ac = acetate.

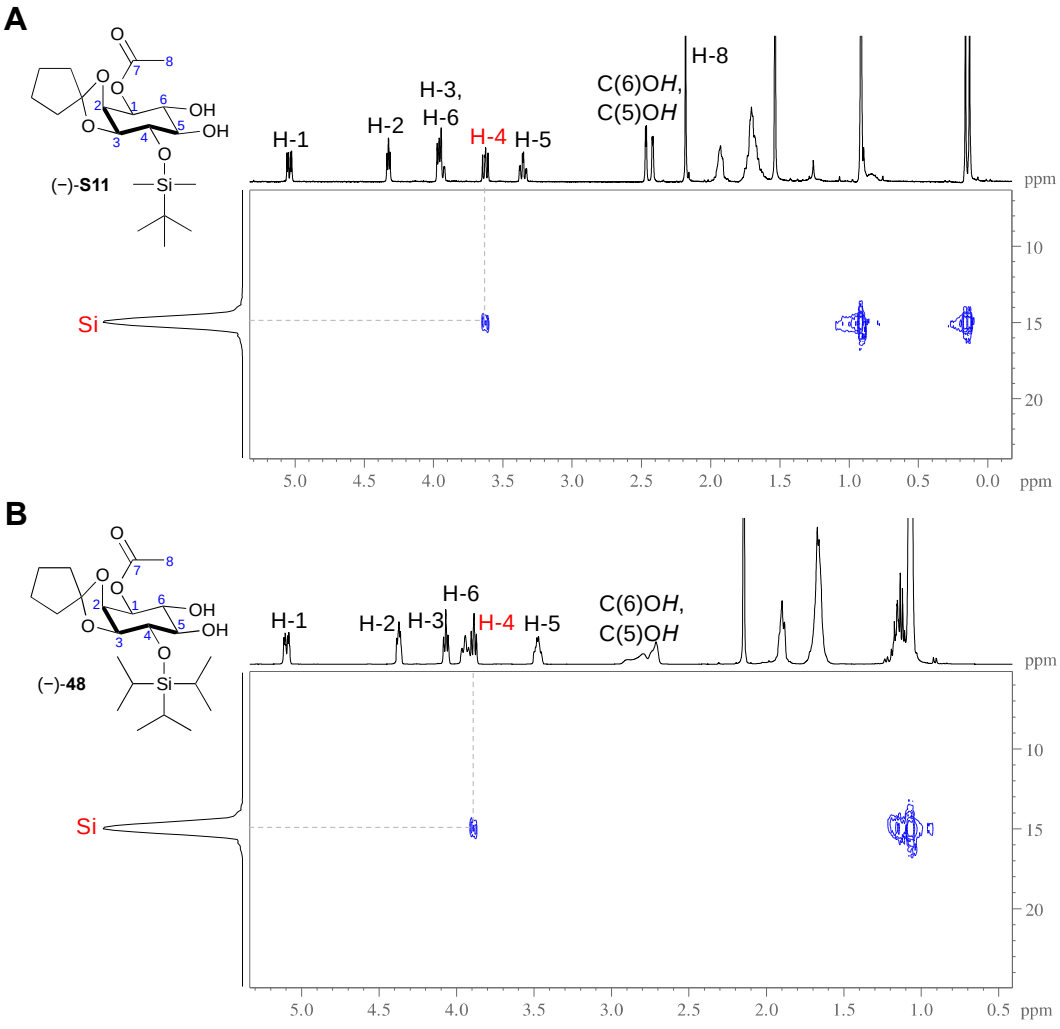


Figure S4. Regioselective silylation of (−)-**46** to give (−)-**S11** and (−)-**48**. (A) ^{1}H-^{29}Si HMBC for (−)-**S11** accounting for the position of the TBDMS ethers on the *myo*-inositol ring. (B) ^{1}H-^{29}Si HMBC for (−)-**48** accounting for the position of the TIPS ethers on the *myo*-inositol ring. The ^{1}H and ^{29}Si NMR spectra were acquired at 500 MHz and 99 MHz, respectively, in $CDCl_3$. TBDMS = *tert*-butyldimethylsilyl; TIPS = triisopropylsilyl.

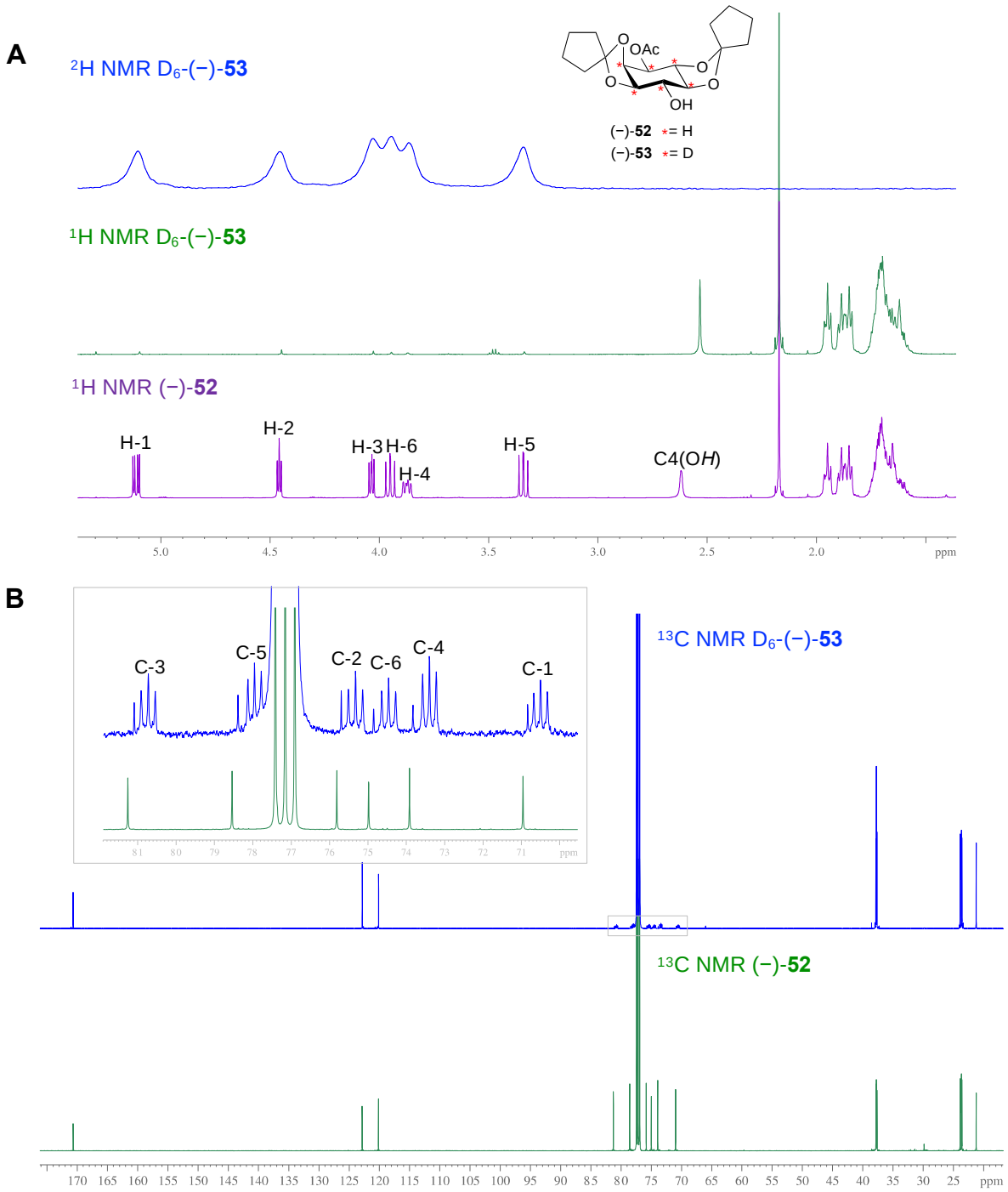


Figure S5. NMR spectra of deuterated and protonated *myo*-inositol intermediates (−)-**52** and (−)-**53**. (A) Comparing the ^{1}H NMR of (−)-**52** (purple) with the ^{1}H NMR (green) and ^{2}H NMR (blue) of D_6-(−)-**53**. The ^{2}H NMR spectrum of D_6-(−)-**53** shows six deuterium signals in distinct environments. These can be assigned by comparison with the ^{1}H NMR spectrum of (−)-**52**. The ^{1}H NMR and ^{2}H NMR spectra were acquired at 500 and 96 MHz, respectively, in $CDCl_3$. (B) ^{13}C NMR spectra of (−)-**52** (green) and of D_6-(−)-**53** (blue). The signals for the deuterated carbons around the *myo*-inositol ring in D_6-(−)-**53** are observed as triplets of weak intensity with an isotopic shift of ~0.3 ppm upfield as compared to the protonated analogue (−)-**52**. A small signal for the residual protonated D_5 compounds can also be observed. Both ^{13}C NMR spectra were acquired at 126 MHz in $CDCl_3$. Ac = acetate.

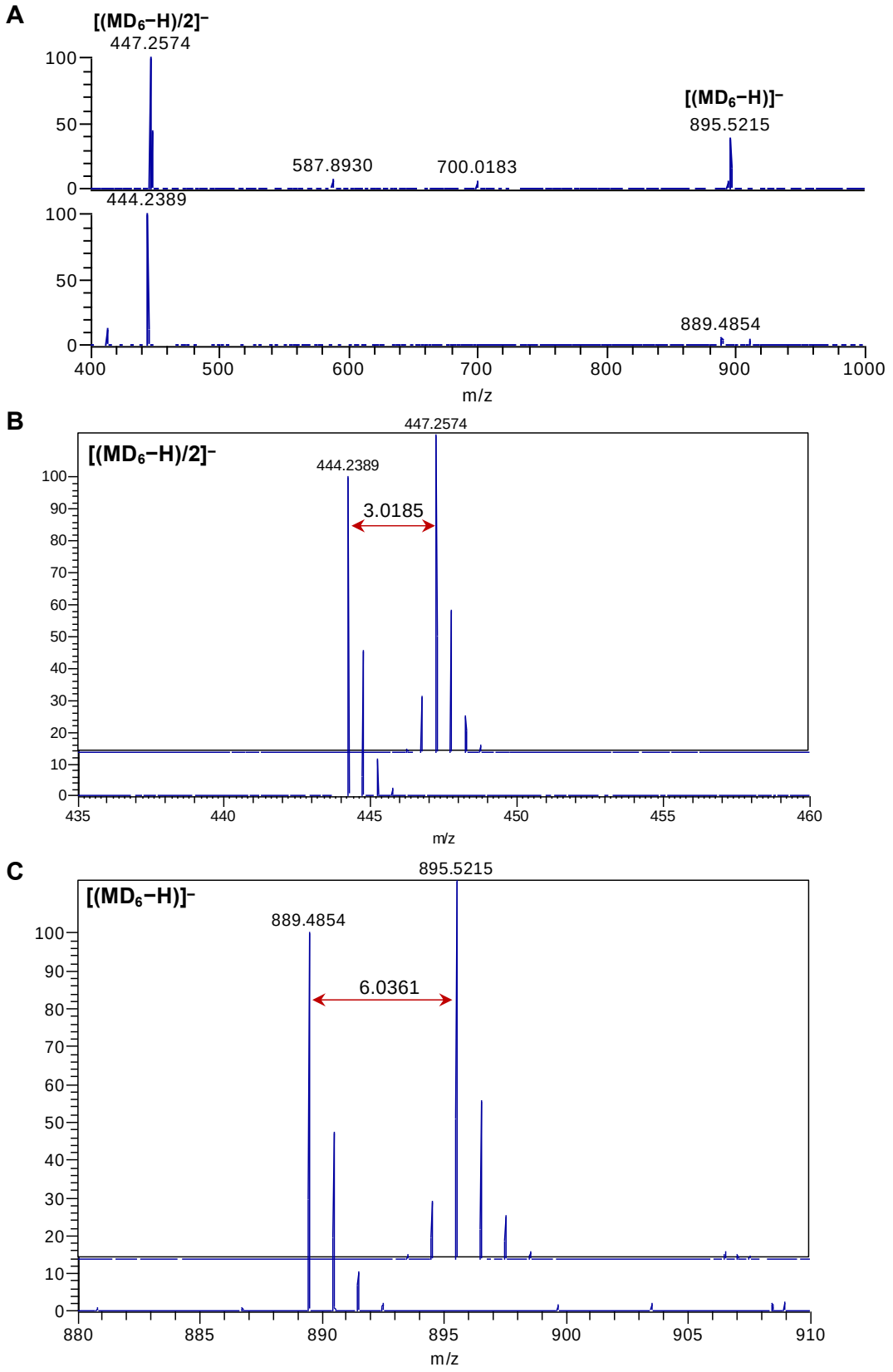


Figure S6. Mass spectra for PtdIns4*P* and D_6-PtdIns4*P*. (A) Comparison of the high-resolution mass spectra for PtdIns4*P* (bottom) and D_6-PtdIns4*P* (top). (B) Expansion of the peaks corresponding to $[(MD_6–H)/2]^-$ for PtdIns4*P* (−)-**64** (bottom) and D_6-PtdIns4*P* (−)-**65** (top). (C) Expansion of the peaks corresponding to $[(MD_6–H)]^-$ for PtdIns4*P* (−)-**64** (bottom) and D_6-PtdIns4*P* (−)-**65** (top). The mass differences are marked with a red arrow.

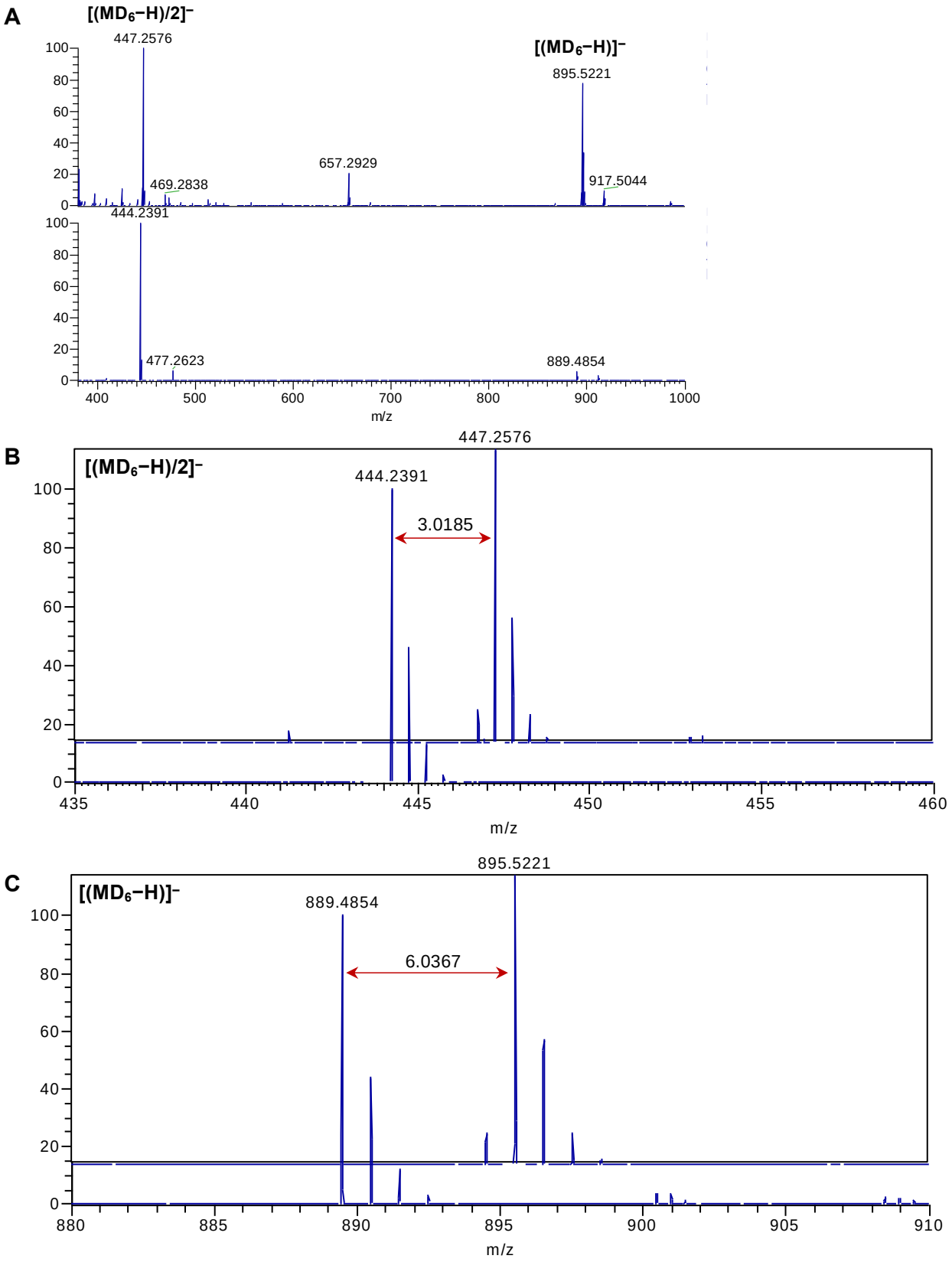


Figure S7. Mass spectra for PtdIns5*P* and D_6 PtdIns5*P*. (A) Comparison of the high resolution mass spectra for PtdIns5*P* (bottom) and D_6-PtdIns5*P* (top). (B) Expansion of the peaks corresponding to $[(MD_6–H)/2]^-$ for PtdIns5*P* (–)-**73** (bottom) and D_6-PtdIns5*P* (–)-**74** (top). (C) Expansion of the peaks corresponding to $[(MD_6–H)]^-$ for PtdIns5*P* (–)-**73** (bottom) and D_6-PtdIns5*P* (–)-**74** (top). The mass differences are marked with a red arrow.

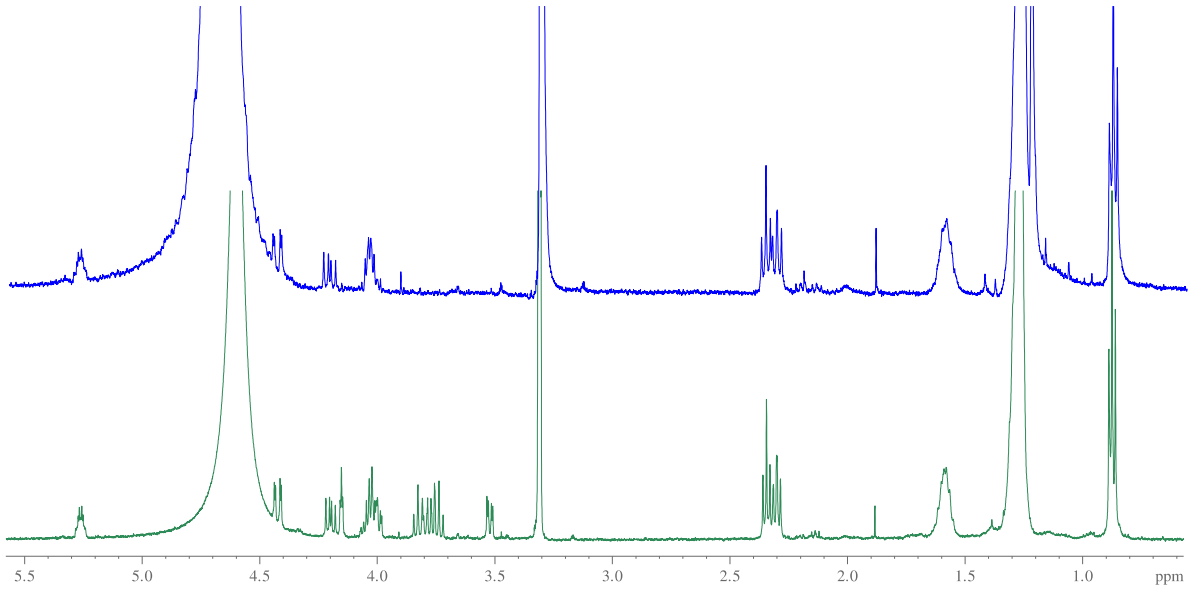


Figure S8. Comparison of the ^{1}H NMR spectrum acquired for dipalmitoyl PtdIns4*P* (−)-**64** (green) and dipalmitoyl D_6-PtdIns4P (−)-**65** (blue). Both ^{1}H NMR spectra were acquired at 500 MHz, in $CD_3OD/CDCl_3/D_2O$ 4:3:1.

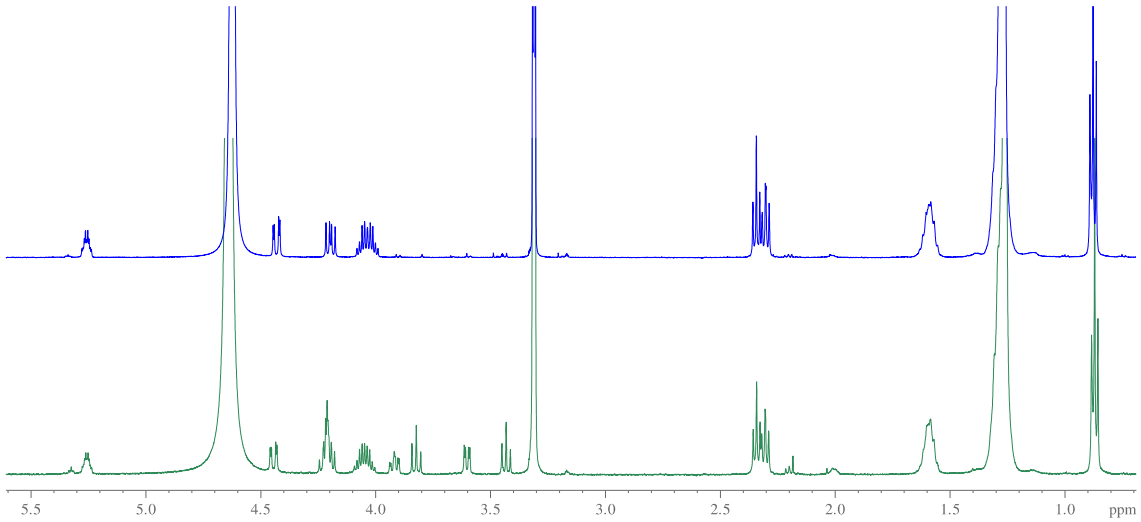
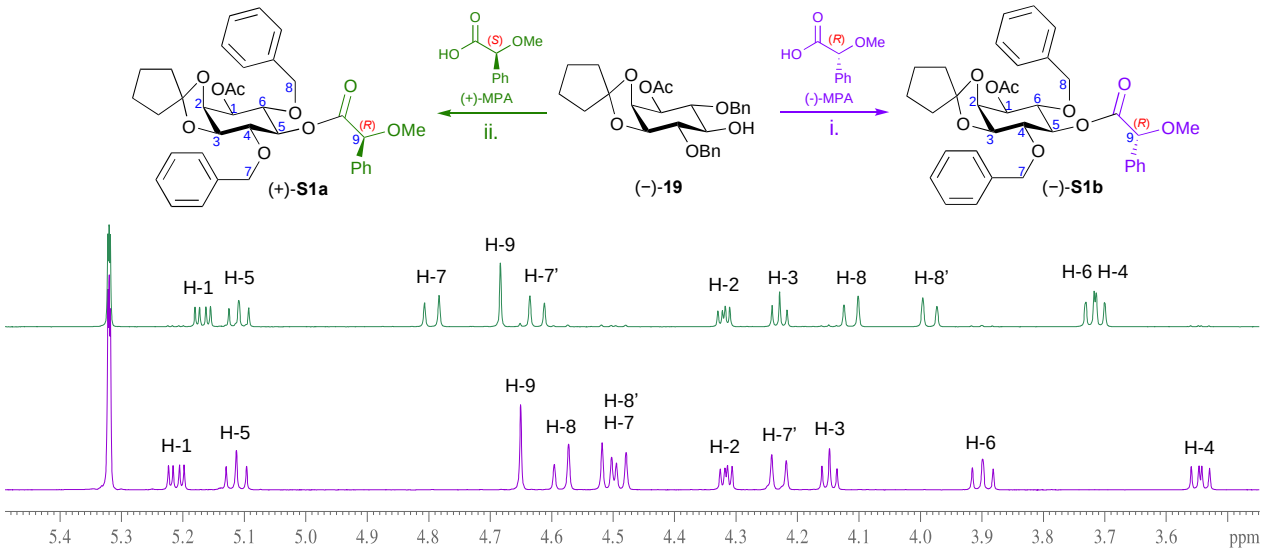
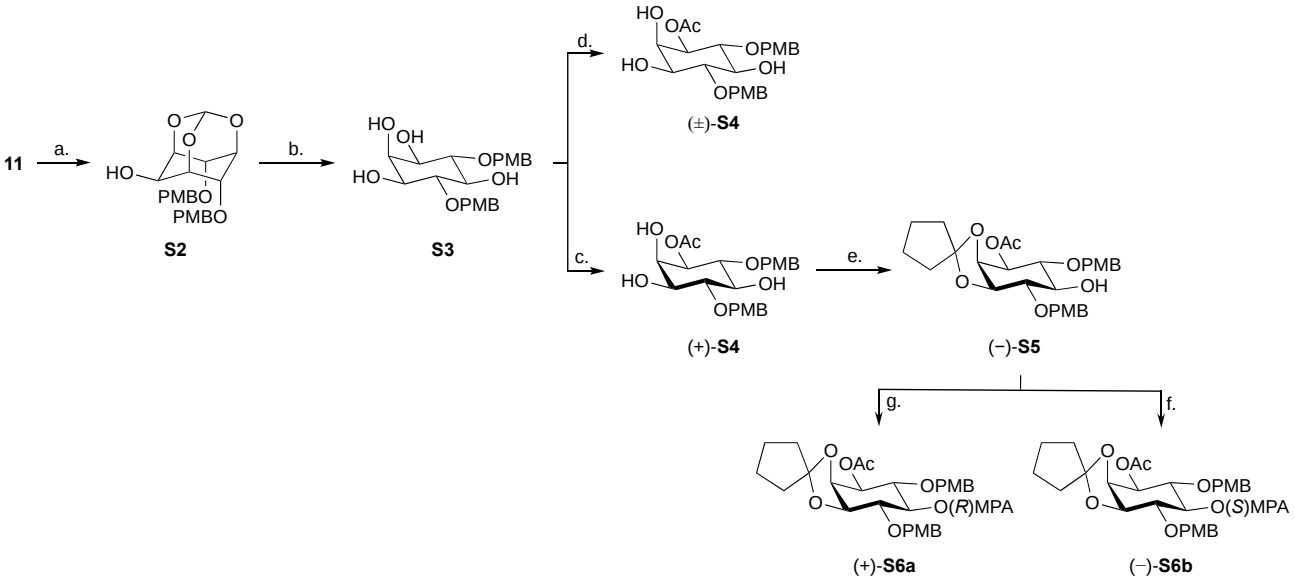


Figure S9. Comparison of the ^{1}H NMR obtained for PtdIns5*P* (−)-**73** (green) and D_6-PtdIns5*P* (−)-**74** (blue). Both ^{1}H NMR spectra were acquired at 500 MHz, in $CD_3OD/CDCl_3/D_2O$ 4:3:1.

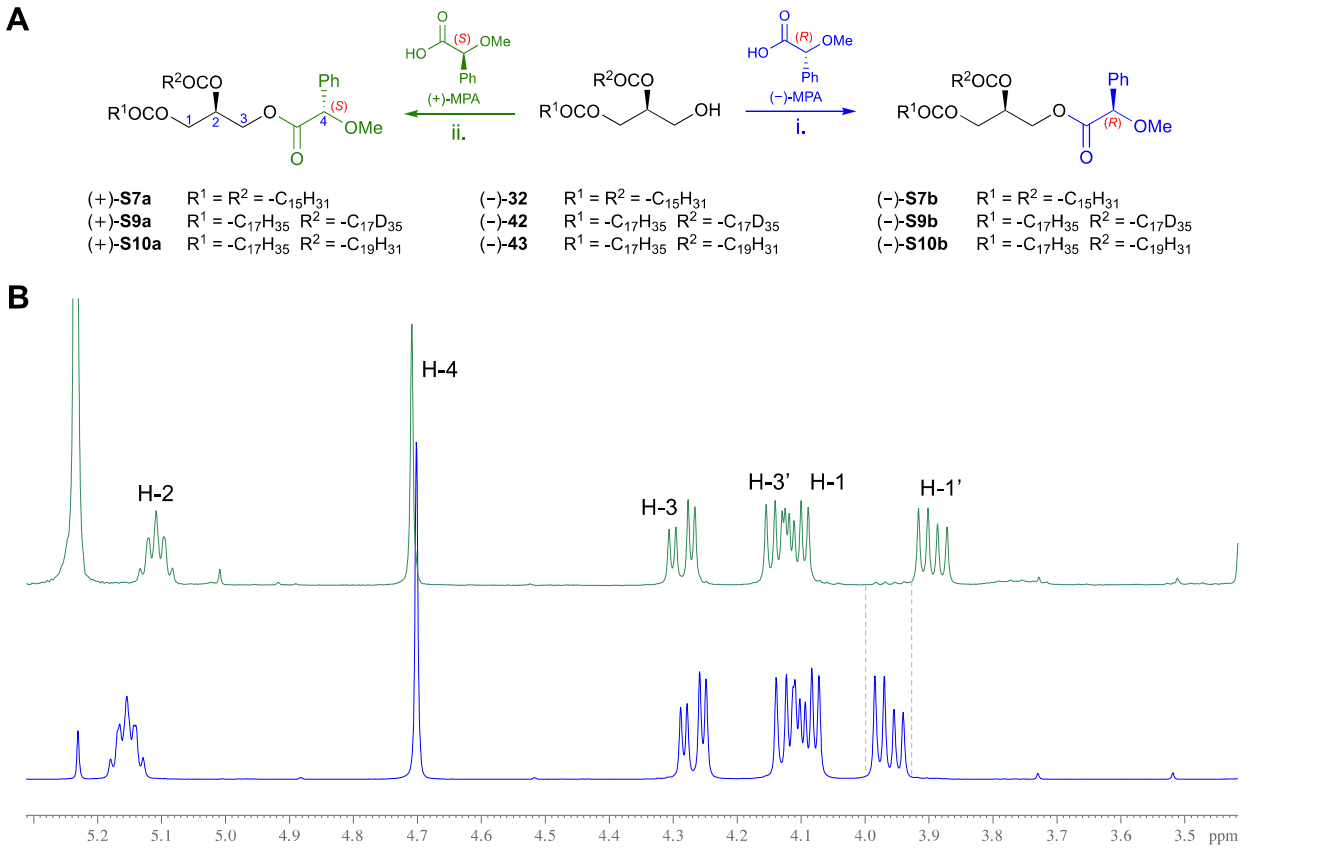
2. Supplementary Schemes



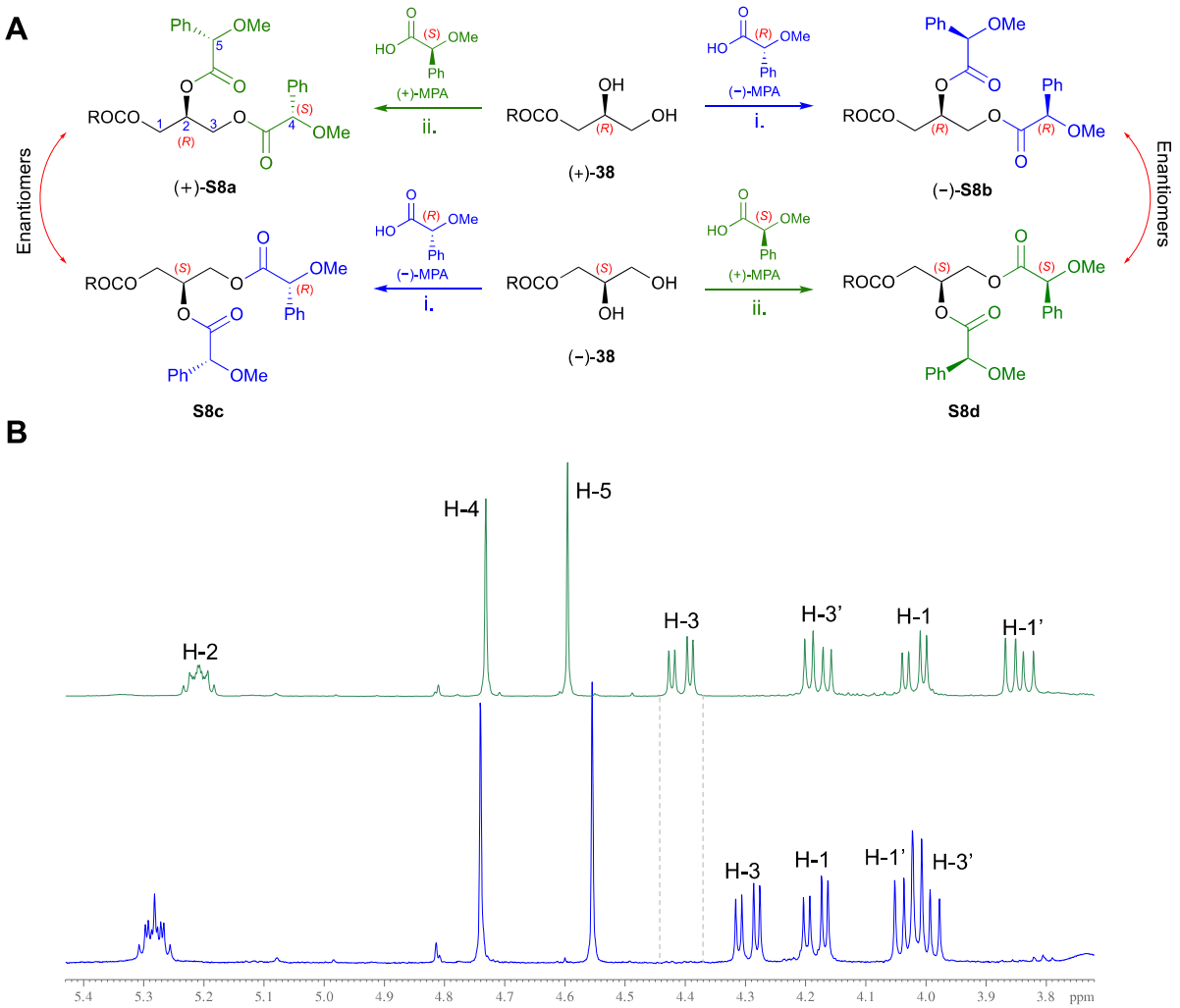
Scheme S1. Derivatisation of (−)-**19** with each enantiomer of MPA gave two diastereoisomers the (*S*)-MPA-ester (+)-**S1a** (green) and the (*R*)-MPA-ester (−)-**S1b** (purple). The ^{1}H NMR spectra (500 MHz, CD_2Cl_2) of these diastereoisomers were used for assignment of the absolute configuration. *Reagents and conditions*: i. EDC, 4-DMAP, CH_2Cl_2, RT, 24 h, 72% ii. EDC, 4-DMAP, CH_2Cl_2, RT, 3 d, 52%. Ac = acetate; Bn = benzyl; Me = methyl; Ph = phenyl; MPA = α-methoxy-phenylacetic acid.



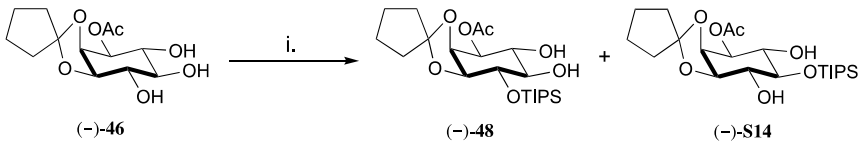
Scheme S2. Synthesis of enantiomerically pure (−)-**S4** *via* an enzymatic desymmetrisation step using Lipozyme TL-IM®, and derivatisation to give (−)-**S6b** and (−)-**S6b**. *Reagents and conditions*: a. i. NaH, DMF, RT, 1 h ii. PMBCl, RT, 17 h, 55% b. $HCl_{(aq.)}$, MeOH/H_2O, pH 2–3, 45 °C, 24 h, 74% c. Lipozyme TL-IM®, vinyl acetate/hexane (1:1), 45 °C, 15 h, 95%, >99% *e.e.* d. Ac_2O, Et_3N, 4-DMAP, CH_2Cl_2, −20 °C to −10 °C, 30 h, 9% e. 1,1-Dimethoxycyclopentane **18**, PTSA·H_2O, CH_2Cl_2, RT, 15 h, 94% f. (*R*)-MPA, EDC, 4-DMAP, CH_2Cl_2, RT, 17.5 h, 7% g. (*S*)-MPA, EDC, 4-DMAP, CH_2Cl_2, RT, 17.5 h, 6%. Ac = acetate; PMB = 4-methoxybenzyl; MPA = α-methoxyphenylacetic acid.



Scheme S3. Determination of the *e.e.* values of diglycerides (−)-**32**, (−)-**42** and (−)-**43**. (A) Derivatisation of diglycerides. *Reagents and conditions*: i. (*R*)-MPA, EDC, 4-DMAP, CH_2Cl_2, RT, 24 h, 79% (−)-**S7b**; 86%, 70% D_{35}, 30% D_{34} (−)-**S9b**; 49% (−)-**S10b** ii. (*S*)-MPA, EDC, 4-DMAP, CH_2Cl_2, RT, 24 h, 55% (+)-**S7b**; 94%, 71% D_{35}, 29% D_{34} (+)-**S9b**; 74% (+)-**S10b** (B) Example ^{1}H NMR spectra of the crude diastereoisomers (+)-**S9a** and (−)-**S9b** revealing that the *e.e.* of (−)-**42** is 96%. Multiple re-crystallisations of the product was found to improve the *e.e.* (data not shown). Me = methyl; Ph = phenyl; MPA = α-methoxy-phenylacetic acid.



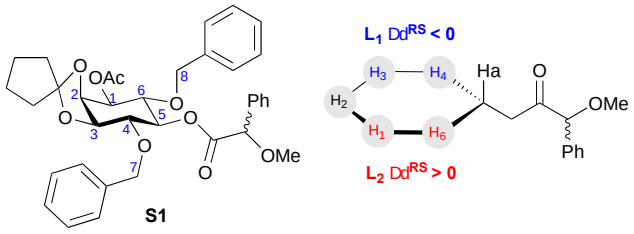
Scheme S4. Determination of the *e.e.* of diglyceride (+)-**38**. (A) Derivatisation of diglycerides. *Reagents and conditions*: (*R*)-MPA, EDC, 4-DMAP, CH_2Cl_2, RT, 24 h, 83% ii. (*S*)-MPA, EDC, 4-DMAP, CH_2Cl_2, RT, 24 h, 89%. (B) Comparing the ^1H NMR spectra (500 MH, in $CDCl_3$) of the crude diastereoisomers (+)-**8a** and (−)-**8b** obtained from the derivatisation of diol (+)-**38**. Analysis of these spectra shows that the *e.e.* of (+)-**38** is greater than 99%. R = -$C_{17}H_{35}$; Me = methyl; Ph = phenyl; MPA = α-methoxy-phenylacetic acid.



Scheme S5. Regioselective silylation of (−)-**46**. *Reagents and conditions*: i. TIPSOTf (2.2 eq), 2,6-lutidine, THF, −78 °C, 16.5 h, 71% (−)-**48**, 20% (−)-**S14**. TBDMS = *tert*-butyldimethylsilyl; TIPS = triisopropylsilyl; Ac = acetate.

3. Supplementary Tables

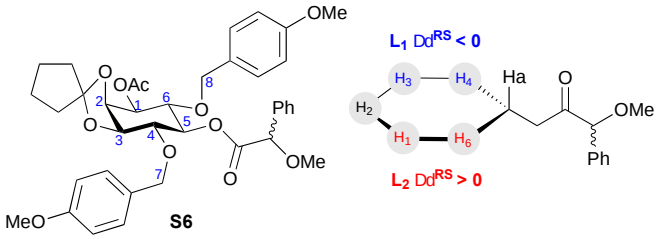
Table S1. Calculation of the differences in chemical shifts $\Delta\delta^{RS}$ for relevant protons signals in the ^{1}H NMR spectra of (+)-**S1a** and (−)-**S1b**.



Position	δ^R (−)-**S1b**[a]	δ^S (+)-**S1a**[a]	$\Delta\delta^{RS}$	L_1 or L_2
1	5.21	5.17	0.04	L_2
2	4.32	4.32	0.00	N/A
3	4.15	4.23	−0.08	L_1
4	3.54	3.72	−0.18	L_1
5	5.11	5.11	0.00	N/A
6	3.90	3.72	0.18	L_2
7	4.49	4.79	−0.30	L_1
7’	4.23	4.62	−0.39	L_1
8	4.58	4.11	0.47	L_2
8’	4.51	3.98	0.53	L_2

[a] The chemical shift (δ) values quoted were obtained from the ^{1}H NMR spectra shown in Scheme S1, run at 500 MHz, in CD_2Cl_2. Me = methyl; Ac = acetate; Ph = phenyl.

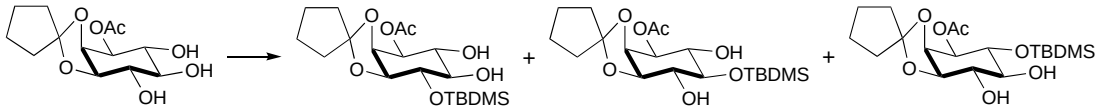
Table S2: Calculation of the differences in chemical shifts $\Delta\delta^{RS}$ for relevant protons signals in the ^{1}H NMR spectra of (+)-**S6a** and (−)-**S6b**.



Position	δ^R (−)-S6b[a]	δ^S (+)-S6a[a]	$\Delta\delta^{RS}$	L_1 or L_2
1	5.22	5.20	0.02	N/A
2	4.35	4.37	−0.02	N/A
3	4.11	4.20	−0.09	L_1
4	3.54	3.71	−0.17	L_1
5	5.14	5.15	0.01	N/A
6	3.88	3.71	0.17	L_2
7	4.43	4.69	−0.26	L_1
7’	4.27	4.58	−0.31	L_1
8	4.51	4.07	0.44	L_2
8’	4.43	3.98	0.45	L_2

[a] The chemical shift (δ) values quoted were obtained from the ^{1}H NMR spectra for (+)-**S6a** and (−)-**S6b** (see Supplementary Information, NMR spectra), run at 500 MHz, in CD_2Cl_2. Me = methyl; Ac = acetate; Ph = phenyl.

Table S3: Summary of reaction conditions for the silylation of (−)-**46**.

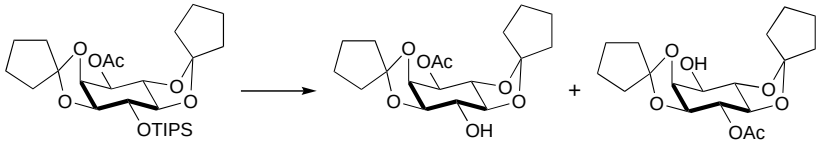


(−)-**46** (−)-**S11** (−)-**S12** (−)-**S13**

Entry	Reagent(s) (eq)	Base (eq)	Solvent	Temperature [°C]	Time [hours]	Yield S11:S12:S13 [%][a]
1	TBDMSCl (1.01) imidazole (1.5)	Pyridine	Pyridine	−10 to RT	52	-[b]
2	TBDMSCl (1.01) imidazole (1.5)	-	DMF	RT	120	-[b]
3[c]	TBDMSOTf (1.0)	2,6-Lutidine (1.5)	CH_2Cl_2	−78 to RT	71	10:0:0
4	TBDMSOTf (1.1)	Et_3N (1.3)	CH_2Cl_2	0 to RT	30	28:27:8
5	TBDMSOTf (1.1)	Pyridine	Pyridine	0 to RT	23	40:36:19
6	TBDMSOTf (1.1)	Pyridine	Pyridine	−30	24	49:36:11
7	TBDMSOTf (1.0)	2,6-Lutidine (1.5)	THF	−78	25	55:33:8

[a] Isolated yields [b] None of the desired product (−)-**S11** was formed; only starting material was recovered [c] After 23 hours of reaction at −78 °C TLC analysis indicated that most of the starting material remained, more TBDMSOTf and 2,6-lutidine were therefore added. TBDMS = *tert*-butyldimethylsilyl; TIPS = triisopropylsilyl; Ac = acetate.

Table S4: Screening of reaction conditions for the desilylation of (−)-**50**



(−)-**50** (−)-**52** **S15**

Entry	Reagents (eq)	Temperature [°C]	Solvent	Time [hours]	Yield [%]
1	$Et_3N{\cdot}3HF$ (5)	40	THF	41	-[a]
2	Pyr·HF (5)	RT	THF/Pyridine	120	39 (−)-**52**/**S15** 2.9:1.0[b]
3	TAS-F (3)	RT	DMF	1.5	75[c]

[a] The product (−)-**52** was not observed and none of the starting material could be recovered [b] Ratio determined by ^{1}H NMR analysis [c] Isolated yield. Ac = acetate; TIPS = triisopropylsilyl; Pyr. = pyridine.

4. Supplementary Results and Discussion

4.1 Confirming the absolute configuration of (−)-19 and (−)-S5

Although Laumen *et al*. had confirmed the absolute configuration of 1d-(−)-**9** through chemical correlation,[1] no other studies had been conducted since to support this assignment. Despite numerous crystallisation trials, the crystals obtained for (−)-**9** were of very poor quality, and could not be used for X-ray crystallographic analysis. As described by Wenzel[2] and Seco *et al.*,[3] diastereoisomeric derivatisation coupled with ^{1}H NMR experiments can be used to calculate both the *e.e.* of a compound and assign its absolute stereochemistry. Notably, methods have been developed for the determination of the absolute configuration of inositol derivates[4,5] using Trost's conformational model.[6] Therefore, we chose to confirm the stereochemistry of (−)-**19** and (−)-**S5** *via* NMR methods. Assignment of the absolute configuration by NMR was undertaken using the procedures by Seco *et al*.,[3] and following the sequence of steps described below:

*a) Derivatisation of alcohol (−)-**19** and (−)-**S5** with each enantiomer, (R)- and (S)-, of a chosen chiral anisotropy reagent.* Although α-methoxy-α-trifluoromethylphenylacetic acid (MTPA), also called Mosher's acid,[7] is the most well-known chiral derivatising agent, α-methoxyphenylacetic acid (MPA) was found to be more reliable for the stereochemical assignment of secondary alcohols.[3] As such, esterification of (−)-**19** with each enantiomer of MPA in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) and 4-DMAP yielded the two diastereoisomeric esters (+)-**S1a** and (−)-**S1b** (Scheme S1). Similarly, esterification of (−)-**S5** provided two diastereoisomeric esters (+)-**S6a** and (−)-**S6b** (Scheme S2). Each diastereoisomer provided a different ^{1}H NMR spectrum as illustrated in Scheme S1. These spectra were analysed and compared, to determine the absolute configuration of (−)-**19** and (−)-**S5**.

b) Conformational model for the chiral anisotropy reagent

The stereogenic centre under consideration features the MPA ester, an α-proton, and two substituents L_1 and L_2 (Figures S2). The substituent facing the aryl ring of the MPA ester experience an anisotropic shielding effect due to the local induced magnetic field of the aromatic ring. The protons on this substituent therefore appear more upfield (lower δ) by ^{1}H NMR. This shielding effect will be experienced by a different substituent (L_1 or L_2) in each of the two diastereoisomers (+)-**S1a** and (−)-**S1b**. As such, the difference in the chemical shift value ($\Delta\delta^{RS}$) of the substituent's proton signal in each diastereoisomer is a measure of the anisotropic effect. The sign of $\Delta\delta^{RS}$ is an indication of the relative spacial arrangement of L_1 and L_2 with reference to the phenyl ring on the MPA ester. The protons that are shielded in the diastereoisomer containing (*R*)-MPA (−)-**S1b** will give a negative $\Delta\delta^{RS}$ and those that are shielded in (+)-**S1a** will give a positive $\Delta\delta^{RS}$. Determination of the absolute configuration can be achieved unequivocally when the system considered is conformationally locked, resulting in large Δδ values. The conformational model developed by Trost[6] for MPA esters is closely related to the model for MTPA esters developed by Dale and Mosher's.[7] These empirical models were later evaluated and rationalised through computational modelling and dynamic NMR.[8,9] These studies showed that the *syn*-periplanar and *anti*-periplanar conformers are the two main conformers for the MPA esters of secondary alcohols. Contrastingly, MTPA esters of secondary alcohols are known to have three main conformers. This conformational complexity is the reason why MTPA is currently recognised as an unreliable chiral derivatising agent. The *syn*-periplanar conformation, in which the MPA methoxy, MPA carbonyl, and α-proton are placed in the same plane, was found to be the most stable (Figure S2). According to this conformational model, therefore, protons H-1 and H-6 of (+)-**S1a** and

protons H-3 and H-4 of (−)-**S1b** are expected to be shielded, if the configuration of (−)-**19** is indeed (−)-1d-1-*O*-acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-*myo*-inositol. The parameter $\Delta\delta^{RS}$ for this configuration is thus expected to be positive for protons H-1 and H-6 and negative for protons H-3 and H-4 (Figure S2).

c) *The ^{1}H NMR spectra of the diastereoisomers were analysed and the chemical shift differences ($\Delta\delta^{RS}$) were calculated.* As shown in Table S1 and S2, $\Delta\delta^{RS}$ was indeed negative for protons H-3, H-4 and H-7 and positive for protons H-1, H-6 and H-8 for both sets of enantiomers: (+)-**S1a** and (−)-**S1b** and (+)-**S6a** and (−)-**S6b**. This matched our prediction using the conformational model in Figure S2. According to this study, the configuration of (−)-**9** was therefore assigned as (−)-1d-1-*O*-acetyl-4,6-di-*O*-benzyl-*myo*-inositol[1] and that of (−)-**S4** was assigned as (+)-1d-1-*O*-Acetyl-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol.

4.2 Synthesis of phosphoramidite fragments (+)-34, (+)-35, (+)-44 and (+)-45.

To synthesise dipalmitoyl and distearoyl PtdIns4*P* and PtdIns5*P* derivatives, diacylglycerol (−)-1,2-dipalmitoyl-*sn*-glycerol (−)-**35** and diacylglycerol (−)-1,2-distearoyl-*sn*-glycerol (−)-**36** were prepared from (+)-1,2-*O*-isopropylidene-glycerol (+)-**30** with modifications to the reported literature procedures.[10,11] First, intermediates (−)-**32** and (−)-**33** were obtained from esterification of diol (−)-**31** (Scheme 4A). The 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)-mediated PMB cleavage previously employed in the literature,[10] however, afforded the desired product mixed with DDQ-related contaminants, which had to be removed by column chromatography. Silica-promoted ester exchange led to the isomerisation of diglycerides (−)-**32** and (−)-**33**, as indicated by ^{1}H NMR analysis. This, in turn, suggested concurrent racemisation. To avoid this, the desired product (−)-**32** and (−)-**33** were obtained through Pd/C-catalysed hydrogenolysis (Scheme 4A). Purification by column chromatography was not necessary in this case, avoiding migration and racemisation. The enantiomeric purity of these intermediates was confirmed to be greater than 99% by ^{1}H NMR analysis of the corresponding (*R*)- and (*S*)-MPA esters (Supplementary Results and Discussion 4.3). Finally, a 1*H*-tetrazole-mediated coupling of (−)-**32** and (−)-**33** with (benzyloxy)bis(*N*,*N*-diisopropylamino)phosphine **34** provided (+)-**35** and (+)-**36** (Scheme 4A), which were employed in the synthesis of saturated PtdIns4*P* and PtdIns5*P* analogues.

As 1-stearoyl-2-arachidonyl PtdInsP_ns are enriched in mammals, it was desirable to extend this strategy to the synthesis of unsaturated, mixed diglyceride derivatives. However, the synthetic methodology described above could not be applied to the synthesis of such derivatives, owing to the incompatibility of the hydrogenolysis step. A synthesis of enantiomerically pure mixed diglycerides was therefore optimised, based on previous literature.[12,13] First, (*R*)-(−)-2,3-isopropylidene-*sn*-glycerol (−)-**30** was acylated smoothly with stearoyl chloride in the presence of 4-DMAP to provide (−)-**37** in 76% yield (Scheme 4B). Conditions for the deprotection of an acetonide on frameworks such as (−)-**37** have been thoroughly investigated.[12,14] Notably, Mori *et al.*[14] demonstrated that commonly employed conditions including Amberlyst 15 (H^+ form) in MeOH/CH_2Cl_2,[13,15,16] led to acyl migration. Conversely, deprotection with 80% aqueous acetic acid (AcOH) at 50 °C for 2 hours, followed by crystallisation, gave the desired product with no racemisation.[14] Deprotection of (−)-**37** under these conditions was successful in our hands, giving (+)-**38** in 70% yield after crystallisation (Scheme 4B). As these acyl glycerides are prone to acyl migration, it is essential to monitor their *e.e.* values during the synthesis. Analysis of the corresponding bis-(*R*)- and bis-(*S*)-MPA esters by ^{1}H NMR analysis revealed that the *e.e.* of (+)-**38** was >99% (Supplementary Results and Discussion 4.3). Regioselective protection of the primary alcohol on (+)-**38** with DMT, as described in by Kubiak and Bruzik,[13] was followed by condensation with D_{35}-stearic acid to give the DMT-protected precursor (+)-**40** (Scheme 4B).

Deprotection of acid-labile groups at the *sn*-3 position had been accomplished on similar derivatives by Gaffney and Reese,[12] as well as Kubiak and Bruzik,[13] with dichloroacetic acid or trifluoroacetic acid (TFA) and pyrrole as a carbocation scavenger. In our hands, however, these conditions yielded a mixture of the expected products (−)-**42**, and the acyl migration side-product. As aqueous AcOH is routinely applied to the deprotection of DMT protecting groups, we hypothesised that the conditions used for the cleavage of the acetonide on (−)-**37** would be applicable to the deprotection of (+)-**40**. Indeed, treatment with 80% aqueous AcOH at 50 °C for 3.5 hours followed by crystallisation from pentane/Et_2O furnished (−)-**42** in high yield. This product was not contaminated by any migration regioisomer, and the *e.e.* was 96%, as determined by MPA ^{1}H NMR analysis (Supplementary Results and Discussion 4.3). Preparation of the phosphoramidite fragment (+)-**44** was then undertaken using a 1*H*-tetrazole-mediated coupling of diglyceride (−)-**42** to benzyloxybis(*N*,*N*-diisopropylamino)phosphine **34** (Scheme 4B). Using the developed procedure, we prepared 1-stearoyl-2-arachidonyl phosphoramidite (+)-**45** (Scheme 4B), for use in the synthesis of unsaturated PtdIns*P* analogues. In this case, however, intermediate (−)-**43** could not be crystallised and was found to be more prone to acyl migration. Optimisation of the procedure for this system involved using AcOH/formic acid/H_2O (7:2:1) at RT, followed by filtration through reverse-phase silica to remove the DMTOH side product. The unsaturated phosphoramidite (+)-**45** was subsequently obtained from this intermediate (Scheme 4B).

4.3 Determining the *e.e.*s of (−)-32, (+)-38, (−)-42 and (−)-43 by NMR

The *e.e.* values of (−)-**32**, (+)-**38**, (−)-**42** and (−)-**43** were determined by NMR, as described by Wenzel[2] and Seco *et al*.[3] Derivatisation of (−)-**32**, (+)-**38**, (−)-**42** and (−)-**43** with each enantiomer ((*R*)- and (*S*)-) of MPA was achieved by condensation with excess (*S*)-MPA or (*R*)-MPA in the presence of 4-DMAP and EDC (Schemes S3A and S4A). The *e.e.* values of the substrates were determined by comparing the crude ^{1}H NMR spectra of diastereoisomers (+)-**S7a** and (−)-**S7b**, (+)-**S8a** and (−)-**S8b**, (+)-**S9a** and (−)-**S9b**, (+)-**S10a** and (−)-**S10b**. This is essential, as diastereoisomers may be separated during the purification step. The crude ^{1}H NMR spectra of each set of diastereoisomers feature proton signals with distinct chemical shifts (Scheme S3B and Scheme S4B).

For instance, if the diol (+)-**38** is not enantiomerically pure, diastereoisomer **S8c** will also be formed in the reaction with (*R*)-MPA and diastereoisomer **S8d** in the reaction with (*S*)-MPA. As **S8c** is the enantiomer of (+)-**S8a**, these diastereoisomers will have identical ^{1}H NMR spectra. The same applies for **S8d** and (−)-**S8b**. As such, if signals for **S8c** (equivalent to that of (+)-**S8a**) are observed in the crude ^{1}H NMR spectra of (−)-**S8b** the e.e. can be calculated by integrating the signals corresponding to (−)-**S8b** and **S8c**. If no residual signals are observed, the e.e. is presumed to be greater than 99%. This was indeed the case for (+)-**S8a** and (−)-**S8b**. The *e.e.* of diol (+)-**38** was therefore greater than 99% (Scheme S4). Similarly, the *e.e.* values of (−)-**32**, (−)-**42** and (−)-**43** were shown to be greater than 96% (Scheme S3).

4.4 Regioselective protection of (−)-46 at the 4-*O*-position

Previous revious studies in our laboratory had demonstrated that the 4-*O*-position of inositol frameworks similar to (−)-**46** can be regioselectively protected as 4-*O*-pivalate esters. However, attempts to regioselectively silylate (−)-**46** using TBDMSCl, under standard conditions, proved unsuccessful (Table S3; Entries 1 and 2). Even at room temperature and after extended reaction times, only the starting material remained. Contrastingly, the more reactive silylating agent *tert*-butyldimethylsilyl triflate (TBDMSOTf)[17] led to the formation of the expected product (−)-**S11** (Table S3; Entry 3) in 10% isolated yield, with significant amounts of the starting material (−)-**46** remaining. The low conversion observed in this transformation was later

attributed to the poor solubility of the starting material (−)-**46** in CH_2Cl_2 at −78 °C. In the presence of other bases such as pyridine or triethylamine,[18] and at higher temperatures, formation of the regioisomers (−)-**S12** and (−)-**S13** was observed (Table S3; Entries 4 and 5). The relative ratio of the regioisomers obtained was not significantly altered when the reaction was carried out at −30 °C (Table S3; Entry 6). Finally, we found that (−)-**46** could be fully solubilised in THF at −78 °C. Treatment with TBDMSOTf in the presence of the preferred milder base, 2,6-lutidine, resulted in the full conversion of (−)-**46**, with (−)-**S11** as the major regioisomer (Table S3; Entry 7). Difficulties were encountered when purifying the mixture of the three regioisomers, as (−)-**S11** and (−)-**S13** were found to have very similar polarities. Each regioisomer isolated in this study was fully characterised using 2D NMR experiments including ^{1}H-^{29}Si and ^{1}H-^{13}C HMBC (Figure S4A). The regioselectivity of this reaction was significantly improved when (−)-**46** was protected with the bulkier and more stable triisopropylsilyl (TIPS) group. Treatment with up to 2.2 equivalents of triisopropylsilyl triflate (TIPSOTf), under the optimised reaction conditions, yielded the desired regioisomer (−)-**48** in good yields (Scheme S5), as determined by ^{1}H-^{29}Si and ^{1}H-^{13}C HMBC NMR (Figure S4B). Although (−)-**S14** was also isolated, the difference in polarity between the two regioisomers greatly facilitated the purification of (−)-**48**.

To account for the regioselectivity of these transformations, it was essential to think beyond steric factors alone. Steric crowding around the 4-position is alleviated by the conformationally restricted 2,3-cyclopentylidene acetal. In contrast, the 1-position acetyl group occludes the 6-positoin hydroxyl group to some degree. In addition, previous work, focusing on carbohydrate regioselectivity, demonstrates that geometrically favourable hydrogen bonding between the hydroxyl protons and the neighbouring ether oxygen of the *cis*-acetal is mostly responsible for the enhanced nucleophilicity of the hydroxyl groups observed.[19-21] The 3-position oxygen is a better H-bond acceptor than that of the acetyl group, due to the inductive electron-donating effect of the cyclopentylidene group. Taken together, these considerations provide an explanation for the regioselectivity observed in protection of compound (−)-**46**.

4.5 Cleavage of the 4-*O*-TIPS ether on (−)-50

Previous studies in our laboratory had shown that $Et_3N{\cdot}3HF$ could efficiently cleave silyl groups at the 1-*O*-position, on inositol systems featuring both a base-labile acyl group and acid-labile acetal group. The inositol derivative (−)-**50**, however, was found to be unstable in the presence of $Et_3N{\cdot}3HF$. After 41 hours of reaction at 40 °C, the expected product was not observed or isolated and none of the starting material was recovered (Table S4; Entry 1). Appropriate mild conditions for the deprotection of TIPS on acid- and base-sensitive substrates such as (−)-**50** were therefore sought.

Deprotection of (−)-**50** was attempted using Pyr·HF (Table S4; Entry 2).[22] We envisaged that the substrate would be more stable in the presence of a weaker base. After five days stirring at room temperature, purification by column chromatography afforded a mixture of two inseparable regioisomers. It appeared that following deprotection of the silyl ether, the reaction conditions facilitated partial intermolecular transesterification of the 1-*O*-acetate ester to give the expected product (−)-**52** and the side product **S15** in a ratio of 2.9:1.0 (Table S4), as identified by NMR analysis. This type of acyl migration had been previously described on furanosides by Chevallier and Migaud.[23] Evidence suggests that optimisation of the reaction concentration would minimise intermolecular acyl migration, however, considering the low overall yield of this transformation, we decided to explore alternative reagents. The pentacoordinated silicate tris(dimethylamino)sulfonium difluorotrimethylsilicate, $[(Me_2N)_3S]^+[F_2SiMe_3]^-$ (TAS-F) has been shown to be a soluble, mild and anhydrous source of nucleophilic fluoride.[24] In addition, the electron donating ability of the three $(CH_3)_2N$ substituents on the sulfonium anion in TAS-F renders it non-electrophilic.[25] This reagent has been shown to be successful in the desilylation of highly complex, acid-

and base-sensitive substrates,[26-28] as well as inositol derivatives.[29] Therefore, (−)-**50** was stirred with three equivalents of TAS-F at RT for two and a half hours. Work-up and purification by column chromatography over silica gel provided (−)-**52** in 75% yield (Table S4; Entry 3).

5. Synthetic Procedures and Characterisation data

5.1 General Methods

^{1}H NMR spectra were recorded on Bruker DPX 200 (200 MHz), Bruker AVIIIHD 400 nanobay (400 MHz), Bruker AVII 500 (500 MHz) with dual ^{13}C(^{1}H) cryoprobe, or Bruker AVIIIHD 500 (500 MHz) spectrometer in the stated solvents as a reference for the internal deuterium lock. The chemical shift data for each signal are given as δ_H in units of parts per million (ppm) relative to tetramethylsilane (TMS) where δ_H (TMS) = 0.00 ppm. The spectra are calibrated using the solvent peak with the data provided by Fulmer *et al*.[30] The multiplicity of each signal is indicated by s (singlet); br s (broad singlet); d (doublet); dd (doublet of doublets), ddd (doublet of doublet of doublets), t (triplet), q (quartet), dq (double of quartet) or m (multiplet). The number of protons (n) for a given resonance signal is indicated by nH. Where appropriate, coupling constants (*J*) are quoted in Hz and are recorded to the nearest 0.1 Hz. Identical proton coupling constants (*J*) are averaged in each spectrum and reported to the nearest 0.1 Hz. The coupling constants are determined by analysis using Bruker TopSpin version 3.2 software. ^{1}H spectra were assigned using 2D NMR experiments including COSY, HMBC, HSQC, ^{29}Si-^{1}H HMBC and ^{31}P-^{1}H HMBC. ^{13}C NMR spectra were recorded on a Bruker AVIIIHD 400 nanobay (101 MHz), or Bruker AVII 500 (126 MHz) spectrometer, with dual ^{13}C(^{1}H) cryoprobe, in the stated solvents, with broadband proton decoupling and an internal deuterium lock. The chemical shift data for each signal are given as δ_C in units of parts per million (ppm) relative to tetramethylsilane (TMS) where δ_C (TMS) = 0.00 ppm. The spectra are calibrated using the solvent peak with the data provided by Fulmer *et al*.[30] The shift values of resonances are quoted to 1 decimal place unless peaks have similar chemical shifts, in which case 2 decimal places are used. Where appropriate, the multiplicity of each signal is indicated by d (doublet), t (triplet) or m (multiplet). A subscript D (e.g. t_D) indicates splitting caused by deuterium (I = 1); and a subscript P (e.g. d_P) indicated splitting caused by phosphorus (I = 1/2). Coupling constants (J_P and J_D) are quoted in Hz and are recorded to the nearest 0.1 Hz. These were determined using Bruker TopSpin version 3.2 software. ^{13}C spectra were assigned using 2D NMR experiments including HMBC and HSQC. ^{31}P NMR spectra were recorded on a Bruker AVIIIHD 400 nanobay (162 MHz), or Bruker AVIIIHD 500 (202 MHz) spectrometer in the stated solvents as a reference for the internal deuterium lock, using a broadband proton decoupling pulse sequence. The chemical shift for each signal are given as δ_P in units of parts per million (ppm) relative to 85% phosphoric acid as an external reference where δ_P (H_3PO_4) = 0.00 ppm. Signals are singlets unless otherwise stated. ^{31}P spectra were assigned using ^{1}H-^{31}P NMR experiments as necessary. ^{2}H NMR spectra were recorded on a Bruker AVII 500 (77 MHz) or Bruker AVIIIHD 600 (92 MHz) spectrometer in the stated solvents using a drop of relevant deuterated solvent as a reference for the internal deuterium lock. Signals are typically broad singlets. The chemical shift data for each signal are given as δ_D in units of parts per million (ppm) relative to tetramethylsilane (TMS) where δ_D (TMS) = 0.00 ppm. The spectra are calibrated using the solvent peak with the data provided by Fulmer *et al*.[30] The spectra are assigned by matching the signals to those obtained in the ^{1}H spectra of the protonated counterparts.

When two diastereoisomers are present in the sample, A and B denotes each of the two diastereoisomers without distinguishing between them. A is arbitrarily assigned to the diastereoisomer with the highest ppm shift and B to the diastereoisomer with the lowest ppm shift, in ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra. In cases of multiplets which are assigned to multiple protons, where possible resonances are quoted in the order in which they appear as assigned by 2D NMR experiments.

Low resolution electrospray ionisation spectra were acquired on a Waters LCT Premier spectrometer or Agilent 6120 Quadrupole spectrometer. High resolution mass spectra were recorded on a Bruker MicroTOF spectrometer, operating in

positive or negative mode, as indicated, from solutions of MeOH, MeCN or H_2O. *m/z* values are reported in Daltons and followed by their percentage abundance in parentheses. Electron ionisation/field ionisation (EI/FI) was carried out on a Waters GCT with a temperature programmed solids probe inlet. MALDI was carried out on a Waters MALDI Micro MX. When a compound was not observed by LRMS, only HRMS is quoted.

Where not explicitly stated in a chemical structure, deuterium atoms are indicated by a red asterisk next to the relevant carbon. The deuterium incorporation of deuterated compounds is shown after the yield. Mass spectrometry techniques were used to calculate the incorporation shown and are ^{13}C corrected.

Specific optical rotations were measured using either a Perkin Elmer Model 241 polarimeter or Schmidt + Haensch UniPol L2000 polarimeter, in cells with a path length of 1 dm, using a sodium lamp at 589 nm. The concentration (*c*) is expressed in g/100 mL (equivalent to g/0.1 dm^3) Specific rotations are denoted $[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{T}}$ and are given in implied units of $10^{-1}degcm^2g^{-1}$ at the temperature stated.

Melting points were determined using a Leica Galen III hot stage microscope and are uncorrected. The solvents of crystallisation are shown in parentheses. Infrared (IR) spectra were obtained from neat samples, either as liquids or solids using a diamond ATR module. The spectra were recorded on a Bruker Tensor 27 spectrometer. Absorption maxima are reported in wavenumbers (cm^{-1}) and reported as s (strong), m (medium), w (weak) or br (broad). Only the main, relevant peaks have been assigned.

Thin layer chromatography (TLC) was carried out on normal phase Merck silica gel 60 F_{254} aluminium-supported chromatography sheets. Visualisation was by absorption of UV light (λ_{max} 254 nm), exposure to iodine vapour or thermal development after dipping in either an ethanolic solution of ninhydrin or an aqueous solution of potassium permanganate. Reaction progress was monitored at appropriate times either by TLC or by ^{31}P NMR. Normal phase silica gel flash column chromatography was performed either manually using VWR Prolabo silica gel 60 (240–400 mesh) under a positive pressure of nitrogen or on a Biotage SP1 automated column chromatography system using KP-Sil® SNAP Flash Silica Cartridges. Reversed phase silica gel column chromatography was carried out using C18 Fluka silica gel, eluting with the appropriate solvents under a positive pressure of compressed nitrogen. Chemicals were purchased from Acros UK, Apollo Scientific, Enamine, Sigma Aldrich UK, Alfa Aesar UK, Fisher Scientific UK, Fluka UK, Fluorochem, Merck, Argo International Limited and TCI-Europe. All reagents were purified, when necessary, by standard techniques.[31] In particular, Et_3N, pyridine and DIPEA were dried by stirring over solid KOH pellets overnight followed by fractional distillation. DIPA was distilled from NaH. These were stored under Ar and over 3 Å molecular sieves. PCl_3 was heated under reflux to expel dissolved HCl, then distilled and stored under Ar over 4 Å molecular sieves. Anhydrous solvents were obtained under the following conditions: Et_2O, toluene and CH_2Cl_2 were dried by passing through a column of activated basic alumina according to the Grubbs' procedure.[32] Anhydrous DMF, DMSO, MeOH and MeCN were purchased from Sigma Aldrich UK in SureSeal™ bottles and used without further purification. Anhydrous THF was distilled from sodium metal, using benzophenone as an indicator.[31] All other solvents were used as supplied (analytical or HPLC grade) without purification. Where appropriate and if not otherwise stated, all non-aqueous reactions were performed in a flame dried flask under an inert atmosphere. Hexane refers to a mixture of hexane isomers and petroleum ether refers to the fraction of light petroleum ether boiling within the range of 40–60 °C. Brine refers to a saturated aqueous solution of sodium chloride. Rochelle's salt refers to an aqueous solution of potassium sodium tartrate tetrahydrate. *In vacuo* refers to the removal of solvents under reduced pressure using a Büchi™ rotary evaporator in a water bath at 40 °C, unless otherwise stated. Vacuum transfer refers to the removal of solvents on a manifold linked to a high vacuum pump at RT. Lyophilisation refers to the removal of H_2O from aqueous solutions by freeze drying using a CHRIST Alpha 1-2 LD lyophiliser. Celite® refers to Celite® 545 filter aid, treated with sodium carbonate, flux-calcined

which was purchased from Sigma Aldrich. Glass microfiber filter refers to Whatman® borosilicate glass microfiber filters, Grade GF/B. Compound purity was determined by analytical high-performance liquid chromatography (HPLC) on a PerkinElmer Flexar system with a Binary LC Pump and UV/VIS LC Detector using: a) a reversed phase Dionex Acclaim® 120 column (C18, 5 µm, 4.6 × 150 mm) with H_2O/MeCN/TFA 95:5:0.1 (A) and MeCN/ H_2O/TFA 95:5:0.1 (B) or H_2O/MeCN 95:5 (A) and MeCN/H_2O 95:5 (B) as eluents; or b) a normal phase HyperSil GOLD™ Silica column (5 µm, 4.6 × 150 mm) with heptane or hexane (A) and IPA (B) as eluents. Gradient methods of 19 to 25 minutes were employed with a constant flow rate, and detection at 254 or 220 nm (Methods 1, 2, 3, 5, 6 and 7). In certain cases, isocratic methods were employed (Methods 4 and 8). Samples were injected by dissolving in the relevant solvent system. The methods are described below:

Method 1: A = H_2O/MeCN/TFA 95:5:0.1; B = MeCN/ H_2O/TFA 95:5:0.1; 1.0 mL.min^{-1}; 254 nm.

Method 2: A = H_2O/MeCN 95:5; B = MeCN/ H_2O 95:5; 1.0 mL.min^{-1}; 254 nm.

Method 3: A = H_2O/MeCN 95:5; B = MeCN/ H_2O 95:5; 1.0 mL.min^{-1}; 220 nm.

Method 4: Isocratic; MeCN; 1.5 mL.min^{-1}; 254 nm.

Method 5: Normal Phase; A = Heptane; B = IPA; 1.0 mL.min^{-1}; 254 nm.

Method 6: Normal Phase; A = Hexane; B = IPA; 2.0 mL.min^{-1}; 254 nm.

Method 7: Normal Phase; A = Hexane; B = IPA; 1.5 mL.min^{-1}; 254 nm.

Method 8: Normal Phase; Isocratic; Hexane; 1.0 mL.min^{-1}; 254 nm.

Table S5. Reverse Phase HPLC gradient for Method 1, Method 2 and Method 3

Step length (min)	Elapsed time (min)	%A	%B
1	1	100	0
10	11	0	100
3	14	0	100
1	15	100	0
5	20	100	0

Table S6. Normal Phase HPLC gradient for Method 5.

Step length (min)	Elapsed time (min)	%A	%B
1	1	95	5
12	13	5	95
5	18	5	95
1	19	95	5
6	25	95	5

Table S7. Normal Phase HPLC gradient for Method 6.

Step length (min)	Elapsed time (min)	%A	%B
1	1	98	2
5	6	90	10
13	19	90	10

Table S8. Normal Phase HPLC gradient for Method 7.

Step length (min)	Elapsed time (min)	%A	%B
1	1	98	2
15	16	90	10
3	19	90	10

Enantiomeric purity was determined by chiral analytical high-performance liquid chromatography (HPLC) on a PerkinElmer Flexar system with a Binary LC Pump and UV/VIS LC Detector using a ChiralPak® AD-H column (5 µm, 4.6 × 150 mm) with IPA (A) and heptane (B) as eluents. Isocratic methods of 45 minutes were employed with a constant flow rate of 1.0 mL.min^{-1} or 0.8 mL.min^{-1} and detection at 220 or 254 nm as indicated. Samples were injected by dissolving in the relevant solvent system. The enantiomeric excess (*e.e*) was determined using the following equation: *e.e*. = ((*R*−*S*)/*R*+*S*)) × 100 where *R* and *S* stand for the individual enantiomers and *R* + *S* = 1. Semi preparative HPLC was performed on a Dionex P680 HPLC pump using a reversed phase Agilent ZORBAX 300SB-C18 column (5 µm, 9.4 × 250 mm) with H_2O/MeCN/TFA 95:5:0.1 (A) and MeCN/ H_2O/TFA 95:5:0.1 (B) as eluents. A gradient method of 29 minutes was employed with a constant flow rate of 3.0 mL.min^{-1} and detection at 254 nm. Samples were injected by dissolving in MeCN/H_2O. The method used is described below:

Method 1: A = H_2O/MeCN/TFA 95:5:0.1; B = MeCN/ H_2O/TFA 95:5:0.1; 3.0 mL/min^{-1}; 254 nm.

Table S9. Semi-preparative HPLC gradient for Method 1.

Step length (min)	Elapsed time (min)	%A	%B
1	2	100	0
3	5	74	26
20	25	74	26
2	27	0	100
2	29	100	0

5.2 Cell Studies

Lipid Extraction Delivery of deuterated phosphatidyl inositol-4- and 5-phosphate probes D_6-PtdInd4*P* [(−)-65], D_{41}-PtdInd4*P* [(−)-67,] and D_6-PtdIns5*P* [(−)-76] into cells

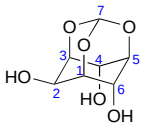
The delivery of the phosphatidylinositol-4- and 5-phosphate probes to MCF-7 cells was carried out as reported previously.[33] Briefly, MCF-7 cells (ATCC) were plated in 6 well plates at 1×105 cells/mL, 2 mL per well in RPMI media with GlutaMAX (Gibco, UK) supplemented with 10% foetal calf serum. Cells were incubated overnight at 37 °C, 5% CO_2. Subsequently, cells were washed once in serum free RPMI media and then incubated in serum free media for 1 h. Unlabelled Shuttle PIP Carrier 1 (Neomycin B Sulfate, Echelon Biosciences US) was combined at a 1 to 1 molar ratio (~100 µM final concentration each) with (−)-**65**, (−)-**67**, or (−)-**76** for 10 minutes in a test tube at room temperature. The complex was then diluted in serum free RPMI media so that the final concentration on cells of both the carrier and the specific deuterated PIP was either 10 µM, 1 µM or 0.1 µM. Cells in the carrier only control was treated with a final concentration of 10 µM of Neomycin B Sulfate. After 60 minutes, the media containing the carrier/PtdInd*P* complex was removed, cells were washed in serum free RPMI media, killed in 1 mL ice-cold aqueous 1 M HCl, then scraped and collected into an Eppendorf tube. Cells were pelleted in a microfuge (15000 × g, 10 min at 4 °C), the supernatant removed, and cell pellets were snap-frozen in liquid nitrogen and stored at −80°C.

Lipid Extraction

Cell pellets were resuspended in 920 µL of MeOH:$CHCl_3$:$H_2O_{(acidic)}$ 2:1:0.79 (*v/v*) containing the internal standards C17:0/C16:0-PtdIP_3 (10 ng) and C17:0/C16:0-PtdIns (100 ng). Lipids were then extracted using an acidified Folch phase partition and derivatised with TMS-diazomethane.[34] The derivatised phosphoinositides were measured by HPLC-MS.[35] Response ratios relative to the C17:0/C16:0-PtdIns internal standard were calculated for both endogenous C38:4 and C32:0 PtdInsP species and the deuterated PtdInsP probes (−)-**65**, (−)-**67**, or (−)-**76**.

5.3 Synthetic Protocols, Characterisation data, and Compound Assignments

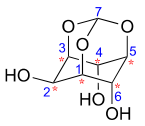
***myo*-Inositol 1,3,5-orthoformate 11**



To a solution of *myo*-inositol **1** (20.0 g, 111 mmol, 1.0 eq) in DMF (80 mL) were added triethylorthoformate (82.5 g, 555 mmol, 5.0 eq) and PTSA·H_2O (8.45 g, 44.5 mmol, 0.40 eq). The reaction mixture was stirred at 105 °C for 3 days, then allowed to cool to RT. The solution was neutralised by addition of solid $NaHCO_3$ (10 g). The volatile components were removed *in vacuo* to give a yellow paste which was taken up in MeOH (300 mL). The mixture was cooled to −20 °C for 13 hours, then filtered to remove excess solid $NaHCO_3$ and sodium tosylate by-products. The filtrate was concentrated *in vacuo* to give a brown oil which was taken up in MeOH (50 mL) and cooled to −20 °C for 2 days. The resulting colourless crystalline solid was isolated by filtration, washed with $CHCl_3$ (25 mL), and dried. The remaining filtrate was concentrated *in vacuo* and purified by column chromatography over silica gel (CH_2Cl_2/MeOH 9.5:0.5) to give another batch of the crystalline solid. The combined materials provided **11** (14.9 g, 65%): R_f 0.40 (MeCN/EtOAc 8:2); m.p. 300–302 °C (MeOH, sealed tube) [lit.[36,37] 300–302 °C (MeOH, sealed tube)]; ^{1}H NMR (400 MHz; D_6-DMSO) δ_H 5.48 (1H, br s, C(2)O*H*), 5.44–5.36 (2H, m, C(4)O*H* and C(6)O*H*), 5.31 (1H, d, *J* 6.2, H-7) 4.31–4.24 (2H, dd, *J* 3.9, 3.9 H-1 and H-3), 4.09–4.04 (1H, m, H-5), 4.02–3.98 (1H, m, H-2), 3.97–3.92 (2H, m, H-4 and H-6); ^{13}C NMR (101 MHz;

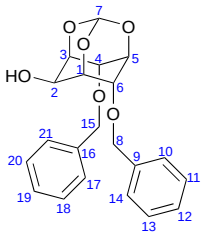
D_6-DMSO) δ 101.9 (C-7), 74.4 (C-1, C-3), 69.3 (C-5), 67.5 (C-4, C-6), 58.6 (C-2); LRMS *m/z* (ESI$^+$) 191.2 ([M+H]$^+$, 100%). These data are in good agreement with the literature values.[36,37]

D_6-*myo*-Inositol orthoformate 12



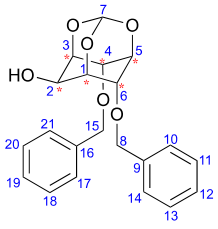
To a solution of D_6 *myo*-inositol **10** (608 mg, 3.27 mmol, 1.0 eq) in DMF (2.8 mL) were added triethylorthoformate (2.72 mL, 16.3 mmol, 5.0 eq) and PTSA·H_2O (248 mg, 1.31 mmol, 0.40 eq). The reaction mixture was stirred at 105 °C for 3 days, then allowed to cool to RT. The solvent was then concentrated *in vacuo* and the residue obtained was purified by column chromatography over silica gel (CH_2Cl_2/MeOH 10:0, 9.9:0.1, 9.8:0.2, 9.7:0.3, 9.6:0.4, 9.5:0.5) to afford **12** (200 mg, 31%, 89% D_6, 11% D_5) as a colourless solid: R_f 0.40 (MeCN/EtOAc 8:2); m.p. 299–301 °C (MeOH, sealed tube); ^{1}H NMR (500 MHz; D_6-DMSO) δ_H 5.45 (1H, s, C(2)O*H*), 5.43 (2H, br s, C(4)O*H*, C(6)O*H*), 5.27 (1H, s, H-7); ^{13}C NMR (126 MHz; D_6-DMSO) δ_C 101.8 (C-7), 73.8 (t$_D$, J_D 24.0, C-1, C-3), 68.6 (t$_D$, J_D 23.7, C-5), 66.8 (t$_D$, J_D 22.9, C-4, C-6), 58.0 (t$_D$, J_D 21.9, C-2); ^{2}H NMR (77 MHz; DMSO; D_6-DMSO) δ_D 4.24 (2D, br s, D-1 and D-3), 4.12–3.74 (4D, br s, D-5, D-2, D-4 and D-6); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3385 (O-H) (br), 3291 (O-H) (br), 3013 (w), 2360 (w), 2179 (w), 1410 (m), 1335 (m), 1258 (m), 1155 (s), 1096 (s), 1069 (s), 1044 (s), 995 (s), 955 (s), 935 (s); LRMS *m/z* (ESI$^+$) 218.0 ([MD_5+Na]$^+$, 11%), 219.0 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^-$) found 194.07178 [MD_5−H]$^-$, 195.07791 [MD_6−H]$^-$ ($C_7H_4D_6O_6Na$ requires 195.07812 [MD_6−H]$^-$). The X-ray crystal structure of this compound is represented in Figure 1, and the data can be found in the X-ray Crystallographic data section of the Supplementary Information.

4,6-Di-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate 13



LiH (167 mg, 21.0 mmol, 4.0 eq) was gradually added to a solution of **11** (1.00 g, 5.26 mmol, 1.0 eq) in anhydrous DMF (15 mL), and the resulting solution was stirred at RT for 30 minutes. Benzyl bromide (1.44 mL, 12.1 mmol, 2.3 eq) was then added dropwise and the solution was stirred for a further 48 hours. After quenching the reaction with H_2O (30 mL), the aqueous phase was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with H_2O (4 × 30 mL), and brine (2 × 30 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue obtained was filtered through a short plug of silica gel (Petroleum ether/EtOAc 6:4) then crystallised (EtOAc) to yield 13 (1.37 g, 71%) as a colourless solid: R_f 0.48 (Petroleum ether/EtOAc 5:5); m.p. 123–124 °C (EtOAc) [lit.[38] 122–124 °C (EtOAc); lit.[39] 124–125 °C (EtOAc)]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.31–7.26 (10H, m, H-10 to H-14 and H-17 to H-21), 5.47 (1H, d, *J* 1.0, H-7), 4.67 (2H, d, J_{AB} 11.5, H-8 and H-15), 4.59 (2H, d, J_{AB} 11.5, H-8' and H-15'), 4.48–4.45 (1H, m, H-2), 4.38 (2H, dd, *J* 3.7, 3.7, H-4 and H-6), 4.25–4.18 (3H, m, H-1, H-3 and H-5), 3.04 (1H, d, *J* 11.5, C(2)O*H*); LRMS *m/z* (ESI$^+$) 393.1 ([M+Na]$^+$, 100%). These data are in good agreement with the literature values.[37-40]

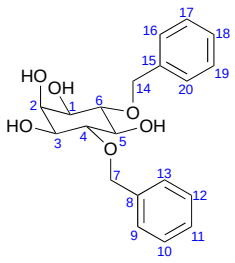
D_6-4,6-Di-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate 14



LiH (22 mg, 2.55 mmol, 4.0 eq) was gradually added to a solution of the orthoformate **12** (125 mg, 0.637 mmol, 1.0 eq, 89% D_6, 11% D_5) in anhydrous DMF (1.8 mL), and the resulting solution was stirred at RT for 30 minutes. Benzyl bromide (174 µL, 1.47 mmol, 2.3 eq) was then added dropwise and the solution was stirred for a further 48 hours. The reaction was quenched by addition of H_2O (3 mL) and the aqueous phase was extracted with EtOAc (4 × 5 mL). The combined organic layers were washed with H_2O (4 × 5 mL) and brine (4 × 5 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue

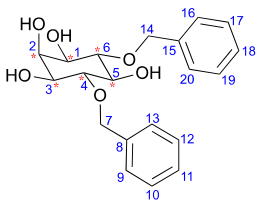
was purified by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4) to yield **14** (185 mg, 77%, 91% D_6, 9% D_5) as a colourless solid: R_f 0.48 (Petroleum ether/EtOAc 5:5); m.p. 125–127 °C (MeOH); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.29–7.22 (10H, m, H-10 to H-14 and H-17 to H-21), 5.44 (1H, s, H-7), 4.64 (2H, d, J_{AB} 11.5, H-8 and H-15), 4.56 (2H, d, J_{AB} 11.5, H-8' and H-15'); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 137.6 (C-9, C-16), 128.6 (C-11, C-13, C-18, C-20), 128.0 (C-12, C-19), 127.8 (C-10, C-14, C-17, C-21), 103.4 (C-7), 73.2 (t_D, J_D 22.6, C-4, C-6), 72.5 (t_D, J_D 24.2, C-1, C-3), 71.8 (C-8, C-15), 67.4 (t_D, J_D 23.7, C-2), 61.0 (t_D, J_D 22.7, C-5); ^{2}H NMR (77 MHz; $CHCl_3$; $CDCl_3$) δ_D 4.44 (1D, br s, D-2), 4.36 (2D, br s, D-4 and D-6), 4.22 (3D, br s, D-1, D-3 and D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3503 (m), 3020 (w), 2981 (w), 2360 (w), 2342 (w), 1498 (m), 1452 (m), 1390 (m), 1316 (m), 1245 (m), 1208 (m), 1165 (s), 1117 (m), 1107 (m), 1082 (s), 1021 (m), 996 (m), 968 (m), 936 (m), 866 (s), 783 (m), 746 (s), 730 (s), 695 (s); LRMS *m/z* (ESI$^+$) 398.2 ([MD_5+Na]$^+$, 9%), 399.2 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 398.16238 [MD_5+Na]$^+$, 399.16829 [MD_6+Na]$^+$ ($C_{21}H_{16}D_6O_6Na$ requires 399.16852 [MD_6+Na]$^+$); RP-HPLC (Method 2) t_R = 12.59 min, 99.96%.

4,6-Di-*O*-benzyl-*myo*-inositol 15



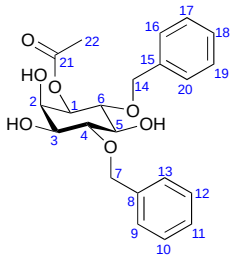
The protected orthoformate **13** (1.00 g, 2.70 mmol, 1.0 eq) was dissolved in MeOH (2.7 ml) and PTSA·H_2O (514 mg, 2.70 mmol, 1.0 eq) was added. The solution was stirred for 24 hours, then concentrated *in vacuo*. The residue was filtered through a short plug of silica gel (EtOAc) then crystallised (Hexane/CH_2Cl_2) to yield **15** (890 mg, 92%) as a colourless, fluffy, crystalline solid: R_f 0.40 (EtOAc); m.p. 140–141 °C (Hexane/CH_2Cl_2) [lit.[1] 138.5–139 °C (Hexane/CH_2Cl_2)]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.40–7.28 (10H, m, H-9 to H-13 and H-16 to H-20), 4.90 (2H, d, J_{AB} 11.4, H-7 and H-14), 4.84 (2H, d, J_{AB} 11.4, H-7' and H-14'), 4.13 (1H, dd, *J* 2.9, 2.9, H-5), 3.70–3.64 (2H, m, H-4 and H-6), 3.58–3.52 (3H, m, H-1, H-2 and H-3), 2.37 (4H, br s, C(1)O*H*, C(2)O*H*, C(3)O*H* and C(5)O*H*); LRMS *m/z* (ESI$^+$) 383.1 ([M+Na]$^+$, 100%). These data are in good agreement with the literature values.[41]

D_6-4,6-Di-*O*-benzyl-*myo*-inositol 16



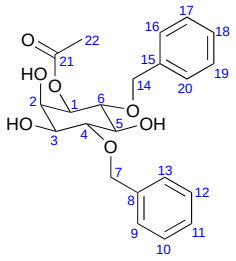
The protected orthoformate **14** (179 mg, 0.476 mmol, 1.0 eq, 91% D_6, 9% D_5) was dissolved in MeOH (0.50 mL) and PTSA·H_2O (90 mg, 0.476 mmol, 1.0 eq) was added. The solution was stirred for 24 hours then concentrated *in vacuo*. The residue obtained was filtered through a short pad of silica gel (EtOAc) then crystallised (Hexane/CH_2Cl_2) to yield **16** (150 mg, 86%, 92% D_6, 8% D_5) as a colourless, fluffy, crystalline solid: R_f 0.40 (EtOAc); m.p. 144–145 °C (Hexane/CH_2Cl_2); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.41–7.28 (10H, m, H-9 to H-13 and H-16 to H-20), 4.90 (2H, d, J_{AB} 11.5, H-7 and H-14), 4.84 (2H, d, J_{AB} 11.5, H-7' and H-14'), 2.69 (1H, br s, C(5)O*H*), 2.52 (1H, br s, C(2)O*H*), 2.51 (2H, br s, C(1)O*H* and C(3)O*H*); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 138.6 (C-8, C-15), 128.8 (C-10, C-12, C-17, C-19), 128.2 (C-9, C-11, C-13, C-16, C-18, C-20), 81.1 (t_D, J_D 21.9, C-4, C-6), 75.2 (C-7, C-14), 74.3 (t_D, J_D 21.7, C-2), 71.4 (t_D, J_D 21.7, C-1, C-3), 71.1 (t_D, J_D 22.7, C-5); ^{2}H NMR (77 MHz; $CHCl_3$; $CDCl_3$) δ_D 4.10 (1D, br s, D-5), 3.65 (2D, br s, D-4 and D-6), 3.53 (3D, br s, D-1, D-2 and D-3); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3658 (O-H) (br), 3529 (O-H) (br), 3435 (O-H) (br), 3354 (O-H) (br), 2981 (s), 2885 (m), 1496 (w), 1473 (w), 1455 (w), 1384 (m), 1306 (w), 1251 (w), 1206 (m), 1176 (m), 1139 (m), 1083 (m), 1060 (m), 1038 (m), 1027 (m), 1013 (m), 992 (m), 980 (m), 966 (m), 952 (m), 936 (m), 754 (m), 704 (s), 696 (s); LRMS *m/z* (ESI$^+$) 388.2 ([MD_5+Na]$^+$, 9%), 389.2 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 388.17803 [MD_5+Na]$^+$, 389.18402 [MD_6+Na]$^+$ ($C_{20}H_{18}D_6O_6Na$ requires 389.18417 [MD_6+Na]$^+$); RP-HPLC (Method 2) t_R = 9.66 min, 97.15%.

(−)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (−)-9



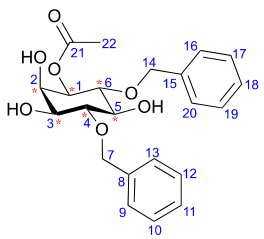
The immobilised Lipozyme® TL-IM (150 mg) was added to a solution of **15** (50 mg, 0.139 mmol, 1.0 eq) in vinyl acetate (12.5 mL) and hexane (12.5 mL). After stirring at 45 °C for 15 hours the reaction mixture was filtered through a pad of Celite®, washed with hexane (3 × 2 mL) and the combined filtrates were concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 8:2) to give (−)-**9** (55 mg, 98%, >99% *ee*) as a colourless solid: $[\alpha]_D^{25}$ = −39.1 (*c* 1.0, MeOH) [lit.[41] $[\alpha]_D^{20}$ = −39.3 (*c* 1.0, MeOH); lit.[1] $[\alpha]_D^{20}$ = −39.1 (*c* 1.0, MeOH)]; Chiral HPLC (Heptane/IPA 85:15, 1.0 mL.min^{-1}, 254 nm) t_R = 15.65 min, 99.45% (−)-**9**, >99% *e.e.* (other enantiomer not observed, t_R = 18.89 min). All other data (R_f, m.p., ^{1}H NMR, ^{13}C NMR, IR) matched those of the racemic product (±)-**9** and that of the literature values.[1,41] See Figure S1.

(±)-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (±)-9



To a solution of **15** (150 mg, 0.416 mmol, 1.0 eq) in anhydrous CH_2Cl_2 (4.0 mL) and at −20 °C were added acetic anhydride (39 µL, 0.416 mmol, 1.0 eq), Et_3N (64 µL, 0.458 mmol, 1.1 eq) and 4-DMAP (3 mg, 0.0208 mmol, 0.050 eq). The reaction mixture was stirred at −20 °C for 18 hours, then warmed to −15 °C, and stirred for a further 12 hours. The solution was diluted in CH_2Cl_2 (5 mL) and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 mL), and brine (2 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 4:6) to give a mixture of regioisomers containing (±)-**9**. Separation of this mixture was achieved by semi-preparative, reverse phase HPLC (Method 1) to give (±)-**9** (11 mg, 7%) as a colourless solid: R_f 0.67 (EtOAc); m.p. 97–98 °C (EtOAc) [lit.[41] 96–97 °C]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.39–7.27 (10H, m, H-16 to H-20 and H-9 to H-13), 4.99 (1H, d, J_{AB} 11.4, H-7), 4.88 (1H, dd, *J* 10.0, 2.7, H-1), 4.80 (1H, d, J_{AB} 11.4, H-14), 4.75 (1H, d, J_{AB} 11.4, H-7'), 4.74 (1H, d, J_{AB} 11.4, H-14'), 4.22 (1H, dd, *J* 2.8, 2.7, H-2), 3.92 (1H, dd, *J* 10.0, 9.6, H-6), 3.71 (1H, dd, *J* 9.6, 9.6, H-4), 3.66–3.57 (2H, m, H-5 and H-3), 2.49 (1H, d, *J* 2.1, C(5)O*H*), 2.44 (1H, d, *J* 3.2, C(3)O*H*), 2.39 (1H, s, C(2)O*H*), 2.08 (3H, s, H-22); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.3 (C-21), 138.6, 138.5 (C-8, C-15), 128.9, 128.8 (C-10, C-12, C-17, C-19), 128.21, 128.1 (C-11, C-18), 128.18, 127.8 (C-9, C-13, C16, C-20), 80.8 (C-4), 79.7 (C-6), 75.5 (C-14), 75.3 (C-7), 75.1 (C-5), 73.5 (C-1), 71.4 (C-3), 70.2 (C-2), 21.2 (C-22); LRMS *m/z* (ESI$^+$) 425.1 ([M+Na]$^+$, 100%); Chiral HPLC (Heptane/IPA 85:15, 1.0 mL.min^{-1}, 254 nm) t_R = 15.29 min, 50.90% (−)-151, t_R = 18.89 min, 49.07% (+)-151 [lit.[41] (Chiralcel OD-H column, Hexane/IPA 70:30, 0.8 mL.min^{-1}) t_R = 43.6 min (+)-**9**; t_R = 50.5 min (−)-**9**]. These data are in good agreement with the literature values.[1,41] See Figure S1.

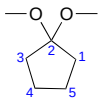
D_6-(−)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (−)-17



The immobilised Lipozyme® TL-IM (403 mg) was added to a solution of **16** (140 mg, 0.382 mmol, 1.0 eq, 92% D_6, 8% D_5) in vinyl acetate (33 mL) and hexane (33 mL). After stirring at 45 °C for 15 hours, the reaction mixture was filtered through a pad of Celite®, washed with hexane (3 × 10 mL), and the combined filtrates were concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 8:2) to give (−)-**17** (128 mg, 84%, >99% *e.e.*, 89% D_6, 11% D_5) as a colourless solid: R_f 0.64 (EtOAc); $[\alpha]_D^{25} = -38.8$ (*c* 1.0, MeOH); m.p. 97–98 °C (EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.39–7.27 (10H, m, H-9 to H-13 and H-16 to H-20), 4.98 (1H,

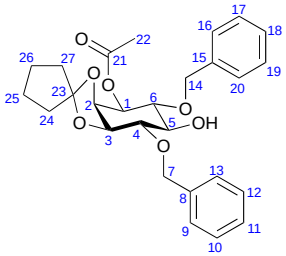
d, J_{AB} 11.4, H-7), 4.80 (1H, d, J_{AB} 11.7, H-14), 4.75 (1H, d, J_{AB} 11.4, H-7'), 4.74 (1H, d, J_{AB} 11.7, H-14'), 2.53 (1H, br s, C(5)O*H*), 2.50 (1H, br s, C(2)O*H*), 2.48 (1H, br s, C(3)O*H*), 2.08 (3H, s, H-22); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.3 (C-21), 138.6, 138.5 (C-8, C-15), 128.8, 128.7 (C-10, C-12, C-17, C-19), 128.19, 128.0 (C-11, C-18), 128.17, 127.7 (C-9, C-13, C-16, C-20), 80.3 (t_D, J_D 22.0, C-4), 79.1 (t_D, J_D 22.0, C-6), 75.4 (C-14), 75.2 (C-7), 74.4 (t_D, J_D 21.8, C-5), 73.0 (t_D, J_D 22.2, C-1), 70.8 (t_D, J_D 21.5, C-3), 69.6 (t_D, J_D 23.0, C-2), 21.2 (C-22); ^{2}H NMR (77 MHz; $CHCl_3$; $CDCl_3$) δ_D 4.85 (1D, br s, D-1), 4.19 (1D, br s, D-2), 3.91 (1D, br s, D-6), 3.68 (1D, br s, D-4), 3.59 (2D, br s, D-3 and D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3658 (O-H) (br), 2981 (s), 2888 (m), 1737 (C=O) (w), 1494 (w), 1473 (w), 1462 (w), 1381 (m), 1253 (m), 1209 (w), 1155 (m), 1090 (m), 1072 (m), 1031 (m), 1011 (m), 953 (m); LRMS *m/z* (ESI$^+$) 430.2 ([MD_5+Na]$^+$, 12%), 431.2 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 430.18850 [MD_5+Na]$^+$, 431.19456 [MD_6+Na]$^+$ ($C_{22}H_{20}D_6O_7Na$ requires 431.19473 [MD_6+Na]$^+$); RP-HPLC (Method 2) t_R = 10.71 min, 98.70%; Chiral HPLC (Heptane/IPA 85:15, 1.0 mL.min^{-1}, 254 nm) t_R = 15.89 min, 99.97% (−)-**17**, >99% *e.e.* (other enantiomer not observed, t_R = 18.89 min). See Figure S1.

1,1-Dimethoxycyclopentane 18



To a solution of cyclopentanone (6.31 mL, 71.3 mmol, 1.0 eq) in hexane (48 mL) were added K-10 montmorillonite clay (10.8 g) and trimethylorthoformate (17.9 mL, 159 mmol, 2.3 eq). The suspension was stirred rapidly for 18 hours at RT. The dark brown reaction mixture was then filtered through a pad of Celite® and washed with hexane (2 × 10 mL) and Et_2O (2 × 10 mL). The combined filtrates were concentrated *in vacuo* to give **18** (7.08 g, 88%) as a yellow oil. Analysis by ^{1}H NMR showed that the product was ~97% pure. This compound was therefore used in subsequent steps without further purification: R_f 0.51 (Petroleum ether/EtOAc 8:2); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 3.20 (6H, s, C(2)OC*H*$_3$), 1.80–1.71 (4H, m, H-3 and H-1), 1.69–1.61 (4H, m, H-4 and H-5); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 112.3 (C-2), 49.4 (C(2)O*C*H$_3$), 34.3 (C-3, C-1), 23.3 (C-4, C-5); HRMS *m/z* (EI/FI$^+$) found 130.0997 [M]$^+$ ($C_7H_{14}O_2$ requires 130.0994 [M]$^+$). These data are in good agreement with the literature values.[12,42]

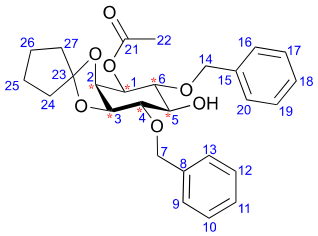
(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-*myo*-inositol (−)-19



To a clear solution of (−)-**9** (800 mg, 1.99 mmol, 1.0 eq) and **18** (4.55 mL, 33.2 mmol, 17 eq) in CH_2Cl_2 (5.0 mL) was added PTSA·H_2O (30 mg, 0.159 mmol, 0.080 eq). The resulting green solution was stirred at RT for 18 hours. The dark purple solution was then quenched with Et_3N (22 µL, 0.159 mmol, 0.080 eq) and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) to give (−)-**19** (857 mg, 92%) as a yellow-brown oil: R_f 0.86 (Petroleum ether/EtOAc 2:8); $[\alpha]_D^{25}$ = −23.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.41–7.26 (10H, m, H-9 to H-13 and H-16 to H-20), 5.19 (1H, dd, *J* 8.3, 3.8, H-1), 4.93 (1H, d, J_{AB} 11.6, H-7), 4.82 (1H, d, J_{AB} 11.6, H-14), 4.76 (1H, d, J_{AB} 11.6, H-14'), 4.72 (1H, d, J_{AB} 11.6, H-7'), 4.33 (1H, dd, *J* 5.7, 3.8, H-2), 4.20–4.14 (1H, m, H-3), 3.85–3.76 (1H, m, H-6), 3.68–3.60 (2H, m, H-5 and H-4), 2.66 (1H, s, C(5)O*H*), 2.08 (3H, s, H-22), 1.98–1.84 (2H, m, H-24 or H-27), 1.79–1.62 (6H, m, H-25, H-26 and H-24 or H-27); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.3 (C-21), 138.5, 138.3 (C-8, C-15), 128.6, 128.2, 128.0, 127.9, 127.7 (C-9 to C-13, C-16 to C-20), 120.1 (C-23), 81.1 (C-4), 79.5 (C-6), 78.5 (C-3), 74.5 (C-14), 74.4 (C-2), 73.7 (C-5), 73.5 (C-7), 71.3 (C-1), 37.4, 37.2 (C-24, C-27), 24.0, 23.6 (C-25, C-26), 21.2 (C-22); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3471 (O-H) (br), 2972 (w), 2874 (w), 1742 (C=O) (m), 1454 (m), 1370 (m), 1335 (m), 1234 (s), 1103 (s), 1070 (s), 1028 (s), 972 (m), 911 (m), 732 (s), 697 (s); LRMS *m/z* (ESI$^+$) 469.2 ([M+H]$^+$, 38%), 491.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 491.2032 [M+Na]$^+$ ($C_{27}H_{32}O_7Na$ requires 491.2040 [M+Na]$^+$); NP-HPLC (Method 5) t_R = 6.36 min,

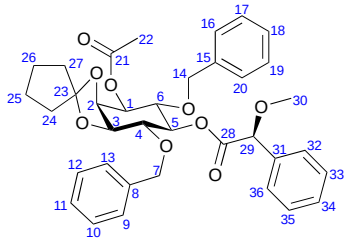
90.41%; Chiral HPLC (Heptane/IPA 85:15, 1.0 mL.min^{-1}, 254 nm) t_R = 16.75 min, 99% (−)-**19**, >99% *e.e.* (other enantiomer not observed).[43]

D_6-(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-*myo*-inositol (−)-20



To a clear solution of (−)-**17** (99 mg, 0.242 mmol, 1.0 eq, 89% D_6, 11% D_5) and **18** (565 µL, 4.11 mmol, 17 eq) in CH_2Cl_2 (0.60 mL) was added PTSA·H_2O (4 mg, 0.0194 mmol, 0.080 eq). The resulting green solution was allowed to stir at RT for 19 hours. The dark purple solution was then quenched with Et_3N (3 µL, 0.0194 mmol, 0.080 eq) and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) to give (−)-**20** (100 mg, 87%, 91% D_6, 9% D_5) as a yellow-brown oil: R_f 0.86 (Petroleum ether/EtOAc 2:8); $[\alpha]_D^{25} = -29.4$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.41–7.26 (10H, m, H-9 to H-13 and H-16 to H-20), 4.92 (1H, d, J_{AB} 11.6, H-7), 4.82 (1H, d, J_{AB} 11.5, H-14), 4.76 (1H, d, J_{AB} 11.5, H-14'), 4.72 (1H, d, J_{AB} 11.6, H-7'), 2.70 (1H, br s, C(5)O*H*), 2.09 (3H, s, H-22), 1.98–1.84 (2H, m, H-24 or H-27), 1.79–1.58 (6H, m, H-25, H-26 and H-24 or H-27); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.3 (C-21), 138.4, 138.2 (C-8, C-15), 128.5, 128.1, 127.7 (C-9, C-10, C-12, C-13, C-16, C-17, C-19, C-20), 127.9, 127.8 (C-11, C-18), 120.0 (C-23), 80.4 (t_D, J_D 21.7, C-4), 78.9 (t_D, J_D 21.8, C-6), 77.8 (t_D, J_D 22.8, C-3), 74.4 (C-14), 73.9 (t_D, J_D 22.9, C-2), 73.4 (C-7), 73.1 (t_D, J_D 21.6, C-5), 70.8 (t_D, J_D 22.1, C-1), 37.4, 37.2 (C-24, C-27), 24.0, 23.5 (C-25, C-26), 21.2 (C-22); ^{2}H NMR (92 MHz; $CHCl_3$; $CDCl_3$) δ_D 5.19 (1D, br s, D-1), 4.34 (1D, br s, D-2), 4.19 (1D, br s, D-3), 3.81 (1D, br s, D-6), 3.64 (2H, br s, D-5 and D-4); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3486 (O-H) (br), 2962 (w), 2873 (w), 1738 (C=O) (m), 1370 (w), 1337 (m), 1309 (m), 1232 (m), 1211 (m), 1101 (s), 1070 (s), 1026 (s), 995 (s), 911 (m), 733 (s), 697 (s); LRMS *m/z* (ESI$^+$) 496.2 ([MD_5+Na]$^+$, 10%), 497.2 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 496.23569 [MD_5+Na]$^+$, 497.24162 [MD_6+Na]$^+$ ($C_{27}H_{26}D_6O_7Na$ requires 497.24168 [MD_6+Na]$^+$); RP-HPLC (Method 2) t_R = 14.21 min, 100%.

(+)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-((*S*)-α-methoxyphenyl-acetoxy)-*myo*-inositol (+)-S1a

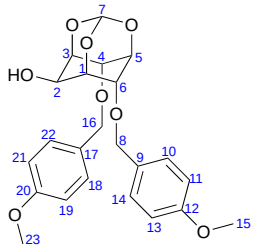


(*S*)-(+)-α-Methoxyphenylacetic acid (13 mg, 0.0768 mmol, 2.0 eq), 1-ethyl-3-(3-dimethylamino-propyl)carbodiimide (20 mg, 0.104 mmol, 2.7 eq) and DMAP (2.3 mg, 0.0192 mmol, 0.50 eq) were added to a solution of (−)-**19** (18 mg, 0.0384 mmol, 1.0 eq) in CH_2Cl_2 (0.4 mL). After 48 hours, the reaction mixture was diluted with CH_2Cl_2 (3 mL), and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 5 mL), brine (5 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2) afforded (+)-**S1a** (16 mg, 68%) as a colourless solid: R_f 0.26 (Petroleum ether/EtOAc 8:2); $[\alpha]_D^{25}$ = +4.8 (*c* 0.55, $CHCl_3$); m.p. 105–107 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz, CD_2Cl_2) δ_H 7.42–7.37 (2H, m, H-32 and H-36), 7.36–7.19 (11H, m, H-33 to H-35, H-17 to H-19 and H-9 to H-13), 7.10–7.05 (2H, m, H-16 and H-20), 5.17 (1H, dd, *J* 8.9, 3.7, H-1), 5.11 (1H, dd, *J* 8.2, 8.2, H-5), 4.79 (1H, d, J_{AB} 11.8, H-7), 4.68 (1H, s, H-29), 4.62 (1H, d, J_{AB} 11.8, H-7'), 4.32 (1H, dd, *J* 6.0, 3.7, H-2), 4.23 (1H, dd, *J* 6.1, 6.0, H-3), 4.11 (1H, d, J_{AB} 11.4, H-14), 3.98 (1H, d, J_{AB} 11.4, H-14'), 3.74–3.69 (1H, m, H-4 and H-6), 3.30 (3H, s, H-30), 1.94 (3H, s, H-22), 1.96–1.91 (2H, m, H-24 and H-27), 1.74–1.58 (6H, m, H-24', H-27', H-25 and H-26); ^{13}C NMR (126 MHz, CD_2Cl_2) δ_C 170.1 (C-21), 169.9 (C-28), 138.57, 138.42 (C-8, C-15), 136.6 (C-31), 129.2, 129.0, 128.7, 128.5 (C-10 to C-12, C-17 to C-19 and C-33 to C-35), 128.2, 128.1, 127.8, 127.7 (C-9, C-13, C-16, C-20, C-32, C-36), 120.3 (C-23), 82.9 (C-29), 79.1 (C-4), 78.1 (C-3), 77.3 (C-6), 75.2 (C-5), 74.3 (C-2), 73.9 (C-14), 73.3 (C-7), 70.7 (C-1), 57.6 (C-30), 37.23, 37.17 (C-24, C-27), 24.2, 23.7 (C-25, C-27), 21.1 (C-22); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3089

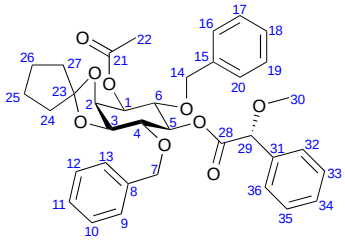
(w), 3063 (w), 3032 (w), 2956 (m), 2829 (w), 2359 (w), 2337 (w), 1748 (C=O) (s), 1497 (w), 1455 (m), 1370 (m), 1337 (m), 1234 (s), 1200 (C-O) (m), 1177 (m), 1109 (s), 1073 (m), 1029 (m), 1005 (m), 973 (m), 737 (m), 698 (m); LRMS *m/z* (ESI$^+$) 639.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 639.25568 [M+Na]$^+$ ($C_{36}H_{40}O_9Na$ requires 639.25645 [M+Na]$^+$).[1] This compound was employed for the determination of the absolute configuration of (−)-**19** by ^{1}H NMR. See Supplementary Results and Discussion, Scheme S1, Figure S2 and Table S1.

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-((*R*)-α-methoxyphenyl- acetoxy)-*myo*-inositol (−)-S1b

(*R*)-(−)-α-Methoxyphenylacetic acid (13 mg, 0.0768 mmol, 2.0 eq), 1-ethyl-3-(3-dimethylamino-propyl)carbodiimide (20 mg, 0.104 mmol, 2.7 eq) and DMAP (2.3 mg, 0.0192 mmol, 0.50 eq) were added to a solution of (−)-**19** (18 mg, 0.0384 mmol, 1.0 eq) in CH_2Cl_2 (0.4 mL). After 24 hours stirring at RT, the reaction mixture was diluted with CH_2Cl_2 (3 mL), and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 5 mL), brine (5 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3) afforded (−)-**S1b** (17 mg, 72%) as a colourless solid: R_f 0.26 (Petroleum ether/EtOAc 8:2); $[\alpha]_D^{25}$ = −5.5 (*c* 0.34, $CHCl_3$); m.p. 105–107 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz, CD_2Cl_2) δ_H 7.41–7.36 (2H, m, H-32 and H-36), 7.35–7.18 (11H, m, H-33 to H-35, H-10 to H-12 and H-16 to H-20), 7.10–7.05 (2H, m, H-9 and H-13), 5.21 (1H, dd, *J* 8.7, 3.8, H-1), 5.11 (1H, dd, *J* 8.5, 8.4, H-5), 4.65 (1H, s, H-29), 4.58 (1H, d, J_{AB} 11.6, H-14), 4.51 (1H, d, J_{AB} 11.6, H-14'), 4.49 (1H, d, J_{AB} 12.0, H-7), 4.32 (1H, dd, *J* 6.0, 3.8, H-2), 4.23 (1H, d, J_{AB} 12.0, H-7'), 4.15 (1H, dd, *J* 6.1, 6.0, H-3), 3.90 (1H, dd, *J* 8.7, 8.4, H-6), 3.54 (1H, dd, *J* 8.5, 6.1, H-4), 3.30 (3H, s, H-30), 2.03 (3H, s, H-22), 1.90–1.83 (1H, m, H-24 or H-27), 1.82–1.75 (1H, m, H-24 or H-27), 1.69–1.58 (6H, m, H-24', H-27', H-25 and H-26); ^{13}C NMR (126 MHz, CD_2Cl_2) δ_C 170.2 (C-21), 170.0 (C-28), 138.52, 138.47 (C-8, C-15), 136.5 (C-31), 129.1, 129.0, 128.7, 128.4 (C-10 to C-12, C-17 to C-19 and C-33 to C-35), 128.1, 128.0, 127.9, 127.73, 127.67 (C-9, C-13, C-16, C-20, C-32, C-36), 120.3 (C-23), 83.0 (C-29), 79.2 (C-4), 78.1 (C-3), 77.3 (C-6), 75.2 (C-5), 74.6 (C-14), 74.3 (C-2), 73.0 (C-7), 71.0 (C-1), 57.7 (C-30), 37.3, 37.1 (C-24, C-27), 24.2, 23.7 (C-25, C-27), 21.2 (C-22); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3089 (w), 3063 (w), 3032 (w), 2956 (m), 2829 (w), 2360 (w), 2337 (w), 1748 (C=O) (s), 1497 (w), 1455 (m), 1434 (w), 1370 (m), 1337 (m), 1234 (s), 1200 (C-O) (s), 1177 (C-O) (s), 1109 (s), 1073 (s), 1029 (m), 1005 (m), 973 (m), 913 (m), 873 (w), 737 (m), 698 (m); LRMS *m/z* (ESI$^+$) 639.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 639.25598 [M+Na]$^+$ ($C_{36}H_{40}O_9Na$ requires 639.25645 [M+Na]$^+$).[1] This compound was employed for the determination of the absolute configuration of (−)-**19** by ^{1}H NMR. See Supplementary Results and Discussion, Scheme S1, Figure S2 and Table S1.



4,6-Di-*O*-(4-methoxybenzyl)-*myo*-inositol 1,3,5-orthoformate S2

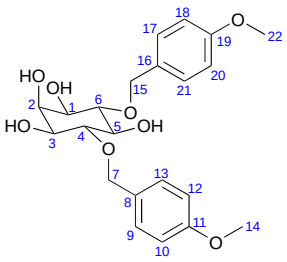


Sodium hydride (3.02 g, 75.4 mmol, 2.05 eq, 60% dispersion in mineral oil) was suspended in anhydrous DMF (200 mL) and cooled to 0 ºC. To this suspension was added dropwise a solution of *myo*-inositol orthoformate **11** (7.00 g, 36.8 mmol, 1.0 eq) in anhydrous DMF (150 mL). The suspension was stirred for 1 hour at RT, then PMBCl (11.3 mL, 82.8 mmol, 2.25 eq) was added dropwise at 0 ºC. The suspension was warmed to RT and stirred for a further 17 hours. The reaction was quenched with H_2O (60 mL) and the aqueous layer was extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with H_2O (2 × 30 mL), and brine (2 × 30 mL),

[1] HPLC data was not acquired on this compound as it seemed to be breaking down on both normal phase and reversed phase columns.

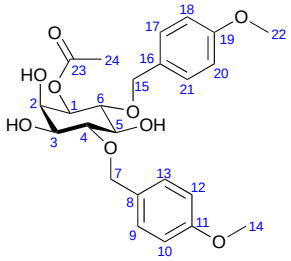
then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5, 4:6) gave **S2** (9.08 g, 55%) as a colourless solid: R_f 0.71 (EtOAc); m.p. 118–119 °C (EtOAc); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.22–7.13 (4H, m, H-10, H-14, H-18 and H-22), 6.86–6.77 (4H, m, H-11, H-13, H-19 and H-21), 5.46 (1H, s, H-7), 4.58 (2H, d, *J* 11.0, H-8 and H-16), 4.50 (2H, d, *J* 11.0, H-8' and H-16'), 4.43–4.38 (1H, m, H-2), 4.36–4.32 (2H, m, H-4 and H-6), 4.22–4.13 (3H, m, H-1, H-3 and H-5), 3.80 (6H, s, H-15 and H-23), 3.03 (1H, d, *J* 11.5, C(2)O*H*); ν_{max}(thin film)/cm^{-1} 3476 (O-H) (br), 3001 (w), 2958 (w), 2872 (w), 2837 (w), 1613 (m), 1586 (w), 1513 (s), 1464 (w), 1442 (w), 1403 (w), 1378 (w), 1349 (w), 1302 (m), 1245 (s), 1160 (s), 1136 (m), 1097 (s), 1031 (m), 988 (s), 956 (m), 938 (m), 889 (m), 818 (m), 808 (m), 778 (w), 764 (w), 731 (w); LRMS *m/z* (ESI$^+$) 453.2 ([M+Na]$^+$, 100%). These data are in good agreement with the literature values.[40,44]

4,6-Di-*O*-(4-methoxybenzyl)-*myo*-inositol S3



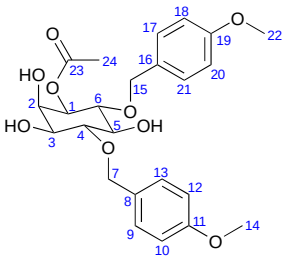
To a solution of the orthoformate **S2** (1.66 g, 3.86 mmol, 1.0 eq) in MeOH/H_2O (73 mL, 10:1 *v/v*) was added 8 drops of 2M HCl until a pH of 2–3 was reached. The reaction was stirred at 35 °C for 18 hours and at 45 °C for 23 hours. The reaction was then cooled to RT and diluted with EtOAc (200 mL). $NaHCO_3$ was added (200 mL) and the aqeuous layers were extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with $NaHCO_3$ (3 × 100 mL), then dried ($MgSO_4$), filtered, and evaporated *in vacuo*. The solid obtained was crystallised from EtOAc to give **S3** (1.20 g, 74%) as colourless crystals: R_f 0.64 (EtOAc); m.p. 144–145 °C (EtOAc); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.34–7.28 (4H, m, H-9, H-13, H-17 and H-21), 6.93–6.87 (4H, m, H-10, H-12, H-18 and H-20), 4.83 (2H, d, J_{AB} 11.1, H-7 and H-15), 4.77 (2H, d, J_{AB} 11.1, H-7' and H-15'), 4.16–4.12 (1H, m, H-2), 3.81 (6H, s, H-14 and H-22), 3.64 (2H, dd, *J* 9.5, 9.3, H-4 and H-6), 3.55–3.48 (3H, m, H-1, H-3 and H-5), 2.56–2.54 (1H, m, -O*H*), 2.46 (1H, d, *J* 2.2, -O*H*), 2.43 (1H, s, -O*H*), 2.42 (1H, s, -O*H*); LRMS *m/z* (ESI$^+$) 443.2 ([M+Na]$^+$, 100%). These data are in good agreement with the literature values.[40]

(+)-1D-1-*O*-Acetyl-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol (+)-S4



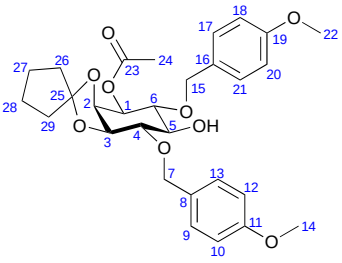
The immobilised Lipozyme® TL-IM (2.82 g) was added to a solution of **S3** (1.10 g, 1.62 mmol, 1.0 eq) in vinyl acetate (60 mL) and hexane (60 mL). After stirring at 45 °C for 15 hours the reaction mixture was filtered through a pad of Celite®, washed with hexane (3 × 20 mL) and the combined filtrates were concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2) to give (+)-**S4** (1.15 g, 95%, >99% *e.e.*) as a colourless foam: $[\alpha]_D^{25}$ = +24.0 (*c* 1.0, CH_3Cl); Chiral HPLC (Heptane/IPA 85:15, 1.0 mL.min^{-1}, 254 nm) t_R = 55.84 min, 96.97% (+)-**S4**, >99% *e.e.* (other enantiomer not observed, t_R = 59.93 min). All other data (R_f, m.p., ^{1}H NMR, ^{13}C NMR, IR) matched those of the racemic product (±)-**S4**.

(±)-1-*O*-Acetyl-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol (±)-S4



To a solution of **S3** (93 mg, 0.221 mmol, 1.0 eq) in anhydrous CH_2Cl_2 (4.0 mL) and at −20 °C were added acetic anhydride (21 µL, 0.221 mmol, 1.0 eq), Et_3N (34 µL, 0.243 mmol, 1.1 eq) and 4-DMAP (1.4 mg, 0.0111 mmol, 0.050 eq). The reaction mixture was stirred at −20 °C for 18 hours, then warmed to −15 °C, and stirred for a further 12 hours. The solution was diluted in CH_2Cl_2 (5 mL) and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 mL), and brine (2 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue obtained was purified twice by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5, 4:6) to give (±)-**S4** (9.5 mg, 9%) as a colourless solid: R_f 0.31 (2:8 Petroleum ether/EtOAc); m.p. 126–130 °C (EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.32–7.27 (2H, m, H-9 and H-13), 7.26–7.22 (2H, m, H-17 and H-21), 6.92–6.86 (4H, m, H-10, H-12, H-18 and H-20), 4.91 (1H, d, J_{AB} 11.2, H-7), 4.85 (1H, dd, *J* 10.1, 2.8, H-1), 4.74 (1H, d, J_{AB} 11.2, H-15), 4.66 (1H, d, J_{AB} 11.2, H-7'), 4.64 (1H, d, J_{AB} 11.2, H-15'), 4.22–4.18 (1H, m, H-2), 3.89 (1H, dd, *J* 10.1, 9.5, H-6), 3.80 (6H, H-14 and H-22), 3.67 (1H, dd, *J* 9.5, 9.5, H-4), 3.60–3.53 (2H, m, H-3 and H-5), 2.48 (1H, d, *J* 2.0, C(5)O*H*), 2.44 (1H, d, *J* 3.2, C(3)O*H*), 2.43 (1H, br s, C(2)O*H*), 2.12 (3H, s, H-24); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.3 (C-23), 159.6, 159.5 (C-11, C-19), 130.7, 130.6 (C-8, C-16), 129.9 (C-9, C-13), 129.5 (C-17, C-21), 114.3, 114.2 (C-10, C-12, C-18, C-20), 80.4 (C-4), 79.3 (C-6), 75.1 (C-15), 75.0 (C-5), 74.9 (C-7), 73.5 (C-1), 71.3 (C-3), 70.1 (C-2), 55.4 (C-14, C-22), 21.3 (C-24); $\bar{\nu}_{max}$(solid)/cm^{-1} 3494 (O-H) (br), 3347 (O-H) (br), 2959 (w), 2915 (w), 2839 (w), 1726 (C=O) (m), 1613 (m), 1514 (s), 1467 (w), 1371 (m), 1300 (w), 1241 (s), 1183 (m), 1173 (m), 1114 (s), 1075 (s), 1020 (s), 945 (m), 916 (w), 887 (w), 850 (w), 814 (s), 773 (w), 760 (w), 729 (m), 707 (m); LRMS *m/z* (ESI$^+$) 485.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 485.17805 [M+Na]$^+$ ($C_{24}H_{30}O_9Na$ requires 485.17820 [M+Na]$^+$); RP-HPLC (Method 2) t_R = 9.56 min, 98.09%; Chiral HPLC (Heptane/IPA 85:15, 1.0 mL.min^{-1}, 254 nm) t_R = 55.09 min, 47.75% (−)-**S4**, t_R = 59.93 min, 52.25% (+)-**S4**.

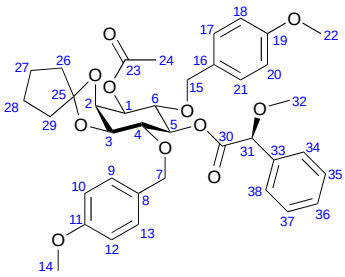
(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol (−)-S5



To a clear solution of (+)-**S4** (1.09 g, 2.36 mmol, 1.0 eq) and **18** (6 mL, 40.2 mmol, 17 eq) in CH_2Cl_2 (13 mL) was added PTSA·H_2O (36 mg, 0.189 mmol, 0.080 eq). The resulting green solution was stirred at RT for 15 hours. The black solution was then quenched with Et_3N (26 µL, 0.189 mmol, 0.080 eq) and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3) to give (−)-**S5** (1.17 g, 94%) as a yellow-brown oil: R_f 0.83 (2:8 Petroleum ether/EtOAc); $[\alpha]_D^{25}$ = −25.3 (*c* 1.0, CH_3Cl); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.33–7.29 (2H, m, H-9 and H-13), 7.27–7.23 (2H, m, H-17 and H-21), 6.90–6.85 (4H, m, H-10, H-12, H-18 and H-20), 5.15 (1H, dd, *J* 8.2, 3.8, H-1), 4.84 (1H, d, *J* 11.0, H-7), 4.72 (1H, d, *J* 11.2, H-15), 4.68 (1H, d, *J* 11.2, H-15'), 4.63 (1H, d, *J* 11.0, H-7'), 4.31 (1H, dd, *J* 5.8, 3.8, H-2), 4.14 (1H, dd, *J* 6.1, 5.8, H-3), 3.80 (3H, s, H-14 or H-22), 3.80 (3H, s, H-14 or H-22), 3.77 (1H, dd, *J* 8.2, 8.0, H-6), 3.63–3.56 (2H, m, H-4 and H-5), 2.62 (1H, d, *J* 1.9, C(5)O*H*), 2.11 (3H, s, H-24), 1.98–1.85 (2H, m, H-26 or H-29), 1.77–1.61 (6H, m, H-27, H-28, H-26 or H-29); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.3 (C-23), 159.5, 159.4 (C-11, C-19), 130.5, 130.4 (C-8, C-16), 129.8 (C-9, C-13), 129.4 (C-17, C-21), 120.0 (C-25), 114.0 (C-10, C-12, C-18, C-20), 80.7 (C-4), 79.1 (C-6), 78.5 (C-3), 74.4 (C-2), 74.2 (C-15), 73.6 (C-5), 73.2 (C-7), 71.3 (C-1), 55.4 (C-14, C-22), 37.5, 37.2 (C-26, C-29), 24.0, 23.6 (C-27, C-28), 21.3 (C-24); $\bar{\nu}_{max}$(solid)/cm^{-1} 3657 (O-H) (br), 2980 (s), 2889 (m), 1741 (w), 1613 (w), 1514 (w), 1473 (w), 1462 (w), 1382 (m), 1249 (m), 1152 (m), 1073 (m), 1035 (w),

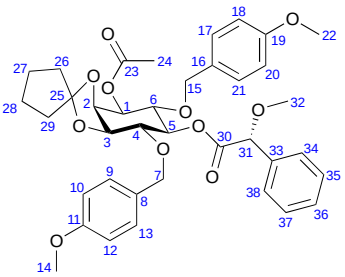
955 (m), 820 (w); LRMS *m/z* (ESI$^+$) 551.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 551.22508 [M+Na]$^+$ ($C_{29}H_{36}O_9Na$ requires 551.22515 [M+Na]$^+$); RP-HPLC (Method 2) t_R = 13.12 min, 96.19%.

(+)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-(4-methoxybenzyl)-5-*O*-((*S*)-α-methoxyphenylacetoxy)-*myo*-inositol (+)-S6a



(*S*)-(+)-α-Methoxyphenylacetic acid (32 mg, 0.189 mmol, 2.0 eq), 1-ethyl-3-(3-dimethylamino propyl)carbodiimide (49 mg, 0.255 mmol, 2.7 eq) and DMAP (6 mg, 0.0473 mmol, 0.50 eq) were added to a solution of (−)-**S5** (50 mg, 0.0946 mmol, 1.0 eq) in CH_2Cl_2 (3 mL). After 17.5 hours, the reaction mixture was diluted with CH_2Cl_2 (3 mL), and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 4 mL), brine (4 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3) afforded (+)-**S6a** (4.5 mg, 7%) as a colourless solid: R_f 0.33 (Petroleum ether/EtOAc 7:3); $[\alpha]_D^{25}$ = +17.8 (*c* 0.22, CH_3Cl); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.44–7.39 (2H, m, H-34 and H-38), 7.30–7.24 (3H, m, H-35 to H-37), 7.23–7.20 (2H, m, H-17 and H-21), 6.92–6.88 (2H, m, H-9 and H-13), 6.87–6.83 (2H, m, H-18 and H-20), 6.80–6.74 (2H, m, H-10 and H-12), 5.20 (1H, dd, *J* 8.9, 3.6, H-1), 5.15 (1H, dd, *J* 6.9, 6.9, H-5), 4.69 (1H, s, H-31), 4.69 (1H, d, J_{AB} 11.6, H-7), 4.58 (1H, d, J_{AB} 11.6, H-7'), 4.37 (1H, dd, *J* 6.2, 3.6, H-2), 4.20 (1H, dd, *J* 6.2, 6.1, H-3), 4.07 (1H, d, J_{AB} 11.3, H-15), 3.98 (1H, d, J_{AB} 11.3, H-15'), 3.80 (3H, s, H-14 or H-22), 3.78 (3H, s, H-14 or H-22), 3.74–3.69 (2H, m, H-4 and H-6), 3.35 (3H, s, H-32), 1.99 (3H, s, H-24), 1.98–1.89 (2H, m, H-26 and H-29), 1.76–1.62 (6H, m, H-26', H-29', H-27 and H-28); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.1 (C-23), 169.7 (C-30), 159.4, 159.2 (C-11, C-19), 136.2 (C-33), 130.22, 130.17 (C-8, C-16), 129.6, 129.01, 128.98 (C-9, C-13, C-17, C-21), 128.8 (C-36), 127.5 (C-34, C-38, C-35, C-37), 120.0 (C-25), 113.8, 113.7 (C-18, C-20, C-10, C-12), 82.7 (C-31), 77.8 (C-4), 77.4 (C-3), 76.6 (C-6), 75.7 (C-5), 73.8 (C-2), 73.1 (C-15), 72.4 (C-7), 70.5 (C-1), 57.5 (C-32), 55.44, 55.40 (C-14, C-22), 36.7, 36.6 (C-26, C-29), 24.1, 23.5 (C-27, C-28), 21.1 (C-24); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2936 (m), 2876 (w), 2836 (w), 1747 (C=O) (s), 1613 (m), 1586 (w), 1514 (s), 1456 (w), 1370 (w), 1336 (w), 1302 (w), 1246 (s), 1176 (m), 1109 (m), 1075 (m), 1033 (m), 822 (m), 773 (m); LRMS *m/z* (ESI$^+$) 699.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 699.27766 [M+Na]$^+$ ($C_{38}H_{44}O_{11}Na$ requires 699.27758 [M+Na]$^+$); RP-HPLC (Method 2) t_R = 14.71 min, 96.93%. This compound was employed for the determination of the absolute configuration of (−)-**S5** by ^{1}H NMR. See Supplementary Results and Discussion, Scheme S2 and Table S2.

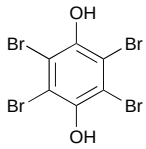
(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-(4-methoxybenzyl)-5-*O*-((*R*)-α-methoxyphenylacetoxy)-*myo*-inositol (−)-S6b



(*R*)-(−)-α-Methoxyphenylacetic acid (32 mg, 0.189 mmol, 2.0 eq), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (49 mg, 0.255 mmol, 2.7 eq) and DMAP (6 mg, 0.0473 mmol, 0.50 eq) were added to a solution of (−)-**S5** (50 mg, 0.0946 mmol, 1.0 eq) in CH_2Cl_2 (3 mL). After 17.5 hours, the reaction mixture was diluted with CH_2Cl_2 (3 mL), and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 4 mL), brine (4 mL), then dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3) afforded (−)-**S6b** (4.1 mg, 6%) as a colourless solid: R_f 0.33 (Petroleum ether/EtOAc 7:3); $[\alpha]_D^{25}$ = −17.5 (*c* 0.19, CH_3Cl); ^{1}H NMR (500 MHz; CDCl3) δ_H 7.43–7.38 (2H, m, H-34 and H-38), 7.29–7.23 (3H, m, H-35 to H-37), 7.14–7.09 (2H, m, H-17 and H-21), 7.05–7.00 (2H, m, H-9 and H-

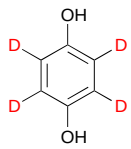
13), 6.86–6.82 (2H, m, H-18 and H-20), 6.81–6.76 (2H, m, H-10 and H-12), 5.22 (1H, dd, *J* 8.8, 3.7, H-1), 5.14 (1H, dd, *J* 7.5, 7.5, H-5), 4.64 (1H, s, H-31), 4.51 (1H, d, J_{AB} 11.5, H-15), 4.43 (2H, d, J_{AB} 11.5, H-15' and H-7), 4.35 (1H, dd, *J* 6.2, 3.7, H-2), 4.27 (1H, d, J_{AB} 11.5, H-7'), 4.11 (1H, dd, *J* 6.2, 6.1, H-3), 3.88 (1H, dd, *J* 8.8, 7.5, H-6), 3.80 (3H, s, H-14 or H-22), 3.79 (3H, s, H-14 or H-22), 3.54 (1H, dd, *J* 7.5, 6.1, H-4), 3.34 (3H, s, H-32), 2.07 (3H, s, H-24), 1.92–1.85 (1H, m, H-26 or H-29), 1.79–1.72 (1H, m, H-26 or H-29), 1.71–1.57 (6H, m, H-26', H-29', H-27 and H-28); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.2 (C-23), 169.8 (C-30), 159.4 (C-19), 159.2 (C-11), 136.0 (C-33), 130.3 (C-16), 130.2 (C-8), 129.32, 129.31 (C-9, C-13, C-17, C-21), 128.9 (C-36), 128.7 (C-35, C-37), 127.4 (C-34, C-38), 120.0 (C-25), 113.9 (C-18, C-20), 113.7 (C-10, C-12), 82.8 (C-31), 77.9 (C-4), 77.5 (C-3), 76.6 (C-6), 75.6 (C-5), 73.8 (C-2), 73.7 (C-15), 72.2 (C-7), 70.8 (C-1), 57.5 (C-32), 55.43, 55.41 (C-14, C-22), 36.8, 36.6 (C-26, C-29), 24.1, 23.4 (C-27, C-28), 21.2 (C-24); $\bar{\nu}_{max}$(thin film)/cm^{-1} 32980 (s), 2972 (s), 2888 (m), 1748 (C=O) (w), 1613 (w), 1514 (w), 1473 (w), 1462 (w), 1382 (w), 1302 (m), 1250 (m), 1153 (m), 1074 (m), 1036 (m), 965 (m), 955 (m), 820 (w); LRMS *m/z* (ESI$^+$) 699.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 699.27756 [M+Na]$^+$ ($C_{38}H_{44}O_{11}Na$ requires 699.27758 [M+Na]$^+$); RP-HPLC (Method 2) t_R = 14.73 min, 95.60%. This compound was employed for the determination of the absolute configuration of (−)-**S5** by ^{1}H NMR. See Supplementary Results and Discussion, Scheme S2 and Table S2.

2,3,5,6-Tetrabromoquinol S16



The procedure from Head was followed.[45] Quinol **21** (2.20 g, 50 mmol, 1.0 eq) was suspended in AcOH (40 mL) and the suspension was cooled to 0 °C. To this suspension was added a solution of bromine (4.3 mL, 167 mmol, 3.3 eq) in AcOH (10 mL), dropwise, *via* a dropping funnel over a period of 30 minutes. The reaction mixture was warmed to RT and stirred for 24 hours. Water (10 mL) was added and the reaction was heated under reflux for 2 hours. The resulting suspension was cooled to RT and the precipitate was filtered to afford **S16** as a orange solid (7.96 g, 93%): R_f 0.32 (CH_2Cl_2); m.p. 242–243 °C (decomposed, from AcOH) [lit.[45] 243–244 °C, decomposed]; ^{1}H NMR (400 MHz; D_6-DMSO) δ_H 9.96 (2H, s, O*H*); ^{13}C NMR (101 MHz; D_6-DMSO) δ_C 146.9 (*C*-OH), 115.9 (*C*-Br); LRMS *m/z* (ESI$^-$) 421.6 ([M^{79}Br$_4$−H]$^-$, 88%), 423.6 ([M^{79}Br$_3$^{81}Br−H]$^-$, 100%), 425.6 ([M^{79}Br$_2$^{81}Br$_2$−H]$^-$, 92%), 427.6 ([M^{79}Br^{81}Br$_3$−H]$^-$, 23%). These data are in good agreement with the literature values.[45,46]

2,3,5,6-Tetradeuteroquinol 22

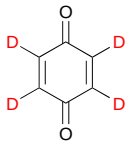


Method 1 - A suspension of **S16** (7.95 g, 18.7 mmol, 1.0 eq.) in D_2O (50 mL) was heated under reflux for 30 min. After this time, the suspension was cooled to RT and Pd/C (10% *w/w*, 710 mg, 0.67 mmol, 0.036 eq) as well as powdered zinc dust (2.39 g, 36.5 mmol, 1.95 eq) were added. The reaction mixture was heated under reflux for 4 hours. Further zinc dust (1.19 g, 18.3 mmol, 0.95 eq) was added to the reaction mixture and continued heating under reflux for 18 h. The reaction mixture was cooled to room temperature and was diluted with MeOH (50 mL). The suspension was filtered through Celite® followed by a plug of silica and the resulting filtrate was concentrated *in vacuo* to give a brown oil. The product was purified by column chromatography over silica gel on a Biotage system (EtOAc/Petroleum ether Gradient 5–40%) to afford **22** as a brown crystalline solid (420 mg, 20%, >95% D_4): R_f 0.51 (Petroleum ether/EtOAc 1:1); m.p. 169–170 °C (from EtOAc) [lit.[47] 171–173 °C]; ^{1}H NMR (400 MHz; D_6-DMSO) δ_H 8.63 (2H, s, O*H*); ^{13}C NMR (126 MHz; D_6-DMSO) δ_C 150.1 (*C*-O), 115.8 (t_D, J_D 23.8, *C*-D); ^{2}H NMR (77 MHz; DMSO; D_6-DMSO) δ_D 6.58; $\bar{\nu}_{max}$(thin film)/cm^{-1} 3245 (O-H) (w), 1409 (C=C) (s), 1315 (C=C) (m), 1220 (C-O) (m), 1126 (C-O) (s); HRMS *m/z* (F$^+$) Found 114.0621 [M]$^+$ ($C_6H_2O_2D_4$ requires 114.0619); NP-HPLC (Method 5) t_R = 4.8 min, 98.5%. These data are in good agreement with the literature values.[47]

Method 2 - The procedure from Desiraju *et al.* was followed.[47] Acetyl chloride (40 mL, 56 mmol, 2.9 eq) was cooled to 0 °C in an ice bath and D_2O (20 mL, 111 mmol, 5.8 eq) was added, dropwise, over a period of 1 hour (Slowly, care must be taken to avoid large release of HCl gas). The solution was stirred at 0 °C for 10 minutes then zinc powder (4.0 g, 61 mmol, 3.2 eq) was added, portion-wise, at 0 °C over a period of 10 minutes. Once addition was complete, quinol **21** (2.1 g, 19 mmol, 1.0 eq) was added to the solution and the reaction mixture was heated under reflux for 18 hours. The solution was cooled to RT and H_2O (80 mL) was added. The product was extracted with Et_2O (3 × 150 mL) and the combined organic components were was washed with saturated aqueous $NaHCO_3$ (3 × 50 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford **22** as a colourless solid (1.81 g, 86%, D_4 46%, 36% D_3, 17% D_2, <1% D_1, D_0 not observed). Full characterisation data was not obtained on this partially deuterated sample.

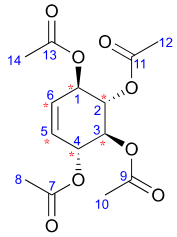
Method 3 - The procedure from Zimmermann *et al.* was followed.[48] A suspension of quinol **21** (20.0 g, 18.1 mmol, 1.0 eq) and D_2SO_4 (1 mL, 96–98 wt.% in D_2O, 99.5% D, 13.7 mmol, 0.75 eq) in D_2O (50 mL) was placed under an atmosphere of nitrogen and the reaction suspension was heated under reflux for 24 hours. The reaction suspension was cooled to RT and the product was extracted using Et_2O (3 × 100 mL). The combined organic extracts were dried ($MgSO_4$) filtered, and concentrated *in vacuo* to give a colourless solid. This procedure was repeated (heated under reflux in fresh D_2O and D_2SO_4 followed by extraction) twice more to afford **22** as a colourless solid (19.72 g, 95%, 93% D_4, 7% D_3). All other characterisation data matched those reported above.

2,3,5,6-Tetradeuterobenzoquinone 23



The procedure from Ikemoto *et al.* was followed.[49] To a solution of **22** (1.14 g, 10.0 mmol, 1.0 eq., >95% D_4) and iodine (126 mg, 1.0 mmol, 0.1 eq) in isopropanol (5 mL) was added aqueous H_2O_2 (35% *w/w*, 1.7 ml, 20 mmol, 2.0 eq) and the solution was heated to 45 °C for 2 hours. TLC analysis of the reaction mixture (Petroleum ether/EtOAc 4:1) indicated that the reaction was complete. The reaction mixture was cooled in an ice bath for 30 minutes and the solid was filtered to afford **23** as yellow needles (986 mg, 89%, >95% D_4): R_f 0.59 (Petroleum ether/EtOAc 4:1); m.p. 112–114 °C (sublimed, from isopropanol) [lit.[50] 113 °C (from H_2O)]; ^{2}H NMR (77 MHz; DMSO; D_6-DMSO) δ_D 6.87; ^{13}C NMR (126 MHz; D_6-DMSO) δ_C 188.3 (*C*-O), 136.6 (t_D, J_D 25.8, *C*-D); $\bar{\nu}_{max}$(thin film)/cm^{-1} 1638 (C=C) (s), 1558 (C=C) (m), 1264 (C=O) (m), 1238 (C=O) (m); HRMS *m/z* (F^+) Found 112.0462 $[M]^+$ ($C_6D_4O_2$ requires 112.0462). These data are in good agreement with the literature values.[49,50]

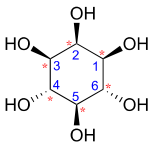
D_6 (±)-(1*RS*,2*SR*,3*SR*,4*RS*)-Cyclohex-5-ene-1,2,3,4-tetrayl-tetracetate (±)-26



A solution of D_4-benzoquinone **23** (2.90 g, 25.9 mmol, 1.0 eq, 93% D_4, 7% D_3) in $CHCl_3$ (75 mL) was cooled to 0 °C and a solution of bromine (1.33 mL, 25.9 mmol, 1.0 eq) in $CHCl_3$ (75 mL) was added dropwise *via* a dropping funnel over a period of 2 hours. The reaction mixture was stirred at RT for another hour at 0 °C. TLC analysis of the reaction mixture (Petroleum ether/EtOAc 4:1) indicated that the reaction was complete. The solvent was removed *in vacuo*, the resulting yellow solid (±)-**24** was dissolved in Et_2O (110 mL), and the solution was cooled to 0 °C. A solution of $NaBD_4$ (2.28 g, 54.4 mmol, 2.1 eq) in D_2O (40 mL) was added, portionwise, over a period of 5 minutes with vigorous stirring. The reaction mixture was stirred vigorously at 0 °C for 2 hours. TLC analysis of the reaction mixture (Petroleum ether/EtOAc 4:1) indicated that the reaction was complete. The phases were separated and the organic components were extracted from the aqueous layer using Et_2O (2 × 100 mL), combined, dried

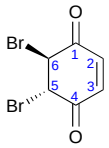
($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting colourless solid (±)-**25** (7.08 g) was dissolved in Ac_2O (75 mL) and K_2CO_3 (21.3 g, 154 mmol, 6.0 eq) was added. The suspension was stirred at RT for 2 hours. TLC analysis of the reaction mixture (Petroleum ether/EtOAc 1:1) indicated the reaction was complete. Glacial AcOH (75 mL) was added and the reaction mixture was heated under reflux for 45 hours. Mass spectrometry analysis of the reaction mixture ($[M+K]^+$ = 383.1, no brominated species observed) indicated that the reaction was complete. The reaction was cooled down to 0 °C, MeOH (50 mL) was added to quench Ac_2O and the reaction was stirred at 0 °C for 2 hours. The reaction mixture was concentrated *in vacuo* (Büchi water bath at 60 °C) to give a brown oil. The product was purified by column chromatography over silica gel (Petroleum ether/EtOAc 4:1), followed by crystallisation from EtOH to afford (±)-**26** as colourless crystals (2.40 g, 29% over three steps, D_6 90%, D_5 10%): R_f 0.16 (Petroleum ether/EtOAc 4:1); m.p. 81–83 °C (from EtOH); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 2.05 (6H, s, H-8, H-14), 2.03 (6H, s, H-10, H-12); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.3 (C-7, C-13), 169.9 (C-9, C-11), 127.0 (t_D, J_D 25.2, C-5, C-6), 71.0 (t_D, J_D 23.0, C-1, C-4), 70.8 (t_D, J_D 23.0, *C*-2, *C*-3), 20.9 (*C*-8, *C*-14), 20.6 (*C*-10, *C*-12); ^{2}H NMR (77 MHz; $CHCl_3$; D_6-DMSO) δ 5.65 (D-5, D-6), 5.48 (D-1, D-4), 5.22 (D-2, D-3); $\bar{\nu}_{max}$(thin film)/cm^{-1} 1745 (C=O) (s), 1431 (C-H) (w), 1372 (C-H) (m), 1241 (C-H) (s), 1222 (C-H) (s), 1196 (C-O) (s), 1118 (C-O) (m), 1091 (C-O) (m), 1023 (C-O) (s), 969 (C-H) (m), 954 (C-D) (m); LRMS *m/z* (ESI^+) 342.1 ($[MD_5+Na]^+$, 11%) 343.1 ($[MD_6+Na]^+$, 100%); HRMS *m/z* (ESI^+) Found 342.1204 $[MD_5+Na]^+$ ($C_{14}H_{13}D_5O_8Na$ requires 342.1213), 343.1265 $[MD_6+Na]^+$ ($C_{14}H_{12}D_6O_8Na$ requires 343.1271). The X-ray crystal structure of this compound is represented in Figure 1 and the data can be found in the X-ray Crystallographic data section of the Supplementary Information.

D_6-*myo*-Inositol 10



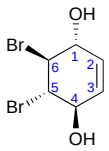
To a vigorously stirred solution of (±)-**26** (1.96 g, 6.11 mmol, 1.0 eq, 90% D_6, 10% D_5) in MeCN (60 mL) at 0 °C was added a solution of $RuCl_3 \cdot 3H_2O$ (80 mg, 0.31 mmol, 0.05 eq) and $NaIO_4$ (1.96 g, 9.18 mmol, 1.5 eq) in H_2O (15 mL) and the resulting solution was stirred at 0 °C for 4 minutes. TLC analysis of the reaction mixture (Petroleum ether/EtOAc 4:1) indicated that the reaction was complete. The reaction mixture was quenched with aqueous $Na_2S_2O_3$ (10% *w/v*, 50 mL) and the organic components were extracted with EtOAc (3 × 50 mL). The organic components were washed with saturated aqueous NaCl (50 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting solid containing (±)-**27** and (±)-**28** was dissolved in a mixture of MeOH (21 mL) and H_2O (9 mL), Et_3N (10.2 mL, 73.0 mmol, 12.0 eq) was added, and the reaction solution was stirred at RT for 2 hours. After this time, the reaction solution was concentrated *in vacuo* and the resulting solid crystallised from 1:1 EtOH/H_2O to afford **10** as colourless cubes (621 mg, 55%, 90% D_6, 10% D_6): R_f 0.82 (EtOH/H_2O 1:1); m.p. 226–229 °C (from EtOH/H_2O) [**1**, 220–221 °C (from EtOH/H_2O)]; ^{1}H NMR (400 MHz; D_6-DMSO) δ 4.47 (1H, s, O*H*-5), 4.42 (2H, s, O*H*-4, O*H*-6), 4.40 (1H, s, O*H*-2), 4.27 (2H, s, O*H*-1, O*H*-3); ^{13}C NMR (126 MHz; D_6-DMSO) δ 74.6 (t_D, J_D 20.4, C-2), 72.2 (t_D, J_D 20.4, C-4, C-6), 72.1 (t_D, J_D 20.4, C-5), 71.3 (t_D, J_D 20.4, C-1, C-3); ^{2}H NMR (77 MHz; DMSO; D_6-DMSO) δ_D 3.66 (D-2), 3.33 (D-4, D-6), 3.08 (D-1, D-3), 2.88 (D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3215 (O-H) (br, m), 1413 (C-H) (m), 1365 (C-H) (m), 1201 (C-H) (s), 1144 (C-O) (m), 1107 (C-O) (m); LRMS *m/z* (ESI^+) 208.1 ($[MD_5+Na]^+$, 11%) 209.1 ($[MD_6+Na]^+$, 100%); HRMS *m/z* (ESI^+) Found 208.0843 $[MD_5+Na]^+$ ($C_6H_7O_6D_5Na$ requires 208.0840), 209.0903 $[MD_6+Na]^+$ ($C_6H_6O_6D_6Na$ requires 209.0902).

(±)-*trans*-5,6-Dibromocyclohex-2-ene-1,4-dione (±)-S17



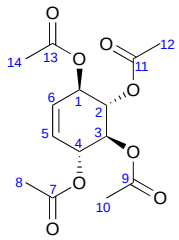
The procedure from Adelt *et al.* was followed.[51] A solution of *p*-benzoquinone (5.4 g, 50 mmol, 1.0 eq) in $CHCl_3$ (150 mL) was cooled to 0 °C and bromine (2.58 mL, 50 mmol, 1.0 eq) in $CHCl_3$ (50 mL) was added, dropwise, over a period of 30 min at 0 °C *via* a dropping funnel. The solution was stirred at 0 °C for 1 hour producing a bright red solution. TLC analysis of the reaction mixture (Petroleum ether/ EtOAc 4:1) indicated the reaction was complete. The solvent was removed *in vacuo* to afford (±)-**S17** as a light yellow solid (13.4 g, 100%) which was used without further purification: R_f 0.54 (Petroleum ether/EtOAc 4:1); m.p. 84–85 °C (from isopropanol) [lit.[51] 82-83 °C]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 6.72 (2H, t, *J* 0.8, H-2, H-3), 4.80 (2H, t, *J* 0.8, H-5, H-6); LRMS *m/z* (ESI^-) 264.8 ($[M^{79}Br_2- H]^-$, 51%), 266.8 ($[M^{79}Br^{81}Br-H]^-$, 100%), 268.8 ($[M^{81}Br_2-H]^-$, 47%). These data are in good agreement with the literature values.[51]

(±)-*trans*-5,6-Dibromocyclohex-2-ene-1,4-diol (±)-S18



The procedure from Adelt *et al.* was followed.[51] A solution of (±)-**S17** (13.4 g, 50 mmol, 1.0 eq) in Et_2O (225 mL) was cooled to –5 °C and a solution of $NaBH_4$ (4.73 g, 125 mmol, 2.5 eq) in H_2O (75 mL) was added portionwise over a period of 10 min. The resulting biphasic mixture was stirred vigorously for 1 hour. TLC analysis of the reaction mixture (Petroleum ether/EtOAc 4:1) indicated the reaction was complete. The phases were separated, and the organic components were extracted using Et_2O (3 × 100 mL). The combined organic components were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to afford (±)-**S18** as a colourless solid (10.99 g, crude), which was used without further purification. An analytical sample was prepared by crystallisation from 1:1 acetone/pentane: R_f 0.32 (Petroleum ether/EtOAc 2:1); m.p. 149–150 °C (from acetone/pentane) [lit.[51] 149 °C]; ^{1}H NMR (400 MHz; D_6-acetone) δ_H 5.75 (2H, s, H-2, H-3), 4.89 (2H, dt, *J* 6.4, 1.1, O*H*), 4.52 (2H, dd, *J* 5.4, 2.6, *H*-5, *H*-6), 4.23 (2H, dd, *J* 5.4, 2.6, H-1, H-4); LRMS *m/z* (ESI^-) 268.6 ($[M^{79}Br_2-H]^-$, 71%), 270.6 ($[M^{79}Br^{81}Br-H]^-$, 100%), 272.6 ($[M^{81}Br_2-H]^-$, 82%). These data are in good agreement with the literature values.[51]

(±)-(1*RS*,2*SR*,3*SR*,4*RS*)-Cyclohex-5-ene-1,2,3,4-tetrayl tetraacetate (±)-S19

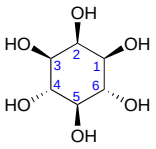


A modification of the procedure from Guo *et al.* was followed.[52] To a solution of (±)-**S18** (10.99 g, crude) in Ac_2O (300 mL) was added solid K_2CO_3 (34.6 g, 250 mmol, 6.0 eq relative to *p*-benzoquinone) portionwise over 10 minutes at 0 °C. The reaction mixture was stirred for at RT for 2 hours. TLC analysis of the reaction mixture (Petroleum ether/EtOAc 1:1) indicated the reaction was complete. Glacial AcOH (300 mL) was added and the reaction mixture was heated under reflux for 96 hours. Mass spectrometry analysis of the reaction mixture showed the reaction was complete ($[M+K]^+$ = 337.1, no brominated species observed). The reaction mixture was cooled to RT and concentrated *in vacuo*. The resulting oil was suspended in saturated aqueous $NaHCO_3$ (200 mL) and the product was extracted using Et_2O (3 × 200 mL). The organic components were combined, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting oil was azeotroped three times with cyclohexane. The crude was purified by column chromatography over silica gel on a Biotage system (Petroleum ether/EtOAc 5-40%). The product was crystallised by dissolving in boiling Et_2O, and dropwise addition of boiling petroleum ether until the solution was cloudy, followed by cooling to −20 °C for 1 hour to afford **S19** as colourless needles (5.54 g, 35% over 3 steps): R_f 0.85 (Petroleum ether/Et_2O 1:1); m.p. 84–85 °C (from Petroleum ether/Et_2O), 88–89 °C (from EtOH) [lit.[53] 85–85.5 °C, lit.[54] 86–88 °C, lit.[55] 92–93 °C]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 5.73 (2H, s, H-5, H-6), 5.62 (2H, dd, *J* 5.5, 2.6, H-1, H-4), 5.36 (2H, dd, *J* 5.5, 2.6, H-2, H-3), 2.09 (6H, s, H-8 and

H-14), 2.07 (6H, s, H-10 and H-12); LRMS *m/z* (ESI$^+$) 337.1 ([M+Na]$^+$, 100%). These data are in good agreement with the literature.[53,56]

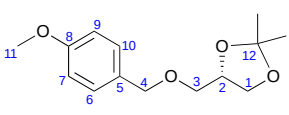
Multistep Procedure from p-*benzoquinone:* To a solution of *p*-benzoquinone (10.8 g, 100 mmol, 1.0 eq) in CH_2Cl_2 (300 mL) at 0 °C was added a solution of Br_2 (5.15 mL, 100 mmol, 1.0 eq) in CH_2Cl_2 (100 mL) *via* a dropping funnel over a period of 1 hour. TLC analysis of the reaction mixture (Petroleum ether/EtOAc 4:1) indicated the reaction was complete. After this time, the solution was concentrated *in vacuo* to afford a yellow solid (±)-**S17**. The solid was dissolved in Et_2O (450 mL), cooled to 0 °C and a solution of $NaBH_4$ (3.78 g, 100 mmol, 1.0 eq) in H_2O (150 mL) was added dropwise *via* a dropping funnel over 1 hour. The reaction mixture was stirred vigorously for a further 1 hour at 0 °C. TLC analysis of the reaction mixture (Petroleum ether/EtOAc 4:1) indicated the reaction was complete. The phases were separated and the organic components were extracted using Et_2O (3 × 300 mL), combined, dried (Na_2SO_4) filtered, and concentrated *in vacuo* to afford a colourless solid (±)-**S18**. The solid was dissolved in Ac_2O (500 mL) and K_2CO_3 (69.2 g, 500 mmol, 5.0 eq) was added, portionwise, over 30 minutes. The reaction suspension was stirred at RT for 2 hours, after which time glacial AcOH (500 mL) was added. The reaction mixture was heated to reflux for 48 hour, cooled, and concentrated *in vacuo*. Mass spectrometry analysis of the reaction mixture ([M+K]$^+$= 337.1, no brominated species observed) showed the reaction was complete. The resulting brown solid was partitioned between Et_2O (500 mL) and water (500 mL), and the organic components were washed with water (2 × 500 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The product was purified by column chromatography over silica gel on a Biotage system (5-40% EtOAc in petroleum ether), followed by crystallisation from EtOH to afford (±)-**S19** as colourless needles (9.98 g, 32% over 3 steps). The data matched those reported above.

***myo*-Inositol 1**



To a vigorously stirred solution of (±)-**S19** (1.06 g, 3.37 mmol, 1.0 eq) in MeCN (32 mL) was added a solution of $NaIO_4$ (1.08 g, 5.05 mmol, 1.5 eq) and $RuCl_3{\cdot}3H_2O$ (45 mg, 0.17 mmol, 0.05 eq) in H_2O (8 mL) and the mixture was stirred vigorously for 8 minutes. TLC analysis (Petroleum ether/EtOAc 4:1) indicated the reaction was complete. Aqueous $Na_2S_2O_3$ (10% *w/v*, 50 mL) was added and the organic components were extracted with EtOAc (3 × 100 mL), combined, dried (Na_2SO_4) filtered, and concentrated *in vacuo*. The resulting solid was dissolved in a mixture of MeOH (14 mL) and H_2O (6 mL), NEt_3 (5.64 mL, 40.4 mmol, 12.0 eq) was added and the reaction solution was stirred at RT for 2 hours. After this time, the reaction solution was concentrated *in vacuo* to give a brown solid. The product was crystallised from 1:1 EtOH/H_2O, filtered and the crystals washed with Et_2O (20 mL) to afford **1** as colourless needles (496 mg, 82%): R_f 0.81 (EtOH/H_2O 1:1); m.p. 220–221 °C (from EtOH/ H_2O 1:1) [lit.[57] 220–221 °C (from aq. EtOH)]; ^{1}H NMR (400 MHz; D_6-DMSO) δ_H 4.56 (1H, d, *J* 4.3, O*H*-5), 4.51 (2H, d, *J* 4.5, O*H*-4, O*H*-6), 4.48 (1H, d, *J* 3.1, O*H*-2), 4.36 (2H, d, *J* 5.5, O*H*-1, O*H*-3), 3.69 (1H, dt, *J* 3.1, 2.8, H-2), 3.33 (2H, ddd, *J* 9.2, 9.2, 4.5, H-4, H-6), 3.11 (2H, ddd, *J* 9.2, 5.5, 2.8, H-1, H-3), 2.89 (1H, td, *J* 9.2, 4.3, H-5); ^{13}C NMR (101 MHz; D_6-DMSO) δ_C 75.3 (C-5), 72.8 (C-4, C-6), 72.7 (C-2), 71.9 (C-1, C-3); LRMS *m/z* (ESI$^+$) 203.1 ([M+Na]$^+$, 100%). These data are in good agreement with the literature values, as well as in comparison to commercial sources of *myo*-inositol **1**.[57-59]

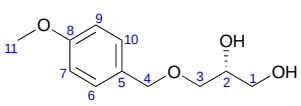
(*S*)-(+)-1,2-*O*-Isopropylidene-3-*O*-(4-methoxybenzyl)-*sn*-glycerol (+)-S20



(*S*)-(+)-1,2-Isopropylidene-*sn*-glycerol (+)-**30** (935 µL, 7.56 mmol, 1.0 eq) was added dropwise to a suspension of NaH (480 mg, 12.0 mmol, 1.6 eq, 60% dispersion in mineral oil) in anhydrous DMF (5.0 mL) and at 0 °C. The solution obtained was warmed to RT, stirred for 1 hour, then

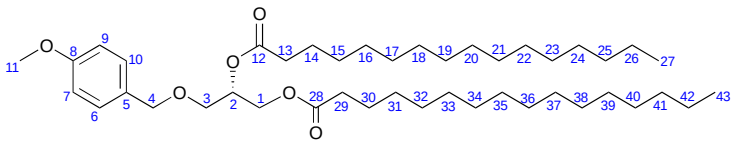
cooled to 0 °C. PMBCl (1.53 mL, 11.0 mmol, 1.5 eq) was added dropwise, and the solution was warmed to RT and stirred for a further 14 hours. The reaction was then quenched by addition of H_2O (10 mL) and the aqueous layer was extracted with Et_2O (3 × 15 mL). The combined organic layers were washed with H_2O (3 × 15 mL), then brine (2 × 15 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 8:2) afforded (+)-**S20** (1.87 g, 98%) as a colourless oil: R_f 2.3 (Petroleum ether/EtOAc 8:2); $[\alpha]_D^{20}$ = +21.1 (*c* 1.0, $CHCl_3$) [lit.[60] $[\alpha]_D^{21}$ = +21.8 (*c* 1.0, $CHCl_3$)]; ^{1}H NMR (200 MHz; $CDCl_3$) δ_H 7.32–7.20 (2H, m, H-6 and H-10), 6.92–6.83 (2H, m, H-7 and H-9), 4.54 (1H, d, J_{AB} 11.7, H-4), 4.47 (1H, d, J_{AB} 11.7, H-4'), 4.35–4.21 (1H, m, H-2), 4.04 (1H, dd, J_{XY} 8.2, 6.4, H-3), 3.81 (3H, s, H-11), 3.72 (1H, dd, J_{XY} 8.2, 6.4, H-3'), 3.53 (1H, dd, J_{XY} 9.7, 5.7, H-1), 3.43 (1H, dd, J_{XY} 9.7, 6.3, H-1'), 1.42 (3H, s, C(12)CH_3), 1.36 (3H, s, C(12)CH_3); LRMS *m/z* (ESI$^+$) 275.0 ([M+Na]$^+$, 100%). These data are in good agreement with the literature values.[60,61]

(*R*)-(−)-3-*O*-(4-Methoxybenzyl)-*sn*-glycerol (−)-31



PTSA·H_2O (500 mg, 2.62 mmol, 0.22 eq) was added to solution of acetal (+)-**S20** (3.00 g, 11.9 mmol, 1.0 eq) in MeOH (83 mL). After stirring at RT for 2 hours the reaction was neutralised with Et_3N (360 µL, 2.62 mmol, 0.22 eq) and the solvent was removed *in vacuo*. Purification by column chromatography over silica gel (Hexane/EtOAc 4:6, 2:8) gave the diol (−)-**31** (6.80 g, 81%) as a colourless solid: R_f 0.35 (EtOAc); $[\alpha]_D^{20}$ = −2.2 (*c* 2.0, $CHCl_3$) [lit.[61] $[\alpha]_D^{22}$ = −1.1 (*c* 3.04, $CHCl_3$)]; m.p. 40–41 °C (EtOAc) [lit.[61] 41–43 °C (EtOAc)]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.27–7.22 (2H, m, H-6 and H-10), 6.91–6.87 (2H, m, H-7 and H-9), 4.49 (2H, s, H-4), 3.92–3.84 (1H, m, H-2), 3.81 (3H, s, H-11), 3.71 (1H, dd, J_{XY} 11.4, 3.9, H-1), 3.63 (1H, dd, J_{XY} 11.4, 5.4, H-1'), 3.56 (1H, dd, J_{XY} 9.6, 3.9, H-3), 3.52 (1H, dd, J_{XY} 9.6, 6.2, H-3'); LRMS *m/z* (ESI$^+$) 235.1 ([M+Na]$^+$, 100%). These data are in good agreement with the literature values.[61]

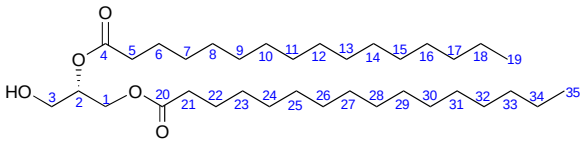
(*S*)-(+)-1,2-Di-*O*-palmitoyl-3-*O*-(4-methoxybenzyl)-*sn*-glycerol (+)-S21



To a stirred solution of the protected diol (−)-**31** (200 mg, 0.942 mmol, 1.0 eq) in anhydrous CH_2Cl_2 (4.0 mL) was added anhydrous pyridine (190 µL, 2.36 mmol, 2.5 eq) and 4-DMAP (6 mg, 0.0470 mmol, 0.050 eq). The solution was cooled to 0 °C and palmitoyl chloride (629 µL, 2.07 mmol, 2.2 eq) was added dropwise over 10 minutes. After stirring for 15 minutes at this temperature, the solution was allowed to warm to RT and was stirred for a further 14 hours. The reaction was quenched with H_2O (2 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 4 mL) and the combined organic layers were washed successively with a 2.0 M aqueous solution of HCl (2.5 mL), H_2O (3 mL) and brine (3 mL). The combined organic layers were then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/CH_2Cl_2 5:5) afforded (+)-**S21** (592 mg, 91%) as a colourless solid: R_f 0.78 (EtOAc); $[\alpha]_D^{20}$ = +10.2 (*c* 2.0, $CHCl_3$) [lit.[62] $[\alpha]_D^{27}$ = +11.3 (*c* 6.8, $CHCl_3$)]; m.p. 62–63 °C (CH_2Cl_2) [lit.[62] 63.5–64 °C]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.25–7.19 (2H, m, H-6 and H-10), 6.89–6.83 (2H, m, H-7 and H-9), 5.26–5.18 (1H, m, H-2), 4.48 (1H, d, J_{AB} 11.7, H-4), 4.44 (1H, d, J_{AB} 11.7, H-4'), 4.33 (1H, dd, J_{XY} 11.9, 3.6, H-1), 4.17 (1H, dd, J_{XY} 11.9, 6.4, H-1'), 3.79 (3H, s, H-11), 3.59–3.51 (2H, m, H-3), 2.34–2.23 (4H, m, H-13 and H-29), 1.59–1.45 (4H, m, H-14 and H-30), 1.26 (48H, br s, H-15 to H-26 and H-31 to H-42), 0.88 (6H, t, *J* 6.5, H-27 and H-43); ^{13}C NMR (101 MHz; $CDCl_3$) δ_C 173.6, 173.3 (C-12, C-28), 159.5 (C-8) 130.0 (C-5), 129.4 (C-6, C-10), 114.0 (C-7, C-9), 73.1 (C-4), 70.2 (C-2), 68.1 (C-3), 62.8 (C-1), 55.4 (C-11), 34.5, 34.3 (C-13, C-29), 32.1 (C-25, C-41), 29.9–29.8, 29.7, 29.51, 29.49, 29.29, 29.26 (C-15 to C-24 and C-31 to C-40), 25.12, 25.05 (C-14, C-30), 22.8 (C-

26, C-42), 14.3 (C-27, C-43); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2955 (m), 2916 (s), 2849 (s), 1730 (C=O) (s), 1612 (w), 1514 (m), 1472 (m), 1443 (m), 1358 (w), 1263 (m), 1244 (m), 1197 (m), 1171 (s), 1109 (s), 1084 (m), 1030 (m), 1016 (m), 947 (w), 831 (m), 816 (m), 718 (m); HRMS *m/z* (EI/FI) found 688.5432 $[M]^+$ ($C_{43}H_{76}O_6$ requires 688.5642 $[M]^+$). These data are in good agreement with the literature values.[62]

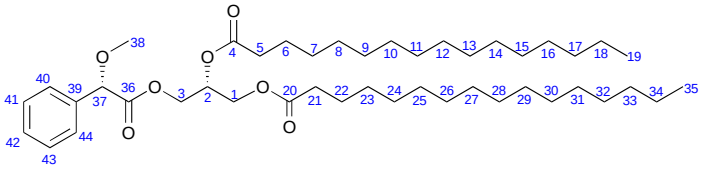
(*S*)-(−)-1,2-Di-*O*-palmitoyl-*sn*-glycerol (−)-32



Method 1 – DDQ (182 mg, 0.802 mmol, 2.05 eq) was added to a stirred solution of (+)-**S21** (270 mg, 0.391 mmol, 1.0 eq) in CH_2Cl_2 (16 mL) and H_2O (1.0 mL). The reaction mixture was stirred for 14 hours at RT, then quenched with a saturated aqueous solution of $NaHCO_3$ (18 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 9 mL). The combined organic phases were washed with a saturated aqueous solution of $NaHCO_3$ (13 mL), and brine (2 × 13 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/Et_2O 6:4) afforded the alcohol (−)-**32** (186 mg, 84%) as a colourless solid. Formation of the small amounts of the regioisomers was observed by ^{1}H NMR, suggesting that concurrent racemisation may be taking place. Data is given below.

Method 2 – To a solution of (+)-**S12** (1.48 g, 2.15 mmol, 1.0 eq) in EtOAc (155 mL) under $N_{2(g)}$, was added 10% Pd/C (389 mg, 0.362 mmol, 0.17 eq). The flask was purged with 3 balloons of $H_{2(g)}$. After stirring at RT for 2 hours under $H_{2(g)}$, the reaction mixture was filtered through a pad of Celite®, washed with EtOAc (3 × 20 mL), and the combined filtrates were concentrated *in vacuo* to give the alcohol (−)-**32** (1.17 g, 96%, 99% *e.e.*) as a colourless solid: R_f 0.71 (Hexane/EtOAc 6:4); $[\alpha]_D^{20}$ = −2.4 (*c* 1.0, $CHCl_3$) [lit.[63] $[\alpha]_D^{25}$ = −2.6 (*c* 8.0, $CHCl_3$); lit.[62] $[\alpha]_D^{25}$ = −2.69 (*c* 3.9, $CHCl_3$);]; m.p. 67–68 °C (Pentane/EtOAc) [lit.[63] 67–69 °C (Hexane/Et_2O); lit.[62] 66–67 °C (Pentane/EtOAc)]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 5.12–5.05 (1H, m, H-2), 4.32 (1H, dd, J_{XY} 11.9, 5.1, H-1), 4.23 (1H, dd, J_{XY} 11.9, 5.1, H-1'), 3.76–3.70 (2H, m, H-3), 2.34 (2H, t, *J* 7.5, H-5 or H-21), 2.32 (2H, t, *J* 7.5, H-5 or H-21), 2.06 (1H, t, *J* 6.3, C(3)O*H*), 1.63–1.57 (4H, m, H-6 and H-22), 1.26 (48H, br s, H-7 to H-18 and H-23 to H-34), 0.88 (6H, t, *J* 6.6, H-19 and H-35); LRMS *m/z* (ESI$^+$) 551.1 ($[M-OH]^+$, 100%). These data are in good agreement with the literature values.[63] The *e.e.* of (−)-**32** was calculated by ^{1}H NMR: See Supplementary Results and Discussion, Scheme S3A.

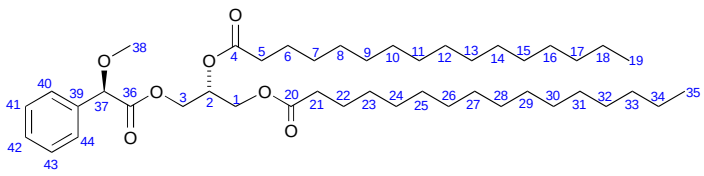
(*R*)-(+)-3-((*S*)-2-Methoxy-2-phenylacetoxy)-1,2-dipalmitoyl-*sn*-glycerol (+)-S7a



(+)-**S7a** was prepared similarly to (+)-**S7b** from (−)-**32** using (+)-(*S*)-α-methoxyphenyl-acetic acid to afford **S7a** as a colourless film (35 mg, 55%): R_f 0.63 (Petroleum ether/EtOAc 4:1); $[\alpha]_D^{25}$ = +8.8 (*c* 3.2, $CHCl_3$); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.44–7.30 (5H, m, H-40 to H-44), 5.17 (1H, dddd, *J* 5.1, 5.1, 5.1, 5.1, H-2), 4.77 (1H, s, H-37), 4.35 (1H, dd, J_{XY} 11.9, 5.1, H-1), 4.19 (1H, dd, J_{XY} 11.9, 5.1, H-1'), 4.17 (1H, dd, J_{XY} 11.9, 5.1, H-3), 3.96 (1H, dd, J_{XY} 11.9, 5.1, H-3'), 3.40 (3H, s, H-38), 2.26 (2H, dd, *J* 7.6, H-21), 2.17 (1H, dd, *J* 7.6, H-5), 2.16 (1H, dd, *J* 7.6, H-5'), 1.62–1.48 (4H, m, H-6 and H-22), 1.35–1.17 (48H, m, H-7 to H-18 and H-23 to H-34), 0.93–0.82 (6H, m, H-19 and H-35); ^{13}C NMR (101 MHz; $CDCl_3$) δ_C 173.2 (C-4), 172.7 (C-20), 170.2 (C-36), 135.9 (C-39), 128.9 (C-42), 128.7 (C-40, C-44), 127.2 (C-41, C-43), 82.3 (C-37), 68.6 (C-2), 62.6 (C-1), 61.8 (C-3), 57.4 (C-38), 34.04 (C-5), 34.00 (C-21), 31.9 (C-18), 29.71 (C-34), 29.68, 29.6, 29.51, 29.49, 29.4, 29.3, 29.11, 29.08 (C-7 to C-16, C-23 to C-32), 24.83 (C-6), 24.75 (C-22), 22.7 (C-17, C-33), 14.1 (C-19, C-35); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2922 (C-H) (s), 2852 (C-H) (s), 1741 (C=O) (s), 1467 (C-H) (m), 1237 (C-O) (m), 1168 (C-O) (s), 1117 (C-O) (s); LRMS *m/z* (ESI$^+$)

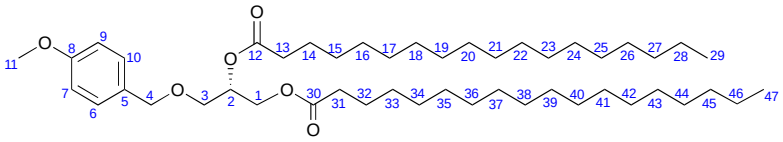
739.5 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) Found 739.5477 [M+Na]$^+$ ($C_{44}H_{76}O_7Na$ requires 739.5483). This compound was employed for determining the *e.e.* of (–)-**32** by ^{1}H NMR. See Supplementary Results and Discussion, Scheme S3A.

(*R*)-(+)-3-((*R*)-2-Methoxy-2-phenylacetoxy)-1,2-dipalmitoyl-*sn*-glycerol (–)-S7b



A solution of (–)-**32** (50 mg, 0.09 mmol, 1.0 eq), (–)-(*R*)-α-methoxyphenylacetic acid (28 mg, 0.17 mmol, 2.2 eq.), EDC·HCl (35 mg, 0.18 mmol, 2.4 eq) and 4-dimethylamino-pyridine (1.9 mg, 0.01 mmol, 0.1 eq.) in CH_2Cl_2 (1 mL) was stirred at RT for 2 hours. TLC analysis of the reaction mixture (Petroleum ether/EtOAc 4:1) indicated the reaction was complete. The reaction solution was diluted with CH_2Cl_2 (30 mL) and the organic components were washed with aqueous HCl (1 M, 20 mL), saturated aqueous $NaHCO_3$ (20 mL), and saturated NaCl (20 mL), dried (Na_2O_4), filtered, and concentrated *in vacuo*. The product was purified by column chromatography over silica gel on a Biotage system (2–20% EtOAc in petroleum ether) to afford (+)-**S7b** as a colourless film (50 mg, 79%): R_f 0.59 (Petroleum ether/EtOAc 4:1); $[\alpha]_D^{26}$ = −7.5 (*c* 4.4, $CHCl_3$); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.43–7.29 (5H, m, H-40 to H-44), 5.22 (1H, dddd, *J* 4.5, 4.5, 4.5, 4.5, H-2), 4.76 (1H, s, H-37), 4.33 (1H, dd, J_{XY} 11.9, 4.5, H-1), 4.18 (1H, dd, J_{XY} 11.9, 4.5, H-1'), 4.16 (1H, dd, J_{XY} 11.9, 4.5, H-3), 4.03 (1H, dd, J_{XY} 11.9, 4.5, H-3'), 3.41 (3H, s, H-38), 2.25 (2H, t, *J* 7.7, H-21), 2.18 (1H, ddd, *J* 7.6, 7.6, 7.6, H-5), 2.14 (1H, ddd, *J* 7.6, 7.6, 7.6, H-5'), 1.62–1.48 (4H, m, H-6 and H-22), 1.32–1.21 (48H, m, H-7 to H-18) and H-23 to H-34), 0.90–0.85 (6H, m, H-19 and H-35); ^{13}C NMR (101 MHz; $CDCl_3$) δ_C 173.3 (C-4), 172.9 (C-20), 170.3 (C-36), 136.1 (C-39), 129.0 (C-42), 128.8 (C-40, C-44), 127.3 (C-41, C-43), 82.4 (C-37), 68.7 (C-2), 63.0 (C-1), 61.9 (C-3), 57.5 (C-38), 34.13 (C-5), 34.1 (C-21), 32.1 (C-18), 29.82 (C-34), 29.79, 29.75, 29.63, 29.6, 29.5, 29.41, 29.38, 29.23, 29.19 (C-7 to C-16, C-23 to C-32), 24.94 (C-6), 24.88 (C-22), 22.8 (C-17, C-33), 14.3 (C-19, C-35); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2916 (C-H) (s), 2849 (C-H) (s), 1749 (C=O) (s), 1731 (C=O) (s), 1467 (C-H) (m), 1286 (C-H) (m), 1266 (C-H) (m), 1245 (C-H) (m), 1225 (C-O) (s), 1198 (C-O) (s), 1176 (C-O) (s), 1148 (C-O) (s), 1118 (C-O) (s), 1097 (C-O) (s), 1089 (C-O) (m), 1019 (C-O) (m); LRMS *m/z* (ESI$^+$) 739.5 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) Found 739.5478 [M+Na]$^+$ ($C_{44}H_{76}O_7$ requires 739.5483). This compound was employed for determining the *e.e.* of (–)-**32** by ^{1}H NMR. See Supplementary Results and Discussion, Scheme S3A.

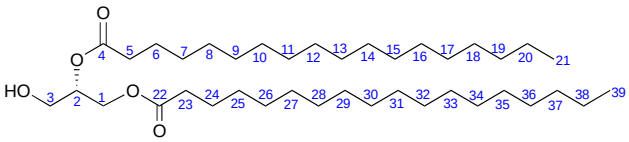
(*S*)-(+)-1,2-Di-*O*-stearoyl-3-*O*-(4-methoxyphenyl)-*sn*-glycerol (+)-S22



(+)-**S22** was synthesised similarly to (+)-**S21**, from (–)-**31** (500 mg, 2.36 mmol, 1.0 eq) and stearoyl chloride (1.75 mL, 5.19 mmol, 2.2 eq). Purification by column chromatography over silica gel (Petroleum ether/EtOAc 95:5, 9:1, 8:2) afforded (+)-**S22** (1.78, 99%) as a colourless solid: R_f 0.70 (Petroleum ether/EtOAc 1:1); m.p. 63–64 °C (CH_2Cl_2); $[\alpha]_D^{25}$ = +3.1 (*c* 0.19, $CHCl_3$); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.25–7.20 (2H, m, H-6 and H-10), 6.90–6.84 (2H, m, H-7 and H-9), 5.26–5.18 (1H, m, H-2), 4.49 (1H, d, J_{AB} 11.7, H-4), 4.44 (1H, d, J_{AB} 11.7, H-4'), 4.33 (1H, dd, J_{XY} 11.9, 3.6, H-1), 4.17 (1H, dd, J_{XY} 11.9, 6.4, H-1'), 3.80 (3H, s, H-11), 3.59–3.51 (2H, m, H-3), 2.34–2.23 (4H, m, H-13 and H-31), 1.67–1.54 (4H, m, H-14 and H-32), 1.26 (56H, br s, H-15 to H-28 and H-31 to H-46), 0.88 (6H, t, *J* 6.6, H-29 and H-47); ^{13}C NMR (101 MHz; $CDCl_3$) δ_C 173.6, 173.3 (C-12, C-30), 159.5 (C-8), 130.0 (C-5), 129.4 (C-6, C-10), 114.0 (C-7, C-9), 73.1 (C-4), 70.2 (C-2), 68.1 (C-3), 62.9 (C-1), 55.4 (C-11), 34.5, 34.3 (C-13, C-31), 32.1 (C-27, C-45), 29.9–29.7, 29.6, 29.5, 29.4, 29.29, 29.25 (C-15 to C-26 and C-33 to C-44), 25.1, 25.0 (C-14, C-32), 22.8 (C-28, C-46), 14.3 (C-29, C-47); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2955 (m), 2916 (s), 2849 (s), 1730 (s), 1612 (w), 1514 (m), 1472 (m), 1391

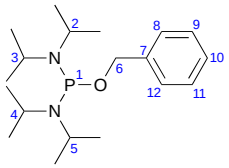
(w), 1236 (m), 1171 (s), 1109 (s); HRMS *m/z* (EI/FI) found 744.6075 $[M]^+$ ($C_{47}H_{84}O_6$ requires 744.6268 $[M]^+$). The data are in good agreement with the literature values.[64]

(*S*)-(−)-1,2-Di-*O*-stearoyl-*sn*-glycerol (−)-33



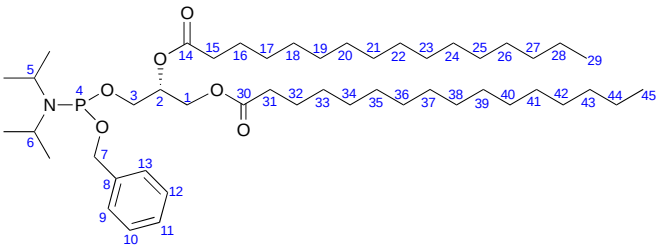
(−)-**33** was synthesised similarly to (−)-**32** from (+)-**S22** (1.70 g, 2.23 mmol, 1.0 eq) to give (−)-**33** (1.30 g, 91%) as a colourless solid: R_f 0.16 (EtOAc); m.p. 75–76 °C (CH_2Cl_2) [lit.[64] 75–77 °C]; $[\alpha]_D^{25}$ = −2.4 (*c* 0.75, CH_2Cl_2) [lit.[64] $[\alpha]_D^{25}$ = −2.50 (*c* 0.060, CH_2Cl_2)]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 5.12–5.50 (1H, m, H-2), 4.32 (1H, dd, *J* 12.0, 5.4, H-1), 4.24 (1H, dd, *J* 12.0, 5.4, H-1'), 3.76–3.70 (2H, m, H-3), 2.33 (4H, app. q, *J* 8.03, H-13 and H-29), 1.99 (1H, t, *J* 5.9, C(3)OH), 1.68-1.57 (4H, m, H-14 and H-30), 1.26 (56H, br s, H-15 to H-28 and H-31 to H-44), 0.88 (6H, t, *J* 6.6, H-29 and H-45). The data are in good agreement with the literature values.[64]

Benzyloxy bis(*N*,*N*-diisopropylamino)phosphine 34



PCl_3 (9.55 mL, 109 mmol, 1.0 eq) was dissolved in anhydrous Et_2O (200 mL) and anhydrous pyridine (7.06 mL, 87.4 mmol, 0.80 eq). The resulting mixture was cooled to −78 °C and benzyl alcohol (11.3 mL, 109 mmol, 1.0 eq) in anhydrous Et_2O (50 mL) was added dropwise, *via* cannula, over 1 hour. The mixture was warmed to RT and stirred for a further 19 hours. The resulting colourless precipitate (pyridinium hydrochloride) was removed by Schlenk filtration under Ar and the remaining solid was washed further with anhydrous Et_2O (2 × 25 mL). The supernatant containing 309 was placed under Ar and cooled to −10 °C. DIPA (84.2 mL, 0.601 mmol, 5.5 eq) was added dropwise, *via* cannula, over 2.5 hours so as to keep the temperature below −5 °C. The mixture was stirred at −10 °C for 1 hour then warmed to RT and stirred for 48 hours. The resulting colourless precipitate (DIPA hydrochloride salt) was removed by Schlenk filtration under Ar and washed with anhydrous Et_2O (2 × 25 mL). The supernatant was concentrated *in vacuo* to yield **34** (30.5 g, crude) as a yellow oil. This unstable phosphine was used in subsequent steps without further purification or characterisation. The product was stored under Ar at −20 °C and was checked by ^{31}P NMR before each use: ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.42–7.20 (5H, m, H-8 to H-12), 4.65 (2H, d, *J* 7.3, H-6), 3.65–3.52 (4H, m, H-2, H-3, H-4 and H-5), 1.21–1.16 (24H, m, C(2)CH_3, C(3)CH_3, C(4)CH_3 and C(5)CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ_P 123.6 (P-1). These data are in good agreement with the literature values.[65-67]

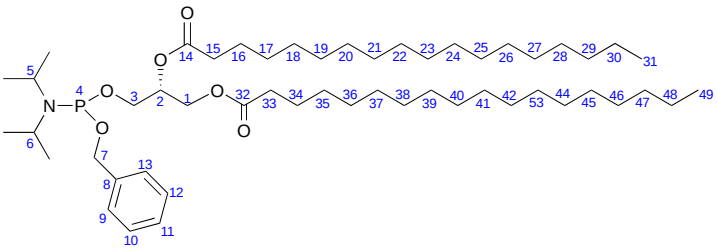
(*R*)-(+)-Benzyloxy-*N*,*N*-diisopropyl-(1,2-di-*O*-palmitoyl-*sn*-glycer-3-yl)phosphoramidite (+)-35



A solution of alcohol (−)-**32** (521 mg, 1.54 mmol, 2.5 eq) in anhydrous CH_2Cl_2 (17 mL) was added dropwise, over 45 minutes, *via* cannula, to a solution of benzyloxy-bis(*N*,*N*-diisopropyl- amino)phosphine **S23** (350 mg, 0.615 mmol, 1.0 eq) and 1*H*-tetrazole (4.1 mL, 1.85 mmol, 3.0 eq, 0.45 M in MeCN) in anhydrous CH_2Cl_2 (28 mL). The reaction mixture was stirred at RT for 18 hours, then diluted with CH_2Cl_2 (20 mL) and quenched by addition of a saturated aqueous solution of $NaHCO_3$ (20 mL). The organic phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by column chromatography over silica gel (Hexane/EtOAc/Et_3N 8:1.5:0.5) to give phosphoramidite (+)-**35** (446 mg, 90%) as a colourless waxy solid, and

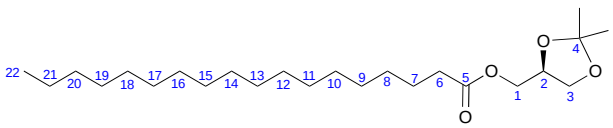
containing a mixture of two diastereoisomers. This phosphoramidite was synthesised fresh and used directly in subsequent steps without further characterisation: R_f 0.72 (Hexane/EtOAc 8:2); $[\alpha]_D^{25}$ = +6.8 (*c* 3.0, $CHCl_3$) [lit.[11] $[\alpha]_D^{24}$ = +6.2 (*c* 1.21, $CHCl_3$)]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.37–7.23 (10H, m, H-9 to H-13 Diast. A and B), 5.22–5.15 (2H, m, H-2 Diast. A and B), 4.79–4.62 (4H, m, H-7, Diast. A and B), 4.35 (1H, dd, J_{XY} 8.3, 3.7, H-1 Diast. A), 4.32 (1H, dd, J_{XY} 8.2, 3.8, H-1 Diast. B), 4.20–4.13 (2H, m, H-1' Diast. A and B), 3.83–3.58 (8H, m, H-5, H-6 and H-3 Diast. A and B), 2.29 (8H, t, *J* 7.6, H-15 and H-31 Diast. A and B), 1.64–1.55 (8H, m, H-16 and H-32), 1.32–1.16 (96H, m, C-17 to C-28 and C-33 to C-44 Diast. A and B), 1.20–1.15 (24H, m, C(5)CH_3 and C(6)CH_3 Diast. A and B), 0.88 (12H, t, *J* 6.8, H-29 and H-45 Diast. A and B); ^{31}P NMR (400 MHz; $CDCl_3$) δ_P 148.7 (P-4, Diast. A), 148.5 (P-4, Diast. B); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2962 (m), 2924 (s), 2854 (m), 2360 (w), 2341 (w), 1744 (C=O) (s), 1464 (w), 1310 (w), 1184 (m), 1158 (m), 1125 (w), 1024 (P-O) (m), 976 (m), 771 (w), 731 (w). These data are in good agreement with the literature values.[11,68]

(*R*)-(+)-Benzyloxy-*N*,*N*-diisopropyl-(1,2-di-*O*-stearoyl-*sn*-glycer-3-yl)phosphoramidite (+)-36



Phosphoramidite (+)-**36** was synthesised similarly to (+)-**35** using alcohol (−)-**33**, to afford (+)-**36** (470 mg, 87%) as a colourless waxy solid, and containing a mixture of two diastereoisomers. This phosphoramidite was synthesised fresh before each use and used directly in subsequent steps without further characterisation: R_f 0.72 (Hexane/EtOAc 8:2); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.37–7.23 (10H, m, H-9 to H-13 Diast. A and B), 5.22–5.15 (2H, m, H-2 Diast. A and B), 4.79–4.62 (4H, m, H-7, Diast. A and B), 4.35 (1H, dd, J_{XY} 8.3, 3.7, H-1 Diast. A), 4.32 (1H, dd, J_{XY} 8.2, 3.8, H-1 Diast. B), 4.20–4.13 (2H, m, H-1' Diast. A and B), 3.83–3.58 (8H, m, H-5, H-6, H-3 and H-3' Diast. A and B), 2.29 (8H, t, *J* 7.6, H-15 and H-31 Diast. A and B), 1.64–1.55 (8H, m, H-16 and H-32), 1.32–1.16 (96H, m, H-17 to H-28 and H-33 to H-44 Diast. A and B), 1.20–1.15 (24H, m, C(5)CH_3 and C(6)CH_3 Diast. A and B), 0.88 (12H, t, *J* 6.8, H-29 and H-45 Diast. A and B); ^{31}P NMR (400 MHz; $CDCl_3$) δ_P 148.7 (P-4, Diast. A), 148.5 (P-4, Diast. B). These data are in good agreement with the literature values.[11,68]

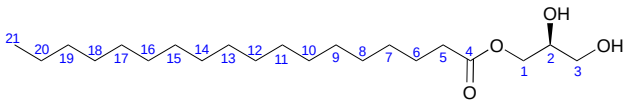
(*S*)-(−)-1-*O*-Stearoyl-2,3-*O*-isopropylidene-*sn*-glycerol (−)-37



A solution of *N*,*N*'-dicyclohexylcarbodiimide (3.12 g, 15.1 mmol, 2.0 eq) in anhydrous CH_2Cl_2 (27 mL) was added dropwise to a stirred solution of (*R*)-(−)-2,3-isopropylidene-*sn*-glycerol (−)-**36** (1.00 g, 7.57 mmol, 1.0 eq), stearic acid (2.15 g, 7.57 mmol, 1.0 eq) and 4-DMAP (55 mg, 0.454 mmol, 0.060 eq) in anhydrous CH_2Cl_2 (20 mL) over 30 minutes, at 0 °C. The reaction mixture was gradually warmed to RT, and was stirred for a further 12 hours. The mixture was then diluted with hexane (10 mL), filtered through Celite® and washed with hexane (3 × 10 mL). The combined filtrate and washings were concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Hexane/EtOAc 20:1) to give (−)-**37** (2.29 g, 76%) as a colourless solid: R_f 0.43 (Hexane/EtOAc 20:1); $[\alpha]_D^{25}$ = −7.9 (*c* 4.0, Hexane) [lit.[14] $[\alpha]_D^{23}$ = −7.38 (*c* 3.95, Hexane)]; m.p. 40–41 °C (Pentane/EtOAc) [lit.[14] 40–41 °C]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 4.35–4.28 (1H, m, H-2), 4.17 (1H, dd, J_{XY} 11.7, 4.6, H-1), 4.09 (1H, dd, J_{XY} 11.7, 5.6, H-1'), 4.08 (1H, dd, J_{XY} 8.3, 6.1, H-3), 3.74 (1H, dd, J_{XY} 8.3, 6.2, H-3'), 2.34 (2H, t, *J* 7.6, H-6), 1.67–1.56 (2H, m, H-7), 1.44 (3H, s, C(4)CH_3), 1.37 (3H, s, C(4)CH_3), 1.33–1.23 (28H, m, H-8 to H-21), 0.88 (3H, t, *J* 6.8, H-22); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.5 (C-5), 109.8 (C-4), 73.7 (C-2),

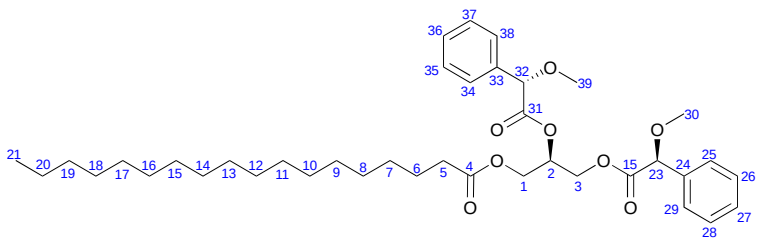
66.4 (C-3), 64.5 (C-1), 34.1 (C-6), 32.0 (C-20), 29.75, 29.72, 29.69, 29.6, 29.5, 29.4, 29.3, 29.2 (C-8 to C-19), 26.7 (C(4)CH_3), 25.4 (C(4)CH_3), 24.9 (C-7), 22.7 (C-21), 14.1 (C-22); LRMS *m/z* (ESI$^-$) 415.1 ([M−OH]$^-$, 100%). These data are in good agreement with the literature values.[12-14]

(*S*)-(+)-1-*O*-Stearoyl-*sn*-glycerol (+)-38



Aqueous acetic acid (AcOH/H_2O 4:1 *v/v*, 5 mL) was added to solid (−)-**37** (500 mg, 1.25 mmol, 1.0 eq), and the mixture was stirred at 50 °C for 2 hours. The reaction mixture was cooled to RT and diluted in Et_2O (10 mL). The organic layer was washed with H_2O (8 mL), a saturated aqueous solution of $NaHCO_3$ (8 mL), and brine (8 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The colourless solid obtained was crystallised from Pentane/EtOAc to give (+)-**38** (314 mg, 70%, >99% *e.e.*) as silver, shiny crystals: R_f 0.25 (Petroleum ether/EtOAc 7:3); $[\alpha]_D^{25}$ = +3.9 (*c* 2.9, Pyridine) [lit.[14] $[\alpha]_D^{23}$ = +4.10 (*c* 2.58, Pyridine)]; m.p. 74–75 °C (Pentane/EtOAc) [lit.[14] 73–74 °C]; ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 4.21 (1H, dd, J_{XY} 11.7, 4.5, H-1), 4.15 (1H, dd, J_{XY} 11.7, 6.1, H-1'), 3.98–3.89 (1H, m, H-2), 3.70 (1H, ddd, J_{XY} 11.4, 6.6, 4.0, H-3), 3.60 (1H, ddd, J_{XY} 11.4, 5.7, 5.7, H-3'), 2.53 (1H, br s, C(2)O*H*), 2.35 (2H, t, *J* 7.7, H-5), 2.10 (1H, br s, C(3)O*H*), 1.67–1.58 (2H, m, H-6), 1.36–1.19 (28H, m, H-7 to H-20), 0.87 (3H, t, *J* 6.8, H-21); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 174.5 (C-4), 70.4 (C-2), 65.3 (C-1), 63.5 (C-3), 34.3 (C-5), 32.1 (C-19), 29.83, 29.79, 29.74, 29.6, 29.5, 29.4, 29.3 (C-7 to C-18), 25.0 (C-6), 22.8 (C-20), 14.3 (C-21); LRMS *m/z* (ESI$^+$) 381.3 ([M+Na]$^+$, 100%). These data are in good agreement with the literature values.[12-14] The *e.e.* of (+)-**38** was calculated by ^{1}H NMR: See Supplementary Results and Discussion and Scheme S4.

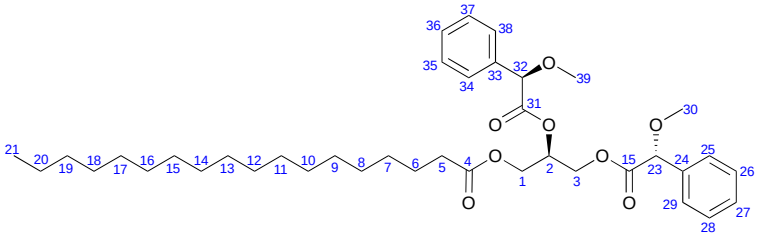
(*R*)-(+)-1-*O*-Stearoyl-2,3-di-*O*-((*S*)-α-methoxyphenylacetoxy)-*sn*-glycerol (+)-S8a



(*S*)-(+)-α-Methoxyphenylacetic acid (37 mg, 0.223 mmol, 4.0 eq), 1-ethyl-3-(3-dimethylamino propyl)carbodiimide (58 mg, 0.301 mmol, 5.4 eq) and 4-DMAP (3 mg, 0.0278 mmol, 0.50 eq) were added to a solution of (+)-**38** (20 mg, 0.0558 mmol, 1.0 eq) in CH_2Cl_2 (0.50 mL). After 24 hours stirring at RT, the reaction mixture was diluted with CH_2Cl_2 (3 mL), and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 5 mL), and brine (5 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3) afforded (+)-**S8a** (32 mg, 89%) as a colourless solid: R_f 0.59 (Petroleum ether/EtOAc 6:4); $[\alpha]_D^{25}$ = +51.7 (*c* 1.0, $CHCl_3$); m.p. 50–51 °C; ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.44–7.29 (10H, m, H-25 to H-29 and H-34 to H-38), 5.24–5.18 (1H, m, H-2), 4.73 (1H, s, H-23), 4.60 (1H, s, H-32), 4.41 (1H, dd, J_{XY} 12.1, 3.9, H-3), 4.18 (1H, dd, J_{XY} 12.1, 5.4, H-3'), 4.02 (1H, dd, J_{XY} 11.9, 4.3, H-1), 3.85 (1H, dd, J_{XY} 11.9, 6.7, H-1'), 3.40 (3H, s, H-30 or H-39), 3.38 (3H, s, H-30 or H-39), 2.07–1.95 (2H, m, H-5), 1.47–1.39 (2H, m, H-6), 1.32–1.18 (28H, m, H-7 to H-20), 0.88 (3H, t, *J* 6.9, H-21); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.1 (C-4), 170.3 (C-22), 169.9 (C-31), 136.02, 136.00 (C-24, C-33), 129.1, 128.9, 128.7 (C-26 to C-28, C-35 to C-37), 127.3 (C-25, C-29), 127.2 (C-34, C-38), 82.3 (C-23), 82.2 (C-32), 69.7 (C-2), 62.58 (C-3), 62.57 (C-1), 57.52, 57.50 (C-30, C-39), 33.8 (C-5), 32.1 (C-19), 29.84, 29.80, 29.76, 29.6, 29.5, 29.4, 29.2 (C-7 to C-18), 24.7 (C-6), 22.8 (C-20), 14.3 (C-21); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2980 (m), 2971 (m), 2923 (s), 2853 (m), 1744 (C=O) (s), 1494 (w), 1456 (m), 1380 (m), 1251 (m), 1198 (m), 1166 (C-O) (s), 1116 (C-O) (s), 1076 (m), 1029 (w), 998 (w), 967 (w), 731 (m), 697 (m); LRMS *m/z* (ESI$^+$) 677.4 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 677.40230 [M+Na]$^+$ ($C_{39}H_{58}O_8Na$ requires 677.40239 [M+Na]$^+$); RP-

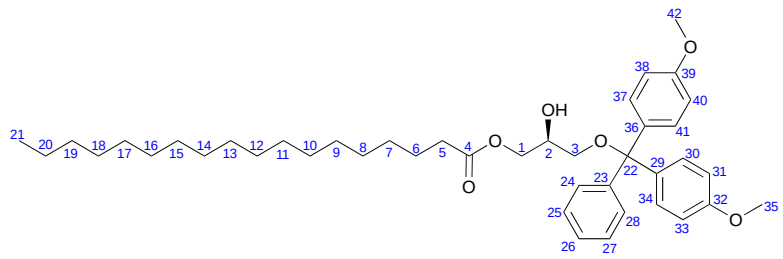
HPLC (Method 4) t_R = 8.27 min, 98.61%. This compound was employed for determining the *e.e.* of (+)-**38** by ^{1}H NMR: See Supplementary Results and Discussion and Scheme S4.

(*R*)-(−)-1-*O*-Stearoyl-2,3-di-*O*-((*R*)-α-methoxyphenylacetoxy)-*sn*-glycerol (−)-S8b



(*R*)-(−)-α-Methoxyphenylacetic acid (37 mg, 0.223 mmol, 4.0 eq), 1-ethyl-3-(3-dimethylamino propyl)carbodiimide (58 mg, 0.301 mmol, 5.4 eq) and 4-DMAP (3 mg, 0.0278 mmol, 0.50 eq) were added to a solution of (+)-**38** (20 mg, 0.0558 mmol, 1.0 eq) in CH_2Cl_2 (0.50 mL). After 24 hours stirring at RT, the reaction mixture was diluted with CH_2Cl_2 (3 mL), and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 5 mL), and brine (5 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3) afforded (−)-**S8b** (30 mg, 83%) as a colourless solid: R_f 0.63 (Petroleum ether/EtOAc 6:4); $[\alpha]_D^{25}$ = −47.7 (*c* 0.97, $CHCl_3$); m.p. 44–45 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.45–7.29 (10H, m, H-25 to H-29 and H-34 to H-38), 5.31–5.25 (1H, m, H-2), 4.74 (1H, s, H-23), 4.56 (1H, s, H-32), 4.30 (1H, dd, J_{XY} 12.0, 4.1, H-3), 4.18 (1H, dd, J_{XY} 12.1, 4.2, H-1), 4.03 (1H, dd, J_{XY} 12.1, 6.1, H-1'), 4.00 (1H, dd, J_{XY} 12.0, 6.3, H-3'), 3.37 (3H, s, H-30 or H-39), 3.34 (3H, s, H-30 or H-39), 2.20 (2H, t, *J* 8.0, H-5), 1.59–1.50 (2H, m, H-6), 1.33–1.21 (28H, m, H-7 to H-20), 0.88 (3H, t, *J* 6.9, H-21); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.2 (C-4), 170.2, 170.1 (C-22, C-31), 136.1, 136.0 (C-24, C-33), 129.02, 129.00, 128.8 (C-26 to C-28, C-35 to C-37), 127.28, 127.26 (C-25, C-29, C-34, C-38), 82.5 (C-23), 82.2 (C-32), 69.8 (C-2), 62.6 (C-3), 61.7 (C-1), 57.5 (C-30, C-39), 34.0 (C-5), 32.1 (C-19), 29.84, 29.80, 29.76, 29.6, 29.5, 29.4, 29.2 (C-7 to C-18), 24.9 (C-6), 22.8 (C-20), 14.3 (C-21); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2923 (s), 2853 (m), 1742 (C=O) (s), 1495 (w), 1455 (m), 1349 (w), 1318 (w), 1245 (m), 1198 (C-O) (s), 1166 (C-O) (s), 1113 (C-O) (s), 1076 (m), 1029 (m), 997 (m), 730 (s), 697 (s); LRMS *m/z* (ESI$^+$) 677.4 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 677.40268 [M+Na]$^+$ ($C_{39}H_{58}O_8Na$ requires 677.40239 [M+Na]$^+$); RP-HPLC (Method 4) t_R = 7.93 min, 98.76%. This compound was employed for determining the *e.e.* of (+)-**38** by ^{1}H NMR: See Supplementary Results and Discussion and Scheme S4.

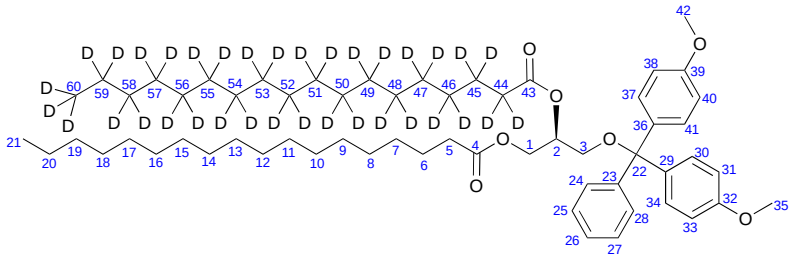
(*S*)-(+)-1-*O*-Stearoyl-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-39



To a solution of (+)-**38** (200 mg, 0.558 mmol, 1.0 eq) in anydrous pyridine (5 mL) was added 4,4'-dimethoxytrityl chloride (227 mg, 0.669 mmol, 1.2 eq) in one portion. After 50 minutes stirring at RT, the yellow solution was concentrated *in vacuo* at RT. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 9.5:0.5, 9:1, 8.5:1.5, 8:2, 7:3) to give (+)-**39** (249 mg, 67%) as a colourless oil: R_f 0.54 (Petroleum ether/EtOAc 7:3); $[\alpha]_D^{25}$ = +3.0 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.43–7.39 (2H, m, H-24 and H-28), 7.33–7.26 (6H, m, H-30, H-34, H-37, H-41, H-25 and H-27), 7.24–7.20 (1H, m, H-26), 6.85–6.81 (4H, m, H-31, H-33, H-38 and H-40), 4.20 (1H, dd, J_{XY} 11.5, 4.3, H-1), 4.16 (1H, dd, J_{XY} 11.5, 6.2, H-1'), 4.01–3.95 (1H, m, H-2), 3.79 (6H, s, H-35 and H-42), 3.22 (1H, dd, J_{XY} 9.5, 5.0, H-3), 3.19 (1H, dd, J_{XY} 9.5, 5.5, H-3'), 2.42 (1H, d, *J* 5.2, C(2)O*H*), 2.28 (2H, t, *J* 7.6, H-5), 1.62–1.54 (2H, m, H-6), 1.34–1.20 (28H, m, H-7 to H-20), 0.88 (3H, t, *J* 6.9, H-21); ^{13}C

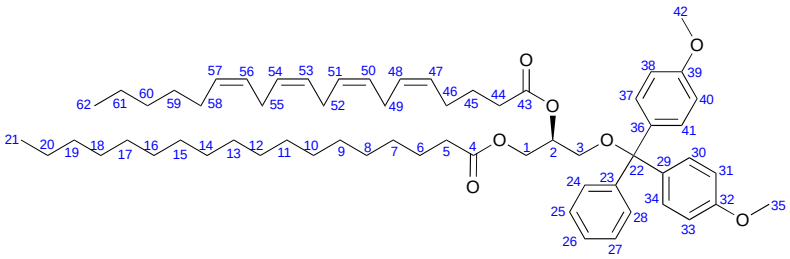
NMR (126 MHz; $CDCl_3$) δ_C 174.1 (C-4), 158.7 (C-32, C-39), 144.7 (C-23), 135.9 (C-29, C-36), 130.1 (C-30, C-34, C-37, C-41), 128.2 (C-24, C-28), 128.0 (C-25, C-27), 127.0 (C-26), 113.3 (C-31, C-33, C-38, C-40), 86.4 (C-22), 69.5 (C-2), 65.8 (C-1), 64.1 (C-3), 55.3 (C-35, C-42), 34.3 (C-5), 32.1 (C-19), 29.84, 29.80, 29.76, 29.6, 29.5, 29.4, 29.3 (C-7 to C-18), 25.0 (C-6), 22.8 (C-20), 14.3 (C-21); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3480 (O-H) (br), 2980 (m), 2922 (s), 2852 (m), 1737 (C=O) (m), 1608 (m), 1582 (w), 1509 (s), 1463 (m), 1445 (m), 1415 (w), 1379 (w), 1300 (m), 1249 (s), 1175 (C-O) (s), 1155 (m), 1116 (m), 1076 (m), 1035 (m), 982 (m), 902 (w), 828 (m), 791 (w), 771 (w), 754 (w), 726 (w), 702 (m); HRMS *m/z* (ESI^+) found 683.42851 $[M+Na]^+$ ($C_{42}H_{60}O_6Na$ requires 683.42821 $[M+Na]^+$); RP-HPLC (Method 2) t_R = 6.88 min, 96.13%. These data are in good agreement with the literature values.[13]

D_{35}-(*S*)-(+)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-40



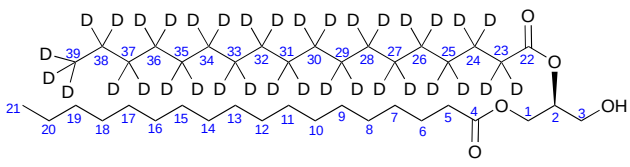
To a stirred solution of (+)-**39** (600 mg, 0.908 mmol, 1.0 eq), D_{35} stearic acid (290 mg, 0.908 mmol, 1.0 eq, Sigma Aldrich 98 atom % D) and 4-DMAP (30 mg, 0.245 mmol, 0.27 eq) in anhydrous CH_2Cl_2 (14 mL) was added *N*,*N*'-dicyclohexylcarbodiimide (227 mg, 1.10 mmol, 1.21 eq). The reaction mixture was stirred at RT for 24 hours and the solvent was concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/Et_2O 10:0, 9.5:0.5, 9:1, 8.5:1.5, 8:2) to give (+)-**40** (795 mg, 91%, 70% D_{35}, 30% D_{34}) as a colourless solid: R_f 0.88 (Petroleum ether/EtOAc 7:3); $[\alpha]_D^{25}$ = +11.3 (*c* 1.0, $CHCl_3$); m.p. 31–32 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.43–7.39 (2H, m, H-24 and H-28), 7.33–7.27 (6H, m, H-25, H-27, H-30, H-34, H-37 and H-41), 7.24–7.19 (1H, m, H-26), 6.85–6.79 (4H, m, H-31, H-33, H-38 and H-40), 5.28–5.22 (1H, m, H-2), 4.34 (1H, dd, J_{XY} 11.7, 3.8, H-1), 4.23 (1H, dd, J_{XY} 11.7, 6.8, H-1'), 3.79 (6H, s, H-35 and H-42), 3.23 (1H, dd, J_{XY} 9.9, 4.8, H-3), 3.20 (1H, dd, J_{XY} 9.9, 5.2, H-3'), 2.28 (2H, t, *J* 7.6, H-5), 1.59–1.50 (2H, m, H-6), 1.34–1.18 (28H, m, H-7 to H-20), 0.88 (3H, t, *J* 6.9, H-21); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.6 (C-4), 173.3 (C-43), 158.6 (C-39, C-32), 144.7 (C-23), 135.91, 135.88 (C-29, C-36), 130.16, 130.13 (C-30, C-34, C-37, C-41), 128.2 (C-24, C-28), 128.0 (C-25, C-27), 127.0 (C-26), 113.3 (C-31, C-33, C-38, C-40), 86.2 (C-22), 70.6 (C-2), 63.1 (C-1), 62.2 (C-3), 55.3 (C-35, C-42), 34.3 (C-5), 34.2–33.4 (m_D, C-44), 32.1 (C-19), 31.1–30.2 (m_D, C-58), 29.9, 29.83, 29.81, 29.79, 29.7, 29.5, 29.4, 29.3 (C-7 to C-18), 28.9–27.7 (m_D, C-46 to C-57), 25.0 (C-6), 24.4–23.7 (m_D, C-45), 22.8 (C-20), 21.9–21.1 (m_D, C-59), 14.3 (C-21), 13.5–12.6 (m_D, C-60); ^{2}H NMR (96 MHz; $CDCl_3$) δ_D 2.29 (2D, br s, D-44), 1.57 (2D, br s, D-45), 1.19 (28D, br s, D-46 to D-59), 0.83 (3D, br s, D-60); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2981 (s), 2919 (m), 2851 (m), 2194 (w), 2088 (w), 1739 (C=O) (m), 1608 (w), 1509 (m), 1468 (w), 1446 (w), 1381 (w), 1298 (w), 1250 (s), 1174 (s), 1088 (m), 1034 (m), 953 (w), 828 (m), 724 (w), 702 (w); HRMS *m/z* (ESI^+) found 983.90219 ($[MD_{34}+Na]^+$, 33%), 984.90804 ($[MD_{35}+Na]^+$, 100%) ($C_{60}H_{59}D_{35}O_7Na$ requires 984.90886 $[MD_{35}+Na]^+$); NP-HPLC (Method 8) t_R = 1.39 min, 100%.

(*S*)-(+)-1-*O*-Stearoyl-2-*O*-arachidonyl-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-41



To a solution of (+)-**39** (553 mg, 0.837 mmol, 1.0 eq) in CH_2Cl_2 (13 mL) was added DCC (242 mg, 1.17. mmol, 1.4 eq), 4-DMAP (61 mg, 0.502 mmol, 0.60 eq) and arachidonic acid (301 µL, 0.912 mmol, 1.09 eq). The solution was stirred at RT in the dark for 5 hours and the solvent was evaporated *in vacuo* at RT. Purification by column chromatography over silica gel (Petroleum ether/Et_2O 10:0 to 8.8:1.3) yielded (+)-**41** (681 mg, 86%) as a colourless oil: R_f 0.35 (Petroleum ether/Et_2O 8:2); $[\alpha]_D^{25}$ = +9.0 *c* 0.50, CH_3Cl); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.43–7.38 (2H, m, H-24 and H-28), 7.32–7.26 (6H, m, H-25, H-27, H-30, H-34, H-37 and H-41), 7.23–7.19 (1H, m, H-26), 6.84–6.79 (4H, m, H-31, H-33, H-38 and H-40), 5.43–5.30 (8H, m, H-47, H-48, H-50, H-51, H-53, H-54, H-56 and H-57), 5.28–5.21 (1H, m, H-2), 4.35 (1H, dd, J_{XY} 11.6, 3.7, H-1), 4.23 (1H, dd, J_{XY} 11.6, 6.7, H-1'), 3.79 (6H, s, H-35 and H-42), 3.23 (1H, dd, J_{XY} 9.7, 5.0, H-3), 3.21 (1H, dd, J_{XY} 9.7, 5.1, H-3'), 2.87–2.76 (6H, m, H-49, H-52 and H-55), 2.38–2.31 (2H, m, H-44), 2.23 (2H, t, *J* 7.5, H-5), 2.15–2.09 (2H, m, H-46), 2.08–2.02 (2H, m, H-58), 1.72 (2H, tt, *J* 7.5, 7.5, H-45), 1.59–1.51 (2H, m, H-6), 1.39–1.21 (34H, m, H-7 to H-20 and H-59 to H-61), 0.89 (3H, t, *J* 7.0, H-21 or H-62), 0.88 (3H, t, *J* 7.0, H-21 or H-62); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.5 (C-4), 172.9 (C-43), 158.7 (C-32, C-39), 144.7 (C-23), 135.91, 135.88 (C-29, C-36), 130.6 (C-57), 130.2, 130.1 (C-30, C-34, C-37, C-41), 129.1, 129.0 (C-47, C-48), 128.7, 128.4 (C-50, C-51, C-53, C-54), 128.3, 128.2 (C-24, C-28), 128.00, 127.97 (C-25, C-27), 127.7 (C-56), 127.0 (C-26), 113.3 (C-31, C-33, C-38, C-40), 86.2 (C-22), 70.7 (C-2), 63.0 (C-1), 62.1 (C-3), 55.3 (C-35, C-42), 34.3 (C-5), 33.9 (C-44), 32.1 (C-19), 31.7 (C-60), 29.9, 29.83, 29.81, 29.79, 29.6, 29.51, 29.49, 29.43, 29.3 (C-7 to C-18, C-59), 27.4 (C-58), 26.7 (C-46), 25.79, 25.76 (C-49, C-52, C-55), 25.0 (C-6, C-45), 22.8 (C-20), 22.7 (C-61), 14.3, 14.2 (C-21, C-62); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3011 (w), 2923 (s), 2853 (m), 1741 (C=O) (s), 1608 (m), 1582 (w), 1509 (s), 1463 (m), 1446 (m), 1417 (w), 1376 (w), 1301 (m), 1249 (s), 1175 (s), 1151 (s), 1089 (m), 1036 (s), 977 (w), 913 (w), 902 (w), 828 (s), 725 (m), 701 (s); HRMS *m/z* (ESI$^+$) found 969.65858 $[M+Na]^+$ ($C_{62}H_{90}O_7Na$ requires 969.65788 $[M+Na]^+$); NP-HPLC (Method 8) t_R = 1.45 min, 100%.

D_{35}-(*S*)-(−)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glycerol (−)-42

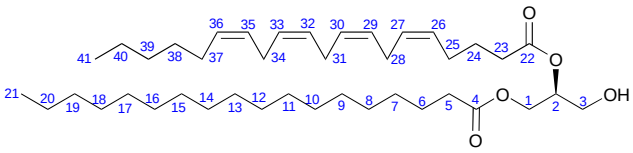


<u>Method 1</u> – TFA (0.3 µL) was added to a solution of (+)-**40** (30 mg, 0.0312 mmol, 1.0 eq, 70% D_{35}, 30% D_{34}) and pyrrole (4 mg, 0.0596 mmol, 1.9 eq) in anhydrous CH_2Cl_2 (0.20 mL). After stirring at RT for 2 hours, further TFA (0.3 µL) was added. The solution was then stirred for a further hour, and the solvent was concentrated *in vacuo*. The solid obtained was crystallised from Hexane/Et_2O to give (−)-**42** (10 mg, 54%) as a colourless solid. Analysis by ^{1}H NMR revealed that (−)-**42** was contaminated with some migration product in a ratio of 3.3:1.0, suggesting that (−)-**42** may not be enantiomerically pure.

<u>Method 2</u> – Aqueous acetic acid ($AcOH/H_2O$ 4:1 *v/v*, 5 mL) was added to solid (+)-**40** (923 mg, 0.959 mmol, 1.0 eq, 70% D_{35}, 30% D_{34}), and the mixture was stirred at 50 °C for 3.5 hours. The solution was then cooled to RT and concentrated *in vacuo*. The colourless solid obtained was crystallised from Pentane/Et_2O to give (−)-**42** (596 mg, 94%, 72% D_{35}, 28% D_{34}, 96% *e.e.*) as a colourless solid: R_f 0.19 (Petroleum ether/Et_2O 7:3); $[\alpha]_D^{25}$ = −2.9 (*c* 1.0, $CHCl_3$); m.p. 72–73 °C (Pentane/Et_2O); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 5.11–5.06 (1H, m, H-2), 4.32 (1H, dd, J_{XY} 11.9, 4.5, H-1), 4.24 (1H, dd, J_{XY} 11.9, 5.7, H-1'), 3.77–3.68 (2H, m,

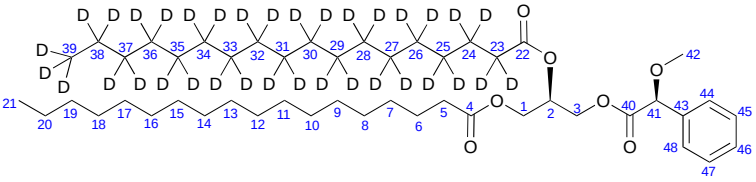
H-3), 2.32 (2H, t, *J* 7.6, H-5), 2.03 (1H, dd, *J* 6.5, 6.5, C(3)O*H*), 1.65–1.58 (2H, m, H-6), 1.34–1.20 (28H, m, H-7 to H-20), 0.88 (3H, t, *J* 7.0, H-21); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 174.0 (C-4), 173.7 (C-22), 72.2 (C-2), 62.1 (C-1), 61.7 (C-3), 34.3 (C-5), 34.1–33.3 (m_D, C-23), 32.1 (C-19), 31.1–30.2 (m_D, C-37), 29.85, 29.81, 29.77, 29.6, 29.5, 29.4, 29.3 (C-7 to C-18), 28.9–27.7 (m_D, C-25 to C-36), 25.0 (C-6), 24.4–23.6 (m_D, C-24), 22.8 (C-20), 21.9–21.1 (m_D, C-38), 14.3 (C-21), 13.5–12.7 (m_D, C-39); ^{2}H NMR (96 MHz; $CDCl_3$) δ_D 2.31 (2D, br s, D-23), 1.58 (2D, br s, D-24), 1.20 (28D, br s, D-25 to D-38), 0.83 (3D, br s, D-39); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3501 (O-H) (w), 2955 (w), 2918 (s), 2850 (s), 2193 (m), 2088 (m), 1729 (C=O) (s), 1709 (C=O) (s), 1600 (w), 1468 (m), 1451 (m), 1389 (m), 1367 (m), 1328 (m), 1317 (m), 1276 (s), 1256 (m), 1241 (m), 1222 (m), 1164 (m), 1147 (m), 1089 (s), 1062 (s), 1039 (m), 1027 (m), 1010 (m), 724 (m); HRMS *m/z* (ESI$^+$) found 681.77168 ([MD_{34}+Na]$^+$, 34%), 682.77748 ([MD_{35}+Na]$^+$, 100%) ($C_{39}H_{41}D_{35}O_5Na$ requires 682.77818 [MD_{35}+Na]$^+$). The *e.e.* of (−)-**42** was calculated by ^{1}H NMR: See Supplementary Results and Discussion and Scheme S3.

(*S*)-1-*O*-Stearoyl-2-*O*-arachidonyl-*sn*-glycerol (−)-43



To (+)-**41** (210 mg, 0.222 mmol, 1.0 eq) was added AcOH/Formic Acid/H_2O (3 mL, 7:2:1 *v*/*v*/*v*) to give a bright orange solution. This solution was stirred at RT for 4 hours. Conversion was monitored by TLC analysis (Petroleum ether/Et_2O 7:3) until a minimal amount of starting material could be observed (in certain cases, heating to 30 °C was needed, although it is important to be aware that over-heating may result in acyl migration). When the reaction was judged finished, Et_2O (10 mL) and H_2O (10 mL) were added. The aqueous layer was extracted with Et_2O (4 × 10 mL) and the combined organic layers were washed with H_2O (4 × 10 mL) and $NaHCO_3$ (3 × 10 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. A 20 mL syringe was loaded with C-18 RP silica gel (~12 mL) and washed with MeCN (3 × 20 mL). The crude compound was loaded onto the column with MeCN and DMTOH side product was flushed off the column by eluting with MeCN (50 mL). The silica was then washed out of the column with CH_2Cl_2 (10 mL) and triturated with CH_2Cl_2 (5–6 × 30 mL) until (−)-**43** could no longer be observed by TLC analysis. The combined CH_2Cl_2 washings were evaporated *in vacuo* to give (−)-**43** (132 mg, 92%, 95% *e.e.*) as a colourless oil, contaminated with the starting material (+)-**41** in an 8:1 ratio, as determined by ^{1}H NMR analysis: ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 5.44–5.30 (8H, m, H-26, H-27, H-29, H-30, H-32, H-33, H-35, H-36), 5.11–5.04 (1H, m, H-2), 4.31 (1H, dd, J_{XY} 11.9, 4.5, H-1), 4.22 (1H, dd, J_{XY} 11.9, 5.6, H-1'), 3.74–3.69 (2H, m, H-3), 2.86–2.77 (6H, m, H-28, H-31 and H-34), 2.36 (2H, t, *J* 7.6, H-5), 2.31 (2H, t, *J* 7.6, H-23), 2.15–2.00 (2H, m, H-25 and H-37), 1.72 (2H, tt, *J* 7.5, 7.5, H-6), 1.66–1.54 (2H, m, H-24), 1.39–1.19 (34H, m, H-7 to H-20 and H-38 to H-40), 0.92–0.84 (6H, m, H-21 and H-41); HRMS *m/z* (ESI$^+$) found 645.54488 [M+H]$^+$ ($C_{41}H_{73}O_5$ requires 645.54525 [M+H]$^+$). This compound was employed in subsequent steps without further purification or characterisation. The *e.e.* of (−)-**43** was calculated by ^{1}H NMR: See Supplementary Results and Discussion and Scheme S3.

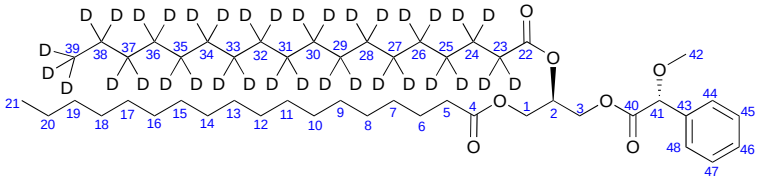
D_{35}-(*R*)-(+)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-((*S*)-α-methoxyphenylacetoxy)-*sn*-glycerol (+)-9a



(*S*)-(+)-α-Methoxyphenylacetic acid (19 mg, 0.115 mmol, 3.8 eq), 1-ethyl-3-(3-dimethylamino propyl)carbodiimide (30 mg, 0.158 mmol, 5.2 eq) and 4-DMAP (3 mg, 0.0242 mmol, 0.80 eq) were added to a solution of (−)-**42** (20 mg, 0.0303 mmol, 1.0 eq, 72% D_{35}, 28% D_{34}) in CH_2Cl_2 (1 mL). After stirring at RT for 24

hours, the reaction mixture was diluted with CH_2Cl_2 (3 mL), and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 5 mL), and brine (5 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/Et_2O 10:0, 9:1, 8:2, 7:3) provided (+)-**9a** (23 mg, 94%, 71% D_{35}, 29% D_{34}) as a colourless solid: R_f 0.44 (Petroleum ether/Et_2O 7:3); $[\alpha]_D^{25}$ = +20.7 (*c* 0.79, $CHCl_3$); m.p. 58–60 °C (Pentane/Et_2O); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.44–7.40 (2H, m, H-45 and H-47), 7.38–7.30 (3H, m, H-44, H-46 and H-48), 5.20–5.14 (1H, m, H-2), 4.77 (1H, s, H-41), 4.35 (1H, dd, J_{XY} 11.9, 4.1, H-3), 4.20 (1H, dd, J_{XY} 11.9, 5.7, H-3'), 4.28 (1H, dd, J_{XY} 11.9, 4.4, H-1), 3.96 (1H, dd, J_{XY} 11.9, 5.9, H-1'), 3.41 (3H, s, H-42), 2.26 (2H, t, *J* 7.5, H-5), 1.61–1.52 (2H, m, H-6), 1.33–1.20 (28H, m, H-7 to H-20), 0.88 (3H, t, *J* 6.9, H-21); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.3 (C-4), 172.9 (C-22), 170.3 (C-40), 136.0 (C-43), 129.0 (C-46), 128.8 (C-44, C-48), 127.3 (C-45, C-47), 82.5 (C-41), 68.7 (C-2), 62.7 (C-3), 61.9 (C-1), 57.5 (C-42), 34.1 (C-5), 33.9–33.0 (m_D, C-23), 32.1 (C-19), 31.1–30.3 (m_D, C-37), 29.85, 29.81, 29.77, 29.6, 29.5, 29.4, 29.2 (C-7 to C-18), 28.9–27.7 (m_D, C-25 to C-36), 25.0 (C-6), 24.2–23.4 (m_D, C-24), 22.8 (C-20), 21.9–21.1 (m_D, C-38), 14.3 (C-21), 13.5–12.7 (m_D, C-39); ^{2}H NMR (96 MHz; $CDCl_3$) δ_D 2.15 (2D, br s, D-23), 1.48 (2D, br s, D-24), 1.20 (28D, br s, D-25 to D-38), 0.83 (3D, br s, D-39); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2919 (s), 2851 (m), 2193 (m), 2087 (m), 1737 (C=O) (s), 1469 (m), 1385 (w), 1261 (m), 1250 (m), 1213 (m), 1191 (m), 1166 (s), 1149 (s), 1117 (s), 1088 (s), 1032 (m), 981 (m), 947 (m), 932 (m), 726 (s), 695 (m); HRMS *m/z* (ESI$^+$) found 829.82428 ([MD_{34}+H]$^+$, 34%), 830.82988 ([MD_{35}+H]$^+$, 100%) ($C_{48}H_{49}D_{35}O_7Na$ requires 830.83061 [MD_{35}+Na]$^+$); RP-HPLC (Method 8) t_R = 1.45 min, 96.86%. This compound was employed for determining the *e.e.* of (+)-**42** by ^{1}H NMR: See Supplementary Results and Discussion and Scheme S3.

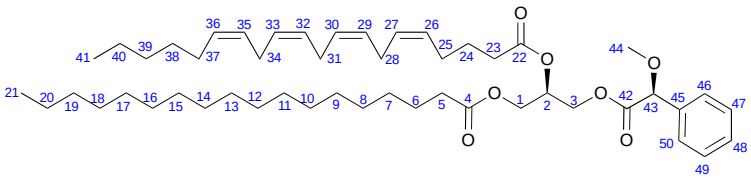
D_{35}-(*R*)-(−)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-((*R*)-α-methoxyphenylacetoxy)-*sn*-glycerol (−)-9b



(*R*)-(−)-α-Methoxyphenylacetic acid (19 mg, 0.115 mmol, 3.8 eq), 1-ethyl-3-(3-dimethylamino propyl)carbodiimide (30 mg, 0.158 mmol, 5.2 eq) and 4-DMAP (3 mg, 0.0242 mmol, 0.80 eq) were added to a solution of (−)-**42** (20 mg, 0.0303 mmol, 1.0 eq, 72% D_{35}, 28% D_{34}) in CH_2Cl_2 (1 mL). After stirring at RT for 24 hours, the reaction mixture was diluted with CH_2Cl_2 (3 mL), and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 5 mL), and brine (5 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/Et_2O 10:0, 9:1, 8:2, 7:3) gave (−)-**9b** (21 mg, 86%, 70% D_{35}, 30% D_{34}) as a colourless solid: R_f 0.44 (Petroleum ether/Et_2O 7:3); $[\alpha]_D^{25}$ = −19.6 (*c* 1.0, $CHCl_3$); m.p. 58–60 °C (Pentane/Et_2O); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.44–7.39 (2H, m, H-45 and H-47), 7.38–7.30 (3H, m, H-44, H-46 and H-48), 5.25–5.19 (1H, m, H-2), 4.77 (1H, s, H-41), 4.34 (1H, dd, J_{XY} 12.1, 4.0, H-3), 4.18 (1H, dd, J_{XY} 12.1, 6.1, H-3'), 4.16 (1H, dd, J_{XY} 12.0, 4.9, H-1), 4.03 (1H, dd, J_{XY} 12.0, 5.7, H-1'), 3.41 (3H, s, H-42), 2.26 (2H, t, *J* 7.6, H-5), 1.61–1.52 (2H, m, H-6), 1.33–1.20 (28H, m, H-7 to H-20), 0.88 (3H, t, *J* 6.9, H-21); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.3 (C-4), 172.9 (C-22), 170.4 (C-40), 136.1 (C-43), 129.0 (C-46), 128.8 (C-44, C-48), 127.3 (C-45, C-47), 82.4 (C-41), 68.6 (C-2), 63.0 (C-3), 61.9 (C-1), 57.5 (C-42), 34.1 (C-5), 33.9–32.9 (m_D, C-23), 32.1 (C-19), 31.1–30.2 (m_D, C-37), 29.85, 29.81, 29.77, 29.6, 29.5, 29.4, 29.2 (C-7 to C-18), 28.9–27.6 (m_D, C-25 to C-36), 25.0 (C-6), 24.2–23.4 (m_D, C-24), 22.8 (C-20), 21.9-21.1 (m_D, C-38), 14.3 (C-21), 13.5–12.7 (m_D, C-39); ^{2}H NMR (96 MHz; $CDCl_3$) δ_D 2.13 (2D, br s, D-23), 1.48 (2D, br s, D-24), 1.19 (28D, br s, D-25 to D-38), 0.83 (3D, br s, D-39); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2918 (s), 2850 (m), 2193 (m), 2088 (m), 1736 (C=O) (s), 1469 (m), 1286 (m), 1274 (m), 1211 (m),1177 (s), 1115 (s), 1089 (m), 1058 (m), 744 (m), 724 (m), 698 (m); HRMS *m/z* (ESI$^+$) found 829.82412 ([MD_{34}+Na]$^+$, 35%), 830.82983 ([MD_{35}+Na]$^+$, 100%) ($C_{48}H_{49}D_{35}O_7Na$

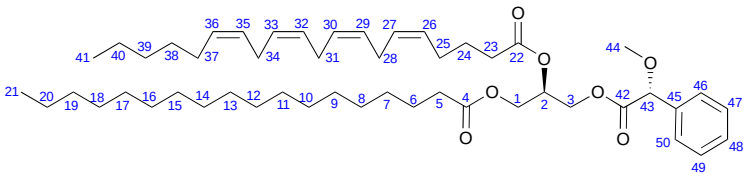
requires 830.83061 [MD_{35}+Na]$^+$); RP-HPLC (Method 8) t_R = 1.45 min, 96.86%. This compound was employed for determining the *e.e.* of (+)-**42** by ^{1}H NMR: See Supplementary Results and Discussion and Scheme S3.

(*R*)-(+)-1-*O*-Stearoyl-2-*O*-arachidonyl-3-*O*-((*S*)-α-methoxyphenylacetoxy)-*sn*-glycerol (+)-S10a



(S)-(+)-α-Methoxyphenylacetic acid (5 mg, 0.0310 mmol, 2.0 eq), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (8 mg, 0.0419 mmol, 2.7 eq) and 4-DMAP (1 mg, 0.00775 mmol, 0.50 eq) were added to a solution of (−)-**43** (10 mg, 0.0155 mmol, 1.0 eq) in CH_2Cl_2 (0.5 mL). After stirring at RT for 4 hours, the reaction mixture was diluted with CH_2Cl_2 (5 mL), and the organic layer was washed with a saturated aqueous solution of $NaHCO_3$ (2 × 3 mL), and brine (3 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/Et_2O 10:0, 9:1, 8:2, 7:3) gave (+)-**S10a** (9 mg, 74%) as a colourless film: $[\alpha]_D^{25}$ = +45.5 (*c* 0.33, CH_3Cl); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.44–7.39 (2H, m, H-47 and H-49), 7.39–7.31 (3H, m, H-46, H-48 and H-50), 5.44–5.30 (8H, m, H-26, H-27, H-29, H-30, H-32, H-33, H-35 and H-36), 5.20–5.14 (1H, m, H-2), 4.77 (1H, s, H-43), 4.36 (1H, dd, J_{XY} 11.8, 4.2, H-3), 4.20 (1H, dd, J_{XY} 11.8, 5.8, H-3'), 4.18 (1H, dd, J_{XY} 11.8, 4.3, H-1), 3.97 (1H, dd, J_{XY} 11.8, 5.8, H-1'), 3.40 (3H, s, H-44), 2.86–2.78 (6H, m, H-28, H-31 and H-34), 2.26 (2H, t, *J* 7.6, H-5), 2.19 (2H, td, *J* 11.3, 3.5, H-23), 2.11–2.02 (4H, m, H-25 and H-37), 1.65–1.54 (4H, m, H-6 and H-24), 1.39–1.21 (34H, m, H-7 to H-20 and H-38 to H-40), 0.91–0.85 (6H, m, H-21 and H-41); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.3 (C-4), 172.6 (C-22), 170.3 (C-42), 136.1 (C-45), 130.7 (C-36), 129.1, 129.0, 128.9, 128.83, 128.76, 128.5, 128.2, 128.0 (C-26, C-27, C-48, C-46, C-50, C-29, C-30, C-32, C-33), 127.7 (C-35), 127.3 (C-47, C-49), 82.5 (C-43), 68.9 (C-2), 62.7 (C-3), 61.9 (C1), 57.5 (C-44), 34.1 (C-5), 33.6 (C-23), 32.1 (C-19), 31.7 (C-39), 29.84, 29.80, 29.77, 29.6, 29.50, 29.46, 29.40, 29.2 (C-7 to C-18, C-38), 27.4 (C-37), 26.6 (C-25), 25.8, 25.7 (C-28, C-31, C-34), 25.0, 24.7 (C-6, C-24), 22.8 (C-20), 22.7 (C-40), 14.3, 14.2 (C-21, C-41); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2936 (br), 2876 (w), 2836 (w), 1747 (C=O) (s), 1613 (m), 1586 (w), 1514 (s), 1456 (w), 1370 (w), 1336 (w), 1302 (w), 1246 (s), 1176 (m), 1109 (s), 1075 (m), 1033 (m), 773 (m), 699 (m); HRMS *m/z* (ESI$^+$) found 793.59728 [M+H]$^+$ ($C_{50}H_{81}O_7$ requires 793.59768 [M+H]$^+$). This compound was employed for determining the *e.e.* of (+)-**43** by ^{1}H NMR: See Supplementary Results and Discussion and Scheme S3.

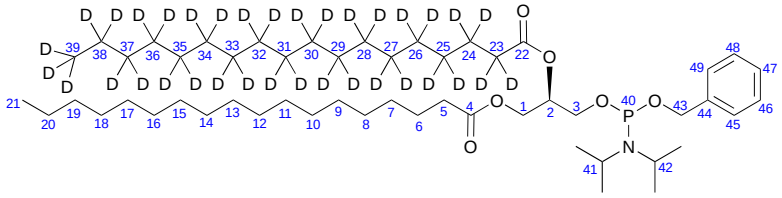
(*R*)-(−)-1-*O*-Stearoyl-2-*O*-arachidonyl-3-*O*-((*R*)-α-methoxyphenylacetoxy)-*sn*-glycerol (−)-S10b



(−)-**S10b** was prepared from (−)-**43**, similarly to (+)-**S10a**, using (*R*)-(−)-α-methoxyphenylacetic acid (5 mg, 0.0310 mmol, 2.0 eq) to afford (−)-**S10b** (6 mg, 49%) as a colourless film: $[\alpha]_D^{25}$ = −44.3 (*c* 0.27, $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.43–7.39 (2H, m, H-47 and H-49), 7.38–7.31 (3H, m, H-46, H-48 and H-50), 5.44–5.29 (8H, m, H-26, H-27, H-29, H-30, H-32, H-33, H-35 and H-36), 5.25–5.19 (1H, m, H-2), 4.77 (1H, s, H-43), 4.34 (1H, dd, J_{XY} 11.9, 4.1, H-3), 4.19 (1H, dd, J_{XY} 11.9, 6.2, H-3'), 4.16 (1H, dd, J_{XY} 11.9, 4.5, H-1), 4.03 (1H, dd, J_{XY} 11.9, 5.8, H-1'), 3.41 (3H, s, H-44), 2.86–2.78 (6H, m, H-28, H-31 and H-34), 2.26 (2H, t, *J* 7.5, H-5), 2.23–2.13 (2H, m, H-23), 2.11–2.02 (4H, m, H-25 and H-37), 1.65–1.54 (4H, m, H-6 and H-24), 1.39–1.21 (34H, m, H-7 to H-20 and H-38 to H-40), 0.91–0.85 (6H, m, H-21 and H-41); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.3 (C-4), 172.6 (C-22), 170.4 (C-42), 136.1 (C-45), 130.7 (C-36), 129.1, 129.0, 128.92, 128.84, 128.77, 128.5, 128.2, 128.0 (C-26, C-27, C-48, C-46, C-50, C-29, C-30, C-32, C-33), 127.7 (C-35), 127.3 (C-47, C-49), 82.4 (C-43), 68.8 (C-2), 63.0 (C-3), 61.9 (C1), 57.5 (C-44), 34.1 (C-5), 33.5 (C-23), 32.1 (C-19), 31.7 (C-39), 29.85, 29.81, 29.77,

29.6, 29.51, 29.47, 29.40, 29.2 (C-7 to C-18, C-38), 27.4 (C-37), 26.6 (C-25), 25.78, 25.77 (C-28, C-31, C-34), 24.9, 24.8 (C-6, C-24), 22.8 (C-20), 22.7 (C-40), 14.3, 14.2 (C-21, C-41); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3011 (w), 2955 (m), 2924 (s), 2854 (m), 1745 (C=O) (s), 1456 (m), 1378 (m), 1259 (m), 1238 (m), 1197 (m), 1168 (m), 1148 (m), 1117 (m), 1104 (m), 1027 (m), 967 (w), 726 (m), 697 (m); HRMS *m/z* (ESI$^+$) found 793.59729 [M+H]$^+$ ($C_{50}H_{81}O_7$ requires 793.59768 [M+H]$^+$). This compound was employed for determining the *e.e.* of (+)-**43** by ^{1}H NMR: See Supplementary Results and Discussion and Scheme S3.

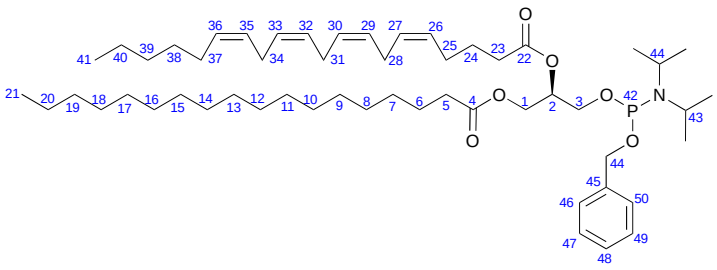
D_{35}-(*R*)-(+)-Benzyloxy-*N,N*-diisopropyl-(1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glyceryl) phosphoramidite (+)-44



A solution of alcohol (−)-**42** (200 mg, 0.303 mmol, 1.0 eq, 72% D_{35}, 28% D_{34}) in anhydrous CH_2Cl_2 (9 mL) was added dropwise, over 45 minutes and *via* cannula, to a solution of benzyloxy bis(*N*,*N*-diisopropylamino) phosphine **34** (256 mg, 0.757 mmol, 2.5 eq) and 1*H*-tetrazole (2.02 mL, 0.909 mmol, 3.0 eq, 0.45 M in MeCN) in anhydrous CH_2Cl_2 (15 mL). The reaction mixture was stirred at RT for 18 hours, diluted with CH_2Cl_2 (10 mL), and quenched by addition of a saturated aqueous solution of $NaHCO_3$ (10 mL). The organic phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (10 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Hexane/EtOAc/Et_3N 8:1.5:0.5) to give phosphoramidite (+)-**44** (143 mg, 90%, 70% D_{35}, 30% D_{34}) as a colourless waxy solid, containing a mixture of two diastereoisomers. This phosphoramidite was synthesised fresh before each use: R_f 0.84 (Petroleum ether/EtOAc 8:2); $[\alpha]_D^{25}$ = +4.5 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.39–7.22 (10H, m, C-45 to C-49 Diast. A and B), 5.23–5.15 (2H, m, H-2 Diast. A and B), 4.82–4.62 (4H, m, H-43), 4.36 (1H, dd, *J* 11.7, 3.7, H-1 Diast. A), 4.34 (1H, dd, *J* 11.9, 3.7, H-1 Diast. B), 4.18 (1H, dd, *J* 11.7, 5.2, H-1' Diast. A), 4.17 (1H, dd, *J* 11.9, 5.0, H-1' Diast. B), 3.83–3.69 (4H, m, H-3), 3.69–3.56 (4H, m, H-41 and H-42), 2.29 (4H, t, *J* 7.8, H-5 Diast. A and B), 1.66–1.54 (4H, m, H-6 Diast. A and B), 1.35–1.23 (56H, m, H-7 to H-20 Diast. A and B), 1.20 (3H, s, C(41)C*H*$_3$ or C(42)C*H*$_3$ Diast. A), 1.19 (3H, s, C(41)C*H*$_3$ or C(42)C*H*$_3$ Diast. A), 1.18 (3H, s, C(41)C*H*$_3$ or C(42)C*H*$_3$ Diast. B), 1.17 (3H, s, C(41)C*H*$_3$ or C(42)C*H*$_3$ Diast. B), 0.88 (3H, t, *J* 6.8, H-21); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.5 (C-4 Diast A and B), 173.2 (C-22 Diast. A and B), 139.5 (d_P, J_P 3.5, C-44 Diast. A), 139.4 (d_P, J_P 3.4, C-44 Diast. B), 128.40, 128.36 (C-46, C-48 Diast. A and B), 127.4, 127.3 (C-47 Diast. A and B), 127.12, 127.08 (C-45, C-49 Diast. A and B), 70.95 (d_P, J_P 4.4, C-2 Diast. A), 70.87 (d_P, J_P 5.1, C-2 Diast. B), 65.6 (d_P, J_P 3.5, C-43 Diast. A), 65.4 (d_P, J_P 3.6, C-43 Diast. B), 62.6 (d_P, J_P 4.7, C-1 Diast. A and B), 61.9 (d_P, J_P 16.9, C-3 Diast. A), 61.7 (d_P, J_P 16.7, C-3 Diast. B), 43.3, 43.2 (C-41, C-42 Diast. A and B), 34.3 (C-5 Diast. A and B), 32.1 (C-19 Diast. A and B), 29.85, 29.82, 29.79, 29.6, 29.5, 29.4, 29.3 (C-7 to C-18 Diast. A and B), 28.9–27.7 (m_D, C-25 to C-36 Diast. A and B), 25.1 (C-6 Diast. A and B), 24.83, 24.75, 24.72, 24.67, 24.65 (C(41)*C*H$_3$ and C(42)*C*H$_3$ Diast. A and B), 22.8 (C-20 Diast. A and B), 14.3 (C-21 Diast. A and B)[2]; ^{31}P NMR (162 MHz; $CDCl_3$) δ_P 148.8 (P-40 Diast. A), 148.6 (P-40 Diast. B); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2964 (m), 2924 (s), 2854 (m), 2197 (m), 2095 (m), 1742 (C=O) (s), 1456 (m), 1396 (w), 1364 (m), 1255 (m), 1200 (m), 1184 (m), 1127 (m), 1080 (m), 1059 (m), 1024 (P-O) (s), 975 (P-O) (s), 877 (w), 830 (w), 760 (m), 730 (s), 695 (m), 641 (w); HRMS *m/z* (ESI$^+$) found 896.91706 ([MD_{34}+H]$^+$, 35%), 897.92254 ([MD_{35}+H]$^+$, 100%) ($C_{52}H_{62}D_{35}O_6NP$ requires 897.92449 [MD_{35}+Na]$^+$).

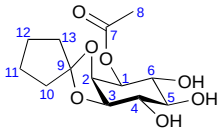
[2] Due to the instability of this compound in solution, only a minimal number of scans could be used for acquiring the ^{13}C NMR spectrum, this was not enough to observe the peaks corresponding to C-23, C-24, C-37, C-38 and C-39. These, however, can be inferred by comparison with the ^{13}C NMR of the equivalent non-deuterated compound. ^{2}H NMR was also not acquired for the same reasons.

(*R*)-Benzyloxy-*N,N*-diisopropyl-(1-*O*-stearoyl-2-*O*-arachidonyl-*sn*-glycer-3-yl)phosphoramidite (+)-45



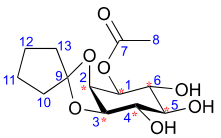
Phosphoramidite (+)-**45** was synthesised similarly to (+)-**44** using alcohol (−)-**43**, to afford which was purified by column chromatography over silica gel (Hexane/EtOAc/Et_3N 9.5:0:0.5, 9:0.5:0.5) to give (+)-**45** (88%) as a colourless oil, and containing a mixture of two diastereoisomers. This unstable phosphoramidite was synthesised fresh before each use and used directly in subsequent steps without further characterisation: ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.38–7.22 (10H, m, H-46 to H-50 Diast. A and B), 5.45–5.29 (16H, m, H-26, H-27, H-29, H-30, H-32, H-33, H-35 and H-36 Diast. A and B), 5.23–5.16 (2H, m, H-2 Diast. A and B), 4.81–4.59 (4H, m, H-44, Diast. A and B), 4.36 (1H, dd, J_{XY} 8.8031, 3.6680, H-1 Diast. A), 4.33 (1H, dd, J_{XY} 8.6809, 3.7902, H-1 Diast. B), 4.20–4.13 (2H, m, H-1' Diast. A and B), 3.83–3.56 (8H, m, H-43, H-44, H-3 and H-3' Diast. A and B), 2.88–2.74 (12H, m, H-28, H-31 and H-34), 2.31 (4H, t, *J* 7.5805, H-5 Diast. A and B), 2.29 (4H, t, *J* 7.5805, H-23 Diast. A and B), 2.14–2.02 (8H, m, H-25 and H-37 Diast. A and B), 1.64–1.55 (8H, m, H-6 and H-24), 1.39–1.21 (68H, m, H-7 to H-20 and H-38 to H-40 Diast. A and B), 1.21–1.15 (24H, m, C(43)C*H*$_3$ and C(44)C*H*$_3$ Diast. A and B), 0.92–0.85 (12H, m, H-21 and H-41 Diast. A and B); ^{31}P NMR (400 MHz; $CDCl_3$) δ_P 148.8 (P-42, Diast. A), 148.6 (P-42, Diast. B).

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-*myo*-inositol (−)-46



To a solution of (−)-**19** (3.06 g, 6.53 mmol, 1.0 eq) in EtOAc (124 mL) was added 10% Pd/C (1.04 g, 0.979 mmol, 0.15 eq) in one portion. After bubbling two balloons of $H_{2(g)}$ through the reaction, the mixture was stirred vigorously for 2 hours under an atmosphere of $H_{2(g)}$, then filtered through a pad of Celite® and concentrated *in vacuo* to give (−)-**46** (1.78 g, 94%) as a colourless solid: R_f 0.087 (Petroleum ether/EtOAc 2:8); $[\alpha]_D^{25}$ = −36.9 (*c* 0.68, $CHCl_3$); m.p. 156–158 °C (EtOAc); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 5.00 (1H, dd, *J* 9.9, 4.1, H-1), 4.31 (1H, dd, *J* 4.6, 4.1, H-2), 4.05 (1H, dd, *J* 7.5, 4.6, H-3), 3.92 (1H, ddd, *J* 9.9, 9.9, 3.3, H-6), 3.65 (1H, ddd, *J* 10.1, 7.5, 2.6, H-4), 3.39 (1H, ddd, *J* 10.1, 9.9, 2.0, H-5), 3.05 (1H, s, C(5)O*H*), 2.78 (1H, s, C(4)O*H*), 2.67 (1H, s, C(6)O*H*), 2.20 (3H, s, H-8), 2.01–1.89 (2H, m, H-10 or H-13), 1.78–1.61 (6H, m, H-11, H-12 and H-10 or H-13); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 171.1 (C-7), 120.4 (C-9), 78.4 (C-3), 74.7 (C-4), 74.5 (C-2), 73.6 (C-5), 72.1 (C-1), 70.7 (C-6), 37.99, 37.97 (C-10, C-13), 23.9, 23.7 (C-11, C-12), 21.2 (C-8); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3656 (O-H) (m), 3537 (O-H) (br), 2980 (w), 2965 (w), 2936 (w), 2886 (w), 1721 (C=O) (s), 1376 (m), 1332 (m), 1261 (s), 1236 (m), 1186 (m), 1111 (s), 1100 (s), 1069 (m), 1035 (m), 973 (s), 871 (m); LRMS *m/z* (ESI$^-$) 333.1 ([M+FA−H]$^-$, 100%), 323.0 ([M+Cl]$^-$, 7%); HRMS *m/z* (ESI$^+$) found 289.12819 [M+H]$^+$ ($C_{13}H_{20}O_7$ requires 289.12818 [M+H]$^+$); RP-HPLC (Method 3) t_R = 15.04 min, 98.99%.[69]

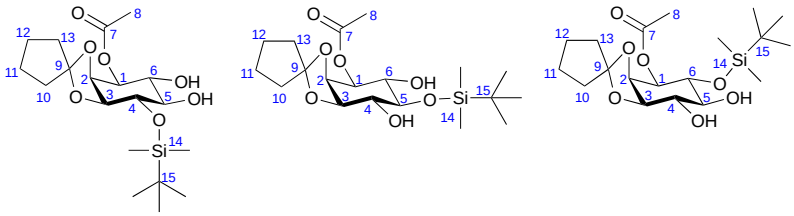
D_6-(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-*myo*-inositol (−)-47



To a solution of (−)-**20** (430 mg, 0.906 mmol, 1.0 eq, 84% D_6, 16% D_5) in EtOAc (17 mL) was added 10% Pd/C (145 mg, 0.136 mmol, 0.15 eq) in one portion. After bubbling two balloons of $H_{2(g)}$ through the reaction, the mixture was stirred vigorously for 2 hours under an atmosphere of $H_{2(g)}$, then filtered through a pad of Celite® and concentrated *in vacuo* to give (−)-**47** (204 mg, 76%, 84% D_6, 16% D_5) as a colourless solid: R_f 0.087 (Petroleum ether/EtOAc 2:8); $[\alpha]_D^{25}$ = −39.0 (*c* 0.70, $CHCl_3$); m.p. 156–159 °C (EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 4.50 (1H,

s, C(5)O*H*), 4.08 (1H, s, C(4)O*H*), 3.89 (1H, br s, C(6)O*H*), 2.18 (3H, s, H-8), 2.01–1.88 (2H, m, H-10 or H-13), 1.77–1.56 (6H, m, H-11, H-12 and H-10 or H-13); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 171.2 (C-7), 120.2 (C-9), 78.1–77.5 (m_D, C-3), 74.4–73.7 (m_D, C-4, C-2), 73.3–72.7 (m_D, C-5), 71.5–71.0 (m_D, C-1), 70.5–69.9 (m_D, C-6), 37.93, 37.89 (C-10, C-13), 23.9, 23.7 (C-11, C-12), 21.2 (C-8); ^{2}H NMR (92 MHz; $CHCl_3$; $CDCl_3$) δ_D 5.04 (1D, br s, D-1), 4.24 (1D, br s, D-2), 3.92 (2D, br s, D-3 and D-6), 3.60 (1D, br s, D-4), 3.40 (1D, br s, D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3659 (O-H) (br), 3508 (O-H) (br), 3332 (O-H) (br), 2980 (s), 2888 (m), 1723 (C=O) (w), 1473 (w), 1461 (w), 1381 (m), 1337 (w), 1253 (m), 1150 (m), 1101 (m), 1044 (m), 989 (m), 955 (m), 877 (w), 799 (w); LRMS *m/z* (ESI$^+$) 316.2 ([MD_5+Na]$^+$, 18%), 317.2 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 316.14147 [MD_5+Na]$^+$, 317.14751 [MD_6+Na]$^+$ ($C_{13}H_{14}D_6O_7Na$ requires 317.14778 [MD_6+Na]$^+$).

(–)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol (–)-S11; (–)-1D-1-*O*-acetyl-2,3-*O*-cyclopentylidene-5-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol (–)-S12; (–)-1D-1-*O*-acetyl-2,3-*O*-cyclopentylidene-6-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol (–)-S13



Method 1 – To a solution of triol (–)-**46** (50 mg, 0.173 mmol, 1.0 eq) and imidazole (18 mg, 0.260 mmol, 1.5 eq) in anhydrous pyridine (0.80 mL) was added TBDMSCl (26 mg, 0.175 mmol, 1.01 eq) at −10 °C. After 12 hours of stirring at −10 °C the reaction mixture was warmed to RT. After 52 hours of stirring at RT, no product could be observed.

Method 2 – To a solution of triol (–)-**46** (50 mg, 0.173 mmol, 1.0 eq) and imidazole (18 mg, 0.260 mmol, 1.5 eq) in anhydrous DMF (0.60 mL) was added TBDMSCl (26 mg, 0.173 mmol, 1.0 eq). After stirring at RT for 5 days, no product could be observed.

Method 3 – To a solution of triol (–)-**46** (25 mg, 0.0867 mmol, 1.0 eq) and 2,6-lutidine (15 µL, 0.130 mmol, 1.5 eq) in anhydrous CH_2Cl_2 (0.80 mL) was added TBDMSOTf (20 µL, 0.0867 mmol, 1.0 eq) at −78 °C. The reaction mixture was stirred for 21 hours and warmed to RT. After 2 hours of stirring, 2,6-lutidine (15 µL, 0.130 mmol, 1.5 eq) and TBDMSOTf (20 µL, 0.0867 mmol, 1.0 eq) were added sequentially and the reaction mixture was stirred at RT for 48 hours. The reaction mixture was concentrated *in vacuo* and the residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 6:4, 5:5) to give (–)-**S11** (3 mg, 10%) as a colourless solid: R_f 0.55 (Petroleum ether/EtOAc 5:5); $[\alpha]_D^{25}$ = −25.0 (*c* 1.0, $CHCl_3$); m.p. 108–112 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 5.04 (1H, dd, *J* 9.9, 4.3, H-1), 4.32 (1H, dd, *J* 4.5, 4.3, H-2), 3.99–3.90 (2H, m, H-3 and H-6), 3.63 (1H, dd, *J* 8.9, 6.8, H-4), 3.34 (1H, ddd, *J* 8.9, 8.9, 2.7, H-5), 2.47 (1H, d, *J* 2.8, C(6)O*H*), 2.42 (1H, d, *J* 2.7, C(5)O*H*), 2.18 (3H, s, H-8), 1.98–1.88 (2H, m, H-10 or H-13), 1.76–1.62 (6H, m, H-11, H-12 and H-10 or H-13), 0.91 (9H, s, C(15)C*H*$_3$), 0.16 (3H, s, Si(14)C*H*$_3$), 0.13 (3H, s, Si(14)C*H*$_3$); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 171.0 (C-7), 120.0 (C-9), 79.0 (C-3), 76.1 (C-4), 75.0 (C-5), 74.4 (C-2), 72.1 (C-1), 70.4 (C-6), 37.32, 37.27 (C-10, C-13), 26.0 (C(15)*C*H$_3$), 23.6, 23.3 (C-11, C-12), 21.2 (C-8), 18.3 (C-15), −4.1, −4.7 (Si(14)*C*H$_3$); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3561 (O-H) (br), 2961 (w), 2930 (w), 2855 (w), 1725 (C=O) (s), 1430 (w), 1376 (w), 1331 (m), 1254 (Si-CH$_3$) (s), 1201 (m), 1163 (m), 1130 (m), 1100 (Si-O) (m), 1047 (m), 994 (m), 968 (m), 912 (m), 872 (m), 855 (s), 834 (s), 780 (s), 730 (m), 672 (m); LRMS *m/z* (ESI$^+$) 425.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 403.21494 [M+H]$^+$ ($C_{19}H_{35}O_7Si$ requires 403.21466 [M+H]$^+$).

Method 4 – To a solution of triol (−)-**46** (15 mg, 0.0520 mmol, 1.0 eq) and Et_3N (9 µL, 0.0676 mmol, 1.3 eq) in anhydrous CH_2Cl_2 (0.30 mL) was added TBDMSOTf (13 µL, 0.0572 mmol, 1.1 eq) at 0 °C. The reaction mixture was stirred for 2 hours and warmed to RT. After 28 hours of stirring, the solvent was concentrated *in vacuo* and the residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 9.5:0.5, 9:1, 8:2, 7:3, 6:4, 5:5) to give (−)-**S11** (6 mg, 28%) as a colourless solid as well as (−)-**S13** (2 mg, 8%) and (−)-**S12** (6 mg, 27%) as colourless oils: (−)-**S12** R_f 0.79 (Petroleum ether/EtOAc 5:5); $[\alpha]_D^{25}$ = −23.5 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 5.00 (1H, dd, *J* 9.6, 4.1, H-1), 4.29 (1H, dd, *J* 4.8, 4.1, H-2), 3.97 (1H, dd, J 7.6, 4.8, H-3), 3.85 (1H, ddd, *J* 9.6, 9.2, 2.8, H-6), 3.57 (1H, ddd, *J* 9.8, 7.6, 2.6, H-4), 3.33 (1H, dd, *J* 9.8, 9.2, H-5), 2.27 (1H, d, *J* 2.6, C(4)O*H*), 2.22 (1H, d, *J* 2.8, C(6)O*H*), 2.18 (3H, s, H-8), 2.02–1.90 (2H, m, H-10 or H-13), 1.82–1.60 (6H, m, H-11, H-12 and H-10 or H-13), 0.92 (9H, s, C(15)CH_3), 0.15 (6H, Si(14)CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.9 (C-7), 120.2 (C-9), 78.3 (C-3), 75.6 (C-5), 75.1 (C-4), 74.3 (C-2), 71.9 (C-1), 71.1 (C-6), 38.0, 37.9 (C-10, C-13), 26.1 (C(15)*C*H$_3$), 23.9, 23.7 (C-11, C-12), 21.2 (C-8), 18.5 (C-15), −4.2, −4.4 (Si(14)*C*H$_3$); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3479 (O-H) (br), 2954 (m), 2930 (m), 2895 (w), 2856 (w), 2361 (w), 2341 (w), 1728 (C=O) (m), 1373 (m), 1333 (m), 1247 (Si-CH$_3$) (s), 1143 (s), 1109 (s), 1035 (s), 972 (m), 838 (s), 780 (s); LRMS *m/z* (ESI$^+$) 425.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 425.19632 [M+Na]$^+$ ($C_{19}H_{34}O_7NaSi$ requires 425.19660 [M+Na]$^+$); (−)-**S13**: R_f 0.61 (Petroleum ether/EtOAc 5:5); $[\alpha]_D^{25}$ = −25.2 (*c* 0.30, $CHCl_3$); ^{1}H NMR (500 MHz; CD_2Cl_2) δ_H 4.94 (1H, dd, *J* 9.1, 4.0, H-1), 4.27 (1H, dd, *J* 5.0, 4.0, H-2), 3.95 (1H, dd, *J* 7.5, 5.0, H-3), 3.87 (1H, dd, *J* 9.1, 8.8, H-6), 3.61 (1H, ddd, *J* 10.2, 7.5, 2.8, H-4), 3.29 (1H, ddd, *J* 10.2, 8.8, 2.9, H-5), 2.54 (1H, d, *J* 2.8, C(4)O*H*), 2.44 (1H, d, *J* 2.9, C(5)O*H*), 2.11 (3H, s, H-8), 2.99–1.87 (2H, m, H-10 or H-13), 1.76–1.56 (6H, m, H-11, H-12 and H-10 or H-13), 0.89 (9H, s, C(15)CH_3), 0.14 (3H, s, Si(14)CH_3), 0.13 (3H, s, Si(14)CH_3); ^{13}C NMR (126 MHz; CD_2Cl_2) δ_C 170.4 (C-7), 120.1 (C-9), 78.4 (C-3), 74.8 (C-5), 74.6 (C-2), 74.4 (C-4), 72.8 (C-1), 72.3 (C-6), 38.1, 38.0 (C-10, C-13), 25.9 (C(15)*C*H$_3$), 24.2, 23.9 (C-11, C-12), 21.4 (C-8), 18.4 (C-15), −4.2, −4.4 (Si(CH_3); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3445 (O-H) (br), 2980 (s), 2971 (s), 2930 (m), 2890 (m), 2858 (m), 2360 (w), 2341 (w), 1745 (C=O) (m), 1473 (w), 1462 (w), 1380 (m), 1249 (m), 1144 (m), 1117 (m), 1072 (m), 1036 (m), 967 (m), 871 (w), 838 (m), 780 (m); LRMS *m/z* (ESI$^+$) 425.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 425.19632 [M+Na]$^+$ ($C_{19}H_{34}O_7NaSi$ requires 425.19660 [M+Na]$^+$). Spectral data for (−)-**S11** are identical to those reported above.

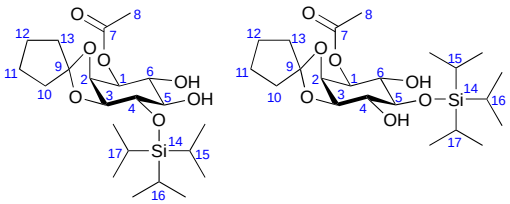
Method 5 – To a solution of triol (−)-**46** (12 mg, 0.0416 mmol, 1.0 eq) in anhydrous pyridine (0.30 mL) was added TBDMSOTf (11 µL, 0.0458 mmol, 1.1 eq) at 0 °C. The reaction mixture was stirred for 2 hours and warmed to RT. After 23 hours of stirring, the solvent was concentrated *in vacuo* and the residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 9.5:0.5, 9:1, 8:2, 7:3, 6:4, 5:5) to give (−)-**S11** (7 mg, 40%) as a colourless solid as well as (−)-**S13** (3 mg, 19%) and (−)-**S12** (6 mg, 36%) as colourless oils. Spectral data are identical to those reported above.

Method 6 – To a solution of triol (−)-**46** (100 mg, 0.347 mmol, 1.0 eq) in anhydrous pyridine (1.2 mL) was added TBDMSOTf (88 µL, 0.382 mmol, 1.1 eq) at −30 °C. The reaction mixture was stirred for 24 hours and the solvent was then concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) to give (−)-**S11** (68 mg, 49%) as a colourless solid as well as (−)-**S13** (15 mg, 11%) and (−)-**S12** (51 mg, 36%) as colourless oils. Spectral data are identical to those reported above.

Method 7 – To a solution of triol (−)-**46** (100 mg, 0.347 mmol, 1.0 eq) and 2,6-lutidine (61 µL, 0.520 mmol, 1.5 eq) in anhydrous THF (3.6 mL) was added TBDMSOTf (81 µL, 0.347 mmol, 1.0 eq) at −78 °C. After stirring for 24 hours, TBDMSOTf (40 µL, 0.175 mmol, 0.505 eq) and 2,6-lutidine (31 µL, 0.267 mmol, 0.77 eq) were added sequentially and the solution was allowed to stir for another 2 hours. H_2O (5 mL) was then added and the aqueous layer was extracted with EtOAc (4 × 5 mL). The combined organic layers were washed with H_2O (5 mL) and brine (5 mL), then dried ($MgSO_4$), filtered, and concentrated

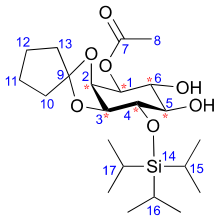
in vacuo. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 6:4, 5:5) afforded (−)-**S11** (76 mg, 55%) as a colourless solid as well as (−)-**S13** (46 mg, 33%) and (−)-**S12** (11 mg, 8%) as colourless oils. Spectral data are identical to those reported above.

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-*myo*-inositol (−)-48 & (−)-1D-1-*O*-acetyl-2,3-*O*-cyclopentyli- dene-5-*O*-(triisopropylsilyl)-*myo*-inositol (−)-S14



To a solution of triol (−)-**46** (350 mg, 1.21 mmol, 1.0 eq) and 2,6-lutidine (435 µL, 3.74 mmol, 3.08 eq) in anhydrous THF (13 mL) was added TIPSOTf (718 µL, 2.67 mmol, 2.2 eq) dropwise at −78 °C. After 16.5 hours of stirring, H_2O (10 mL) was added and the aqueous layer was extracted with EtOAc (4 × 15 mL). The combined organic layers were washed with H_2O (15 mL) and brine (15 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 6:4, 5:5) afforded (−)-**48** (384 mg, 71%) as a colourless solid and the regioisomer (−)-**S14** (109 mg, 20%) as a colourless oil: (−)-**48** R_f 0.76 (Petroleum ether/EtOAc 5:5); $[\alpha]_D^{25} = -40.5$ (*c* 1.0, $CHCl_3$); m.p. 80–83 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 5.12 (1H, dd, *J* 9.8, 3.9, H-1), 4.40 (1H, dd, *J* 5.9, 3.9, H-2), 4.09 (1H, dd, *J* 5.9, 5.8, H-3), 3.97 (1H, dd, *J* 9.8, 7.5, H-6), 3.90 (1H, dd, *J* 7.3, 5.8, H-4), 3.50 (1H, dd, *J* 7.5, 7.3, H-5), 2.17 (3H, s, H-8), 1.96–1.88 (2H, m, H-10 or H-13), 1.73–1.63 (6H, m, H-11, H-12 and H-10 or H-13), 1.21–1.12 (3H, m, H-15, H-16 and H-17), 1.09 (12H, s, C(15)CH_3 and C(17)CH_3), 1.08 (6H, s, C(16)CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 171.0 (C-7), 119.9 (C-9), 78.9 (C-3), 76.6 (C-5), 75.4 (C-4), 73.9 (C-2), 72.2 (C-1), 71.3 (C-6), 36.62, 36.61 (C-10, C-13), 23.8, 23.2 (C-11, C-12), 21.3 (C-8), 18.3, 18.2 (C(15)CH_3, C(16)CH_3, C(17)CH_3), 12.6 (C-15, C-16, C-17); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3495 (O-H) (br), 3274 (O-H) (br), 2943 (m), 2892 (m), 2866 (m), 1720 (C=O) (s), 1464 (m), 1433 (w), 1374 (m), 1332 (m), 1242 (s), 1142 (s), 1117 (s), 1101 (Si-O) (s), 1040 (s), 998 (s), 988 (s), 919 (m), 882 (s), 829 (m), 730 (m), 680 (s), 655 (s); LRMS *m/z* (ESI$^+$) 467.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 445.26144 [M+H]$^+$ ($C_{22}H_{41}O_7Si$ requires 445.26161 [M+H]$^+$); (−)-**S14** R_f 0.83 (Petroleum ether/EtOAc 5:5); $[\alpha]_D^{25} = -15.3$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 4.99 (1H, dd, *J* 9.4, 4.0, H-1), 4.30 (1H, dd, *J* 5.0, 4.0, H-2), 3.98 (1H, dd, *J* 7.3, 5.0, H-3), 3.86 (1H, dd, *J* 9.4, 9.3, H-6), 3.59 (1H, dd, *J* 9.6, 7.3, H-4), 3.52 (1H, dd, *J* 9.6, 9.3, H-5), 2.18 (3H, s, H-8), 2.01–1.91 (2H, m, H-10 or H-13), 1.77–1.59 (6H, m, H-11, H-12 and H-10 or H-13), 1.23–1.15 (3H, m, H-15, H-16 and H-17), 1.10 (12H, s, C(15)CH_3 and C(17)CH_3), 1.08 (6H, s, C(16)CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.9 (C-7), 120.2 (C-9), 78.3 (C-3), 76.1 (C-5), 75.4 (C-4), 74.1 (C-2), 72.2 (C-1), 71.4 (C-6), 37.9, 37.8 (C-10, C-13), 23.9, 23.6 (C-11, C-12), 21.2 (C-8), 18.4 (C(15)CH_3, C(16)CH_3, C(17)CH_3), 13.0 (C-15, C-16, C-17); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3477 (O-H) (br), 2943 (m), 2893 (m), 2866 (m), 1728 (C=O) (m), 1465 (w), 1372 (m), 1333 (m), 1239 (s), 1146 (s), 1106 (Si-O) (s), 1034 (s), 972 (m), 918 (m), 882 (s), 819 (m), 756 (s), 734 (s), 717 (m), 678 (s); LRMS *m/z* (ESI$^+$) 467.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 467.24342 [M+Na]$^+$ ($C_{22}H_{40}O_7NaSi$ requires 467.24355 [M+Na]$^+$).

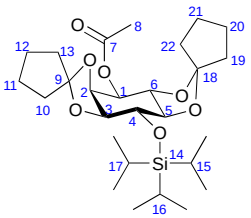
D_6-(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-*myo*-inositol (−)-49



To a solution of triol (−)-**47** (190 mg, 0.646 mmol, 1.0 eq, 84% D_6, 16% D_5) and 2,6-lutidine (232 µL, 1.99 mmol, 3.08 eq) in anhydrous THF (7.0 mL) was added TIPS triflate (382 µL, 1.42 mmol, 2.2 eq) dropwise at −78 °C. After 16 hours of stirring at −78 °C, H_2O (5 mL) was added and the aqueous layer was extracted with EtOAc (4 × 8 mL). The combined organic layers were washed with H_2O (5 mL) and brine (5 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column

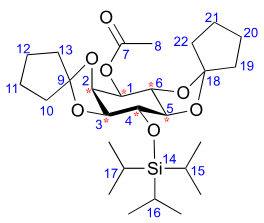
chromatography over silica gel (Petroleum ether/EtOAc 7:3, 6:4, 5:5) gave (−)-**49** (214 mg, 74%, 84% D_6, 16% D_5) as a colourless solid: R_f 0.76 (Petroleum ether/EtOAc 5:5); $[\alpha]_D^{25}$ = −58.3 (*c* 0.58, $CHCl_3$); m.p. 82–83 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 2.57 (1H, br s, C(5)O*H*), 2.42 (1H, br s, C(6)O*H*), 2.17 (3H, s, H-8), 1.97-1.87 (2H, m, H-10 or H-13), 1.77–1.63 (6H, m, H-11, H-12 and H-10 or H-13), 1.21–1.12 (3H, m, H-15, H-16 and H-17), 1.09 (12H, s, C(15)CH_3 and C(17)CH_3), 1.08 (6H, s, C(16)CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 171.1 (C-7), 119.9 (C-9), 78.3 (t_D, J_D 22.9, C-3), 76.2 (t_D, J_D 22.0, C-5), 74.7 (t_D, J_D 22.1, C-4), 73.4 (t_D, J_D 23.4, C-2), 71.3 (t_D, J_D 22.2, C-1), 70.9 (t_D, J_D 22.3, C-6), 36.59, 36.55 (C-10, C-13), 23.8, 23.2 (C-11, C-12), 21.3 (C-8), 18.3, 18.2 (C(15)*C*H$_3$, C(16)*C*H$_3$, C(17)*C*H$_3$), 12.6 (C-15, C-16, C-17); ^{2}H NMR (92 MHz; $CHCl_3$; $CDCl_3$) δ_D 5.11 (1D, br s, D-1), 4.40 (1D, br s, D-2), 4.08 (1D, br s, D-3), 3.94 (1D, br s, D-6), 3.91 (1D, br s, D-4), 3.49 (1D, br s, D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3655 (O-H) (w), 3501 (O-H) (w), 2980 (s), 2972 (s), 2891 (w), 2867 (w), 2184 (w), 2162 (w), 2049 (w), 2036 (w), 2019 (w), 1995 (w), 1719 (C=O) (m), 1463 (m), 1433 (m), 1377 (m), 1337 (m), 1243 (m), 1201 (s), 1153 (s), 1125 (s), 1105 (s), 1062 (s), 1043 (Si-O) (s), 1010 (s), 985 (m), 960 (m), 920 (s), 882 (m), 799 (m), 680 (s); LRMS *m/z* (ESI$^+$) 472.2 ([MD_5+Na]$^+$, 18%), 473.2 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ES$^+$) found 472.27366 [MD_5+Na]$^+$, 473.27972 [MD_6+Na]$^+$ ($C_{22}H_{34}D_6O_7NaSi$ requires 473.28121 [MD_6+Na]$^+$).

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-50



To a clear solution of (−)-**48** (310 mg, 0.697 mmol, 1.0 eq) and **18** (1.62 mL, 11.9 mmol, 17 eq) in CH_2Cl_2 (1.6 mL) was added PTSA·H_2O (7 mg, 0.0349 mmol 0.050 eq). The resulting yellow solution was stirred at 30 °C for 18 hours. The brown reaction mixture obtained was then quenched with Et_3N (5 µL, 0.0349 mmol, 0.050 eq) and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/Et_2O 10:0, 9.5:0.5, 9:1) to give (−)-**50** (303 mg, 85%) as a colourless oil: R_f 0.20 (Petroleum ether/EtOAc 7:3); $[\alpha]_D^{25}$ = −26.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 5.06 (1H, dd, *J* 10.6, 4.6, H-1), 4.44 (1H, dd, *J* 5.3, 4.6, H-2), 4.00 (1H, dd, *J* 5.8, 5.3, H-3), 3.95 (1H, dd, *J* 10.0, 5.8, H-4), 3.91 (1H, dd, *J* 10.6, 9.8, H-6), 3.29 (1H, dd, *J* 10.0, 9.8, H-5), 2.16 (3H, s, H-8), 1.94–1.76 (6H, m, H-19, H-22 and H-10 or H-13), 1.75–1.55 (10H, m, H-11, H-12, H-20, H-21 and H-10 or H-13), 1.17–1.09 (3H, m, H-15, H-16 and H-17), 1.08 (12H, s, C(15)CH_3 and C(17)CH_3), 1.07 (6H, s, C(16)CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.7 (C-7), 121.8 (C-18), 119.5 (C-9), 82.9 (C-3), 79.7 (C-5), 75.6 (C-2), 75.0 (C-4), 74.6 (C-6), 71.4 (C-1), 37.51, 37.47 (C-19, C-22), 37.28, 37.21 (C-10, C-13), 23.5, 23.4, 23.3 (C-11, C-12, C-20, C-21), 21.2 (C-8), 18.07, 18.06 (C(15)*C*H$_3$, C(17)*C*H$_3$, C(16)*C*H$_3$), 12.5 (C-15, C-16, C-17); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2944 (m), 2893 (m), 2867 (m), 1745 (C=O) (m), 1464 (w), 1433 (w), 1370 (m), 1330 (m), 1237 (s), 1172 (m), 1115 (s), 1040 (Si-O) (m), 974 (m), 909 (m), 882 (m), 829 (m), 757 (m), 741 (m), 680 (s); LRMS *m/z* (ESI$^+$) 511.4 ([M+H]$^+$, 4%), 533.3 ([M+Na]$^+$, 82%); HRMS *m/z* (ESI$^+$) found 533.29045 [M+Na]$^+$ ($C_{27}H_{46}O_7NaSi$ requires 533.29050 [M+Na]$^+$).

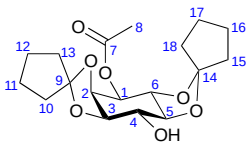
D_6-(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-51



To a clear solution of (−)-**49** (204 mg, 0.453 mmol, 1.0 eq, 84% D_6, 16% D_5) and **18** (1.10 mL, 7.70 mmol, 17 eq) in CH_2Cl_2 (1.05 mL) was added PTSA·H_2O (4 mg, 0.0226 mmol 0.050 eq). The resulting yellow solution was then stirred at 30 °C for 16 hours. The brown reaction obtained was then quenched with Et_3N (3 µL, 0.0226 mmol, 0.050 eq) and concentrated *in vacuo*. The residue obtained was purified by column chromatography over silica gel (Petroleum ether/Et_2O 10:0, 9.5:0.5, 9:1) to give (−)-**51** (167 mg, 71%, 85% D_6, 15% D_5) as a colourless oil: R_f 0.20 (Petroleum ether/EtOAc 7:3); $[\alpha]_D^{25}$ = −35.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 2.16 (3H, s, H-8), 1.95–1.75 (6H, m, H-19, H-22 and H-10 or H-13), 1.75–

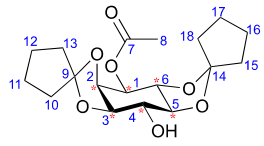
1.56 (10H, m, H-11, H-12, H-20, H-21 and H-10 or H-13), 1.17–1.09 (3H, m, H-15, H-16 and H-17), 1.08 (12H, s, C(15)CH_3 and C(17)CH_3), 1.07 (6H, s, C(16)CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.7 (C-7), 121.8 (C-18), 119.4 (C-9), 82.3 (t_D, J_D 22.9, C-3), 79.1 (t_D, J_D 21.6, C-5), 75.1 (t_D, J_D 24.5, C-2), 74.5 (t_D, J_D 21.7, C-4), 74.1 (t_D, J_D 22.9, C-6), 71.0 (t_D, J_D 22.5, C-1), 37.52, 37.48 (C-19, C-22) 37.3, 37.2 (C-10, C-13), 23.5, 23.4, 23.3 (C-11, C-12, C-20, C-21), 21.2 (C-8), 18.07, 18.06 (C(15)CH_3, C(17)CH_3, C(16)CH_3), 12.5 (C-15, C-16 and C-17); ^{2}H NMR (92 MHz; $CHCl_3$; $CDCl_3$) δ_D 5.04 (1D, br s, D-1), 4.43 (1D, br s, D-2), 3.93 (3D, br s, D-3, D-4 and D-6), 3.29 (1D, br s, D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2980 (s), 2971 (s), 2890 (m), 2867 (m), 1741 (C=O) (m), 1463 (m), 1433 (w), 1372 (m), 1337 (m), 1249 (m), 1204 (m), 1180 (m), 1105 (s), 1080 (m), 1053 (m), 1026 (Si-O) (s), 1001 (m), 971 (m), 920 (m), 882 (m), 801 (m), 775 (m), 678 (m); LRMS *m/z* (ESI$^+$) 538.4 ([MD_5+Na]$^+$, 17%), 539.4 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 538.32239 [MD_5+Na]$^+$, 539.32819 [MD_6+Na]$^+$ ($C_{27}H_{40}D_6O_7NaSi$ requires 539.32816 [MD_6+Na]$^+$).

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-52



To a solution of (−)-**50** (56 mg, 0.110 mmol, 1.0 eq) in DMF (5 mL) was added TAS-F (91 mg, 0.329 mmol, 3.0 eq) in one portion. After stirring at RT for 2.5 hours the reaction was quenched with phosphate buffer (5 mL, pH 7.4, 50 mM NaH_2PO_4/Na_2HPO_4, 150 mM NaCl) and dissolved with EtOAc (5 mL). The aqueous layer was extracted with EtOAc (4 × 10 mL). The combined organic layers were washed with H_2O (2 × 10 mL), brine (2 × 10 mL) and an aqueous solution of LiCl (10% *w/v*, 10 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4) afforded (−)-**52** (30 mg, 77%) as a colourless solid: R_f 0.24 (Petroleum ether/EtOAc 6:4); $[\alpha]_D^{25} = -53.2$ (*c* 0.70, $CHCl_3$); m.p. 157–159 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 5.11 (1H, dd, *J* 10.6, 4.5, H-1), 4.46 (1H, dd, *J* 4.7, 4.5, H-2), 4.04 (1H, dd, *J* 6.5, 4.7, H-3), 3.95 (1H, dd, *J* 10.6, 9.3, H-6), 3.87 (1H, dd, *J* 10.9, 6.5, H-4), 3.34 (1H, dd, *J* 10.9, 9.3, H-5), 2.62 (1H, br s, C(4)O*H*), 2.17 (3H, s, H-8), 1.99–1.82 (6H, m, H-15 and H-18, H-10 or H-13), 1.76–1.58 (10H, m, H-11, H-12, H-16, H-17 and H-10 or H-13); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.7 (C-7), 122.8 (C-14), 120.1 (C-9), 81.3 (C-3), 78.5 (C-5), 75.8 (C-2), 75.0 (C-6), 73.9 (C-4), 71.0 (C-1), 37.8, 37.73 (C-15, C-18), 37.72, 37.6 (C-10, C-13), 23.9, 23.64, 23.62, 23.55 (C-11, C-12, C-16 and C-17), 21.2 (C-8); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3460 (O-H) (br), 2970 (m), 2876 (w), 1741 (C=O) (m), 1433 (w), 1372 (m), 1332 (m), 1236 (s), 1201 (m), 1154 (m), 1118 (s), 1091 (s), 1040 (s), 971 (m), 907 (m), 730 (s); LRMS *m/z* (ESI$^+$) 377.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 377.15693 [M+Na]$^+$ ($C_{18}H_{26}O_7Na$ requires 377.15707 [M+Na]$^+$).

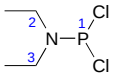
D_6-(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-53



To a solution of (−)-**51** (157 mg, 0.304 mmol, 1.0 eq, 85% D_6, 15% D_5) in DMF (14 mL) was added TAS-F (251 mg, 0.911 mmol, 3.0 eq) in one portion. After stirring at RT for 3 hours, the reaction was quenched with phosphate buffer (10 mL, pH 7.4, 50 mM NaH_2PO_4/Na_2HPO_4, 150 mM NaCl) and dissolved with EtOAc (15 mL). The aqueous layer was extracted with EtOAc (4 × 15 mL). The combined organic layers were washed with H_2O (2 × 15 mL), brine (2 × 15 mL) and an aqueous solution of LiCl (10% *w/v*, 15 mL), then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4) afforded (−)-**53** (96 mg, 88%, 84% D_6, 16% D_5) as a colourless solid: R_f 0.24 (Petroleum ether/EtOAc 6:4); $[\alpha]_D^{25}$ = −55.6 (*c* 0.79, $CHCl_3$); m.p. 160–162 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 2.53 (1H, br s, C(4)O*H*), 2.17 (3H, s, H-8), 1.99–1.82 (6H, m, H-15 and H-18, H-10 or H-13), 1.76–1.58 (10H, m, H-11, H-12, H-16, H-17 and H-10 or H-13); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.7 (C-7), 122.8 (C-14), 120.1 (C-9), 80.7 (t_D, J_D 23.0, C-3), 78.0 (t_D, J_D 21.8, C-5), 75.3 (t_D, J_D 23.4, C-2),

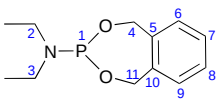
74.5 (t_D, J_D 22.9, C-6), 73.4 (t_D, J_D 22.4, C-4), 70.5 (t_D, J_D 22.5, C-1), 37.8, 37.7, 37.6 (C-15, C-18, C-10, C-13), 23.9, 23.65, 23.63, 23.56 (C-11, C-12, C-16 and C-17), 21.2 (C-8); ^{2}H NMR (92 MHz; $CHCl_3$; $CDCl_3$) δ_D 5.11 (1D, br s, D-1), 4.46 (1D, br s, D-2), 4.03 (1D, br s, D-3), 3.94 (1D, br s, D-6), 3.86 (1D, br s, D-4), 3.34 (1D, br s, D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3504 (O-H) (br), 2941 (m), 2185 (w), 2162 (w), 1737 (C=O) (m), 1433 (w), 1370 (m), 1337 (m), 1307 (w), 1250 (m), 1227 (m), 1197 (m), 1157 (w), 1131 (m), 1104 (s), 1062 (m), 1014 (s), 991 (s), 969 (m), 873 (m), 864 (m), 797 (m), 733 (m); LRMS *m/z* (ESI$^+$) 382.2 ([MD_5+Na]$^+$, 18%), 383.2 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 382.18863 [MD_5+Na]$^+$, 383.19459 [MD_6+Na]$^+$ ($C_{18}H_{20}D_6O_7Na$ requires 383.19473 [MD_6+Na]$^+$).

Dichloro-*N*,*N*-diethylphosphoramidite S23



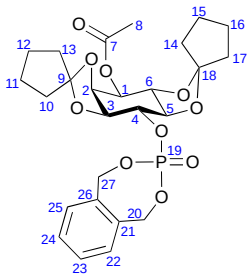
A solution of freshly distilled diethylamine (6.03 mL, 58.3 mmol, 2.0 eq) in anhydrous Et_2O (58 mL) was added *via* cannula, over 45 minutes, to a solution of PCl_3 219 (2.54 mL, 29.1 mmol, 1.0 eq) in anhydrous Et_2O (174 mL) at –78 °C. After addition was complete, the reaction mixture was stirred at –78 °C for 1.5 hour, then warmed to RT, and stirred for a further 18 hours. The resulting precipitate was removed by Schlenk filtration under Ar and washed with Et_2O (2 × 50 mL). The filtrate was concentrated *in vacuo* to give **S23** (4.00 g, crude) as a colourless oil that was used without further purification or characterisation. Analysis by ^{31}P NMR showed that this compound was ~95% pure. The product was stored under Ar at −20 °C and was checked by ^{31}P NMR before each use: ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 3.32 (4H, dq, *J* 14.2, 6.8, H-2 and H-3), 1.18 (6H, t, *J* 7.1, C(2)CH_3 and C(3)CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ_P 162.43 (P-1). These data are in good agreement with the literature values.[70]

(1,5-Dihydro-2,4,3-benzodioxaphosphepin-3-yl)diethylamine 54



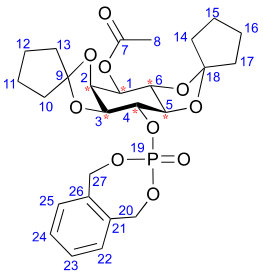
A solution of triethylamine (8.11 mL, 58.3 mmol, 2.0 eq) and 1,2-benzenedimethanol (4.02 g, 29.1 mmol, 1.0 eq) in a mixture of THF (40 mL) and Et_2O (160 mL) was added to a solution of **S24** (5.06 g, 29.1 mmol, 1.0 eq) in anhydrous Et_2O (200 mL) at –78 °C, *via* cannula, over 1 hour. The reaction mixture was warmed to RT and stirred for a further 18 hours. The resulting precipitate was removed by Schlenk filtration under Ar and washed with Et_2O (2 × 50 mL). The filtrate was concentrated *in vacuo* to give **54** (5.23 g, crude) as a colourless oil. Analysis by ^{31}P NMR showed that the product was ~87% pure. This unstable phosphoramidite was therefore used in subsequent steps without further purification or characterisation. The product was stored under Ar at −20 °C and was checked by ^{31}P NMR before each use: ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.30–7.16 (4H, m, H-6 to H-9), 5.18 (2H, dd, J_{ABX} 13.8, 7.0, H-4 and H-11), 4.91 (2H, dd, J_{ABX} 19.4, 13.8, H-4' and H-11'), 3.19 (4H, dq, *J* 9.9, 7.1, H-2 and H-3), 1.11 (6H, t, *J* 7.1, C(2)CH_3 and C(3)CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ_P 145.32 (P-1). These data are in good agreement with the literature values.[70]

(−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-55



To a solution of (−)-**52** (48 mg, 0.135 mmol, 1.0 eq) and phosphoramidite **54** (97 mg, 0.406 mmol, 3.0 eq) in CH_2Cl_2 (2.3 mL) was added 1*H*-tetrazole (903 µL, 0.406 mmol, 3.0 eq, 0.45 M in MeCN). After stirring at RT for 1.5 hour, the cloudy reaction mixture was cooled to −78 °C and *m*CPBA (91 mg, 0.406 mmol, 3.0 eq, 77%) was added in a single portion. The reaction mixture was then gradually warmed to RT over 20 minutes, stirred for 1 hour and quenched with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 3 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 3 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 3 × 3 mL), brine (3 × 3 mL), and a saturated aqueous solution of $NaHCO_3$ (3 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) afforded (−)-**55** (57 mg, 79%) as an amorphous solid: R_f 0.60 (Petroleum ether/Et_2O 4:6); $[\alpha]_D^{25} = -26.4$ (*c* 1.0, $CHCl_3$); m.p. 193–195 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.39–7.31 (2H, m, H-22 and H-25), 7.31–7.24 (2H, m, H-23 and H-24), 5.34–5.25 (2H, m, H-27 and H-20), 5.20–5.05 (3H, m, H-20', H-27' and H-1), 4.63 (1H, ddd, *J* 10.8, 9.8, 6.6, H-4), 4.46 (1H, dd, *J* 4.5, 4.3, H-2), 4.26 (1H, dd, *J* 6.6, 4.5, H-3), 4.01 (1H, dd, *J* 10.4, 9.5, H-6), 3.51 (1H, dd, *J* 10.8, 9.5, H-5), 2.17 (3H, s, H-8), 2.19–2.11 (1H, m, H-10 or H-13), 2.00–1.50 (15H, m, H-11, H12, H-14 to H-17, H-10', H-13' and H-10 or H-13); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.6 (C-7), 135.5, 135.4 (C-21, C-26), 129.20, 129.17 (C-22, C-25), 129.0, 128.9 (C-23, C-24), 123.0 (C-18), 120.6 (C-9), 79.4 (d_P, J_P 3.8, C-3), 79.3 (d_P, J_P 5.8, C-4), 76.1 (C-5), 75.9 (C-2), 74.9 (C-6), 70.4 (C-1), 68.80 (d_P, J_P 5.8, C-20 or C-27), 68.75 (d_P, J_P 6.1, C-20 or C-27), 37.8, 37.7 (C-14, C-17), 37.7, 37.5 (C-10, C-13), 24.0, 23.8, 23.63, 23.60 (C-11, C-12, C-15, C-16), 21.2 (C-8); ^{31}P NMR (162 MHz; $CDCl_3$) δ_P −2.10 (P-19); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2961 (w), 2895 (w), 1742 (C=O) (m), 1453 (w), 1371 (w), 1332 (m), 1289 (m), 1226 (m), 1200 (m), 1119 (m), 1090 (m), 1013 (P-O) (s), 973 (m), 917 (m), 849 (m), 777 (w), 729 (s); LRMS *m/z* (ESI$^+$) 559.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 559.17018 [M+Na]$^+$ ($C_{26}H_{33}O_{10}NaP$ requires 559.17035 [M+Na]$^+$); RP-HPLC (Method 2) t_R = 12.67 min, 100%.

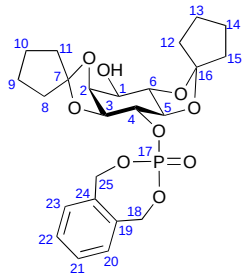
D_6-(−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-56



To a solution of (−)-**53** (90 mg, 0.250 mmol, 1.0 eq, 85% D_6, 15% D_5) and phosphoramidite **54** (179 mg, 0.749 mmol, 3.0 eq) in CH_2Cl_2 (4.3 mL) was added 1*H*-tetrazole (1.66 mL, 0.749 mmol, 3.0 eq, 0.45 M in MeCN). After stirring at RT for 1 hour, the cloudy reaction mixture was cooled to −78 °C and *m*CPBA (168 mg, 0.749 mmol, 3.0 eq, 77%) was added in a single portion. The reaction mixture was gradually warmed to RT over 20 minutes, stirred for 1 hour, and quenched with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 5 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 3 × 10 mL), brine (3 × 10 mL), and a saturated aqueous solution of $NaHCO_3$ (10 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) afforded (−)-**56** (120 mg, 88%, 84% D_6, 16% D_5) as an amorphous solid: R_f 0.60 (Petroleum ether/EtOAc 4:6); $[\alpha]_D^{25}$ = −27.2 (*c* 0.88, $CHCl_3$); m.p. 197–199 °C (Hexane/EtOAc); ^{1}H NMR (500 MHz; CD_2Cl_2) δ_H 7.47–7.42 (2H, m, H-22 and H-25), 7.37–7.31 (2H, m, H-23 and H-24), 5.37–5.29 (2H, m, H-20 and H-27), 5.13–5.01 (2H, m, H-20' and H-27'), 2.14 (3H, s, H-8), 2.13–2.06 (1H, m, H-10 or H-13), 1.97–1.55 (15H, m, H-11, H12, H-14 to H-17, H-10', H-13' and H-10 or H-13); ^{13}C NMR (126 MHz; CD_2Cl_2) δ_C 170.5 (C-7), 136.1,

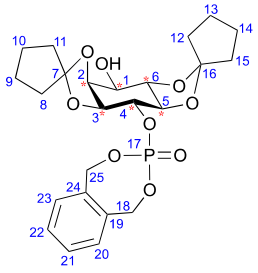
136.0 (C-21, C-26), 129.60, 129.59 (C-22, C-25), 129.43, 129.40 (C-23, C-24), 123.1 (C-18), 120.7 (C-9), 79.6–78.6 ($m_{D,P}$, C-3, C-4), 77.0–76.4 ($m_{D,P}$, C-5), 75.9 (t_D, J_D 23.3, C-2), 74.8 (t_D, J_D 22.7, C-6), 70.0 (t_D, J_D 21.9, C-1), 69.22 (d_P, J_P 5.3, C-20 or C-27), 69.17 (d_P, J_P 5.2, C-20 or C-27), 38.03, 37.96 (C-14, C-17), 37.91, 37.7 (C-10, C-13), 24.2, 24.1, 23.9, 23.8 (C-11, C-12, C-15, C-16), 21.1 (C-8); ^{31}P NMR (162 MHz; CD_2Cl_2) δ_C −1.41 (P-19); ^{2}H NMR (92 MHz; $CHCl_3$; $CDCl_3$) δ_D 5.12 (1D, br s, D-1), 4.63 (1D, br s, D-4), 4.47 (1D, br s, D-2), 4.26 (1D, br s, D-3), 4.02 (1D, br s, D-6), 3.52 (1D, br s, D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2958 (w), 2899 (w), 2875 (w), 2162 (w), 1738 (C=O) (m), 1433 (w), 1365 (w), 1338 (w), 1289 (m), 1245 (m), 1225 (m), 1203 (m), 1100 (m), 1054 (m), 999 (P-O) (s), 973 (P-O) (s), 953 (m), 877 (m), 849 (m), 786 (m), 736 (m); LRMS *m/z* (ESI$^+$) 564.2 ([MD_5+Na]$^+$, 19%), 565.2 ([MD_6+Na]$^+$, 100%); HRMS m/z (ESI$^+$) found 542.21897 [MD_5+H]$^+$, 543.22511 [MD_6+H]$^+$ ($C_{26}H_{28}D_6O_{10}P$ requires 543.22607 [MD_6+H]$^+$); RP-HPLC (Method 2) t_R = 12.01 min, 97.45%.

(+)-1D-2,3-*O*-Cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (+)-57



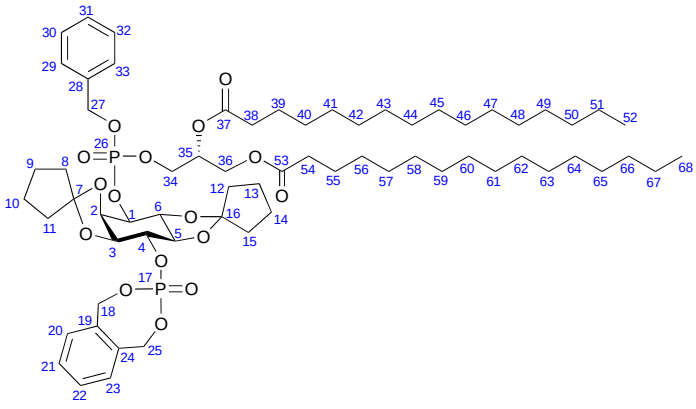
To a solution of (−)-**55** (53 mg, 0.0984 mmol, 1.0 eq) in MeOH (9 mL) was added ground K_2CO_3 (27 mg, 0.197 mmol, 2.0 eq). The reaction mixture was stirred at RT for 1 hour. The solvent was then partially removed *in vacuo* at RT and H_2O (5 mL) was added to the resulting residue. The aqueous layer was extracted with EtOAc (4 × 6 mL) and the combined organic layers were washed with H_2O (6 mL) and brine (2 × 6 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) afforded (+)-**57** (36 mg, 74%) as an amorphous, colourless foam: R_f 0.32 (Petroleum ether/EtOAc 8:3); $[\alpha]_D^{25}$ = +15.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz; CD_2Cl_2) δ_H 7.43–7.36 (2H, m, H-20 and H-23), 7.36–7.30 (2H, m, H-21 and H-22), 5.37–5.29 (2H, m, H-18 and H-25), 5.09 (1H, dd, J_{ABX} 20.6, 11.4, H-18' or H-25'), 5.05 (1H, dd, J_{ABX} 20.6, 11.5, H-18' or H-25'), 4.56 (1H, ddd, *J* 10.9, 9.6, 6.5, H-4), 4.33 (1H, dd, *J* 4.7, 4.5, H-2), 4.26 (1H, dd, *J* 6.5, 4.7, H-3), 4.00 (1H, ddd, *J* 9.3, 9.7, 4.5, H-1), 3.79 (1H, dd, *J* 10.3, 9.7, H-6), 3.43 (1H, dd, *J* 10.3, 9.6, H-5), 2.40 (1H, d, *J* 9.3, C(1)O*H*), 2.14–2.04 (1H, m, H-8 or H-11), 1.96–1.83 (5H, m, H-8 or H-11, H-8', H-11' and H-12 or H-15), 1.82–1.61 (10H, m, H-9, H-10, H-13, H-14 and H-12 or H-15); ^{13}C NMR (126 MHz; CD_2Cl_2) δ_C 136.14, 136.05 (C-19, C-24), 129.61, 129.58 (C-20, C-23), 129.43, 129.40 (C-21, C-22), 122.9 (C-16), 120.6 (C-7), 80.1 (d_P, J_P 5.2, C-4), 80.0 (d_P, J_P 3.4, C-3), 78.9 (C-6), 78.7 (C-2), 77.0 (d_P, J_P 4.5, C-5), 69.8 (C-1), 69.24 (d_P, J_P 3.3, C-18 or C-25), 69.17 (d_P, J_P 3.0, C-18 or C-25), 38.0, 37.90 (C-12, C-15), 37.89, 37.7 (C-8, C-11), 24.1, 24.0, 23.84, 23.81 (C-9, C-10, C-13, C-14); ^{31}P NMR (162 MHz; CD_2Cl_2) δ_P −1.47 (P-17); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3398 (O-H) (br), 2959 (w), 2894 (w), 2874 (w), 1333 (m), 1289 (m), 1224 (w), 1197 (w), 1156 (w), 1121 (m), 1056 (m), 1014 (P-O) (s), 975 (m), 887 (w), 860 (w), 850 (w), 777 (w), 732 (w), 701 (w); LRMS *m/z* (ESI$^+$) 517.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 517.15925 [M+Na]$^+$ ($C_{24}H_{31}O_9NaP$ requires 517.15979 [M+Na]$^+$); RP-HPLC (Method 2) t_R = 11.53 min, 99.33%.

D_6-(+)-1D-2,3-*O*-Cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (+)-58



To a solution of (−)-**56** (110 mg, 0.203 mmol, 1.0 eq, 84% D_6, 16% D_5) in MeOH (19 mL) was added ground K_2CO_3 (56 mg, 0.405 mmol, 2.0 eq). The reaction mixture was stirred at RT for 1 hour. The solvent was then partially removed *in vacuo* at RT and H_2O (10 mL) was added. The aqueous layer was extracted with EtOAc (4 × 10 mL) and the combined organic layers were then washed with H_2O (10 mL) and brine (2 × 10 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) yielded (+)-**58** (87 mg, 86%, 84% D_6, 16% D_5) as an amorphous, colourless foam: R_f 0.32 (Petroleum ether/EtOAc 8:3); $[\alpha]_D^{25}$ = +20.3 (*c* 0.46 in $CHCl_3$); ^{1}H NMR (500 MHz; CD_2Cl_2) δ_H 7.42–7.37 (2H, m, H-20 and H-23), 7.36–7.31 (2H, m, H-21 and H-22), 5.38–5.29 (2H, m, H-18 and H-25), 5.08 (1H, dd, J_{ABX} 20.7, 13.6, H-18' or H-25'), 5.05 (1H, dd, J_{ABX} 20.8, 13.9, H-18' or H-25'), 2.37 (1H, s, C(1)O*H*), 2.12–2.04 (1H, m, H-8 or H-11), 1.96–1.83 (5H, m, H-8 or H-11, H-8', H-11' and H-12 or H-15), 1.81–1.59 (10H, m, H-9, H-10, H-13, H-14 and H-12 or H-15); ^{13}C NMR (126 MHz; CD_2Cl_2) δ_C 136.1, 136.0 (C-19, C-24), 129.60, 129.58 (C-20, C-23), 129.43, 129.41 (C-21, C-22), 122.9 (C-16), 120.6 (C-7), 80.1–79.0 ($m_{D,P}$, C-4, C-3), 78.3 (t_D, J_D 25.5, C-6), 78.1 (t_D, J_D 23.9, C-2), 76.7–76.1 ($m_{D,P}$, C-5), 69.4–68.9 ($m_{D,P}$, C-1), 69.22 (d_P, J_P 3.7, C-18 or C-25), 69.16 (d_P, J_P 3.7, C-18 or C-25), 38.0, 37.9 (C-12, C-15), 37.9,[3] 37.7 (C-8, C-11), 24.1, 24.0, 23.82, 23.78 (C-9, C-10, C-13, C-14); ^{31}P NMR (162 MHz; CD_2Cl_2) δ_C −2.28 (P-17); ^{2}H NMR (92 MHz; $CHCl_3$; $CDCl_3$) δ_D 4.59 (1D, br s, D-4), 4.32 (2D, br s, D-2 and D-3), 4.03 (1D, br s, D-1), 3.80 (1D, br s, D-6), 3.46 (1D, br s, D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3407 (O-H) (br), 2962 (w), 2874 (w), 2361 (w), 2342 (w), 1454 (w), 1433 (w), 1374 (m), 1338 (m), 1290 (m), 1224 (m), 1201 (m), 1121 (m), 1103 (m), 1056 (m), 1016 (P-O) (s), 999 (s), 979 (m), 928 (m), 851 (m), 753 (m), 734 (m); LRMS *m/z* (ESI$^+$) 522.2 ([MD_5+Na]$^+$, 19%), 523.2 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 500.20862 [MD_5+Na]$^+$, 501.21477 [MD_6+H]$^+$ ($C_{24}H_{26}D_6O_9P$ requires 501.21551 [MD_6+H]$^+$); RP-HPLC (Method 2) t_R = 10.67 min, 98.00%.

(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-59



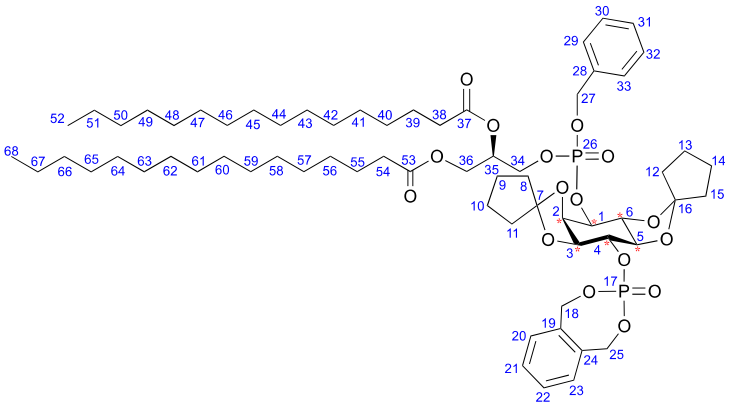
Method 1 – To a solution of (+)-**57** (34 mg, 0.0688 mmol, 1.0 eq) and phosphoramidite (+)-**34** (277 mg, 0.344 mmol, 5.0 eq) in anhydrous CH_2Cl_2 (3.5 mL) was added 1*H*-tetrazole (764 µL, 0.344 mmol, 5.0 eq, 0.45 M in MeCN) dropwise. The cloudy reaction mixture was stirred at RT for 4 hours, then cooled to −78 °C and *m*CPBA (77 mg, 0.344 mmol, 5.0 eq, 77%) was added in one portion. The reaction mixture was stirred for 1 hour, warmed to RT, and stirred for a further 18 hours. The reaction was quenched by addition of an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 3 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 3 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 2 × 3 mL), and brine (2 × 3 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Three consecutive purifications by column

[3] Overlapping peaks

chromatography over silica gel were then carried out (Purification 1 - Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4; Purification 2 – CH_2Cl_2/MeOH 10:0, 9.5:0.5; Purification 3 - Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4) yielding (−)-**59** (11 mg, 13%) as a colourless, gummy solid, and containing a mixture of two diastereoisomers: R_f 0.34 (Petroleum ether/EtOAc 1:1); $[\alpha]_D^{25} = -1.9$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz; CD_2Cl_2) δ_H 7.46–7.30 (18H, m, H-20 to H-23 and H-29 to H-33 Diast. A and B), 5.38–5.29 (4H, m, H-18 and H-25, Diast. A and B), 5.26–5.18 (2H, m, H-35 Diast. A and B), 5.17–5.06 (6H, m, H-27, H-27' and H-18' or H-25' Diast. A and B), 5.05 (2H, dd, J_{ABX} 13.6, 11.4, H-18' or H-25' Diast. A and B), 4.81–4.70 (2H, m, H-1 Diast. A and B), 4.60 (2H, ddd, *J* 10.8, 9.4, 6.7, H-4 Diast. A and B), 4.46 (2H, ddd, *J* 6.9, 4.4, 4.3, H-2 Diast A and B), 4.30 (2H, ddd, *J* 12.0, 4.0, 4.0, H-36 Diast. A and B), 4.25 (2H, dd, *J* 6.7, 4.4, H-3 Diast. A and B), 4.23–4.10 (6H, m, H-34, H-34' and H-36' Diast. A and B), 4.04 (2H, dd, *J* 9.8, 9.7, H-6 Diast. A and B), 3.50 (2H, ddd, *J* 10.8, 9.7, 4.3, H-5 Diast. A and B), 2.34–2.24 (8H, m, H-38 and H-54 Diast. A and B), 2.18–2.07 (2H, m, H-8 or H-11 Diast A and B), 2.01–1.68 (30H, m, H-8', H-11', H-8 or H-11, H-12, H-15, H-9, H-10, H-13, H-14 Diast. A and B), 1.63–1.50 (8H, m, H-39 and H-55 Diast. A and B), 1.37–1.19 (96H, m, H-40 to H-51 and H-56 to H-67 Diast. A and B), 0.88 (12H, t, *J* 6.8, H-52 and H-68 Diast. A and B); ^{13}C NMR (126 MHz; CD_2Cl_2) δ_C 173.43, 173.41 (C-53 Diast. A and B), 173.05, 173.03 (C-37 Diast. A and B), 136.17 (d_P, J_P 7.6, C-28 Diast. A), 136.1–136.0 (m_P, C-28 Diast. B, C-19 or C-24 Diast. A and B), 135.96 (C-19 or C-24 Diast. A and B), 129.61, 129.60, 129.43, 129.40, 129.05, 129.02, 129.0, 128.96 (C-20 to C-23, C-30 to C-32 Diast. A and B), 128.4, 128.3 (C-29, C-33 Diast. A and B), 123.4 (C-16 Diast. A), 123.3 (C-16 Diast. B), 120.9 (C-7 Diast. A and B), 79.9 (d_P, J_P 3.4, C-3 Diast. A and B), 79.2 (d_P, J_P 5.0, C-4 Diast. A and B), 77.6 (C-2 Diast. A and B), 76.9 (d_P, J_P 3.6, C-5 Diast. A and B), 76.1 (d_P, J_P 6.5, C-6 Diast. A and B), 74.6 (d_P, J_P 4.8, C-1 Diast. A), 74.5 (d_P, J_P 4.8, C-1 Diast. B), 70.2 (d_P, J_P 5.7, C-27 Diast. A), 70.0 (d_P, J_P 5.6, C-27 Diast. B), 69.7 (d_P, J_P 7.3, C-35 Diast. A), 69.6 (d_P, J_P 7.2, C-35 Diast. B), 69.23 (d_P, J_P 4.6, C-18 or C-25 Diast. A and B), 69.17 (d_P, J_P 4.7, C-18 or C-25 Diast. A and B), 66.2 (d_P, J_P 5.7, C-34 Diast. A), 65.9 (d_P, J_P 5.1, C-34 Diast. B), 62.05, 61.96 (C-36 Diast. A and B), 38.0, 37.92, 37.87, 37.84, 37.7 (C-12, C-15, C-8, C-11 Diast. A and B), 34.5, 34.3 (C-38, C-54 Diast. A and B), 32.3 (C-50, C-66 Diast. A and B), 30.11, 30.09, 30.07, 29.9, 29.8, 29.7, 29.52, 29.49 (C-40 to C-49, C-56 to C-65 Diast. A and B), 25.2 (C-39, C-55 Diast. A and B), 24.20, 24.18, 24.1, 23.8 (C-9, C-10, C-13, C-14 Diast. A and B), 23.1 (C-51, C-67 Diast. A and B), 14.3 (C-52, C-68 Diast. A and B); ^{31}P NMR (162 MHz; CD_2Cl_2) δ_P −2.17 (P-26 Diast. A), −2.22 (P-26 Diast. B), −3.32 (P-17); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2955 (m), 2918 (s), 2850 (s), 2361 (w), 2340 (w), 1743 (C=O) (m), 1435 (w), 1419 (w), 1332 (w), 1285 (m), 1171 (m), 1118 (m), 1015 (P-O) (s), 922 (w), 907 (w), 861 (w), 741 (m); LRMS *m/z* (ESI$^+$) 1237.6 ([M+Na]$^+$, 100%), 1238.6 ([M+Na+H]$^+$, 57%); HRMS *m/z* (ESI$^+$) found 1215.68389 [M+H]$^+$ ($C_{66}H_{105}O_{16}P_2$ requires 1215.68724 [M+H]$^+$); NP-HPLC (Method 7) t_R = 4.86 min, 100%.

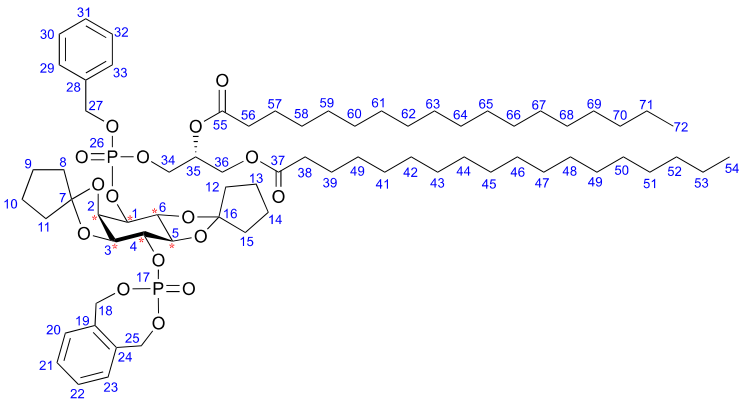
Method 2 – To a solution of (+)-**57** (50 mg, 0.101 mmol, 1.0 eq) and phosphoramidite (+)-**34** (244 mg, 0.303 mmol, 3.0 eq) in anhydrous CH_2Cl_2 (5.0 mL) was added 1*H*-tetrazole (674 µL, 0.303 mmol, 3.0 eq, 0.45 M in MeCN) dropwise. The cloudy reaction mixture was stirred at RT for 19.5 hours, then cooled to −78 °C and *m*CPBA (68 mg, 0.303 mmol, 3.0 eq, 77%) was added in one portion. The reaction mixture was stirred for 1 hour, warmed to RT, stirred for a further 3 hours, then quenched by addition of an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 5 mL). After stirring for 15 minutes, the aqueous phase was extracted with CH_2Cl_2 (4 × 5 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 2 × 3 mL), and brine (2 × 3 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4, 5:5) yielded (−)-**59** (68 mg, 55%) as a colourless, gummy solid, and containing a mixture of two diastereoisomers. Spectral data are identical to those reported above.

D_6-(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxa-phosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-60



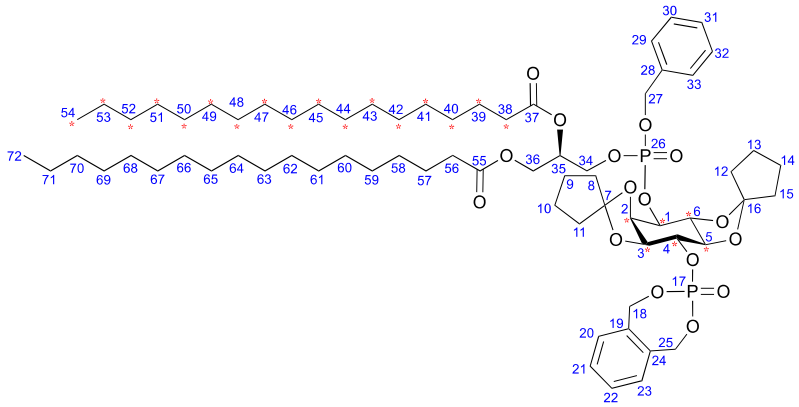
To a solution of (+)-**58** (20 mg, 0.0400 mmol, 1.0 eq, 84% D_6, 16% D_5) and phosphoramidite (+)-**34** (97 mg, 0.120 mmol, 3.0 eq) in anhydrous CH_2Cl_2 (2.0 mL) was added 1*H*-tetrazole (266 µL, 0.120 mmol, 3.0 eq, 0.45 M in MeCN) dropwise. The cloudy reaction mixture was stirred at RT for 21 hours, then cooled to −78 °C and *m*CPBA (27 mg, 0.120 mmol, 3.0 eq, 77%) was added in one portion. The reaction mixture was stirred for 1 hour, warmed to RT, then stirred for a further 3 hours. The reaction was quenched by addition of an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 3 mL) and stirred for 15 minutes. The aqueous phase was extracted with CH_2Cl_2 (4 × 3 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 2 × 3 mL), and brine (2 × 3 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purifications by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4, 5:5) yielded (−)-**60** (27 mg, 55%, 87% D_6, 13% D_5) as a colourless, gummy solid: R_f 0.34 (Petroleum ether/EtOAc 5:5); $[\alpha]_D^{25}$ = −1.9 (*c* 0.52, $CHCl_3$); ^{1}H NMR (400 MHz; CD_2Cl_2) δ_H 7.43–7.31 (18H, m, H-20 to H-23 and H-29 to H-33 Diast. A and B), 5.36–5.29 (4H, m, H-18 and H-25 Diast. A and B), 5.25–5.18 (2H, m, H-35 Diast. A and B), 5.16–5.06 (6H, m, H-27 and H-18’ or H-25’ Diast. A and B), 5.05 (2H, dd, J_{ABX} 14.0, 14.0, H-18’ or H-25’ Diast. A and B), 4.30 (2H, ddd, J_{XY} 12.0, 4.4, 4.4, H-36 Diast. A and B), 4.22–4.09 (6H, m, H-34 and H-36’ Diast. A and B), 2.33–2.25 (8H, m, H-38 and H-54 Diast. A and B), 2.16–2.08 (2H, m, H-8 or H-11 Diast A and B), 1.98–1.63 (30H, m, H-8 or H-11, H-8’, H-11’, H-12, H-15, H-9, H-10, H-13, H-14 Diast. A and B), 1.63–1.49 (8H, m, H-39 and H-55 Diast. A and B), 1.34–1.19 (96H, m, H-40 to H-51 and H-56 to H-67 Diast. A and B), 0.88 (12H, t, *J* 6.9, H-52 and H-68 Diast. A and B); ^{13}C NMR (126 MHz; CD_2Cl_2) δ_C 173.45, 173.43 (C-53 Diast. A and B), 173.06, 173.05 (C-37 Diast. A and B), 136.2 (d_P, J_P 7.3, C-28 Diast. A), 136.12–136.00 (m_P, C-28 Diast. B, C-19 or C-24 Diast. A and B), 135.96 (C-19 or C-24 Diast. A and B), 129.6, 129.43, 129.40, 129.05, 129.02, 128.99, 128.96 (C-20 to C-23, C-30 to C-32 Diast. A and B), 128.4, 128.3 (C-29, C-33 Diast. A and B), 123.35 (C-16 Diast. A), 123.32 (C-16 Diast. B), 120.9 (C-7 Diast. A and B), 79.8–79.1 ($m_{D,P}$, C-3 Diast. A and B), 79.1–78.5 ($m_{D,P}$, C-4 Diast. A and B), 77.4–76.8 ($m_{D,P}$, C-2 Diast. A and B), 76.6–76.1 ($m_{D,P}$, C-5 Diast. A and B), 75.8–75.2 ($m_{D,P}$, C-6 Diast. A and B), 74.5–73.8 ($m_{D,P}$, C-1 Diast. A and B), 70.2 (d_P, J_P 5.7, C-27 Diast. A), 70.0 (d_P, J_P 5.7, C-27 Diast. B), 69.7 (d_P, J_P 6.7, C-35 Diast. A), 69.6 (d_P, J_P 6.7, C-35 Diast. B), 69.23 (d_P, J_P 4.8, C-18 or C-25 Diast. A and B), 69.18 (d_P, J_P 4.8, C-18 or C-25 Diast. A and B), 66.2 (d_P, J_P 5.7, C-34 Diast. A), 65.9 (d_P, J_P 5.1, C-34 Diast. B), 62.04, 61.96 (C-36 Diast. A and B), 38.0, 37.93, 37.88, 37.85, 37.7 (C-12, C-15, C-8, C-11 Diast. A and B), 34.5, 34.3 (C-38, C-54 Diast. A and B), 32.3 (C-50, C-66 Diast. A and B), 30.11, 30.09, 30.06, 29.9, 29.8, 29.7, 29.52, 29.49 (C-40 to C-49, C-56 to C-65 Diast. A and B), 25.2 (C-39, C-55 Diast. A and B), 24.20, 24.17, 24.08, 23.8 (C-9, C-10, C-13, C-14 Diast. A and B), 23.1 (C-51, C-67 Diast. A and B), 14.3 (C-52, C-68 Diast. A and B); ^{31}P NMR (162 MHz; CD_2Cl_2) δ_P −2.15 (P-26 Diast. A), −2.20 (P-26 Diast. B), −3.32 (P-17); ^{2}H NMR (92 MHz; $CHCl_3$; $CDCl_3$) δ_D 4.62 (2D, br s, D-1 and D-4), 4.46 (1D, br s, D-2), 4.25 (1D, br s, D-3), 4.02 (1D, br s, D-6), 3.45 (1D, br s, D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2955 (m), 2924 (s), 2853 (m), 2359 (w), 2339 (w), 1743 (C=O) (m), 1435 (w), 1418 (w), 1377 (w), 1339 (w), 1292 (m), 1207 (m), 1176 (m), 1156 (m), 1104 (m), 1020 (P-O) (s), 885 (w), 851 (w), 775 (w), 733 (w); LRMS *m/z* (ESI$^+$) 1242.6 ([MD_5+Na]$^+$, 4%), 1243.6 ([MD_6+Na]$^+$, 13%); HRMS *m/z* (ESI$^+$) found 1242.69965 [MD_5+Na]$^+$, 1243.70607 [MD_6+Na]$^+$ ($C_{66}H_{98}D_6O_{16}NaP_2$ requires 1243.70684 [MD_6+Na]$^+$); NP-HPLC (Method 6) t_R = 4.82 min, 100%.

D_6-(−)-1D-1-*O*-(1,2-Di-*O*-stearoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphos-phep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-61



To a solution of (+)-**58** (20 mg, 0.340 mmol, 1.0 eq, 84% D_6, 16% D_5) and phosphoramidite (+)-**35** (88 mg, 0.102 mmol, 3.0 eq) in anhydrous CH_2Cl_2 (2.0 mL) was added 1*H*-tetrazole (227 µL, 0.102 mmol, 3.0 eq, 0.45 M in MeCN) dropwise. The cloudy reaction mixture was stirred at RT for 18 hours, then cooled to −78 °C and *m*CPBA (23 mg, 0.102 mmol, 3.0 eq, 77%) was added in one portion. The reaction mixture was stirred at −78 °C for 1 hour, warmed to RT, then stirred for a further 30 minutes. The reaction was quenched by addition of an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 3 mL) and stirred for 15 minutes. The aqueous phase was extracted with CH_2Cl_2 (4 × 3 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 2 × 3 mL), and brine (2 × 3 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purifications by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 4:6, 3:7, 2:8) yielded (−)-**61** (28 mg, 64%, 87% D_6, 13% D_5) as a colourless, gummy solid: R_f 0.34 (Petroleum ether/EtOAc 1:1); ^{1}H NMR (500 MHz; CD_2Cl_2) δ_H 7.44–7.31 (18H, m, H-20 to H-23 and H-29 to H-33 Diast. A and B), 5.37–5.29 (4H, m, H-18 and H-25, Diast. A and B), 5.25–5.19 (2H, m, H-35 Diast. A and B), 5.16–5.06 (6H, m, H-27, H-27' and H-18' or H-25' Diast. A and B), 5.05 (2H, dd, J_{ABX} 13.7928, 13.7928, H-18' or H-25' Diast. A and B), 4.30 (2H, ddd, J_{XY} 12.0194, 4.3743, 4.3743, H-36 Diast. A and B), 4.22–4.10 (6H, m, H-34 and H-36' Diast. A and B), 2.32–2.25 (8H, m, H-38 and H-56 Diast. A and B), 2.15–2.07 (2H, m, H-8 or H-11 Diast A and B), 1.98–1.63 (30H, m, H-8 or H-11, H-8', H-11', H-12, H-15, H-9, H-10, H-13, H-14 Diast. A and B), 1.63–1.49 (8H, m, H-39 and H-57 Diast. A and B), 1.34–1.19 (112H, m, H-40 to H-53 and H-58 to H-71 Diast. A and B), 0.88 (12H, t, *J* 6.9, H-54 and H-72 Diast. A and B); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.5, 173.4 (C-37 Diast. A and B), 173.1 (C-55 Diast. A and B), 136.2 (d_P, J_P 7.5, C-28 Diast. A), 136.1–135.9 (m_P, C-28 Diast. B, C-19, C-24 Diast. A and B), 129.6, 129.44, 129.41, 120.06, 129.03, 129.00, 128.96 (C-20 to C-23, C-30 to C-32 Diast. A and B), 128.4, 128.3 (C-29, C-33 Diast. A and B), 123.36 (C-16 Diast. A), 123.34 (C-16 Diast. B), 120.9 (C-7 Diast. A and B), 79.8–79.1 ($m_{D,P}$, C-3 Diast. A and B), 79.1–78.5 ($m_{D,P}$, C-4 Diast. A and B), 77.4–76.8 ($m_{D,P}$, C-2 Diast. A and B), 76.6–76.1 ($m_{D,P}$, C-5 Diast. A and B), 75.8–75.2 ($m_{D,P}$, C-6 Diast. A and B), 74.5–73.8 ($m_{D,P}$, C-1 Diast. A and B), 70.2 (d_P, J_P 5.7, C-27 Diast. A), 70.0 (d_P, J_P 5.7, C-27 Diast. B), 69.7 (d_P, J_P 7.4, C-35 Diast. A), 69.6 (d_P, J_P 7.4, C-35 Diast. B), 69.25 (d_P, J_P 4.9, C-18 or C-25 Diast. A and B), 69.19 (d_P, J_P 4.9, C-18 or C-25 Diast. A and B), 66.2 (d_P, J_P 5.7, C-34 Diast. A), 65.9 (d_P, J_P 5.5, C-34 Diast. B), 62.05, 61.97 (C-36 Diast. A and B), 38.0, 37.93, 37.88, 37.85, 37.7 (C-12, C-15, C-8, C-11 Diast. A and B), 34.5, 34.3 (C-38, C-56 Diast. A and B), 32.3 (C-52, C-70 Diast. A and B), 30.11, 30.06, 29.9, 29.8, 29.7, 29.52, 29.49 (C-40 to C-51, C-58 to C-69 Diast. A and B), 25.2 (C-39, C-57 Diast. A and B), 24.20, 24.17, 24.07, 23.8 (C-9, C-10, C-13, C-14 Diast. A and B), 23.1 (C-53, C-71 Diast. A and B), 14.3 (C-54, C-72 Diast. A and B); ^{31}P NMR (126 MHz; $CDCl_3$) δ_P −1.99 (P-17), −2.16 (P-26 Diast. A), −2.22 (P-26 Diast. B); ^{2}H NMR (92 MHz; $CDCl_3$) δ_P 5.11–3.77 (5D, br, D-1, D-4, D-2, D-3 and D-6), 3.44 (1D, br s, D-5); ν_{max}(thin film)/cm^{-1} 32955 (w), 2917 (s), 2850 (s), 1743 (C=O) (m), 1467 (w), 1434 (w), 1377 (w), 1339 (m), 1289 (w), 1208 (m), 1176 (m), 1103 (m), 1018 (s), 925 (w), 851 (w), 752 (m), 734 (m), 698 (w), 666 (w), 624 (m); HRMS *m/z* (ESI$^+$) found 1277.78737 $[M+H]^+$ ($C_{50}H_{81}O_7$ requires 1277.78750 $[M+H]^+$); NP-HPLC (Method 7) 7.83 min, 99.49%.

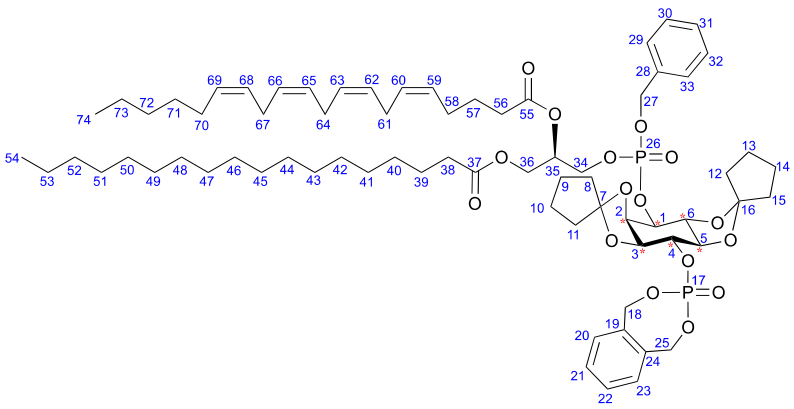
D_{41}-(−)-1D-1-*O*-(1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclo-pentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-62



To a solution of (+)-**58** (20 mg, 0.0400 mmol, 1.0 eq, 84% D_6, 16% D_5) and phosphoramidite (+)-**44** (108 mg, 0.120 mmol, 3.0 eq) in anhydrous CH_2Cl_2 (2.0 mL) was added 1*H*-tetrazole (266 µL, 0.120 mmol, 3.0 eq, 0.45 M in MeCN) dropwise. The cloudy reaction mixture was stirred at RT for 22 hours, then cooled to −78 °C and *m*CPBA (27 mg, 0.120 mmol, 3.0 eq, 77%) was added in one portion. The reaction mixture was stirred for 1 hour, warmed to RT, and stirred for a further 2 hours. The reaction was quenched by addition of an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 3 mL) and stirred for a further 15 minutes. The aqueous phase was extracted with CH_2Cl_2 (4 × 3 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 2 × 3 mL), brine (2 × 3 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4, 5:5) gave (−)-**62** (34 mg, 65%, 62% D_{41}, 29% D_{40}, 9% D_{39}) as a colourless, gummy solid: R_f 0.34 (Petroleum ether/EtOAc 5:5); $[\alpha]_D^{25}$ = −5.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz; CD_2Cl_2) δ_H 7.44–7.31 (18H, m, H-20 to H-23 and H-29 to H-33 Diast. A and B), 5.37–5.29 (4H, m, H-18 and H-25, Diast. A and B), 5.25–5.18 (2H, m, H-35 Diast. A and B), 5.16–5.06 (6H, m, H-27 and H-18’ or H-25’ Diast. A and B), 5.05 (2H, dd, J_{ABX} 13.8, 13.8, H-18’ or H-25’ Diast. A and B), 4.30 (2H, ddd, J_{XY} 12.0, 4.3, 4.3, H-36 Diast. A and B), 4.22–4.10 (6H, m, H-34 and H-36’ Diast. A and B), 2.28 (2H, t, *J* 7.6, H-56 Diast. A), 2.27 (2H, t, *J* 7.6, H-56 Diast. B), 2.16–2.08 (2H, m, H-8 or H-11 Diast A and B), 1.98–1.63 (30H, m, H-8 or H-11, H-8’, H-11’, H-12, H-15, H-9, H-10, H-13, H-14 Diast. A and B), 1.63–1.50 (4H, m, H-57 Diast. A and B), 1.34–1.21 (56H, m, H-58 to H-71 Diast. A and B), 0.88 (6H, t, *J* 6.9, H-71 Diast. A and B); ^{13}C NMR (126 MHz; CD_2Cl_2) δ_C 173.45, 173.43 (C-55 Diast. A and B), 173.1 (C-37 Diast. A and B), 136.2 (d_P, J_P 7.4, C-28 Diast. A), 136.11–136.00 (m, C-28 Diast. B, C-19 or C-24 Diast. A and B), 135.96 (C-19 or C-24 Diast. A and B), 129.61, 129.60, 129.44, 129.40, 129.05, 129.02, 129.00 (C-20 to C-23, C-30 to C-32 Diast. A and B), 128.4, 128.3 (C-29, C-33 Diast. A and B), 123.35 (C-16 Diast. A), 123.33 (C-16 Diast. B), 120.9 (C-7 Diast. A and B), 79.8–79.1 ($m_{D,P}$, C-3 Diast. A and B), 79.1–78.5 ($m_{D,P}$, C-4 Diast. A and B), 77.4–76.8 ($m_{D,P}$, C-2 Diast. A and B), 76.6–76.1 ($m_{D,P}$, C-5 Diast. A and B), 75.8–75.2 ($m_{D,P}$, C-6 Diast. A and B), 74.5–73.8 ($m_{D,P}$, C-1 Diast. A and B), 70.2 (d_P, J_P 5.7, C-27 Diast. A), 70.0 (d_P, J_P 5.7, C-27 Diast. B), 69.64 (d_P, J_P 6.7, C-35 Diast. A), 69.58 (d_P, J_P 6.8, C-35 Diast. B), 69.24 (d_P, J_P 4.8, C-18 or C-25 Diast. A and B), 69.19 (d_P, J_P 4.8, C-18 or C-25 Diast. A and B), 66.2 (d_P, J_P 5.5, C-34 Diast. A), 65.9 (d_P, J_P 5.2, C-34 Diast. B), 62.05, 61.97 (C-36 Diast. A and B), 38.0, 37.94, 37.88, 37.85, 37.7 (C-12, C-15, C-8, C-11 Diast. A and B), 34.3 (C-56 Diast. A and B), 34.2–33.3 (m_D, C-38 Diast. A and B), 32.3 (C-70 Diast. A and B), 31.3–30.6 (m_D, C-52 Diast. A and B), 30.11, 30.06, 29.9, 29.8, 29.7, 29.5 (C-58 to C-69 Diast. A and B), 29.2–28.0 (m_D, C-40 to C-51 Diast. A and B), 25.2 (C-57 Diast. A and B), 24.4–23.6 (m_D, C-39 Diast. A and B), 24.19, 24.17, 24.1, 23.8 (C-9, C-10, C-13, C-14 Diast. A and B), 23.1 (C-71 Diast. A and B), 22.2–21.4 (m_D, C-53 Diast. A and B), 14.3 (C-72 Diast. A and B), 13.6–12.7 (m_D, C-54 Diast. A and B); ^{31}P NMR (162 MHz; CD_2Cl_2) δ_P −2.17 (P-26 Diast. A), −2.22 (P-26 Diast. B), −3.30 (P-17); ^{2}H NMR (92 MHz; $CHCl_3$; $CDCl_3$) δ_D 4.69 (1D, br s, D-1), 4.53 (1D, br s, D-4), 4.40 (1D, br s, D-2), 4.20 (1D, br s, D-3), 3.99 (1D, br s, D-6), 3.45 (1D, br s, D-5), 2.21 (2D, br s, D-38), 1.49 (2D, br s, D-39), 1.15 (28D, br s, D-40 to D-53), 0.78 (3D, br s, D-54); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2920 (s), 2851 (m), 2359 (w), 2339 (w), 2194 (w), 2088 (w), 1743 (C=O) (m), 1468 (w), 1339 (w), 1289 (m), 1208 (m), 1175 (m), 1143 (m), 1104 (m), 1019 (P-O)

(s), 885 (w), 851 (w), 733 (w), 698 (w); HRMS *m/z* (ESI$^+$) found 1310.9918 ([MD_{39}+H]$^+$, 11%), 1312.00179 ([MD_{40}+H]$^+$, 43%), 1313.00682 ([MD_{41}+H]$^+$, 100%) ($C_{70}H_{72}D_{41}O_{16}P_2$ requires 1313.00718 [MD_{41}+H]$^+$); NP-HPLC (Method 6) 4.63 min, 99.80%.

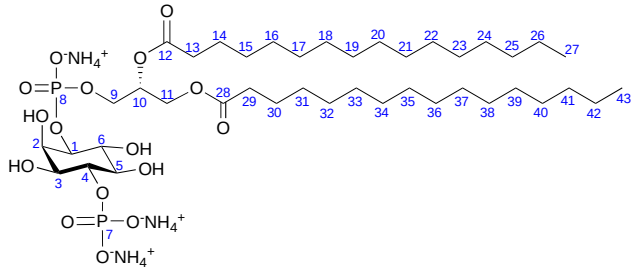
D_6-(−)-1D-1-*O*-(1-*O*-stearoyl-2-*O*-arachidonyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-63



To a solution of (+)-**58** (17 mg, 0.0340 mmol, 1.0 eq, 84% D_6, 16% D_5) and phosphoramidite (+)-**45** (90 mg, 0.102 mmol, 3.0 eq) in anhydrous CH_2Cl_2 (2.0 mL) was added 1*H*-tetrazole (226 µL, 0.102 mmol, 3.0 eq, 0.45 M in MeCN) dropwise. The cloudy reaction mixture was stirred at RT for 3.5 hours, then cooled to −78 °C and *m*CPBA (23 mg, 0.102 mmol, 3.0 eq, 77%) was added in one portion. The reaction mixture was stirred at −78 °C for 25 minutes, warmed to RT, then stirred for a further 15 minutes. The reaction was quenched by addition of an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 3 mL) and stirred for 15 minutes. The aqueous phase was extracted with CH_2Cl_2 (4 × 3 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 2 × 3 mL), and brine (2 × 3 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purifications by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4, 5:5, 5:6) yielded (−)-**63** (36 mg, 79%, 82% D_6, 18% D_5) as a colourless, gummy solid: R_f 0.55 (Petroleum ether/EtOAc 1:1); $[\alpha]_D^{25}$ = −3.2 (*c* 0.52, CH_3Cl); ^{1}H NMR (500 MHz; CD_2Cl_2) δ_H 7.44–7.31 (18H, m, H-20 to H-23 and H-29 to H-33 Diast. A and B), 5.44–5.29 (24H, m, H-18, H-25, H-59, H-60, H-62, H-63, H-65, H-66, H-68 and H-69 Diast. A and B), 5.25–5.18 (2H, m, H-35 Diast. A and B), 5.15–5.02 (6H, m, H-27 and H-18' or H-25' Diast. A and B), 5.05 (2H, dd, J_{ABX} 13.8, 13.8, H-18' or H-25' Diast. A and B), 4.30 (2H, ddd, J_{XY} 12.0, 4.9, 4.4, H-36 Diast. A and B), 4.23–4.10 (6H, m, H-34 and H-36' Diast. A and B), 2.87–2.77 (12H, m, H-61, H-64 and H-67), 2.35–2.25 (8H, m, H-38 and H-56), 2.15–2.08 (10H, m H-58, H-70 and H-8 or H-11 Diast. A and B), 1.98–1.62 (30H, m, H-8 or H-11, H-8', H-11', H-12, H-15, H-9, H-10, H-13 and H-14 Diast. A and B), 1.62–1.48 (8H, m, H-39 and H-57 Diast. A and B), 1.39–1.20 (68H, m, H-40 to H-53 and H-71 to H-73 Diast. A and B), 0.91–0.85 (12H, m, H-54 and H-74 Diast. A and B); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 173.5, 173.4 (C-37 Diast. A and B), 172.8 (C-55 Diast. A and B), 136.2 (d_P, J_P 7.5, C-28 Diast. A), 136.1–135.9 (m_P, C-28 Diast. B, C-19, C-24 Diast. A and B), 130.8 (C-69), 129.61, 129.60, 129.44, 129.40, 129.3, 129.2, 129.1, 129.03, 129.00, 128.96, 128.91 (C-20 to C-23, C-30 to C-32, C-59 and C-60 Diast. A and B), 128.6, 128.5, 128.4, 128.3, 128.2 (C-62, C-63, C-65, C-66, C-29 and C-33 Diast. A and B), 127.9 (C-68), 123.4 (C-16 Diast. A), 123.3 (C-16 Diast. B), 120.9 (C-7 Diast. A and B), 79.8–79.0 ($m_{D,P}$, C-3 Diast. A and B), 79.0–78.5 ($m_{D,P}$, C-4 Diast. A and B), 77.5–76.8 ($m_{D,P}$, C-2 Diast. A and B), 76.6–76.1 ($m_{D,P}$, C-5 Diast. A and B), 75.8–75.2 ($m_{D,P}$, C-6 Diast. A and B), 74.5–73.8 ($m_{D,P}$, C-1 Diast. A and B), 70.2 (d_P, J_P 5.7, C-27 Diast. A), 70.0 (d_P, J_P 5.5, C-27 Diast. B), 69.8 (d_P, J_P 7.6, C-35 Diast. A), 69.7 (d_P, J_P 7.4, C-35 Diast. B), 69.24 (d_P, J_P 5.0, C-18 or C-25 Diast. A and B), 69.19 (d_P, J_P 4.8, C-18 or C-25 Diast. A and B), 66.2 (d_P, J_P 5.6, C-34 Diast. A), 65.9 (d_P, J_P 5.2, C-34 Diast. B), 62.0, 61.9 (C-36 Diast. A and B), 38.0, 37.94, 37.88, 37.85, 37.7 (C-12, C-15, C-8 and C-11 Diast. A and B), 34.3 (C-38 Diast. A and B), 33.9 (C-56 Diast. A and B), 32.3 (C-52 Diast. A and B), 31.9 (C-72 Diast. A and B), 30.10, 30.06, 29.9, 29.8, 29.74, 29.71, 29.5 (C-40 to C-51 Diast. A and B and C-71 Diast. A and B), 27.6 (C-70, Diast. A and B), 26.9 (C-58 Diast. A and B), 25.98, 25.97 (C-61, C-64 and C-67 Diast. A and B), 25.2, 25.1 (C-39 and C-57 Diast. A and B), 24.20, 24.17, 24.1, 23.8 (C-9, C-10, C-13, C-14 Diast. A and B), 23.1, 23.0 (C-53 and C-73

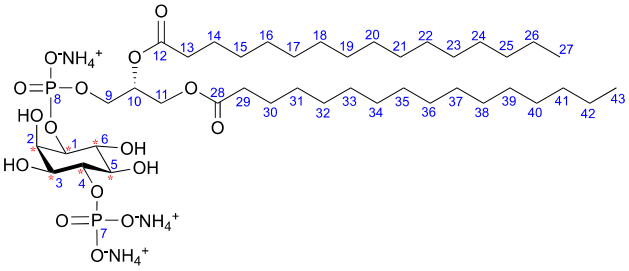
Diast. A and B), 14.3, 14.2 (C-54 and C-74 Diast. A and B); ^{31}P NMR (126 MHz; CD_2Cl_2) δ_P −2.13 (P-26 Diast. A), −2.18 (P-26 Diast. B), −3.29 (P-17); ^{2}H NMR (92 MHz; $CDCl_3$) δ_P 5.07–3.76 (5D, br, D-1, D-4, D-2, D-3 and D-6), 3.44 (1D, br s, D-5); $\bar{\nu}_{max}$(thin film)/cm^{-1} 33014 (w), 2925 (m), 2854 (m), 1743 (C=O) (m), 1457 (w), 1435 (w), 1338 (w), 1292 (m), 1207 (w), 1145 (w), 1104 (m), 1019 (s), 886 (w), 851 (w), 777 (w), 733 (w), 696 (w), 669 (w), 624 (w); HRMS *m/z* (ESI$^+$) found 1297.75594 $[M+H]^+$ ($C_{50}H_{81}O_7$ requires 1297.75620 $[M+H]^+$); NP-HPLC (Method 7) 7.43 min, 96.42%.

(−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-64



To a solution of (−)-**59** (10 mg, 0.00823 mmol, 1.0 eq) in toluene (0.5 mL) was added TMSBr (21 µL, 0.165 mmol, 20 eq). The solution was heated to 70 °C for 12 hours, then cooled to 0 °C and concentrated by vacuum transfer. The residue was dissolved in toluene (0.75 mL) and concentrated again by vacuum transfer. This was repeated three times. The residue was then dissolved in MeOH (0.50 mL), stirred at 0 °C for 1 hour and the solution was concentrated *in vacuo* at 0 °C. The residue obtained was dissolved in the minimal amount of MeOH/CH_2Cl_2 (1:1, *v/v*) and purified by column chromatography over silica gel ($CHCl_3$/MeOH/2.2 M NH_4OH 5:3.9:1.1).[71] The combined fractions were partially concentrated *in vacuo* at 0 °C, then H_2O (30 mL) was added. Lyophilising this solution gave (−)-**64** (6 mg, 68%) as a colourless, fluffy solid.[72] The compound was stored at −80 °C as the ammonium salt: R_f 0.60 ($CHCl_3$/MeOH/2.2 M NH_4OH 5:3.9:1.1); $[\alpha]_D^{25} = -11.7$ (*c* 0.050, MeOH/$CHCl_3$/H_2O 4:3:1); ^{1}H NMR (500 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_H 5.28–5.23 (1H, m, H-10), 4.44 (1H, dd, *J* 12.1, 2.7, H-11), 4.25–4.17 (3H, m, H-11', H-4 and H-2), 4.10–4.00 (2H, m, H-9), 3.95–3.89 (1H, m, H-1), 3.82 (1H, dd, *J* 9.6, 9.4, H-6), 3.60 (1H, dd, *J* 9.6, 2.7, H-3), 3.43 (1H, dd, *J* 9.4, 9.2, H-5), 2.37–2.28 (4H, m, H-13 and H-29), 1.65–1.54 (4H, m, H-14 and H-30), 1.36–1.21 (48H, m, H-15 to H-26 and H-31 to H-42), 0.87 (6H, t, *J* 6.9, H-27 and H-43); ^{13}C NMR (126 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_C 175.2, 174.9 (C-12, C-28), 78.4 (C-4), 77.3 (d_P, J_P 6.1, C-1), 74.8 (C-5), 72.4 (d_P, J_P 5.7, C-6), 72.1 (C-2), 71.7 (d_P, J_P 2.9, C-3), 71.5 (d_P, J_P 8.7, C-10), 64.5 (d_P, J_P 6.0, C-9), 63.8 (C-11), 35.0, 34.9 (C-13, C-29), 32.7 (C-25, C-41), 30.43, 30.39, 30.35, 30.30, 30.17, 30.10, 29.92, 29.88 (C-15 to C-24 and C-31 to C-40), 25.74, 25.66 (C-14, C-30), 23.4 (C-26, C-42), 14.5 (C-27, C-43); ^{31}P NMR (162 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_P 7.86 (P-7), 3.76 (P-8); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3660 (O-H) (w), 3221 (O-H) (br), 2981 (s), 2917 (m), 2890 (m), 2850 (m), 1737 (C=O) (m), 1464 (w), 1382 (m), 1250 (m), 1152 (s), 1061 (s), 953 (P-O) (s), 805 (w); HRMS *m/z* (ESI$^-$) found 889.48442 $[M-H]^-$ ($C_{41}H_{79}O_{16}P_2$ requires 889.48488 $[M-H]^-$). These data are in good agreement with the literature values.[10,73]

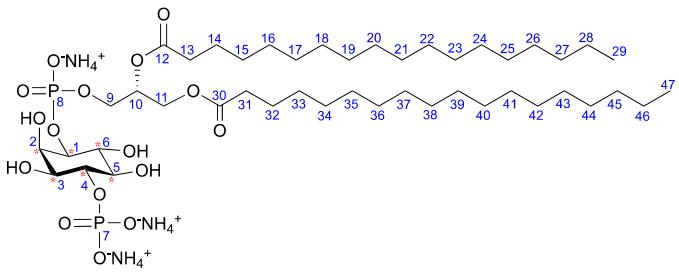
D_6-(−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-65



To a solution of (−)-**60** (12 mg, 0.00982 mmol, 1.0 eq, 87% D_6, 13% D_5) in toluene (0.50 mL) was added TMSBr (20 µL, 0.147 mmol, 15 eq). The solution was stirred at RT for 12 hours, then cooled to 0 °C and concentrated by vacuum transfer. The residue was dissolved in toluene (0.6 mL) and concentrated again by vacuum transfer. This was repeated three times. The residue was then dissolved in MeOH (0.5 mL), stirred at 0 °C for 1 hour and the solution was concentrated *in vacuo* at 0 °C. The residue obtained was dissolved in the minimal amount of MeOH/CH_2Cl_2 (1:1 *v/v*) and purified by column chromatography

over silica gel ($CHCl_3$/MeOH/2.2 M NH_4OH 5:3.9:1.1). The combined fractions were partially concentrated *in vacuo* at 0 °C, then H_2O (30 mL) was added. Lyophilising this solution yielded (−)-**65** (7 mg, 75%, 86% D_6, 14% D_5) as a colourless, fluffy solid. The compound was stored at −80 °C as the ammonium salt: R_f 0.60 ($CHCl_3$/MeOH/2.2 M NH_4OH 5:3.9:1.1); $[\alpha]_D^{25}$ = −9.9 (*c* 0.06, MeOH/$CHCl_3$/H_2O 4:3:1); ^{1}H NMR (500 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_H 5.29–5.23 (1H, m, H-10), 4.43 (1H, dd, J_{XY} 12.1, 2.5, H-11), 4.20 (1H, dd, J_{XY} 12.1, 7.8, H-11'), 4.09–3.98 (2H, m, H-9), 2.37–2.27 (4H, m, H-13 and H-29), 1.65–1.54 (4H, m, H-14 and H-30), 1.36-1.21 (48H, m, H-15 to H-26 and H-31 to H-42), 0.88 (6H, t, *J* 6.9, H-27 and H-43); ^{13}C NMR (126 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_C 175.2, 174.9 (C-12, C-28), 71.4 (d_P, J_P 8.5, C-10), 64.5 (d_P, J_P 4.8, C-9), 63.8 (C-11), 35.0, 34.9 (C-13, C-29), 32.7 (C-25, C-41), 30.43, 30.38, 30.31, 30.2, 30.1, 29.93, 29.88 (C-15 to C-24 and C-31 to C-40), 25.7, 25.6 (C-14, C-30), 23.4 (C-26, C-42), 14.6 (C-27, C-43);[4] ^{31}P NMR (162 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_P 1.72 (P-7), −0.18 (P-8); ^{2}H NMR (92 MHz; CH_3OH/$CHCl_3$/H_2O 4:3:1; $CDCl_3$) δ_D 4.30 (br s, inositol ring), 3.04 (br s, inositol ring), 3.03 (br s, inositol ring); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3211 (O-H) (br), 3070 (O-H) (br), 2956 (w), 2917 (m), 2850 (m), 1738 (C=O) (m), 1464 (m), 1417 (m), 1196 (m), 1169 (m), 1089 (s), 1064 (s), 1033 (s), 1013 (P-O) (s), 993 (s), 897 (m), 873 (m), 720 (m), 681 (m), 615 (s); HRMS *m/z* (ESI$^-$) found 894.51613 ([MD_5−H]$^-$, 16%), 895.52186 ([MD_6−H]$^-$, 100%) ($C_{41}H_{73}D_6O_{16}P_2$ requires 895.52254 [MD_6−H]$^-$).

D_6-(−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-66

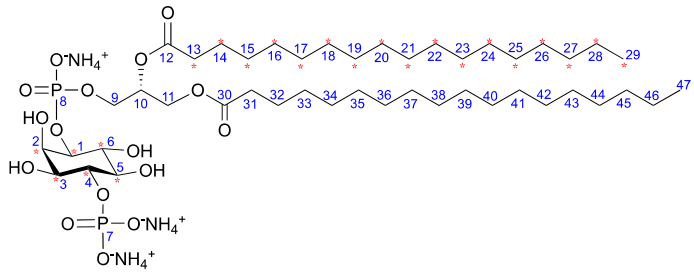


To a solution of (−)-**61** (14 mg, 0.0110 mmol, 1.0 eq, 87% D_6, 13% D_5) in toluene (0.40 mL) was added TMSBr (22 µL, 0.164 mmol, 15 eq). The solution was stirred at RT for 14 hours, then heated to 70 °C for 1 hour, cooled to 0 °C, and concentrated by vacuum transfer. The residue was dissolved in toluene (0.5 mL) and concentrated again by vacuum transfer. This was repeated three times. The residue was then dissolved in MeOH (0.5 mL), stirred at 0 °C for 1 hour and the solution was concentrated *in vacuo* at 0 °C. The residue obtained was dissolved in the minimal amount of MeOH/CH_2Cl_2 (1:1 *v/v*) and purified by column chromatography over silica gel ($CHCl_3$/MeOH/2.2 M NH_4OH 9:7:2). The combined fractions were partially concentrated *in vacuo* at 0 °C, then H_2O (30 mL) was added. Lyophilising this solution yielded (−)-**66** (4 mg, 36%, 84% D_6, 16% D_5) as a colourless, fluffy solid. The compound was stored at −80 °C as the ammonium salt: R_f 0.60 ($CHCl_3$/MeOH/2.2 M NH_4OH 9:7:2); $[\alpha]_D^{25}$ = −46.3 (*c* 0.025, MeOH/$CHCl_3$/H_2O 4:3:1); ^{1}H NMR (500 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_H 5.29–5.23 (1H, m, H-10), 4.43 (1H, dd, J_{XY} 12.3, 2.5, H-11), 4.20 (1H, dd, J_{XY} 12.0, 7.9, H-11'), 4.09–3.98 (2H, m, H-9), 2.37–2.27 (4H, m, H-13 and H-31), 1.66–1.54 (4H, m, H-14 and H-32), 1.38-1.22 (56H, m, H-15 to H-28 and H-33 to H-46), 0.88 (6H, t, *J* 6.9, H-29 and H-47); ^{13}C NMR (126 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_C 175.2, 174.9 (C-12, C-30), 71.4 (d_P, J_P 8.6, C-10), 64.5 (d_P, J_P 6.3, C-9), 63.8 (C-11), 35.0, 34.9 (C-13, C-31), 32.7 (C-27, C-44), 30.50, 30.45, 30.39, 30.35, 30.2, 30.13, 30.10, 29.96, 29.91 (C-15 to C-26 and C-33 to C-44), 25.8, 25.7 (C-14, C-32), 23.4 (C-29, C-46), 14.6 (C-29, C-47);[5] ^{31}P NMR (162 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_P 1.82 (P-7), −0.19 (P-8); ^{2}H NMR (92 MHz; CH_3OH/$CHCl_3$/H_2O 4:3:1; $CDCl_3$) δ_D 4.35 (br s, inositol ring), 4.13 (br s, inositol ring), 3.03 (br t, inositol ring); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3587 (O-H) (br), 3354 (O-H) (br), 3295 (O-H) (br), 3203 (O-H) (br), 2957 (w), 2917 (m), 2850 (m), 1740 (w), 1719 (w), 1663 (w), 1633 (w), 1464 (m), 1258

[4] Due to the instability of this compound in solution, only a minimal number of scans could be used for acquiring the ^{13}C NMR spectrum, this was not enough to observe the peaks corresponding to C-1, C-2, C-3, C-4, C-5 and C-6. Those can be inferred by comparison with the ^{13}C NMR spectrum of the equivalent non-deuterated compounds.

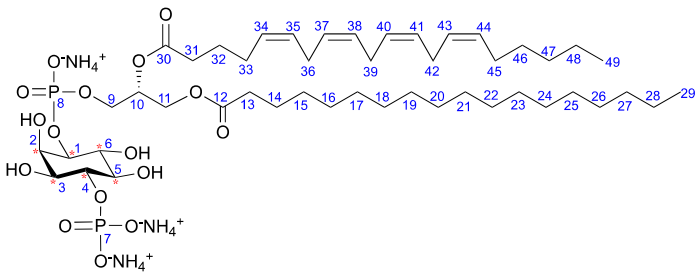
(m), 1210 (m), 1195 (m), 1171 (m), 1080 (s), 1062 (s), 1032 (s), 1015 (s), 997 (s), 895 (m), 872 (m), 802 (m), 720 (m), 676 (m); HRMS *m/z* (ESI$^+$) found 951.58298 [M−H]$^-$ ($C_{45}H_{81}D_6O_{16}P_2$ requires 951.58514 [M−H]$^-$).

D_{41}-(−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-67



To a solution of (−)-**62** (13 mg, 0.00990 mmol, 1.0 eq, 62% D_{41}, 29% D_{40}, 9% D_{39}) in toluene (0.30 mL) was added TMSBr (20 µL, 0.148 mmol, 15 eq). The solution was stirred at RT for 12 hours, heated to 70 °C for 45 minutes, then cooled to 0 °C and concentrated by vacuum transfer. The residue was dissolved in toluene (0.5 mL) and concentrated again by vacuum transfer. This was repeated three times. The residue was then dissolved in MeOH (0.4 mL), stirred at 0 °C for 1 hour and the solution was concentrated *in vacuo* at 0 °C. The residue obtained was dissolved in the minimal amount of MeOH/CH_2Cl_2 (1:1 *v/v*) and purified by column chromatography over silica gel ($CHCl_3$/MeOH/2.2 M NH_4OH 5:3.9:1.1). The combined fractions were partially concentrated *in vacuo* at 0 °C, then H_2O (30 mL) was added. Lyophilising this solution gave (−)-**67** (6 mg, 58%, 59% D_{41}, 31% D_{40}, 10% D_{39}) as a colourless, fluffy solid. The compound was stored at −80 °C as the ammonium salt: R_f 0.60 ($CHCl_3$/MeOH/2.2 M aqueous solution of NH_4OH 5:3.9:1.1); $[\alpha]_D^{25}$ = −26.1 (*c* 0.04, MeOH/$CHCl_3$/H_2O 4:3:1); ^{1}H NMR (500 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_H 5.30–5.22 (1H, m, H-10), 4.44 (1H, dd, J_{XY} 12.2, 2.5, H-11), 4.20 (1H, dd, J_{XY} 12.2, 7.8, H-11'), 4.09–3.98 (2H, m, H-9), 2.33–2.27 (2H, m, H-31), 1.63–1.55 (2H, m, H-32), 1.34–1.21 (28H, m, H-33 to H-46), 0.87 (3H, t, *J* 6.9, H-47); ^{13}C NMR (126 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_C 175.2, 175.1 (C-12, C-30), 71.4 (d_P, J_P 8.5, C-10), 64.5 (d_P, J_P 4.8, C-9), 63.8 (C-11), 34.9 (C-31), 32.7 (C-45), 30.43, 30.38, 30.3, 30.12, 30.09, 30.0 (C-33 to C-44), 29.6–28.4 (m_D, C-15 to C-26), 25.7 (C-32), 23.4 (C-46), 14.6 (C-47);[6] ^{31}P NMR (162 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_P 1.98 (P-7), −0.15 (P-8); ^{2}H NMR (92 MHz; CH_3OH/$CHCl_3$/H_2O 4:3:1; $CDCl_3$) δ_H 4.35 (br s, inositol ring), 3.04 (br s, inositol ring), 2.14–1.76 (2D, m, D-13), 1.42–1.07 (2D, m, D-14), 1.08–0.64 (28D, m, D-15 to D-28), 0.50 (3D, br s, D-29); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3219 (O-H) (br), 2920 (m), 2851 (m), 2361 (m), 2341 (m), 2194 (w), 2162 (w), 2087 (w), 2035 (w), 1979 (w), 1774 (C=O) (w), 1737 (C=O) (m), 1468 (m), 1419 (m), 1262 (w), 1170 (m), 1067 (P-O) (s), 873 (w), 721 (m), 694 (m), 615 (m); HRMS *m/z* (ESI$^-$) found 984.79065 ([MD_{39}−H]$^-$, 13%), 985.79674 ([MD_{40}−H]$^-$, 45%), 986.80280 ([MD_{41}−H]$^-$, 100%) ($C_{45}H_{46}D_{41}O_{16}P_2$ requires 986.80373 [MD_{41}−H]$^-$).

D_6-(−)-1D-(1-*O*-Stearoyl-2-*O*-arachidonyl)-phosphatidylinositol-4-phosphate triammonium salt (−)-68

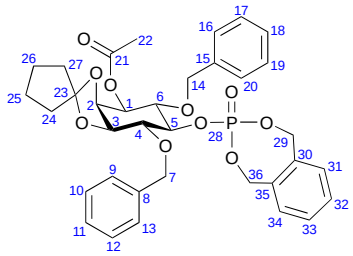


To a solution of (−)-**63** (12 mg, 0.00925 mmol, 1.0 eq, 82% D_6, 18% D_5) in toluene (0.50 mL) was added TMSBr (18 µL, 0.139 mmol, 15 eq). The solution was stirred at RT for 13 hours in the dark, then heated to 70 °C for 45 minutes, cooled to 0 °C, and concentrated by vacuum transfer. The residue was dissolved in toluene (0.6 mL) and concentrated again by vacuum transfer. This was repeated three times. The residue was then dissolved in MeOH (0.5 mL),

[6] Due to the instability of this compound in solution, only a minimal number of scans could be used for acquiring the ^{13}C NMR spectrum, this was not enough to observe the peaks corresponding to C-1, C-2, C-3, C-4, C-5 and C-6 as well as C-13, C-14, C-27, C-28 and C-29. These, however, can be inferred by comparison with the ^{13}C NMR of the equivalent non-deuterated compound.

stirred at 0 °C for 1 hour and the solution was concentrated *in vacuo* at 0 °C. The residue obtained was dissolved in the minimal amount of MeOH/CH_2Cl_2 (1:1 *v/v*) and purified by column chromatography over silica gel ($CHCl_3$/MeOH/2.2 M NH_4OH 9:7:2). The combined fractions were partially concentrated *in vacuo* at 0 °C, then H_2O (30 mL) was added. Lyophilising this solution yielded (−)-**68** (5 mg, 53%, 86% D_6, 14% D_5) as a colourless, fluffy solid. The compound was stored at −80 °C as the ammonium salt: R_f 0.63 ($CHCl_3$/MeOH/2.2 M NH_4OH 9:7:2); $[\alpha]_D^{25}$ = −55.9 (*c* 0.02, MeOH/$CHCl_3$/H_2O 4:3:1); ^{1}H NMR (500 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_H 5.46–5.31 (8H, m, H-34, H-35, H-37, H-38, H-40, H-41, H-43 and H-44), 5.31–5.24 (1H, m, H-10), 4.45 (1H, dd, J_{XY} 12.3, 2.5, H-11), 4.21 (1H, dd, J_{XY} 12.3, 7.6, H-11'), 4.10–3.99 (2H, m, H-9), 2.87–2.67 (6H, m, H-36, H-39 and H-42), 2.41–2.35 (2H, m, H-13), 2.31 (2H, dd, *J* 8.1, 6.9, H-31), 2.16–1.97 (4H, m, H-33 and H-45), 1.76–1.54 (4H, m, H-14 and H-32), 1.41–1.20 (34H, m, H-15 to H-28 and H-46 to H-48), 0.92–0.86 (6H, m, H-29 and H-49); ^{13}C NMR (126 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_C 175.3 (C-12), 174.8 (C-30), 131.2 (C-44), 129.72, 129.69, 129.4, 129.1. 129.0, 128.7, 128.4 (C-34, C-35, C-37, C-38, C-40, C-41, C-43), 71.6 (d_P, J_P 8.8, C-10), 64.5 (d_P, J_P 4.8, C-9), 63.9 (C-11), 35.0, 34.5 (C-13, C-31), 32.7, 32.3 (C-27, C-47), 30.5, 30.45, 30.39, 30.2, 30.0 (C-15 to C-26 and C-46), 28.0 (C-45), 27.3 (C-33), 26.47, 26.44, 26.43 (C-36, C-39, C-42), 25.7, 25.6 (C-14, C-32), 23.5, 23.4 (C-28, C-48), 14.70, 14.69 (C-29, C-49); ^{31}P NMR (126 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_P 2.25 (P-7), −0.19 (P-8); ^{2}H NMR (92 MHz; CD_3OD/$CDCl_3$/D_2O 4:3:1) δ_P 4.42 (br s), 4.20 (br s); ν_{max}(thin film)/cm^{-1} 3224 (O-H) (br), 3012 (m), 2957 (m), 2922 (s), 2852 (m), 2361 (w), 2341 (w), 1736 (m), 1655 (w), 1455 (m), 1438 (m), 1379 (m), 1315 (m), 1171 (s), 1146 (s), 1064 (s), 1029 (s), 1006 (s), 983 (s), 857 (m), 805 (m), 720 (m), 683 (m), 638 (m), 615 (m); HRMS *m/z* (ESI$^+$) found 971.55350 $[M-H]^-$ ($C_{47}H_{77}D_6O_{16}P_2$ requires 971.55275 $[M-H]^-$).

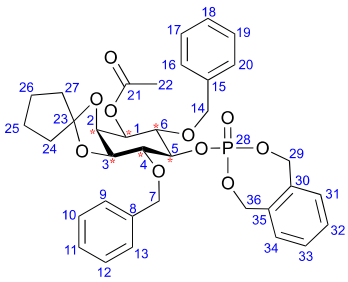
(−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-69



To a solution of (−)-**19** (400 mg, 0.854 mmol, 1.0 eq) and phosphoramidite **54** (613 mg, 2.56 mmol, 3.0 eq) in CH_2Cl_2 (15 mL) was added 1*H*-tetrazole (5.70 mL, 2.56 mmol, 3.0 eq, 0.45 M in MeCN). After stirring at RT for 1 hour, the cloudy reaction mixture was cooled to −78 °C and *m*CPBA (574 mg, 2.56 mmol, 3.0 eq, 77%) was added in a single portion. The reaction mixture was gradually warmed to RT over 20 minutes, then stirred for 1 hour and finally quenched with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 10 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 3 × 10 mL), brine (3 × 10 mL), and a saturated aqueous solution of $NaHCO_3$ (10 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) afforded (−)-**69** (509 mg, 92%) as an amorphous, colourless foam: R_f 0.66 (Petroleum ether/Et_2O 4:6); $[\alpha]_D^{25}$ = −8.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.44–7.39 (2H, m, H-9 and H-13), 7.37–7.24 (10H, m, H-10 to H-12, H-16 to H-20, H-32 and H-33), 7.20–7.14 (2H, m, H-31 and H-34), 5.25 (1H, dd, *J* 8.6, 3.7, H-1), 5.22–5.07 (2H, m, H-29 and H-36), 5.06–4.93 (2H, m, H-29' and H-36'), 4.86 (1H, d J_{AB} 11.3, H-14), 4.85 (1H, d J_{AB} 11.6, H-7), 4.76 (1H, dd J_{AB} 11.6, H-7'), 4.69 (1H, dd, J_{AB} 11.3, H-14'), 4.68–4.61 (1H, m, H-5), 4.39 (1H, dd, *J* 6.2, 3.7, H-2), 4.23 (1H, dd, *J* 6.2, 6.1, H-3), 4.04 (1H, dd, *J* 8.6, 7.0, H-6), 3.90 (1H, dd, *J* 7.8, 6.1, H-4), 2.05 (3H, s, H-22), 1.98–1.84 (2H, m, H-24 or H-27), 1.75–1.61 (6H, m, H-25, H-26 and H-24 or H-27); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.2 (C-21), 138.2, 138.1 (C-8, C-15), 135.42, 135.39 (C-30, C-35), 129.1, 129.0, 128.43, 128.35, 128.1, 127.9, 127.7 (C-32, C-33, C-9 to C-13 and C-16 to C-20), 128.8 (C-31, C-34), 120.2 (C-23), 80.7 (d_P, J_P 6.7, C-5), 79.3 (d_P, J_P 2.9, C-4), 78.0 (d_P, J_P 3.8, C-6), 77.6 (C-3), 74.4 (C-14), 73.8 (C-2), 73.3 (C-7), 70.5 (C-1), 68.4 (d_P, J_P 5.7, C-29, C-36), 36.9, 36.7 (C-24, C-27), 24.1, 23.5 (C-25, C-26), 21.2 (C-22); ^{31}P NMR (162 MHz; $CDCl_3$) δ_P −0.27 (P-28); $\bar{\nu}_{max}$(thin

film)/cm^{-1} 2981 (s), 2888 (m), 2363 (w), 2337 (w), 1745 (C=O) (m), 1497 (w), 1374 (m), 1290 (m), 1237 (m), 1152 (m), 1108 (m), 1073 (m), 1015 (P-O) (s), 977 (m), 860 (w), 735 (m), 699 (m); LRMS *m/z* (ESI$^+$) 673.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 673.21543 [M+Na]$^+$ ($C_{35}H_{39}O_{10}NaP$ requires 673.21730 [M+Na]$^+$); RP-HPLC (Method 2) t_R = 14.73 min, 96.87%.

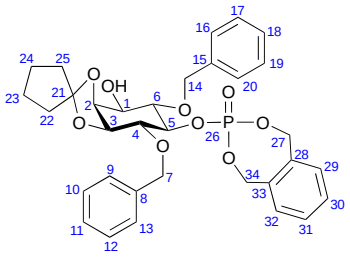
D_6-(−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-70



To a solution of (−)-**20** (100 mg, 0.211 mmol, 1.0 eq, 91% D_6, 9% D_5) and phosphoramidite 303 (151 mg, 0.632 mmol, 3.0 eq) in CH_2Cl_2 (3.7 mL) was added 1*H*-tetrazole (1.40 mL, 0.632 mmol, 3.0 eq, 0.45 M in MeCN). After stirring at RT for 1 hour, the cloudy reaction mixture was cooled to −78 °C and *m*CPBA (142 mg, 0.632 mmol, 3.0 eq, 77%) was added in a single portion. The reaction mixture was gradually warmed to RT over 20 minutes, stirred for 1 hour and quenched with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 10 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 2 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 3 × 2 mL), brine (3 × 2 mL), and a saturated aqueous solution of $NaHCO_3$ (2 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) afforded (−)-**70** (85 mg, 61%, 88% D_6, 12% D_5) as an amorphous, colourless foam: R_f 0.66 (Petroleum ether/Et_2O 4:6); $[\alpha]_D^{25}$ = −6.6 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz; $CDCl_3$) δ_H 7.44–7.38 (2H, m, H-9 and H-13), 7.38–7.24 (10H, m, H-10 to H-12, H-16 to H-10, H-32 and H-33), 7.21–7.14 (2H, m, H-31 and H-34), 5.22–5.07 (2H, m, H-29 or H-36), 5.06–4.94 (2H, m, H-29 or H-36), 4.85 (1H, d, J_{AB} 11.2, H-14), 4.84 (1H, d, J_{AB} 11.6, H-7), 4.76 (1H, d, J_{AB} 11.6, H-7'), 4.69 (1H, d, J_{AB} 11.2, H-14'), 2.05 (3H, s, H-22), 1.98–1.84 (2H, m, H-24 and H-27), 1.74–1.62 (6H, m, H-25, H-26, H-24' and H-27'); ^{13}C NMR (126 MHz; $CDCl_3$) δ_C 170.2 (C-21), 138.2, 138.1 (C-8, C-15), 135.43, 135.39 (C-30, C-35), 128.8 (C-31, C-34), 129.1, 129.0, 128.43, 128.36, 128.1, 127.9, 127.74, 127.73 (C-32, C-33, C-9 to C-13 and C-16 to C-20), 120.1 (C-23), 80.6–79.9 ($m_{D,P}$, C-5), 79.0–78.4 ($m_{D,P}$, C-4), 78.1–76.8 ($m_{D,P}$, C-6, C-3), 74.3 (C-14), 73.5–72.9 (m_D, C-2), 73.2 (C-7), 70.3–69.7 (m_D, C-1), 68.4 (d_P, J_P 5.6, C-29, C-36), 36.9, 36.7 (C-24, C-27), 24.1, 23.5 (C-25, C-26), 21.2 (C-22); ^{13}C NMR (126 MHz; CD_2Cl_2)[7] δ_C 170.2 (C-21), 138.58, 138.55 (C-8, C-15), 135.83, 135.79 (C-30, C-35), 129.1 (C-31, C-34), 129.34, 129.31, 128.7, 128.6, 128.34, 128.27, 128.05, 127.99 (C-32, C-33, C-9 to C-13 and C-16 to C-20), 120.4 (C-23), 80.5–79.9 ($m_{D,P}$, C-5), 79.6–79.0 ($m_{D,P}$, C-4), 77.9–77.1 ($m_{D,P}$, C-6, C-3), 74.6 (C-14), 73.9–73.4 (m_D, C-2), 73.5 (C-7), 70.4–69.8 (m_D, C-1), 68.7 (d_P, J_P 7.7, C-29, C-36), 37.2, 37.0 (C-24, C-27), 24.2, 23.7 (C-25, C-26), 21.2 (C-22); ^{31}P NMR (162 MHz; $CDCl_3$) δ_P 0.25 (P-28); ^{2}H NMR (92 MHz; $CHCl_3$; $CDCl_3$) δ_D 5.18 (1D, br s, D-1), 4.53 (1D, br s, D-5), 4.30 (1D, br s, D-2), 4.20 (1D, br s, D-3), 3.96 (1D, br s, D-6), 3.83 (1D, br s, D-4); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2981 (s), 2972 (s), 2888 (m), 1742 (C=O) (w), 1473 (w), 1461 (s), 1382 (m), 1339 (w), 1252 (m), 1153 (m), 1074 (m), 1015 (P-O) (m), 967 (m), 955 (m), 850 (w), 777 (w), 735 (w), 699 (w); LRMS *m/z* (ESI$^+$) 678.2 ([MD_5+Na]$^+$, 13%), 679.2 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 678.24795 [MD_5+Na]$^+$, 679.25368 [MD_6+Na]$^+$ ($C_{35}H_{33}D_6O_{10}NaP$ requires 679.25497 [MD_6+Na]$^+$); RP-HPLC (Method 2) t_R = 14.20 min, 100%.

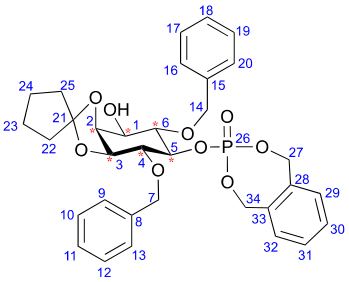
[7] ^{13}C NMR data was run in both $CDCl_3$ and CD_2Cl_2 as some of the peaks were obscured under the solvent peak in $CDCl_3$

(+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (+)-71



To a solution of (−)-**69** (200 mg, 0.307 mmol, 1.0 eq) in MeOH (28 mL) was added ground K_2CO_3 (85 mg, 0.615 mmol, 2.0 eq). The reaction mixture was stirred at RT for 1 hour. The solvent was then partially removed *in vacuo* at RT and H_2O (10 mL) was added to the resulting residue. The aqueous layer was extracted with EtOAc (4 × 10 mL) and the combined organic layers were washed successively with H_2O (10 mL) and brine (2 × 10 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) afforded (+)-**71** (139 mg, 74%) as a colourless oil: R_f 0.59 (Petroleum ether/EtOAc 2:8); $[\alpha]_D^{25}$ = +3.1 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz; CD_2Cl_2)[8] δ_H 7.45–7.38 (4H, m, H-9, H-13, H-16 and H-20), 7.38–7.25 (8H, m, H-10 to H-12, H-17 to H-19, H-30 and H-31), 7.25–7.18 (2H, m, H-29 and H-32), 5.16–5.06 (3H, m, H-27 or H-34, H-27' and H-34'), 5.00 (1H, dd, J_{ABX} 17.8, 13.8, H-27 or H-34), 4.88 (1H, d, J_{AB} 11.1, H-7 or H-14), 4.87 (1H, d, J_{AB} 11.6, H-7 or H-14), 4.723 (1H, d, J_{AB} 11.6, H-7' or H-14'), 4.719 (1H, d, J_{AB} 11.1, H-7' or H-14'), 4.55 (1H, ddd, *J* 8.4, 8.4, 6.5, H-5), 4.33 (1H, dd, *J* 6.5, 3.7, H-2), 4.23 (1H, dd, *J* 6.5, 6.5, H-3), 4.00 (1H, ddd, *J* 7.7, 4.1, 3.7, H-1), 3.98–3.90 (2H, m, H-4 and H-6), 2.50 (1H, d, *J* 4.1, C(1)O*H*), 2.00–1.91 (2H, m, H-22 or H-25), 1.81–1.62 (6H, m, H-23, H-24 and H-22 or H-25); ^{13}C NMR (101 MHz; CD_2Cl_2) δ_C 138.8, 138.6 (C-8, C-15), 135.9, 135.8 (C-28, C-33), 129.35, 129.32, 129.12, 129.11 (C-29 to C-32), 128.7, 128.6, 128.5, 128.3, 128.1, 127.9 (C-9 to C-13, C-16 to C-20), 120.1 (C-21), 81.0 (d_P, J_P 6.9, C-5), 80.5 (d_P, J_P 3.7, C-4 or C-6), 80.4 (d_P, J_P 3.7, C-4 or C-6), 78.0 (C-3), 75.6 (C-2), 74.3 (C-7 or C-14), 73.6 (C-7 or C-14), 69.4 (C-1), 68.74 (d_P, J_P 6.1, C-27 or C-34), 68.68 (d_P, J_P 6.1, C-27 or C-34), 36.88, 36.87 (C-22, C-25), 24.2, 23.6 (C-23, C-24); ^{31}P NMR (162 MHz; CD_2Cl_2) δ_P −0.31 (P-26); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3398 (O-H) (br), 2981 (m), 2972 (m), 2889 (m), 2361 (w), 2341 (w), 1497 (w), 1454 (w), 1380 (w), 1335 (w), 1278 (m), 1265 (m), 1150 (m), 1103 (m), 1089 (m), 1014 (s), 1001 (P-O) (s), 980 (m), 868 (m), 734 (m), 698 (m), 677 (m), 624 (m); LRMS *m/z* (ESI$^+$) 631.2 ([M+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 631.20654 [M+Na]$^+$ ($C_{33}H_{37}O_9NaP$ requires 631.20674 [M+Na]$^+$); RP-HPLC (Method 2) t_R = 13.95 min, 100%.

D_6-(+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep -2-yl)-*myo*-inositol (+)-72

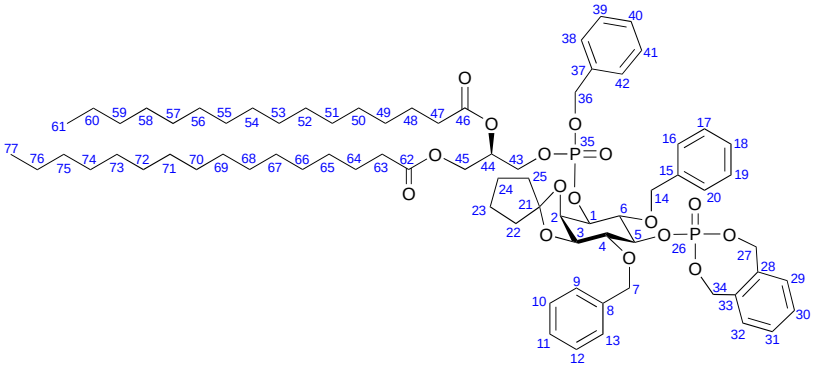


To a solution of (−)-**70** (80 mg, 0.122 mmol, 1.0 eq, 88% D_6, 12% D_5) in MeOH (11 mL) was added ground K_2CO_3 (34 mg, 0.244 mmol, 2.0 eq). The reaction mixture was stirred at RT for 1 hour. The solvent was then partially removed *in vacuo* at RT and H_2O (5 mL) was added to the resulting residue. The aqueous layer was extracted with EtOAc (4 × 10 mL) and the combined organic layers were then washed with H_2O (5 mL) and brine (2 × 5 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 9:1, 8:2, 7:3, 6:4, 5:5) afforded (+)-**72** (66 mg, 89%, 89% D_6, 11% D_5) as a colourless oil: R_f 0.28 (Petroleum ether/EtOAc 4:6); $[\alpha]_D^{25}$ = +2.8 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz; CD_2Cl_2) δ_H 7.44–7.38 (4H, m, H-9, H-13, H-16 and H-20), 7.38–7.25 (8H, m, H-10 to H-12, H-17 to H-19, H-30 and H-31), 7.25–7.19 (2H, m, H-29 and H-32), 5.16–5.07 (3H, m, H-27 or H-34, H-27' and H-34'), 5.00 (1H, dd, J_{ABX} 17.9, 13.8, H-27 or H-34), 4.88 (1H, d, J_{AB} 11.3, H-7 or H-14), 4.87 (1H, d, J_{AB} 11.3, H-7 or H-14), 4.73 (2H, d, J_{AB} 11.3, H-7' and H-14'), 2.56 (1H, br s, C(1)O*H*), 2.00–1.91 (2H, m, H-22 or H-25), 1.81–1.62 (6H, m, H-23, H-24 and H-22 or H-25); ^{13}C NMR (126 MHz; CD_2Cl_2) δ_C 138.7, 138.6 (C-8,

[8] This compound was found to be unstable in $CDCl_3$. When left in solution for more than 30 minutes, deprotection of the cyclopentylidene protecting group was observed. Characterisation was therefore carried out in CD_2Cl_2 as well as is $CDCl_3$. This is true for any sterically congested, cyclopentylidene containing compounds in this series.

C-15), 135.9, 135.8 (C-28, C-33), 129.34, 129.31, 129.12, 129.11, 128.7, 128.6, 128.5, 128.3, 128.1, 127.9 (C-9 to C-13, C-16 to C-20, C-29 to C-32), 120.1 (C-21), 81.0–80.2 ($m_{P,D}$, C-5), 80.2-79.5 ($m_{P,D}$, C-4, C-6), 77.4 (t_D, J_D 22.8, C-3), 75.1 (t_D, J_D 22.9, C-2), 74.2, 73.5 (C-7, C-14), 68.9 (t_D, J_D 28.4, C-1), 68.72 (d_P, J_P 7.8, C-27 or C-34), 68.67 (d_P, J_P 6.6, C-27 or C-34), 24.2 (C-22, C-25), 23.6 (C-23, C-24), 2.00–1.91 (2H, m, H-22 or H-25), 1.81–1.62 (6H, m, H-23, H-24 and H-22 or H-25); ^{31}P NMR (162 MHz; CD_2Cl_2) δ_C −1.02 (P-26); ^{2}H NMR (77 MHz; CH_2Cl_2; CD_2Cl_2) δ_D 4.53 (1D, br s, D-5), 4.32 (1D, br s, D-2), 4.23 (1D, br s, D-3), 3.96 (3D, br s, D-1, D-4 and D-6); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3398 (O-H) (br), 3063 (w), 3030 (w), 2959 (w), 2873 (w), 1497 (w), 1454 (w), 1433 (w), 1385 (w), 1337 (w), 1284 (m), 1208 (m), 1155 (m), 1097 (m), 1073 (m), 1050 (m), 1016 (P-O) (s), 860 (m), 777 (m), 735 (m), 699 (m); LRMS *m/z* (ESI$^+$) 636.2 ([MD_5+Na]$^+$, 12%), 637.2 ([MD_6+Na]$^+$, 100%); HRMS *m/z* (ESI$^+$) found 614.25673 [MD_5+H]$^+$, 615.26287 [MD_6+H]$^+$ ($C_{33}H_{32}D_6O_9P$ requires 615.26246 [MD_6+H]$^+$); RP-HPLC (Method 2) t_R = 13.34 min, 96.87%.

(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-73

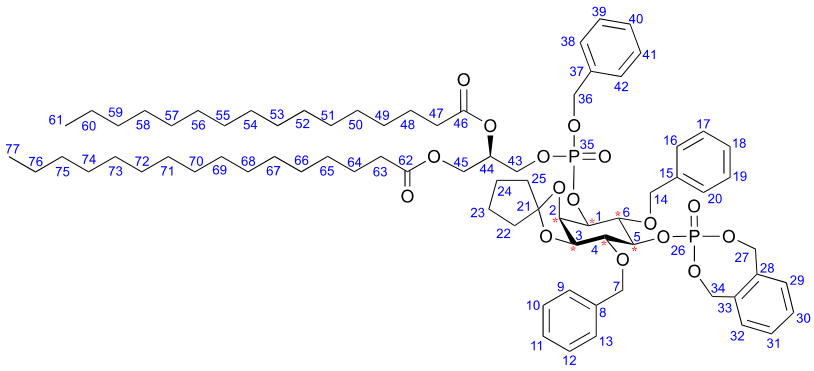


Method 1 – To a solution of (+)-**71** (64 mg, 0.104 mmol, 1.0 eq) and phosphoramidite (+)-**34** (423 mg, 0.522 mmol, 5.0 eq) in anhydrous CH_2Cl_2 (5.4 mL) was added 1*H*-tetrazole (470 µL, 0.522 mmol, 5.0 eq, 0.45 M in MeCN) dropwise. The cloudy reaction mixture was stirred at RT for 4 hours, then cooled to −78 °C and *m*CPBA (117 mg, 0.522 mmol, 5.0 eq, 77%) was added in one portion. The reaction mixture was stirred for 1 hour, warmed to RT, and stirred for a further 20.5 hours. The reaction was quenched by addition of an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 5 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 5 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 2 × 3 mL), brine (2 × 3 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Three consecutive purifications by column chromatography over silica gel were then carried out (Purification 1 - Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4, 5:5; Purification 2 - CH_2Cl_2/MeOH 10:0, 9.5:0.5; Purification 3 - Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4) to give (−)-**73** (58 mg, 42%) as a colourless, gummy solid, and containing a mixture of two diastereoisomers: R_f 0.34 (Petroleum ether/EtOAc 5:5); $[\alpha]_D^{25}$ = −1.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz; CD_2Cl_2) δ_H 7.43–7.24 (34H, m, H-9 to H-13, H-16 to H-20, H-38 to H-42, H-30 and H-31 Diast. A and B), 7.24–7.19 (4H, m, H-29 and H-32 Diast. A and B), 5.20–5.15 (1H, m, H-44 Diast. A), 5.15–4.92 (13H, m, H-44 Diast. B, H-27, H-34 and H-36 Diast. A and B), 4.87–4.79 (4H, m, H-7 and H-14 Diast. A and B), 4.76–4.70 (4H, m, H-7' and H-14' Diast. A and B), 4.69 (1H, ddd, *J* 9.7, 8.4, 2.0, H-1 Diast. A), 4.68 (1H, ddd, *J* 9.7, 8.5, 1.9, H-1 Diast. B), 4.63–4.56 (2H, m, H-5 Diast. A and B), 4.48 (2H, ddd, *J* 9.7, 6.3, 3.8, H-2 Diast. A and B), 4.27–4.21 (3H, m, H-3 Diast. A and B, H-45 Diast. A), 4.19–4.04 (7H, m, H-45' Diast. A, H-45 Diast. B, H-43 Diast. A and B, H-43' Diast. A, H-6 Diast. A and B), 4.04–3.98 (1H, m, H-43' Diast. B), 3.94 (1H, dd, J_{XY} 12.0, 6.1, H-45' Diast. B), 3.89 (2H, ddd, *J* 7.8, 5.8, 2.1, H-4 Diast. A and B), 2.30–2.19 (8H, m, H-47 and H-63 Diast. A and B), 2.00–1.88 (4H, m, H-22 and H-25 Diast. A and B), 1.76–1.63 (12H, m, H-22', H-25', H-23 and H-24 Diast. A and B), 1.63–1.48 (8H, m, H-48 and H-64 Diast. A and B), 1.35–1.19 (96H, m, H-49 to H-60 and H-65 to H-76 Diast. A and B), 0.88 (12H, t, *J* 6.9, H-61 and H-77 Diast. A and B); ^{13}C NMR (126 MHz; CD_2Cl_2) δ_C 173.41, 173.36 (C-62 Diast. A and B), 173.1, 173.0 (C-46 Diast. A and B), 138.45, 138.37, 138.32 (C-8, C-15 Diast. A and B), 136.24 (d_P, J_P 7.8, C-37 Diast. A), 136.17 (d_P, J_P 7.9, C-37 Diast. B), 135.81, 135.76 (C-28, C-33 Diast. A and B), 129.36, 129.34, 129.11, 128.97, 128.95,

128.92, 128.85, 128.7, 128.6, 128.4, 128.33, 128.29, 128.25, 128.11, 128.06, 128.04 (C-9 to C-13, C-16 to C-20, C-29 to C-32, C-38 to C-42 Diast. A and B), 120.4 (C-21 Diast. A and B), 80.4 (d_P, J_P 6.1, C-5 Diast A and B), 79.5 (d_P, J_P 2.8, C-4 Diast A and B), 78.7–78.4 (m_P, C-6 Diast. A and B), 77.6 (C-3 Diast. A and B), 75.63 (d_P, J_P 4.8, C-1 Diast. A), 75.59 (d_P, J_P 4.6, C-1 Diast. B), 74.6 (C-2, C-7 Diast. A and B), 73.5 (C-14 Diast. A and B), 69.9 (d_P, J_P 2.6, C-36 Diast. A), 69.8 (d_P, J_P 2.3, C-36 Diast. B), 69.7 (d_P, J_P 4.8, C-44 Diast. A), 69.6 (d_P, J_P 5.6, C-44 Diast. B), 68.7 (d_P, J_P 7.0, C-27 and C-34 Diast. A and B), 66.0 (d_P, J_P 5.2, C-43 Diast. A), 65.9 (d_P, J_P 4.9, C-43 Diast. B), 62.0 (C-45 Diast. A), 61.9 (C-45 Diast. B), 36.9, 36.78, 36.76 (C-22, C-25 Diast. A and B), 34.5, 34.4, 34.33, 34.30 (C-47, C-63 Diast. A and B), 32.3 (C-59, C-75 Diast. A and B), 30.12, 30.07, 29.9, 29.8, 29.7, 29.52, 29.49, 29.48 (C-49 to C-58 and C-65 to C-74 Diast. A and B), 25.23, 25.20 (C-48, C-64 Diast. A and B), 24.23, 24.20, 23.6 (C-23, C-24 Diast. A and B), 23.1 (C-60, C-76 Diast. A and B), 14.3 (C-61, C-77 Diast. A and B); ^{31}P NMR (162 MHz; CD_2Cl_2) δ_P −0.90 (P-26), −1.80 (P-35 Diast. A), −1.94 (P-35 Diast. B); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2924 (s), 2853 (m), 1743 (C=O) (m), 1456 (w), 1285 (m), 1266 (m), 1173 (m), 1156 (m), 1112 (m), 1073 (m), 1012 (P-O) (s), 866 (w), 735 (m), 697 (m); LRMS *m/z* (ESI$^+$) 1351.5 ([M+Na]$^+$, 9%); HRMS *m/z* (ESI$^+$) found 1351.70985 [M+Na]$^+$ ($C_{75}H_{110}O_{16}NaP_2$ requires 1351.71613 [M+Na]$^+$); NP-HPLC (Method 7) t_R = 4.07 min, 48.36% Diast. A, t_R = 4.42 min, 49.32% Diast. B.

Method 2 – To a solution of (+)-**71** (30 mg, 0.0493 mmol, 1.0 eq) and phosphoramidite (+)-**34** (423 mg, 0.148 mmol, 3.0 eq) in anhydrous CH_2Cl_2 (4.0 mL) was added 1*H*-tetrazole (329 µL, 0.148 mmol, 3.0 eq, 0.45 M in MeCN) dropwise. The cloudy reaction mixture was stirred at RT for 22 hours, then cooled to −78 °C and *m*CPBA (33 mg, 0.148 mmol, 3.0 eq, 77%) was added in one portion. The reaction mixture was stirred for 1 hour, warmed to RT, stirred for a further 3 hours, then quenched by addition of an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 5 mL). After stirring for 15 minutes, the aqueous phase was extracted with CH_2Cl_2 (4 × 5 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 2 × 3 mL), and brine (2 × 3 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4, 5:5) yielded (−)-**73** (54 mg, 82%) as a colourless, gummy solid, and containing a mixture of two diastereoisomers. Spectral data are identical to those reported above.

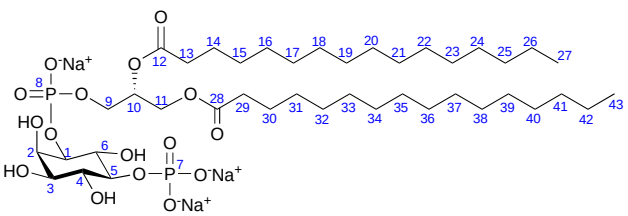
D_6-(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-74



To a solution of (+)-**72** (49 mg, 0.0797 mmol, 1.0 eq, 89% D_6, 11% D_5) and phosphoramidite (+)-**34** (193 mg, 0.239 mmol, 3.0 eq) in anhydrous CH_2Cl_2 (4.1 mL) was added 1*H*-tetrazole (531 µL, 0.239 mmol, 3.0 eq, 0.45 M in MeCN) dropwise. The cloudy reaction mixture was stirred at RT for 20 hours, then cooled to −78 °C and *m*CPBA (54 mg, 0.239 mmol, 3.0 eq, 77%) was added in one portion. The reaction mixture was stirred for 1 hour, warmed to RT, and stirred for a further 2 hours. The reaction was quenched by addition of an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 5 mL), then stirred for 15 minutes. The aqueous phase was extracted with CH_2Cl_2 (4 × 5 mL) and the combined organic layers were washed with an aqueous solution of $Na_2S_2O_3$ (10% *w/v*, 2 × 3 mL), and brine (2 × 3 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by column chromatography over silica gel (Petroleum ether/EtOAc 10:0, 9:1, 8:2, 7:3, 6:4,

5:5) yielded (−)-**74** (50 mg, 46%, 88% D_6, 12% D_5) as a colourless, waxy solid: R_f 0.34 (Petroleum ether/EtOAc 5:5); $[\alpha]_D^{25}$ = −2.0 (*c* 0.83, $CHCl_3$); ^{1}H NMR (500 MHz; CD_2Cl_2) δ_H 7.43–7.24 (34H, m, H-9 to H-13, H-16 to H-20, H-38 to H-42, H-30 and H-31 Diast. A and B), 7.24–7.19 (4H, m, H-29 and H-32 Diast. A and B), 5.21–5.14 (1H, m, H-44 Diast. A), 5.13–4.93 (13H, m, H-44 Diast. B, H-27, H-34 and H-36 Diast. A and B), 4.86–4.79 (4H, m, H-7 and H-14 Diast. A and B), 4.77–4.70 (4H, m, H-7' and H-14' Diast. A and B), 4.26 (1H, dd, J_{ABX} 11.9, 4.0, H-45 Diast. A), 4.20–4.04 (5H, m, H-45' Diast. A, H-45 Diast. B, H-43 Diast. A and B, H-43' Diast. A), 4.04–3.99 (1H, m, H-43' Diast. B), 3.95 (1H, dd, J_{ABX} 11.9, 5.9, H-45' Diast. B), 2.32–2.19 (8H, m, H-47 and H-63 Diast. A and B), 2.01–1.89 (4H, m, H-22 and H-25 Diast. A and B), 1.76–1.63 (12H, m, H-22', H-25', H-23 and H-24 Diast. A and B), 1.62–1.49 (8H, m, H-48 and H-64 Diast. A and B), 1.35–1.18 (96H, m, H-49 to H-60 and H-65 to H-76 Diast. A and B), 0.89 (12H, t, *J* 6.9, H-61 and H-77 Diast. A and B); ^{13}C NMR (126 MHz; CD_2Cl_2) δ_C 173.41, 173.37 (C-62 Diast. A and B), 173.07, 173.05 (C-46 Diast. A and B), 138.5, 138.41, 138.36 (C-8, C-15 Diast. A and B), 136.3 (d_P, J_P 7.5, C-37 Diast. A), 136.2 (d_P, J_P 7.5, C-37 Diast. B), 135.85, 135.80 (C-28, C-33 Diast. A and B), 129.39, 129.36, 129.1, 128.99, 128.96, 128.94, 128.87, 128.7, 128.6, 128.38, 128.36, 128.33, 128.27, 128.13, 128.06, 128.04 (C-9 to C-13, C-16 to C-20, C-29 to C-32, C-38 to C-42 Diast. A and B), 120.4 (C-21 Diast. A and B), 80.3–79.7 ($m_{D,P}$, C-5 Diast. A and B), 79.3–78.7 ($m_{D,P}$, C-4 Diast A and B), 78.4–77.7 ($m_{D,P}$, C-6 Diast. A and B), 77.4–76.8 ($m_{D,P}$, C-3 Diast. A and B), 75.5–74.9 ($m_{D,P}$, C-1 Diast. A and B), 74.52, 74.51 (C-7 Diast. A and B), 74.3–73.8 ($m_{D,P}$, C-2 Diast. A and B), 73.4 (C-14 Diast. A and B), 69.90 (d_P, J_P 2.2, C-36 Diast. A), 69.86 (d_P, J_P 2.5, C-36 Diast. B), 69.71 (d_P, J_P 6.6, C-44 Diast. A), 69.67 (d_P, J_P 6.4, C-44 Diast. B), 68.7 (d_P, J_P 6.2, C-27 and C-34 Diast. A and B), 66.1 (d_P, J_P 5.0, C-43 Diast. A), 65.9 (d_P, J_P 5.3, C-43 Diast. B), 62.0 (C-45 Diast. A), 61.9 (C-45 Diast. B), 36.9, 36.75, 36.73 (C-22, C-25 Diast. A and B), 34.50, 34.45, 34.35, 34.33 (C-47, C-63 Diast. A and B), 32.4 (C-59, C-75 Diast. A and B), 30.13, 30.11, 30.09, 29.9, 29.8, 29.7, 29.55, 29.51 (C-49 to C-58 and C-65 to C-74 Diast. A and B), 25.27, 25.26, 25.22 (C-48, C-64 Diast. A and B), 24.3, 24.2, 23.6 (C-23, C-24 Diast. A and B), 23.1 (C-60, C-76 Diast. A and B), 14.3 (C-61, C-77 Diast. A and B); ^{31}P NMR (162 MHz; CD_2Cl_2) δ_P −0.93 (P-26), −1.78 (P-35 Diast. A), −1.92 (P-35 Diast. B); ^{2}H NMR (96 MHz; $CHCl_3$; $CDCl_3$) δ_D 4.63 (3D, br s, D-1, D-5 and D-2), 4.11 (3D, br s, D-3, D-6 and D-4); $\bar{\nu}_{max}$(thin film)/cm^{-1} 2918 (m), 2850 (m), 1739 (C=O) (m), 1467 (w), 1455 (w), 1417 (w), 1382 (w), 1338 (m), 1210 (m), 1170 (m), 1099 (m), 1072 (m), 1050 (m), 1015 (P-O) (s), 1000 (P-O) (s), 865 (m), 733 (m), 696 (m); LRMS *m/z* (ESI$^+$) 1357.6 ([MD_6+Na]$^+$, 0.7%); HRMS *m/z* (ESI$^+$) found 1356.74890 [MD_5+Na]$^+$, 1357.75281 [MD_6+Na]$^+$ ($C_{75}H_{104}D_6O_{16}NaP_2$ requires 1357.75379 [MD_6+Na]$^+$); NP-HPLC (Method 7) t_R = 3.92 min, 47.13% Diast. A, t_R = 4.27 min, 50.47% Diast. B.

(−)-1D-Dipalmitoyl-phosphatidylinositol 5-phosphate trisodium salt (−)-75

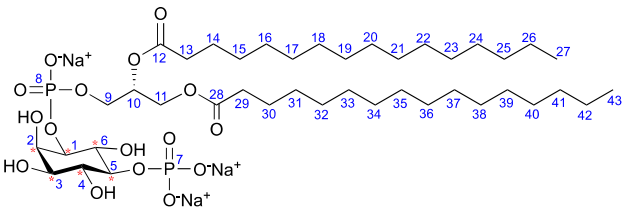


To a solution of (−)-**73** (34 mg, 0.0256 mmol, 1.0 eq) in a mixtue of ^{t}BuOH (1.36 mL) and H_2O (0.24 mL) was added palladium black (55 mg, 0.512 mmol, 20 eq) under $N_{2(g)}$. The flask was then purged with 3 balloons of $H_{2(g)}$, and stirred at RT under $H_{2(g)}$ for 17 hours. $NaHCO_3$ (6 mg, 0.0767 mmol, 3.0 eq) was then added in one portion and the reaction mixture was stirred for a further 4 hours under $H_{2(g)}$. The reaction mixture was filtered through a glass microfiber filter and washed with H_2O (4 × 20 mL). The combined aqueous filtrates were lyophilised to give (−)-**75** (23 mg, 94%) as a fluffy, colourless solid. The compound was stored at −80 °C as the sodium salt: $[\alpha]_D^{25}$ = −18.1 (*c* 0.076, MeOH/$CHCl_3$/H_2O 4:3:1)[9] [lit.[10] $[\alpha]_D^{28}$ = −4.7 (*c* 0.58, $CHCl_3$)]; ^{1}H NMR (500 MHz; CD_3OD/$CDCl_3$/ D_2O

[9] The optical rotation of this compound could not be obtained in $CHCl_3$ or H_2O due to solubility issues.

4:3:1)[10] δ_H 5.29–5.23 (1H, m, H-10), 4.42 (1H, dd, J_{XY} 12.2, 2.5, H-11), 4.20 (1H, dd, J_{XY} 12.2, 7.8, H-11'), 4.15 (1H, dd, *J* 2.9, 2.8, H-2), 4.08–3.98 (3H, m, H-9 and H-1), 3.85–3.71 (3H, m, H-6, H-5 and H-4), 3.52 (1H, dd, *J* 9.6, 2.9, H-3), 2.37–2.27 (4H, m, H-13 and H-29), 1.65–1.53 (4H, m, H-14 and H-30), 1.34–1.21 (48H, m, H-15 to H-26 and H-31 to H-42), 0.87 (6H, t, *J* 6.9, H-27 and H-43); ^{13}C NMR (126 MHz; $CD_3OD/CDCl_3/D_2O$ 4:3:1) δ_C 175.3, 175.0 (C-12, C-28), 78.5 (C-5), 77.0 (d_P, J_P 6.3, C-1), 73.0 (d_P, J_P 2.3, C-4), 72.2 (C-2), 72.1–71.9 (m_P, C-6), 71.9 (C-3), 71.4 (d_P, J_P 8.7, C-10), 64.4 (d_P, J_P 4.6, C-9), 63.8 (C-11), 35.0, 34.9 (C-13, C-29), 32.7 (C-25, C-41), 30.5, 30.43, 30.37, 30.3, 30.2, 30.11, 30.08, 29.94, 29.89 (C-15 to C-24, C-31 to C-40), 25.7, 25.6 (C-14, C-30), 23.4 (C-26, C-42), 14.6 (C-27, C-43); ^{31}P NMR (162 MHz; $CD_3OD/CDCl_3/D_2O$ 4:3:1) δ_P 5.39 (P-7), 0.08 (P-8); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3216 (O-H) (br), 2957 (m), 2917 (s), 2850 (s), 1737 (C=O) (m), 1631 (m), 1468 (m), 1379 (m), 1244 (m), 1199 (m), 1097 (P-O) (s), 1041 (P-O) (s), 971 (s), 865 (m), 821 (m), 721 (m); HRMS *m/z* (ESI$^-$) found 889.48524 $[M-H]^-$ ($C_{41}H_{79}O_{16}P_2$ requires 889.48488 $[M-H]^-$). These data are in good agreement with the literature values.[10,74,75]

D_6-(−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-76



To a solution of (−)-**74** (10 mg, 0.00749 mmol, 1.0 eq, 88% D_6, 12% D_5) in a mixture of ^{t}BuOH (400 µL) and H_2O (70 µL) was added palladium black (24 mg, 0.225 mmol, 30 eq) under $N_{2(g)}$. The flask was purged with 3 balloons of $H_{2(g)}$. After stirring at RT under $H_{2(g)}$ for 21 hours, $NaHCO_3$ (6 mg, 0.0767 mmol, 3.0 eq) was added in one portion and the reaction mixture was stirred for a further 2 minutes under $H_{2(g)}$. The reaction mixture was then filtered through a microfiber pad and washed with H_2O (2 × 5 mL). The combined aqueous filtrates were lyophilised to give (−)-**76** (6 mg, 86%, 90% D_6, 10% D_5) as a fluffy, colourless solid. The compound was stored at −80 °C as the sodium salt: R_f 0.60 ($CHCl_3$/MeOH/2.2 M NH_4OH 5:3.9:1.1); $[\alpha]_D^{25}$ = −16.2 (*c* 0.054, MeOH/$CHCl_3$/H_2O 4:3:1); ^{1}H NMR (500 MHz; $CD_3CD/CDCl_3/D_2O$ 4:3:1) δ_H 5.30–5.25 (1H, m, H-10), 4.43 (1H, dd, J_{XY} 12.2, 2.5, H-11), 4.21 (1H, dd, J_{XY} 12.2, 8.0, H-11'), 4.09–3.99 (2H, m, H-9), 2.38–2.28 (4H, m, H-13 and H-29), 1.65–1.53 (4H, m, H-14 and H-30), 1.34–1.21 (48H, m, H-15 to H-26 and H-31 to H-42), 0.87 (6H, t, *J* 6.9, H-27 and H-43); ^{13}C NMR (126 MHz; $CD_3CD/CDCl_3/D_2O$ 4:3:1) δ_C 175.4, 175.2 (C-12, C-28), 71.5 (d_P, J_P 8.8, C-10), 64.5 (d_P, J_P 4.7, C-9), 64.0 (C-11), 35.1, 35.0 (C-13, C-29), 32.7 (C-25, C-41), 30.55, 30.52, 30.50, 30.48, 30.45, 30.43, 30.39, 30.37, 30.3, 30.2, 30.1, 30.0, 29.7 (C-15 to C-24, C-31 to C-40), 25.8, 25.7 (C-14, C-30), 23.4 (C-26, C-42), 14.6 (C-27, C-43);[11] ^{31}P NMR (162 MHz; $CD_3CD/CDCl_3/D_2O$ 4:3:1) δ_P 5.37 (P-7), 0.005 (P-8); ^{2}H NMR (96 MHz; MeOH/$CHCl_3$/H_2O 4:3:1; $CDCl_3$) δ_D 4.33 (br s, inositol ring), 3.04 (br s, inositol ring), 3.01 (br s, inositol ring); $\bar{\nu}_{max}$(thin film)/cm^{-1} 3301 (O-H) (br), 2957 (w), 2917 (m), 2850 (m), 1735 (C=O) (m), 1627 (m), 1467 (m), 1380 (s), 1355 (s), 1244 (m), 1199 (m), 1101 (s), 1022 (P-O) (s), 970 (P-O) (s), 833 (s), 682 (s), 648 (s), 638 (s); HRMS *m/z* (ESI$^-$) found 894.51615 ($[MD_5-H]^-$, 11%), 895.52192 ($[MD_6-H]^-$, 100%) ($C_{41}H_{73}D_6O_{16}P_2$ requires 895.52254 $[MD_6-H]^-$).

5.4 Crystallography

Single crystal X-ray diffraction data were collected using a (Rigaku) Oxford Diffraciton Supernova A diffractomter (λ = 1.54184 Å) and reduced using CrysAlisPro. The structures were solved using SuperFlip[76] and refined using CRYSTALS[77,78,79]. Full re-

[10] The spectra were calibrated to CD_3OD

[11] Due to the instability of this compound in solution, only a minimal number of scans could be used for acquiring the ^{13}C NMR spectrum, this was not enough to observe the peaks corresponding to C-1, C-2, C-3, C-4, C-5 and C-6. Those can be inferred however by comparison with the ^{13}C NMR spectrum of the equivalent non-deuterated compounds.

finement details can be found in the CIF. Crystallographic data have also been deposited with the Cambridge Crystallographic Data Centre (CCDC 2049548 & 2049549) and copies of these data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

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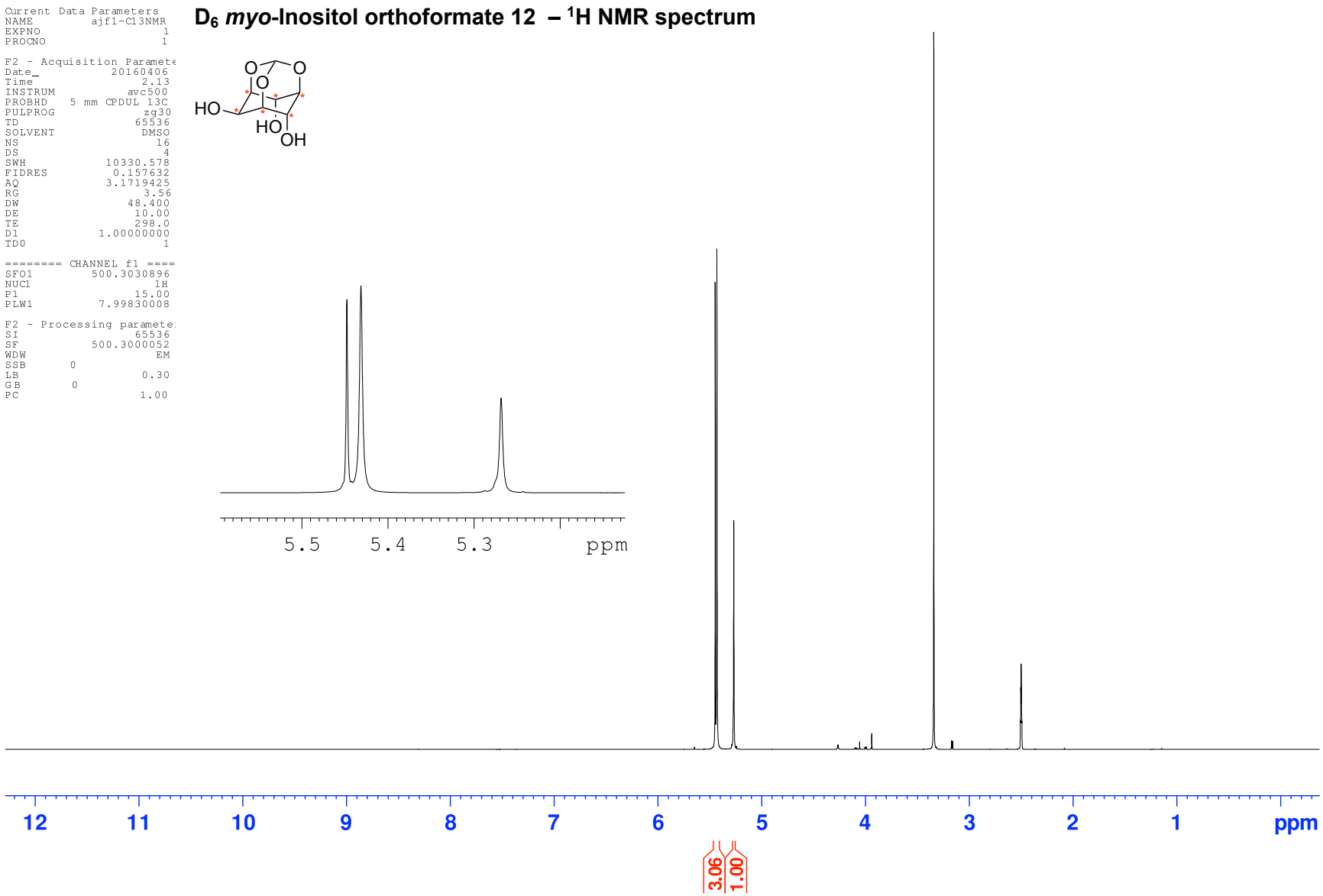
7. Author Contributions

The research programme was conceived by SJC. AMJ and SJC designed all of the experiments relating to the synthesis of PtdIns4*P* and PtdIns5*P* and analysed the data. AMJ performed all of the experiments relating to the synthesis of PtdIns4*P* and PtdIns5*P.* AMS and SJC designed all experiments relating to the synthesis of deuterated *myo*-inositol and analysed the data relating to these experiments. AMS performed all experiments relating to the synthesis of deuterated *myo*-inositol. SJC supervised the work and acquired the funding. AMJ and SJC wrote the manuscript. HJS and VF contributed to the supervision of the project. VF and DB designed and performed the cell studies. ALT obtained the X-ray crystal structures.

8 Nuclear Magnetic Resonance (NMR) and Mass Spectra



D_6 *myo*-Inositol orthoformate 12 – ^{13}C NMR spectrum

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TD0                   1

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P1               10.00 usec
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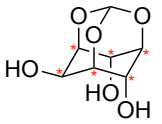
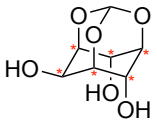


D_6 myo-Inositol orthoformate 12 – ^2H NMR spectrum

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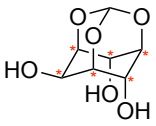

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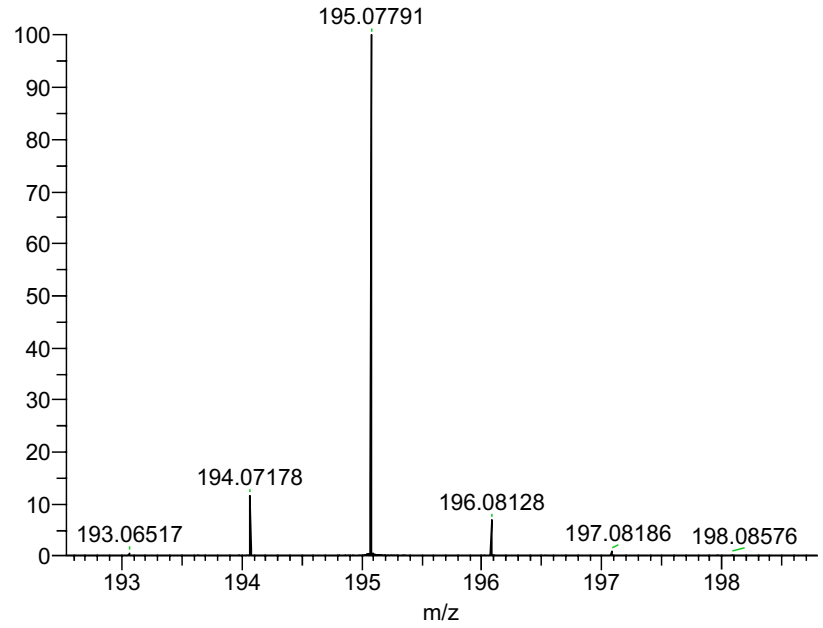

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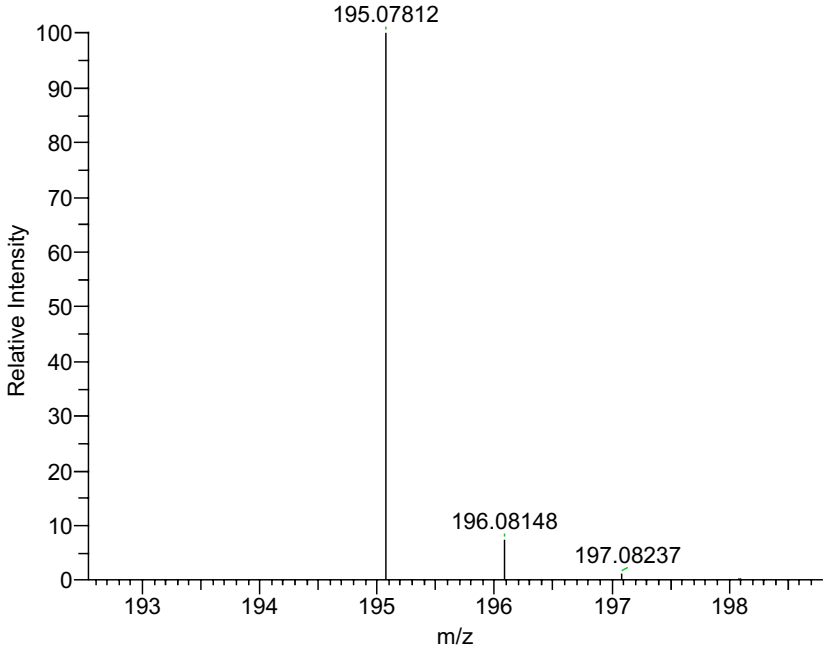

NL: 9.14E5
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Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
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D_6 4,6-Di-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate 14 – ^{1}H NMR spectrum

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PROCNO                 1

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PROBHD   5 mm CPDUL 13C
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                  3.56
DW                48.400 use
DE                10.00 use
TE                298.0 K   c
D1           1.00000000 sec c
TD0                   1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1               1H
P1                15.00 usec
PLW1           7.99830008 W

F2 - Processing parameters
SI                65536
SF           500.3000267 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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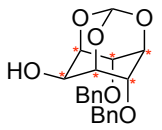
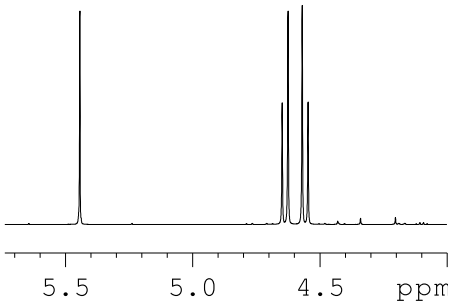
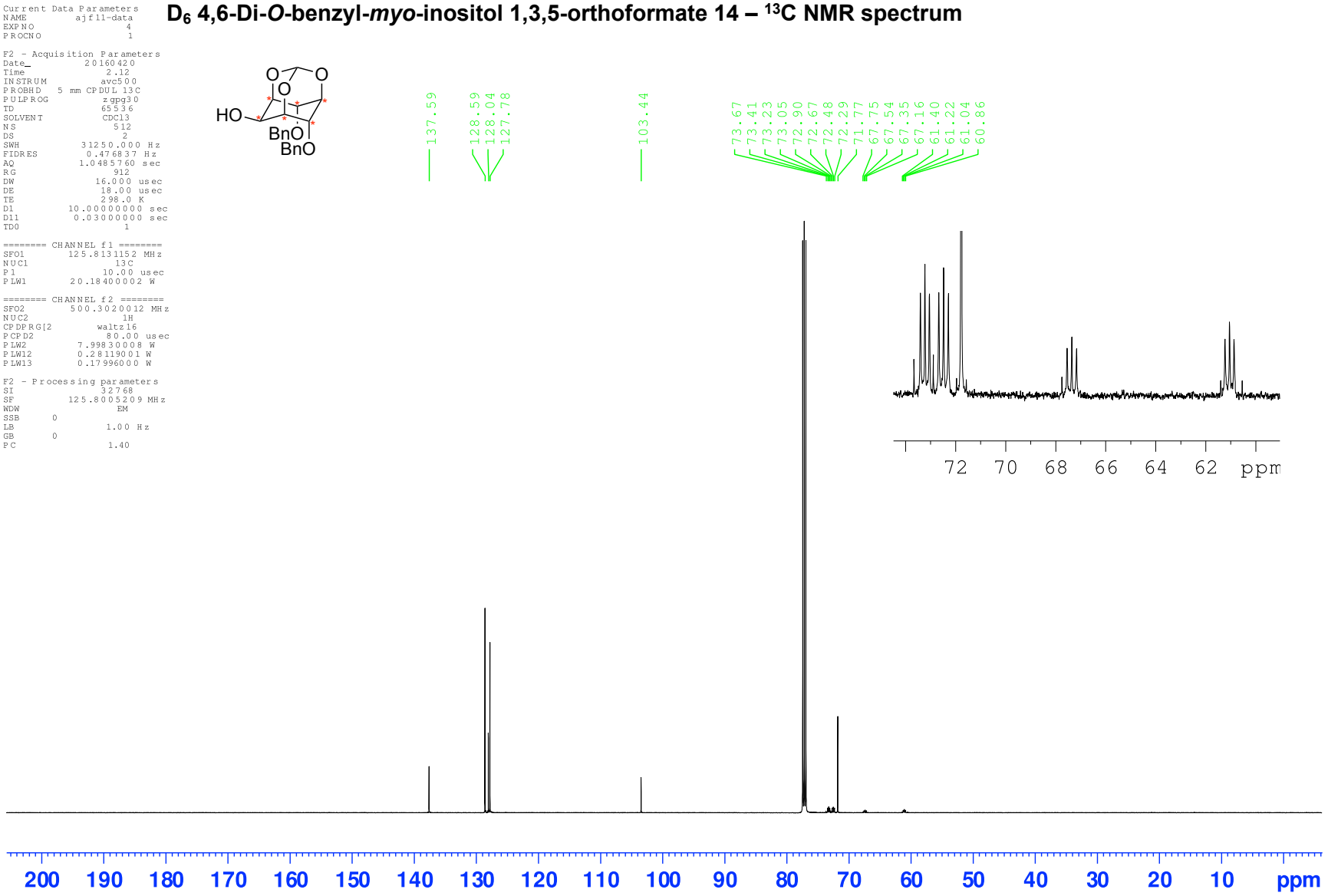
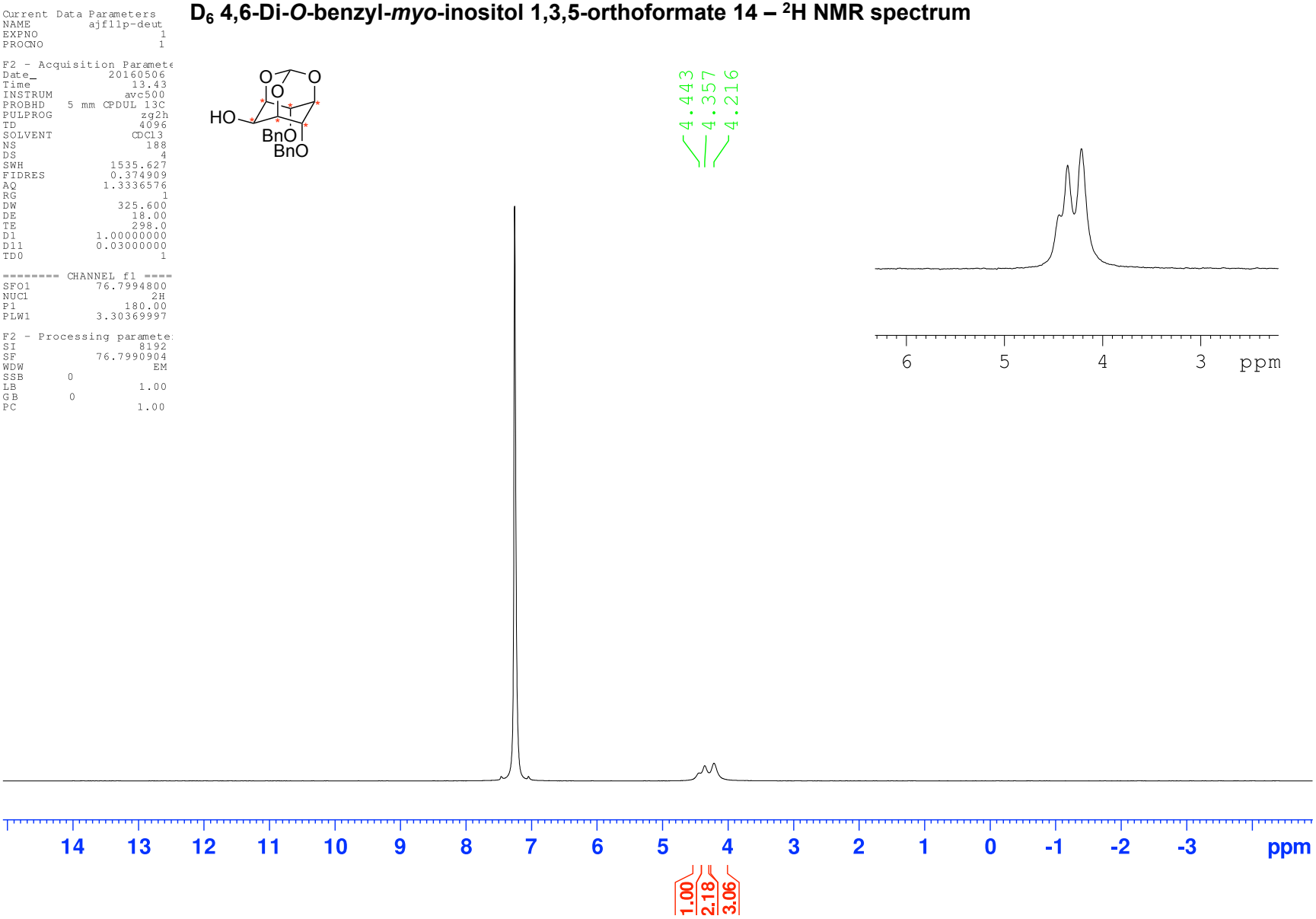




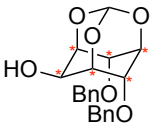
D_6 4,6-Di-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate 14 – ^{13}C NMR spectrum



D_6 4,6-Di-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate 14 – ^2H NMR spectrum



D_6 4,6-Di-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate 14 – Mass spectrum



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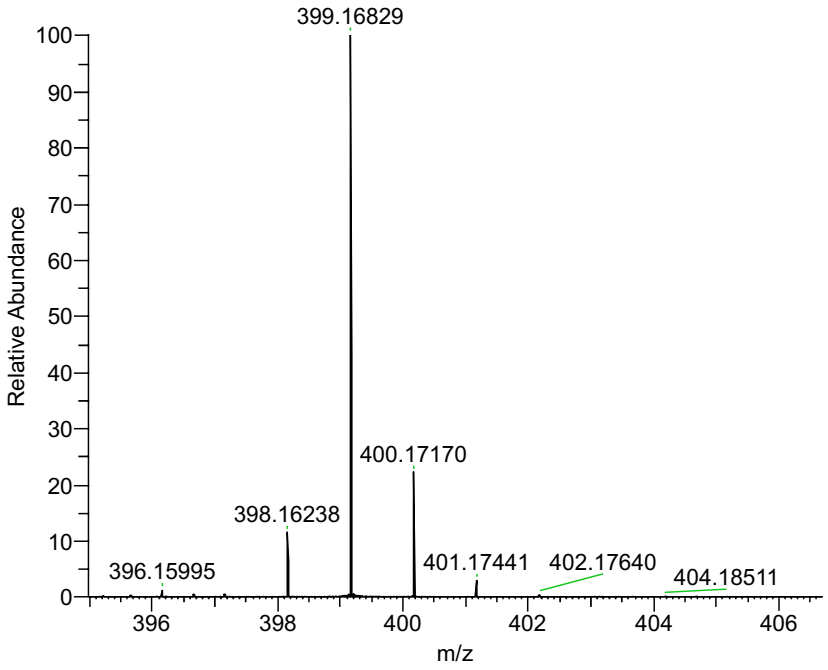
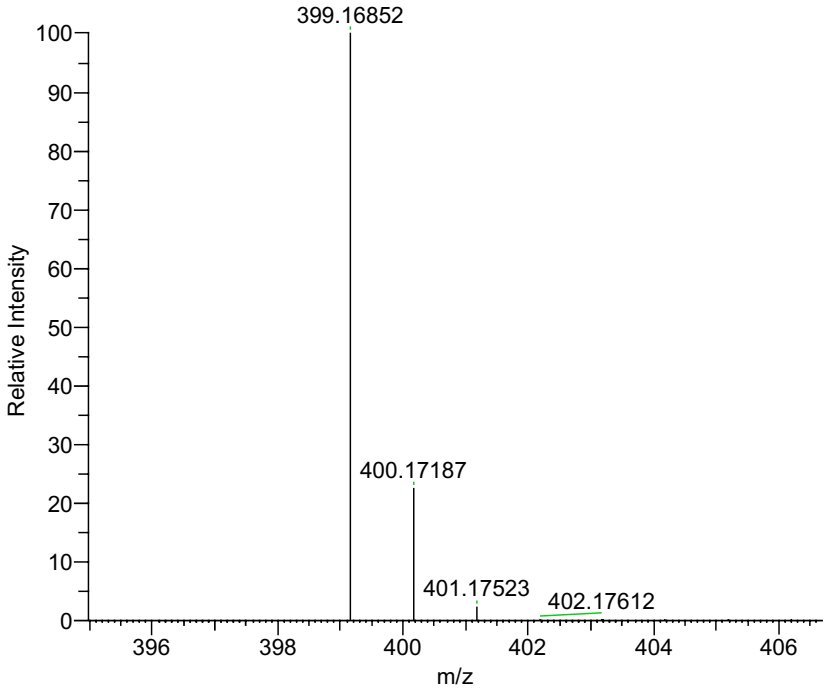


NL: 1.20E8
ESI56916 #12-26 RT: 0.15-0.28 AV: 7 NL: 1.20E+008
T: FTMS {1,1} + p ESI Full lock ms [80.00-1600.00]

Measured Spectrum



NL: 7.85E5
C21H16[2]H6O6Na1: $C_{21}H_{16}{}^{2}H_{6}O_{6}Na$
Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
399.16827	$C_{21}H_{16}{}^{2}H_{6}O_{6}{}^{23}Na$	10.5	-0.62	399.16852

D_6 4,6-Di-*O*-benzyl-*myo*-inositol 16 – ^{1}H NMR spectrum

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Current Data Parameters
NAME         ajf14p-data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160421
Time              15.26
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719425 sec
RG                 3.56
DW               48.400 usec
DE               10.00 usec
TE               298.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1               1H
P1               15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI                65536
SF           500.3000134 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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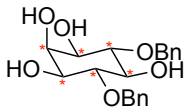
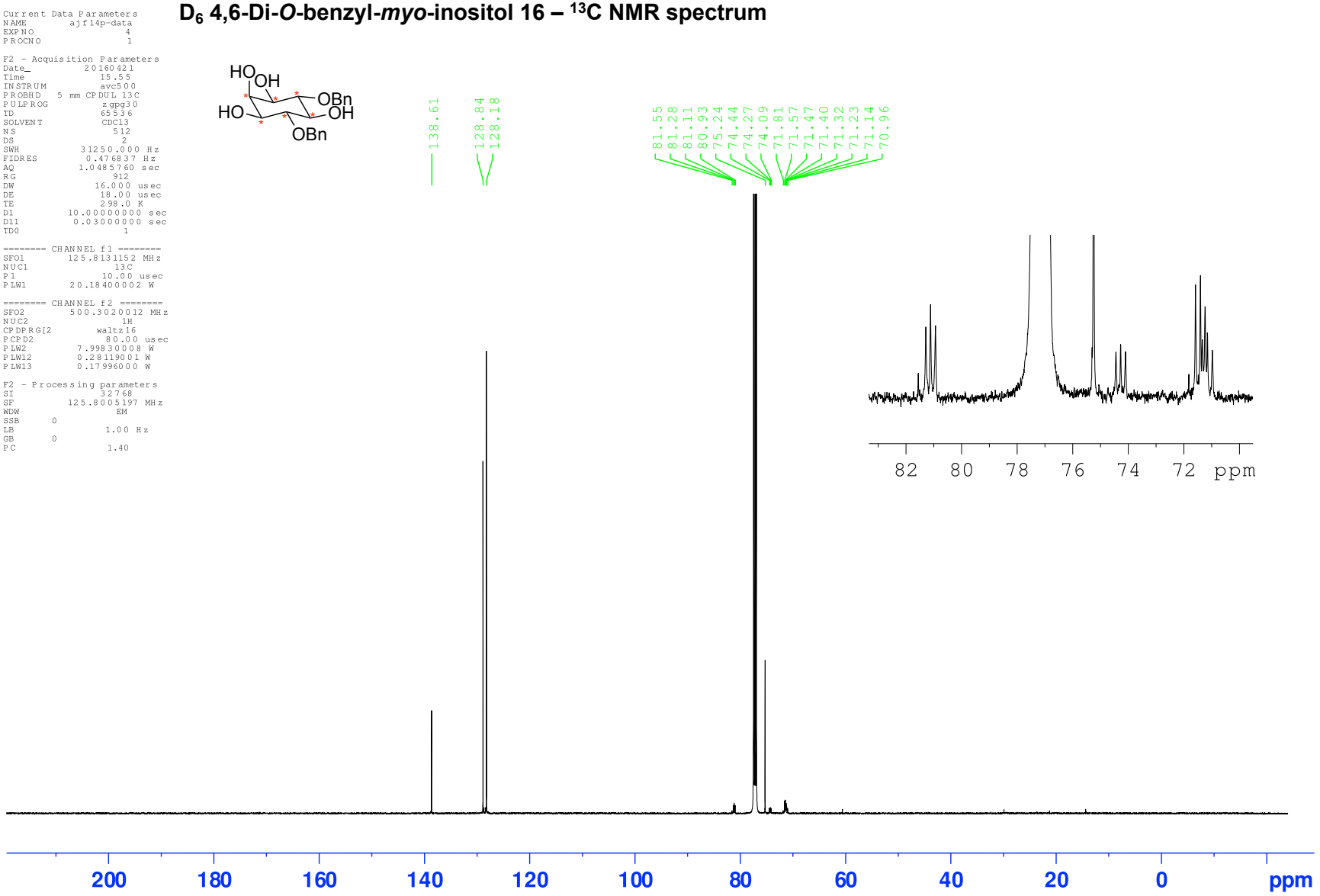
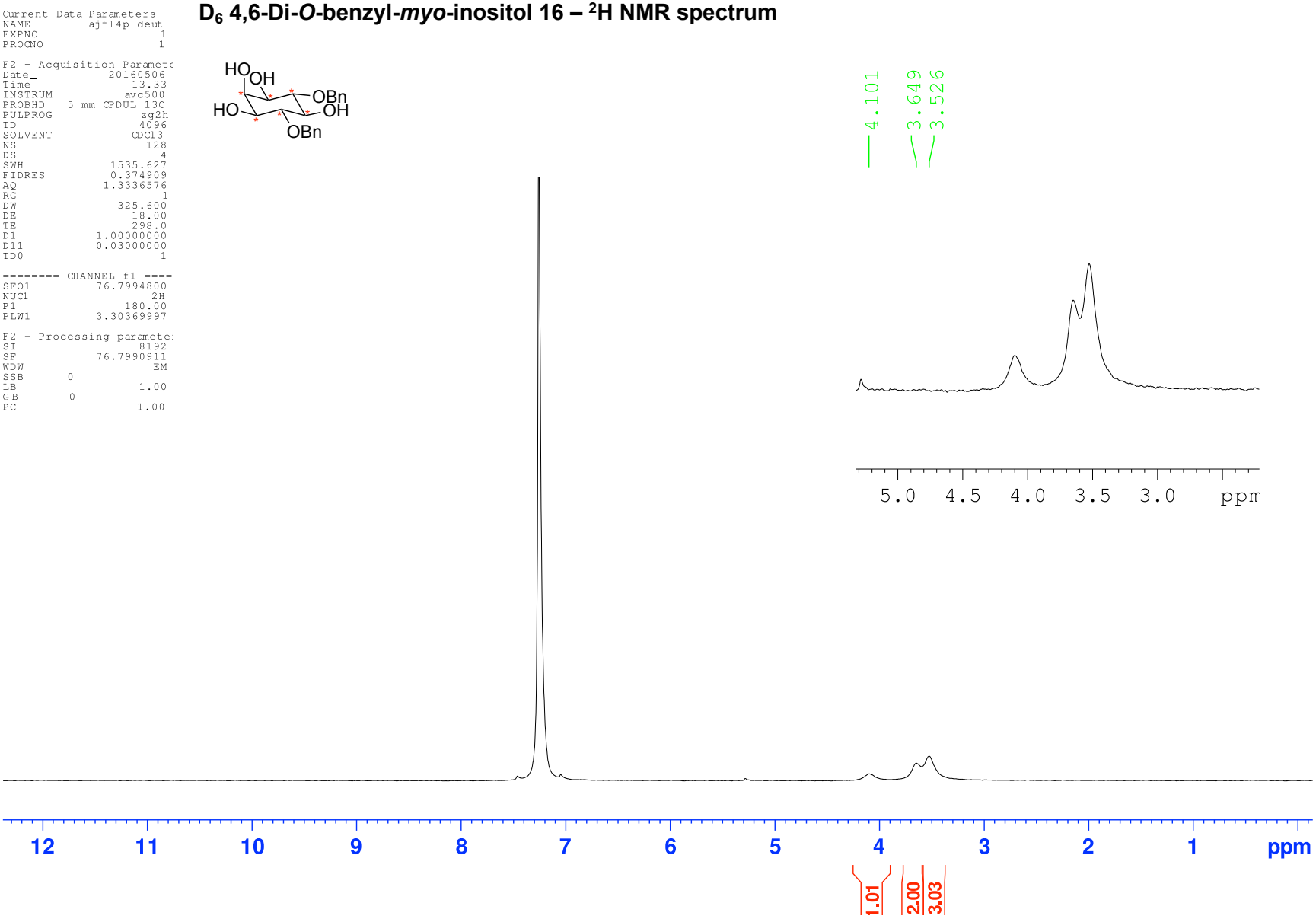


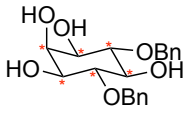
D_6 4,6-Di-*O*-benzyl-*myo*-inositol 16 – ^{13}C NMR spectrum



D_6 4,6-Di-*O*-benzyl-*myo*-inositol 16 – ^2H NMR spectrum



D_6 4,6-Di-*O*-benzyl-*myo*-inositol 16 – Mass spectrum



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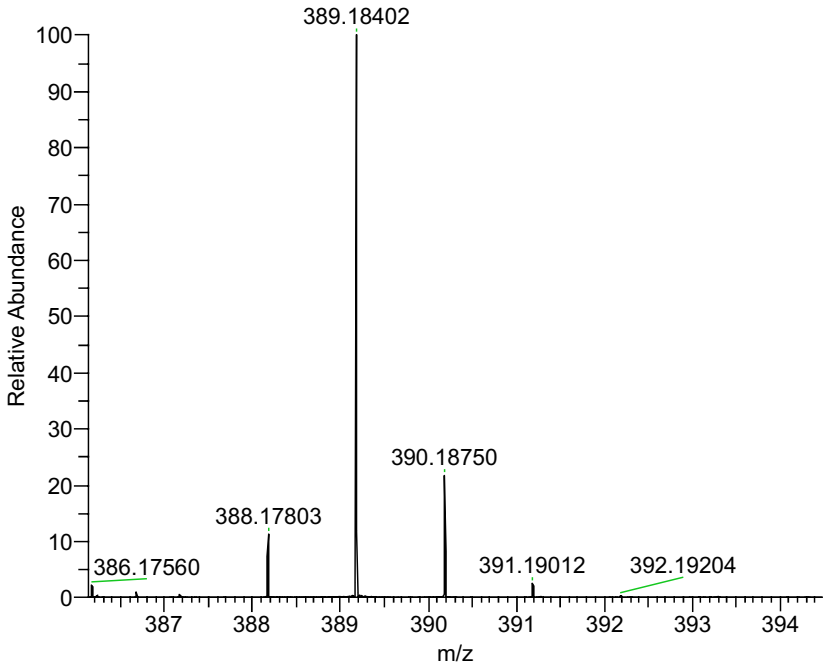
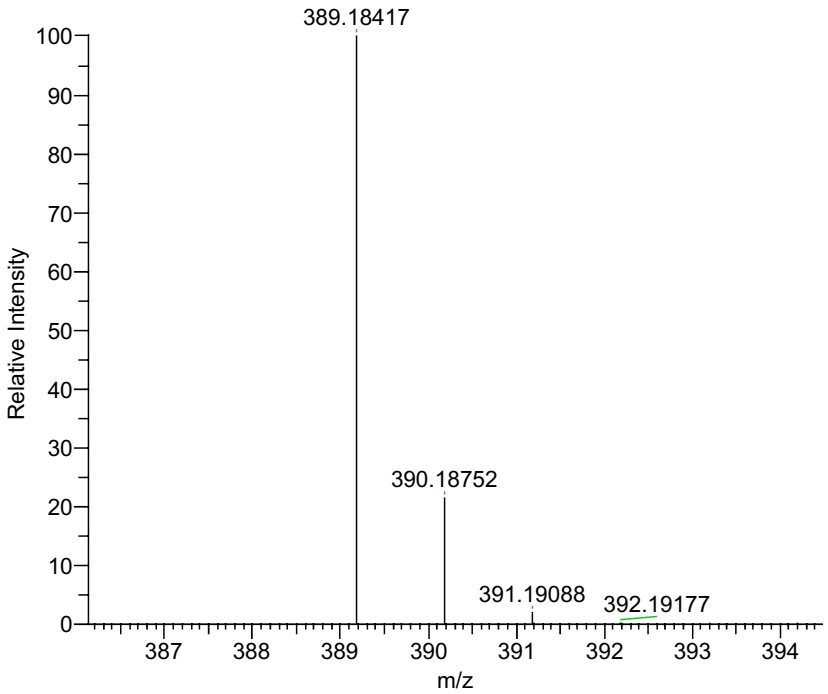


NL: 3.94E7
ESI56917 #12-27 RT: 0.14-0.3 AV: 8 NL: 3.94E+007
T: FTMS {1,1} + p ESI Full lock ms [80.00-1600.00]

Measured Spectrum



NL: 7.93E5
C20H18[2]H6O6Na1: $C_{20}H_{18}{}^{2}H_{6}O_{6}Na$
Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
389.18402	$C_{20}H_{18}{}^{2}H_{6}O_{6}{}^{23}Na$	8.5	-0.38	389.18417

(−)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (−)-9 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME                 ajc71p
EXPNO                     1
PROCNO                    1

F2 - Acquisition Paramete
Date_              20150302
Time                  22.55
INSTRUM              avb400
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820
FIDRES             0.122266
AQ                 4.0894465
RG                     70.94
DW                    62.400
DE                      6.50
TE                     298.0
D1                1.00000000
TD0                       1

======== CHANNEL f1 ====
SFO1             400.1320007
NUC1                      1H
P1                     10.00
PLW1            14.58800030

F2 - Processing paramete
SI                    65536
SF               400.1300096
WDW                      EM
SSB          0
LB                     0.30
GB           0
PC                     1.00
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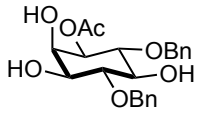
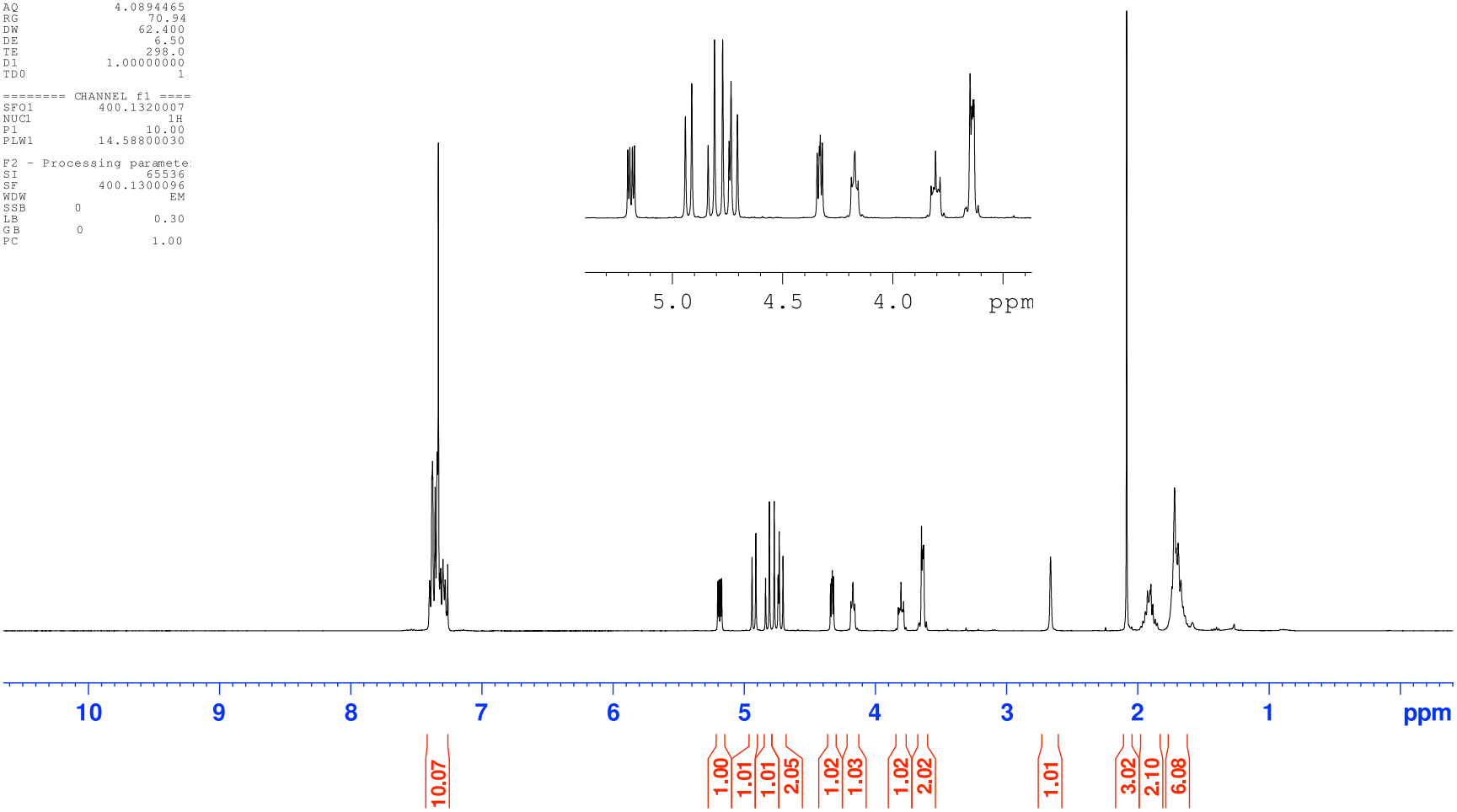
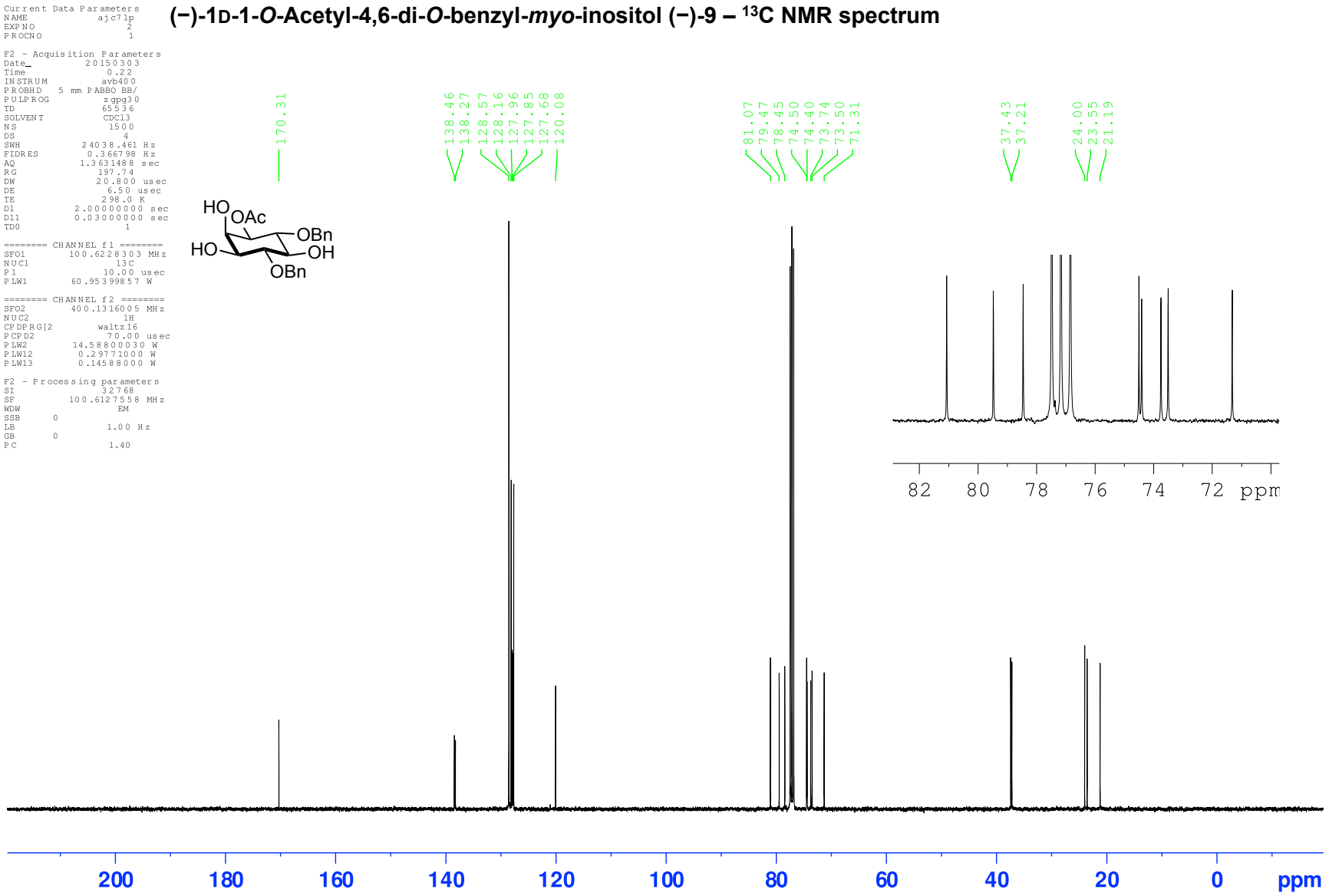
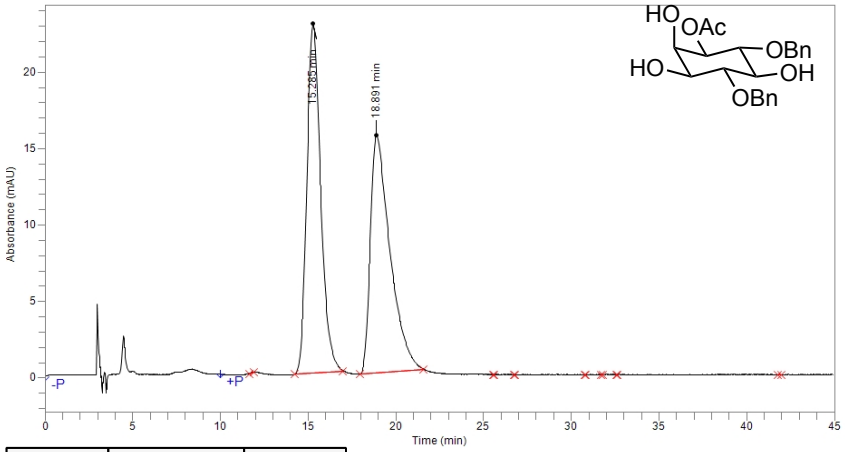




(−)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (−)-9 – ^{13}C NMR spectrum

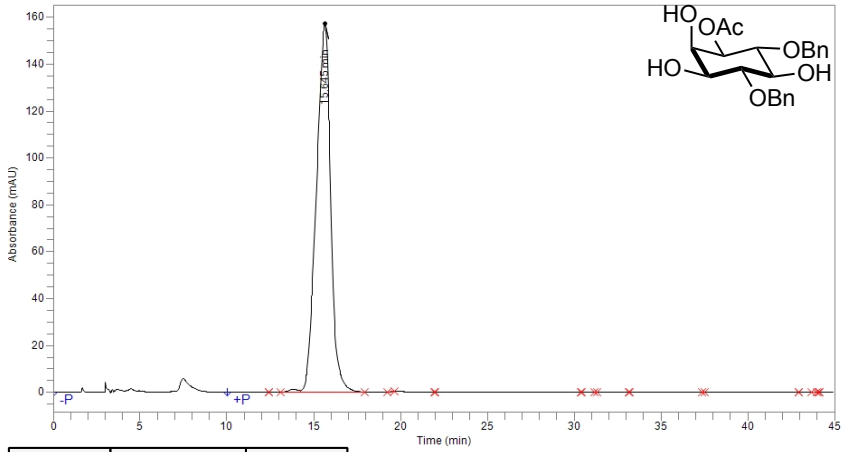


(±)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (±)-9 – Chiral HPLC (Heptane/IPA 85:15, 1.0 mL.min^{-1}, 254 nm)



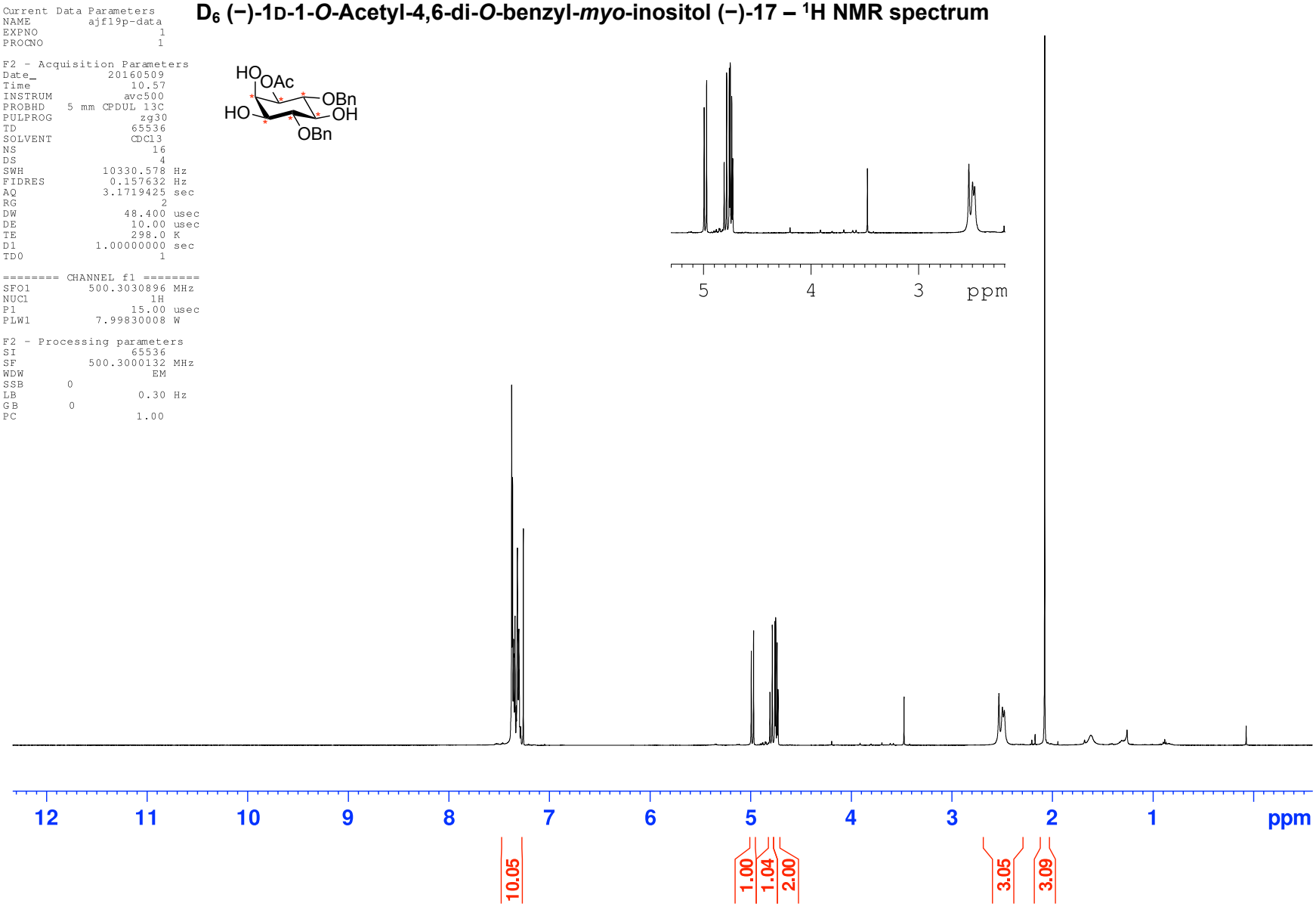
Time	Area	Area %
11.895	372	0.02
15.285	1,253,208	50.90
18.891	1,208,110	49.07
25.571	28	0.00
26.768	33	0.00
30.783	39	0.00
31.730	59	0.00
32.605	28	0.00
41.809	162	0.01
Total	2,462,039	100.00

(−)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (−)-9 – Chiral HPLC (Heptane/IPA 85:15, 1.0 mL.min^{-1}, 254 nm)

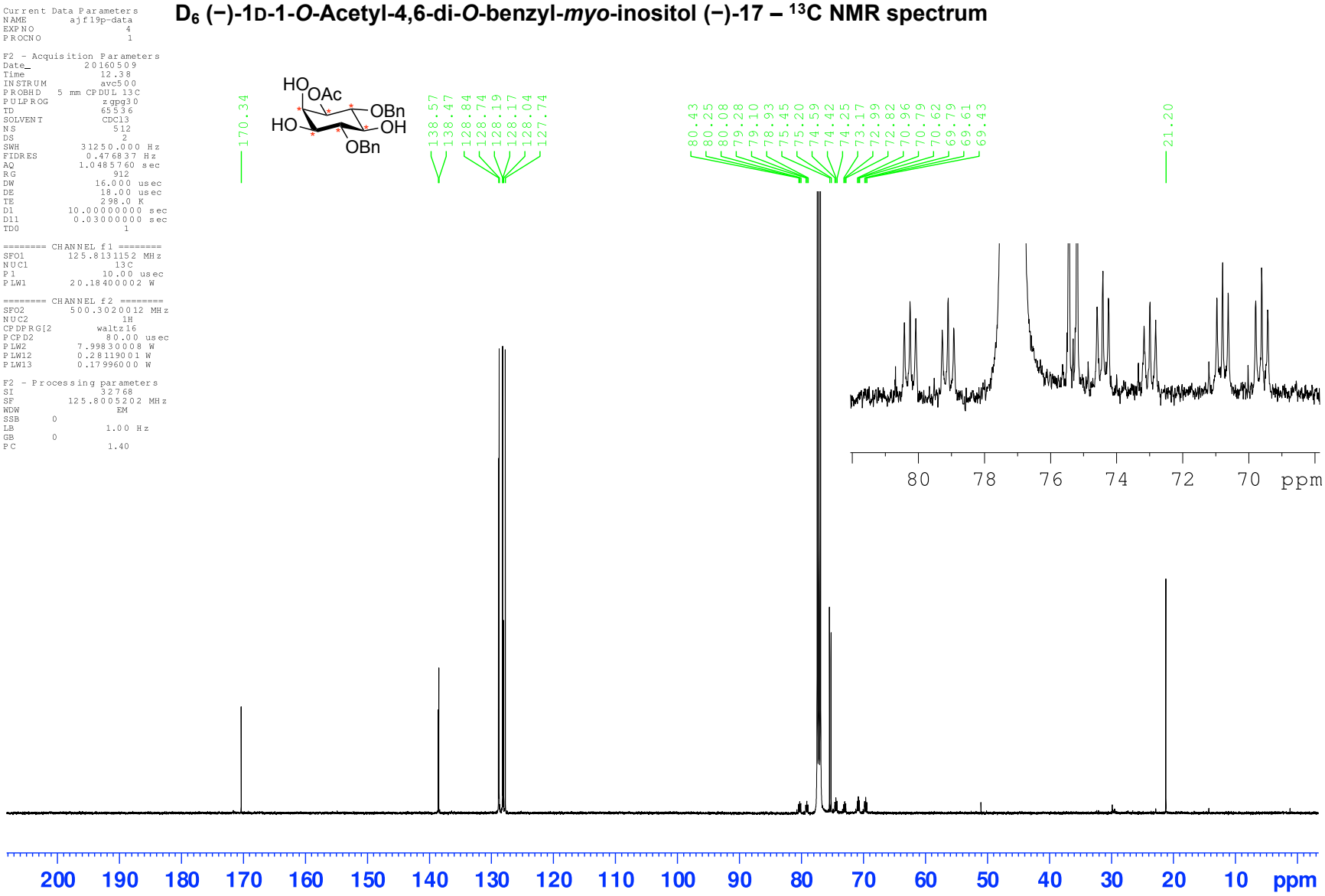


Time	Area	Area %
12.421	34	0.00
13.812	48,653	0.54
15.645	9,026,166	99.45
19.634	425	0.00
21.959	26	0.00
30.416	47	0.00
31.206	126	0.00
33.152	42	0.00
37.415	137	0.00
42.948	28	0.00
43.951	249	0.00
44.147	76	0.00
Total	9,076,008	100.00

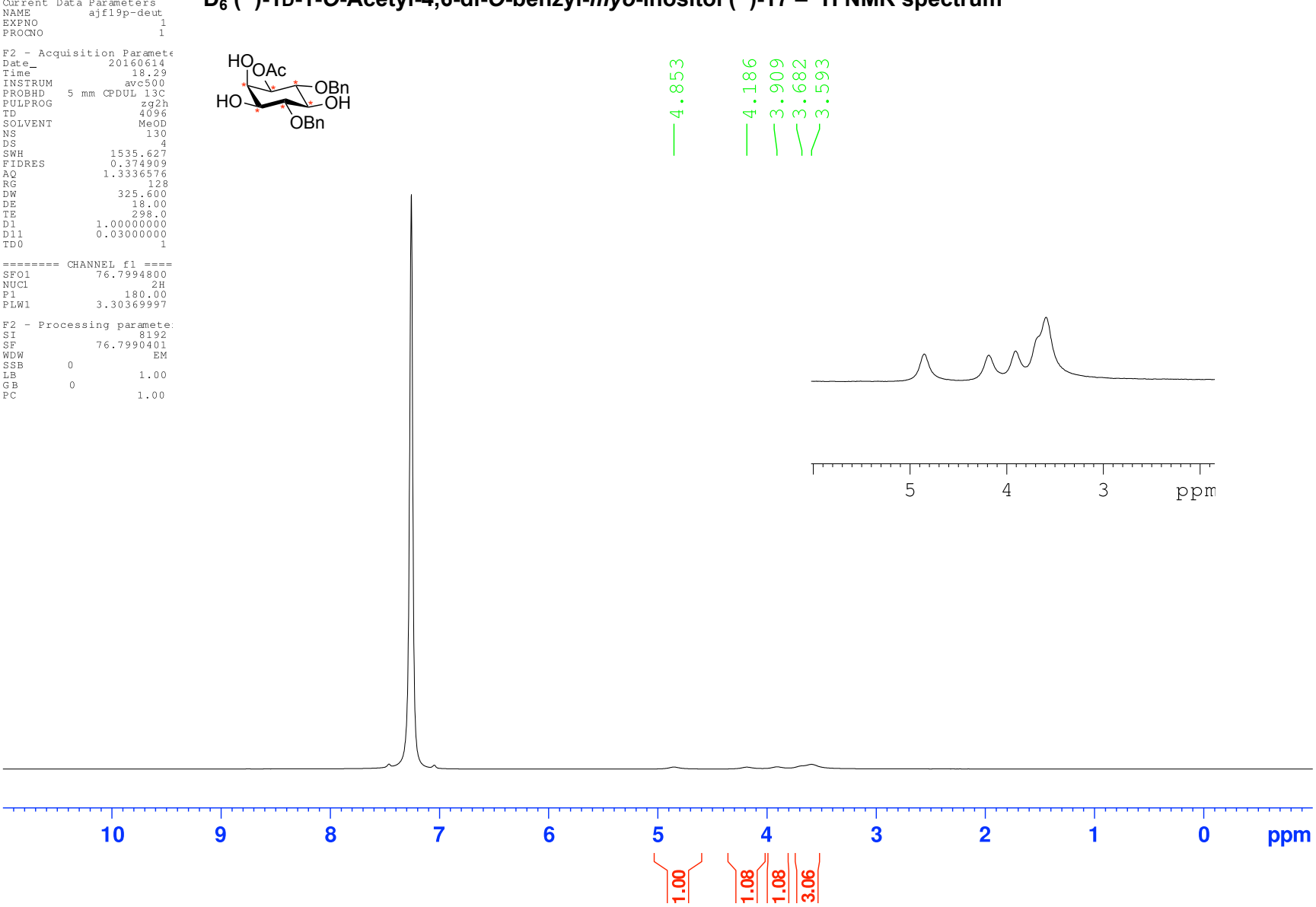
D_6 (−)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (−)-17 – ^{1}H NMR spectrum



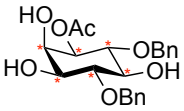
D_6 (−)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (−)-17 – ^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (−)-17 – ^{2}H NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (−)-17 – Mass spectrum



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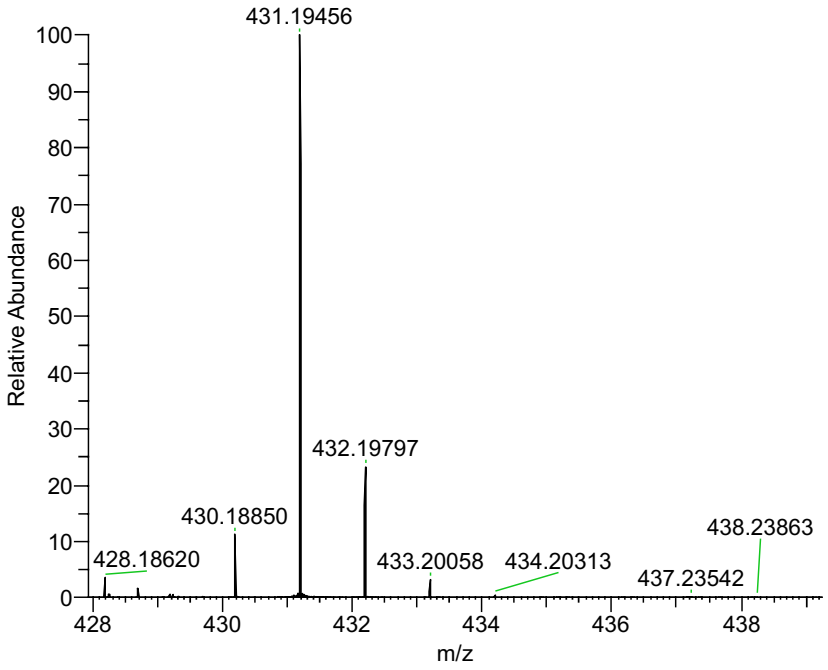
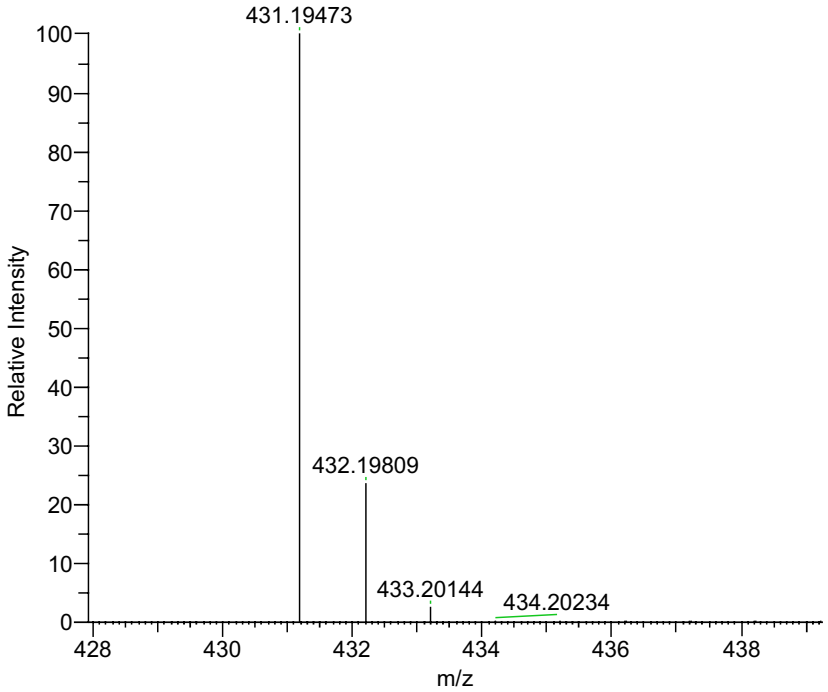


NL: 3.53E7
ESI56918 #12-27 RT: 0.14-0.3 AV: 8 NL: 3.53E+007
T: FTMS {1,1} + p ESI Full lock ms [80.00-1600.00]

Measured Spectrum

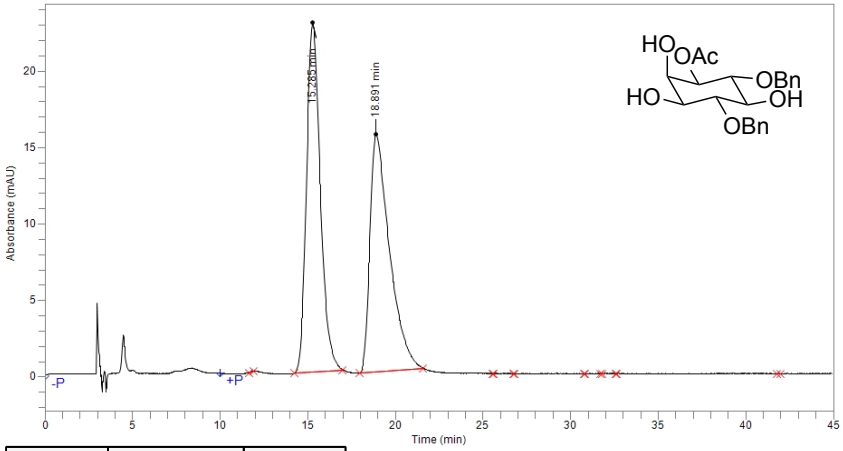


NL: 7.74E5
C22H20[2]H6O7Na1: $C_{22}H_{20}{}^{2}H_{6}O_{7}Na$
Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

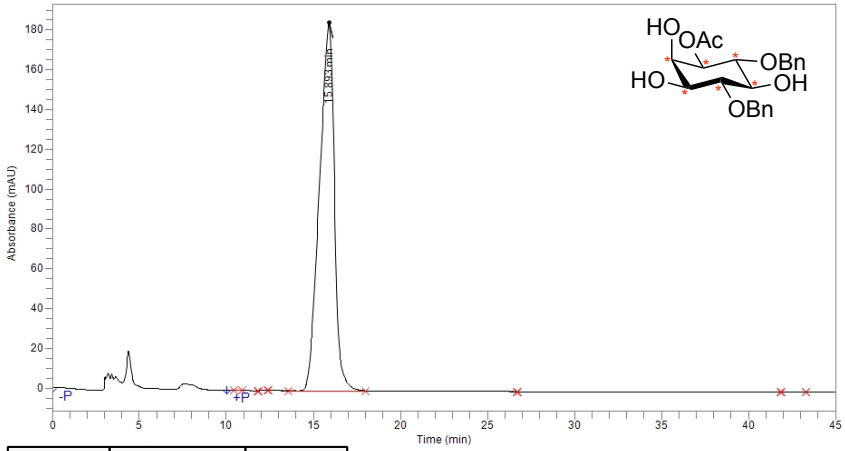
m/z	Formula	RDB	Delta ppm	Theo. Mass
431.19455	$C_{22}H_{20}{}^{2}H_{6}O_{7}{}^{23}Na$	9.5	-0.43	431.19473

(±)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (±)9 – Chiral HPLC (Heptane/IPA 85:15, 1.0 mL.min^{-1}, 254 nm)



Time	Area	Area %
11.895	372	0.02
15.285	1,253,208	50.90
18.891	1,208,110	49.07
25.571	28	0.00
26.768	33	0.00
30.783	39	0.00
31.730	59	0.00
32.605	28	0.00
41.809	162	0.01
Total	2,462,039	100.00

D_6 (−)-1D-1-*O*-Acetyl-4,6-di-*O*-benzyl-*myo*-inositol (−)-17 – Chiral HPLC (Heptane/IPA 85:15, 1.0 mL.min^{-1}, 254 nm)



Time	Area	Area %
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11.845	39	0.00
12.405	31	0.00
13.608	775	0.01
15.893	11,038,336	99.97
26.708	30	0.00
41.897	42	0.00
43.301	6	0.00
Total	11,041,710	100.00

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-*myo*-inositol (−)-19 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME                 ajc71p
EXPNO                     1
PROCNO                    1

F2 - Acquisition Paramete
Date_             20150302
Time                 22.55
INSTRUM              avb400
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820
FIDRES             0.122266
AQ                 4.0894465
RG                     70.94
DW                    62.400
DE                      6.50
TE                     298.0
D1                1.00000000
TD0                       1

======== CHANNEL f1 ====
SFO1             400.1320007
NUC1                      1H
P1                     10.00
PLW1            14.58800030

F2 - Processing paramete
SI                    65536
SF               400.1300096
WDW                      EM
SSB       0
LB                     0.30
GB        0
PC                     1.00
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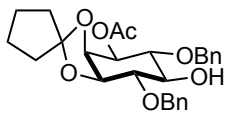
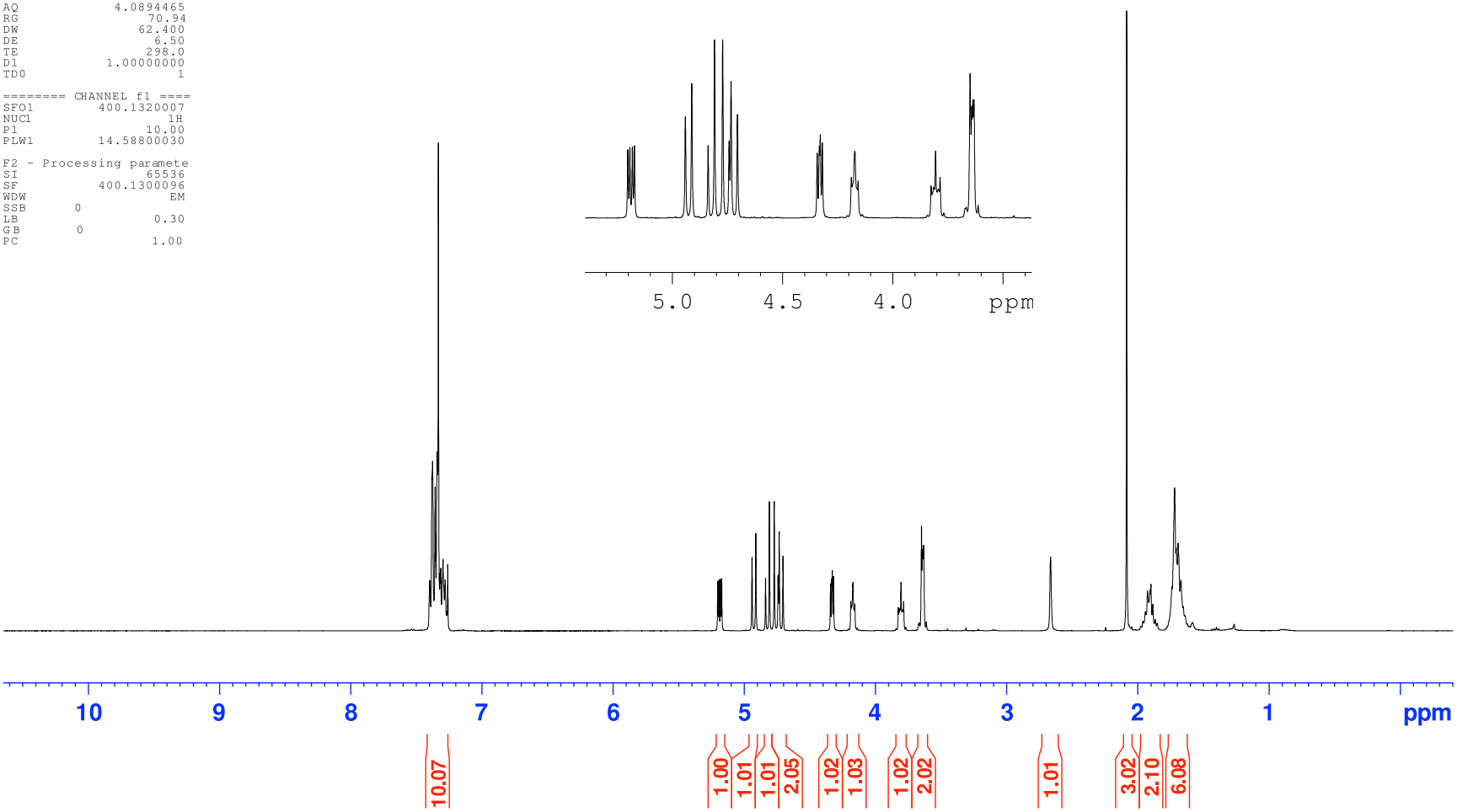
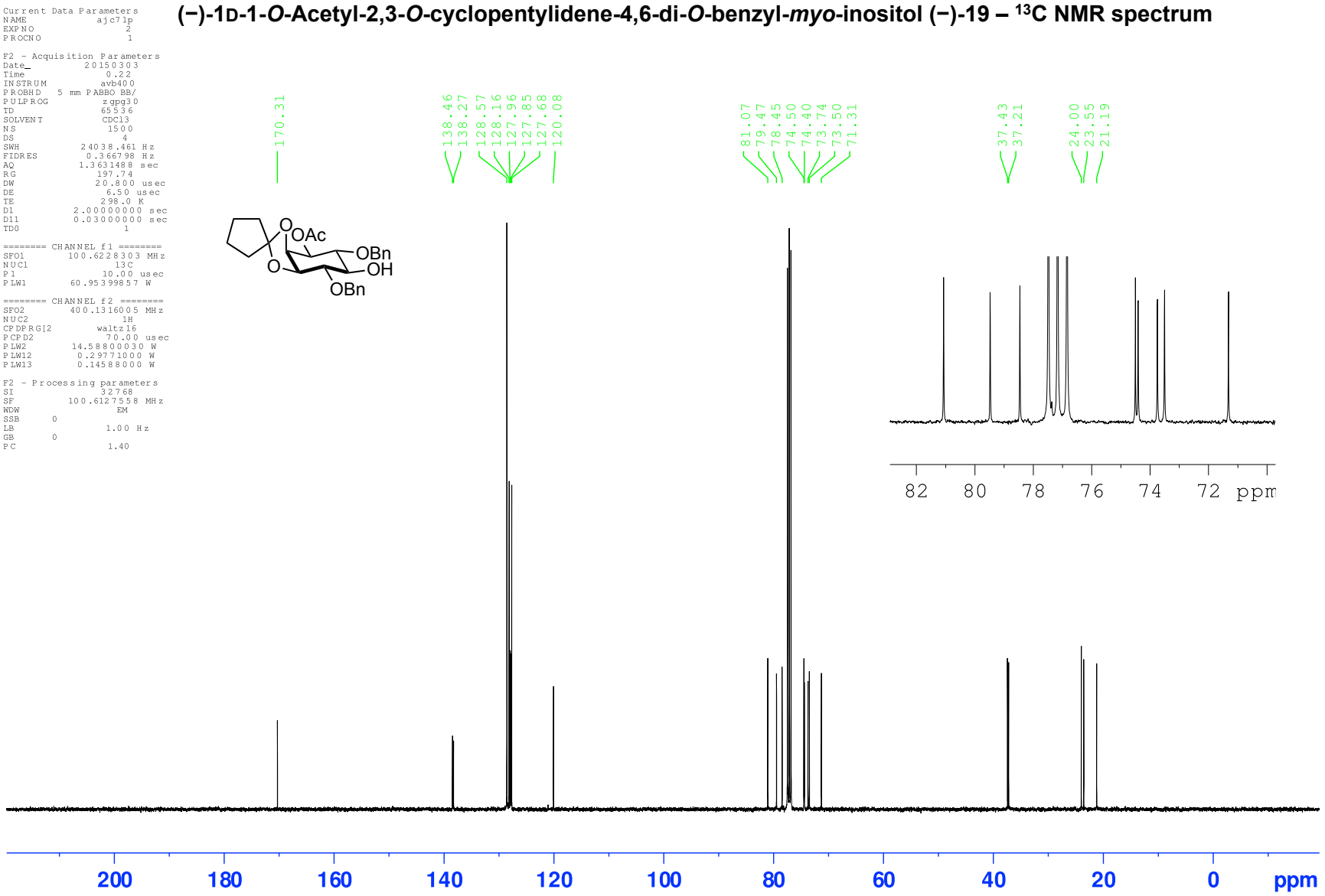




(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-*myo*-inositol (−)-19 – ^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-*myo*-inositol (−)-20 – ^{1}H NMR spectrum

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Current Data Parameters
NAME          ajf23p-data
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
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Time                18.38
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PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719425 sec
RG                  3.56
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.3030896 MHz
NUC1                1H
P1                15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI                 65536
SF            500.3000133 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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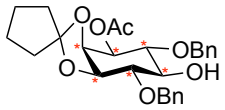
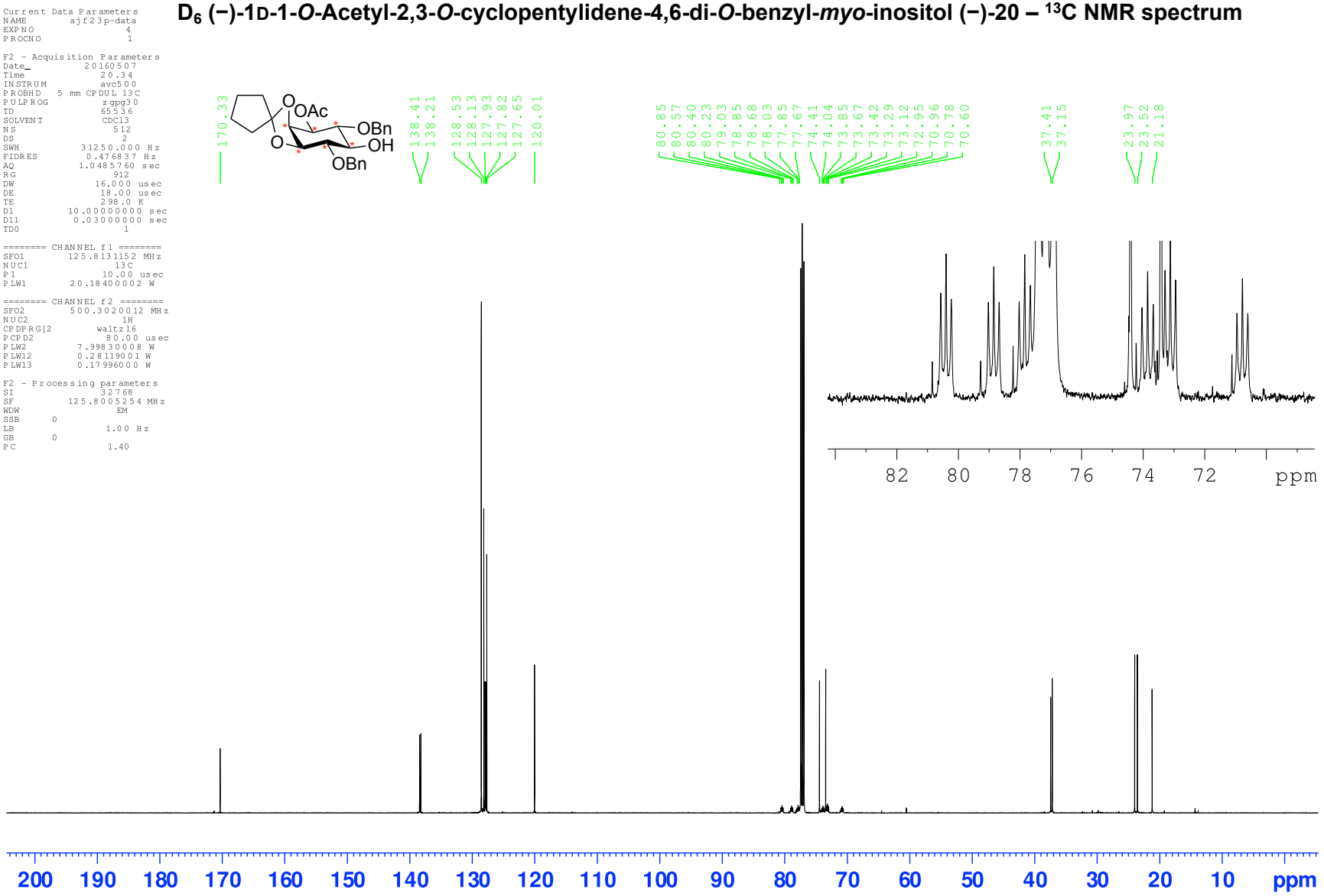


D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-*myo*-inositol (−)-20 – ^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-*myo*-inositol (−)-20 – ^{2}H NMR spectrum

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Current Data Parameters
NAME      ajf23p-DNMRdata
EXPNO                   2
PROCNO                  1

F2 - Acquisition Paramete
Date_            20161219
Time                10.16
INSTRUM             av600
PROBHD    Z130037_0008 (
PULPROG             zg2h
TD                  8192
SOLVENT              D2O
NS                     78
DS                      2
SWH             1842.299
FIDRES          0.449780
AQ              2.2233088
RG                  60.94
DW                271.400
DE                  18.00
TE                  298.0
D1              1.00000000
D11             0.03000000
TD0                     1
SFO1            92.1316525
NUC1                   2H
P1                 378.00
PLW1            1.75000000

F2 - Processing paramete
SI                  16384
SF              92.1312808
WDW                    EM
SSB       0
LB                   0.30
GB        0
PC                   1.00
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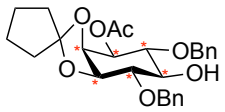
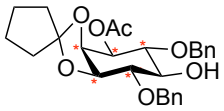
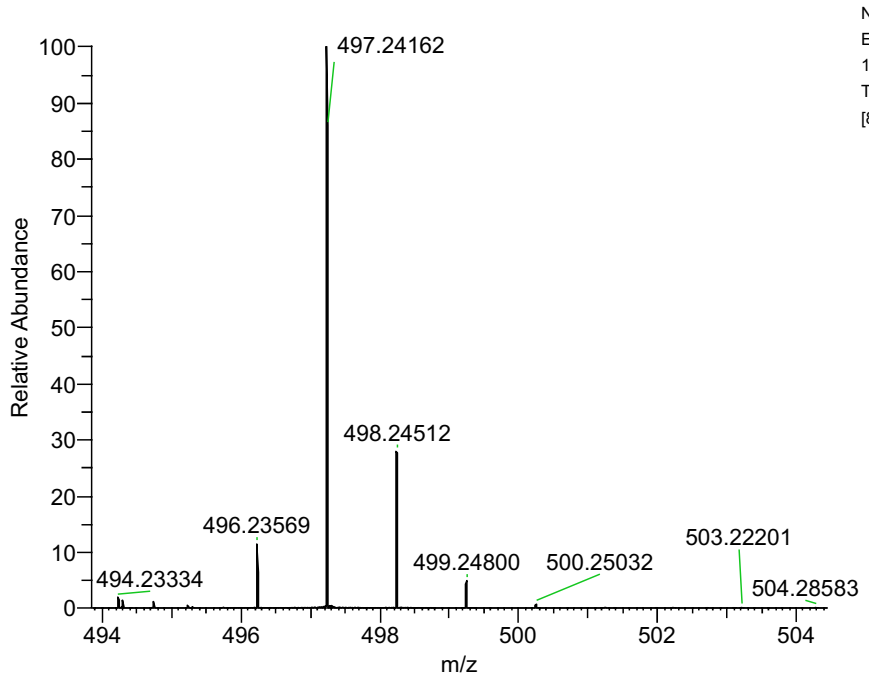


D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-*myo*-inositol (−)-20 – Mass spectrum

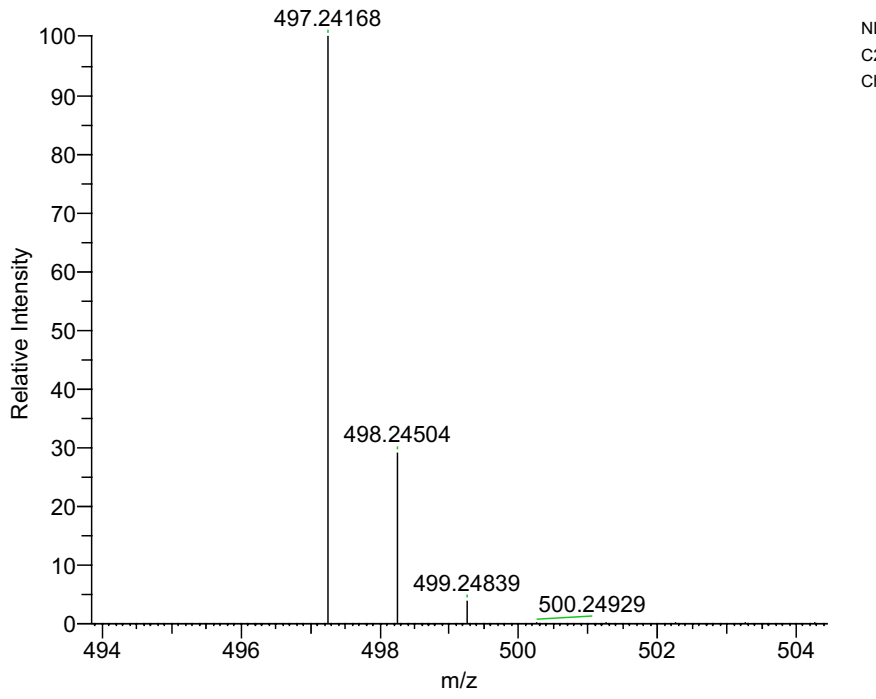


W:\data\May 16\ESI56919.raw 09/05/2016 10:56 am



NL: 1.17E8
ESI56919 #12-27 RT: 0.14-0.3 AV: 8 NL: 1.17E+008
T: FTMS {1,1} + p ESI Full ms [80.00-1600.00]

Measured Spectrum



NL: 7.33E5
C27H26[2]H6O7Na1: $C_{27}H_{26}{}^{2}H_{6}O_{7}Na$
Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
497.24161	$C_{27}H_{26}{}^{2}H_{6}O_{7}{}^{23}Na$	11.5	-0.16	497.24168

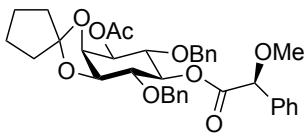
(+)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-((*S*)-α-methoxyphenylacetoxy)-*myo*-inositol (+)-S1a – ^{1}H NMR spectrum

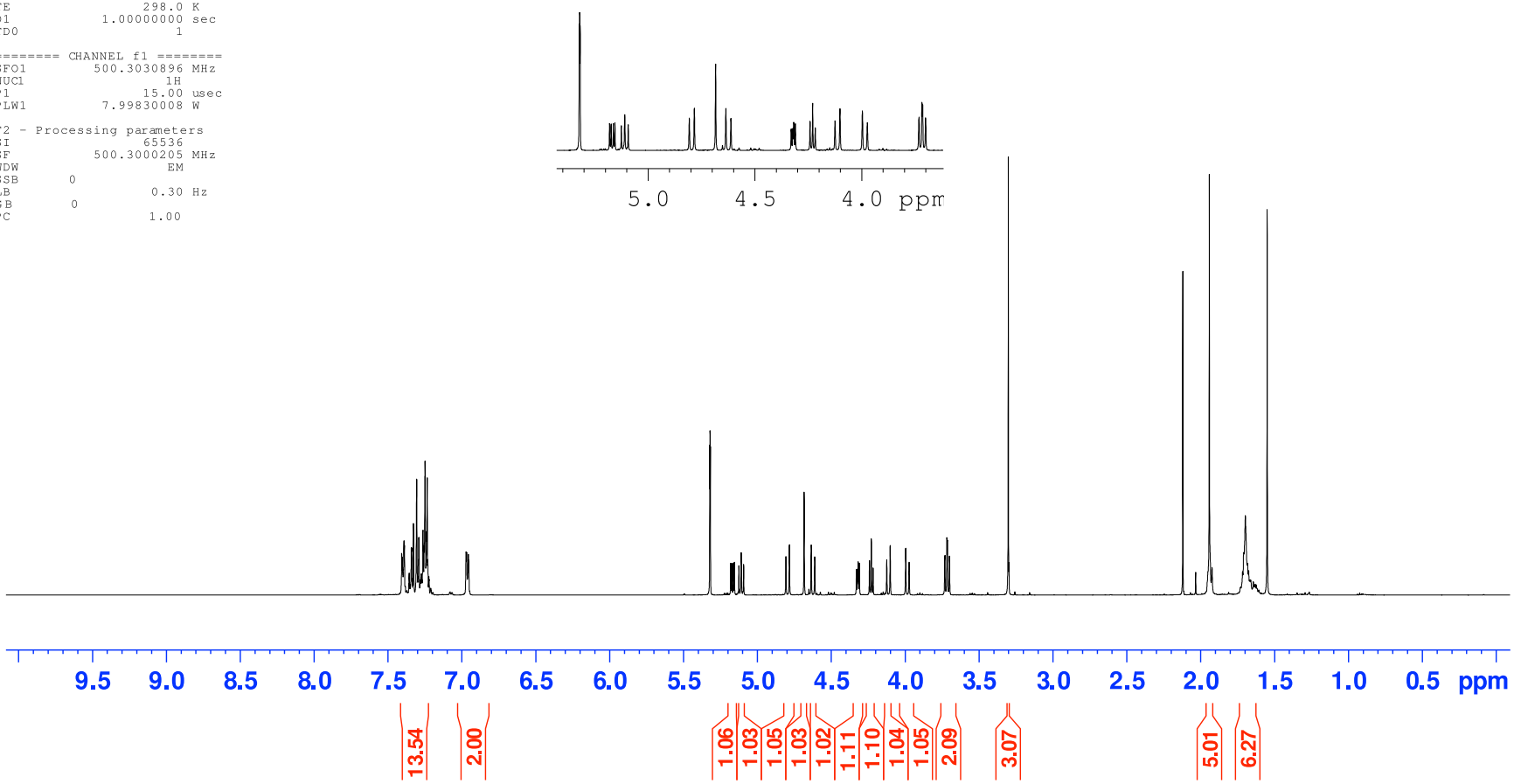
```
Current Data Parameters
NAME      ajl33(S)-data
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_          20170320
Time              11.21
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT          CD2Cl2
NS                  16
DS                   4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719425 sec
RG                2.56
DW               48.400 usec
DE               10.00 usec
TE               298.0 K
D1            1.00000000 sec
TD0                  1

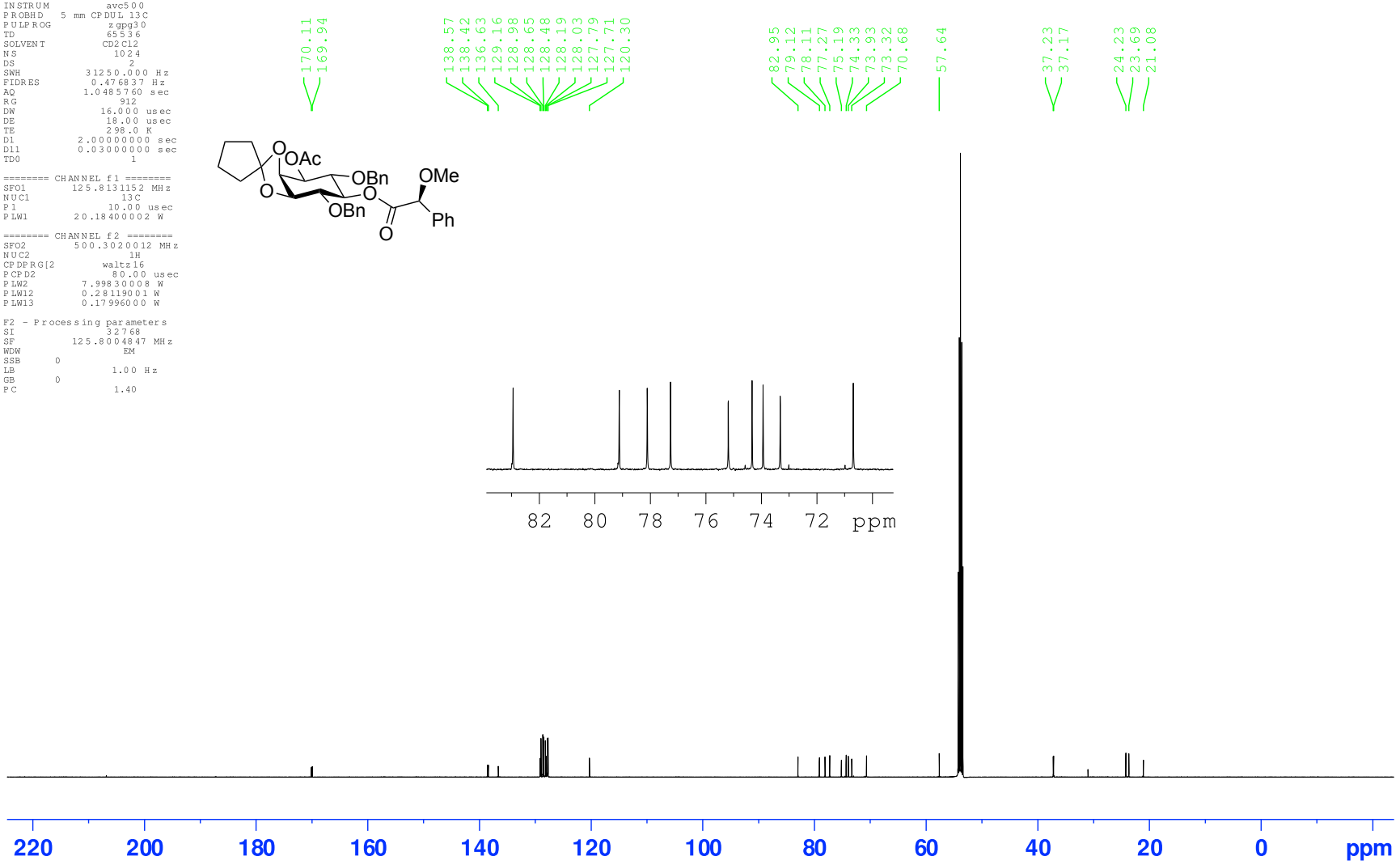
======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1               1H
P1               15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI               65536
SF          500.3000205 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```





(+)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-((*S*)-α-methoxyphenylacetoxy)-*myo*-inositol (+)-S1a – ^{13}C NMR spectrum



Current Data Parameters
NAME aj133(S)-data
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170320
Time 11.52
INSTRUM avc500
PROBHD 5 mm CPDUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CD2Cl2
NS 1024
DS 2
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0485760 sec
RG 912
DW 16.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.8131152 MHz
NUC1 13C
P1 10.00 usec
PLW1 20.18400002 W

======== CHANNEL f2 ========
SFO2 500.3020012 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 7.99830008 W
PLW12 0.28119001 W
PLW13 0.17996000 W

F2 - Processing parameters
SI 32768
SF 125.8004847 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

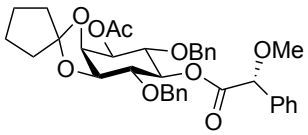
(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-((*R*)-α-methoxyphenylacetoxy)-*myo*-inositol
(−)-S1b – ^{1}H NMR spectrum

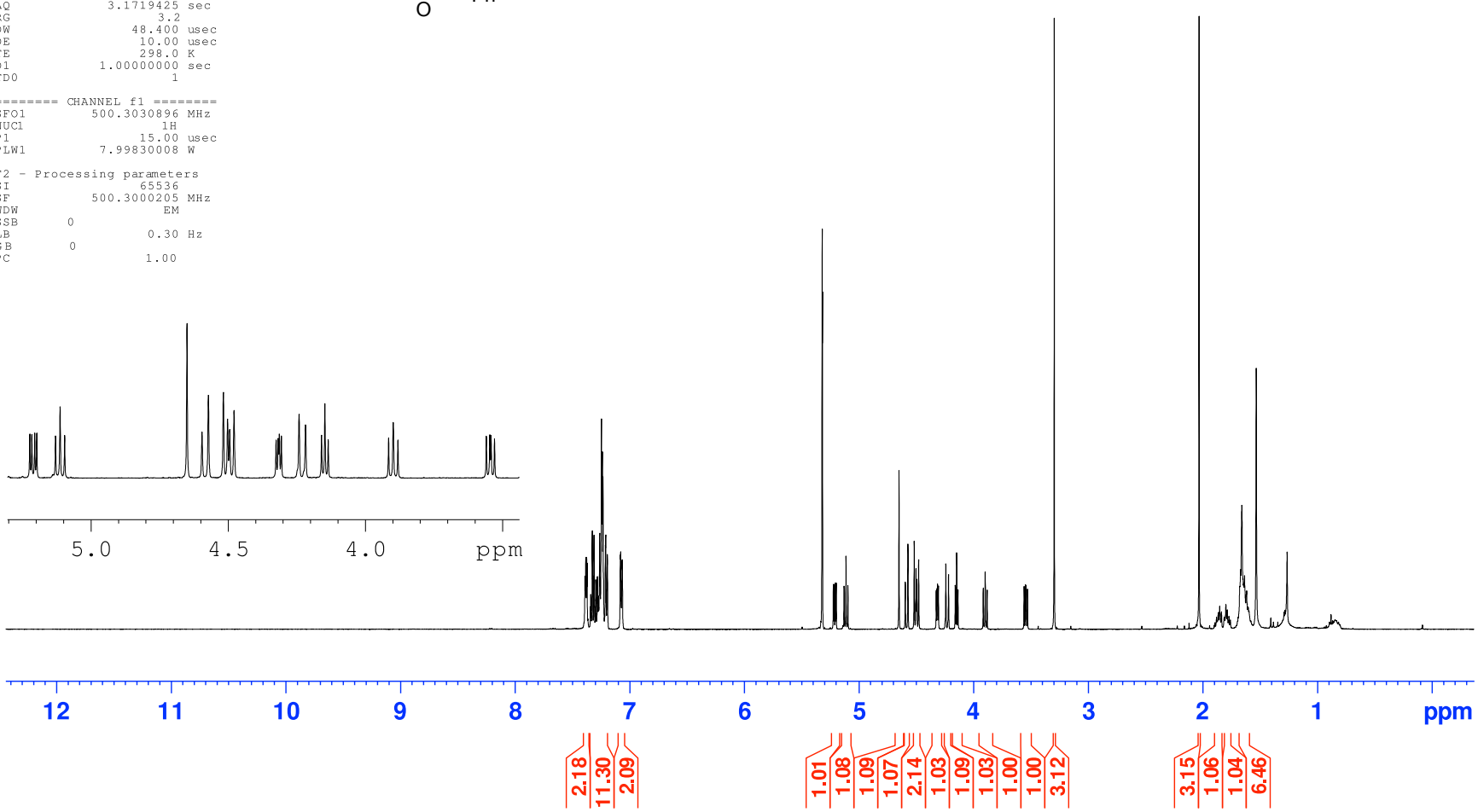
```
Current Data Parameters
NAME      ajf70p(R)-data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160930
Time              19.28
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT          CD2Cl2
NS                  16
DS                   4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                   3.2
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                  1

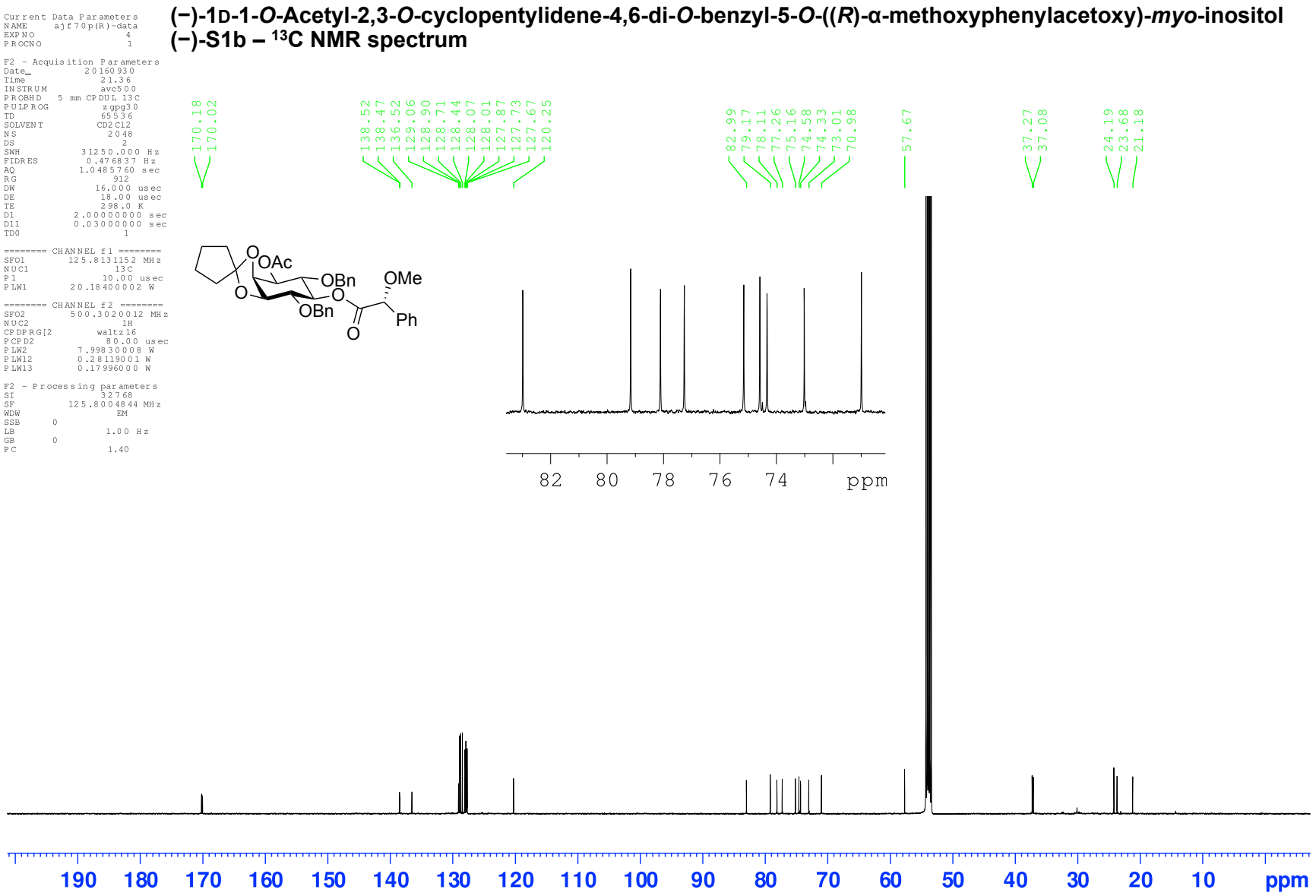
======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1               1H
P1                15.00 usec
PLW1           7.99830008 W

F2 - Processing parameters
SI                65536
SF           500.3000205 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```





(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-((*R*)-α-methoxyphenylacetoxy)-*myo*-inositol
(−)-S1b – ^{13}C NMR spectrum



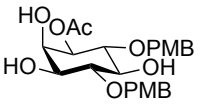
(+)-1D-1-*O*-Acetyl-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol (+)-S4 – ^{1}H NMR

```
Current Data Parameters
NAME         ajg51p-data
EXPNO                  1
PROCNO                 1

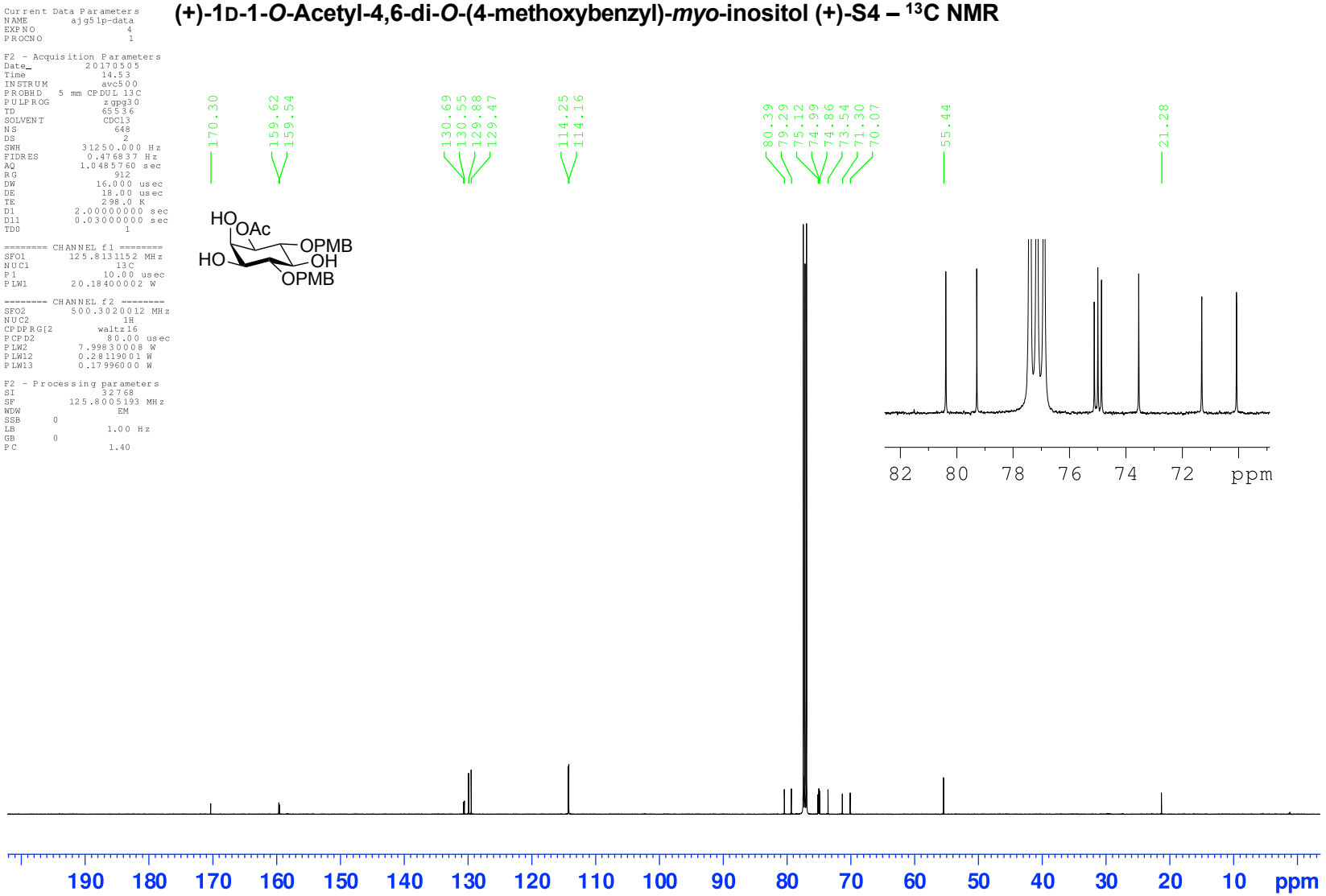
F2 - Acquisition Parameters
Date_           20170505
Time               13.56
INSTRUM          avc500
PROBHD    5 mm CPDUL 13C
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719425 sec
RG                  3.2
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1                   1H
P1                 15.00 usec
PLW1         7.99830008 W

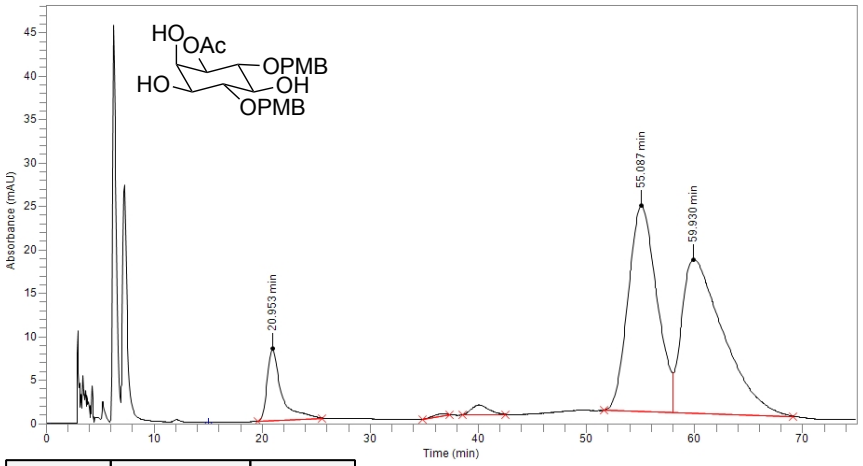
F2 - Processing parameters
SI                 65536
SF          500.3000129 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



(+)-1D-1-*O*-Acetyl-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol (+)-S4 – ^{13}C NMR

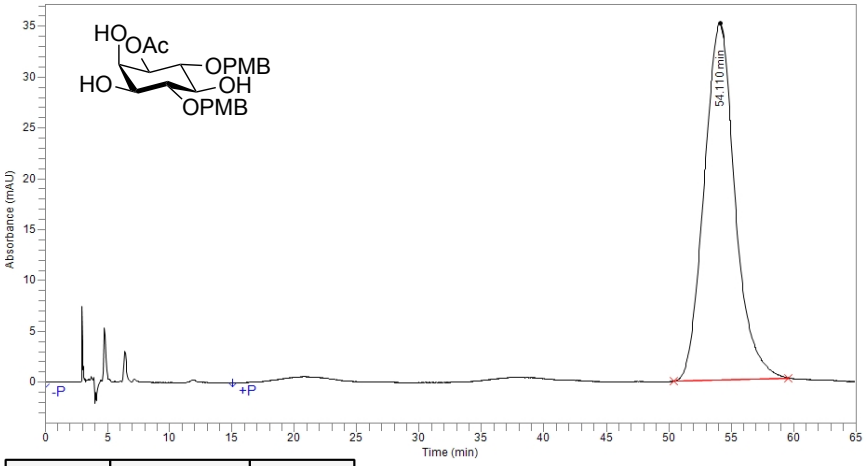


(±)-1D-1-*O*-Acetyl-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol (±)-S4
Chiral HPLC



Time	Area	Area %
20.953	754,314	7.51
36.678	23,142	0.23
40.120	123,678	1.23
55.087	4,367,527	43.47
59.930	4,778,153	47.56
Total	10,046,813	100.00

(−)-1D-1-*O*-Acetyl-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol (+)-S4
Chiral HPLC



Time	Area	Area %
54.110	6,042,298	100.00
Total	6,042,298	100.00

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol (−)-S5 – ^{1}H NMR

```
Current Data Parameters
NAME          ajg58p-data
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170511
Time                9.46
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                   2.8
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          500.3030896 MHz
NUC1                   1H
P1                 15.00 usec
PLW1           7.99830008 W

F2 - Processing parameters
SI                 65536
SF            500.3000133 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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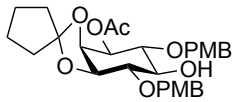
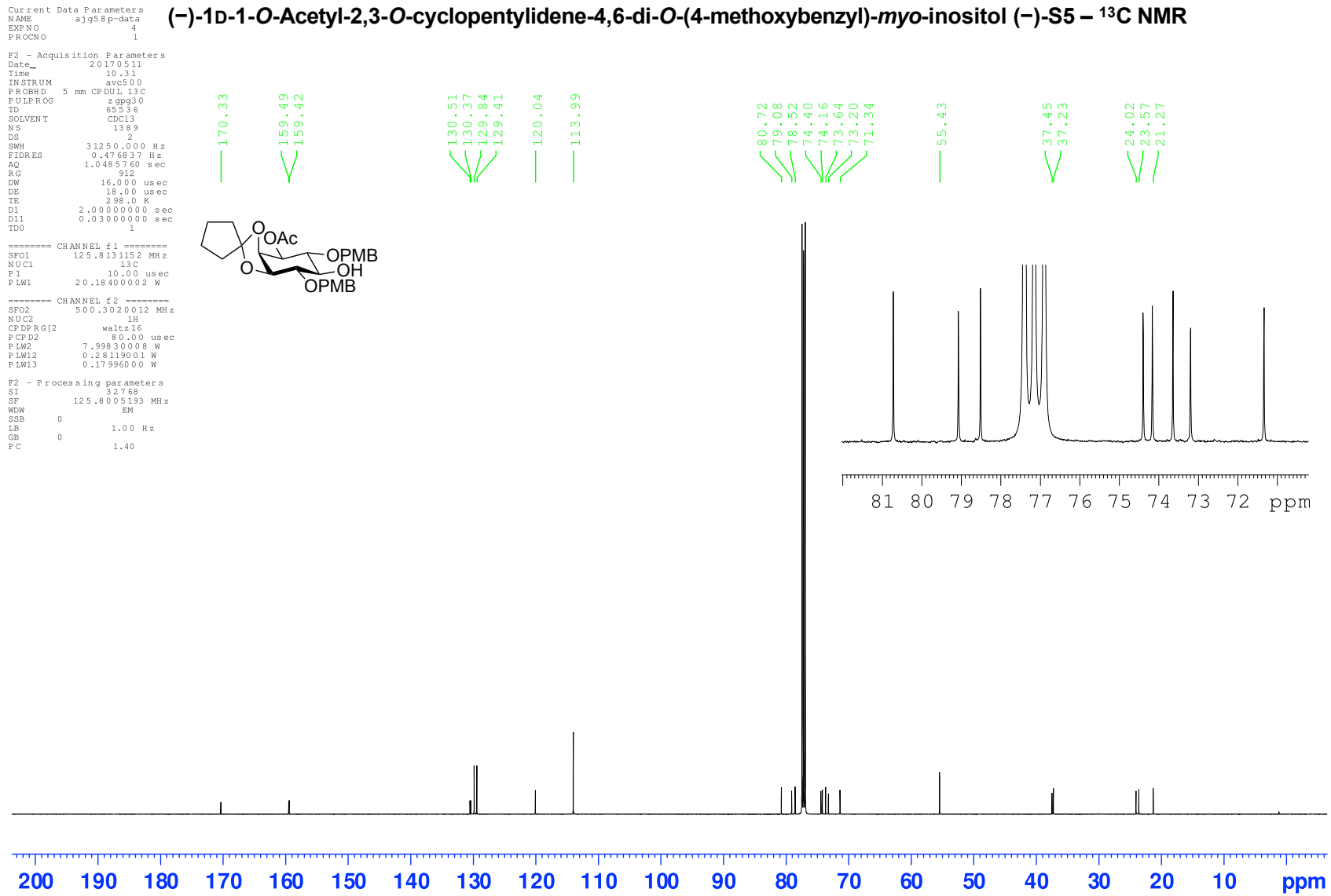
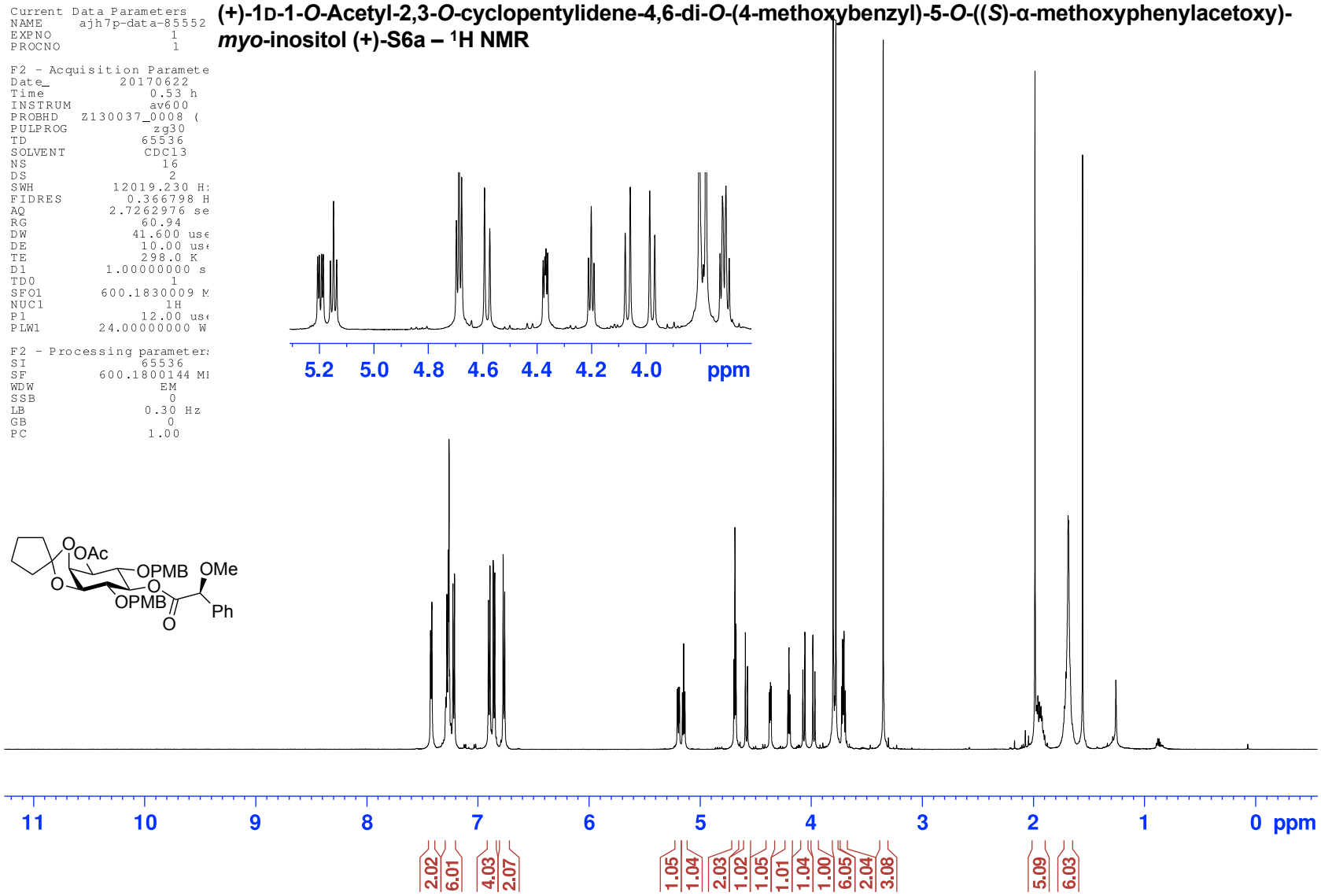


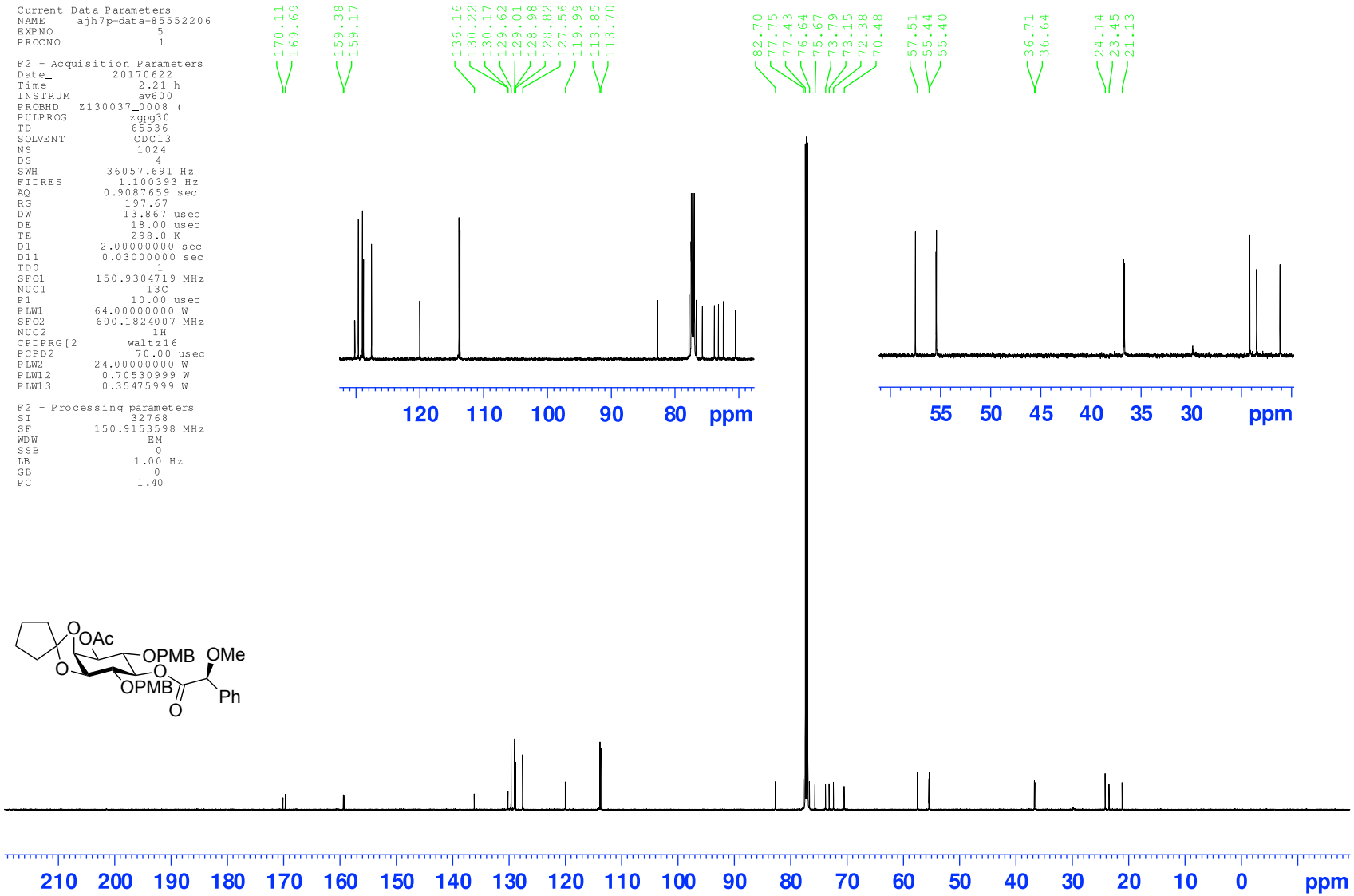
(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-(4-methoxybenzyl)-*myo*-inositol (−)-S5 – ^{13}C NMR



(+)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-(4-methoxybenzyl)-5-*O*-((*S*)-α-methoxyphenylacetoxy)-*myo*-inositol (+)-S6a – ^{1}H NMR



(+)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-(4-methoxybenzyl)-5-*O*-((*S*)-α-methoxyphenylacetoxy)-*myo*-inositol (+)-S6a – ^{13}C NMR



(−) 1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-(4-methoxybenzyl)-5-*O*-((*R*)-α-methoxyphenylacetoxy)-*myo*-inositol (−) S6b – ^{1}H NMR

```
Current Data Parameters
NAME      ajh7(R)p-data-85562206
EXPNO                          1
PROCNO                         1

F2 - Acquisition Parameters
Date_               20170622
Time                   12.32 h
INSTRUM                av600
PROBHD    Z130037_0008 (
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                12019.230 Hz
FIDRES             0.366798 Hz
AQ                 2.7262976 sec
RG                     60.94
DW                    41.600 usec
DE                    10.00 usec
TE                    298.0 K
D1                 1.00000000 sec
TD0                        1
SFO1             600.1830009 MHz
NUC1                      1H
P1                    12.00 usec
PLW1            24.00000000 W

F2 - Processing parameters
SI                     65536
SF               600.1800148 MHz
WDW                       EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
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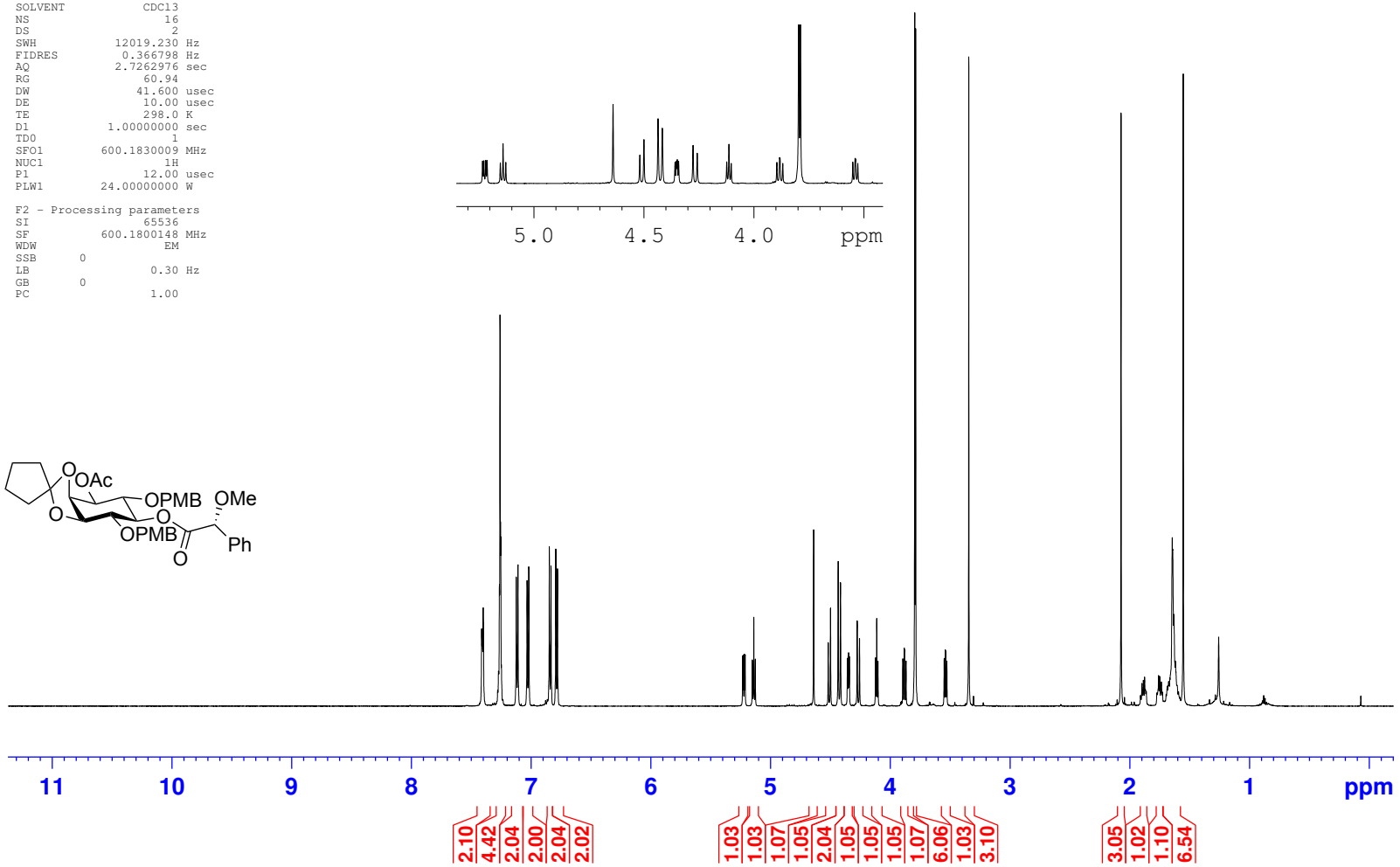

(−) 1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4,6-di-*O*-(4-methoxybenzyl)-5-*O*-((*R*)-α-methoxyphenylacetoxy)-*myo*-inositol (−) S6b – ^{13}C NMR

```
Current Data Parameters
NAME      ajh7(R)p-data-85562206
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170622
Time              13.59 h
INSTRUM            av600
PROBHD    Z130037_0008 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           36057.691 Hz
FIDRES         1.100393 Hz
AQ            0.9087659 sec
RG               197.67
DW               13.867 usec
DE                18.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        150.9304719 MHz
NUC1                13C
P1                10.00 usec
PLW1        64.00000000 W
SFO2        600.1824007 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             70.00 usec
PLW2        24.00000000 W
PLW12        0.70530999 W
PLW13        0.35475999 W

F2 - Processing parameters
SI                32768
SF          150.9153597 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
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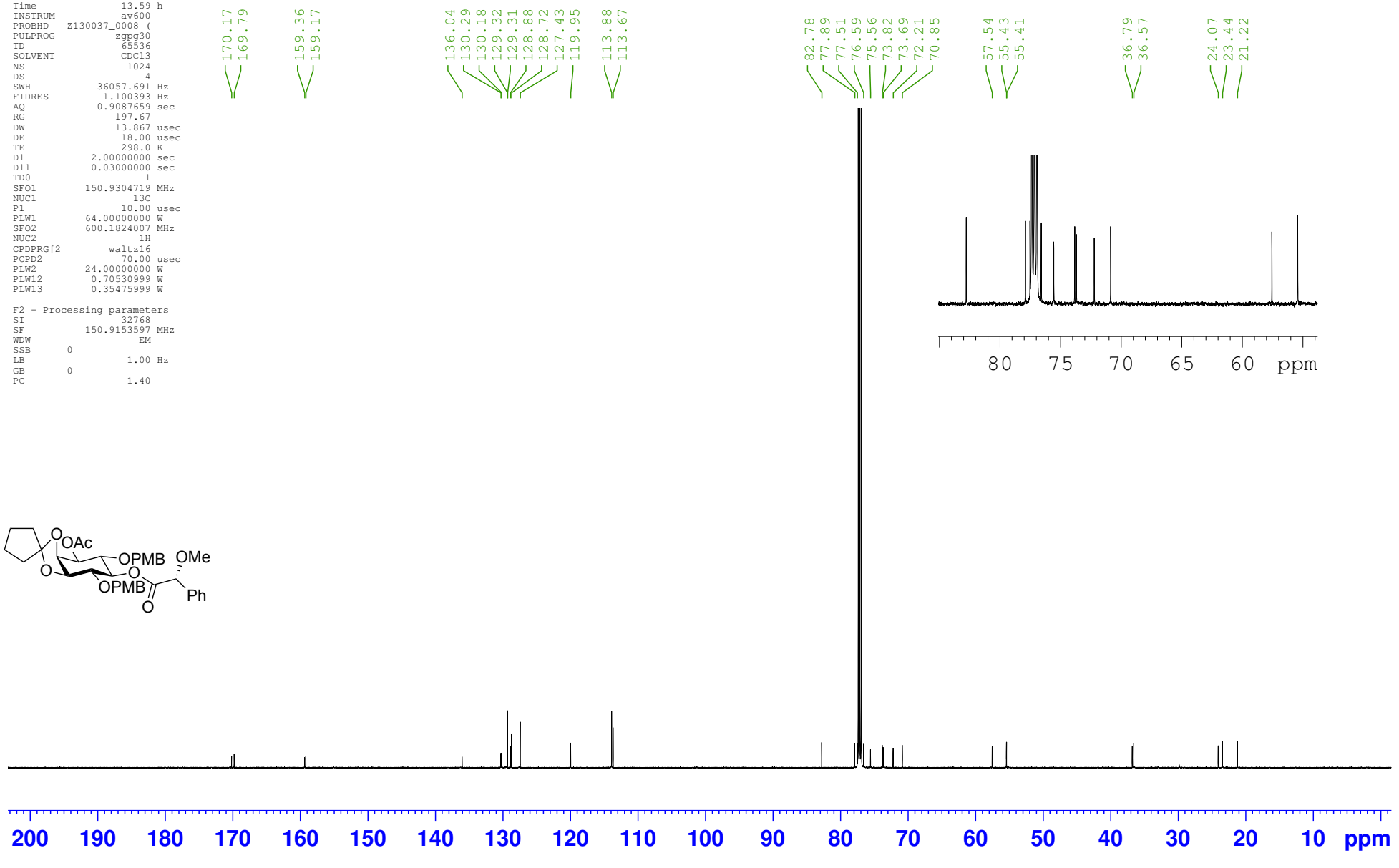
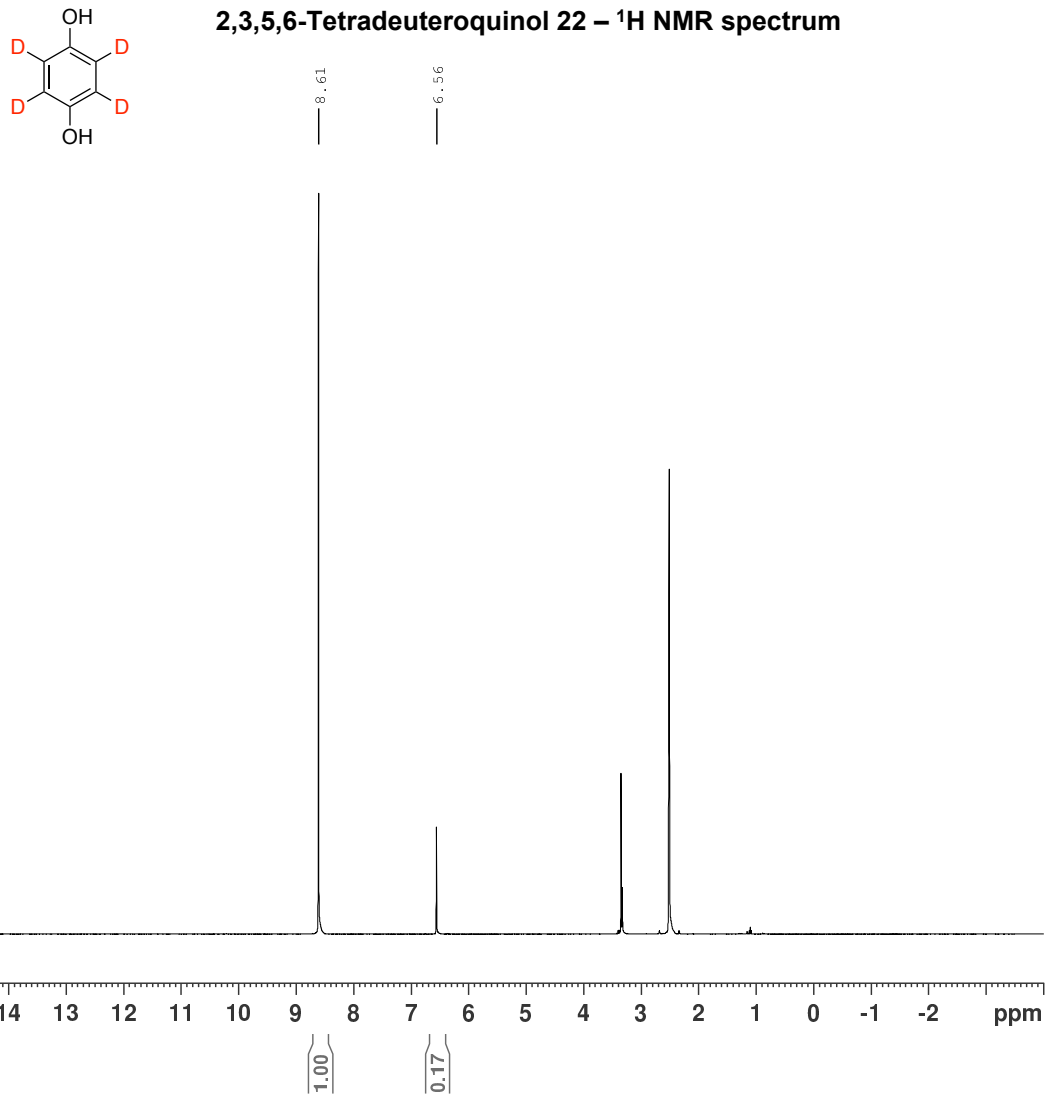


2,3,5,6-Tetradeuteroquinol 22 – ^{1}H NMR spectrum

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Current Data Parameters
NAME       AS-126-01_1H
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20160418
Time              23.12 h
INSTRUM           avh400
PROBHD   Z108618_0873 (
PULPROG             zg60
TD                 65536
SOLVENT             DMSO
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ             4.0894465 sec
RG                 88.17
DW                62.400 usec
DE                 6.50 usec
TE                296.7 K
D1           1.00000000 sec
TD0                    1
SFO1        400.1324008 MHz
NUC1                  1H
P1                14.00 usec
PLW1        14.36999989 W

F2 - Processing parameters
SI                 32768
SF          400.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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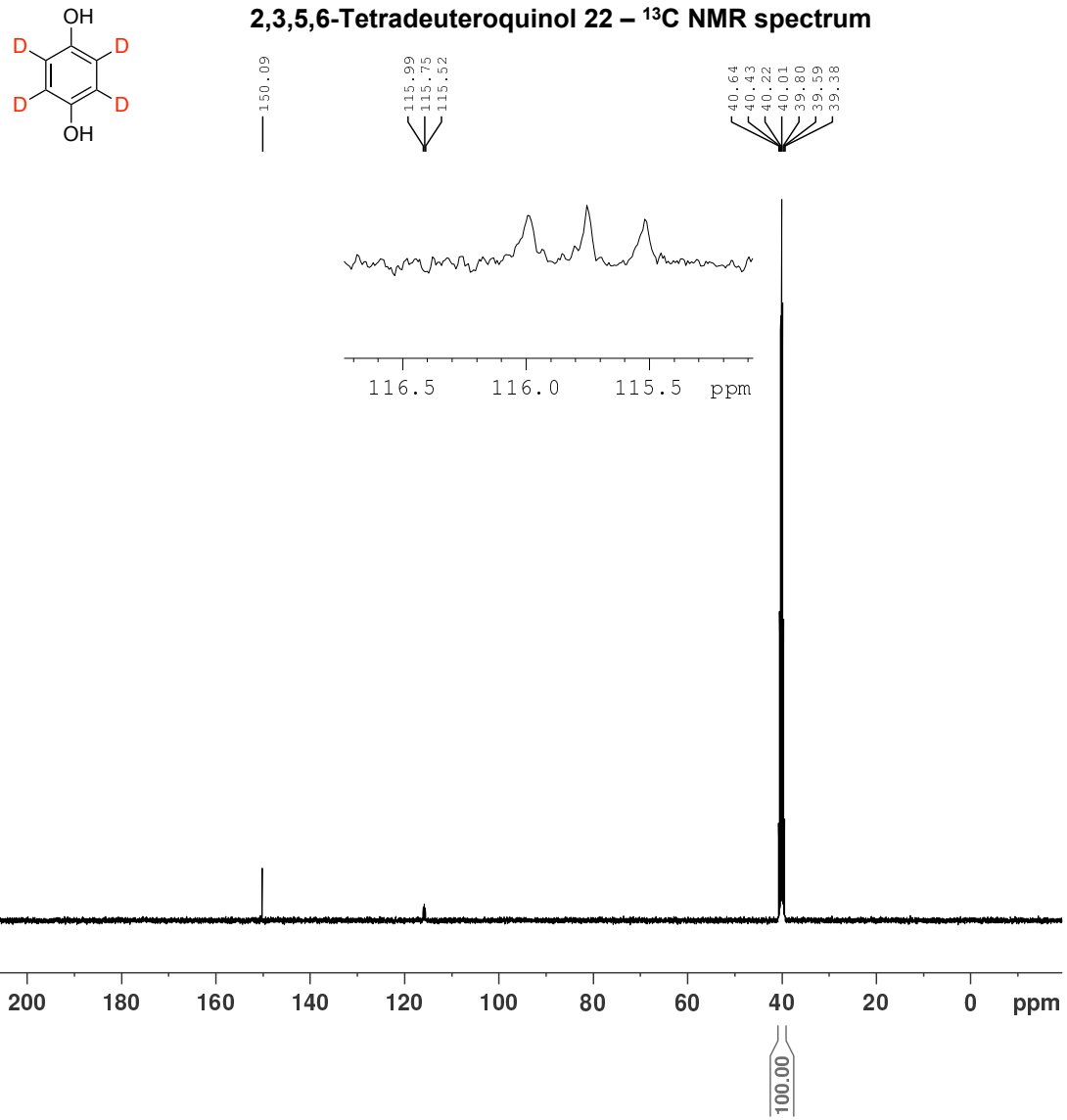


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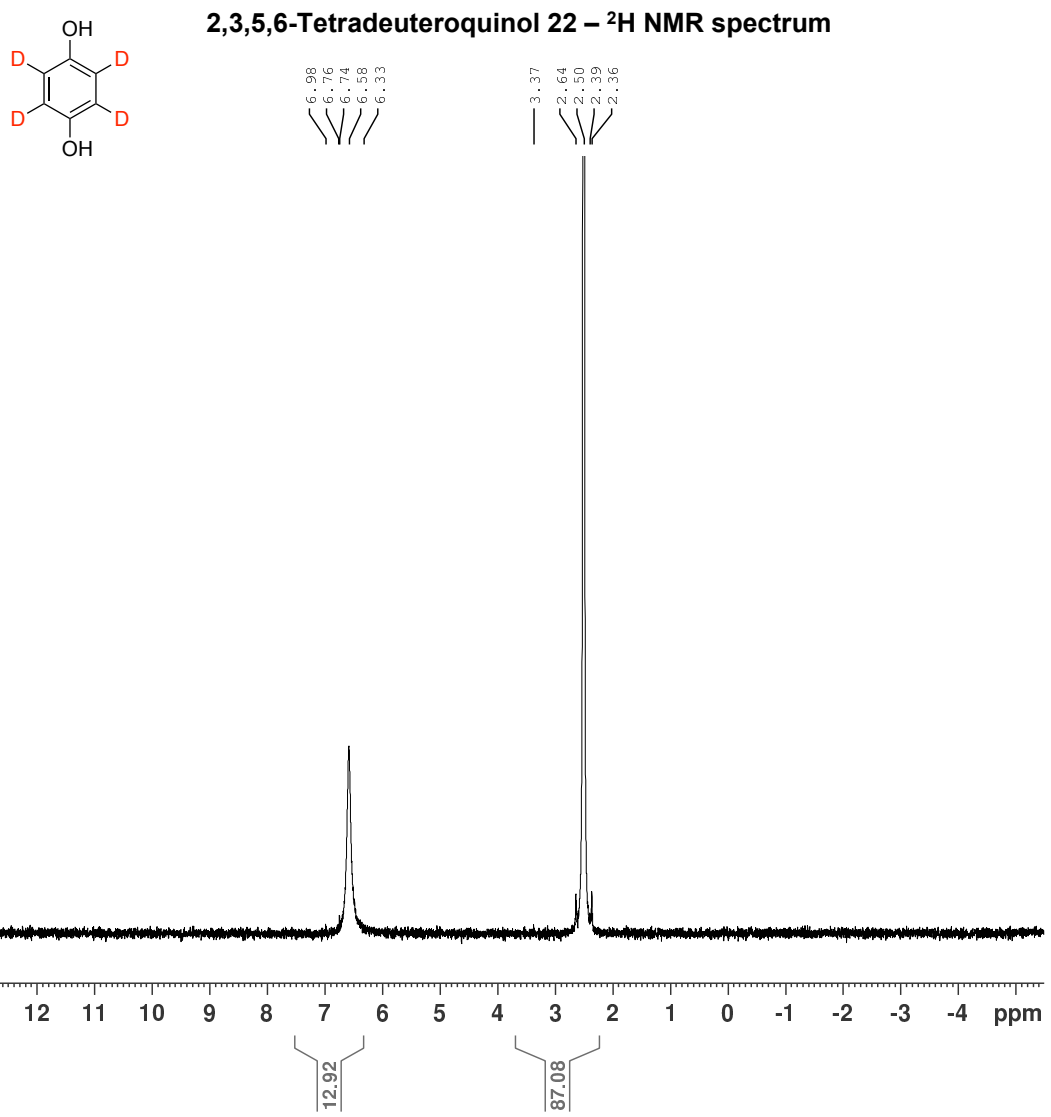
Current Data Parameters
NAME       AS-153-01 13C
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20140429
Time              12.00
INSTRUM           avb400
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT             DMSO
NS                  350
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG                197.74
DW                20.800 usec
DE                 6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

-------- CHANNEL f1 --------
SFO1         100.6228303 MHz
NUC1                 13C
P1                10.00 usec
PLW1         60.95399857 W

-------- CHANNEL f2 --------
SFO2         400.1316005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             70.00 usec
PLW2         14.58800030 W
PLW12         0.29771000 W
PLW13         0.14588000 W

F2 - Processing parameters
SI                32768
SF           100.6127690 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



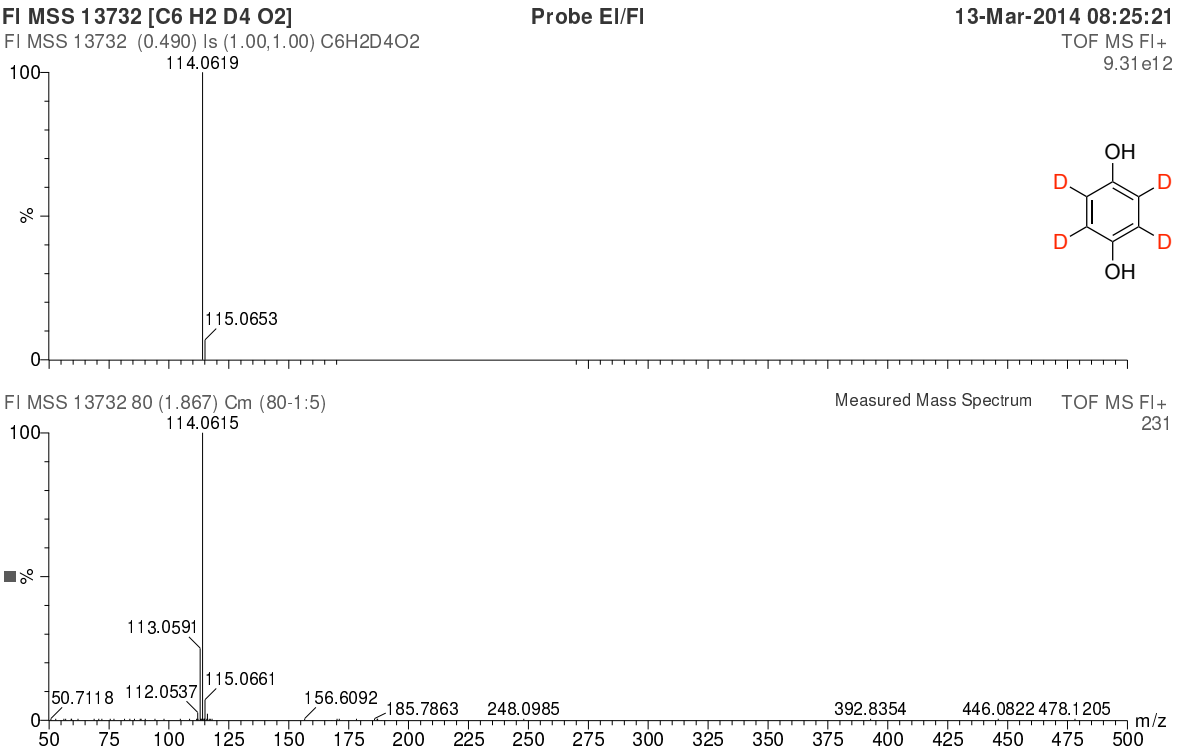

```
Current Data Parameters
NAME         AS-126-01 D
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140314
Time               15.04
INSTRUM          avb500
PROBHD   5 mm PATXI 1H/
PULPROG            zg2h
TD                 8192
SOLVENT            CDCl3
NS                   16
DS                    2
SWH            1534.684 Hz
FIDRES        0.187339 Hz
AQ            2.6689537 sec
RG                    4
DW              325.800 usec
DE                6.50 usec
TE               298.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

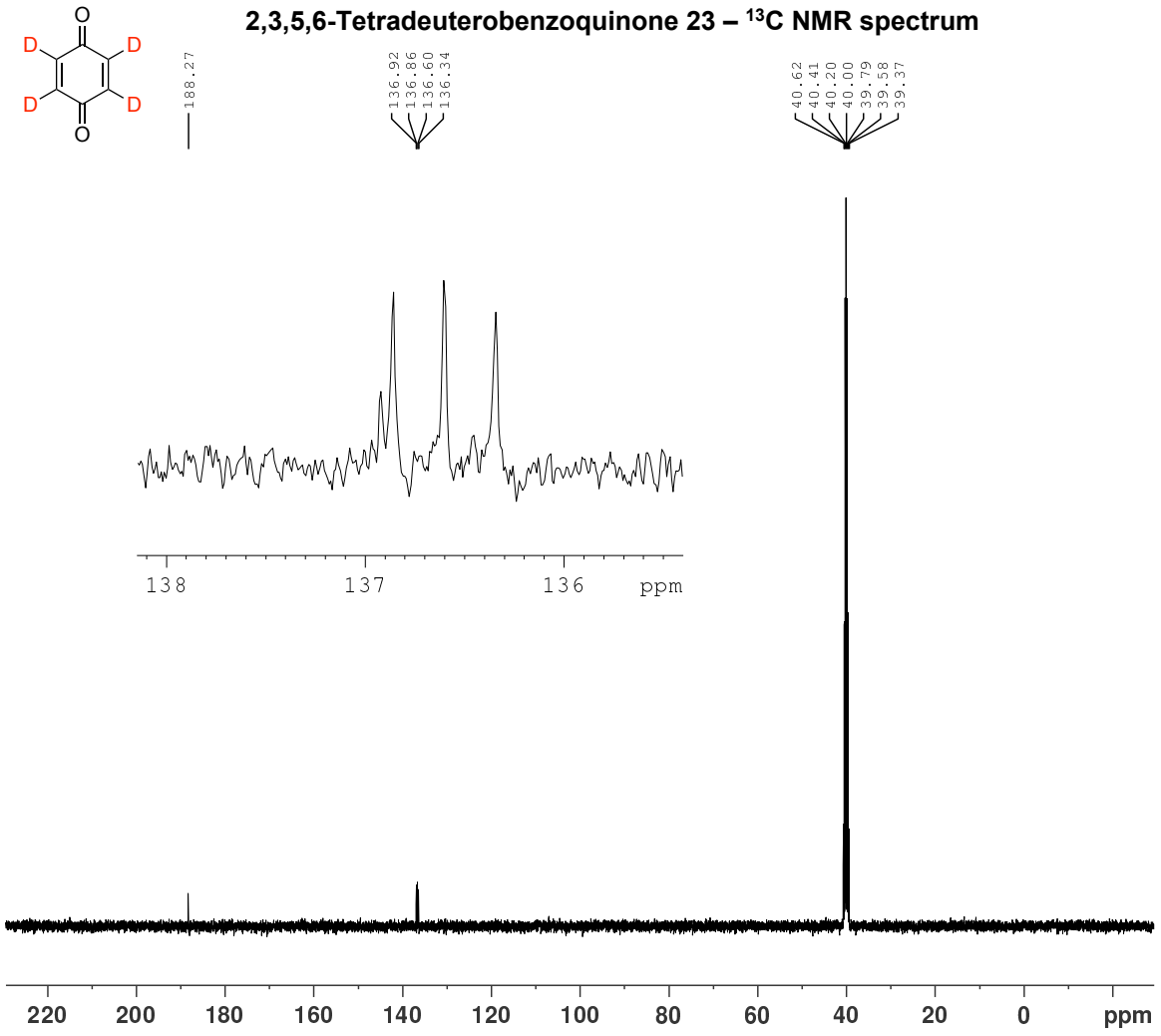
======== CHANNEL f1 ========
SFO1         76.7503579 MHz
NUC1                2H
P1               200.00 usec
PLW1        11.60799980 W

F2 - Processing parameters
SI                32768
SF           76.7500122 MHz
WDW                  no
SSB       0
LB        0 Hz
GB        0
PC                1.00
```

2,3,5,6-Tetradeuteroquinol 22 – Mass spectrum



2,3,5,6-Tetradeuterobenzoquinone 23 – ^{13}C NMR spectrum




```
Current Data Parameters
NAME                  AS-154-01
EXPNO                         2
PROCNO                        1

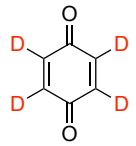
F2 - Acquisition Parameters
Date_              20140430
Time                      2.29
INSTRUM                 avf400
PROBHD    5 mm PABBO BB/
PULPROG                 zgpg30
TD                       32768
SOLVENT                   DMSO
NS                          256
DS                            4
SWH                 26041.666 Hz
FIDRES               0.794729 Hz
AQ                  0.6291456 sec
RG                      205.43
DW                    19.200 usec
DE                     6.50 usec
TE                     297.8 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1           100.6530073 MHz
NUC1                      13C
P1                       9.00 usec
PLW1           58.70000076 W

======== CHANNEL f2 ========
SFO2           400.2516010 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                   90.00 usec
PLW2           16.70000076 W
PLW12           0.32991999 W
PLW13           0.26723999 W

F2 - Processing parameters
SI                       32768
SF             100.6429430 MHz
WDW                        EM
SSB          0
LB                       1.00 Hz
GB           0
PC                       1.40
```

2,3,5,6-Tetradeuterobenzoquinone 23 – ^{2}H NMR spectrum



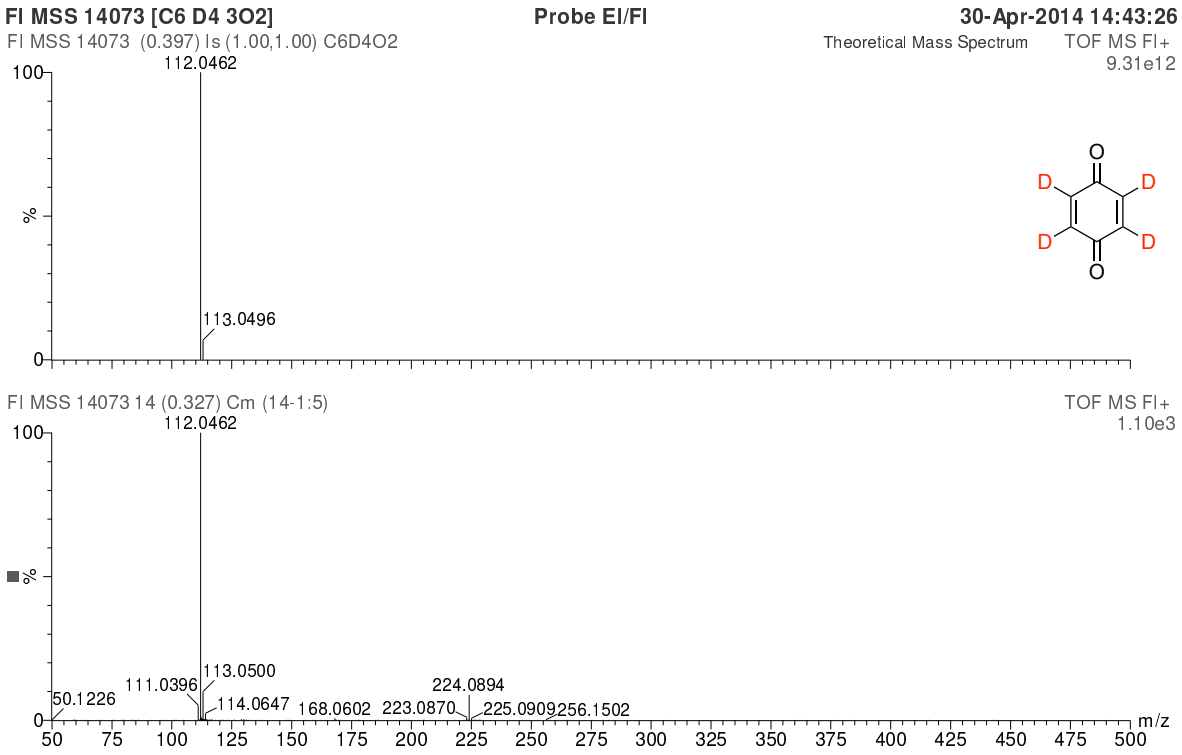

```
Current Data Parameters
NAME         AS-154-01 D
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140429
Time              15.06
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg2h
TD                 4096
SOLVENT            DMSO
NS                  191
DS                    4
SWH           1535.627 Hz
FIDRES        0.374909 Hz
AQ           1.3336576 sec
RG                  1.6
DW              325.600 usec
DE                18.00 usec
TE                298.0 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0                   1

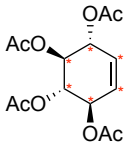
======== CHANNEL f1 ========
SFO1         76.7994801 MHz
NUC1                2H
P1               320.00 usec
PLW1        1.00000000 W

F2 - Processing parameters
SI                 8192
SF           76.7990951 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.00
```

2,3,5,6-Tetradeuterobenzoquinone 23 – Mass spectrum



D_6 (±)-(1*RS*,2*SR*,3*SR*,4*RS*)-Cyclohex-5-ene-1,2,3,4-tetrayl-tetracetate (±)-26 – ^{1}H NMR spectrum



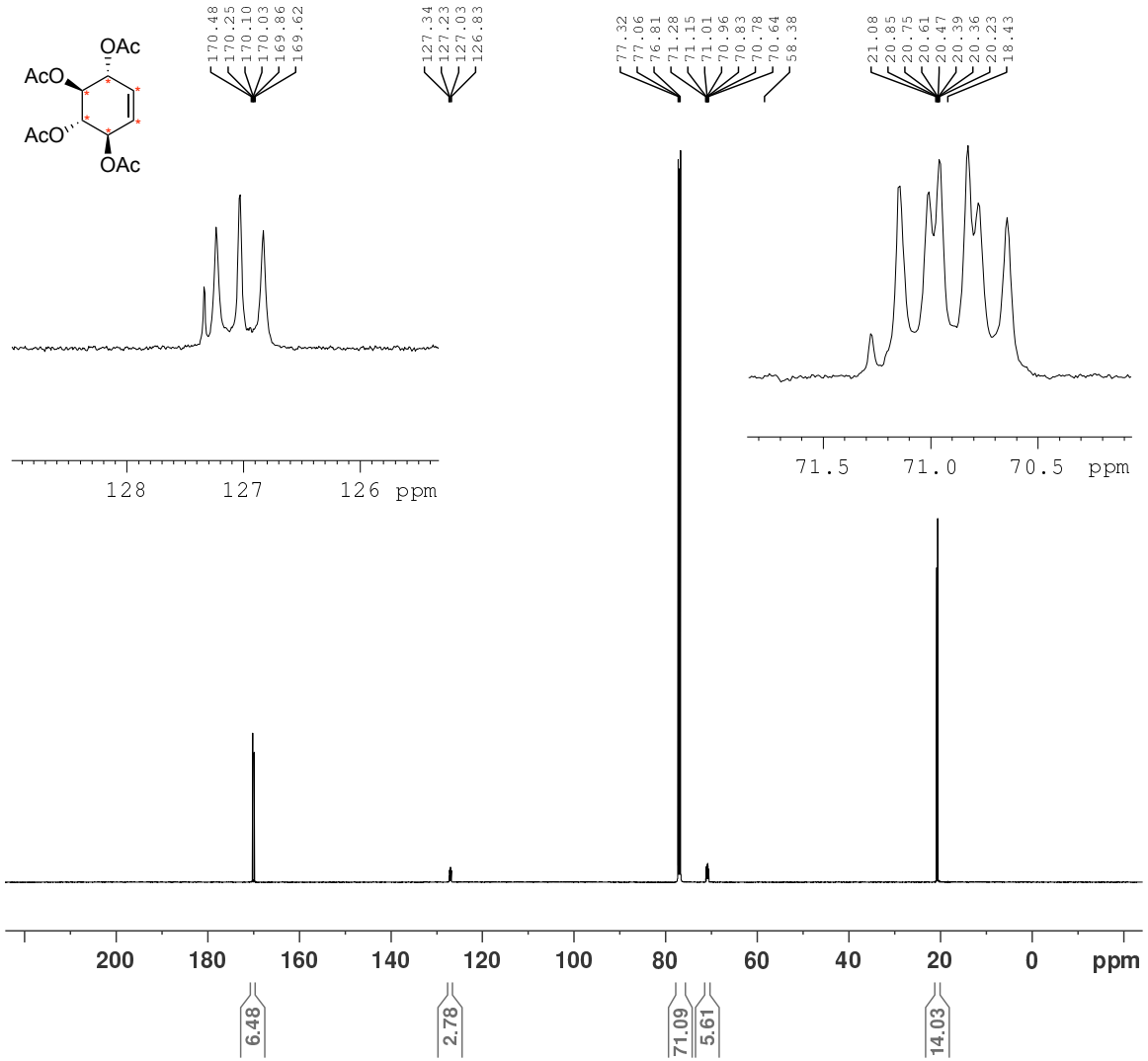

```
Current Data Parameters
NAME         AS-254-01 1H
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141014
Time               15.04
INSTRUM          avg400
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10000.000 Hz
FIDRES         0.152588 Hz
AQ             3.2767999 sec
RG                 321.1
DW                50.000 usec
DE                 6.50 usec
TE                294.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.2024714 MHz
NUC1                1H
P1                12.23 usec
PLW1         11.30000019 W

F2 - Processing parameters
SI                 65536
SF           400.2000131 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

D_6 (±)-(1*RS*,2*SR*,3*SR*,4*RS*)-Cyclohex-5-ene-1,2,3,4-tetrayl-tetracetate (±)-26 – ^{13}C NMR spectrum




```
Current Data Parameters
NAME       AS-254-01 13C
EXPNO                1
PROCNO               1

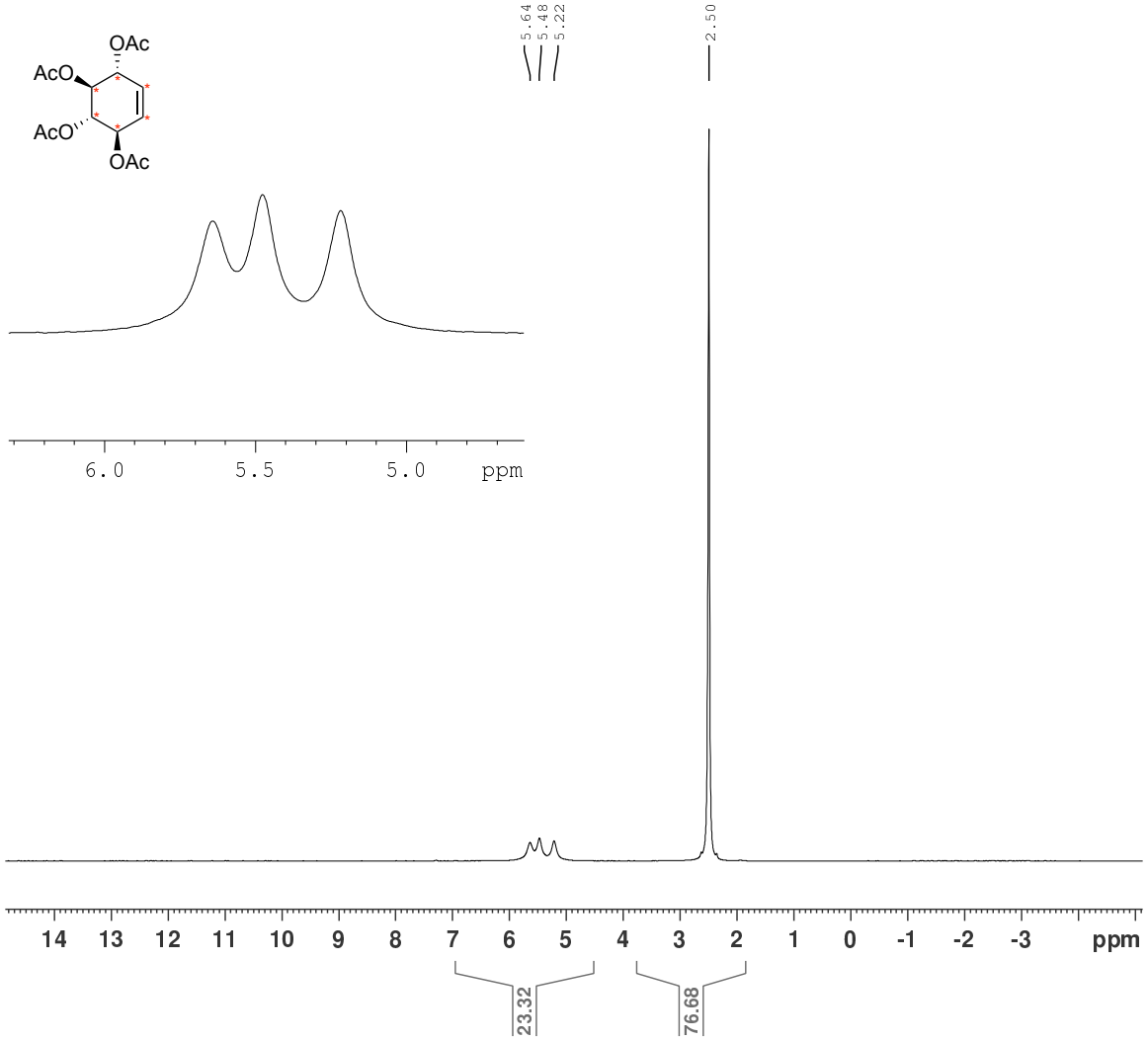
F2 - Acquisition Parameters
Date_          20141015
Time              10.36
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           31250.000 Hz
FIDRES        0.476837 Hz
AQ            1.0485760 sec
RG                  912
DW               16.000 usec
DE               18.00 usec
TE               298.0 K
D1           10.00000000 sec
D11           0.03000000 sec
TD0                  1

-------- CHANNEL f1 --------
SFO1        125.8131152 MHz
NUC1               13C
P1               10.00 usec
PLW1        20.18400002 W

-------- CHANNEL f2 --------
SFO2        500.3020012 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         7.99830008 W
PLW12        0.28119001 W
PLW13        0.17996000 W

F2 - Processing parameters
SI                32768
SF          125.8005351 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

D_6 (±)-(1*RS*,2*SR*,3*SR*,4*RS*)-Cyclohex-5-ene-1,2,3,4-tetrayl-tetracetate (±)-26 – ^2H NMR spectrum




```
Current Data Parameters
NAME         AS-254-01 D
EXPNO                  1
PROCNO                 1

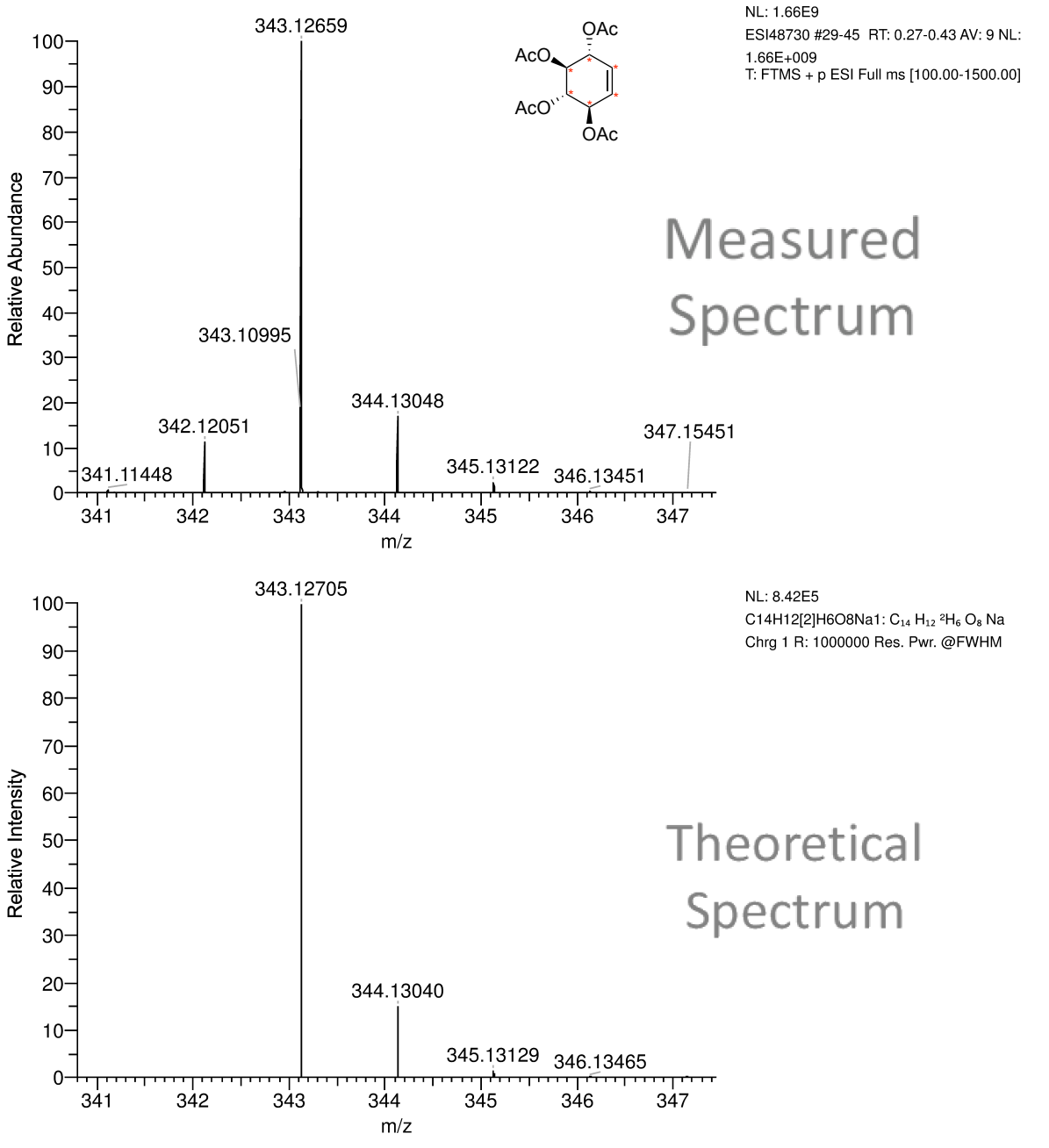
F2 - Acquisition Parameters
Date_           20141015
Time               13.41
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg2h
TD                 4096
SOLVENT           CDCl3
NS                   154
DS                     4
SWH           1535.627 Hz
FIDRES        0.374909 Hz
AQ           1.3336576 sec
RG                     1
DW              325.600 usec
DE               18.00 usec
TE               298.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         76.7994800 MHz
NUC1                  2H
P1               180.00 usec
PLW1         3.30369997 W

F2 - Processing parameters
SI                  8192
SF           76.7991064 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```

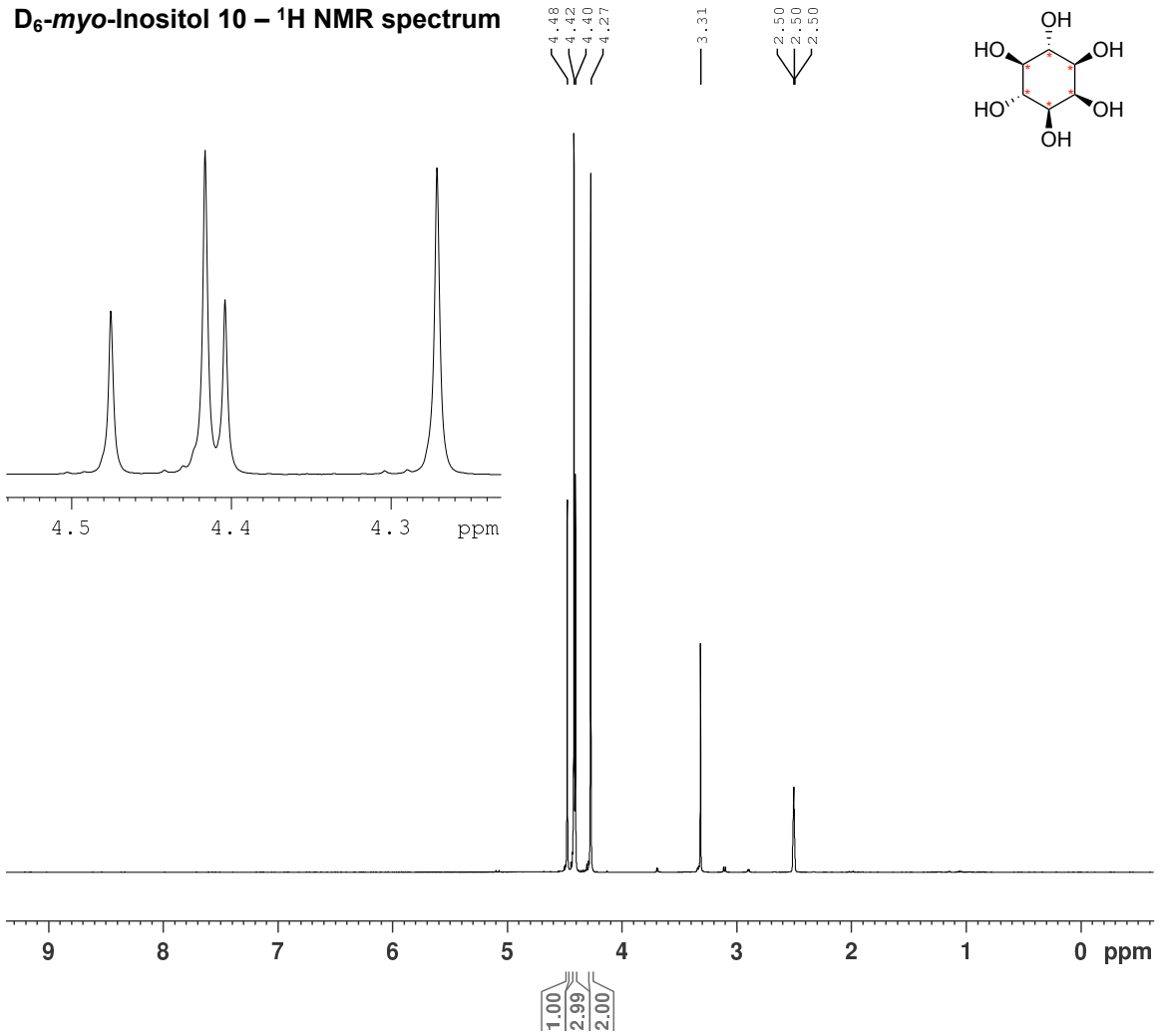
D_6 (±)-(1*RS*,2*SR*,3*SR*,4*RS*)-Cyclohex-5-ene-1,2,3,4-tetrayl-tetracetate (±)-26 – Mass spectrum

R:\data\MSservice\Oct 14\ESI48730.raw 16/10/2014 8:41 am



m/z	Formula	RDB	Delta ppm	Theo. Mass
343.12659	$C_{14}H_{12}{}^{2}H_6O_8{}^{23}Na$	5.5	-1.35	343.12705

D_6-*myo*-Inositol 10 – ^{1}H NMR spectrum



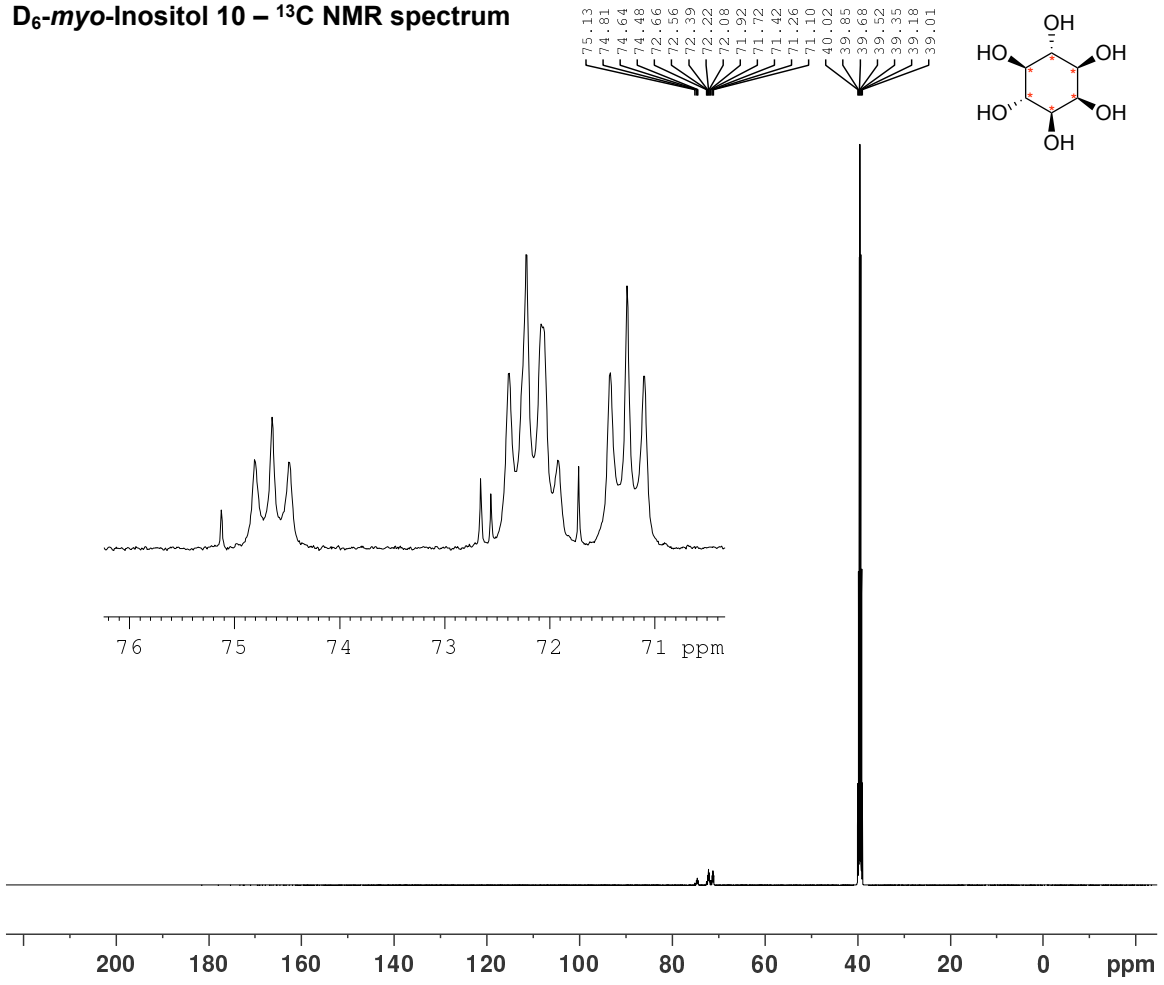

```
Current Data Parameters
NAME                 AS-533-01
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_               20151120
Time                    13.22
INSTRUM                 avb400
PROBHD    5 mm PABBO BB/
PULPROG                  zg30
TD                      65536
SOLVENT                  DMSO
NS                          16
DS                           2
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894465 sec
RG                       157.2
DW                      62.400 usec
DE                       6.50 usec
TE                      298.0 K
D1                1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1              400.1320007 MHz
NUC1                        1H
P1                       10.00 usec
PLW1              14.58800030 W

F2 - Processing parameters
SI                      65536
SF                400.1300035 MHz
WDW                        EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```

D_6-*myo*-Inositol 10 – ^{13}C NMR spectrum




```
Current Data Parameters
NAME       AS-533-01_500
EXPNO                  1
PROCNO                 1

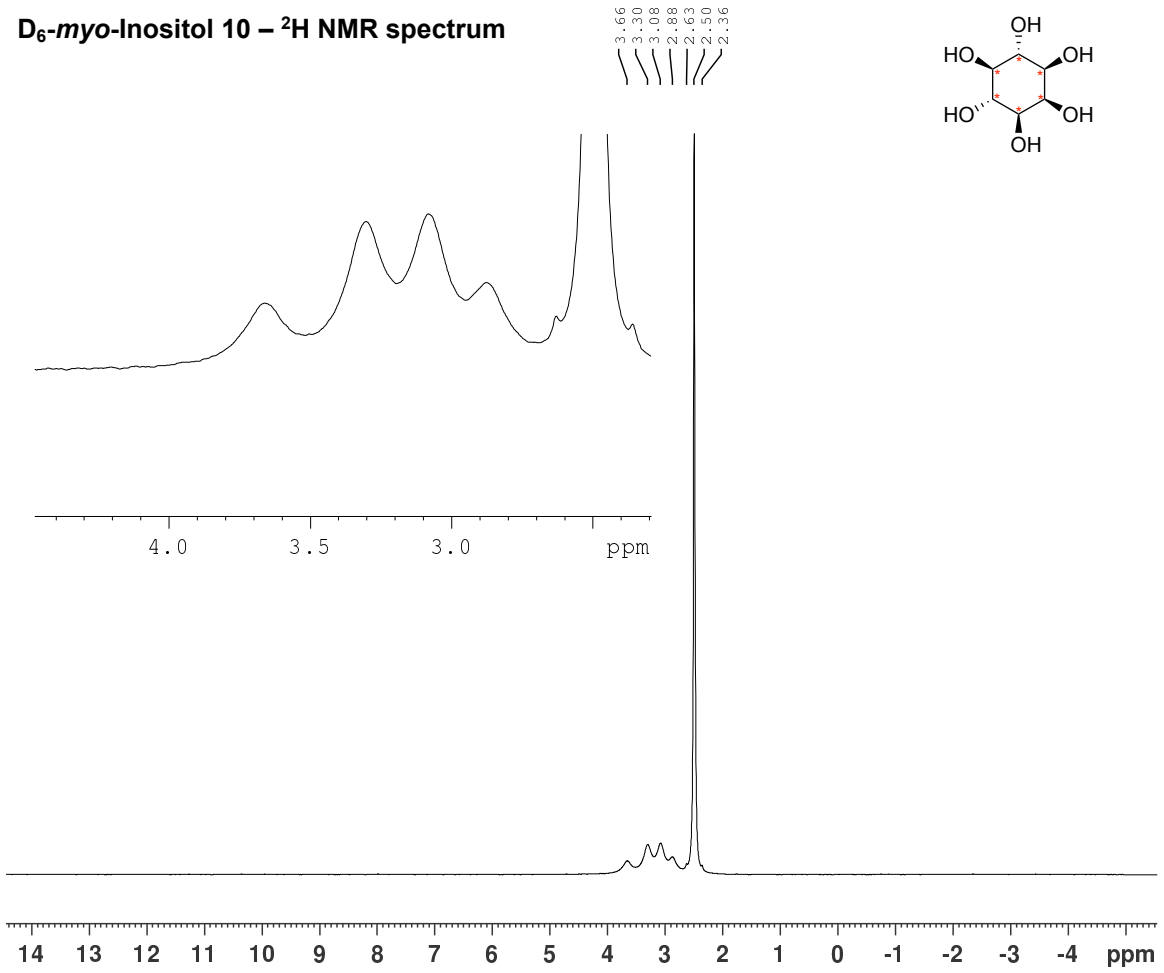
F2 - Acquisition Parameters
Date_           20151122
Time               9.25
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                 3072
DS                    2
SWH           31250.000 Hz
FIDRES        0.476837 Hz
AQ            1.0485760 sec
RG                  912
DW               16.000 usec
DE               18.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

-------- CHANNEL f1 --------
SFO1         125.8131152 MHz
NUC1                13C
P1                10.00 usec
PLW1        20.18400002 W

-------- CHANNEL f2 --------
SFO2         500.3020012 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2         7.99830008 W
PLW12        0.28119001 W
PLW13        0.17996000 W

F2 - Processing parameters
SI                 32768
SF           125.8005917 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

D_6-*myo*-Inositol 10 – ^2H NMR spectrum




```
Current Data Parameters
NAME         AS-533-01_D
EXPNO                  1
PROCNO                 1

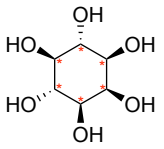
F2 - Acquisition Parameters
Date_           20151123
Time               16.48
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg2h
TD                 4096
SOLVENT           CDCl3
NS                    65
DS                     4
SWH            1535.627 Hz
FIDRES         0.374909 Hz
AQ            1.3336576 sec
RG                     1
DW              325.600 usec
DE               18.00 usec
TE               298.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

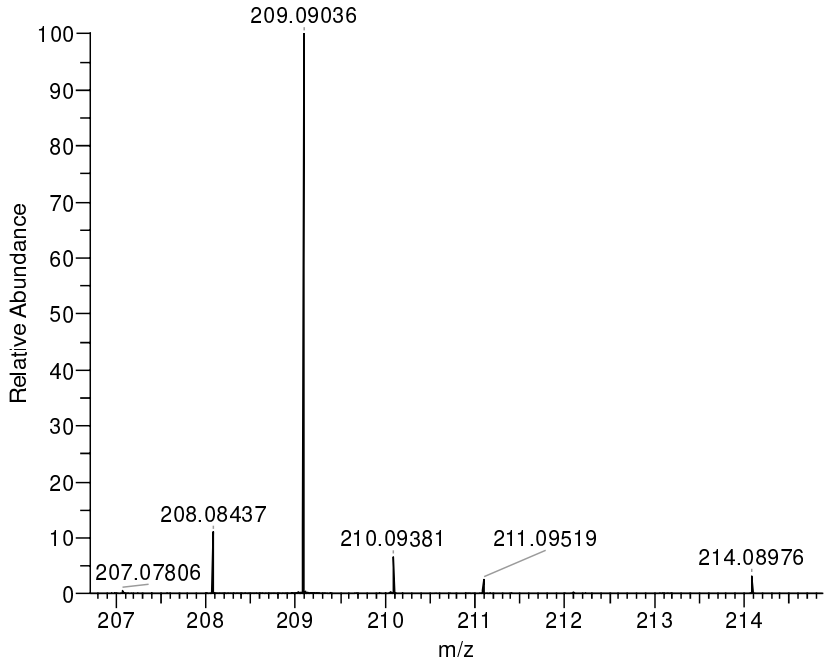
======== CHANNEL f1 ========
SFO1         76.7994800 MHz
NUC1                2H
P1               180.00 usec
PLW1         3.30369997 W

F2 - Processing parameters
SI                  8192
SF           76.7991383 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.00
```

D_6-*myo*-Inositol 10 – Mass spectrum

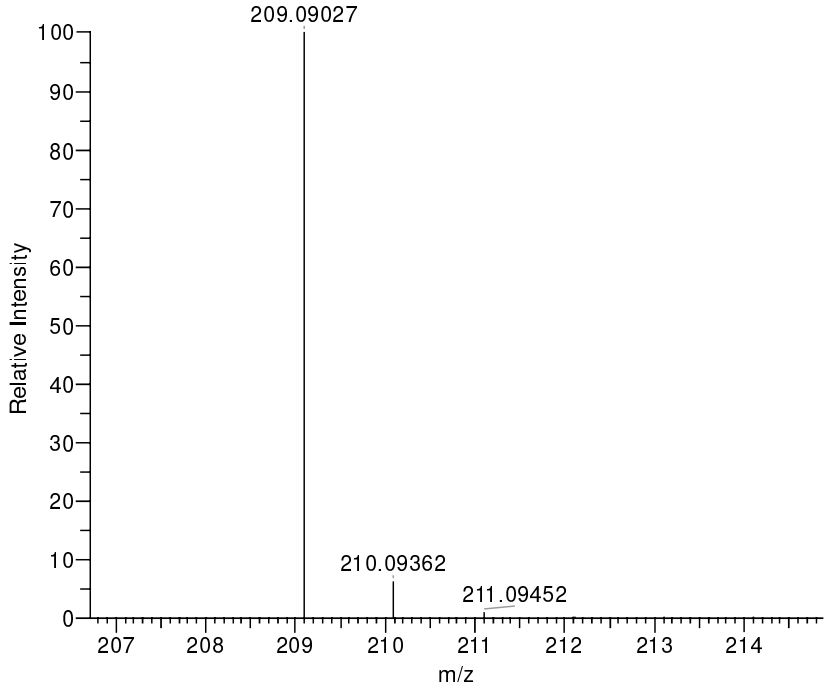
W:\data\Nov 15\ESI54796.raw 23/11/2015 8:46 am





NL: 1.44E7
ESI54796 #11-26 RT: 0.12-0.29 AV: 8 NL: 1.44E+007
T: FTMS {1,1} + p ESI Full lock ms [80.00-1600.00]

Measured Spectrum

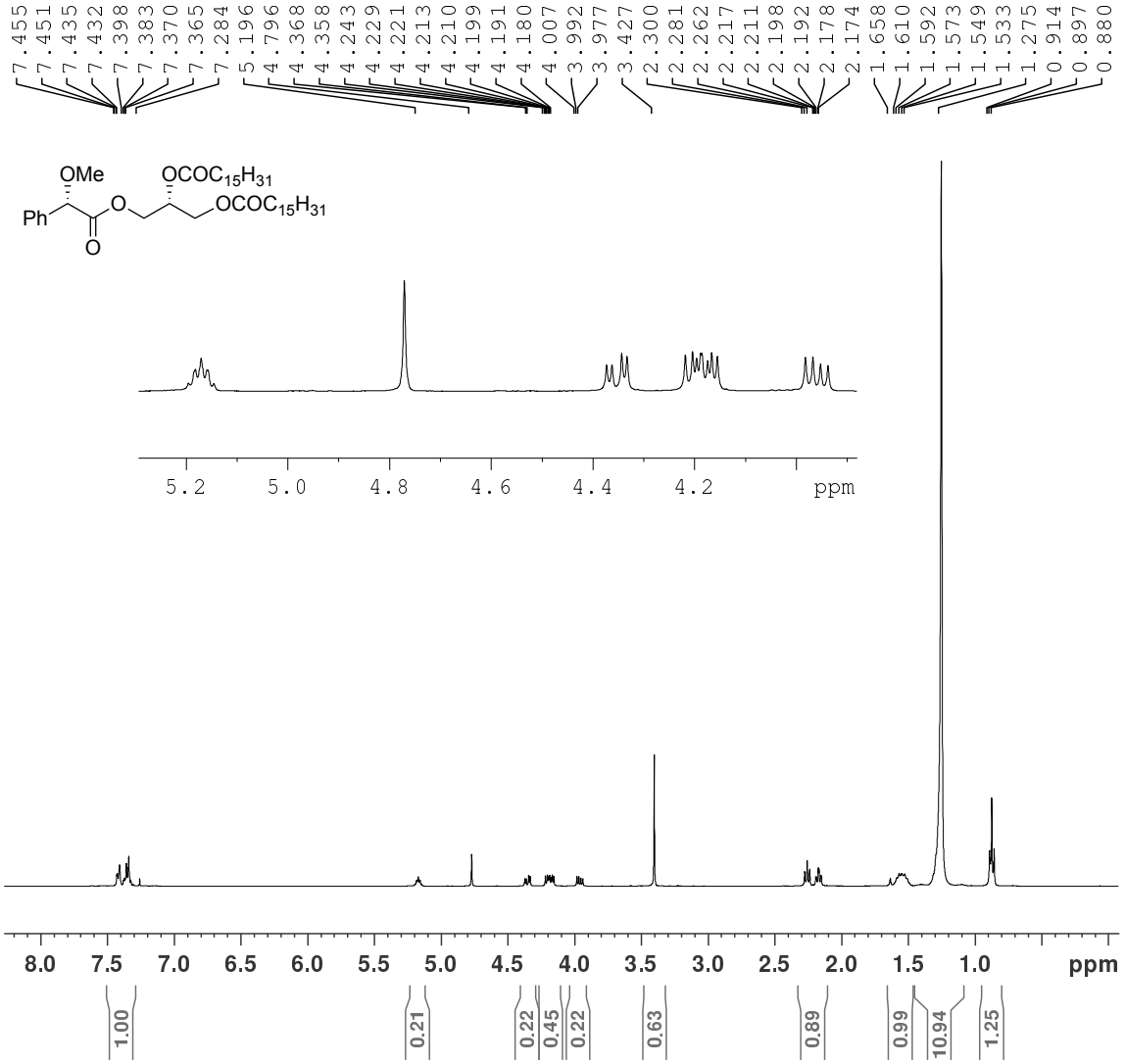


NL: 9.23E5
C6H6[2]H6O6Na1: $C_6\,H_6\,^2H_6\,O_6\,Na$ Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

Index	m/z	Formula	Score	RDB	Delta ppm	OriginalFormula	Theo. Mass
1	209.09036	$C_6H_6{}^2H_6O_6{}^{23}Na$	0	0.5	0.44	C6H6[2]H6O6...	209.09027

(*R*)-(+)-3-((*S*)-2-Methoxy-2-phenylacetoxy)-1,2-dipalmitoyl-*sn*-glycerol (+)-S7a – ^{1}H NMR spectrum



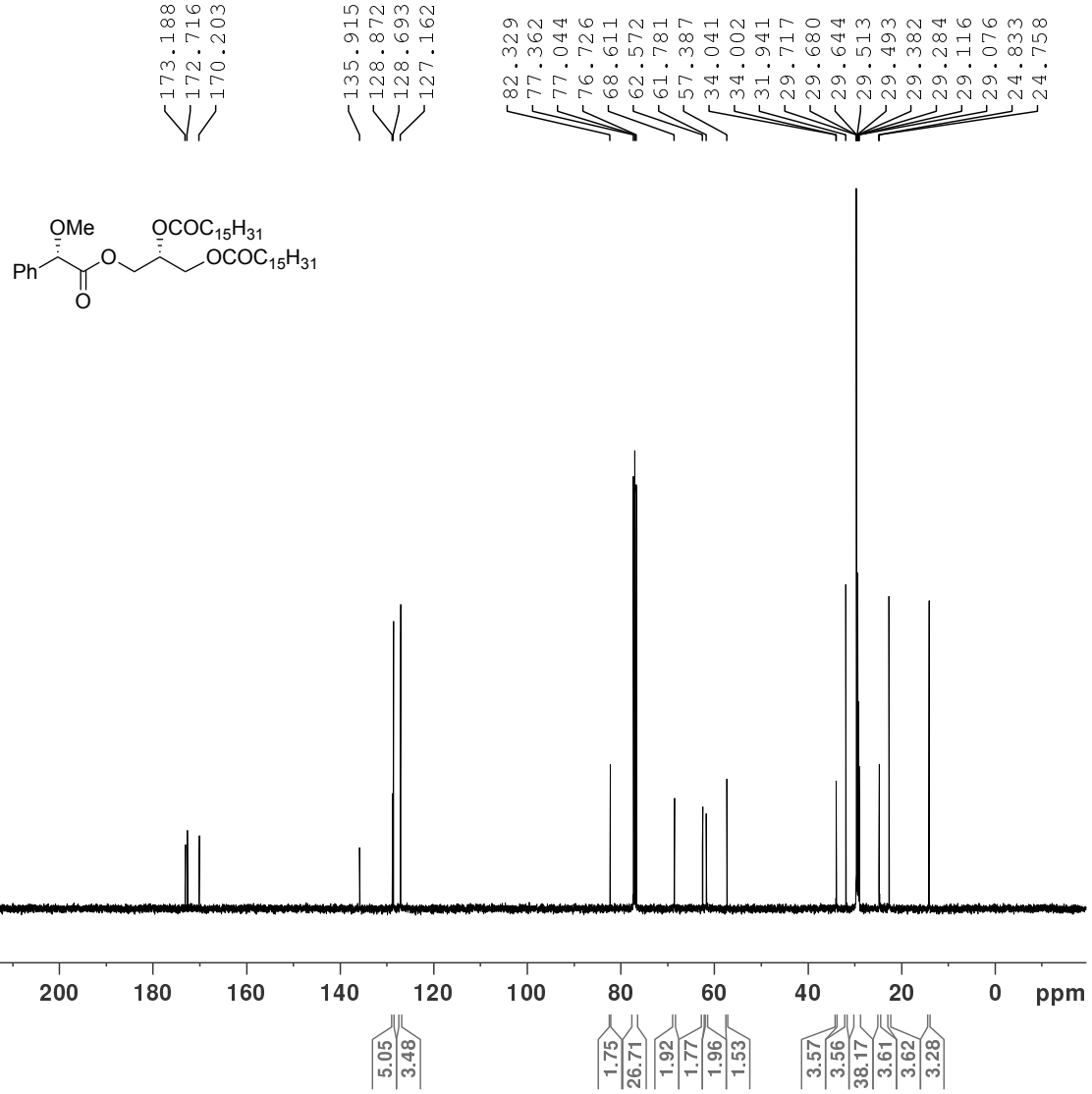

```
Current Data Parameters
NAME                  AS-431-S
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20150626
Time                     16.57
INSTRUM                avg400
PROBHD    5 mm PABBO BB/
PULPROG                  zg60
TD                      65536
SOLVENT                 CDCl3
NS                           8
DS                           2
SWH                 10000.000 Hz
FIDRES                0.152588 Hz
AQ                    3.2767999 sec
RG                       27.94
DW                       50.000 usec
DE                        6.50 usec
TE                       294.4 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                400.2024714 MHz
NUC1                        1H
P1                       14.00 usec
PLW1                14.00000000 W

F2 - Processing parameters
SI                           65536
SF                  400.2000101 MHz
WDW                             EM
SSB          0
LB                        0.30 Hz
GB           0
PC                        1.00
```

(*R*)-(+)-3-((*S*)-2-Methoxy-2-phenylacetoxy)-1,2-dipalmitoyl-*sn*-glycerol (+)-S7a – ^{13}C NMR spectrum




```
Current Data Parameters
NAME                  AS-431-S
EXPNO                        3
PROCNO                       1

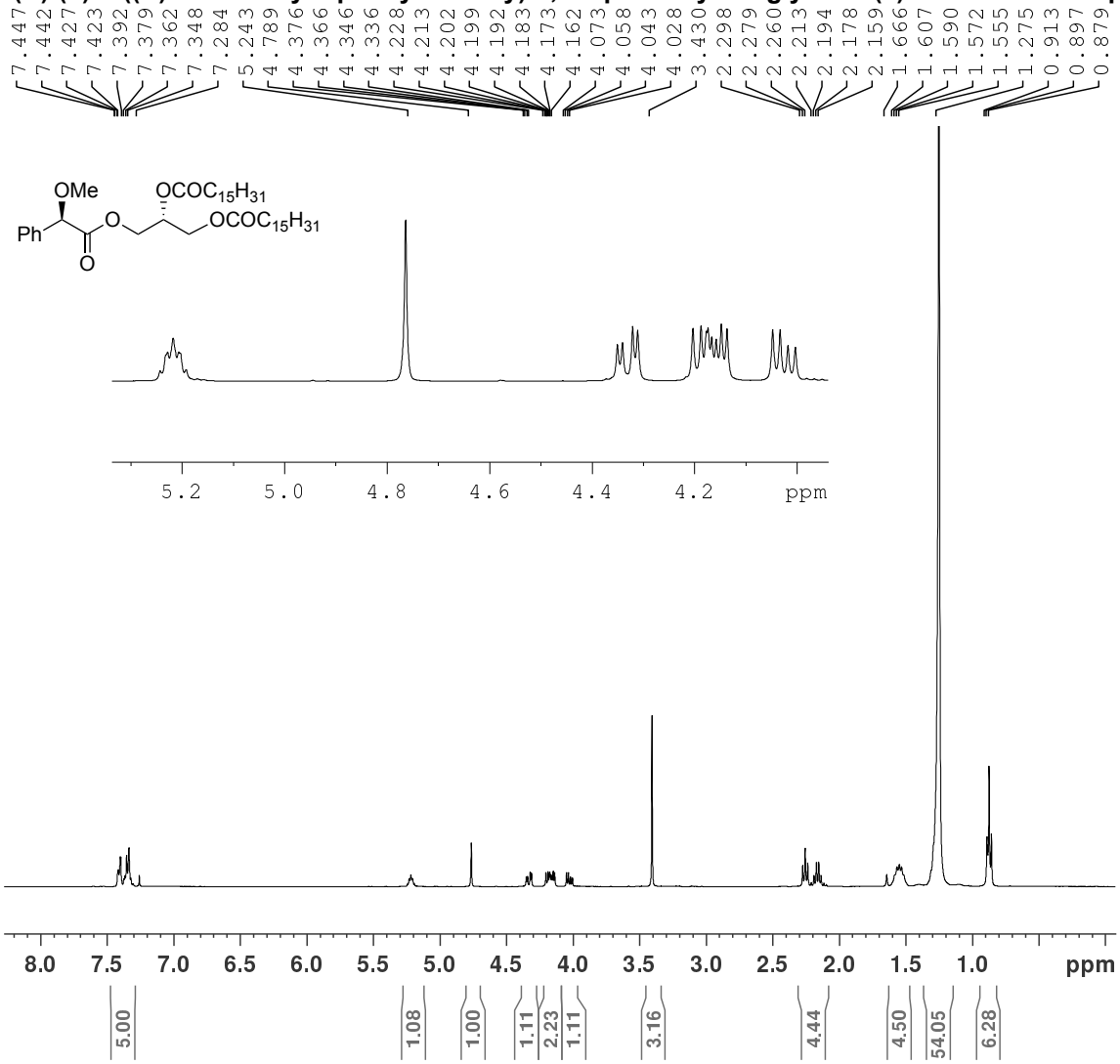
F2 - Acquisition Parameters
Date_                 20150626
Time                     20.06
INSTRUM                avg400
PROBHD   5 mm PABBO BB/
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        256
DS                          4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631488 sec
RG                      206.87
DW                      20.800 usec
DE                       6.50 usec
TE                      295.5 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1               100.6404326 MHz
NUC1                       13C
P1                       10.00 usec
PLW1               56.00000000 W

======== CHANNEL f2 ========
SFO2               400.2016008 MHz
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                    90.00 usec
PLW2               14.00000000 W
PLW12               0.33877000 W
PLW13               0.27440000 W

F2 - Processing parameters
SI                       32768
SF                 100.6303700 MHz
WDW                         EM
SSB          0
LB                       1.00 Hz
GB           0
PC                       1.40
```

(*R*)-(+)-3-((*R*)-2-Methoxy-2-phenylacetoxy)-1,2-dipalmitoyl-*sn*-glycerol (–)-S7b – ^{1}H NMR spectrum



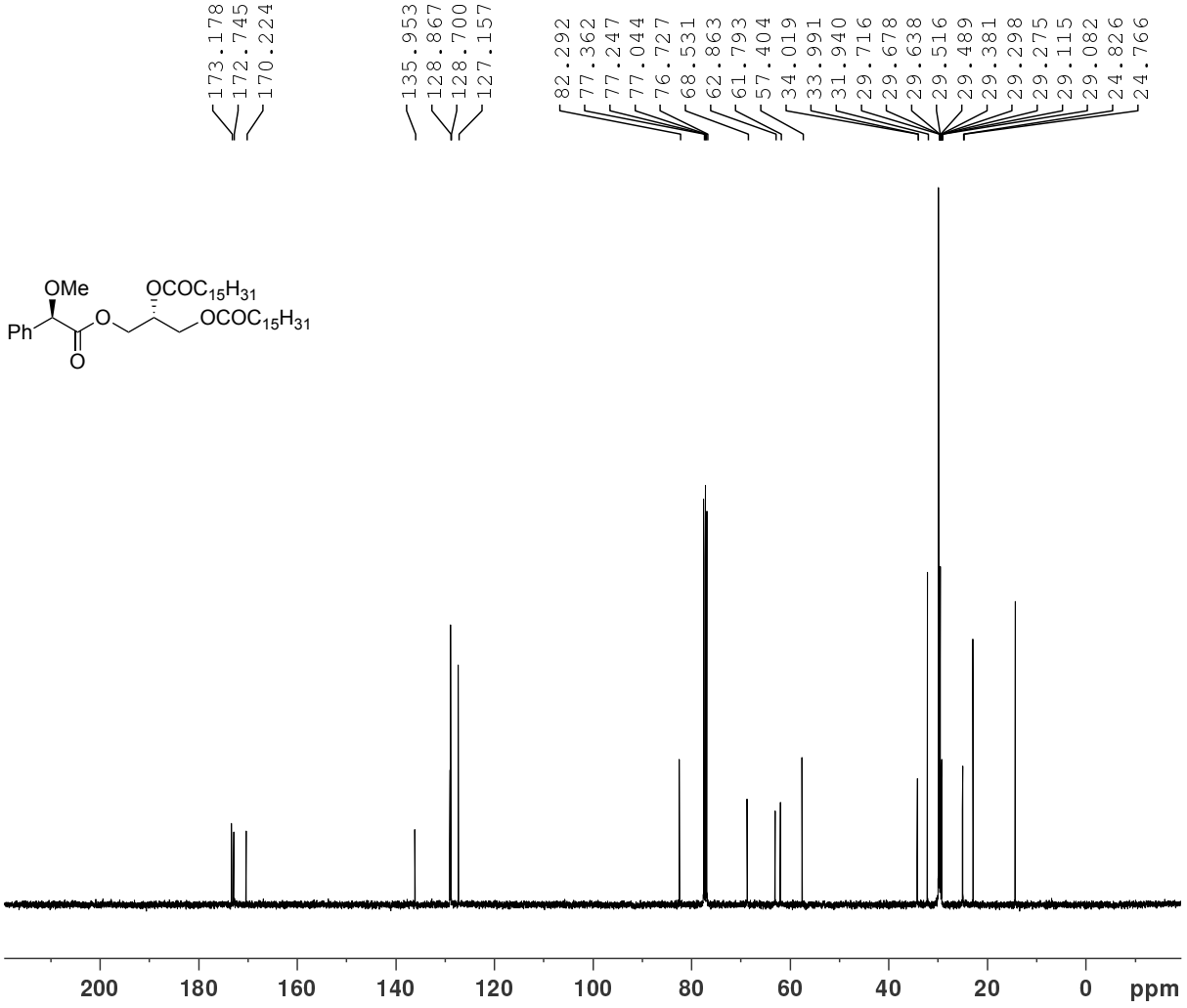

```
Current Data Parameters
NAME                  AS-431-R
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20150626
Time                     18.12
INSTRUM                avg400
PROBHD    5 mm PABBO BB/
PULPROG                  zg60
TD                      65536
SOLVENT                 CDCl3
NS                           8
DS                           2
SWH                10000.000 Hz
FIDRES             0.152588 Hz
AQ                 3.2767999 sec
RG                       27.94
DW                      50.000 usec
DE                       6.50 usec
TE                      294.1 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1              400.2024714 MHz
NUC1                       1H
P1                      14.00 usec
PLW1              14.00000000 W

F2 - Processing parameters
SI                       65536
SF                400.2000101 MHz
WDW                        EM
SSB          0
LB                       0.30 Hz
GB           0
PC                       1.00
```

(*R*)-(+)-3-((*R*)-2-Methoxy-2-phenylacetoxy)-1,2-dipalmitoyl-*sn*-glycerol (–)-S7b – ^{13}C NMR spectrum




```
Current Data Parameters
NAME                  AS-431-R
EXPNO                        3
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20150627
Time                      4.39
INSTRUM                avg400
PROBHD   5 mm PABBO BB/
PULPROG                zgpg30
TD                        65536
SOLVENT                  CDCl3
NS                         256
DS                           4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                   1.3631488 sec
RG                      206.87
DW                      20.800 usec
DE                       6.50 usec
TE                      295.5 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
SFO1                100.6404326 MHz
NUC1                        13C
P1                        10.00 usec
PLW1                56.00000000 W

======== CHANNEL f2 ========
SFO2                400.2016008 MHz
NUC2                        1H
CPDPRG[2                waltz16
PCPD2                     90.00 usec
PLW2                14.00000000 W
PLW12                0.33877000 W
PLW13                0.27440000 W

F2 - Processing parameters
SI                       32768
SF                  100.6303591 MHz
WDW                         EM
SSB          0
LB                        1.00 Hz
GB           0
PC                        1.40
```

(*R*)-(+)-1-*O*-Stearoyl-2,3-di-*O*-((*S*)-α-methoxyphenylacetoxy)-*sn*-glycerol (+)-S8a – ^{1}H NMR spectrum

```
Current Data Parameters
NAME      ajf76(S)-data-Hnmr
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20160927
Time                  20.42
INSTRUM             avc500
PROBHD    5 mm CPDUL 13C
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       4
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ                3.1719425 sec
RG                     3.56
DW                   48.400 usec
DE                   10.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           500.3030896 MHz
NUC1                   1H
P1                   15.00 usec
PLW1            7.99830008 W

F2 - Processing parameters
SI                   65536
SF             500.3000133 MHz
WDW                    EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
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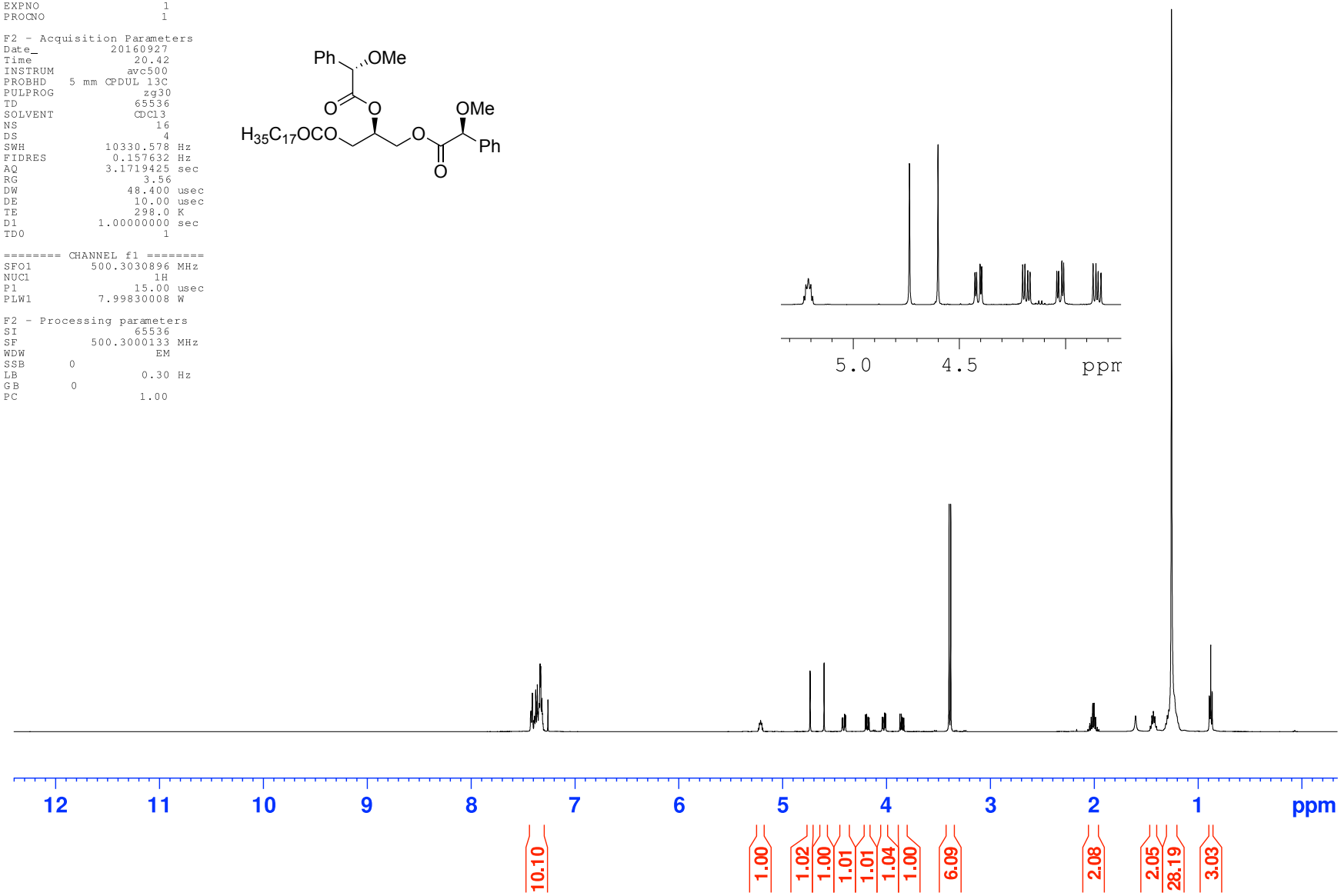
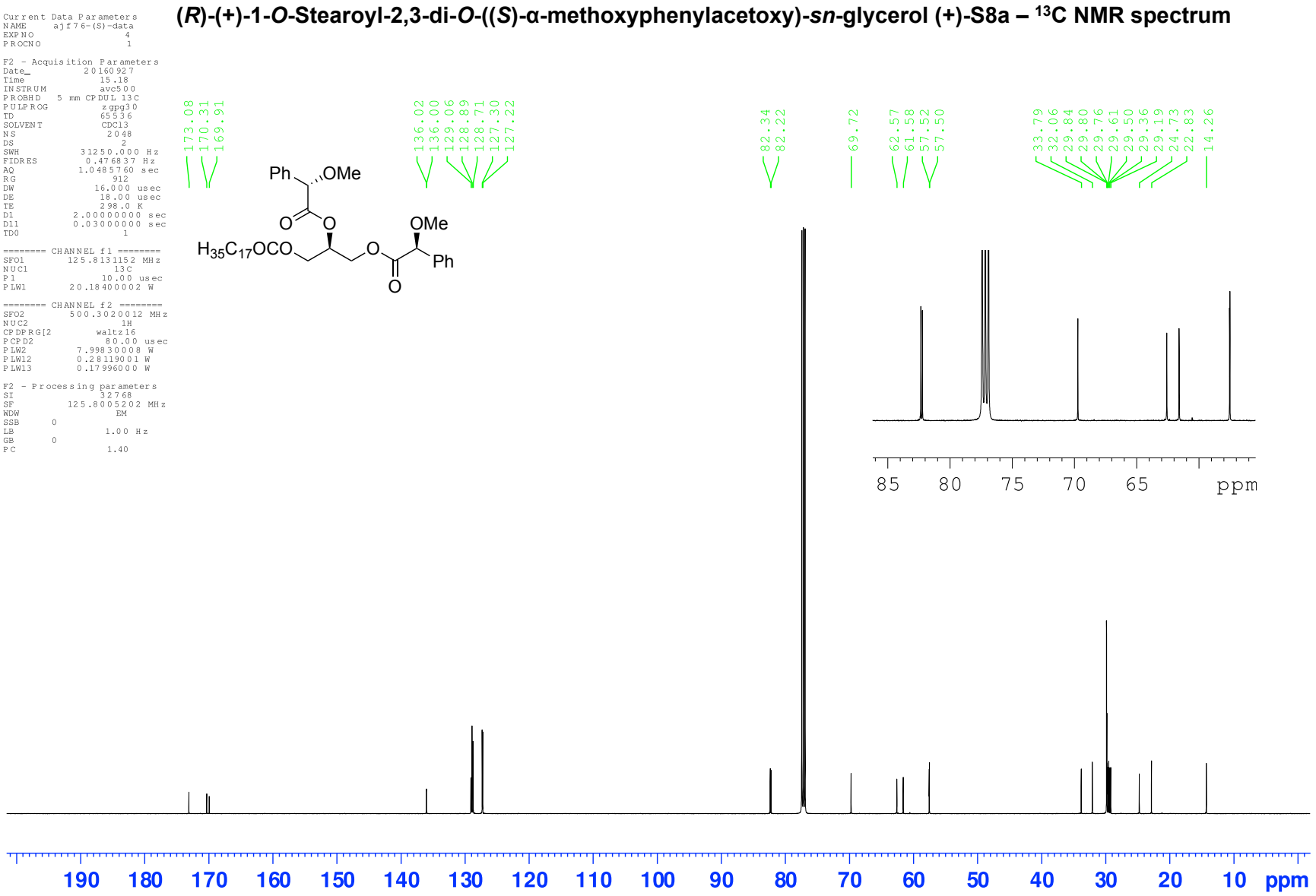


(*R*)-(+)-1-*O*-Stearoyl-2,3-di-*O*-((*S*)-α-methoxyphenylacetoxy)-*sn*-glycerol (+)-S8a – ^{13}C NMR spectrum



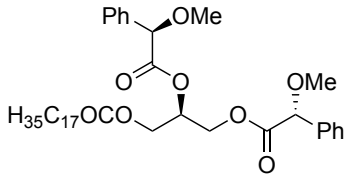
(*R*)-(−)-1-*O*-Stearoyl-2,3-di-*O*-((*R*)-α-methoxyphenylacetoxy)-*sn*-glycerol (−)-S8b – ^{1}H NMR spectrum

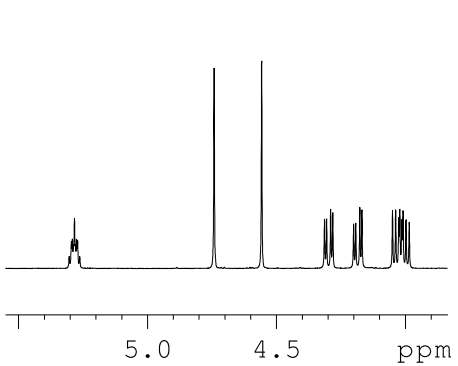
```
Current Data Parameters
NAME      ajf76-(R)-data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160927
Time              16.25
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   4
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719425 sec
RG                3.56
DW               48.400 usec
DE               10.00 usec
TE               298.0 K
D1           1.00000000 sec
TD0                  1

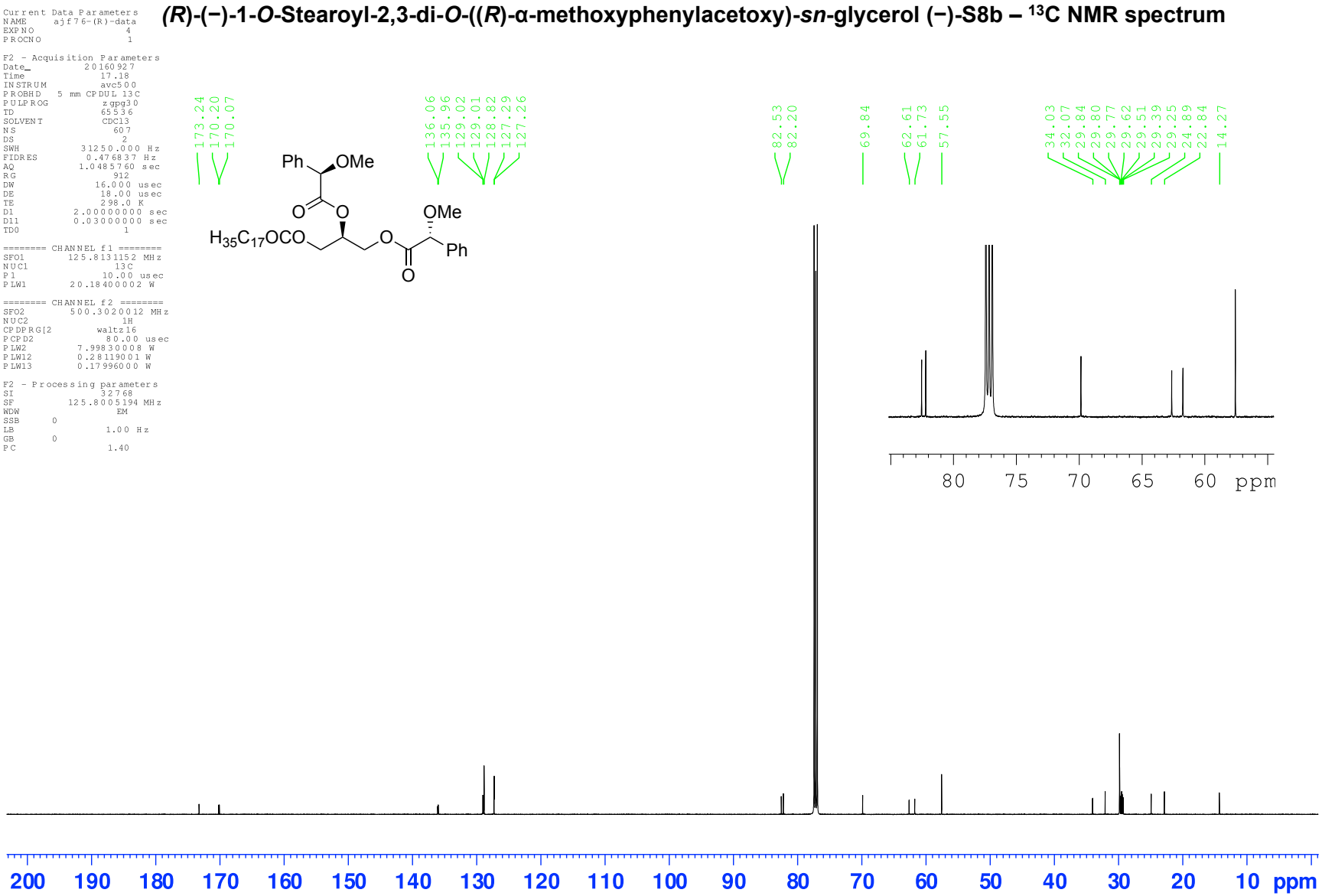
======== CHANNEL f1 ========
SFO1       500.3030896 MHz
NUC1               1H
P1               15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI               65536
SF         500.3000136 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```





(*R*)-(−)-1-*O*-Stearoyl-2,3-di-*O*-((*R*)-α-methoxyphenylacetoxy)-*sn*-glycerol (−)-S8b – ^{13}C NMR spectrum



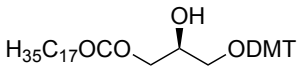
(*S*)-(+)-1-*O*-Stearoyl-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-39 – ^{1}H NMR spectrum

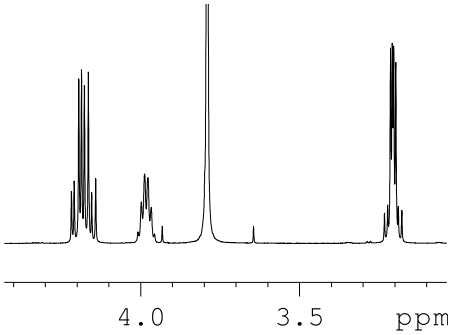
```
Current Data Parameters
NAME         ajf73p-data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161010
Time              16.37
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719425 sec
RG                 3.56
DW               48.400 usec
DE               10.00 usec
TE               298.0 K
D1           1.00000000 sec
TD0                  1

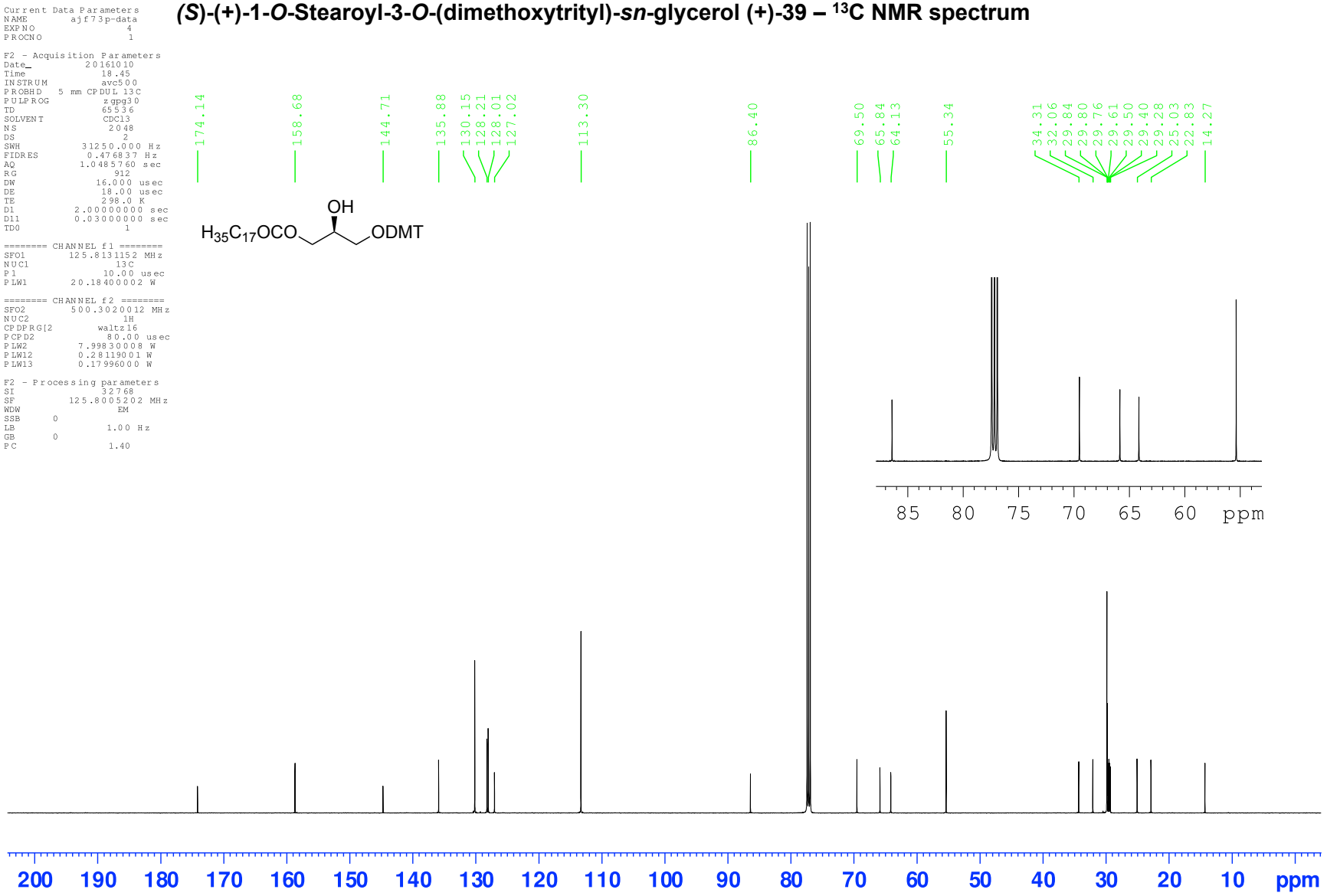
======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1               1H
P1               15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI               65536
SF          500.3000132 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```

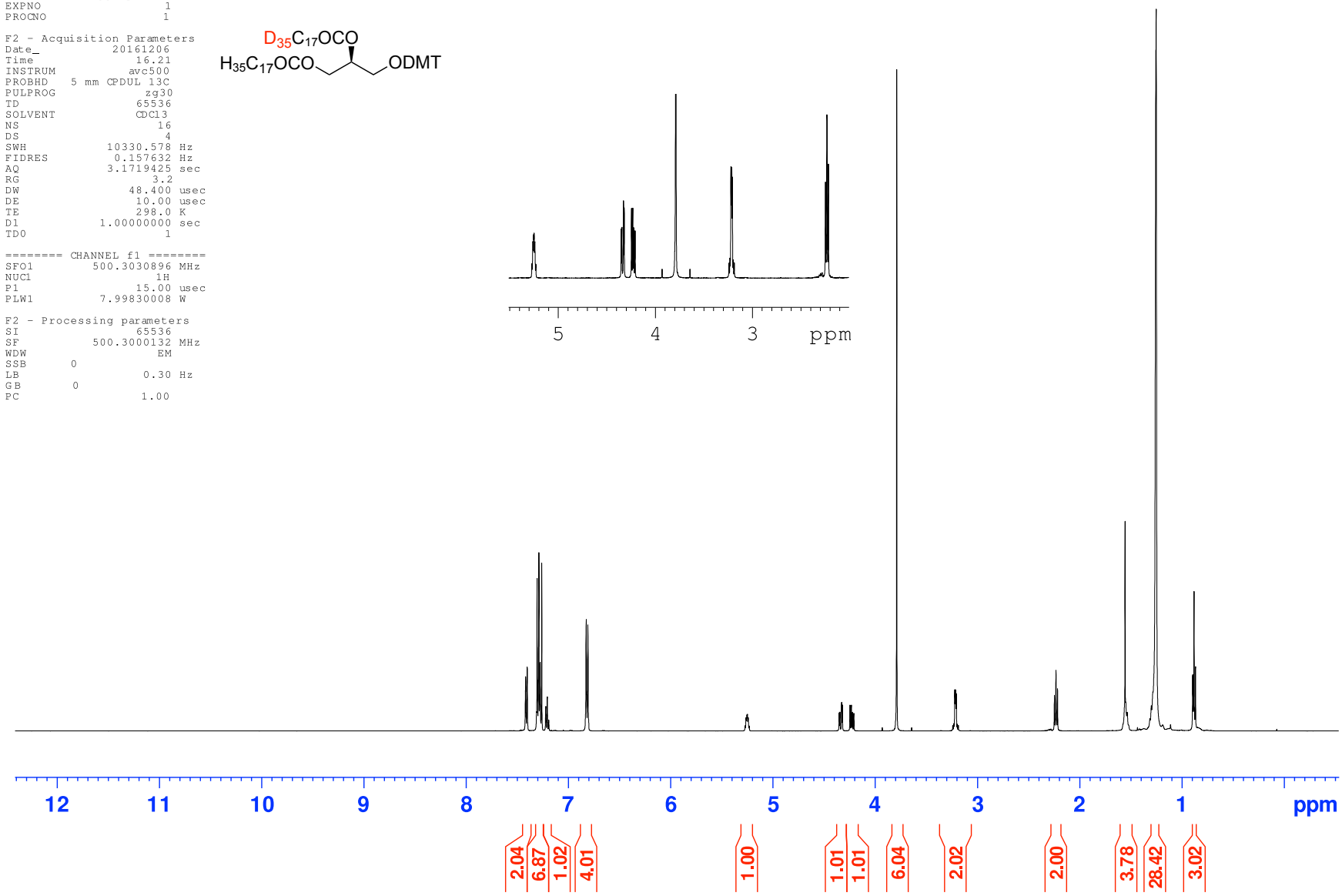




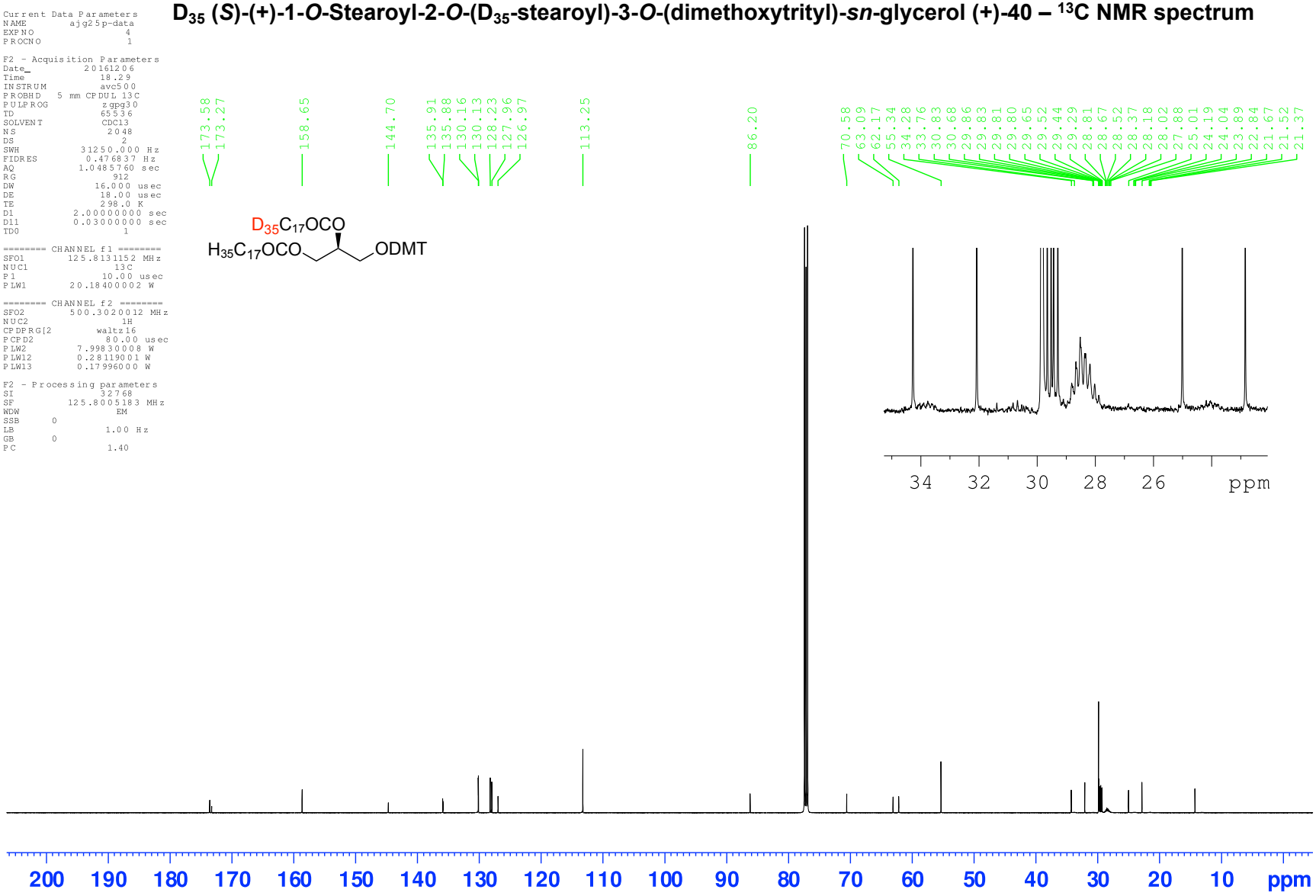
(*S*)-(+)-1-*O*-Stearoyl-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-39 – ^{13}C NMR spectrum



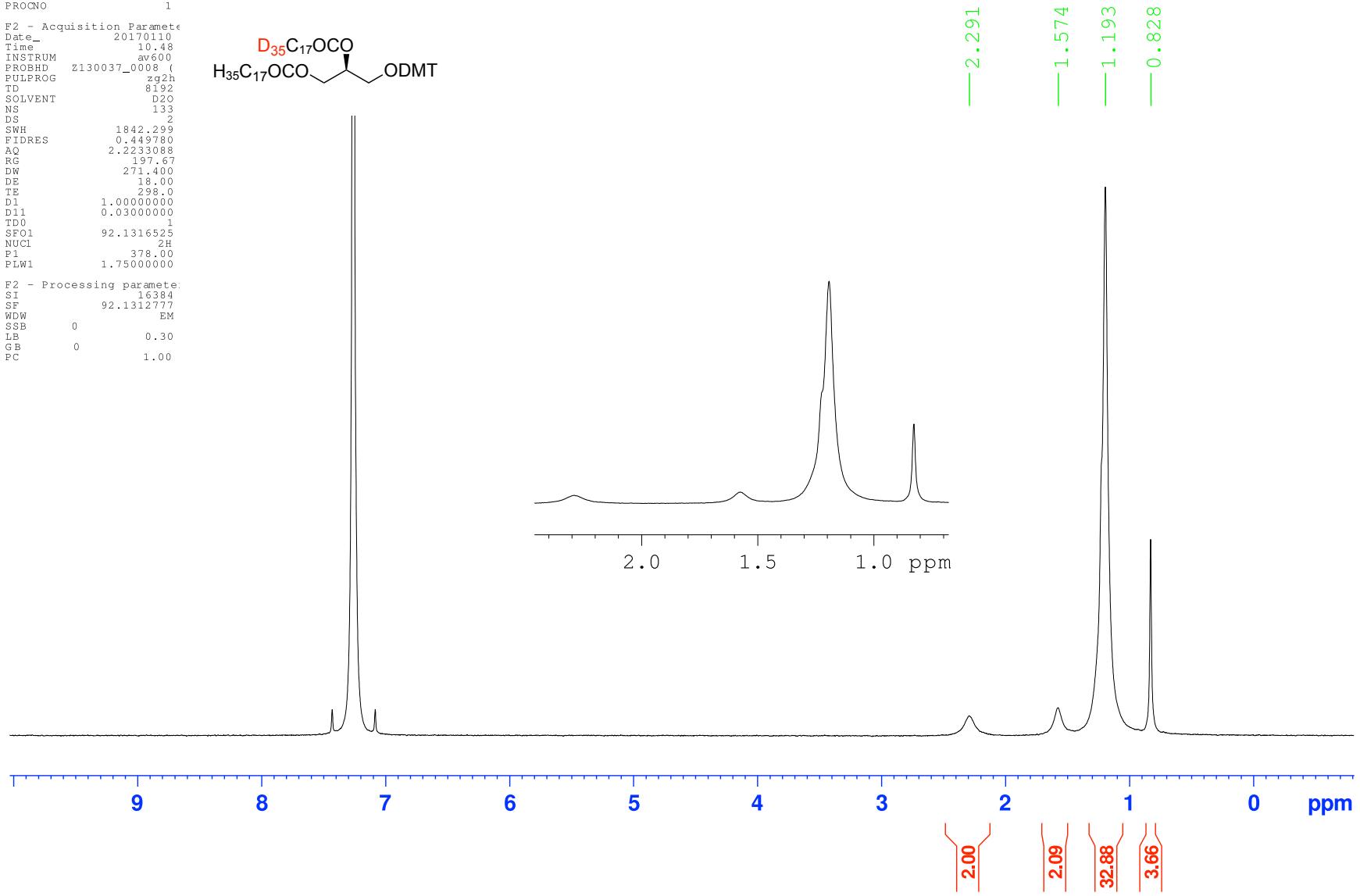
D_{35} (*S*)-(+)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-40 – ^{1}H NMR spectrum



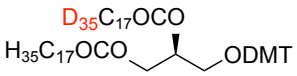
D_{35} (*S*)-(+)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-40 – ^{13}C NMR spectrum



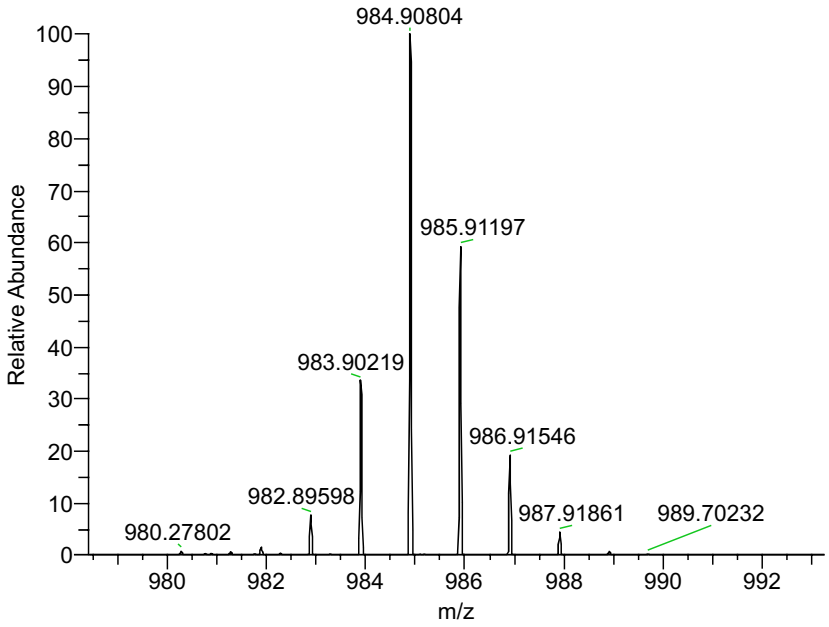
D_{35} (*S*)-(+)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-40 – ^{2}H NMR spectrum



D_{35} (*S*)-(+)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-40 – Mass spectrum

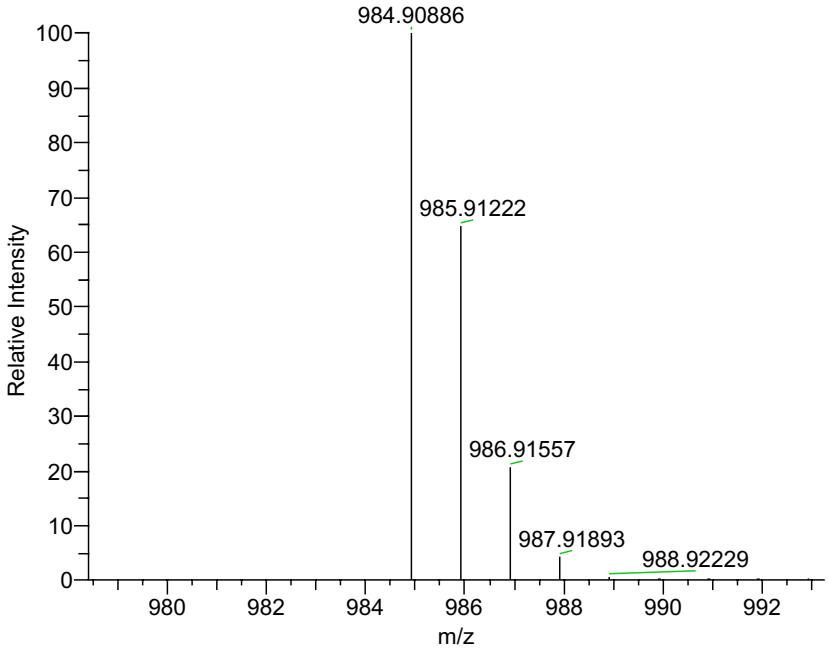


S:\data\Nov 16\ESI59933.raw 23/11/2016 10:46 am



NL: 4.07E6
ESI59933 #15-25 RT: 0.17-0.28 AV: 6 NL: 6.53E+007
T: FTMS {1,1} + p ESI Full lock ms [80.00-1600.00]

Measured Spectrum



NL: 5.12E5
C60H59[2]H35O7Na1: C_{60} H_{59} $^{2}H_{35}$ O_{7} Na
Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
984.90802	$C_{60}H_{59}{}^{2}H_{35}O_{7}{}^{23}Na$	13.5	-0.86	984.90886

)

(*S*)-(+)-1-*O*-Stearoyl-2-*O*-arachidonyl-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-41 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME      ajh5p-data-85412206
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20170622
Time                10.37 h
INSTRUM             av600
PROBHD    Z130037_0008 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH            12019.230 Hz
FIDRES          0.366798 Hz
AQ             2.7262976 sec
RG                  60.94
DW                 41.600 usec
DE                 10.00 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                     1
SFO1         600.1830009 MHz
NUC1                   1H
P1                 12.00 usec
PLW1         24.00000000 W

F2 - Processing parameters
SI                  65536
SF           600.1800149 MHz
WDW                    EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
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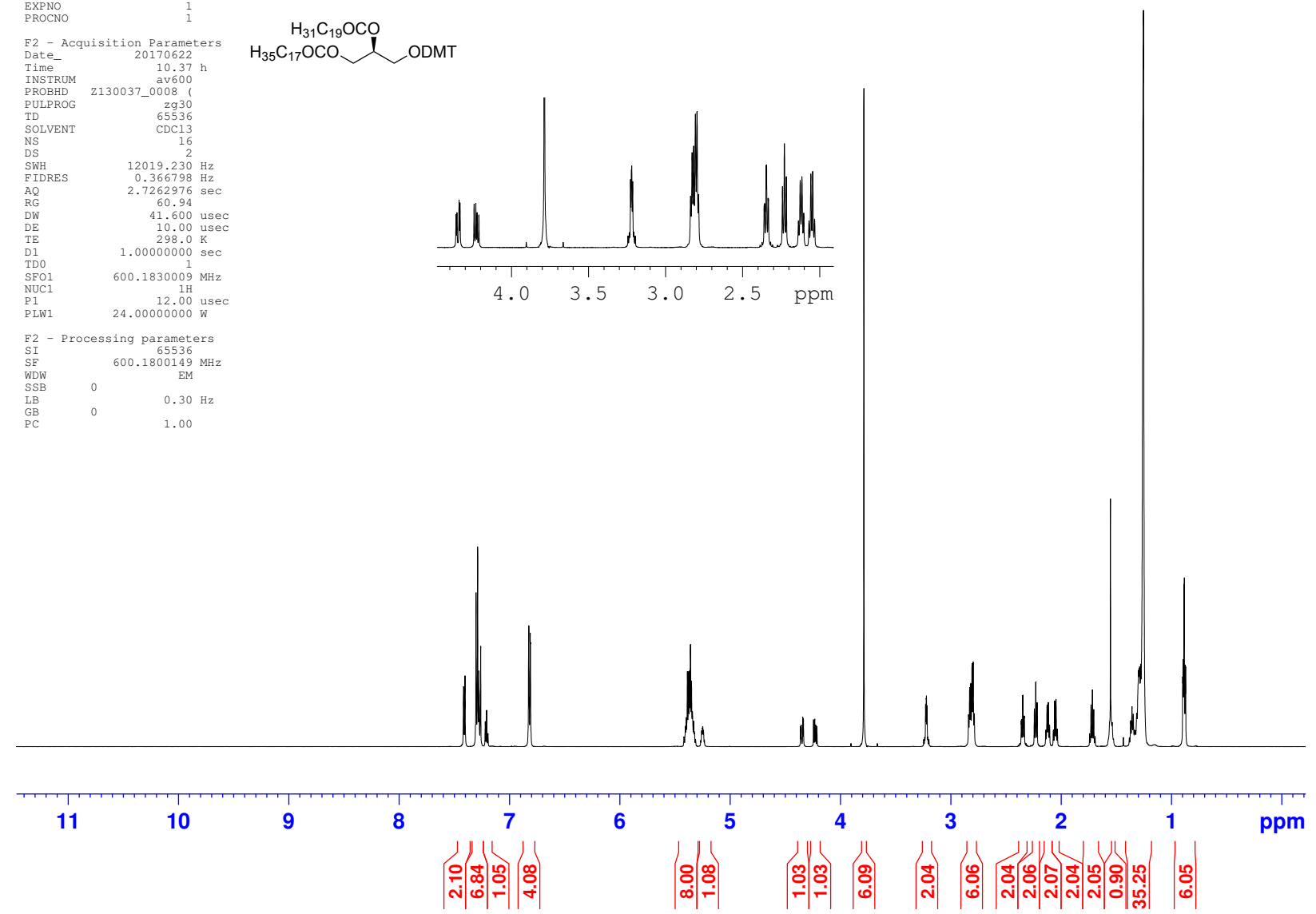
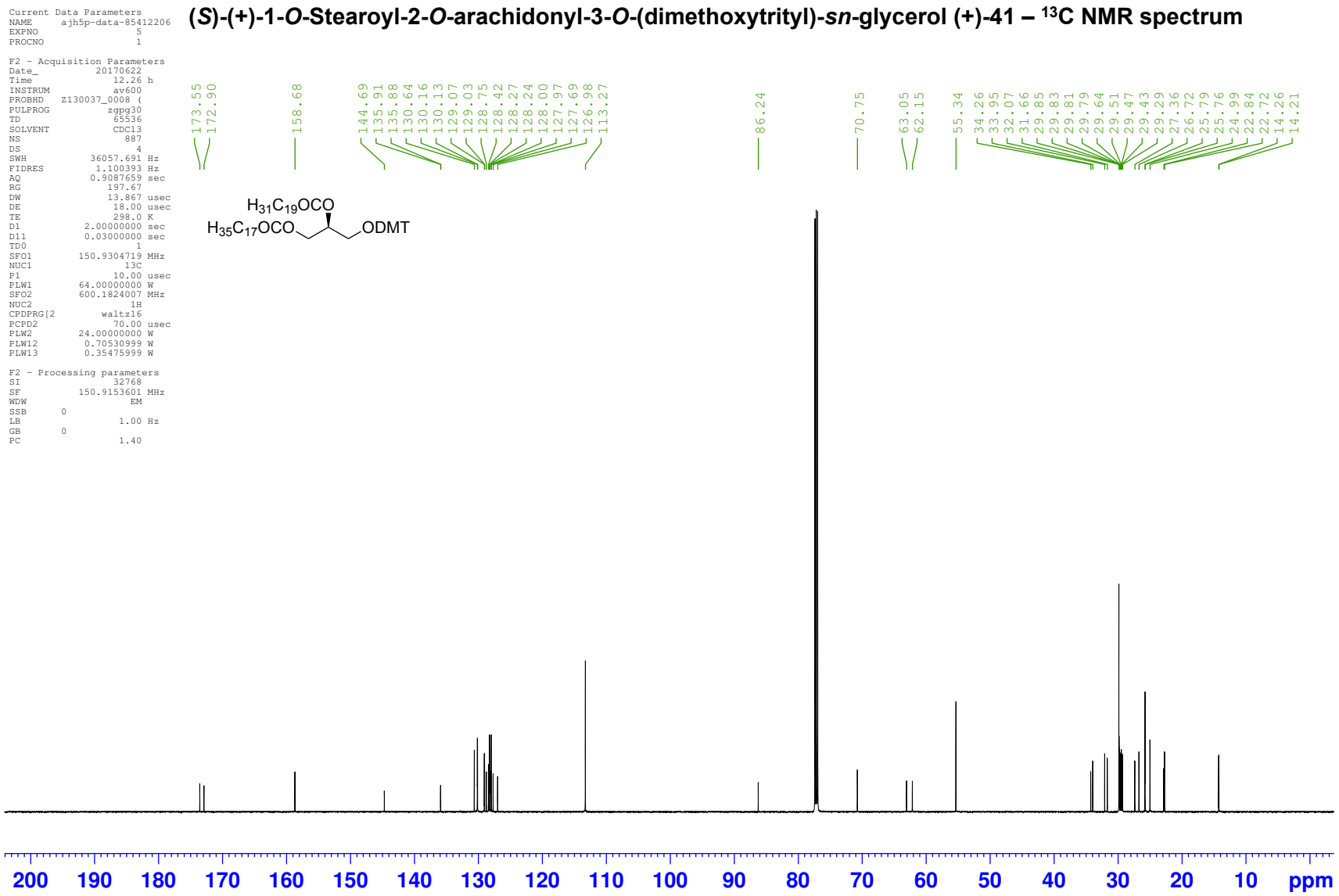


(*S*)-(+)-1-*O*-Stearoyl-2-*O*-arachidonyl-3-*O*-(dimethoxytrityl)-*sn*-glycerol (+)-41 – ^{13}C NMR spectrum



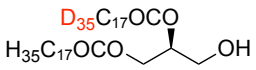
D_{35} (*S*)-(−)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glycerol (−)-42 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME         ajg38p-data2
EXPNO                   1
PROCNO                  1

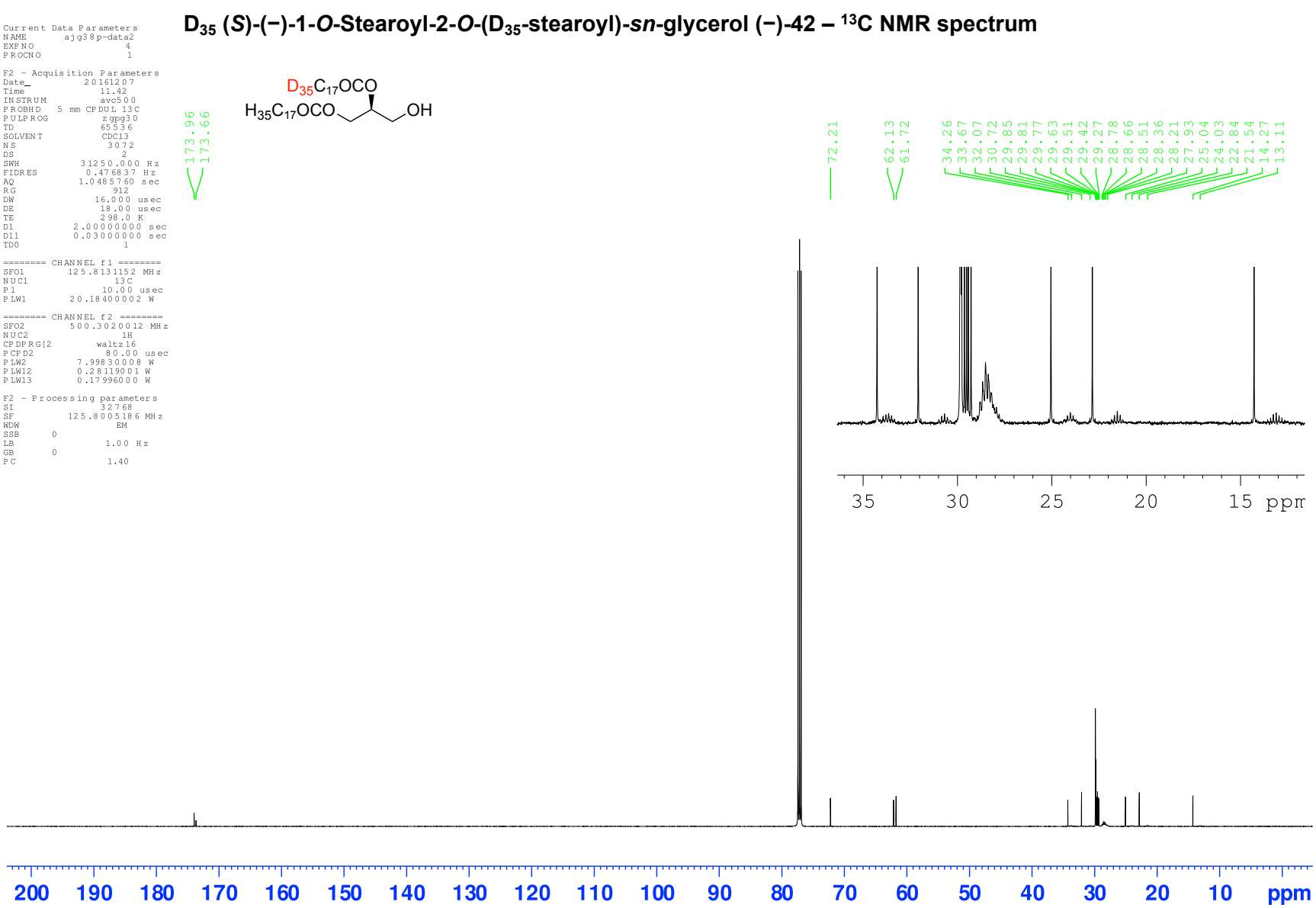
F2 - Acquisition Parameters
Date_           20161207
Time              10.40
INSTRUM         avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                  3.56
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1                1H
P1                15.00 usec
PLW1         7.99830008 W

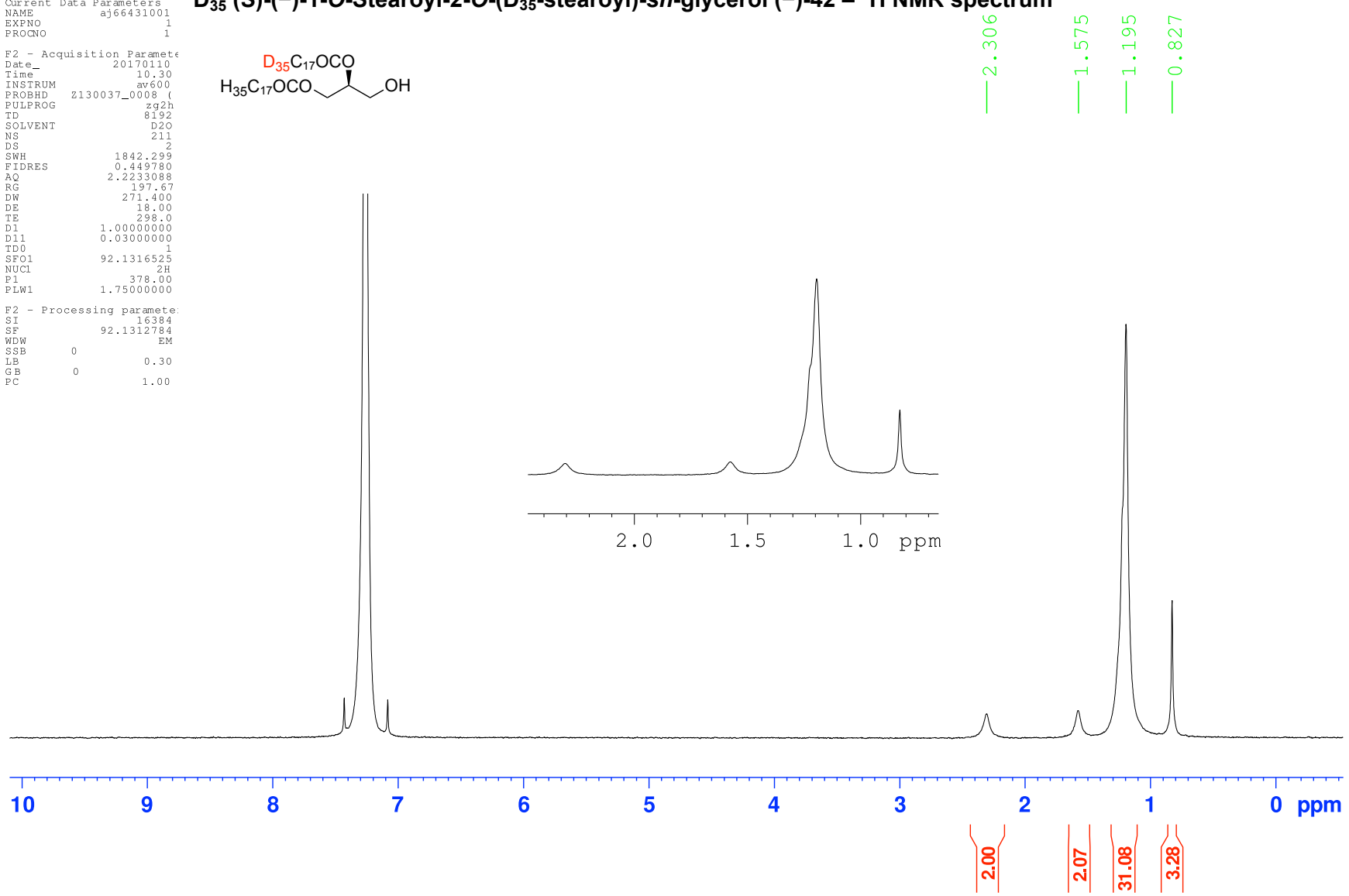
F2 - Processing parameters
SI                65536
SF          500.3000135 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```



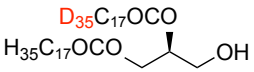
D_{35} (*S*)-(−)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glycerol (−)-42 – ^{13}C NMR spectrum



D_{35} (*S*)-(−)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glycerol (−)-42 – ^{2}H NMR spectrum



D_{35} (*S*)-(−)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glycerol (−)-42 – Mass spectrum



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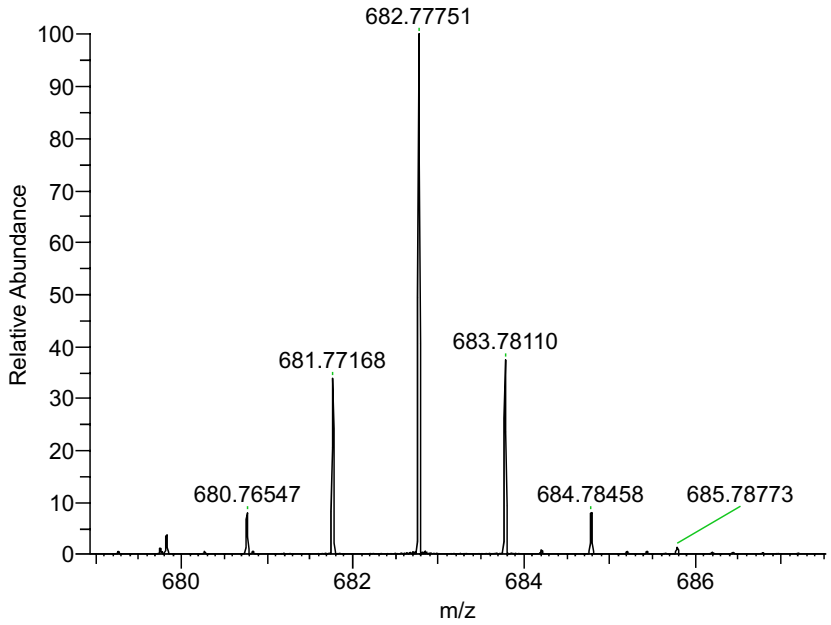
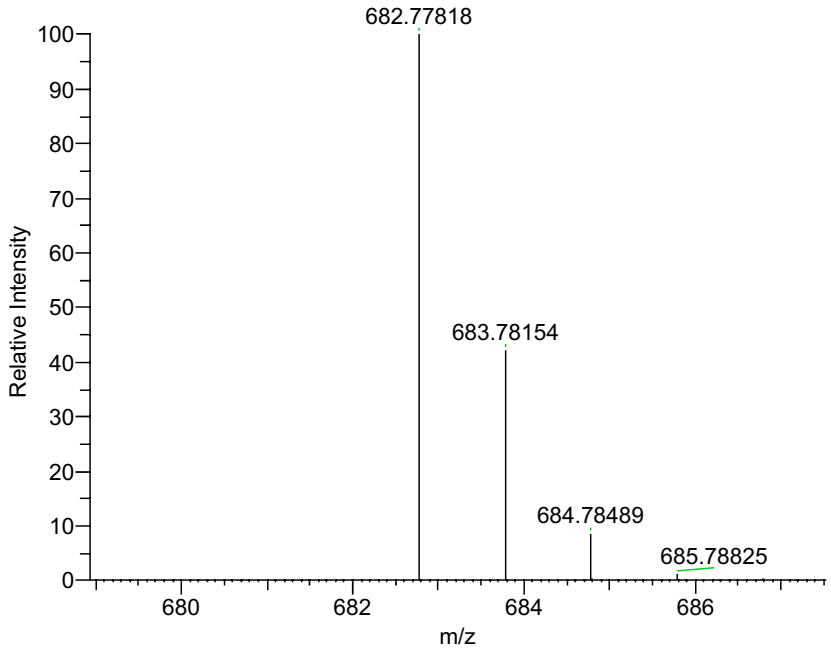


NL: 1.06E7
ESI60072 #15-25 RT: 0.17-0.28 AV: 6 NL: 1.06E+007
T: FTMS {1,1} + p ESI Full lock ms [80.00-1600.00]

Measured Spectrum



NL: 6.46E5
C39H41[2]H35O5Na1: $C_{39}H_{41}{}^{2}H_{35}O_5Na$
Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
682.77753	$C_{39}H_{41}{}^{2}H_{35}O_5{}^{23}Na$	1.5	-0.96	682.77818

)

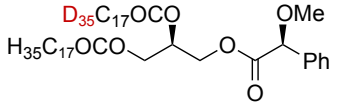
D_{35} (*R*)-(+)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-((*S*)-α-methoxyphenylacetoxy)-*sn*-glycerol (+)-9a – ^{1}H NMR spectrum

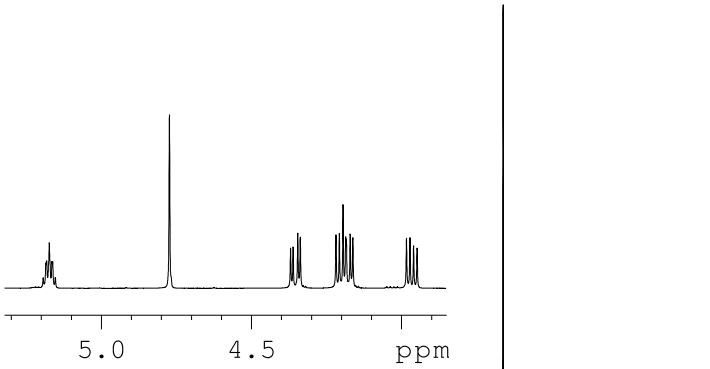
```
Current Data Parameters
NAME      ajg43p(S)-data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161208
Time               13.50
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                  3.56
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1

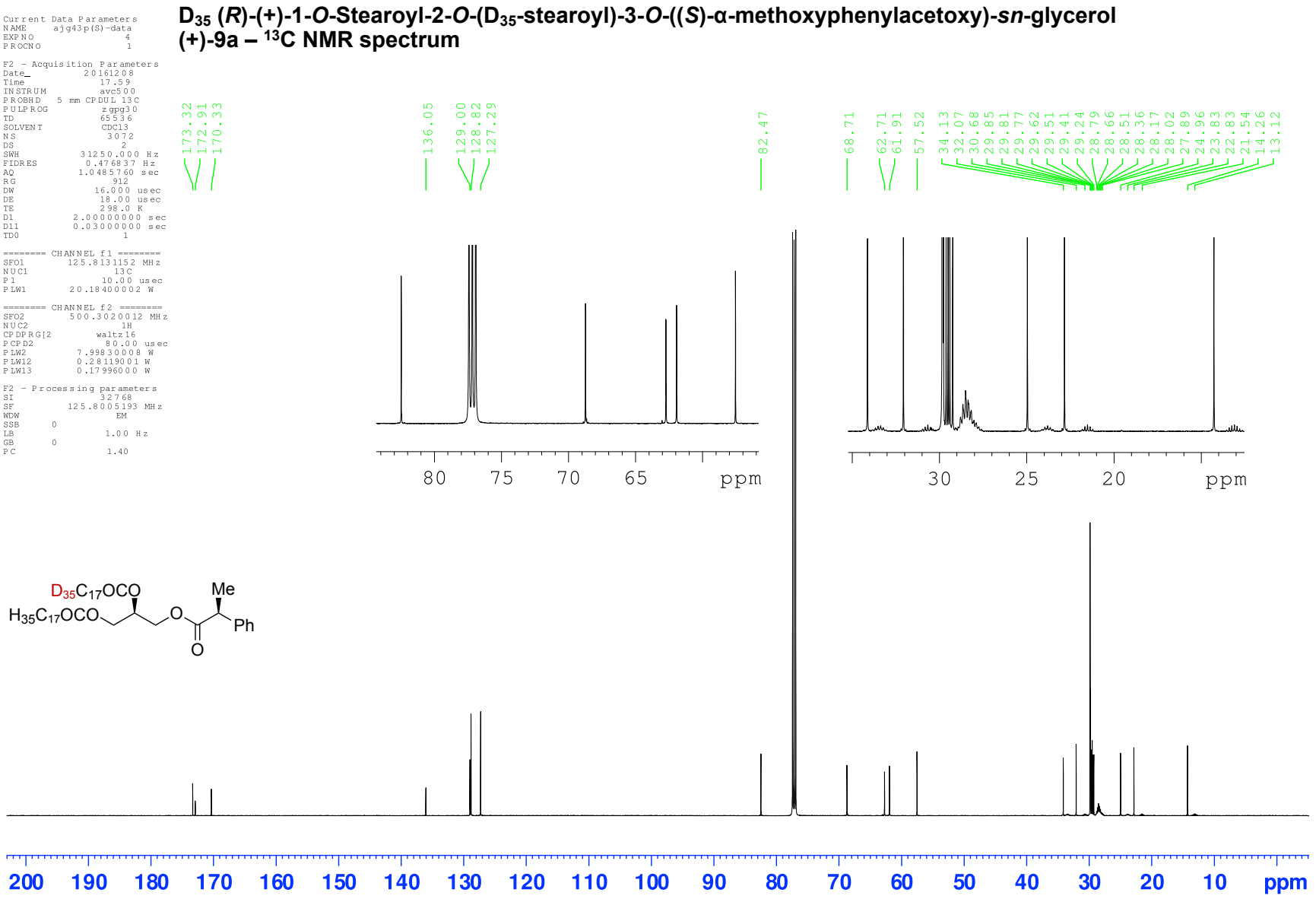
======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1                1H
P1                15.00 usec
PLW1           7.99830008 W

F2 - Processing parameters
SI                65536
SF          500.3000132 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

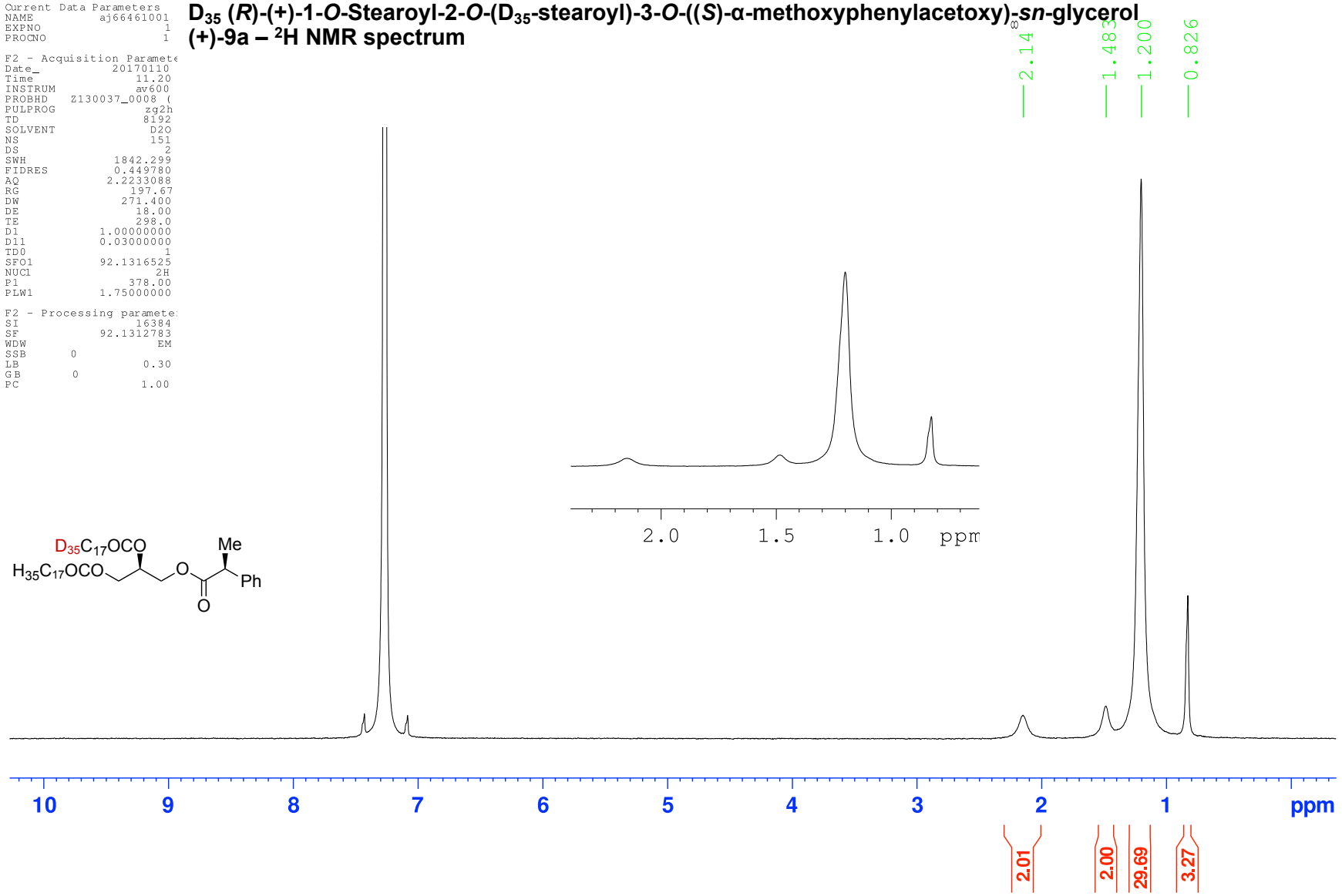




D_{35} (*R*)-(+)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-((*S*)-α-methoxyphenylacetoxy)-*sn*-glycerol (+)-9a – ^{13}C NMR spectrum



D_{35} (*R*)-(+)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-((*S*)-α-methoxyphenylacetoxy)-*sn*-glycerol (+)-9a – ^{2}H NMR spectrum



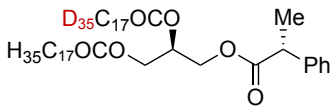
D_{35} (*R*)-(−)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-((*R*)-α-methoxyphenylacetoxy)-*sn*-glycerol (−)-9b – ^{1}H NMR spectrum

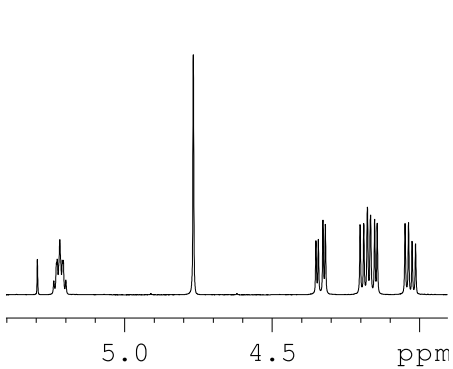
```
Current Data Parameters
NAME      ajg43(R)-data2
EXPNO                  1
PROCNO                 1

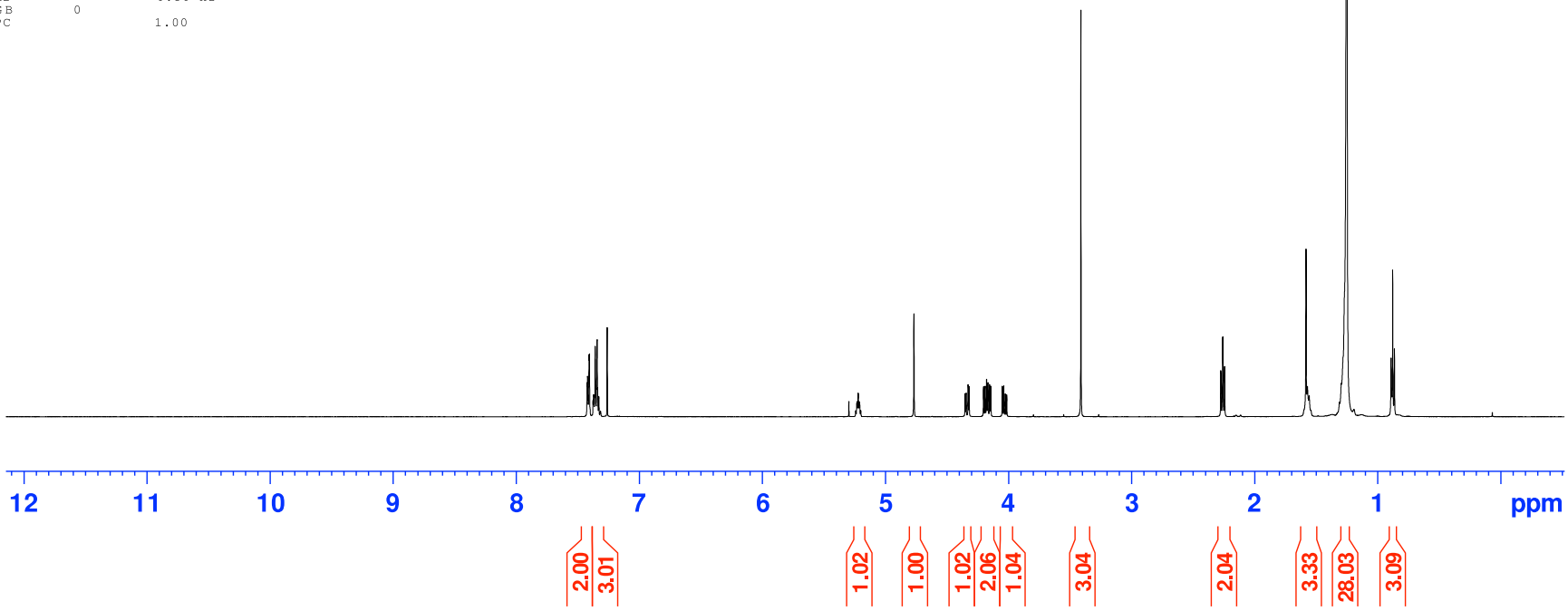
F2 - Acquisition Parameters
Date_           20161213
Time              11.52
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                3.56
DW               48.400 use
DE               10.00 use
TE               298.0 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1               1H
P1               15.00 usec
PLW1          7.99830008 W

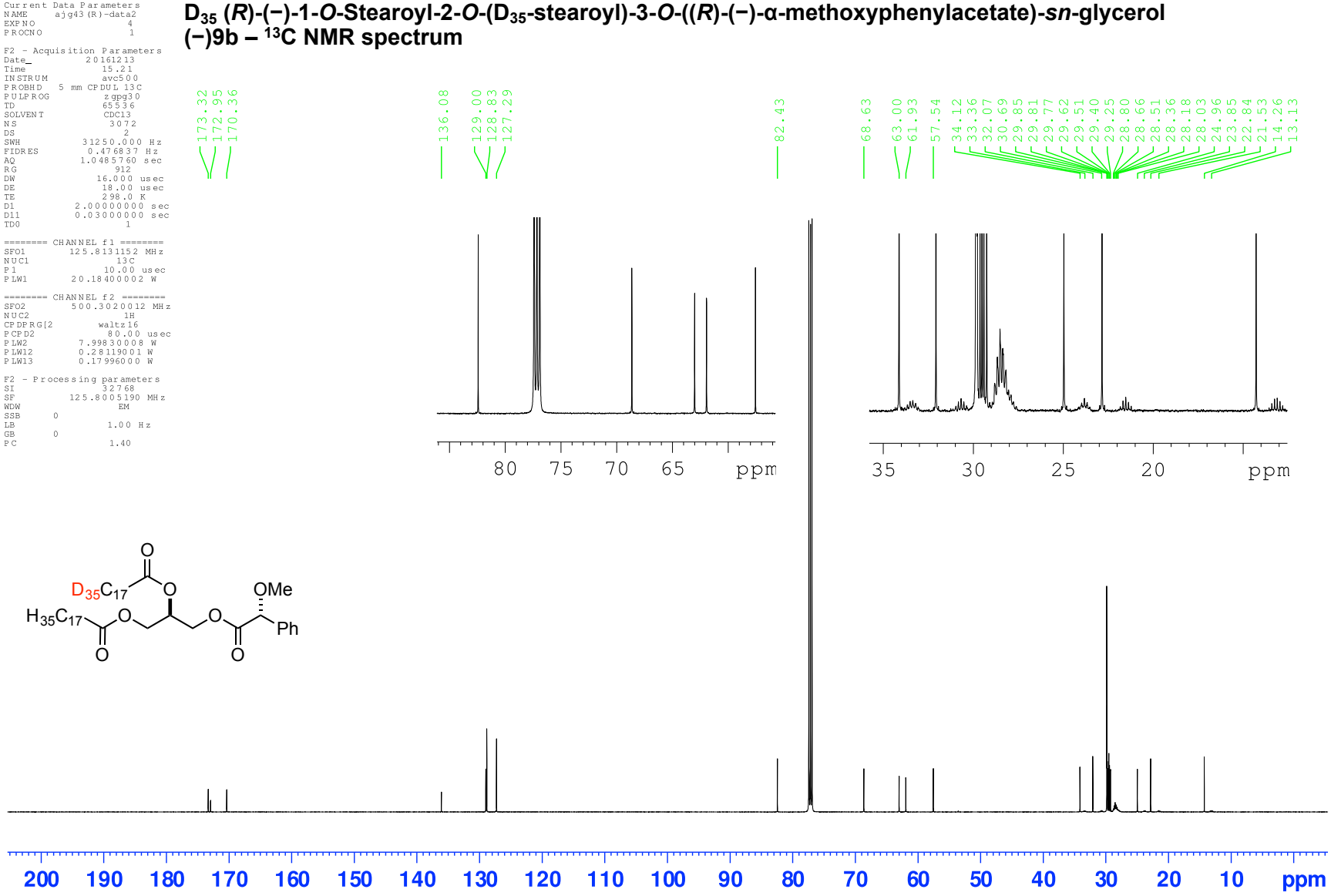
F2 - Processing parameters
SI               65536
SF          500.3000135 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```



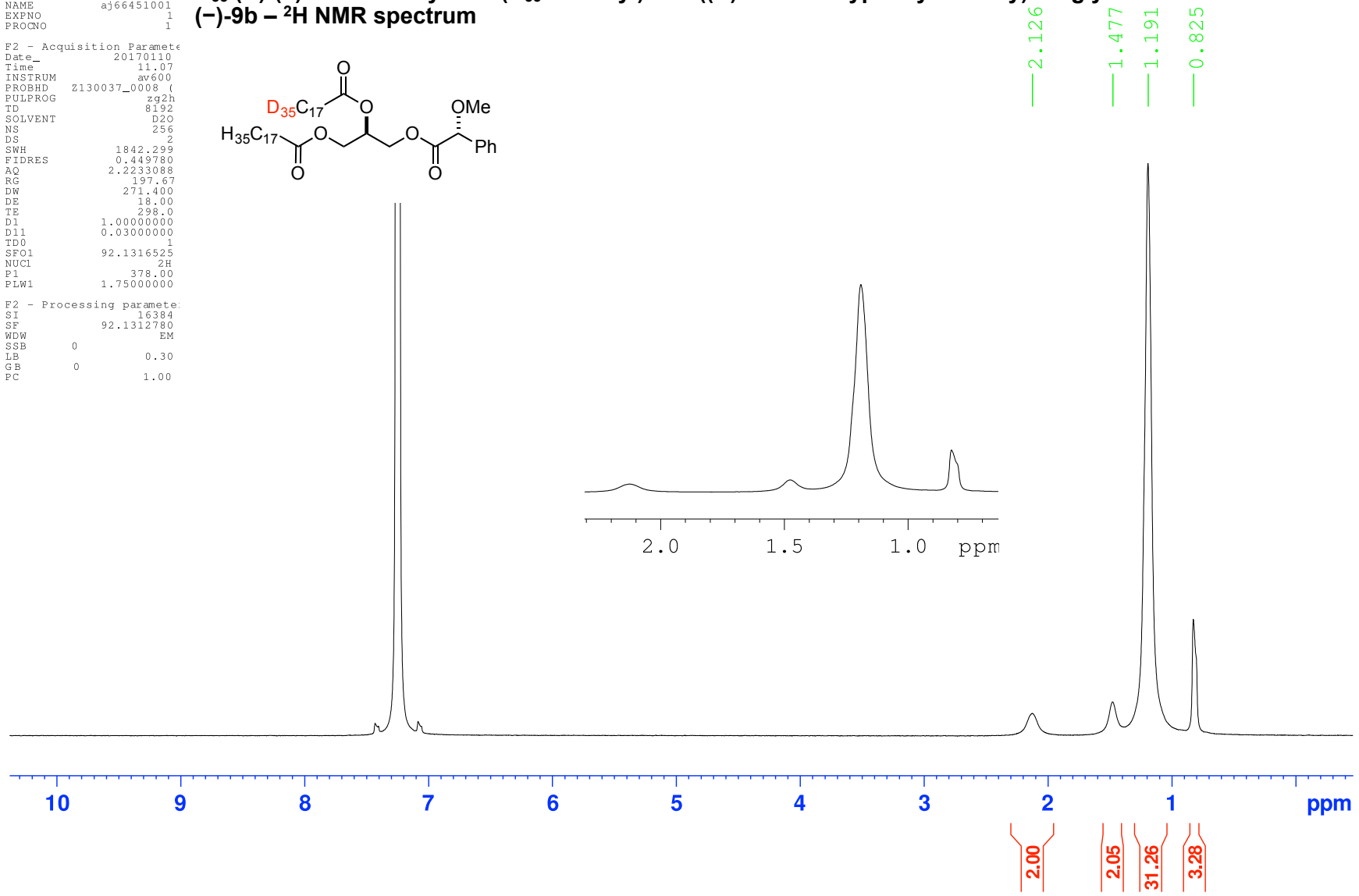




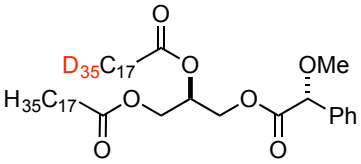
D_{35} (*R*)-(−)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-((*R*)-(−)-α-methoxyphenylacetate)-*sn*-glycerol (−)9b – ^{13}C NMR spectrum



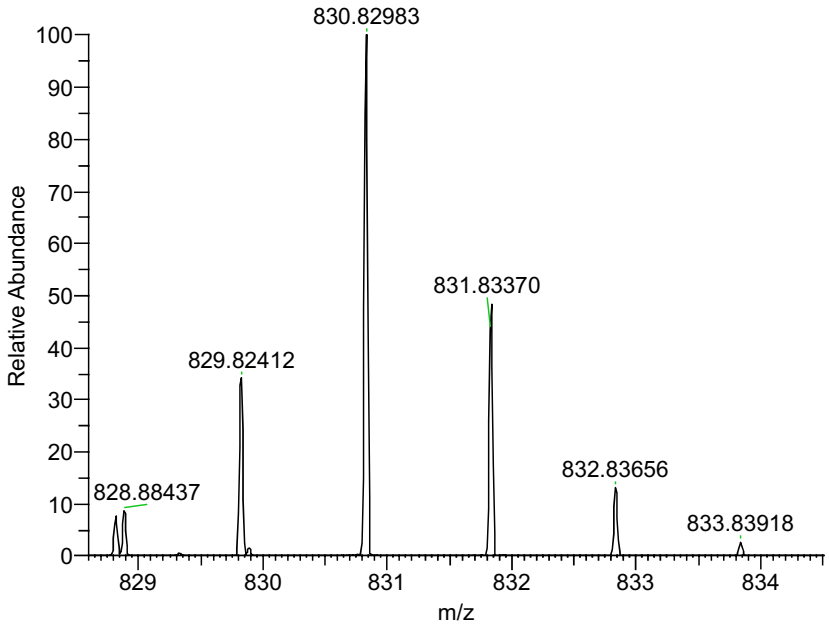
D_{35} (*R*)-(−)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-((*R*)-α-methoxyphenylacetoxy)-*sn*-glycerol (−)-9b – ^{2}H NMR spectrum



D_{35} (*R*)-(−)-1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-3-*O*-((*R*)-α-methoxyphenylacetoxy)-*sn*-glycerol (−)-9b – Mass spectrum

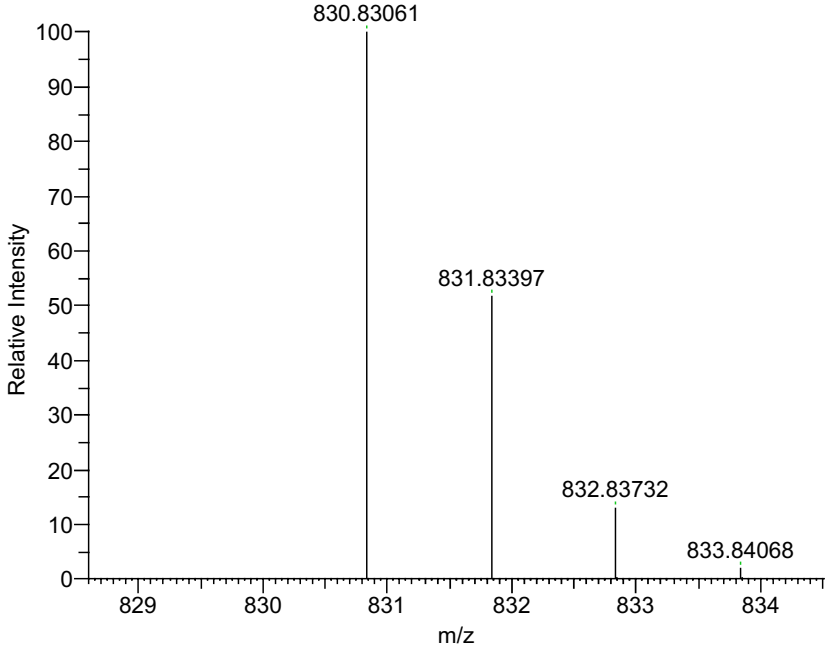


X:\data\Dec 16\ESI60219.raw 14/12/2016 3:19 pm



NL: 4.96E6
ESI60219 #13-27 RT: 0.15-0.31 AV: 8 NL: 3.11E+007
T: FTMS {1,1} + p ESI Full lock ms [80.00-1600.00]

Measured Spectrum



NL: 5.83E5
C48H49[2]H35O7Na1: $C_{48}H_{49}{}^{2}H_{35}O_7Na$
Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
830.82983	$C_{48}H_{49}{}^{2}H_{35}O_7{}^{23}Na$	6.5	-0.94	830.83061

(*R*)-(+)-1-*O*-Stearoyl-2-*O*-arachidonyl-3-*O*-((*S*)-α-methoxyphenylacetoxy)-*sn*-glycerol (+)-S10a

^{1}H NMR spectrum

```
Current Data Parameters
NAME      ajh17(S)p-data-865907
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_           20170707
Time                1.15
INSTRUM           avb500
PROBHD    5 mm PATBO BB-
PULPROG             zg60
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1719425 sec
RG                   114
DW                48.400 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.9825000 MHz
NUC1                   1H
P1                  15.00 usec
PLW1        32.00000000 W

F2 - Processing parameters
SI                 32768
SF           499.9800129 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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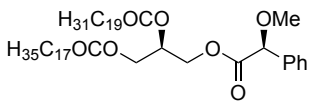
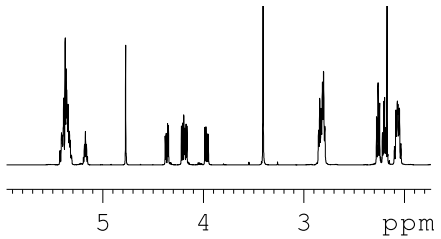
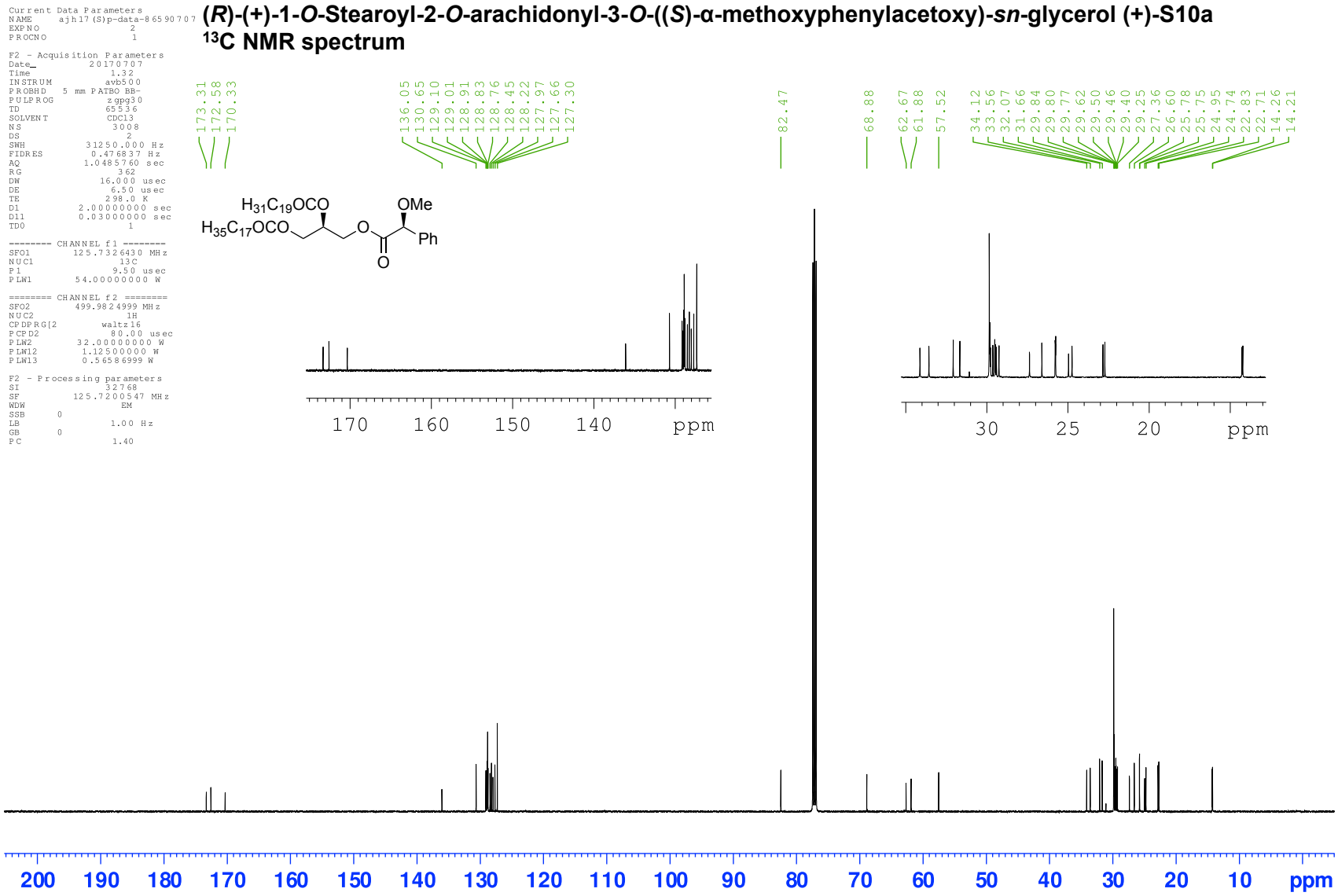




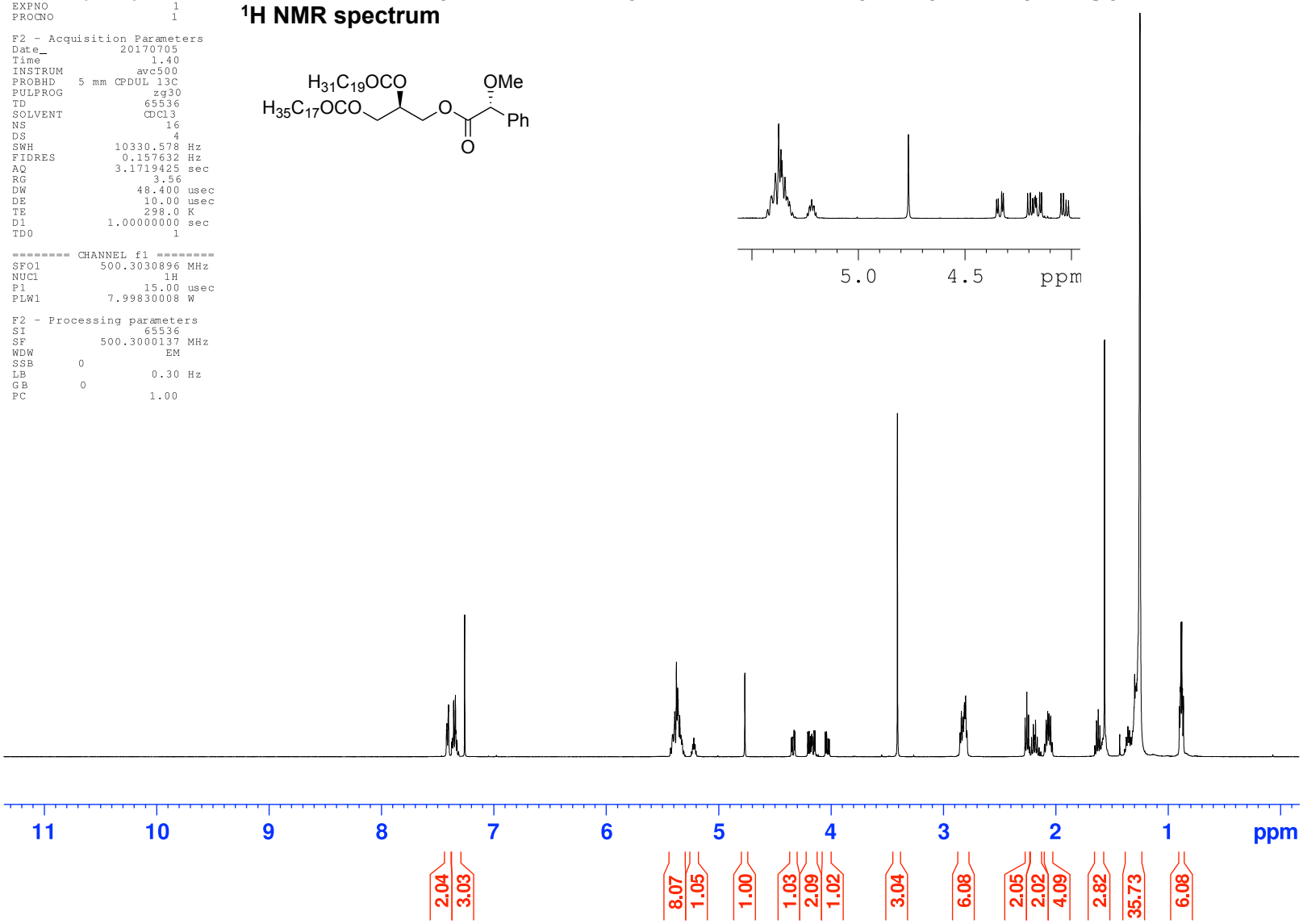
(*R*)-(+)-1-*O*-Stearoyl-2-*O*-arachidonyl-3-*O*-((*S*)-α-methoxyphenylacetoxy)-*sn*-glycerol (+)-S10a

^{13}C NMR spectrum



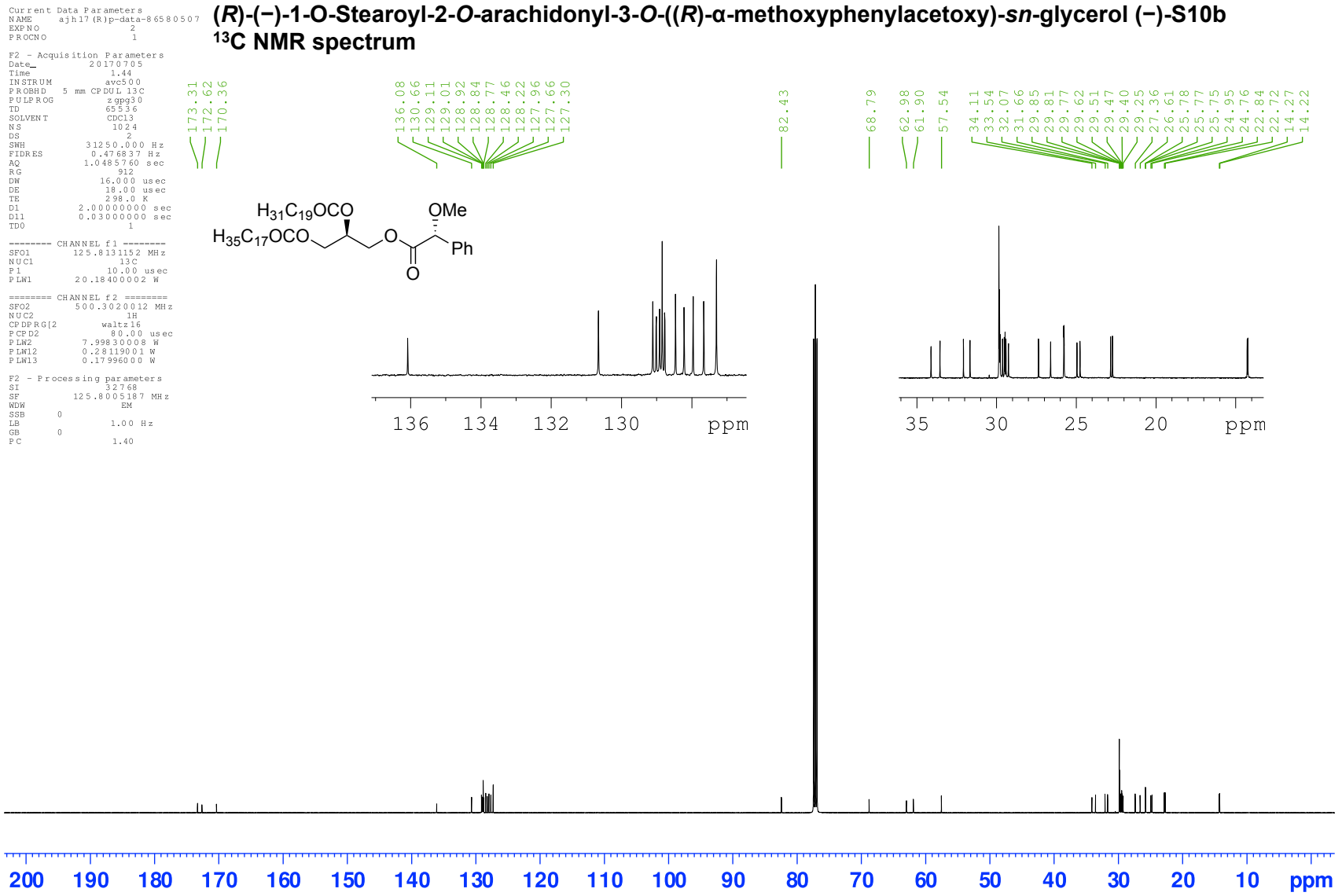
(*R*)-(−)-1-O-Stearoyl-2-*O*-arachidonyl-3-*O*-((*R*)-α-methoxyphenylacetoxy)-*sn*-glycerol (−)-S10b

^{1}H NMR spectrum



(*R*)-(−)-1-O-Stearoyl-2-*O*-arachidonyl-3-*O*-((*R*)-α-methoxyphenylacetoxy)-*sn*-glycerol (−)-S10b

^{13}C NMR spectrum

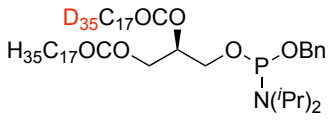


D_{35} (*R*)-(+)-Benzyloxy-*N,N*-diisopropylamino-(1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glyceryl) phosphoramidite (+)-44 – ^{1}H NMR spectrum

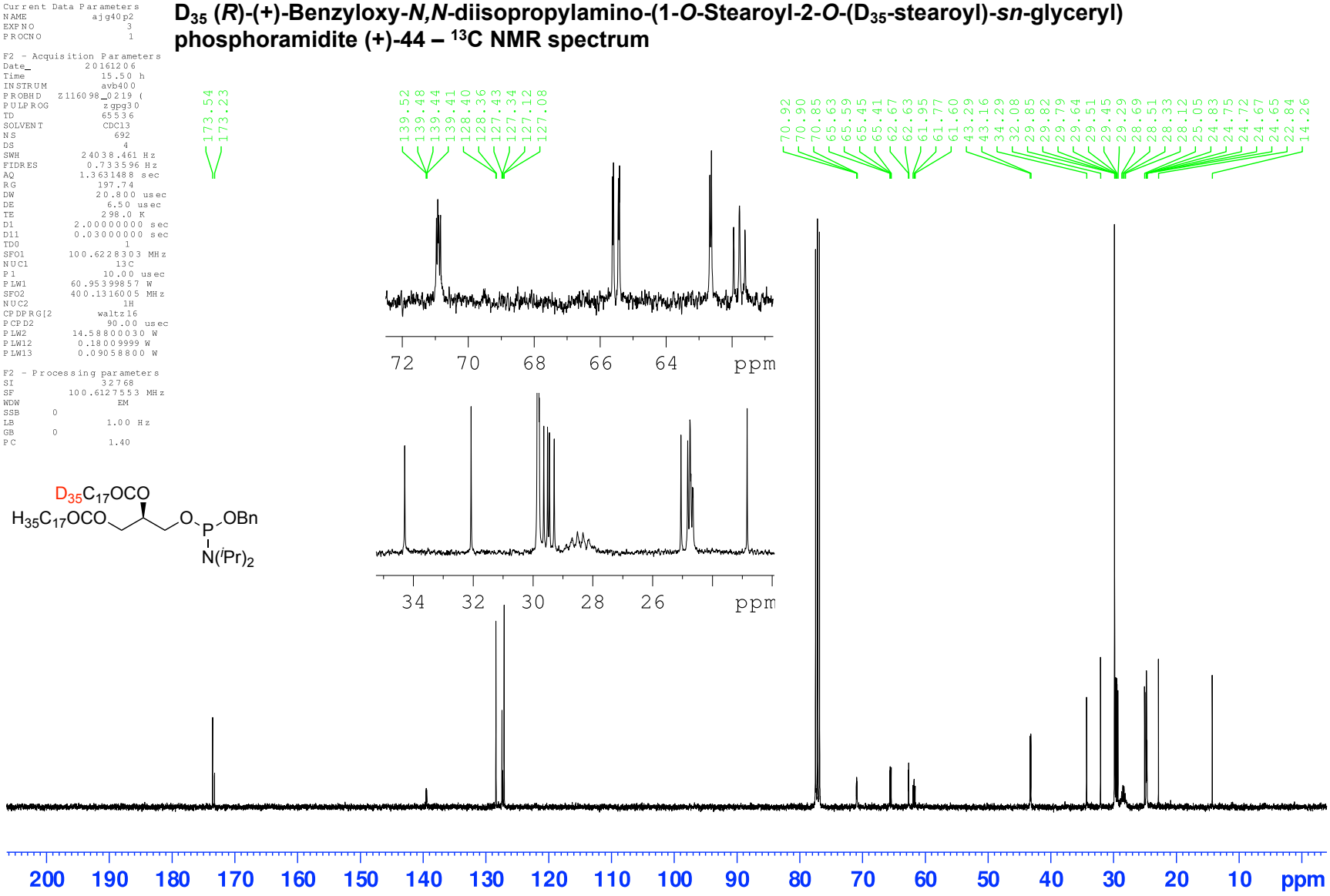
```
Current Data Parameters
NAME                  ajg40p2
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20161206
Time                  15.07 h
INSTRUM              avb400
PROBHD    Z116098_0219 (
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                 4.0894465 sec
RG                    30.76
DW                   62.400 usec
DE                    6.50 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                       1
SFO1           400.1320007 MHz
NUC1                   1H
P1                   10.00 usec
PLW1           14.58800030 W

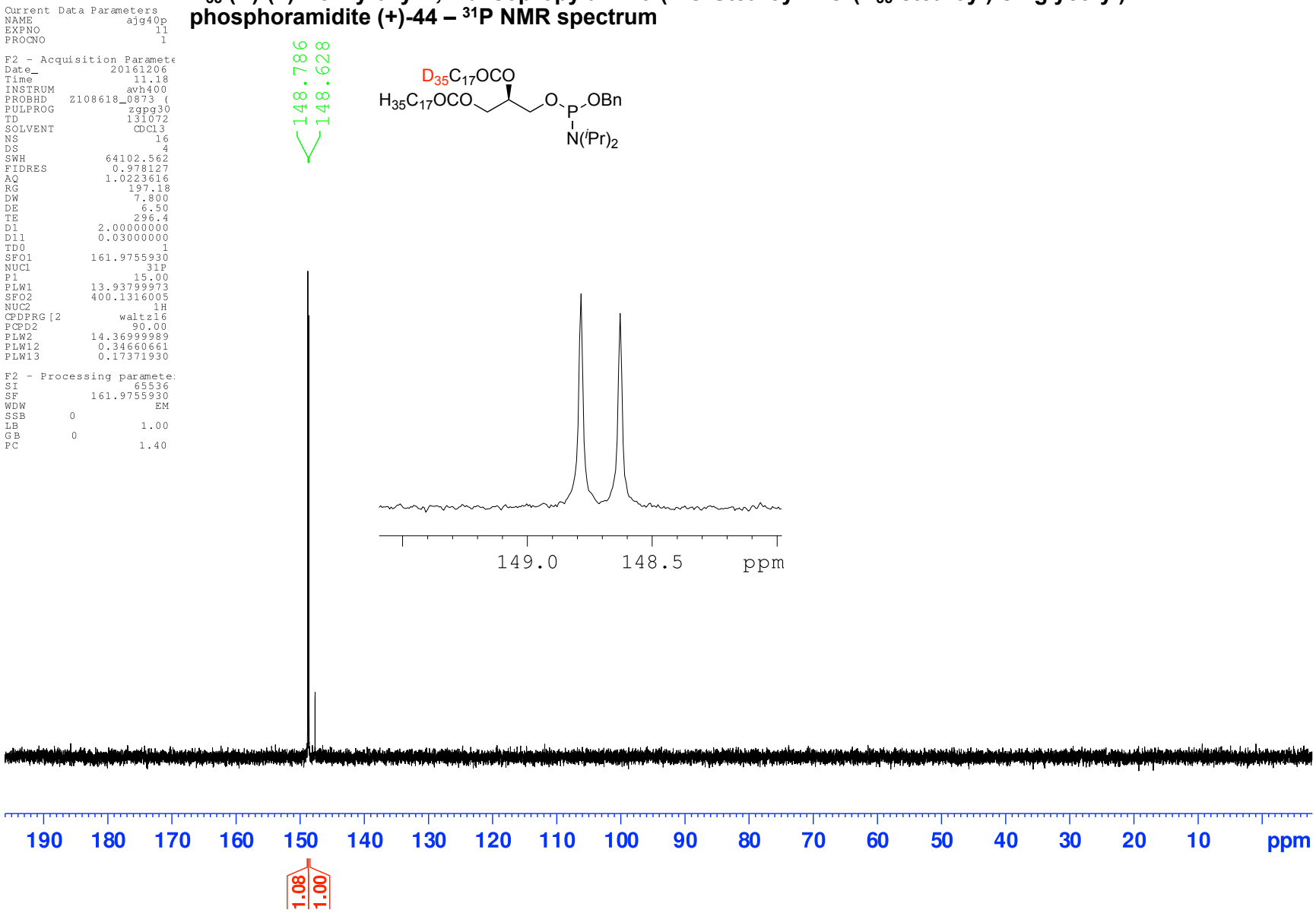
F2 - Processing parameters
SI                    65536
SF             400.1300099 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```



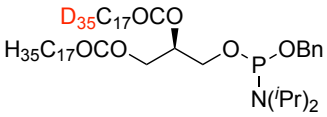
D_{35} (*R*)-(+)-Benzyloxy-*N,N*-diisopropylamino-(1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glyceryl) phosphoramidite (+)-44 – ^{13}C NMR spectrum



D_{35} (*R*)-(+)-Benzyloxy-*N*,*N*-diisopropylamino-(1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glyceryl) phosphoramidite (+)-44 – ^{31}P NMR spectrum



D_{35} (*R*)-(+)-Benzyloxy-*N*,*N*-diisopropylamino-(1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glyceryl) phosphoramidite (+)-44 – Mass spectrum



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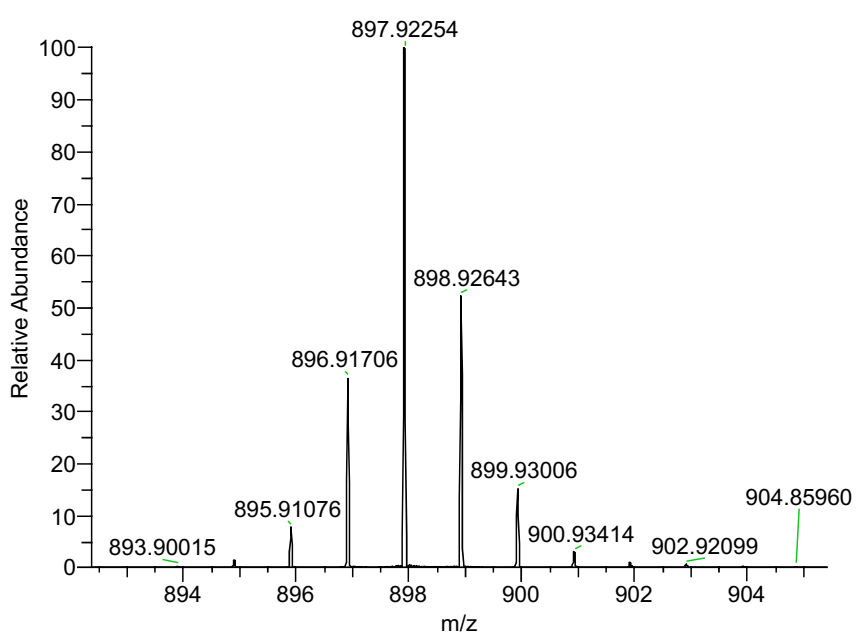

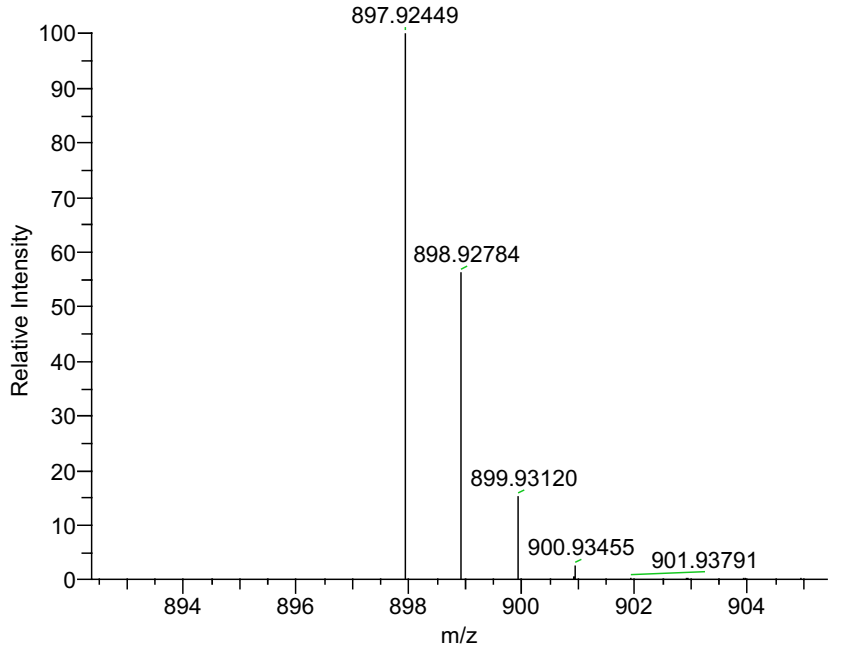

m/z	Formula	RDB	Delta ppm	Theo. Mass
897.92255	$C_{52}H_{62}{}^{2}H_{35}O_6NP$	5.5	-2.16	897.92449

(*R*)-Benzyloxy-*N*,*N*-diisopropyl-(1-*O*-stearoyl-2-*O*-arachidonyl-*sn*-glycer-3-yl)phosphoramidite (+)-45
^{1}H NMR spectrum

```
Current Data Parameters
NAME                 ajh15p
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20170626
Time                  5.23 h
INSTRUM              avg400
PROBHD    Z108618_0816 (
PULPROG                zg60
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES            0.244532 Hz
AQ                4.0894465 sec
RG                    91.39
DW                   62.400 use
DE                    6.50 use
TE                   362.2 K
D1              1.00000000 sec
TD0                       1
SFO1           400.2024012 MHz
NUC1                    1H
P1                   14.00 use
PLW1           14.00000000 W

F2 - Processing parameters
SI                    32768
SF             400.2000103 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                    1.00
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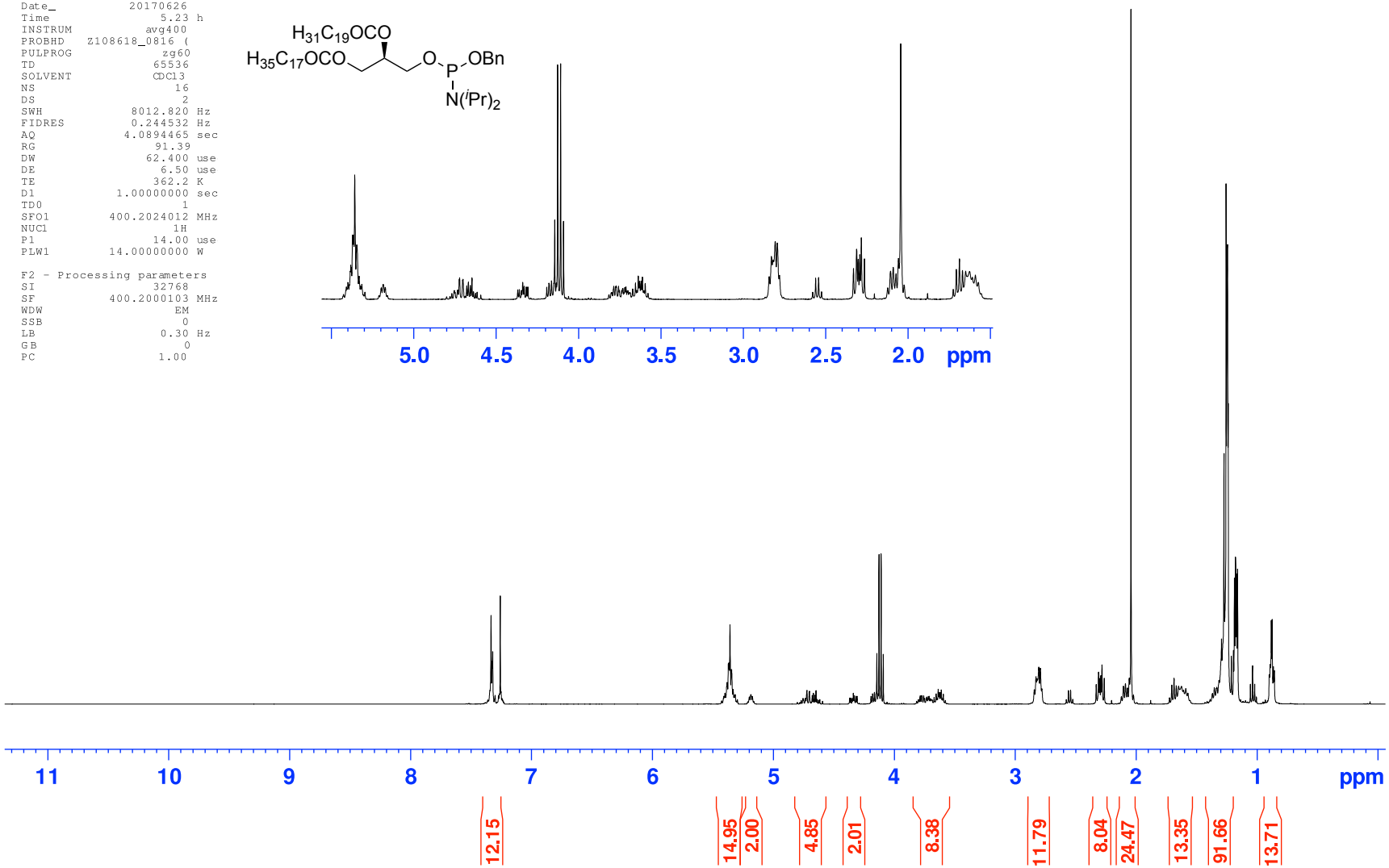
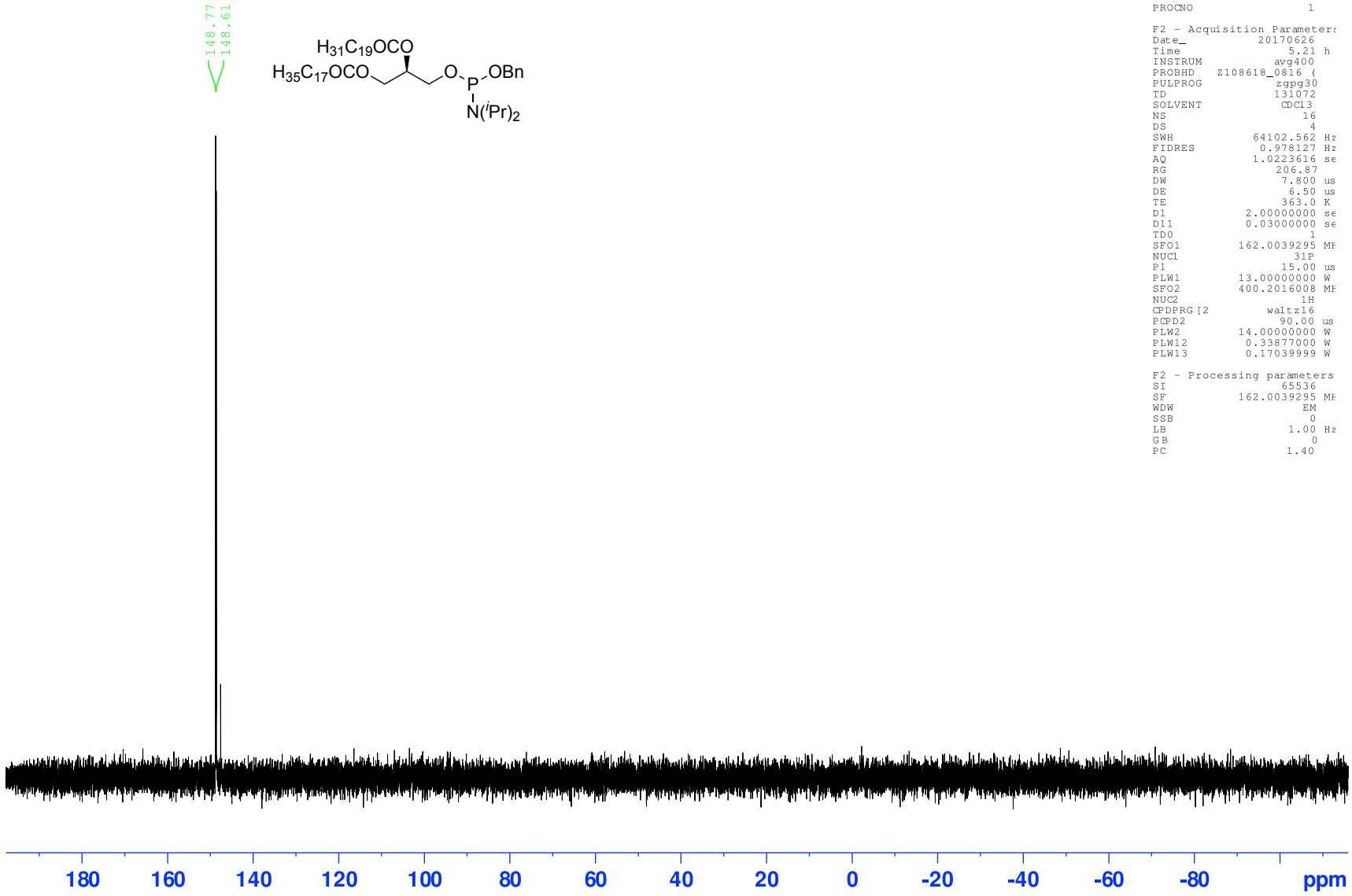


(*R*)-Benzyloxy-*N*,*N*-diisopropyl-(1-*O*-stearoyl-2-*O*-arachidonyl-sn-glycer-3-yl)phosphoramidite (+)-45

^{31}P NMR spectrum

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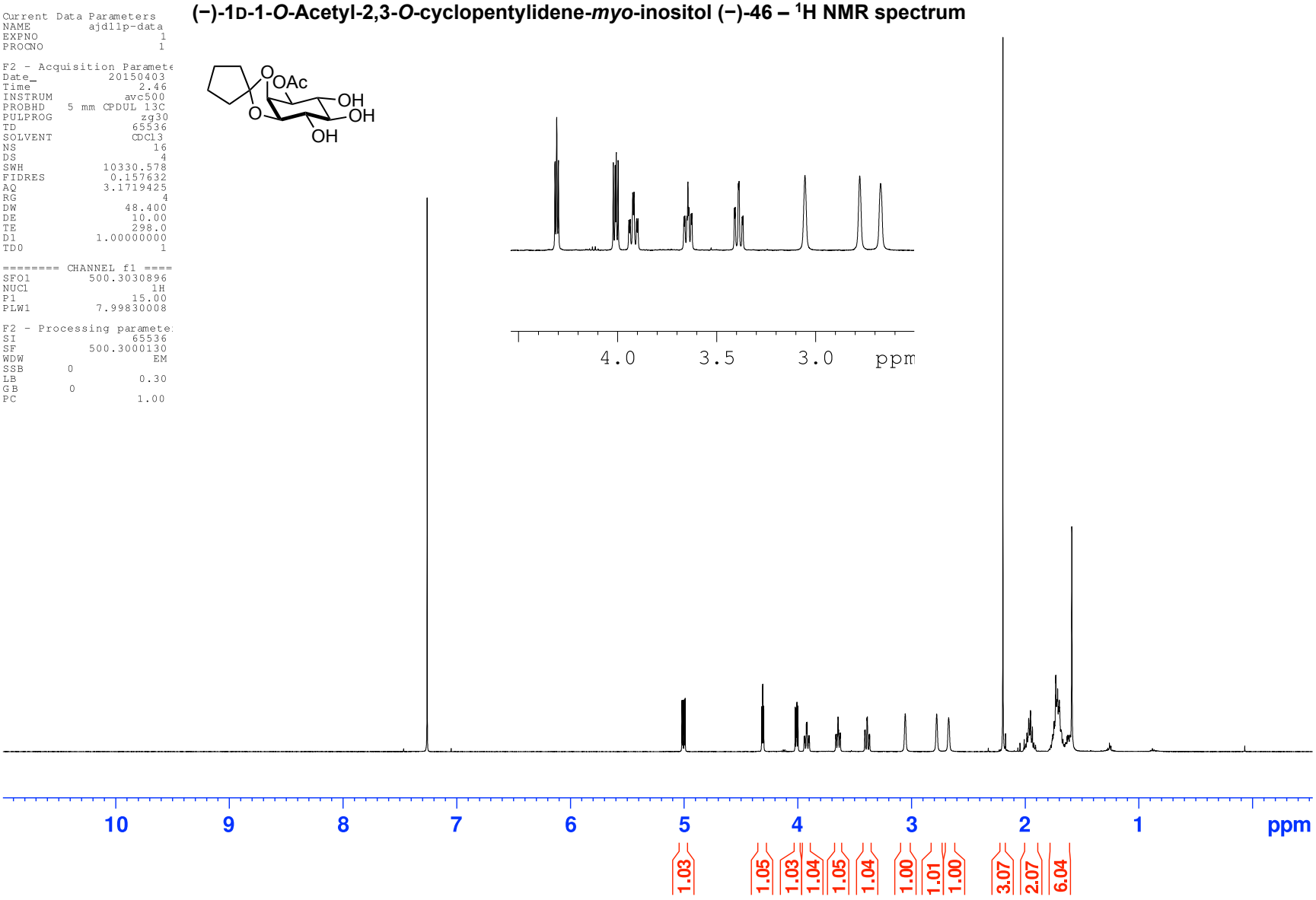
Current Data Parameters
NAME                  ajh15p
EXPNO                      1
PROCNO                     1

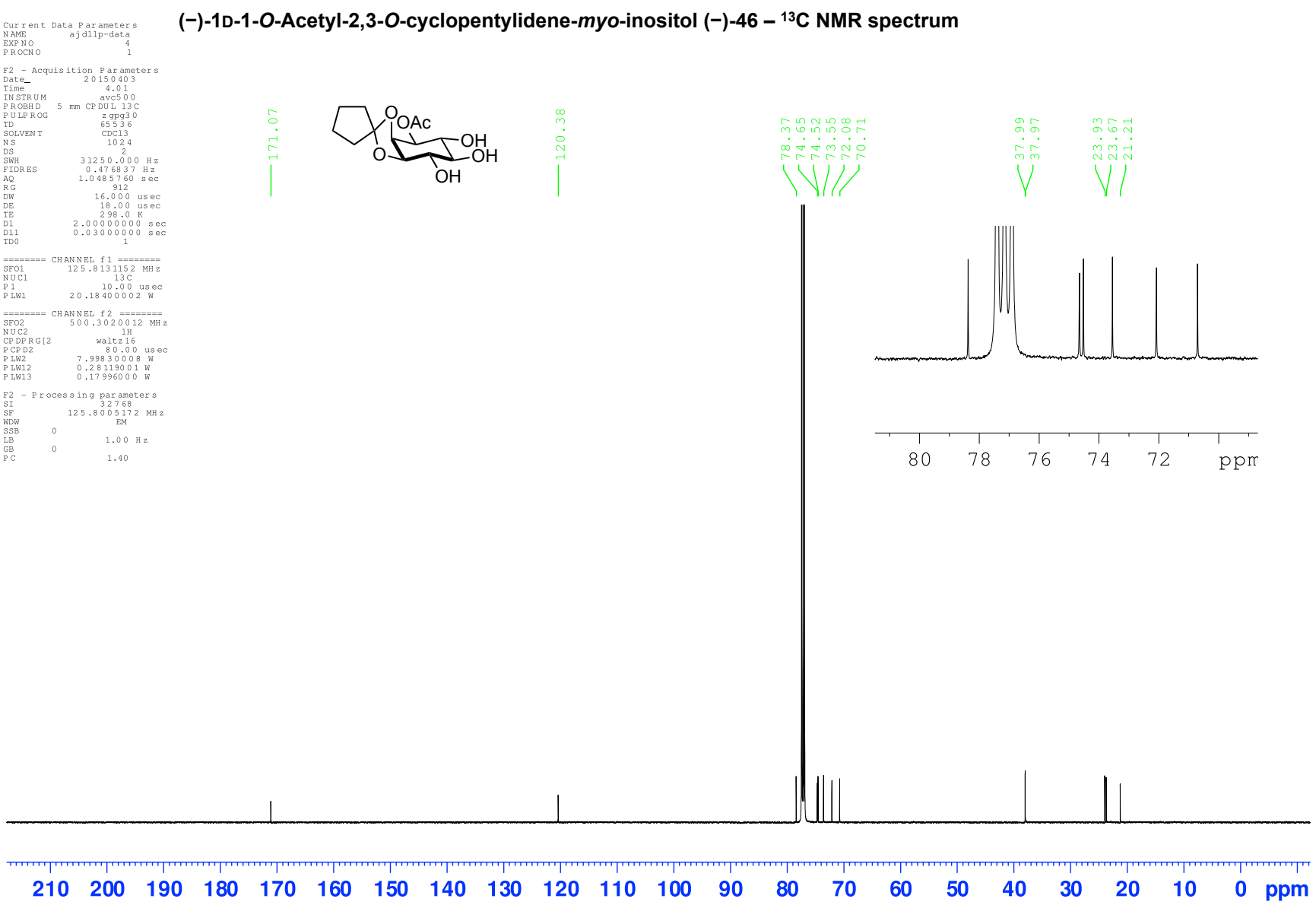
F2 - Acquisition Parameters
Date_              20170626
Time                   5.21 h
INSTRUM              avg400
PROBHD    Z108618_0816 (
PULPROG              zgpg30
TD                   131072
SOLVENT               CDCl3
NS                        16
DS                         4
SWH                64102.562 Hz
FIDRES             0.978127 Hz
AQ                 1.0223616 se
RG                    206.87
DW                     7.800 us
DE                     6.50 us
TE                     363.0 K
D1              2.00000000 se
D11             0.03000000 se
TD0                        1
SFO1           162.0039295 MH
NUC1                   31P
P1                    15.00 us
PLW1           13.00000000 W
SFO2           400.2016008 MH
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                 90.00 us
PLW2           14.00000000 W
PLW12           0.33877000 W
PLW13           0.17039999 W

F2 - Processing parameters
SI                     65536
SF             162.0039295 MH
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                     1.40
```

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-*myo*-inositol (−)-46 – ^{1}H NMR spectrum



(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-*myo*-inositol (−)-46 – ^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-*myo*-inositol (−)-47 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME         ajg9p-data2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161101
Time              17.08
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg30
TD                65536
SOLVENT            CDCl3
NS                    16
DS                     4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                     4
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.3030896 MHz
NUC1                1H
P1                15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI                 65536
SF            500.3000135 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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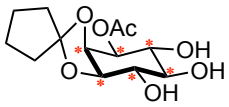
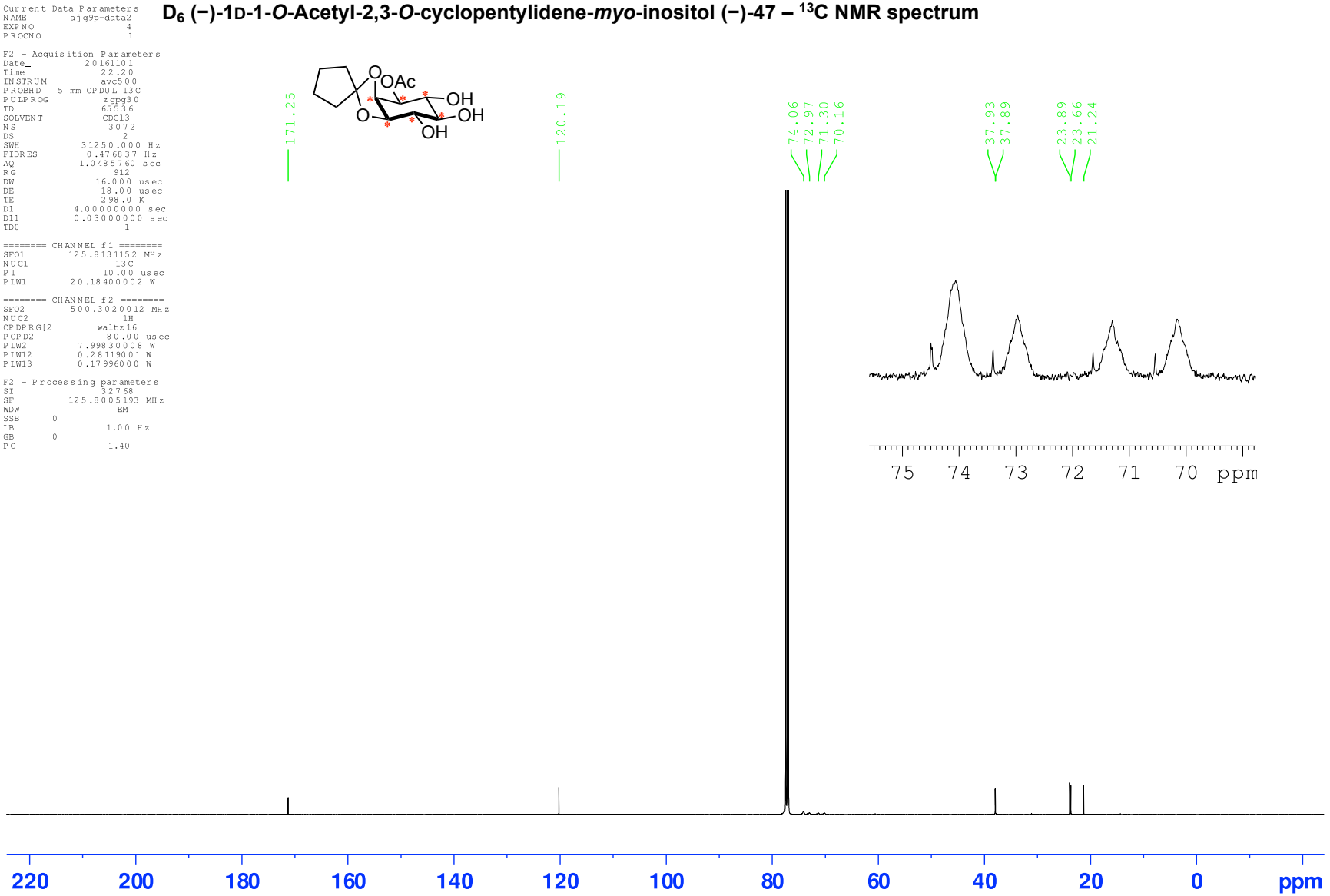
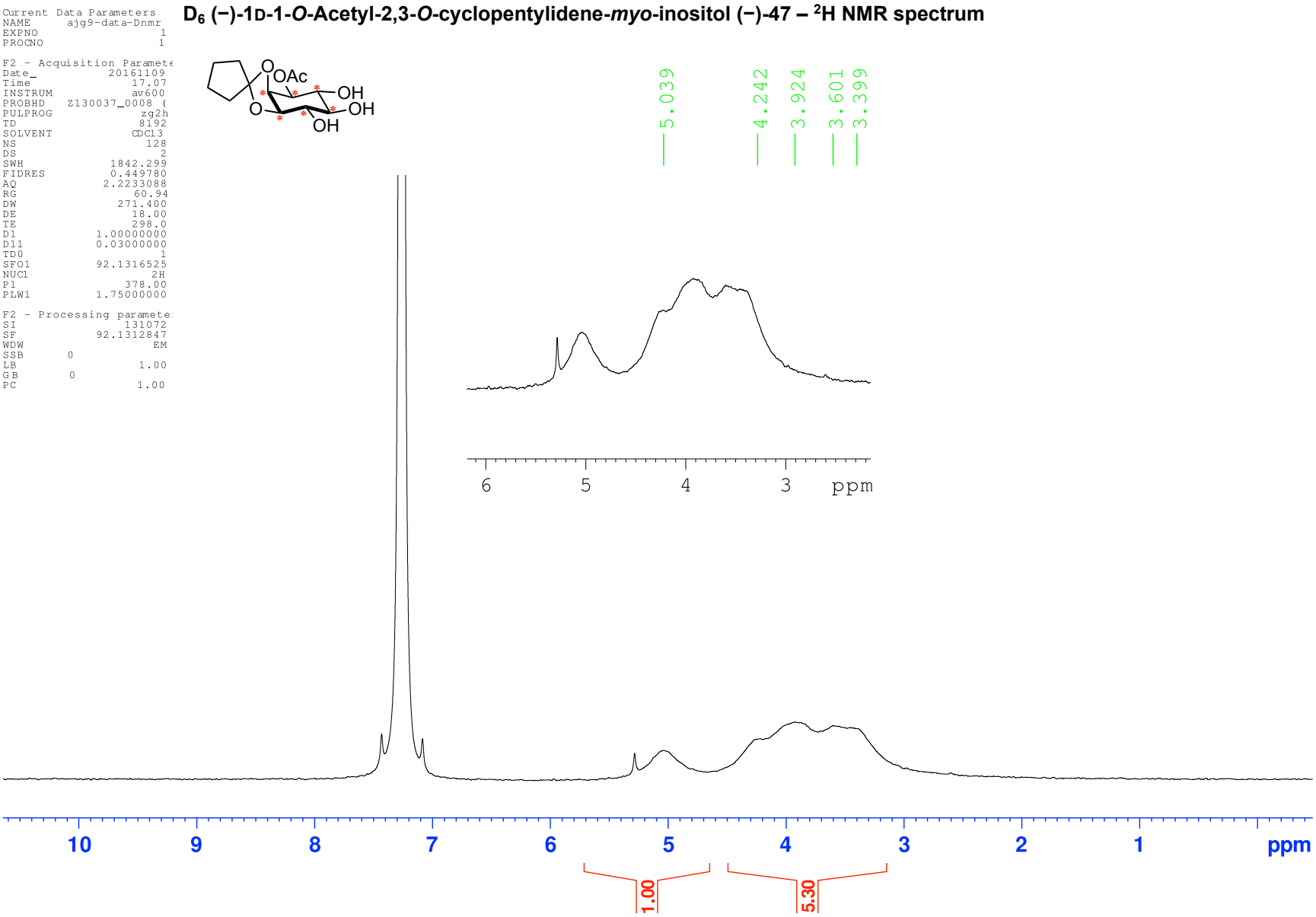


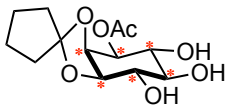
D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-*myo*-inositol (−)-47 – ^{13}C NMR spectrum



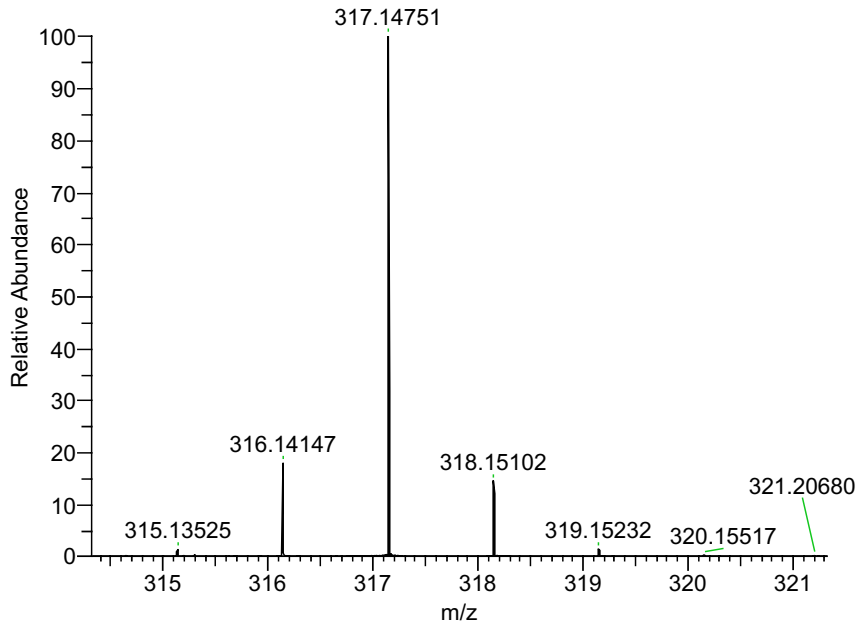
D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-*myo*-inositol (−)-47 – ^{2}H NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-*myo*-inositol (−)-47 – Mass spectrum

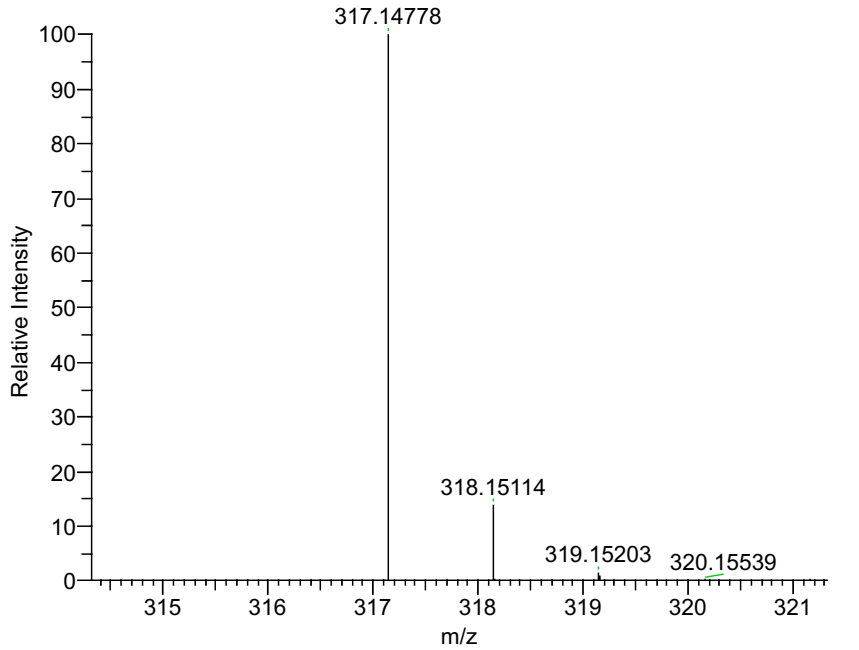


S:\data\Nov 16\ESI59700.raw 08/11/2016 2:59 pm



NL: 5.87E7
ESI59700 #15-25 RT: 0.17-0.28 AV: 6 NL: 5.87E+007
T: FTMS {1,1} + p ESI Full lock ms [80.00-1600.00]

Measured Spectrum

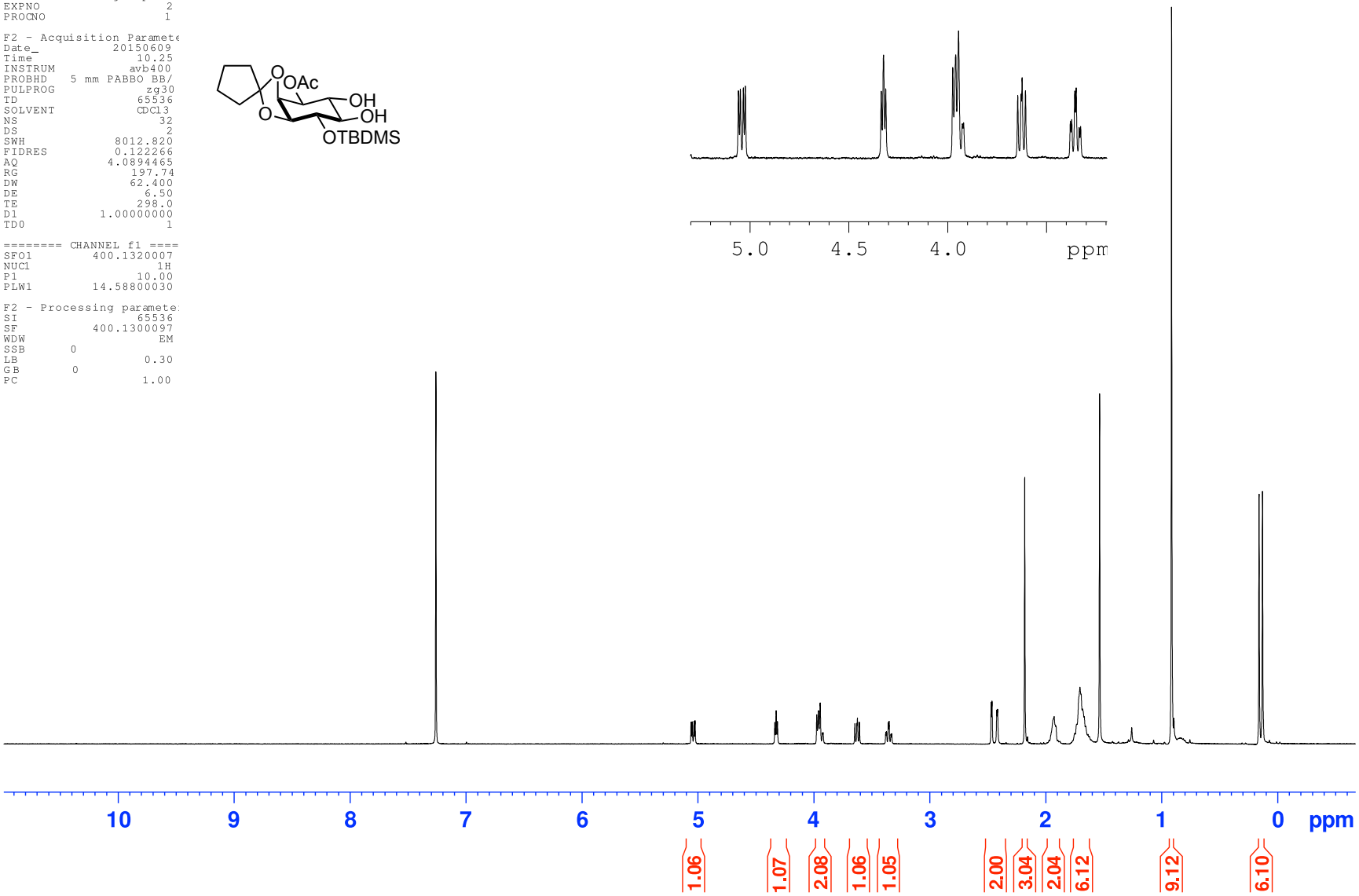


NL: 8.53E5
C13H14[2]H6O7Na1: $C_{13}H_{14}{}^{2}H_6O_7Na$
Chrg 1 R: 1000000 Res. Pwr. @FWHM

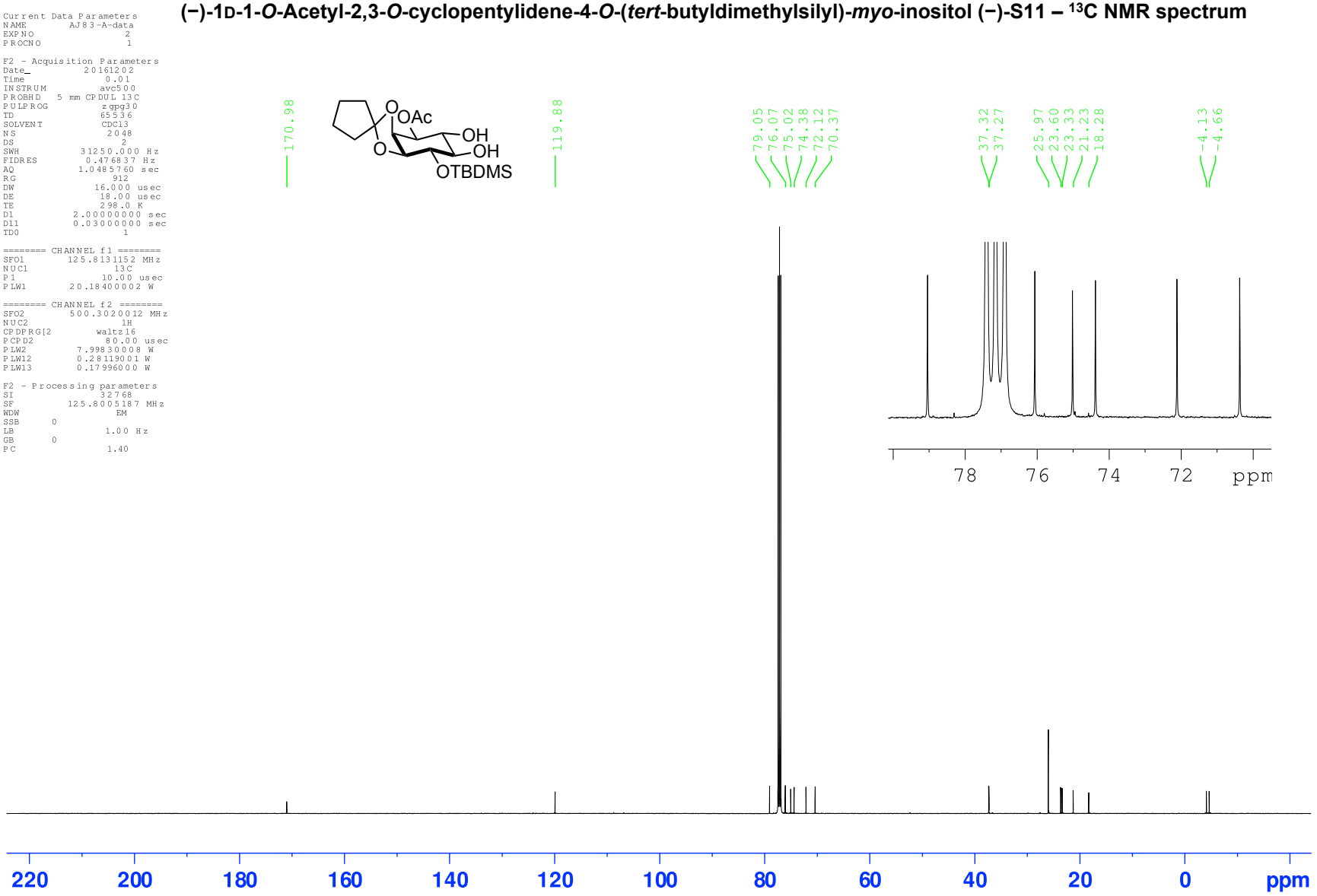
Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
317.14752	$C_{13}H_{14}{}^{2}H_6O_7{}^{23}Na$	3.5	-0.83	317.14778

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol (−)-S11 – ^{1}H NMR spectrum



(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol (−)-S11 – ^{13}C NMR spectrum



(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol (−)-S11
^{1}H-^{29}Si HMBC NMR spectrum

```
Current Data Parameters
NAME     ajd29p-f3-Si-H
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20150505
Time              11.25
INSTRUM          avx500
PROBHD   Z113652_0208 (
PULPROG      hmbcgpndqf
TD                 4096
SOLVENT           CDCl3
NS                    2
DS                   16
SWH            6009.615 Hz
FIDRES          1.467191 Hz
AQ             0.3407872 sec
RG                191.37
DW                83.200 usec
DE                 6.50 usec
TE                298.0 K
CNST13          6.0000000
d0             0.00000300 sec
D1             2.00000000 sec
d6             0.08333334 sec
D16            0.00020000 sec
in0      0 sec
ST1CNT                0
d0orig         0.00000300 sec
ph1loop               0
t1loop                0
SFO1         500.1323506 MHz
NUC1                 1H
P1                10.00 usec
p2                20.00 usec
PLW1         20.50000000 W
SFO2          99.3617620 MHz
NUC2                29Si
P3                12.50 usec
PLW2         80.00000000 W
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1              70.00 %
GPZ2              30.00 %
GPZ3              59.90 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                  128
SFO1           99.36176 MHz
FIDRES         77.659042 Hz
SW              100.042 ppm
FnMODE                QF

F2 - Processing parameters
SI                  2048
SF          500.1300096 MHz
WDW                 SINE
SSB                    4
LB       0 Hz
GB       0
PC                 1.40

F1 - Processing parameters
SI                  1024
MC2                   QF
SF           99.3624076 MHz
WDW                QSINE
SSB      0
LB       0 Hz
GB       0
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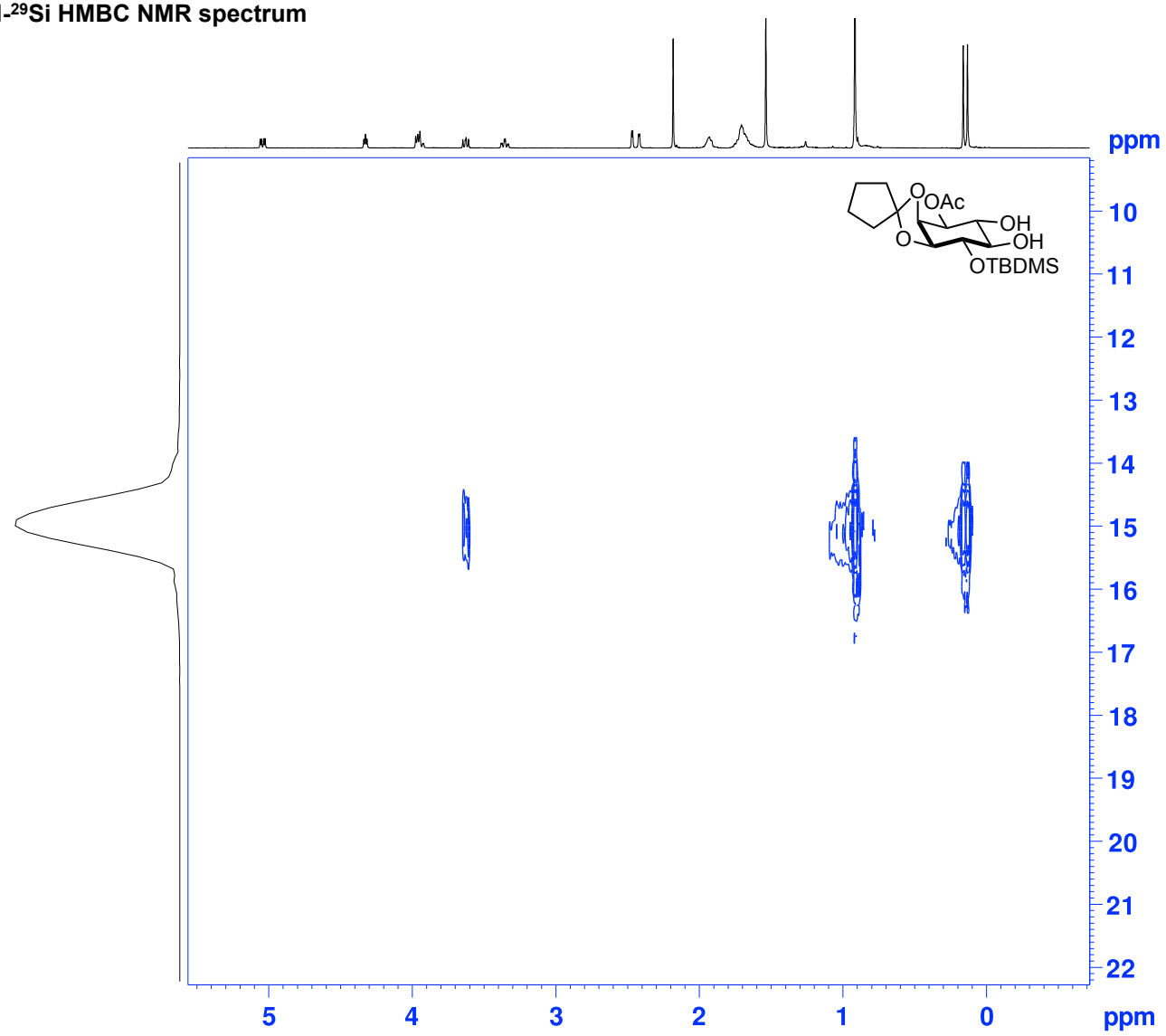
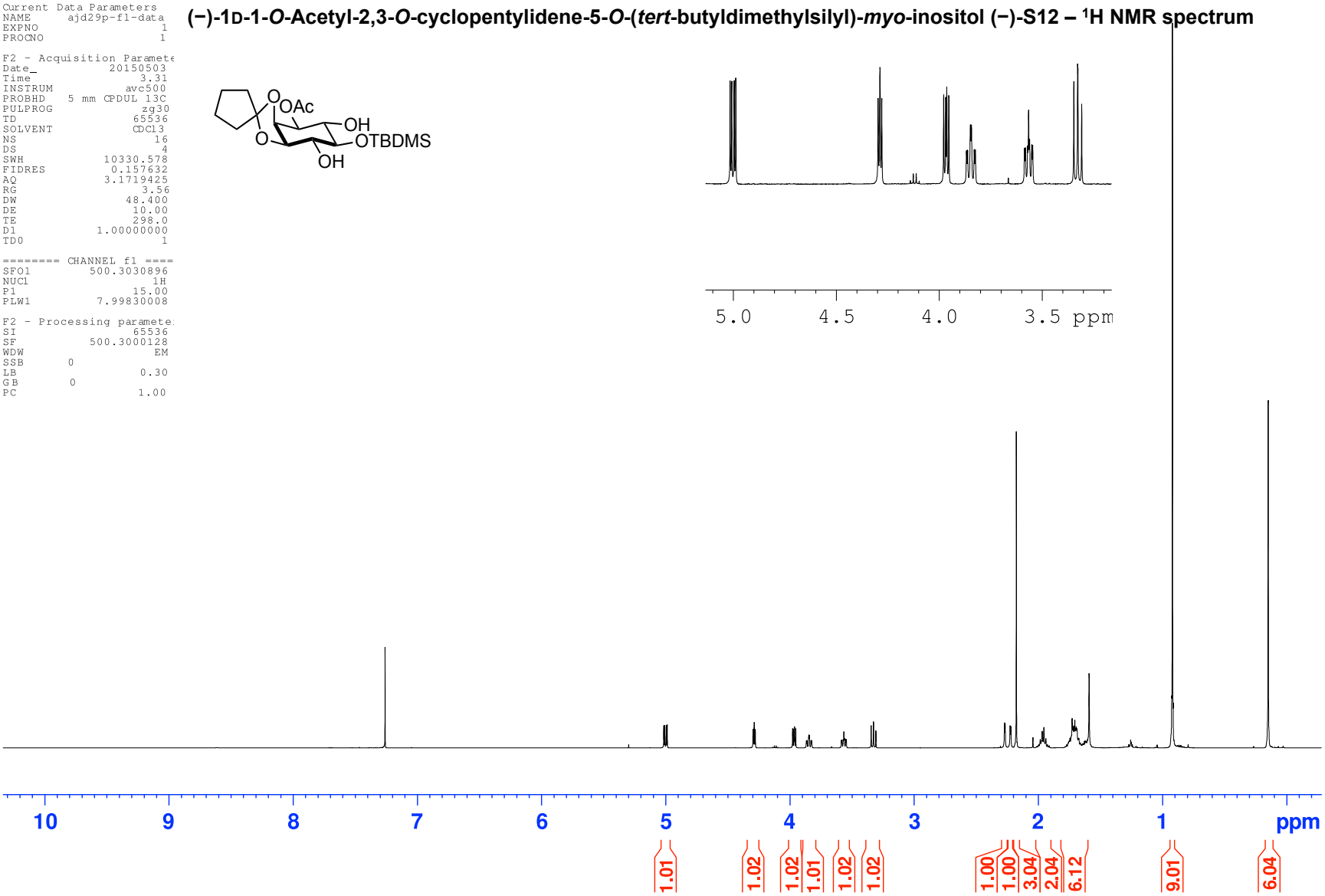
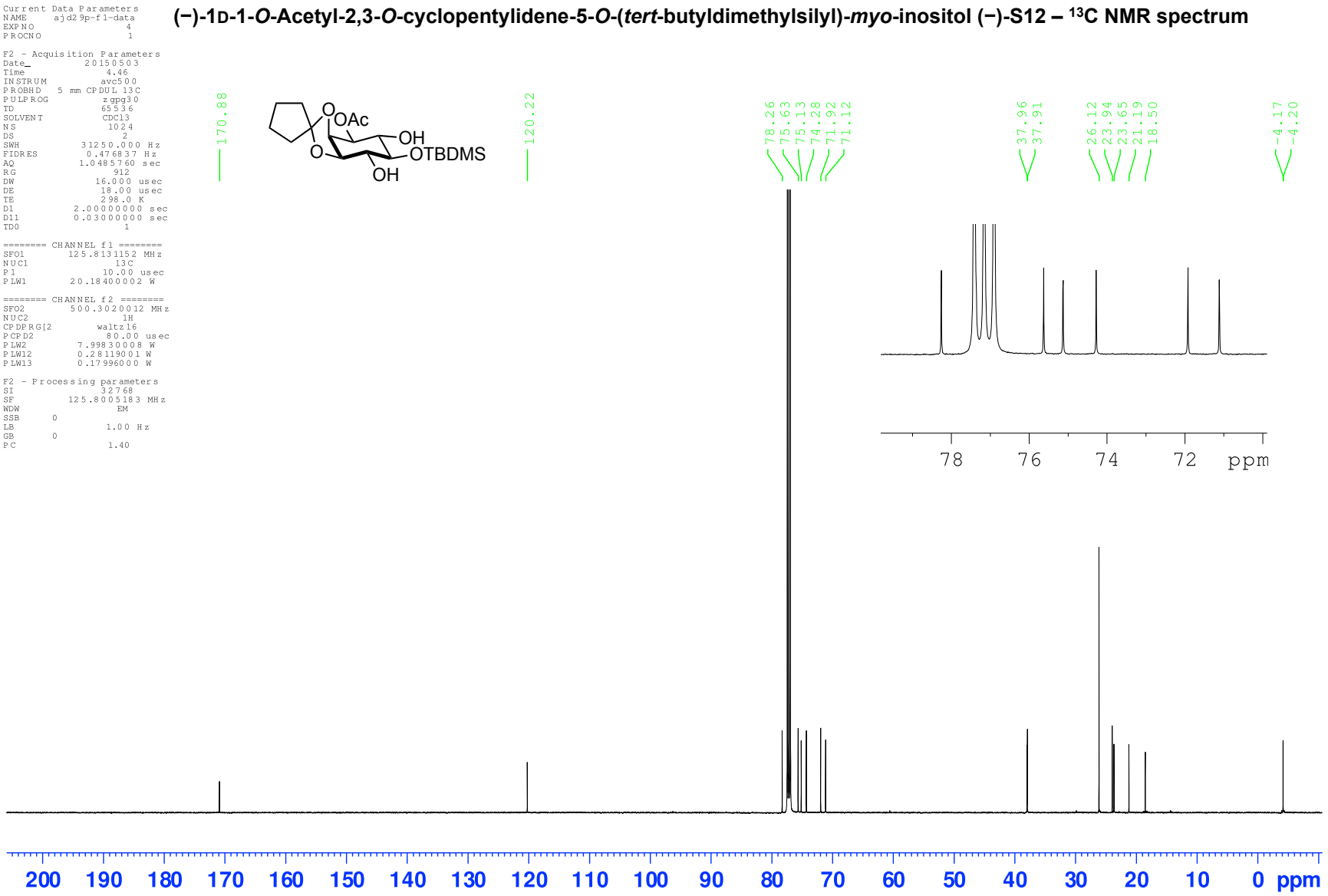


(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol (−)-S12 – ^{1}H NMR spectrum



(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol (−)-S12 – ^{13}C NMR spectrum



(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-6-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol (−)-S13 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME        aj83p-C-data
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160930
Time              16.47
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT          CD2Cl2
NS                   16
DS                    4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                    2
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1                1H
P1                15.00 usec
PLW1           7.99830008 W

F2 - Processing parameters
SI                65536
SF           500.3000207 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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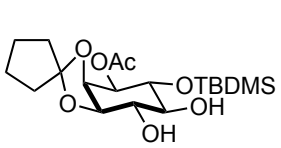
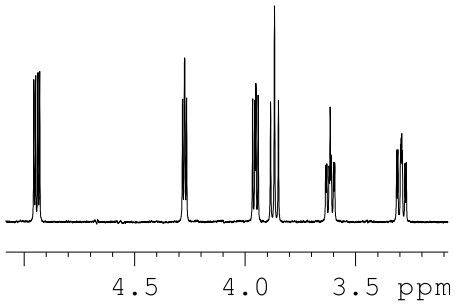
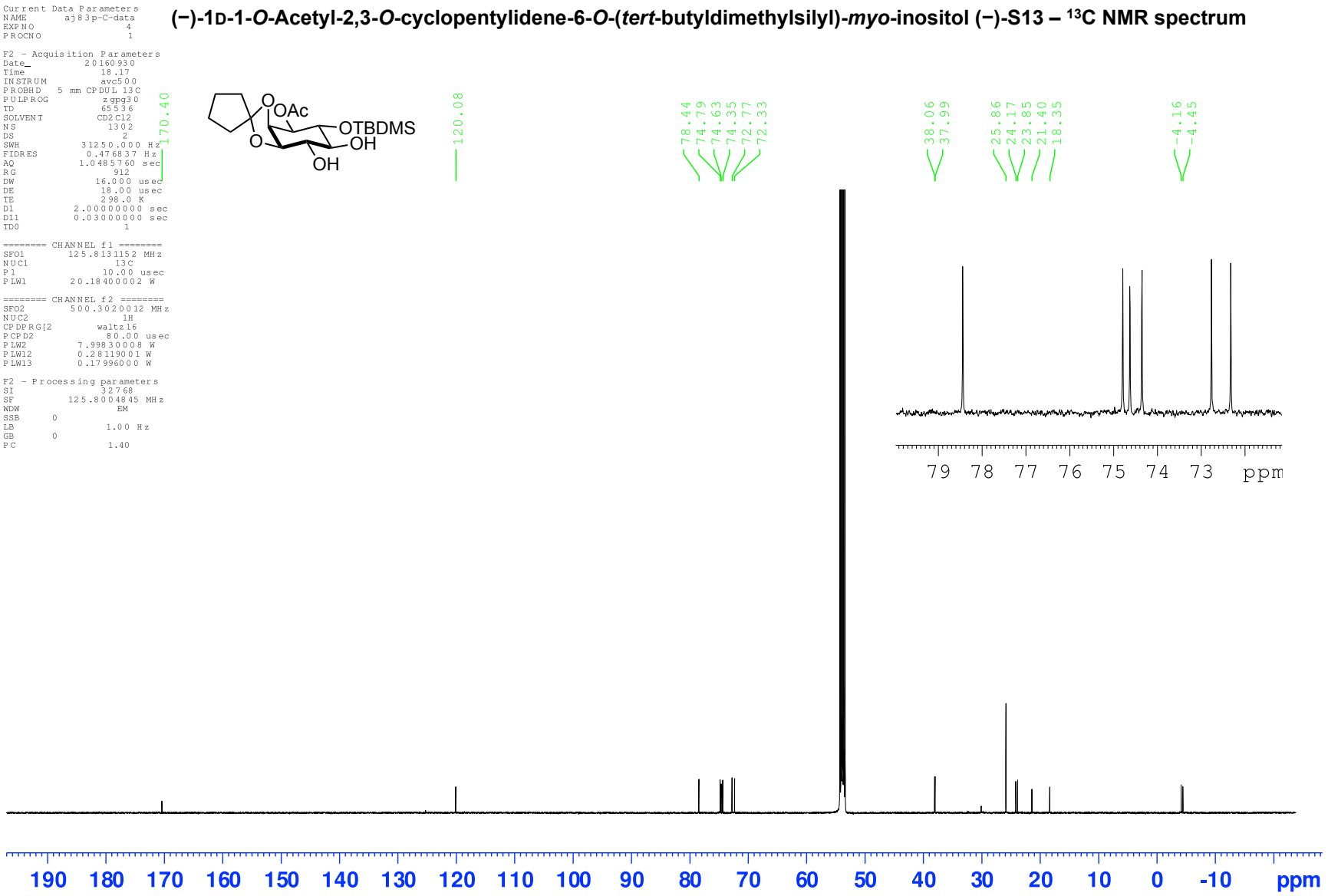




(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-6-*O*-(*tert*-butyldimethylsilyl)-*myo*-inositol (−)-S13 – ^{13}C NMR spectrum



(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-*myo*-inositol (−)-48 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME          ajf40p-400
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160609
Time               8.48 h
INSTRUM          avh400
PROBHD   Z108618_0873 (
PULPROG           zg60
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH            8012.820 Hz
FIDRES         0.244532 Hz
AQ             4.0894465 sec
RG                15.33
DW                62.400 usec
DE                 6.50 usec
TE                296.6 K
D1           1.00000000 sec
TD0                  1
SFO1         400.1324008 MHz
NUC1                 1H
P1                14.00 usec
PLW1         14.36999989 W

F2 - Processing parameters
SI                32768
SF           400.1300101 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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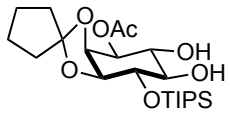
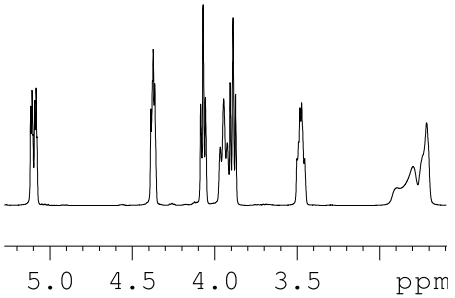
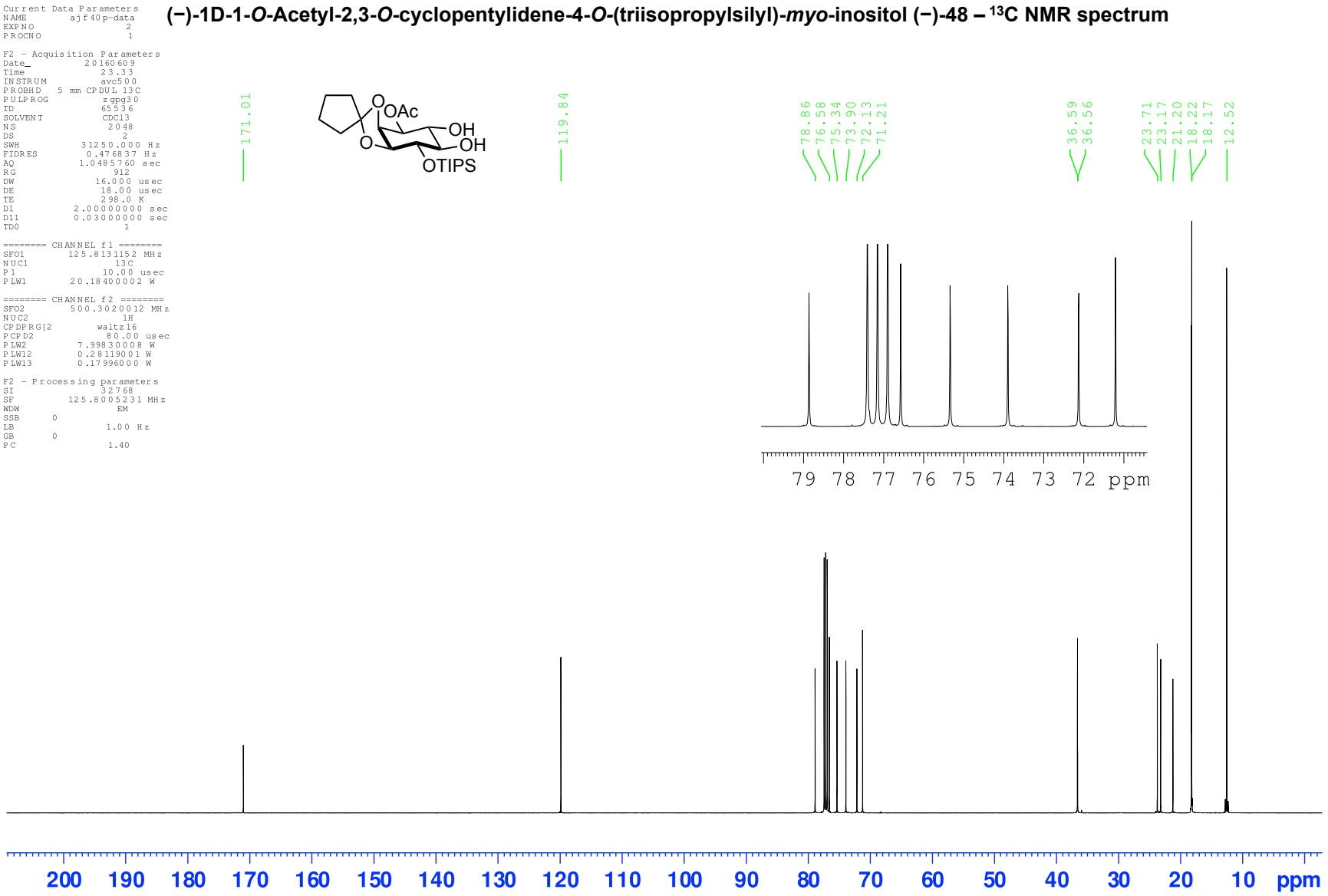




(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-*myo*-inositol (−)-48 – ^{13}C NMR spectrum



(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-*myo*-inositol (−)-48
^{1}H-^{29}Si HMBC NMR spectrum

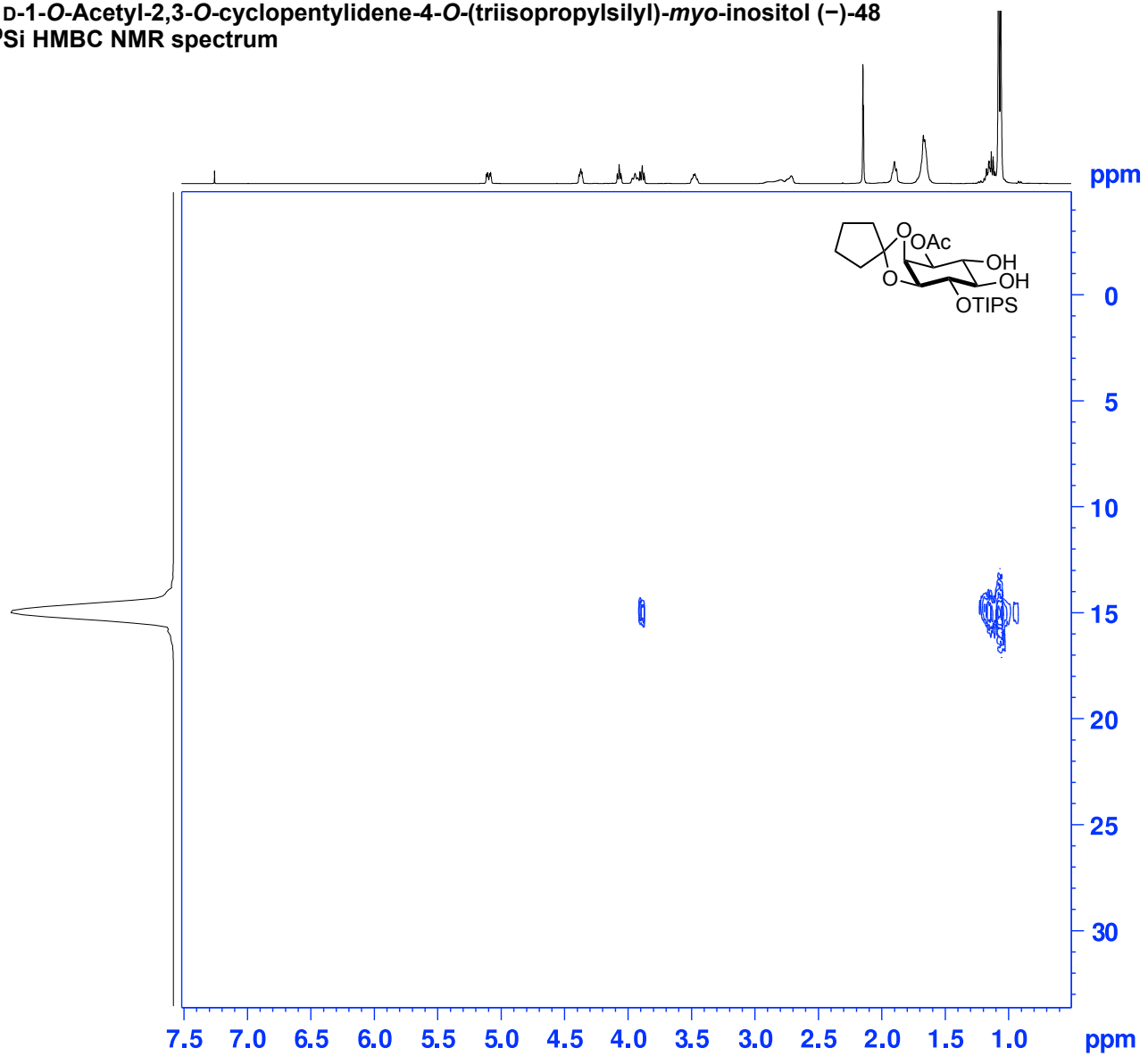
```
Current Data Parameters
NAME      ajd65p-f2-Si-H
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20150709
Time             11.46
INSTRUM          avx500
PROBHD   Z113652_0208 (
PULPROG      hmbcgpndqf
TD                 4096
SOLVENT           CDCl3
NS                   16
DS                   16
SWH            6009.615 Hz
FIDRES          1.467191 Hz
AQ             0.3407872 sec
RG                191.37
DW                83.200 usec
DE                 6.50 usec
TE                298.0 K
CNST13         6.0000000
d0            0.00000300 sec
D1            2.00000000 sec
d6            0.08333334 sec
D16           0.00020000 sec
in0      0 sec
ST1CNT                0
d0orig        0.00000300 sec
ph1loop               0
t1loop                0
SFO1         500.1323506 MHz
NUC1                 1H
P1                10.00 usec
p2                20.00 usec
PLW1         20.50000000 W
SFO2          99.3617620 MHz
NUC2                29Si
P3                12.50 usec
PLW2         80.00000000 W
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1              70.00 %
GPZ2              30.00 %
GPZ3              59.90 %
P16             1000.00 usec

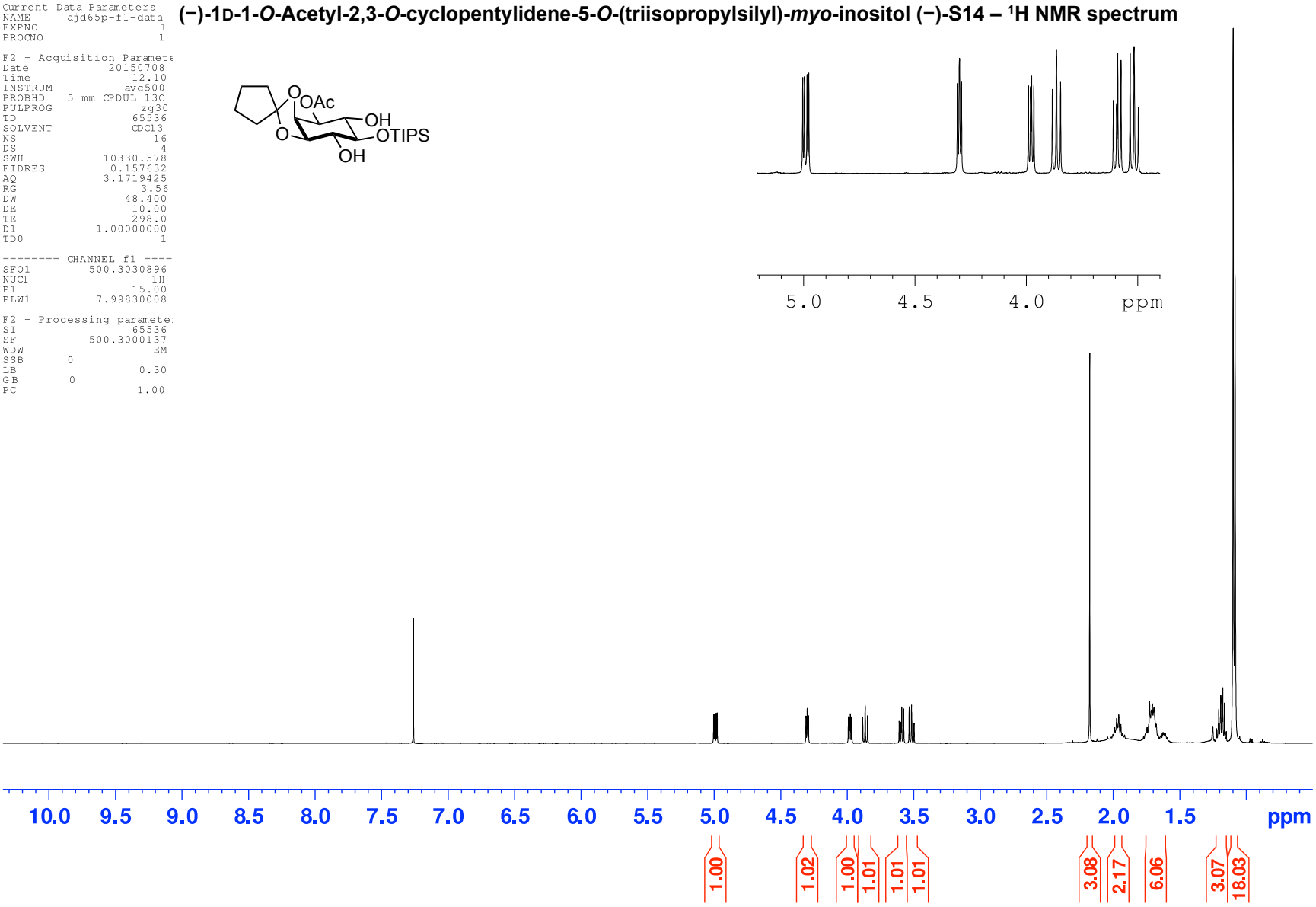
F1 - Acquisition parameters
TD                  128
SFO1           99.36176 MHz
FIDRES         77.659042 Hz
SW              100.042 ppm
FnMODE                QF

F2 - Processing parameters
SI                  2048
SF           500.1300197 MHz
WDW                 SINE
SSB                    4
LB       0 Hz
GB       0
PC                  1.40

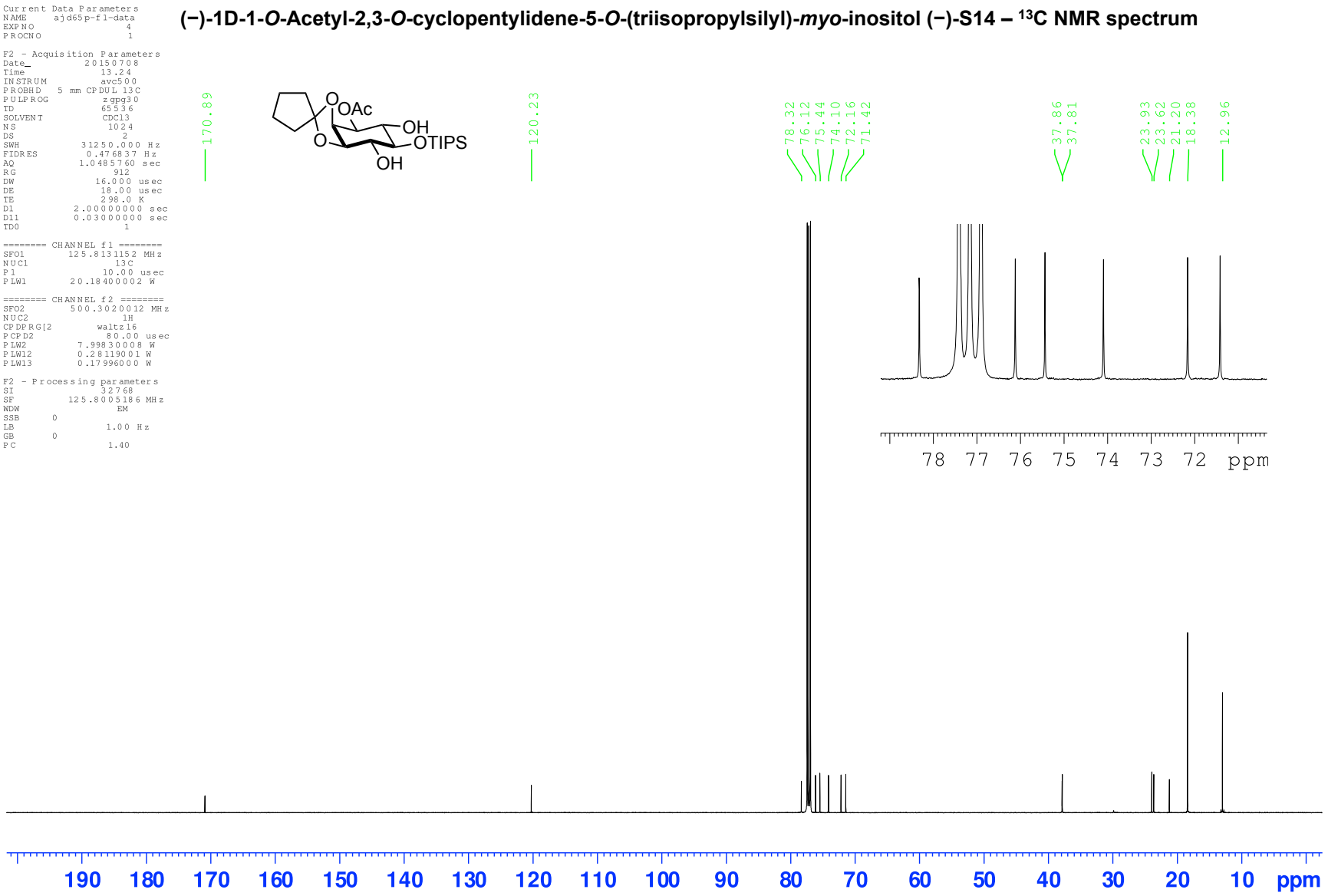
F1 - Processing parameters
SI                  1024
MC2                   QF
SF            99.3617619 MHz
WDW                QSINE
SSB      0
LB       0 Hz
GB       0
```



(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5-*O*-(triisopropylsilyl)-*myo*-inositol (−)-S14 – ^{1}H NMR spectrum



(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5-*O*-(triisopropylsilyl)-*myo*-inositol (−)-S14 – ^{13}C NMR spectrum



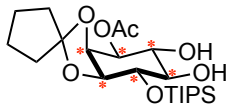
D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-*myo*-inositol (−)-49 – ^{1}H NMR spectrum

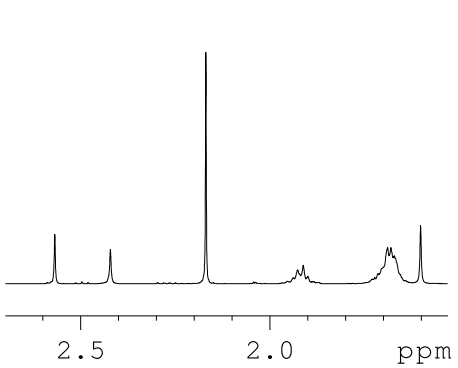
```
Current Data Parameters
NAME         ajg11-p-data
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20161101
Time                23.28
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719425 sec
RG                  3.56
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

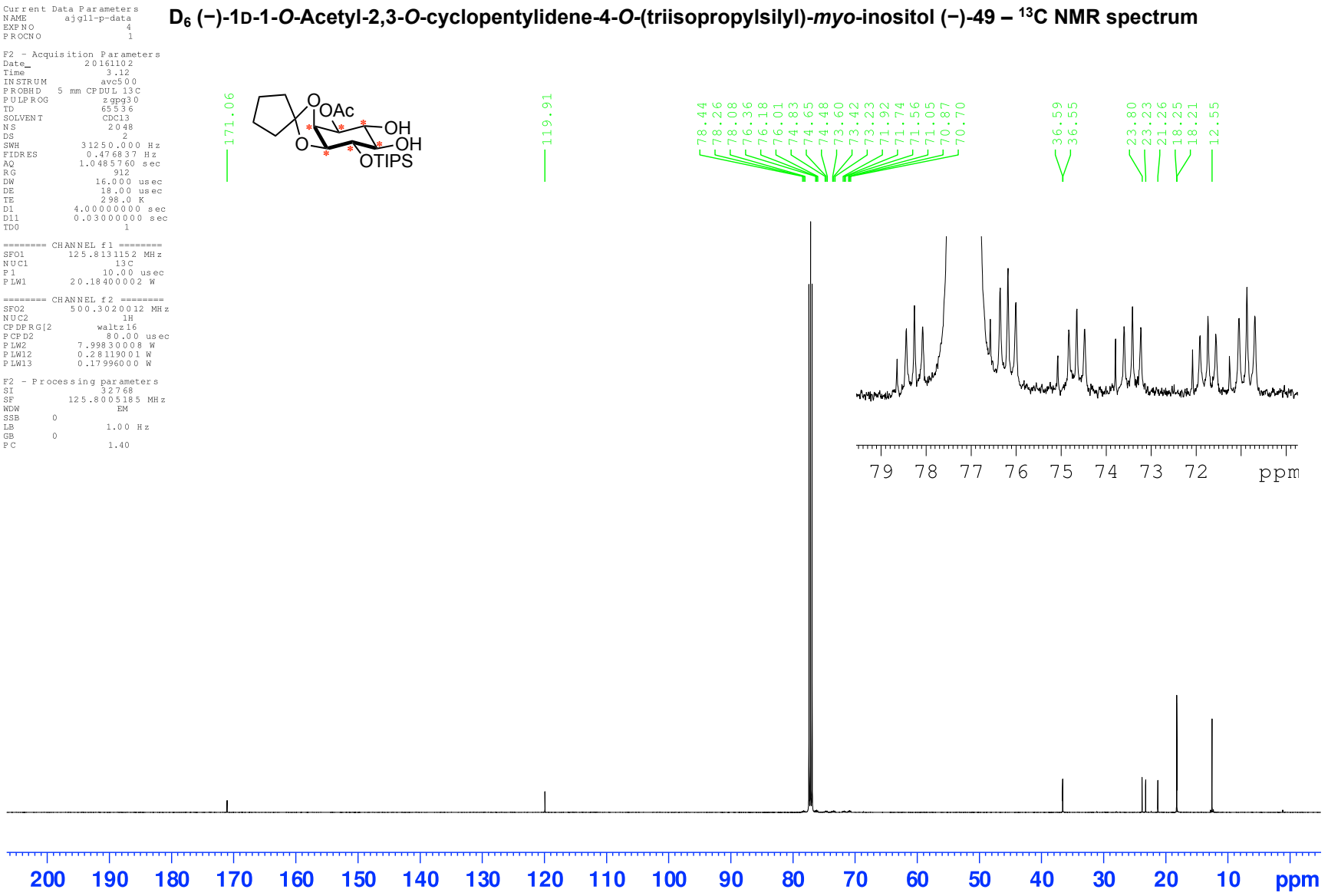
======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1                   1H
P1                  15.00 usec
PLW1         7.99830008 W

F2 - Processing parameters
SI                 65536
SF          500.3000133 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```





D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-*myo*-inositol (−)-49 – ^{13}C NMR spectrum

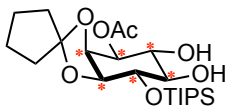


D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-*myo*-inositol (−)-49 – ^{2}H NMR spectrum

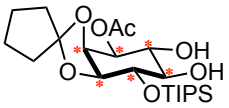
```
Current Data Parameters
NAME      ajg11-data-DNMR
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20161109
Time               16.41
INSTRUM            av600
PROBHD    Z130037_0008 (
PULPROG            zg2h
TD                 8192
SOLVENT           CDCl3
NS                   69
DS                    2
SWH           1842.299
FIDRES        0.449780
AQ            2.2233088
RG                60.94
DW               271.400
DE                18.00
TE                298.0
D1           1.00000000
D11          0.03000000
TD0                   1
SFO1         92.1316525
NUC1                 2H
P1                378.00
PLW1         1.75000000

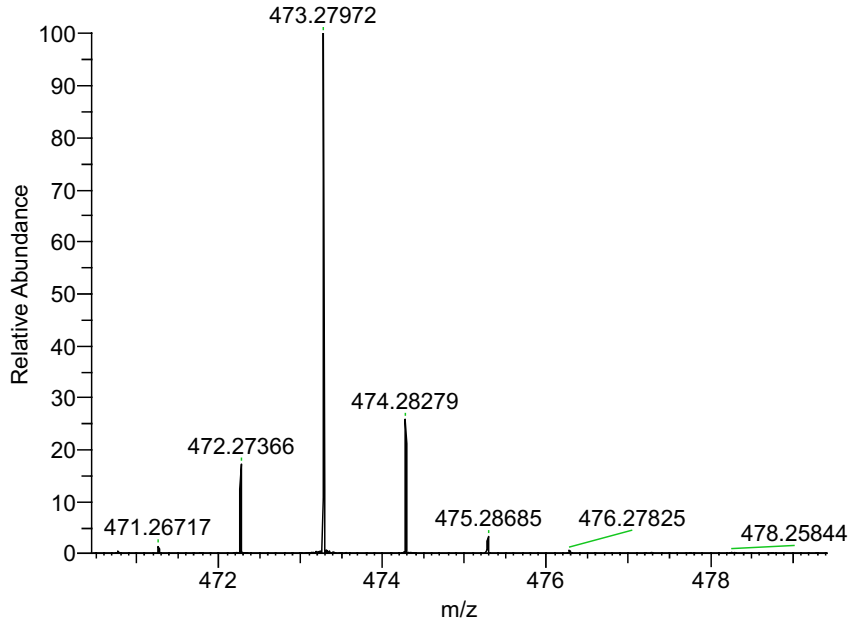
F2 - Processing paramete
SI                16384
SF           92.1312840
WDW                  EM
SSB       0
LB                 0.30
GB        0
PC                 1.00
```



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)- *myo*-inositol (−)-49 – Mass spectrum

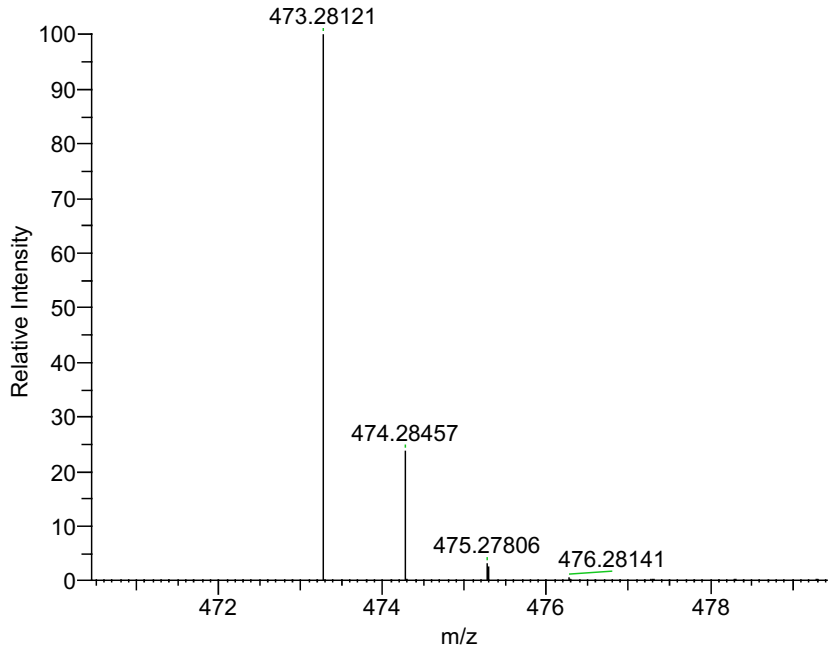


S:\data\Nov 16\ESI59716.raw 08/11/2016 3:38 pm



NL: 5.97E7
ESI59716 #15-25 RT: 0.17-0.28 AV: 6 NL: 5.97E+007
T: FTMS {1,1} + p ESI Full ms [80.00-1600.00]

Measured Spectrum



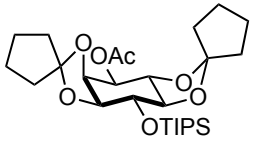
NL: 7.13E5
C22H34[2]H6O7Na1Si1: C_{22} H_{34} $^{2}H_{6}$ O_{7} Na Si Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
473.27972	$C_{22}H_{34}{}^{2}H_{6}O_{7}{}^{23}Na{}^{28}Si$	3.5	-3.14	473.28121

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-50

^{1}H NMR spectrum

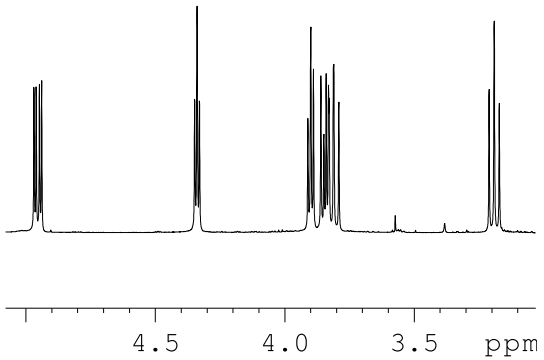


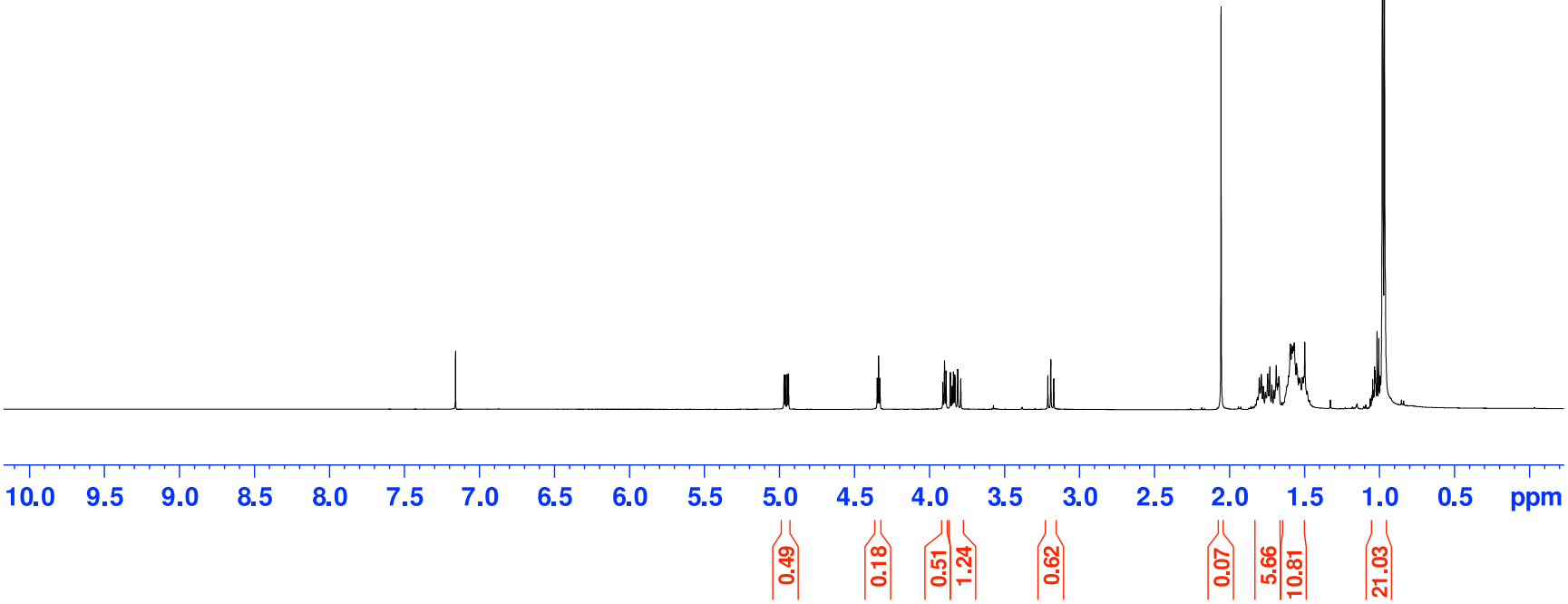

```
Current Data Parameters
NAME         ajel6p-data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20150915
Time              21.07
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           10330.578
FIDRES         0.157632
AQ            3.1719425
RG                  3.2
DW                48.400
DE                10.00
TE                298.0
D1           1.00000000
TD0                    1

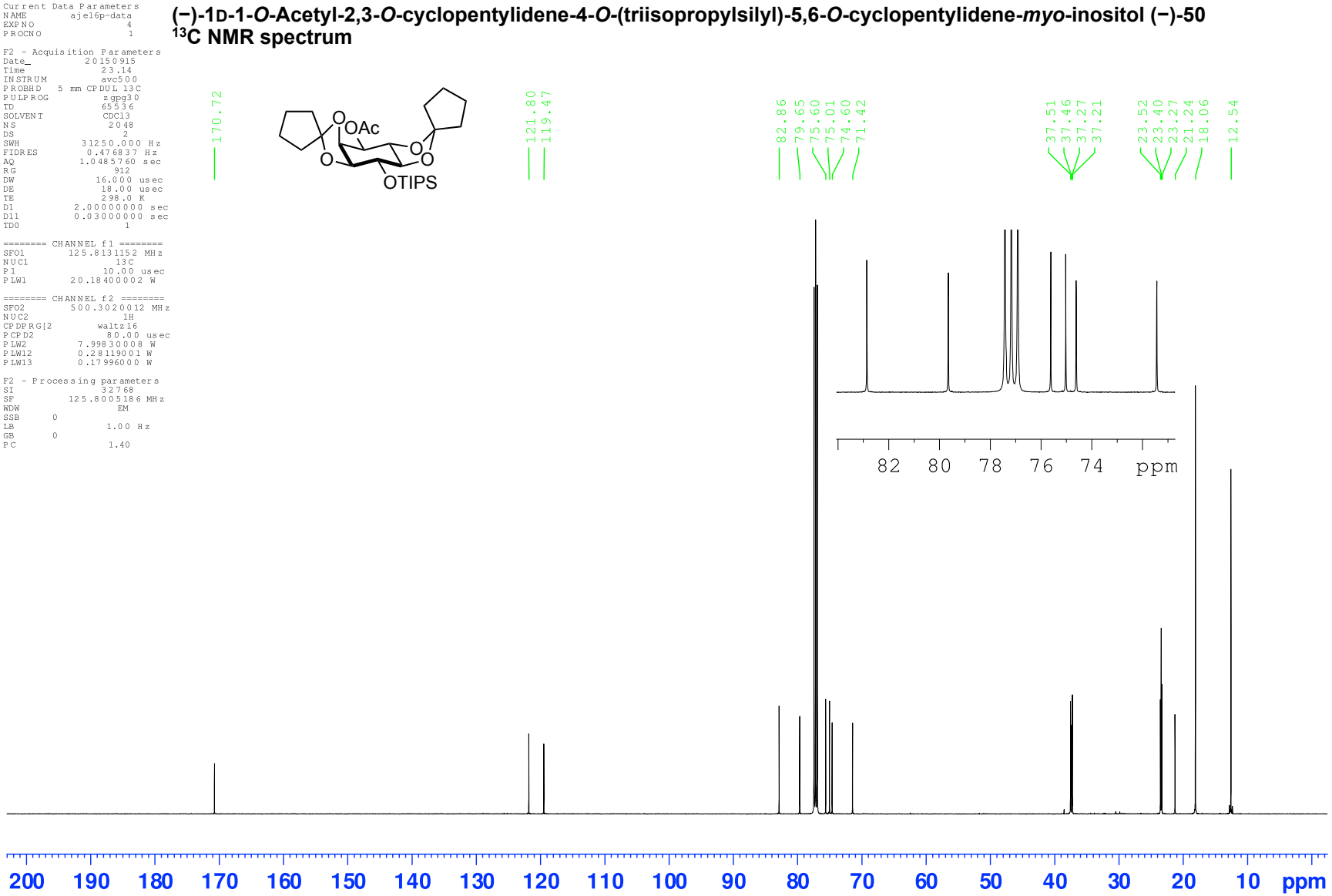
======== CHANNEL f1 ====
SFO1         500.3030896
NUC1                1H
P1                15.00
PLW1          7.99830008

F2 - Processing paramete
SI                65536
SF           500.3000634
WDW                  EM
SSB       0
LB                 0.30
GB        0
PC                 1.00
```





(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-50
^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-5,6-*O*-cyclopentylidene- *myo*-inositol (−)-51

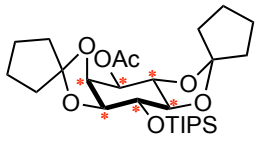
^{1}H NMR spectrum

```
Current Data Parameters
NAME         ajg12p-data
EXPNO                  1
PROCNO                 1

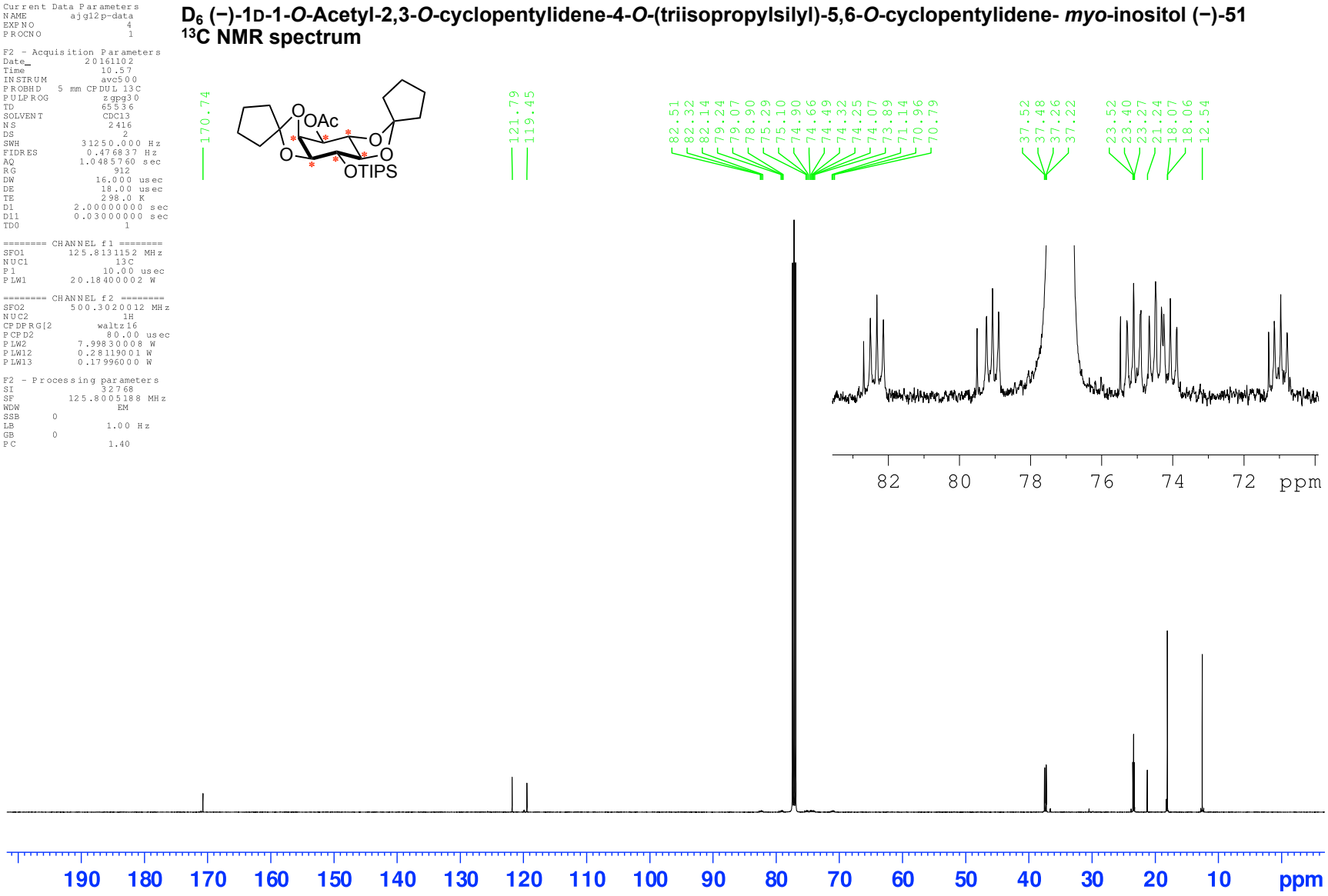
F2 - Acquisition Parameters
Date_           20161102
Time                9.53
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                  2.56
DW                 48.400 usec
DE                 10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.3030896 MHz
NUC1                1H
P1                15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI                 65536
SF           500.3000135 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-5,6-*O*-cyclopentylidene- *myo*-inositol (−)-51
^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-5,6-*O*-cyclopentylidene- *myo*-inositol (−)-51
^2H NMR spectrum

```
Current Data Parameters
NAME      ajg12p-data-Dnmr
EXPNO                    2
PROCNO                   1

F2 - Acquisition Paramete
Date_             20161110
Time                 10.15
INSTRUM              av600
PROBHD    Z130037_0008 (
PULPROG              zg2h
TD                   8192
SOLVENT             CDCl3
NS                    128
DS                      2
SWH              1842.299
FIDRES           0.449780
AQ               2.2233088
RG                   60.94
DW                  271.400
DE                   18.00
TE                   298.0
D1               1.00000000
D11              0.03000000
TD0                      1
SFO1             92.1316525
NUC1                    2H
P1                   378.00
PLW1             1.75000000

F2 - Processing paramete
SI                  131072
SF               92.1312838
WDW                     EM
SSB       0
LB                    0.30
GB        0
PC                    1.00
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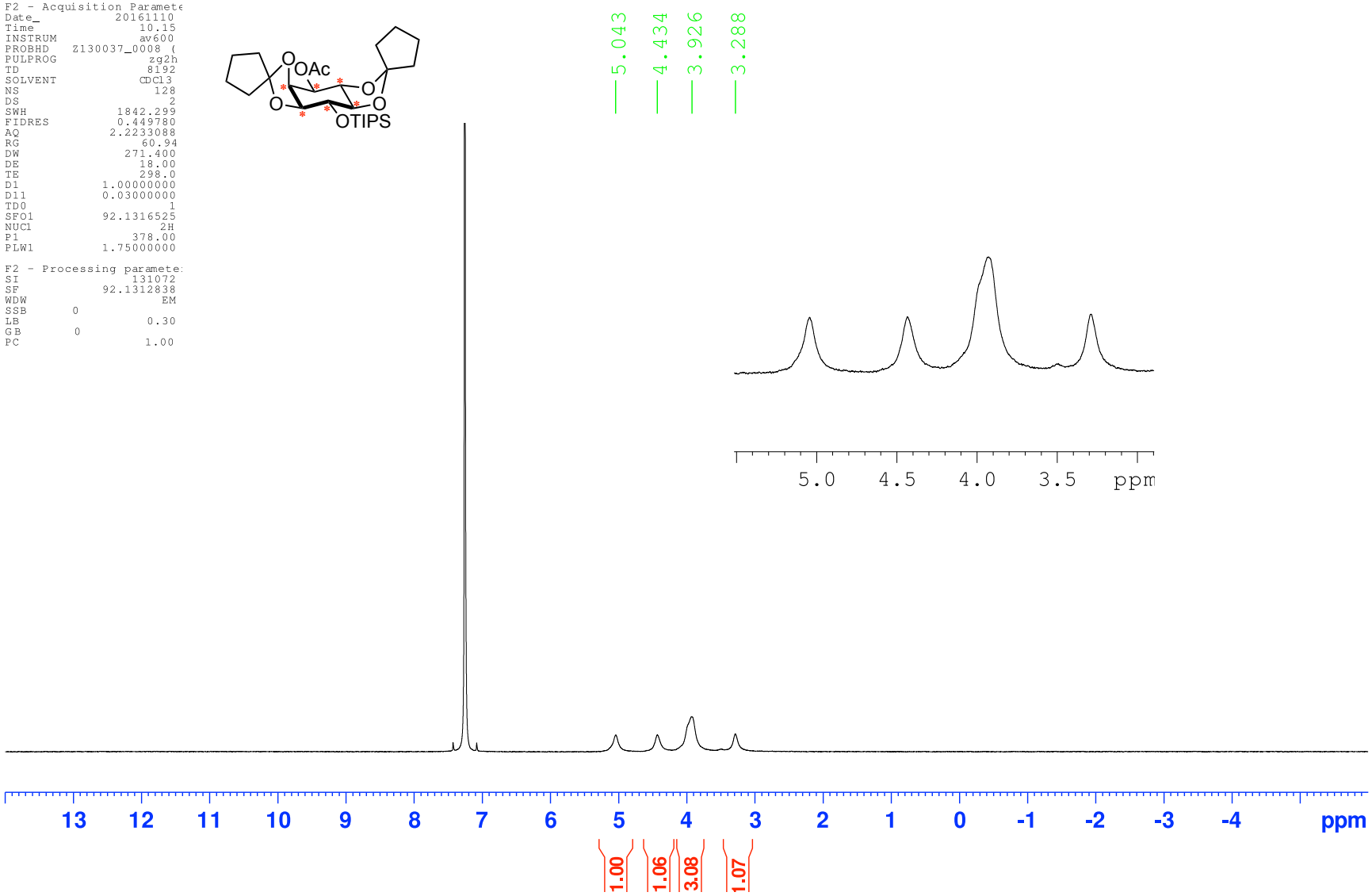
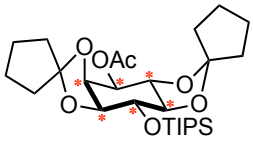
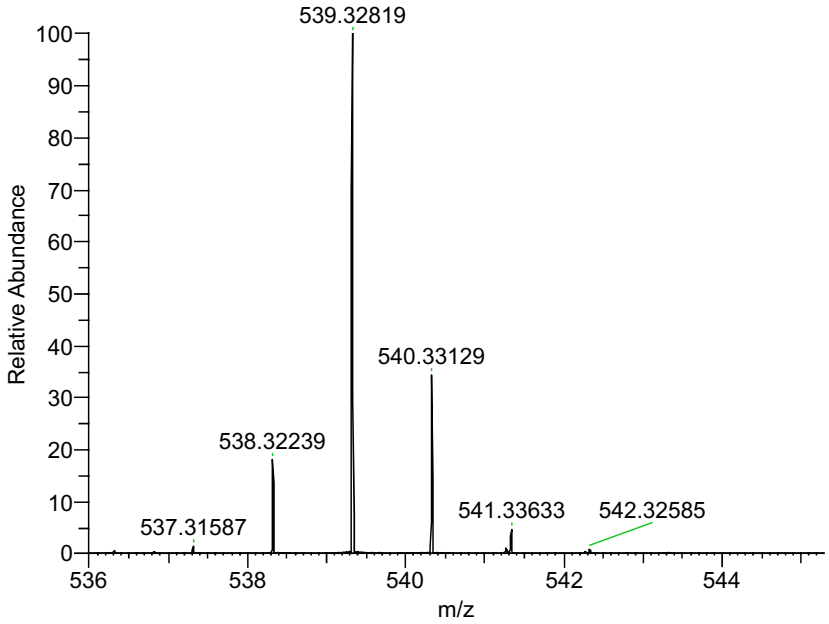


D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-4-*O*-(triisopropylsilyl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-51 – Mass spectrum

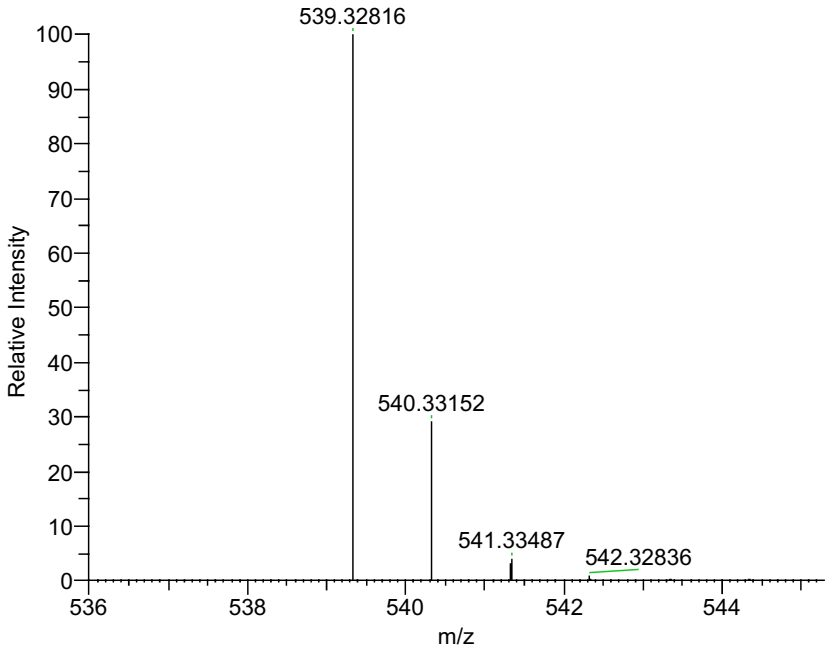


S:\data\Nov 16\ESI59717.raw 08/11/2016 3:54 pm



NL: 4.94E7
ESI59717 #15-25 RT: 0.17-0.28 AV: 6 NL: 4.94E+007
T: FTMS {1,1} + p ESI Full lock ms [80.00-1600.00]

Measured Spectrum

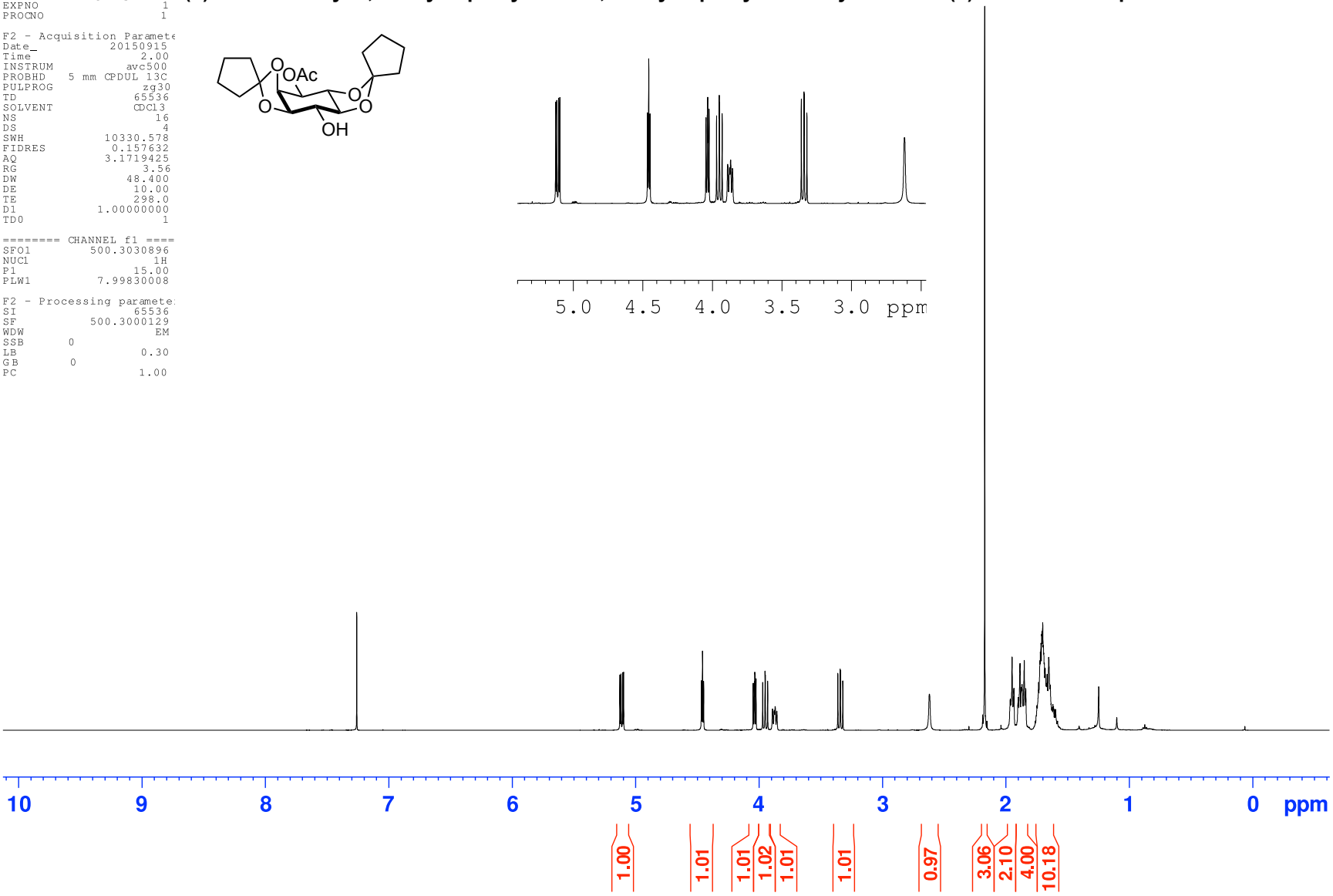


NL: 6.75E5
C27H40[2]H6O7Na1Si1: C_{27} H_{40} $^{2}H_{6}$ O_{7} Na Si Chrg 1 R: 1000000 Res. Pwr. @FWHM

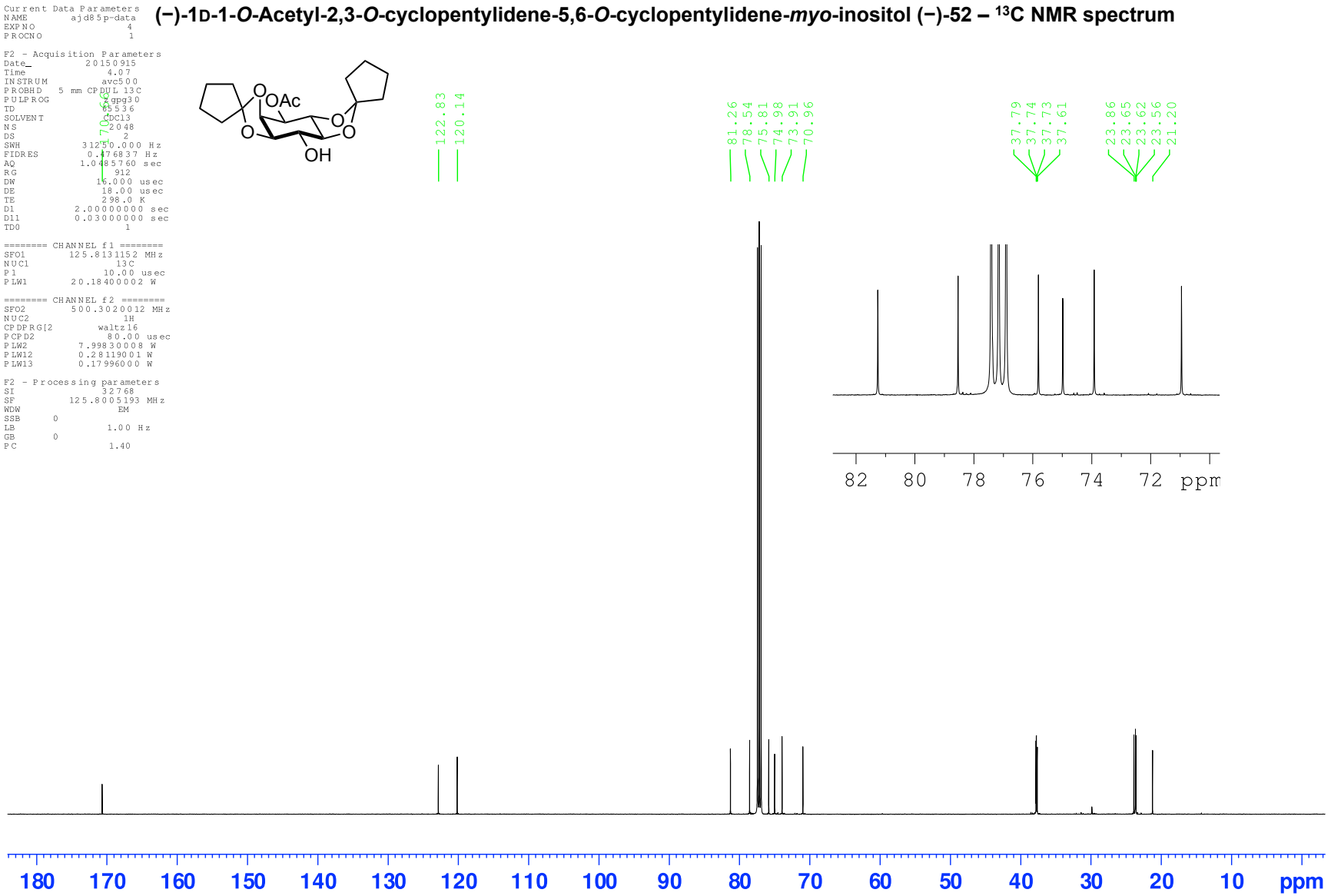
Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
539.32819	$C_{27}H_{40}{}^{2}H_{6}O_{7}{}^{23}Na{}^{28}Si$	5.5	0.04	539.32816

(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-52 – ^{1}H NMR spectrum



(−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-52 – ^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-53 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME         ajg13p-data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161102
Time              13.32
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                  2.25
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1                1H
P1                15.00 usec
PLW1         7.99830008 W

F2 - Processing parameters
SI                65536
SF          500.3000137 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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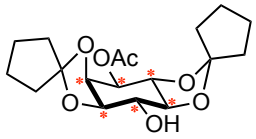
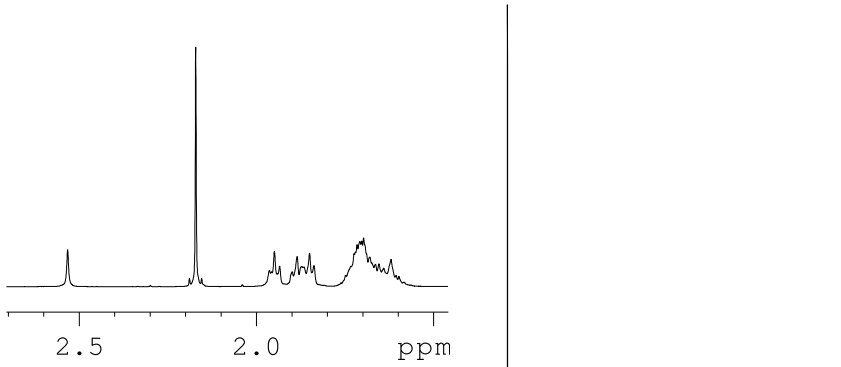
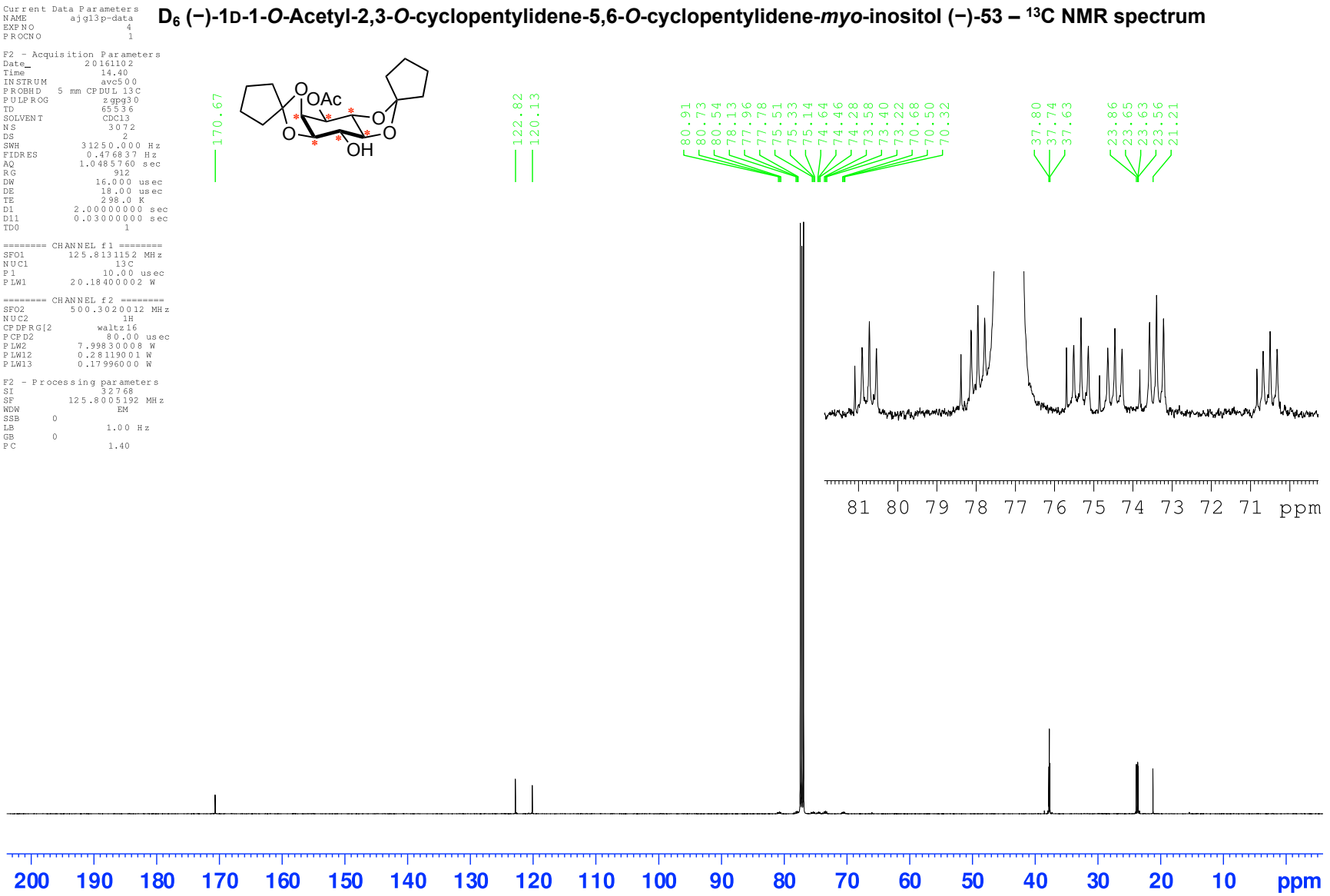
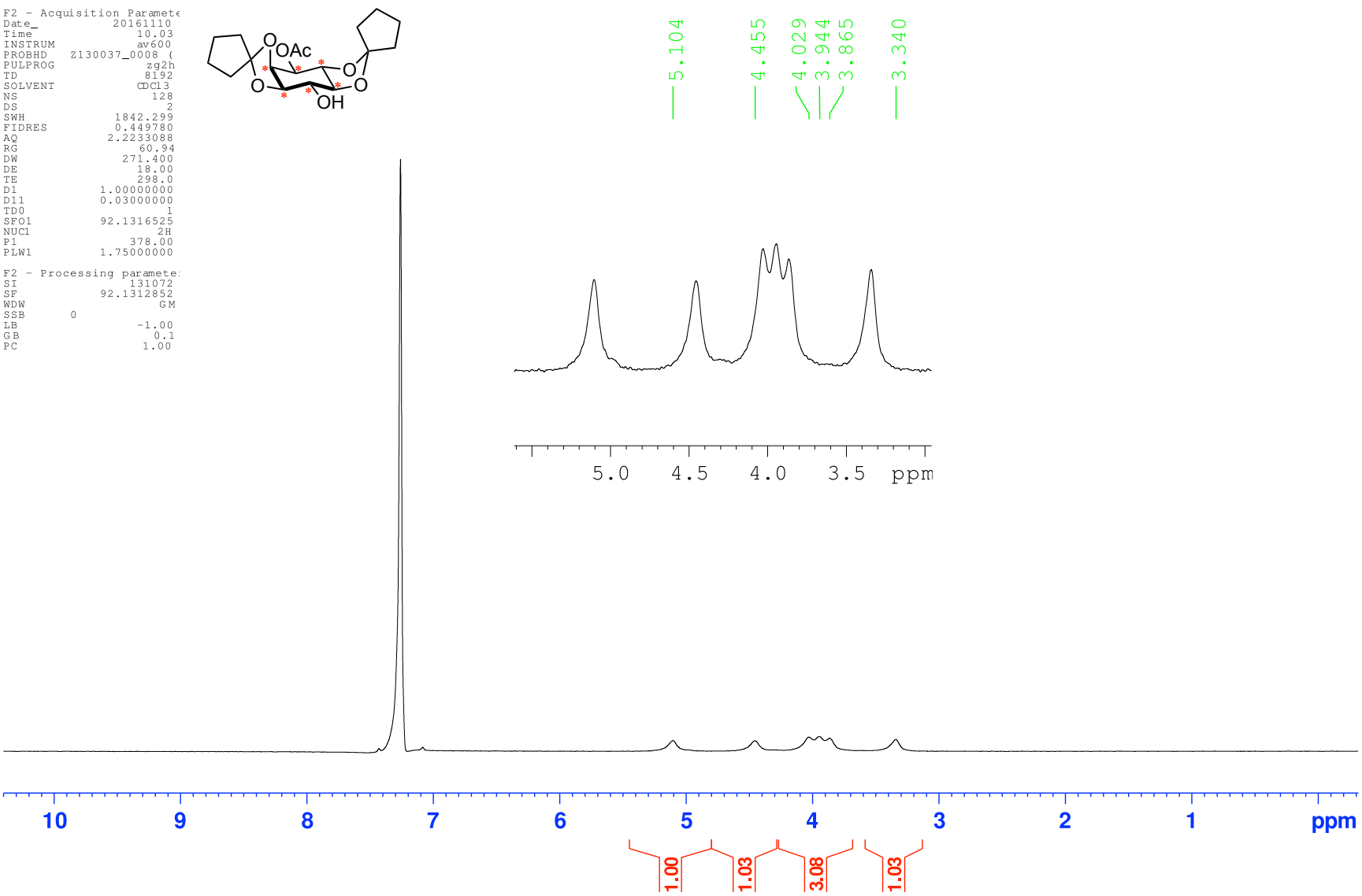




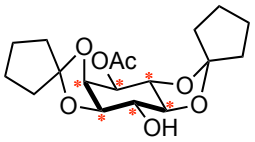
D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-53 – ^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-53 – ^{2}H NMR spectrum



D_6 (−)-1D-1-*O*-Acetyl-2,3-*O*-cyclopentylidene-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-53 – Mass spectrum



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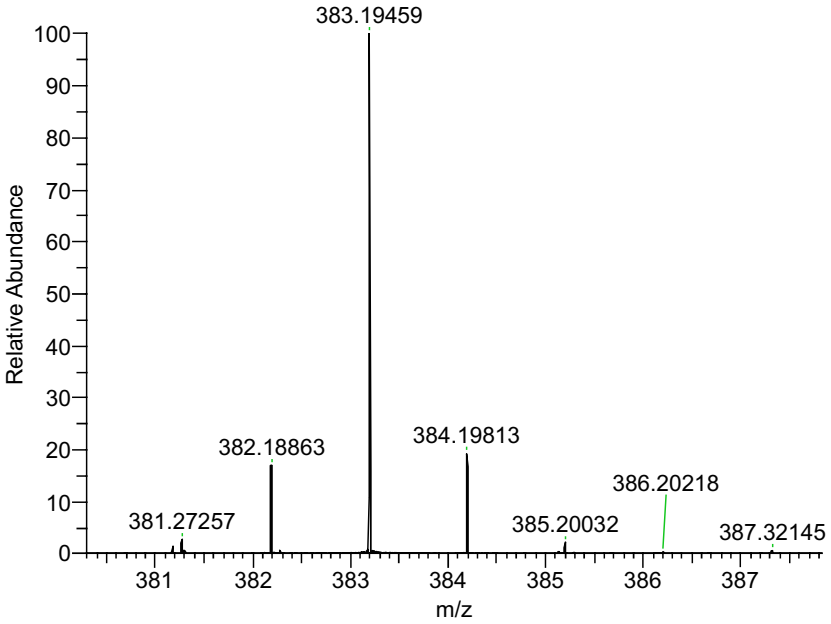
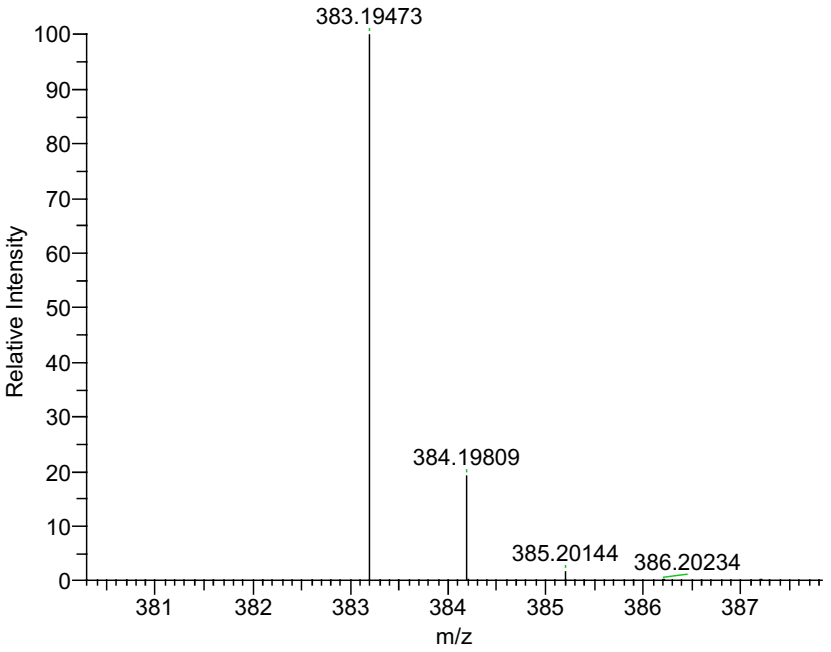


NL: 5.73E7
ESI59718 #15-24 RT: 0.17-0.26 AV: 5 NL: 5.73E+007
T: FTMS {1,1} + p ESI Full lock ms [80.00-1600.00]

Measured Spectrum



NL: 8.08E5
C18H20[2]H6O7Na1: C_{18} H_{20} $^{2}H_{6}$ O_{7} Na
Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
383.19458	$C_{18}H_{20}{}^{2}H_{6}O_{7}{}^{23}Na$	5.5	-0.4	383.19473

(−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-55 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME        aje73p-data2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20160122
Time               14.03
INSTRUM          avg400
PROBHD   5 mm PABBO BB/
PULPROG            zg60
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH           10000.000
FIDRES        0.152588
AQ            3.2767999
RG                66.06
DW                50.000
DE                  6.50
TE                294.0
D1            1.00000000
TD0                   1

======== CHANNEL f1 ====
SFO1          400.2024714
NUC1                   1H
P1                 14.00
PLW1          14.00000000

F2 - Processing paramete
SI                65536
SF          400.2000098
WDW                   EM
SSB       0
LB                 0.30
GB        0
PC                 1.00
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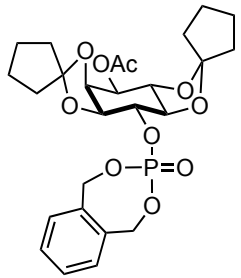
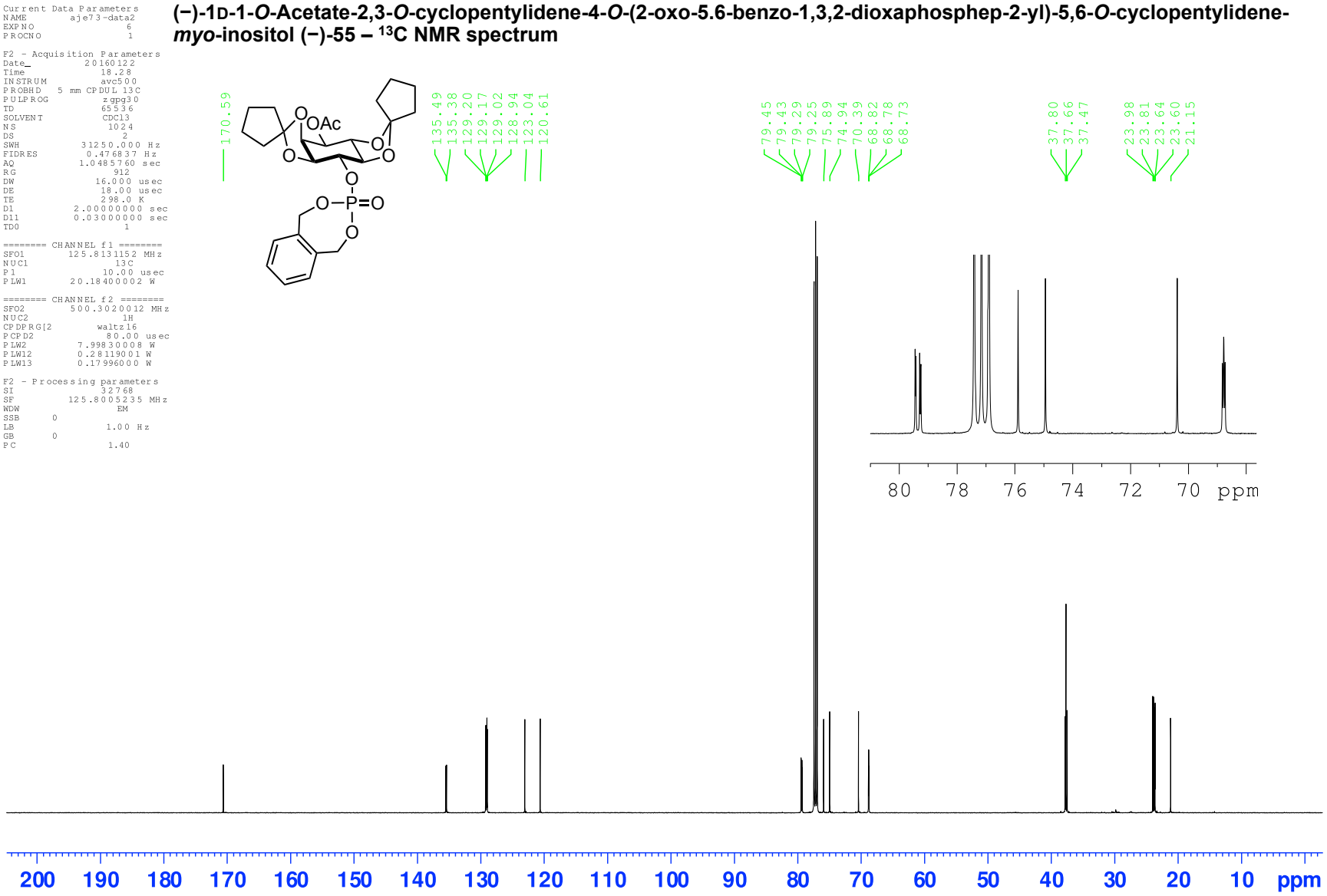


(−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-55 – ^{13}C NMR spectrum



(−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-55 – ^{31}P NMR spectrum

```
Current Data Parameters
NAME                 aje73
EXPNO                    1
PROCNO                   1

F2 - Acquisition Paramete
Date_               20160216
Time                   12.02
INSTRUM              avh400
PROBHD    Z108618_0873 (
PULPROG              zgpg30
TD                   131072
SOLVENT               CDCl3
NS                       16
DS                        4
SWH                64102.562
FIDRES             0.978127
AQ                 1.0223616
RG                    197.18
DW                     7.800
DE                      6.50
TE                     297.1
D1              2.00000000
D11             0.03000000
TD0                       1
SFO1           161.9755930
NUC1                   31P
P1                    15.00
PLW1           13.93799973
SFO2           400.1316005
NUC2                   1H
CPDPRG[2            waltz16
PCPD2                 90.00
PLW2           14.36999989
PLW12           0.34660661
PLW13           0.17371930

F2 - Processing paramete
SI                    65536
SF             161.9755930
WDW                      EM
SSB       0
LB                     1.00
GB        0
PC                     1.40
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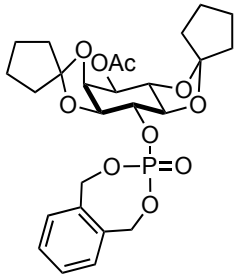

D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)- 5,6-*O*-cyclopentylidene-*myo*-inositol (−)-56 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME         ajg15p-data2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161107
Time              18.13
INSTRUM         avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                3.56
DW               48.400 usec
DE               10.00 usec
TE               298.0 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1               1H
P1               15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI               65536
SF          500.3009811 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
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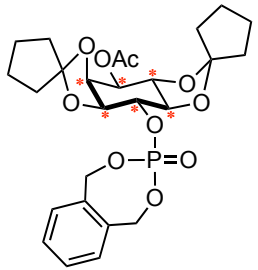
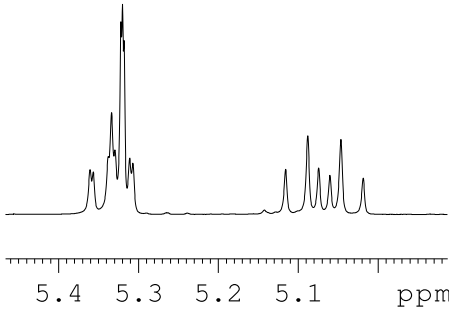
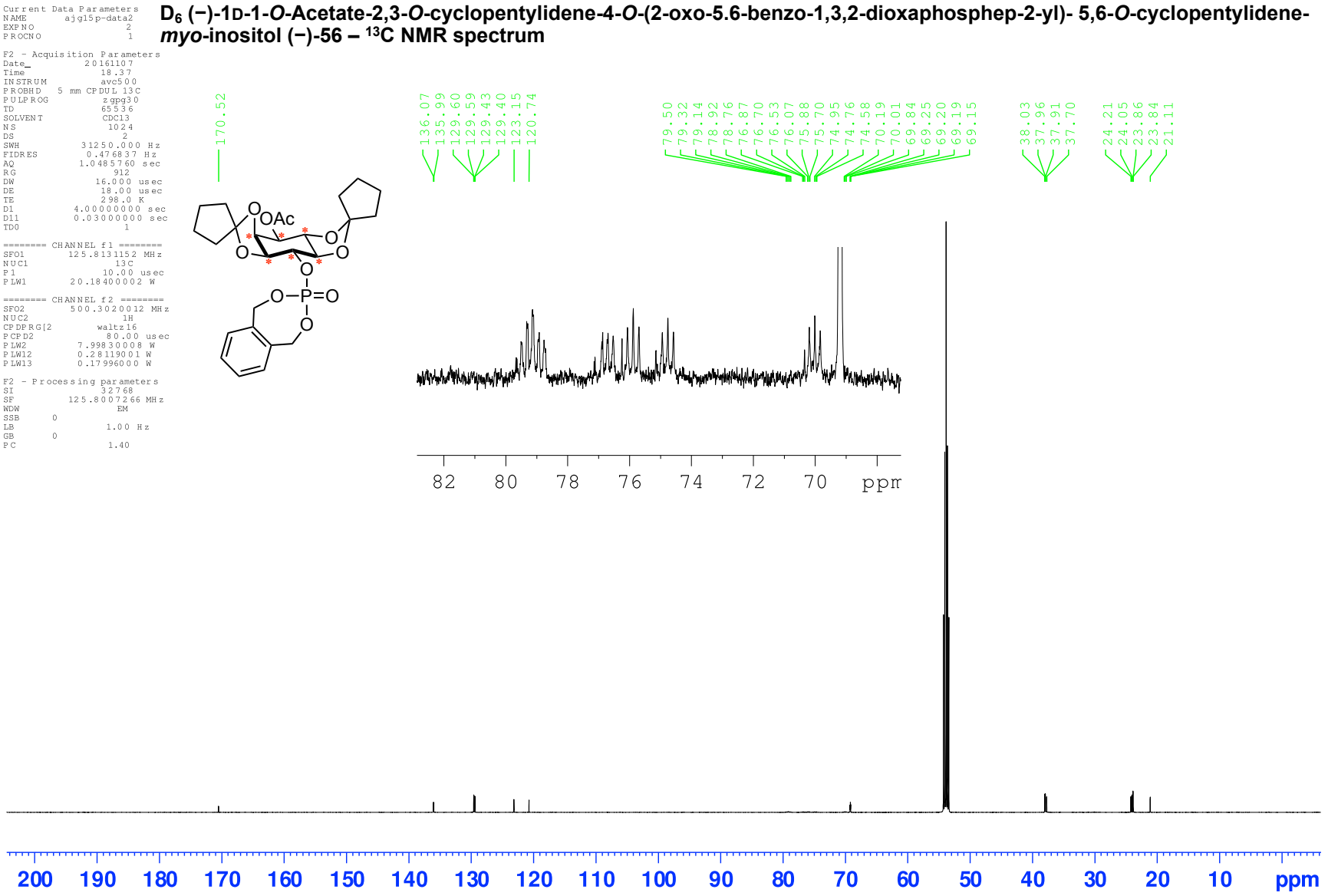




D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)- 5,6-*O*-cyclopentylidene-*myo*-inositol (−)-56 – ^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)- 5,6-*O*-cyclopentylidene-*myo*-inositol (−)-56 - ^{31}P NMR spectrum

```
Current Data Parameters
NAME                 ajg15p
EXPNO                     1
PROCNO                    1

F2 - Acquisition Paramete
Date_               20161102
Time                   17.37
INSTRUM                avb400
PROBHD    Z116098_0219 (
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          4
SWH                 64102.562
FIDRES              1.956255
AQ                  0.5111808
RG                     197.74
DW                      7.800
DE                      6.50
TE                     298.1
D1                 2.00000000
D11                0.03000000
TD0                         1
SFO1               161.9755930
NUC1                       31P
P1                      8.00
PLW1               54.00000000
SFO2               400.1316005
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                   90.00
PLW2               14.58800030
PLW12               0.18009999
PLW13               0.09058800

F2 - Processing paramete
SI                      32768
SF                 161.9755930
WDW                        EM
SSB          0
LB                      1.00
GB           0
PC                      1.40
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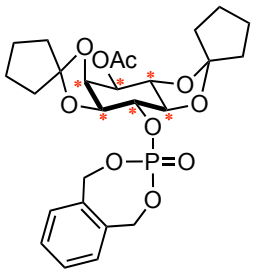
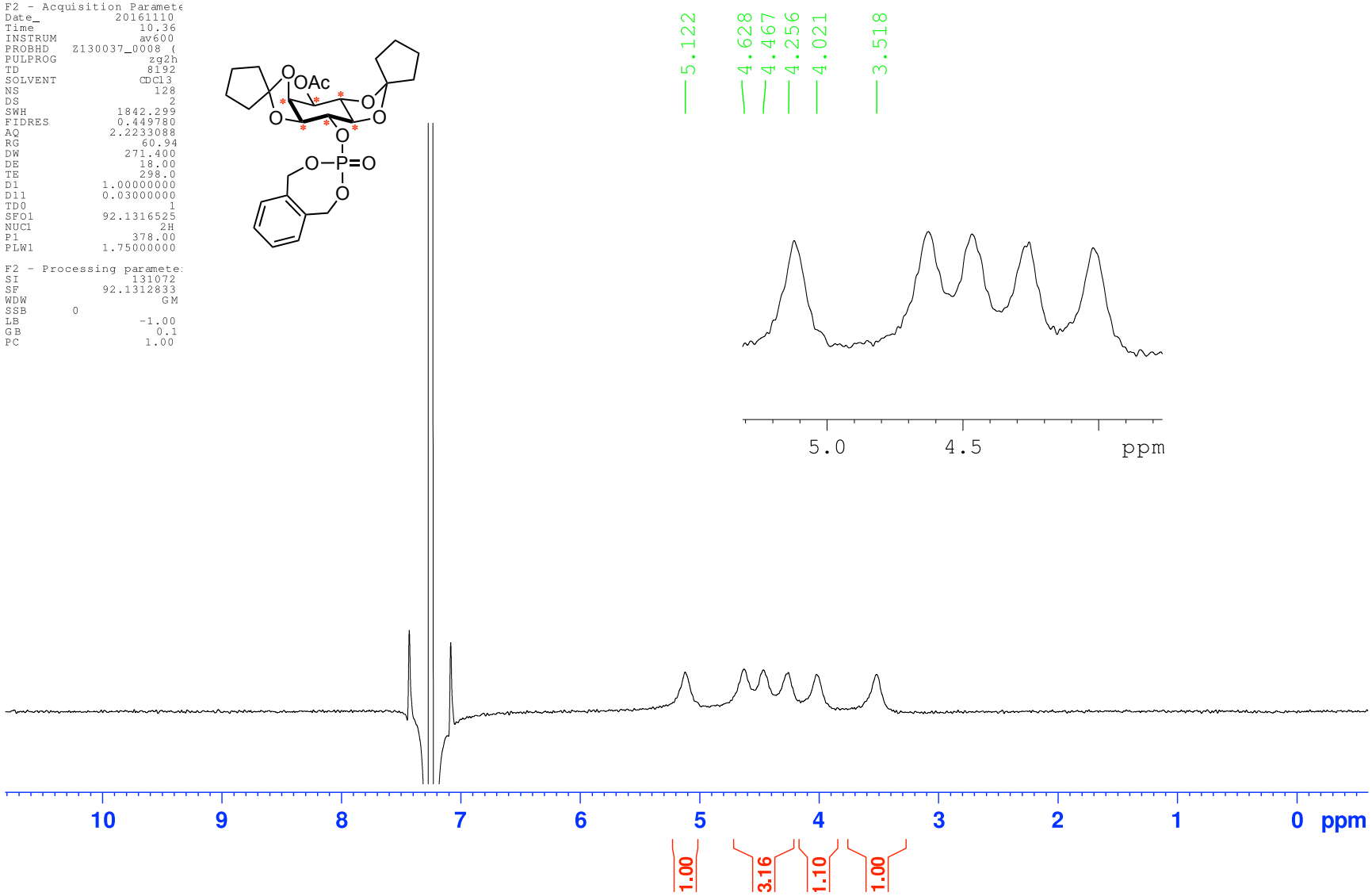
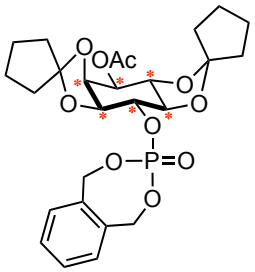


D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)- 5,6-*O*-cyclopentylidene-*myo*-inositol (−)-56 – ^{2}H NMR spectrum





D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol

(−)-56 – Mass spectrum

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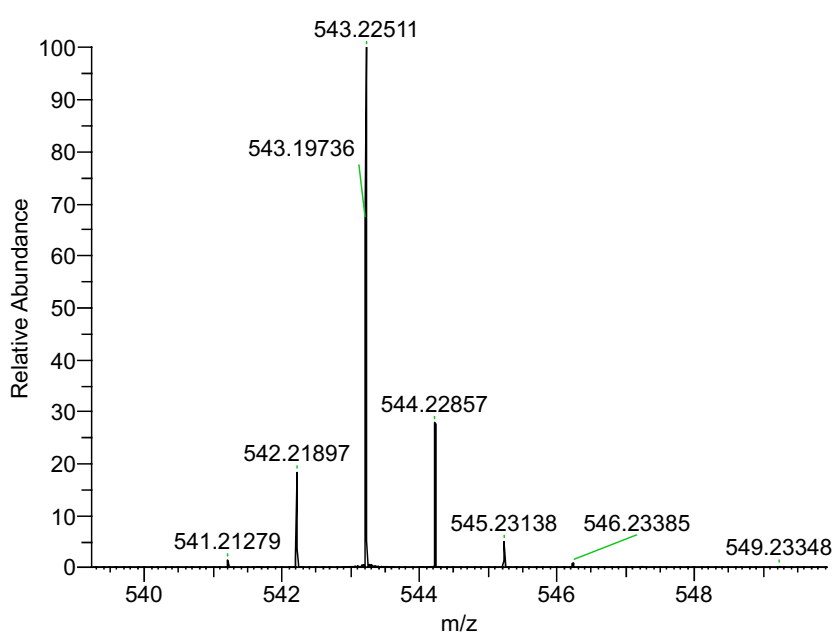
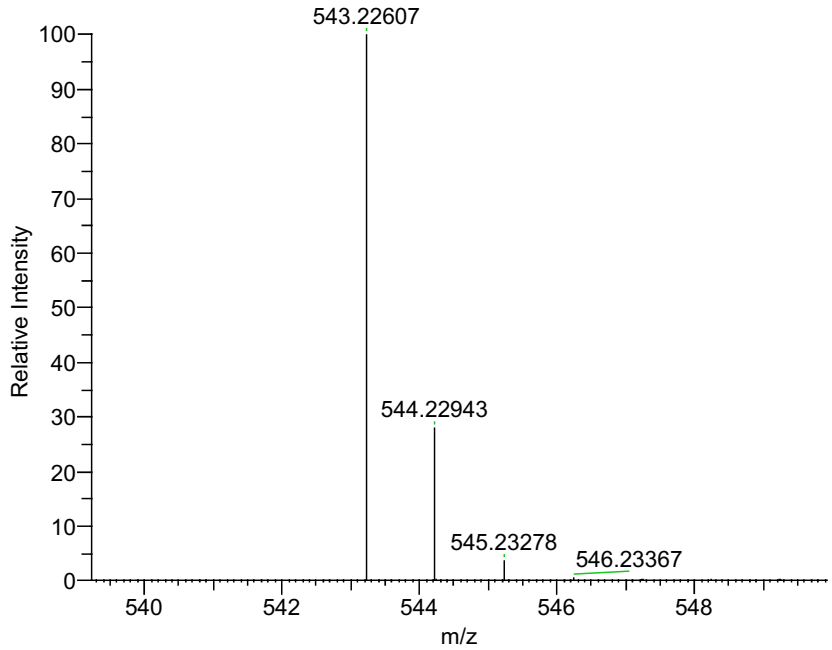


NL: 3.81E7
ESI59703 #15-25 RT: 0.17-0.28 AV: 6 NL: 5.29E+007
T: FTMS {1,1} + p ESI Full ms [80.00-1600.00]

Measured Spectrum

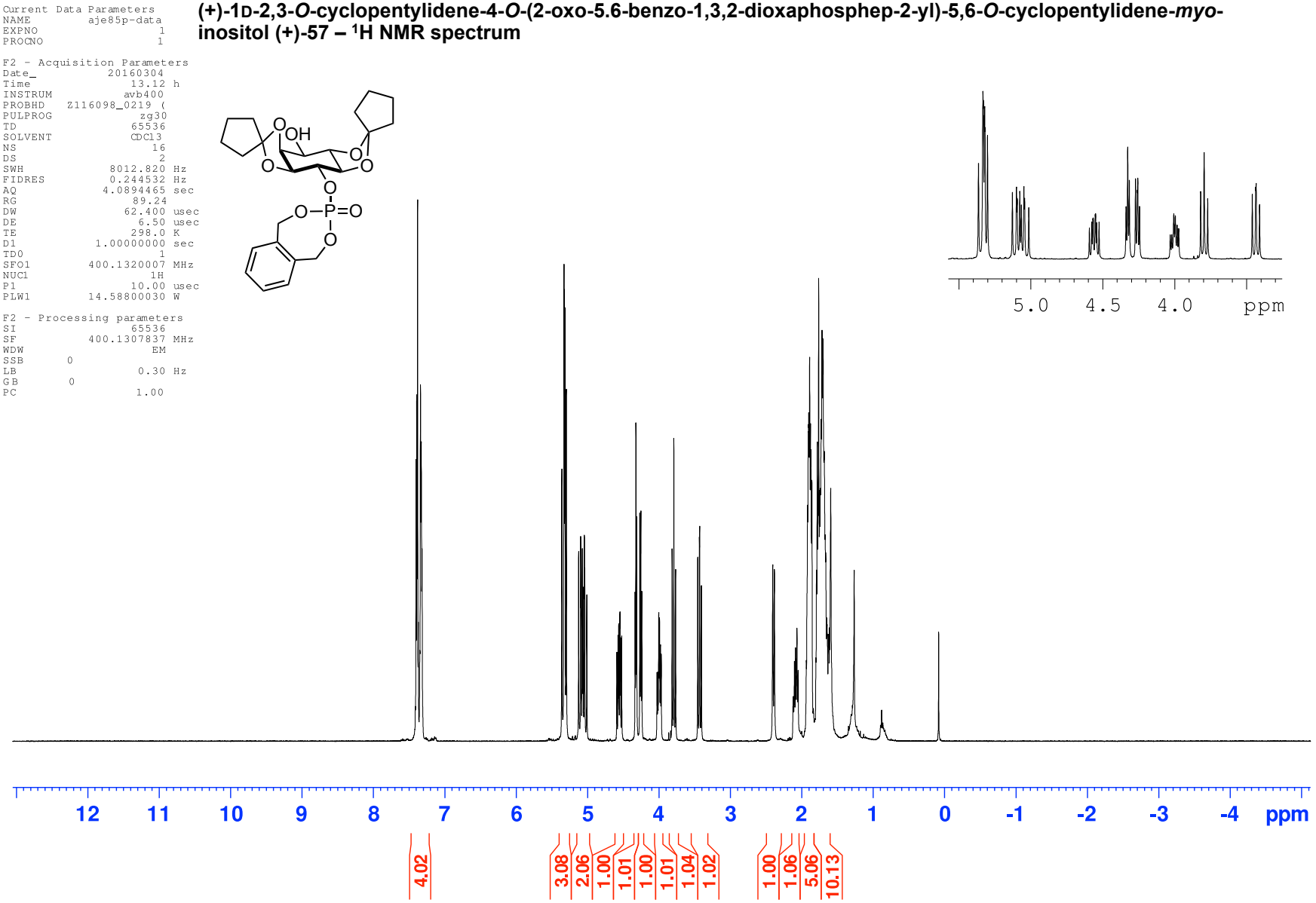


NL: 7.35E5
C26H28[2]H6O10P1: $C_{26}H_{28}{}^{2}H_{6}O_{10}P$
Chrg 1 R: 1000000 Res. Pwr. @FWHM

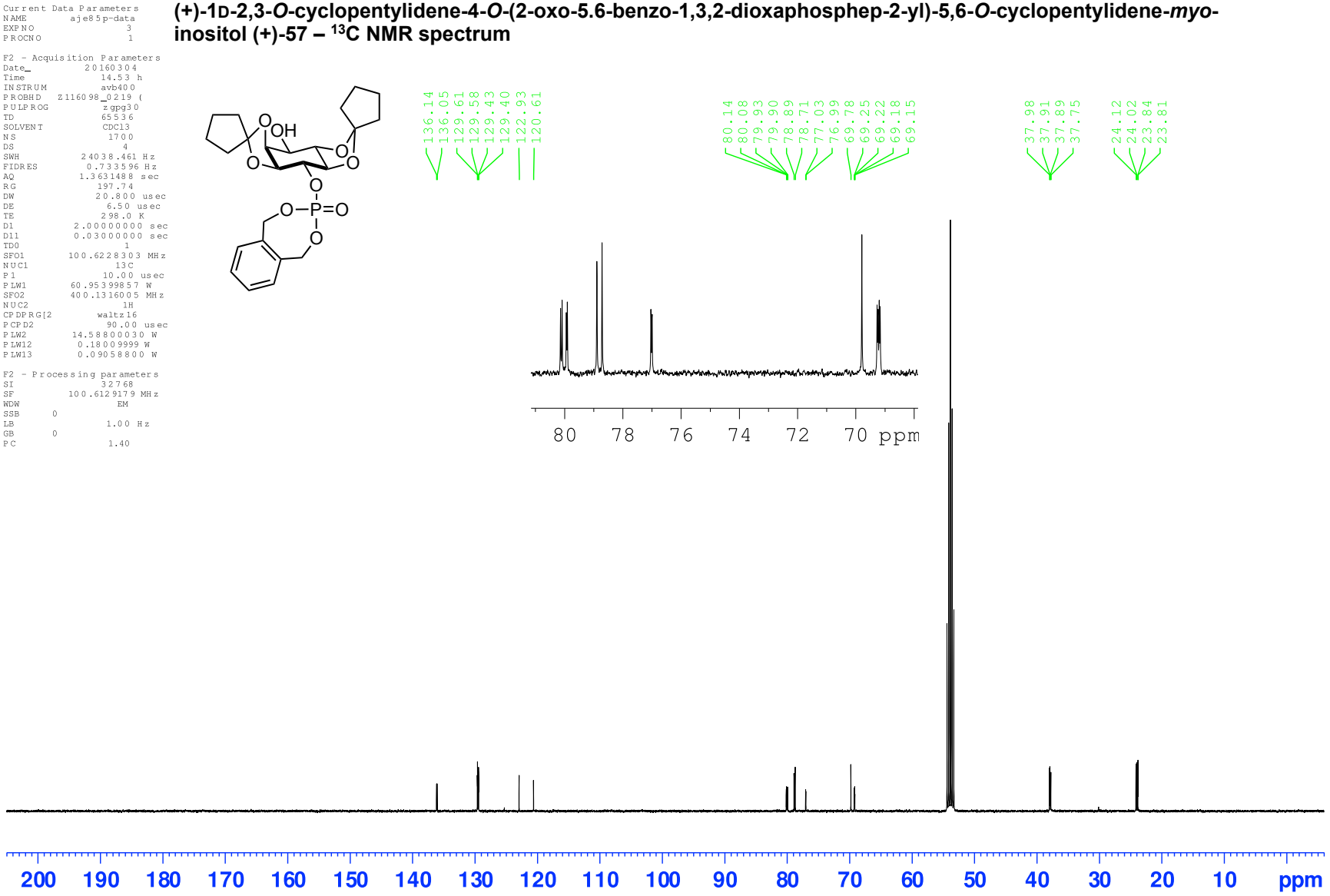
Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
543.22510	$C_{26}H_{28}{}^{2}H_{6}O_{10}P$	10.5	-1.79	543.22607

(+)-1D-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (+)-57 – ^{1}H NMR spectrum



(+)-1D-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (+)-57 – ^{13}C NMR spectrum

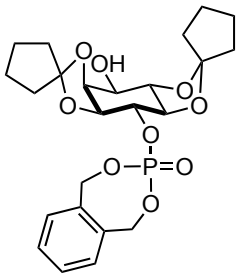


(+)-1D-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (+)-57 – ^{31}P NMR spectrum

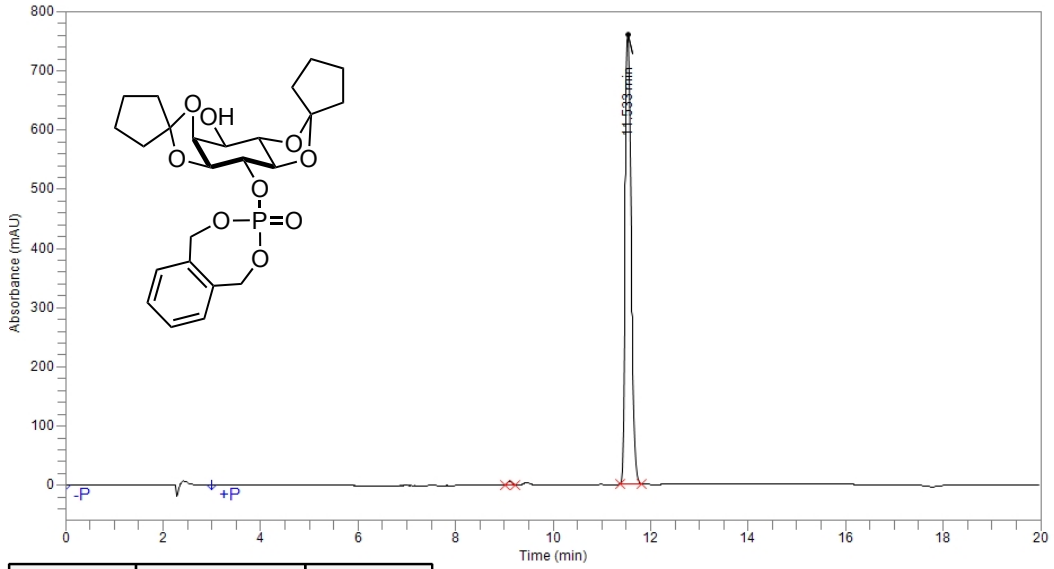
```
Current Data Parameters
NAME         aje85p-data
EXPNO                  2
PROCNO                 1

F2 - Acquisition Paramete
Date_           20160304
Time              13.14
INSTRUM          avb400
PROBHD    Z116098_0219 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           64102.562
FIDRES         1.956255
AQ             0.5111808
RG                197.74
DW                 7.800
DE                  6.50
TE                298.1
D1            2.00000000
D11           0.03000000
TD0                    1
SFO1          161.9755930
NUC1                31P
P1                 8.00
PLW1          54.00000000
SFO2          400.1316005
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00
PLW2          14.58800030
PLW12          0.18009999
PLW13          0.09058800

F2 - Processing paramete
SI                 32768
SF            161.9755930
WDW                   EM
SSB       0
LB                 1.00
GB        0
PC                 1.40
```



(+)-1D-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)- 5,6-*O*-cyclopentylidene-*myo*-inositol (+)-57 – RP-HPLC (Method 2)



Time	Area	Area %
9.101	44,427	0.67
11.533	6,576,972	99.33
Total	6,621,399	100.00

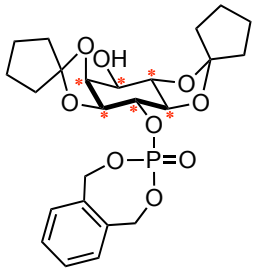
D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (+)-58 – ^{1}H NMR spectrum

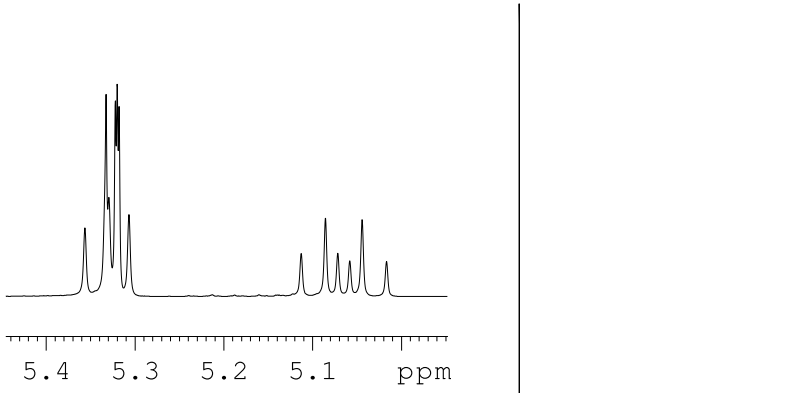
```
Current Data Parameters
NAME          ajg17p-data
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161109
Time              14.16
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT          CD2Cl2
NS                  16
DS                   4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                 3.2
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1               1H
P1                15.00 usec
PLW1           7.99830008 W

F2 - Processing parameters
SI                65536
SF          500.3000205 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```





D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (+)-58 – ^{13}C NMR spectrum

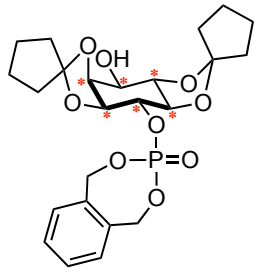
```
Current Data Parameters
NAME         ajg17p-data
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_          20161109
Time              14.24
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zgpg30
TD                65536
SOLVENT           CD2Cl2
NS                   973
DS                     2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ             1.0485760 sec
RG                   912
DW               16.000 usec
DE               18.000 usec
TE                298.0 K
D1            4.00000000 sec
D11           0.03000000 sec
TD0                    1

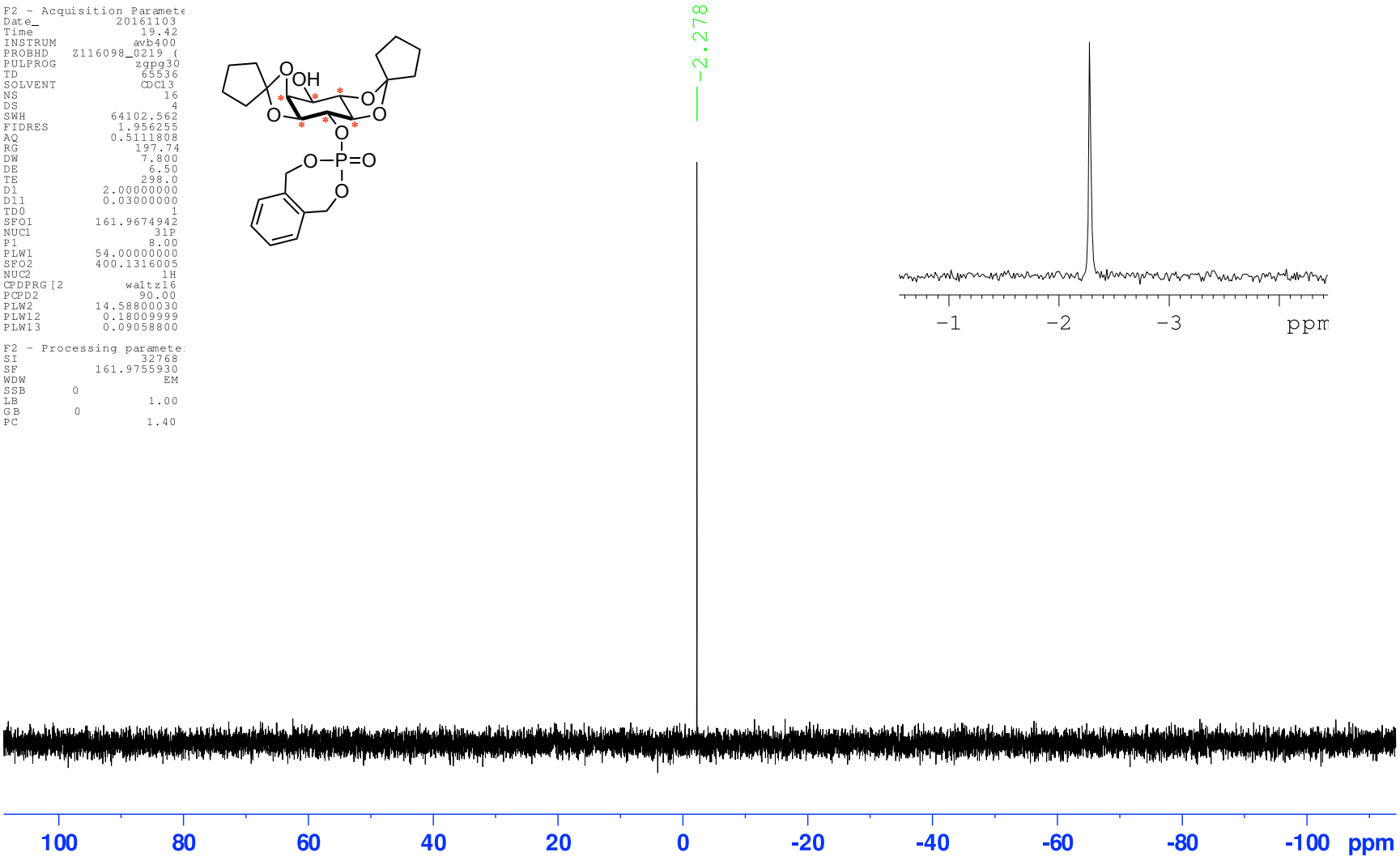
======== CHANNEL f1 ========
SFO1         125.8131152 MHz
NUC1               13C
P1               10.00 usec
PLW1         20.18400002 W

======== CHANNEL f2 ========
SFO2         500.3020012 MHz
NUC2               1H
CPDPRG[2         waltz16
PCPD2             80.00 usec
PLW2          7.99830008 W
PLW12         0.28119001 W
PLW13         0.17996000 W

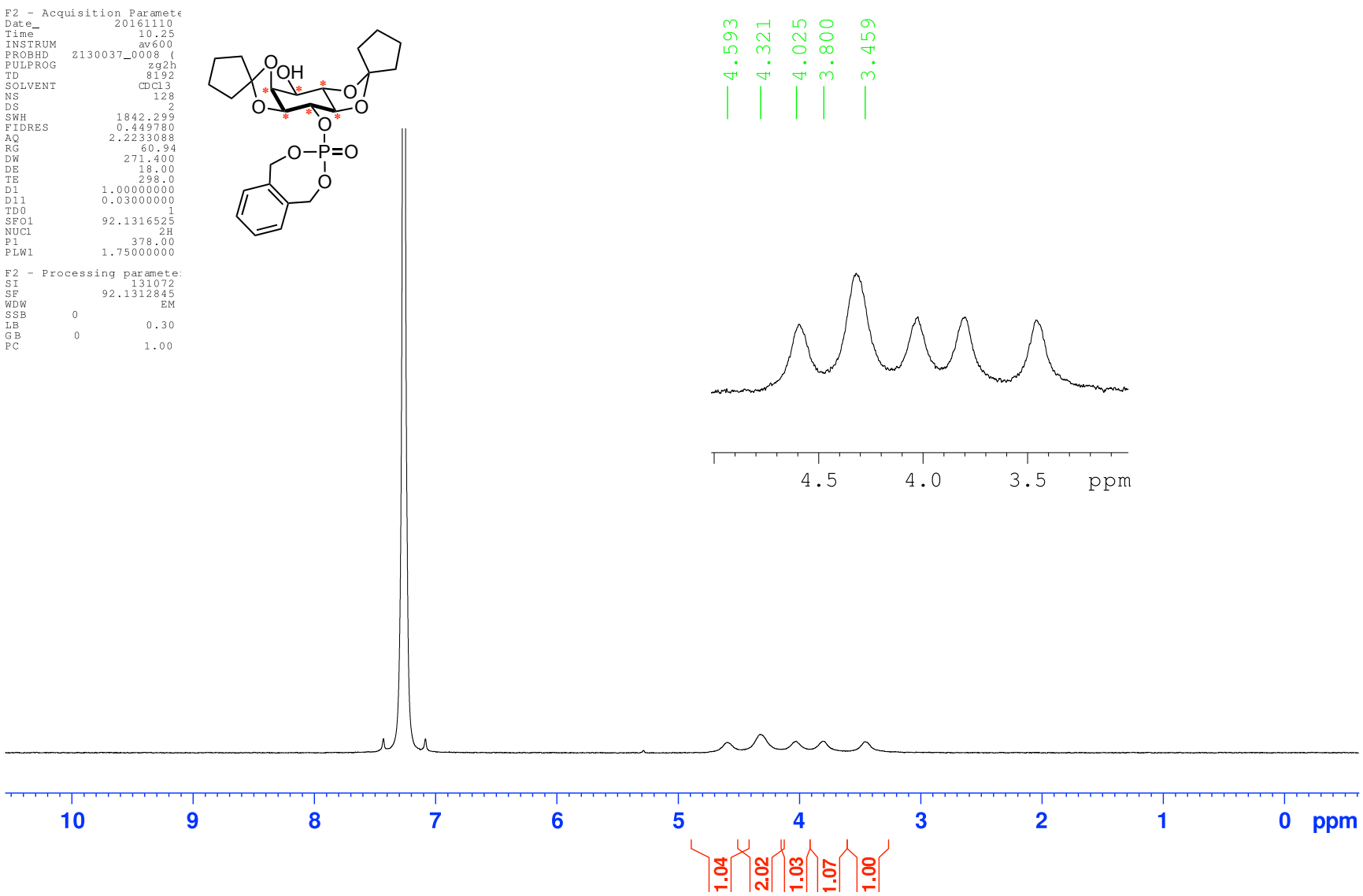
F2 - Processing parameters
SI                 32768
SF           125.8004851 MHz
WDW                EM
SSB       0
LB               2.00 Hz
GB        0
PC                1.40
```



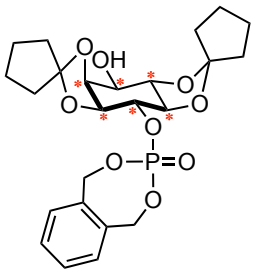
D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (+)-58 – ^{31}P NMR spectrum



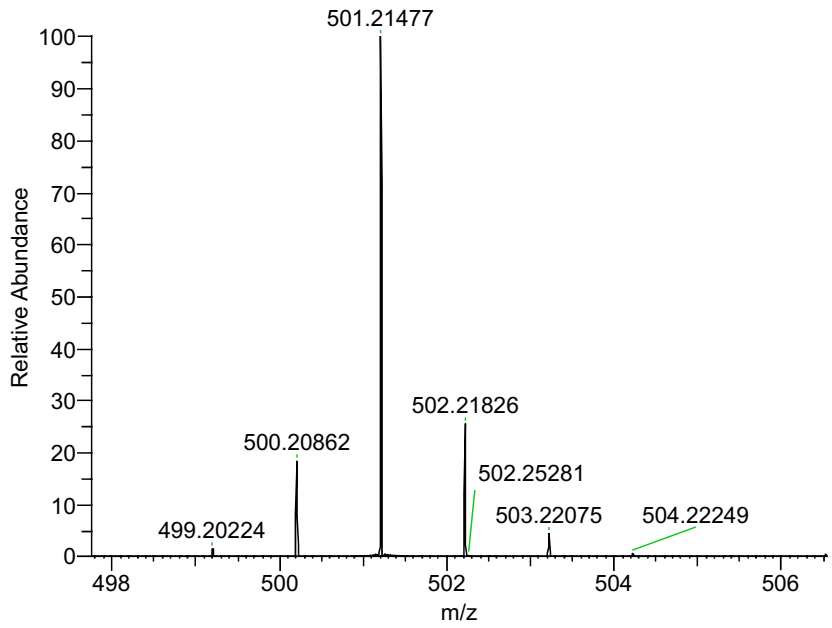
D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (+)-58 – ^2H NMR spectrum



D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4-*O*-(2-oxo-5.6-benzo- 1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (+)-58 Mass spectrum

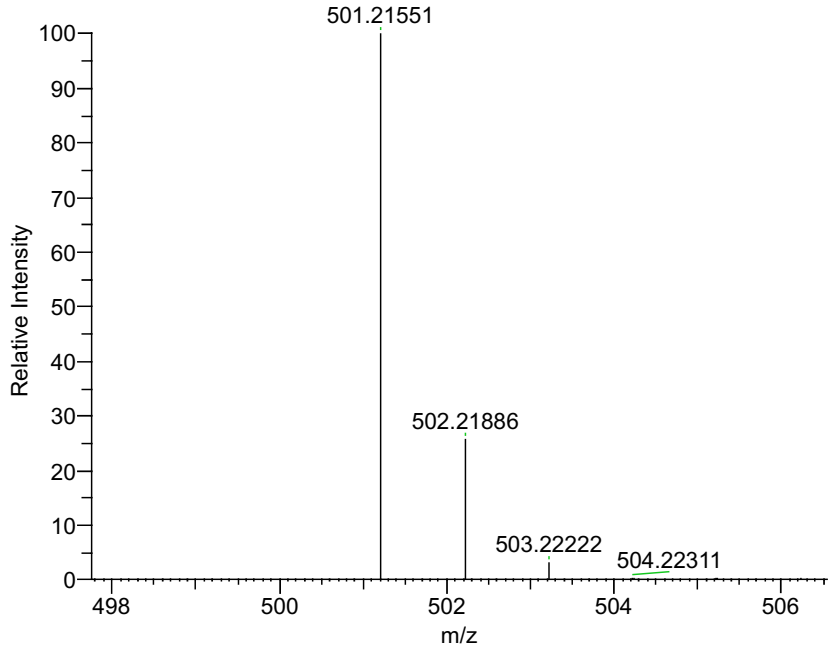


S:\data\Nov 16\ESI59702.raw 08/11/2016 3:07 pm



NL: 4.16E7
ESI59702 #15-25 RT: 0.17-0.28 AV: 6 NL: 5.29E+007
T: FTMS {1,1} + p ESI Full ms [80.00-1600.00]

Measured Spectrum

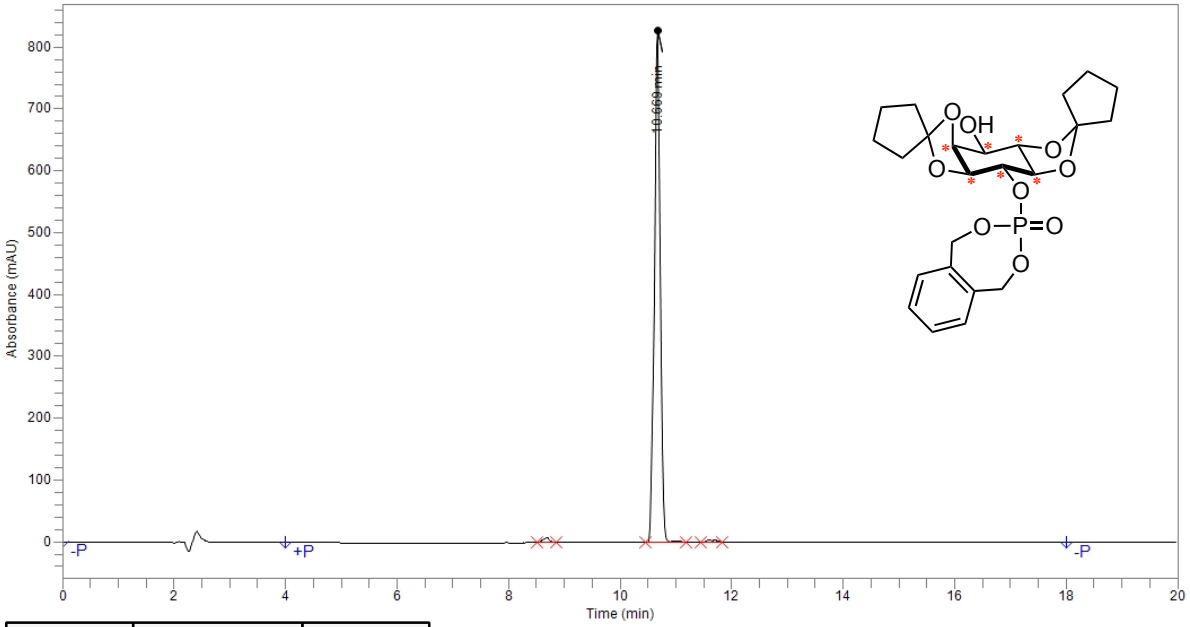


NL: 7.53E5
C24H26[2]H6O9P1: $C_{24}H_{26}{}^{2}H_{6}O_{9}P$ Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
501.21475	$C_{24}H_{26}{}^{2}H_{6}O_{9}P$	9.5	-1.5	501.21551

D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)- 5,6-*O*-cyclopentylidene-*myo*-inositol (+)-58 - RP-HPLC (Method 2)



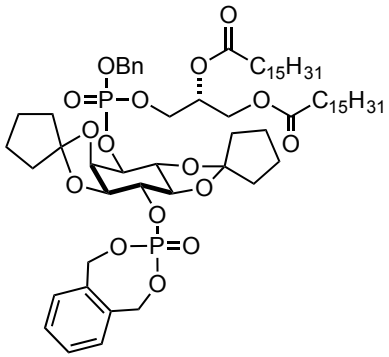
Time	Area	Area %
8.696	73043	1.22
10.669	5891278	98.00
11.034	10323	0.17
11.581	20951	0.35
11.703	15863	0.26
Total	6011459	100.00

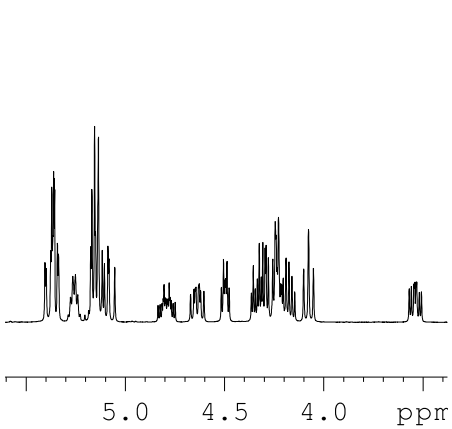
(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-59 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME                 ajf80p
EXPNO                    10
PROCNO                    1

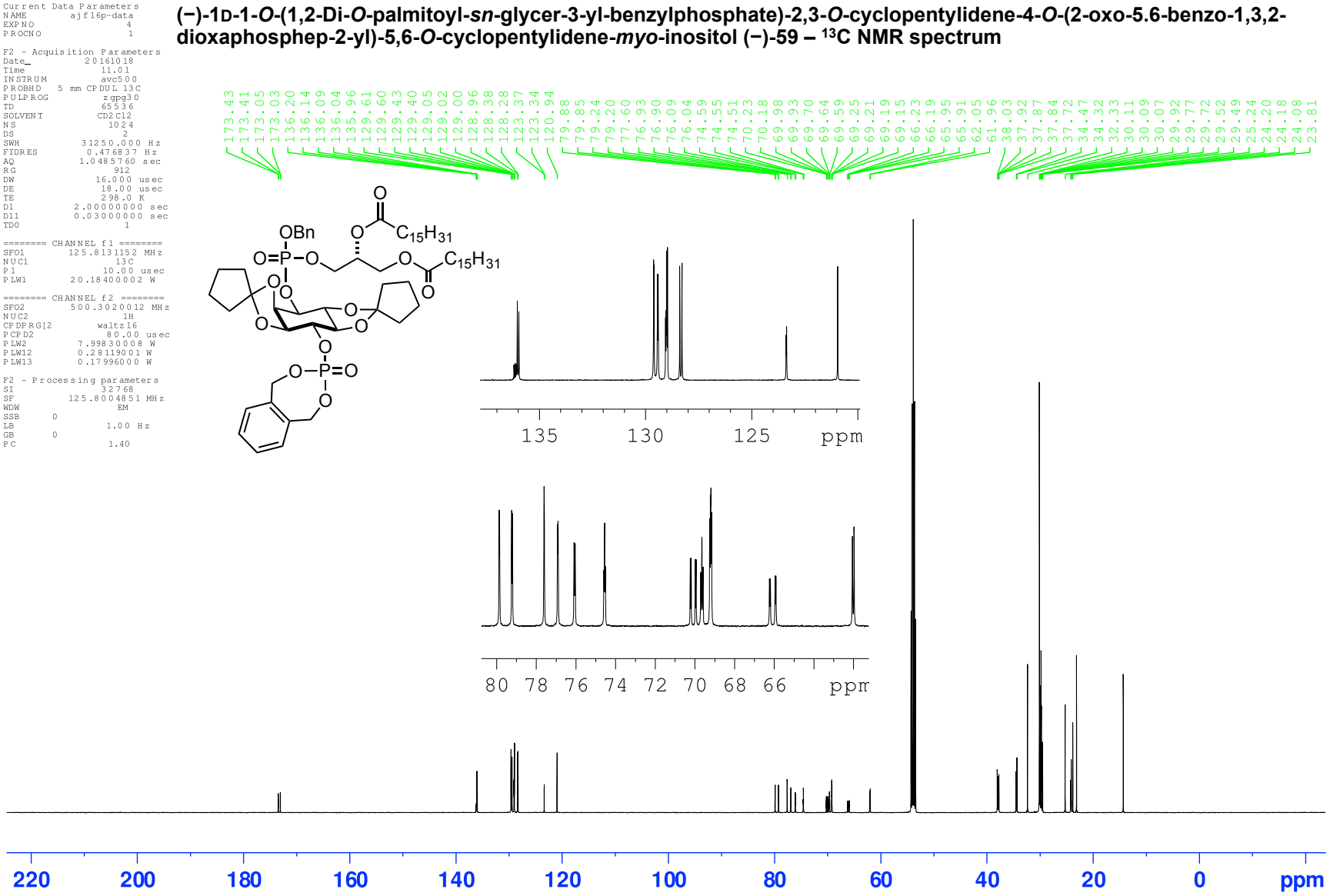
F2 - Acquisition Parameters
Date_              20161010
Time                 14.01 h
INSTRUM              avh400
PROBHD    Z108618_0873 (
PULPROG              zg60
TD                  65536
SOLVENT             CD2Cl2
NS                      16
DS                       2
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                 4.0894465 sec
RG                     30.75
DW                    62.400 usec
DE                     6.50 usec
TE                   296.3 K
D1              1.00000000 sec
TD0                      1
SFO1           400.1324008 MHz
NUC1                    1H
P1                    14.00 usec
PLW1           14.36999989 W

F2 - Processing parameters
SI                   32768
SF             400.1300000 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```





(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-59 – ^{13}C NMR spectrum

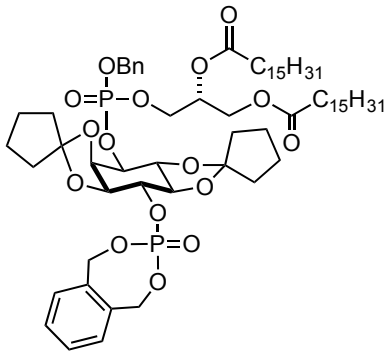


(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-59 – ^{31}P NMR spectrum

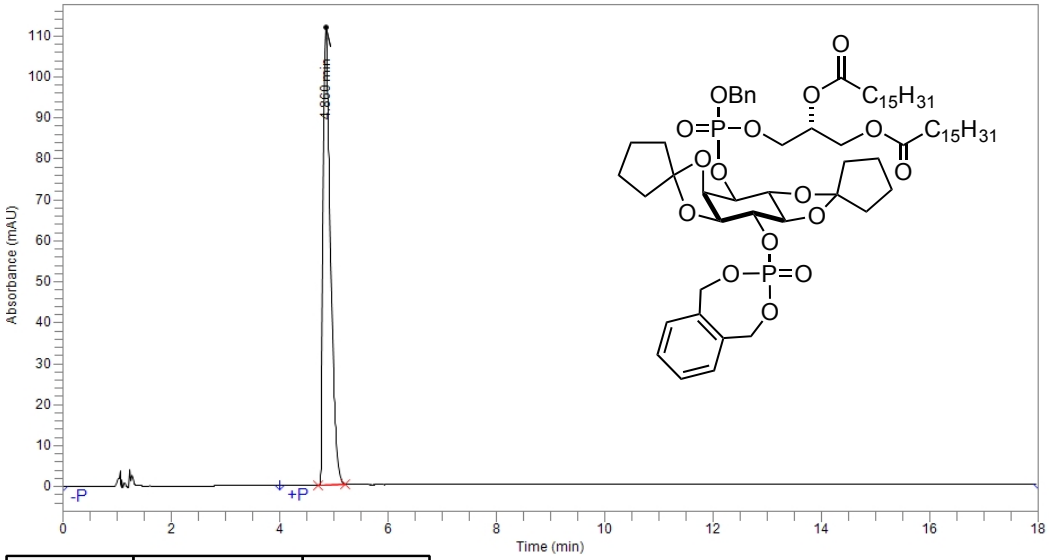
```
Current Data Parameters
NAME                 ajf80p
EXPNO                    11
PROCNO                    1

F2 - Acquisition Paramete
Date_               20161010
Time                   14.03
INSTRUM              avh400
PROBHD    Z108618_0873 (
PULPROG              zgpg30
TD                   131072
SOLVENT              CD2Cl2
NS                       16
DS                        4
SWH                64102.562
FIDRES             0.978127
AQ                 1.0223616
RG                    197.18
DW                     7.800
DE                      6.50
TE                     296.7
D1                2.00000000
D11               0.03000000
TD0                       1
SFO1           161.9755930
NUC1                    31P
P1                    15.00
PLW1           13.93799973
SFO2           400.1316005
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 90.00
PLW2           14.36999989
PLW12           0.34660661
PLW13           0.17371930

F2 - Processing paramete
SI                    65536
SF             161.9755930
WDW                      EM
SSB       0
LB                     1.00
GB        0
PC                     1.40
```



(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-59 - NP-HPLC (Method 7)



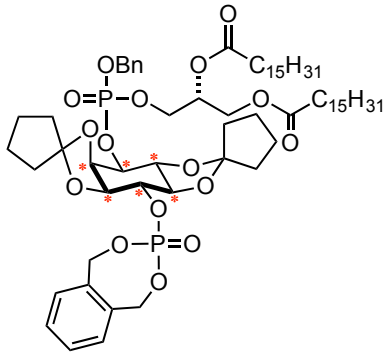
Time	Area	Area %
4.860	1,050,011	100.00
Total	1,050,011	100.00

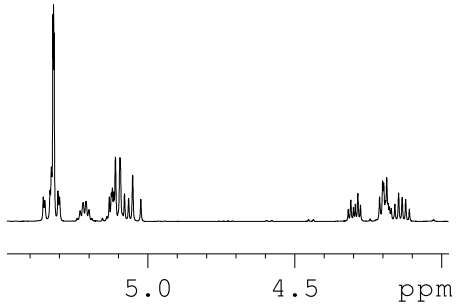
D$_6$ (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-60 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME          ajg21p-data
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161129
Time              10.26 h
INSTRUM           avx500
PROBHD    Z113652_0208 (
PULPROG             zg60
TD                 65536
SOLVENT           CD2Cl2
NS                    16
DS                     2
SWH           10000.000 Hz
FIDRES            0.305176 Hz
AQ                3.2767999 sec
RG                   44.54
DW                  50.000 usec
DE                   6.50 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                    1
SFO1          500.1325006 MHz
NUC1                  1H
P1                  10.00 usec
PLW1          20.50000000 W

F2 - Processing parameters
SI                 65536
SF            500.1300193 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```





D$_6$ (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-60 – ^{13}C NMR spectrum

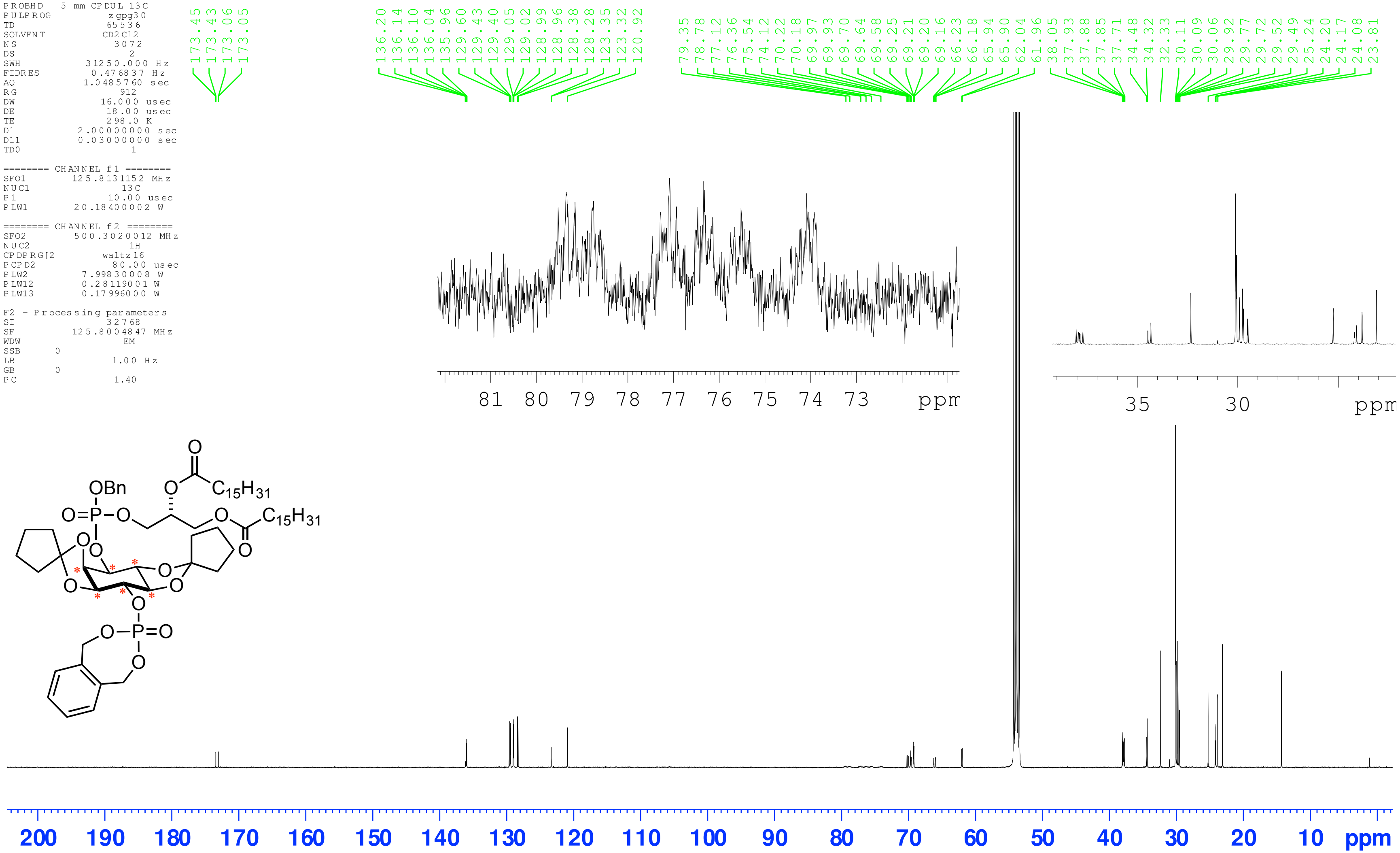
```
Current Data Parameters
NAME          ajg21p-data2
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20161129
Time                 11.08
INSTRUM             avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zgpg30
TD                   65536
SOLVENT            CD2Cl2
NS                    3072
DS                       2
SWH            31250.000 Hz
FIDRES          0.476837 Hz
AQ             1.0485760 sec
RG                     912
DW                  16.000 usec
DE                   18.00 usec
TE                   298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         125.8131152 MHz
NUC1                   13C
P1                   10.00 usec
PLW1          20.18400002 W

======== CHANNEL f2 ========
SFO2         500.3020012 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2            7.99830008 W
PLW12           0.28119001 W
PLW13           0.17996000 W

F2 - Processing parameters
SI                   32768
SF           125.8004847 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

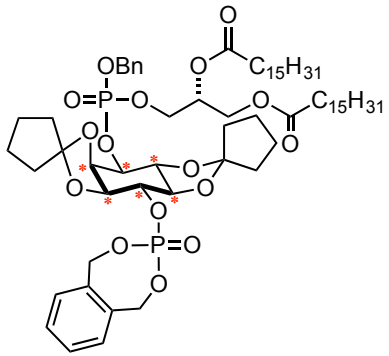


D_6 (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-60 – ^{31}P NMR spectrum

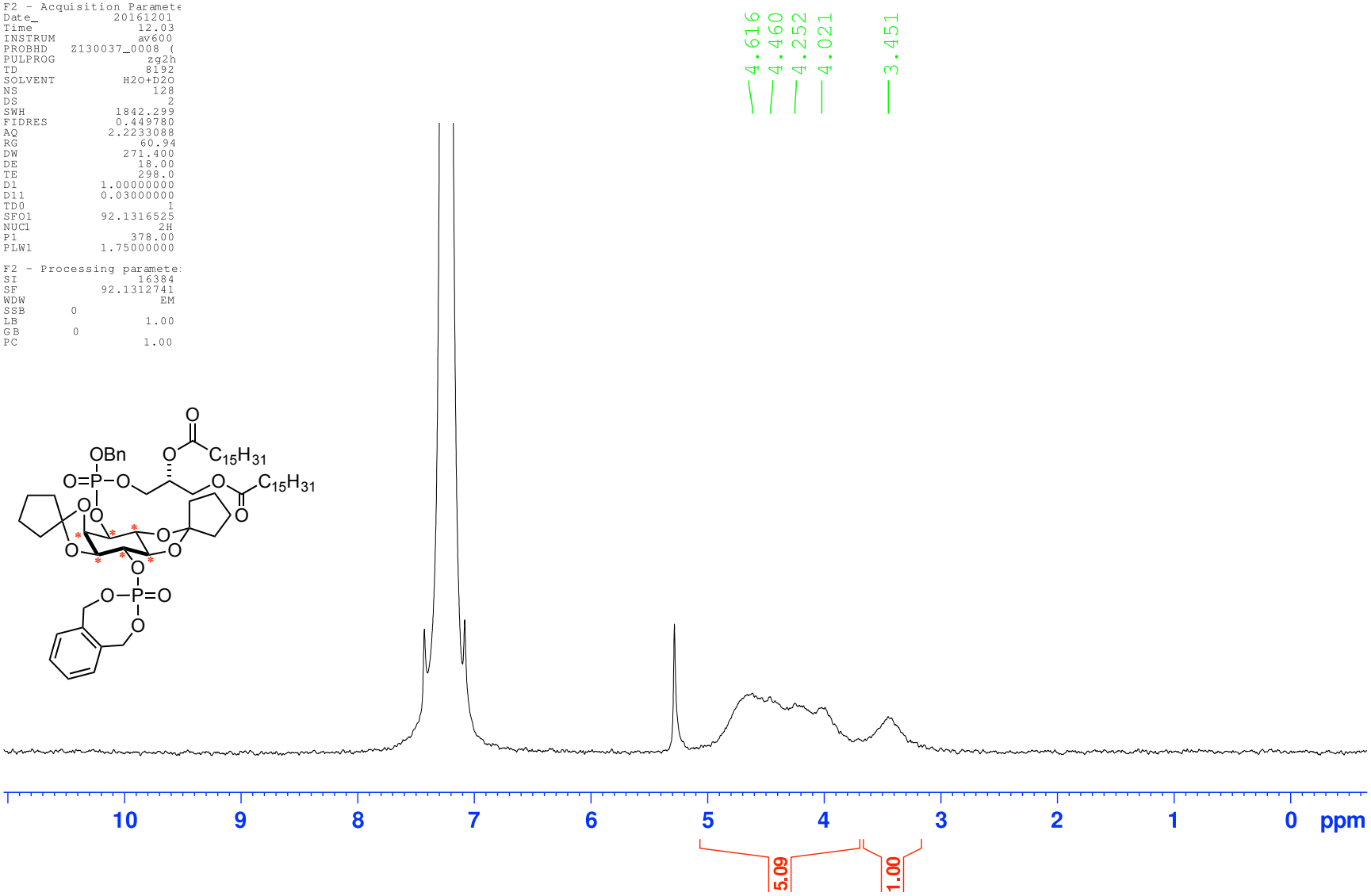
```
Current Data Parameters
NAME                 ajg21p
EXPNO                    11
PROCNO                    1

F2 - Acquisition Paramete
Date_              20161120
Time                  15.03
INSTRUM             avh400
PROBHD    Z108618_0873 (
PULPROG             zgpg30
TD                  131072
SOLVENT             CD2Cl2
NS                      16
DS                       4
SWH                64102.562
FIDRES             0.978127
AQ                 1.0223616
RG                    197.18
DW                     7.800
DE                      6.50
TE                     296.0
D1                 2.00000000
D11                0.03000000
TD0                       1
SFO1               161.9755930
NUC1                     31P
P1                     15.00
PLW1               13.93799973
SFO2               400.1316005
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                  90.00
PLW2               14.36999989
PLW12               0.34660661
PLW13               0.17371930

F2 - Processing paramete
SI                       65536
SF                 161.9755930
WDW                         EM
SSB          0
LB                      1.00
GB           0
PC                      1.40
```



D$_6$ (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-60 – ^{2}H NMR spectrum



D_6 (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene- 4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-60 – Mass spectrum

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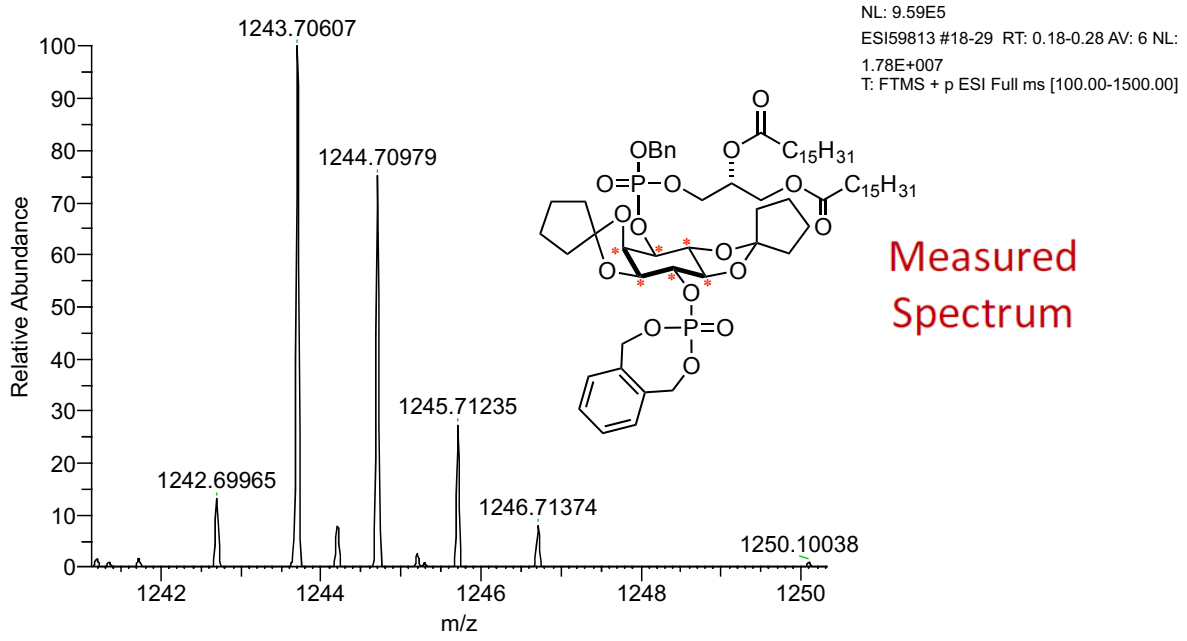
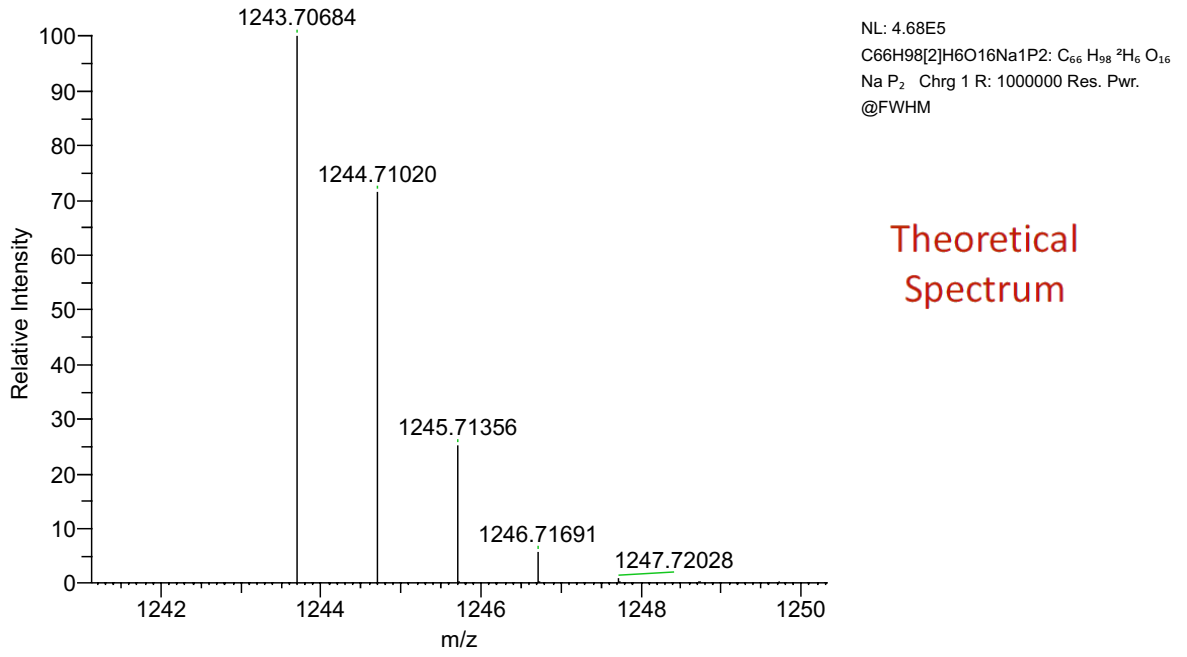
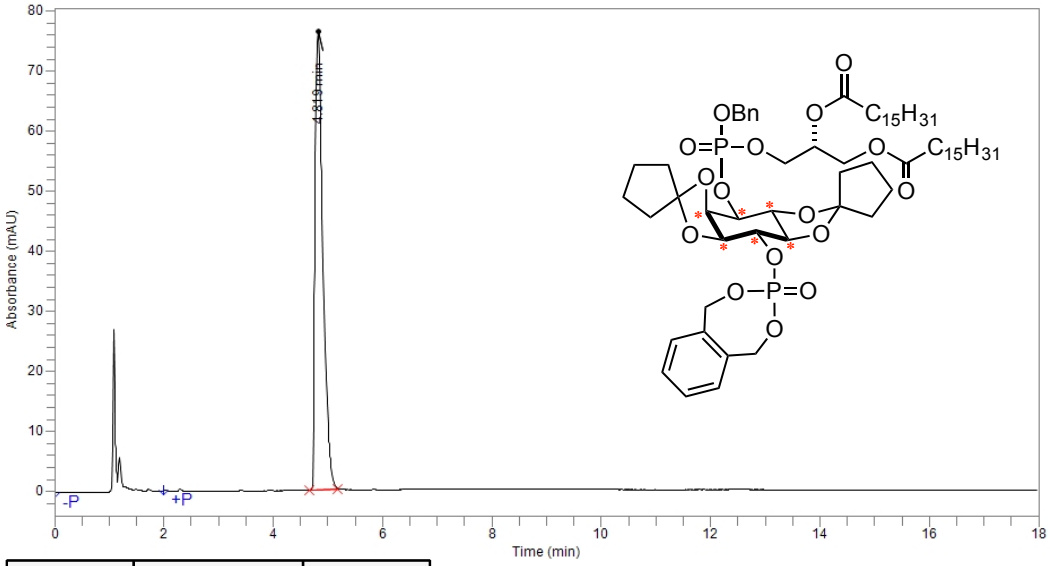




m/z	Formula	RDB	Delta ppm	Theo. Mass
1243.70605	$C_{66}H_{98}{}^{2}H_{6}O_{16}{}^{23}NaP_2$	15.5	-0.63	1243.70684

D_6 (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-60 – NP-HPLC (Method 6)



Time	Area	Area %
4.819	765,265	100.00
Total	765,265	100.00

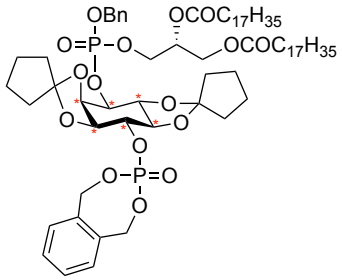
D_6 (−)-1D-1-O-(1,2-Di-*O*-stearoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphos-phep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-61
^{1}H NMR spectrum

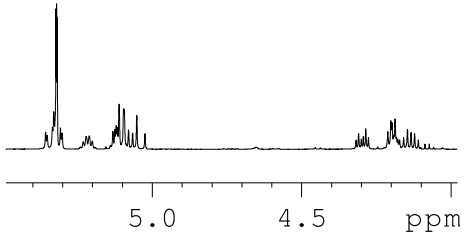
```
Current Data Parameters
NAME      ajg80p-data-85862706
EXPNO                        1
PROCNO                       1

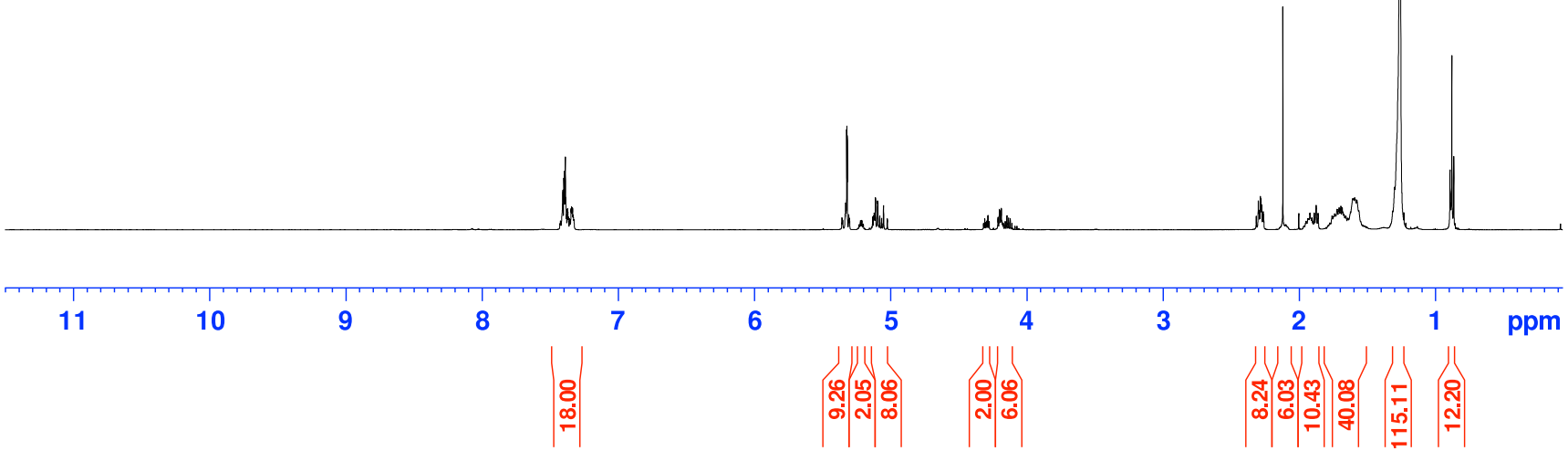
F2 - Acquisition Parameters
Date_              20170627
Time                   6.15
INSTRUM              avc500
PROBHD    5 mm CPDUL 13C
PULPROG                zg30
TD                    65536
SOLVENT             CD2Cl2
NS                        16
DS                         4
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                3.1719425 sec
RG                      3.2
DW                   48.400 usec
DE                   10.00 usec
TE                   298.0 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           500.3030896 MHz
NUC1                    1H
P1                   15.00 usec
PLW1           7.99830008 W

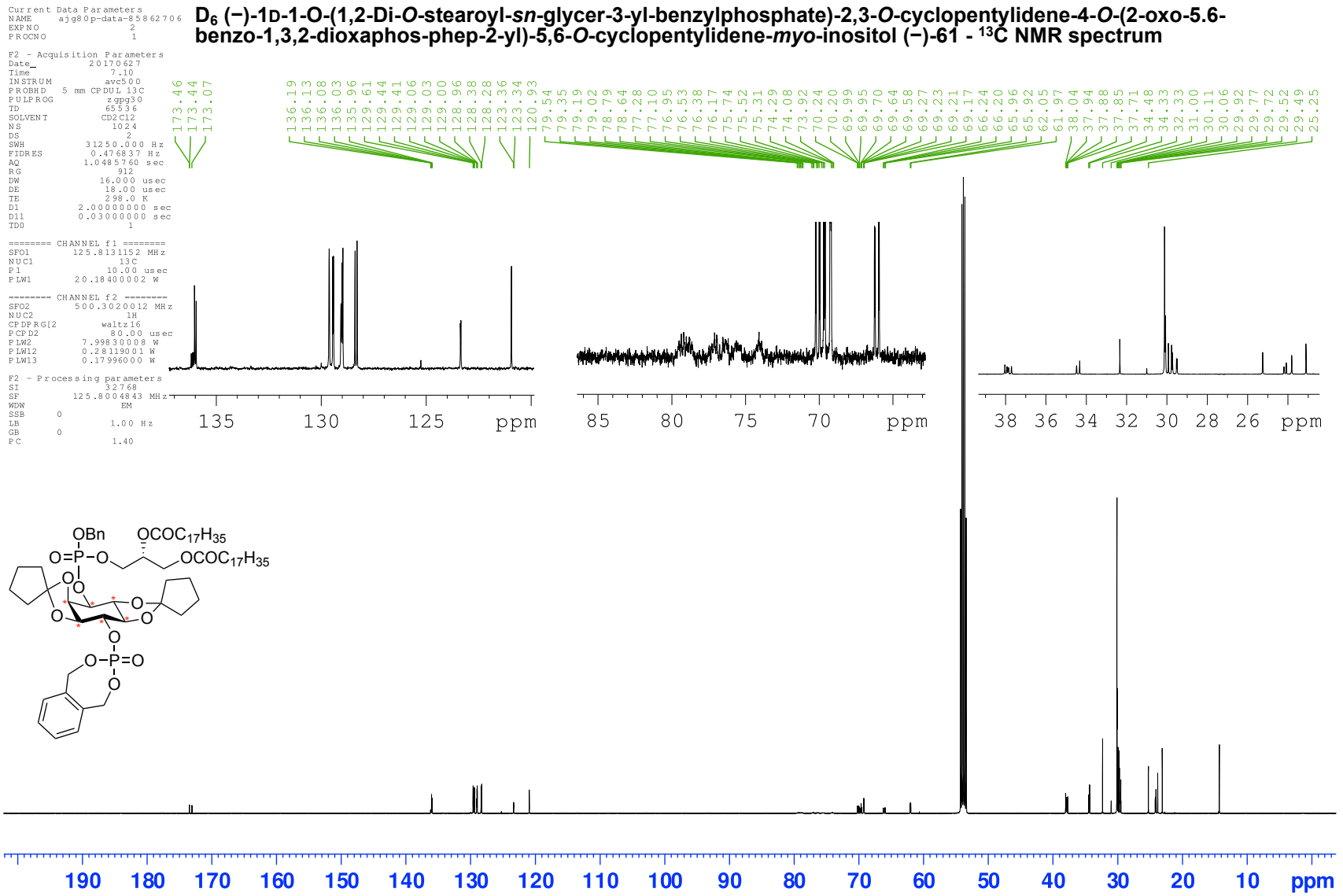
F2 - Processing parameters
SI                    65536
SF             500.3000205 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```







D_6 (−)-1D-1-O-(1,2-Di-*O*-stearoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphos-phep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-61 - ^{13}C NMR spectrum



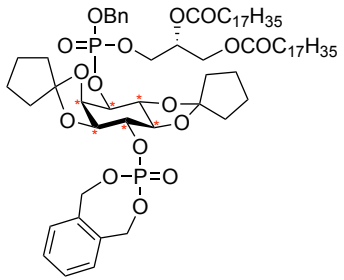
D_6 (−)-1D-1-O-(1,2-Di-*O*-stearoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphos-phep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-61 - ^{2}H NMR spectrum

```
Current Data Parameters
NAME      ajg80p-DNMR-86570507
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_            20170705
Time                7.31
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg2h
TD                  4096
SOLVENT            CDCl3
NS                   1024
DS                      4
SWH              1535.627 Hz
FIDRES           0.374909 Hz
AQ              1.3336576 sec
RG                      1
DW                325.600 usec
DE                 18.00 usec
TE                 298.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          76.7994800 MHz
NUC1                  2H
P1                180.00 usec
PLW1          3.30369997 W

F2 - Processing parameters
SI                   8192
SF            76.7990896 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
```

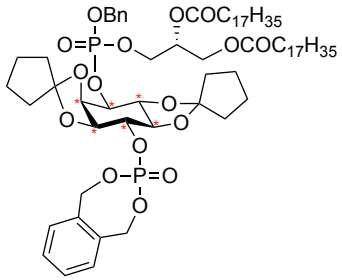


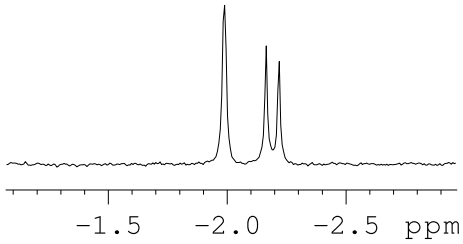
D_6 (−)-1D-1-O-(1,2-Di-*O*-stearoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphos-phep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-61 - ^{31}P NMR spectrum

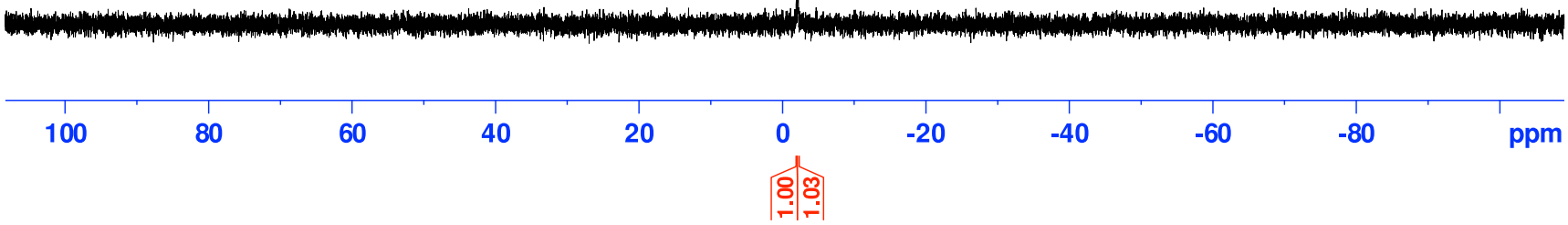
```
Current Data Parameters
NAME                 ajg80p
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20170622
Time                   0.47 h
INSTRUM              avg400
PROBHD    Z108618_0816 (
PULPROG              zgpg30
TD                   131072
SOLVENT                CDCl3
NS                        16
DS                         4
SWH                64102.562 Hz
FIDRES             0.978127 Hz
AQ                 1.0223616 sec
RG                    206.87
DW                     7.800 usec
DE                     6.50 usec
TE                     352.4 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1
SFO1             162.0039295 MHz
NUC1                     31P
P1                    15.00 usec
PLW1             13.00000000 W
SFO2             400.2016008 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                 90.00 usec
PLW2             14.00000000 W
PLW12             0.33877000 W
PLW13             0.17039999 W

F2 - Processing parameters
SI                       65536
SF               162.0039295 MHz
WDW                        EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```







D_6 (−)-1D-1-O-(1,2-Di-*O*-stearoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphos-phep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-61 Mass spectrum

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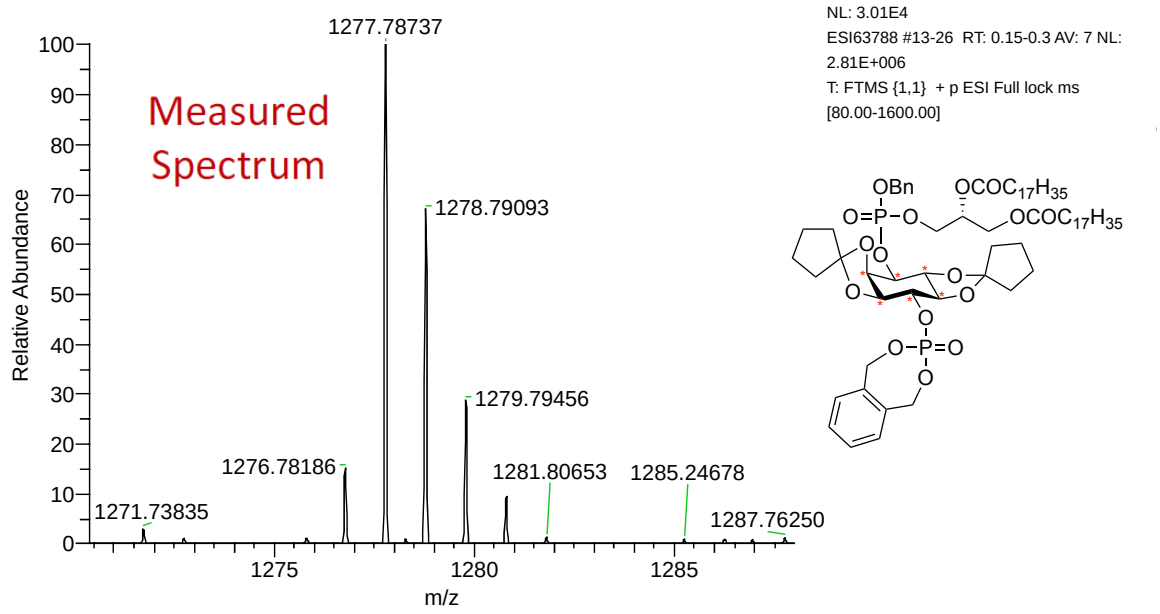
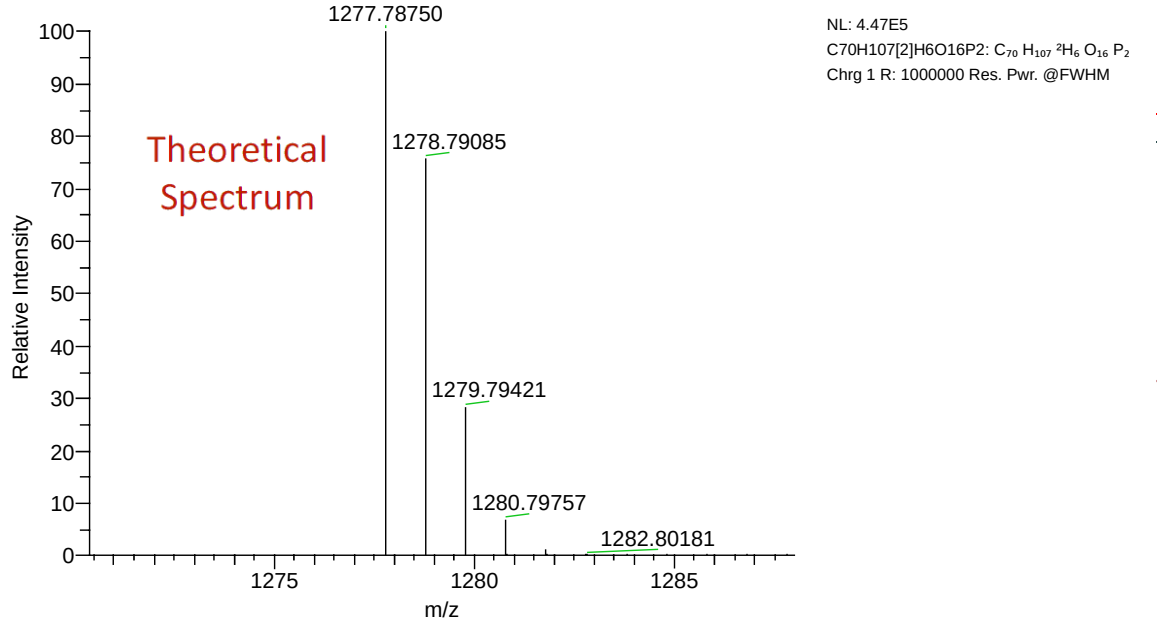
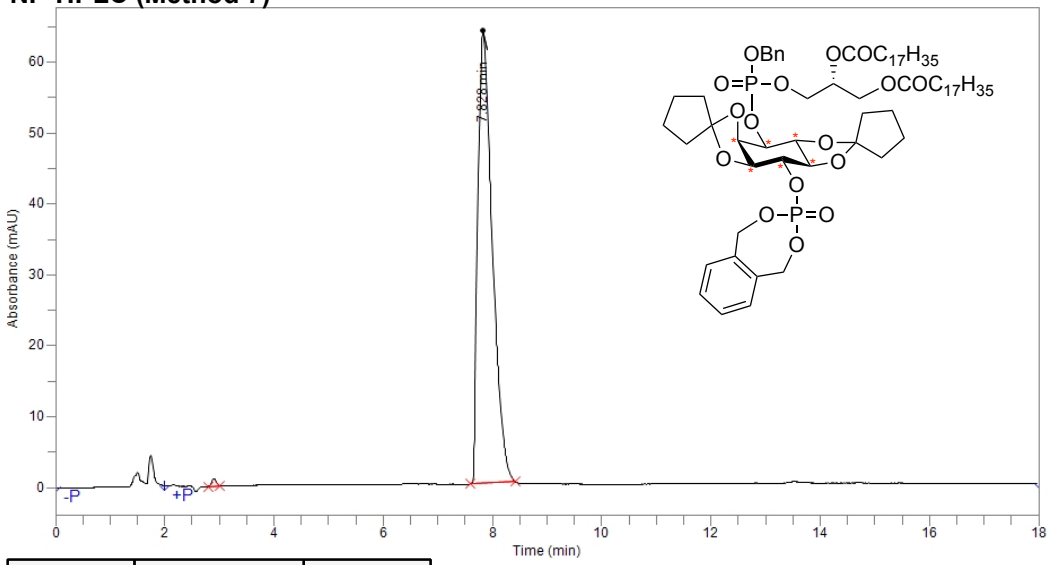




m/z	Formula	RDB	Delta ppm	Theo. Mass
1277.78735	$C_{70}H_{107}{}^{2}H_6O_{16}P_2$	15.5	-0.11	1277.78750

D_6 (−)-1D-1-O-(1,2-Di-*O*-stearoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphos-phep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-61
NP-HPLC (Method 7)



Time	Area	Area %
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7.828	1,167,870	99.49
Total	1,173,834	100.00

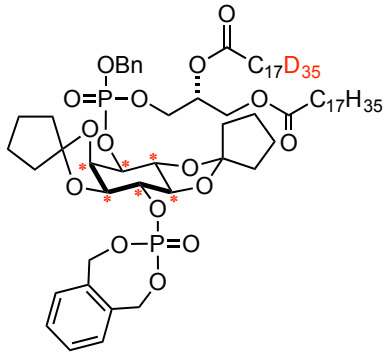
D_{41} (−)-1D-1-*O*-(1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene- 4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-62 – ^{1}H NMR spectrum

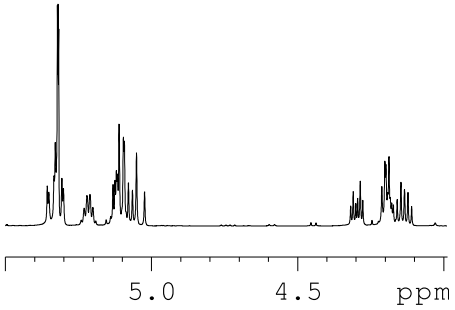
```
Current Data Parameters
NAME          ajg41p-data
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161216
Time              11.31
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT          CD2Cl2
NS                 256
DS                   4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                2.25
DW               48.400 usec
DE               10.00 usec
TE               298.0 K
D1            1.00000000 sec
TD0                  1

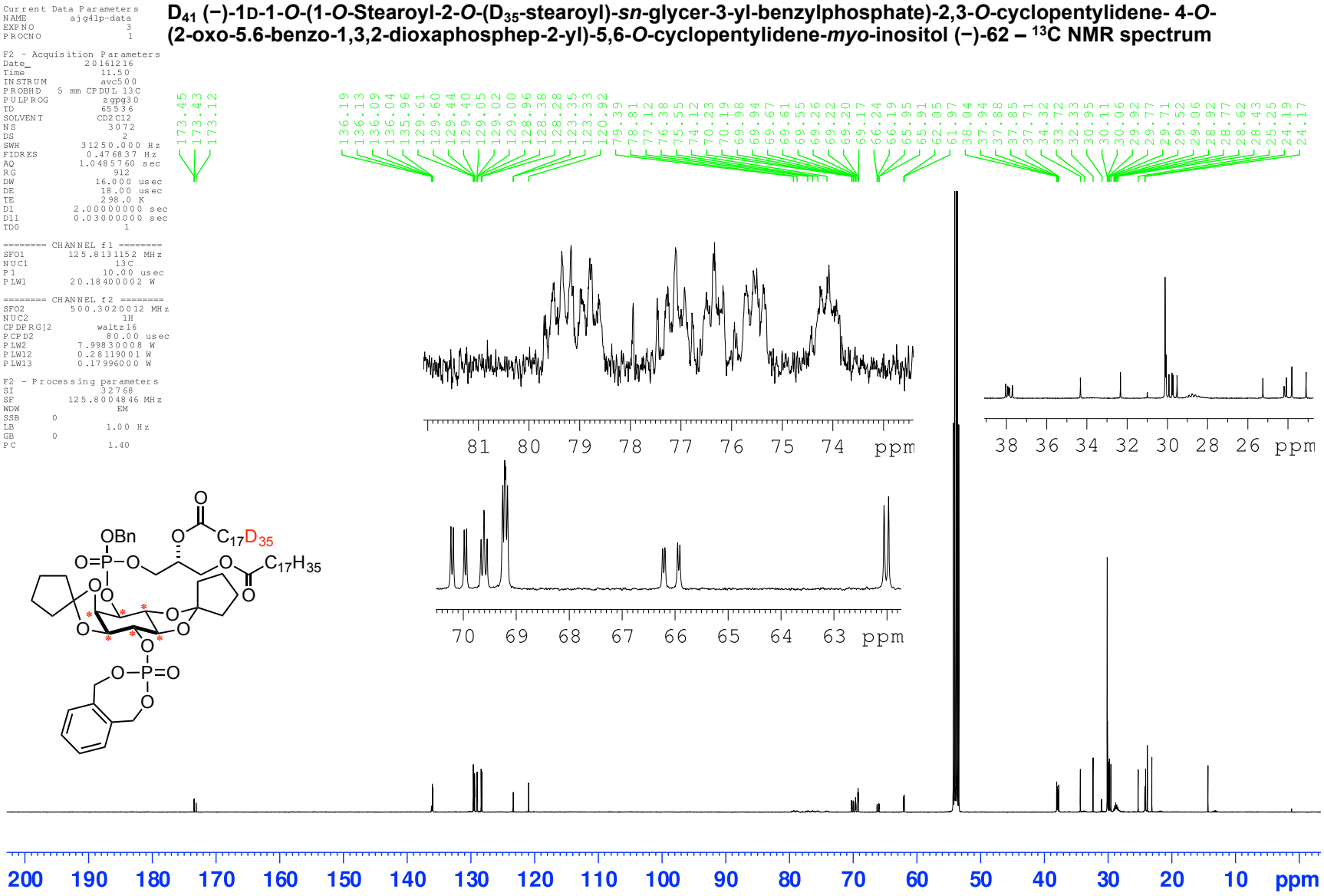
======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1               1H
P1               15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI                65536
SF          500.3000206 MHz
WDW                EM
SSB       0
LB               0.30 Hz
GB        0
PC               1.00
```





D_{41} (−)-1D-1-*O*-(1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene- 4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-62 – ^{13}C NMR spectrum



D_{41} (−)-1D-1-*O*-(1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene- 4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-62 – ^{31}P NMR spectrum

```
Current Data Parameters
NAME                 ajg41p-2
EXPNO                       2
PROCNO                      1

F2 - Acquisition Paramete
Date_               20161209
Time                   14.07
INSTRUM                avb400
PROBHD     Z116098_0219 (
PULPROG              zgpg30
TD                    65536
SOLVENT              CD2Cl2
NS                        80
DS                         4
SWH                64102.562
FIDRES              1.956255
AQ                 0.5111808
RG                    197.74
DW                     7.800
DE                      6.50
TE                     298.0
D1                2.00000000
D11               0.03000000
TD0                         1
SFO1           161.9674942
NUC1                      31P
P1                      8.00
PLW1              54.00000000
SFO2              400.1316005
NUC2                      1H
CPDPRG[2               waltz16
PCPD2                  90.00
PLW2              14.58800030
PLW12              0.18009999
PLW13              0.09058800

F2 - Processing paramete
SI                      32768
SF                 161.9755930
WDW                        EM
SSB          0
LB                      1.00
GB           0
PC                      1.40
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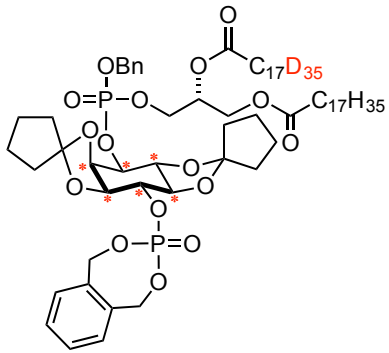
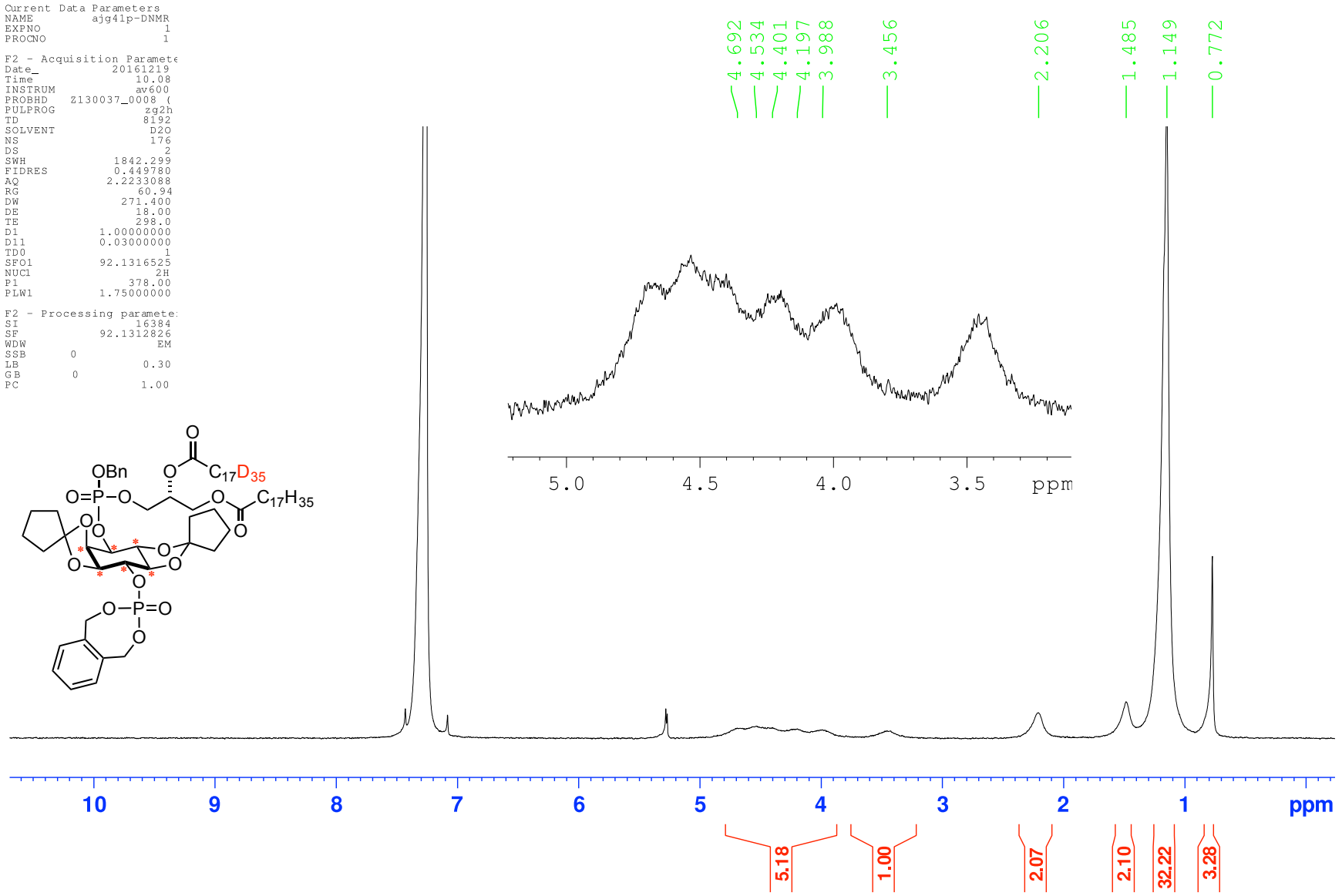


D_{41} (−)-1D-1-*O*-(1-*O*-Stearoyl-2-*O*-(D35-stearoyl)-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene- 4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-62 – ^{31}P NMR spectrum



D_{41} (−)-1D-1-*O*-(1-*O*-Stearoyl-2-*O*-(D35-stearoyl)-*sn*-glycer-3-yl-benzylphosphate)- 2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-62 – Mass spectrum

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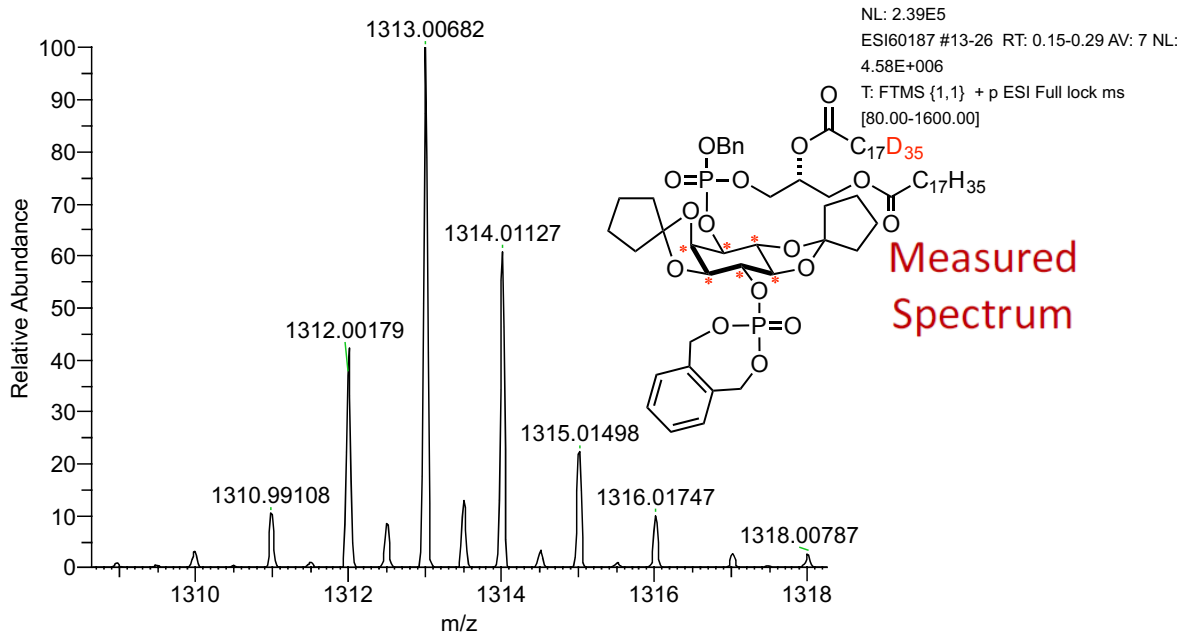
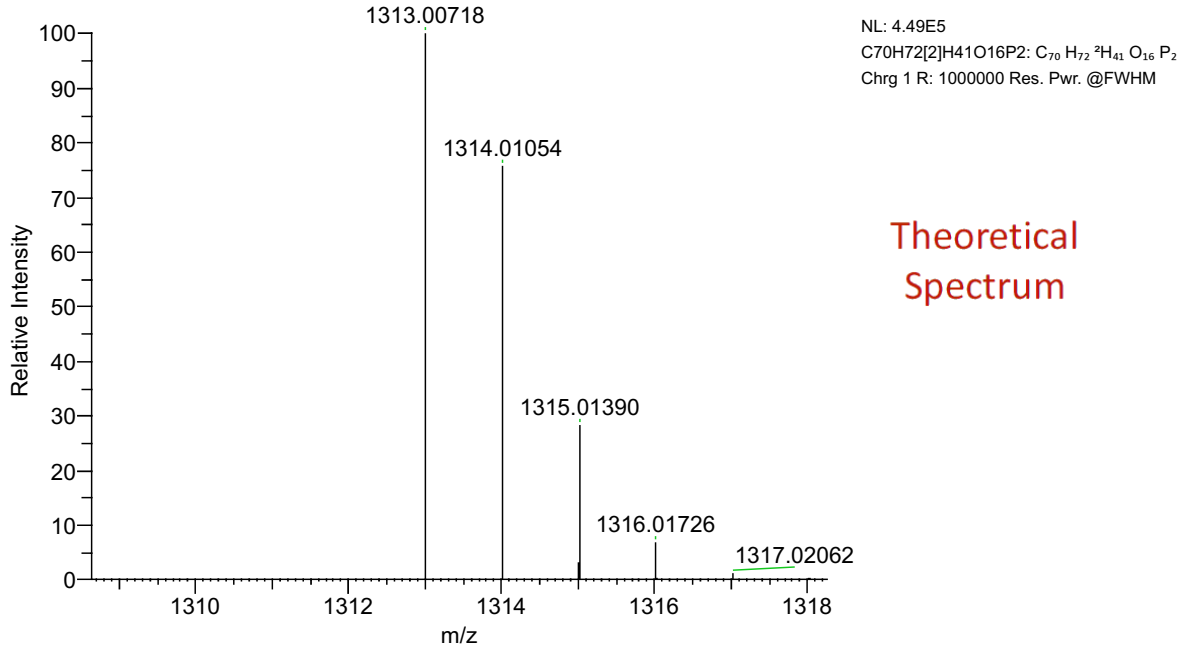
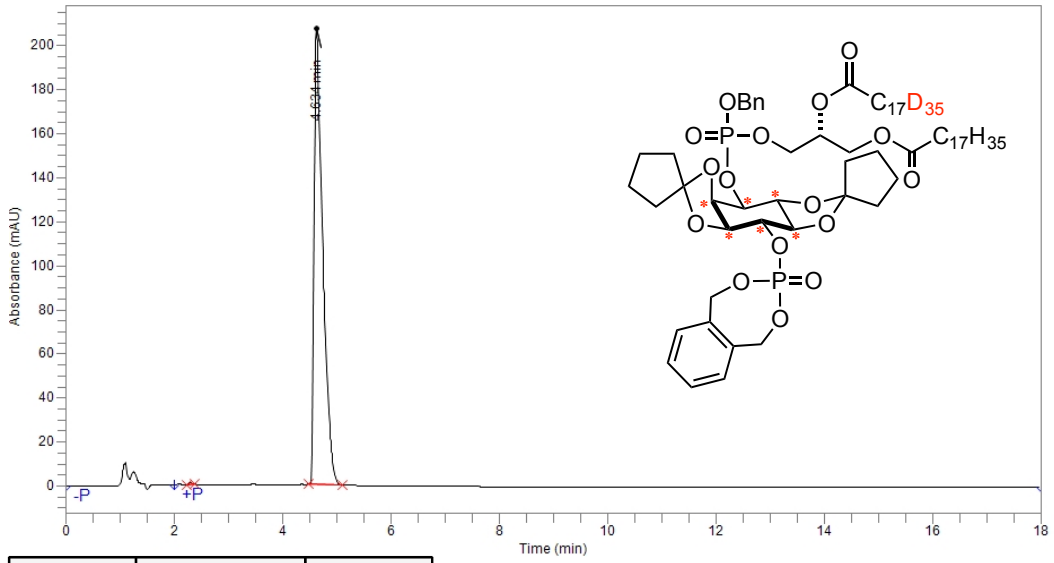




m/z	Formula	RDB	Delta ppm	Theo. Mass
1313.00684	$C_{70}H_{72}{}^{2}H_{41}O_{16}P_2$	15.5	-0.26	1313.00718

D_{41} (−)-1D-1-*O*-(1-*O*-Stearoyl-2-*O*-(D_{35}-stearoyl)-*sn*-glycer-3-yl-benzylphosphate)- 2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*- cyclopentylidene-*myo*-inositol (−)-62 – NP-HPLC (Method 6)



Time	Area	Area %
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4.634	2,290,414	99.80
Total	2,295,080	100.00

D_6 (−)-1D-1-*O*-(1-*O*-stearoyl-2-*O*-arachidonyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-63

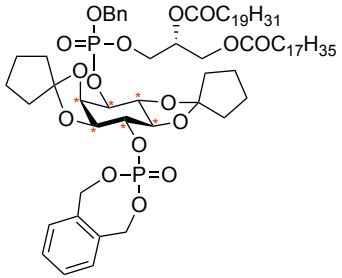
^{31}P NMR spectrum

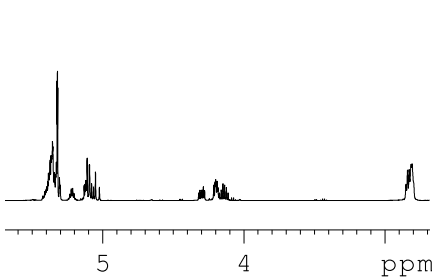
```
Current Data Parameters
NAME      ajh16p-data-86312806
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20170628
Time                   6.06
INSTRUM              avc500
PROBHD    5 mm CPDUL 13C
PULPROG               zg30
TD                   65536
SOLVENT             CD2Cl2
NS                       16
DS                        4
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                3.1719425 sec
RG                     3.56
DW                  48.400 usec
DE                  10.00 usec
TE                  298.0 K
D1              1.00000000 sec
TD0                      1

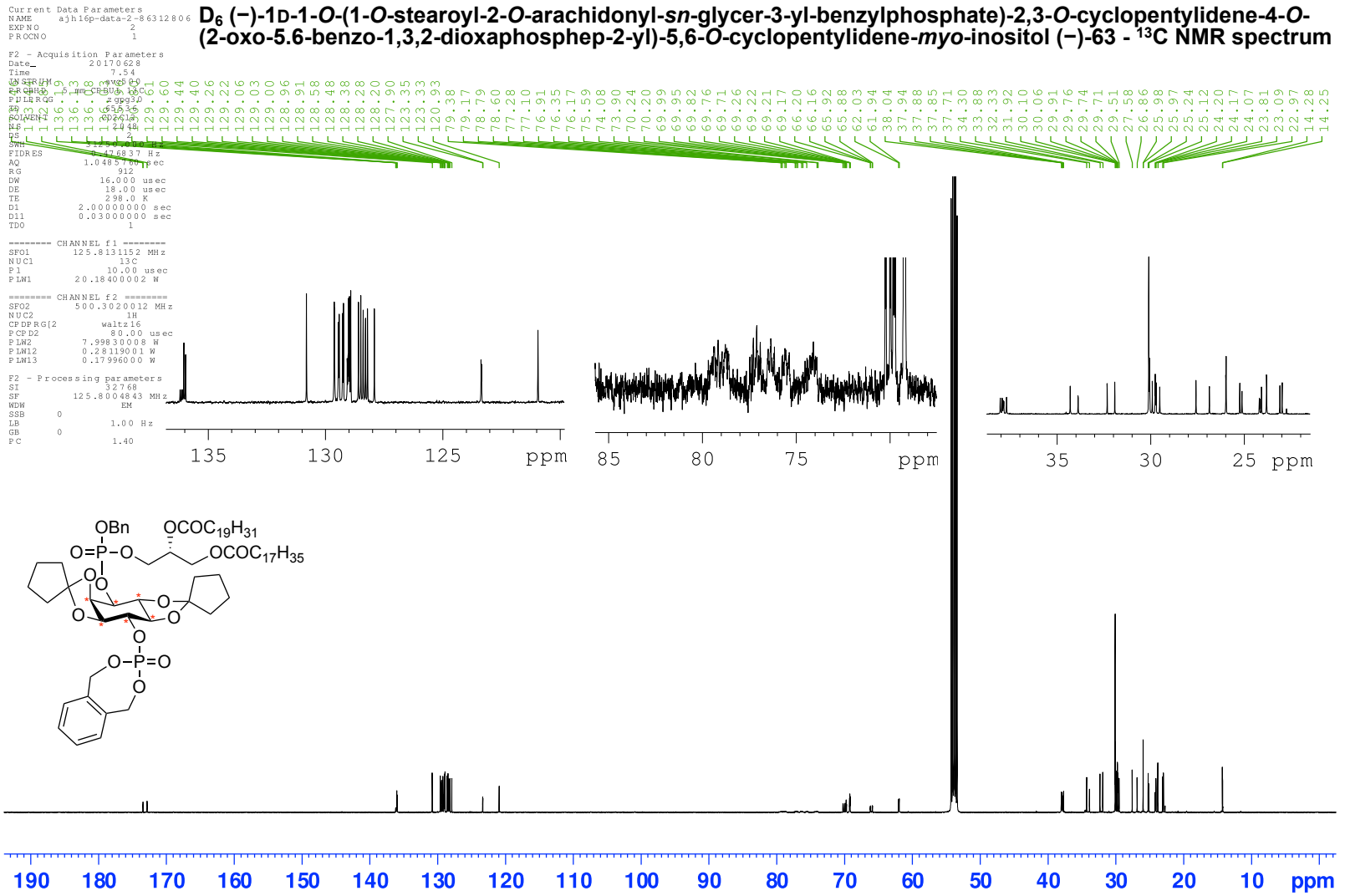
======== CHANNEL f1 ========
SFO1           500.3030896 MHz
NUC1                    1H
P1                   15.00 usec
PLW1            7.99830008 W

F2 - Processing parameters
SI                   65536
SF              500.3000206 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```





D_6 (−)-1D-1-*O*-(1-*O*-stearoyl-2-*O*-arachidonyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-63 - ^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-(1-*O*-stearoyl-2-*O*-arachidonyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-63 - ^{2}H NMR spectrum

```
Current Data Parameters
NAME      ajh16p-DNMR-86560507
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_            20170705
Time                6.45
INSTRUM           avc500
PROBHD    5 mm CPDUL 13C
PULPROG             zg2h
TD                  4096
SOLVENT            CDCl3
NS                   1024
DS                      4
SWH            1535.627 Hz
FIDRES          0.374909 Hz
AQ             1.3336576 sec
RG                      1
DW               325.600 usec
DE                 18.00 usec
TE                 298.0 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          76.7994800 MHz
NUC1                   2H
P1                180.00 usec
PLW1          3.30369997 W

F2 - Processing parameters
SI                   8192
SF            76.7990896 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.00
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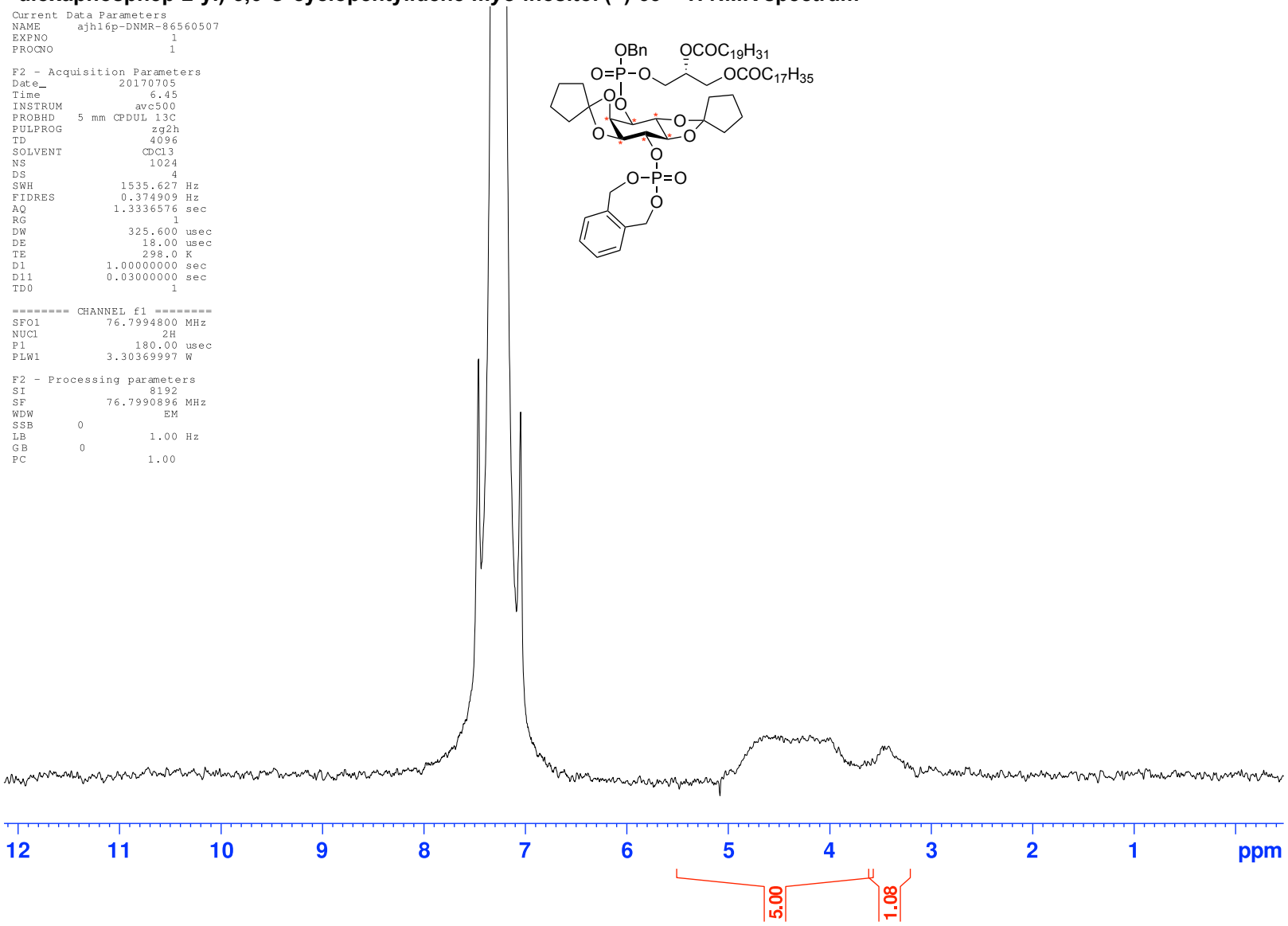
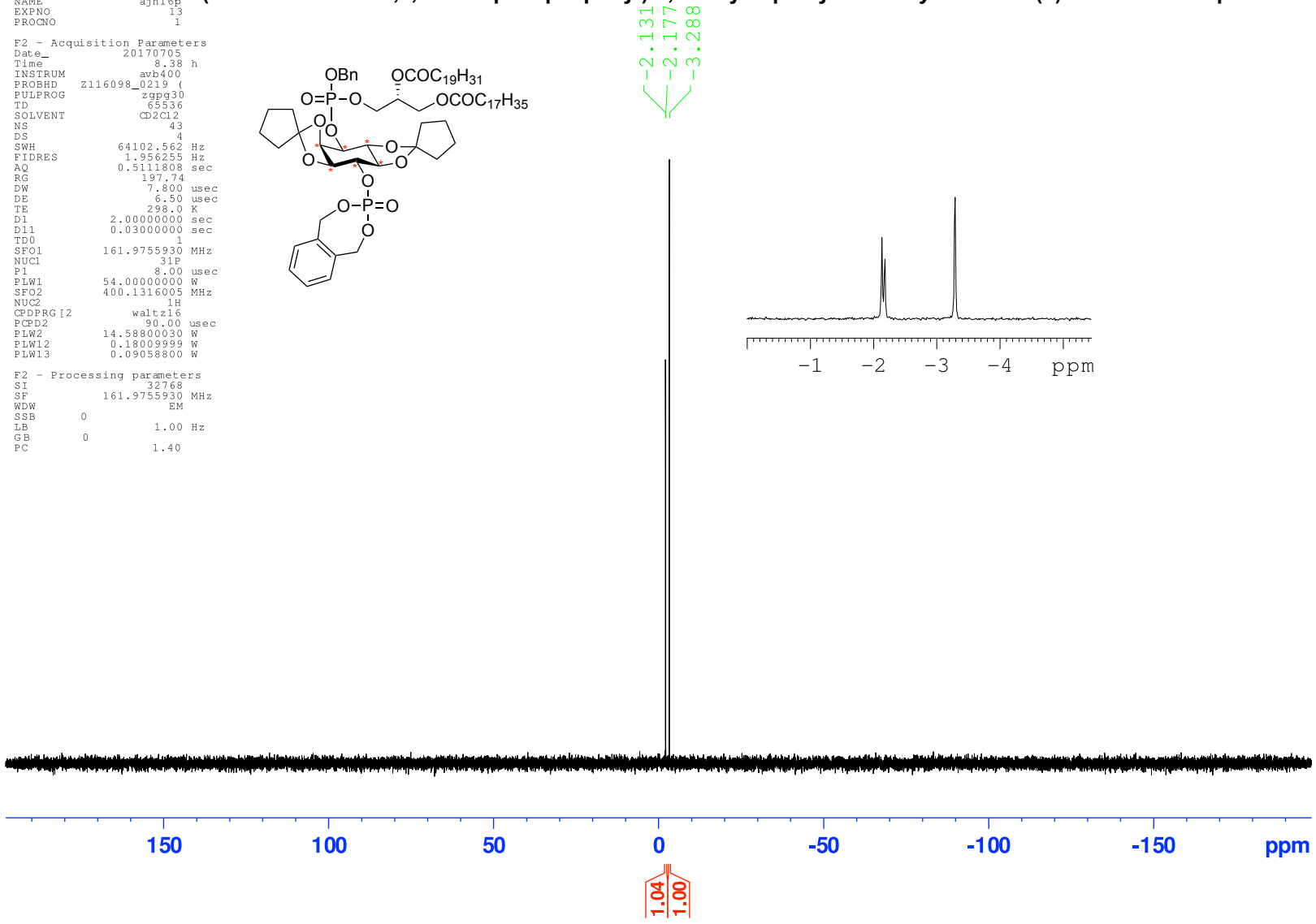
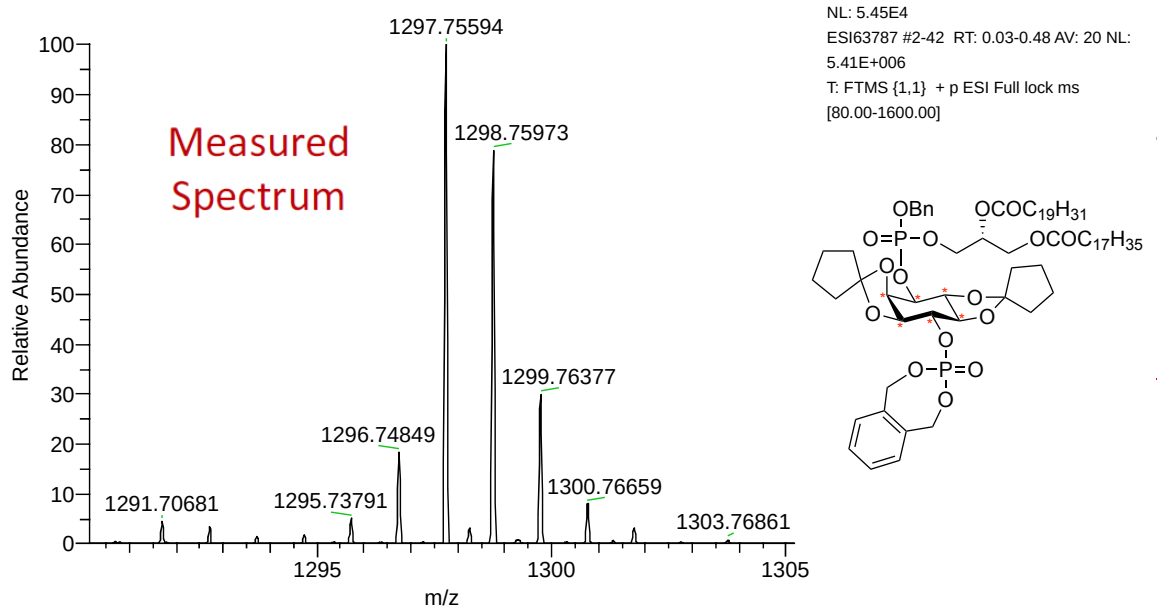


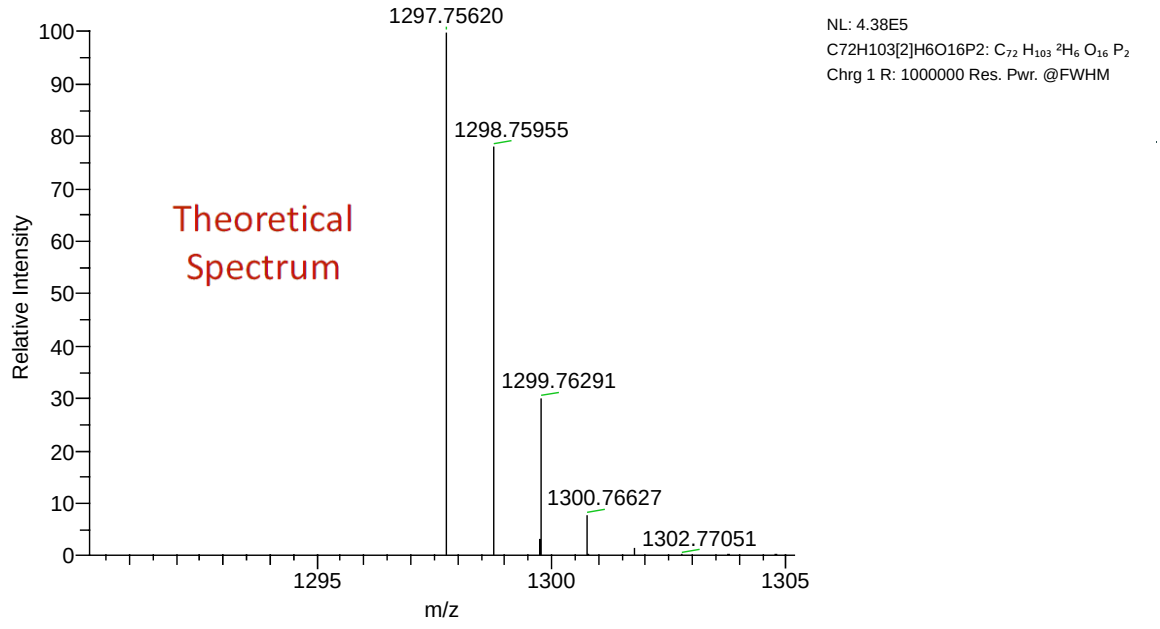
D_6 (−)-1D-1-*O*-(1-*O*-stearoyl-2-*O*-arachidonyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-63 - ^{31}P NMR spectrum



D_6 (−)-1D-1-*O*-(1-*O*-stearoyl-2-*O*-arachidonyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-63 - Mass spectrum

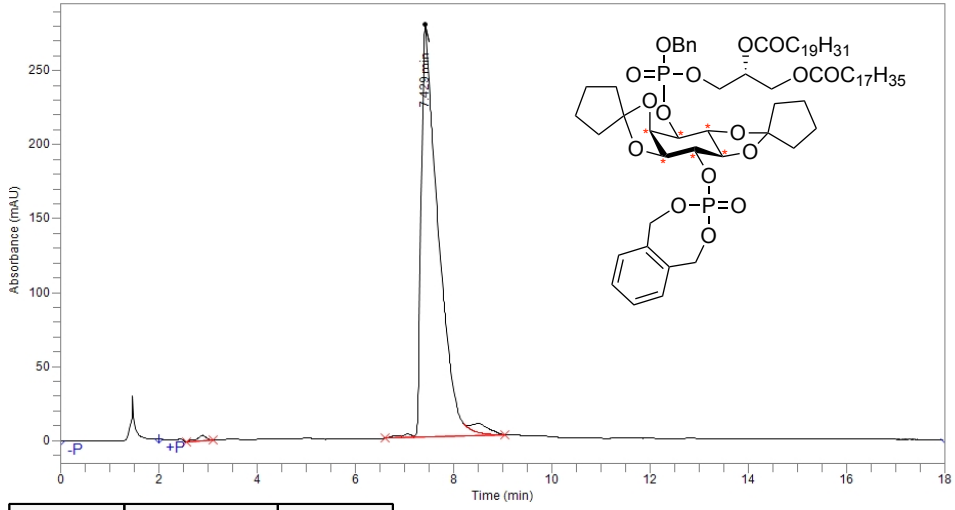
X:\data\Jun 17\ESI63787.raw 29/06/2017 4:19 pm





m/z	Formula	RDB	Delta ppm	Theo. Mass
1297.75598	$C_{72}H_{103}{}^{2}H_6O_{16}P_2$	19.5	-0.17	1297.75620

D_6 (−)-1D-1-*O*-(1-*O*-stearoyl-2-*O*-arachidonyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-5,6-*O*-cyclopentylidene-*myo*-inositol (−)-63 - NP-HPLC (Method 7)



Time	Area	Area %
2.899	49,543	0.72
6.848	21,700	0.31
7.070	27,504	0.40
7.429	6,669,523	96.42
8.505	148,620	2.15
Total	6,916,891	100.00

(−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-64 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME      ajfPI(4)P-data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160610
Time              10.48
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT           MeOD
NS                  16
DS                   4
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719425 sec
RG                 2.25
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1                1H
P1                15.00 usec
PLW1         7.99830008 W

F2 - Processing parameters
SI                 65536
SF          500.3000110 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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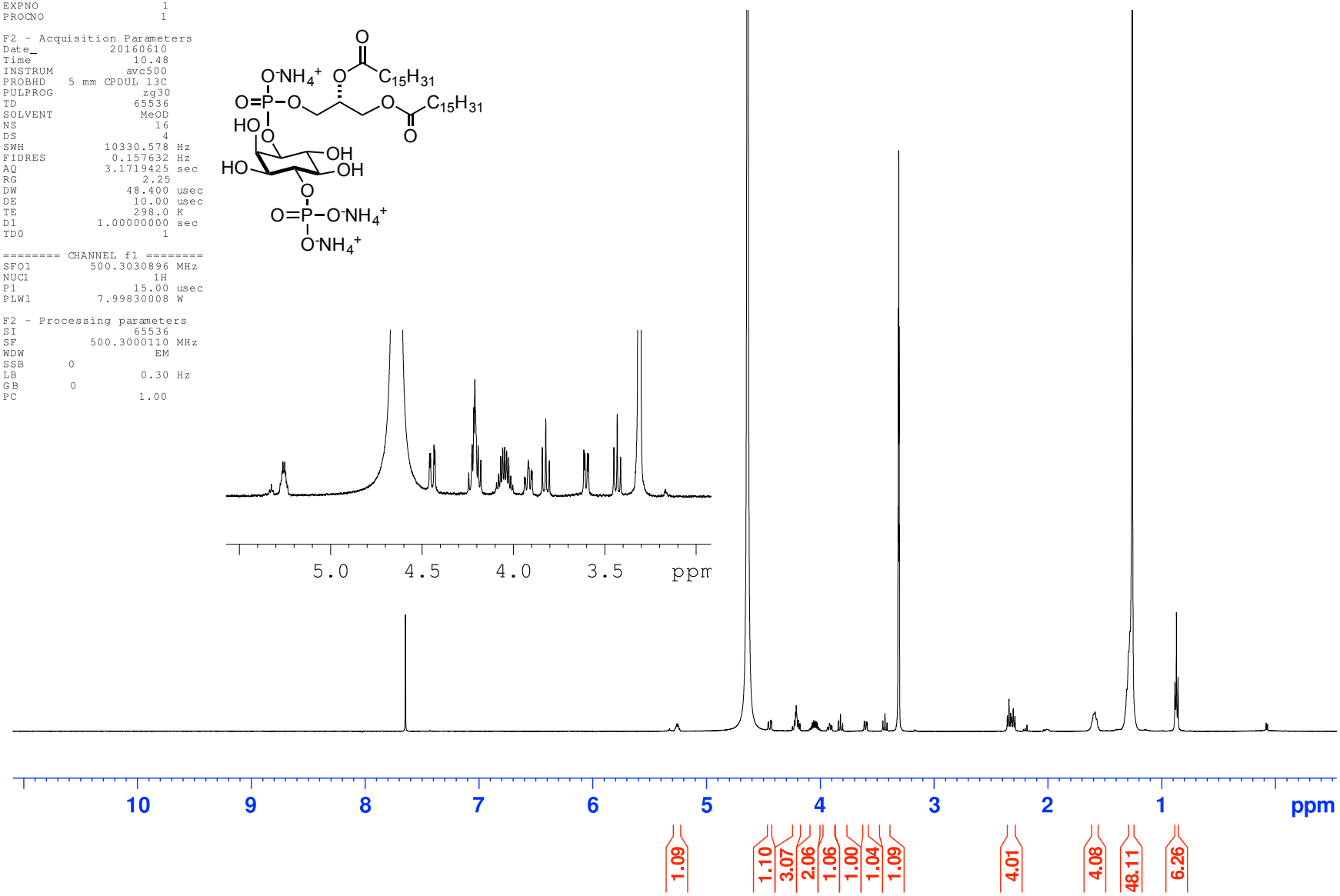
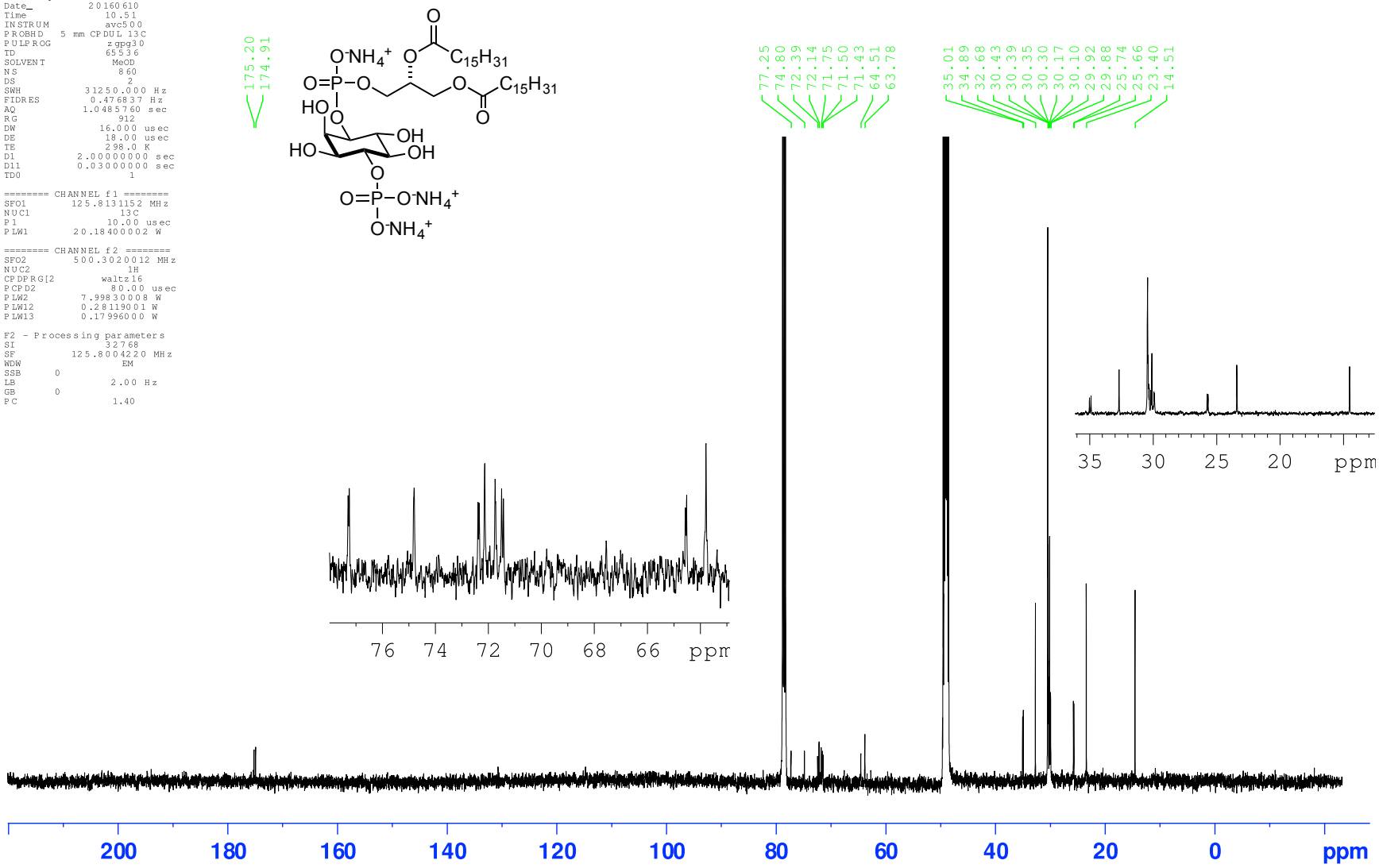


(−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-64 – ^{13}C NMR spectrum



(−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-64 – ^{1}H-^{13}C HSQC

```
Current Data Parameters
NAME      ajfPI(4)P-data
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160610
Time              11.41
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG  hsqcedetgpsp.3
TD                 1024
SOLVENT            MeOD
NS                    2
DS                   16
SWH           5000.000 Hz
FIDRES        4.882812 Hz
AQ           0.1024000 sec
RG                 2050
DW             100.000 usec
DE               10.00 usec
TE               298.0 K
CNST2       145.0000000
D0           0.00000300 sec
D1           1.00000000 sec
D4           0.00172414 sec
D11          0.03000000 sec
D16          0.00020000 sec
D21          0.00340000 sec
IN0          0.00001990 sec

======== CHANNEL f1 ========
SFO1        500.3025015 MHz
NUC1                1H
P1                15.00 usec
P2                30.00 usec
P28       0 usec
PLW1         7.99830008 W

======== CHANNEL f2 ========
SFO2        125.8131151 MHz
NUC2                13C
CPDPRG[2           garp
P3                10.00 usec
P14              500.00 usec
P31             1900.00 usec
PCPD2             70.00 usec
PLW0      0 W
PLW2        20.18400002 W
PLW12        0.41192001 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3              0.500
SPOFFS3   0 Hz
SPW3         3.08389997 W
SPNAM[18  Crp60_xfilt.2
SPOAL18             0.500
SPOFFS18 0 Hz
SPW18        0.73894000 W

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                  256
SFO1            125.8131 MHz
FIDRES         98.146988 Hz
SW               199.706 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                 1024
SF          500.3000103 MHz
WDW               QSINE
SSB                   2
LB        0 Hz
GB        0
PC                1.40

F1 - Processing parameters
SI                  512
MC2        echo-antiecho
SF          125.8004332 MHz
WDW               QSINE
SSB                   2
LB        0 Hz
GB        0
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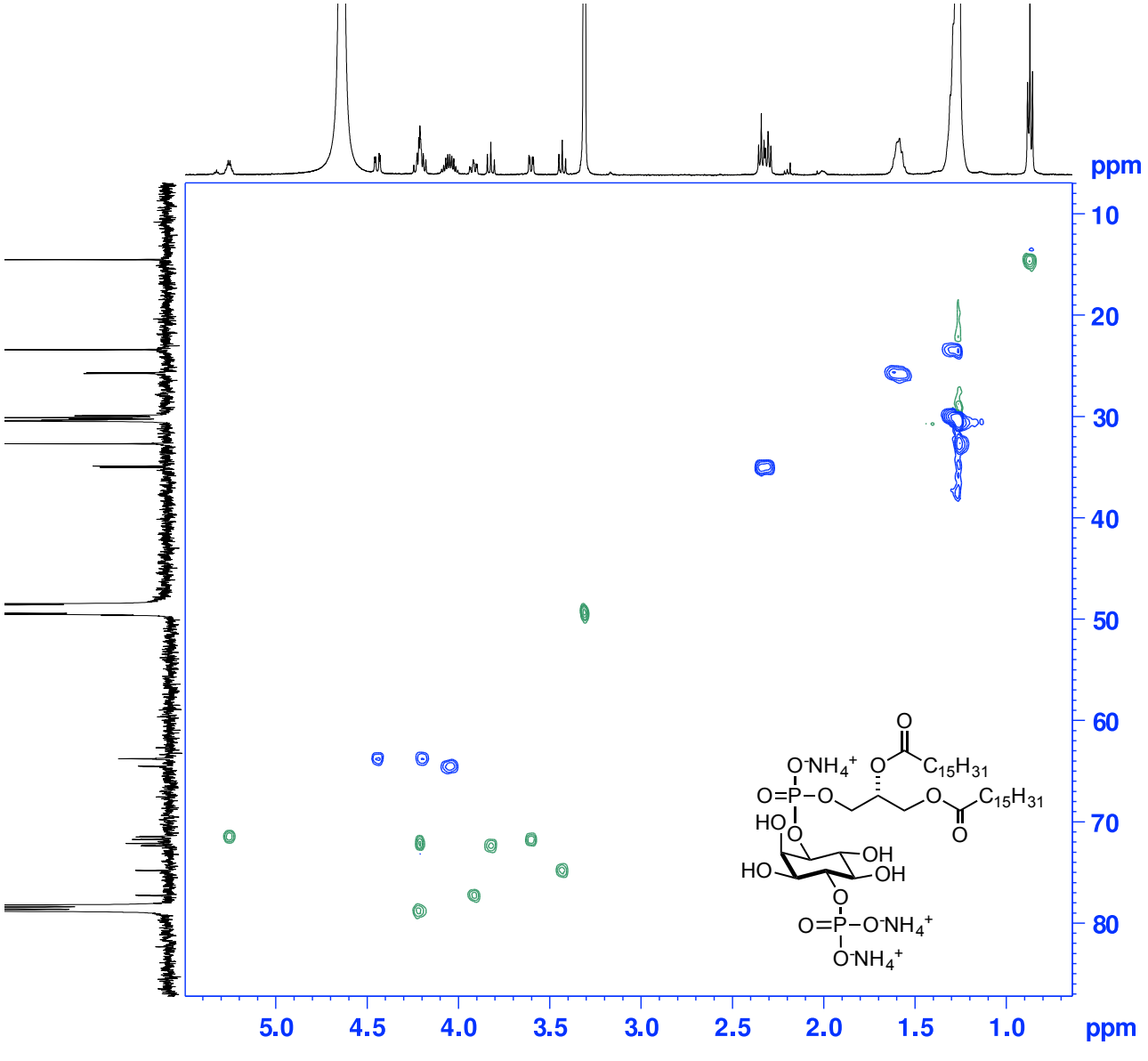
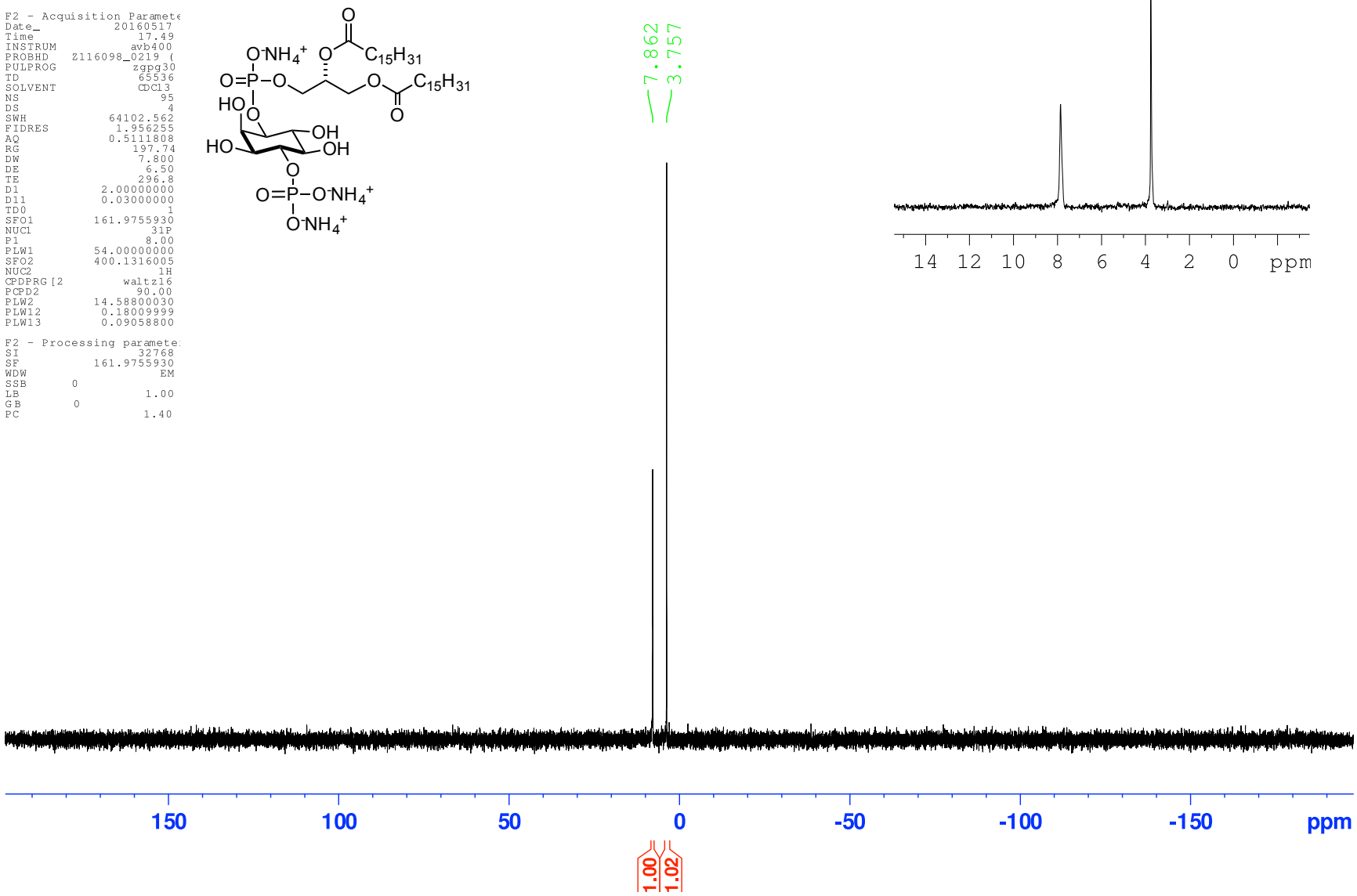


(−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-64 – ^{31}P NMR spectrum



(−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-64 – ^{1}H-^{31}P HMBC

```
Current Data Parameters
NAME        ajf26p-PI4P
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20160517
Time              18.01
INSTRUM           avb400
PROBHD   Z116098_0219 (
PULPROG      hmbcgpndqf
TD                 2048
SOLVENT           CDCl3
NS                    2
DS                   16
SWH            4795.396 Hz
FIDRES          2.341502 Hz
AQ            0.2135381 sec
RG               197.74
DW             104.267 usec
DE               6.50 usec
TE              296.4 K
CNST13         8.0000000
d0           0.00000300 sec
D1           1.50000000 sec
d6           0.06250000 sec
D16          0.00020000 sec
in0      0 sec
ST1CNT                0
d0orig       0.00000300 sec
ph1loop               0
t1loop                0
SFO1         400.1320007 MHz
NUC1                 1H
P1                10.00 usec
p2                20.00 usec
PLW1         14.58800030 W
SFO2         161.9755930 MHz
NUC2                31P
P3                 8.00 usec
PLW2         53.95100021 W
GPNAM[1]     SMSQ10.100
GPNAM[2]     SMSQ10.100
GPNAM[3]     SMSQ10.100
GPZ1              70.00 %
GPZ2              30.00 %
GPZ3              80.50 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   79
SFO1           161.9756 MHz
FIDRES       282.549744 Hz
SW             137.807 ppm
FnMODE              QF

F2 - Processing parameters
SI                 1024
SF          400.1315733 MHz
WDW                SINE
SSB      0
LB       0 Hz
GB       0
PC                 1.40

F1 - Processing parameters
SI                 1024
MC2                 QF
SF          161.9755972 MHz
WDW                SINE
SSB      0
LB       0 Hz
GB       0
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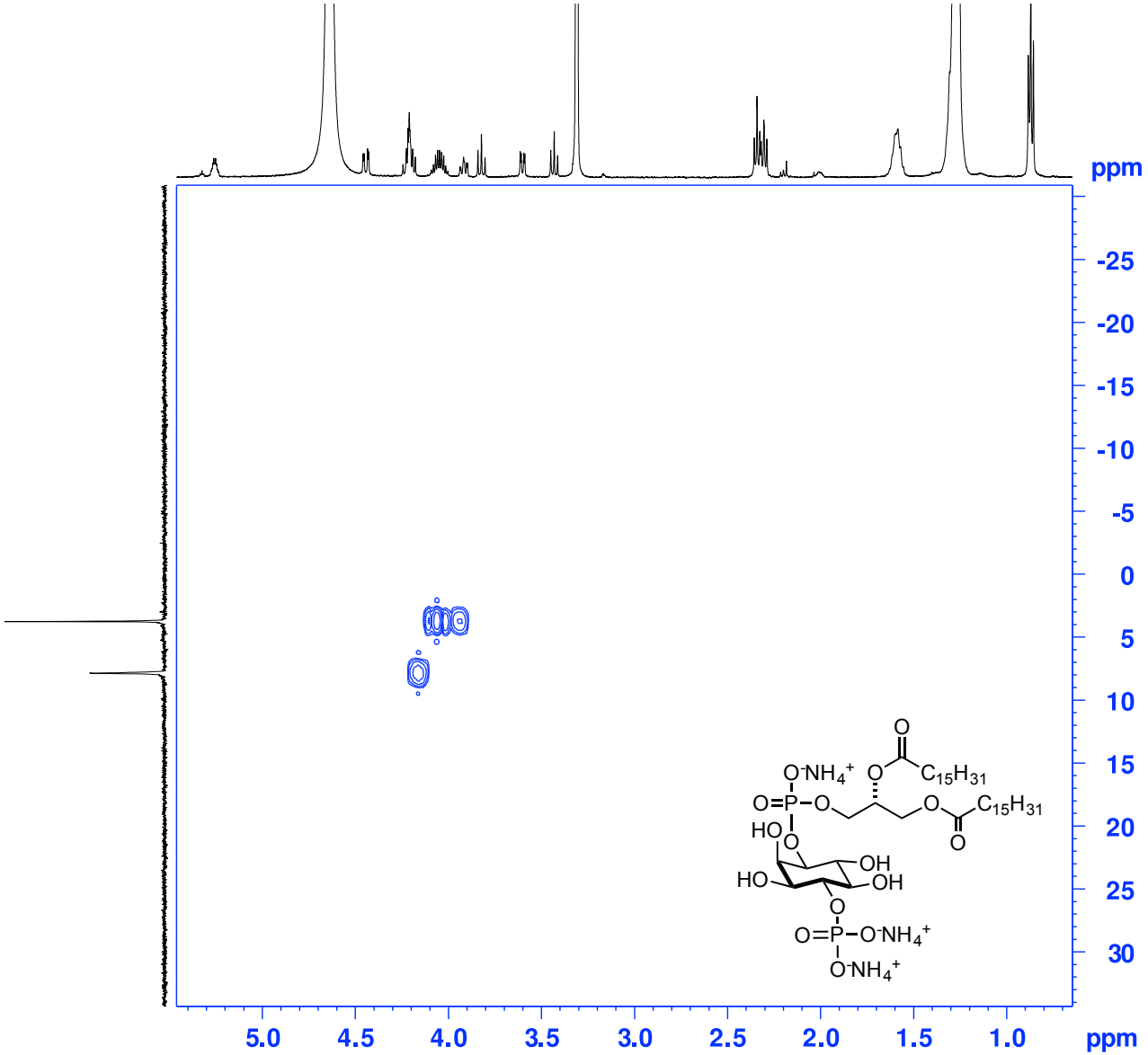
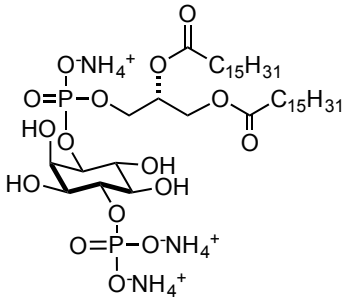
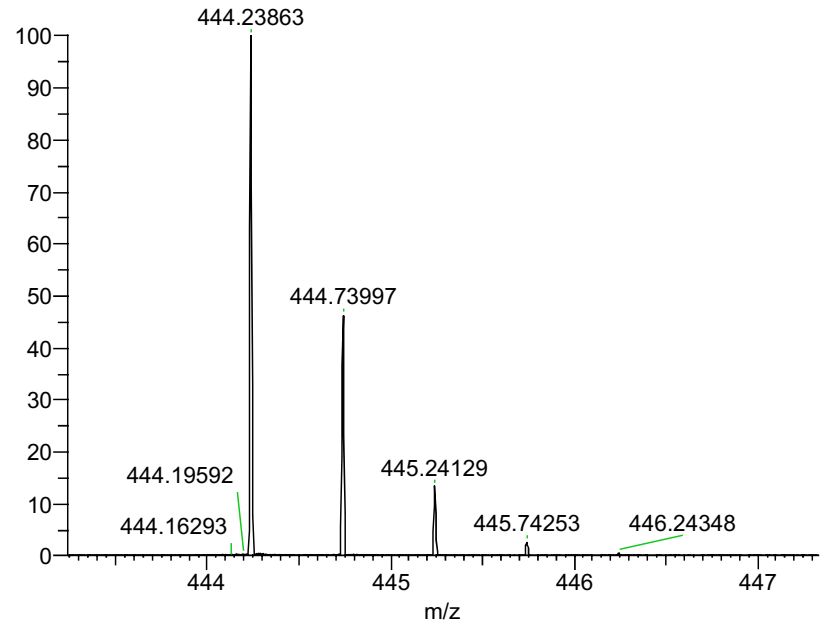


(−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-64 – Mass Spectrum

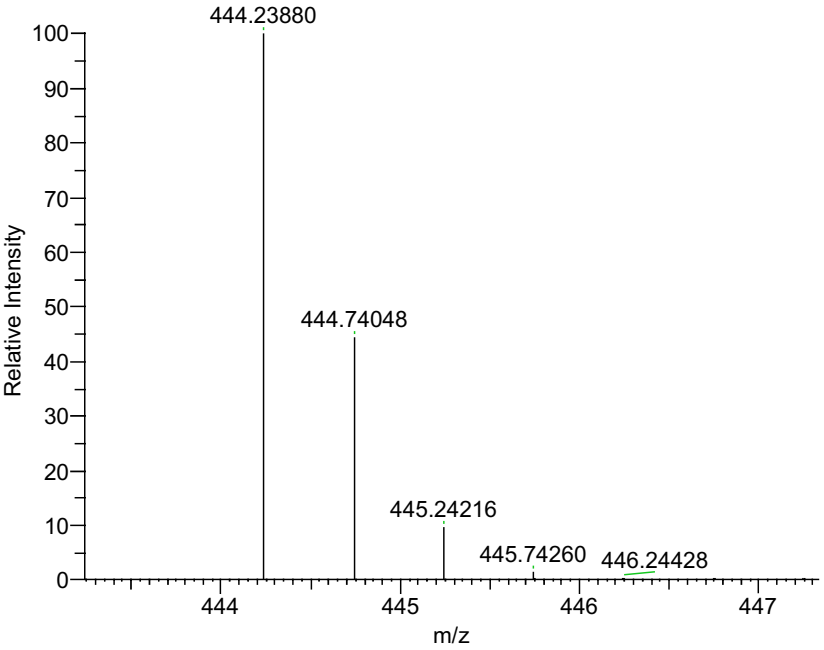


S:\data\June 16\ESI57677.raw 13/06/2016 10:29 am



NL: 4.48E7
ESI57677 #12-20 RT: 0.13-0.22 AV: 5 NL: 4.48E7
T: FTMS {1,2} - p ESI Full ms [80.00-1600.00]

Measured Spectrum

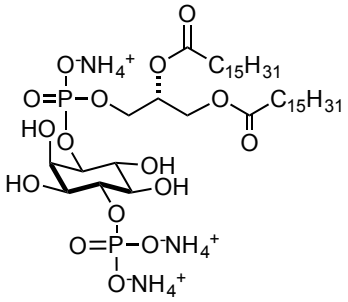


NL: 6.13E5
C41H78O16P2: $C_{41}H_{78}O_{16}P_2$ Chrg -2 R: 1000000 Res. Pwr. @FWHM

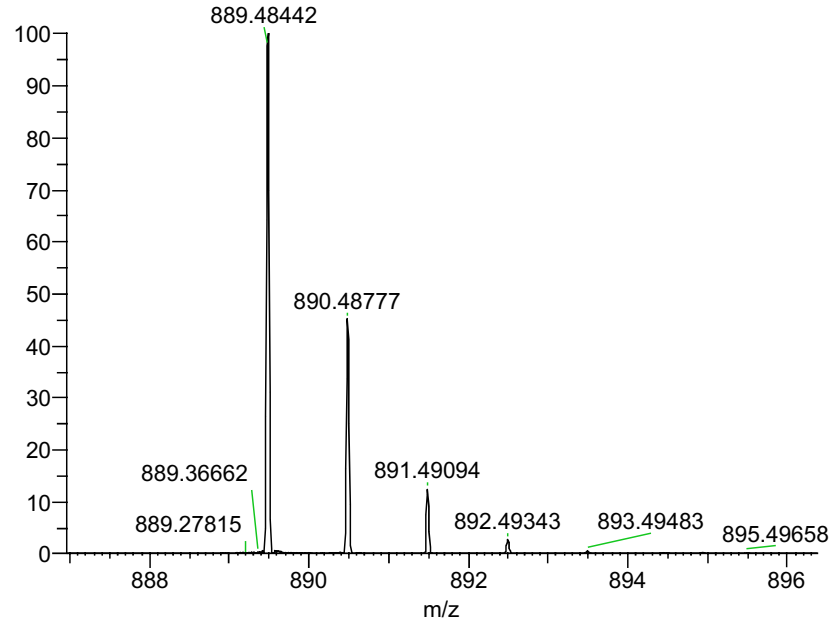
Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
444.23862	$C_{41}H_{78}O_{16}P_2$	4	-0.42	444.23880

(−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-64 – Mass Spectrum

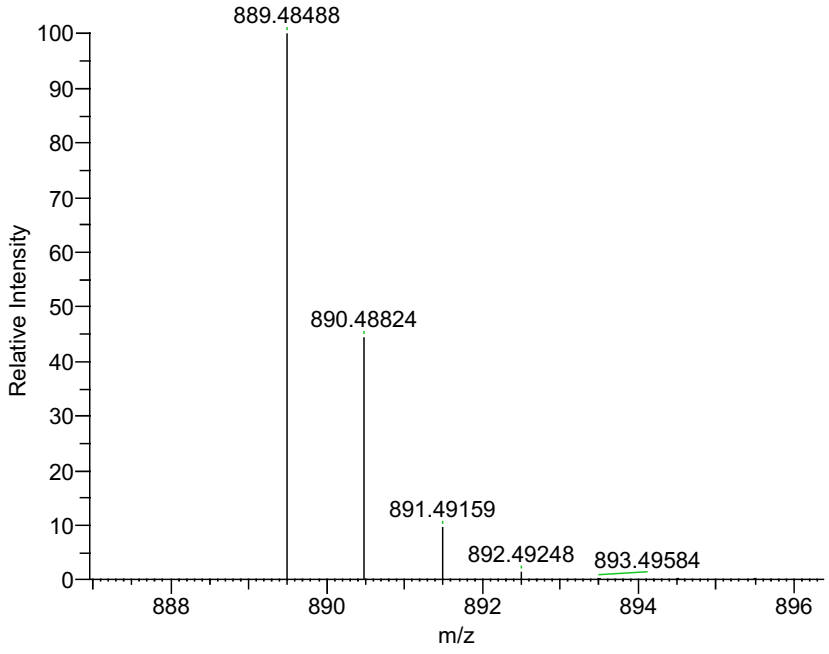


Q:\MassStore-Research Groups\STUART CONWAY GROUP\Amelie...06/12/2016 12:37 pm



NL: 7.78E6
ESI57677 #13-24 RT: 0.16-0.27 AV: 6 NL: 3.86E7
T: FTMS {1,2} - p ESI Full ms [80.00-1600.00]

Measured Spectrum



NL: 6.13E5
C41H79O16P2: $C_{41}H_{79}O_{16}P_2$ Chrg -1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
889.48444	$C_{41}H_{79}O_{16}P_2$	3.5	-0.5	889.48488

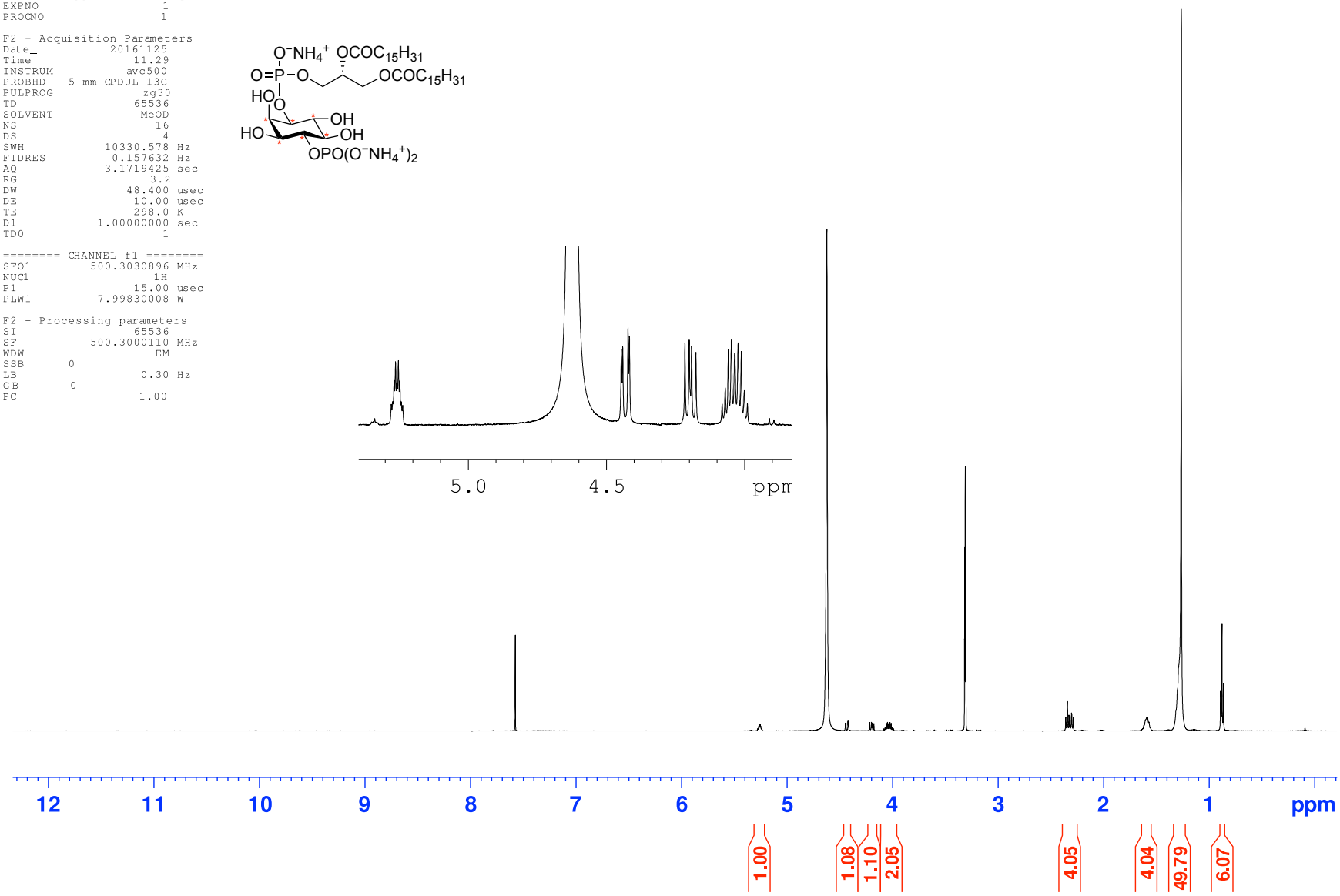
D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-65 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME      ajg28-D6PI(4)P-Vpure
EXPNO                       1
PROCNO                      1

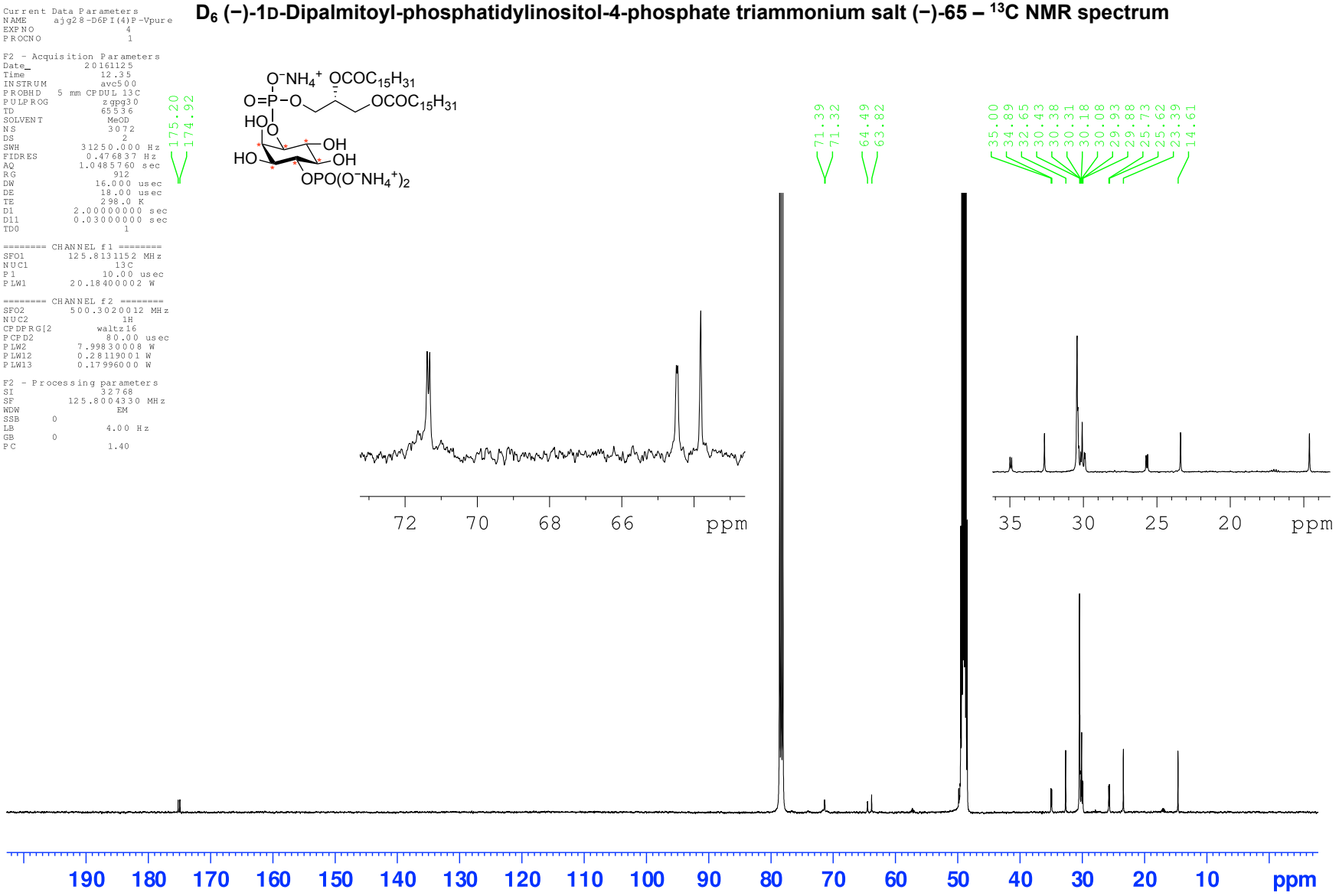
F2 - Acquisition Parameters
Date_              20161125
Time                  11.29
INSTRUM              avc500
PROBHD    5 mm CPDUL 13C
PULPROG               zg30
TD                   65536
SOLVENT               MeOD
NS                      16
DS                       4
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ                3.1719425 sec
RG                      3.2
DW                   48.400 usec
DE                   10.00 usec
TE                   298.0 K
D1               1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.3030896 MHz
NUC1                    1H
P1                   15.00 usec
PLW1           7.99830008 W

F2 - Processing parameters
SI                   65536
SF            500.3000110 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
```



D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-65 – ^{13}C NMR spectrum



D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-65 – ^{1}H-^{13}C HSQC NMR spectrum

```
Current Data Parameters
NAME      ajg28-D6PI(4)P-Vpure
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_              20161125
Time                  11.41
INSTRUM              avc500
PROBHD    5 mm CPDUL 13C
PULPROG   hsqcedetgpsp.3
TD                    1024
SOLVENT               MeOD
NS                       8
DS                      16
SWH                5000.000 Hz
FIDRES             4.882812 Hz
AQ                0.1024000 sec
RG                     2050
DW                  100.000 usec
DE                   10.00 usec
TE                   298.0 K
CNST2          145.0000000
D0                0.00000300 sec
D1                1.00000000 sec
D4                0.00172414 sec
D11               0.03000000 sec
D16               0.00020000 sec
D21               0.00340000 sec
IN0               0.00002400 sec

======== CHANNEL f1 ========
SFO1           500.3025015 MHz
NUC1                    1H
P1                   15.00 usec
P2                   30.00 usec
P28         0 usec
PLW1            7.99830008 W

======== CHANNEL f2 ========
SFO2           125.8099180 MHz
NUC2                   13C
CPDPRG[2               garp
P3                   10.00 usec
P14                 500.00 usec
P31                1900.00 usec
PCPD2                70.00 usec
PLW0        0 W
PLW2           20.18400002 W
PLW12           0.41192001 W
SPNAM[3]  Crp60,0.5,20.1
SPOAL3                0.500
SPOFFS3   0 Hz
SPW3            3.08389997 W
SPNAM[18   Crp60_xfilt.2
SPOAL18               0.500
SPOFFS18  0 Hz
SPW18           0.73894000 W

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPZ1                 80.00 %
GPZ2                 20.10 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                     256
SFO1             125.8099 MHz
FIDRES          81.380211 Hz
SW                165.594 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                    1024
SF             500.3000105 MHz
WDW                  QSINE
SSB                      2
LB          0 Hz
GB          0
PC                    1.40

F1 - Processing parameters
SI                     512
MC2          echo-antiecho
SF             125.8004502 MHz
WDW                  QSINE
SSB                      2
LB          0 Hz
GB          0
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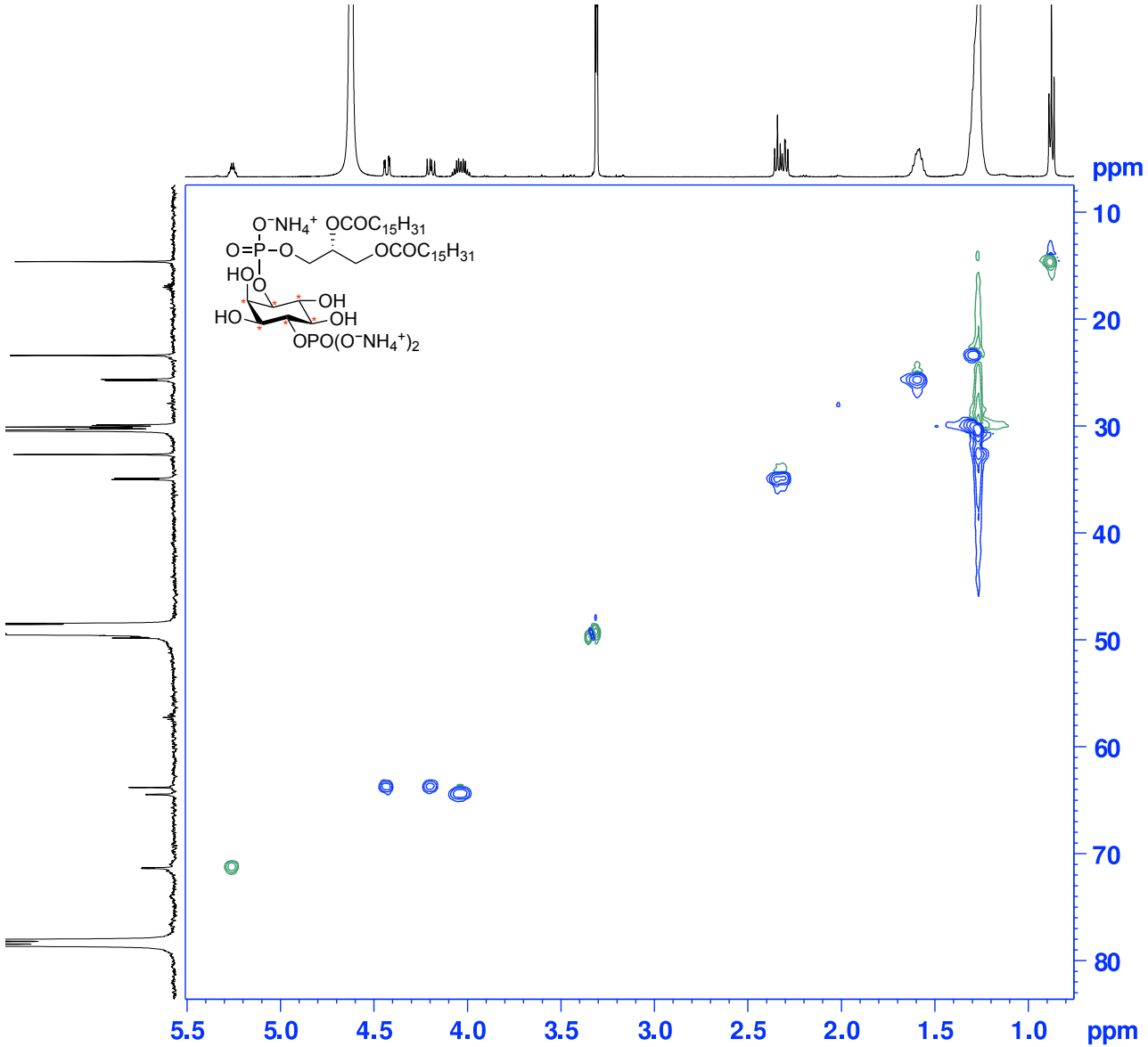
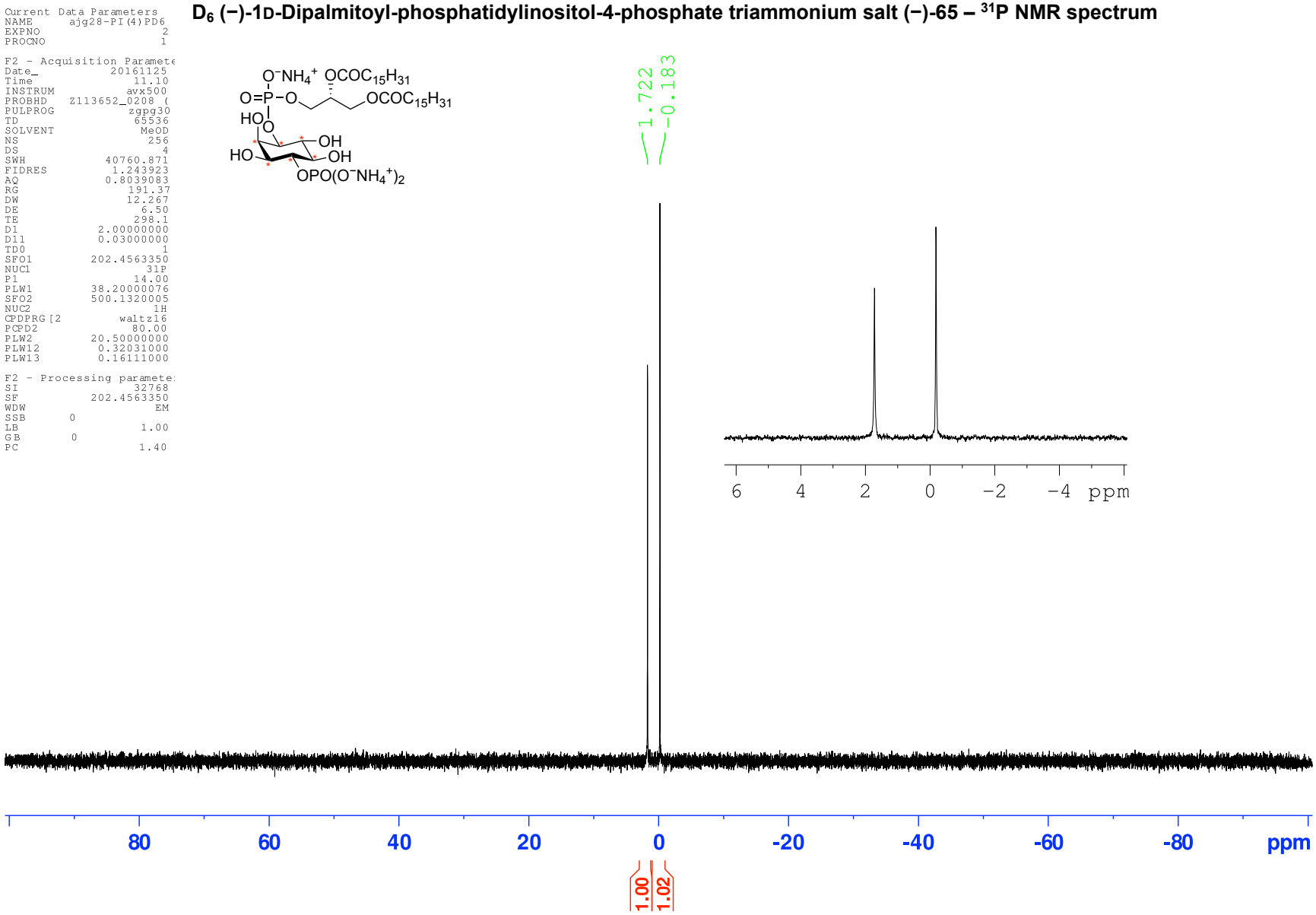


D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-65 – ^{31}P NMR spectrum



D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-65 – ^{1}H-^{31}P HMBC NMR spectrum

```
Current Data Parameters
NAME     ajg28-PI(4)PD6
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20161125
Time              11.11
INSTRUM           avx500
PROBHD   Z113652_0208 (
PULPROG      hmbcgpndqf
TD                 4096
SOLVENT            MeOD
NS                    2
DS                   16
SWH            6009.615 Hz
FIDRES          1.467191 Hz
AQ             0.3407872 sec
RG                191.37
DW                83.200 usec
DE                 6.50 usec
TE                298.0 K
CNST13         8.0000000
d0            0.00000300 sec
D1            2.00000000 sec
d6            0.06250000 sec
D16           0.00020000 sec
in0      0 sec
ST1CNT                0
d0orig        0.00000300 sec
ph1loop               0
t1loop                0
SFO1         500.1323506 MHz
NUC1                 1H
P1                10.00 usec
p2                20.00 usec
PLW1         20.50000000 W
SFO2         202.4563350 MHz
NUC2                31P
P3                14.00 usec
PLW2         38.20000076 W
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1              70.00 %
GPZ2              30.00 %
GPZ3              80.50 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                   48
SFO1           202.4563 MHz
FIDRES       421.727386 Hz
SW             99.987 ppm
FnMODE               QF

F2 - Processing parameters
SI                 2048
SF          500.1300534 MHz
WDW                SINE
SSB                   4
LB       0 Hz
GB       0
PC                1.40

F1 - Processing parameters
SI                 1024
MC2                  QF
SF          202.4563278 MHz
WDW               QSINE
SSB      0
LB       0 Hz
GB       0
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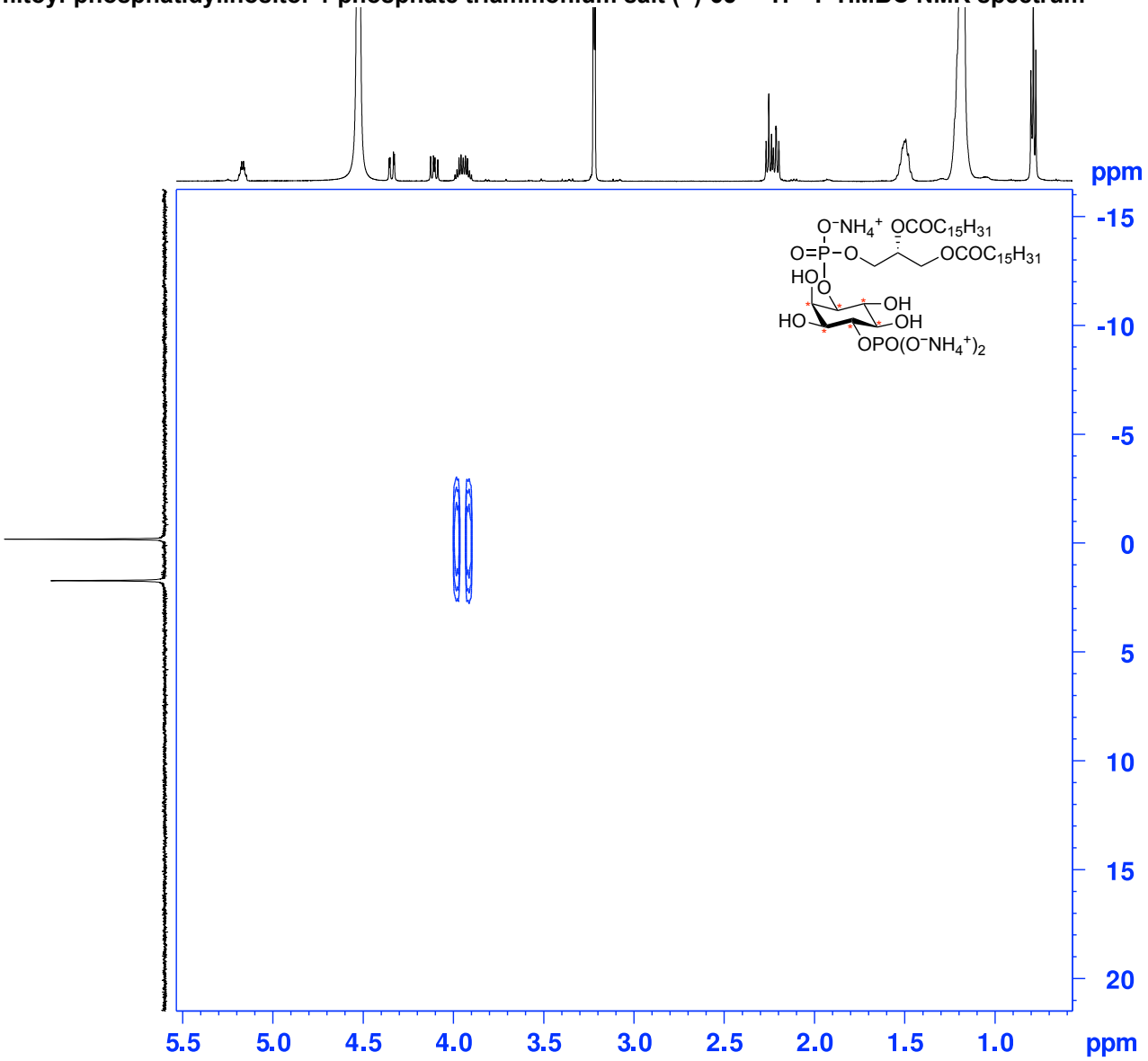

D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-65 – ^2H NMR spectrum

```
Current Data Parameters
NAME      ajg28p-PI(4)P-D1
EXPNO                    7
PROCNO                   1

F2 - Acquisition Paramete
Date_             20161207
Time                 11.07
INSTRUM              av600
PROBHD    Z130037_0008 (
PULPROG              zg2h
TD                   8192
SOLVENT               D2O
NS                     602
DS                       2
SWH              1842.299
FIDRES           0.449780
AQ               2.2233088
RG                   60.94
DW                  271.400
DE                    18.00
TE                   298.0
D1               1.00000000
D11              0.03000000
TD0                      1
SFO1             92.1316525
NUC1                     2H
P1                  378.00
PLW1             1.75000000

F2 - Processing paramete
SI                   16384
SF               92.1313451
WDW                     EM
SSB       0
LB                    1.00
GB        0
PC                    1.00
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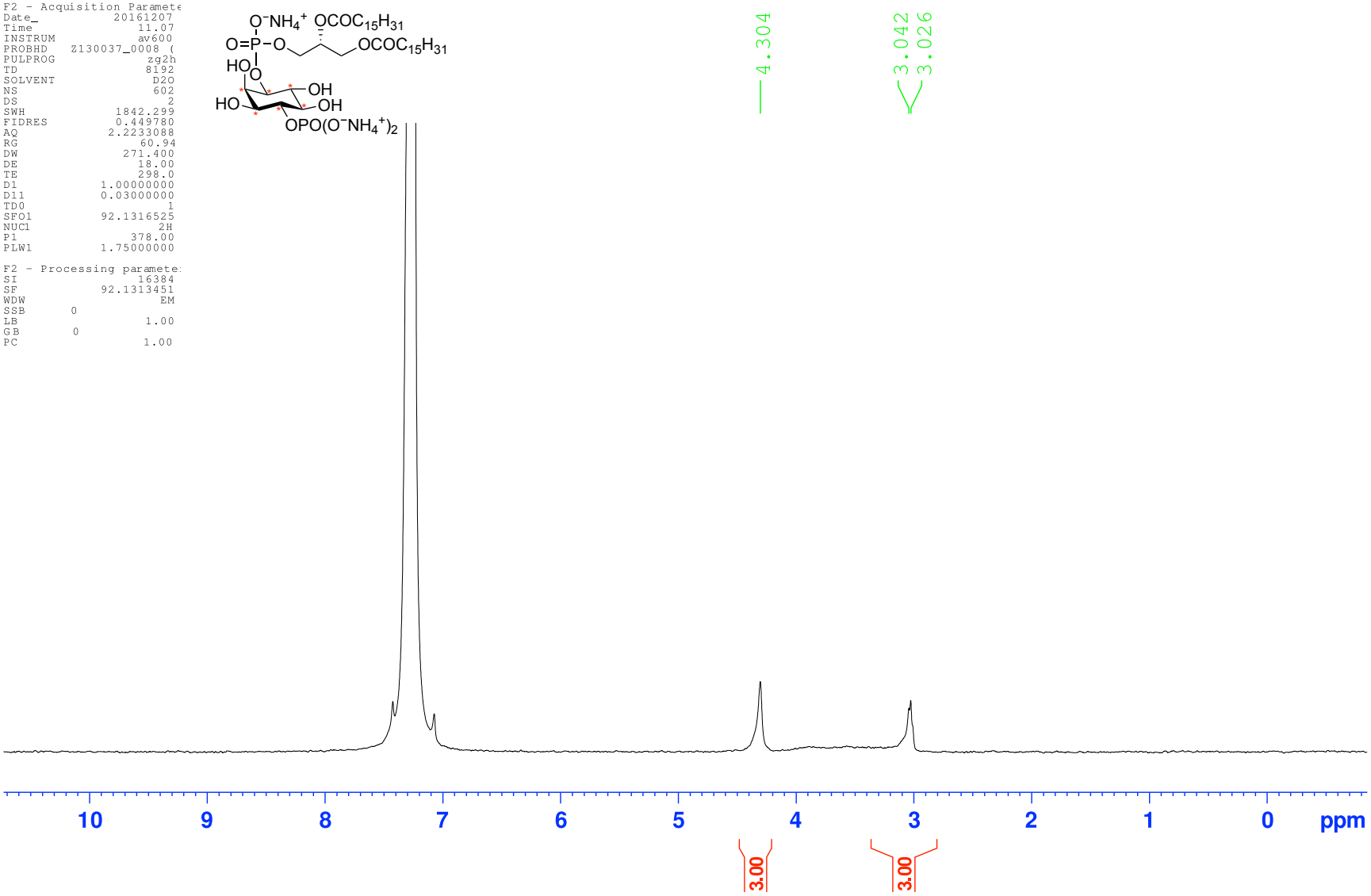
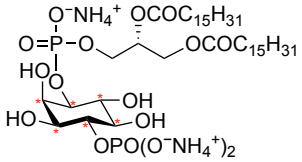
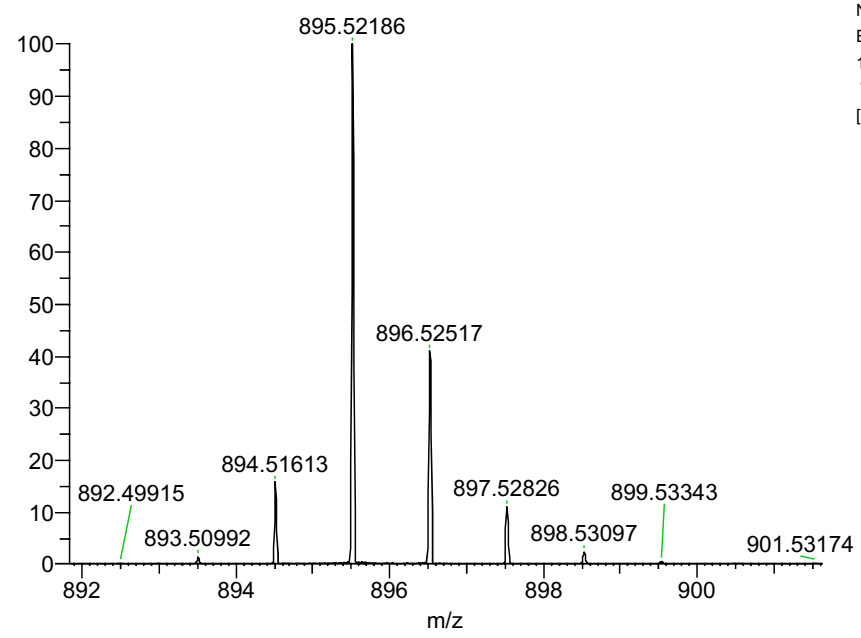


D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-65 – Mass spectrum

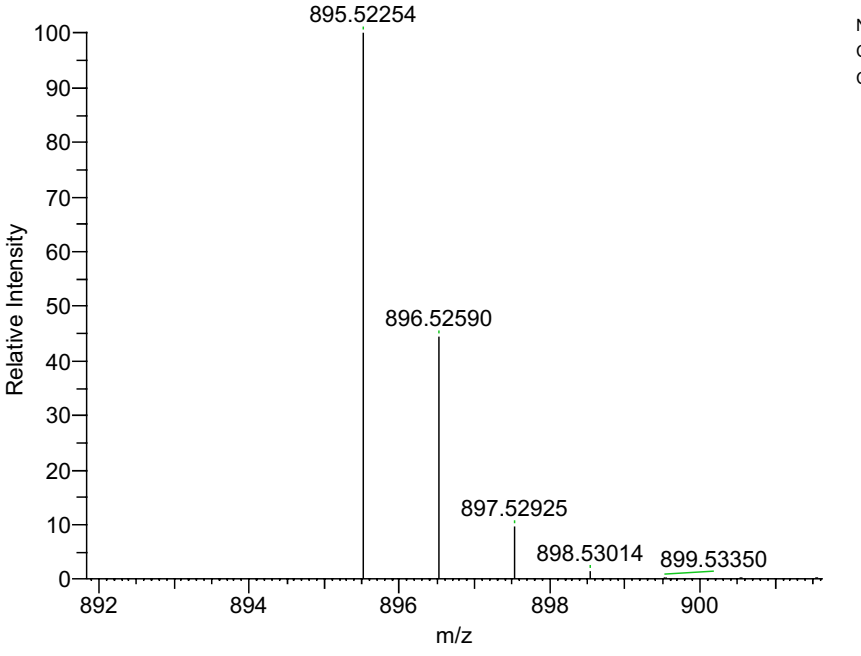


S:\data\Dec 16\ESI59994.raw 06/12/2016 12:35 pm



NL: 5.23E6
ESI59994 #11-33 RT: 0.14-0.37 AV: 11 NL: 1.30E7
T: FTMS {1,2} - p ESI Full ms [80.00-1600.00]

Measured Spectrum



NL: 6.14E5
C41H73[2]H6O16P2: $C_{41}H_{73}{}^{2}H_{6}O_{16}P_{2}$
Chrg -1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
895.52185	$C_{41}H_{73}{}^{2}H_{6}O_{16}P_{2}$	3.5	-0.77	895.52254

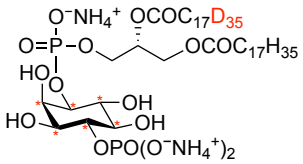
D_{41} (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-67 – ^{1}H NMR spectrum

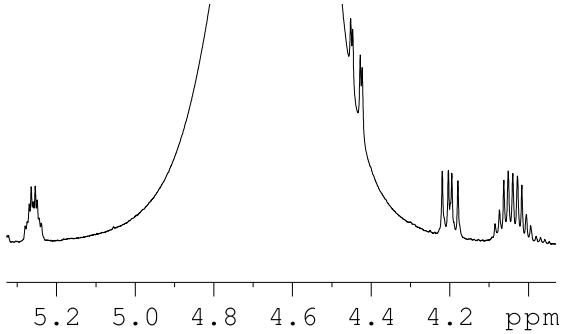
```
Current Data Parameters
NAME      ajg45p-D41PI(4)P
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20161214
Time              14.18
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                   128
DS                     4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                  3.56
DW                 48.400 usec
DE                 10.00 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1

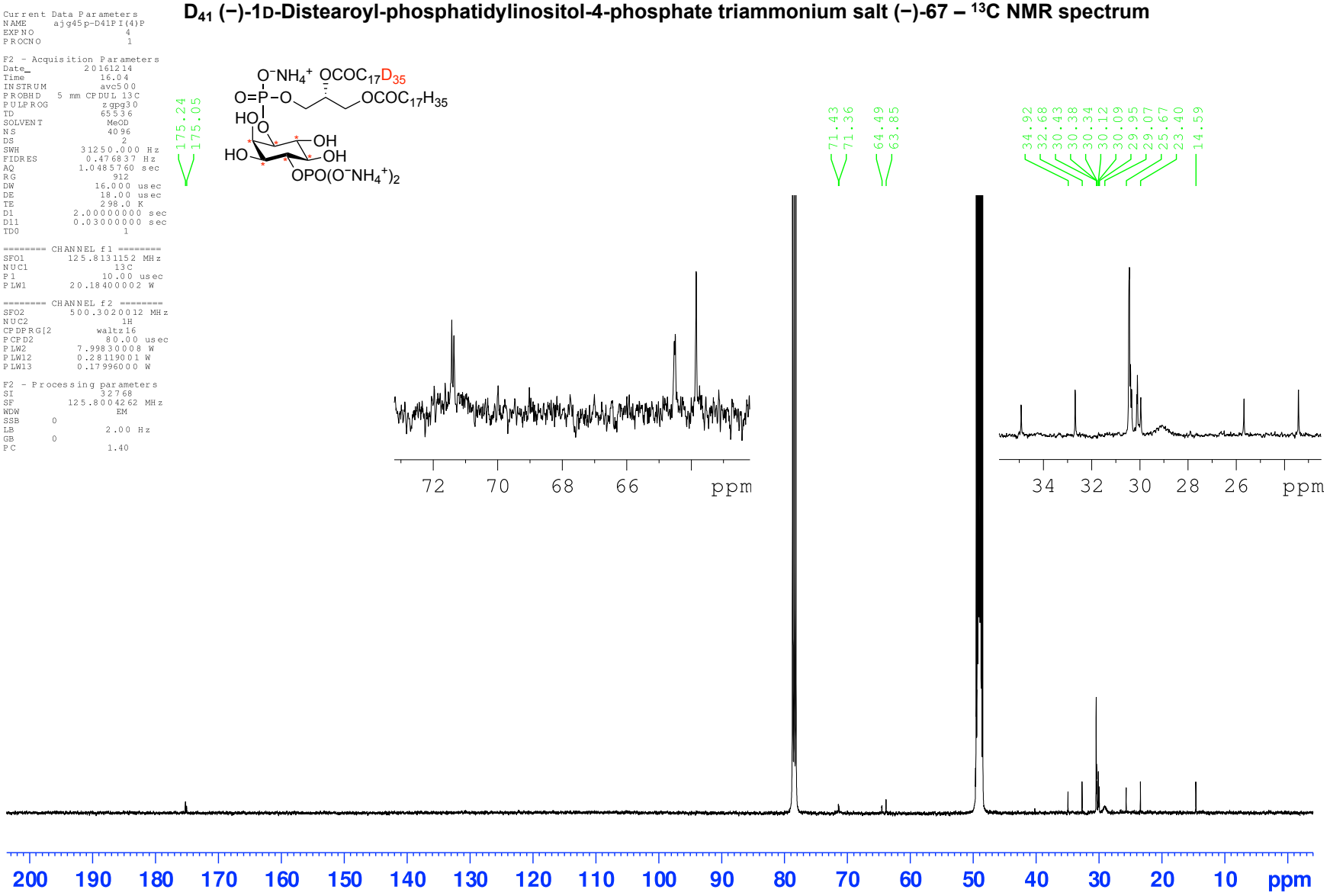
======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1                   1H
P1                  15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI                 65536
SF            500.3000110 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```





D_{41} (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-67 – ^{13}C NMR spectrum



D_{41} (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-67 – ^{1}H-^{13}C HSQC NMR spectrum

```
Current Data Parameters
NAME      ajg45p-D41PI(4)P
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_           20161214
Time               15.08
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG  hsqcedetgpsp.3
TD                 1024
SOLVENT             MeOD
NS                   16
DS                   16
SWH             2463.054 Hz
FIDRES          2.405326 Hz
AQ             0.2078720 sec
RG                  2050
DW               203.000 usec
DE                10.00 usec
TE                298.0 K
CNST2        145.0000000
D0             0.00000300 sec
D1             0.89452791 sec
D4             0.00172414 sec
D11            0.03000000 sec
D16            0.00020000 sec
D21            0.00340000 sec
IN0            0.00002400 sec

======== CHANNEL f1 ========
SFO1         500.3015539 MHz
NUC1                   1H
P1                 15.00 usec
P2                 30.00 usec
P28       0 usec
PLW1           7.99830008 W

======== CHANNEL f2 ========
SFO2         125.8099180 MHz
NUC2                  13C
CPDPRG[2             garp
P3                 10.00 usec
P14               500.00 usec
P31              1900.00 usec
PCPD2              70.00 usec
PLW0       0 W
PLW2         20.18400002 W
PLW12         0.41192001 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3               0.500
SPOFFS3   0 Hz
SPW3          3.08389997 W
SPNAM[18  Crp60_xfilt.2
SPOAL18              0.500
SPOFFS18 0 Hz
SPW18          0.73894000 W

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPZ1                80.00 %
GPZ2                20.10 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                   186
SFO1            125.8099 MHz
FIDRES       112.007172 Hz
SW              165.594 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           500.3000116 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                   512
MC2        echo-antiecho
SF           125.8004343 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
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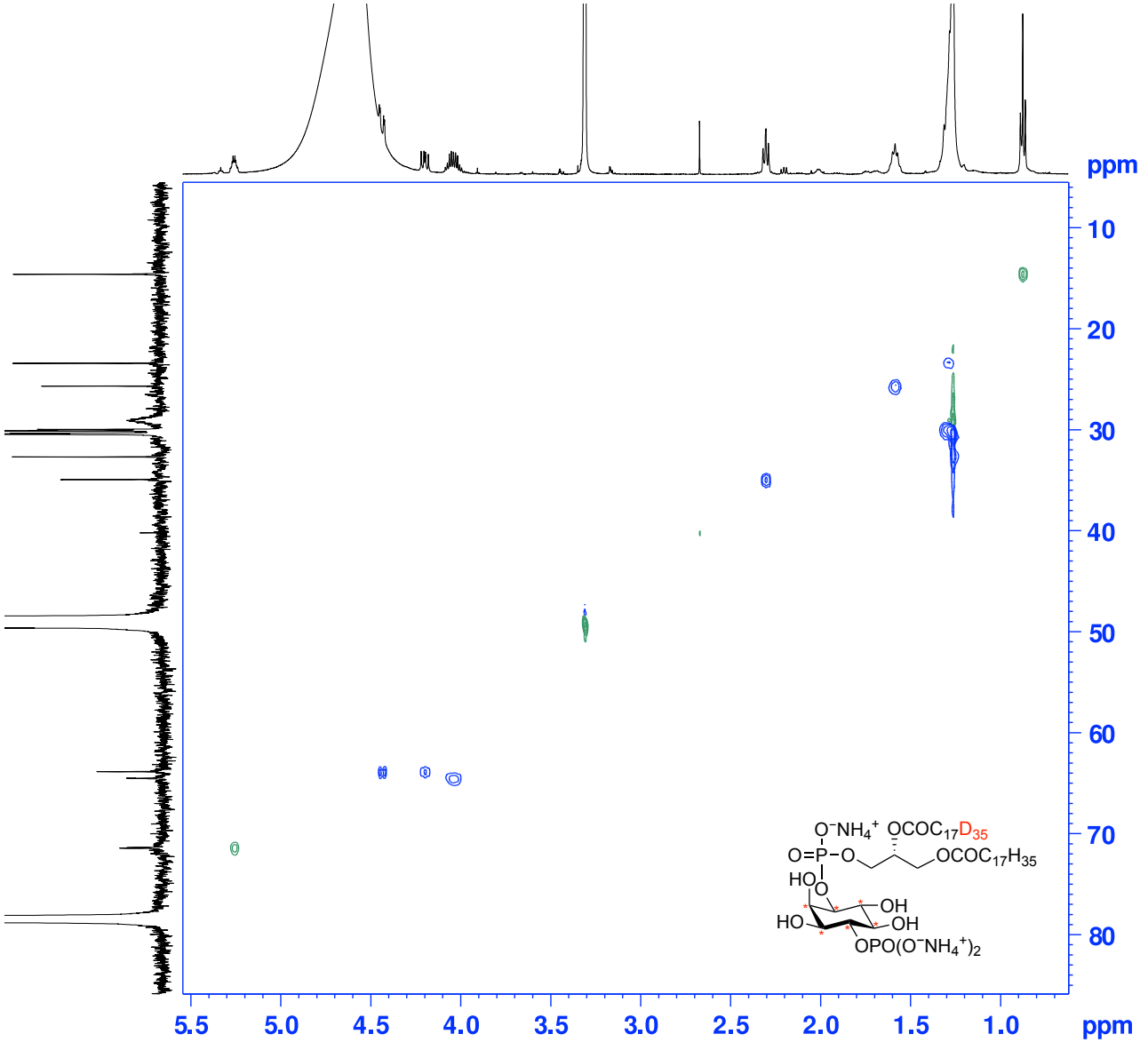
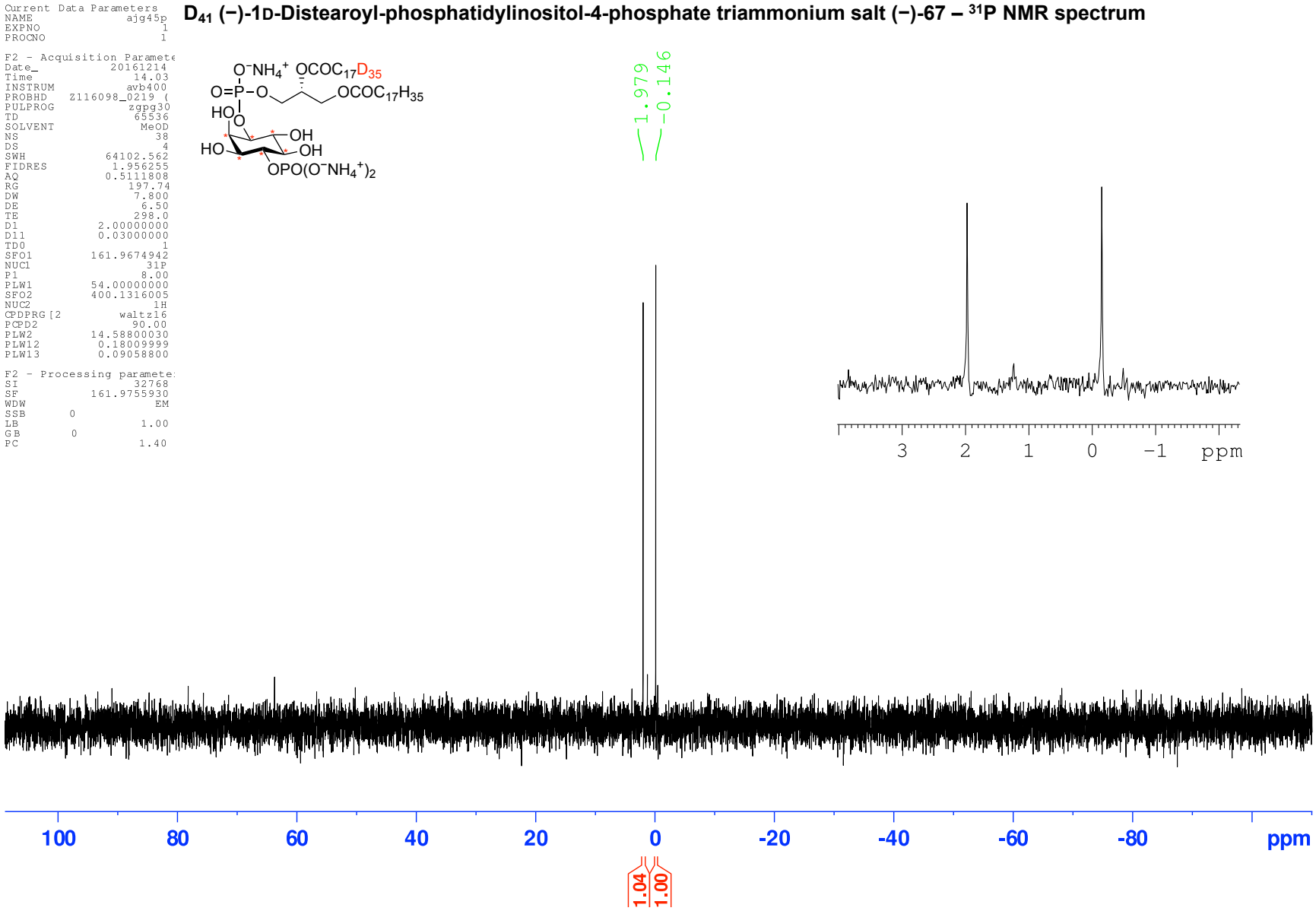


D_{41} (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-67 – ^{31}P NMR spectrum



D_{41} (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-67 – ^{1}H-^{31}P HMBC NMR spectrum

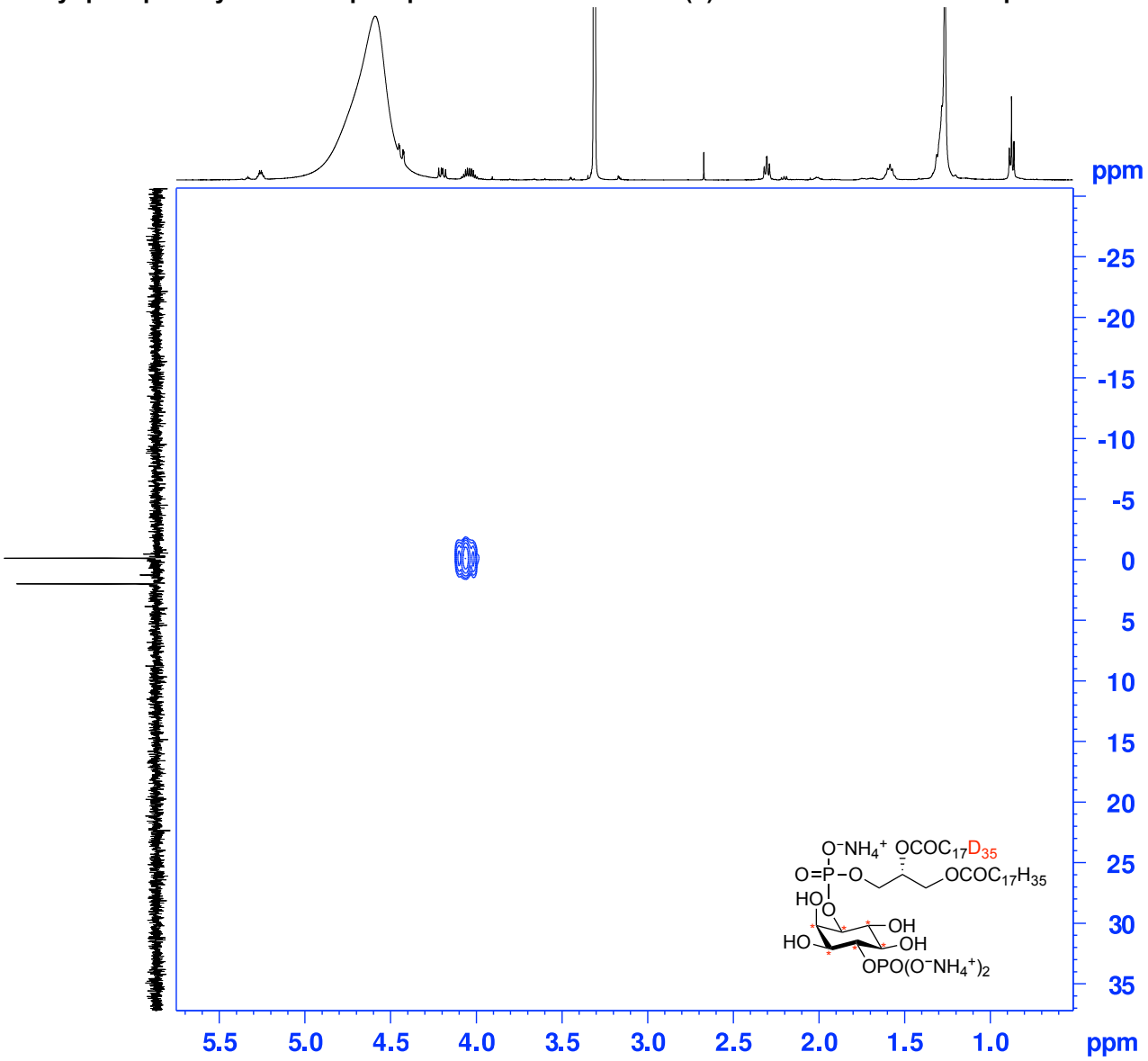
```
Current Data Parameters
NAME            ajg45p
EXPNO                2
PROCNO               1

F2 - Acquisition Parameters
Date_         20161214
Time             14.05
INSTRUM          avb400
PROBHD   Z116098_0219 (
PULPROG      hmbcgpndqf
TD                2048
SOLVENT           MeOD
NS                   2
DS                  16
SWH           4795.396 Hz
FIDRES         2.341502 Hz
AQ           0.2135381 sec
RG               197.74
DW              104.267 usec
DE                6.50 usec
TE               298.0 K
CNST13         8.0000000
d0           0.00000300 sec
D1           1.50000000 sec
d6           0.06250000 sec
D16          0.00020000 sec
in0      0 sec
ST1CNT               0
d0orig       0.00000300 sec
ph1loop              0
t1loop               0
SFO1        400.1320007 MHz
NUC1                 1H
P1                10.00 usec
p2                20.00 usec
PLW1        14.58800030 W
SFO2        161.9755930 MHz
NUC2                31P
P3                 8.00 usec
PLW2        53.95100021 W
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1               70.00 %
GPZ2               30.00 %
GPZ3               80.50 %
P16              1000.00 usec

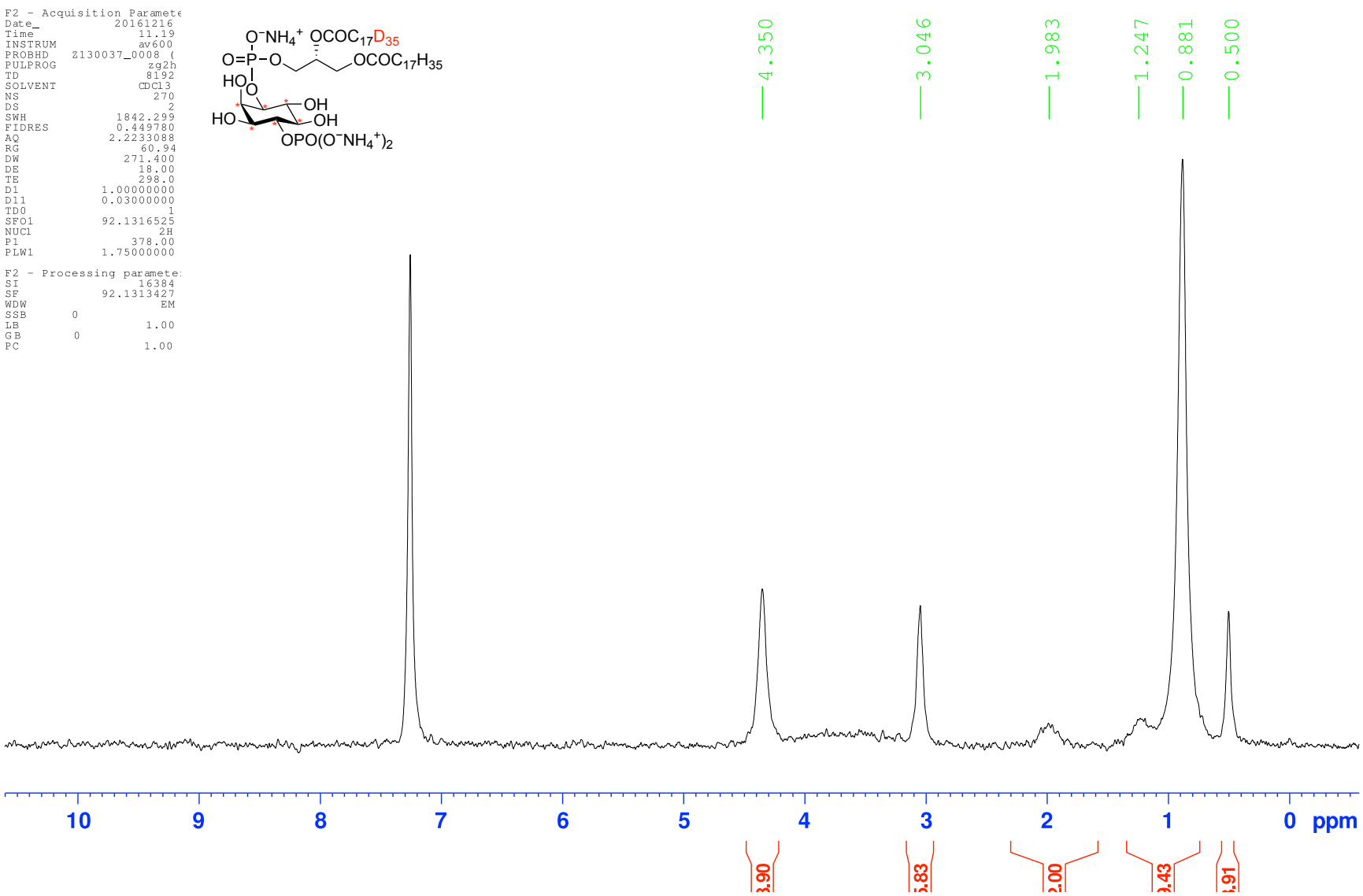
F1 - Acquisition parameters
TD                   51
SFO1           161.9756 MHz
FIDRES       437.675079 Hz
SW             137.807 ppm
FnMODE              QF

F2 - Processing parameters
SI                 1024
SF          400.1300000 MHz
WDW                SINE
SSB      0
LB       0 Hz
GB       0
PC                 1.40

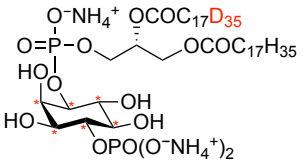
F1 - Processing parameters
SI                 1024
MC2                 QF
SF          161.9755930 MHz
WDW                SINE
SSB      0
LB       0 Hz
GB       0
```



D_{41} (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-67 – ^2H NMR spectrum



D41 (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-67 – ^{2}H NMR spectrum



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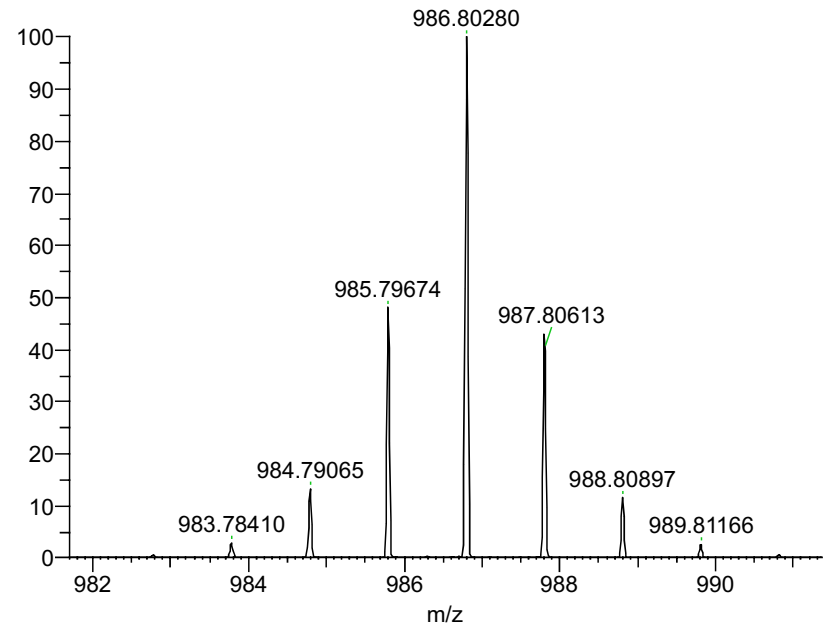
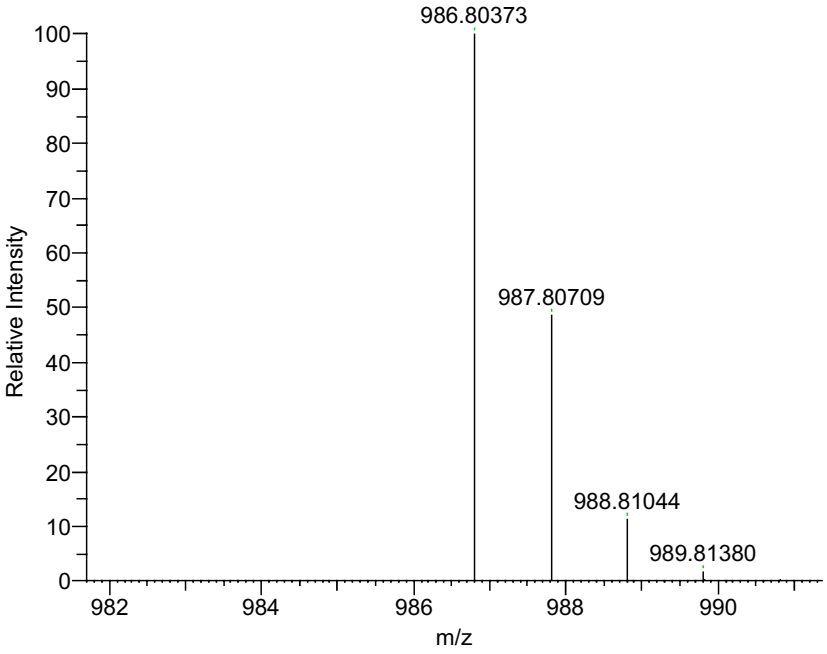


NL: 7.71E5
ESI60247 #10-34 RT: 0.11-0.39 AV: 13 NL: 7.95E6
T: FTMS {1,2} - p ESI Full ms [80.00-1600.00]

Measured Spectrum

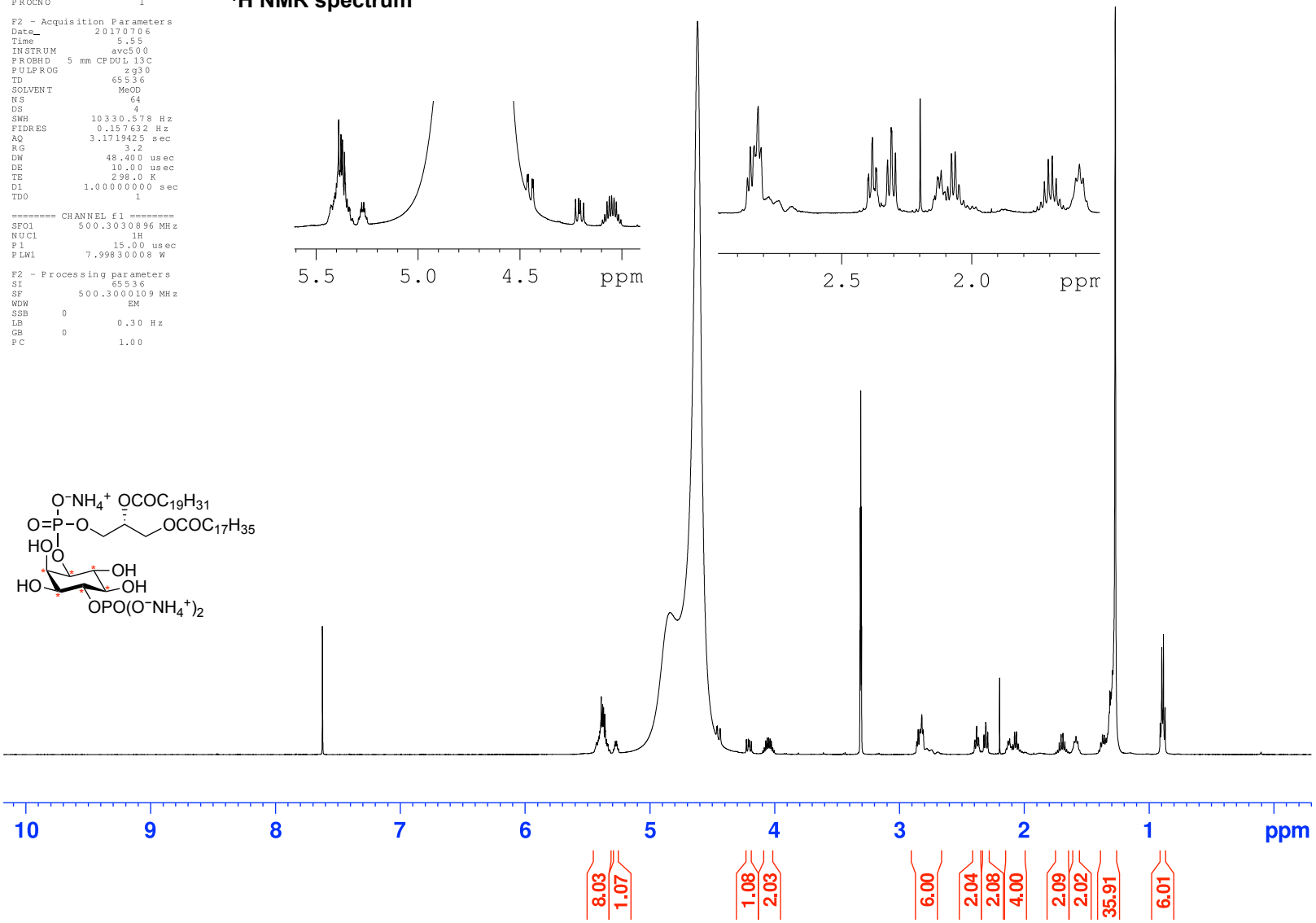


NL: 5.90E5
c45h46D41O16P2: $C_{45}H_{46}D_{41}O_{16}P_2$ pa
Chrg 1 R: 1000000 Res. Pwr. @FWHM

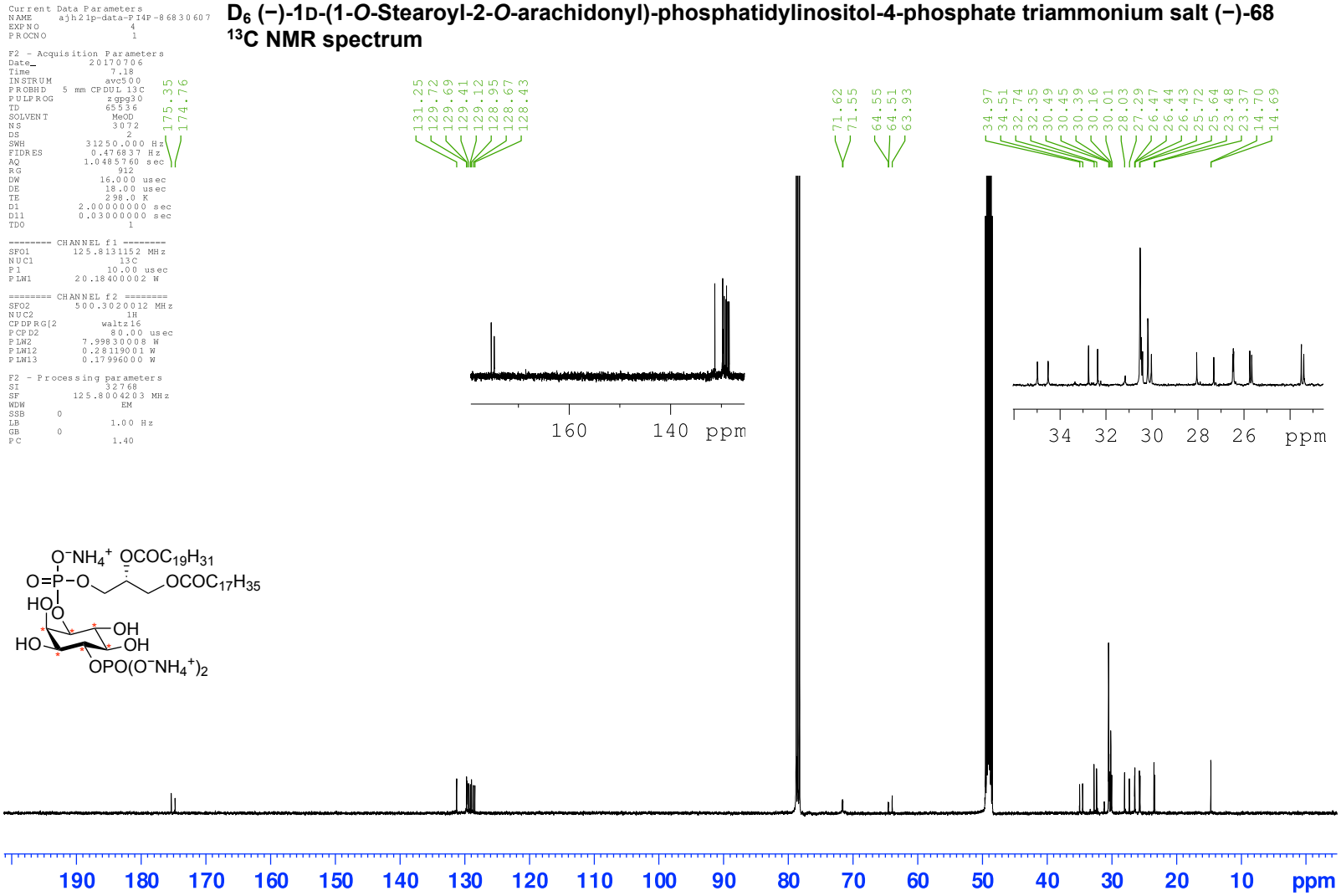
Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
986.80280	$C_{45}H_{46}{}^2H_{41}O_{16}P_2$	3.5	-0.95	986.80373

D_6 (−)-1D-(1-*O*-Stearoyl-2-*O*-arachidonyl)-phosphatidylinositol-4-phosphate triammonium salt (−)-68
^{1}H NMR spectrum

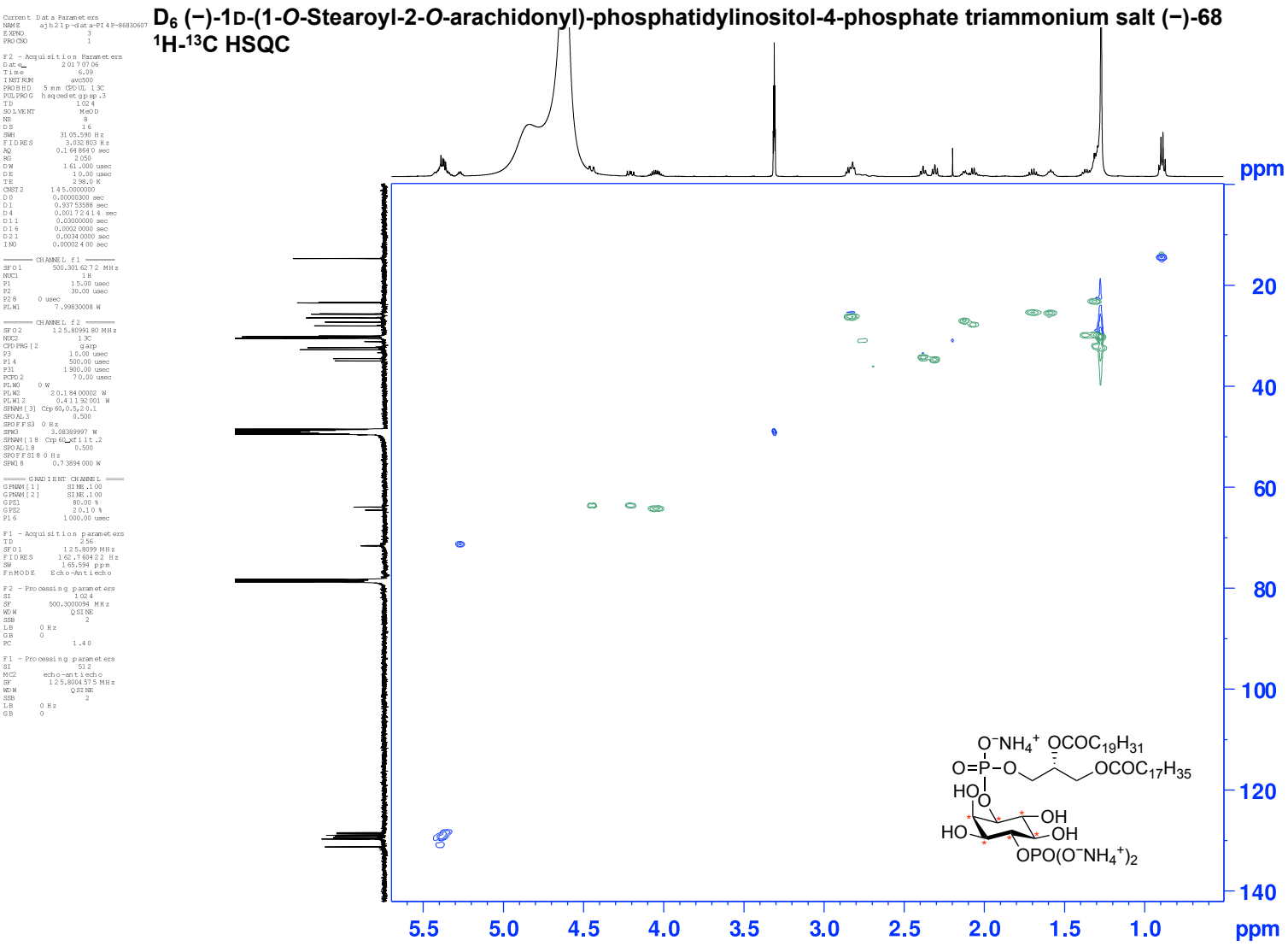


D_6 (−)-1D-(1-*O*-Stearoyl-2-*O*-arachidonyl)-phosphatidylinositol-4-phosphate triammonium salt (−)-68
^{13}C NMR spectrum



D_6 (−)-1D-(1-*O*-Stearoyl-2-*O*-arachidonyl)-phosphatidylinositol-4-phosphate triammonium salt (−)-68

^1H-^{13}C HSQC



D_6 (−)-1D-(1-*O*-Stearoyl-2-*O*-arachidonyl)-phosphatidylinositol-4-phosphate triammonium salt (−)-68

^{31}P NMR spectrum

```
Current Data Parameters
NAME         ajh21p-main
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170706
Time                5.27 h
INSTRUM           avb400
PROBHD    Z116098_0219 (
PULPROG          zgpg30
TD                65536
SOLVENT            MeOD
NS                    53
DS                     4
SWH             64102.562 Hz
FIDRES          1.956255 Hz
AQ              0.5111808 sec
RG                 197.74
DW                  7.800 usec
DE                  6.50 usec
TE                 298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         161.9755930 MHz
NUC1                31P
P1                  8.00 usec
PLW1         54.00000000 W
SFO2         400.1316005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         14.58800030 W
PLW12         0.18009999 W
PLW13         0.09058800 W

F2 - Processing parameters
SI                 32768
SF          161.9755930 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
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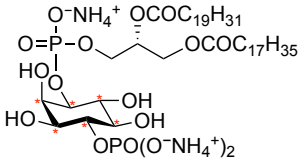
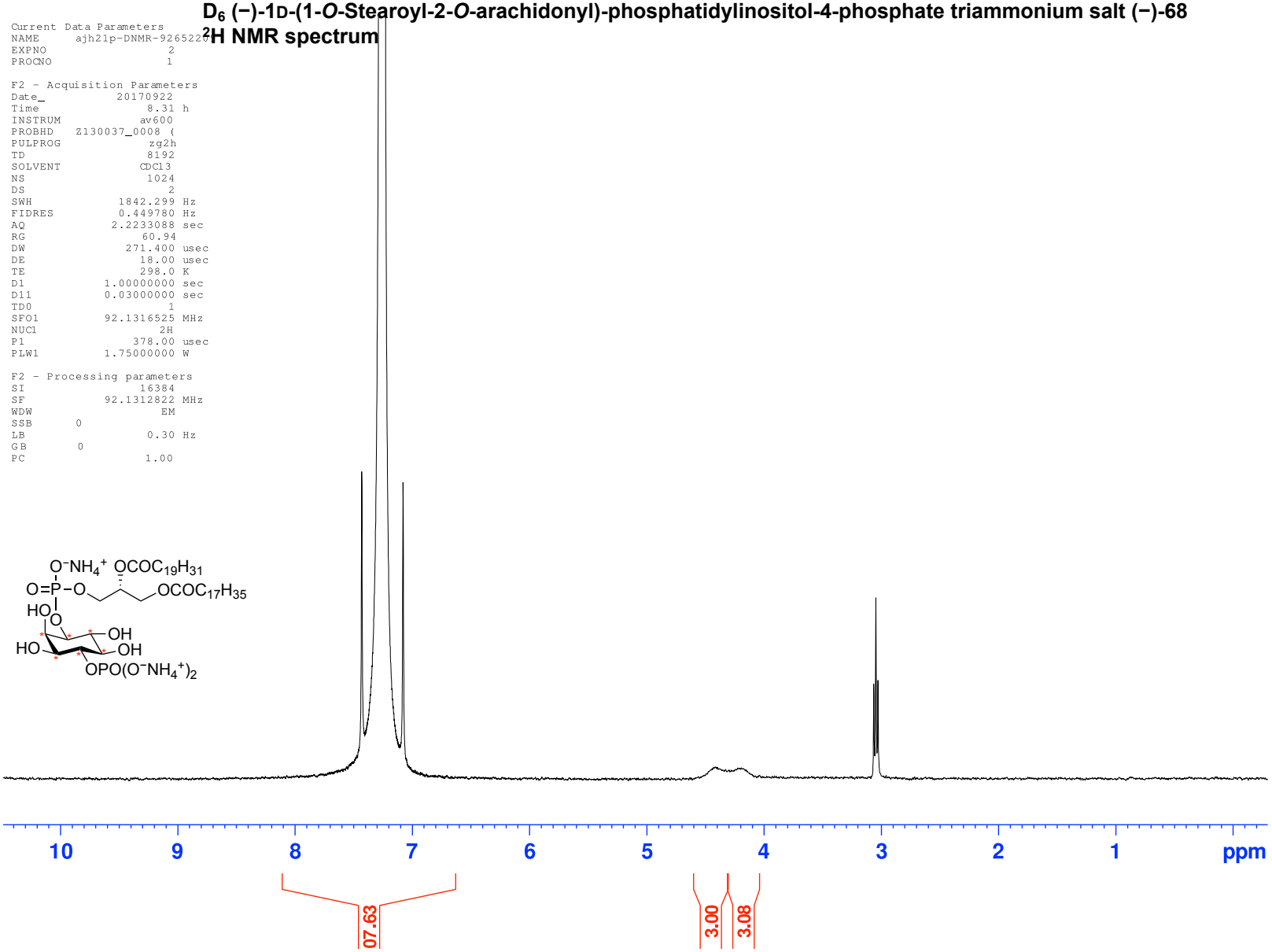


D_6 (−)-1D-(1-*O*-Stearoyl-2-*O*-arachidonyl)-phosphatidylinositol-4-phosphate triammonium salt (−)-68

^2H NMR spectrum



D_6 (−)-1D-(1-*O*-Stearoyl-2-*O*-arachidonyl)-phosphatidylinositol-4-phosphate triammonium salt (−)-68 - Mass Spectrum

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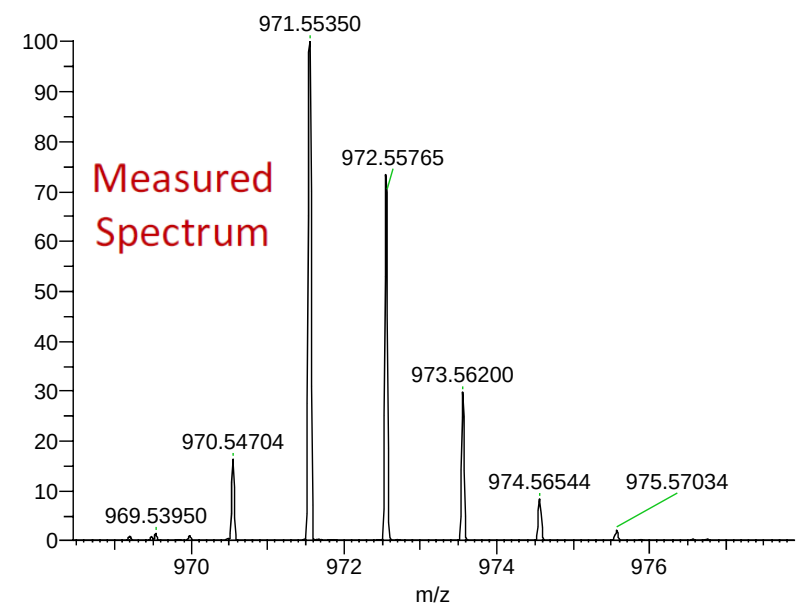
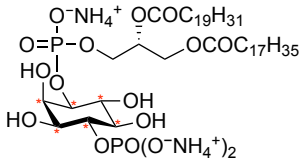
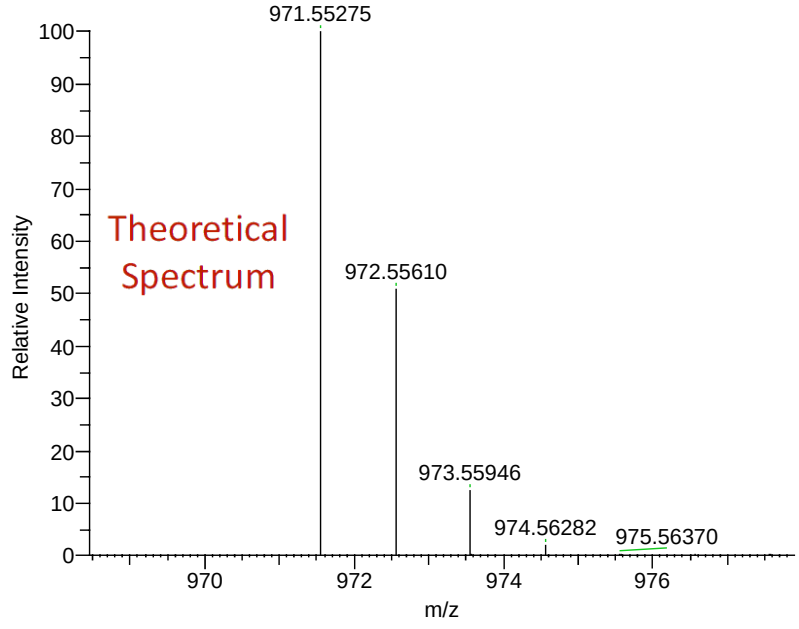


NL: 1.24E5
ESI64566 #14-28 RT: 0.16-0.34 AV: 8 NL: 6.06E5
T: FTMS {1,2} - p ESI Full ms [80.00-1600.00]



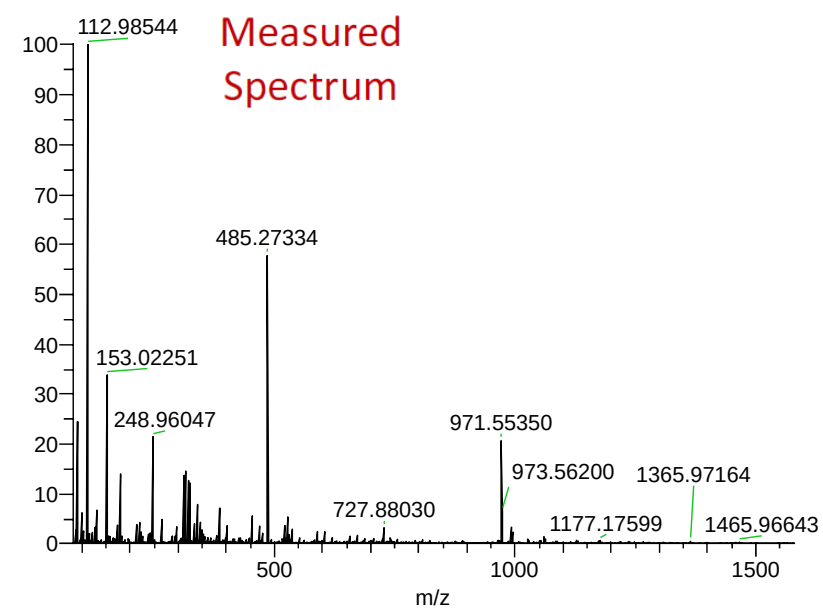


NL: 5.75E5
C47H77[2]H6O16P2: C_{47} H_{77} $^2H_6$ O_{16} P_2
Chrg 1 R: 1000000 Res. Pwr. @FWHM

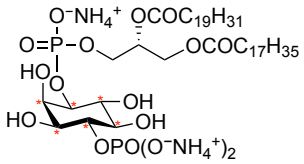
m/z	Formula	RDB	Delta ppm	Theo. Mass
971.55353	$C_{47}H_{77}{}^2H_6O_{16}P_2$	7.5	0.8	971.55275

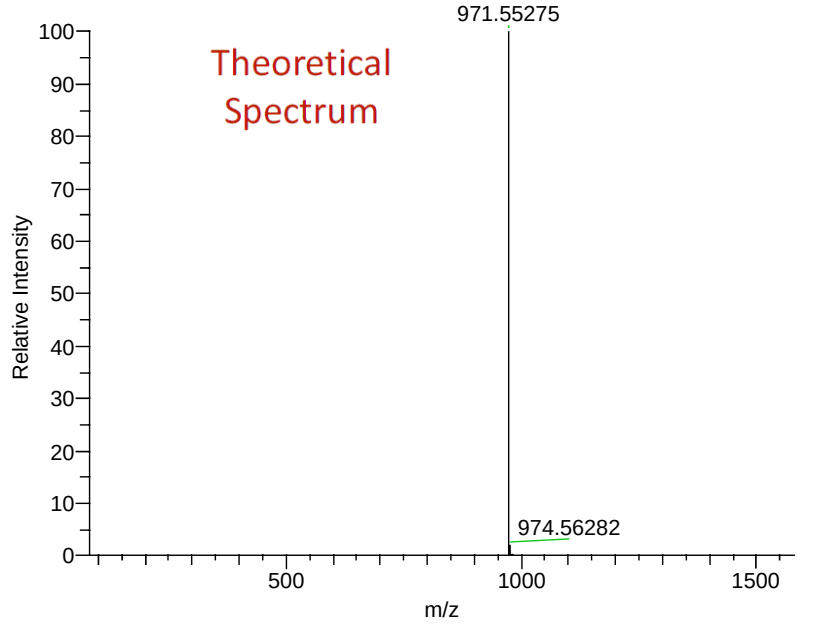
D_6 (−)-1D-(1-*O*-Stearoyl-2-*O*-arachidonyl)-phosphatidylinositol-4-phosphate triammonium salt (−)-68 - Mass Spectrum

S:\data\Aug 17\ESI64566.raw 04/08/2017 3:15 pm



NL: 6.06E5
ESI64566 #14-28 RT: 0.16-0.34 AV: 8 NL: 6.06E5
T: FTMS {1,2} - p ESI Full ms [80.00-1600.00]

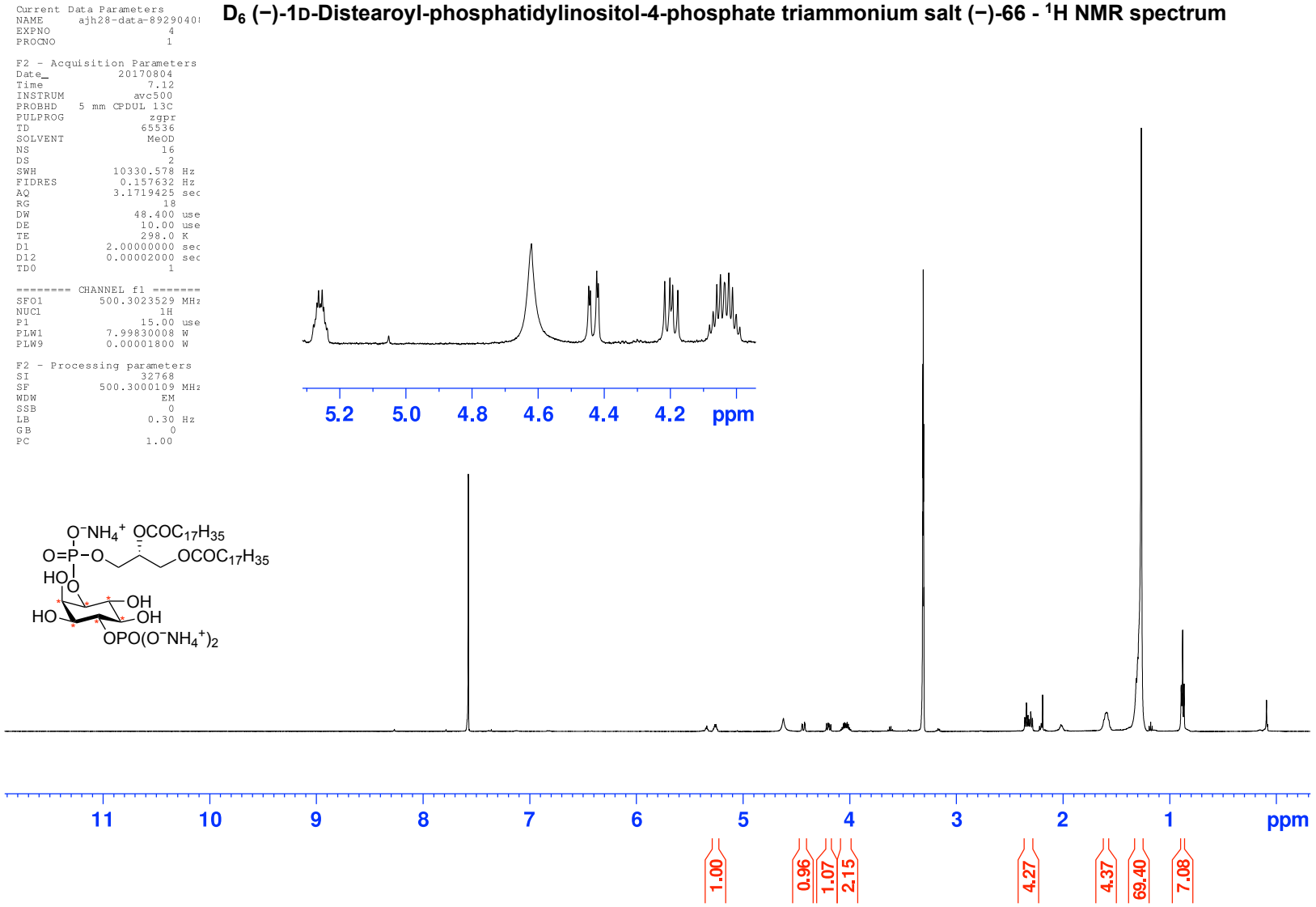




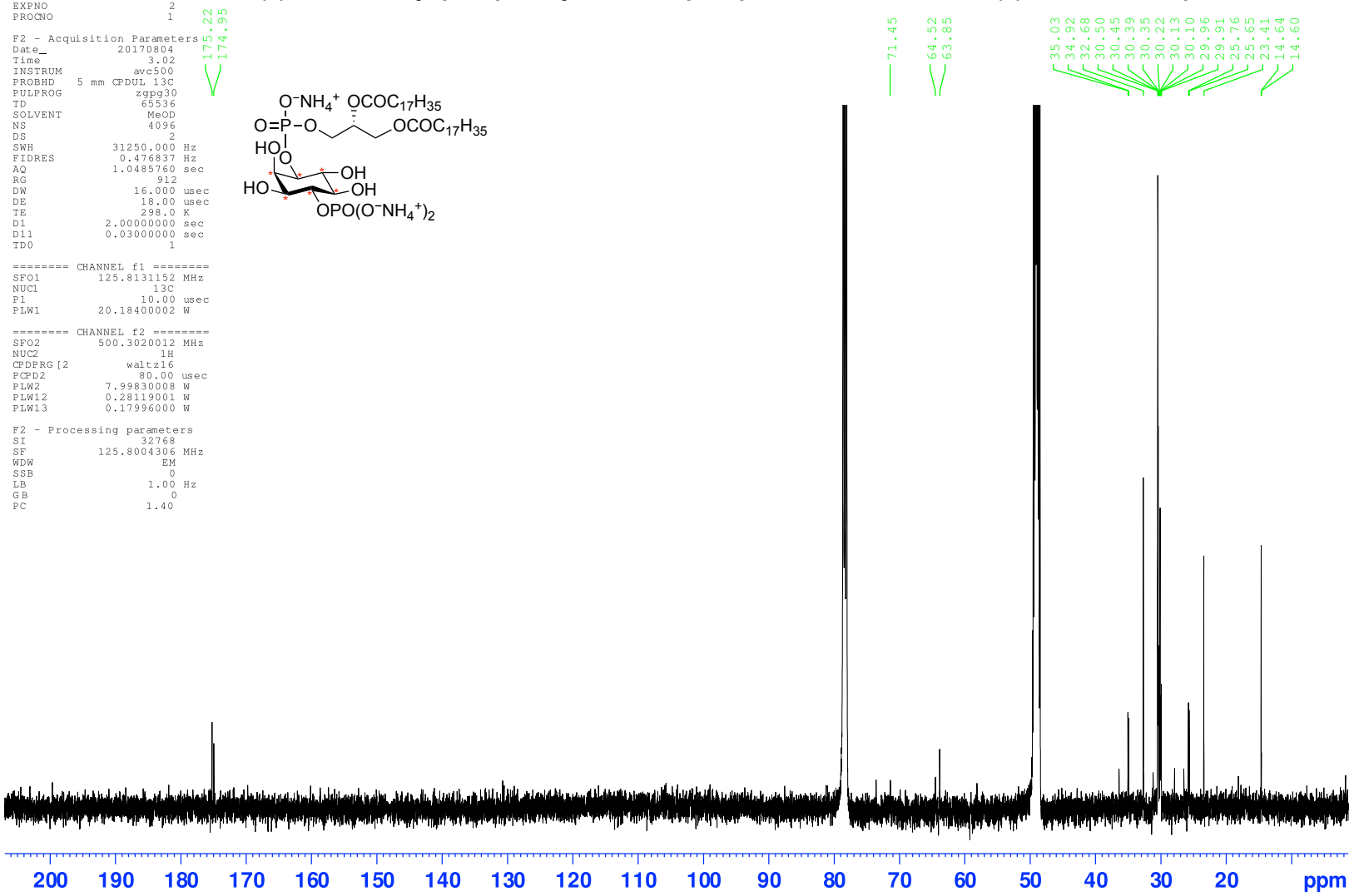
NL: 5.75E5
C47H77[2]H6O16P2: $C_{47}H_{77}{}^{2}H_{6}O_{16}P_{2}$
Chrg 1 R: 1000000 Res. Pwr. @FWHM

m/z	Formula	RDB	Delta ppm	Theo. Mass
971.55353	$C_{47}H_{77}{}^{2}H_{6}O_{16}P_{2}$	7.5	0.8	971.55275

D_6 (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-66 - ^{1}H NMR spectrum



D_6 (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-66 - ^{13}C NMR spectrum



D_6 (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-66 - ^{31}P NMR spectrum

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Current Data Parameters
NAME                 ajh28p
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20170803
Time                   4.50 h
INSTRUM              avb400
PROBHD    Z116098_0219 (
PULPROG              zgpg30
TD                    65536
SOLVENT                MeOD
NS                      100
DS                        4
SWH                64102.562 Hz
FIDRES             1.956255 Hz
AQ                 0.5111808 sec
RG                    197.74
DW                     7.800 usec
DE                     6.50 usec
TE                    298.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                       1
SFO1            161.9755930 MHz
NUC1                    31P
P1                     8.00 usec
PLW1            54.00000000 W
SFO2            400.1316005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 90.00 usec
PLW2            14.58800030 W
PLW12            0.18009999 W
PLW13            0.09058800 W

F2 - Processing parameters
SI                    32768
SF              161.9755930 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
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PC                     1.40
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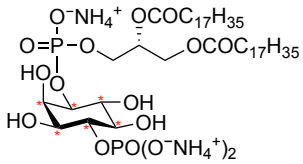
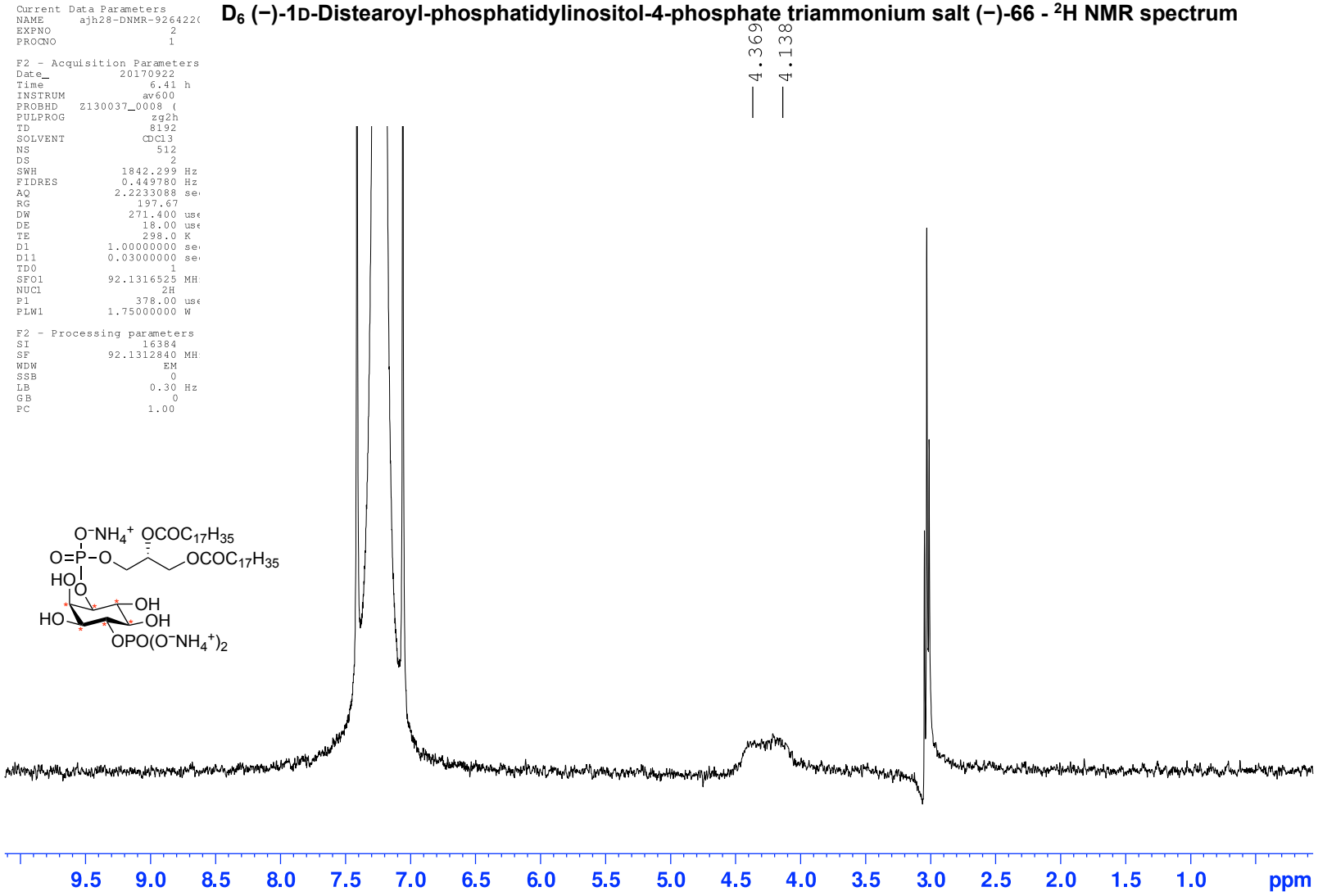
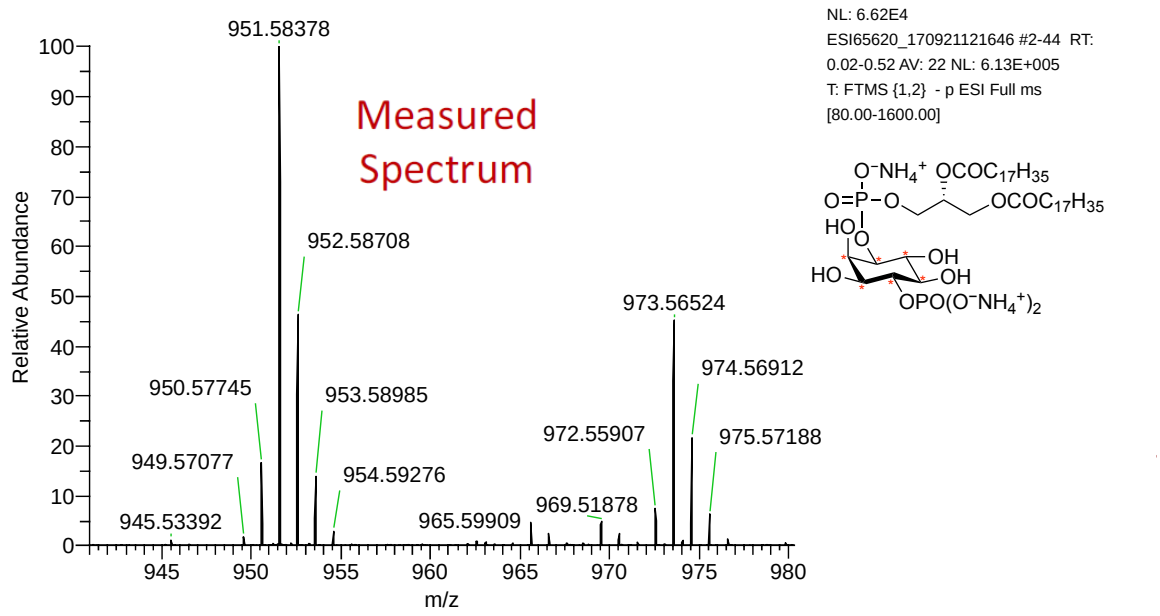


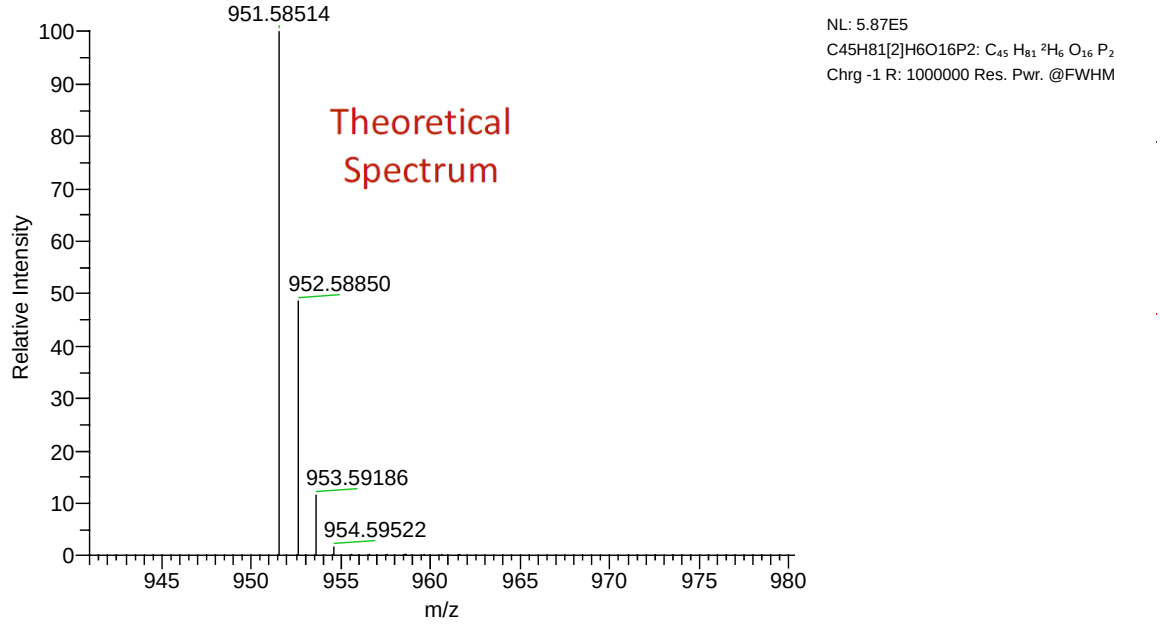
D_6 (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-66 - ^2H NMR spectrum



D_6 (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-66
Mass spectrum

X:\data\Sep 17\ESI65620_170921121646.raw 21/09/2017 1:01 pm

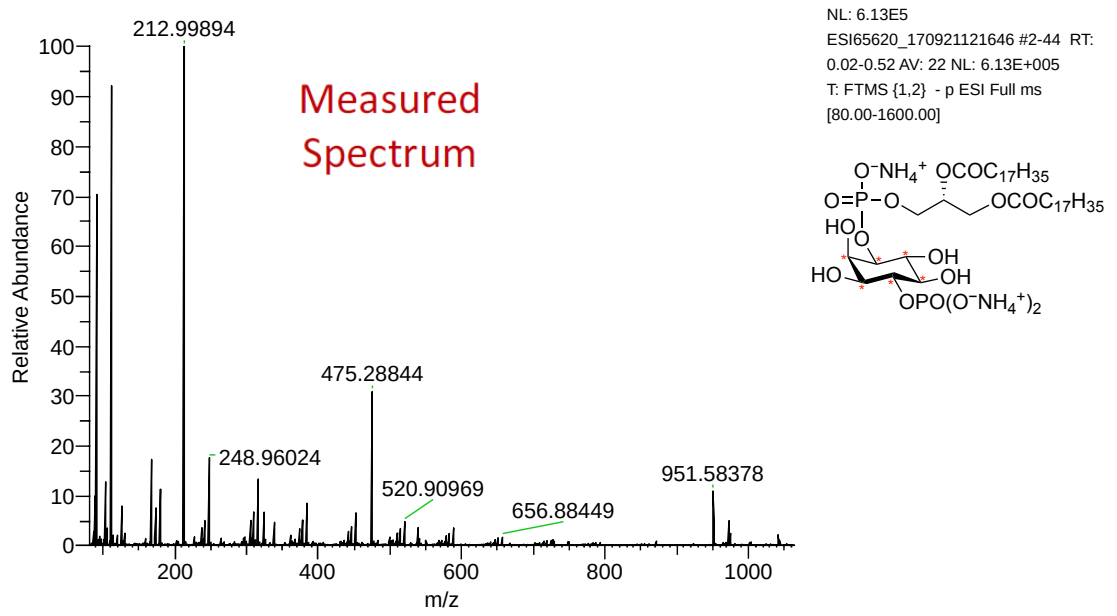


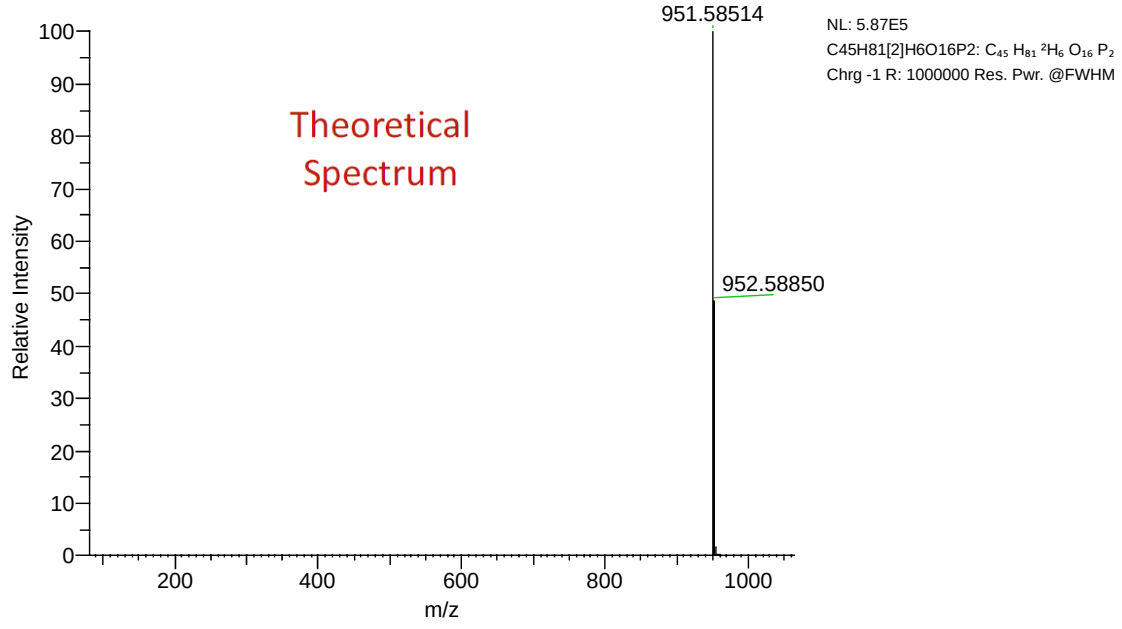


m/z	Formula	RDB	Delta ppm	Theo. Mass
951.58380	$C_{45}H_{81}{}^{2}H_6O_{16}P_2$	3.5	-1.41	951.58514

D_6 (−)-1D-Distearoyl-phosphatidylinositol-4-phosphate triammonium salt (−)-66
Mass spectrum

X:\data\Sep 17\ESI65620_170921121646.raw 21/09/2017 1:03 pm





m/z	Formula	RDB	Delta ppm	Theo. Mass
951.58380	$C_{45}H_{81}{}^{2}H_6O_{16}P_2$	3.5	-1.41	951.58514

(−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-69 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME         aje74p-data2
EXPNO                   4
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160122
Time              16.01 h
INSTRUM           avb400
PROBHD    Z116098_0219 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ              4.0894465 sec
RG                 56.66
DW                62.400 usec
DE                 6.50 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1
SFO1        400.1320007 MHz
NUC1                1H
P1                10.00 usec
PLW1        14.58800030 W

F2 - Processing parameters
SI                 65536
SF          400.1300107 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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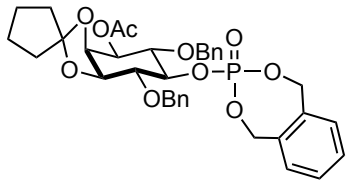
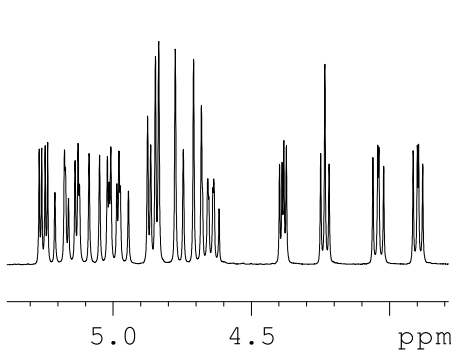
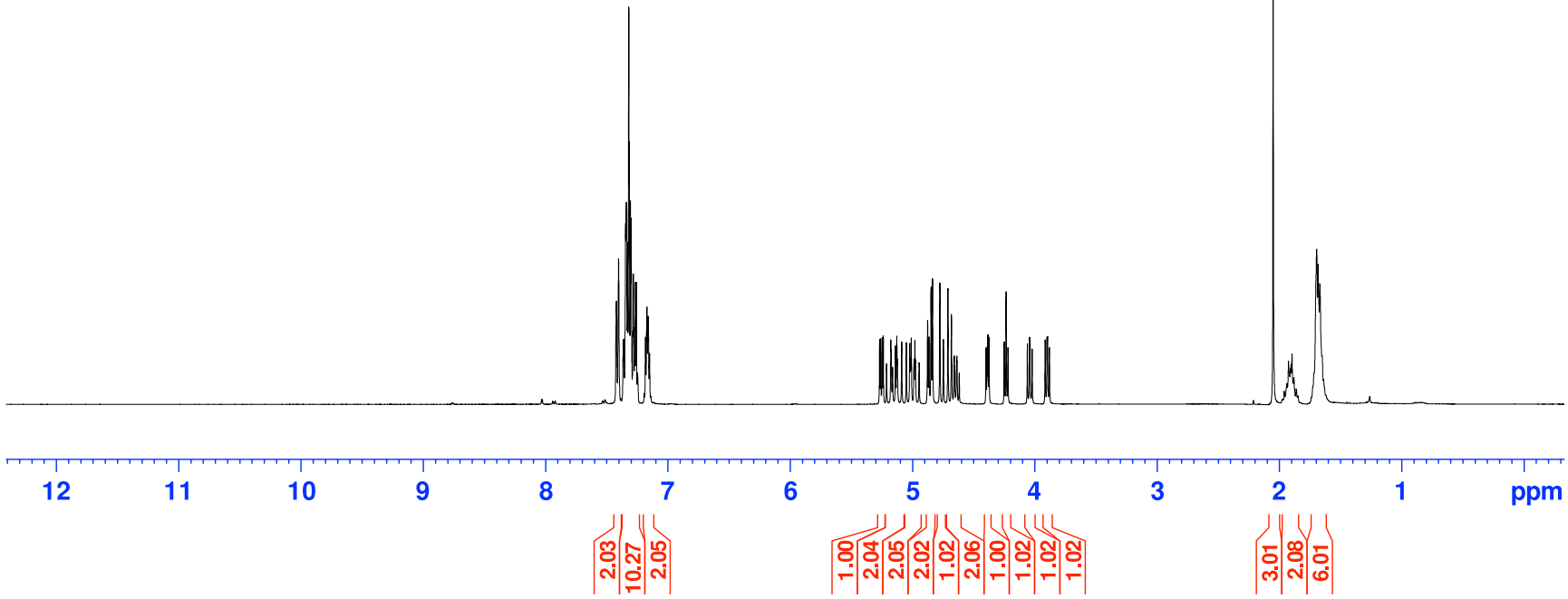
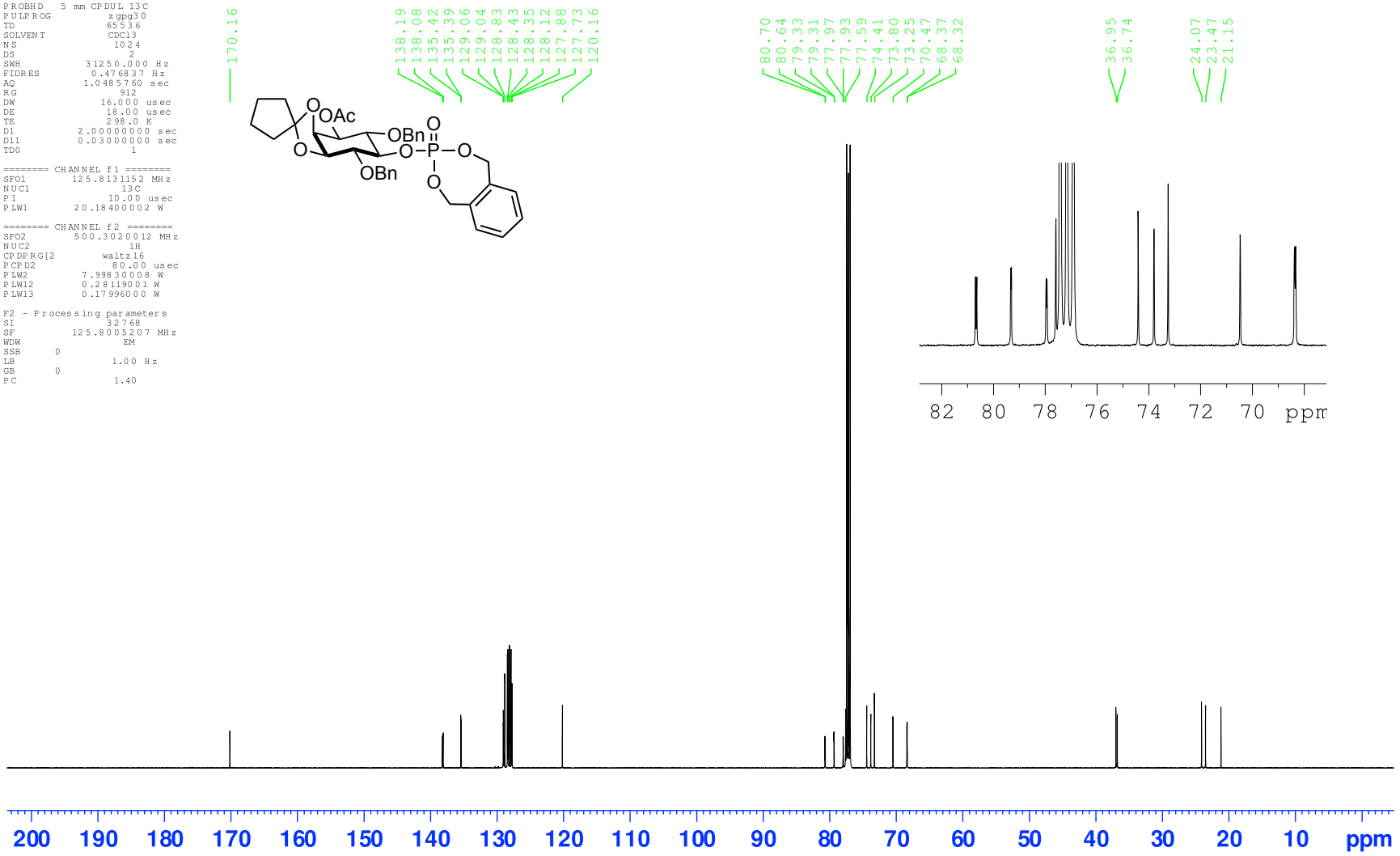


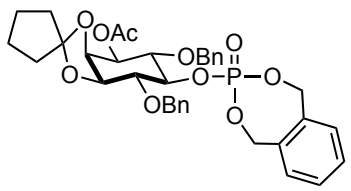




(−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-69 – ^{13}C NMR spectrum



(−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-69 – ^{31}P NMR spectrum

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Current Data Parameters
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EXPNO                  3
PROCNO                 1

F2 - Acquisition Paramete
Date_           20160122
Time              15.58
INSTRUM          avb400
PROBHD    Z116098_0219 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   50
DS                    4
SWH           64102.562
FIDRES         1.956255
AQ             0.5111808
RG                197.74
DW                 7.800
DE                 6.50
TE                298.0
D1           2.00000000
D11          0.03000000
TD0                   1
SFO1        161.9755930
NUC1               31P
P1                 8.00
PLW1        54.00000000
SFO2        400.1316005
NUC2               1H
CPDPRG[2        waltz16
PCPD2             90.00
PLW2        14.58800030
PLW12        0.18009999
PLW13        0.09058800

F2 - Processing paramete
SI                32768
SF          161.9755930
WDW                  EM
SSB       0
LB                 1.00
GB        0
PC                 1.40
```

D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-70 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME         ajf52p-data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160713
Time              10.25
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   4
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ            3.1719425 sec
RG                   2
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1               1H
P1                15.00 usec
PLW1          7.99830008 W

F2 - Processing parameters
SI                65536
SF          500.3000132 MHz
WDW                EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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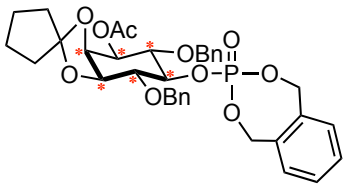
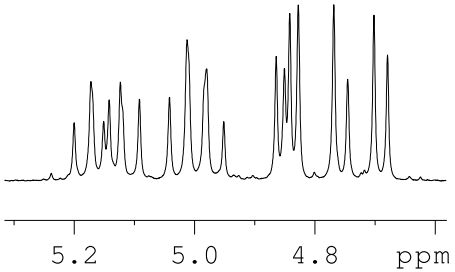
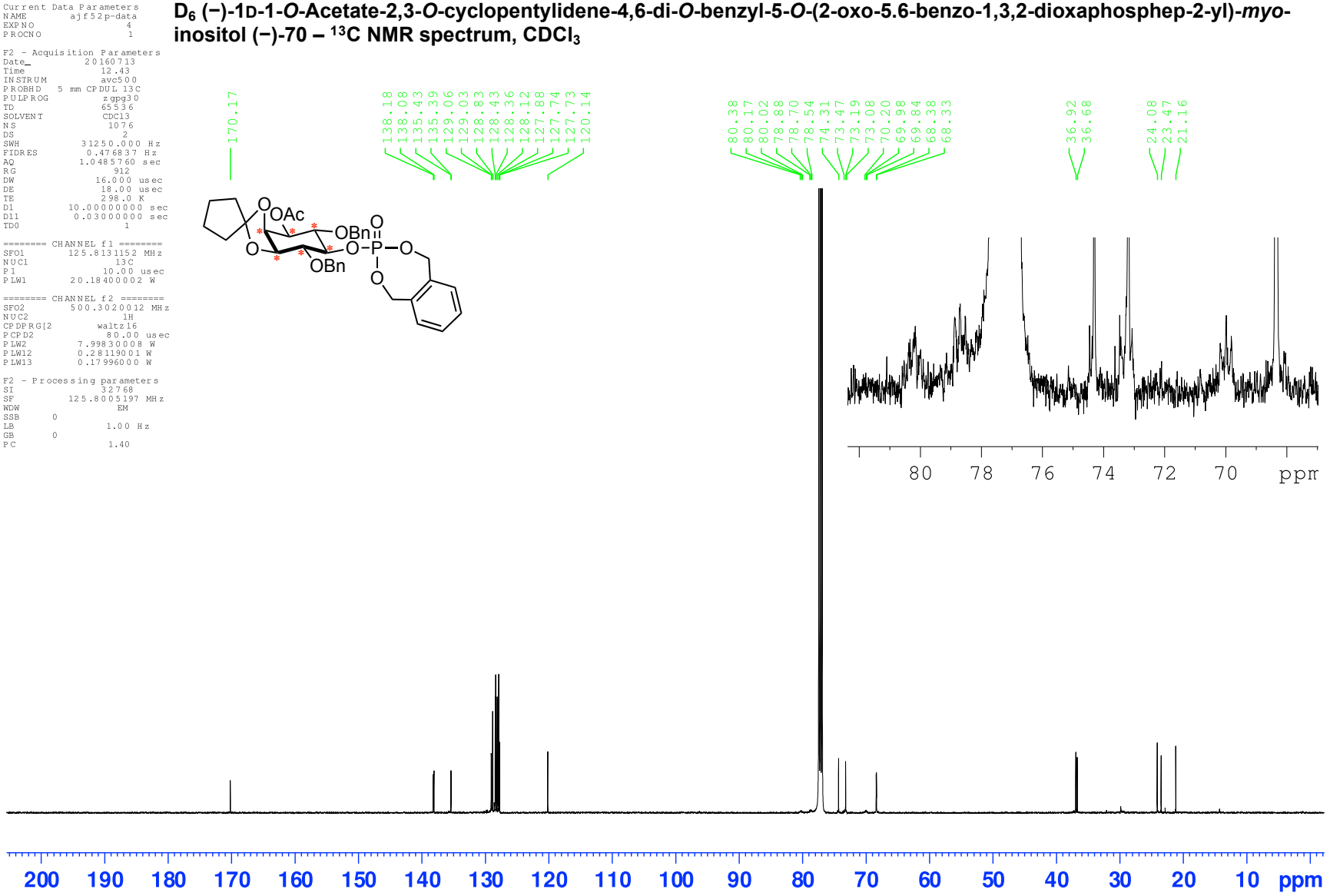
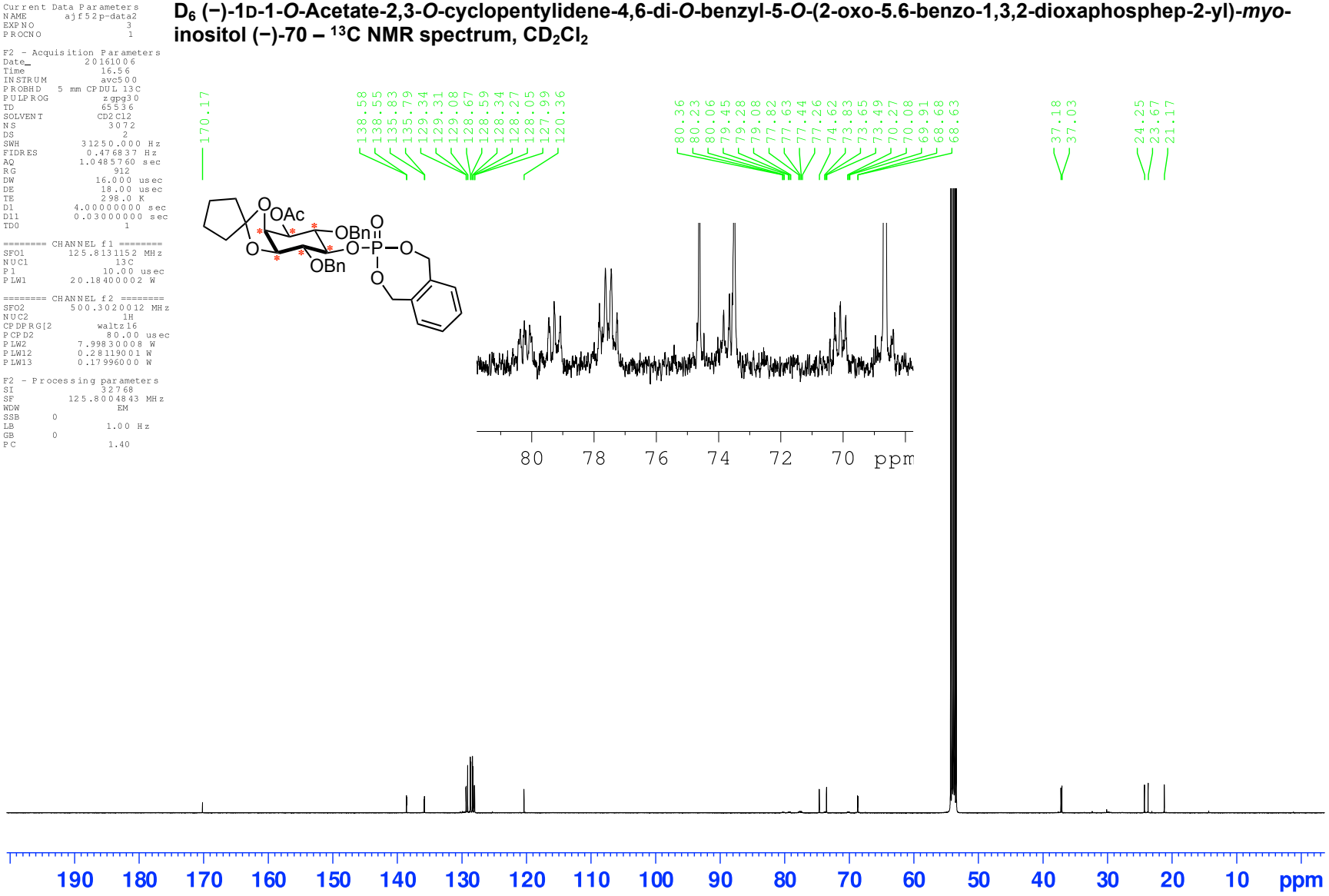




D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-70 – ^{13}C NMR spectrum, $CDCl_3$



D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-70 – ^{13}C NMR spectrum, CD_2Cl_2



D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-70 – ^{31}P NMR spectrum

```
Current Data Parameters
NAME        ajf52p-dataP
EXPNO                  2
PROCNO                 1

F2 - Acquisition Paramete
Date_           20160713
Time               15.58
INSTRUM          avx500
PROBHD    Z113652_0208 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  128
DS                    4
SWH           40760.871
FIDRES         1.243923
AQ             0.8039083
RG               191.37
DW               12.267
DE                 6.50
TE                298.0
D1           2.00000000
D11          0.03000000
TD0                   1
SFO1         202.4563350
NUC1                31P
P1                14.00
PLW1         38.20000076
SFO2         500.1320005
NUC2                1H
CPDPRG[2         waltz16
PCPD2              80.00
PLW2         20.50000000
PLW12         0.32031000
PLW13         0.16111000

F2 - Processing paramete
SI                 32768
SF           202.4563350
WDW                   EM
SSB       0
LB                 1.00
GB        0
PC                 1.40
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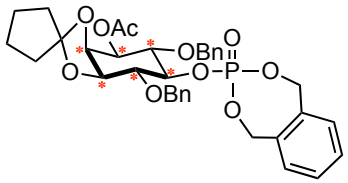
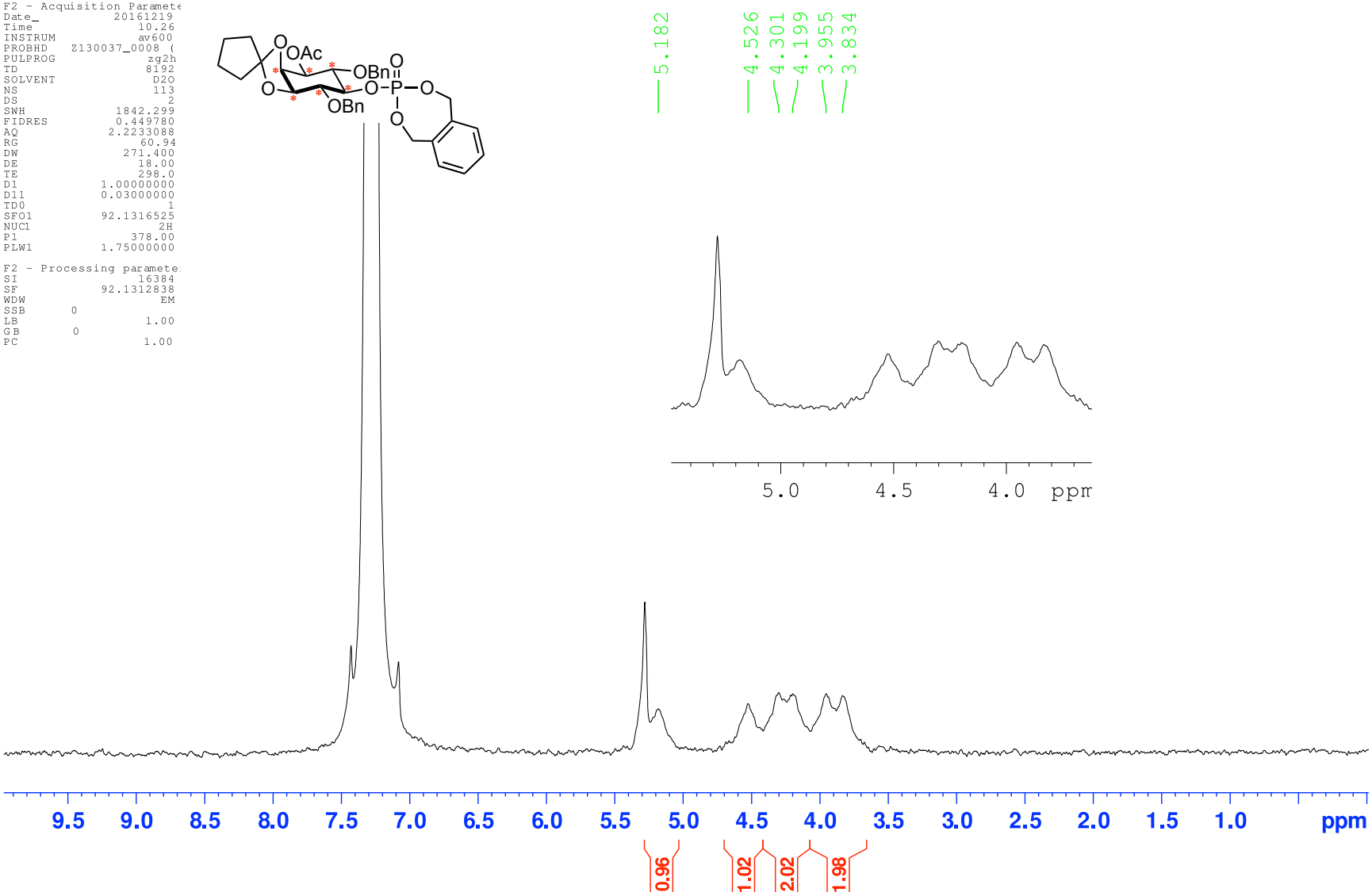
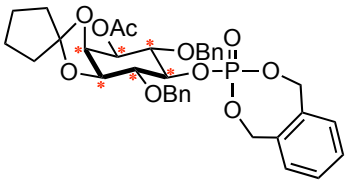


D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-70 – ^{2}H NMR spectrum



D_6 (−)-1D-1-*O*-Acetate-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-70 – Mass spectrum



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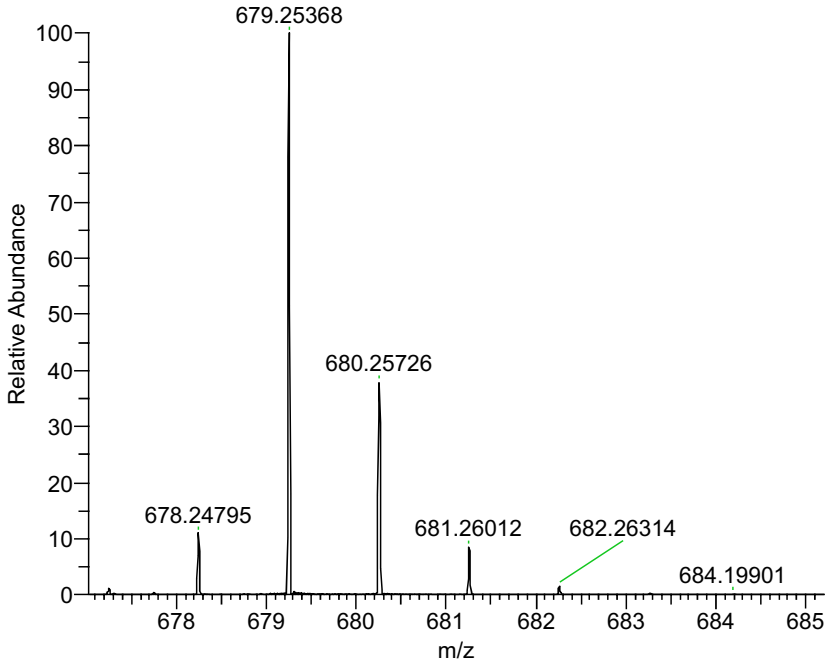
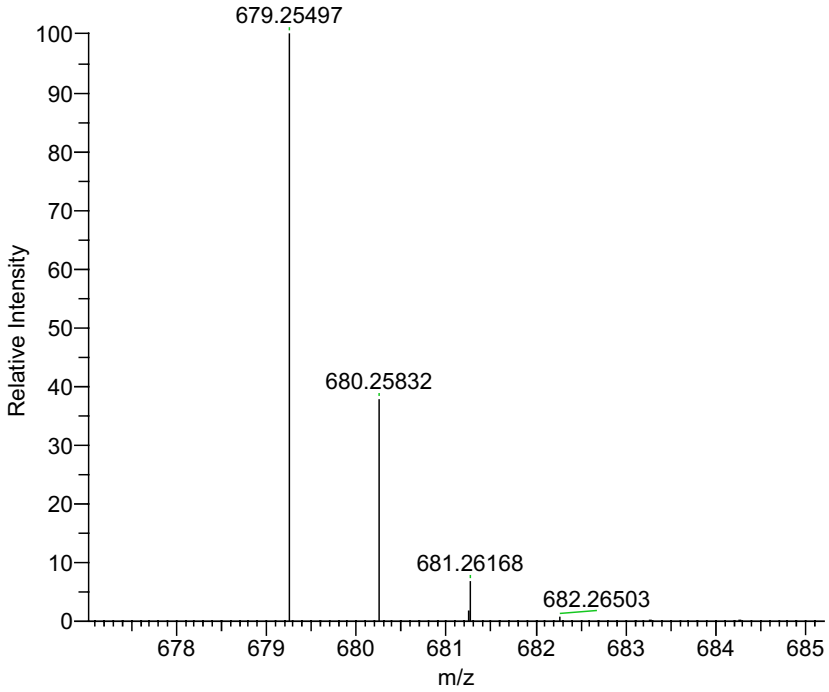


NL: 7.40E7
ESI58013 #12-27 RT: 0.15-0.3 AV: 8 NL: 8.67E+007
T: FTMS {1,1} + p ESI Full ms [80.00-1600.00]

Measured Spectrum



NL: 6.67E5
C35H33[2]H6O10Na1P1: $C_{35}H_{33}{}^{2}H_{6}O_{10}$ Na P Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
679.25366	$C_{35}H_{33}{}^{2}H_{6}O_{10}{}^{23}NaP$	16.5	-1.92	679.25497

(+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (+)-71 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME      ajf83p-data2-b
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161108
Time              15.08 h
INSTRUM           avb400
PROBHD   Z116098_0219 (
PULPROG            zg30
TD                65536
SOLVENT           CD2Cl2
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.244532 Hz
AQ             4.0894465 sec
RG                89.24
DW               62.400 usec
DE                6.50 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1
SFO1         400.1320007 MHz
NUC1                 1H
P1                10.00 usec
PLW1         14.58800030 W

F2 - Processing parameters
SI                65536
SF           400.1300156 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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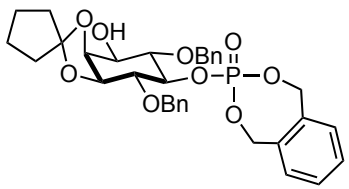
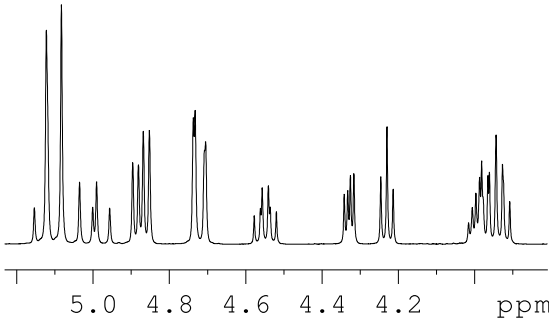
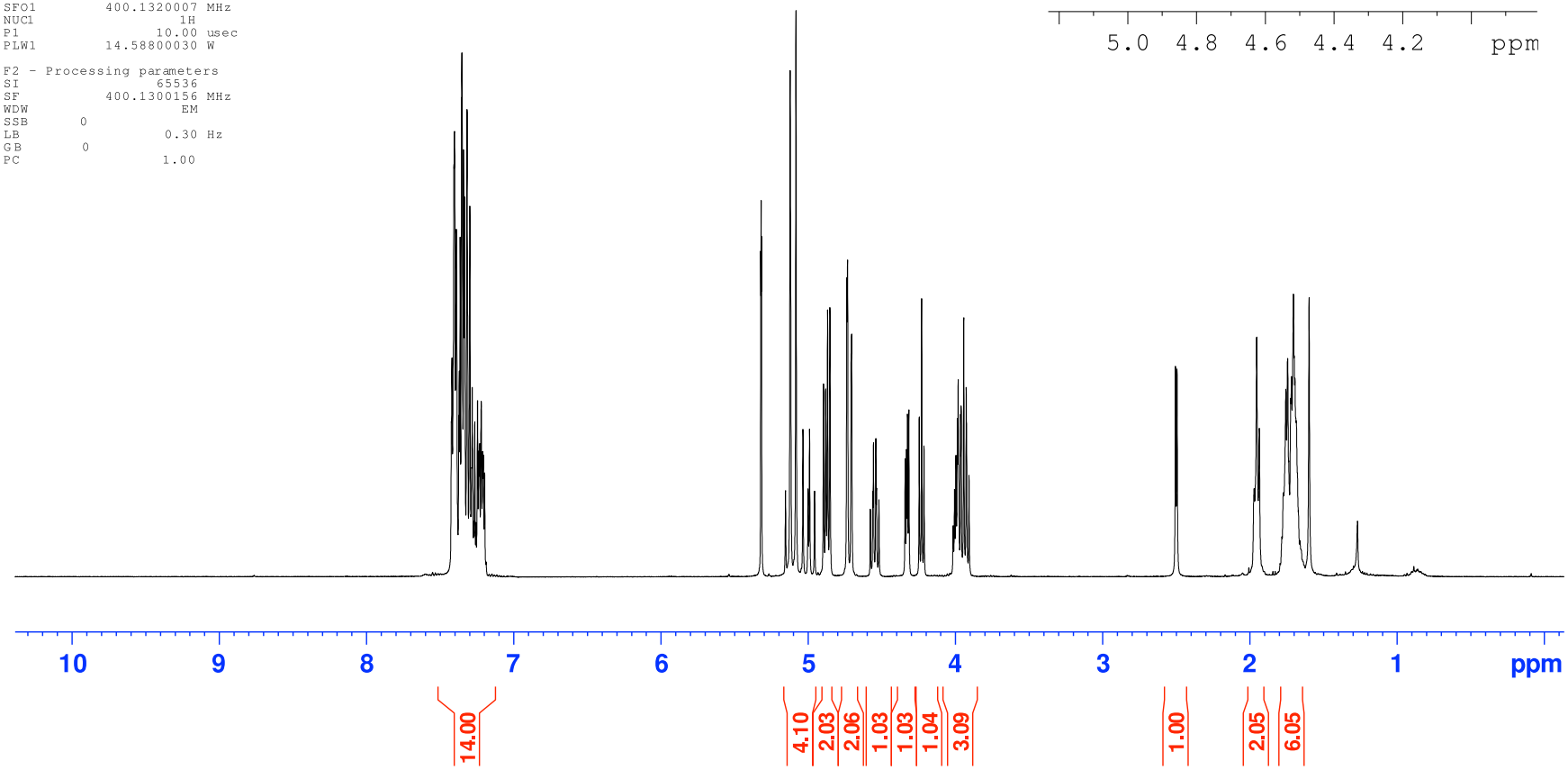
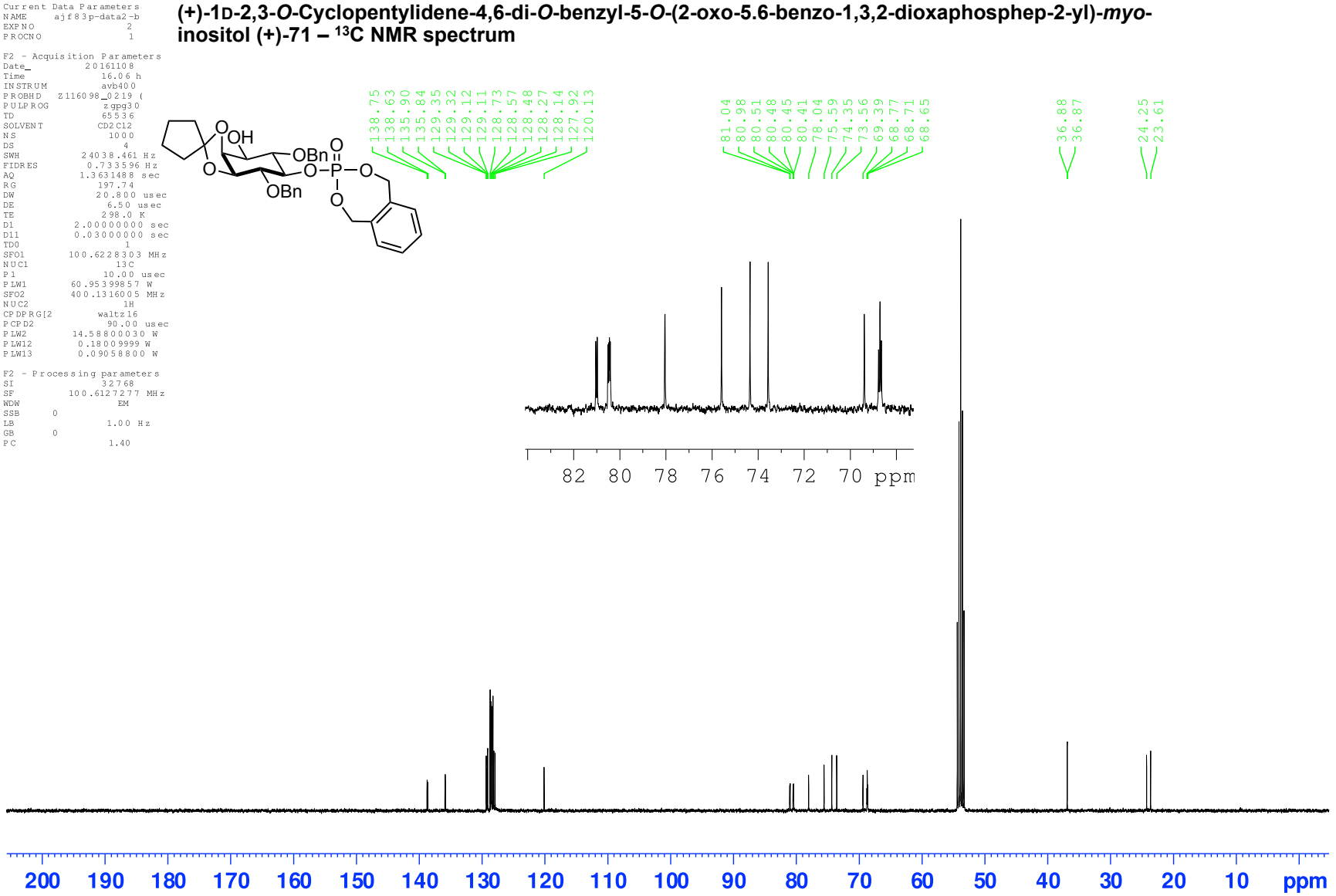






(+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (+)-71 – ^{13}C NMR spectrum



(+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (+)-71 – ^{31}P NMR spectrum

```
Current Data Parameters
NAME        ajf83p-data2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Paramete
Date_           20161005
Time              11.38
INSTRUM          avb400
PROBHD    Z116098_0219 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    4
SWH           64102.562
FIDRES         1.956255
AQ             0.5111808
RG                197.74
DW                 7.800
DE                  6.50
TE                298.0
D1           2.00000000
D11          0.03000000
TD0                   1
SFO1        161.9674942
NUC1               31P
P1                 8.00
PLW1        54.00000000
SFO2        400.1316005
NUC2               1H
CPDPRG[2       waltz16
PCPD2             90.00
PLW2        14.58800030
PLW12        0.18009999
PLW13        0.09058800

F2 - Processing paramete
SI                32768
SF          161.9755930
WDW                  EM
SSB       0
LB                 1.00
GB        0
PC                 1.40
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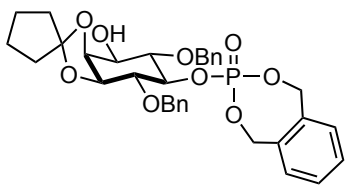
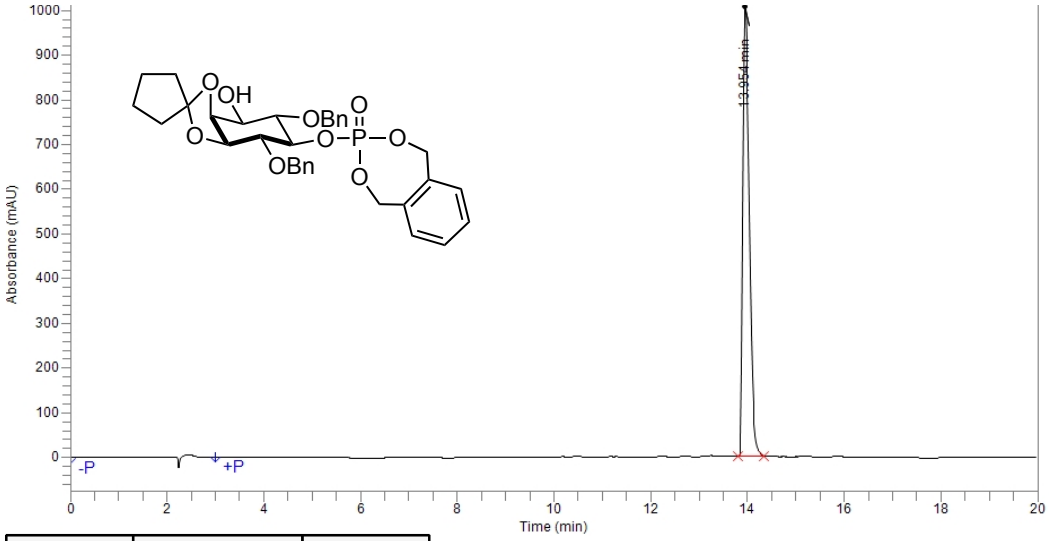


(+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (+)-71 – RP-HPLC (Method 2)



Time	Area	Area %
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Total	9,287,838	100.00

D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (+)-72 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME         ajf59p-data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160718
Time              11.58
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg30
TD                65536
SOLVENT          CD2Cl2
NS                   16
DS                    4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                   3.2
DW                48.400 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1                1H
P1                15.00 usec
PLW1           7.99830008 W

F2 - Processing parameters
SI                 65536
SF            500.3000206 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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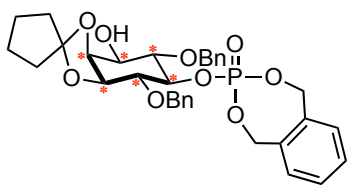
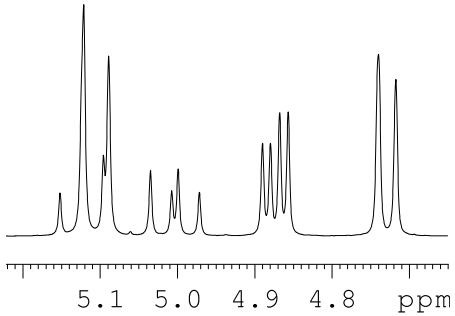
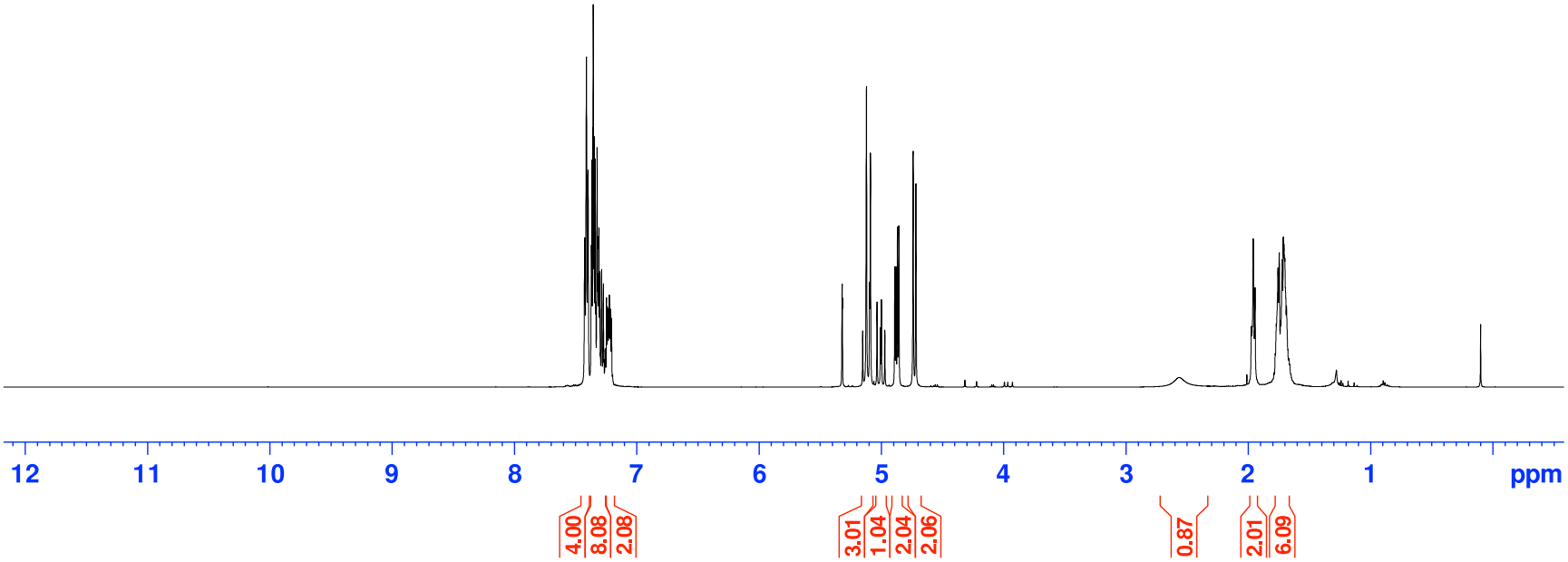
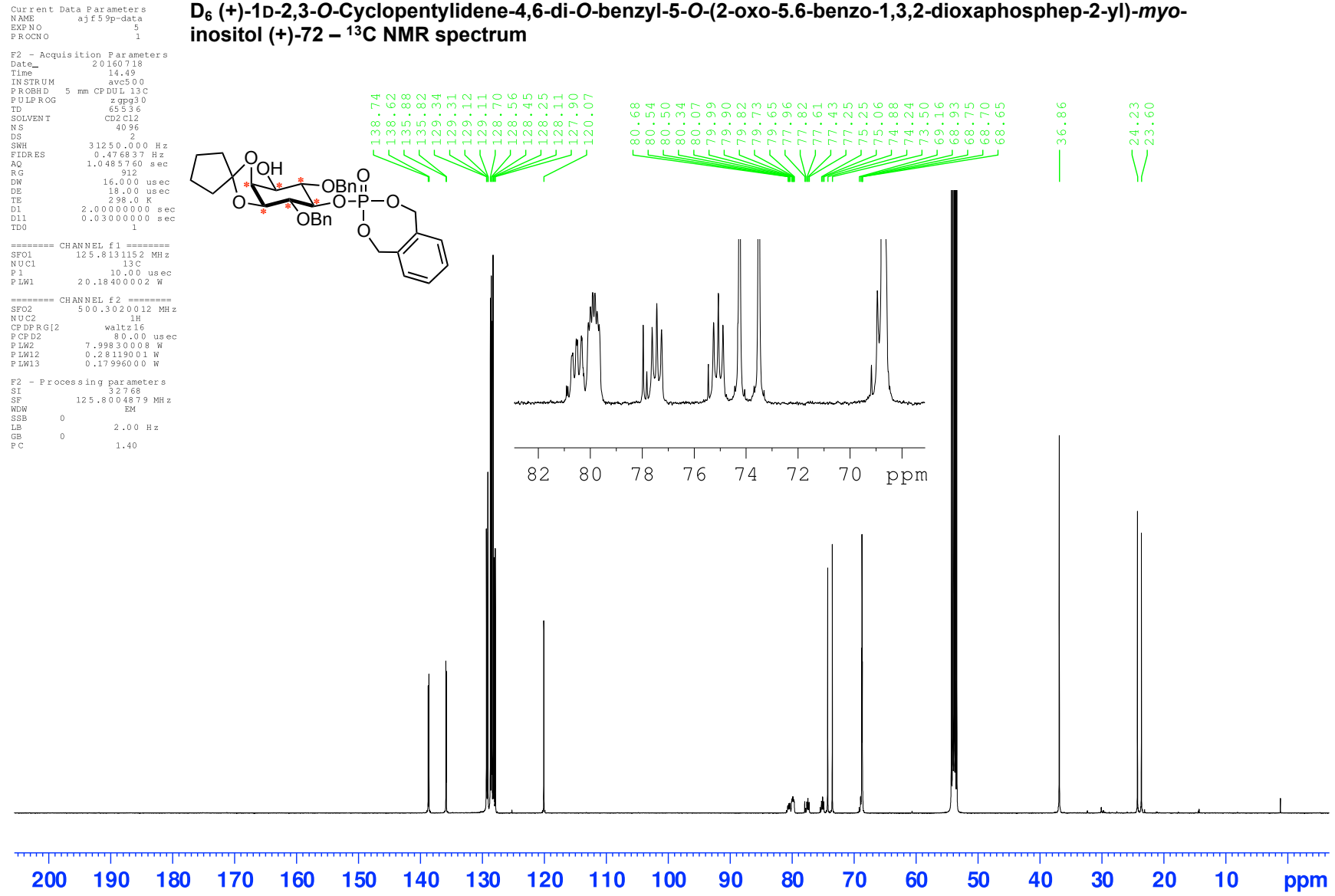


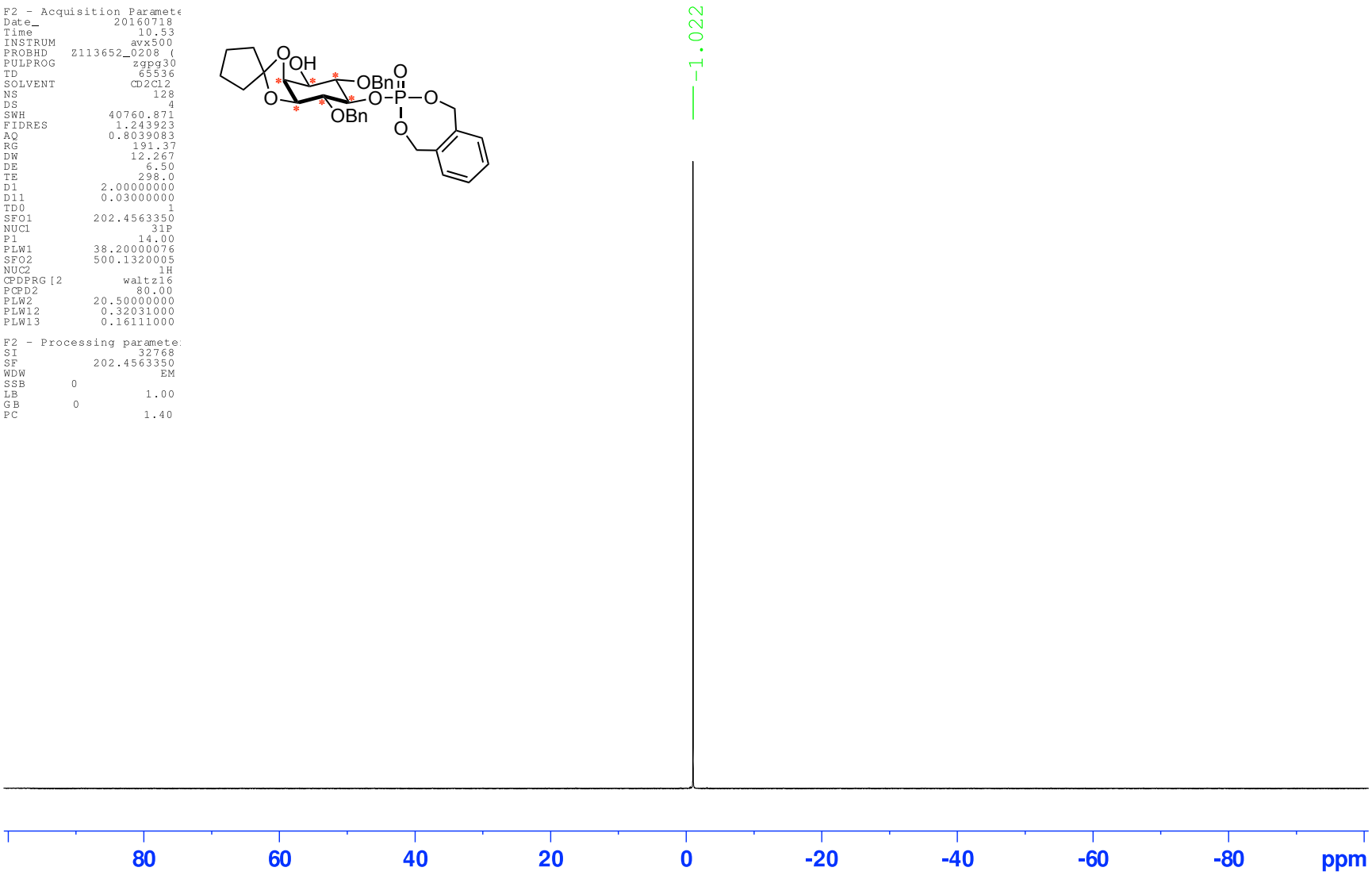




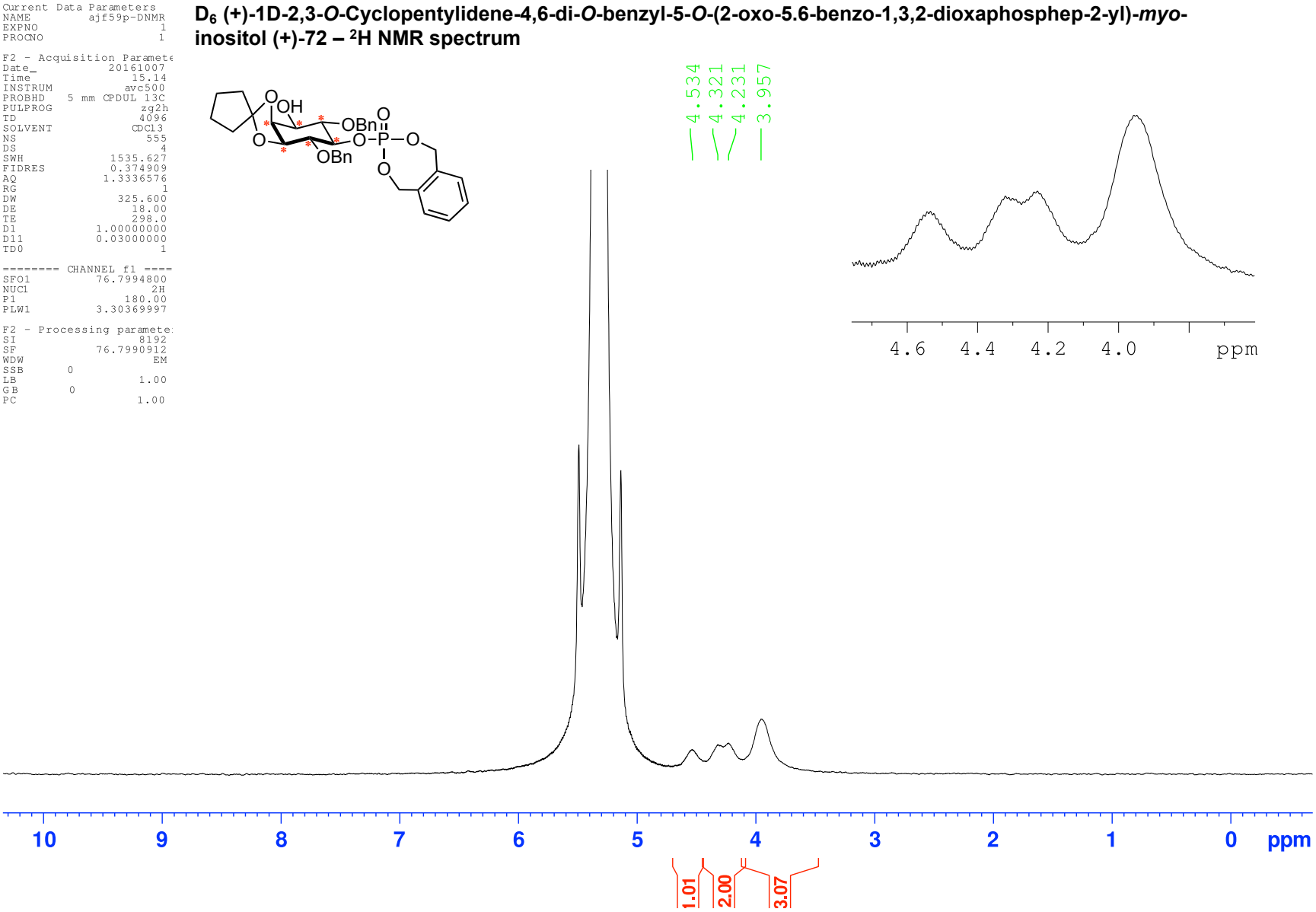
D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (+)-72 – ^{13}C NMR spectrum



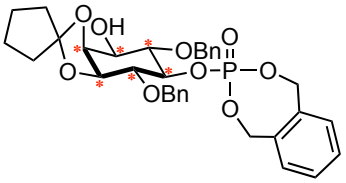
D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (+)-72 – ^{31}P NMR spectrum



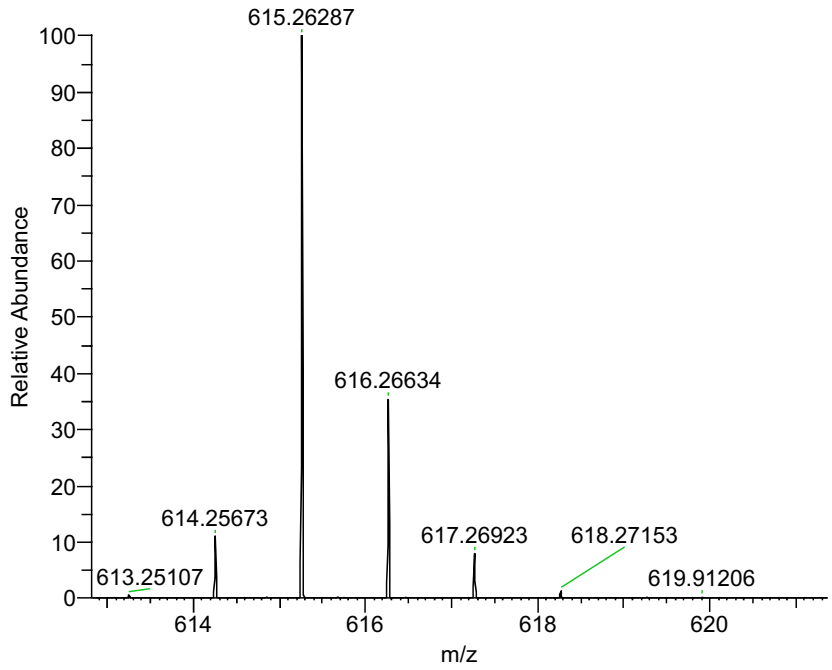
D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (+)-72 – ^{2}H NMR spectrum



D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep -2-yl)-*myo*-inositol (+)-72 – Mass spectrum

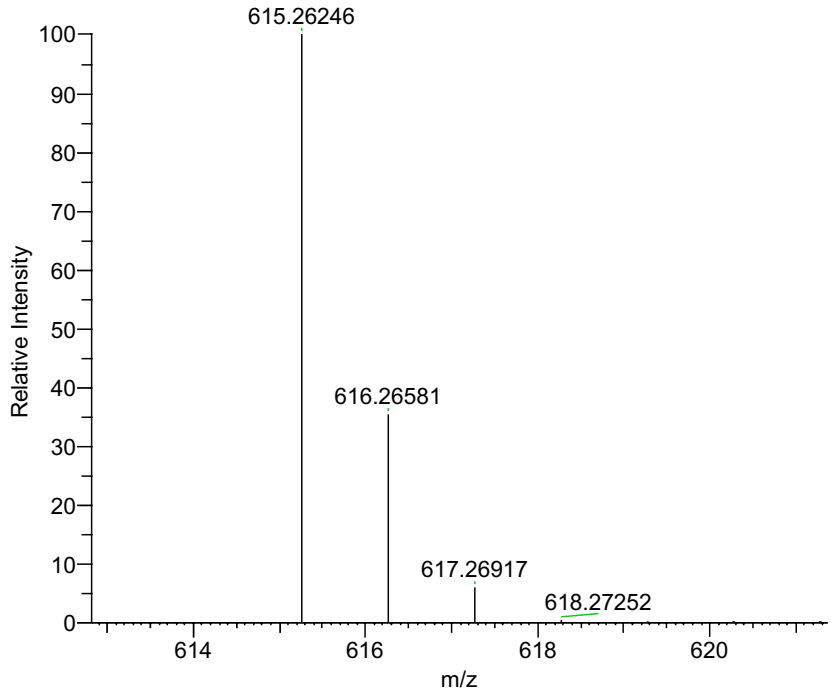


W:\data\Sep 16\ESI59268.raw 28/09/2016 9:38 am



NL: 7.87E7
ESI59268 #14-31 RT: 0.14-0.29 AV: 9 NL: 1.27E+008
T: FTMS + p ESI Full ms [100.00-1500.00]

Measured Spectrum

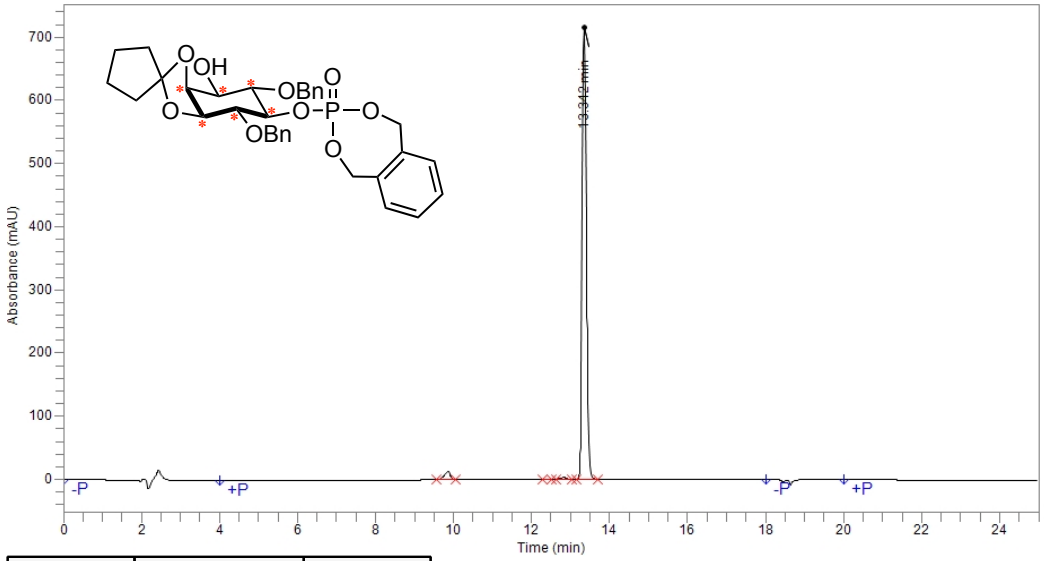


NL: 6.83E5
C33H32[2]H6O9P1: $C_{33}H_{32}{}^{2}H_{6}O_{9}P$ Chrg 1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
615.26288	$C_{33}H_{32}{}^{2}H_{6}O_{9}P$	15.5	0.69	615.26246

D_6 (+)-1D-2,3-*O*-Cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep -2-yl)-*myo*-inositol (+)-72 – RP-HPLC (Method 2)



Time	Area	Area %
9.857	141,121	2.59
12.399	3,681	0.07
12.815	25,784	0.47
13.342	5,275,487	96.87
Total	5,446,073	100.00

(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-73 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME          aje83p-data
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20160316
Time              12.27
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG            zg30
TD                65536
SOLVENT           CD2Cl2
NS                   16
DS                    4
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719425 sec
RG                  3.56
DW                 48.400 usec
DE                 10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        500.3030896 MHz
NUC1                1H
P1                15.00 usec
PLW1         7.99830008 W

F2 - Processing parameters
SI                65536
SF          500.3000205 MHz
WDW                 EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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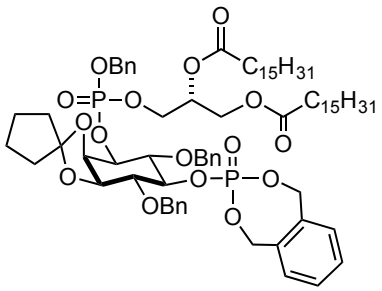
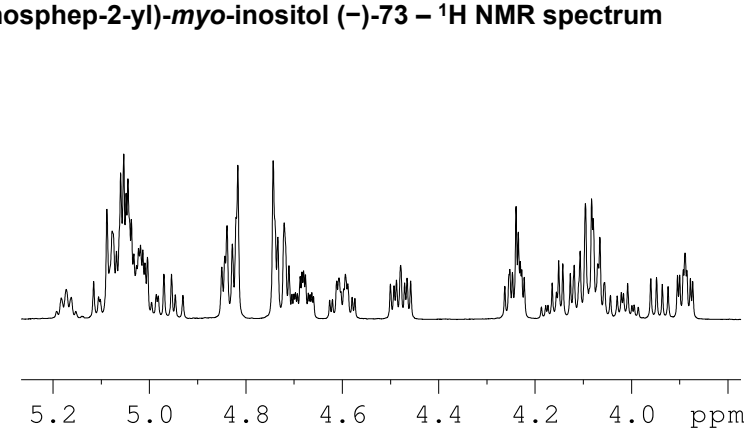
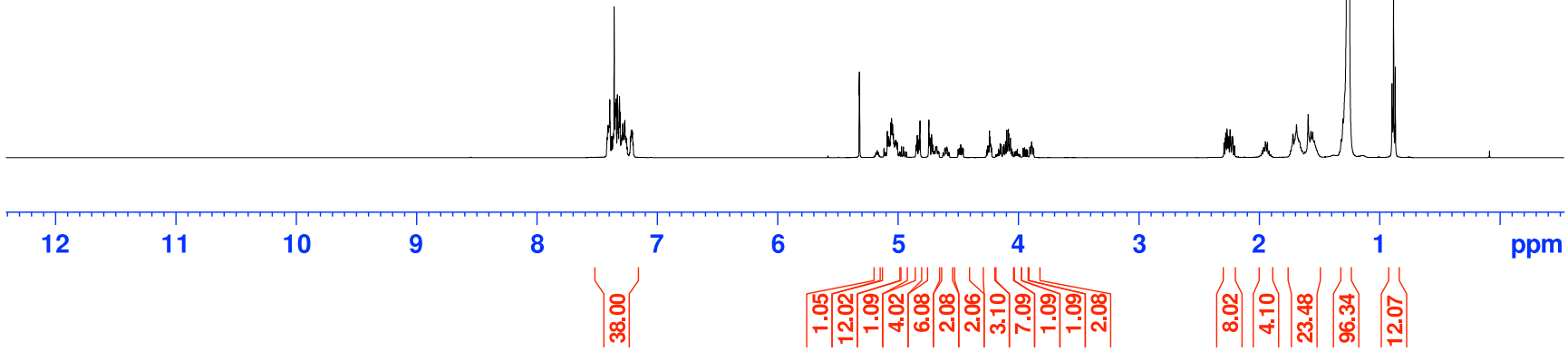
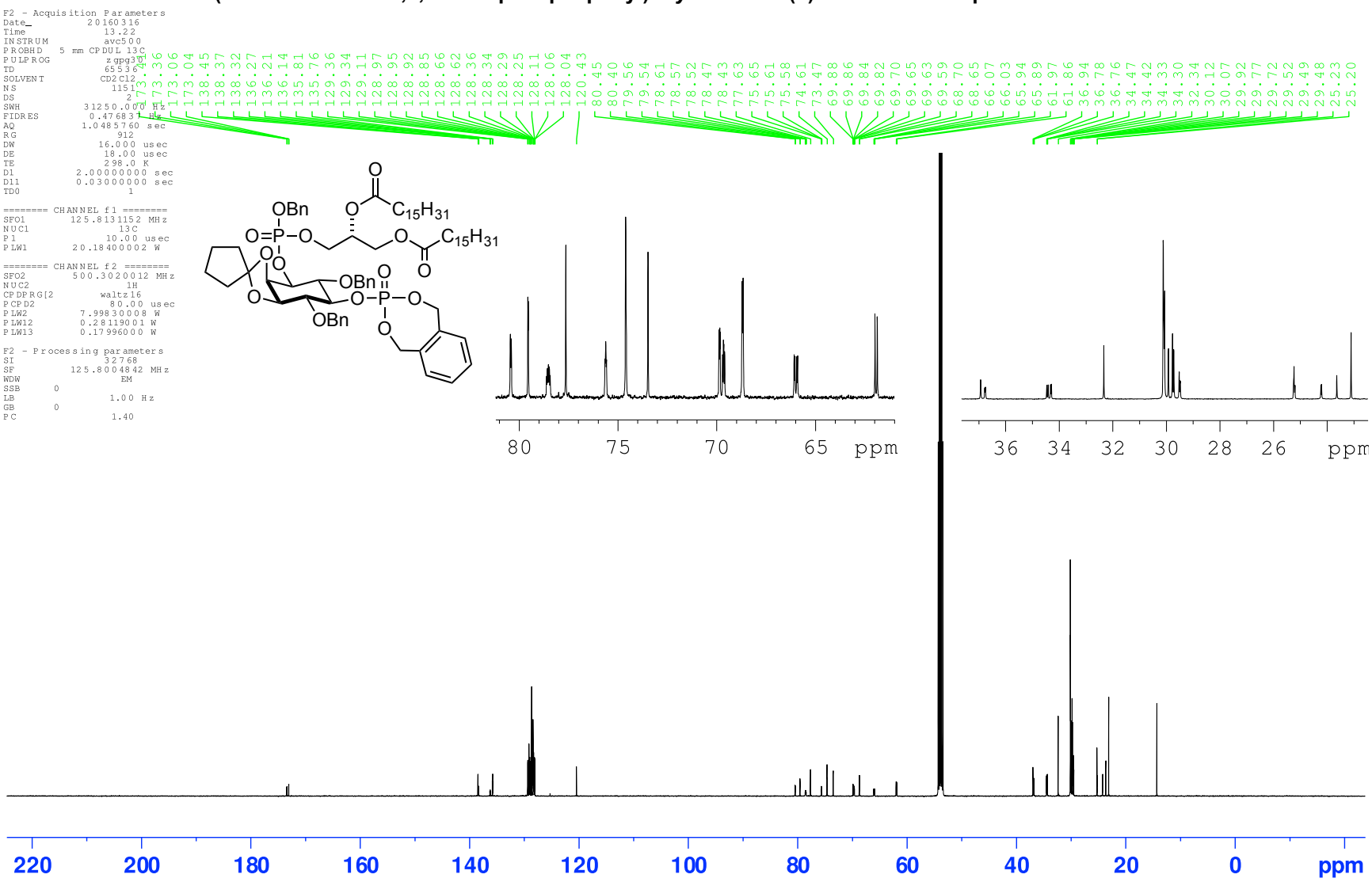


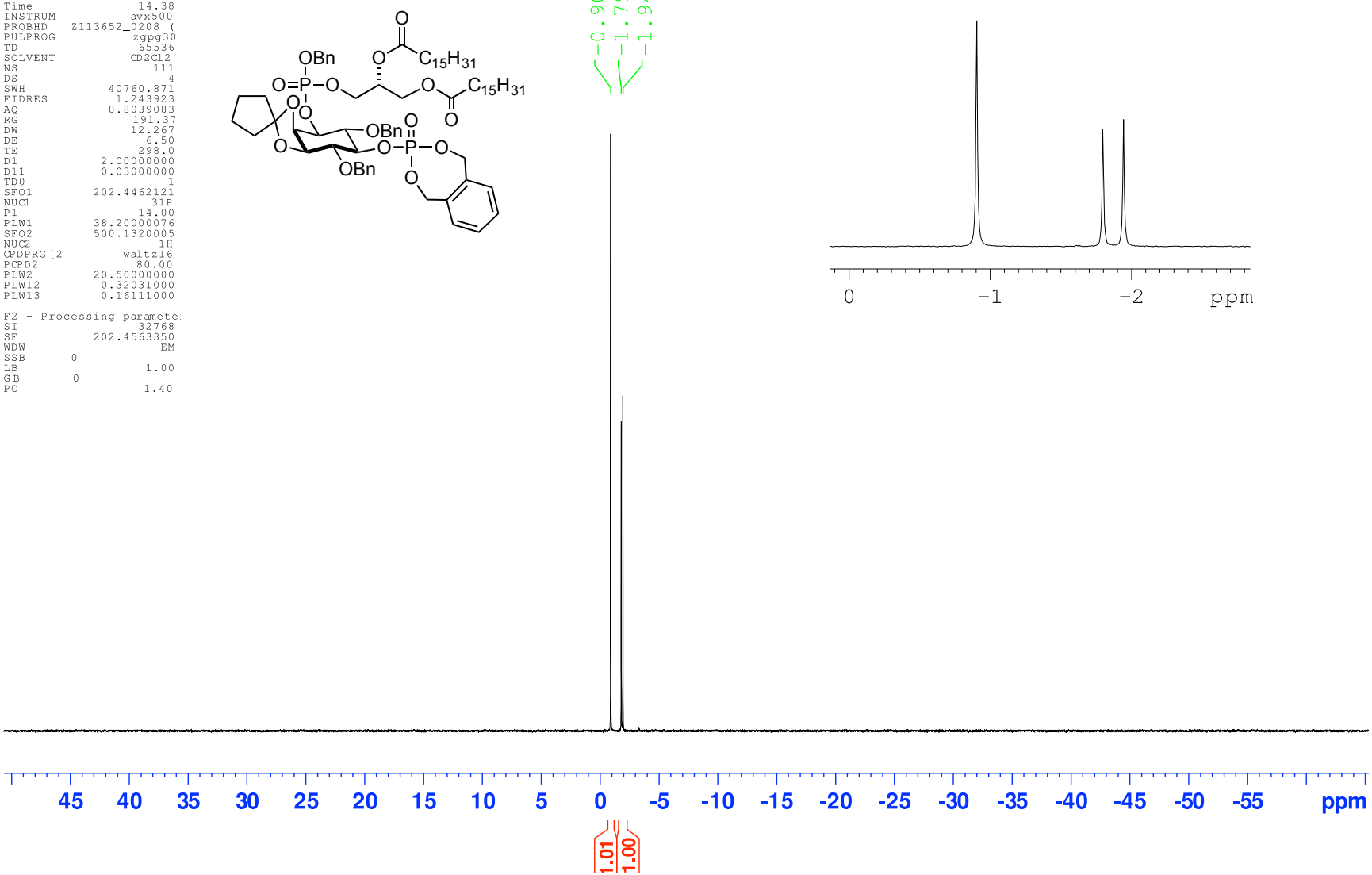




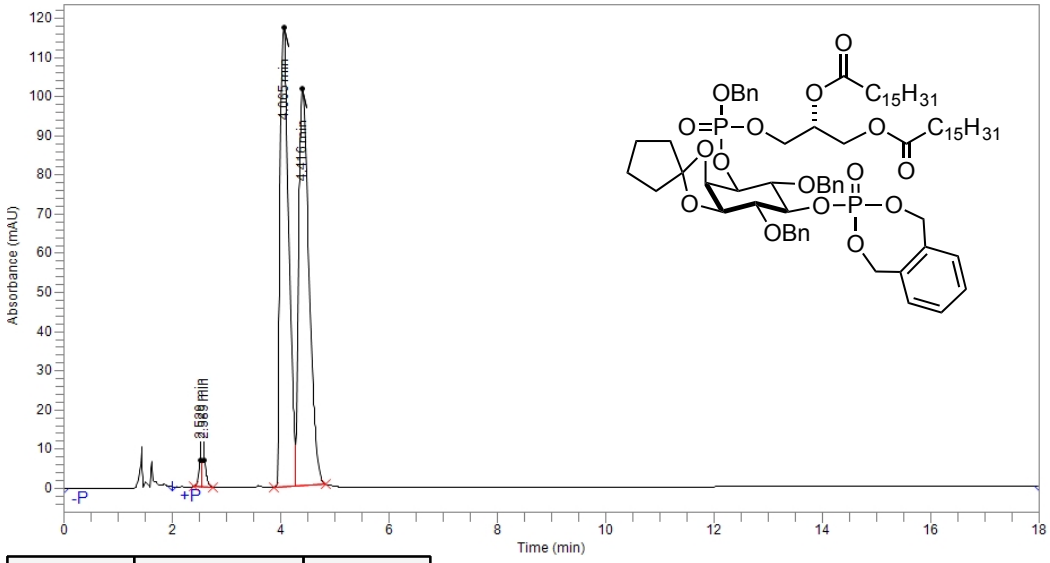
(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-73 – ^{13}C NMR spectrum



(−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-73 – ^{31}P NMR spectrum



(−)-1D-1-*O*-(2,3-Di-*O*-palmitoyl-*sn*-glyceryl-1-benzylphosphate)-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-73 – NP-HPLC (Method 7)



Time	Area	Area %
2.529	29,723	1.09
2.589	33,437	1.23
4.065	1,314,178	48.36
4.416	1,340,319	49.32
Total	2,717,656	100.00

D_6 (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-74 – ^{1}H NMR spectrum

```
Current Data Parameters
NAME          ajf81p-data
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20161012
Time              11.04 h
INSTRUM             av600
PROBHD    Z130037_0008 (
PULPROG             zg30
TD                 65536
SOLVENT           CD2Cl2
NS                    16
DS                     2
SWH           12019.230 Hz
FIDRES         0.366798 Hz
AQ             2.7262976 sec
RG                 22.67
DW                41.600 usec
DE                10.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1
SFO1         600.1830009 MHz
NUC1                1H
P1                12.00 usec
PLW1         24.00000000 W

F2 - Processing parameters
SI                 65536
SF           600.1800237 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
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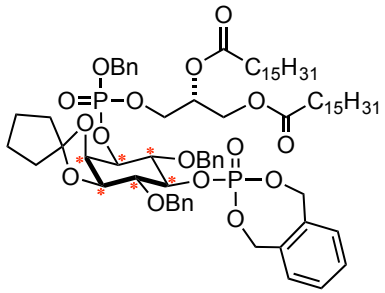
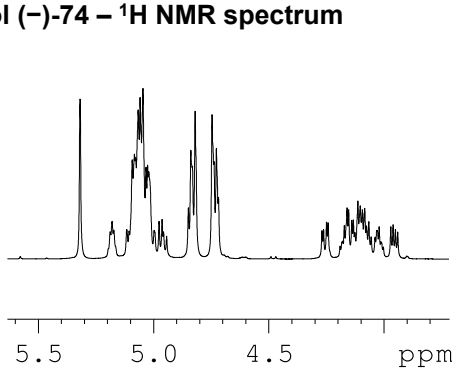
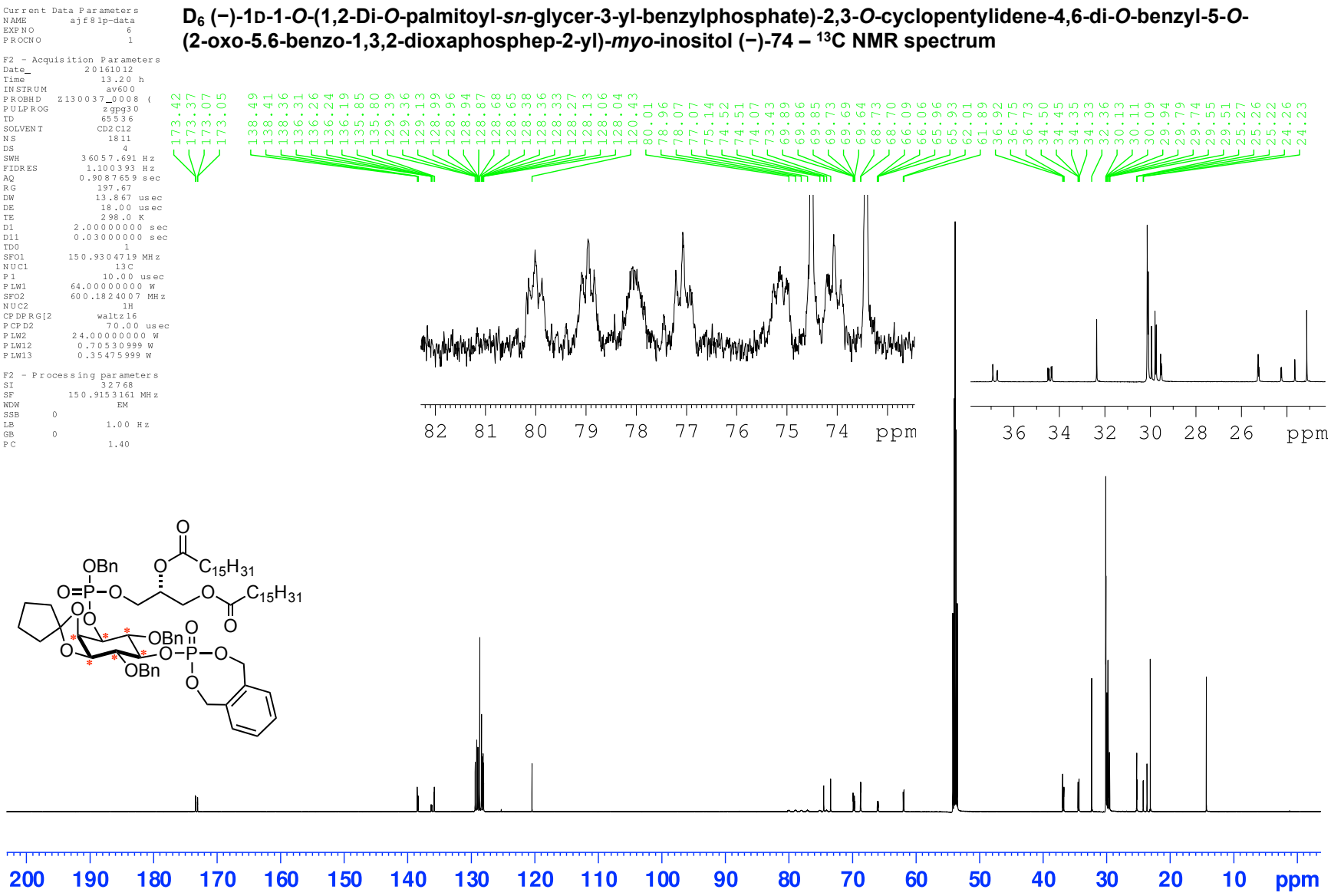
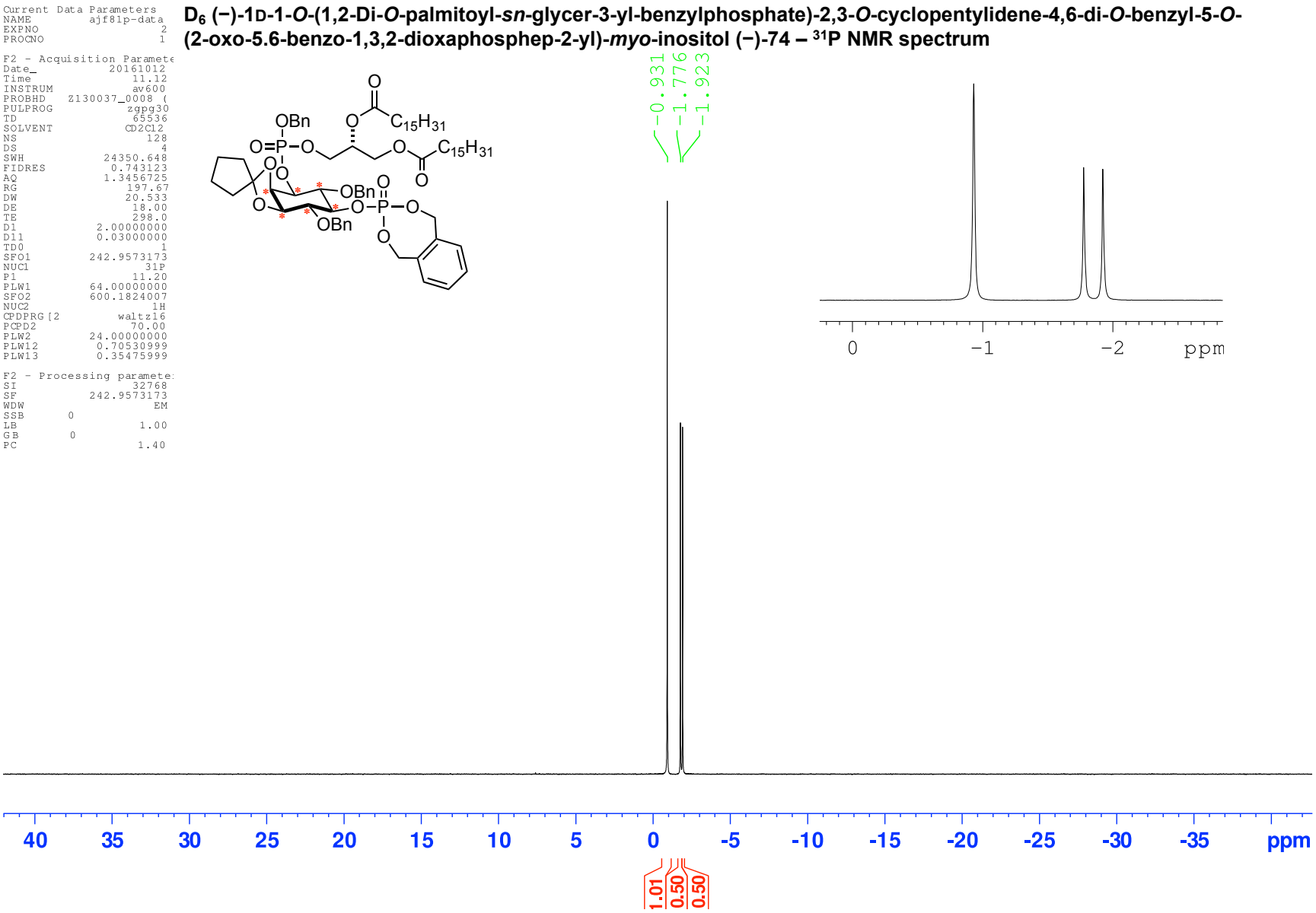




D_6 (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-74 – ^{13}C NMR spectrum



D_6 (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-74 – ^{31}P NMR spectrum



D_6 (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-2,3-*O*-cyclopentylidene-4,6-di-*O*-benzyl-5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-74 – ^{2}H NMR spectrum

```
Current Data Parameters
NAME       ajf81dataDnmr
EXPNO                  2
PROCNO                 1

F2 - Acquisition Paramete
Date_           20161110
Time              10.54
INSTRUM           av600
PROBHD    Z130037_0008 (
PULPROG           zg2h
TD                8192
SOLVENT           CDCl3
NS                 128
DS                   2
SWH           1842.299
FIDRES        0.449780
AQ            2.2233088
RG                60.94
DW               271.400
DE                18.00
TE                298.0
D1           1.00000000
D11          0.03000000
TD0                  1
SFO1         92.1316525
NUC1                2H
P1               378.00
PLW1         1.75000000

F2 - Processing paramete
SI                16384
SF           92.1312845
WDW                  EM
SSB       0
LB                1.00
GB        0
PC                1.00
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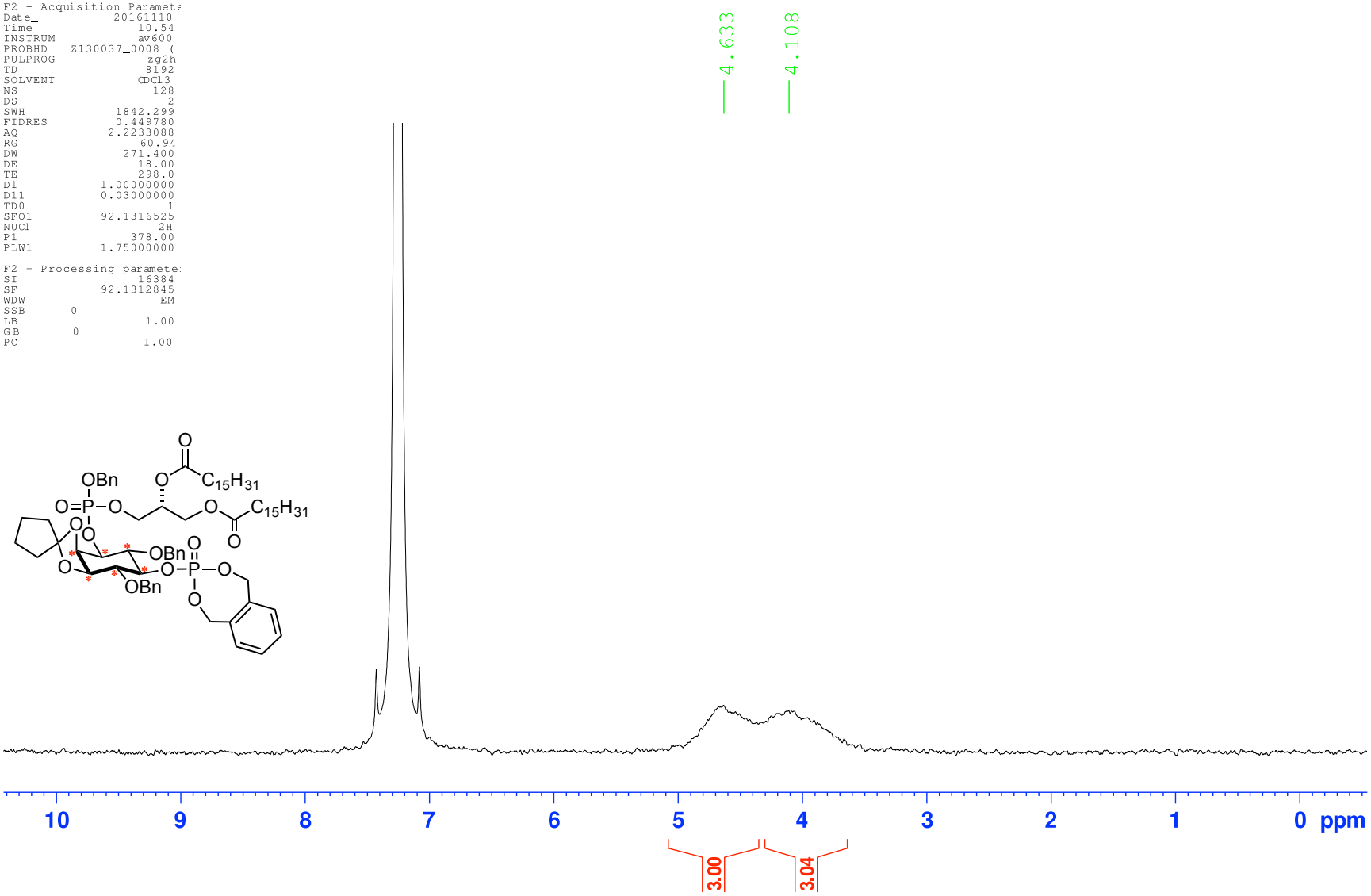
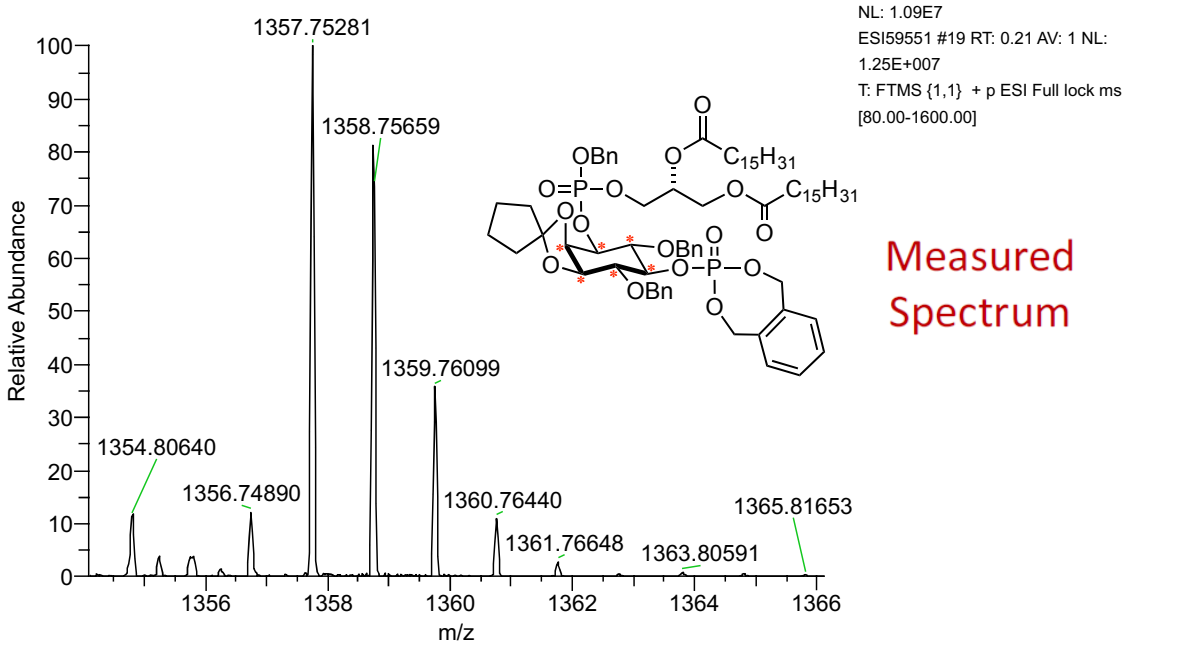
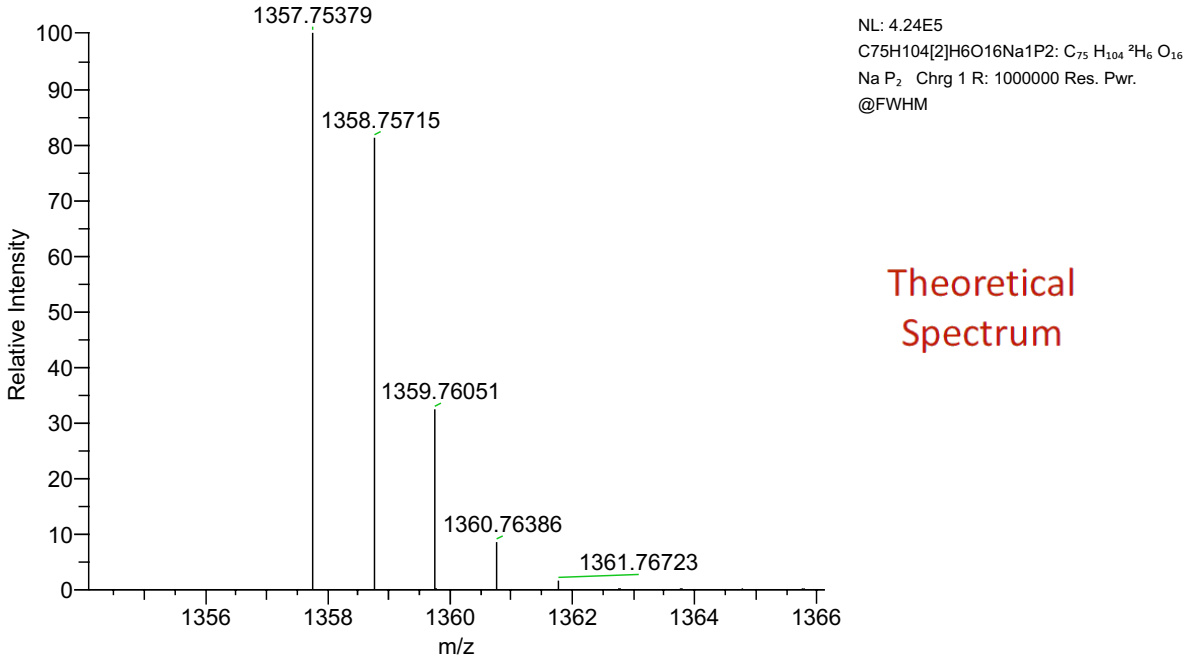


D_6 (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-4,6-di-*O*-benzyl- 5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-74 – Mass spectrum

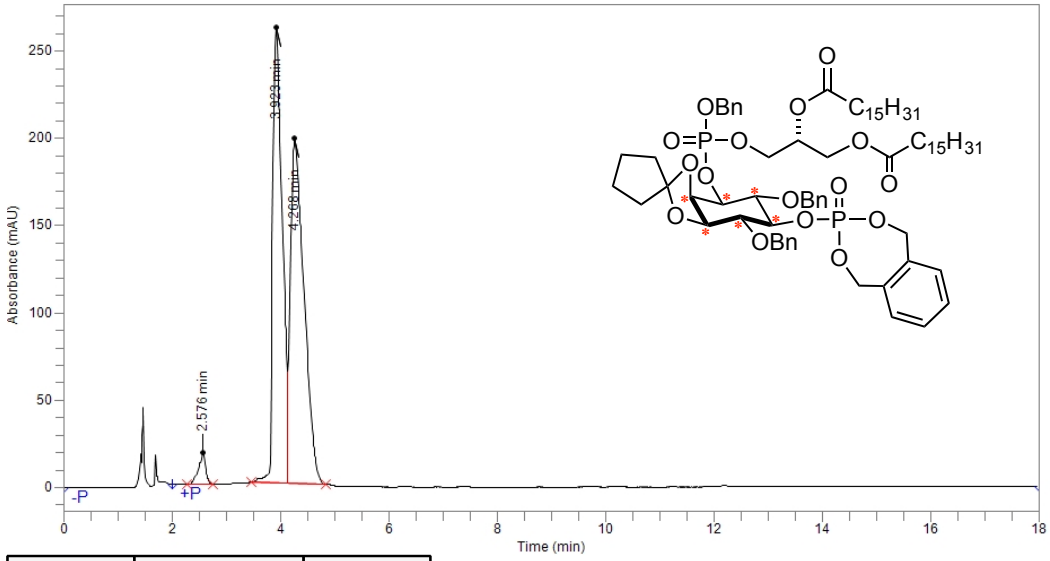
X:\data\Oct 16\ESI59551.raw 25/10/2016 11:13 am





m/z	Formula	RDB	Delta ppm	Theo. Mass
1357.75281	$C_{75}H_{104}{}^{2}H_6O_{16}{}^{23}NaP_2$	21.5	-0.72	1357.75379

D_6 (−)-1D-1-*O*-(1,2-Di-*O*-palmitoyl-*sn*-glycer-3-yl-benzylphosphate)-4,6-di-*O*-benzyl- 5-*O*-(2-oxo-5.6-benzo-1,3,2-dioxaphosphep-2-yl)-*myo*-inositol (−)-74 – NP-HPLC (Method 7)



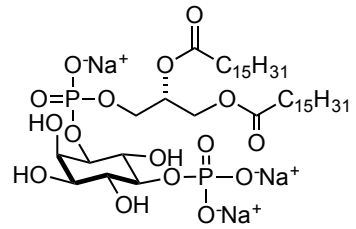
Time	Area	Area %
2.576	163,765	2.40
3.923	3,217,843	47.13
4.268	3,445,914	50.47
Total	6,827,522	100.00

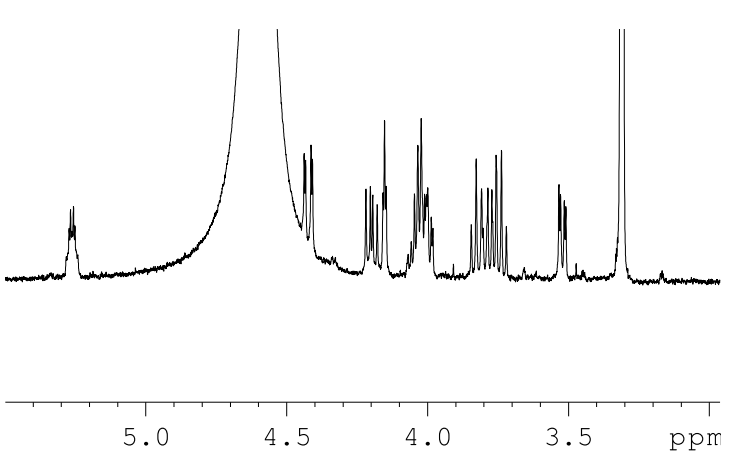
(−)-1D-Dipalmitoyl-phosphatidylinositol 5-phosphate trisodium salt (−)-75 – ^{1}H NMR spectrum

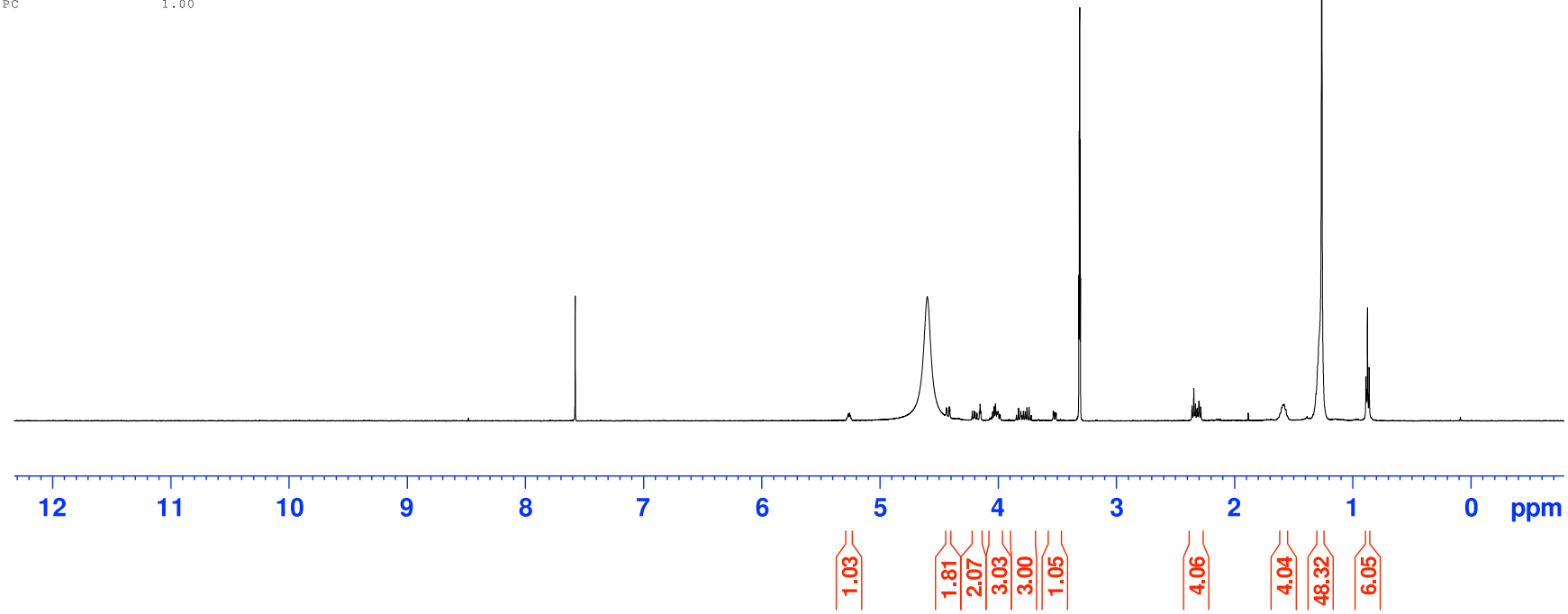
```
Current Data Parameters
NAME      ajfPI(5)P-2data
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20160708
Time              11.37 h
INSTRUM           avx500
PROBHD    Z113652_0208 (
PULPROG             zg60
TD                 65536
SOLVENT             MeOD
NS                    16
DS                     2
SWH           10000.000 Hz
FIDRES            0.305176 Hz
AQ                3.2767999 sec
RG                  106.58
DW                 50.000 usec
DE                  6.50 usec
TE                 298.0 K
D1             1.00000000 sec
TD0                    1
SFO1          500.1325006 MHz
NUC1                  1H
P1                 10.00 usec
PLW1          20.50000000 W

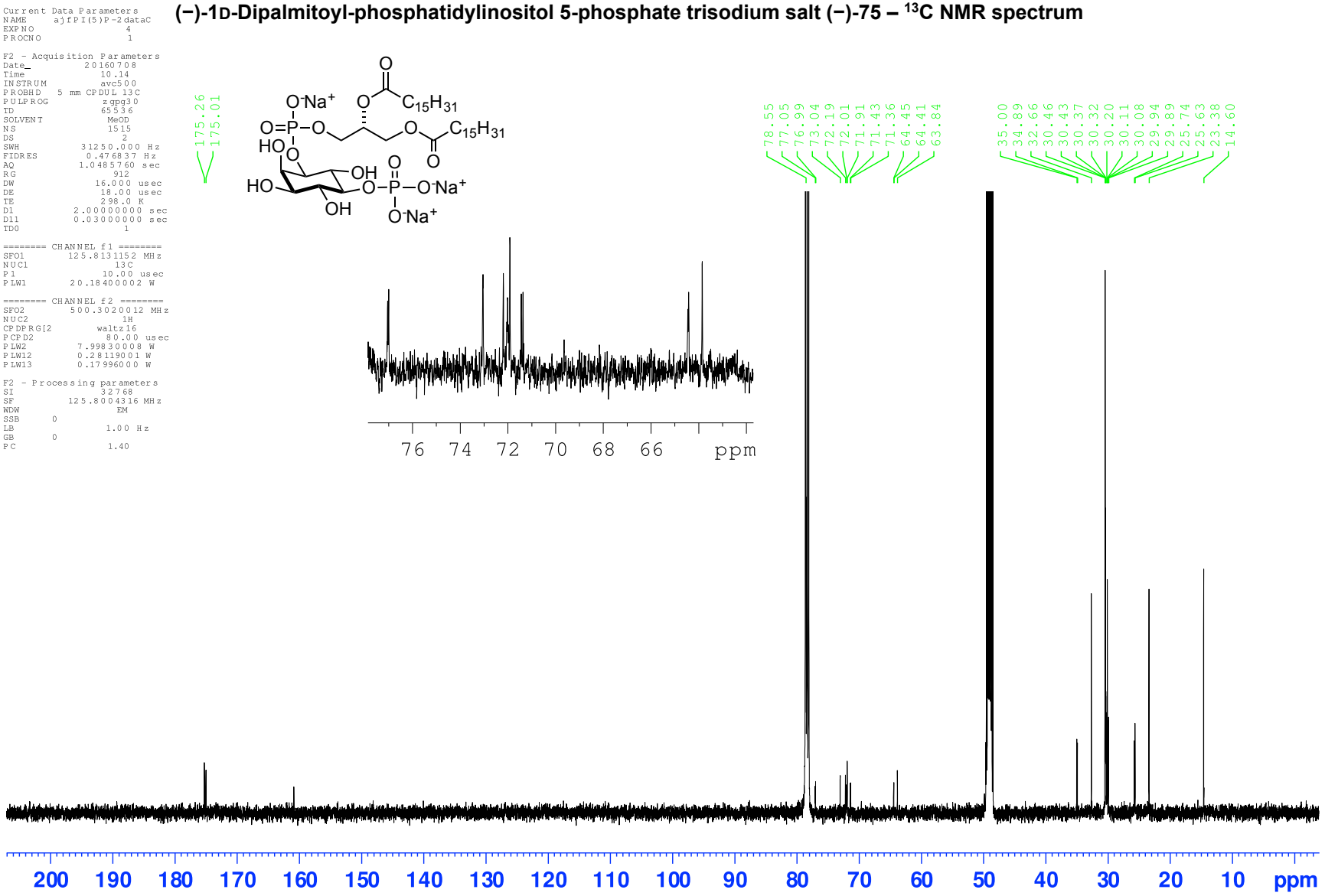
F2 - Processing parameters
SI                 65536
SF            500.1300099 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```







(−)-1D-Dipalmitoyl-phosphatidylinositol 5-phosphate trisodium salt (−)-75 – ^{13}C NMR spectrum



(−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-75 – ^{1}H-^{13}C HSQC

```
Current Data Parameters
NAME      ajfPI(5)P-2dataC
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_           20160708
Time                9.53
INSTRUM           avc500
PROBHD    5 mm CPDUL 13C
PULPROG   hsqcedetgpsp.3
TD                  1024
SOLVENT             MeOD
NS                     2
DS                    16
SWH            2463.054 Hz
FIDRES         2.405326 Hz
AQ            0.2078720 sec
RG                  2050
DW              203.000 usec
DE               10.00 usec
TE               298.0 K
CNST2        145.0000000
D0            0.00000300 sec
D1            0.89452791 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
D21           0.00340000 sec
IN0           0.00002400 sec

======== CHANNEL f1 ========
SFO1         500.3015486 MHz
NUC1                   1H
P1                  15.00 usec
P2                  30.00 usec
P28       0 usec
PLW1          7.99830008 W

======== CHANNEL f2 ========
SFO2         125.8099180 MHz
NUC2                  13C
CPDPRG[2             garp
P3                  10.00 usec
P14                500.00 usec
P31               1900.00 usec
PCPD2               70.00 usec
PLW0       0 W
PLW2         20.18400002 W
PLW12         0.41192001 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3               0.500
SPOFFS3   0 Hz
SPW3          3.08389997 W
SPNAM[18  Crp60_xfilt.2
SPOAL18              0.500
SPOFFS18 0 Hz
SPW18          0.73894000 W

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPNAM[2]         SINE.100
GPZ1                80.00 %
GPZ2                20.10 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                   256
SFO1            125.8099 MHz
FIDRES         81.380211 Hz
SW               165.594 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           500.2999982 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                  1.40

F1 - Processing parameters
SI                   512
MC2        echo-antiecho
SF           125.8004291 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
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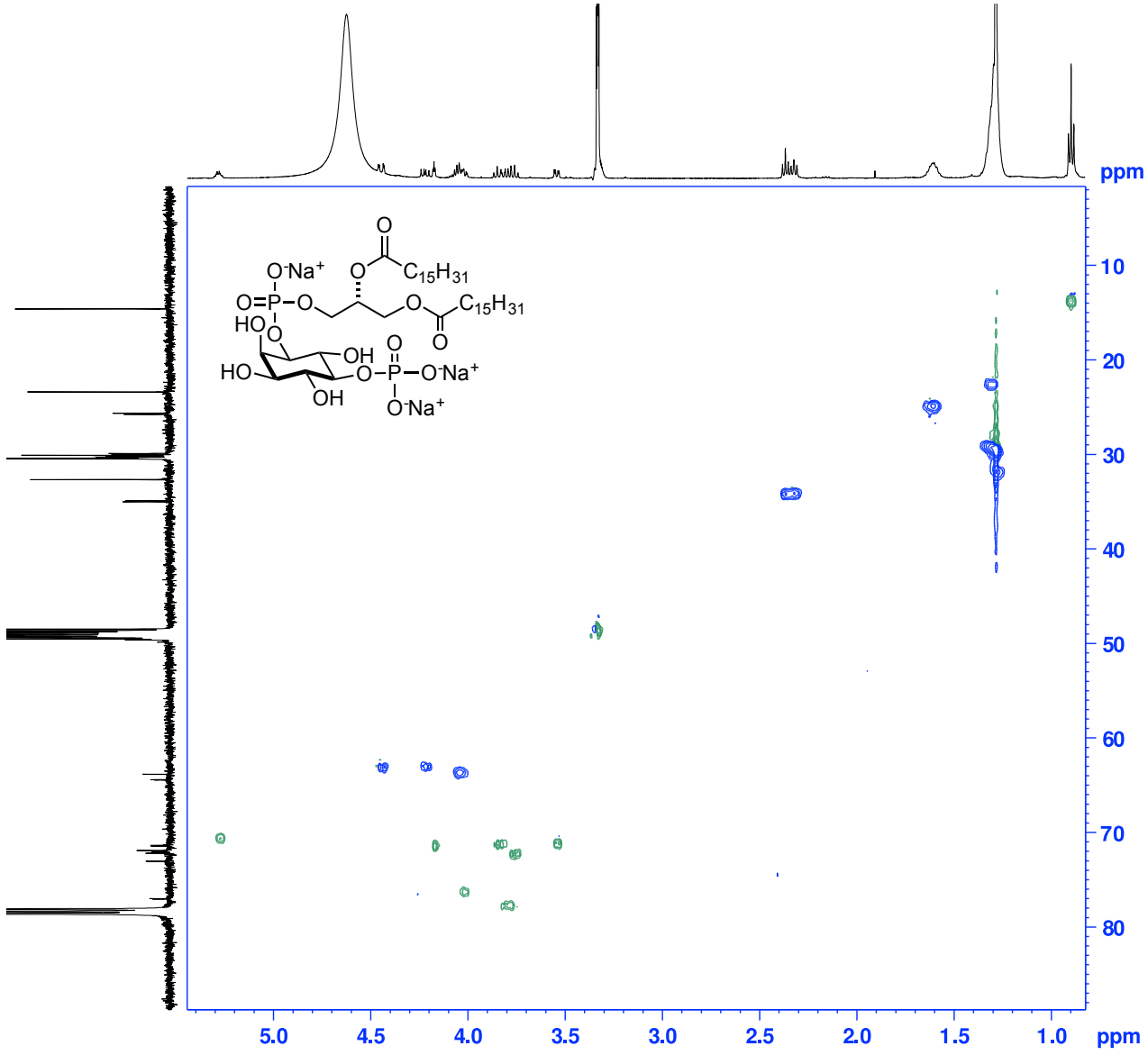

(−)-1D-Dipalmitoyl-phosphatidylinositol 5-phosphate trisodium salt (−)-75 – ^{31}P NMR spectrum

```
Current Data Parameters
NAME      ajfPI(5)P-2data
EXPNO                    2
PROCNO                   1

F2 - Acquisition Paramete
Date_             20160708
Time                 11.35
INSTRUM             avx500
PROBHD    Z113652_0208 (
PULPROG             zgpg30
TD                   65536
SOLVENT               MeOD
NS                      16
DS                       4
SWH              20161.291
FIDRES           0.615274
AQ               1.6252928
RG                  191.37
DW                  24.800
DE                    6.50
TE                  298.1
D1             2.00000000
D11            0.03000000
TD0                      1
SFO1           202.4563350
NUC1                   31P
P1                   14.00
PLW1           38.20000076
SFO2           500.1320005
NUC2                   1H
CPDPRG[2           waltz16
PCPD2                80.00
PLW2           20.50000000
PLW12          0.32031000
PLW13          0.16111000

F2 - Processing paramete
SI                   32768
SF              202.4563350
WDW                     EM
SSB       0
LB                    1.00
GB        0
PC                    1.40
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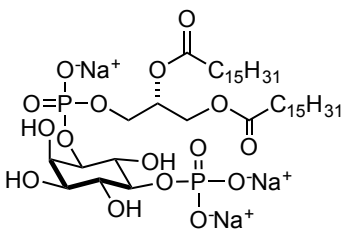
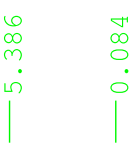
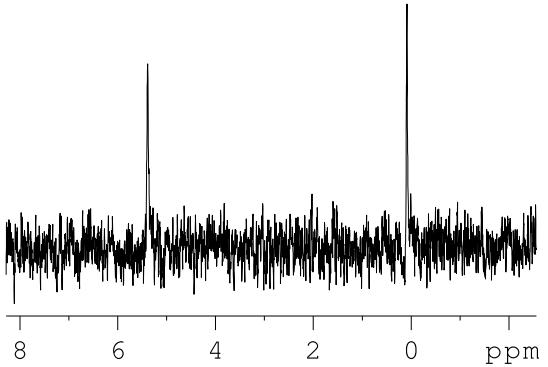
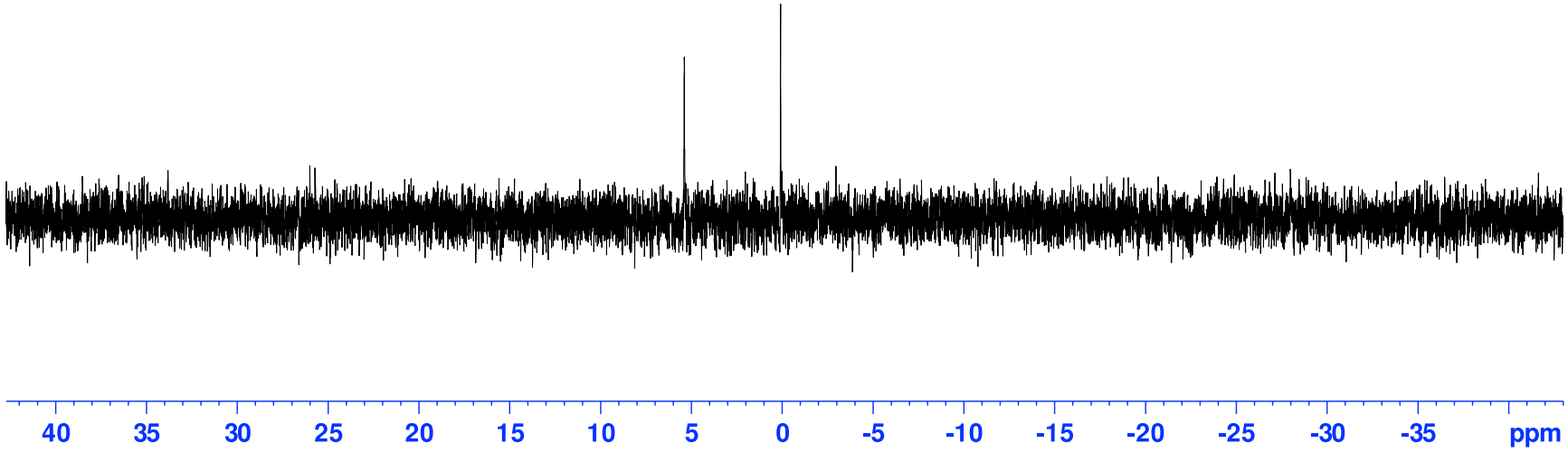
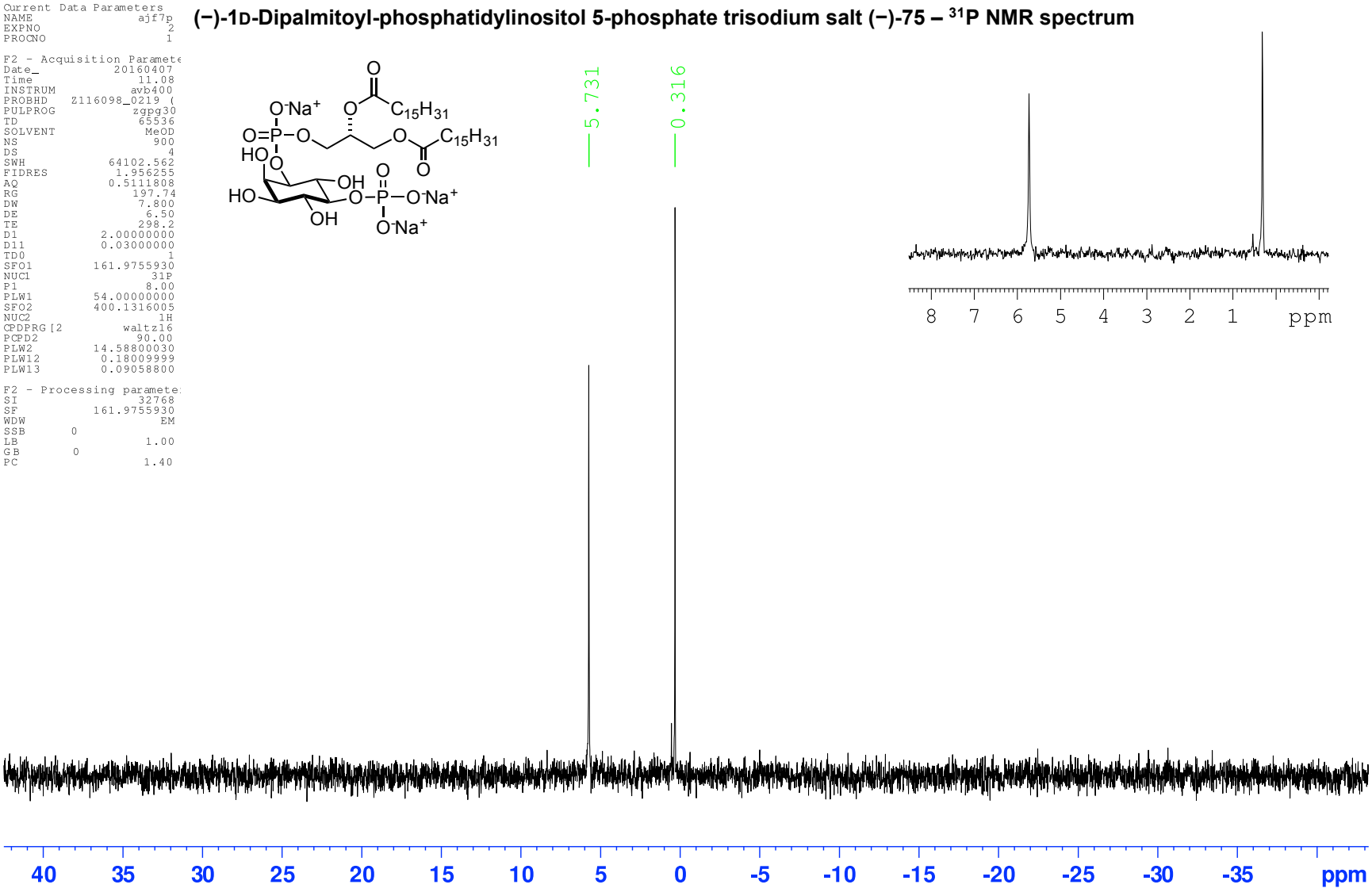








(−)-1D-Dipalmitoyl-phosphatidylinositol 5-phosphate trisodium salt (−)-75 – ^{31}P NMR spectrum



(−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-75 – ^{1}H-^{31}P HMBC

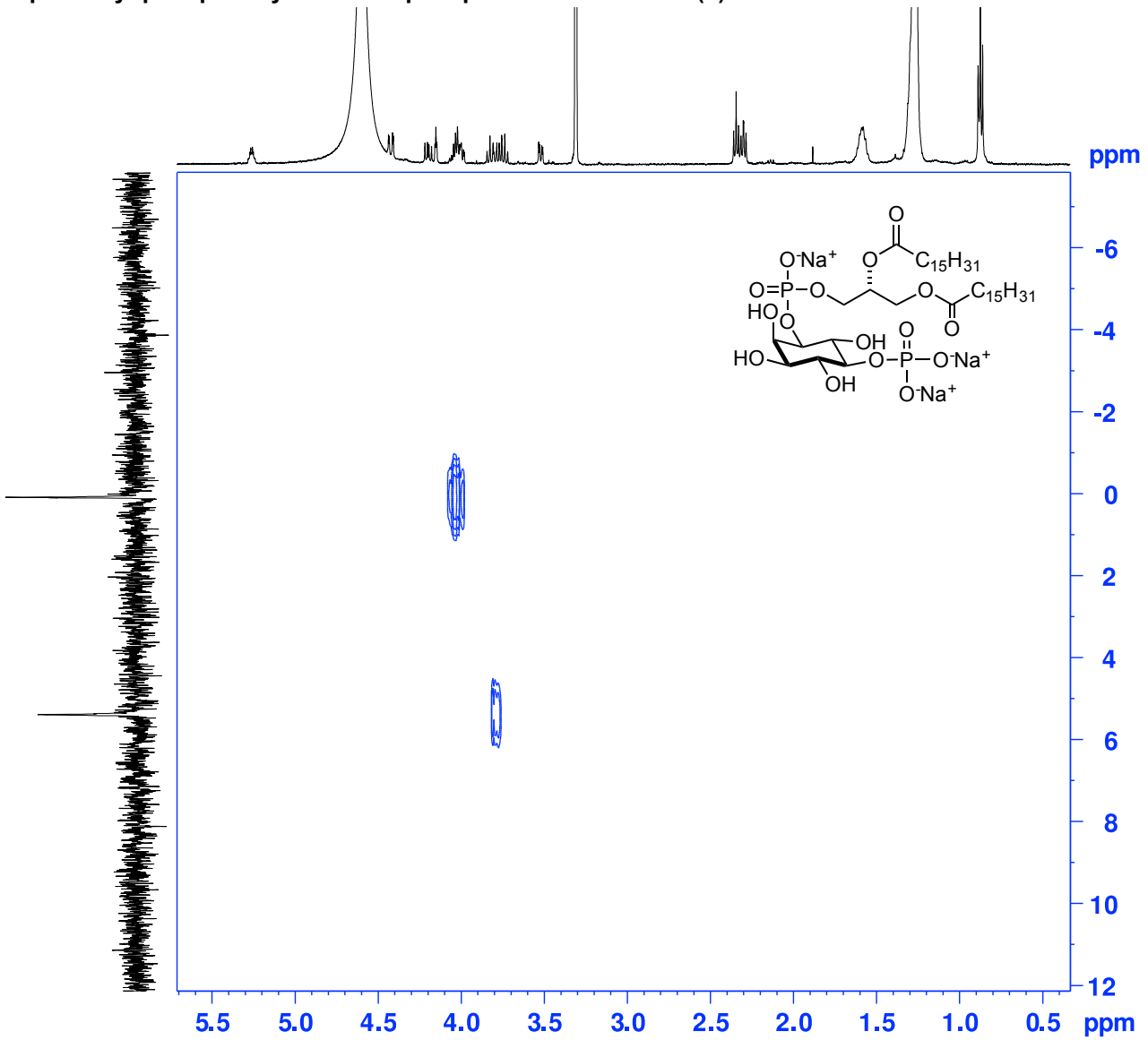
```
Current Data Parameters
NAME      ajfPI(5)P-2data
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_          20160708
Time              11.43
INSTRUM         avx500
PROBHD   Z113652_0208 (
PULPROG      hmbcgpndqf
TD                 4096
SOLVENT            MeOD
NS                    2
DS                   16
SWH            6009.615 Hz
FIDRES          1.467191 Hz
AQ             0.3407872 sec
RG                63.22
DW               83.200 usec
DE                6.50 usec
TE                298.0 K
CNST13         8.0000000
d0            0.00000300 sec
D1            2.00000000 sec
d6            0.06250000 sec
D16           0.00020000 sec
in0       0 sec
ST1CNT                 0
d0orig        0.00000300 sec
ph1loop                0
tlloop                 0
SFO1         500.1323506 MHz
NUC1                  1H
P1                10.00 usec
p2                20.00 usec
PLW1         20.50000000 W
SFO2         202.4563350 MHz
NUC2                 31P
P3                14.00 usec
PLW2         38.20000076 W
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1              70.00 %
GPZ2              30.00 %
GPZ3              80.50 %
P16             1000.00 usec

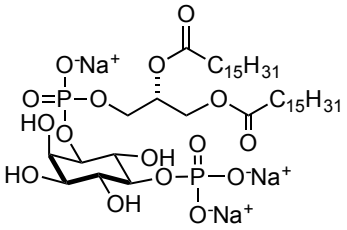
F1 - Acquisition parameters
TD                   128
SFO1            202.4563 MHz
FIDRES         79.073883 Hz
SW               49.993 ppm
FnMODE                QF

F2 - Processing parameters
SI                  2048
SF           500.1300059 MHz
WDW                 SINE
SSB                    4
LB        0 Hz
GB        0
PC                  1.00

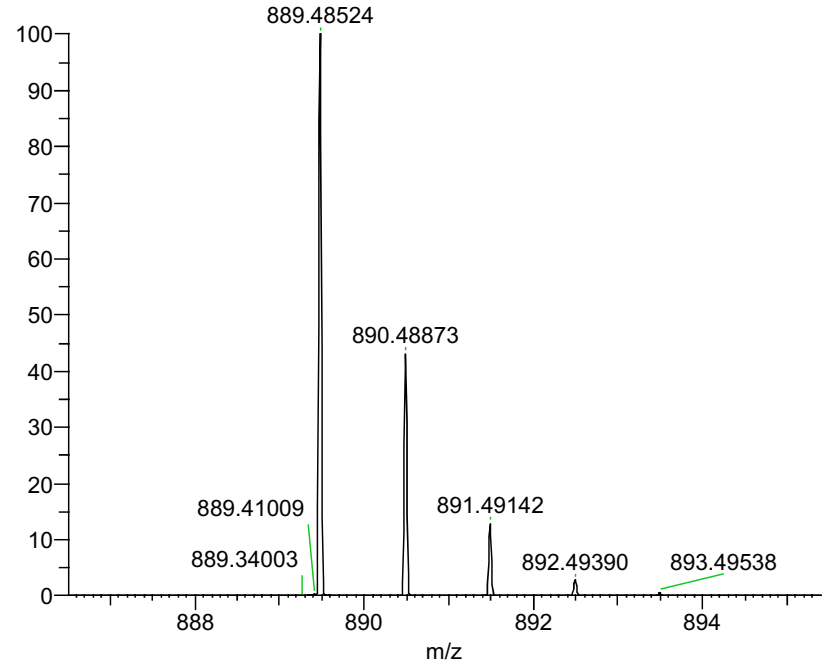
F1 - Processing parameters
SI                  1024
MC2                   QF
SF           202.4563350 MHz
WDW                QSINE
SSB       0
LB        0 Hz
GB        0
```



(−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-75 – Mass Spectrum

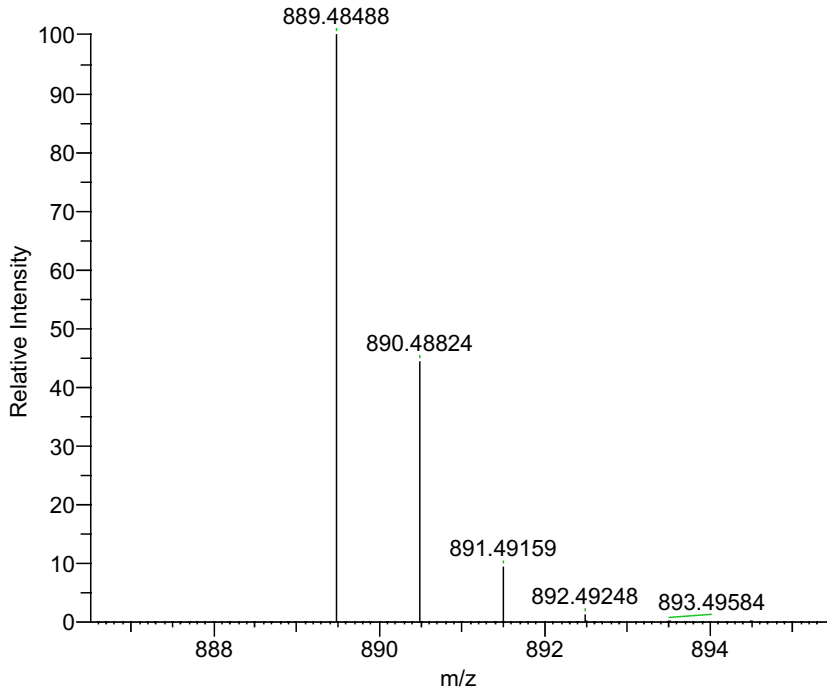


W:\data\July 16\MSS182.raw 21/07/2016 12:30 pm



NL: 1.65E6
MSS182 #13-28 RT: 0.16-0.32 AV: 8 NL: 2.57E7
T: FTMS {1,2} - p ESI Full ms [80.00-1600.00]

Measured Spectrum



NL: 6.13E5
C41H79O16P2: $C_{41}H_{79}O_{16}P_2$ Chrg -1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

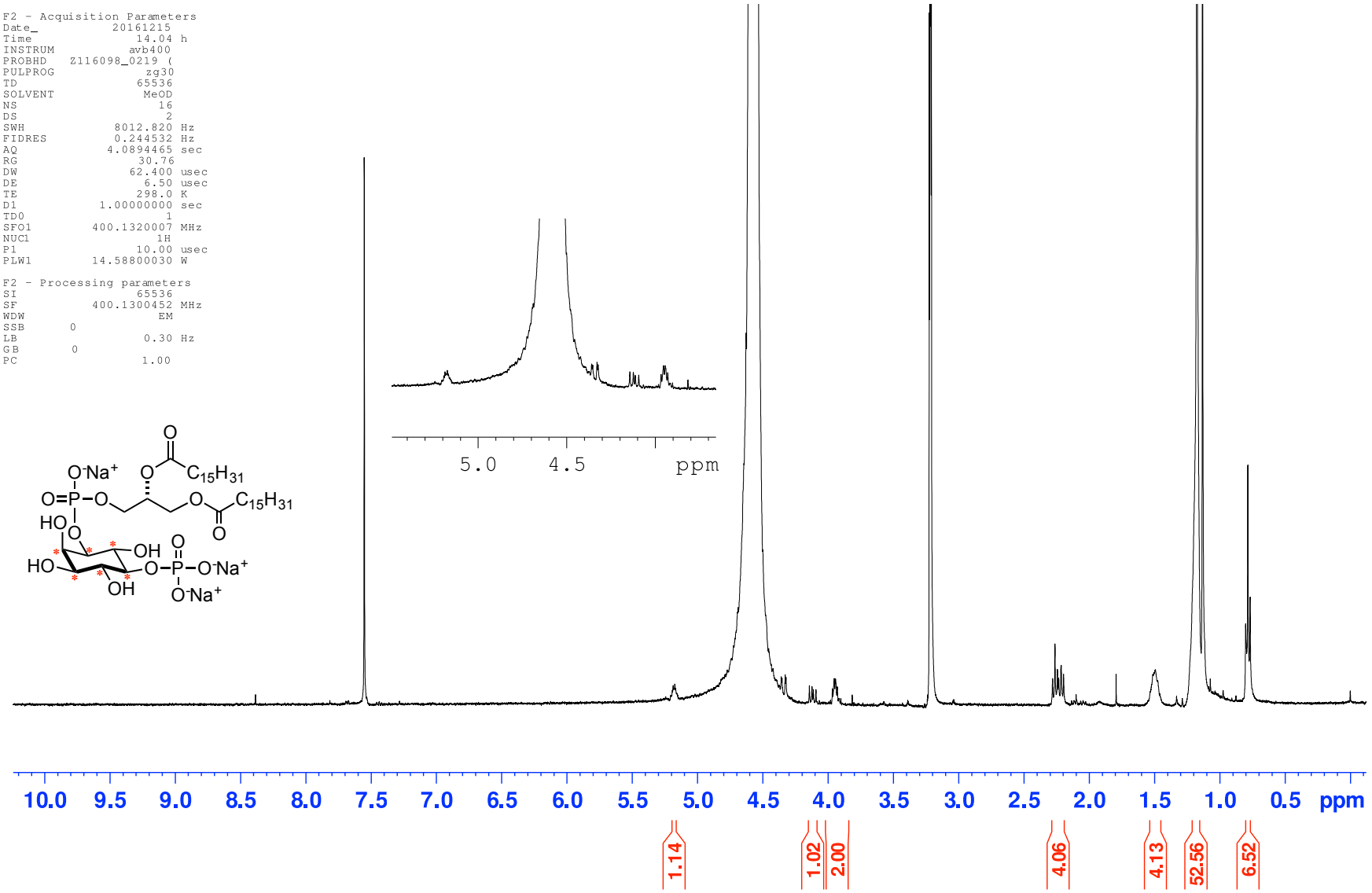
m/z	Formula	RDB	Delta ppm	Theo. Mass
889.48523	$C_{41}H_{79}O_{16}P_2$	3.5	0.39	889.48488

D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-76 – ^{1}H NMR spectrum

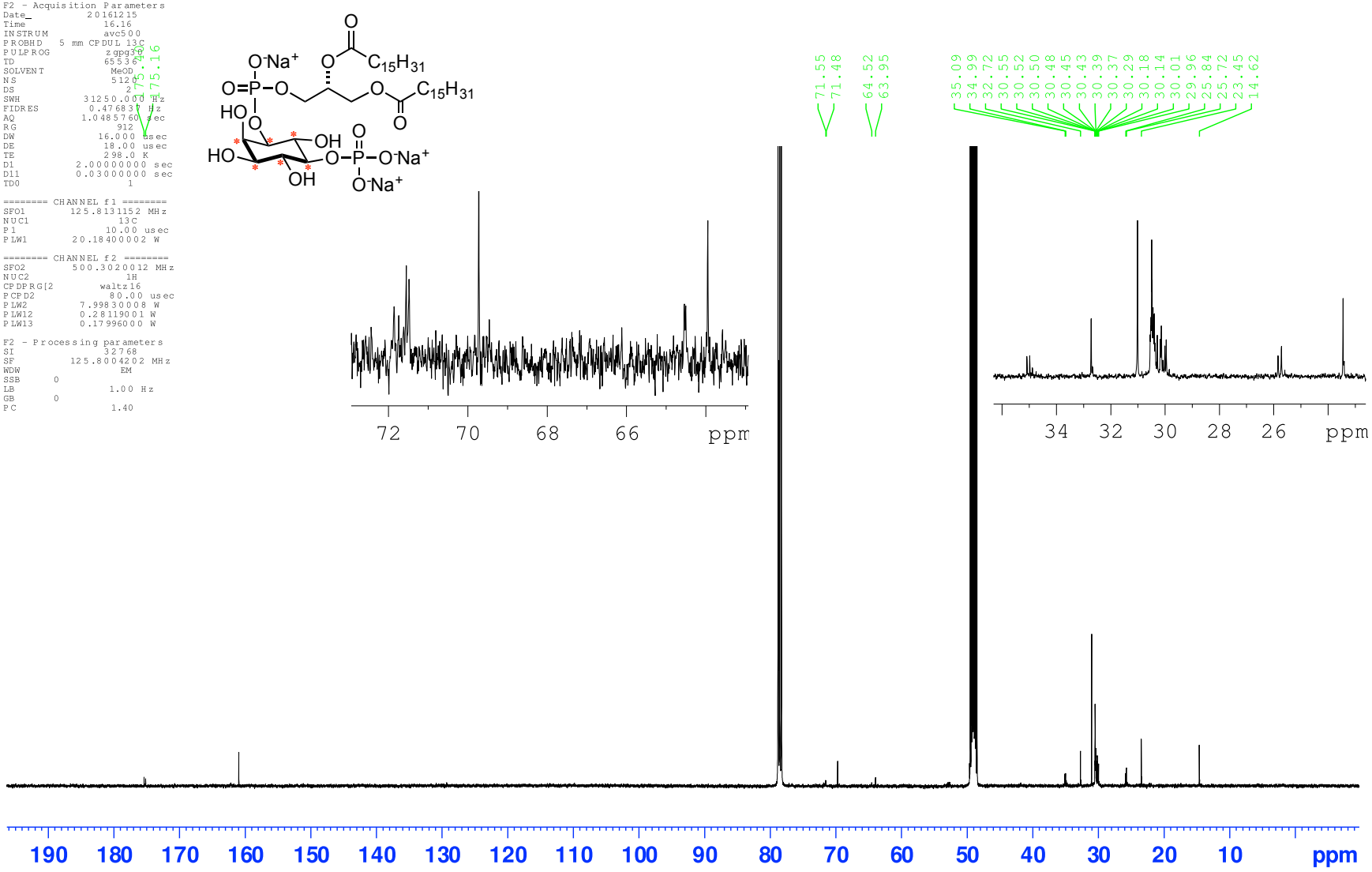
```
Current Data Parameters
NAME                 ajg44p
EXPNO                     3
PROCNO                    1

F2 - Acquisition Parameters
Date_              20161215
Time                 14.04 h
INSTRUM              avb400
PROBHD    Z116098_0219 (
PULPROG                zg30
TD                    65536
SOLVENT                MeOD
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                 4.0894465 sec
RG                     30.76
DW                    62.400 usec
DE                     6.50 usec
TE                    298.0 K
D1              1.00000000 sec
TD0                       1
SFO1           400.1320007 MHz
NUC1                     1H
P1                    10.00 usec
PLW1           14.58800030 W

F2 - Processing parameters
SI                    65536
SF             400.1300452 MHz
WDW                      EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
```



D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-76 – ^{13}C NMR spectrum



D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-76 – ^{1}H-^{13}C HSQC spectrum

```
Current Data Parameters
NAME      ajg44p-PI(5)Pdata
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20161215
Time               14.33
INSTRUM          avc500
PROBHD    5 mm CPDUL 13C
PULPROG   hsqcedetgpsp.3
TD                 1024
SOLVENT            MeOD
NS                   16
DS                   16
SWH            5000.000 Hz
FIDRES         4.882812 Hz
AQ            0.1024000 sec
RG                 2050
DW              100.000 usec
DE               10.00 usec
TE               298.0 K
CNST2       145.0000000
D0            0.00000300 sec
D1            1.00000000 sec
D4            0.00172414 sec
D11           0.03000000 sec
D16           0.00020000 sec
D21           0.00340000 sec
IN0           0.00001990 sec

======== CHANNEL f1 ========
SFO1         500.3025015 MHz
NUC1               1H
P1                15.00 usec
P2                30.00 usec
P28       0 usec
PLW1          7.99830008 W

======== CHANNEL f2 ========
SFO2         125.8131151 MHz
NUC2               13C
CPDPRG[2           garp
P3                10.00 usec
P14              500.00 usec
P31             1900.00 usec
PCPD2             70.00 usec
PLW0      0 W
PLW2         20.18400002 W
PLW12         0.41192001 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3             0.500
SPOFFS3   0 Hz
SPW3          3.08389997 W
SPNAM[18  Crp60_xfilt.2
SPOAL18            0.500
SPOFFS18 0 Hz
SPW18         0.73894000 W

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                  256
SFO1           125.8131 MHz
FIDRES         98.146988 Hz
SW             199.706 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                 1024
SF           500.3000581 MHz
WDW                QSINE
SSB                   2
LB        0 Hz
GB        0
PC                 1.40

F1 - Processing parameters
SI                  512
MC2        echo-antiecho
SF           125.8004232 MHz
WDW                QSINE
SSB                   2
LB        0 Hz
GB        0
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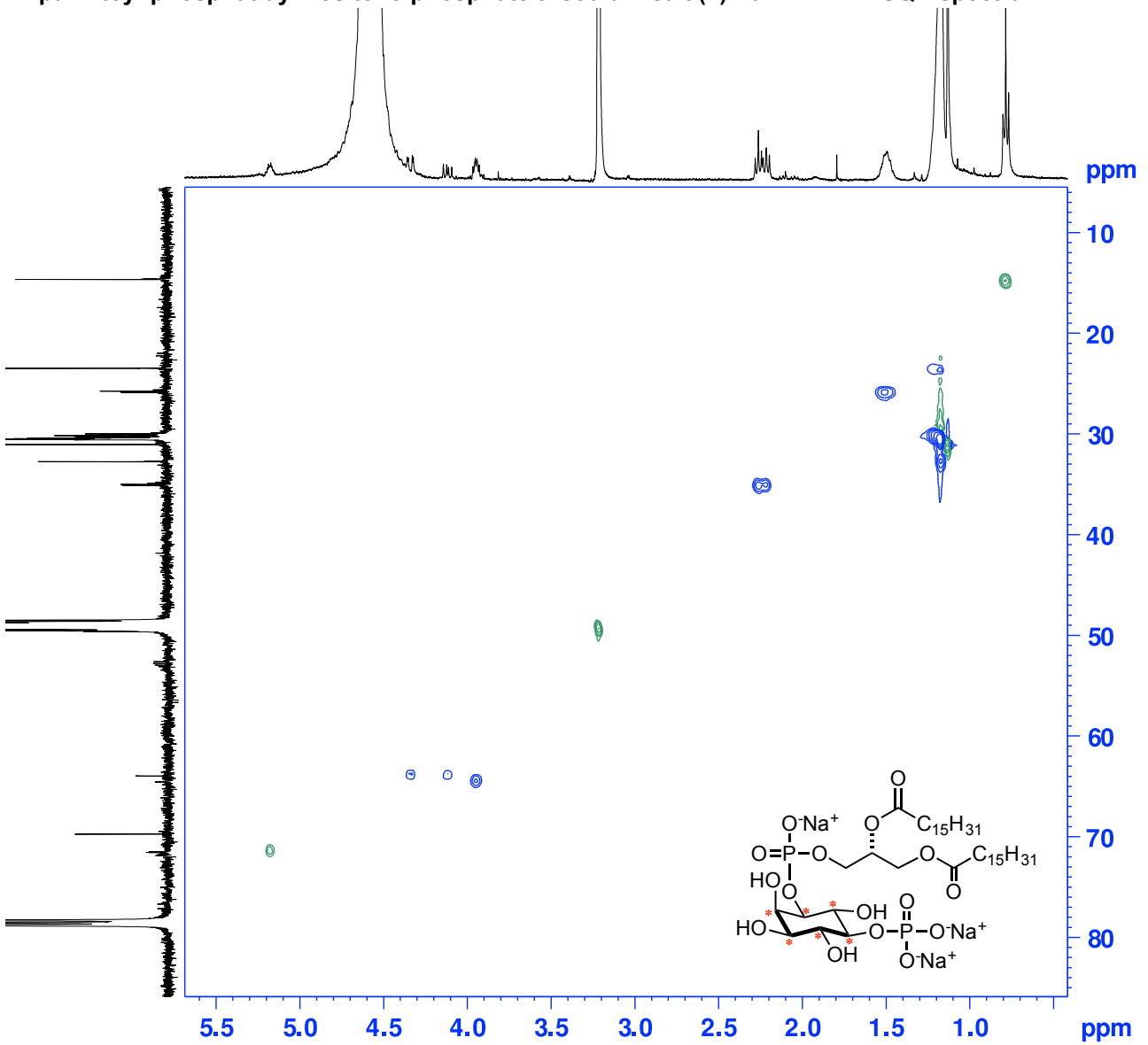
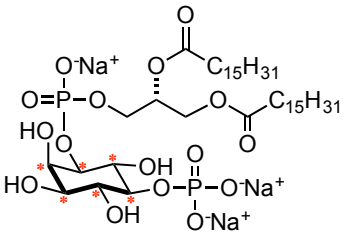


D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-76 – ^{31}P NMR spectrum

```
Current Data Parameters
NAME                 ajg44p
EXPNO                     1
PROCNO                    1

F2 - Acquisition Paramete
Date_             20161215
Time                 13.51
INSTRUM              avb400
PROBHD    Z116098_0219 (
PULPROG              zgpg30
TD                    65536
SOLVENT                MeOD
NS                      120
DS                        4
SWH                64102.562
FIDRES              1.956255
AQ                  0.5111808
RG                     197.74
DW                      7.800
DE                      6.50
TE                     298.1
D1                2.00000000
D11               0.03000000
TD0                       1
SFO1            161.9674942
NUC1                    31P
P1                     8.00
PLW1            54.00000000
SFO2            400.1316005
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                 90.00
PLW2            14.58800030
PLW12            0.18009999
PLW13            0.09058800

F2 - Processing paramete
SI                    32768
SF              161.9755930
WDW                       EM
SSB         0
LB                     1.00
GB          0
PC                     1.40
```



D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-76 – ^{1}H-^{31}P HMBC spectrum

```
Current Data Parameters
NAME             ajg44p
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20161215
Time              13.53
INSTRUM           avb400
PROBHD   Z116098_0219 (
PULPROG      hmbcgpndqf
TD                 2048
SOLVENT            MeOD
NS                    3
DS                   16
SWH            4795.396 Hz
FIDRES          2.341502 Hz
AQ             0.2135381 sec
RG                197.74
DW              104.267 usec
DE                6.50 usec
TE                298.0 K
CNST13         8.0000000
d0            0.00000300 sec
D1            1.50000000 sec
d6            0.06250000 sec
D16           0.00020000 sec
in0       0 sec
ST1CNT                0
d0orig        0.00000300 sec
ph1loop               0
t1loop                0
SFO1         400.1320007 MHz
NUC1                 1H
P1                10.00 usec
p2                20.00 usec
PLW1         14.58800030 W
SFO2         161.9755930 MHz
NUC2                31P
P3                 8.00 usec
PLW2         53.95100021 W
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPNAM[3]      SMSQ10.100
GPZ1              70.00 %
GPZ2              30.00 %
GPZ3              80.50 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                  102
SFO1           161.9756 MHz
FIDRES        218.837540 Hz
SW             137.807 ppm
FnMODE                QF

F2 - Processing parameters
SI                 1024
SF          400.1300446 MHz
WDW                SINE
SSB       0
LB        0 Hz
GB        0
PC                 1.40

F1 - Processing parameters
SI                 1024
MC2                  QF
SF          161.9755849 MHz
WDW                SINE
SSB       0
LB        0 Hz
GB        0
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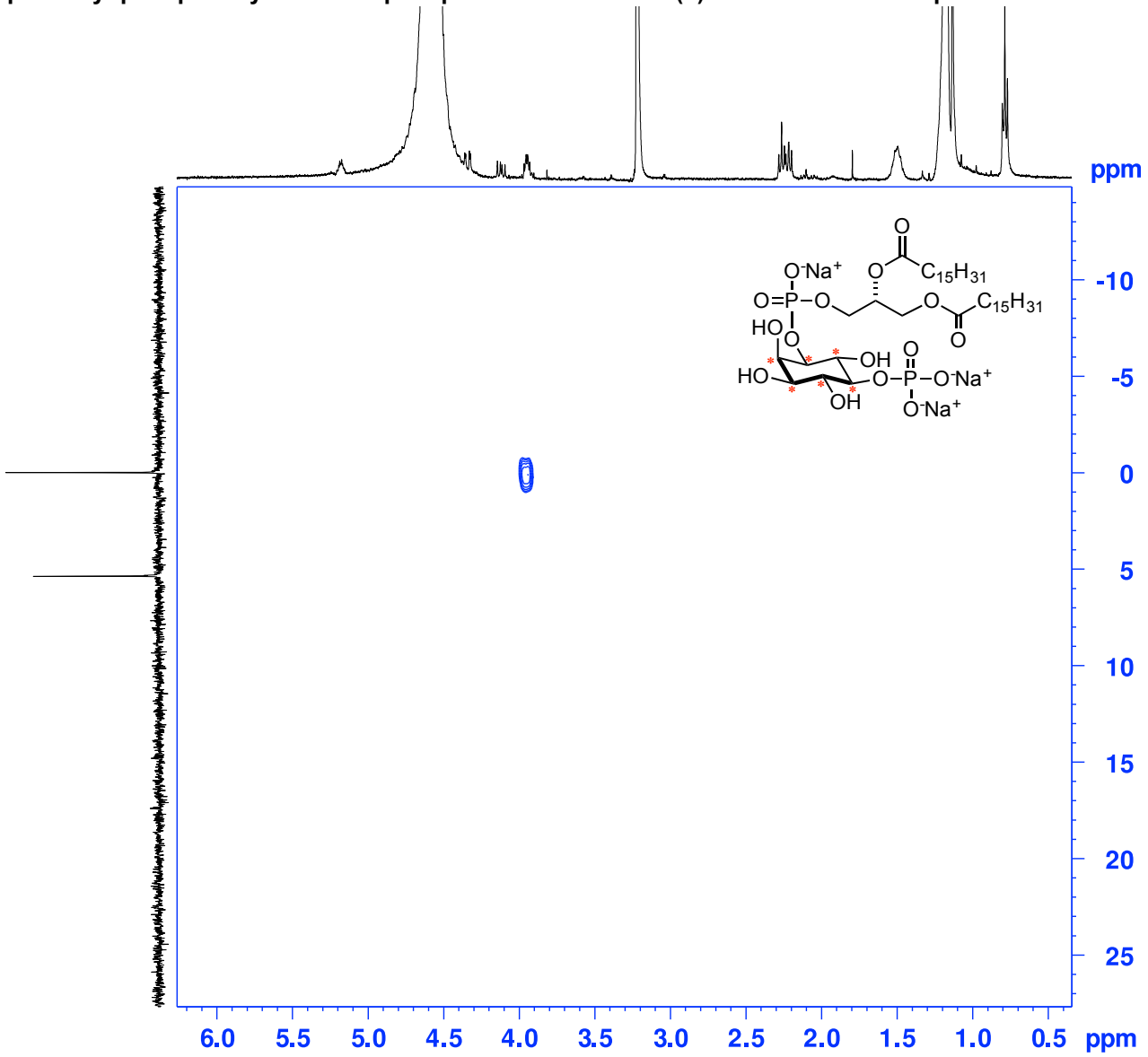
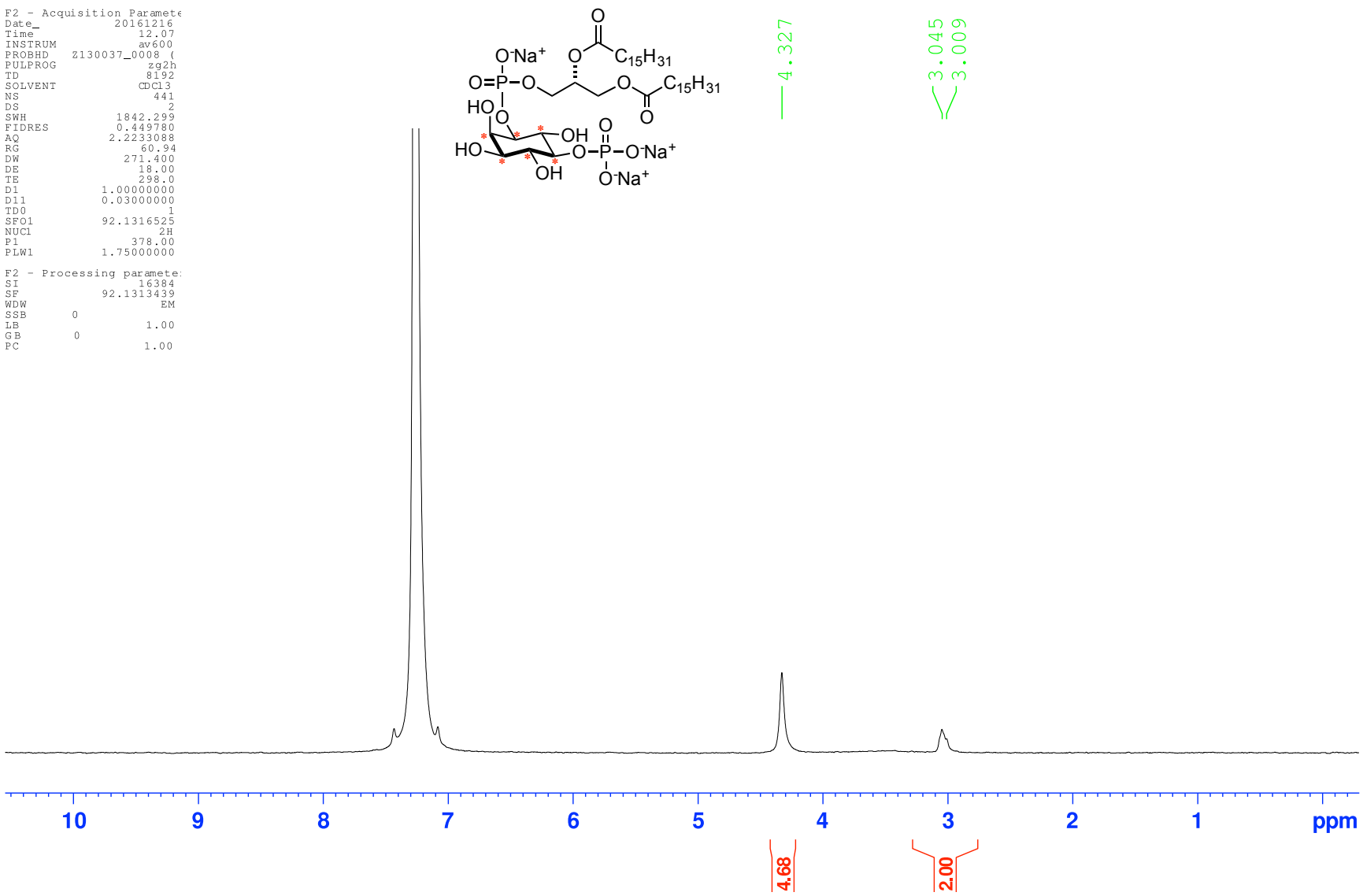
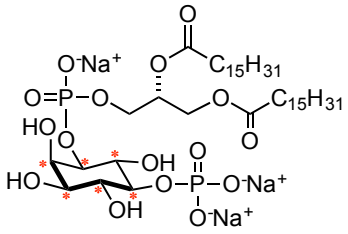


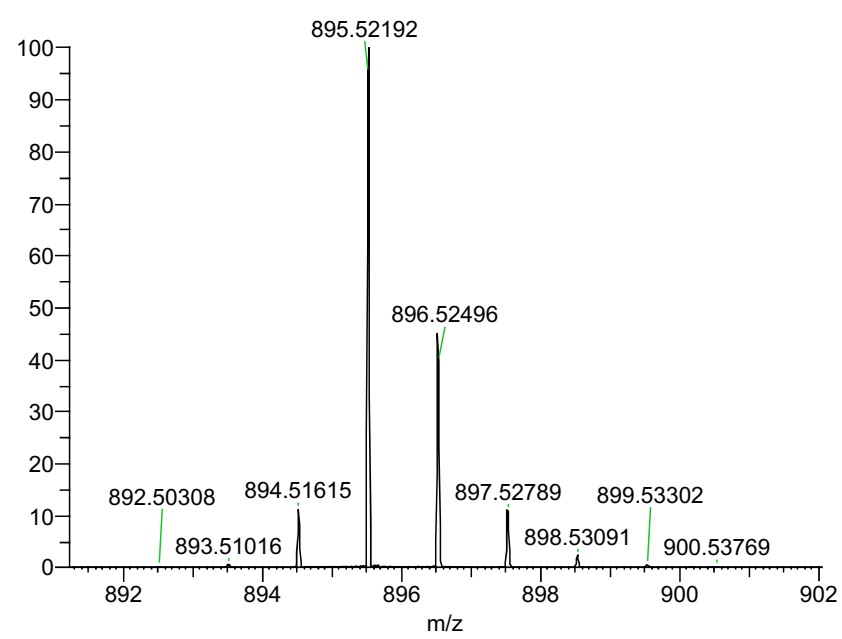
D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-76 – ^2H NMR spectrum



D_6 (−)-1D-Dipalmitoyl-phosphatidylinositol-5-phosphate trisodium salt (−)-76 – Mass spectrum

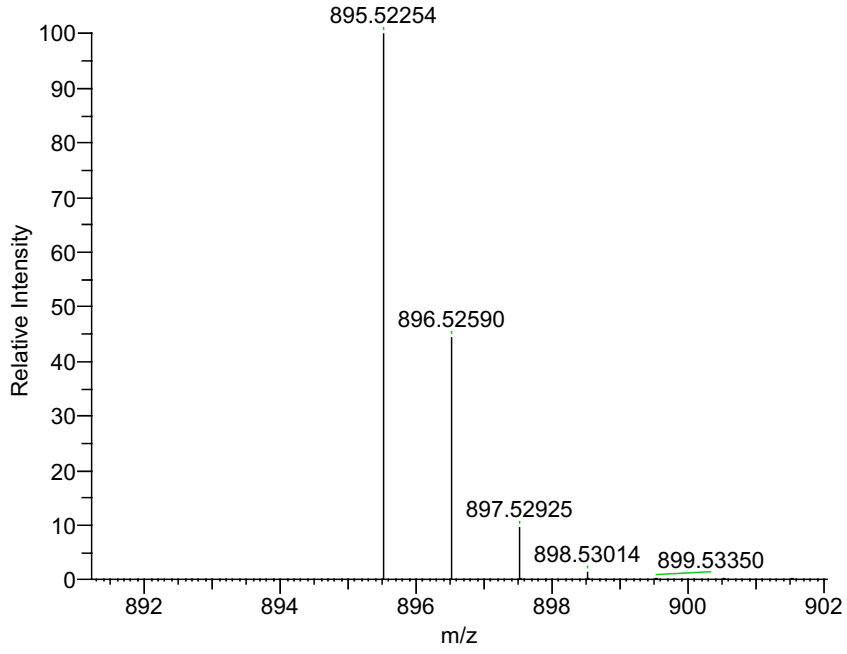


S:\data\Dec 16\ESI59993.raw 06/12/2016 12:32 pm



NL: 6.92E6
ESI59993 #11-24 RT: 0.13-0.27 AV: 7 NL: 6.92E6
T: FTMS {1,2} - p ESI Full ms [80.00-1600.00]

Measured Spectrum



NL: 6.14E5
C41H73[2]H6O16P2: $C_{41}H_{73}{}^{2}H_{6}O_{16}P_{2}$
Chrg -1 R: 1000000 Res. Pwr. @FWHM

Theoretical Spectrum

m/z	Formula	RDB	Delta ppm	Theo. Mass
895.52191	$C_{41}H_{73}{}^{2}H_{6}O_{16}P_{2}$	3.5	-0.7	895.52254

9 X-ray Crystallography data

D_6 *myo*-Inositol orthoformate 12

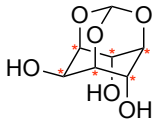


Table 1. Crystal data and structure refinement for 6558.

Identification code	6558	
Empirical formula	C7 H4 D6 O6	
Formula weight	196.19	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 12.1157(4) Å	α= 90°.
	b = 6.1134(2) Å	β= 90°.
	c = 9.9700(3) Å	γ = 90°.
Volume	738.46(4) $Å^3$	
Z	4	
Density (calculated)	1.765 Mg/m^3	
Absorption coefficient	1.332 mm^{-1}	
F(000)	400	
Crystal size	0.38 x 0.20 x 0.12 mm^3	
Theta range for data collection	7.311 to 76.931°.	
Index ranges	-14<=h<=15, -7<=k<=7, -11<=l<=12	
Reflections collected	6213	
Independent reflections	1449 [R(int) = 0.021]	
Completeness to theta = 76.931°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.85 and 0.77	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1447 / 1 / 119	
Goodness-of-fit on F^2	1.0267	
Final R indices [I>2sigma(I)]	R1 = 0.0309, wR2 = 0.0816	
R indices (all data)	R1 = 0.0310, wR2 = 0.0816	
Absolute structure parameter	0.06(15)	
Largest diff. peak and hole	0.30 and -0.20 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 6558. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5497(1)	-661(2)	2772(2)	15
C(2)	6389(1)	-625(2)	3848(2)	17
C(3)	7459(1)	391(2)	3318(2)	17
C(4)	7196(1)	2716(2)	2872(2)	17
C(5)	6308(1)	2770(2)	1787(2)	17
C(6)	5273(1)	1707(2)	2367(2)	16
O(7)	6008(1)	728(2)	4950(1)	19
O(8)	6761(1)	3868(2)	4025(2)	22
O(9)	4956(1)	2911(2)	3551(2)	21
C(10)	5800(1)	2866(2)	4510(2)	20
O(11)	4523(1)	-1724(2)	3215(2)	25
O(12)	7865(1)	-810(2)	2200(2)	25
O(13)	6640(1)	1737(2)	570(2)	20
D(11)	5781	-1486	1996	15
D(21)	6524	-2121	4177	18
D(31)	8009	438	4025	21
D(41)	7867	3479	2583	22
D(51)	6136	4324	1578	20
D(61)	4656	1767	1729	19

Table 3. Bond lengths [Å] and angles [°] for 6558.

C(1)-C(2)	1.5223(19)	C(3)-C(2)-O(7)	107.40(10)
C(1)-C(6)	1.5273(18)	C(1)-C(2)-D(21)	109.814
C(1)-O(11)	1.4174(16)	C(3)-C(2)-D(21)	110.576
C(1)-D(11)	0.986	O(7)-C(2)-D(21)	109.234
C(2)-C(3)	1.5309(18)	C(2)-C(3)-C(4)	107.62(10)
C(2)-O(7)	1.4509(16)	C(2)-C(3)-O(12)	110.69(11)
C(2)-D(21)	0.985	C(4)-C(3)-O(12)	108.97(11)
C(3)-C(4)	1.5229(19)	C(2)-C(3)-D(31)	110.073
C(3)-O(12)	1.4231(17)	C(4)-C(3)-D(31)	109.178
C(3)-D(31)	0.971	O(12)-C(3)-D(31)	110.242
C(4)-C(5)	1.5263(18)	C(3)-C(4)-C(5)	111.98(11)
C(4)-O(8)	1.4476(17)	C(3)-C(4)-O(8)	107.33(11)
C(4)-D(41)	0.980	C(5)-C(4)-O(8)	107.23(11)
C(5)-C(6)	1.5265(18)	C(3)-C(4)-D(41)	110.894
C(5)-O(13)	1.4260(18)	C(5)-C(4)-D(41)	111.493
C(5)-D(51)	0.995	O(8)-C(4)-D(41)	107.669
C(6)-O(9)	1.4435(17)	C(4)-C(5)-C(6)	107.57(11)
C(6)-D(61)	0.981	C(4)-C(5)-O(13)	113.25(11)
O(7)-C(10)	1.4014(18)	C(6)-C(5)-O(13)	111.46(11)
O(8)-C(10)	1.4018(17)	C(4)-C(5)-D(51)	108.440
O(9)-C(10)	1.4007(19)	C(6)-C(5)-D(51)	108.312
C(10)-H(101)	0.975	O(13)-C(5)-D(51)	107.676
O(11)-H(111)	0.831	C(1)-C(6)-C(5)	110.92(11)
O(12)-H(121)	0.826	C(1)-C(6)-O(9)	108.29(11)
O(13)-H(131)	0.823	C(5)-C(6)-O(9)	108.14(11)
		C(1)-C(6)-D(61)	110.031
C(2)-C(1)-C(6)	107.43(11)	C(5)-C(6)-D(61)	111.362
C(2)-C(1)-O(11)	112.24(11)	O(9)-C(6)-D(61)	107.975
C(6)-C(1)-O(11)	111.62(11)	C(2)-O(7)-C(10)	110.61(11)
C(2)-C(1)-D(11)	108.220	C(4)-O(8)-C(10)	111.34(10)
C(6)-C(1)-D(11)	109.836	C(6)-O(9)-C(10)	110.76(10)
O(11)-C(1)-D(11)	107.447	O(8)-C(10)-O(7)	111.47(11)
C(1)-C(2)-C(3)	111.34(11)	O(8)-C(10)-O(9)	111.27(13)
C(1)-C(2)-O(7)	108.40(11)	O(7)-C(10)-O(9)	111.29(11)

O(8)-C(10)-H(101)	107.6	C(1)-O(11)-H(111)	109.5
O(7)-C(10)-H(101)	107.4	C(3)-O(12)-H(121)	109.2
O(9)-C(10)-H(101)	107.6	C(5)-O(13)-H(131)	113.4

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 6558. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	13(1)	17(1)	16(1)	-2(1)	3(1)	-5(1)
C(2)	17(1)	18(1)	15(1)	0(1)	1(1)	1(1)
C(3)	12(1)	25(1)	15(1)	0(1)	-2(1)	4(1)
C(4)	10(1)	22(1)	20(1)	-1(1)	0(1)	-3(1)
C(5)	14(1)	17(1)	20(1)	3(1)	0(1)	0(1)
C(6)	9(1)	22(1)	18(1)	-2(1)	0(1)	1(1)
O(7)	20(1)	24(1)	14(1)	-3(1)	3(1)	-3(1)
O(8)	18(1)	21(1)	25(1)	-8(1)	3(1)	-7(1)
O(9)	13(1)	24(1)	26(1)	-6(1)	2(1)	5(1)
C(10)	15(1)	22(1)	22(1)	-7(1)	3(1)	-2(1)
O(11)	25(1)	30(1)	20(1)	-8(1)	7(1)	-16(1)
O(12)	21(1)	35(1)	21(1)	-1(1)	1(1)	16(1)
O(13)	16(1)	29(1)	15(1)	4(1)	0(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for 6558.

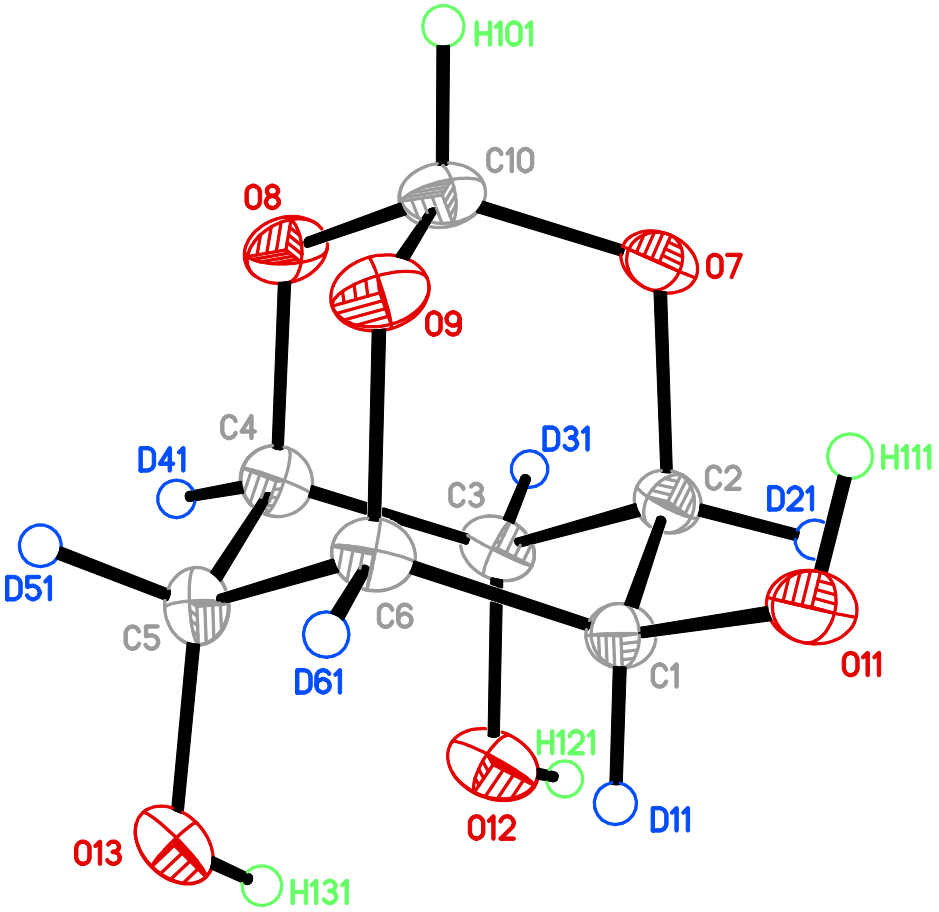
	x	y	z	U(eq)
H(101)	5550	3704	5284	24
H(111)	4367	-1300	3984	37
H(121)	8344	-1673	2458	39
H(131)	7088	741	682	31

Table 6. Hydrogen bonds for 6558 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(11)-H(111)...O(13)#1	0.83	2.01	2.739(2)	145
O(12)-H(121)...O(11)#2	0.83	1.89	2.708(2)	171
O(13)-H(131)...O(8)#3	0.82	2.45	3.033(2)	129
O(13)-H(131)...O(12)	0.82	2.02	2.696(2)	139

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,z+1/2 #2 x+1/2,-y-1/2,z #3 -x+3/2,y-1/2,z-1/2



(±)-(1RS,2SR,3SR,4RS)-Cyclohex-5-ene-1,2,3,4-tetrayl tetraacetate (±)-S19

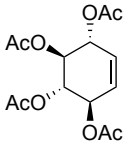


Table 1. Crystal data and structure refinement for 6617.

Identification code	6617	
Empirical formula	C14 H18 O8	
Formula weight	314.29	
Temperature	150 K	
Wavelength	1.54180 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.4164(2) Å	α= 90°.
	b = 6.6513(2) Å	β= 96.9535(17)°.
	c = 11.2592(2) Å	γ = 90°.
Volume	774.33(3) Å^3	
Z	2	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	0.956 mm^{-1}	
F(000)	332	
Crystal size	0.23 x 0.16 x 0.15 mm^3	
Theta range for data collection	3.955 to 76.044°.	
Index ranges	-13<=h<=13, -8<=k<=8, -11<=l<=14	
Reflections collected	8925	
Independent reflections	3187 [R(int) = 0.017]	
Completeness to theta = 74.523°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.87 and 0.73	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2322 / 1 / 200	
Goodness-of-fit on F^2	1.0108	
Final R indices [I>2sigma(I)]	R1 = 0.0229, wR2 = 0.0590	
R indices (all data)	R1 = 0.0230, wR2 = 0.0591	
Absolute structure parameter	0.24(13)	
Largest diff. peak and hole	0.10 and -0.10 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 6617. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3953(1)	227(2)	8615(1)	33
C(2)	5204(1)	-160(2)	8843(1)	32
C(3)	6233(1)	1169(2)	8457(1)	29
C(4)	5694(1)	3214(2)	8051(1)	27
C(5)	4422(1)	2988(2)	7244(1)	27
C(6)	3409(1)	2026(2)	7929(1)	30
O(7)	7194(1)	1443(2)	9493(1)	32
C(8)	8452(1)	1528(2)	9311(1)	35
O(9)	8821(1)	1324(2)	8349(1)	45
C(10)	9285(2)	1950(3)	10456(1)	48
O(11)	6575(1)	4210(2)	7350(1)	29
C(12)	7346(1)	5670(2)	7879(1)	29
O(13)	7341(1)	6174(2)	8903(1)	38
C(14)	8200(1)	6503(2)	7028(1)	35
O(15)	4012(1)	4978(2)	6881(1)	31
C(16)	3695(1)	5359(2)	5707(1)	32
O(17)	3767(1)	4129(2)	4941(1)	57
C(18)	3266(2)	7465(2)	5521(1)	43
O(19)	2339(1)	1276(2)	7098(1)	33
C(20)	1298(1)	2466(2)	6801(1)	35
O(21)	1223(1)	4163(2)	7136(1)	50
C(22)	286(1)	1377(3)	5996(1)	42

Table 3. Bond lengths [Å] and angles [°] for 6617.

C(1)-C(2)	1.323(2)	O(19)-C(20)	1.3516(18)
C(1)-C(6)	1.497(2)	C(20)-O(21)	1.195(2)
C(1)-H(11)	0.925	C(20)-C(22)	1.492(2)
C(2)-C(3)	1.4940(19)	C(22)-H(221)	0.947
C(2)-H(21)	0.956	C(22)-H(222)	0.930
C(3)-C(4)	1.5207(19)	C(22)-H(223)	0.940
C(3)-O(7)	1.4536(15)		
C(3)-H(31)	0.943	C(2)-C(1)-C(6)	123.91(13)
C(4)-C(5)	1.5215(18)	C(2)-C(1)-H(11)	120.2
C(4)-O(11)	1.4419(15)	C(6)-C(1)-H(11)	115.9
C(4)-H(41)	0.952	C(1)-C(2)-C(3)	123.62(13)
C(5)-C(6)	1.5222(18)	C(1)-C(2)-H(21)	119.5
C(5)-O(15)	1.4343(17)	C(3)-C(2)-H(21)	116.8
C(5)-H(51)	0.973	C(2)-C(3)-C(4)	111.37(11)
C(6)-O(19)	1.4538(16)	C(2)-C(3)-O(7)	106.85(10)
C(6)-H(61)	0.960	C(4)-C(3)-O(7)	108.80(11)
O(7)-C(8)	1.3521(16)	C(2)-C(3)-H(31)	111.1
C(8)-O(9)	1.1996(17)	C(4)-C(3)-H(31)	107.4
C(8)-C(10)	1.490(2)	O(7)-C(3)-H(31)	111.4
C(10)-H(101)	0.940	C(3)-C(4)-C(5)	110.78(10)
C(10)-H(102)	0.945	C(3)-C(4)-O(11)	109.83(10)
C(10)-H(103)	0.961	C(5)-C(4)-O(11)	106.48(10)
O(11)-C(12)	1.3520(16)	C(3)-C(4)-H(41)	111.0
C(12)-O(13)	1.2014(16)	C(5)-C(4)-H(41)	110.4
C(12)-C(14)	1.4914(19)	O(11)-C(4)-H(41)	108.2
C(14)-H(141)	0.970	C(4)-C(5)-C(6)	110.21(10)
C(14)-H(142)	0.959	C(4)-C(5)-O(15)	106.69(10)
C(14)-H(143)	0.962	C(6)-C(5)-O(15)	109.38(10)
O(15)-C(16)	1.3470(17)	C(4)-C(5)-H(51)	110.9
C(16)-O(17)	1.1972(18)	C(6)-C(5)-H(51)	109.3
C(16)-C(18)	1.478(2)	O(15)-C(5)-H(51)	110.3
C(18)-H(181)	0.972	C(5)-C(6)-C(1)	110.81(11)
C(18)-H(182)	0.951	C(5)-C(6)-O(19)	109.98(10)
C(18)-H(183)	0.974	C(1)-C(6)-O(19)	105.67(11)

C(5)-C(6)-H(61)	109.7	H(142)-C(14)-H(143)	110.6
C(1)-C(6)-H(61)	111.8	C(5)-O(15)-C(16)	118.82(10)
O(19)-C(6)-H(61)	108.8	O(15)-C(16)-O(17)	123.32(13)
C(3)-O(7)-C(8)	117.99(10)	O(15)-C(16)-C(18)	110.54(12)
O(7)-C(8)-O(9)	123.66(13)	O(17)-C(16)-C(18)	126.14(14)
O(7)-C(8)-C(10)	110.51(12)	C(16)-C(18)-H(181)	110.0
O(9)-C(8)-C(10)	125.82(13)	C(16)-C(18)-H(182)	106.9
C(8)-C(10)-H(101)	111.5	H(181)-C(18)-H(182)	108.7
C(8)-C(10)-H(102)	108.5	C(16)-C(18)-H(183)	108.9
H(101)-C(10)-H(102)	110.6	H(181)-C(18)-H(183)	110.7
C(8)-C(10)-H(103)	109.9	H(182)-C(18)-H(183)	111.5
H(101)-C(10)-H(103)	108.9	C(6)-O(19)-C(20)	119.17(11)
H(102)-C(10)-H(103)	107.4	O(19)-C(20)-O(21)	123.82(13)
C(4)-O(11)-C(12)	118.17(9)	O(19)-C(20)-C(22)	110.65(13)
O(11)-C(12)-O(13)	123.52(12)	O(21)-C(20)-C(22)	125.53(14)
O(11)-C(12)-C(14)	110.66(11)	C(20)-C(22)-H(221)	107.7
O(13)-C(12)-C(14)	125.81(12)	C(20)-C(22)-H(222)	108.0
C(12)-C(14)-H(141)	108.8	H(221)-C(22)-H(222)	110.7
C(12)-C(14)-H(142)	105.4	C(20)-C(22)-H(223)	108.4
H(141)-C(14)-H(142)	108.7	H(221)-C(22)-H(223)	109.6
C(12)-C(14)-H(143)	109.9	H(222)-C(22)-H(223)	112.2
H(141)-C(14)-H(143)	113.1		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 6617. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	31(1)	37(1)	32(1)	4(1)	6(1)	-5(1)
C(2)	36(1)	32(1)	29(1)	4(1)	6(1)	0(1)
C(3)	28(1)	33(1)	25(1)	-1(1)	4(1)	3(1)
C(4)	28(1)	30(1)	24(1)	-1(1)	6(1)	-2(1)
C(5)	29(1)	26(1)	26(1)	-2(1)	2(1)	3(1)
C(6)	25(1)	35(1)	30(1)	-5(1)	2(1)	0(1)
O(7)	26(1)	40(1)	28(1)	1(1)	1(1)	4(1)
C(8)	29(1)	33(1)	42(1)	6(1)	4(1)	2(1)
O(9)	32(1)	61(1)	44(1)	1(1)	11(1)	0(1)
C(10)	33(1)	60(1)	48(1)	5(1)	-6(1)	-2(1)
O(11)	31(1)	32(1)	25(1)	-1(1)	6(1)	-4(1)
C(12)	24(1)	28(1)	33(1)	0(1)	0(1)	4(1)
O(13)	35(1)	45(1)	35(1)	-10(1)	5(1)	-9(1)
C(14)	31(1)	36(1)	40(1)	3(1)	5(1)	-1(1)
O(15)	36(1)	29(1)	27(1)	0(1)	2(1)	4(1)
C(16)	28(1)	38(1)	29(1)	-1(1)	-3(1)	0(1)
O(17)	83(1)	51(1)	32(1)	-9(1)	-14(1)	16(1)
C(18)	47(1)	43(1)	39(1)	8(1)	1(1)	5(1)
O(19)	25(1)	35(1)	38(1)	-5(1)	1(1)	0(1)
C(20)	27(1)	41(1)	36(1)	0(1)	6(1)	2(1)
O(21)	35(1)	46(1)	67(1)	-11(1)	-2(1)	9(1)
C(22)	31(1)	55(1)	39(1)	-4(1)	1(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 6617.

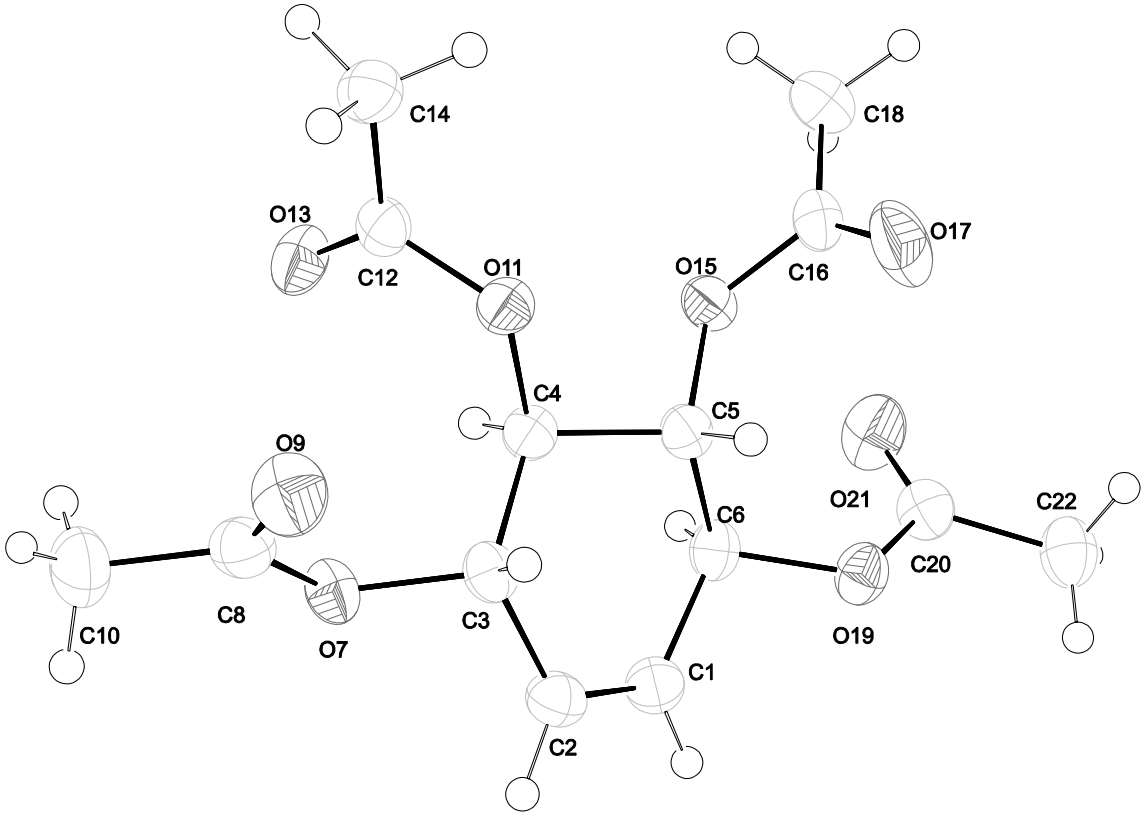
	x	y	z	U(eq)
H(11)	3355	-631	8889	40
H(21)	5483	-1367	9257	39
H(31)	6602	597	7811	34
H(41)	5583	4045	8719	28
H(51)	4532	2169	6548	30
H(61)	3083	3007	8443	33
H(101)	10168	1889	10358	70
H(102)	9086	1009	11035	73
H(103)	9094	3263	10743	73
H(141)	8527	7798	7323	53
H(142)	8911	5582	7050	53
H(143)	7737	6568	6236	53
H(181)	2989	7703	4677	62
H(182)	3995	8294	5766	66
H(183)	2562	7723	5996	64
H(221)	-532	1790	6196	66
H(222)	405	6	6126	66
H(223)	364	1743	5202	66

Table 6. Hydrogen bonds for 6617 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(10)-H(102)...O(21)#1	0.945	2.452	3.379(2)	166.75
C(14)-H(142)...O(21)#2	0.959	2.577	3.501(2)	161.77
C(14)-H(143)...O(17)#3	0.962	2.571	3.326(2)	135.52
C(18)-H(181)...O(11)#3	0.972	2.582	3.458(2)	149.77

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y-1/2,-z+2 #2 x+1,y,z #3 -x+1,y+1/2,-z+1



D_6-(±)-(1RS,2SR,3SR,4RS)-Cyclohex-5-ene-1,2,3,4-tetrayl-tetracetate (±)-26

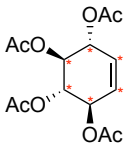


Table 1. Crystal data and structure refinement for 6614.

Identification code	6614	
Empirical formula	C14 H18 O8	
Formula weight	314.29	
Temperature	150 K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.4422(4) Å	α= 90°.
	b = 6.6743(4) Å	β= 97.050(3)°.
	c = 11.2392(3) Å	γ = 90°.
Volume	777.39(6) $Å^3$	
Z	2	
Density (calculated)	1.343 Mg/m^3	
Absorption coefficient	0.953 mm^{-1}	
F(000)	332	
Crystal size	0.25 x 0.10 x 0.01 mm^3	
Theta range for data collection	3.963 to 76.396°.	
Index ranges	-13<=h<=13, -7<=k<=8, -13<=l<=14	
Reflections collected	15703	
Independent reflections	2977 [R(int) = 0.046]	
Completeness to theta = 74.868°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.99 and 0.53	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2962 / 1 / 200	
Goodness-of-fit on F^2	1.0030	
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1143	
R indices (all data)	R1 = 0.0441, wR2 = 0.1182	
Absolute structure parameter	0.3(2)	
Largest diff. peak and hole	0.16 and -0.21 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 6614. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6044(2)	9776(4)	1385(2)	37
C(2)	4791(2)	10149(3)	1156(2)	37
C(3)	3769(2)	8819(3)	1547(2)	33
C(4)	4307(2)	6785(3)	1949(2)	31
C(5)	5581(2)	7002(3)	2759(2)	31
C(6)	6592(2)	7980(3)	2072(2)	34
O(7)	2807(1)	8551(3)	508(1)	36
C(8)	1549(2)	8472(4)	692(2)	39
O(9)	1184(1)	8684(3)	1655(1)	51
C(10)	715(2)	8043(5)	-458(2)	53
O(11)	3431(1)	5791(2)	2653(1)	33
C(12)	2665(2)	4337(3)	2124(2)	33
O(13)	2666(1)	3821(3)	1098(1)	43
C(14)	1809(2)	3505(4)	2976(2)	39
O(15)	5996(1)	5032(2)	3116(1)	35
C(16)	6303(2)	4643(4)	4297(2)	36
O(17)	6220(2)	5856(3)	5065(1)	63
C(18)	6741(2)	2545(4)	4479(2)	48
O(19)	7659(1)	8719(3)	2908(1)	38
C(20)	8699(2)	7539(4)	3190(2)	40
O(21)	8777(2)	5851(3)	2857(2)	58
C(22)	9714(2)	8637(5)	4005(2)	47

Table 3. Bond lengths [Å] and angles [°] for 6614.

C(1)-C(2)	1.326(3)	O(19)-C(20)	1.347(3)
C(1)-C(6)	1.501(3)	C(20)-O(21)	1.193(3)
C(1)-H(11)	0.942	C(20)-C(22)	1.504(3)
C(2)-C(3)	1.495(3)	C(22)-H(221)	0.951
C(2)-H(21)	0.944	C(22)-H(222)	0.957
C(3)-C(4)	1.517(3)	C(22)-H(223)	0.949
C(3)-O(7)	1.454(2)		
C(3)-H(31)	0.971	C(2)-C(1)-C(6)	123.69(19)
C(4)-C(5)	1.524(2)	C(2)-C(1)-H(11)	119.7
C(4)-O(11)	1.442(2)	C(6)-C(1)-H(11)	116.6
C(4)-H(41)	0.967	C(1)-C(2)-C(3)	123.7(2)
C(5)-C(6)	1.528(2)	C(1)-C(2)-H(21)	118.6
C(5)-O(15)	1.427(3)	C(3)-C(2)-H(21)	117.7
C(5)-H(51)	0.978	C(2)-C(3)-C(4)	111.55(15)
C(6)-O(19)	1.453(2)	C(2)-C(3)-O(7)	106.53(14)
C(6)-H(61)	0.980	C(4)-C(3)-O(7)	108.85(17)
O(7)-C(8)	1.356(2)	C(2)-C(3)-H(31)	110.0
C(8)-O(9)	1.199(3)	C(4)-C(3)-H(31)	110.2
C(8)-C(10)	1.495(3)	O(7)-C(3)-H(31)	109.6
C(10)-H(101)	0.945	C(3)-C(4)-C(5)	110.92(16)
C(10)-H(102)	0.958	C(3)-C(4)-O(11)	109.80(15)
C(10)-H(103)	0.960	C(5)-C(4)-O(11)	106.41(14)
O(11)-C(12)	1.348(2)	C(3)-C(4)-H(41)	110.8
C(12)-O(13)	1.204(2)	C(5)-C(4)-H(41)	109.4
C(12)-C(14)	1.495(2)	O(11)-C(4)-H(41)	109.4
C(14)-H(141)	0.968	C(4)-C(5)-C(6)	110.23(14)
C(14)-H(142)	0.954	C(4)-C(5)-O(15)	107.04(16)
C(14)-H(143)	0.957	C(6)-C(5)-O(15)	109.33(15)
O(15)-C(16)	1.352(2)	C(4)-C(5)-H(51)	110.8
C(16)-O(17)	1.194(3)	C(6)-C(5)-H(51)	108.3
C(16)-C(18)	1.479(4)	O(15)-C(5)-H(51)	111.1
C(18)-H(181)	0.967	C(5)-C(6)-C(1)	110.95(15)
C(18)-H(182)	0.968	C(5)-C(6)-O(19)	109.95(14)
C(18)-H(183)	0.956	C(1)-C(6)-O(19)	106.00(17)

C(5)-C(6)-H(61)	109.4	H(142)-C(14)-H(143)	111.4
C(1)-C(6)-H(61)	112.6	C(5)-O(15)-C(16)	118.74(15)
O(19)-C(6)-H(61)	107.9	O(15)-C(16)-O(17)	123.4(2)
C(3)-O(7)-C(8)	117.93(14)	O(15)-C(16)-C(18)	110.50(18)
O(7)-C(8)-O(9)	123.68(19)	O(17)-C(16)-C(18)	126.1(2)
O(7)-C(8)-C(10)	110.38(17)	C(16)-C(18)-H(181)	109.6
O(9)-C(8)-C(10)	125.92(19)	C(16)-C(18)-H(182)	109.8
C(8)-C(10)-H(101)	110.7	H(181)-C(18)-H(182)	110.9
C(8)-C(10)-H(102)	108.8	C(16)-C(18)-H(183)	107.8
H(101)-C(10)-H(102)	109.8	H(181)-C(18)-H(183)	108.3
C(8)-C(10)-H(103)	110.5	H(182)-C(18)-H(183)	110.4
H(101)-C(10)-H(103)	109.3	C(6)-O(19)-C(20)	119.09(17)
H(102)-C(10)-H(103)	107.8	O(19)-C(20)-O(21)	124.2(2)
C(4)-O(11)-C(12)	118.13(14)	O(19)-C(20)-C(22)	110.2(2)
O(11)-C(12)-O(13)	123.90(17)	O(21)-C(20)-C(22)	125.5(2)
O(11)-C(12)-C(14)	110.74(16)	C(20)-C(22)-H(221)	109.1
O(13)-C(12)-C(14)	125.34(19)	C(20)-C(22)-H(222)	109.4
C(12)-C(14)-H(141)	108.7	H(221)-C(22)-H(222)	111.3
C(12)-C(14)-H(142)	110.2	C(20)-C(22)-H(223)	107.7
H(141)-C(14)-H(142)	111.0	H(221)-C(22)-H(223)	109.4
C(12)-C(14)-H(143)	107.4	H(222)-C(22)-H(223)	109.9
H(141)-C(14)-H(143)	108.0		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 6614. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	37(1)	41(1)	35(1)	2(1)	6(1)	-5(1)
C(2)	42(1)	39(1)	30(1)	4(1)	5(1)	0(1)
C(3)	33(1)	40(1)	26(1)	1(1)	4(1)	3(1)
C(4)	32(1)	38(1)	24(1)	-1(1)	5(1)	0(1)
C(5)	33(1)	33(1)	26(1)	-2(1)	2(1)	1(1)
C(6)	33(1)	38(1)	31(1)	-2(1)	4(1)	1(1)
O(7)	33(1)	47(1)	28(1)	2(1)	3(1)	6(1)
C(8)	35(1)	41(1)	42(1)	7(1)	3(1)	1(1)
O(9)	38(1)	69(1)	47(1)	2(1)	12(1)	-1(1)
C(10)	39(1)	66(2)	50(1)	5(1)	-6(1)	0(1)
O(11)	37(1)	37(1)	25(1)	-1(1)	7(1)	-3(1)
C(12)	28(1)	36(1)	34(1)	2(1)	2(1)	4(1)
O(13)	42(1)	53(1)	36(1)	-11(1)	6(1)	-11(1)
C(14)	34(1)	42(1)	41(1)	4(1)	7(1)	-1(1)
O(15)	42(1)	38(1)	26(1)	0(1)	3(1)	5(1)
C(16)	33(1)	45(1)	28(1)	0(1)	-3(1)	1(1)
O(17)	91(1)	60(1)	31(1)	-9(1)	-15(1)	18(1)
C(18)	51(1)	52(2)	40(1)	10(1)	1(1)	7(1)
O(19)	32(1)	41(1)	40(1)	-5(1)	2(1)	0(1)
C(20)	35(1)	48(1)	38(1)	-1(1)	7(1)	2(1)
O(21)	41(1)	55(1)	75(1)	-13(1)	-1(1)	11(1)
C(22)	37(1)	63(2)	41(1)	-3(1)	2(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 6614.

	x	y	z	U(eq)
H(11)	6642	10668	1109	44
H(21)	4523	11327	732	43
H(31)	3374	9455	2188	38
H(41)	4434	5960	1267	36
H(51)	5475	7837	3454	36
H(61)	6934	6980	1556	38
H(101)	-167	8087	-346	78
H(102)	888	9021	-1041	80
H(103)	913	6748	-760	79
H(141)	1457	2241	2664	58
H(142)	2282	3334	3751	59
H(143)	1108	4422	2999	57
H(181)	7015	2316	5322	71
H(182)	7437	2277	4006	72
H(183)	6021	1692	4236	72
H(221)	10544	8245	3823	71
H(222)	9587	10050	3906	71
H(223)	9623	8265	4805	70

Table 6. Hydrogen bonds for 6614 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(10)-H(102)...O(21)#1	0.958	2.441	3.379(3)	166.37
C(14)-H(142)...O(17)#2	0.954	2.538	3.331(3)	140.70
C(18)-H(181)...O(11)#2	0.967	2.587	3.455(3)	149.30

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z #2 -x+1,y-1/2,-z+1