Electronic Supplementary Information

Regio- and Diastereoselective Pd-catalyzed Synthesis of C2-Aryl Glycosides

Table of Contents:

General information:

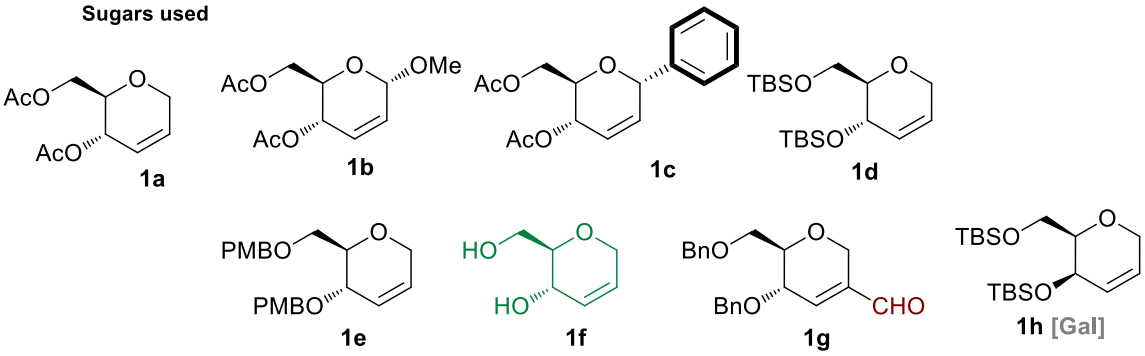
All reactions were carried out under an argon atmosphere in flame-dried glassware, unless otherwise noted. When needed, non-aqueous reagents were transferred under argon via syringe or cannula and dried prior to use. Toluene, THF, Et_2O and CH_2Cl_2 were obtained by passing deoxygenated solvents through activated alumina columns (MBraun SPS-800 Series solvent purification system). Other solvents and reagents were used as obtained from supplier, unless otherwise noted. Analytical TLC was performed using Merck silica gel F254 (230-400 mesh) plates and analyzed by UV light or by staining upon heating with vanillin solution (15 g of vanillin, 250 mL of EtOH, 2.5 mL conc. H_2SO_4). For silica gel chromatography, the flash chromatography technique was used, with Merck silica gel 60 (230-400 mesh) or RediSep Rf Gold Silica Cartridges and p.a. grade solvents unless otherwise noted.

The ^1H NMR and ^{13}C NMR spectra were recorded in either CDCl3 on Bruker Avance 300, 400 and 200 spectrometers. The chemical shifts of ^1H are reported in ppm relative to the solvent residual peak in CDCl3 (δ 7.26), for ^1H NMR. For the ^{13}C NMR spectra, the solvent signals of CDCl3 (δ 77.16) were used as the internal standards.IR spectra were recorded on a Tensor 27 FT-IR spectrometer. Optical rotations were obtained with a Perkin-Elmer 343 polarimeter. High resolution mass spectrometric data were measured using MicroMass LCT Premier Spectrometer.

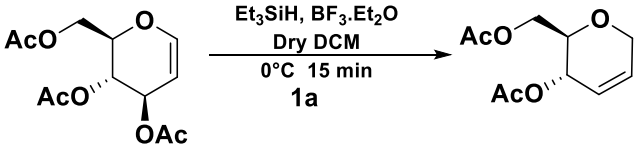
General procedures:

1. General procedures A for 2.3 pseudo-glycals:

Sugars used

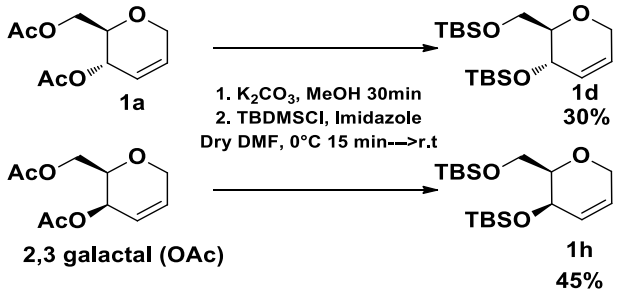


1.1 ((2R, 3S)-3-Acetoxy-3,6-dihydro-2H-pyran-2-yl) methyl acetate [1] 1a:



Tri-O-acetyl-D-glucal (1.0 g, 3.673 mmol) and triethylsilane (512.5 mg, 4.41 mmol) were dissolved in CH_2Cl_2 (5 mL) at room temperature under Ar. The solution was cooled to 0 °C. $BF_3{\cdot}OEt_2$ (521.32 mg, 3.67 mmol) was added dropwise to the solution above at 0 °C under Ar atmosphere. The reaction mixture was stirred 0 °C for 15 min. The reaction mixture was quenched with 10% aqueous $NaHCO_3$ solution (0.5 mL) and diluted with ether (5.5 mL). The whole was washed with H_2O (2 x 5 mL), brine (5 mL), and then dried over $MgSO_4$. Combined organic layers were evaporated. yield **1a** (784.6 mg, 3.66 mmol, 100%, colorless oil). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (dd, *J* = 10.3, 1.4 Hz, 1H), 5.75 (dd, *J* = 10.4, 2.0 Hz, 1H), 5.36 – 5.14 (m, 1H), 4.18 (ddd, *J* = 12.1, 5.8, 4.0 Hz, 4H), 3.71 (ddd, *J* = 5.3, 4.4, 2.3 Hz, 1H), 2.20 – 1.96 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.49 (d, *J* = 41.5 Hz), 133.64 (s), 129.43 (s), 128.59 (t, *J* = 14.6 Hz), 124.22 (s), 73.82 (s), 65.15 (d, *J* = 16.5 Hz), 63.23 (s), 20.85 (d, *J* = 15.8 Hz).

1.2 (2R, 3S) -2-(((tert-Butyldimethylsilyl) oxy) methyl)-3,6-dihydro-2Hpyran-3-ol 1d and 1h:



[1] S. Jung, A. Inoue, S. Nakamura, T. Kishi , A. Uwamizu, M. Sayama, M. Ikubo, Y. O. K. Kano, K. Makide, J. Aok, T. Ohwada. *J. Med. Chem*. 2016, **59**, 3750.

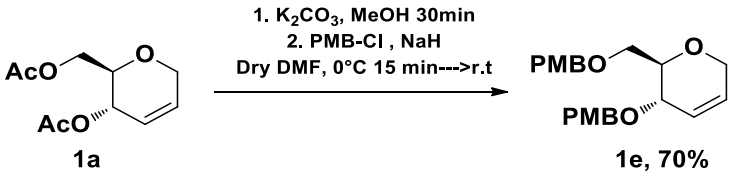
TBS protection[1]*:*

Compound **1a** or **galactal (OAc)** (450 mg, 2.102 mmol) was dissolved in MeOH (9 mL) and K_2CO_3 (75 mg, 0.542 mmol) was added to the solution above. The reaction mixture was stirred at room temperature under argon atmosphere for 30 min. After 30 min, solvent was evaporated, and the residue was dissolved in chloroform. This solution was filtered on Celite and the filtrate was evaporated. Yellow oil was obtained, the yield is quantitative. Compounds obtained in the first step were dissolved in DMF (11 mL) and imidiazole (430 mg) was added to the solution. This was cooled to 0 °C and tert-butyldimethylsilyl chloride (1.26 g) was added. This reaction mixture was stirred at 0 °C under argon atmosphere for 10 min and stirred at room temperature for 15 h. Water was then added (20 mL) to the reaction mixture and the whole was extracted with CH_2Cl_2 (3 x 15 mL). Combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography to yield **1d** (30 %) of a colorless oil or **1h** (45%).

1d: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (d, *J* = 11.0 Hz, 1H), 5.71 (d, *J* = 10.6 Hz, 1H), 4.27 – 4.07 (m, 3H), 3.91 (dd, *J* = 11.2, 1.7 Hz, 1H), 3.74 (dd, *J* = 11.3, 5.7 Hz, 1H), 3.37 – 3.24 (m, 1H), 0.92 (d, *J* = 1.0 Hz, 18H), 0.19 – 0.01 (m, 12H).

1h: ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.90 (d, *J* = 2.4 Hz, 2H), 4.27 (d, *J* = 16.3 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.84 (dd, *J* = 10.7, 5.7 Hz, 1H), 3.76 (dd, *J* = 10.7, 6.4 Hz, 1H), 3.50 (td, *J* = 6.1, 2.2 Hz, 1H), 0.92 (s, 18H), 0.10 (d, *J* = 2.6 Hz, 12H).

1.3 (2R, 3S) -3-((4-methoxybenzyl) oxy)-2-(((4-methoxybenzyl) oxy) methyl)-3,6-dihydro-2H-pyran 1e:



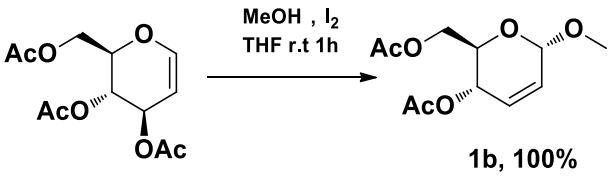
1a **1e, 70%**

PMB protection[2]:

To a stirred solution of **1a** (450 mg) in anhydrous dimethylformamide (DMF), NaH (202 mg, 4 equiv) was added slowly at 0 °C. After stirring the mixture for 15 min, *p*-methoxybenzyl chloride (1.2 mL, 4 equiv) was added. The mixture was stirred for 16 h at room temperature and partitioned between dichloromethane (DCM) and water. The aqueous layer was extracted with DCM and the combined organic layers were dried over anhydrous $MgSO_4$. The filtrate was condensed under reduced pressure and subjected to flash column chromatography to obtain **1e** as a white solid (545 mg, yield 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.88 (t, *J* = 8.7 Hz, 4H), 5.96 – 5.90 (m, 1H), 5.86 (d, *J* = 11.9 Hz, 1H), 4.60 – 4.47 (m, 3H), 4.39 (d, *J* = 11.1 Hz, 1H), 4.21 (s, 2H), 4.04 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 6H), 3.69 (t, *J* = 6.4 Hz, 1H), 3.61 (d, *J* = 7.8 Hz, 2H).

[2] S. Lee, D. Lim, E. Lee, N. Lee, H-G. Lee, J. Cechetto, M. Liuzzi, L.H. Freitas-Junior, J. S. Song, M. A. Bae, S. Oh, L. Ayong, S. B. Park. *J. Med. Chem*. 2014, **57**, 17, 7425.

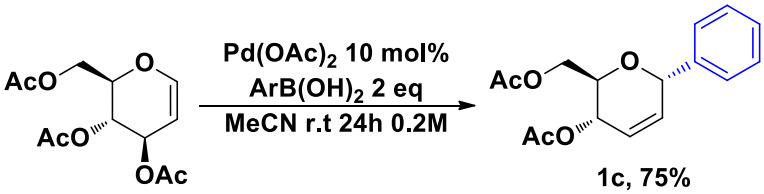
1.4 ((2R, 3S, 6S) -3-acetoxy-6-methoxy-3,6-dihydro-2H-pyran-2-yl) - methyl acetate[3] 1b:



1b, 100%

To a solution of tri-O-acetyl-D-glucal (5 g, 0.18 mol), methanol (1.5 mL) in THF (75 mL) was added iodine (0.90 g, 3.00 mmol). After being stirred on room temperature for 1.5 h under N_2 atmosphere, the mixture was diluted with ether. The resulting dark red coloured mixture was washed with 50 mL of a 10% aq. $Na_2S_2O_3$ soln under stirring until the solution becomes colorless. The aqueous phase was extracted with ether. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated in vacuo and residue was purified by column chromatography to give the product **1b** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77 – 5.71 (m, 1H), 5.18 (d, *J* = 9.6 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.10 (qd, *J* = 12.1, 4.0 Hz, 3H), 3.98 – 3.90 (m, 1H), 3.42 – 3.22 (m, 3H), 2.09 – 1.85 (m, 6H).

1.5 ((2R,3S,6S)-3-acetoxy-6-phenyl-3,6-dihydro-2H-pyran-2-yl) methyl acetate[4] 1f:

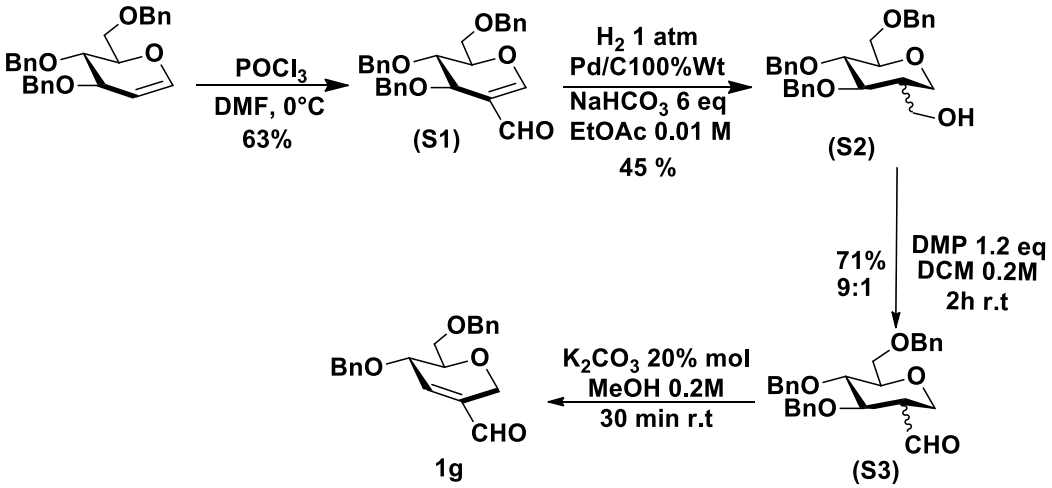


1c, 75%

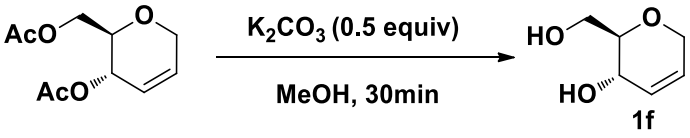
To a mixture of tri-O-acetyl-D-glucal (0.2 mmol) and arylboronic acid (0.4 mmol) in 1 mL of acetonitrile was added $Pd(OAc)_2$ (0.02 mmol). The resulting suspension was stirred at room temperature for 24 h. Then the mixture was diluted with 10 mL of CH_2Cl_2 and filtered through a pad of silica gel. The filtrate was concentrated and subjected to silica gel column chromatography using 80% hexanes/20% ethyl acetate as eluant (yield 75%). **1c:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (dt, *J* = 9.1, 7.2 Hz, 5H), 6.19 (dd, *J* = 10.4, 2.0 Hz, 1H), 5.99 (d, *J* = 10.3 Hz, 1H), 5.31 (d, *J* = 6.6 Hz, 2H), 4.28 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.11 (dd, *J* = 12.0, 3.1 Hz, 1H), 3.93 – 3.79 (m, 1H), 2.07 (d, *J* = 6.6 Hz, 6H).

1.7 (5S,6R) -5-(benzyloxy) -6-((benzyloxy)methyl) -5,6-dihydro-2H-pyran-3-carbaldehyde 1g[5]

[3] P. Singha, G. Panda. *RSC Adv*. 2014, **4**, 31892.
[4] J. Ramnauth, O. Poulin, S. Rakhit, S. P. Maddaford. *Org. Lett.2001*, **313**, 2013-2015.
[5] a) N. G. Ramesh, K.K. Balasubramanian. *Tetrahedon. Lett*. 1991, **32,** 31**,** 3875 (S1); b) H.H. Kinfe, F.M. Mebrahtu, M.M. Manana, K. Madumo, M. S. Sokamisa. *Beilstein J. Org. Chem*. 2015, **11**, 583 (S4).

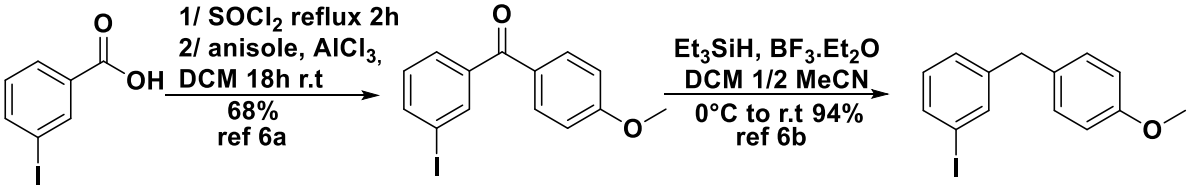


1.6 (2R,3S) -2-(hydroxymethyl)-3,6-dihydro-2H-pyran-3-ol 1f:

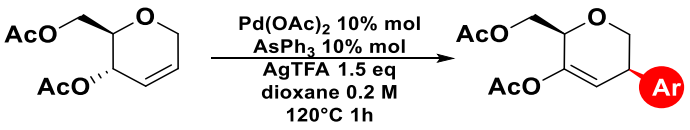


Coompound **1a** (450 mg, 2.102 mmol) was dissolved in MeOH (9 mL) and K_2CO_3 (75 mg, 0.542 mmol) was added to the solution above. The reaction mixture was stirred at room temperature under Ar atmosphere for 30 min. After 30 min, solvent was evaporated and the residue was dissolved in chloroform. This solution was filtered on Celite and the filtrate was evaporated to give **1f** as a yellow oil (quantitative yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.82 (s, 2H), 4.18 (s, 3H), 3.84 (dd, *J* = 7.5, 4.6 Hz, 2H), 3.41 – 3.25 (m, 1H), 2.73 (s, 2H).

1.8 1-iodo-3-(4-methoxybenzyl) benzene[6]:



2 General procedure for C-2 arylation of pseudo-glucal:



[6] a) J. Georgsson, C. Sköld , B. Plouffe, G. Lindeberg , M. Botros, M. Larhed, F. Nyberg, N. Gallo-Payet, A Gogoll, A. Karlén, A. Hallberg. *J. Med. Chem*. 2005, **48**, 6620; b) S.Y. Kang, M.J. Kim, J. S. Lee, J. Lee. *Bioorg. Med. Chem. Lett*. 2011, **21**, 3759.

A reaction tube was charged with 2.3 glucal (0.4 mmol), Pd $(OAc)_2$ (10 mol %), $AsPh_3$ (10% mol), AgTFA (1.5 equiv), aryl iodide (1 equiv) and dioxane (0.2 M, relative to 2.3 glucal). The reaction vessel was purged with argon and sealed, then placed in an oil bath (preheated at 120 °C) for 1 h. The reaction mixture was then allowed to cool to rt and EtOAc (10 mL) was added. The resulting solution was filtered through a pad of Celite, eluting with further EtOAc (2 × 10 mL). The solvent was removed under reduced pressure, and the crude material was purified by flash column chromatography with the specified conditions.

2.1 Optimization reactions of arylation:

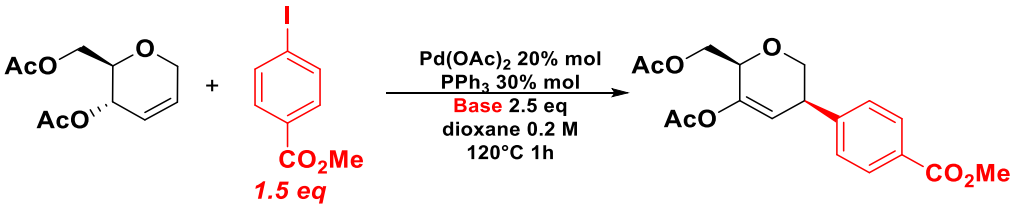
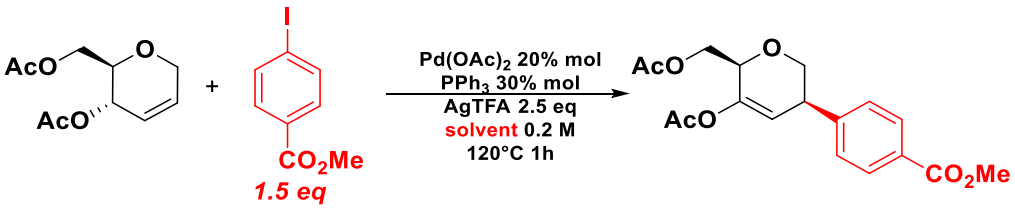


Table S1 Impact of Base

	Base	Time	Conversion	Yield %
1	**Ag_2CO_3**	36h	63 %	37%
2	**Et_3N**	18h	degradation	n.d
3	**DIEPA**	18h	degradation	n.d
4	**Cs_2CO_3**	18h	No reaction	-
5	**AgOAc**	18h	78%	52%
6	**AgTFA**	**1h**	**100 %**	**59%**
7	**$AgSbF_6$**	3h	-	n.d
8	**NaOAc**	18h	No reaction	n.d
9	**AgOTf**	3h	degradation	n.d

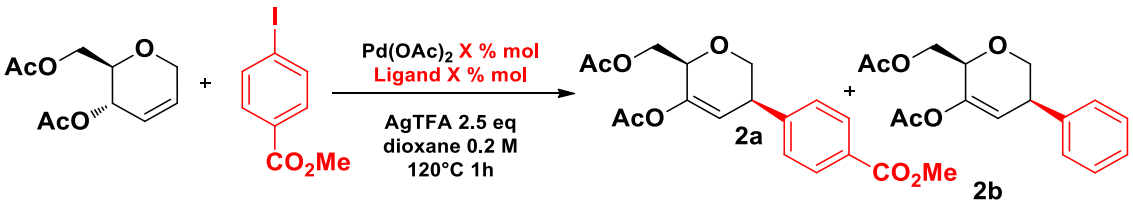
Table S2 Solvent effect



	Solvent	T° C	Time	Conversion	Yield %
1	**Dioxane**	**120**	**1h**	**100 %**	**59%**
1Bis	**Dioxane + 1eq TFA**	120	30min	100 %	40%
2	**HFIP**	120	1h	100 %	22%
3	**AcOH**	**120**	**1h**	**100 %**	**60%**
4	**Ethylene glycol**	120	1h	100 %	15%
5	**DMF**	120	1h	100%	33%

6	**CPME**	120	1h	100 %	27%
7	**PhMe**	120	1h	100 %	32%

Table S3 Impact of *% mol Pd and Ligand:*

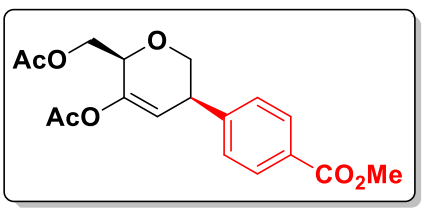


	$Pd(OAc)_2$ X mol%	Ligand X mol%	Time	Conversion	Yield % 2a/2b	
1	**20 mol%**	**PPh_3 30 mol%**	1h	100 %	59%	-
2	**10 mol%**	**PPh_3 15 mol%**	8h	100 %	24%	-
3	**5 mol%**	**PPh_3 7.5 mol%**	24h	100%	23%	-
3	**20 mol%**	**DpePhos 25mol%**	1h	100%	21%	-
4	**20 mol%**	**tBuXPhos 25mol%**	1h	100%	40%	-
4	**20 mol%**	**$AsPh_3$ 30 mol%**	**0.5h**	**100 %**	**74%**	**12%**
5	**10 mol%**	**$AsPh_3$ 15 mol%**	**0.5h**	**82 %**	**77%**	**-**
6	**5 mol%**	**$AsPh_3$ 7.5 mol%**	**1.5h**	**100 %**	**70%**	**-**
8	**10 mol%**	**$AsPh_3$ 10 mol%**	**1 h**	**100%**	**80%**	**-**
9	**10 mol%**	**$AsPh_3$ 10 mol%**	**1 h**	**100%**	**76%[a]**	**-**

[a]1.5 equiv of AgTFA

3. Characterization of compounds:

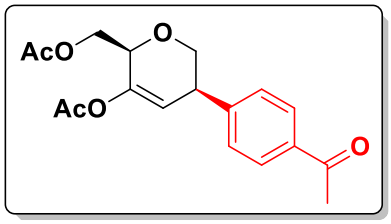
3.1 methyl 4-((3R, 6R) -5-acetoxy-6-(acetoxymethyl)-3,6-dihydro-2H-pyran-3-yl) benzoate 3a:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), methyl 4-iodobenzoate (105 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/Cyclohexane) and arylated compound was obtained (111.3 mg, 80%) as a yellow oil. *Rf (30% EtOAc/Cyclohexane) = 0.25;* $[\alpha]^{19}_D$ = -8 ° (c 0,5 $CHCl_3$). IR (neat, cm^{-1}): 2956, 2928, 1768, 1744, 1718, 1279, 1228, 1182, 1114. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (d, 2H), 7.45 – 7.38 (d, 2H), 5.79 (dd, *J* = 4.9, 1.7 Hz, 1H), 4.51 (dd, *J* = 4.9, 2.4 Hz, 1H), 4.35 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.26 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.07 – 3.98 (m, 1H), 3.92 – 3.83 (m, 5H), 3.66 – 3.60 (m, 1H), 2.15 (d, *J* = 23.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.29 (s), 170.76 (s), 168.78 (s), 166.88 (d, *J* = 22.4 Hz), 146.73 (s), 145.87 (s),

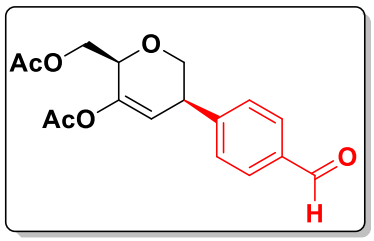
130.55 – 129.45 (m), 128.90 (d, *J* = 38.2 Hz), 128.34 (s), 116.95 (s), 72.14 (s), 68.85 (s), 63.11 (s), 52.16 (s), 41.19 (s), 20.97 (d, *J* = 3.1 Hz). HRMS (ESI+): *m/z* calcd for $[C_{18}H_{20}O_7Na]^+$ 371.1101, found 371.1107.

3.2 ((2R, 5R) -3-acetoxy-5-(4-acetylphenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3b:



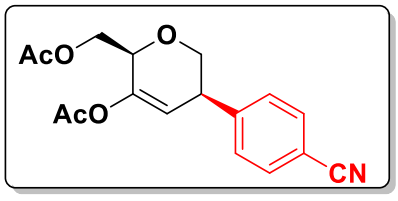
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 1-(4-iodophenyl)ethanone (99 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/Cyclohexane), and arylated compound was obtained (74.4 mg, 56%) as a yellow oil. *Rf (30% EtOAc/Cyclohexane) = 0.10;* $[\alpha]^{18}_D$ = – 18 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2923, 2854, 1767, 1738, 1680, 1607, 1367, 1269,1228,1207, 1148. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 5.80 (d, *J* = 3.6 Hz, 1H), 4.53 (dd, *J* = 4.8, 2.3 Hz, 1H), 4.37 (dd, *J* = 12.0, 5.2 Hz, 1H), 4.27 (dd, *J* = 12.0, 2.6 Hz, 1H), 4.05 (dd, *J* = 11.4, 4.3 Hz, 1H), 3.87 (dd, *J* = 11.4, 3.1 Hz, 1H), 3.65 (s, 1H), 2.59 (s, 3H), 2.19 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.62 (s), 170.59 (s), 168.63 (s), 146.83 (s), 145.80 (s), 137.24 – 136.08 (m), 128.47 (d, *J* = 12.1 Hz), 116.72 (s), 72.04 (s), 68.70 (s), 63.01 (s), 41.04 (s), 26.53 (s), 20.82 (s). HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{18}H_{24}O_6N]^+$ 350.1598, found 350.1599.

3.3 ((2R, 5R) -3-acetoxy-5-(4-formylphenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3c:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 4-iodobenzaldehyde (93 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/Cyclohexane) and arylated compound was obtained (59.9 mg, 47%) as a yellow oil. *Rf (30% EtOAc/Cyclohexane) = 0.10;* $[\alpha]^{19}_D$ = -34 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 2856, 1768, 1739, 1700, 1606, 1425, 1368, 1229,1207, 1148. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 5.81 (d, *J* = 4.2 Hz, 1H), 4.57 – 4.48 (m, 1H), 4.38 (dd, *J* = 12.1, 5.1 Hz, 1H), 4.28 (dd, *J* = 12.1, 2.6 Hz, 1H), 4.06 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.90 (dd, *J* = 11.4, 2.8 Hz, 1H), 3.67 (s, 1H), 2.20 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.75 (s), 191.77 (s), 170.55 (s), 168.60 (s), 148.46 (s), 145.92 (s), 135.36 (s), 129.90 (s), 128.88 (s), 116.51 (s), 72.08 (s), 68.68 (s), 62.95 (s), 41.20 (s), 30.81 (s), 20.79 (s). HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{17}H_{22}O_6N]^+$ 336.1442, found 336.1441.

3.4 ((2R, 5R) -3-acetoxy-5-(4-cyanophenyl) -5,6-dihydro-2H-pyran-2-yl)methyl acetate 3d:

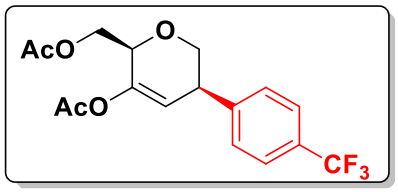


Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 4-iodobenzonitrile (92 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/Cyclohexane), and arylated compound was obtained (63 mg, 50%) as a yellow oil. *Rf (30% EtOAc/Cyclohexane) = 0.28;*

$[\alpha]^{20}_{D}$ = -10 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 1768, 1739, 1368, 1230, 1207, 1126. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 5.79 (d, *J* = 4.5 Hz, 1H), 4.53 (d, *J* = 2.5 Hz, 1H), 4.37 (dd, *J* = 12.1, 5.1 Hz, 1H), 4.29 (d, *J* = 2.5 Hz, 1H), 4.04 (d, *J* = 4.1 Hz, 1H), 3.90 (d, *J* = 2.5 Hz, 1H), 3.64 (s, 1H), 2.20 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.50 (s), 168.57 (s), 146.95 (s), 146.17 (s), 132.26 (s), 129.04 (s), 118.73 (s), 116.17 (s), 110.99 (s), 72.16 (s), 68.69 (s), 62.94 (s), 41.11 (s), 20.81 (s). HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{17}H_{21}O_5N_2]^+$ 333.1445, found 333.1445.

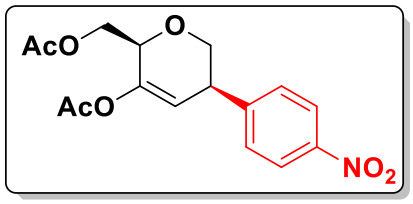
3.5 ((2R, 5R) -3-acetoxy-5-(4-(trifluoromethyl) phenyl)-5,6-dihydro-2H-pyran-2-yl)methyl acetate 3e:

Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 1-iodo-4-(trifluoromethyl)benzene (109 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h.



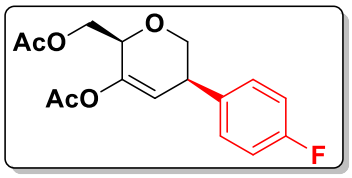
The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/Cyclohexane), and arylated compound was obtained (77.7 mg, 54%) as a yellow oil. *Rf (30% EtOAc/Cyclohexane) =0.39;* $[\alpha]^{18}_{D}$ = −32 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2926, 2854, 1767, 1739, 1368, 1324, 1229, 1207, 1123, 1066. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 5.81 (d, *J* = 4.8 Hz, 1H), 4.54 (dd, *J* = 4.8, 2.3 Hz, 1H), 4.39 (dd, *J* = 12.0, 5.1 Hz, 1H), 4.28 (dd, *J* = 12.0, 2.6 Hz, 1H), 4.06 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.89 (dd, *J* = 11.4, 2.9 Hz, 1H), 3.66 (s, 1H), 2.20 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.57 (s), 168.62 (s), 145.69 (d, *J* = 32.3 Hz), 128.54 (s), 125.58 (t, *J* = 22.4 Hz), 116.66 (s), 72.09 (s), 68.78 (s), 63.00 (s), 40.90 (s), 20.69 – 17.78 (m). ^{19}F NMR (188 MHz, Chloroform-*d*) δ -62.48. HRMS (ESI+): *m/z* calcd for $[C_{17}H_{17}F_3O_5Na]^+$ 381.0920, found 381.0921.

3.6((2R, 5R) -3-acetoxy-5-(4-nitrophenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3f:



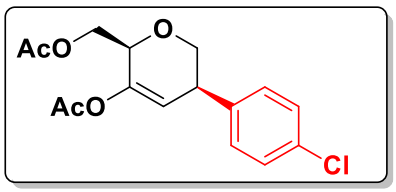
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 1-iodo-4-nitrobenzene (100 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/Cyclohexane) and arylated compound was obtained (92 mg, 69%) as a yellow oil. *Rf (30% EtOAc/Cyclohexane) = 0.27;* $[\alpha]^{18}_{D}$ = −22° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2924, 2854, 1768, 1738, 1688, 1517, 1346, 1228,1206,1186, 1149. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 5.80 (d, *J* = 4.5 Hz, 1H), 4.54 (d, *J* = 2.5 Hz, 1H), 4.38 (dd, *J* = 11.9, 4.9 Hz, 1H), 4.26 (dd, *J* = 12.0, 2.6 Hz, 1H), 4.08 (dd, *J* = 11.5, 4.2 Hz, 1H), 3.96 – 3.85 (m, 1H), 3.69 (s, 1H), 2.20 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.50 (s), 168.54 – 165.99 (m), 149.05 (s), 146.26 (s), 129.12 (s), 123.66 (s), 116.09 (s), 72.23 (s), 68.72 (s), 62.91 (s), 40.93 (s), 20.83 (s). HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{16}H_{21}O_7N_2]^+$ 353.1343, found 353.1345.

3.7((2R, 5R) -3-acetoxy-5-(4-fluorophenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3g:



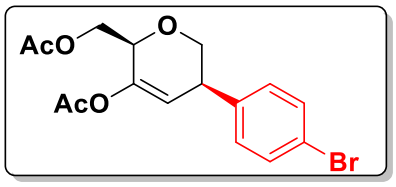
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 1-fluoro-4-iodobenzene (89 mg, 56 µL, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/Cyclohexane) and arylated compound was obtained (72.6 mg, 59%) as a yellow oil. *Rf (30% EtOAc/Cyclohexane) = 0.35*; $[\alpha]^{18}_D$ = −34 (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2924, 2855, 1768, 1732, 1505, 1369, 1217, 1201, 1189, 1148, 1100, 1015. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 8.2, 5.5 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.79 (d, *J* = 4.5 Hz, 1H), 4.52 (d, *J* = 2.6 Hz, 1H), 4.37 (dd, *J* = 12.0, 5.3 Hz, 1H), 4.30 (d, *J* = 2.5 Hz, 1H), 3.83 (dd, *J* = 11.4, 3.3 Hz, 1H), 2.20 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.64, 168.70, 163.58, 160.34, 145.41, 136.97, 129.57, 117.48, 115.41, 115.12, 71.95, 68.98, 63.08, 40.35, 20.82. ^{19}F NMR (188 MHz, Chloroform-*d*) δ -115.35 – -116.82 (m). HRMS (ESI+): *m/z* calcd for $[M.Na]^+$ $[C_{16}H_{17}O_5NaF]^+$ 331.0952, found 331.0949.

3.8((2R, 5R) -3-acetoxy-5-(4-chlorophenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3h:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 1-chloro-4-iodobenzene (96 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/Cyclohexane) and arylated compound was obtained (77.8 mg, 60%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) =0.36;* $[\alpha]^{18}_D$ = -6 ° (c 0,5 $CHCl_3$). IR (neat, cm^{-1}): 2956, 2928, 1767, 1738, 1492, 1368, 1228, 1205, 1186, 1148, 1125. ^{1}H NMR (300 MHz, CDCl3) δ 7.33 – 7.22 (m, 1H), 5.82 – 5.71 (s, 4H), 4.50 (dd, J = 4.8, 2.3 Hz, 1H), 4.35 (dd, J = 12.0, 5.2 Hz, 1H), 4.25 (dd, J = 12.0, 2.7 Hz, 1H), 4.00 (dd, J = 11.4, 4.2 Hz, 1H), 3.82 (dd, J = 11.4, 3.2 Hz, 1H), 3.61 – 3.49 (m, 1H), 2.18 (s, 3H), 2.11 (s, 3H). 13C NMR (75 MHz, CDCl3) δ 170.60 (s), 168.66 (s), 145.58 (s), 139.82 (s), 132.86 (s), 129.51 (s), 128.59 (s), 117.14 (s), 71.97 (s), 68.87 (s), 63.04 (s), 40.47 (s), 20.82 (s). HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{16}H_{21}O_5NCl]^+$ 342.1103, found 342.1103.

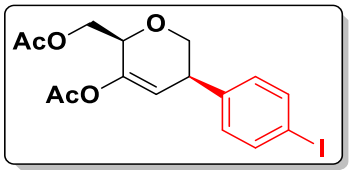
3.8 ((2R, 5R) -3-acetoxy-5-(4-bromophenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3i:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 1-bromo-4-iodobenzene (113 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and reversed arylated compound was obtained (81.2 mg, 55%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.38;* $[\alpha]^{19}_D$ = -26 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 1767, 171738, 1688, 1367, 1228, 1205, 1148, 1125. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 5.69 (d, *J* = 4.1 Hz, 1H), 4.46 – 4.38 (m, 1H), 4.28 (dd, *J* = 12.0, 5.2 Hz, 1H), 4.18 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.93 (dd, *J* = 11.3, 4.2 Hz, 1H), 3.75 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.47 (s, 1H), 2.11 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.60 (s), 168.65 (s), 145.61 (s), 140.35 (s), 131.55 (s), 129.90 (s), 120.95 (s), 117.05 (s), 71.91 (d, *J* =

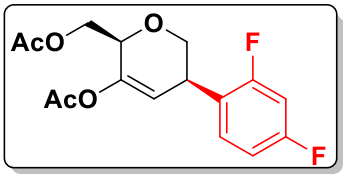
10.0 Hz), 68.81 (s), 63.04 (s), 40.81 (d, *J* = 40.4 Hz), 20.83 (s). HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{16}H_{21}O_5NBr]^+$ 386.0598, found 386.0599.

3.10 ((2R, 5R) -3-acetoxy-5-(4-iodophenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3j:



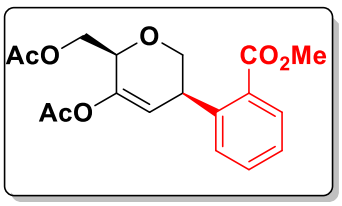
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 1,4-diiodobenzene (132 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane), and arylated compound was obtained (53 mg, 32%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.38;* $[\alpha]^{18}_D$ = −18 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2961, 2925, 2854, 1767, 1740, 1688, 1368, 1229,1207, 1187, 1149. ^{1}H NMR (300 MHz, Chloroform-d) δ 7.66 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 5.78 (d, J = 3.6 Hz, 1H), 4.52 (m, 1H), 4.40 – 4.32 (dd, 1H), 4.27 (dd, J = 12.4 Hz, 1H), 4.02 (dd, J = 11.0, 4.5 Hz, 1H), 3.88 – 3.79 (dd, 1H), 3.55 (m, 1H), 2.20 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.62, 168.66, 145.63, 141.03, 137.56, 130.21, 128.51, 128.13, 127.02, 117.00, 92.43, 71.98, 68.81, 63.05, 40.65, 29.68, 20.85. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{16}H_{21}O_5NI]^+$ 434.0459, found 434.0467.

3.11 ((2R, 5R) -3-acetoxy-5-(2,4-difluorophenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3k:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 2,4-difluoro-1-iodobenzene (96 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (76.7 mg, 60%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.32;* $[\alpha]^{19}_D$ = -10 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 1767, 1739, 1503, 1228, 1202, 1150. ^{1}H NMR (300 MHz, chloroform-d) δ 7.49 (q, J = 8.4 Hz, 1H), 6.90 – 6.75 (m, 2H), 5.75 (d, J = 4.9 Hz, 1H), 4.52 (m, J = 4.5, 2.2 Hz, 1H), 4.38 – 4.31 (dd, 1H), 4.27 (dd, J = 11.9, 2.6 Hz, 1H), 4.03 (dd, J = 12.0, 4.7 Hz, 1H), 3.90 (dd, J = 9.9 Hz, 1H), 2.20 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 170.57, 168.59, 146.23, 130.96 (dd, *J* = 9.3, 5.7 Hz), 128.31 (d, *J* = 28.3 Hz), 116.13, 111.01 (dd, *J* = 20.8, 3.5 Hz), 103.57 (t, *J* = 25.8 Hz), 72.15, 68.03, 63.05, 41.09, 33.13, 20.80. ^{19}F NMR (188 MHz, chloroform-*d*) δ -112.17 (m, *J* = 8.1, 7.6 Hz), -114.30 – -116.41 (m). HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{16}H_{20}O_5NF_2]^+$ 344.1304, found 344.1314.

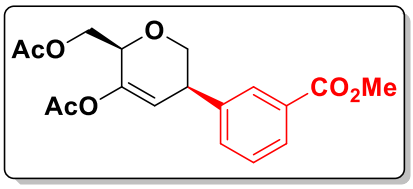
3.12 methyl 2-((3R, 6R) -5-acetoxy-6-(acetoxymethyl) -3,6-dihydro-2H-pyran-3-yl) benzoate 3l:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), methyl 2-iodobenzoate (104 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (68.1 mg, 49%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.28;* $[\alpha]^{20}_D$ = -24 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 1743, 1717, 1231, 1206, 1131, 1108. ^{1}H NMR (300 MHz,

chloroform-*d*) δ 7.93 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 (d, *J* = 14.3 Hz, 1H), 5.76 (d, *J* = 3.9 Hz, 1H), 4.54 (m, *J* = 4.7, 2.4 Hz, 2H), 4.35 (d, *J* = 4.7 Hz, 1H), 4.32 (d, *J* = 2.4 Hz, 1H), 4.14 (dd, *J* = 11.6, 4.1 Hz, 0H), 4.02 – 3.94 (m, 1H), 3.91 (s, *J* = 0.7 Hz, 3H), 2.19 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.67, 168.74, 167.82, 145.82, 142.80, 132.00, 130.70, 130.05, 129.08, 126.76, 117.64, 77.43, 77.01, 76.59, 72.12, 69.26, 63.23, 52.08, 37.32, 20.83. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{18}H_{24}O_7N]^+$ 366.1547, found 366.1551.

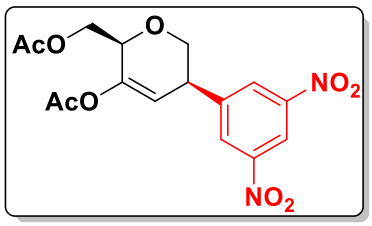
3.13 methyl 3-((3R, 6R) -5-acetoxy-6-(acetoxymethyl) -3,6-dihydro-2H-pyran-3-yl) benzoate 3m:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), methyl 3-iodobenzoate (104 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound (75.1mg, 54%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.27;* $[\alpha]^{19}_D$ = -34 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 1720, 1369, 1285, 1231, 1199, 1109. ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.01 – 7.91 (m, 2H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 5.82 (d, *J* = 4.1 Hz, 1H), 4.54 (m, *J* = 2.6 Hz, 1H), 4.37 (dd, *J* = 5.4 Hz, 1H), 4.29 (dd, *J* = 12.0, 2.4 Hz, 1H), 4.06 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.92 (s, 3H), 3.91 (dd, 1H), 3.74 – 3.62 (m, 1H), 2.20 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.77, 168.69, 166.93, 145.77, 141.75, 132.75, 130.47, 129.20, 128.59, 128.32, 117.00, 72.03, 68.87, 63.11, 52.09, 40.90, 20.82. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{18}H_{24}O_7N]^+$ 366.1547, found 366.1545

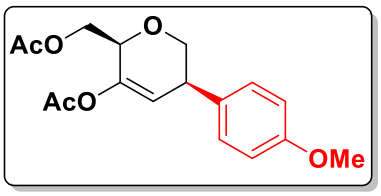
3.14 ((2R, 5R) -3-acetoxy-5-(3,5-dinitrophenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3n:

Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 1-iodo-3,5-dinitrobenzene (118 mg, 0.4 mmol)



and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (53 mg, 32%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) =0.18;* $[\alpha]^{20}_D$ = -28 ° (c 0,5 $CHCl_3$) IR (neat, cm^{-1}): 2956, 2928, 2856, 1767, 1737, 1537, 1367, 1227, 1194, 1154, 1105. ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.89 (t, *J* = 2.1 Hz, 1H), 8.55 (d, *J* = 2.0 Hz, 2H), 5.76 (d, *J* = 5.2 Hz, 1H), 4.57 – 4.47 (m, 1H), 4.43 (dd, *J* = 12.2, 4.2 Hz, 1H), 4.16 (dd, *J* = 12.2, 2.0 Hz, 1H), 4.08 (dd, *J* = 11.7, 3.9 Hz, 1H), 3.90 (dd, *J* = 11.7 Hz, 1H), 3.72 (m, *J* = 4.5 Hz, 1H), 2.14 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.95, 168.44, 148.64, 147.59, 146.71, 128.56, 117.65, 114.58, 72.88, 69.18, 62.57, 40.84, 20.80. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{16}H_{20}O_9N_3]^+$ 398.1194, found 398.1190.

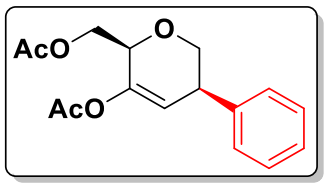
3.15 (2R, 5R) -5-(3-acetoxy-4-methoxyphenyl) -2-(acetoxymethyl)-5,6-dihydro-2H-pyran-3-yl acetate 3o:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 5-iodo-2-methoxyphenyl acetate (117 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified

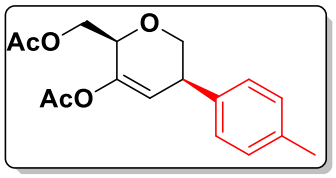
by flash column chromatography (0% grading to 30% AcOEt/cyclohexane), and reversed phase HPLC affording arylated compound (60.5 mg, 40%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.18;* $[\alpha]^{19}_{D}$ = -6 ° (c 0,5 $CHCl_3$). IR (neat, cm^{-1}): 2956, 2928, 2856, 1766, 1738, 1512, 1368, 1269, 1198, 1159, 1124. ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.16 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.78 (d, *J* = 4.6 Hz, 1H), 4.51 (dd, *J* = 4.8, 2.3 Hz, 1H), 4.36 (dd, *J* = 12.0, 5.2 Hz, 1H), 4.27 (dd, *J* = 12.0, 2.6 Hz, 1H), 4.00 (dd, *J* = 11.4, 4.3 Hz, 1H), 3.89 – 3.72 (m, 4H), 3.59 – 3.50 (m, 1H), 2.30 (s, 3H), 2.19 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.70, 168.72, 150.15, 145.33, 139.76, 133.98, 126.34, 122.55, 117.56, 112.40, 71.86, 68.91, 63.10, 55.99, 40.18, 20.80. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{19}H_{26}O_8N]^+$ 396.1653, found 396.1656

3.16 ((2R, 5R) -3-acetoxy-5-phenyl-5,6-dihydro-2H-pyran-2-yl) methyl acetate 3p:



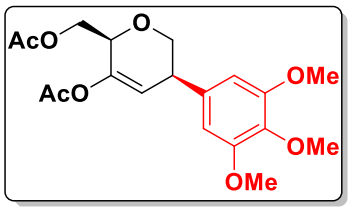
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), iodo-benzene (82 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (62.9 mg, 50%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.52;* $[\alpha]^{18}_{D}$ = −26 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2927, 2858, 1766, 1739, 1688, 1326, 1229,1207,1189, 1148, 1105. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 3.9 Hz, 5H), 5.83 (d, *J* = 4.5 Hz, 1H), 4.53 (s, 1H), 4.38 (dd, *J* = 12.0, 5.5 Hz, 1H), 4.30 (dd, *J* = 12.0, 2.5 Hz, 1H), 4.04 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.87 (dd, *J* = 11.4, 3.8 Hz, 1H), 3.64 (d, *J* = 3.0 Hz, 1H), 2.21 (s, 3H), 2.14 (s, 3H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.71 (s), 168.74 (s), 145.27 (s), 141.16 (s), 128.50 (s), 128.12 (s), 127.01 (s), 117.69 (s), 109.97 (s), 71.85 (s), 68.81 (s), 63.15 (s), 41.08 (s), 20.84 (s). HRMS (ESI+): *m/z* calcd for $[C_{16}H_{18}O_5Na]^+$ 313.1046, found 313.1052.

3.17 ((2R, 5R) -3-acetoxy-5-(p-tolyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3q:



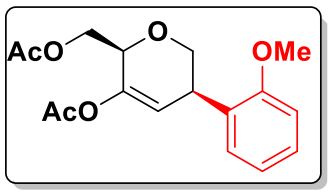
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol),4-iodotoluene (88 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (57.1 mg, 47%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.38;* $[\alpha]^{20}_{D}$ = -12 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 2856, 1768, 1740, 1368, 1229, 1206, 1188, 1042. ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.81 (d, *J* = 4.6 Hz, 1H), 4.52 (m, *J* = 5.0, 2.2 Hz, 1H), 4.37 (dd, *J* = 12.0, 5.5 Hz, 1H), 4.29 (dd, *J* = 12.0, 2.7 Hz, 1H), 4.02 (dd, *J* = 11.3, 4.5 Hz, 1H), 3.83 (dd, *J* = 11.3, 3.9 Hz, 1H), 3.60 (m, *J* = 7.2, 3.6 Hz, 1H), 2.35 (s, 3H), 2.20 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.77, 168.79, 145.11, 138.09, 136.62, 129.19, 127.99, 117.92, 71.80, 68.88, 63.20, 40.69, 20.99, 20.85. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{17}H_{24}O_5N]^+$ 322.1649, found 322.1658.

3.18 ((2R, 5R) -3-acetoxy-5-(3, 4,5-trimethoxyphenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3r:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 5-iodo-1,2,3-trimethoxybenzene (118 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (53.2 mg, 35%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.2;* $[\alpha]^{20}_{D}$ = -58 ° (c 0,5 $CHCl_3$)**;** IR (neat, cm^{-1}): 2956, 2928, 1739, 1722, 1591,1509,1463, 1369, 1229, 1203, 1127. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (s, 2H), 5.88 – 5.68 (d, 1H), 4.51 (dd, *J* = 6.0, 2.3 Hz, 1H), 4.35 (dd, *J* = 11.9, 6.5 Hz, 1H), 4.27 (dd, *J* = 11.9, 2.9 Hz, 1H), 4.01 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.88 (s, 6H), 3.84 (s, 3H), 3.63 – 3.51 (m, 1H), 2.20 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.88 (s), 168.93 (s), 153.47 (s), 145.42 (s), 137.41 (s), 136.98 (s), 118.00 (s), 105.09 (d, *J* = 71.4 Hz), 72.07 (s), 68.91 (s), 63.62 (s), 60.95 (s), 56.40 (s), 41.36 (s), 20.99 (s). HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{19}H_{28}O_8N]^+$ 398.1809, found 398.1819.

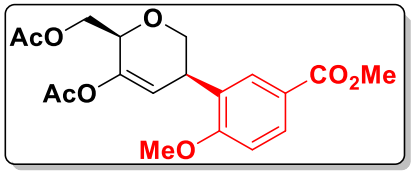
3.19 ((2R, 5R) -3-acetoxy-5-(2-methoxyphenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3s:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 1-iodo-2-methoxybenzene (94 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (63.9mg, 50%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.24;* $[\alpha]^{19}_{D}$ = −10 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 2856, 1738, 1492, 1464, 1253, 1267, 1241, 1206, 1030. ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 5.78 (d, *J* = 3.4 Hz, 1H), 4.52 (m, 1H), 4.30 (d, *J* = 4.6 Hz, 1H), 4.23 (d, *J* = 3.0 Hz, 1H), 4.09 – 3.98 (dd, 2H), 3.90 (dd, *J* = 8.4 Hz, 1H), 3.84 (s, 3H), 2.20 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.73, 168.77, 156.72, 145.52, 129.30, 128.50, 127.99, 120.41, 117.49, 110.13,73.86, 72.01, 67.76, 63.24, 55.27, 34.08, 20.84. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{17}H_{24}O_6N]^+$ 338.1598, found 338.1604.

3.20 methyl 3-((3R, 6R) -5-acetoxy-6-(acetoxymethyl) -3,6-dihydro-2H-pyran-3-yl) -4-methoxybenzoate 3t:

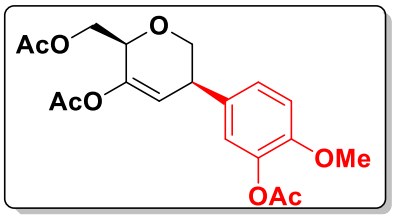
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol),



$Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), methyl 3-iodo-4-methoxybenzoate (117 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (55.9 mg, 37%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.24;* $[\alpha]^{19}_{D}$ = -10 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 2856, 1743, 1712, 1253, 1197, 1152, 1124. ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.04 – 7.90 (m, 2H), 6.91 (d, *J* = 8.5 Hz, 1H), 5.78 (d, *J* = 4.2 Hz, 1H), 4.53 (m, *J* = 2.5 Hz, 1H) 4.35 (dd, *J* = 5.1 Hz, 1H), 4.30 (dd, *J* = 2.5 Hz, 1H), 4.01 (dd, *J* = 8.2, 4.5 Hz, 2H), 3.90 (s, 4H), 3.87 (s, 4H), 2.21 (s, 3H), 2.12 (s, 3H),. ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.09, 168.84, 166.86, 160.49, 146.14, 130.59, 130.46, 129.58, 122.50, 116.59, 109.68, 77.44, 77.02, 76.60, 72.34, 67.74,

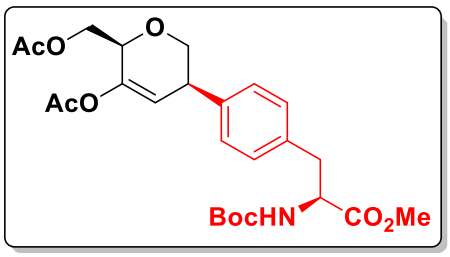
63.12, 55.63, 51.82, 34.18, 20.72. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{19}H_{26}O_8N]^+$ 396.1653, found 396.1651

3.21 ((2R, 5R) -3-acetoxy-5-(4-methoxyphenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3u:



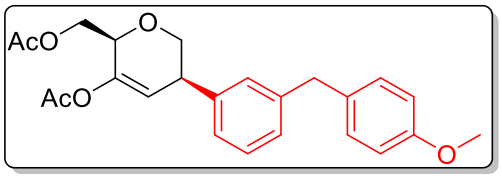
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (12 mg, 0.04 mmol), 1-iodo-4-methoxybenzene (94 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (76.7 mg, 60%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.21*; $[\alpha]^{20}_D$ = 4 ° (c 0,5 $CHCl_3$)**.** IR (neat, cm^{-1}): 2956, 2928, 1767, 1738, 1512, 1368, 1228, 1207, 1178, 1102. ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.27 (d, *J* = 8.6 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 5.79 (d, *J* = 3.5 Hz, 1H), 4.55 – 4.49 (m, 1H), 4.37 (dd, *J* = 12.1, 5.5 Hz, 1H), 4.28 (dd, *J* = 12.1, 2.7 Hz, 1H), 4.01 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.86 – 3.78 (m, 1H), 3.63 – 3.53 (m, 1H), 2.20 (s, 2H), 2.14 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.39, 170.72, 168.77, 158.70, 145.06, 133.26, 129.10, 118.02, 113.96, 110.01, 71.83, 69.00, 63.20, 55.29, 40.29, 20.86. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{17}H_{24}O_6N]^+$ 338.1598, found 338.1600.

3.22 methyl(S)-3-(4-((3R, 6R) -5-acetoxy-6-(acetoxymethyl)-3,6-dihydro-2H-pyran-3-yl) phenyl)-2-((tert-butoxycarbonyl) amino) propanoate 3v:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (83 mg, 0.385 mmol), $Pd(OAc)_2$ (8.6 mg, 0.03 mmol), $AsPh_3$ (12 mg, 0.03 mmol), methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-iodophenyl)propanoate (156 mg, 0.385 mmol) and AgTFA (128 mg, 0.45 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and reversed arylated compound was obtained (85 mg, 45%) as a colorless oil. *Rf (30% EtOAc/cyclohexane) =0.33;*$[\alpha]^{19}_D$ = 20 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 2856, 1742, 1712, 1513, 1391, 1208, 1166, 1103. ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.23 (s, 1H), 7.19 – 7.11 (d, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 5.67 (d, *J* = 4.7, 1.7 Hz, 1H), 4.86 (d, *J* = 7.9 Hz, 1H), 4.50 – 4.37 (m, 2H), 4.25 (dd, *J* = 12.0, 5.5 Hz, 1H), 4.17 (dd, *J* = 12.0, 2.8 Hz, 1H), 3.94 – 3.88 (dd, 1H), 3.73 (dd, *J* = 11.4, 3.8 Hz, 1H), 3.62 (s, 3H), 3.48 (m, *J* = 4.0 Hz, 1H), 3.08 – 2.75 (m, 3H), 2.09 (d, *J* = 0.9 Hz, 3H), 2.03 (d, *J* = 1.0 Hz, 3H), 1.32 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.24, 170.67, 168.73, 145.28, 139.95, 134.76, 133.70, 129.48, 128.33, 117.60, 71.87, 68.81, 63.15, 54.36, 52.16, 40.74, 37.88, 28.28, 20.85. HRMS (ESI+): *m/z* calcd for $[C_{25}H_{33}NO_9Na]^+$ 514.2048, found 514.2045.

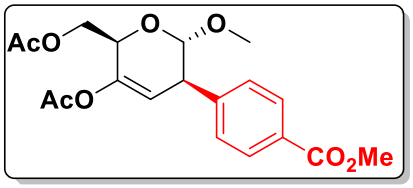
3.23 ((2R,5R) -3-acetoxy-5-(3-(4-methoxybenzyl) phenyl) -5,6-dihydro-2H-pyran-2-yl) methyl acetate 3w:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1a**: (86 mg, 0.4 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), $AsPh_3$ (13 mg, 0.04 mmol), 1-iodo-3-(4-methoxybenzyl)benzene (130 mg, 0.4 mmol)

and AgTFA (134 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 25 % AcOEt/cyclohexane), and reversed phase HPLC affording arylated compound (71 mg, 43 %) as a yellow oil. *Rf (30 % EtOAc/cyclohexane) = 0.46.* IR (neat, cm^{-1}):1766, 1511, 1246, 1228,1201, 1036. ^{1}H NMR (300 MHz, chloroform-d) δ 7.30 – 7.20 (m, 2H), 7.10 (dd, J = 13.2, 7.9 Hz, 4H), 6.86 (d, J = 8.5 Hz, 2H), 5.81 (d, J = 4.4 Hz, 1H), 4.53 (dd, J = 5.0, 2.4 Hz, 2H), 4.39 – 4.32 (m, 1H), 4.29 (dd, J = 12.0, 2.9 Hz, 1H), 4.02 (dd, J = 11.4, 4.6 Hz, 1H), 3.94 (s, 2H), 3.85 (dd, J = 11.6, 3.8 Hz, 1H), 3.81 (s, 3H), 3.64 – 3.57 (m, 1H), 2.21 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.73, 168.75, 158.01, 145.21, 141.82, 141.27, 133.05, 129.82, 128.60, 127.56, 125.79, 117.75, 113.91, 77.45, 77.03, 76.61, 71.83, 68.79, 63.29, 55.24, 41.03, 20.86. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{24}H_{30}NO_6]^+$ 428.2068, found 428.2071.

3.24 methyl 4-((2S, 3R, 6R) -5-acetoxy-6-(acetoxymethyl) -2-methoxy-3,6-dihydro-2H-pyran-3-yl) benzoate 4a:

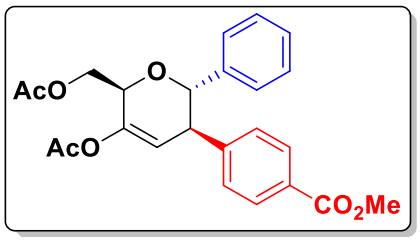


Prepared according to the general procedure for C2-arylation of pseudo-glucal **1b**: (74 mg, 0.3 mmol), Pd(OAc)2 (7 mg, 0.03 mmol), AsPh3 (9 mg, 0.03 mmol), methyl 4-iodobenzoate (79 mg, 0.3 mmol) and AgTFA (100 mg, 0.45 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (38.4 mg, 34%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) =0.24;* $[\alpha]^{19}_{D}$ = 28 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 2856, 1771, 1744, 1720, 1346, 1279, 1229, 1186, 1102. ^{1}H NMR (300 MHz, chloroform-d) δ 8.01 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 5.69 (d, J = 5.2 Hz, 1H), 4.73 (s, 1H), 4.61 (m, 1H), 4.50 (dd, J = 12.1, 4.0 Hz, 1H), 4.30 (dd, J = 12.0, 2.4 Hz, 1H), 3.93 (s, 3H), 3.49 (s, 3H), 2.19 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.60, 168.38, 166.85, 144.97, 144.37, 129.80, 129.21, 128.66, 113.61, 101.31, 77.42, 77.00, 76.57, 66.09, 62.61, 55.78, 52.06, 46.12, 20.88. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{19}H_{26}O_8N]^+$ 396.1653, found 396.1664.

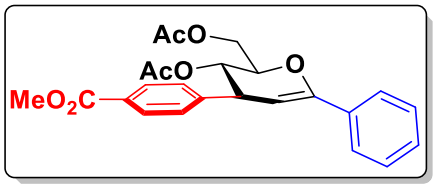
3.25 Compounds 4b an 4b':

Prepared according to the general procedure for C2-arylation of pseudo-glucal **1c**: (116 mg, 0.4 mmol), Pd(OAc)2 (17 mg, 0.04 mmol), AsPh3 (23 mg, 0.04 mmol), methyl 4-iodobenzoate (106 mg, 0.4 mmol) and AgTFA (132 mg, 0.6 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) to furnished a mixture of two regioisomers **4b** and **4b'** (84.6 mg, 48%) in 3:1 ratio (measured by NMR). Both isomers were separated by reversed phase HPLC:

Methyl 4-((2S,3R,6R) -5-acetoxy-6-(acetoxymethyl) -2-phenyl-3,6-dihydro-2H-pyran-3-yl) benzoate 4b as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.23.* $[\alpha]^{19}_{D}$ = 74 ° (c 0,86 $CHCl_3$) IR (neat, cm^{-1}): 2956, 2928, 1746, 1722, 1281, 1237, 1116, 1166. ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.68 – 7.60 (m, 2H), 7.43 – 7.31 (m, 5H), 5.39 (d, *J* = 2.3 Hz, 1H), 5.29 (t, *J* = 9.5 Hz, 1H), 4.49 (dd, *J* = 12.1, 5.2 Hz, 1H), 4.40 – 4.29 (m, 2H), 3.93 (s, 3H), 3.86 (d, *J* = 8.6 Hz, 1H), 2.10 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.81, 169.07, 166.80, 151.99, 146.42, 130.00, 128.78, 128.31, 128.02, 124.90, 98.47, 77.41, 76.99, 76.56, 75.78, 70.46, 62.31, 52.04, 45.84, 20.78, 20.58. HRMS (ESI+): *m/z* calcd for $[M.Na]^+$ $[C_{24}H_{24}NaO_7]^+$ 447.1414, found 447.1420



methyl 4-((2R,4*S*) -3-acetoxy-2-(acetoxymethyl) -6-phenyl-3,4-dihydro-2H-pyran-4-yl) benzoate 4b':

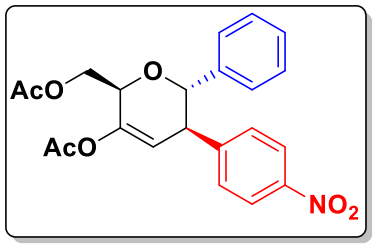


as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.23*; $[\alpha]^{19}_{D}$ = -9 ° (c 0,66 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 1746, 1722, 1281, 1237, 1116, 1166. ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.17 – 7.11 (m, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 5.85 (s, 1H), 4.68 (d, *J* = 8.0 Hz, 1H), 4.61 (d, *J* = 10.1 Hz, 2H), 4.24 (d, *J* = 9.8 Hz, 1H), 3.91 (m, 4H), 2.23 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.65, 168.66, 166.83, 144.98, 138.54, 129.66, 128.61, 128.19, 127.47, 118.27, 78.47, 77.42, 77.00, 76.57, 71.15, 63.30, 52.03, 47.76, 20.95, 20.90. HRMS (ESI+): *m/z* calcd for [M. Na]$^+$ $[C_{24}H_{24}NaO_7]^+$ 447.1414, found 447.1420

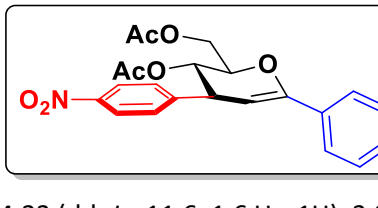
3.26 Compounds 4c and 4c':

Prepared according to the general procedure for C2-arylation of pseudo-glucal **1c**: (92 mg, 0.316 mmol), $Pd(OAc)_2$ (7.2 mg, 0.032 mmol), $AsPh_3$ (10 mg, 0.03 mmol), 1-iodo-4-nitrobenzene (79 mg, 0.316 mmol) and AgTFA (106 mg, 0.375 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane), furnished a mixture of two regioisomers **4c** and **4c'** (67.7 mg, 50%) in 3:1 ratio (measured by NMR). Both isomers were separated by reversed phase HPLC:

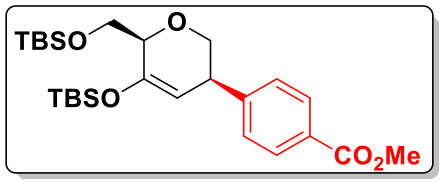
((2R,4*S*)-3-acetoxy-4-(4-nitrophenyl) -6-phenyl-3,4-dihydro-2H-pyran-2-yl) methyl acetate 4c as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.32;* $[\alpha]^{19}_{D}$ = -30.15 ° (c 0,63 $CHCl_3$) IR (neat, cm^{-1}): 2956, 2928, 1743, 1741, 1519, 1347, 1236, 1036. ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.21 (d, *J* = 8.5 Hz, 2H), 7.63 (dd, *J* = 6.4, 2.9 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.39 (dd, *J* = 5.0, 1.6 Hz, 3H), 5.35 (d, *J* = 2.4 Hz, 1H), 5.30 (s, 1H), 4.51 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.42 – 4.30 (m, 2H), 3.92 (dd, *J* = 9.0, 2.2 Hz, 1H), 2.10 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.76, 169.06, 152.55, 148.84, 133.68, 129.03, 128.90, 128.38, 124.94, 123.94, 97.67, 77.42, 77.00, 76.57, 75.75, 70.18, 62.09, 45.88, 20.76. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{22}H_{25}N_2O_7]^+$ 429.1656, found 429.1657



((2R,5R,6*S*) -3-acetoxy-5-(4-nitrophenyl) -6-phenyl-5,6-dihydro-2H-pyran-2-yl) methyl acetate 4c'as a yellow oil. *Rf (30% EtOAc/cyclohexane) =0.32;* $[\alpha]^{19}_{D}$ = 109.8 ° (c 1,02 $CHCl_3$). IR (neat, cm^{-1}): 2956, 2928, 1743, 1741, 1519, 1347, 1236, 1036. ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.30 (dd, *J* = 5.7, 1.8 Hz, 4H), 7.25 – 7.12 (m, 5H), 5.85 (s, 1H), 4.67 (t, *J* = 7.1 Hz, 1H), 4.63 – 4.55 (m, 2H), 4.23 (dd, *J* = 11.6, 1.6 Hz, 1H), 3.98 (d, *J* = 7.8 Hz, 1H), 2.24 (s, 2H), 2.11 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.56, 168.59, 147.56, 145.47, 138.04, 129.45, 128.52, 128.36, 127.46, 123.58, 117.47, 78.42, 77.43, 77.00, 76.58, 71.16, 63.10, 47.56, 20.95. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{22}H_{25}N_2O_7]^+$ 429.1656, found 429.1657.



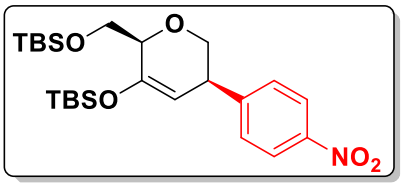
3.27 methyl 4-((3R, 6R) -5-((tert-butyldimethylsilyl) oxy) -6-(((tert-butyldimethylsilyl) oxy) methyl) -3,6-dihydro-2H-pyran-3-yl) benzoate 4d:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1d**: (105 mg, 0.294 mmol), $Pd(OAc)_2$ (7 mg, 0.029 mmol), $AsPh_3$ (9 mg, 0.029 mmol), methyl 4-

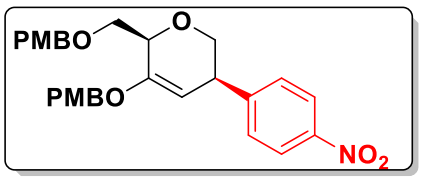
iodobenzoate (77 mg, 0.294 mmol) and AgTFA (98 mg, 0.441 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 10% AcOEt/cyclohexane) and arylated compound was obtained (87.3 mg, 65%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.68;* $[\alpha]^{19}_{D}$ = 6 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2930, 2857, 1721, 1281, 1264, 1101; ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 5.07 (d, *J* = 3.8 Hz, 1H), 4.05 (m, 1H), 3.98 (d, *J* = 3.4 Hz, 2H), 3.92 (s, 3H), 3.89 (d, 1H), 3.83 (dd, *J* = 11.3 Hz, 1H), 3.61 – 3.53 (m, 1H), 0.96 (d, *J* = 7.7 Hz, 18H), 0.22 (s, 6H), 0.11 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.09, 149.90, 148.56, 129.60, 128.49, 128.32, 104.80, 76.58, 68.76, 63.82, 52.03, 51.94, 41.67, 26.91, 26.05, 25.97, 25.86, 25.69, 18.58, 18.44, 18.05, -4.37, -4.52, -5.22. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{26}H_{48}NO_5Si_2]^+$ 510.3066, found 510.3072.

3.28 tert-butyl (((2R, 5R) -3-((tert-butyldimethylsilyl) oxy)-5-(4-nitrophenyl)-5,6-dihydro-2H-pyran-2-yl) methoxy) dimethylsilane 4e:



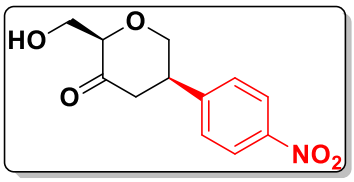
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1d**: (90 mg, 0.25 mmol), $Pd(OAc)_2$ (6 mg, 0.03 mmol), $AsPh_3$ (8 mg, 0.03 mmol), 1-iodo-4-nitrobenzene (63 mg, 0.25 mmol) and AgTFA (83 mg, 0.375 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 10% AcOEt/cyclohexane) and arylated compound was obtained (87.3 mg, 73%) as a yellow oil. *Rf (30% EtOAc/cyclohexane) = 0.8;* $[\alpha]^{20}_{D}$ = 12 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 2856, 1721, 1281, 1264, 1101. ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.14 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 5.04 (d, *J* = 4.7 Hz, 1H), 4.04 (m, 1H), 3.97 (d, *J* = 3.3 Hz, 2H), 3.89 (dd, *J* = 4.3 Hz, 1H), 3.86 (dd, *J* = 3.7 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 18H), 0.20 (s, 6H), 0.10 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.25, 150.54, 129.24, 123.44, 103.98, 68.88, 63.65, 41.57, 26.04, 25.67, 18.61, 18.07, -4.34, -5.22. HRMS (ESI^+): *m/z* calcd for $[M.NH_4]^+$ $[C_{24}H_{45}N_2O_5Si_2]^+$ 497.2862, found 497.2865.

3.29 (3R, 6R) -5-((4-methoxybenzyl) oxy) -6-(((4-methoxybenzyl) oxy) methyl)-3-(4-nitrophenyl)-3,6-dihydro-2H-pyran 4f:



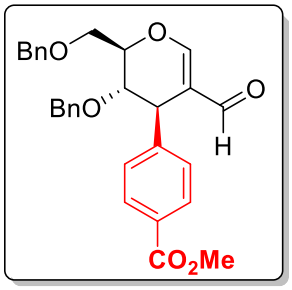
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1e**: (93 mg, 0.25 mmol), $Pd(OAc)_2$ (6 mg, 0.03 mmol), $AsPh_3$ (8 mg, 0.03 mmol), 1-iodo-4-nitrobenzene (63 mg, 0.25 mmol) and AgTFA (83 mg, 0.375 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 30% AcOEt/cyclohexane) and arylated compound was obtained (55.2 mg, 45%) as a yellow oil. Rf (30% EtOAc/cyclohexane) = 0.48; $[\alpha]^{19}_{D}$ = 4 ° (c 0,5 $CHCl_3$); IR (neat, cm^{-1}): 2956, 2928, 2856, 1613, 1513, 1345, 1247, 1173, 1136, 1111. ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.18 (m, 4H), 6.88 (dd, *J* = 8.5, 3.4 Hz, 4H), 4.98 (d, *J* = 5.2 Hz, 1H), 4.76 (s, 2H), 4.56 (d, *J* = 11.3 Hz, 1H), 4.50 (s, 1H), 4.35 (s, 1H), 4.05 – 3.66 (m, 10H), 3.62 – 3.46 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.43, 153.76, 151.38, 146.76, 133.71, 130.38, 129.42, 129.34, 128.88, 128.67, 123.38, 113.93, 96.53, 74.50, 73.32, 69.98, 69.19, 68.87, 55.29, 40.83. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{28}H_{33}N_2O_7]^+$ 509.2282, found 509.2295.

3.30 (2R,5R) -2-(hydroxymethyl) -5-(4-nitrophenyl) dihydro-2H-pyran-3(4H) -one 4g:



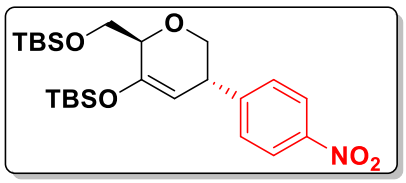
Prepared according to the general procedure for C2-arylation of pseudo-glucal **1f**: (116 mg, 0.89 mmol), $Pd(OAc)_2$ (20 mg, 0.089 mmol), $AsPh_3$ (28 mg, 0.089 mmol), 1-iodo-4-nitrobenzene (222 mg, 0.89 mmol) and AgTFA (295 mg, 1.33 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 60% AcOEt/cyclohexane), and reversed phase HPLC affording arylated compound **4g** (65 mg, 30 %) as a yellow oil. *Rf (80% EtOAc/cyclohexane) = 0.45*.IR (neat, cm^{-1}): 3452, 2956, 2928, 1720, 1519,1347, 1110. ^1H NMR (300 MHz, chloroform-*d*) δ 8.20 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 4.20 (d, *J* = 4.2 Hz, 1H), 4.09 (t, *J* = 4.5 Hz, 1H), 3.98 (t, *J* = 8.3 Hz, 2H), 3.62 (p, *J* = 6.0 Hz, 1H), 3.02 – 2.76 (m, 1H), 2.17 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.61, 149.50, 128.30, 124.04, 82.86, 77.44, 77.02, 76.60, 69.99, 61.80, 43.38, 41.51. HRMS (ESI+): *m/z* calcd for [M. Na]$^+$ $[C_{12}H_{13}NO_5Na]^+$ 274.0686, found 274.0701

3.31 methyl 4-((2R,3S,4R) -3-(benzyloxy) -2-((benzyloxy)methyl) -5-formyl-3,4-dihydro-2H-pyran-4-yl) benzoate 4h:



Prepared according to the general procedure for C2-arylation of pseudo-glucal **1g**: (33 mg, 0.01 mmol), $Pd(OAc)_2$ (2.5 mg, 0.001 mmol), $AsPh_3$ (3 mg, 0.001 mmol), methyl 4-iodobenzoate (26 mg, 0.01 mmol) and AgTFA (33 mg, 0.147 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 25 % AcOEt/cyclohexane), and reversed phase HPLC affording arylated compound **4h** (25.1 mg, 60 %) as a yellow oil. R*f* (30% EtOAc/cyclohexane) = 0.26; $[\alpha]^{17}_D$ = 90° (c 0,3 $CHCl_3$). IR (neat, cm^{-1}): 1721, 1631, 1281, 1182, 1115 ; ^1H NMR (400 MHz, chloroform-*d*) δ 9.30 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.52 (s, 1H), 7.39 – 7.18 (m, 10H), 7.06 – 6.98 (m, 2H), 4.47 (d, *J* = 2.6 Hz, 2H), 4.31 (d, *J* = 10.8 Hz, 1H), 4.21 – 4.15 (m, 1H), 4.04 (d, *J* = 10.8 Hz, 1H), 3.95 – 3.85 (m, 5H), 3.74 (dd, *J* = 10.9, 4.4 Hz, 1H), 3.61 (dd, *J* = 10.9, 3.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.85, 167.01, 164.83, 145.86, 137.38, 137.15, 129.99, 128.96, 128.61, 128.09, 120.14, 80.08, 77.46, 77.14, 76.77, 74.22, 73.76, 67.91, 52.14, 43.78, 27.04. HRMS (ESI$^+$): *m/z* calcd for [M. H]$^+$ $[C_{29}H_{29}O_6]^+$ 473.1959, found 473,1966.

3.32 tert-butyl(((2R,5S) -3-((tert-butyldimethylsilyl) oxy) -5-(4-nitrophenyl) -5,6-dihydro-2H-pyran-2-yl) methoxy) dimethylsilane 4i:



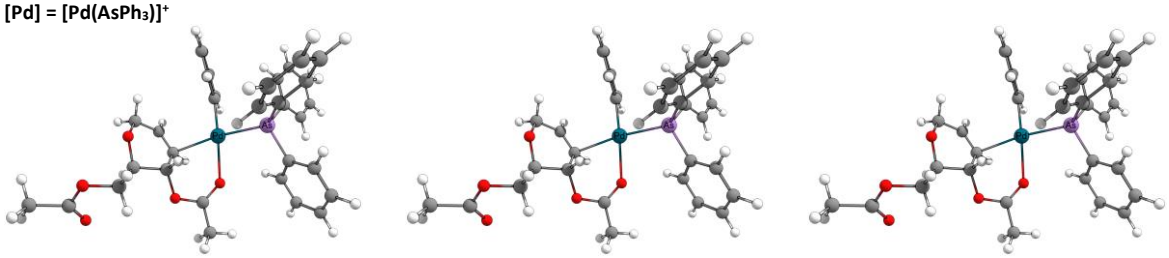
Prepared according to the general procedure for C2-arylation of pseudo-galactal **1h**: (150 mg, 0.426 mmol), $Pd(OAc)_2$ (10 mg, 0.042 mmol), $AsPh_3$ (13 mg, 0.042 mmol), 1-iodo-4-nitrobenzene (107 mg, 0.426 mmol) and AgTFA (142 mg, 0.639 mmol) were employed and the reaction mixture heated for 1 h. The crude material was purified by flash column chromatography (0% grading to 10% AcOEt/cyclohexane), and reversed phase HPLC affording arylated compound **4i** (84.6 mg, 20 %) as a yellow oil. Rf (20% EtOAc/cyclohexane) = 0.73. IR (neat, cm^{-1}): 2956, 2928, 2856, 1665, 1597, 1521, 1472, 1346, 1252, 1212, 1181, 1143, 1109. ^1H NMR (300 MHz, chloroform-*d*) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 5.06 – 5.00 (m, 1H), 4.18 (dd, *J* = 10.9, 4.7 Hz, 1H), 4.12 – 4.06 (m, 1H), 3.97 (dd, *J* = 11.1, 2.4 Hz, 1H), 3.87 (dd, *J* = 11.2, 5.7 Hz, 1H), 3.75 – 3.63 (m, 1H), 3.44 (dd, *J* = 10.9, 6.7 Hz, 1H), 0.94 (d, *J* = 6.6 Hz, 18H), 0.22 (d, *J* = 3.7 Hz, 6H), 0.10 (d, *J* = 1.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.43, 150.33, 146.90, 128.70, 123.73, 104.41, 77.41, 76.99, 76.75, 76.57, 68.82, 63.76, 41.45, 30.18, 26.89, 25.98,

25.60, 18.46, 18.01, -4.36, -4.46, -5.16, -5.25. HRMS (ESI+): *m/z* calcd for $[M.NH_4]^+$ $[C_{24}H_{45}N_2O_5Si_2]^+$ 497.2862, found 497.2882.

4. DFT Computations:

Computational details: Geometries (minima and transition states) were optimized at the B3LYP level of theory at 393.15 K and 1 atm using the Gaussian 16 software package.[7] The double−ζ basis set (LANL2DZ ECP) was used for Pd and As.[8] All other atoms were described by the 6-31G(d) basis set.[9] Frequency calculations were conducted at this level. Single point energy calculations were performed at the M06 level of theory.[10] This method includes dispersion effects. The SDD basis set was used for Pd and As and the 6-311++G(d,p) was used for the other elements.[11] Solvent correction for 1,4-dioxane was obtained with the SMD[12] continuum solvation model as implemented in Gaussian. The values discussed are Gibbs free energies at 393.15 K (ΔG_{393}, kcal/mol).

[Pd] = [Pd(AsPh$_3$)]$^+$



Int-C2-*cis* **Int-C2-*cis*** **Int-C2-*cis***

[Pd] = [Pd(TFA)(AsPh$_3$)]

[7] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[8] a) T. H. Dunning Jr, P. J. Hay, *Modern Theoretical Chemistry*, ed. H. F. Schaefer III, Plenum, New York, 1997, vol. 3; b) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270 ; c) W. R. Wadt, P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284 ; d) P. J. Hay, W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

[9] a) A. D. MacLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639 ; b) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.

[10] Y. Zhao, D. G. Truhlar, *J. Chem. Phys.*, 2006, **125,** 194101.

[11] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297 ; b) F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8,** 1057.

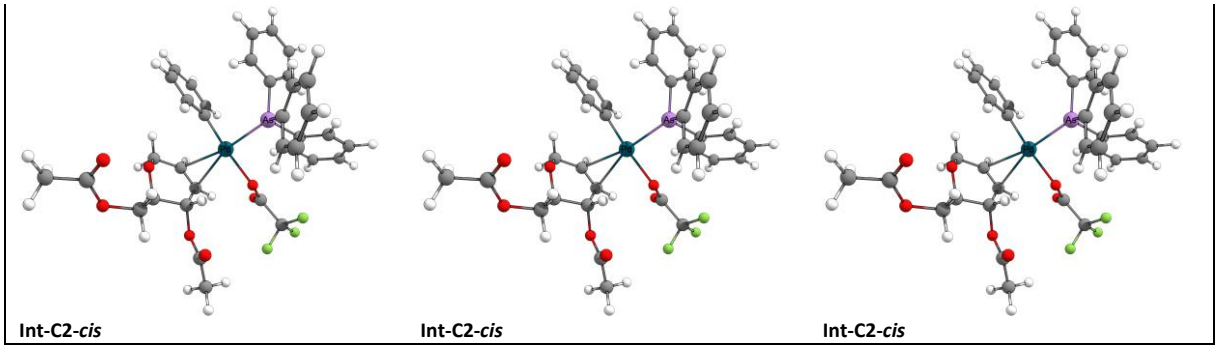


Figure S1. Geometries of selected computed structures (selected distances in Å).

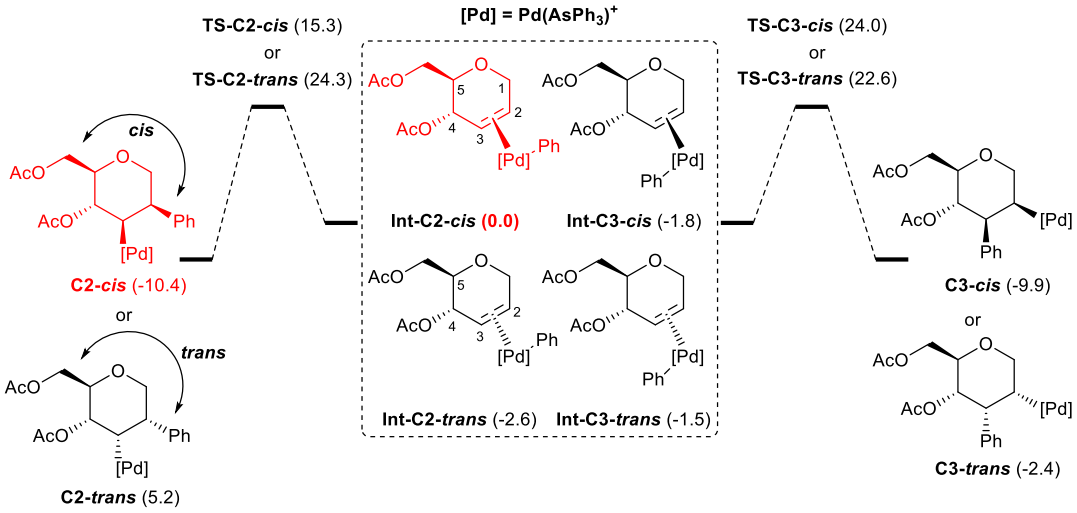


Figure S2. Free energy profile (ΔG_{393}, kcal/mol) of the *syn*-insertion pathways with [Pd] = $Pd(AsPh_3)^+$

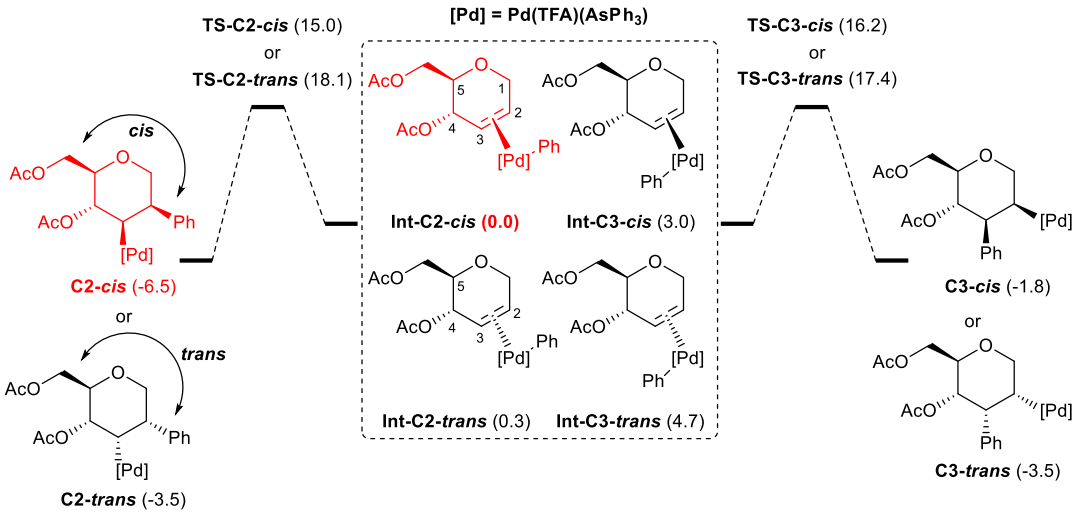
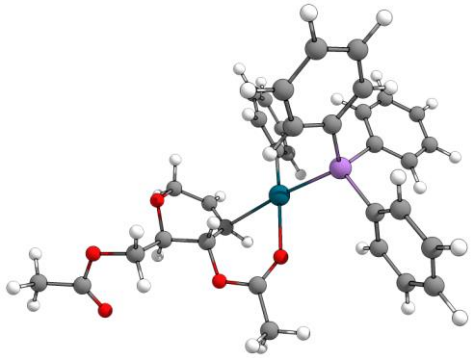
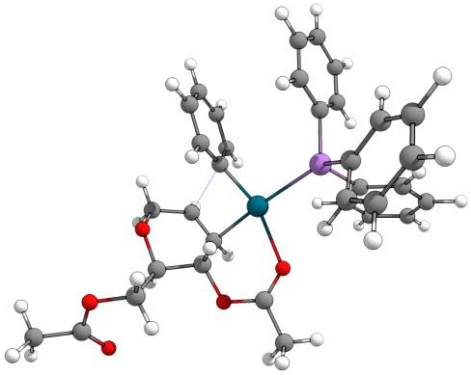


Figure S3. Free energy profile (ΔG_{393}, kcal/mol) of the *syn*-insertion pathways with [Pd] = $Pd(TFA)(AsPh_3)$

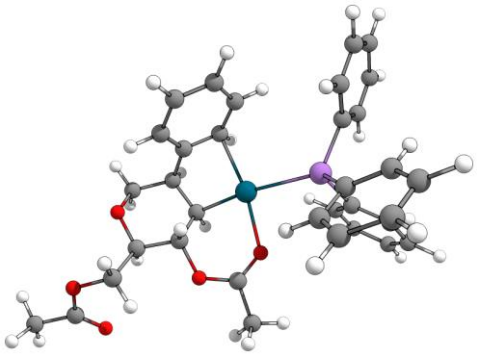
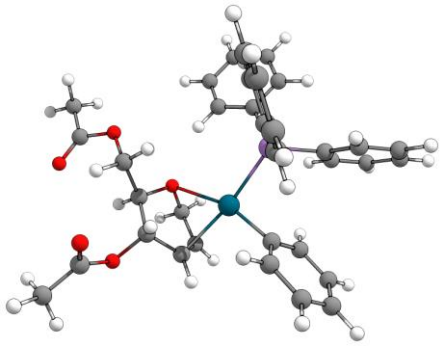
Table S4. Free energies (ΔG_{393}, kcal/mol) of the computed intermediates and transition states referenced to **Int-C2-*cis***

[Pd] = $[Pd(AsPh_3)]^+$					
$TS_{C2\text{-}cis}$	**C2-*cis***	**Int-C3-*cis***	**$TS_{C3\text{-}cis}$**	**C3-*cis***	**Int-C2-*trans***
15.3	-10.4	-1.8	24.0	-9.9	-2.6
$TS_{C2\text{-}trans}$	**C2-*trans***	**Int-C3-*trans***	**$TS_{C3\text{-}trans}$**	**C3-*trans***	
24.3	5.2	-1.5	22.6	-2.4	
[Pd] = $[Pd(TFA)(AsPh_3)]$					
$TS_{C2\text{-}cis}$	**C2-*cis***	**Int-C3-*cis***	**$TS_{C3\text{-}cis}$**	**C3-*cis***	**Int-C2-*trans***
15.0	-6.5	3.0	16.2	-1.8	0.3
$TS_{C2\text{-}trans}$	**C2-*trans***	**Int-C3-*trans***	**$TS_{C3\text{-}trans}$**	**C3-*trans***	
18.1	-3.5	4.7	17.4	-3.5	

Table S5. Coordinates (x,y,z) and energies (Hartree) and imaginary frequencies (cm^{-1}) of the computed minima and transition states.

[Pd] = $[Pd(AsPh_3)]^+$							
 **Int-C2-*cis*** E(RM06) = -1825.35649540				 **$TS_{C2\text{-}cis}$** Frequency -355.1137 E(RM06) = -1825.33270334			
Pd	-0.130805	0.279858	-0.66875	Pd	-0.307201	-0.004311	-0.620876
C	-2.703989	1.911289	-1.404898	C	-2.332118	1.47959	-1.428648
C	-2.464408	0.585136	-1.443969	C	-2.273395	0.069301	-1.32476
C	-3.119566	-0.320005	-0.41799	C	-3.034341	-0.622734	-0.208092
C	-4.474919	0.290489	-0.025091	C	-4.379072	0.095071	0.003639
O	-4.144453	1.56067	0.535954	O	-3.991164	1.421787	0.376284
H	-5.110077	0.395961	-0.914	H	-4.96516	0.10033	-0.923974
H	-2.523238	-0.391959	0.498806	H	-2.500419	-0.550518	0.747336
O	-3.261783	-1.660884	-0.938879	O	-3.182197	-2.026484	-0.510063
H	-2.000829	0.137398	-2.323552	H	-2.160396	-0.496319	-2.25212
C	-3.61658	2.507833	-0.379109	C	-3.444572	2.191494	-0.675943
H	-2.300936	2.575009	-2.165566	H	-2.099928	1.906388	-2.399524
H	-4.430661	3.027382	-0.91544	H	-4.218391	2.396352	-1.438241
H	-3.095954	3.264405	0.220238	H	-3.132676	3.144074	-0.245963
C	-2.123255	-2.353343	-1.077829	C	-2.05166	-2.750338	-0.588921
O	-1.009788	-1.874661	-0.869397	O	-0.921047	-2.271663	-0.506025

C	-2.356391	-3.772938	-1.505262	C	-2.325026	-4.21442	-0.772961
H	-2.955986	-3.794077	-2.420984	H	-3.082245	-4.3639	-1.548016
H	-2.927205	-4.300457	-0.733429	H	-2.72735	-4.627463	0.1594
H	-1.399911	-4.270777	-1.664343	H	-1.40202	-4.73359	-1.031477
C	0.527624	2.155399	-0.60073	C	-0.467067	2.088065	-0.587473
As	2.087209	-0.387196	0.157157	As	2.14082	-0.27155	0.126
C	0.417991	2.897765	0.578626	C	-0.69542	2.639787	0.687711
C	0.950949	2.759926	-1.788337	C	0.210177	2.842793	-1.562908
C	0.698274	4.271119	0.554236	C	-0.22333	3.918162	0.986337
H	0.124369	2.426164	1.512238	H	-1.257709	2.085084	1.433621
C	1.223808	4.132918	-1.801074	C	0.683043	4.118193	-1.253719
H	1.069885	2.180985	-2.700299	H	0.362564	2.439415	-2.560481
C	1.097751	4.888357	-0.632723	C	0.464247	4.657214	0.017449
H	0.608564	4.850601	1.469347	H	-0.401087	4.340599	1.971454
H	1.54324	4.605344	-2.726194	H	1.211723	4.693845	-2.007868
H	1.317885	5.95189	-0.64588	H	0.819235	5.656891	0.249836
C	3.698403	0.427419	-0.606811	C	3.33232	1.290381	0.204397
C	2.239178	-0.114767	2.088919	C	2.395895	-1.133627	1.875625
C	2.317935	-2.314291	-0.121489	C	3.048273	-1.484892	-1.129529
C	3.97545	1.780396	-0.359454	C	3.14442	2.24517	1.214113
C	4.572955	-0.334448	-1.392106	C	4.343296	1.478033	-0.746205
C	5.127715	2.359462	-0.891432	C	3.967667	3.370074	1.275951
H	3.304256	2.38225	0.24478	H	2.363872	2.113063	1.958368
C	5.720025	0.256534	-1.927218	C	5.160093	2.610043	-0.684316
H	4.373097	-1.383786	-1.582593	H	4.504232	0.742554	-1.528484
C	5.998767	1.600722	-1.677434	C	4.975583	3.554852	0.32613
H	5.342004	3.405542	-0.692765	H	3.824204	4.099796	2.068074
H	6.396362	-0.338766	-2.533741	H	5.945838	2.746262	-1.422074
H	6.89312	2.056663	-2.09213	H	5.617011	4.430093	0.376811
C	3.483046	0.112419	2.692407	C	3.512979	-0.869492	2.679136
C	1.082537	-0.185852	2.877364	C	1.434684	-2.058776	2.307271
C	3.563675	0.265697	4.078608	C	3.663378	-1.525375	3.903696
H	4.384194	0.175601	2.090327	H	4.262527	-0.152318	2.359093
C	1.169735	-0.03361	4.261802	C	1.591728	-2.713746	3.529815
H	0.114868	-0.358878	2.411884	H	0.570271	-2.277592	1.685624
C	2.410499	0.193344	4.8624	C	2.704691	-2.446017	4.330163
H	4.529134	0.442804	4.543568	H	4.531274	-1.31545	4.522436
H	0.270998	-0.088496	4.869326	H	0.845043	-3.431479	3.858278
H	2.477664	0.31571	5.939468	H	2.824136	-2.953421	5.283114
C	2.028858	-2.861	-1.379685	C	2.672889	-1.454438	-2.48001
C	2.785618	-3.139042	0.908739	C	4.052271	-2.366959	-0.710249
C	2.224496	-4.223639	-1.60892	C	3.302274	-2.290562	-3.404512
H	1.650798	-2.229935	-2.179457	H	1.889444	-0.776923	-2.813439
C	2.9693	-4.504226	0.675625	C	4.675837	-3.20543	-1.636604
H	3.009862	-2.725687	1.887104	H	4.34618	-2.406452	0.334333
C	2.692509	-5.04615	-0.580584	C	4.303613	-3.167448	-2.98224
H	2.011532	-4.642047	-2.588695	H	3.008566	-2.259633	-4.450046
H	3.33305	-5.14115	1.476714	H	5.452857	-3.888619	-1.305544

H	2.841318	-6.107152	-0.759198	H	4.791101	-3.821389	-3.69959
C	-5.211931	-0.515397	1.036944	C	-5.209375	-0.499632	1.133479
H	-4.665458	-0.473063	1.982566	H	-4.699236	-0.35207	2.088778
H	-5.312435	-1.550281	0.700433	H	-5.359926	-1.565662	0.944376
O	-6.503191	0.032387	1.322538	O	-6.473159	0.156145	1.274982
C	-7.499344	-0.309602	0.455257	C	-7.445523	-0.232034	0.399193
O	-7.308436	-0.986662	-0.530714	O	-7.245075	-1.028392	-0.491217
C	-8.820482	0.257556	0.905822	C	-8.75188	0.450349	0.709827
H	-8.731547	1.332385	1.091184	H	-8.607441	1.530937	0.803118
H	-9.122193	-0.211415	1.848793	H	-9.137024	0.089212	1.669856
H	-9.576817	0.066235	0.144216	H	-9.473234	0.230295	-0.077537
 **C2-*cis*** E(RM06) = -1825.37931626				 **Int-C3-*cis*** E(RM06) = -1825.35723366			
Pd	-0.229415	0.29048	-0.625202	C	1.127948	-2.428264	-0.500905
C	-2.554111	1.843716	-1.508863	C	-2.039819	-2.240074	-1.069299
C	-2.224251	0.384333	-1.193868	C	-2.968936	-1.478533	-0.146294
C	-2.987767	-0.195969	-0.015881	C	-3.205855	-0.026154	-0.631052
C	-4.484979	0.194554	-0.064681	O	-2.116684	0.398306	-1.486832
O	-4.540522	1.61293	-0.087622	H	-4.129391	-0.002761	-1.219091
H	-4.936527	-0.229083	-0.972596	H	-2.584843	-1.487373	0.87948
H	-2.584285	0.148693	0.944226	O	-4.220985	-2.19116	-0.146732
O	-2.94119	-1.653347	-0.018607	C	-1.678831	-1.778805	-2.304615
H	-2.306004	-0.266683	-2.071791	H	-1.797981	-3.25776	-0.775831
C	-4.044348	2.15946	-1.30124	Pd	-0.100712	-0.879766	-0.782283
H	-2.324288	2.030873	-2.565438	C	-2.085695	-0.37844	-2.701123
H	-4.618157	1.761657	-2.151604	H	-1.172468	-2.421909	-3.019271
H	-4.21525	3.23846	-1.247768	H	-3.067662	-0.348433	-3.195493
C	-1.796571	-2.316248	-0.111239	H	-1.352279	0.094751	-3.358364
O	-0.68336	-1.798874	-0.25797	C	-4.872285	-2.292071	1.061852
C	-1.975056	-3.802604	-0.000854	O	-4.423789	-1.83173	2.085392
H	-2.8138	-4.1273	-0.622992	C	-6.183057	-3.010901	0.899518
H	-2.218292	-4.059663	1.036721	H	-6.0635	-3.90698	0.284523
H	-1.055753	-4.309665	-0.294025	H	-6.893076	-2.349651	0.389523
C	-1.550171	2.62766	-0.676254	H	-6.577274	-3.269472	1.882666
As	2.284314	-0.207121	0.046798	As	1.646294	0.648658	0.143204
C	-1.859477	3.296353	0.51683	C	2.075075	-2.756518	-1.469409
C	-0.195167	2.583354	-1.115803	C	0.908667	-3.249733	0.607456
C	-0.857114	3.9579	1.223659	C	2.804022	-3.944916	-1.33048
H	-2.881284	3.303945	0.88116	H	2.262777	-2.10806	-2.31919

C	0.807573	3.259901	-0.379137	C	1.650703	-4.431473	0.735634
H	0.021965	2.279988	-2.142793	H	0.170419	-2.994819	1.363151
C	0.476616	3.938863	0.783554	C	2.595139	-4.779196	-0.231518
H	-1.114527	4.49994	2.129525	H	3.539967	-4.207625	-2.085456
H	1.829734	3.256474	-0.741859	H	1.481316	-5.075831	1.594137
H	1.241534	4.466377	1.344669	H	3.166973	-5.696523	-0.12806
C	3.74365	1.087919	-0.248734	C	1.548477	0.770513	2.098079
C	2.5768	-0.766293	1.909648	C	3.515968	0.264616	-0.295737
C	2.855257	-1.758547	-1.026743	C	1.394594	2.48746	-0.495941
C	3.979975	2.09802	0.69658	C	1.644939	-0.398979	2.867626
C	4.502983	1.055379	-1.425111	C	1.36636	2.008748	2.726756
C	4.96768	3.058163	0.46731	C	1.570377	-0.323281	4.259235
H	3.408421	2.129624	1.620554	H	1.783934	-1.364052	2.389231
C	5.486422	2.021903	-1.652884	C	1.285413	2.074131	4.119828
H	4.34285	0.271956	-2.160062	H	1.290039	2.91875	2.14041
C	5.720574	3.023162	-0.709161	C	1.387815	0.912004	4.88591
H	5.153476	3.828455	1.210814	H	1.651986	-1.229418	4.852634
H	6.074704	1.984318	-2.565397	H	1.144404	3.036161	4.603891
H	6.489307	3.769804	-0.885892	H	1.324993	0.967401	5.968714
C	3.855835	-0.792755	2.484788	C	4.450255	-0.059156	0.693318
C	1.470613	-1.163459	2.672912	C	3.909465	0.321736	-1.64084
C	4.021542	-1.216547	3.805186	C	5.774623	-0.326227	0.335164
H	4.721804	-0.475167	1.911648	H	4.157954	-0.097836	1.737843
C	1.640074	-1.58685	3.992627	C	5.23378	0.05874	-1.990522
H	0.47572	-1.146911	2.235969	H	3.193059	0.584664	-2.415674
C	2.91555	-1.61375	4.559685	C	6.166776	-0.268405	-1.002572
H	5.015357	-1.234148	4.243499	H	6.498507	-0.574079	1.106025
H	0.777139	-1.891482	4.578328	H	5.537022	0.111509	-3.032247
H	3.047409	-1.940292	5.587187	H	7.197533	-0.473749	-1.276303
C	2.393736	-1.849731	-2.347945	C	0.119246	2.940091	-0.860936
C	3.695704	-2.757258	-0.520193	C	2.490177	3.36196	-0.551237
C	2.780603	-2.919125	-3.158532	C	-0.055562	4.262555	-1.275178
H	1.730001	-1.086545	-2.749676	H	-0.739175	2.276786	-0.834608
C	4.074622	-3.829671	-1.330722	C	2.305764	4.681578	-0.967164
H	4.052191	-2.707711	0.504005	H	3.482888	3.020045	-0.275535
C	3.621293	-3.910784	-2.649146	C	1.034452	5.132745	-1.32936
H	2.422795	-2.978937	-4.182649	H	-1.04621	4.608404	-1.555609
H	4.726133	-4.601466	-0.930596	H	3.156855	5.355137	-1.008172
H	3.920265	-4.74537	-3.276804	H	0.895265	6.159846	-1.654026
C	-5.25372	-0.293175	1.160241	C	-3.311739	0.954359	0.528976
H	-4.93686	0.269374	2.042207	H	-4.043755	0.57712	1.24662
H	-5.076099	-1.36099	1.304402	H	-2.343394	1.062618	1.025958
O	-6.658098	-0.045823	1.03837	O	-3.668006	2.272869	0.096509
C	-7.361299	-0.960569	0.31051	C	-4.996196	2.466639	-0.162183
O	-6.836415	-1.897905	-0.249586	O	-5.809741	1.571908	-0.106075
C	-8.832689	-0.637489	0.320744	C	-5.276817	3.90648	-0.504067
H	-8.997735	0.398671	0.009626	H	-4.615959	4.245833	-1.307832
H	-9.227144	-0.738362	1.337734	H	-5.082404	4.53867	0.369216

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	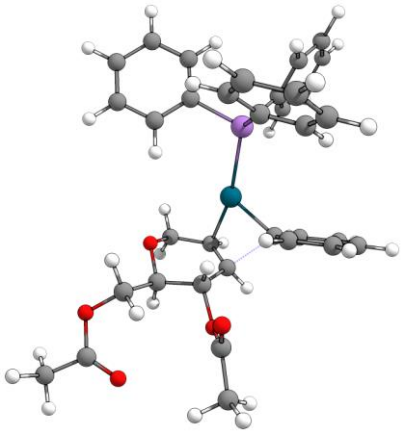				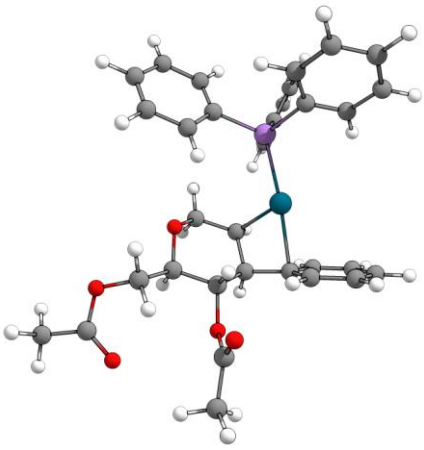		
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C	-0.540507	-2.086008	-0.895194	C	-1.475837	-2.456069	-0.74467
C	-2.195122	-1.038453	-1.516459	C	-2.103556	-1.104023	-1.186325
C	-3.018949	-0.538702	-0.335004	C	-3.059449	-0.485063	-0.149987
C	-3.578729	0.877711	-0.607501	C	-3.262897	1.025059	-0.365115
O	-2.515311	1.719904	-1.060014	O	-1.982625	1.661277	-0.351073
H	-4.356926	0.802233	-1.379896	H	-3.755652	1.191031	-1.334878
H	-2.446126	-0.518446	0.593352	H	-2.697074	-0.625489	0.869553
O	-4.113294	-1.447102	-0.186177	O	-4.318846	-1.154219	-0.307815
C	-1.643577	-0.092341	-2.433328	C	-0.920414	-0.194333	-1.53933
H	-2.568738	-1.971573	-1.922865	H	-2.699334	-1.280627	-2.095033
Pd	0.133578	-0.137913	-1.287298	Pd	0.380029	-1.129816	-0.246875
C	-2.028423	1.369253	-2.334834	C	-1.177787	1.293362	-1.447176
H	-1.399774	-0.450519	-3.435615	H	-0.466546	-0.45253	-2.501733
H	-2.780342	1.574194	-3.120622	H	-1.674579	1.586054	-2.39445
H	-1.1763	2.032749	-2.540382	H	-0.256425	1.875146	-1.373832
C	-4.391372	-1.901877	1.081961	C	-4.943891	-1.636275	0.810357
O	-3.692241	-1.640687	2.034263	O	-4.427176	-1.627878	1.906891
C	-5.662763	-2.699422	1.088181	C	-6.324225	-2.124506	0.474206
H	-5.681916	-3.41231	0.259082	H	-6.300709	-2.784189	-0.398209
H	-6.497643	-2.00293	0.950333	H	-6.940126	-1.255433	0.21671
H	-5.766208	-3.216692	2.042394	H	-6.749471	-2.6431	1.33382
As	2.259596	0.387574	0.096401	As	2.266367	0.430877	0.047149
C	-0.120415	-2.975286	-1.901022	C	-0.777003	-3.223408	-1.71417
C	-0.61193	-2.495416	0.443635	C	-1.598466	-2.99113	0.561481
C	0.278444	-4.265261	-1.550994	C	-0.239097	-4.469993	-1.39759
H	-0.114879	-2.673644	-2.944362	H	-0.697998	-2.851255	-2.732455
C	-0.228298	-3.797288	0.773083	C	-1.04794	-4.239571	0.870106
H	-0.962182	-1.830855	1.225341	H	-2.170027	-2.472437	1.322827
C	0.221795	-4.677051	-0.215756	C	-0.373534	-4.979781	-0.102506
H	0.614668	-4.951268	-2.322862	H	0.273468	-5.044812	-2.162915
H	-0.286509	-4.11933	1.80857	H	-1.168994	-4.637754	1.872941
H	0.513418	-5.688419	0.051203	H	0.038271	-5.954019	0.143596
C	2.313085	-0.146847	1.987814	C	3.242258	-0.361488	1.552593

C	3.974768	-0.237471	-0.619835	C	3.563496	0.468675	-1.419698
C	2.421409	2.348195	0.139935	C	1.948493	2.298002	0.530937
C	2.435155	-1.508058	2.303965	C	3.711833	-1.678459	1.42219
C	2.190838	0.797442	3.013837	C	3.417127	0.328237	2.758371
C	2.444914	-1.916058	3.638597	C	4.361778	-2.294856	2.492113
H	2.534552	-2.250451	1.516459	H	3.592514	-2.217786	0.484826
C	2.19397	0.381423	4.347838	C	4.067736	-0.296338	3.825031
H	2.100939	1.854057	2.78065	H	3.056496	1.346507	2.867228
C	2.321744	-0.972436	4.661646	C	4.538164	-1.604607	3.694132
H	2.551734	-2.970163	3.879323	H	4.731776	-3.310526	2.385839
H	2.1031	1.118861	5.140254	H	4.20897	0.242845	4.757233
H	2.327839	-1.292129	5.699643	H	5.043243	-2.085547	4.526616
C	5.095487	-0.416822	0.202531	C	4.94064	0.501044	-1.160419
C	4.075753	-0.484975	-1.995332	C	3.10191	0.490439	-2.742573
C	6.307095	-0.834133	-0.353118	C	5.84595	0.560316	-2.222485
H	5.025859	-0.240143	1.271788	H	5.309137	0.472855	-0.139325
C	5.28947	-0.898483	-2.546814	C	4.011011	0.552022	-3.79946
H	3.208074	-0.356403	-2.638994	H	2.036048	0.457034	-2.953175
C	6.405383	-1.073417	-1.725465	C	5.383033	0.586742	-3.539509
H	7.17317	-0.972334	0.287815	H	6.912457	0.583891	-2.018371
H	5.361962	-1.087686	-3.614029	H	3.64899	0.568816	-4.823361
H	7.348988	-1.398954	-2.15366	H	6.090146	0.630782	-4.362607
C	1.2427	3.108594	0.188626	C	0.777349	2.635101	1.223504
C	3.663005	2.99541	0.108192	C	2.893122	3.286817	0.221222
C	1.307462	4.503361	0.215864	C	0.559661	3.957805	1.614294
H	0.270366	2.618344	0.215043	H	0.026484	1.880275	1.437495
C	3.72224	4.39048	0.130199	C	2.666425	4.606473	0.614566
H	4.581413	2.41811	0.061197	H	3.797709	3.034873	-0.323905
C	2.54767	5.144408	0.185147	C	1.503167	4.941621	1.312055
H	0.39164	5.086161	0.257898	H	-0.350826	4.21824	2.145705
H	4.68763	4.887757	0.103993	H	3.398452	5.37199	0.374273
H	2.598866	6.229211	0.201545	H	1.329742	5.970444	1.613841
C	-4.164354	1.52466	0.653372	C	-4.095753	1.673854	0.747553
H	-4.473055	0.770477	1.377254	H	-4.747825	0.950041	1.234674
H	-3.404907	2.170263	1.099282	H	-3.415599	2.106007	1.484075
O	-5.272065	2.382882	0.351433	O	-4.88213	2.769697	0.258063
C	-6.488176	1.771411	0.28652	C	-6.125748	2.449582	-0.196157
O	-6.631435	0.574781	0.419751	O	-6.545959	1.313135	-0.231961
C	-7.58599	2.774745	0.048362	C	-6.879567	3.684647	-0.617411
H	-7.326671	3.441256	-0.779419	H	-6.266009	4.304269	-1.278059
H	-7.712268	3.397339	0.941239	H	-7.118696	4.287082	0.266107
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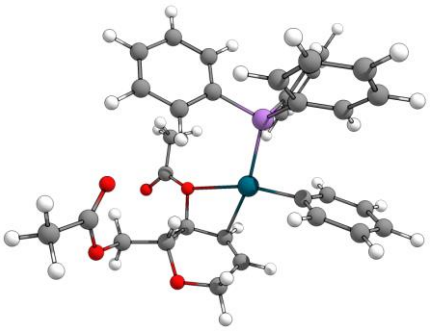
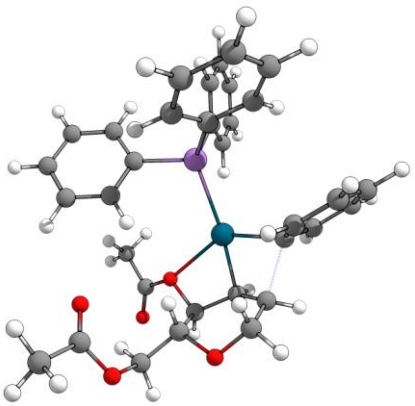


Int-C2-*trans*

E(RM06) = -1825.36360525



$TS_{C2\text{-}trans}$

Frequency -369.5115

E(RM06) = -1825.32132008

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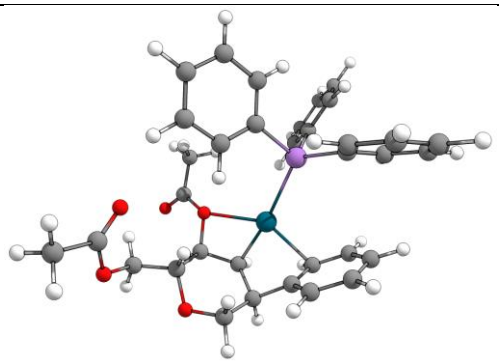
Pd	0.189469	0.991551	-0.659847	Pd	0.258226	0.952766	-0.866074
C	-2.064274	2.815571	-1.098528	C	-1.078204	3.537068	-1.189353
C	-1.067661	2.976612	1.116482	C	-0.628458	3.040079	1.154268
C	1.978444	2.145295	-1.824989	C	1.885223	2.057882	-1.619734
C	2.853392	3.269888	0.216753	C	2.525937	3.012006	0.632988
H	1.134082	3.931013	-1.041759	H	1.453941	4.068417	-1.003448
C	2.980669	1.029579	-1.651092	C	2.97639	1.014338	-1.462767
H	1.409307	2.163259	-2.753834	H	1.619588	2.296294	-2.651876
C	3.650764	1.093662	-0.260068	C	3.572431	1.010094	-0.041241
H	3.719697	1.005452	-2.456292	H	3.760858	1.163758	-2.21246
O	2.173187	-0.187186	-1.734047	O	2.322913	-0.26241	-1.733255
O	3.984774	2.440287	0.037604	O	3.755395	2.359339	0.373134
H	2.933615	0.707617	0.480643	H	2.865962	0.501826	0.631132
C	4.932819	0.270807	-0.192004	C	4.925304	0.30649	0.02533
C	2.676918	-1.233343	-2.498902	C	2.994318	-1.168704	-2.542003
As	-1.455899	-0.655322	0.160435	As	-1.558476	-0.642994	0.069309
H	2.360776	3.069091	1.184343	H	2.004666	2.507482	1.456796
H	3.227627	4.298781	0.254134	H	2.775336	4.024447	0.958924
O	3.763017	-1.167423	-3.013903	O	4.092626	-0.930404	-2.974895
C	1.722586	-2.391138	-2.5605	C	2.181293	-2.4127	-2.75731
H	0.706374	-2.055307	-2.784224	H	1.215566	-2.165314	-3.210189
H	1.699415	-2.897644	-1.589987	H	1.980932	-2.896715	-1.795902
H	2.066604	-3.088331	-3.325237	H	2.73284	-3.089606	-3.410083
C	-2.425526	-0.334625	1.831153	C	-2.391564	-0.278948	1.815732
C	-2.833709	-1.018575	-1.179052	C	-3.093501	-0.9281	-1.119994
C	-0.511973	-2.34987	0.437343	C	-0.76428	-2.429372	0.299386
C	-2.879522	3.917036	-0.801686	C	-2.141487	4.354129	-0.811009
H	-2.155665	2.322387	-2.061707	H	-0.821266	3.441368	-2.240771
C	-1.884587	4.078743	1.395529	C	-1.682789	3.876916	1.522208
H	-0.384406	2.606005	1.875165	H	-0.063596	2.525637	1.924434
C	-2.787698	4.549116	0.439459	C	-2.439086	4.530635	0.545008
H	-3.587122	4.27102	-1.546503	H	-2.722915	4.868386	-1.57059
H	-1.815469	4.560156	2.367276	H	-1.915038	4.011038	2.574361

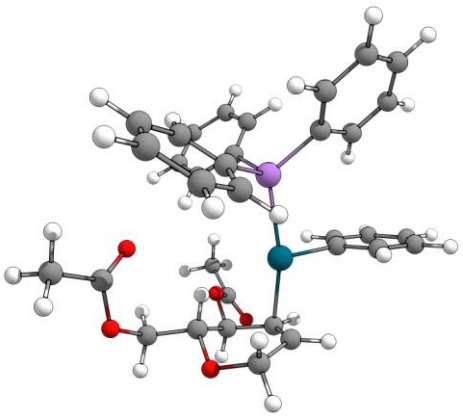
H	-3.422903	5.400856	0.664029	H	-3.25249	5.187304	0.839186
C	-3.458958	0.61311	1.86486	C	-3.371598	0.718965	1.91562
C	-2.085606	-1.045233	2.989102	C	-1.99018	-0.973906	2.963183
C	-4.078765	-1.547358	-0.81252	C	-4.314371	-1.431309	-0.648796
C	-2.547147	-0.780076	-2.530204	C	-2.944583	-0.639634	-2.483341
C	0.75384	-2.330079	1.039918	C	0.562331	-2.509324	0.748216
C	-1.086864	-3.568829	0.052737	C	-1.476469	-3.606157	0.032981
C	-4.153783	0.836218	3.053821	C	-3.951578	1.008208	3.152041
H	-3.726757	1.1734	0.974301	H	-3.696206	1.262803	1.032572
C	-2.781831	-0.809098	4.176818	C	-2.568233	-0.674371	4.199555
H	-1.291777	-1.785202	2.970375	H	-1.239792	-1.756035	2.89738
C	-3.815345	0.128139	4.20994	C	-3.54944	0.31369	4.295715
H	-4.958728	1.565074	3.075768	H	-4.72166	1.771736	3.220199
H	-2.518409	-1.364482	5.072237	H	-2.257239	-1.22246	5.08444
H	-4.358049	0.306039	5.133788	H	-4.003153	0.538755	5.256624
C	-5.025532	-1.83917	-1.797346	C	-5.369601	-1.648014	-1.537758
H	-4.316211	-1.72531	0.231944	H	-4.44851	-1.646517	0.407178
C	-3.496529	-1.074782	-3.509857	C	-4.000785	-0.859676	-3.369346
H	-1.586205	-0.358787	-2.81807	H	-2.00387	-0.240051	-2.856801
C	-4.735897	-1.604561	-3.143057	C	-5.213874	-1.364303	-2.896361
H	-5.98985	-2.248194	-1.510319	H	-6.313327	-2.037909	-1.167127
H	-3.270854	-0.887065	-4.555634	H	-3.877833	-0.63371	-4.424772
H	-5.476073	-1.830741	-3.904907	H	-6.037273	-1.532847	-3.584324
C	1.439051	-3.526118	1.266826	C	1.169471	-3.752922	0.941876
H	1.225498	-1.394896	1.327806	H	1.139671	-1.610232	0.947115
C	-0.396375	-4.761029	0.2808	C	-0.865216	-4.847724	0.221383
H	-2.063059	-3.594256	-0.421742	H	-2.500838	-3.560187	-0.323933
C	0.862608	-4.740986	0.887439	C	0.453671	-4.92289	0.677013
H	2.422141	-3.487251	1.724128	H	2.197244	-3.787615	1.289798
H	-0.843719	-5.705119	-0.016647	H	-1.421717	-5.756946	0.012027
H	1.395136	-5.671867	1.060131	H	0.922692	-5.891945	0.822232
H	4.767971	-0.728682	-0.597722	H	4.91859	-0.600176	-0.580666
H	5.721376	0.772383	-0.756615	H	5.704933	0.982112	-0.332386
O	5.436801	0.175008	1.15018	O	5.293638	-0.016715	1.376045
C	4.850219	-0.739285	1.955706	C	4.721636	-1.126934	1.901016
O	3.892048	-1.407687	1.615076	O	3.877913	-1.777547	1.313781
C	5.548004	-0.81637	3.288853	C	5.280839	-1.434346	3.265567
H	6.53406	-1.276283	3.158125	H	6.30481	-1.810931	3.161252
H	4.957294	-1.419558	3.979061	H	4.667526	-2.193619	3.751969
H	5.708806	0.185512	3.697177	H	5.328071	-0.528978	3.8772



C2-*trans*

E(RM06) = -1825.35898568

C	0.716464	3.227209	-0.364005
C	2.160242	2.985627	-0.860415
Pd	0.268741	0.925738	-0.928642
C	-0.345057	3.202965	-1.324925
C	0.382047	3.53843	0.976363
C	2.000873	1.71003	-1.692781
C	3.203915	2.8135	0.268365
H	2.477919	3.820997	-1.497661
C	2.957342	0.539473	-1.53768
H	1.746484	1.894412	-2.740296
C	3.823432	0.622607	-0.270276
H	3.589927	0.424406	-2.423675
O	2.064621	-0.626979	-1.456472
O	4.26494	1.966822	-0.134938
H	3.210113	0.338881	0.596485
C	5.04714	-0.287024	-0.329913
C	2.409232	-1.753496	-2.200358
As	-1.761935	-0.40246	0.115475
H	2.742122	2.39202	1.17308
H	3.652275	3.775213	0.528036
O	3.406199	-1.769965	-2.873492
C	1.417417	-2.864542	-2.012233
H	0.417019	-2.548923	-2.326077
H	1.360089	-3.1348	-0.953038
H	1.733824	-3.724276	-2.603332
C	-2.982005	0.403114	1.435042
C	-2.979985	-1.150838	-1.234756
C	-1.051655	-1.975291	1.069251
C	-1.669342	3.513195	-0.943712
H	-0.114483	3.150802	-2.3855
C	-0.923965	3.850406	1.327352
H	1.154572	3.583839	1.735146
C	-1.956092	3.835236	0.37214
H	-2.448266	3.521629	-1.700135
H	-1.148951	4.119037	2.35509

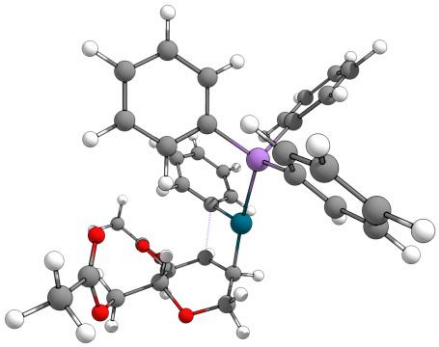


Int-C3-*trans*

E(RM06) = -1825.35635712

C	-1.284371	-2.296574	-0.807461
C	1.90656	-2.573213	-1.020892
Pd	0.189485	-0.95036	-0.808179
C	-1.442141	-3.112735	0.311692
C	-2.055361	-2.457997	-1.956668
C	3.045595	-1.964827	-0.232605
C	1.635929	-2.1377	-2.289231
H	1.428028	-3.459066	-0.615738
C	3.371222	-0.580197	-0.818622
H	3.92077	-2.623271	-0.2848
O	2.684458	-1.774116	1.149304
O	3.636779	-0.734765	-2.2009
H	2.495314	0.083724	-0.665617
C	4.574886	0.080627	-0.158615
C	2.5049	-1.104813	-2.969223
C	2.706299	-2.896337	1.94087
H	0.901627	-2.654625	-2.902968
H	1.913996	-0.210602	-3.236081
As	-1.313242	0.798165	0.140097
H	2.89165	-1.521853	-3.906264
O	2.922452	-3.997656	1.49459
C	2.453948	-2.544716	3.383317
H	3.364882	-2.110224	3.811891
H	2.203158	-3.450187	3.937247
H	1.658354	-1.800206	3.475987
C	-0.654828	2.485138	-0.61483
C	-3.24541	0.813111	-0.174514
C	-1.066658	0.952378	2.077474
C	-2.395569	-4.139485	0.26169
H	-0.846104	-2.969077	1.207664
C	-3.000662	-3.492207	-1.98789
H	-1.942413	-1.802243	-2.814513
C	-3.17075	-4.329279	-0.883923
H	-2.523268	-4.786928	1.124899
H	-3.603819	-3.632009	-2.880742

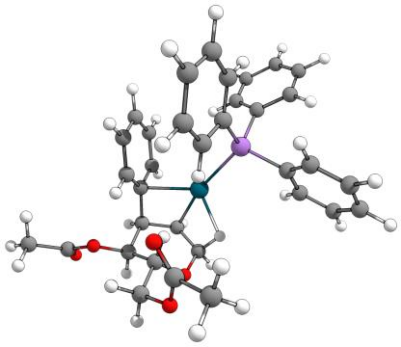
H	-2.969606	4.081856	0.66933	H	-3.906007	-5.127704	-0.915712
C	-4.105636	1.127834	1.013098	C	-0.474163	2.568067	-2.004225
C	-2.695108	0.307819	2.802802	C	-0.376669	3.594204	0.192939
C	-4.24076	-1.672791	-0.911365	C	-3.862466	1.957544	-0.697031
C	-2.546336	-1.181594	-2.56754	C	-4.015616	-0.314931	0.145788
C	0.291621	-1.952034	1.469743	C	0.240122	1.058256	2.580237
C	-1.831374	-3.106899	1.344847	C	-2.160787	0.942819	2.95057
C	-4.937728	1.741622	1.952622	C	-0.02889	3.757648	-2.581773
H	-4.348852	1.199713	-0.043557	H	-0.693733	1.712095	-2.638859
C	-3.525632	0.929726	3.738111	C	0.069869	4.782294	-0.391247
H	-1.836033	-0.262712	3.144551	H	-0.505656	3.538149	1.268874
C	-4.647529	1.64585	3.315619	C	0.2437	4.865485	-1.774482
H	-5.817019	2.286007	1.618977	H	0.101888	3.820451	-3.658252
H	-3.301176	0.843153	4.797551	H	0.27581	5.643891	0.237375
H	-5.297517	2.120254	4.045184	H	0.587468	5.79251	-2.224212
C	-5.045826	-2.228441	-1.908053	C	-5.244472	1.971084	-0.896973
H	-4.605863	-1.634873	0.110808	H	-3.2759	2.835946	-0.945848
C	-3.351847	-1.739728	-3.562478	C	-5.397143	-0.288963	-0.050804
H	-1.578506	-0.760469	-2.834879	H	-3.549746	-1.21036	0.544401
C	-4.602015	-2.265766	-3.231852	C	-6.011935	0.850955	-0.57387
H	-6.021276	-2.630405	-1.649308	H	-5.718744	2.860128	-1.302288
H	-3.006589	-1.758033	-4.592345	H	-5.990605	-1.16307	0.200852
H	-5.231528	-2.697907	-4.004205	H	-7.086758	0.865473	-0.729302
C	0.856128	-3.044451	2.134971	C	0.439268	1.162109	3.958325
H	0.914344	-1.086712	1.256084	H	1.099525	1.087702	1.915675
C	-1.269846	-4.195495	2.014008	C	-1.948192	1.037725	4.328305
H	-2.869968	-3.151085	1.032088	H	-3.17318	0.867763	2.566447
C	0.071206	-4.166273	2.407651	C	-0.651448	1.147109	4.832463
H	1.904737	-3.010867	2.414746	H	1.449013	1.263408	4.345885
H	-1.879707	-5.069854	2.223239	H	-2.798654	1.032329	5.003868
H	0.50357	-5.019957	2.921819	H	-0.490305	1.226376	5.903704
H	4.781424	-1.26331	-0.73816	H	5.491488	-0.419768	-0.478241
H	5.817841	0.17365	-0.951171	H	4.46926	0.027103	0.926713
O	5.652209	-0.452872	0.962595	O	4.73185	1.448148	-0.566442
C	5.043042	-1.325136	1.801418	C	3.915465	2.353711	0.024963
O	4.000734	-1.889404	1.527428	O	3.035047	2.047316	0.805293
C	5.831724	-1.496403	3.073485	C	4.264098	3.758747	-0.392463
H	6.750685	-2.053802	2.859515	H	5.073519	4.130547	0.247079
H	5.237947	-2.048068	3.803016	H	3.392752	4.402326	-0.262513
H	6.128087	-0.524054	3.477246	H	4.616395	3.786767	-1.426084



$TS_{C3\text{-}trans}$

Frequency -343.4402

E(RM06) = -1825.31847441

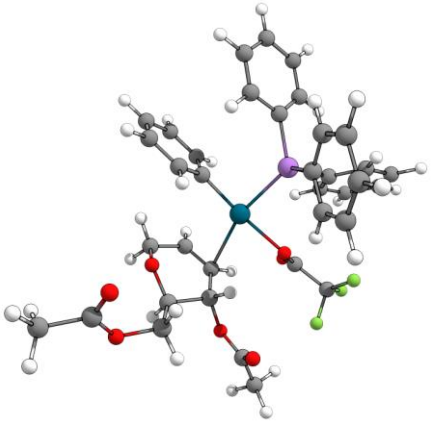


C3-*trans*

E(RM06) = -1825.35979351

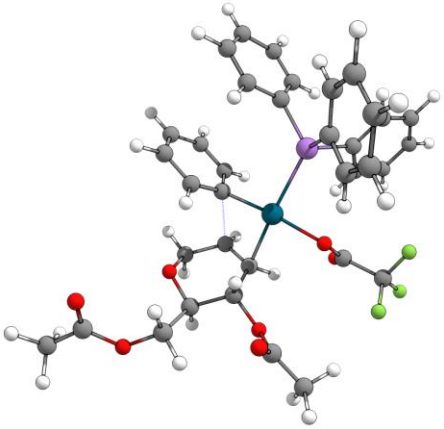
C	1.242495	-1.905397	-0.405398	C	1.981412	-1.936005	-0.143277
C	2.695133	-1.060646	-1.685334	C	2.924006	-1.419586	-1.262786
Pd	0.209458	-0.358076	-1.374724	Pd	0.171381	-0.813363	-1.241028
C	1.411621	-1.697909	0.972275	C	1.976635	-1.49503	1.202491
C	0.961366	-3.185076	-0.913399	C	1.087011	-2.991167	-0.501973
C	3.714374	-0.239658	-0.911012	C	3.911717	-0.294483	-0.894954
C	1.909171	-0.354305	-2.640578	C	1.936272	-0.919767	-2.317466
H	3.020643	-2.062627	-1.932286	H	3.508587	-2.262009	-1.643317
C	3.216846	1.202217	-0.732014	C	3.178549	1.052725	-0.765342
H	4.600854	-0.2182	-1.560411	H	4.629155	-0.209205	-1.717447
O	4.09831	-0.787001	0.351305	O	4.639702	-0.569319	0.310394
O	3.053506	1.747153	-2.038832	O	2.73885	1.414948	-2.07837
H	2.254455	1.2018	-0.198375	H	2.304697	0.959052	-0.108157
C	4.20486	2.081627	0.025239	C	4.061698	2.177147	-0.239812
C	2.040791	1.144908	-2.812456	C	1.823772	0.531296	-2.653342
C	4.912631	-1.893533	0.303932	C	5.679833	-1.462409	0.195871
H	1.547245	-0.907246	-3.510592	H	1.711348	-1.60207	-3.140143
H	1.059926	1.642498	-2.60728	H	0.747725	0.86047	-2.347447
As	-1.959176	0.030018	-0.038011	As	-2.030334	-0.071907	-0.092472
H	2.26511	1.370834	-3.862139	H	1.818018	0.703246	-3.735455
O	5.218491	-2.422849	-0.738355	O	5.931408	-2.030694	-0.839568
C	5.327936	-2.316842	1.686109	C	6.412867	-1.602704	1.502685
H	5.788936	-1.480683	2.220902	H	6.842094	-0.639632	1.798703
H	6.02934	-3.14819	1.612995	H	7.20659	-2.341843	1.393215
H	4.446036	-2.626927	2.256939	H	5.721943	-1.910129	2.294398
C	-2.864961	1.614737	-0.77367	C	-2.671763	1.63849	-0.830964
C	-3.346369	-1.358262	-0.090455	C	-3.612403	-1.228041	-0.240094
C	-1.728524	0.439411	1.866683	C	-1.85516	0.301666	1.829817
C	1.26559	-2.782256	1.841051	C	1.176001	-2.127513	2.146779
H	1.628397	-0.714724	1.372142	H	2.625329	-0.687533	1.515363
C	0.819394	-4.257482	-0.031755	C	0.285584	-3.619907	0.47189
H	0.868219	-3.349471	-1.983193	H	1.148802	-3.432471	-1.493803
C	0.97115	-4.055815	1.343905	C	0.335206	-3.19453	1.791548
H	1.372579	-2.623647	2.910315	H	1.205286	-1.785375	3.176526
H	0.603534	-5.248003	-0.421438	H	-0.345869	-4.453896	0.180886
H	0.866497	-4.892635	2.028145	H	-0.271981	-3.681811	2.54798

C	-3.044564	1.688631	-2.163584	C	-2.700403	1.791365	-2.224768
C	-3.310487	2.663752	0.039015	C	-3.102502	2.688767	-0.011761
C	-4.705101	-1.024996	-0.169304	C	-4.907103	-0.691111	-0.221542
C	-2.961226	-2.704951	-0.034713	C	-3.43864	-2.612481	-0.365494
C	-0.621621	1.208548	2.250918	C	-0.728844	1.016166	2.262128
C	-2.630439	-0.016408	2.836397	C	-2.807278	-0.12395	2.763693
C	-3.668428	2.799134	-2.733367	C	-3.158957	2.980298	-2.793174
H	-2.716239	0.872553	-2.805311	H	-2.378048	0.978833	-2.873435
C	-3.931292	3.775924	-0.536536	C	-3.556823	3.880266	-0.584699
H	-3.176924	2.617468	1.115517	H	-3.083409	2.5842	1.068799
C	-4.110273	3.845309	-1.919167	C	-3.585872	4.027394	-1.972233
H	-3.81069	2.846813	-3.809304	H	-3.183887	3.088824	-3.87383
H	-4.277413	4.586238	0.098851	H	-3.890184	4.691509	0.056422
H	-4.593974	4.71098	-2.362237	H	-3.940672	4.95402	-2.414062
C	-5.669928	-2.034752	-0.188214	C	-6.014376	-1.536185	-0.319024
H	-5.013179	0.015019	-0.220256	H	-5.054908	0.381655	-0.139476
C	-3.930557	-3.709356	-0.050884	C	-4.548483	-3.454198	-0.462202
H	-1.910049	-2.974024	0.022575	H	-2.437898	-3.03494	-0.388796
C	-5.284436	-3.375439	-0.128703	C	-5.83671	-2.916353	-0.43864
H	-6.722043	-1.771845	-0.250591	H	-7.015387	-1.114597	-0.305482
H	-3.628233	-4.751942	-0.007014	H	-4.407338	-4.526867	-0.561193
H	-6.037165	-4.158312	-0.145614	H	-6.700202	-3.570391	-0.518167
C	-0.419998	1.527441	3.594561	C	-0.559592	1.310842	3.615377
H	0.092465	1.56908	1.51594	H	0.025993	1.352093	1.55684
C	-2.423074	0.30283	4.180793	C	-2.630038	0.166269	4.119827
H	-3.489132	-0.616407	2.550547	H	-3.684196	-0.677575	2.441824
C	-1.321159	1.072948	4.560453	C	-1.510192	0.883086	4.54647
H	0.4456	2.122054	3.869903	H	0.317332	1.869988	3.928623
H	-3.125119	-0.051098	4.930543	H	-3.371415	-0.166555	4.840884
H	-1.164964	1.316371	5.607629	H	-1.379259	1.108331	5.601149
H	5.112263	2.222159	-0.566156	H	4.836652	2.423955	-0.968643
H	4.444323	1.615932	0.982725	H	4.516016	1.867002	0.702523
O	3.693622	3.405995	0.239471	O	3.328359	3.397635	-0.049006
C	2.796035	3.556274	1.242248	C	2.523836	3.461137	1.038878
O	2.3639	2.621649	1.89037	O	2.341939	2.518484	1.786929
C	2.437357	5.006492	1.436094	C	1.916801	4.832289	1.184064
H	3.298769	5.543703	1.848571	H	2.699138	5.552267	1.449009
H	1.596689	5.088133	2.125712	H	1.158592	4.816928	1.967485
H	2.19248	5.473067	0.477464	H	1.480442	5.161005	0.236244
[Pd] = [Pd(TFA)($AsPh_3$)]							



Int-C2-*cis*

E(RM06) = -2351.74956784



$TS_{C2\text{-}cis}$

Frequency -348.5265

E(RM06) = -2351.72630937

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C	2.140362	-0.741698	-2.368016	C	-2.114978	0.697468	-2.017725
C	2.202706	0.478651	-1.778197	C	-2.084595	-0.575101	-1.381206
C	3.145778	0.766501	-0.627266	C	-3.092865	-0.919775	-0.294526
C	4.193022	-0.359342	-0.492271	C	-4.385772	-0.085135	-0.454367
O	3.549535	-1.624313	-0.611552	O	-4.040246	1.283655	-0.652232
H	4.93134	-0.239239	-1.302319	H	-4.934694	-0.45965	-1.33345
H	2.604356	0.914191	0.310203	H	-2.69019	-0.768574	0.711082
O	3.794254	2.015094	-0.97055	O	-3.393493	-2.322325	-0.449817
H	1.705454	1.333468	-2.22844	H	-1.716828	-1.421789	-1.958909
Pd	0.054506	-0.266463	-0.855043	Pd	-0.188459	-0.013824	-0.603466
C	3.019208	-1.866973	-1.900253	C	-3.387526	1.518515	-1.878948
H	1.581188	-0.881166	-3.289569	H	-1.664854	0.737734	-3.006749
H	3.834908	-1.993465	-2.637073	H	-4.03928	1.215293	-2.719983
H	2.472517	-2.809853	-1.840795	H	-3.208396	2.591875	-1.949149
C	4.037978	2.898613	0.038253	C	-3.502706	-3.074931	0.682963
O	3.863545	2.645107	1.208728	O	-3.477608	-2.609412	1.800188
C	4.536624	4.209653	-0.515539	C	-3.643433	-4.535345	0.338268
H	3.680149	4.766663	-0.909428	H	-2.651388	-4.931976	0.099462
H	5.241856	4.047652	-1.33501	H	-4.283513	-4.673143	-0.537125
H	5.001078	4.788252	0.284184	H	-4.044563	-5.07374	1.198227
As	-2.129261	-0.29062	0.305492	As	2.186131	0.519971	0.260881
O	0.17142	1.791174	-0.143327	O	0.195947	-2.041658	-0.014909
C	0.396117	-3.169367	-0.366369	C	-1.317094	2.672029	-0.023723
C	-0.818295	-2.684159	-2.398498	C	-0.082207	2.66322	-2.11035
C	0.302355	-4.540305	-0.640065	C	-1.168225	4.058481	0.052367
H	0.920848	-2.840943	0.527563	H	-1.889977	2.154995	0.738872
C	-0.907066	-4.054294	-2.670701	C	0.059142	4.048005	-2.033188
H	-1.266412	-1.975065	-3.090894	H	0.335067	2.128054	-2.960273
C	-0.348831	-4.985954	-1.792596	C	-0.486708	4.749216	-0.95314
H	0.743291	-5.255285	0.050886	H	-1.599437	4.598828	0.891197
H	-1.41727	-4.390541	-3.570466	H	0.593199	4.58065	-2.81568
H	-0.42057	-6.049545	-2.004682	H	-0.385179	5.829685	-0.899539
C	-3.180613	1.307068	-0.13788	C	3.571126	-0.496408	-0.707075

C	-3.432053	-1.74781	0.076856	C	2.890266	2.361456	0.194403
C	-1.876527	-0.158972	2.25262	C	2.515652	0.006732	2.1403
C	-3.113541	1.840049	-1.430922	C	3.245657	-1.090946	-1.932475
C	-4.017732	1.896763	0.818608	C	4.866403	-0.639479	-0.189746
C	-3.883415	2.956747	-1.764607	C	4.211838	-1.813448	-2.638737
H	-2.43758	1.41531	-2.166367	H	2.234846	-1.024601	-2.324518
C	-4.786441	3.011035	0.478286	C	5.828423	-1.358821	-0.899468
H	-4.06516	1.496009	1.826914	H	5.123753	-0.200351	0.770122
C	-4.720689	3.540597	-0.812669	C	5.502435	-1.944728	-2.125833
H	-3.812564	3.376232	-2.763917	H	3.94606	-2.282421	-3.582031
H	-5.430093	3.468888	1.224555	H	6.829836	-1.46817	-0.491355
H	-5.313451	4.413491	-1.072404	H	6.251446	-2.510458	-2.673656
C	-4.716497	-1.482596	-0.415483	C	3.889003	2.733331	-0.714502
C	-3.076494	-3.064962	0.401517	C	2.339254	3.334895	1.040513
C	-5.634948	-2.522989	-0.576549	C	4.335427	4.05631	-0.769846
H	-5.006255	-0.468967	-0.67193	H	4.327598	1.991981	-1.375349
C	-4.000114	-4.099077	0.245487	C	2.792428	4.653652	0.98914
H	-2.078297	-3.292535	0.759969	H	1.555286	3.067732	1.743688
C	-5.280243	-3.830727	-0.244219	C	3.791618	5.017382	0.083398
H	-6.628377	-2.306468	-0.960161	H	5.11355	4.331694	-1.477069
H	-3.712863	-5.115792	0.498736	H	2.362838	5.396734	1.655835
H	-5.996307	-4.638516	-0.369401	H	4.144044	6.04471	0.043685
C	-0.951714	0.781488	2.732882	C	1.875698	-1.143573	2.625949
C	-2.587424	-0.965606	3.149081	C	3.369843	0.733257	2.980371
C	-0.745237	0.904661	4.107637	C	2.09346	-1.556174	3.94218
H	-0.408077	1.416884	2.039394	H	1.222443	-1.719052	1.976246
C	-2.370524	-0.835914	4.523646	C	3.580324	0.314683	4.296783
H	-3.305407	-1.693756	2.785185	H	3.866237	1.628463	2.618504
C	-1.44958	0.096152	5.003354	C	2.94215	-0.828954	4.77936
H	-0.028661	1.633333	4.476404	H	1.594505	-2.447974	4.311755
H	-2.922982	-1.465592	5.216067	H	4.243239	0.884726	4.94276
H	-1.280533	0.192808	6.072489	H	3.105211	-1.151756	5.804296
C	0.025827	2.759861	-0.969845	C	0.345566	-2.8849	-0.969881
O	-0.087412	2.724839	-2.193876	O	0.259251	-2.71075	-2.183811
C	0.062675	4.145659	-0.270923	C	0.683887	-4.301882	-0.433617
F	1.353104	4.503854	-0.030149	F	-0.312432	-4.765373	0.366417
F	-0.576193	4.137779	0.914771	F	1.810071	-4.279651	0.308716
F	-0.486226	5.105802	-1.028331	F	0.855356	-5.191961	-1.419367
C	4.912104	-0.360305	0.84994	C	-5.291393	-0.13741	0.768927
H	5.363471	0.611461	1.052604	H	-5.538065	-1.168288	1.025795
H	4.221315	-0.61701	1.65526	H	-4.815298	0.347903	1.622802
O	5.979259	-1.324407	0.802723	O	-6.528795	0.528013	0.461958
C	5.855292	-2.44013	1.568222	C	-6.772305	1.71682	1.07585
O	4.956364	-2.640445	2.352096	O	-6.060678	2.212497	1.91848
C	7.006854	-3.382216	1.300905	C	-8.060281	2.313343	0.557069
H	6.962664	-4.218052	2.000058	H	-8.297272	3.214708	1.123316
H	7.961928	-2.856952	1.399777	H	-8.877063	1.589583	0.640942
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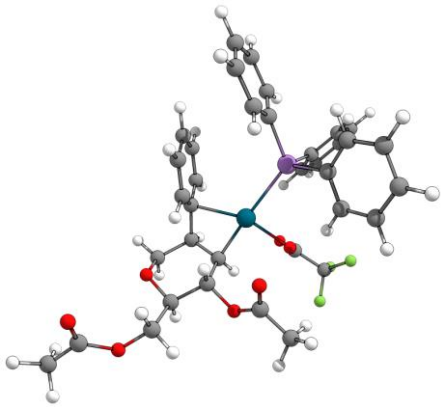

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C	2.200527	0.540837	-1.055317
C	3.114984	0.604488	0.165384
C	4.564166	0.228047	-0.209512
O	4.537671	-1.056972	-0.820501
H	4.970715	0.971185	-0.914557
H	2.789199	-0.067522	0.963469
O	3.105579	1.94578	0.688177
H	2.124506	1.518895	-1.52951
Pd	0.307579	0.002402	-0.486435
C	3.93786	-1.024463	-2.106232
H	2.17679	-0.2348	-3.04844
H	4.492442	-0.325379	-2.753315
H	4.037162	-2.033544	-2.518193
C	2.346788	2.173357	1.801055
O	1.796472	1.296944	2.429315
C	2.292869	3.646358	2.110154
H	1.61156	4.122736	1.3977
H	3.277139	4.108613	1.993023
H	1.919271	3.792815	3.1246
As	-2.186426	-0.571966	0.299906
O	-0.134239	2.064403	-0.179131
C	1.498664	-2.342811	-0.420342
C	0.574376	-2.215864	-2.663688
C	0.687241	-3.46168	-0.1635
H	2.237553	-2.045497	0.314256
C	-0.220473	-3.32232	-2.398395
H	0.531918	-1.733849	-3.636984
C	-0.161416	-3.953479	-1.14585
H	0.737119	-3.943012	0.8082
H	-0.890598	-3.700915	-3.165208
H	-0.791929	-4.812807	-0.940099
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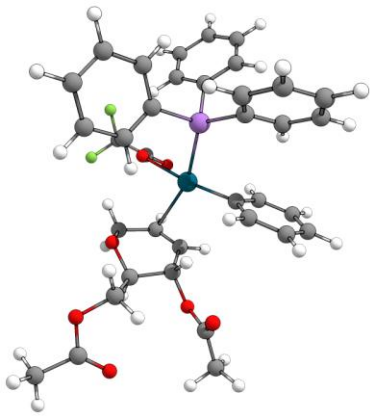

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C	-3.276684	-0.322964	-0.613207
C	-3.813182	0.847976	0.236428
O	-2.760276	1.753481	0.545496
H	-4.584403	1.355425	-0.362598
H	-2.825339	-1.097483	0.009558
O	-4.395885	-0.912423	-1.318298
C	-1.870787	1.450723	-1.6947
H	-2.171378	-0.486826	-2.52475
C	-2.248208	2.415927	-0.601633
H	-1.324669	1.837396	-2.551254
Pd	0.129471	0.104878	-0.882086
H	-3.000817	3.120208	-1.001832
H	-1.384142	2.994229	-0.2717
C	-4.940328	-2.051141	-0.81042
O	-4.501325	-2.638827	0.154332
C	-6.176887	-2.432316	-1.582575
H	-6.030781	-2.29386	-2.656974
H	-6.990368	-1.770655	-1.262635
H	-6.443417	-3.466215	-1.359072
As	2.066637	-0.554891	0.500079
O	0.797343	2.159353	-0.524578
C	0.171183	-2.198108	-2.64926
C	-0.822172	-2.768773	-0.521806
C	-0.074695	-3.496704	-3.111362
H	0.65541	-1.479524	-3.308088
C	-1.077594	-4.063146	-0.990733
H	-1.106332	-2.513658	0.495679
C	-0.703349	-4.430993	-2.283812
H	0.223157	-3.772381	-4.120518
H	-1.569285	-4.779534	-0.337563
H	-0.899252	-5.43713	-2.645329
C	2.362896	-2.427633	1.026126
C	3.829073	0.020976	-0.166694

C	-2.721877	0.271178	2.008838	C	1.90969	0.409618	2.203478
C	-3.15056	0.583731	-2.201518	C	2.468874	-3.412341	0.032641
C	-4.917008	0.156102	-0.601718	C	2.476123	-2.793612	2.373127
C	-4.094739	1.082276	-3.104612	C	2.706685	-4.741502	0.385124
H	-2.097736	0.596237	-2.468373	H	2.344956	-3.153109	-1.014246
C	-5.856457	0.649728	-1.507271	C	2.704172	-4.12741	2.720993
H	-5.24436	-0.185264	0.376262	H	2.387227	-2.045352	3.153843
C	-5.446192	1.111706	-2.761199	C	2.824758	-5.101422	1.729253
H	-3.765793	1.457103	-4.069944	H	2.784959	-5.495916	-0.392659
H	-6.907331	0.680942	-1.231217	H	2.787751	-4.401458	3.769266
H	-6.178799	1.502079	-3.462773	H	3.002946	-6.138079	2.002117
C	-3.635854	-3.086791	-0.313602	C	4.829564	-0.895622	-0.509155
C	-2.298786	-3.14126	1.697445	C	4.060528	1.395611	-0.315715
C	-3.980117	-4.42787	-0.117356	C	6.055064	-0.437019	-1.000084
H	-4.032663	-2.552517	-1.171557	H	4.666582	-1.961826	-0.38906
C	-2.647873	-4.477848	1.896323	C	5.286799	1.84535	-0.805142
H	-1.645142	-2.648437	2.413096	H	3.292349	2.112524	-0.052049
C	-3.488527	-5.125955	0.986727	C	6.284977	0.931156	-1.150169
H	-4.639133	-4.92283	-0.826176	H	6.829067	-1.153449	-1.262365
H	-2.265772	-5.012033	2.762476	H	5.4528	2.912764	-0.92079
H	-3.761513	-6.166411	1.141625	H	7.238107	1.283954	-1.534833
C	-2.105518	1.476913	2.372944	C	0.662076	0.907523	2.597849
C	-3.706255	-0.281063	2.840534	C	3.029876	0.608734	3.022607
C	-2.478399	2.119364	3.556035	C	0.53427	1.586574	3.811533
H	-1.345626	1.917371	1.735222	H	-0.203793	0.790459	1.951736
C	-4.071738	0.365788	4.02311	C	2.896103	1.286765	4.235512
H	-4.183124	-1.220745	2.578361	H	4.00613	0.245876	2.71354
C	-3.458373	1.567322	4.38232	C	1.648258	1.773995	4.63134
H	-1.995504	3.053059	3.831526	H	-0.434915	1.978209	4.107496
H	-4.834797	-0.071373	4.662201	H	3.767771	1.439683	4.866152
H	-3.741906	2.069249	5.30378	H	1.547305	2.307074	5.5729
C	-0.32767	2.714149	-1.272138	C	1.089509	2.750459	-1.625679
O	-0.259364	2.321924	-2.432546	O	1.030776	2.318427	-2.775376
C	-0.664991	4.204738	-0.997803	C	1.512975	4.227118	-1.399988
F	0.446749	4.863769	-0.573859	F	2.547806	4.323842	-0.529456
F	-1.599664	4.335971	-0.035667	F	0.480143	4.9296	-0.87491
F	-1.108719	4.830306	-2.094325	F	1.882795	4.832439	-2.535276
C	5.469747	0.143936	1.010389	C	-4.422997	0.38291	1.557318
H	5.451024	1.091897	1.55305	H	-4.891148	-0.595352	1.453659
H	5.161685	-0.672774	1.66689	H	-3.639043	0.338152	2.316295
O	6.824249	-0.071403	0.582559	O	-5.388144	1.326209	2.064286
C	7.393477	-1.27046	0.880129	C	-6.644942	1.204362	1.574633
O	6.873109	-2.126033	1.557996	O	-6.970946	0.378359	0.747312
C	8.762571	-1.365539	0.248438	C	-7.564608	2.22592	2.20034
H	9.258938	-2.273881	0.591668	H	-7.17734	3.235788	2.030539
H	9.363433	-0.486794	0.502352	H	-7.611399	2.073517	3.283827
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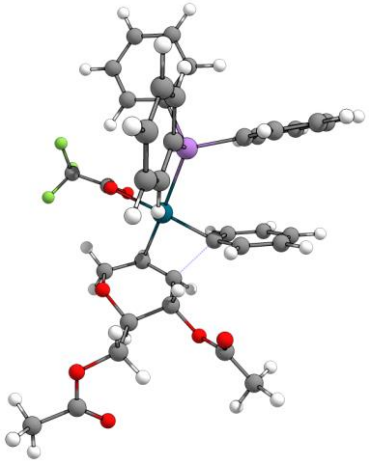

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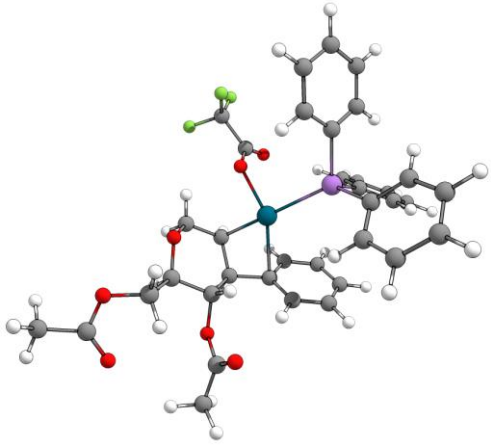

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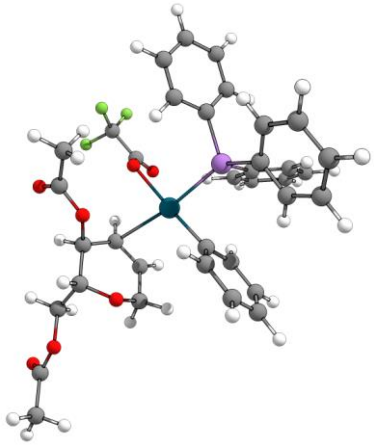
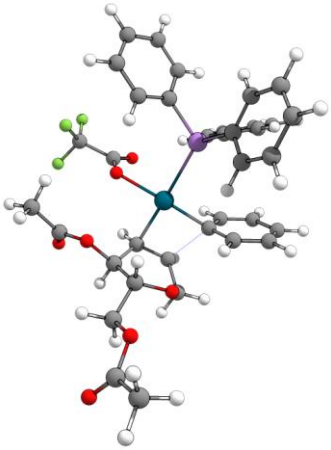
C	-3.160479	-0.735209	-0.354549	C	-3.52751	-0.583136	-0.305664
C	-4.022862	0.443457	0.146868	C	-4.221234	0.733656	0.091367
O	-3.140438	1.494891	0.500413	O	-3.247924	1.738589	0.308905
H	-4.70748	0.758836	-0.655823	H	-4.902355	1.026379	-0.724879
H	-2.597267	-1.124405	0.492826	H	-3.010349	-0.978363	0.570464
O	-3.991832	-1.787832	-0.882762	O	-4.557545	-1.51432	-0.718913
C	-1.877348	1.106241	-1.560037	C	-1.838092	0.928207	-1.522247
H	-2.530434	-0.745602	-2.437487	H	-3.205405	-0.526502	-2.404022
C	-2.538437	2.108071	-0.628119	C	-2.561947	2.093943	-0.881708
H	-1.629074	1.50377	-2.543815	H	-1.527373	1.208445	-2.534422
Pd	-0.022357	0.443557	-0.797908	Pd	-0.08016	0.296954	-0.657857
H	-3.308791	2.648742	-1.209049	H	-3.291942	2.500492	-1.609988
H	-1.826472	2.840373	-0.244276	H	-1.866026	2.890206	-0.615244
C	-4.176162	-2.899676	-0.119344	C	-4.923869	-2.519684	0.114358
O	-3.713022	-3.037524	0.991628	O	-4.343214	-2.786278	1.147282
C	-5.028809	-3.904967	-0.851497	C	-6.151926	-3.217613	-0.409046
H	-4.518116	-4.22934	-1.764467	H	-6.051756	-3.434474	-1.476473
H	-5.976842	-3.44635	-1.149992	H	-7.004301	-2.540368	-0.283338
H	-5.213777	-4.763732	-0.205544	H	-6.3208	-4.136063	0.154468
As	2.134277	-0.38194	0.435862	As	2.248731	-0.50248	0.389389
O	0.504014	2.465677	-0.346474	O	0.302834	2.270953	-0.055148
C	-0.146242	-1.607365	-2.873978	C	-0.439987	-1.36976	-2.535954
C	-0.69534	-2.606534	-0.736812	C	-1.453061	-2.65905	-0.748294
C	0.249241	-2.853245	-3.357179	C	0.530408	-2.372715	-2.705307
H	-0.107983	-0.739271	-3.528192	H	-0.464841	-0.550687	-3.247159
C	-0.307127	-3.85574	-1.22951	C	-0.496382	-3.649992	-0.935959
H	-1.063522	-2.537783	0.281974	H	-2.214053	-2.805973	0.010063
C	0.164038	-3.983396	-2.536879	C	0.500978	-3.510995	-1.911766
H	0.610222	-2.944978	-4.378428	H	1.298084	-2.247378	-3.46212
H	-0.371145	-4.727387	-0.583767	H	-0.525115	-4.540678	-0.314534
H	0.459296	-4.957128	-2.917469	H	1.248417	-4.287581	-2.043829

C	2.889	-2.136614	-0.062933	C	3.473255	-1.202134	-0.992856
C	3.756977	0.746475	0.458826	C	3.348041	0.922005	1.205693
C	1.777816	-0.590024	2.36723	C	2.328707	-1.867666	1.81891
C	3.374582	-2.296783	-1.369227	C	3.655245	-0.412482	-2.140071
C	2.9366	-3.220615	0.821661	C	4.104806	-2.447798	-0.903169
C	3.913331	-3.51741	-1.777599	C	4.470764	-0.868326	-3.177743
H	3.33665	-1.467769	-2.071625	H	3.159385	0.552603	-2.221003
C	3.468893	-4.444904	0.407903	C	4.914133	-2.901911	-1.94947
H	2.564805	-3.113423	1.835962	H	3.970414	-3.067345	-0.021455
C	3.960463	-4.594771	-0.889503	C	5.099058	-2.113793	-3.086365
H	4.293778	-3.626885	-2.789779	H	4.613391	-0.248627	-4.059283
H	3.502937	-5.279002	1.104133	H	5.401843	-3.870417	-1.871371
H	4.379331	-5.5458	-1.20785	H	5.730535	-2.467028	-3.89747
C	5.048709	0.207312	0.3939	C	4.729485	1.013928	0.991734
C	3.590159	2.134355	0.56183	C	2.717001	1.848965	2.046232
C	6.161709	1.051521	0.432696	C	5.471984	2.016531	1.62009
H	5.19356	-0.864994	0.306519	H	5.227722	0.313497	0.328187
C	4.706007	2.972334	0.596208	C	3.462844	2.850418	2.670816
H	2.595247	2.562241	0.601075	H	1.641973	1.812558	2.191304
C	5.992553	2.433667	0.532631	C	4.840504	2.933898	2.461708
H	7.160599	0.625685	0.381271	H	6.542935	2.082185	1.446001
H	4.559646	4.046911	0.659908	H	2.961721	3.573087	3.308524
H	6.860243	3.087822	0.555572	H	5.418314	3.71755	2.944525
C	0.449485	-0.602767	2.810204	C	1.168153	-2.584004	2.136331
C	2.814965	-0.70411	3.303479	C	3.50068	-2.106554	2.55157
C	0.158656	-0.743243	4.169459	C	1.179715	-3.535326	3.160137
H	-0.359982	-0.48463	2.093918	H	0.250336	-2.396208	1.587498
C	2.523204	-0.845142	4.661215	C	3.512977	-3.060302	3.570713
H	3.850456	-0.671339	2.976376	H	4.401949	-1.538842	2.338254
C	1.195289	-0.867299	5.095348	C	2.352873	-3.776939	3.875725
H	-0.875663	-0.748198	4.502418	H	0.270413	-4.079874	3.400888
H	3.333425	-0.930828	5.380572	H	4.426621	-3.237293	4.132243
H	0.970628	-0.972704	6.153361	H	2.362658	-4.514321	4.674023
C	0.738801	3.15031	-1.410286	C	1.11388	2.885458	-0.842944
O	0.755386	2.784119	-2.581159	O	1.748322	2.452456	-1.799683
C	0.958669	4.652328	-1.086782	C	1.190577	4.396211	-0.498479
F	1.866825	4.833	-0.098591	F	1.382729	4.610004	0.818049
F	-0.206771	5.201224	-0.666807	F	0.019583	4.990244	-0.840376
F	1.376829	5.346242	-2.152755	F	2.172845	5.015331	-1.165475
C	-4.836241	0.086727	1.385995	C	-5.020022	0.599712	1.391771
H	-5.415836	-0.821664	1.220364	H	-5.392384	-0.411935	1.543708
H	-4.170691	-0.043529	2.241547	H	-4.376223	0.885802	2.225401
O	-5.721973	1.159355	1.751379	O	-6.128646	1.519876	1.429897
C	-6.933246	1.174454	1.141785	C	-7.303681	1.065678	0.935447
O	-7.283614	0.355403	0.319256	O	-7.461623	-0.044954	0.471709
C	-7.761254	2.337347	1.633833	C	-8.374896	2.1242	1.049449
H	-7.234846	3.27891	1.446395	H	-8.061944	3.034487	0.527892
H	-7.912312	2.259656	2.715621	H	-8.528284	2.389116	2.100906

H	-8.724757	2.339979	1.123174	H	-9.30536	1.749174	0.621996
 **Int-C2-*trans*** E(RM06) = -2351.74674837				 **$TS_{C2\text{-}trans}$** Frequency -318.1512 E(RM06) = -2351.72259572			
C	-0.4082	-2.115765	-0.203513	C	-0.465028	-1.876865	-1.615742
C	-2.599687	-0.444782	-1.416578	C	-2.090743	-0.743824	-2.29058
C	-2.530961	0.797161	-0.881739	C	-2.13666	0.545305	-1.685254
C	-3.381675	1.195452	0.302321	C	-3.346579	0.835749	-0.813363
C	-4.394835	0.104243	0.692662	C	-3.854205	-0.370031	0.005706
O	-3.874771	-1.208191	0.502878	O	-3.552915	-1.643754	-0.578031
H	-4.576556	0.171875	1.76863	H	-3.334744	-0.357279	0.968588
H	-3.905956	2.123943	0.052456	H	-4.133119	1.18575	-1.49876
O	-2.54168	1.490386	1.4425	O	-3.140413	1.87468	0.155961
H	-1.99393	1.586114	-1.396213	H	-1.799702	1.397563	-2.271919
C	-3.484876	-1.50406	-0.825809	C	-3.255143	-1.651944	-1.959618
H	-2.116776	-0.664042	-2.365979	H	-1.724133	-0.802433	-3.310612
H	-2.97111	-2.465965	-0.781756	H	-3.061253	-2.691602	-2.2261
H	-4.363307	-1.635965	-1.483403	H	-4.116855	-1.302125	-2.559079
C	-2.350291	2.813751	1.725321	C	-3.121013	3.155154	-0.316302
O	-2.9206	3.709937	1.1456	O	-3.291631	3.426985	-1.483484
C	-1.338887	3.001767	2.824696	C	-2.872877	4.130419	0.803097
H	-0.391347	3.257534	2.340183	H	-1.856235	3.986296	1.178539
H	-1.207542	2.095197	3.418866	H	-3.569223	3.95027	1.628126
H	-1.64297	3.838783	3.457604	H	-2.983362	5.147654	0.426726
Pd	-0.226184	-0.110916	-0.202651	Pd	-0.34635	0.038451	-0.692247
As	2.184636	-0.528309	0.129478	As	1.934419	-0.478912	0.475843
O	0.058091	2.029893	-0.011929	O	-0.183727	2.076425	-0.035654
C	-0.137701	-2.890203	-1.340349	C	0.439109	-2.050853	-2.680825
C	-0.888265	-2.747008	0.952654	C	-0.835075	-2.996865	-0.850427
C	-0.371181	-4.271887	-1.329258	C	0.992828	-3.30268	-2.945401
H	0.258655	-2.425533	-2.239992	H	0.721558	-1.200103	-3.296088
C	-1.122208	-4.126452	0.960646	C	-0.277446	-4.249834	-1.11931
H	-1.097899	-2.167014	1.847153	H	-1.572876	-2.889977	-0.063012
C	-0.865105	-4.892776	-0.179348	C	0.636197	-4.406119	-2.163995
H	-0.162373	-4.859248	-2.220627	H	1.703714	-3.41485	-3.759368
H	-1.505616	-4.59994	1.861351	H	-0.561626	-5.104808	-0.510893

H	-1.04656	-5.964424	-0.171025	H	1.061793	-5.383485	-2.374895
C	3.014749	-1.061027	-1.570701	C	3.291087	-1.088895	-0.817643
C	3.205401	1.067114	0.653628	C	2.853164	1.035923	1.34919
C	2.794513	-1.874221	1.433551	C	2.027093	-1.808529	1.936135
C	2.602922	-0.3917	-2.733326	C	3.532954	-0.263312	-1.927851
C	4.003872	-2.049367	-1.641643	C	3.966808	-2.308328	-0.699792
C	3.183925	-0.72094	-3.959871	C	4.458165	-0.65495	-2.897303
H	1.845843	0.388816	-2.681946	H	2.997003	0.677135	-2.034678
C	4.575588	-2.373913	-2.874794	C	4.88666	-2.697064	-1.678084
H	4.328218	-2.569167	-0.745518	H	3.779744	-2.959522	0.14846
C	4.165632	-1.712177	-4.033483	C	5.135802	-1.871074	-2.775159
H	2.866262	-0.198232	-4.857917	H	4.646479	-0.008209	-3.750312
H	5.341332	-3.143429	-2.926173	H	5.408836	-3.645326	-1.578611
H	4.611637	-1.966853	-4.991273	H	5.854187	-2.173547	-3.53276
C	4.467528	1.32016	0.101087	C	4.228783	1.25543	1.201575
C	2.677627	1.940004	1.613667	C	2.103425	1.883398	2.175724
C	5.196396	2.438141	0.511065	C	4.84811	2.306867	1.88146
H	4.8809	0.654292	-0.649995	H	4.818249	0.616742	0.550978
C	3.412908	3.054228	2.022253	C	2.726852	2.933526	2.852102
H	1.687696	1.767143	2.020884	H	1.030638	1.748102	2.266604
C	4.671099	3.304345	1.471776	C	4.099228	3.144963	2.709074
H	6.172448	2.632821	0.075048	H	5.915366	2.472005	1.758523
H	2.993217	3.735041	2.757206	H	2.134632	3.594292	3.478824
H	5.237084	4.177716	1.784067	H	4.581431	3.966297	3.232424
C	2.508298	-3.233573	1.236308	C	0.877797	-2.527848	2.28406
C	3.499068	-1.476952	2.577548	C	3.205668	-2.006058	2.670884
C	2.934459	-4.179578	2.169981	C	0.907526	-3.442589	3.340369
H	1.95651	-3.560241	0.361461	H	-0.043716	-2.371739	1.733082
C	3.914007	-2.42804	3.512682	C	3.236128	-2.923961	3.721613
H	3.730273	-0.429674	2.742382	H	4.098465	-1.43423	2.434216
C	3.634919	-3.779944	3.31002	C	2.087077	-3.644813	4.057136
H	2.71034	-5.229982	2.005705	H	0.007481	-3.992217	3.603282
H	4.45932	-2.108365	4.396601	H	4.154904	-3.069494	4.283688
H	3.960609	-4.519124	4.036961	H	2.110921	-4.355198	4.879243
C	0.409671	2.647912	-1.07451	C	0.632484	2.7162	-0.789091
O	0.56046	2.199887	-2.213092	O	1.300609	2.298779	-1.735359
C	0.607862	4.174225	-0.870883	C	0.707238	4.228946	-0.45097
F	0.880968	4.498923	0.413938	F	0.60092	4.466417	0.878112
F	-0.51593	4.833127	-1.223931	F	-0.316873	4.879198	-1.052833
F	1.61609	4.641619	-1.626105	F	1.851689	4.782222	-0.871917
C	-5.721292	0.326303	-0.039087	C	-5.352254	-0.248802	0.252894
H	-5.617018	0.2859	-1.127736	H	-5.923292	-0.44993	-0.659659
H	-6.12953	1.311816	0.211696	H	-5.604418	0.759565	0.598732
O	-6.631226	-0.695344	0.395636	O	-5.706187	-1.205218	1.264597
C	-7.807398	-0.764468	-0.275407	C	-7.032101	-1.341383	1.508586
O	-8.097264	-0.0289	-1.192644	O	-7.88591	-0.707587	0.928963
C	-8.677163	-1.865762	0.283831	C	-7.275465	-2.375283	2.583028
H	-9.589451	-1.943579	-0.308491	H	-8.347346	-2.468521	2.760487

H	-8.931533	-1.647195	1.326593	H	-6.768938	-2.082893	3.508853
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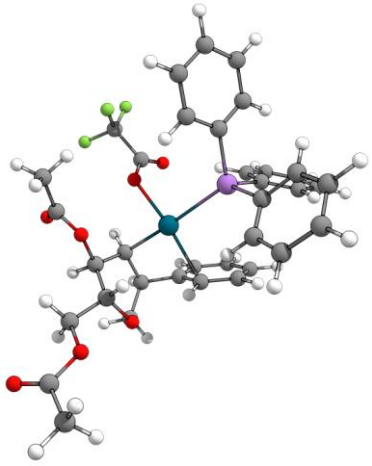
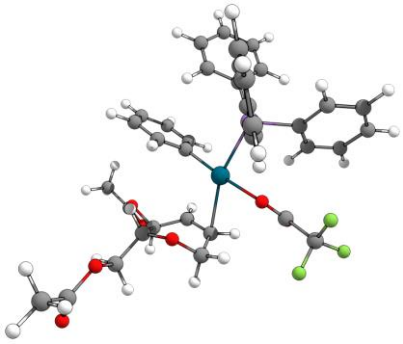
	 **C2-*trans*** E(RM06) = -2351.76027857				 **Int-C3-*trans*** E(RM06) = -2351.73961815		
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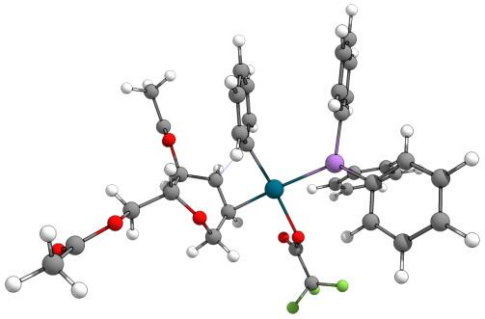
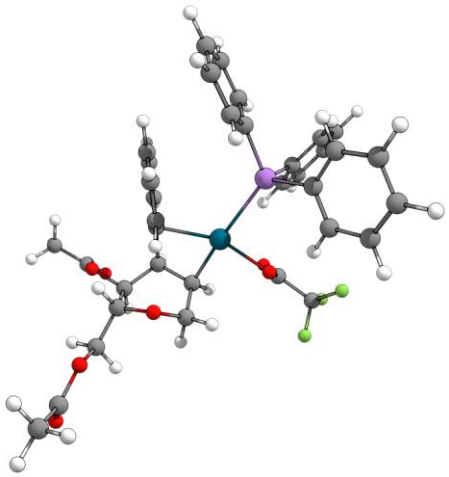
C	-2.382306	-0.552779	-2.614598	C	-2.390738	0.033792	-1.926067
C	-2.117176	0.582405	-1.609555	C	-3.685315	0.334667	-1.217102
C	-3.298146	0.82052	-0.675599	C	-3.815507	-0.35347	0.166408
C	-3.85934	-0.46136	-0.030151	O	-2.906522	-1.432181	0.357332
O	-3.772179	-1.602317	-0.892846	H	-3.55014	0.387708	0.925253
H	-3.243037	-0.698531	0.844355	H	-4.470775	-0.031917	-1.893355
H	-4.078804	1.311592	-1.275439	O	-3.941161	1.734448	-1.00581
O	-3.00065	1.699673	0.421544	C	-1.890092	-1.22223	-1.819384
H	-1.828908	1.515261	-2.094372	H	-2.059143	0.728645	-2.689372
C	-3.682529	-1.303155	-2.281814	Pd	-0.081873	-0.029243	-0.623985
H	-2.473215	-0.152101	-3.632364	C	-2.525847	-2.150054	-0.815045
H	-3.723541	-2.268392	-2.795058	H	-1.144344	-1.605208	-2.512444
H	-4.549729	-0.710731	-2.612398	H	-1.825055	-2.915809	-0.483329
C	-3.039974	3.038101	0.15737	H	-3.395893	-2.657932	-1.269077
O	-3.353054	3.491047	-0.920513	C	-4.411613	2.432666	-2.077709
C	-2.648097	3.835903	1.372887	O	-4.565817	1.941643	-3.1737
H	-1.559015	3.804649	1.469665	C	-4.703197	3.861724	-1.696806
H	-3.084685	3.408723	2.279984	H	-5.092063	4.394612	-2.56519
H	-2.967663	4.87099	1.243561	H	-3.786888	4.339617	-1.336644
Pd	-0.349178	0.00904	-0.697022	H	-5.433037	3.892673	-0.880977
As	1.962783	-0.588338	0.499525	As	2.128106	0.47481	0.371265
O	-0.139988	2.02927	-0.112373	O	0.560021	-2.096723	-0.470955
C	-0.240827	-1.49406	-3.645301	C	-1.190112	2.347948	0.742506
C	-0.885223	-2.260749	-1.425943	C	-0.305082	2.855031	-1.445516
C	0.837817	-2.364	-3.633227	C	-1.538714	3.692652	0.91427
H	-0.418476	-0.857064	-4.507683	H	-1.401123	1.638419	1.539698
C	0.218342	-3.146959	-1.436075	C	-0.652679	4.199823	-1.272718
H	-1.647184	-2.35419	-0.658016	H	0.183399	2.548188	-2.367583
C	1.069324	-3.200832	-2.526445	C	-1.266356	4.624043	-0.091044
H	1.508253	-2.402874	-4.487072	H	-2.018475	4.009989	1.837612
H	0.385034	-3.792791	-0.57905	H	-0.432786	4.916353	-2.060873

H	1.91834	-3.876871	-2.527007	H	-1.523462	5.671355	0.047375
C	3.383225	-1.221035	-0.716937	C	3.56822	-0.534984	-0.501836
C	2.886431	0.866049	1.466189	C	2.863458	2.299961	0.427861
C	1.913641	-1.959867	1.927166	C	2.194821	-0.142142	2.23912
C	3.661958	-0.418755	-1.835257	C	3.496134	-0.794447	-1.875468
C	4.075402	-2.424706	-0.539164	C	4.682835	-0.960902	0.233123
C	4.635048	-0.817854	-2.753457	C	4.538263	-1.474031	-2.510869
H	3.117285	0.510062	-1.987198	H	2.617277	-0.50844	-2.444114
C	5.043418	-2.822186	-1.46693	C	5.721072	-1.63843	-0.407843
H	3.865963	-3.056553	0.318707	H	4.739977	-0.773358	1.301383
C	5.325981	-2.019163	-2.573059	C	5.650366	-1.893597	-1.779611
H	4.850762	-0.18814	-3.612693	H	4.467227	-1.688215	-3.573251
H	5.577887	-3.75743	-1.319875	H	6.581132	-1.972178	0.166445
H	6.081359	-2.327465	-3.291275	H	6.456592	-2.428099	-2.274722
C	4.277228	1.027497	1.421907	C	4.040681	2.611205	-0.264948
C	2.115058	1.73909	2.244839	C	2.202702	3.304917	1.148937
C	4.889245	2.044851	2.157852	C	4.552569	3.910644	-0.231429
H	4.884891	0.36969	0.807875	H	4.562825	1.845287	-0.828731
C	2.73105	2.754974	2.978135	C	2.722211	4.599411	1.185114
H	1.033395	1.648525	2.256562	H	1.276228	3.088608	1.669862
C	4.117978	2.907408	2.938728	C	3.897389	4.905183	0.495287
H	5.968734	2.164779	2.115365	H	5.466179	4.140966	-0.772883
H	2.123206	3.435417	3.567809	H	2.200942	5.369866	1.746496
H	4.595096	3.702114	3.505997	H	4.297938	5.915036	0.521469
C	0.720673	-2.658197	2.155434	C	1.634459	-1.395091	2.533027
C	3.018418	-2.215658	2.752691	C	2.786019	0.617638	3.255568
C	0.63697	-3.611184	3.174478	C	1.669809	-1.875861	3.842812
H	-0.15399	-2.446366	1.546488	H	1.18823	-1.99231	1.742562
C	2.936998	-3.170766	3.767502	C	2.812669	0.128357	4.564557
H	3.941269	-1.659246	2.614855	H	3.223233	1.586491	3.035578
C	1.747279	-3.872521	3.977929	C	2.25424	-1.116018	4.859277
H	-0.296598	-4.141671	3.342569	H	1.237487	-2.847146	4.067122
H	3.800636	-3.360602	4.399465	H	3.271638	0.722141	5.350682
H	1.684317	-4.612223	4.771511	H	2.275409	-1.493896	5.878032
C	0.76187	2.63981	-0.796641	C	0.885844	-2.805724	-1.488268
O	1.513461	2.1995	-1.661229	O	0.92202	-2.494592	-2.676809
C	0.816621	4.152493	-0.451141	C	1.183476	-4.274835	-1.087304
F	0.793102	4.364547	0.887927	F	0.013187	-4.904979	-0.803837
F	-0.259255	4.781375	-0.972711	F	1.959089	-4.354353	0.013388
F	1.917558	4.73883	-0.935262	F	1.787364	-4.959969	-2.067112
C	-5.298181	-0.256234	0.425305	C	-5.256416	-0.796619	0.39557
H	-5.982558	-0.217093	-0.428529	H	-5.951929	0.013805	0.147349
H	-5.397666	0.67794	0.987601	H	-5.513952	-1.662383	-0.224044
O	-5.648351	-1.364213	1.272697	O	-5.392688	-1.138117	1.782792
C	-6.949363	-1.438577	1.640308	C	-6.592425	-1.651579	2.147556
O	-7.788434	-0.634444	1.299116	O	-7.514053	-1.805037	1.376774
C	-7.189806	-2.645989	2.516903	C	-6.601895	-1.997998	3.617857
H	-8.241719	-2.683617	2.801945	H	-6.341719	-1.119328	4.216878

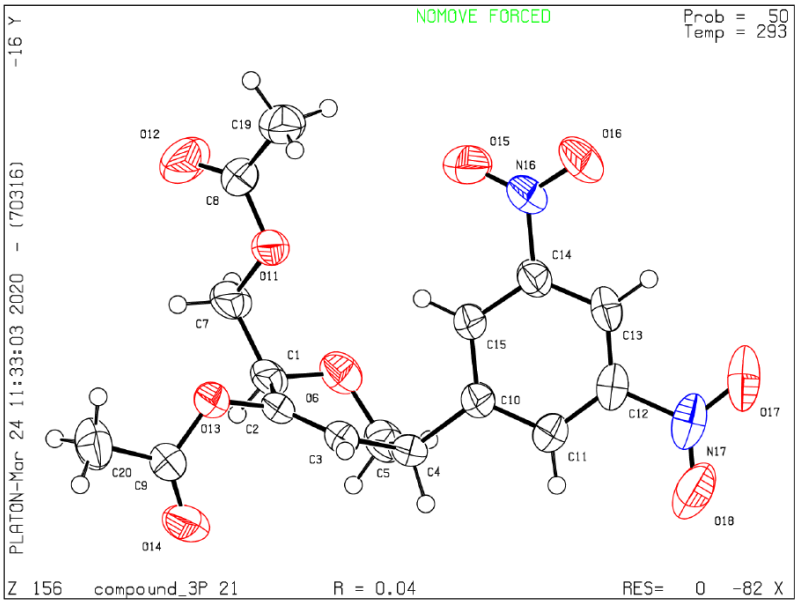
H	-6.562973	-2.592209	3.413236	H	-5.850182	-2.767271	3.824411
H	-6.915309	-3.560627	1.981006	H	-7.590622	-2.362427	3.898531
							
	$TS_{C3\text{-}trans}$ Frequency -321.1934 E(RM06) = -2351.72161818				**C3-*trans*** E(RM06) = -2351.75712049		
C	-1.118224	1.447553	-0.408963	C	-1.709212	1.406544	-0.882116
C	-2.291626	0.057179	-1.451534	C	-2.572299	0.234177	-1.371949
C	-3.718788	0.380233	-1.033794	C	-4.066287	0.307421	-0.994864
C	-4.123433	-0.187256	0.348087	C	-4.348286	0.052787	0.502324
O	-3.193521	-1.134879	0.860441	O	-3.339181	-0.733907	1.136048
H	-4.109548	0.641136	1.060622	H	-4.331084	1.018477	1.017832
H	-4.312992	-0.093562	-1.828681	H	-4.584928	-0.429309	-1.617979
O	-4.070842	1.771732	-1.024377	O	-4.638274	1.60334	-1.280251
C	-1.866579	-1.265966	-1.158161	C	-1.92857	-1.04587	-0.832804
H	-2.027838	0.454295	-2.42493	H	-2.52292	0.23503	-2.46367
Pd	-0.092297	-0.394719	-0.379796	Pd	-0.112346	-0.296159	-0.226078
C	-2.641389	-2.024415	-0.107977	C	-2.711378	-1.69975	0.290886
H	-1.375423	-1.843684	-1.941153	H	-1.648714	-1.754778	-1.612767
H	-1.995203	-2.713045	0.44155	H	-2.068308	-2.302009	0.93714
H	-3.435678	-2.627999	-0.584504	H	-3.471145	-2.382042	-0.134305
C	-4.256598	2.368237	-2.235285	C	-4.99039	1.855364	-2.570494
O	-4.104589	1.793546	-3.290021	O	-4.833249	1.066202	-3.474743
C	-4.670399	3.807242	-2.058806	C	-5.589975	3.23519	-2.696083
H	-4.825115	4.262631	-3.037457	H	-5.869762	3.415655	-3.734416
H	-3.892164	4.34693	-1.50988	H	-4.866062	3.988279	-2.3675
H	-5.590984	3.865932	-1.468904	H	-6.470162	3.325061	-2.051076
As	2.225316	0.516375	0.34015	As	2.397387	0.500249	0.387081
O	0.733858	-2.352535	-0.151133	O	0.577261	-2.292531	-0.148737
C	-1.59069	1.804986	0.868229	C	-1.468425	1.635333	0.49714
C	-0.781226	2.466605	-1.317595	C	-1.190066	2.335076	-1.816664
C	-1.684069	3.148419	1.236565	C	-0.772749	2.789895	0.909258
H	-1.873039	1.028205	1.572595	H	-1.930912	0.989487	1.237954
C	-0.879751	3.808509	-0.947348	C	-0.508428	3.466477	-1.393677
H	-0.435046	2.210954	-2.316146	H	-1.35516	2.161035	-2.876838
C	-1.334284	4.152533	0.329581	C	-0.303755	3.701858	-0.023656
H	-2.036525	3.410784	2.231136	H	-0.613989	2.962324	1.969341
H	-0.596983	4.584521	-1.65398	H	-0.133086	4.175326	-2.126719

H	-1.411599	5.197861	0.616348	H	0.236324	4.58556	0.301605
C	3.628257	0.030406	-0.95911	C	3.658975	0.173129	-1.099959
C	2.513565	2.456548	0.556484	C	2.825759	2.37389	0.858636
C	2.951185	-0.214371	2.028514	C	3.264814	-0.480959	1.875288
C	3.253143	-0.502683	-2.19829	C	3.152002	-0.260999	-2.33091
C	4.987939	0.197043	-0.658729	C	5.042116	0.346611	-0.944151
C	4.231448	-0.856521	-3.132594	C	4.021233	-0.509989	-3.397984
H	2.206374	-0.67802	-2.429145	H	2.088465	-0.441204	-2.457247
C	5.960209	-0.153461	-1.595617	C	5.904913	0.101964	-2.012396
H	5.291165	0.590824	0.307456	H	5.450384	0.665148	0.010864
C	5.582386	-0.678933	-2.834707	C	5.394547	-0.325174	-3.24194
H	3.930701	-1.282	-4.085893	H	3.618259	-0.859097	-4.34461
H	7.012303	-0.023434	-1.355638	H	6.975637	0.237628	-1.883222
H	6.341694	-0.957599	-3.560669	H	6.069001	-0.521323	-4.071369
C	3.187753	3.205496	-0.416783	C	3.356593	3.259004	-0.088166
C	1.978193	3.114365	1.67352	C	2.503423	2.859836	2.135131
C	3.332972	4.587308	-0.26966	C	3.566392	4.602533	0.23634
H	3.610204	2.712563	-1.287039	H	3.616321	2.902002	-1.080204
C	2.131852	4.493436	1.822878	C	2.718636	4.200227	2.460983
H	1.443893	2.552263	2.43445	H	2.093648	2.188983	2.886155
C	2.809489	5.233284	0.851237	C	3.24964	5.076531	1.510481
H	3.862304	5.155907	-1.029897	H	3.984778	5.275868	-0.507429
H	1.721271	4.989142	2.698727	H	2.475423	4.558635	3.458009
H	2.929585	6.307095	0.96834	H	3.419566	6.119534	1.764057
C	2.644557	-1.545393	2.349489	C	2.862219	-1.803289	2.113442
C	3.775604	0.532216	2.880905	C	4.281103	0.082215	2.65988
C	3.161283	-2.115678	3.514976	C	3.472928	-2.546959	3.126317
H	2.019336	-2.137081	1.687012	H	2.087651	-2.257837	1.503407
C	4.285016	-0.044902	4.046969	C	4.883945	-0.665682	3.67389
H	4.018494	1.564088	2.64654	H	4.601367	1.106075	2.492628
C	3.978135	-1.368566	4.365971	C	4.480579	-1.981301	3.909103
H	2.922264	-3.148239	3.755176	H	3.156972	-3.572235	3.299502
H	4.922622	0.542116	4.703189	H	5.66974	-0.218453	4.277504
H	4.375105	-1.81606	5.273448	H	4.950808	-2.562496	4.698058
C	0.937428	-3.051712	-1.208864	C	0.775999	-2.875757	-1.279777
O	0.747294	-2.754021	-2.386007	O	0.630376	-2.437052	-2.415204
C	1.448228	-4.476386	-0.865028	C	1.230139	-4.347259	-1.082863
F	0.433798	-5.216394	-0.356796	F	0.207469	-5.088472	-0.598578
F	2.430121	-4.445395	0.061533	F	2.24932	-4.434498	-0.20032
F	1.921824	-5.116587	-1.942607	F	1.633666	-4.904452	-2.231674
C	-5.541342	-0.748746	0.295502	C	-5.729692	-0.565048	0.687737
H	-6.218112	-0.033452	-0.186628	H	-6.480411	-0.009109	0.114913
H	-5.588972	-1.685357	-0.270318	H	-5.751776	-1.60681	0.349887
O	-5.965993	-0.978634	1.646188	O	-6.050223	-0.504698	2.085925
C	-7.18326	-1.559296	1.788354	C	-7.232175	-1.063877	2.442085
O	-7.891755	-1.855849	0.852106	O	-7.994933	-1.571068	1.649718
C	-7.505746	-1.777386	3.247531	C	-7.443244	-0.966099	3.934684
H	-7.445597	-0.831534	3.795533	H	-7.371158	0.076206	4.261655

H	-6.773826	-2.459342	3.693349	H	-6.662147	-1.526995	4.458999
H	-8.507181	-2.199181	3.338626	H	-8.422933	-1.37134	4.189913

5. Crystal structure determination of Compound 3n

Crystal Data for $C_{16}H_{16}N_2O_9$ (*M* =380.31 g/mol): monoclinic, space group $P2_1$ (no. 4), *a* = 10.3667(3) Å, *b* = 6.84234(18) Å, *c* = 12.9093(4) Å, *β* = 110.345(3)°, *V* = 858.56(4) Å^3, *Z* = 2, *T* = 293(2) K, μ(MoKα) = 0.122 mm^{-1}, *Dcalc* = 1.471 g/cm^3, 40844 reflections measured (6.84° ≤ 2Θ ≤ 52.032°), 3377 unique (R_{int} = 0.0658, R_{sigma} = 0.0280) which were used in all calculations. The final R_1 was 0.0433 (I > 2σ(I)) and wR_2 was 0.1161 (all data).



Experimental

Massive colourless single crystals of **3n** were analyzed on a RIGAKU XtaLabPro diffractometer equipped with a Mo microfocus sealed tube generator coupled to a double-bounce confocal Max-Flux® multilayer optic and a HPAD PILATUS3R 200K detector. The crystals were kept at 293(2) K during data collection. *CrysAlisPro 1.171.39.46* [1] was employed for the data processing, with SCALE3 ABSPACK scaling algorithm implemented for the empirical absorption correction using spherical harmonics. Structure solution was done by intrinsic phasing methods (*SHELXT* program),[2] then the refinement by full-matrix least-squares methods on F^2 using *SHELX-L*.[3] All non-hydrogen atoms of the molecular model improved by anisotropic refinement. Most of the H atoms were identified in difference maps nevertheless they were essentially positioned geometrically using a riding model with U_{iso} set to xU_{eq} ($C_{carrier}$) and x equal to 1.5 when parent atoms are methyl carbons, and 1.2 for the rest of the carbons tertiary CH, secondary CH_2, and aromatic ones. Methyl H atoms were idealized and included as rigid groups allowed to rotate but not tip (AFIX 137). The asymmetric unit of the monoclinic Sohncke space group, P 2_1, is made of one **3n** molecule. Despite several data collections increasing significantly data redundancy (> 8) and trying to optimize Bijvoet pairs measurements to compensate the extremely weak anomalous scattering generated by Mo radiation, the only available source at the that time, the Flack parameter that could be derived using the different approaches [4] was meaningless in any cases to ascertain the absolute configuration in C2, C5 of **3n**. Crystal data, data collection and structure refinement details for one tested crystal are summarized in Table **1**.

CCDC 1992288 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

1 Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England.

2 Sheldrick, G. M. (2015). *Acta Crystallogr.*, **C**71, 3–8.

3 Sheldrick, G. M. (2015). *Acta Crystallogr.*, **A**71, 3–8.

4 Watkin, D.A & Cooper, R I (2016). *Acta Crystallogr.,* **B**72, 661–683.

Table S6 Crystal data and structure refinement for Compound_3n.

Identification code		Compound_3n
Empirical formula		$C_{16}H_{16}N_2O_9$
Formula weight		380.31
Temperature/K		293(2)
Crystal system		monoclinic
Space group		$P2_1$
a	/Å	10.3667(3)
b	/Å	6.84234(18)
c	/Å	12.9093(4)
α/°		90
β/°		110.345(3)
γ/°		90
Volume	/Å^3	858.56(4)
Z		2
ρ_{calc}	(g/cm^3)	1.471
μ	/mm^{-1}	0.122
F(000)		396.0
Crystal size	/mm^3	0.42 × 0.37 × 0.10
Radiation	/Å	Mo*Kα* (λ = 0.71073)
2Θ range for data collection/°		6.84 to 52.032
Index ranges		-12 ≤ h ≤ 12, -8 ≤ k ≤ 8, -15 ≤ l ≤ 15
Reflections collected		40844
Independent reflections		3377 [R_{int} = 0.0658, R_{sigma} = 0.0280]
Data/restraints/parameters		3377/1/247
Goodness-of-fit on F^2		1.074
Final R indexes [$I \geq 2\sigma(I)$]		R_1 = 0.0433, wR_2 = 0.1142
Final R indexes [*all data*]		R_1 = 0.0447, wR_2 = 0.1161
Largest diff. peak/hole / e Å^{-3}		0.47/-0.31

Table S7 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3n**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
C(1)	6502(3)	2932(5)	7689(2)	48.8(7)
C(2)	6058(3)	4999(4)	7390(2)	42.7(6)
C(3)	4860(3)	5505(4)	6661(2)	42.6(6)
C(4)	3887(3)	3981(4)	5981(2)	45.0(6)
C(5)	4646(3)	2048(5)	6105(3)	55.3(7)
O(6)	5384(2)	1624(3)	7235.4(19)	54.9(5)
C(7)	7121(3)	2562(6)	8915(3)	60.3(8)
C(8)	6651(3)	3060(5)	10543(2)	50.8(6)
C(9)	7828(3)	7189(5)	7476(2)	49.6(6)

$C^{(10)}$	2568(2)	3803(4)	6241(2)	41.0(5)
$C^{(11)}$	1309(3)	3760(4)	5381(2)	44.2(6)
$O^{(11)}$	6188.6(18)	3250(3)	9439.1(15)	49.4(5)
$C^{(12)}$	117(3)	3572(4)	5618(2)	46.7(6)
$O^{(12)}$	7746(3)	2339(6)	11031(2)	94.0(11)
$C^{(13)}$	110(3)	3406(4)	6676(2)	48.5(6)
$O^{(13)}$	7043(2)	6360(4)	7984.5(16)	54.7(5)
$C^{(14)}$	1373(3)	3411(4)	7508(2)	45.9(6)
$O^{(14)}$	7657(3)	6889(7)	6531(2)	105.2(14)
$C^{(15)}$	2601(2)	3621(4)	7319(2)	43.0(6)
$O^{(15)}$	2488(3)	2832(7)	9366(2)	93.3(11)
$N^{(16)}$	1397(3)	3172(5)	8647(2)	61.6(7)
$O^{(16)}$	314(3)	3321(6)	8806(2)	90.5(10)
$N^{(17)}$	-1222(3)	3549(4)	4709(3)	61.2(7)
$O^{(17)}$	-2245(2)	3183(5)	4937(3)	83.6(9)
$O^{(18)}$	-1237(3)	3866(5)	3780(3)	89.4(9)
$C^{(19)}$	5664(4)	3757(6)	11051(3)	64.5(8)
$C^{(20)}$	8966(3)	8363(6)	8236(3)	68.2(9)

Table S8 Anisotropic Displacement Parameters ($Å^2×10^3$) for **3n**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
$C^{(1)}$	36.8(12)	66.2(17)	52.2(14)	7.9(13)	26.6(11)	8.9(12)
$C^{(2)}$	35.7(12)	61.0(15)	36.7(12)	1.8(11)	19.2(10)	-5.2(11)
$C^{(3)}$	37.9(12)	52.9(14)	40.8(12)	5.4(10)	18.6(10)	-1.6(10)
$C^{(4)}$	40.5(13)	62.3(16)	35.4(11)	0.2(11)	17.2(10)	-4.5(12)
$C^{(5)}$	50.4(15)	63.4(18)	60.7(17)	-14.1(14)	30.3(14)	-4.3(14)
$O^{(6)}$	51.8(11)	53.7(11)	67.4(13)	4.0(9)	31.1(10)	4.7(9)
$C^{(7)}$	41.5(13)	89(2)	57.9(16)	20.2(16)	27.4(12)	22.2(14)
$C^{(8)}$	44.1(14)	61.2(16)	43.6(12)	6.4(12)	11.0(11)	2.2(12)
$C^{(9)}$	43.1(13)	58.0(15)	49.6(15)	4.1(12)	18.6(11)	-3.9(12)
$C^{(10)}$	36.5(12)	46.7(13)	40.6(12)	-1.0(10)	14.5(9)	-0.6(11)
$C^{(11)}$	42.1(13)	44.4(13)	41.3(12)	-2.8(10)	8.4(10)	-1.4(11)
$O^{(11)}$	37.5(9)	68.5(12)	45.0(9)	12.1(9)	17.6(7)	12.9(8)
$C^{(12)}$	33.1(12)	39.8(12)	58.6(15)	-7.3(11)	5.2(11)	0.5(10)
$O^{(12)}$	63.7(15)	153(3)	58.0(14)	22.1(17)	12.0(12)	38.6(18)
$C^{(13)}$	31.3(12)	51.1(14)	64.3(16)	-7.5(13)	18.2(11)	-3.6(10)
$O^{(13)}$	44.6(10)	80.4(14)	40.6(10)	-5.9(9)	17.0(8)	-14.4(10)
$C^{(14)}$	38.4(13)	54.6(15)	48.8(13)	-4.2(11)	20.4(11)	-3.5(11)
$O^{(14)}$	97(2)	170(4)	54.6(14)	-4.0(18)	34.0(14)	-72(2)
$C^{(15)}$	33.1(12)	56.1(15)	40.4(12)	-1.3(11)	13.6(9)	-1.3(11)
$O^{(15)}$	66.3(16)	164(3)	54.6(13)	21.7(18)	27.5(12)	11.7(19)
$N^{(16)}$	51.1(14)	86.4(19)	56.9(14)	-0.8(14)	31.0(12)	-8.4(13)

$O^{(16)}$	58.3(14)	149(3)	83.6(17)	-10(2)	49.7(13)	-11.7(17)
$N^{(17)}$	43.1(14)	47.0(13)	74.9(18)	-12.3(12)	-3.1(12)	1.9(11)
$O^{(17)}$	34.1(11)	87.7(19)	112(2)	-24.8(16)	4.0(12)	-4.1(11)
$O^{(18)}$	69.6(16)	98(2)	69.1(16)	5.3(15)	-15.4(13)	-8.3(15)
$C^{(19)}$	65.8(19)	81(2)	50.1(15)	1.6(15)	24.9(14)	6.7(18)
$C^{(20)}$	48.7(16)	73(2)	82(2)	-16.3(18)	22.7(15)	-15.3(15)

Table S9 Bond Lengths for **3n**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
$C^{(1)}$	$O^{(6)}$	1.419(4)	$C^{(9)}$	$O^{(13)}$	1.337(3)
$C^{(1)}$	$C^{(2)}$	1.496(4)	$C^{(9)}$	$C^{(20)}$	1.481(4)
$C^{(1)}$	$C^{(7)}$	1.509(4)	$C^{(10)}$	$C^{(15)}$	1.386(3)
$C^{(2)}$	$C^{(3)}$	1.317(4)	$C^{(10)}$	$C^{(11)}$	1.389(3)
$C^{(2)}$	$O^{(13)}$	1.398(3)	$C^{(11)}$	$C^{(12)}$	1.379(4)
$C^{(3)}$	$C^{(4)}$	1.504(4)	$C^{(12)}$	$C^{(13)}$	1.373(4)
$C^{(4)}$	$C^{(5)}$	1.519(4)	$C^{(12)}$	$N^{(17)}$	1.473(3)
$C^{(4)}$	$C^{(10)}$	1.521(3)	$C^{(13)}$	$C^{(14)}$	1.374(4)
$C^{(5)}$	$O^{(6)}$	1.422(4)	$C^{(14)}$	$C^{(15)}$	1.385(3)
$C^{(7)}$	$O^{(11)}$	1.438(3)	$C^{(14)}$	$N^{(16)}$	1.471(4)
$C^{(8)}$	$O^{(12)}$	1.197(4)	$O^{(15)}$	$N^{(16)}$	1.211(4)
$C^{(8)}$	$O^{(11)}$	1.342(3)	$N^{(16)}$	$O^{(16)}$	1.213(3)
$C^{(8)}$	$C^{(19)}$	1.474(4)	$N^{(17)}$	$O^{(18)}$	1.213(5)
$C^{(9)}$	$O^{(14)}$	1.188(4)	$N^{(17)}$	$O^{(17)}$	1.221(4)

Table S10 Bond Angles for **3n.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
$O^{(6)}$	$C^{(1)}$	$C^{(2)}$	110.9(2)	$C^{(15)}$	$C^{(10)}$	$C^{(4)}$	121.2(2)
$O^{(6)}$	$C^{(1)}$	$C^{(7)}$	108.4(2)	$C^{(11)}$	$C^{(10)}$	$C^{(4)}$	119.5(2)
$C^{(2)}$	$C^{(1)}$	$C^{(7)}$	114.2(3)	$C^{(12)}$	$C^{(11)}$	$C^{(10)}$	119.4(2)
$C^{(3)}$	$C^{(2)}$	$O^{(13)}$	123.0(3)	$C^{(8)}$	$O^{(11)}$	$C^{(7)}$	114.7(2)
$C^{(3)}$	$C^{(2)}$	$C^{(1)}$	124.2(3)	$C^{(13)}$	$C^{(12)}$	$C^{(11)}$	122.9(2)
$O^{(13)}$	$C^{(2)}$	$C^{(1)}$	112.8(2)	$C^{(13)}$	$C^{(12)}$	$N^{(17)}$	117.6(3)
$C^{(2)}$	$C^{(3)}$	$C^{(4)}$	120.6(3)	$C^{(11)}$	$C^{(12)}$	$N^{(17)}$	119.5(3)
$C^{(3)}$	$C^{(4)}$	$C^{(5)}$	108.9(2)	$C^{(12)}$	$C^{(13)}$	$C^{(14)}$	116.4(2)
$C^{(3)}$	$C^{(4)}$	$C^{(10)}$	113.5(2)	$C^{(9)}$	$O^{(13)}$	$C^{(2)}$	117.8(2)
$C^{(5)}$	$C^{(4)}$	$C^{(10)}$	112.3(2)	$C^{(13)}$	$C^{(14)}$	$C^{(15)}$	123.2(2)
$O^{(6)}$	$C^{(5)}$	$C^{(4)}$	111.1(2)	$C^{(13)}$	$C^{(14)}$	$N^{(16)}$	117.5(2)
$C^{(1)}$	$O^{(6)}$	$C^{(5)}$	111.4(2)	$C^{(15)}$	$C^{(14)}$	$N^{(16)}$	119.4(2)
$O^{(11)}$	$C^{(7)}$	$C^{(1)}$	109.2(2)	$C^{(14)}$	$C^{(15)}$	$C^{(10)}$	118.9(2)
$O^{(12)}$	$C^{(8)}$	$O^{(11)}$	121.5(3)	$O^{(15)}$	$N^{(16)}$	$O^{(16)}$	124.0(3)

$O^{(12)}$	$C^{(8)}$	$C^{(19)}$	125.3(3)	$O^{(15)}$	$N^{(16)}$	$C^{(14)}$	118.3(2)
$O^{(11)}$	$C^{(8)}$	$C^{(19)}$	113.2(2)	$O^{(16)}$	$N^{(16)}$	$C^{(14)}$	117.7(3)
$O^{(14)}$	$C^{(9)}$	$O^{(13)}$	122.1(3)	$O^{(18)}$	$N^{(17)}$	$O^{(17)}$	124.1(3)
$O^{(14)}$	$C^{(9)}$	$C^{(20)}$	125.1(3)	$O^{(18)}$	$N^{(17)}$	$C^{(12)}$	118.1(3)
$O^{(13)}$	$C^{(9)}$	$C^{(20)}$	112.7(3)	$O^{(17)}$	$N^{(17)}$	$C^{(12)}$	117.8(3)
$C^{(15)}$	$C^{(10)}$	$C^{(11)}$	119.3(2)				

Table S11 Hydrogen Bonds for **3n.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C(5)	H(5A)	O17_$1[1]	0.97	2.59	3.560(4)	176.3
C(7)	H(7B)	O16_$2[2]	0.97	2.64	3.401(4)	135.8
C(11)	H(11)	O14_$3[3]	0.93	2.56	3.274(4)	133.7
C(19)	H(19B)	O(15)	0.96	2.64	3.315(5)	128.0
C(20)	H(20B)	O12_$4[4]	0.96	2.41	3.281(5)	150.5

[1]-X,-1/2+Y,1-Z; [2]1+X,+Y,+Z; [3]1-X,-1/2+Y,1-Z; [4]2-X,1/2+Y,2-Z

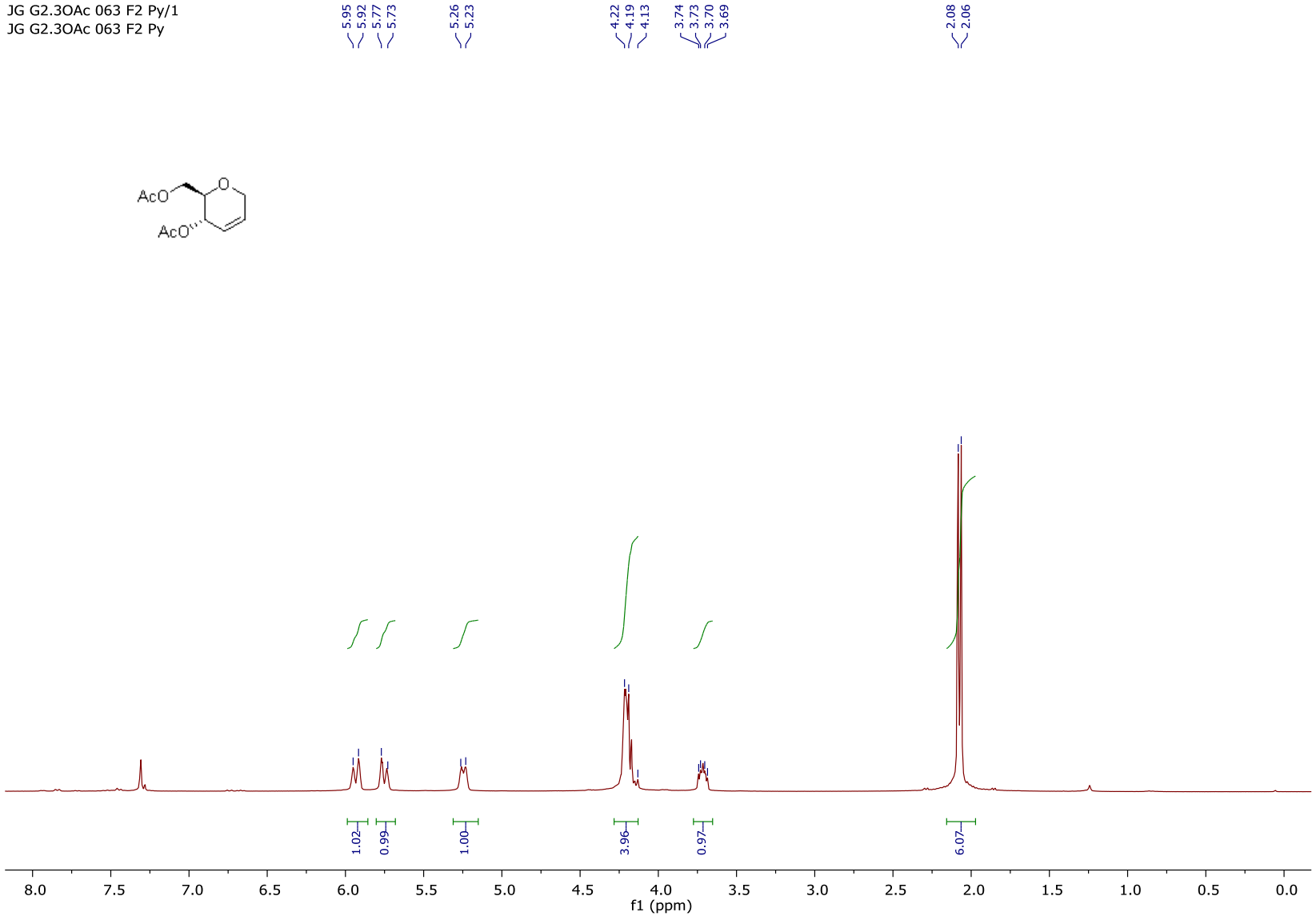
Table S12 Torsion Angles for **3n.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O(6)	C(1)	C(2)	C(3)	-10.4(3)	C(1)	C(7)	O(11)	C(8)	-177.8(3)
C(7)	C(1)	C(2)	C(3)	-133.1(3)	C(10)	C(11)	C(12)	C(13)	-0.6(4)
O(6)	C(1)	C(2)	O(13)	168.6(2)	C(10)	C(11)	C(12)	N(17)	179.3(2)
C(7)	C(1)	C(2)	O(13)	45.8(3)	C(11)	C(12)	C(13)	C(14)	-0.8(4)
O(13)	C(2)	C(3)	C(4)	175.1(2)	N(17)	C(12)	C(13)	C(14)	179.4(2)
C(1)	C(2)	C(3)	C(4)	-6.1(4)	O(14)	C(9)	O(13)	C(2)	4.5(5)
C(2)	C(3)	C(4)	C(5)	-12.5(3)	C(20)	C(9)	O(13)	C(2)	-171.2(3)
C(2)	C(3)	C(4)	C(10)	113.4(3)	C(3)	C(2)	O(13)	C(9)	-79.7(3)
C(3)	C(4)	C(5)	O(6)	48.3(3)	C(1)	C(2)	O(13)	C(9)	101.4(3)
C(10)	C(4)	C(5)	O(6)	-78.3(3)	C(12)	C(13)	C(14)	C(15)	1.7(4)
C(2)	C(1)	O(6)	C(5)	46.9(3)	C(12)	C(13)	C(14)	N(16)	-178.1(3)
C(7)	C(1)	O(6)	C(5)	172.9(2)	C(13)	C(14)	C(15)	C(10)	-1.2(4)
C(4)	C(5)	O(6)	C(1)	-68.5(3)	N(16)	C(14)	C(15)	C(10)	178.6(3)
O(6)	C(1)	C(7)	O(11)	-71.2(3)	C(11)	C(10)	C(15)	C(14)	-0.3(4)
C(2)	C(1)	C(7)	O(11)	52.9(4)	C(4)	C(10)	C(15)	C(14)	-178.3(3)
C(3)	C(4)	C(10)	C(15)	-49.6(4)	C(13)	C(14)	N(16)	O(15)	167.4(4)
C(5)	C(4)	C(10)	C(15)	74.5(3)	C(15)	C(14)	N(16)	O(15)	-12.4(5)
C(3)	C(4)	C(10)	C(11)	132.4(3)	C(13)	C(14)	N(16)	O(16)	-12.3(5)
C(5)	C(4)	C(10)	C(11)	-103.5(3)	C(15)	C(14)	N(16)	O(16)	167.9(4)

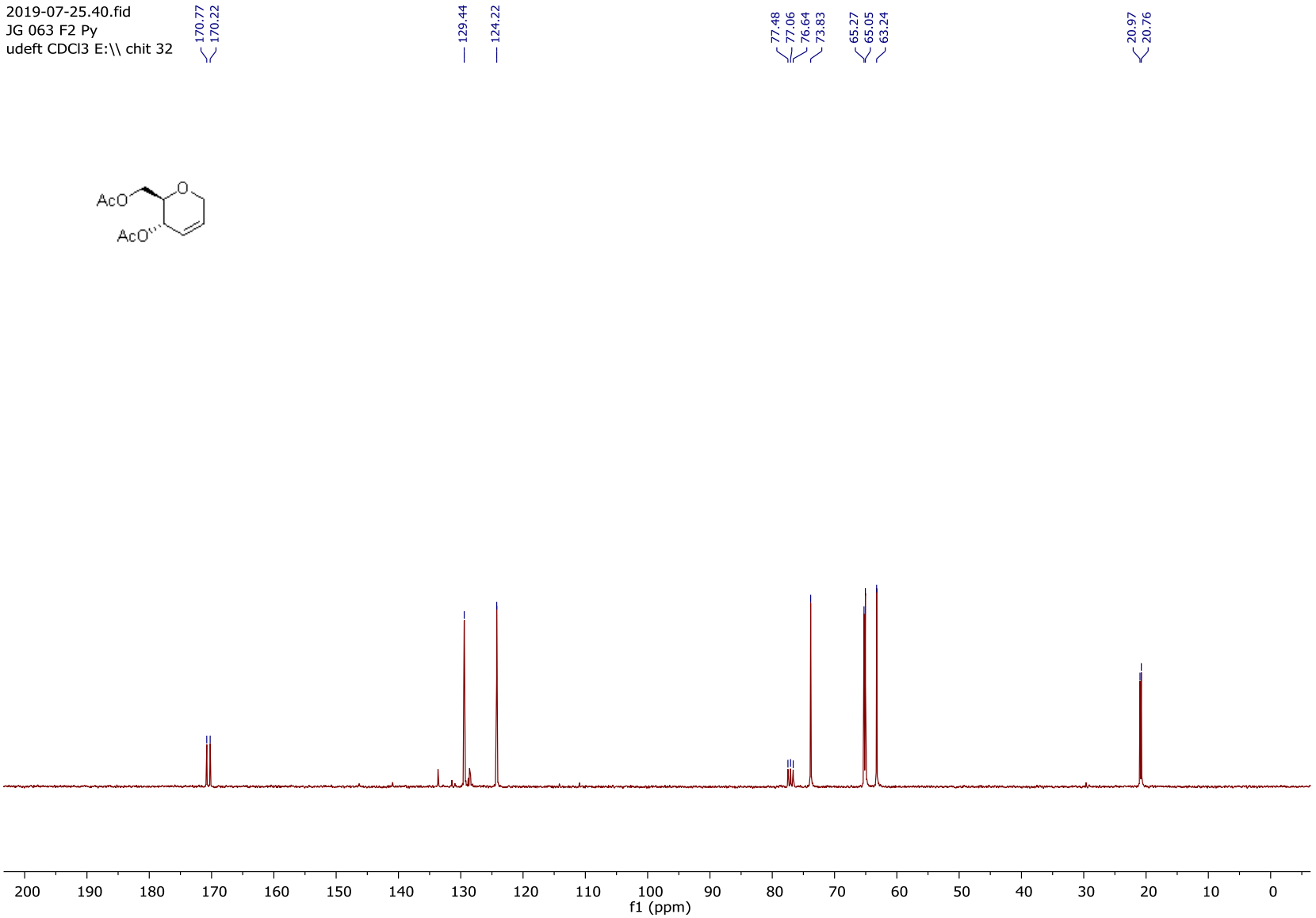
C(15)	C(10)	C(11)	C(12)	1.1(4)	C(13)	C(12)	N(17)	O(18)	173.7(3)
C(4)	C(10)	C(11)	C(12)	179.2(2)	C(11)	C(12)	N(17)	O(18)	-6.2(4)
O(12)	C(8)	O(11)	C(7)	-1.2(5)	C(13)	C(12)	N(17)	O(17)	-7.4(4)
C(19)	C(8)	O(11)	C(7)	-179.3(3)	C(11)	C(12)	N(17)	O(17)	172.7(3)

Table S13 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3n.**

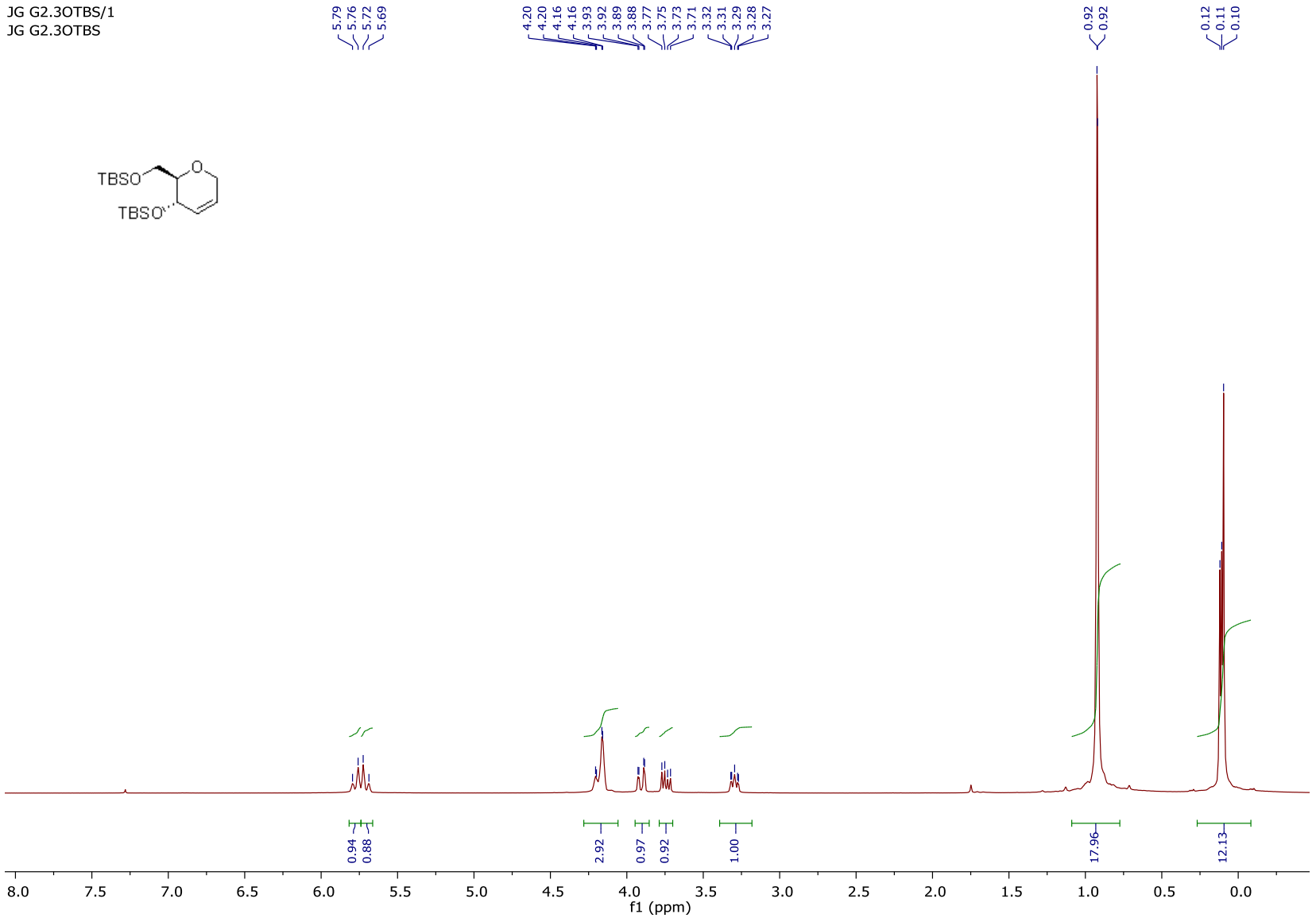
Atom	***x***	***y***	***z***	**U(eq)**
H(1)	7201.23	2617.81	7363.28	59
H(3)	4615.02	6817.76	6565.95	51
H(4)	3624.8	4376.19	5205.27	54
H(5A)	3991.44	1009.2	5786.88	66
H(5B)	5282.43	2105.07	5704.28	66
H(7A)	7286.89	1174.83	9052.39	72
H(7B)	7994.14	3240.48	9217.63	72
H(11)	1270.35	3856.79	4652.22	53
H(13)	-704.09	3296.22	6822.15	58
H(15)	3434.33	3640.7	7905.5	52
H(19A)	6127.77	3925.37	11830.94	97
H(19B)	4938.5	2816.08	10926.89	97
H(19C)	5281.82	4983.68	10726.21	97
H(20A)	9104.65	9510.23	7859.97	102
H(20B)	9793.31	7597.72	8474.47	102
H(20C)	8735.94	8742.16	8866.94	102



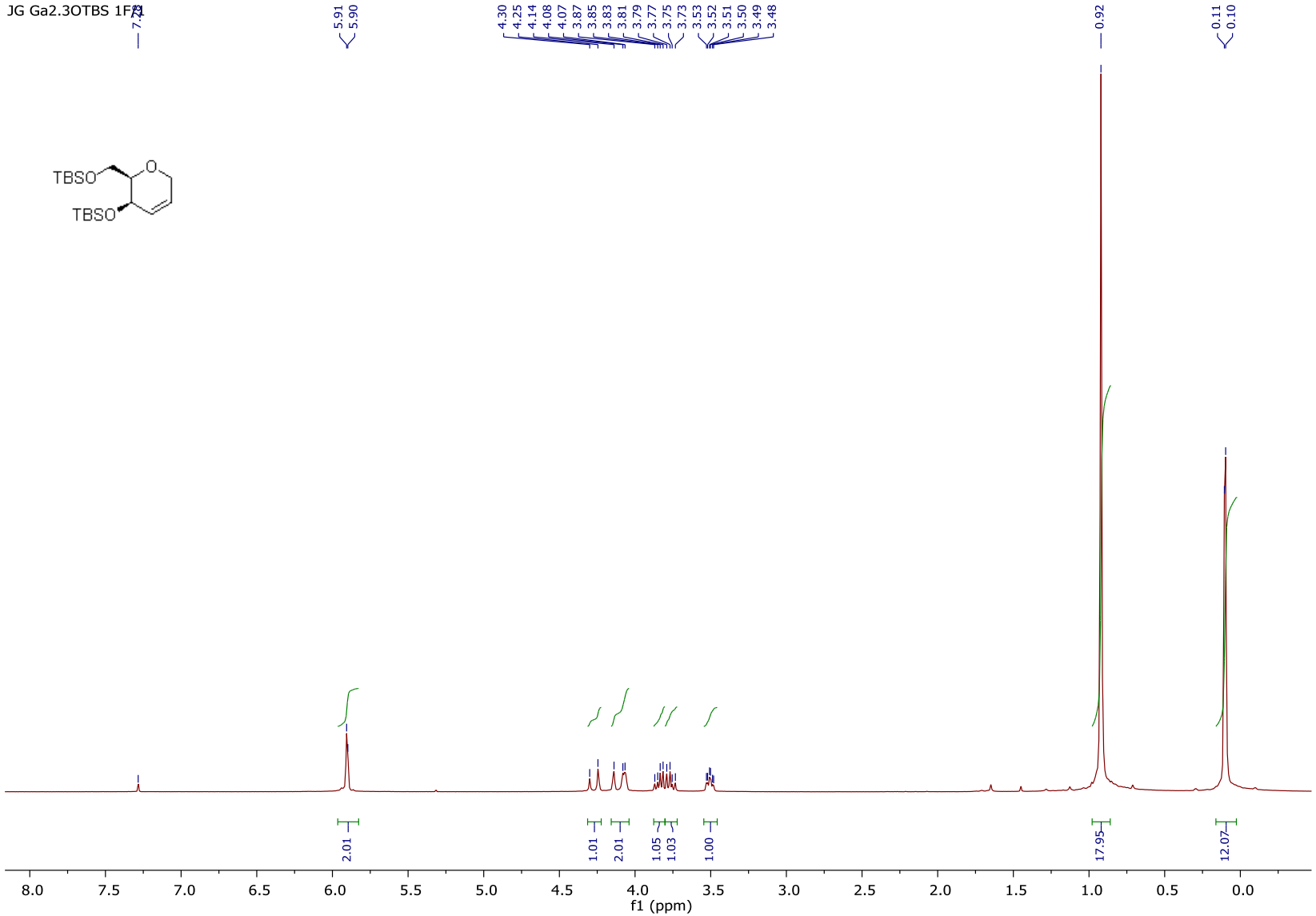
^{1}H NMR spectrum of **1a** (300 MHz, $CDCl_3$)



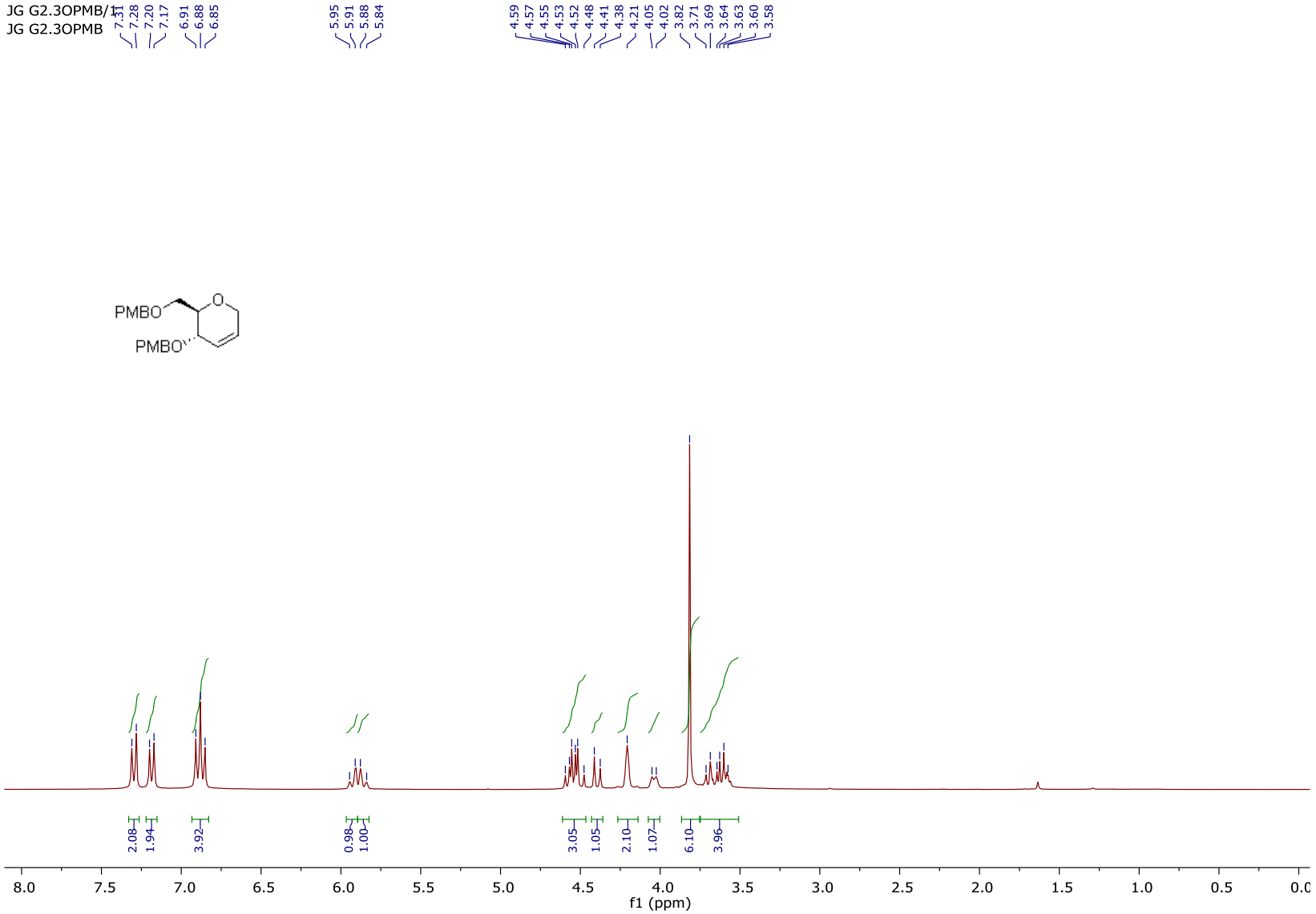
^{13}C NMR spectrum of **1a** (75 MHz, $CDCl_3$)



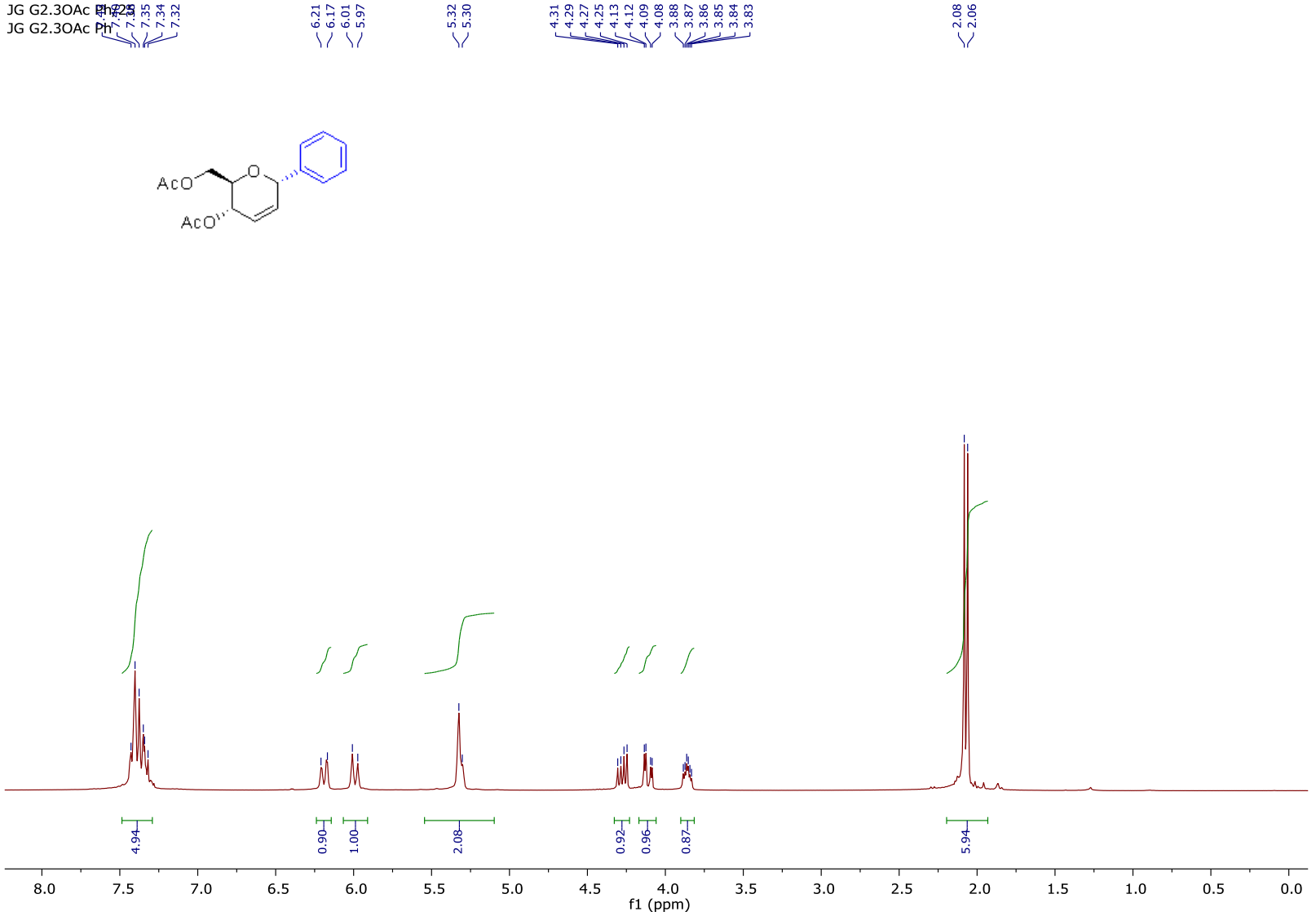
^{1}H NMR spectrum of **1d** (300 MHz, $CDCl_3$)



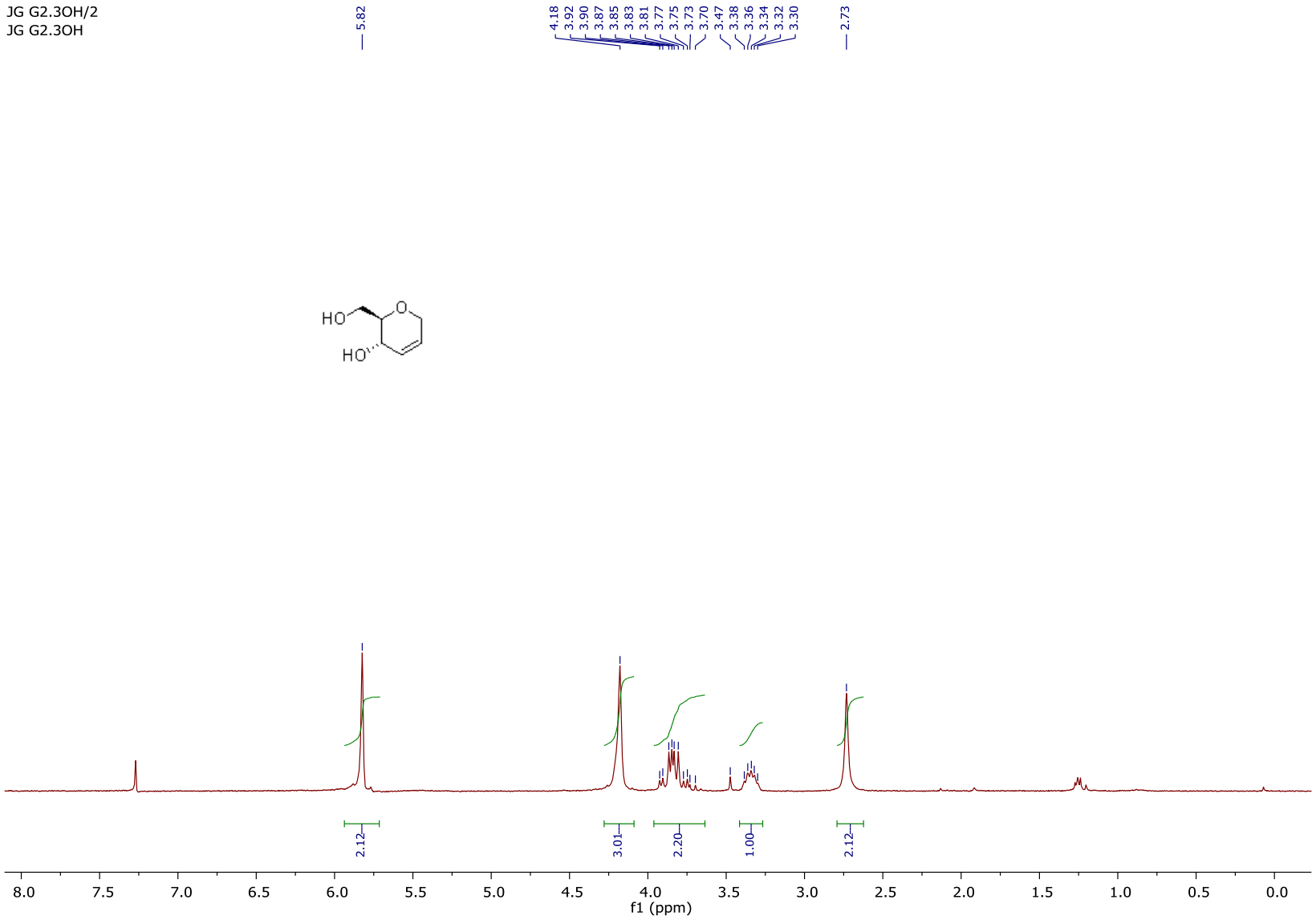
^{1}H NMR spectrum of **1h** (300 MHz, $CDCl_3$)



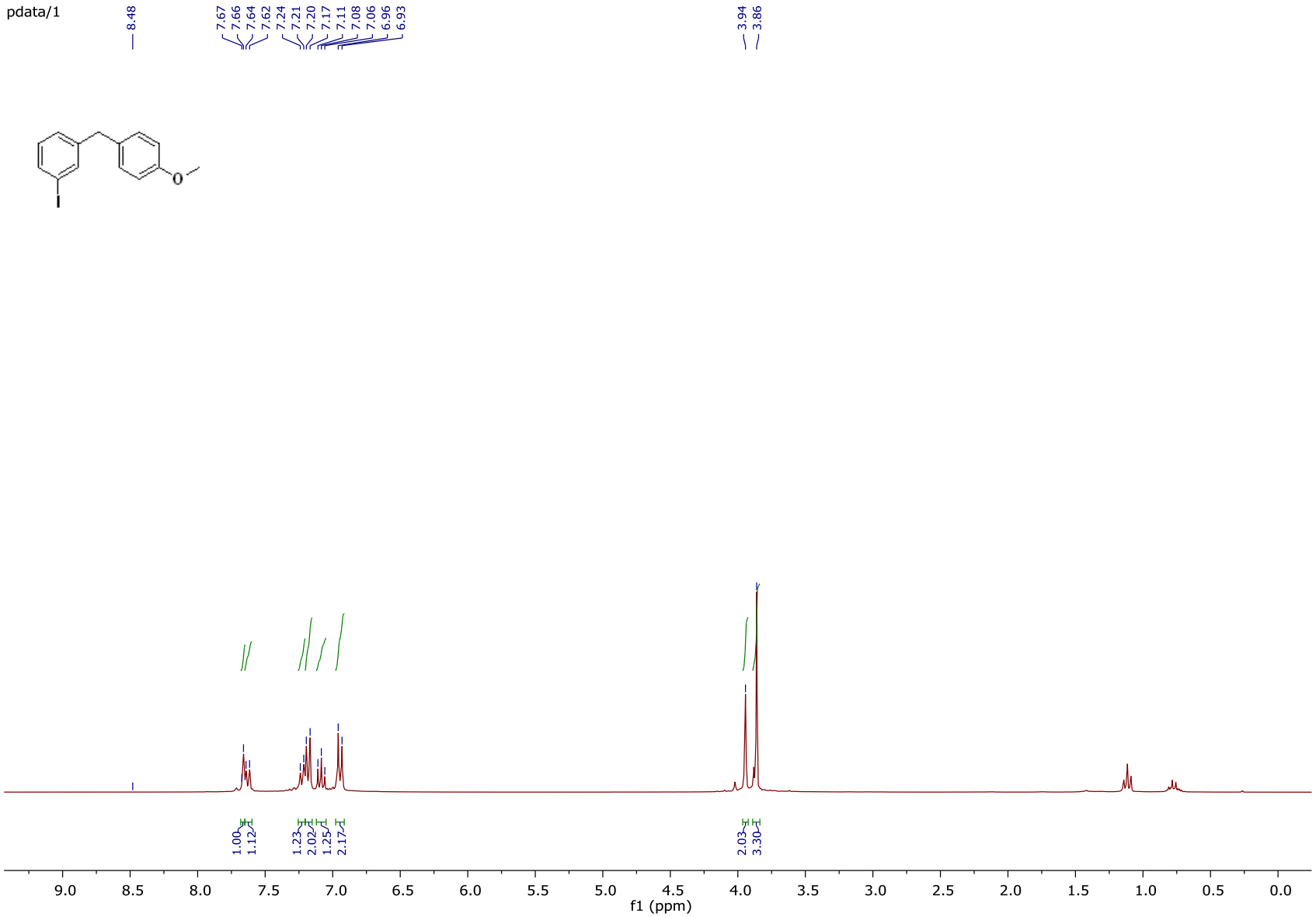
^{1}H NMR spectrum of **1e** (300 MHz, $CDCl_3$)



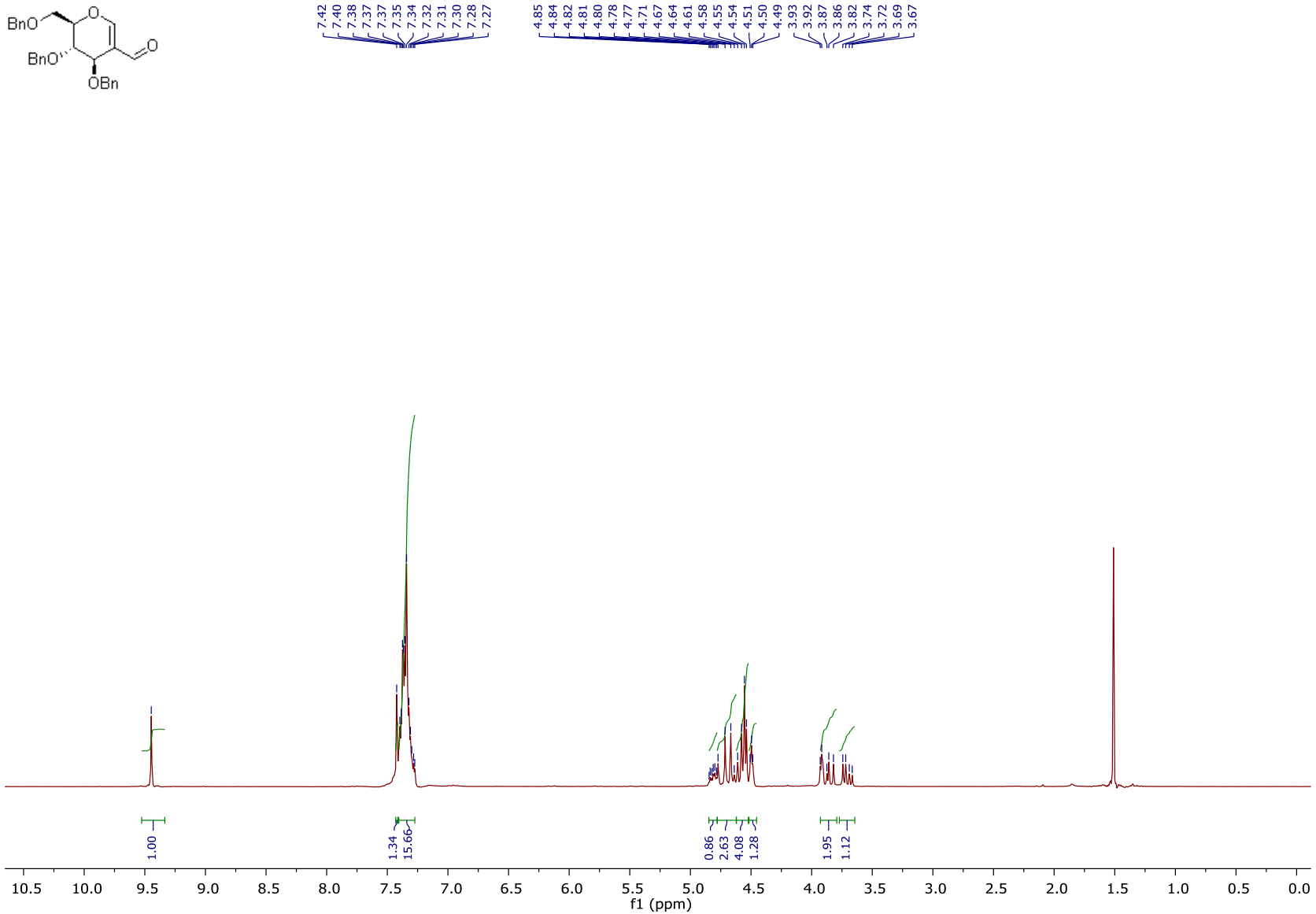
^{1}H NMR spectrum of **1c** (300 MHz, $CDCl_3$)



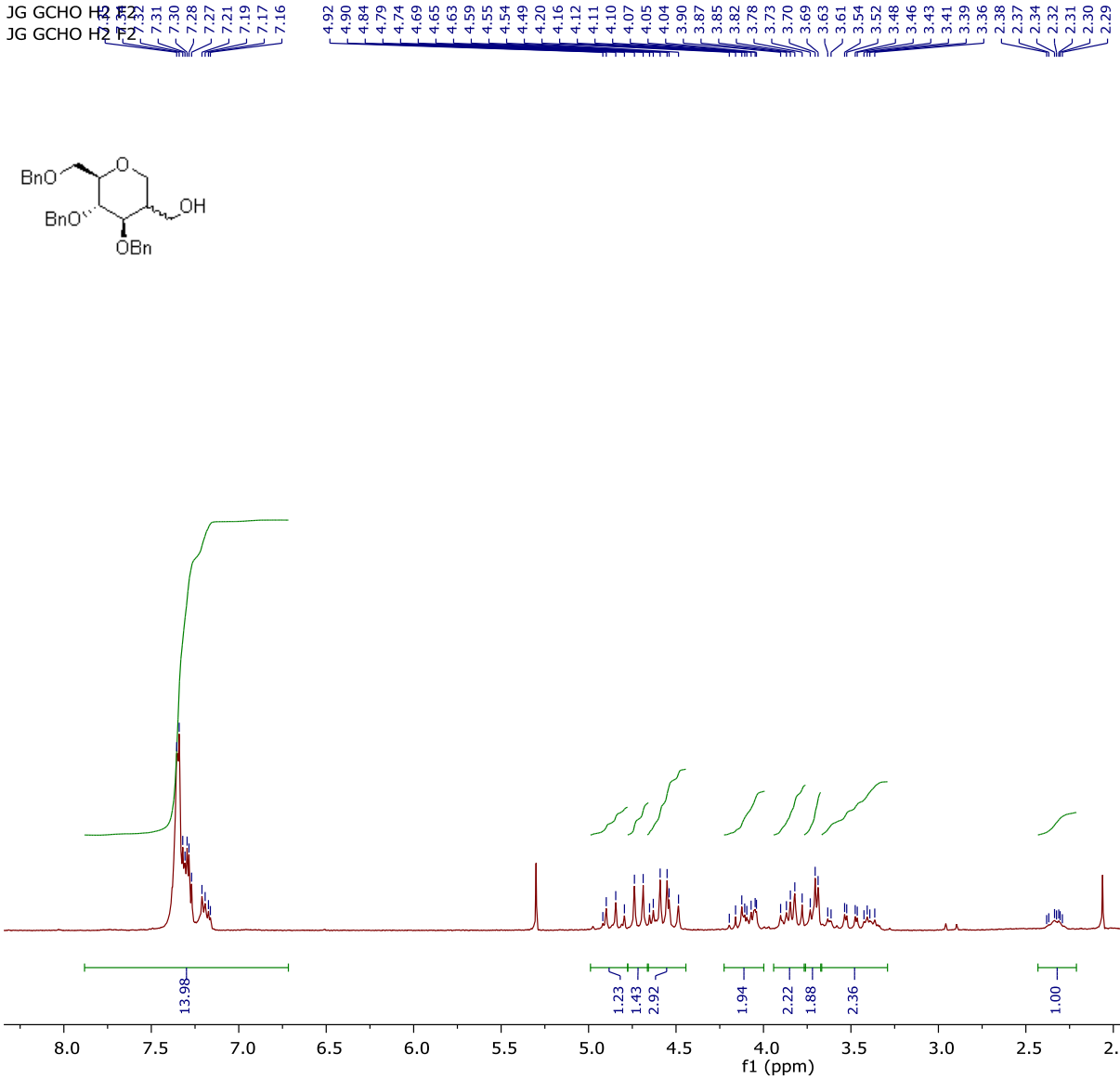
^{1}H NMR spectrum of **1f** (300 MHz, $CDCl_3$)



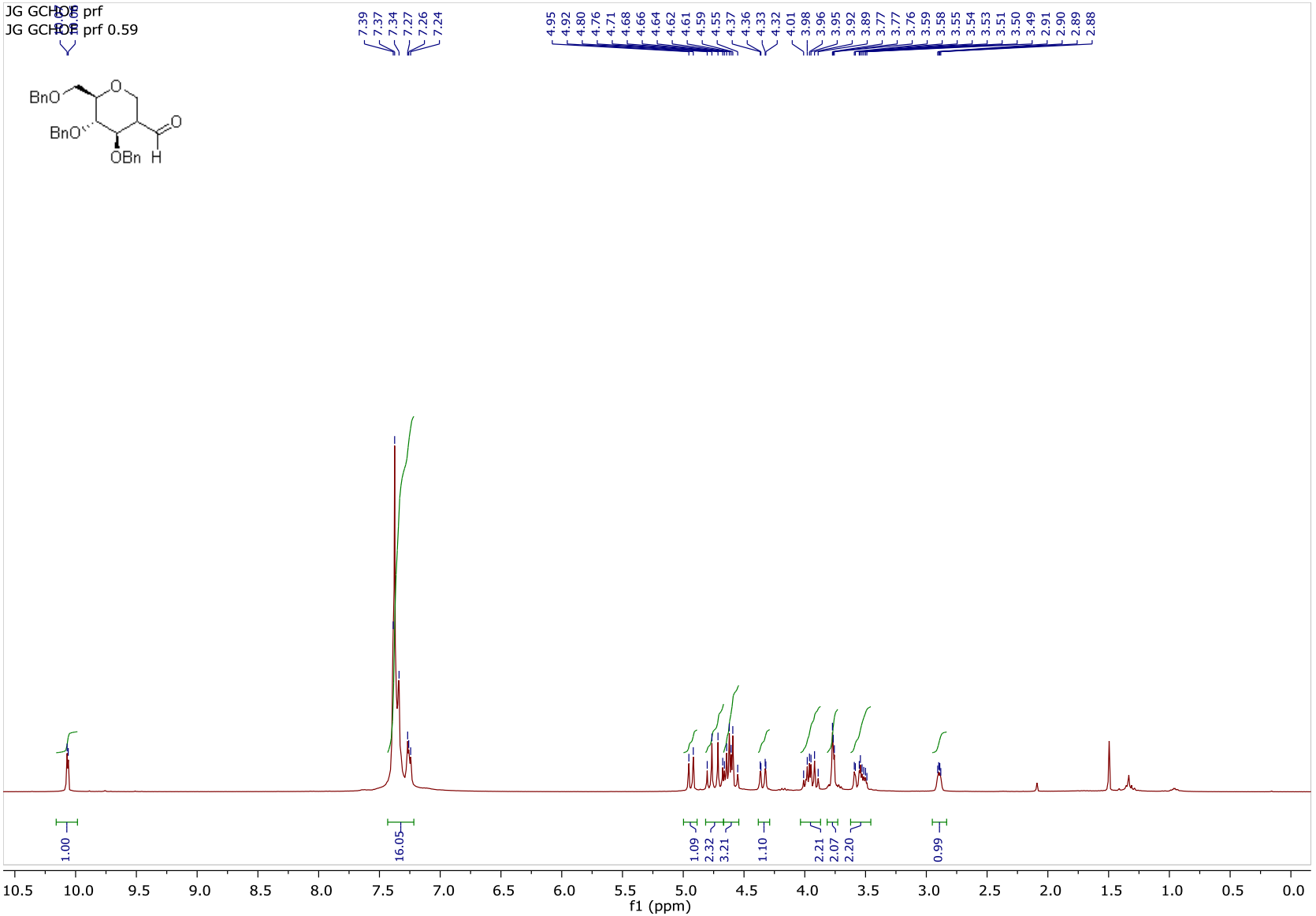
^{1}H NMR spectrum (300 MHz, $CDCl_3$)



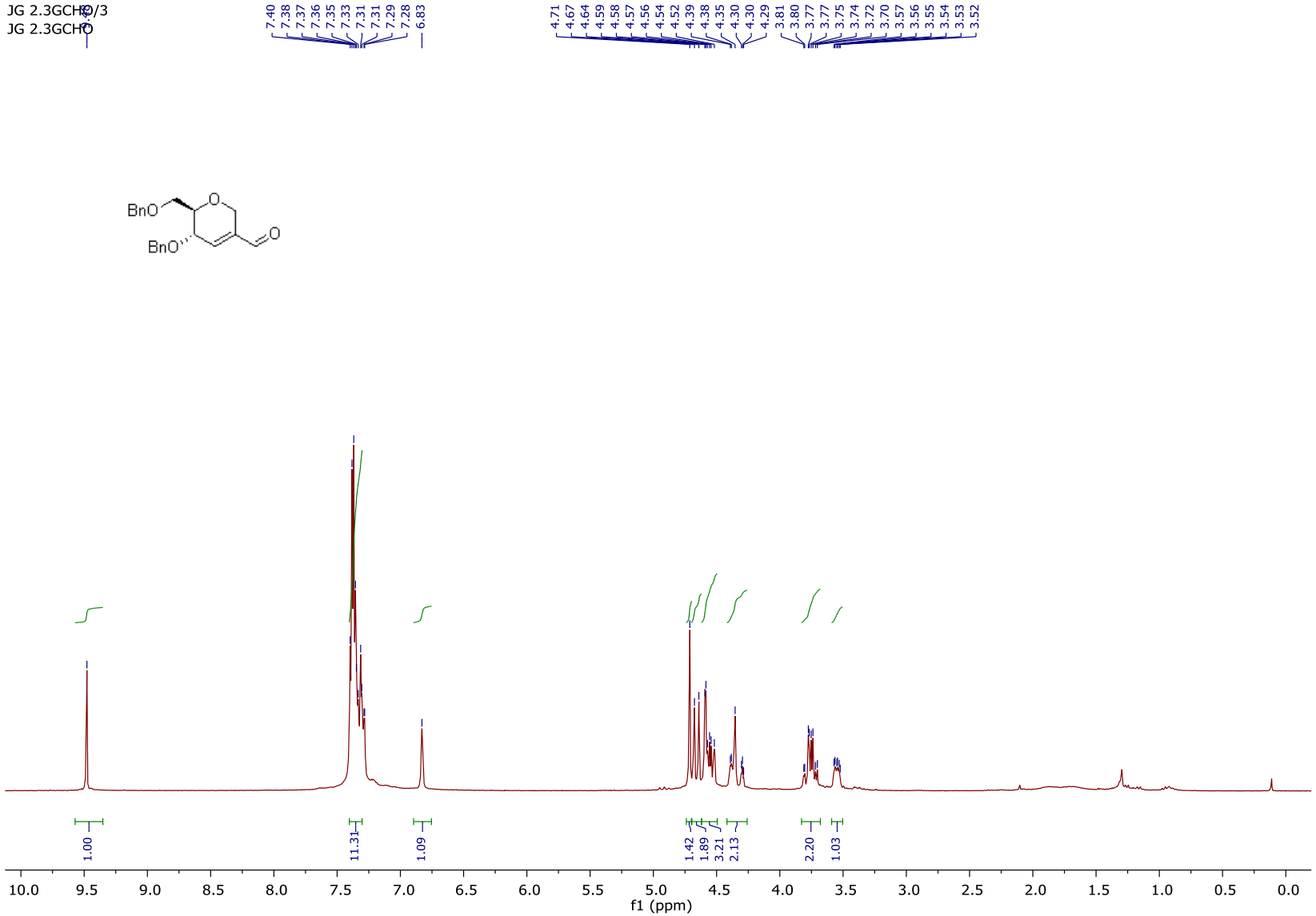
^{1}H NMR spectrum of **S1** (300 MHz, $CDCl_3$)



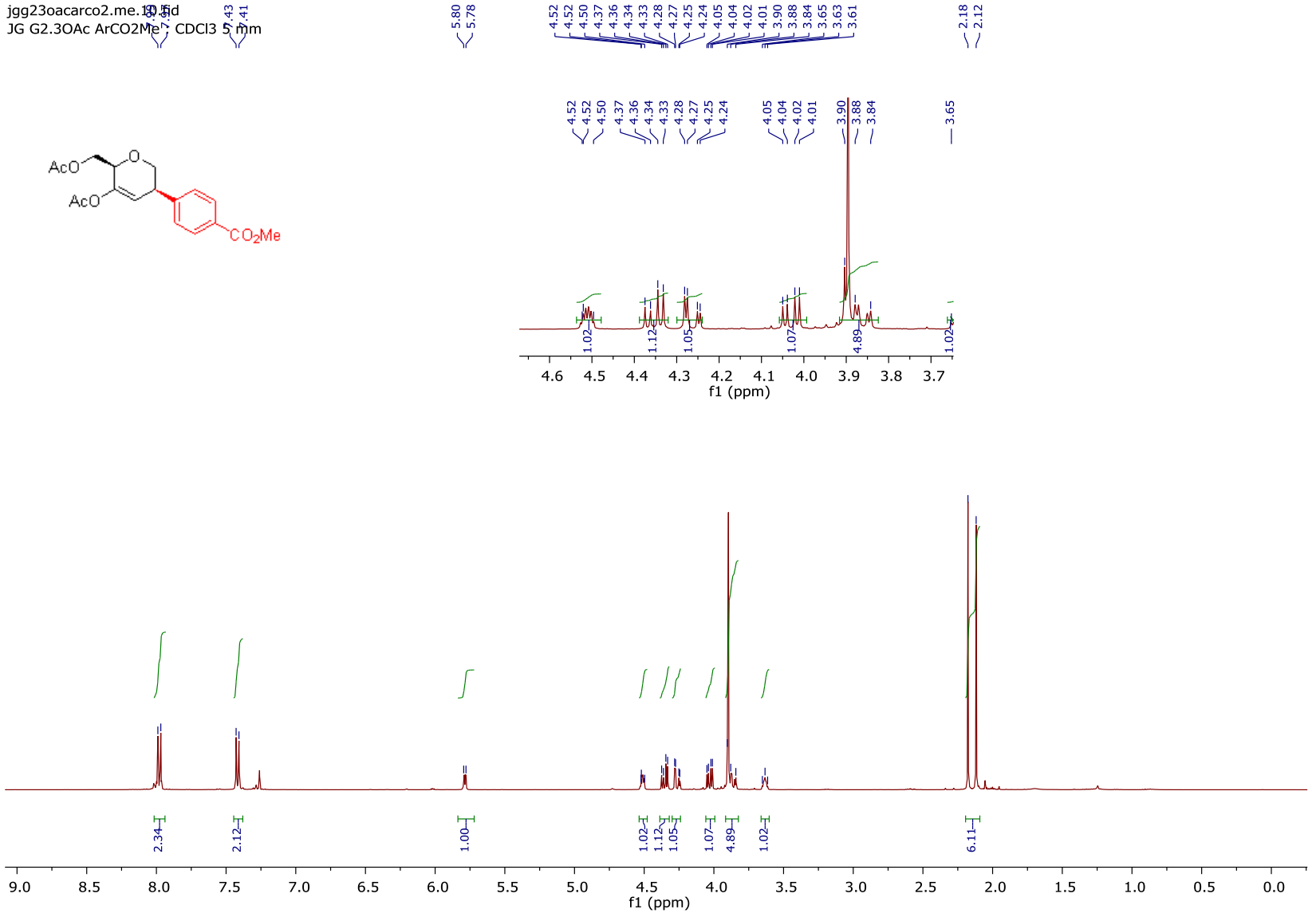
^{1}H NMR spectrum of **S2** (300 MHz, $CDCl_3$)



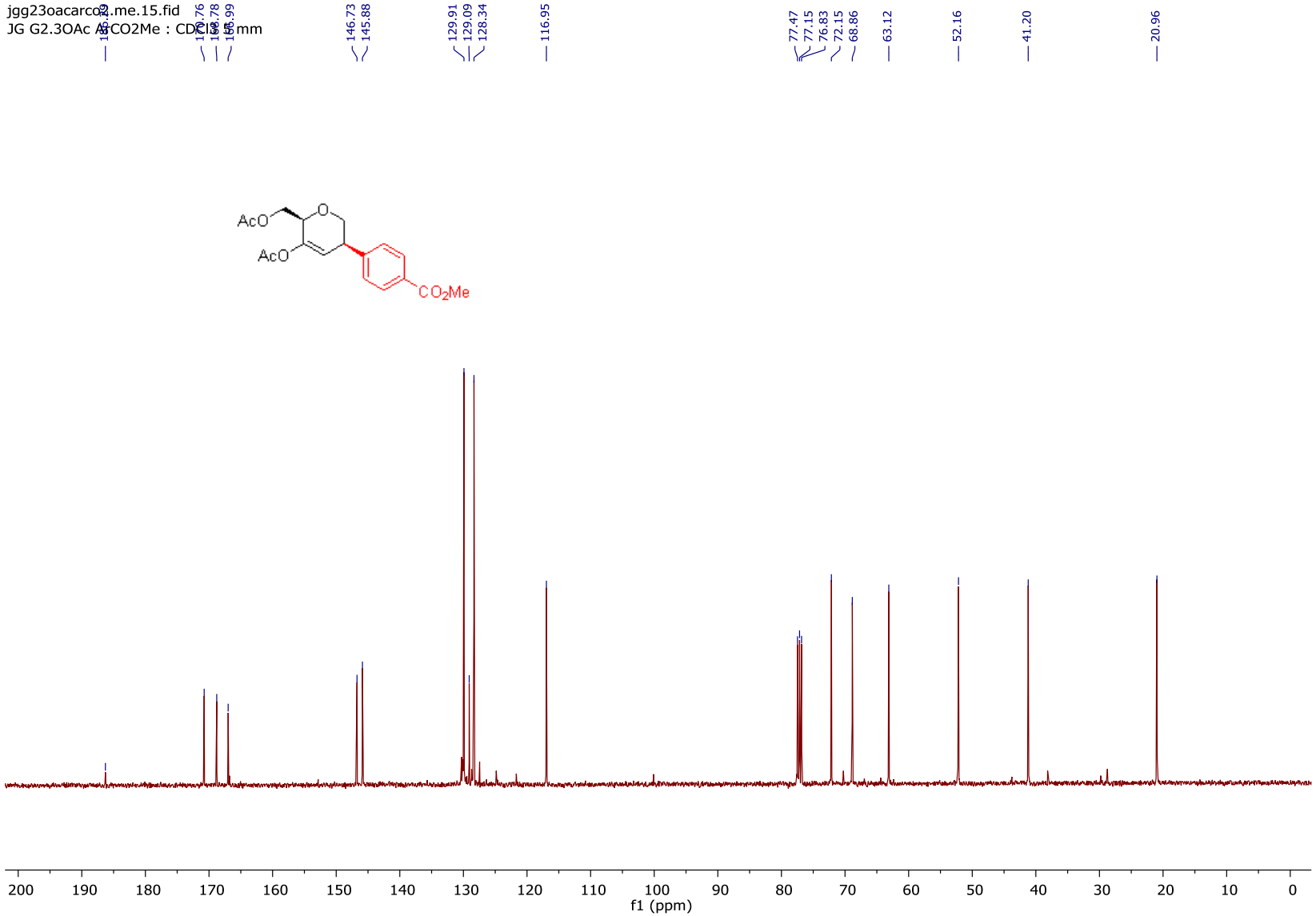
^{1}H NMR spectrum of **S3** (300 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1g** (300 MHz, $CDCl_3$)



^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3a** (101 MHz, $CDCl_3$)

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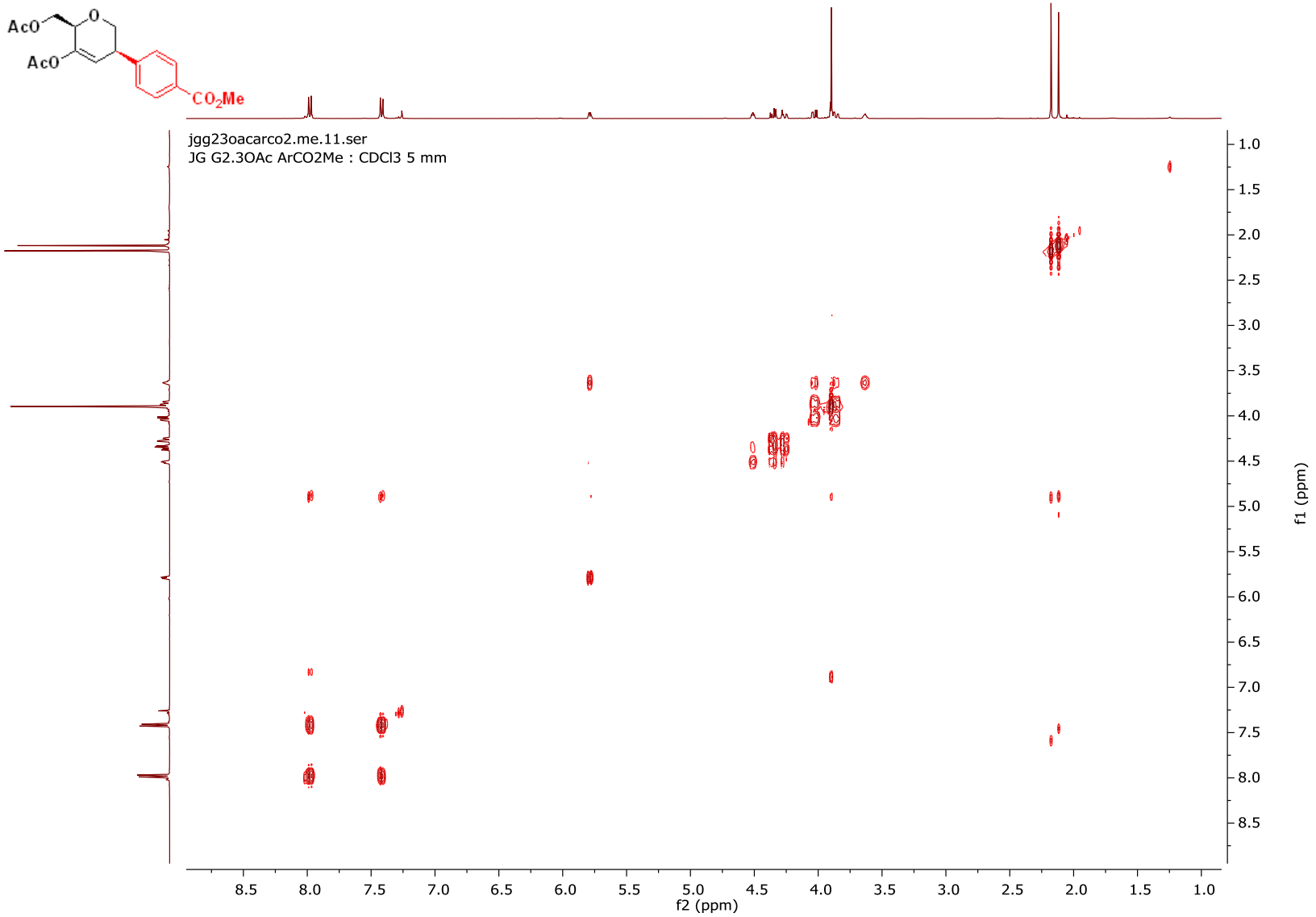
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AcO
O
CO2Me
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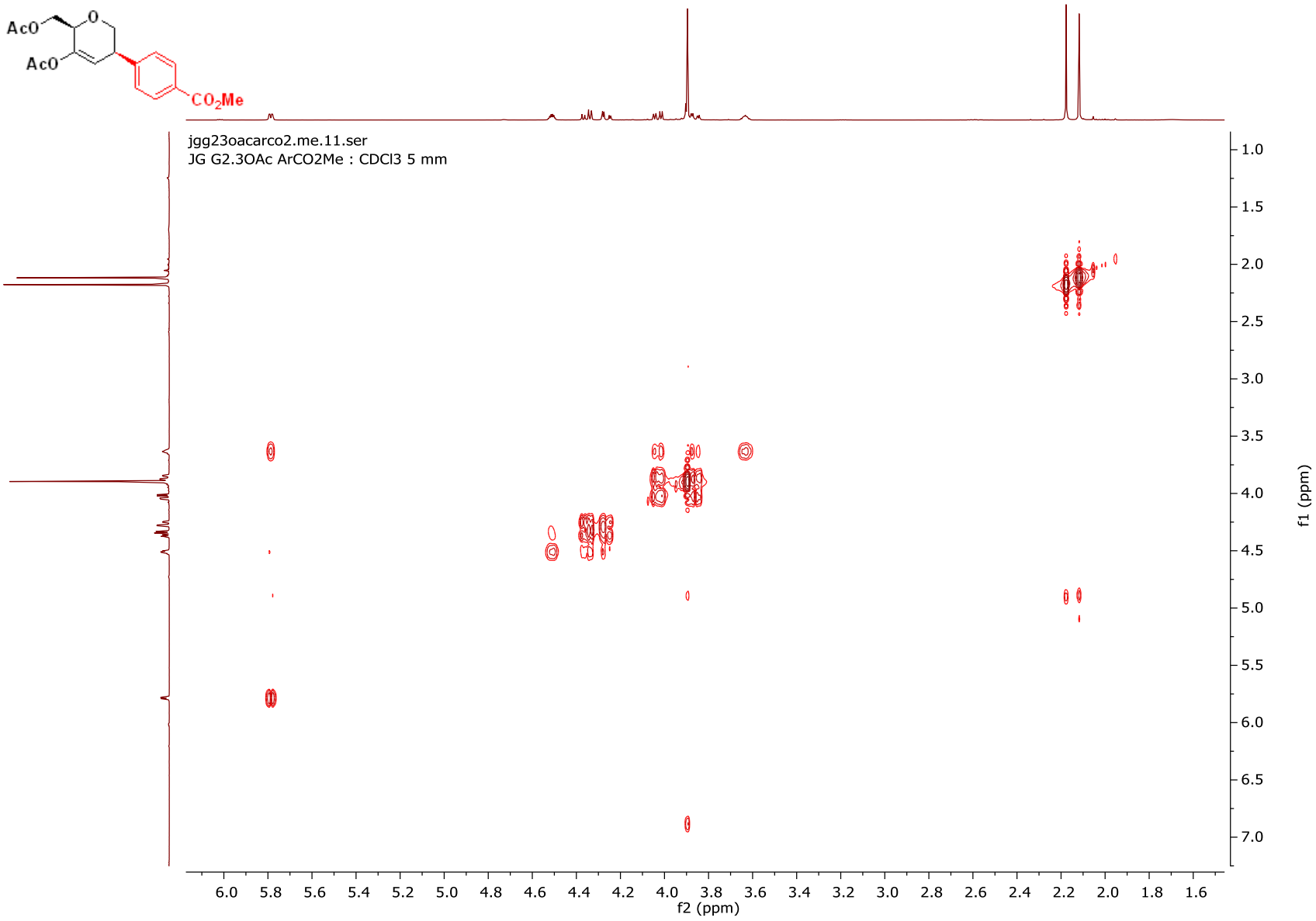
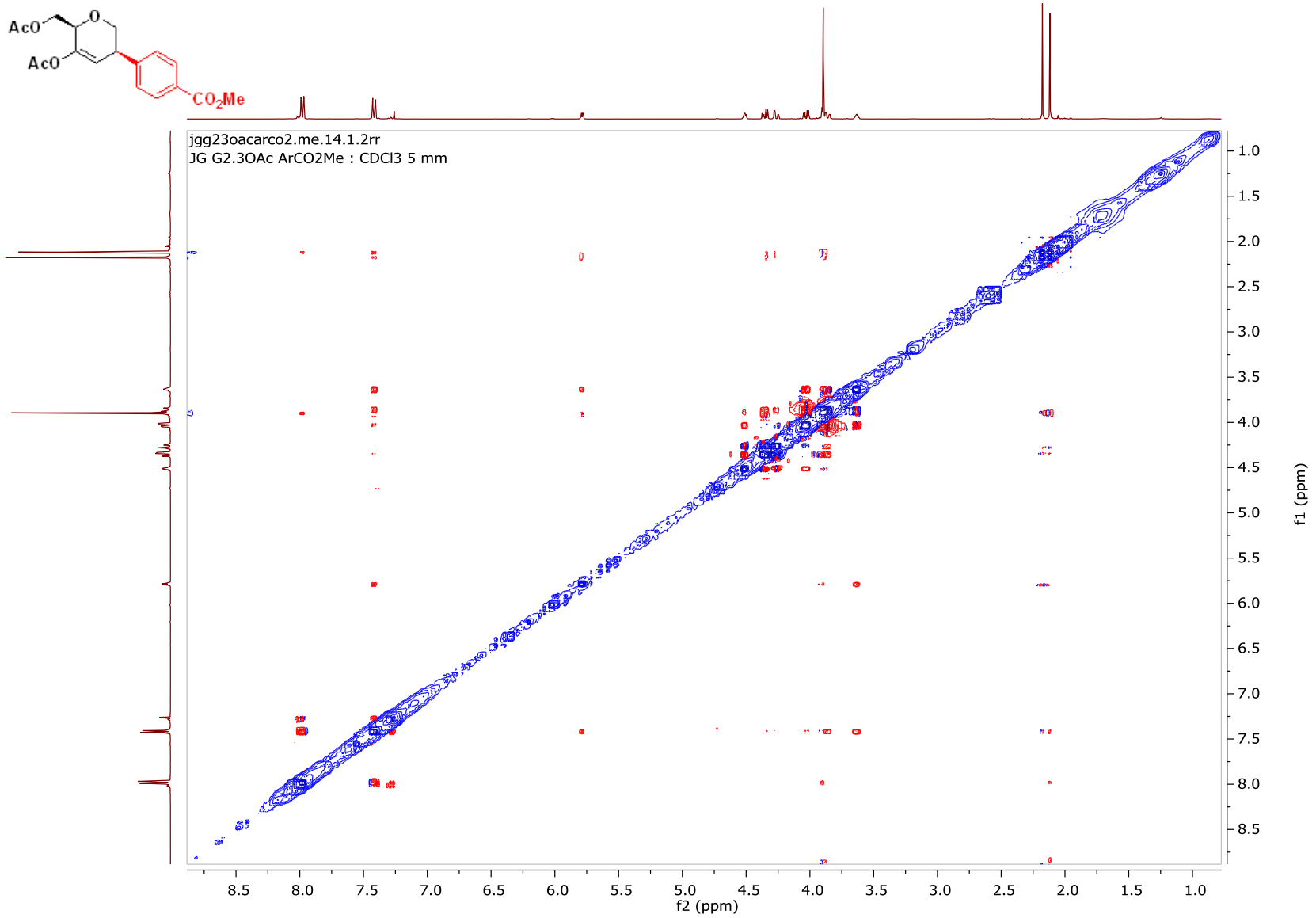
f2 (ppm)
f1 (ppm)


AcO
AcO
O
CO2Me
jgg23oacarco2.me.11.ser
JG G2.3OAc ArCO2Me : CDCl3 5 mm
f2 (ppm)
f1 (ppm)

NOESY :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AcO
O
CO2Me
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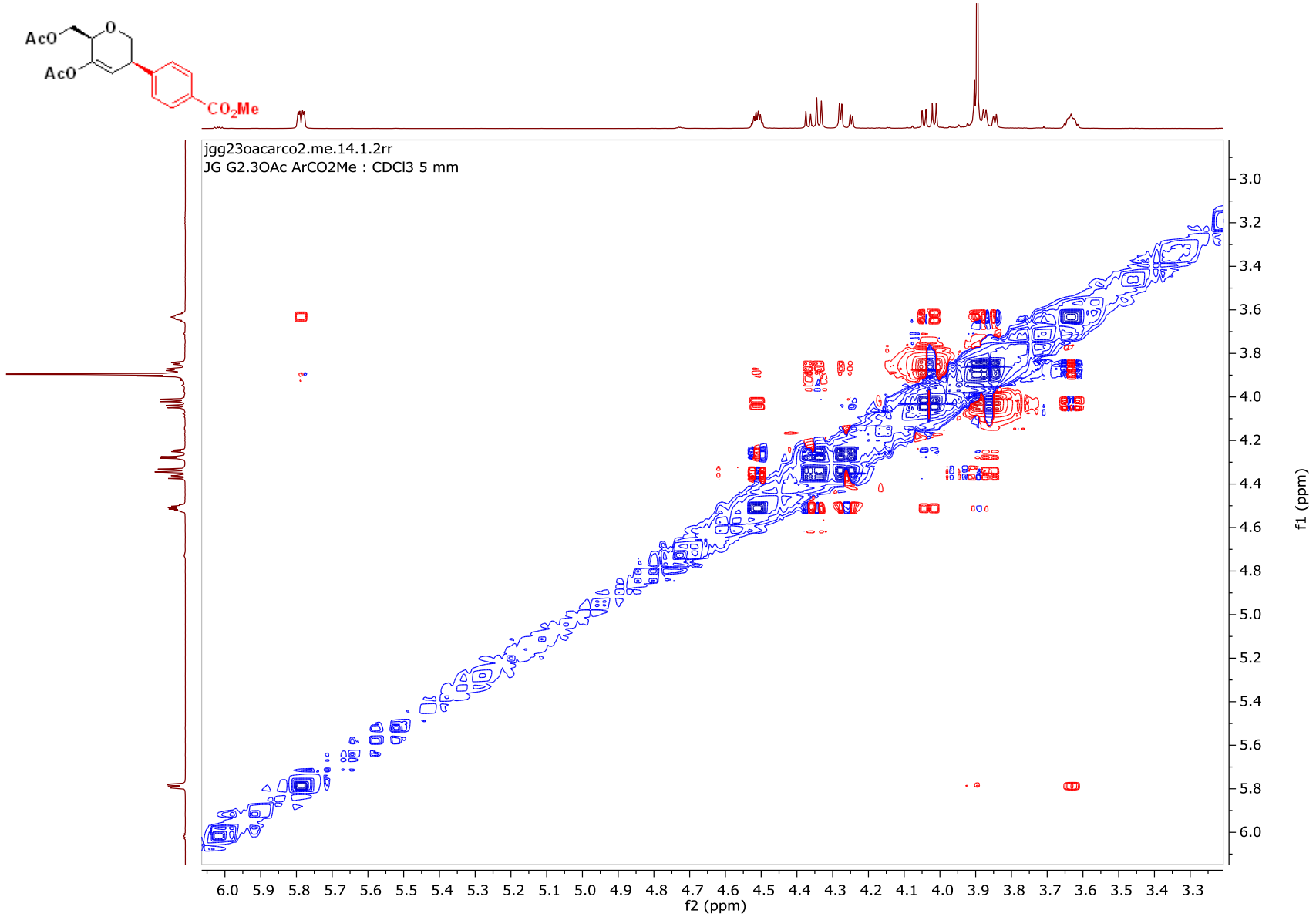
f2 (ppm)
f1 (ppm)


AcO
AcO
O
CO2Me
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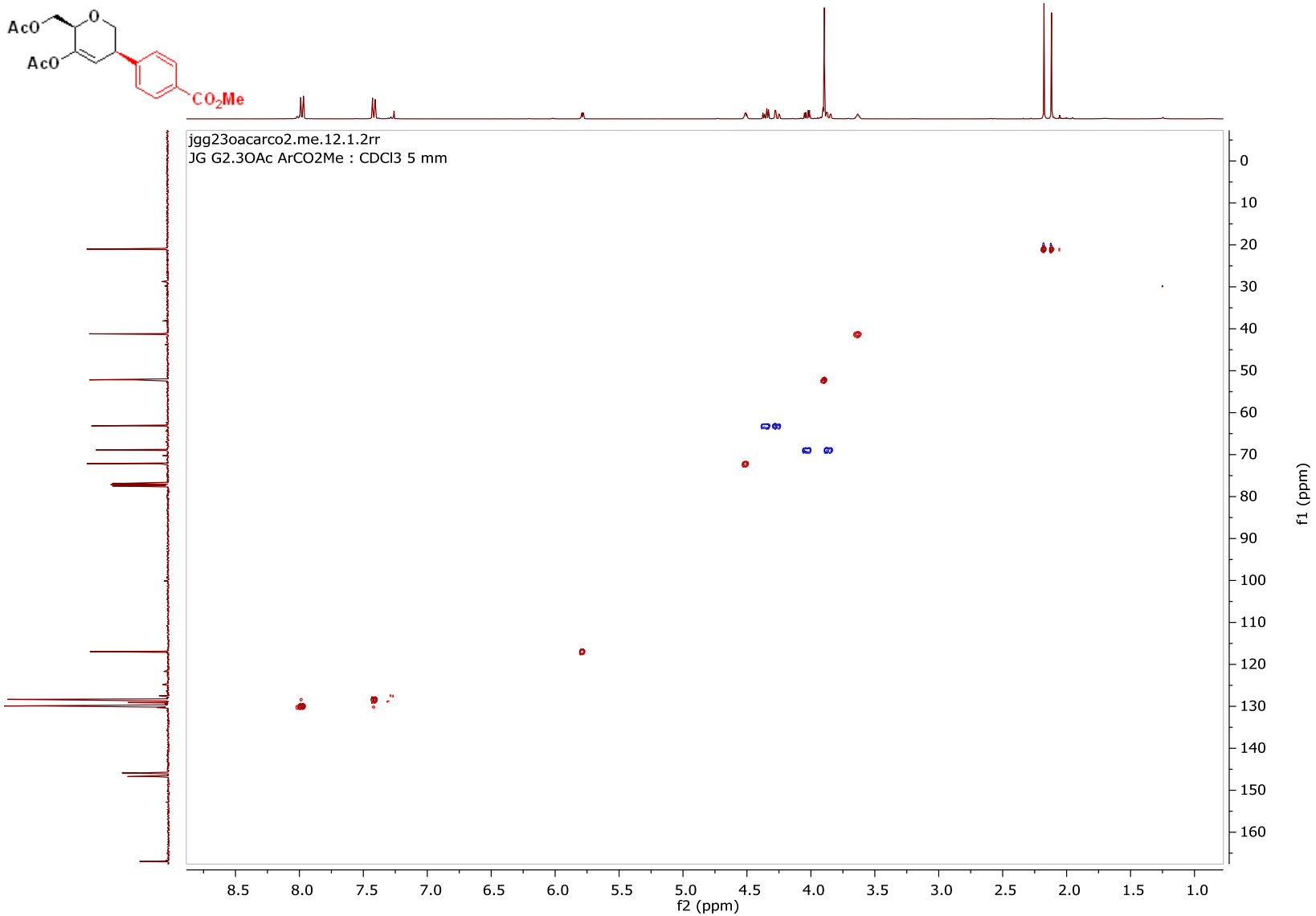
JG G2.3OAc ArCO2Me : CDCl3 5 mm
f1 (ppm)
f2 (ppm)

HSQC :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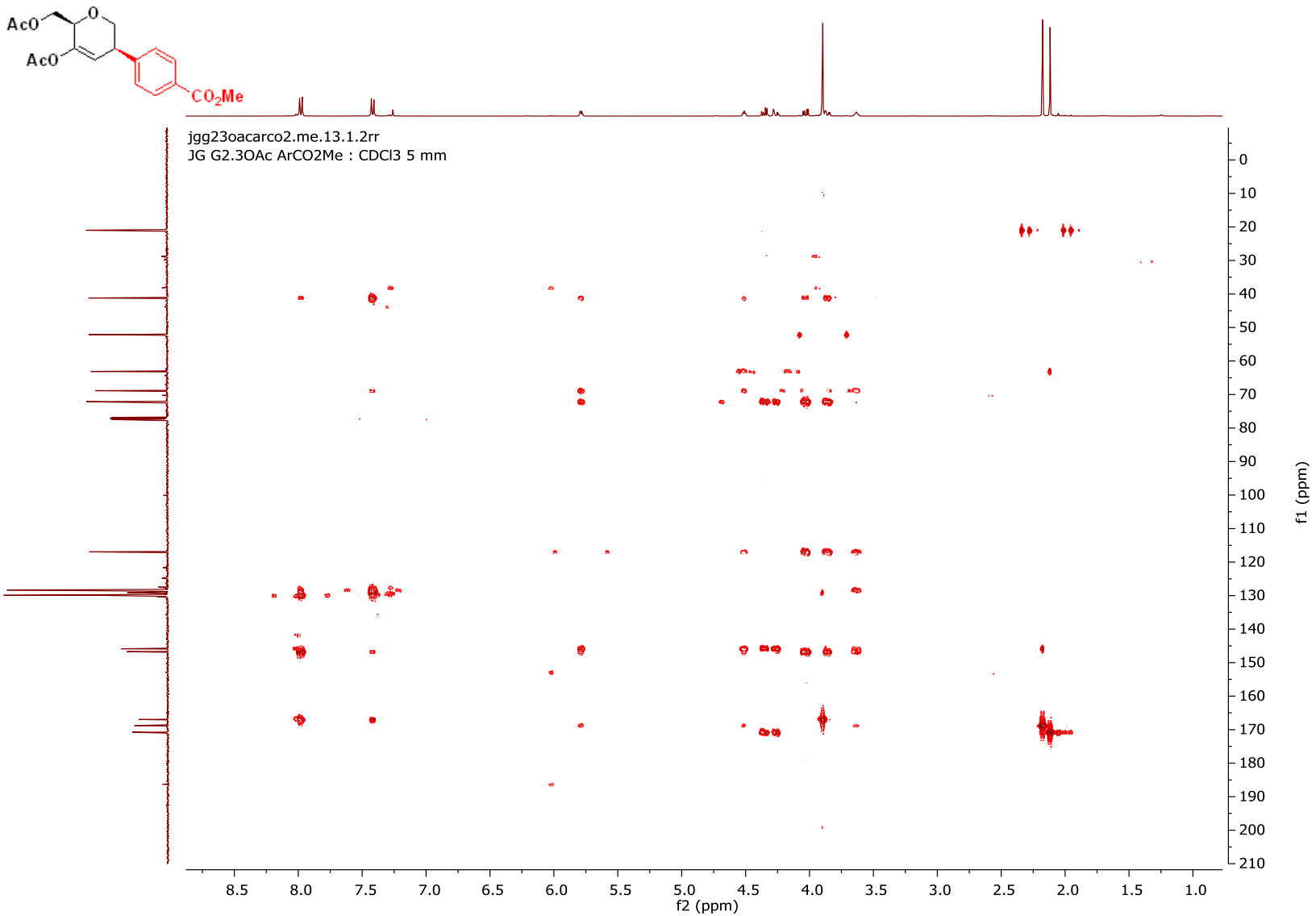
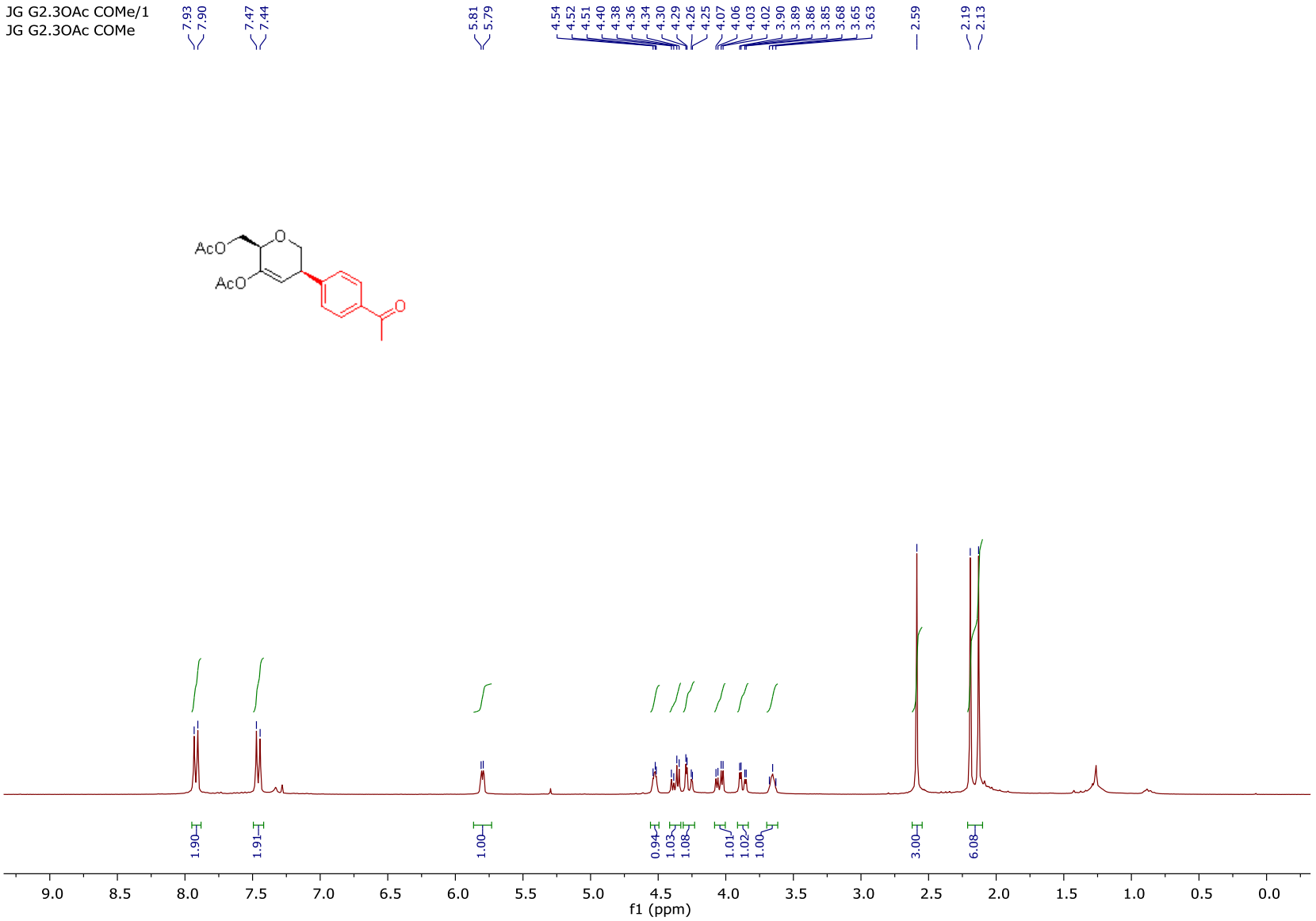
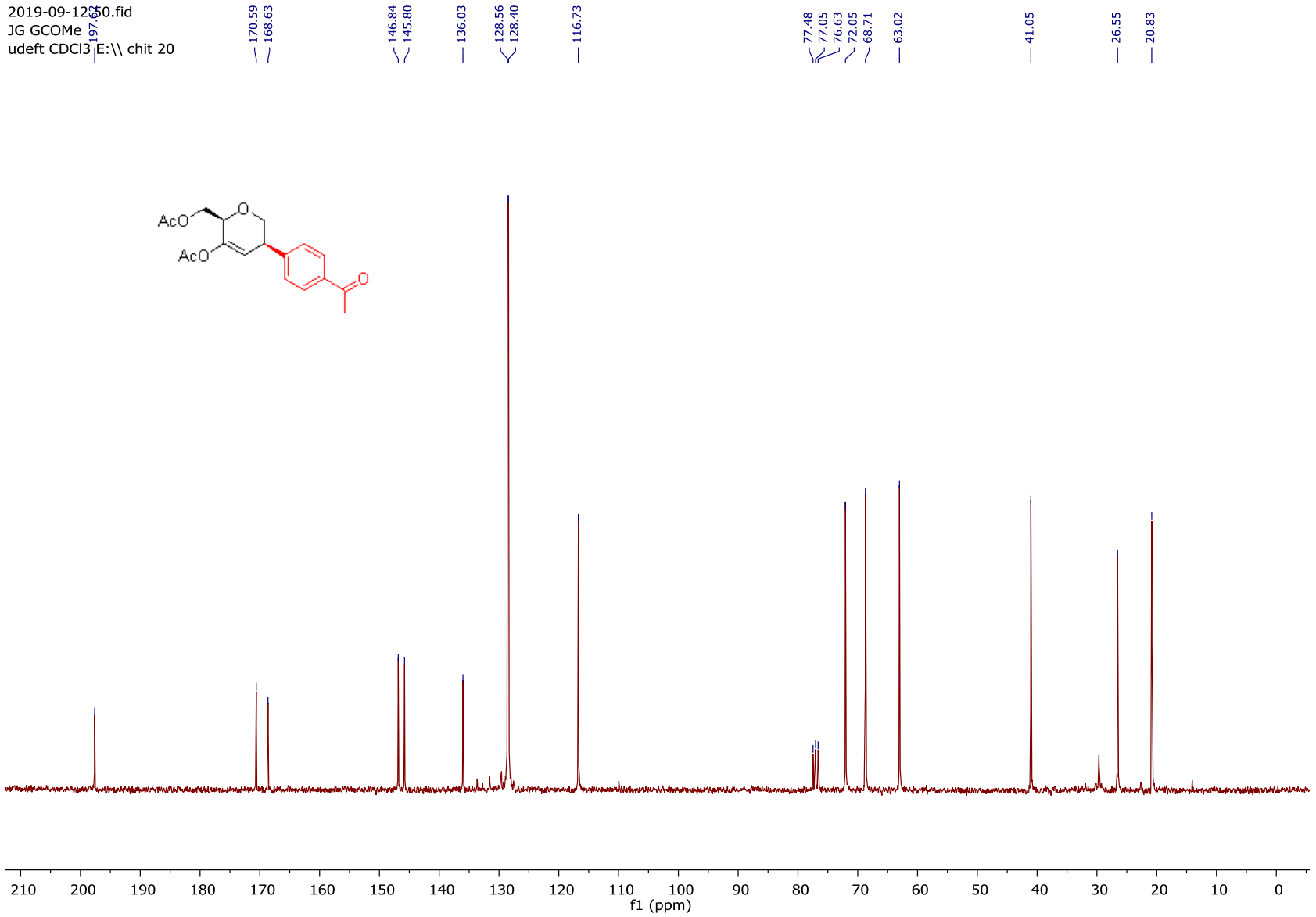
AcO
O
CO2Me
jgg23oacarco2.me.12.1.2rr
JG G2.3OAc ArCO2Me : CDCl3 5 mm
f2 (ppm)
f1 (ppm)

HBMC

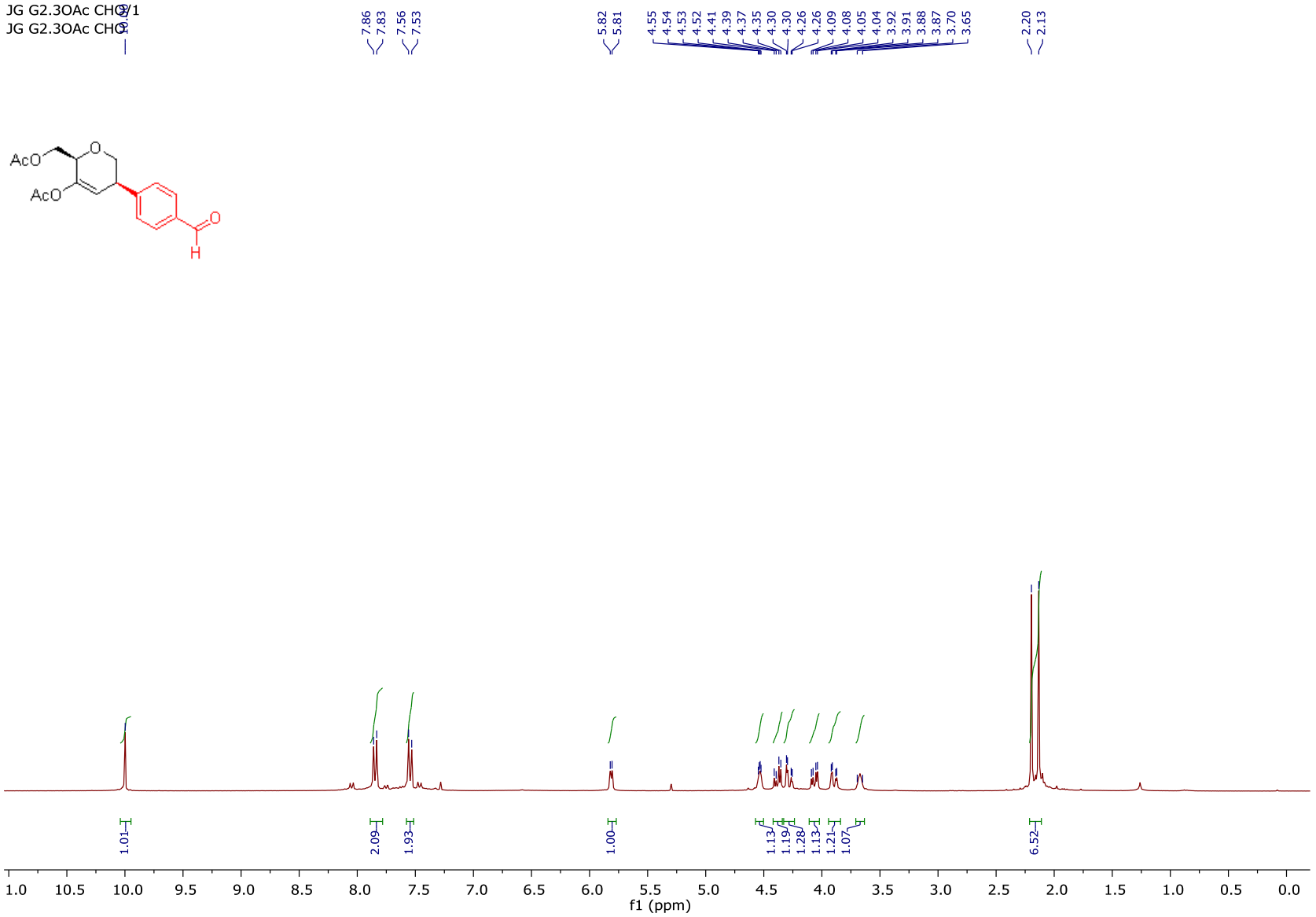

AcO
AcO
O
CO2Me
jgg23oacarco2.me.13.1.2rr
JG G2.3OAc ArCO2Me : CDCl3 5 mm
f2 (ppm)
f1 (ppm)



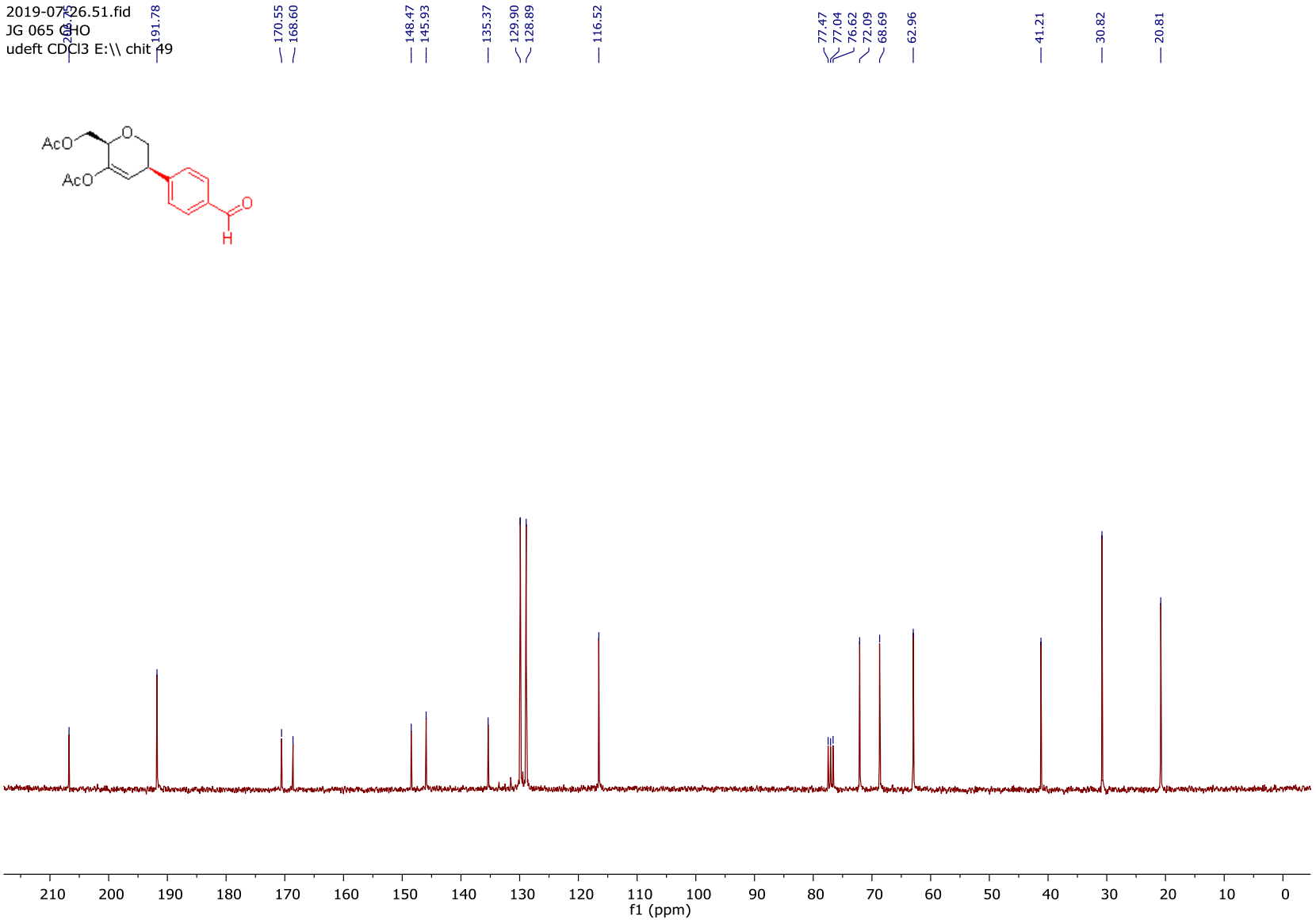
^{1}H NMR spectrum of **3b** (300 MHz, $CDCl_3$)



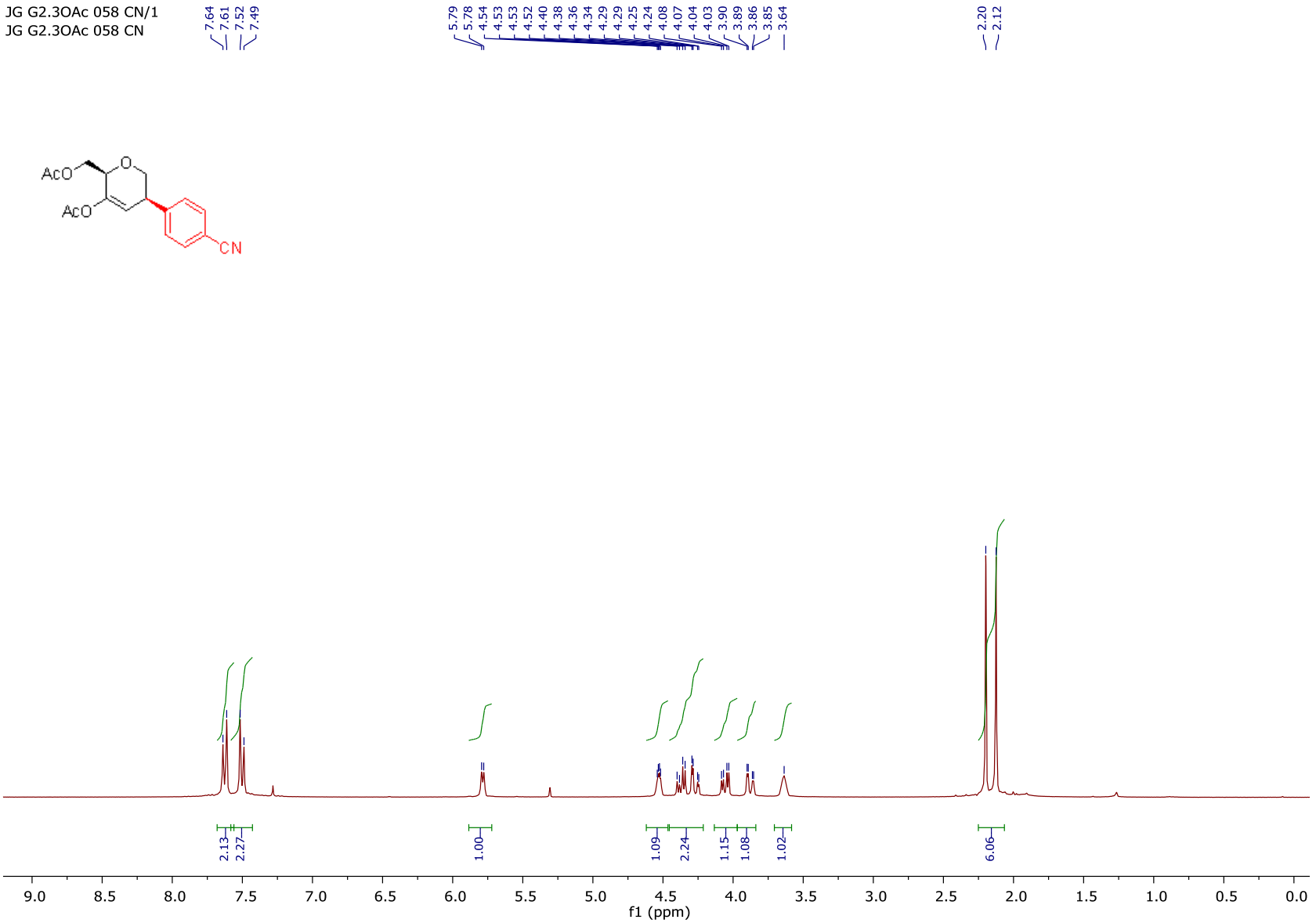
^{13}C NMR spectrum of **3b** (75 MHz, $CDCl_3$)



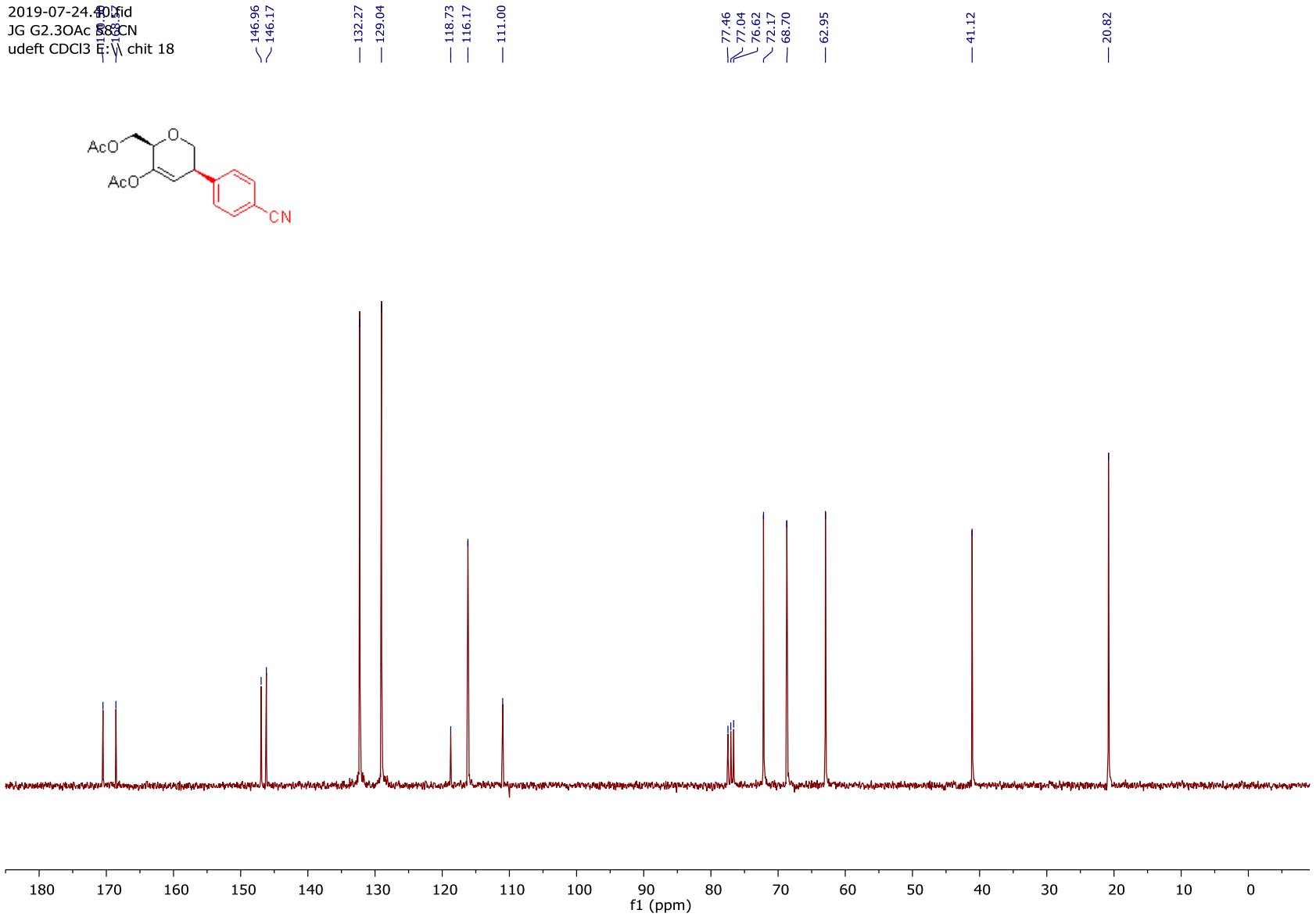
^{1}H NMR spectrum of **3c** (300 MHz, $CDCl_3$)



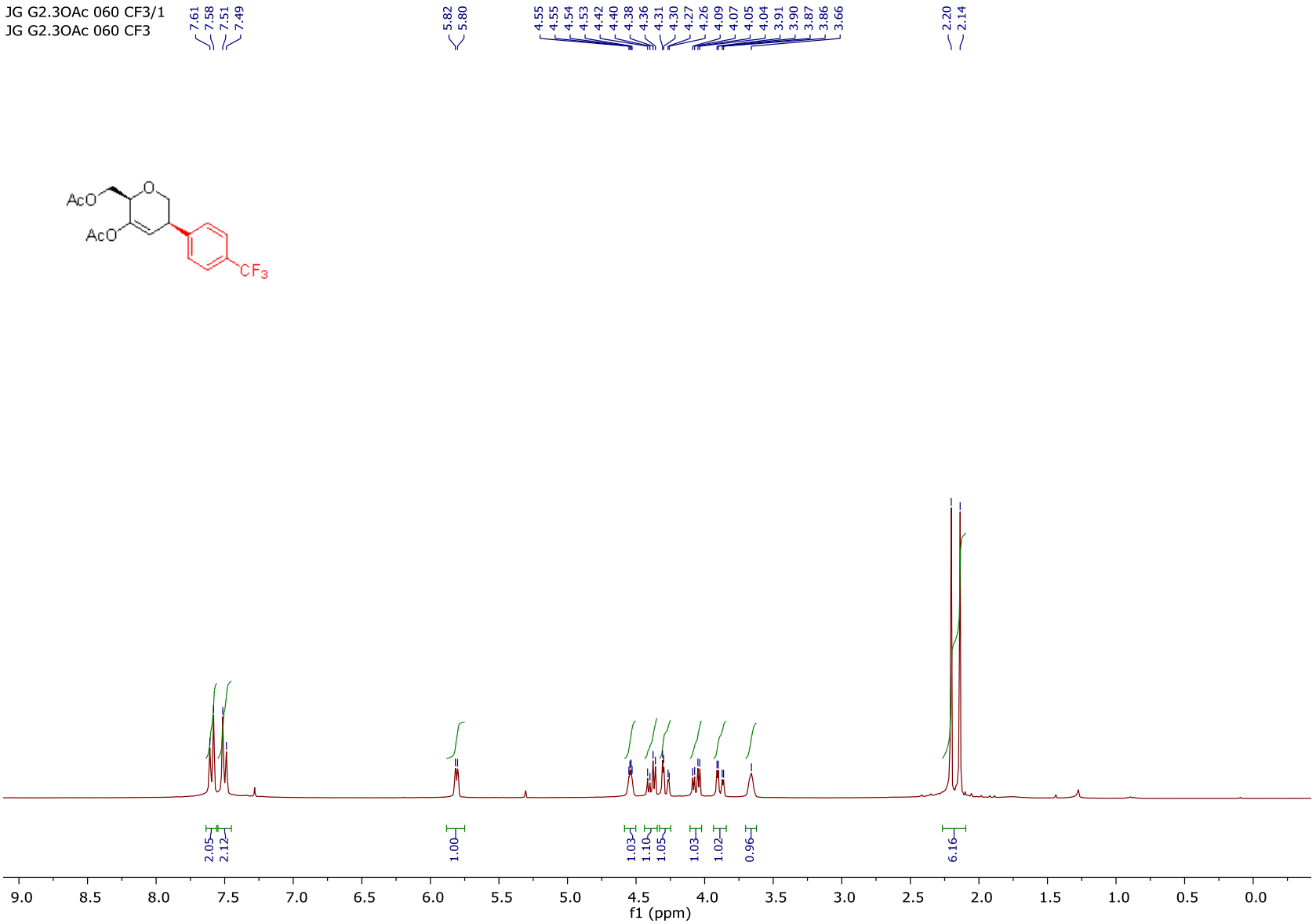
^{13}C NMR spectrum of **3c** (75 MHz, $CDCl_3$)



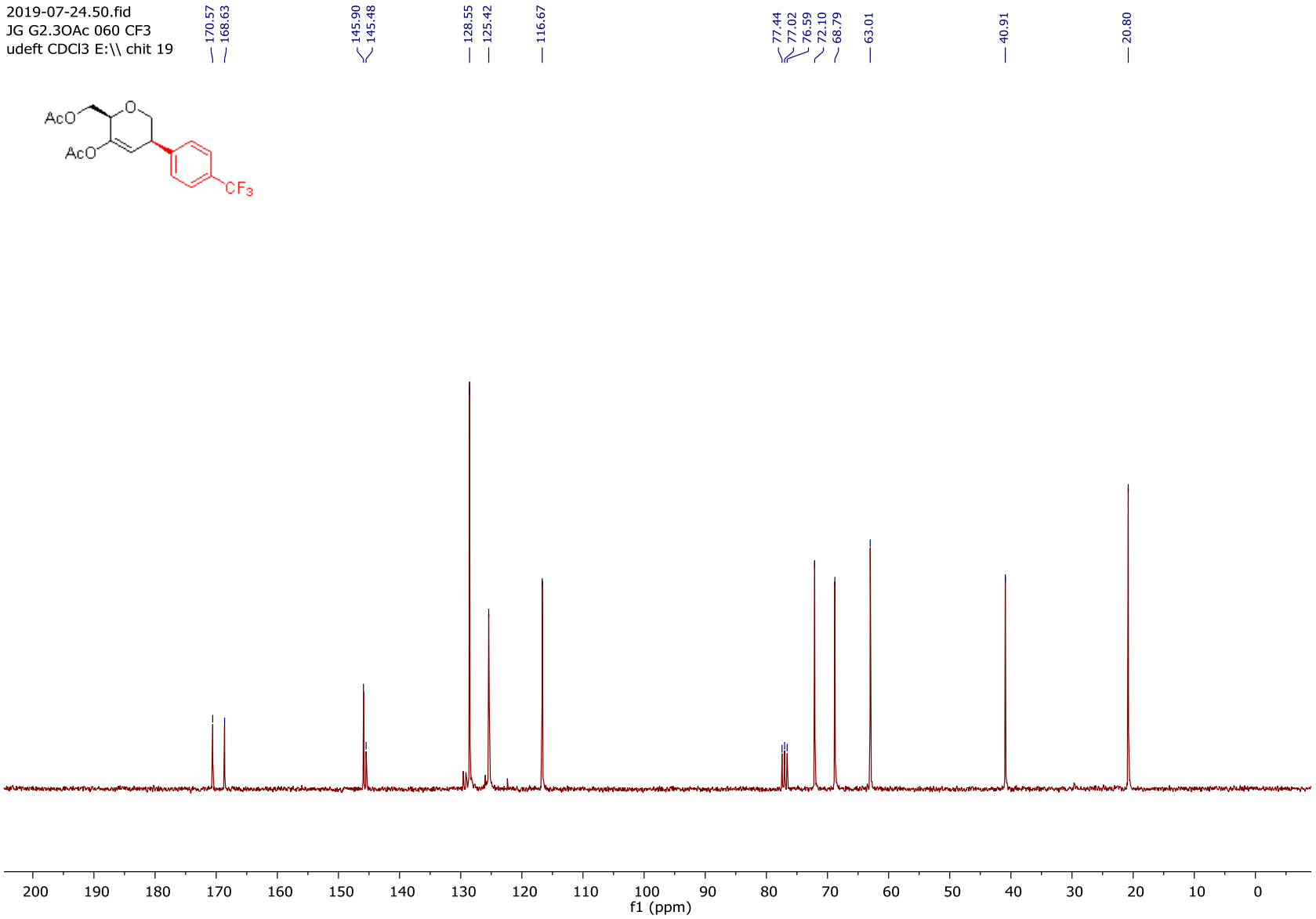
^{1}H NMR spectrum of **3d** (300 MHz, $CDCl_3$)



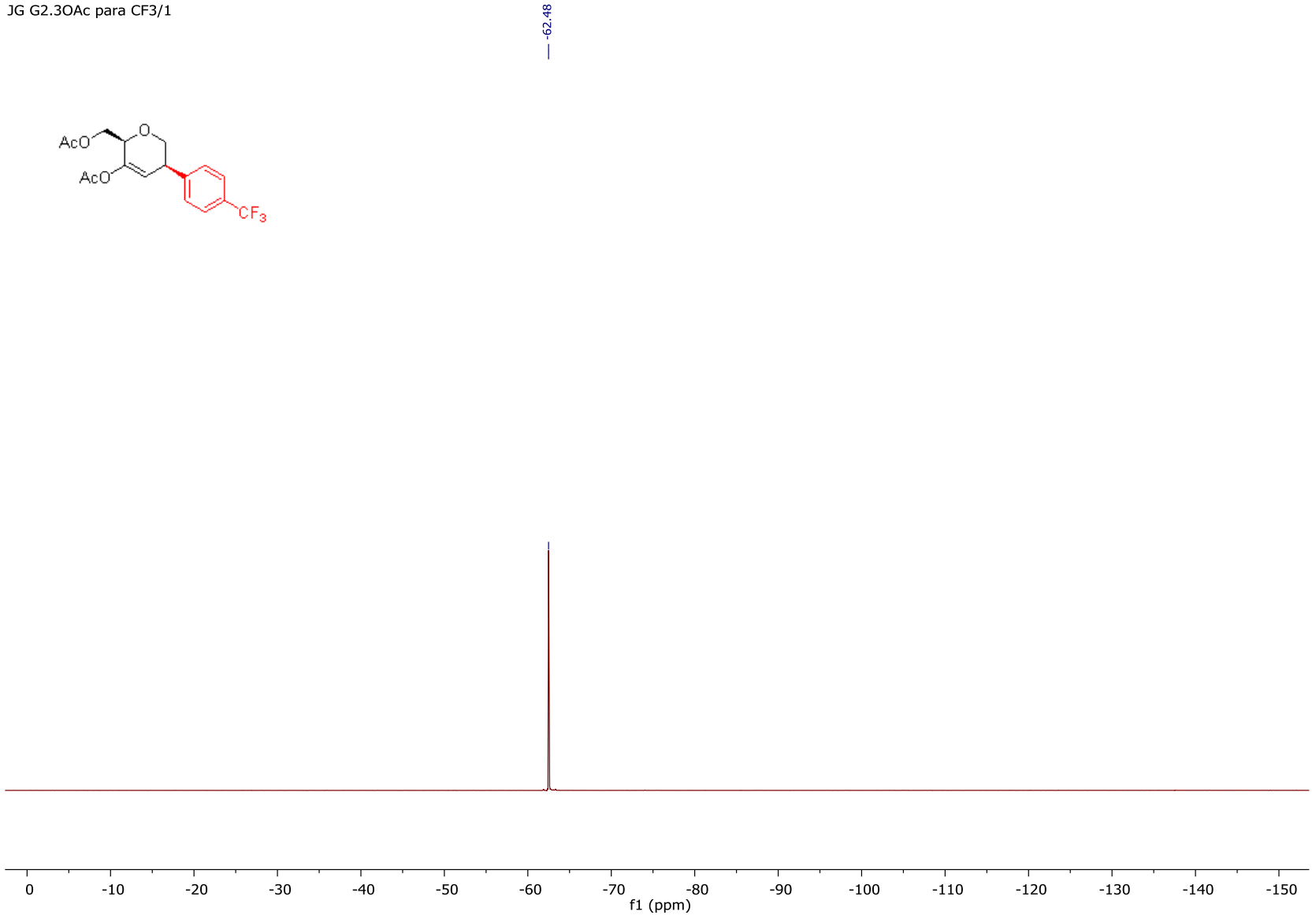
^{13}C NMR spectrum of **3d** (75 MHz, $CDCl_3$)



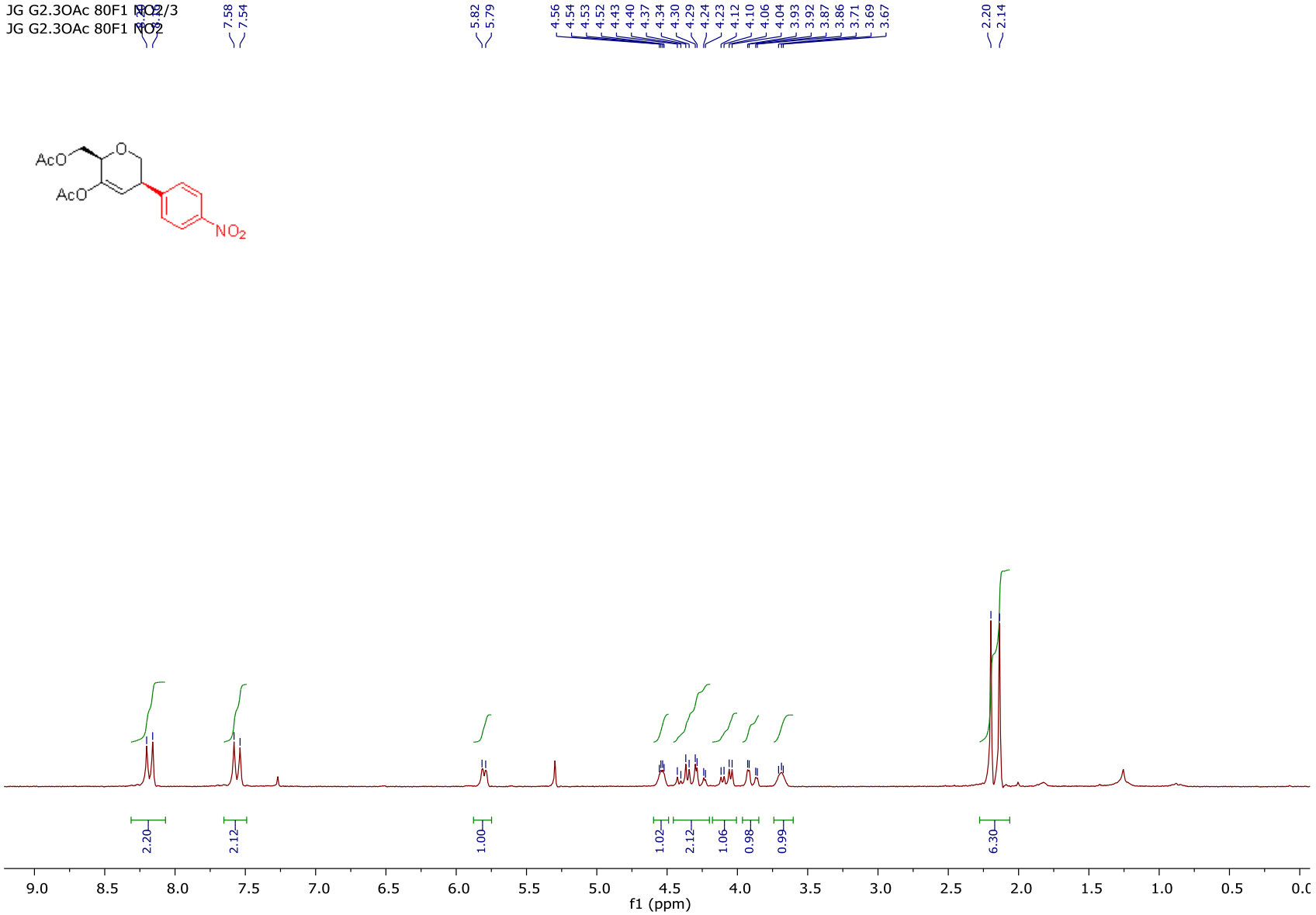
^{1}H NMR spectrum of **3e** (300 MHz, $CDCl_3$)



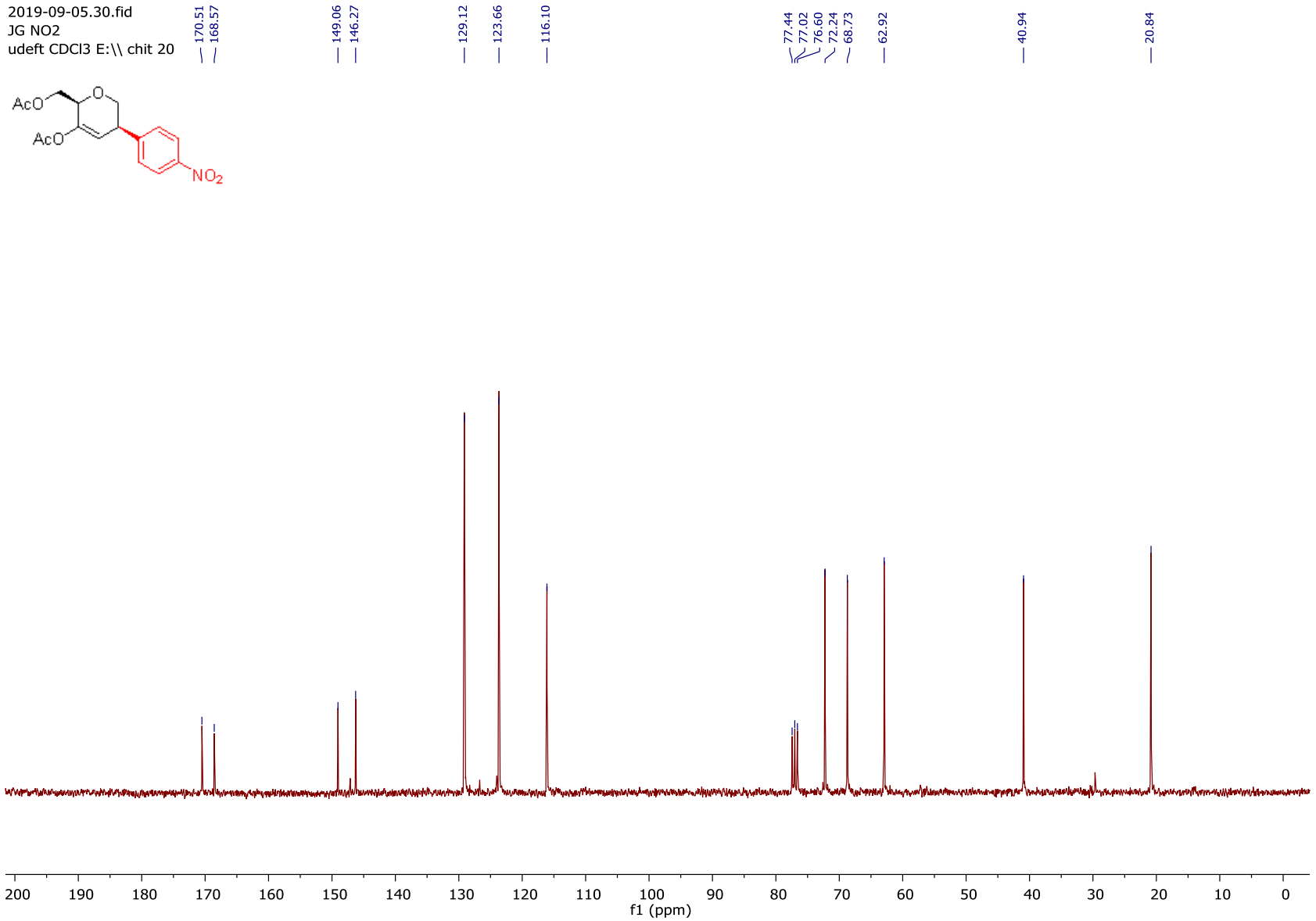
^{13}C NMR spectrum of **3e** (75 MHz, $CDCl_3$)



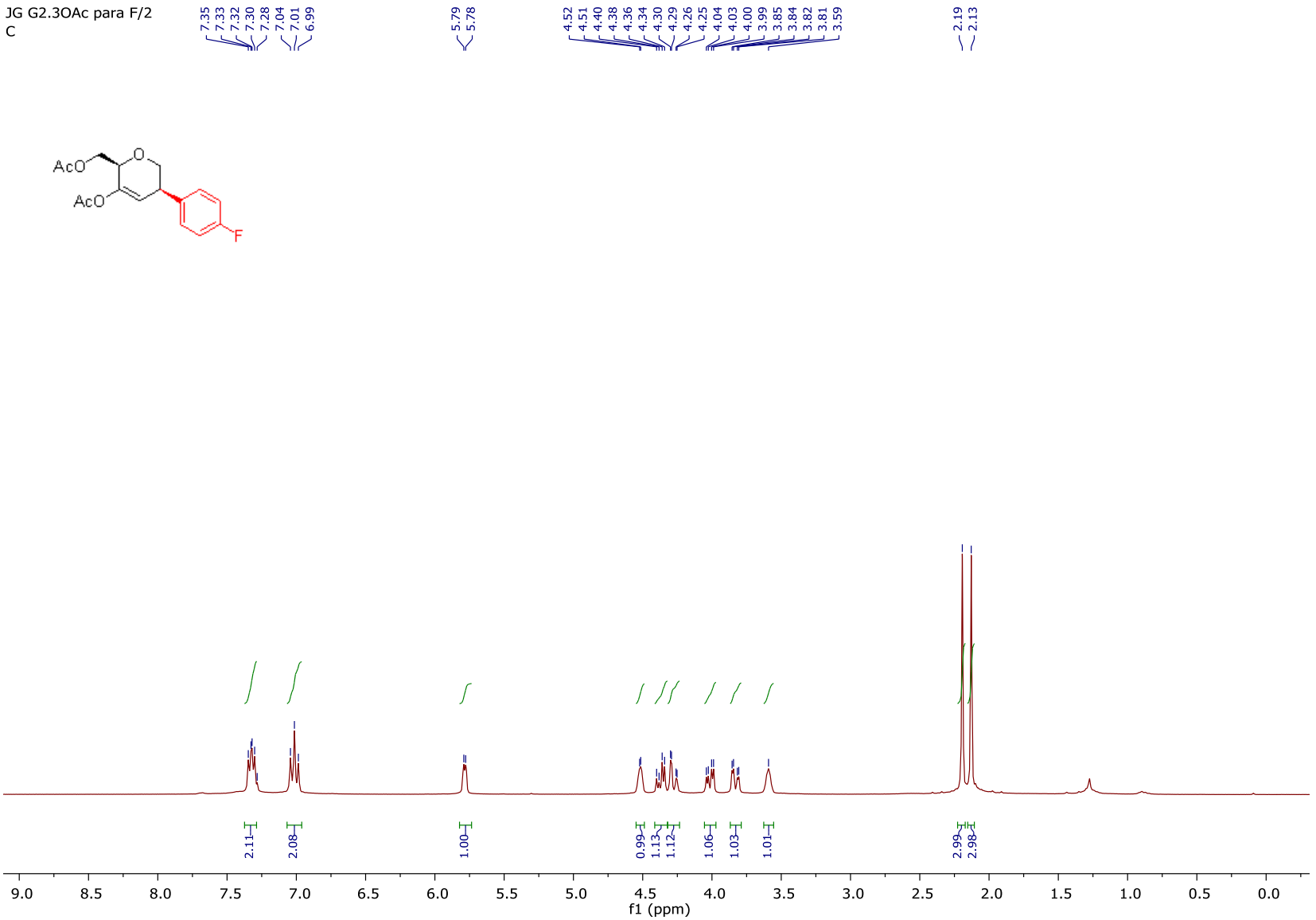
^{19}F NMR spectrum of **3e** (188 MHz, $CDCl_3$)



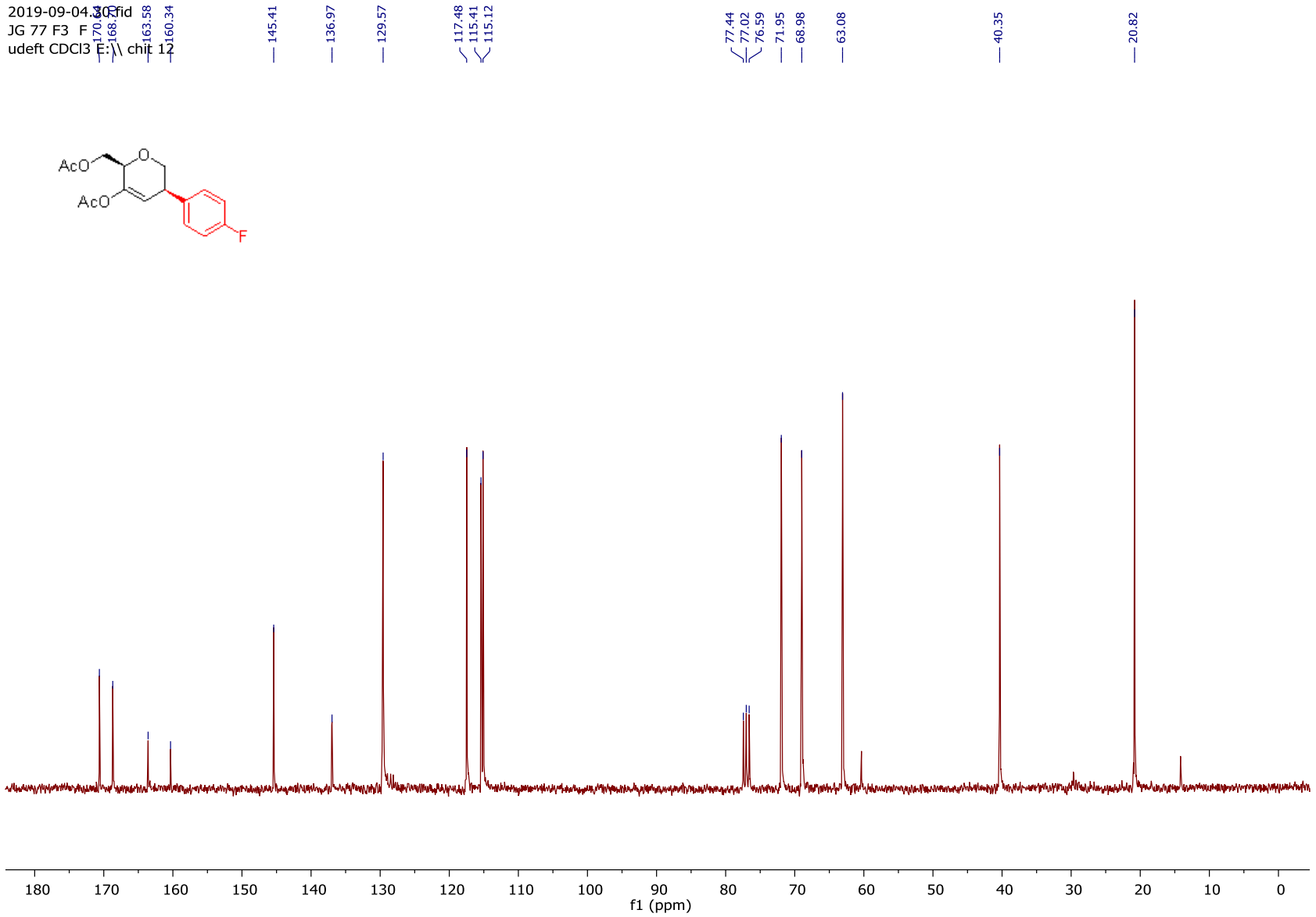
^{1}H NMR spectrum of **3f** (300 MHz, $CDCl_3$)



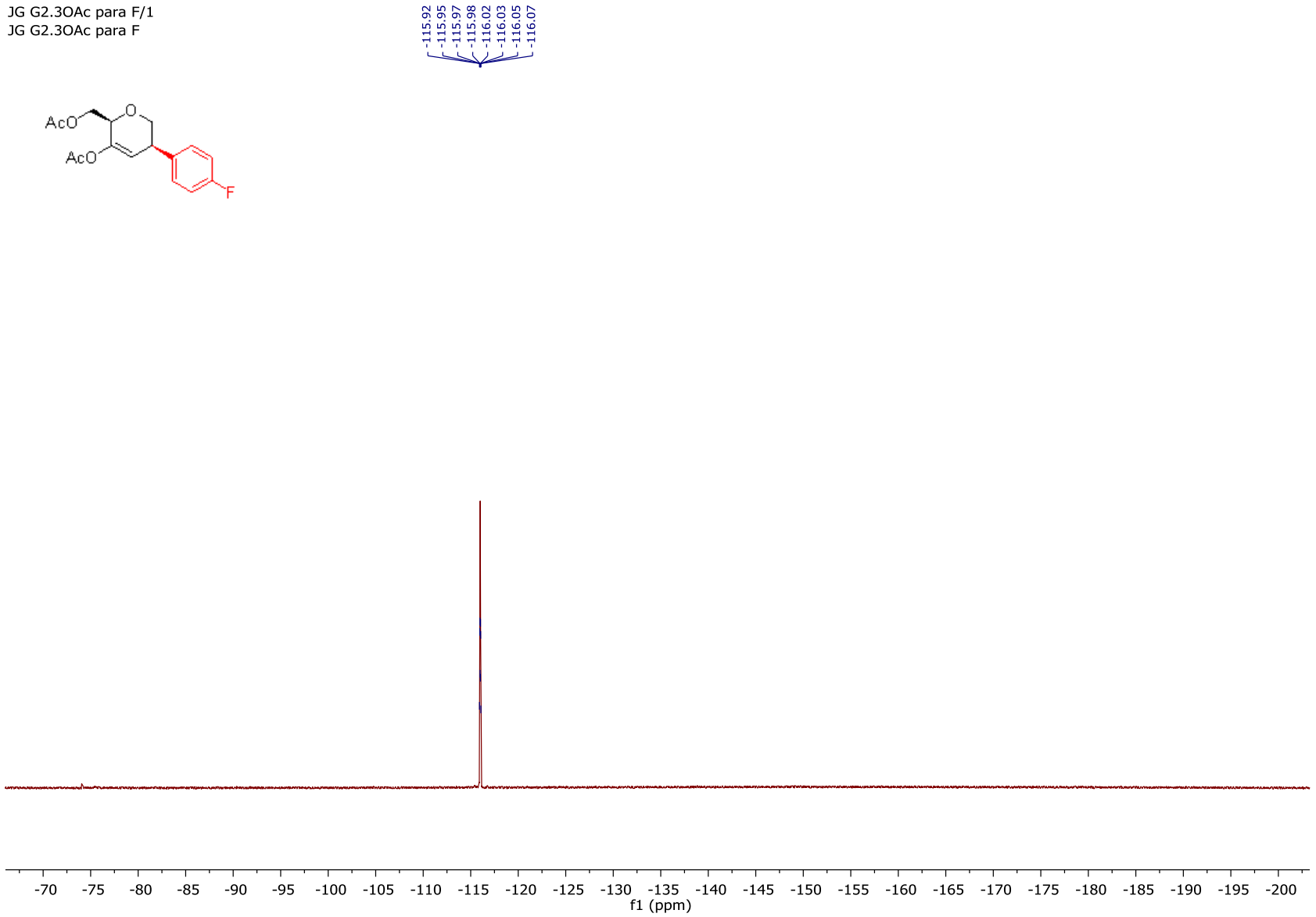
^{13}C NMR spectrum of **3f** (75 MHz, $CDCl_3$)



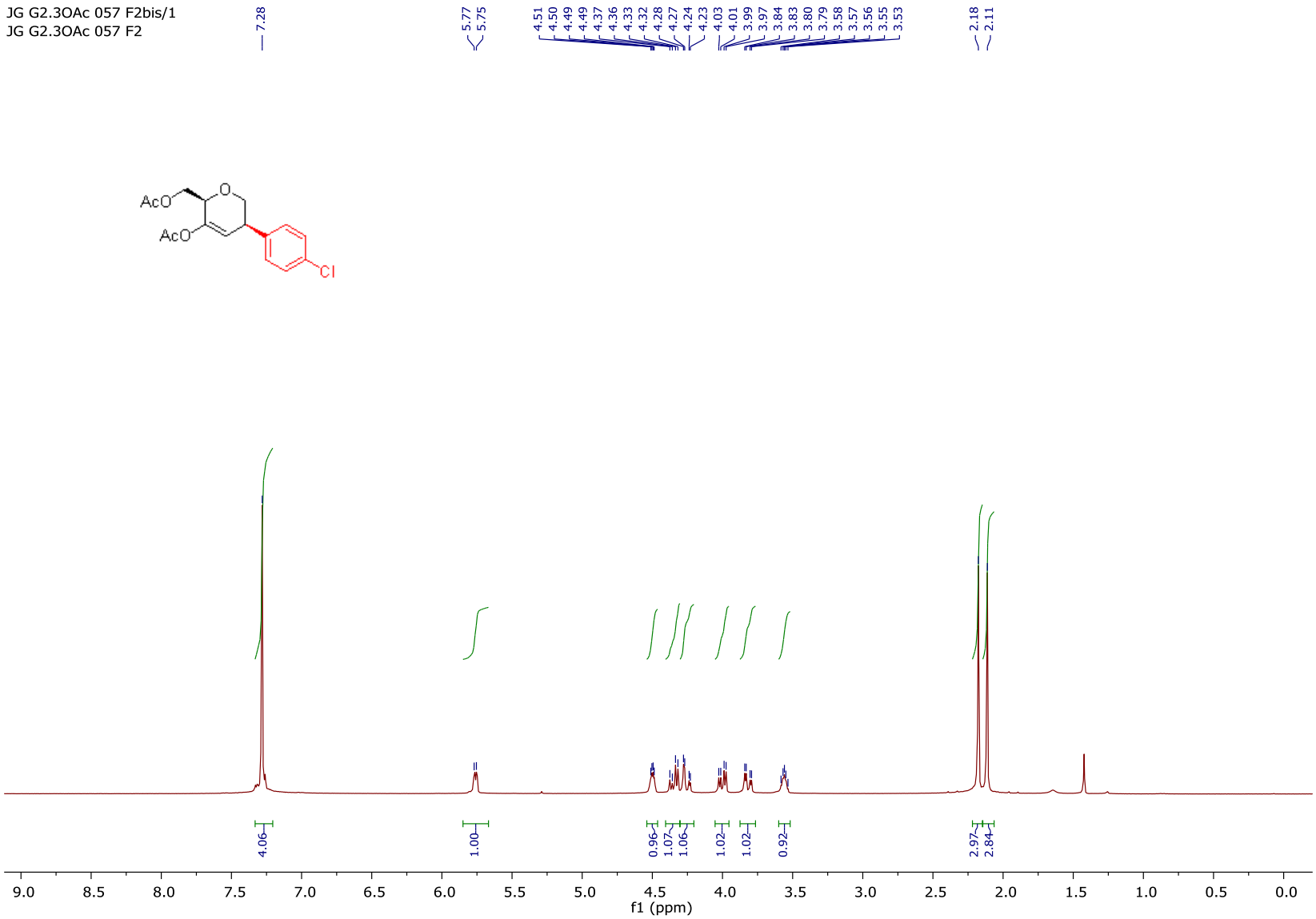
^{1}H NMR spectrum of **3g** (300 MHz, $CDCl_3$)



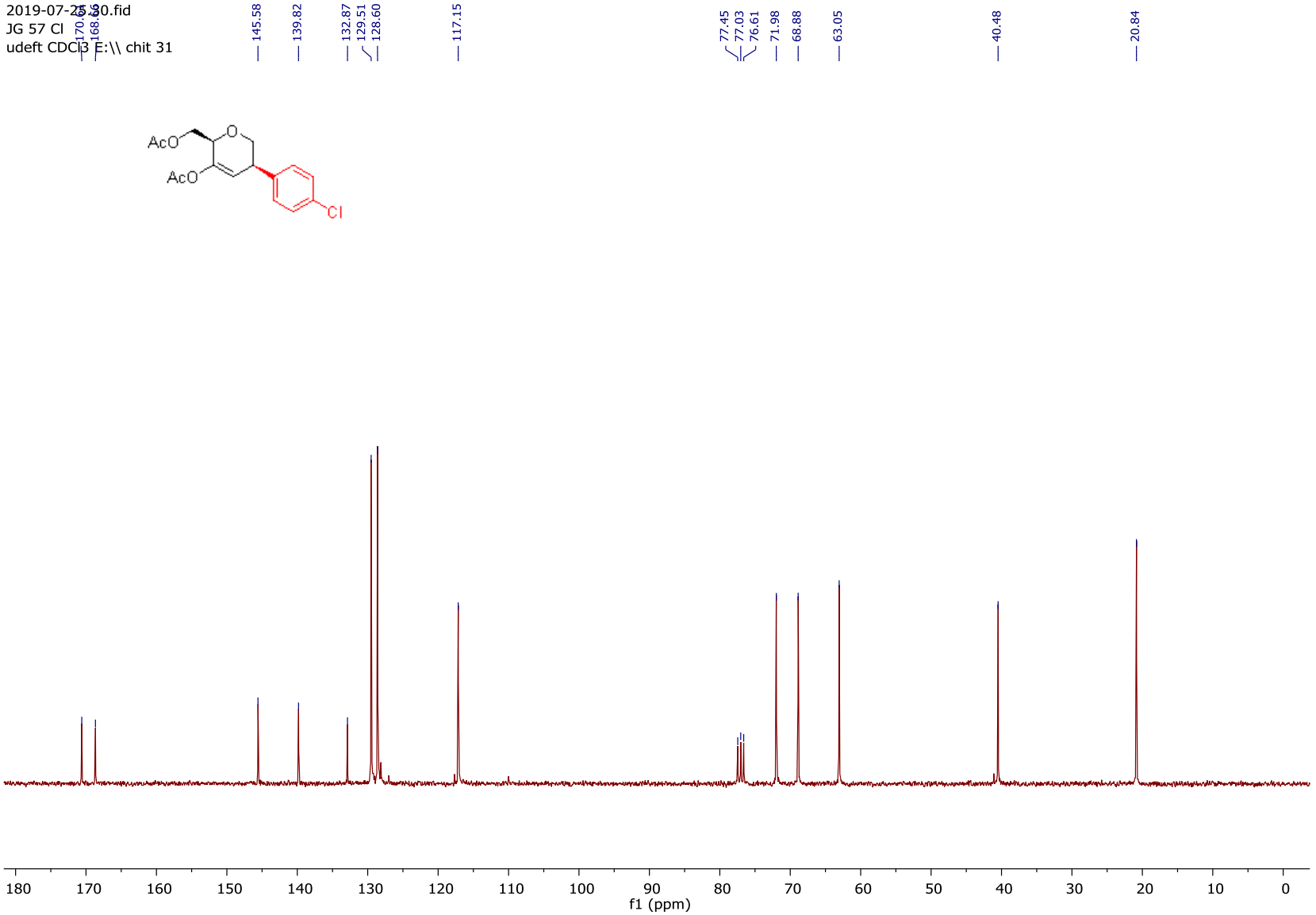
^{13}C NMR spectrum of **3g** (75 MHz, $CDCl_3$)



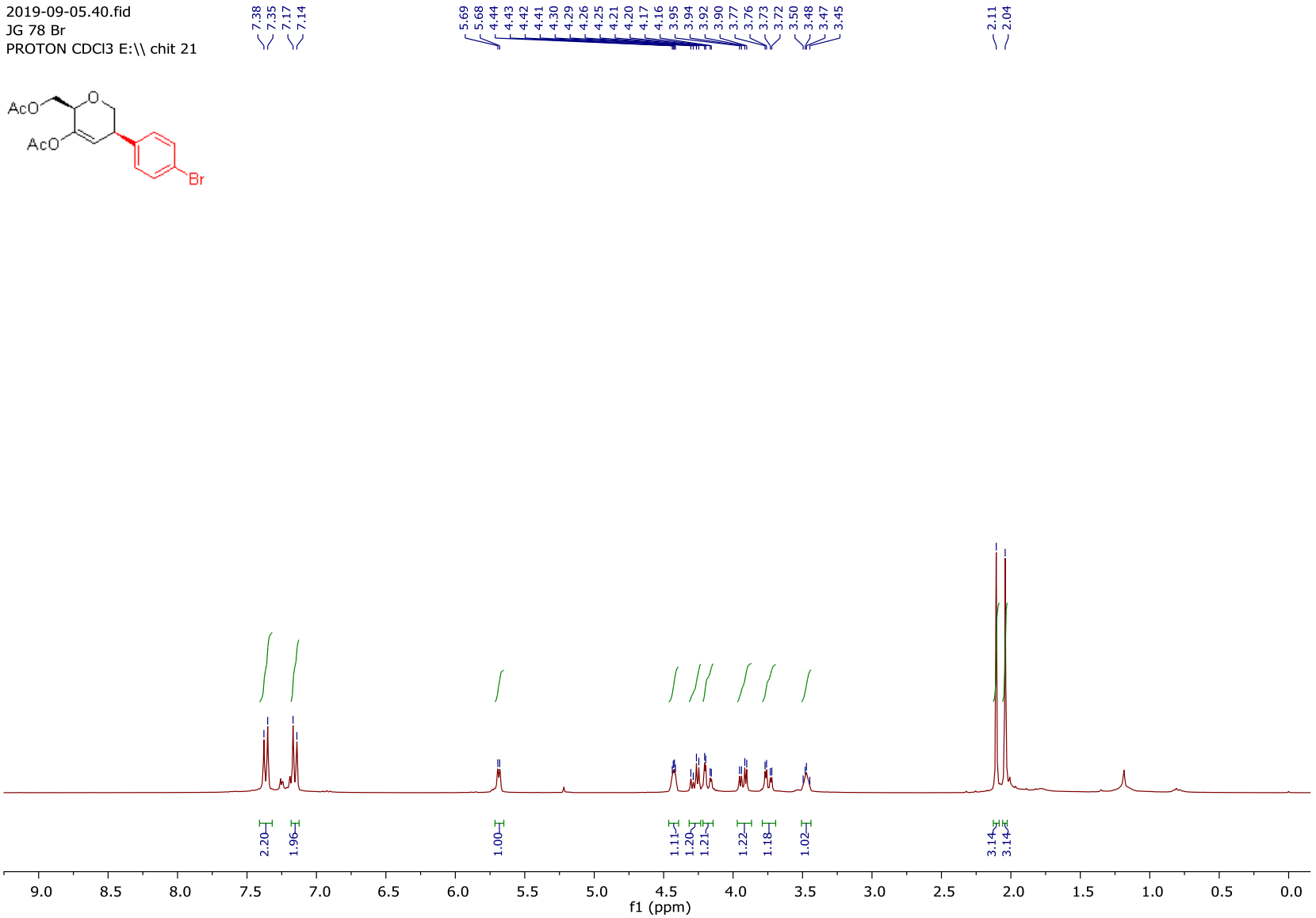
^{19}F NMR spectrum of **3g** (188 MHz, $CDCl_3$



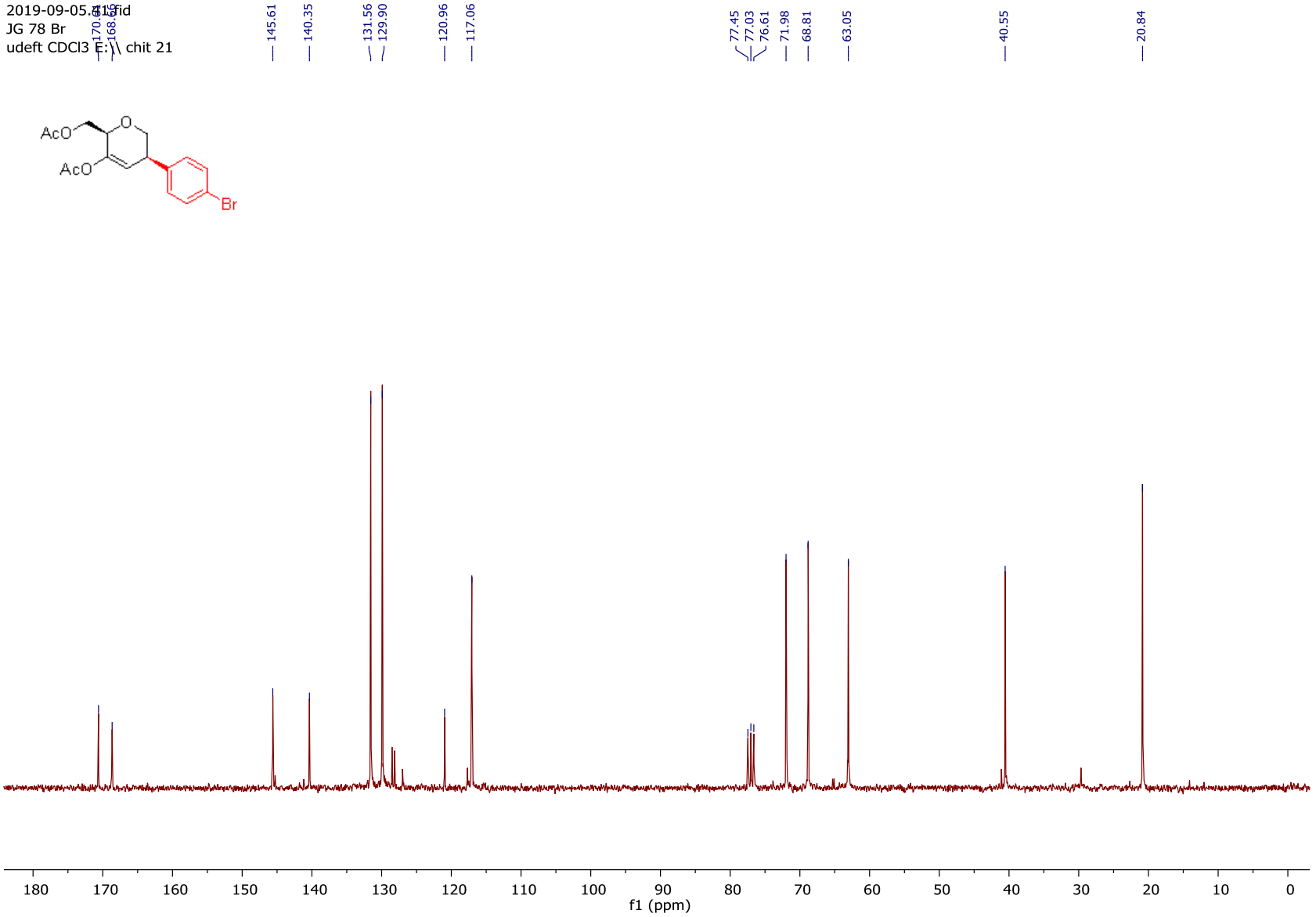
^{1}H NMR spectrum of **3h** (300 MHz, $CDCl_3$)



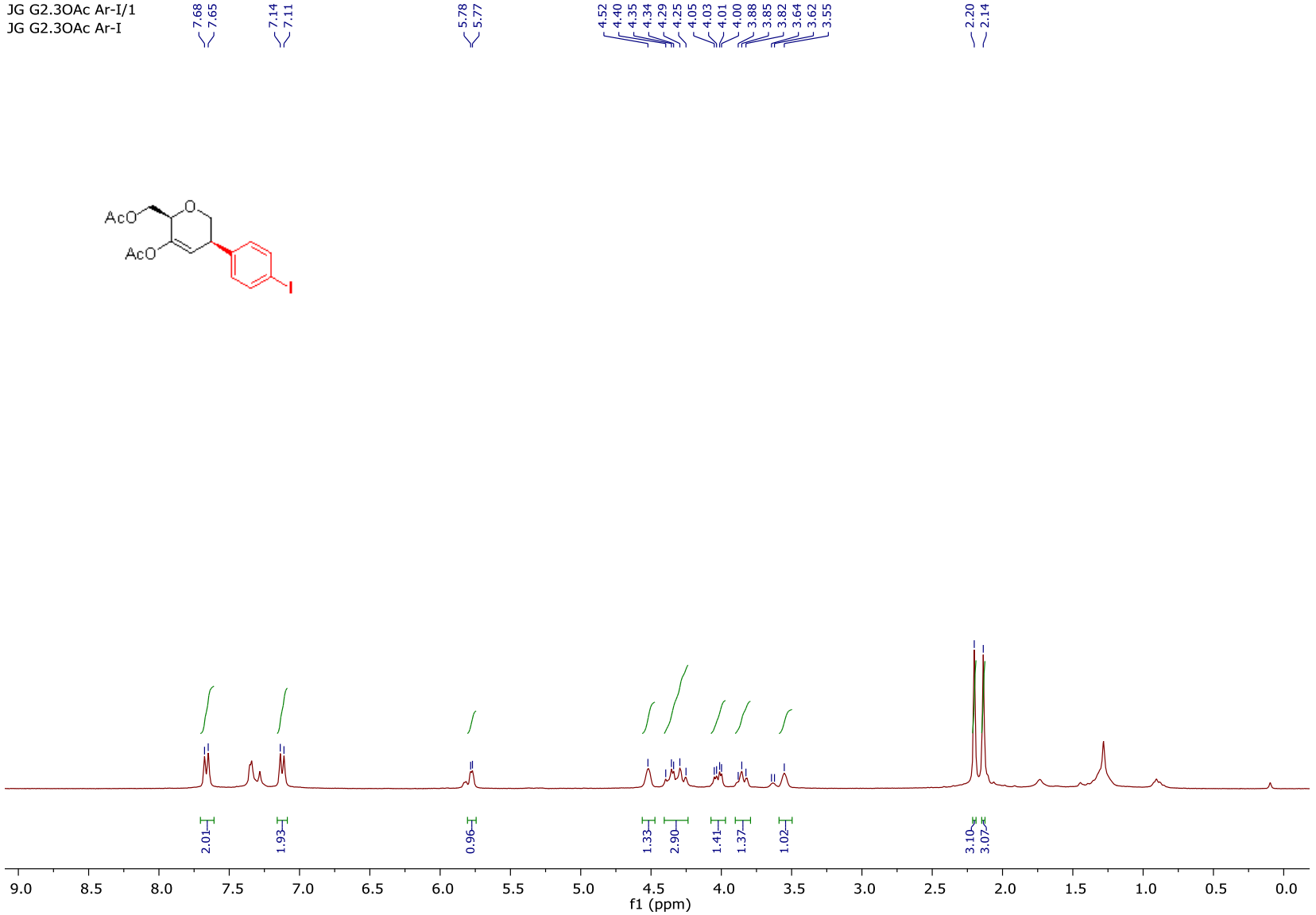
^{13}C NMR spectrum of **3h** (75 MHz, $CDCl_3$)



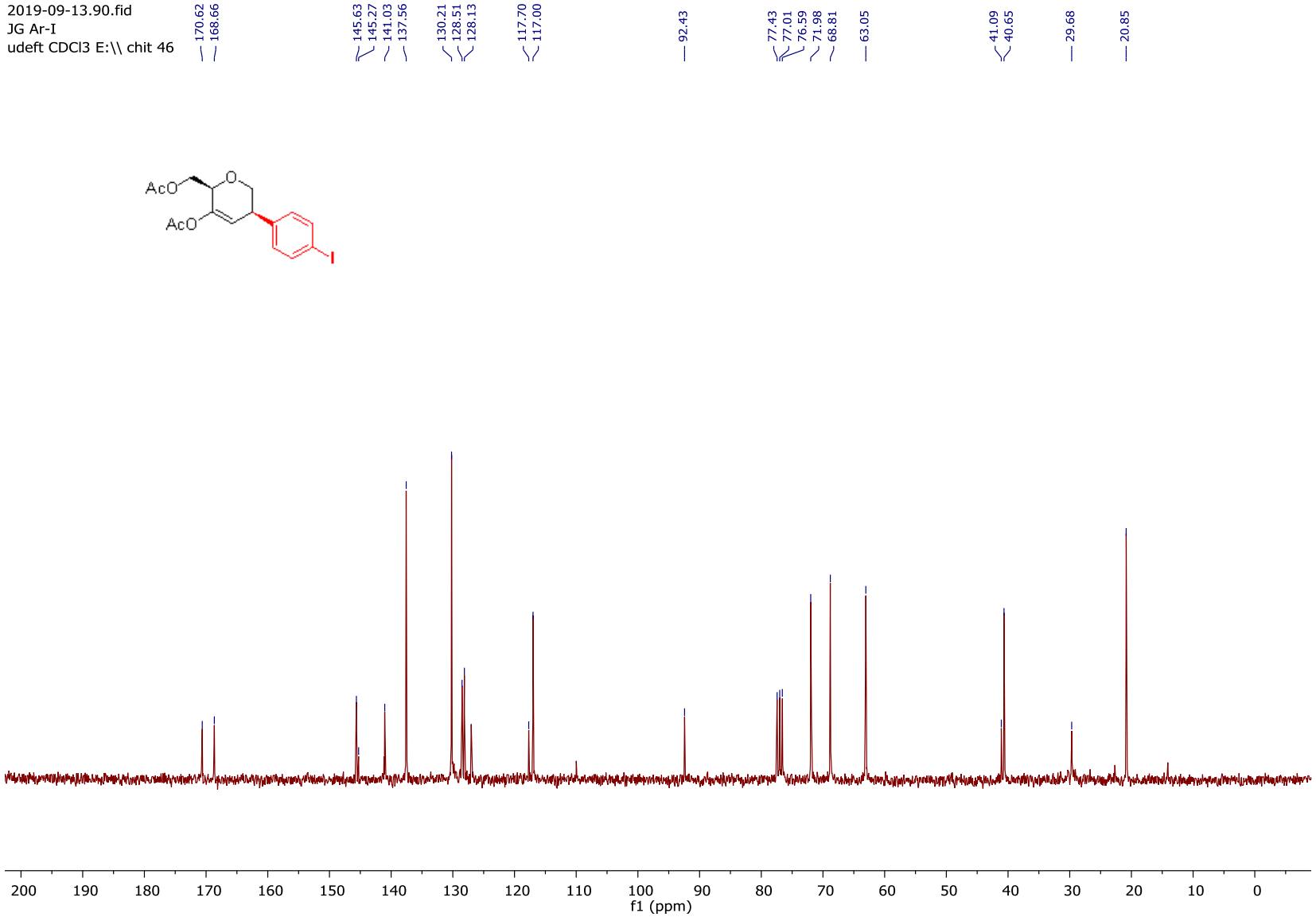
^{1}H NMR spectrum of **3i** (300 MHz, $CDCl_3$)



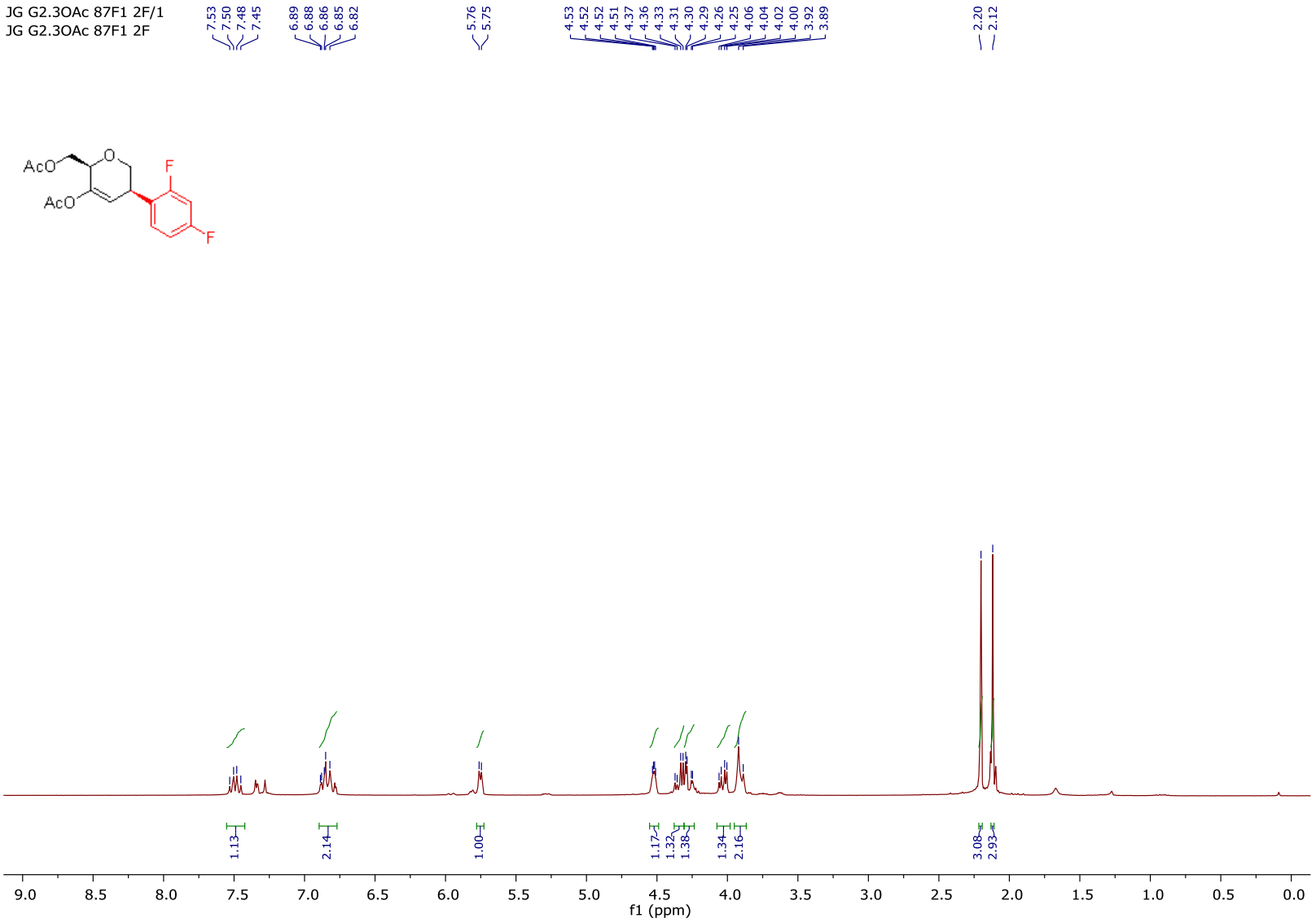
^{13}C NMR spectrum of **3i** (75 MHz, $CDCl_3$)



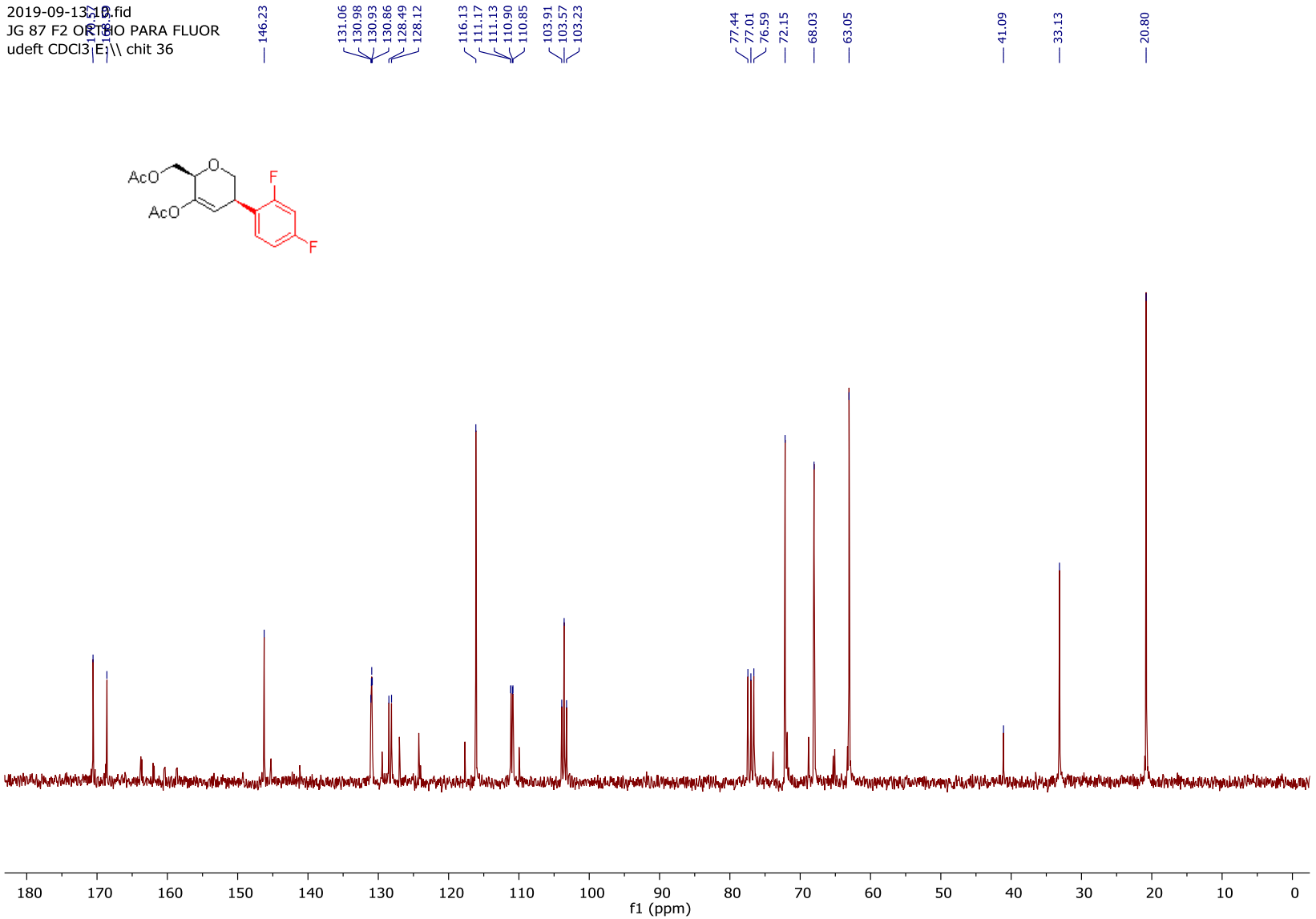
^{1}H NMR spectrum of **3j** (300 MHz, $CDCl_3$)



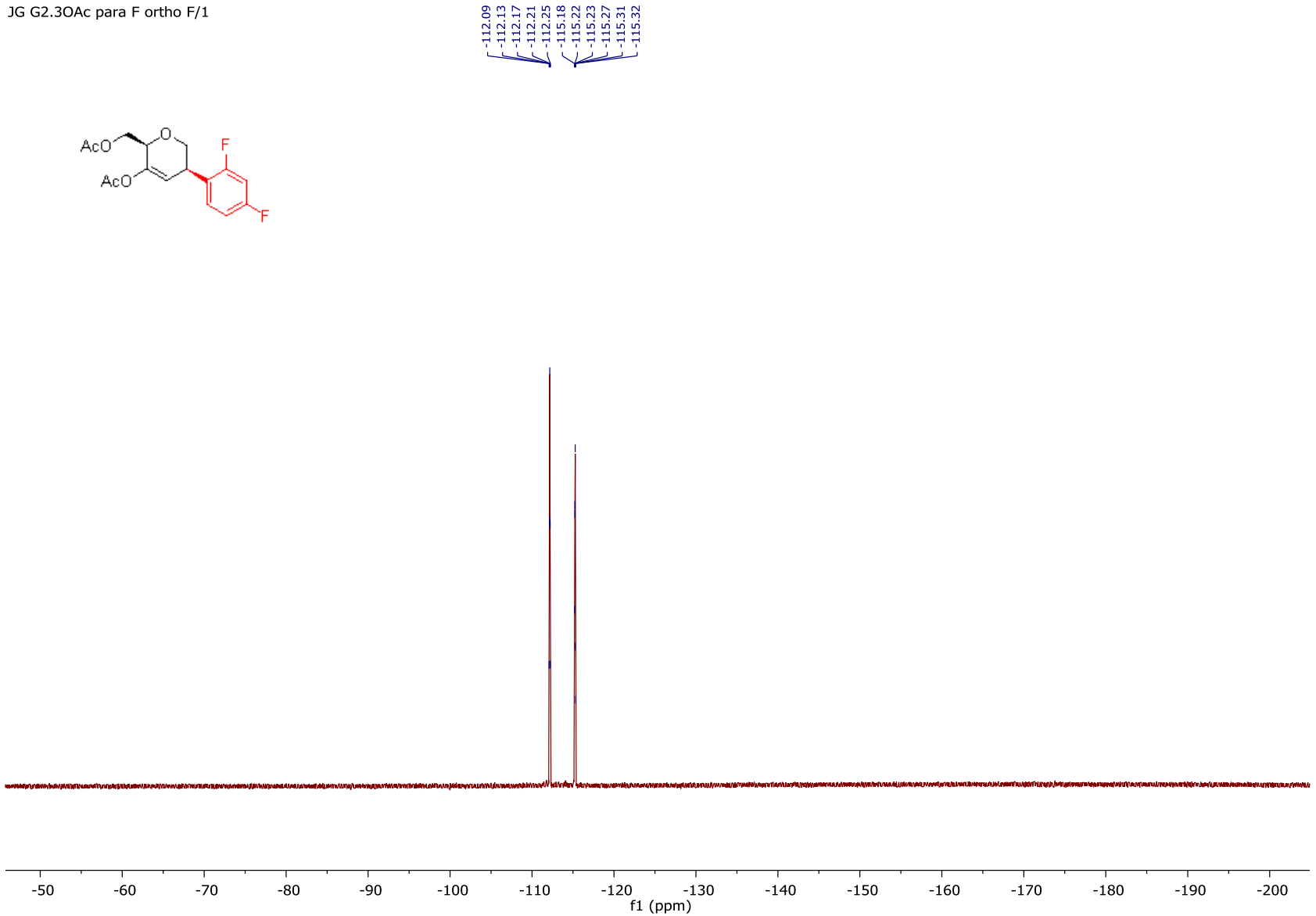
^{13}C NMR spectrum of **3j** (75 MHz, $CDCl_3$)



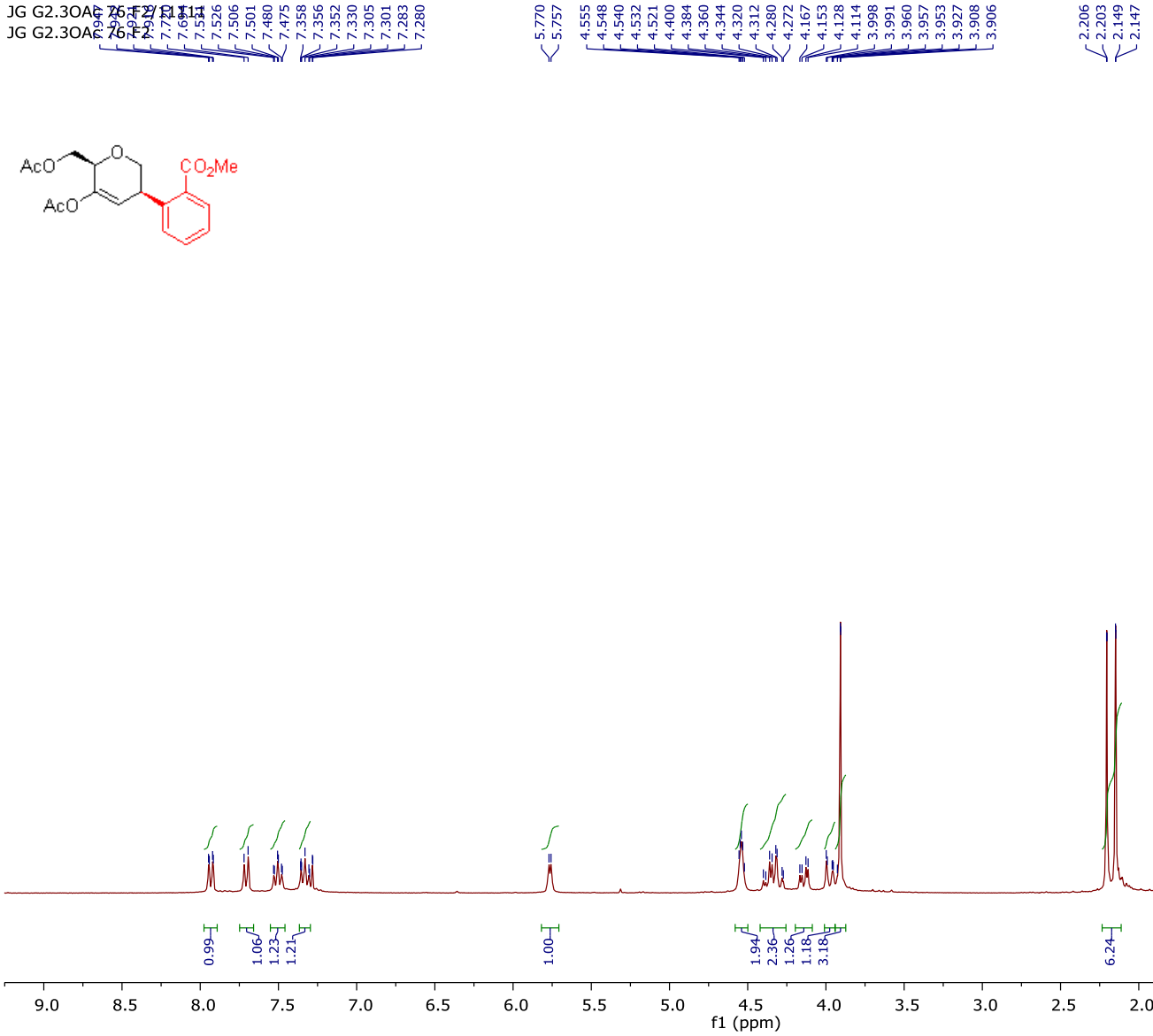
^{1}H NMR spectrum of **3k** (300 MHz, $CDCl_3$)



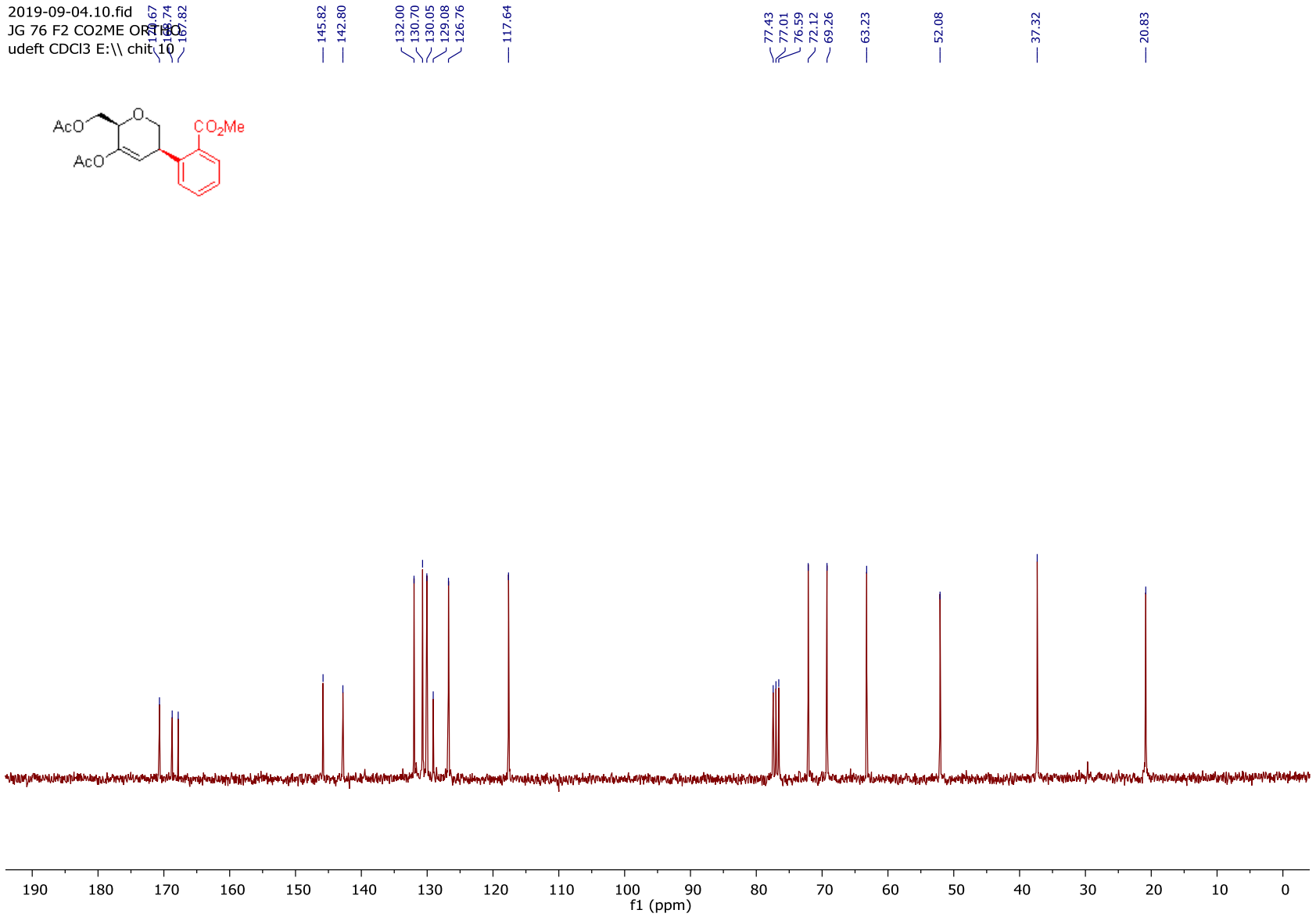
^{13}C NMR spectrum of **3k** (75 MHz, $CDCl_3$)



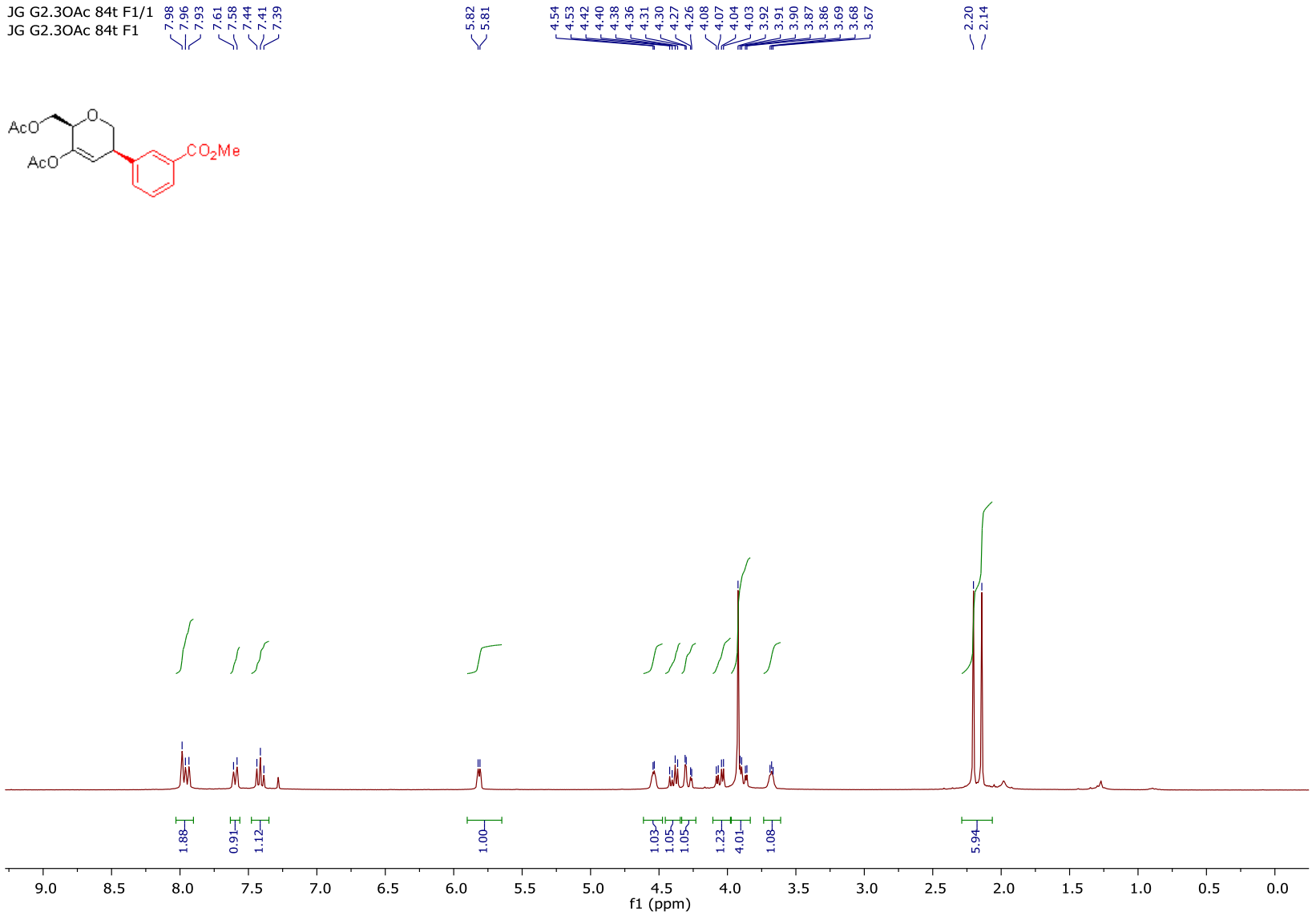
^{19}F NMR spectrum of **3k** (188 MHz, $CDCl_3$)



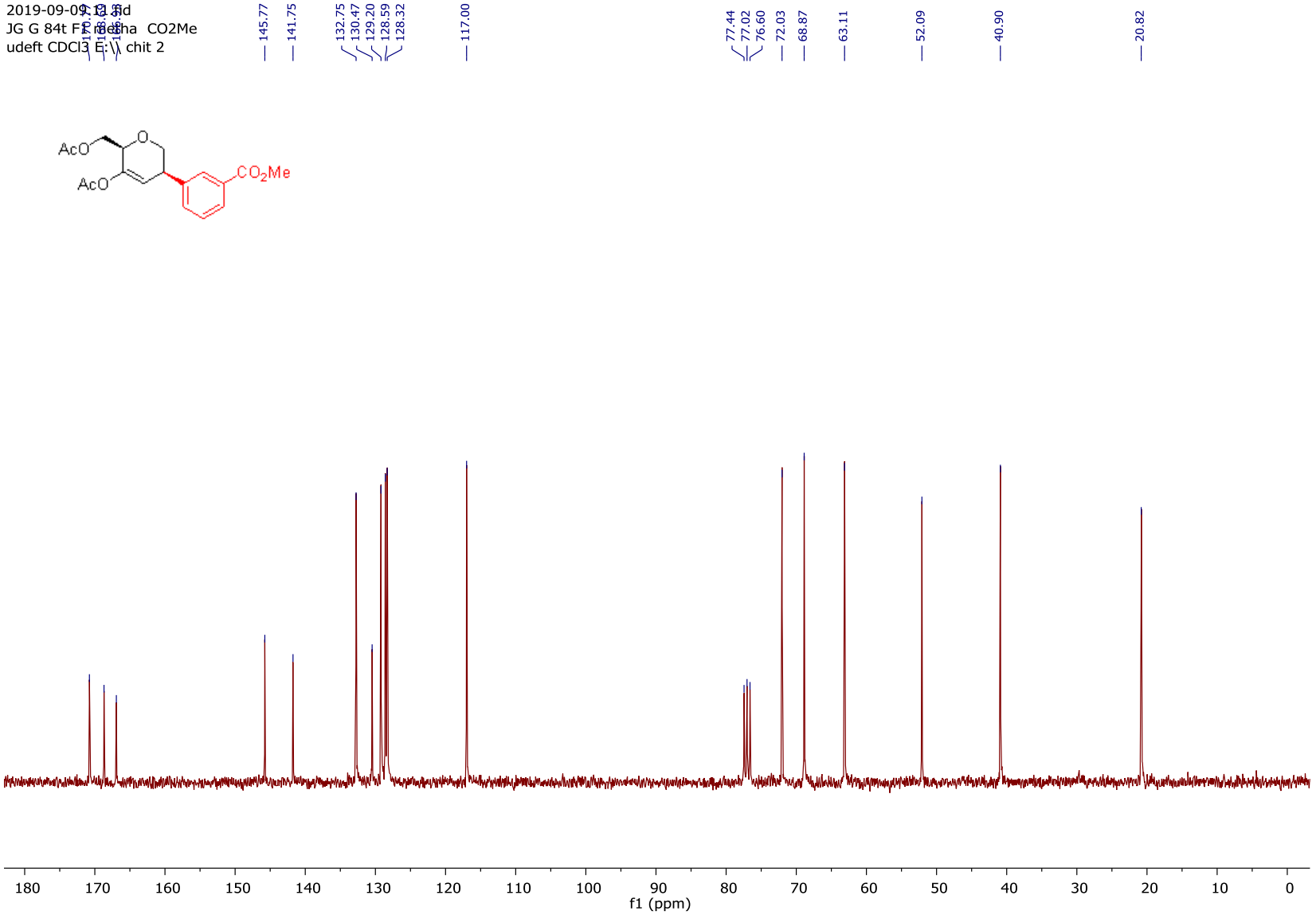
^{1}H NMR spectrum of **3l** (300 MHz, $CDCl_3$)



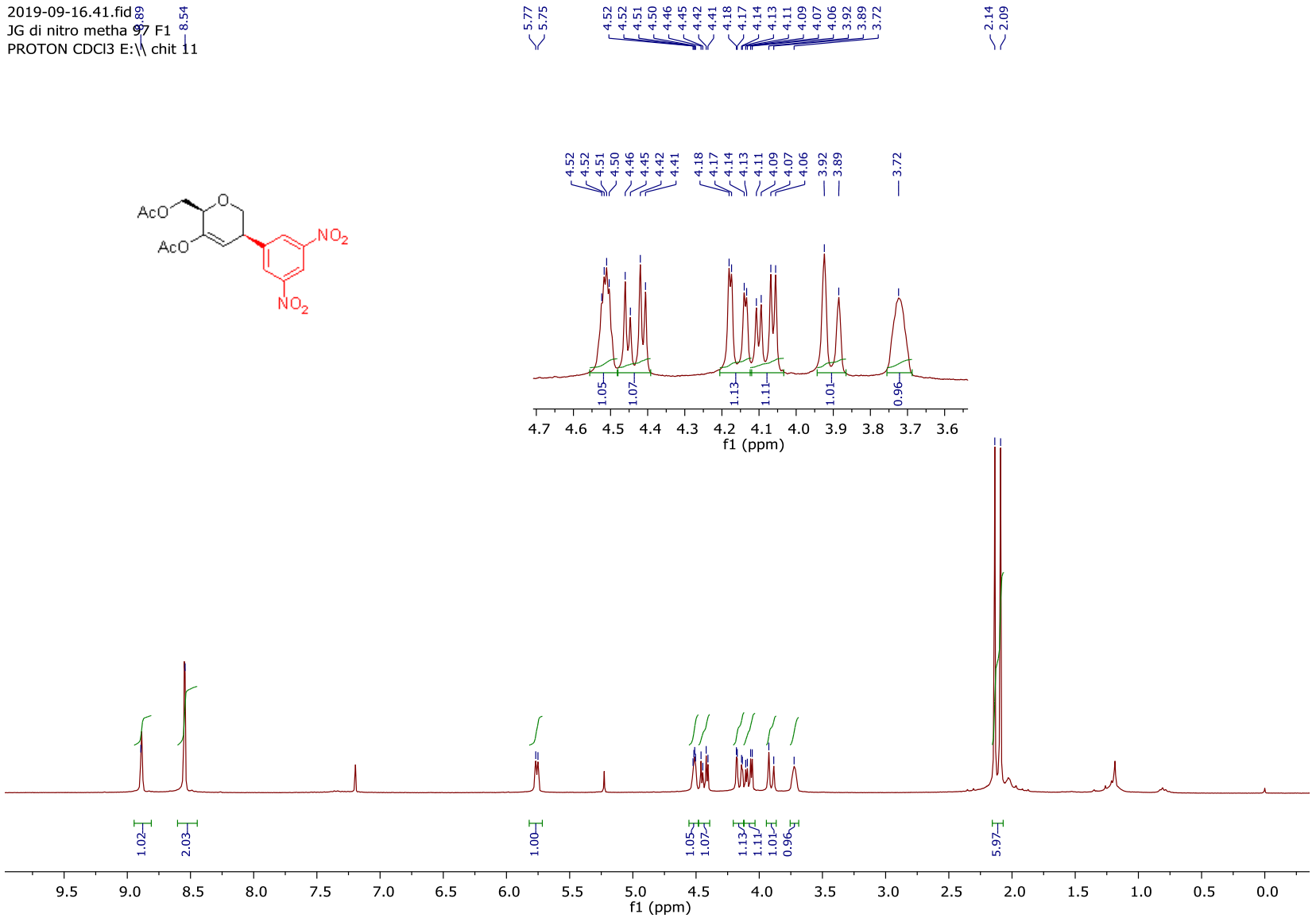
^{13}C NMR spectrum of **3l** (75 MHz, $CDCl_3$)



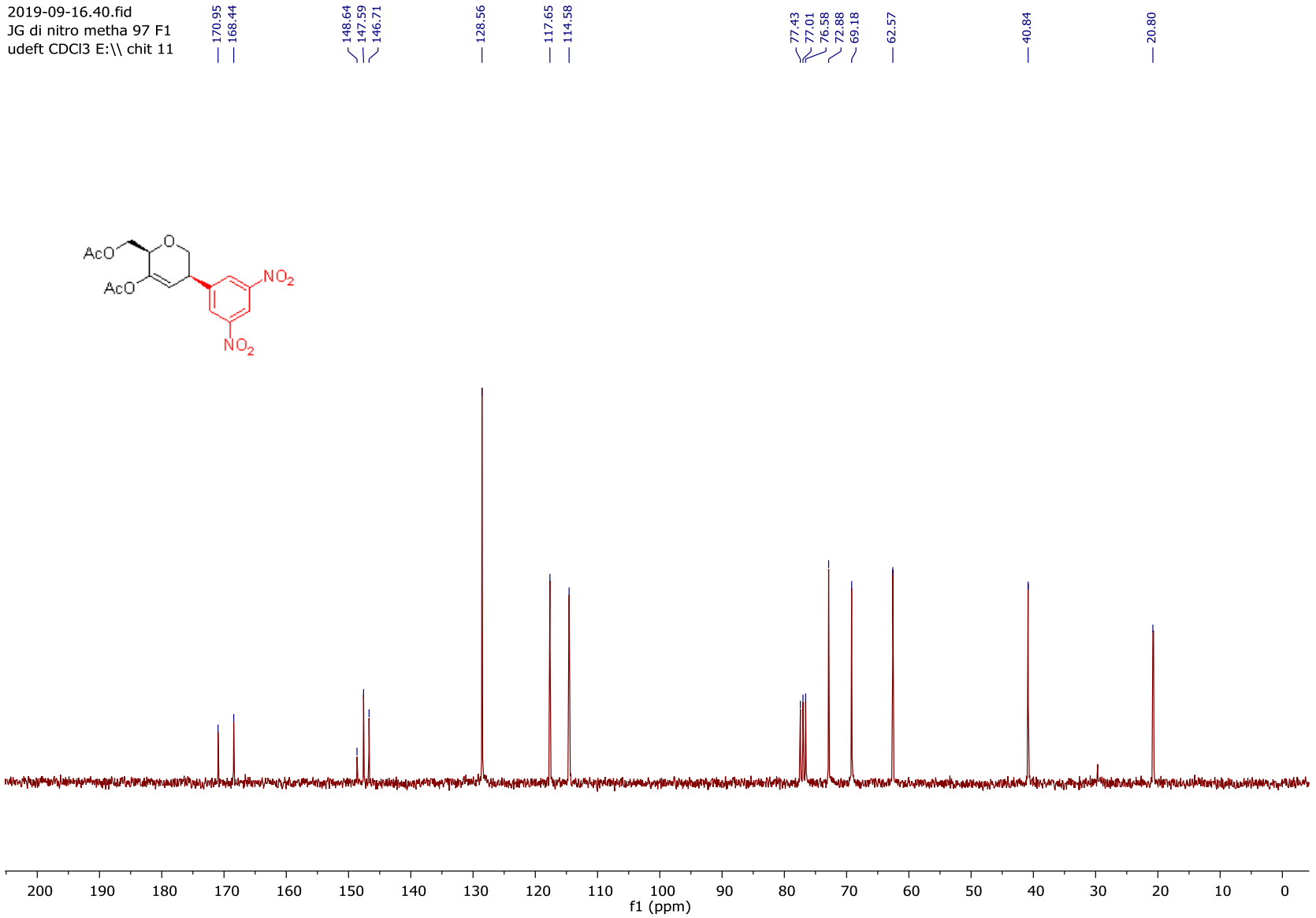
^{1}H NMR spectrum of **3m** (300 MHz, $CDCl_3$)



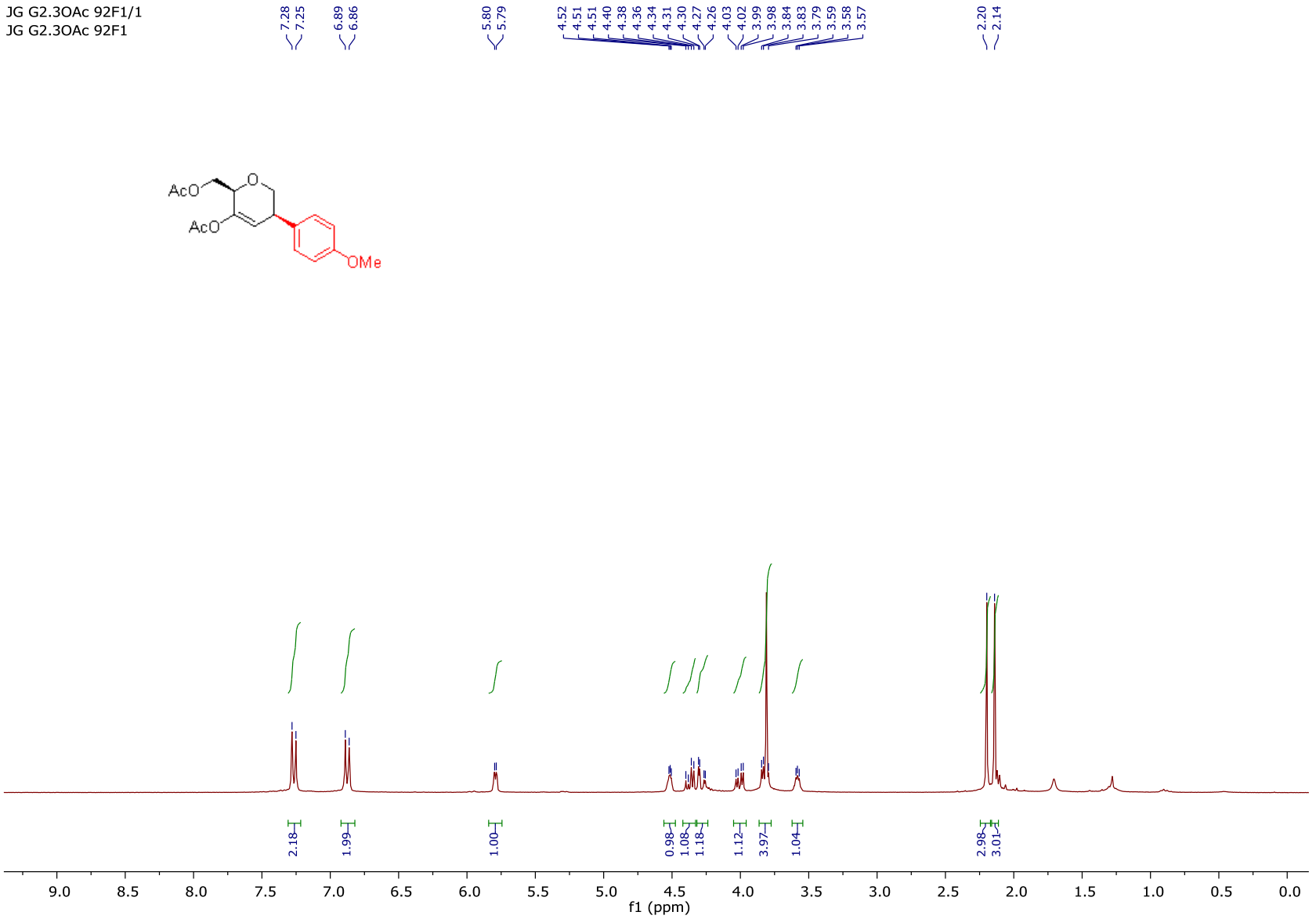
^{13}C NMR spectrum of **3m** (75 MHz, $CDCl_3$)



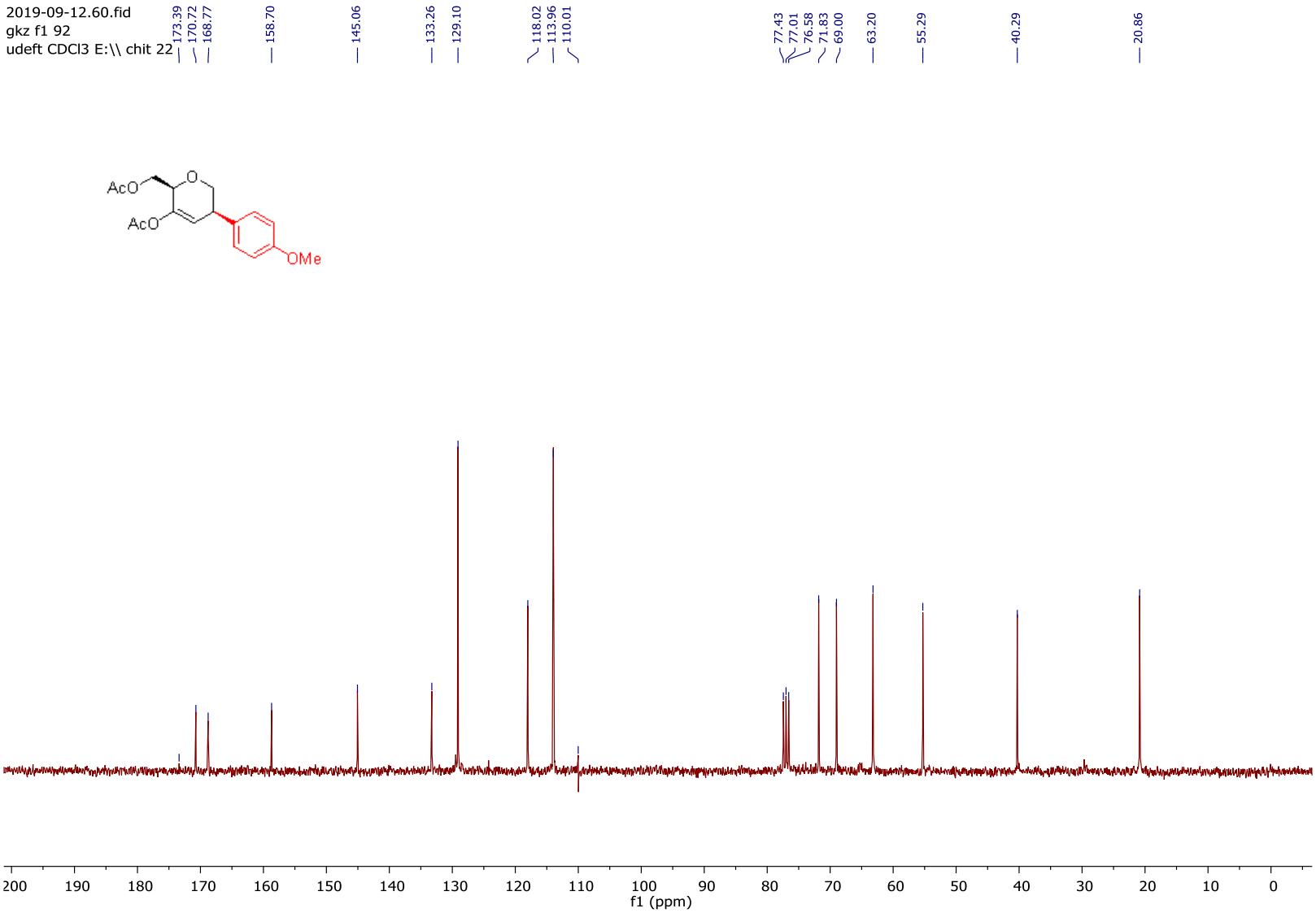
^{1}H NMR spectrum of **3n** (300 MHz, $CDCl_3$)



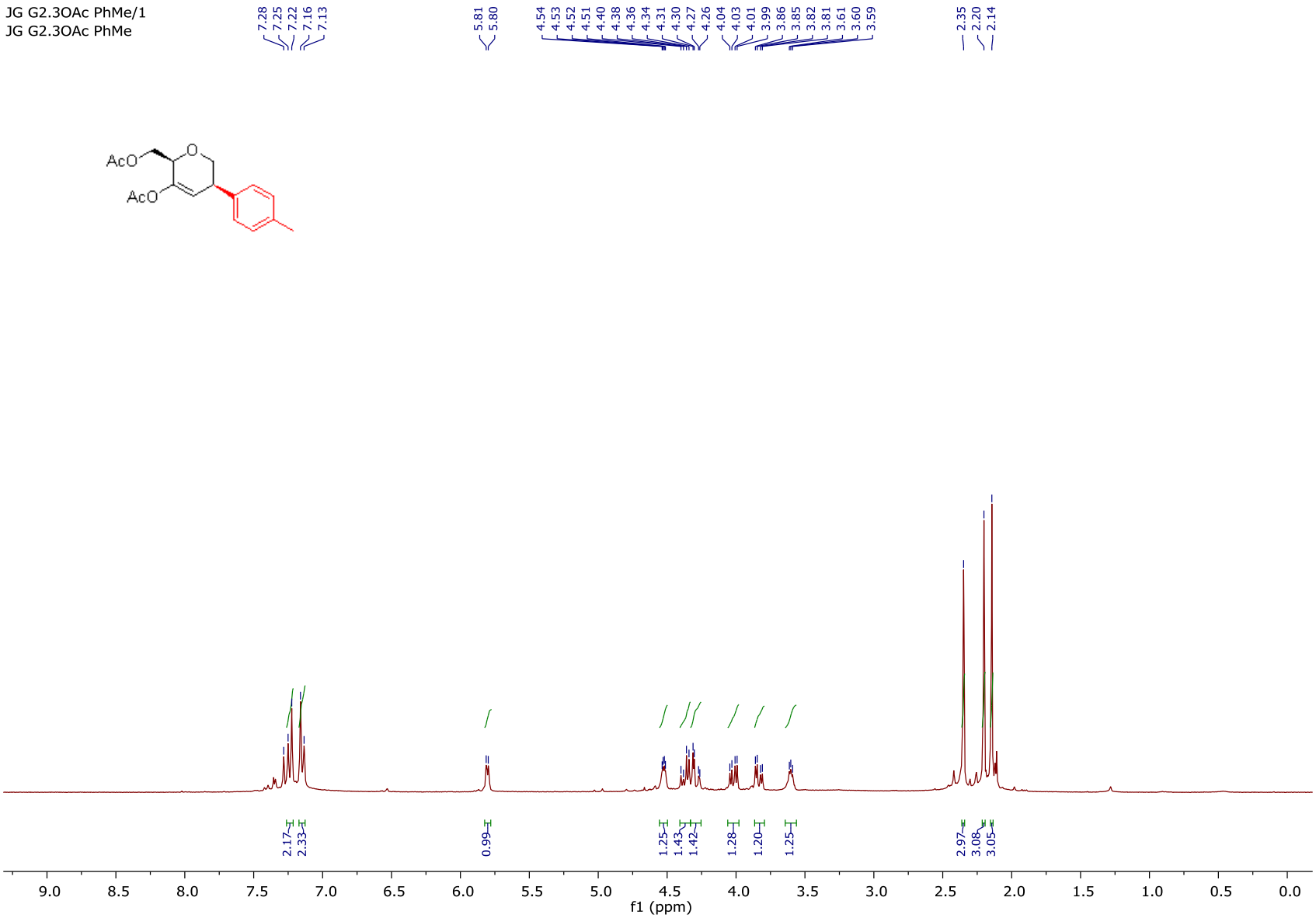
^{13}C NMR spectrum of **3n** (75 MHz, $CDCl_3$)



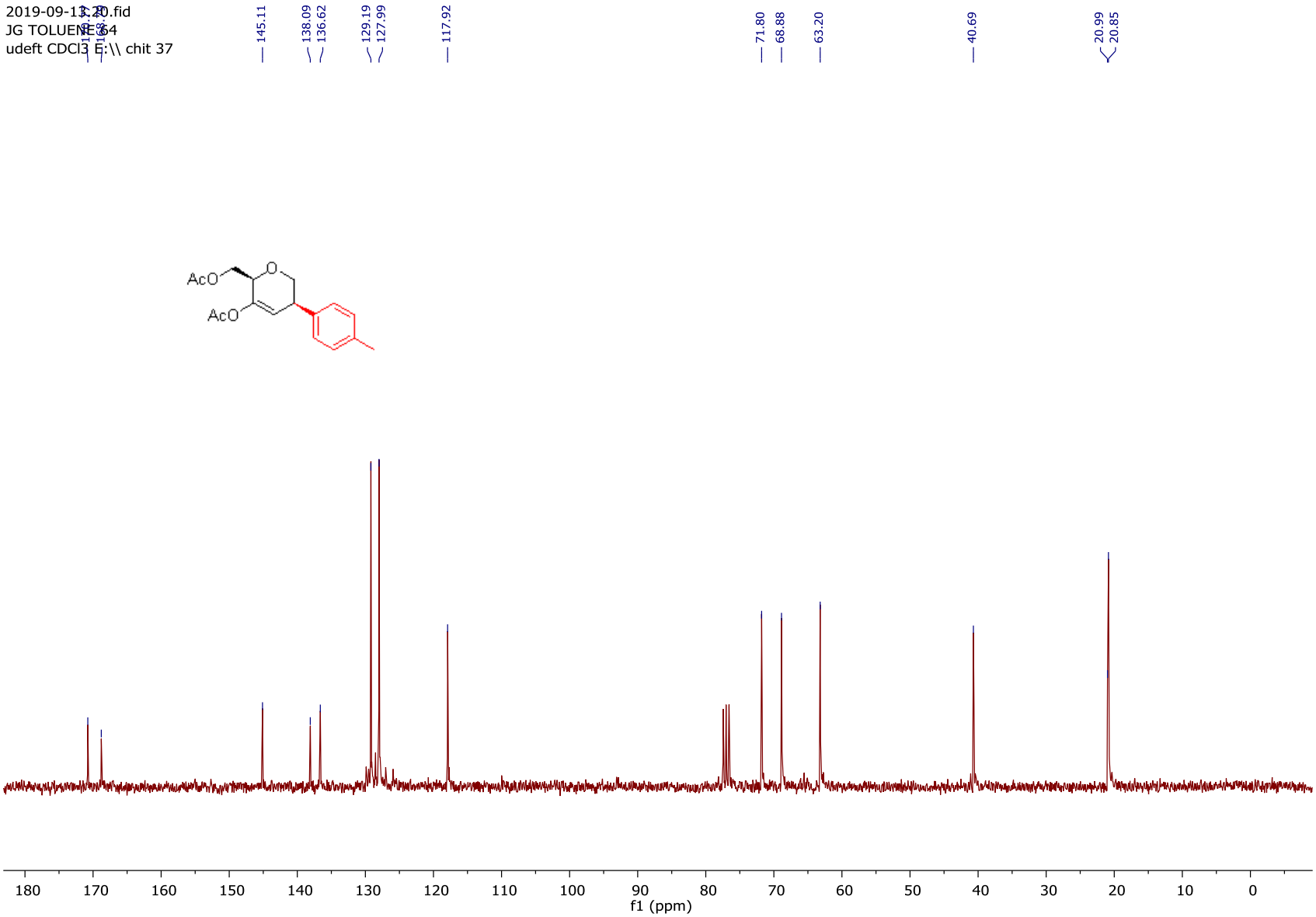
^{1}H NMR spectrum of **3o** (300 MHz, $CDCl_3$)



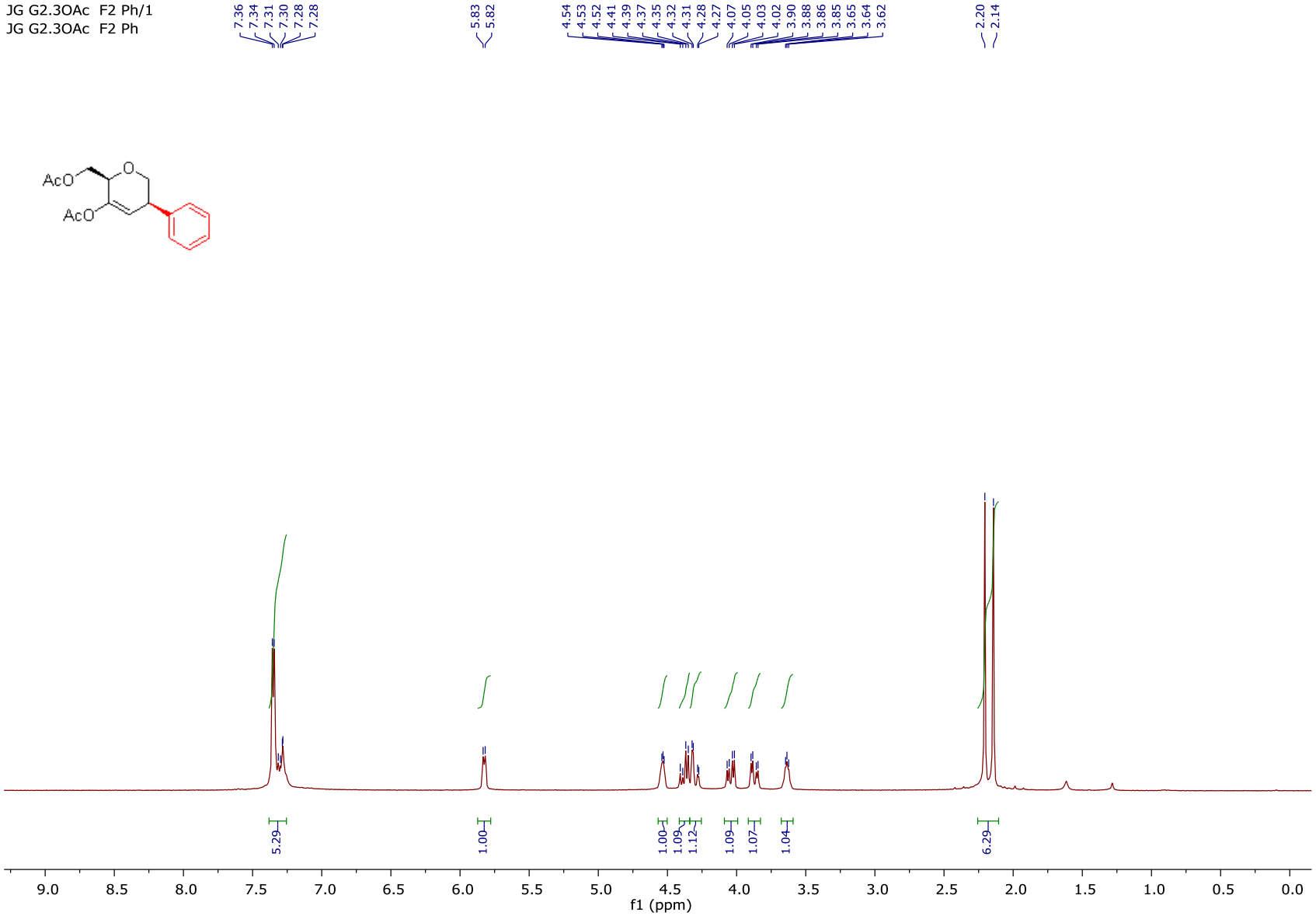
^{13}C NMR spectrum of **3o** (75 MHz, $CDCl_3$)



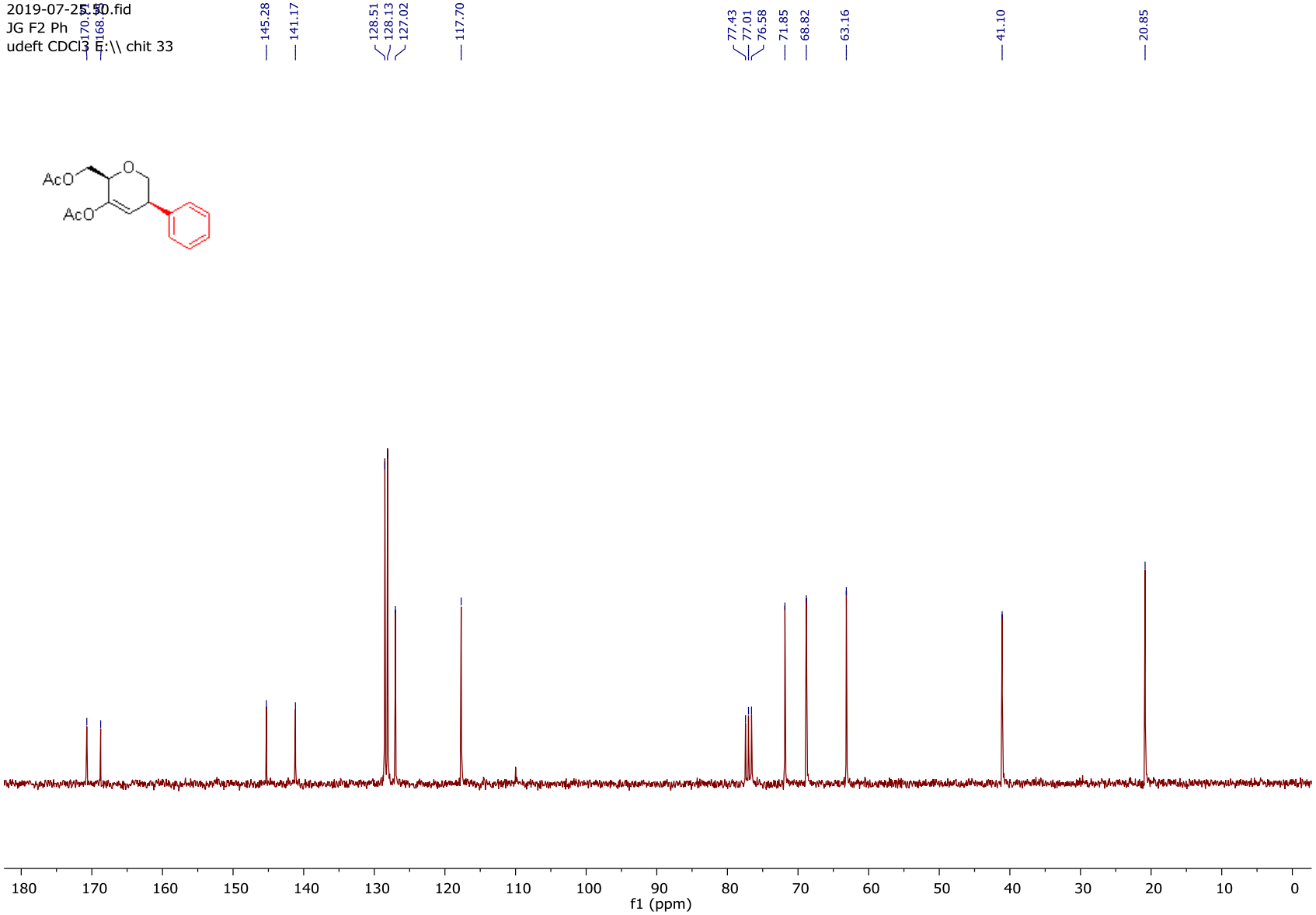
^{1}H NMR spectrum of **3p** (300 MHz, $CDCl_3$)



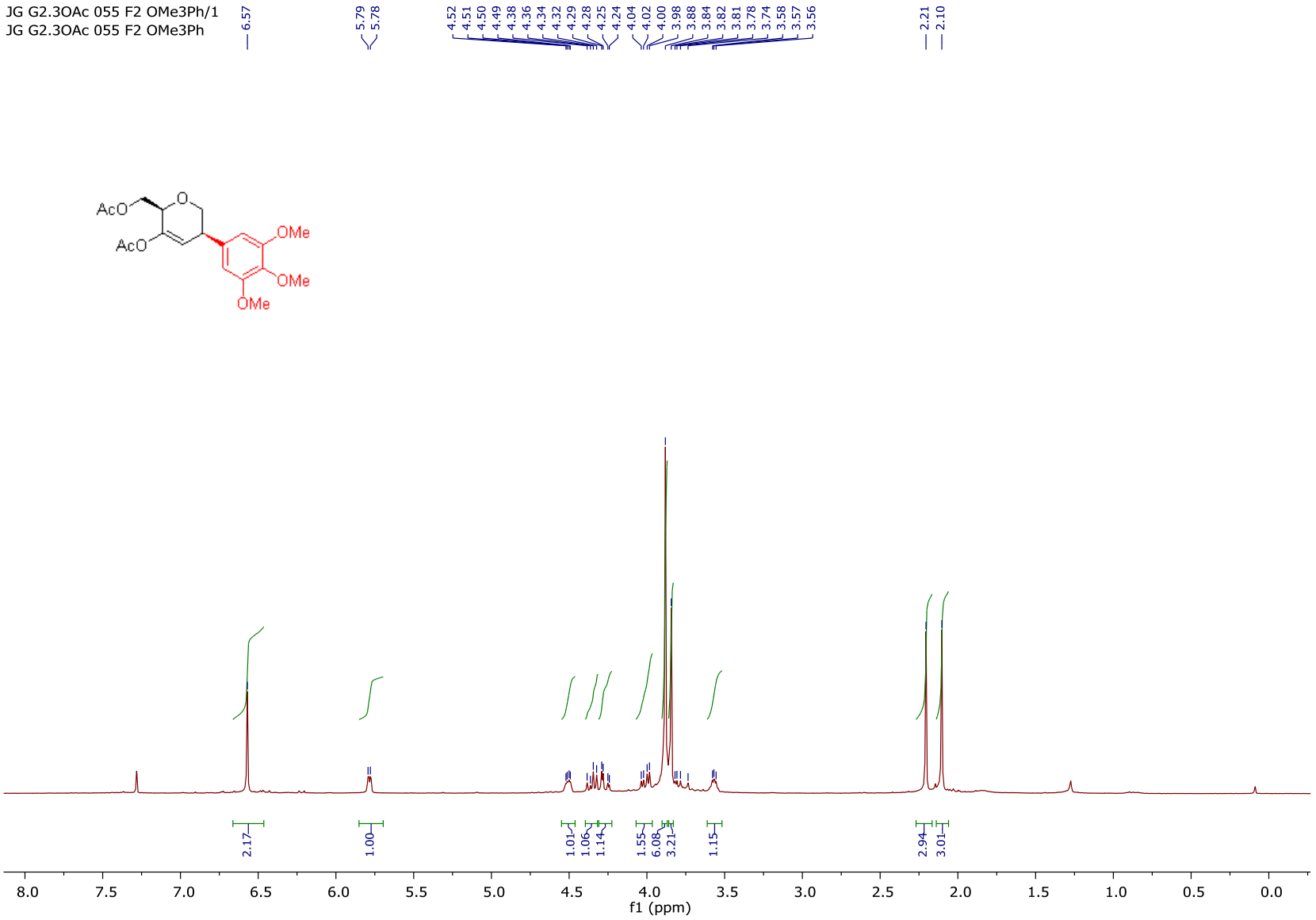
^{13}C NMR spectrum of **3p** (75 MHz, $CDCl_3$)



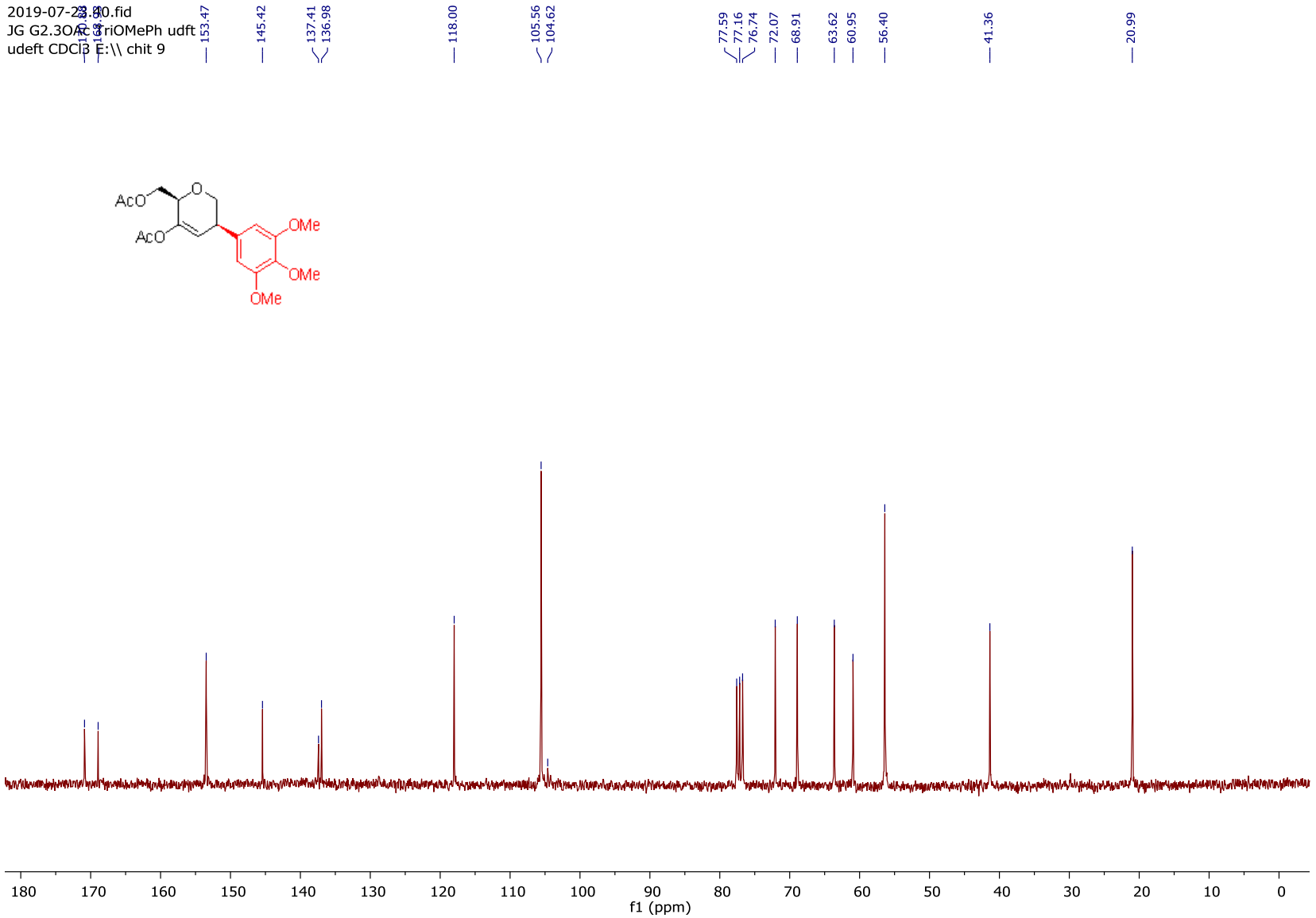
^{1}H NMR spectrum of **3q** (300 MHz, $CDCl_3$)



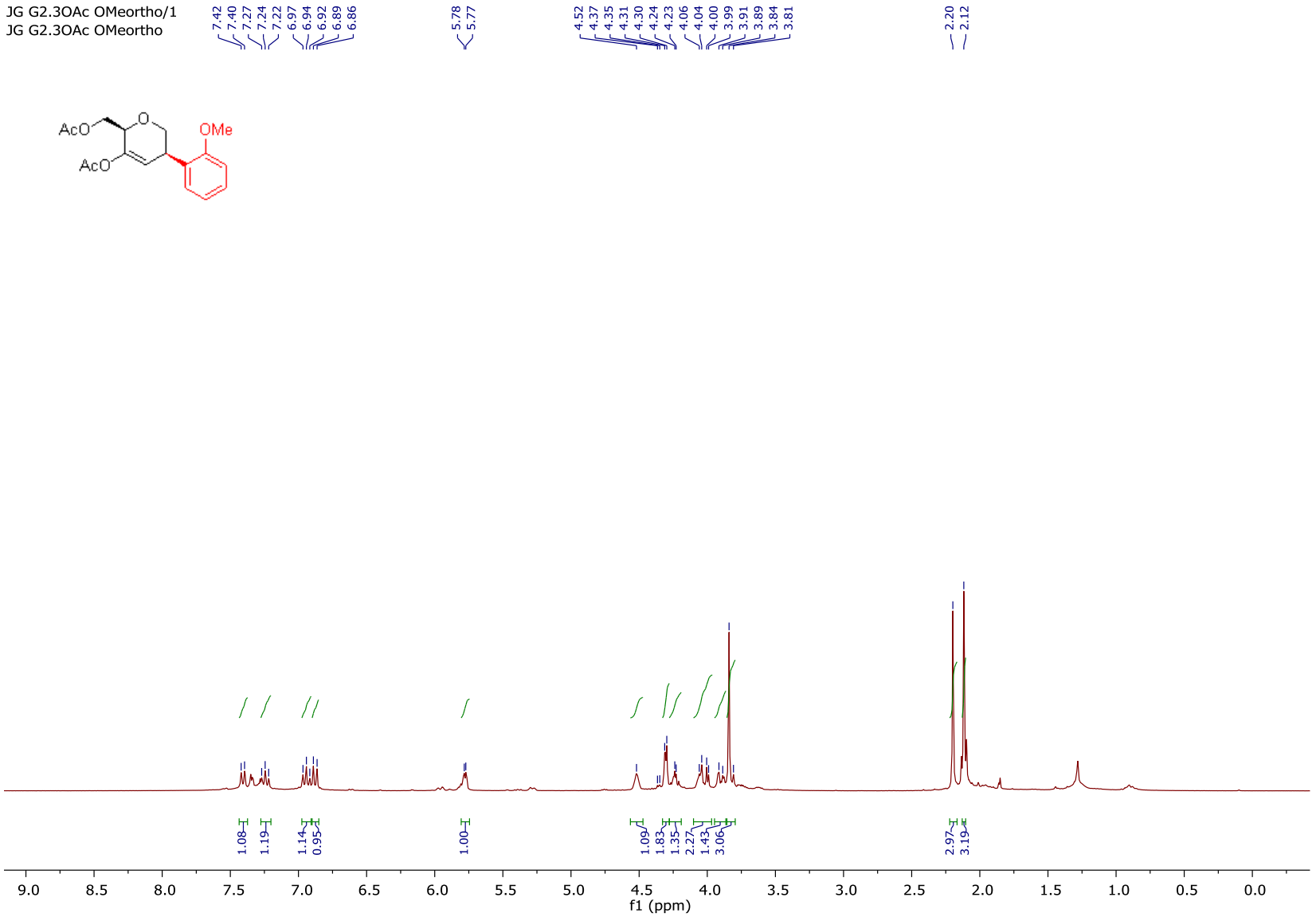
^{13}C NMR spectrum of **3q** (75 MHz, $CDCl_3$)



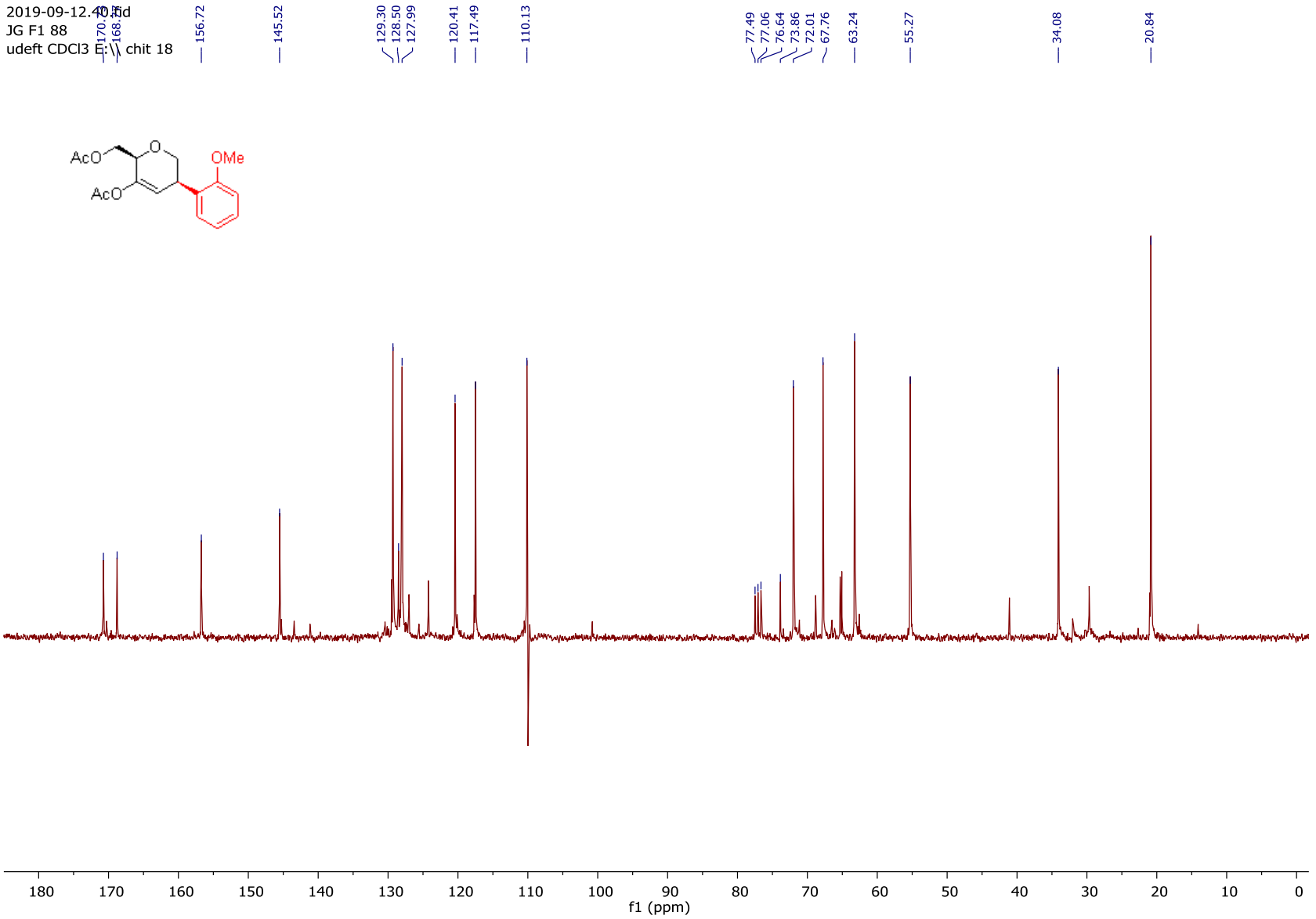
^{1}H NMR spectrum of **3r** (300 MHz, $CDCl_3$)



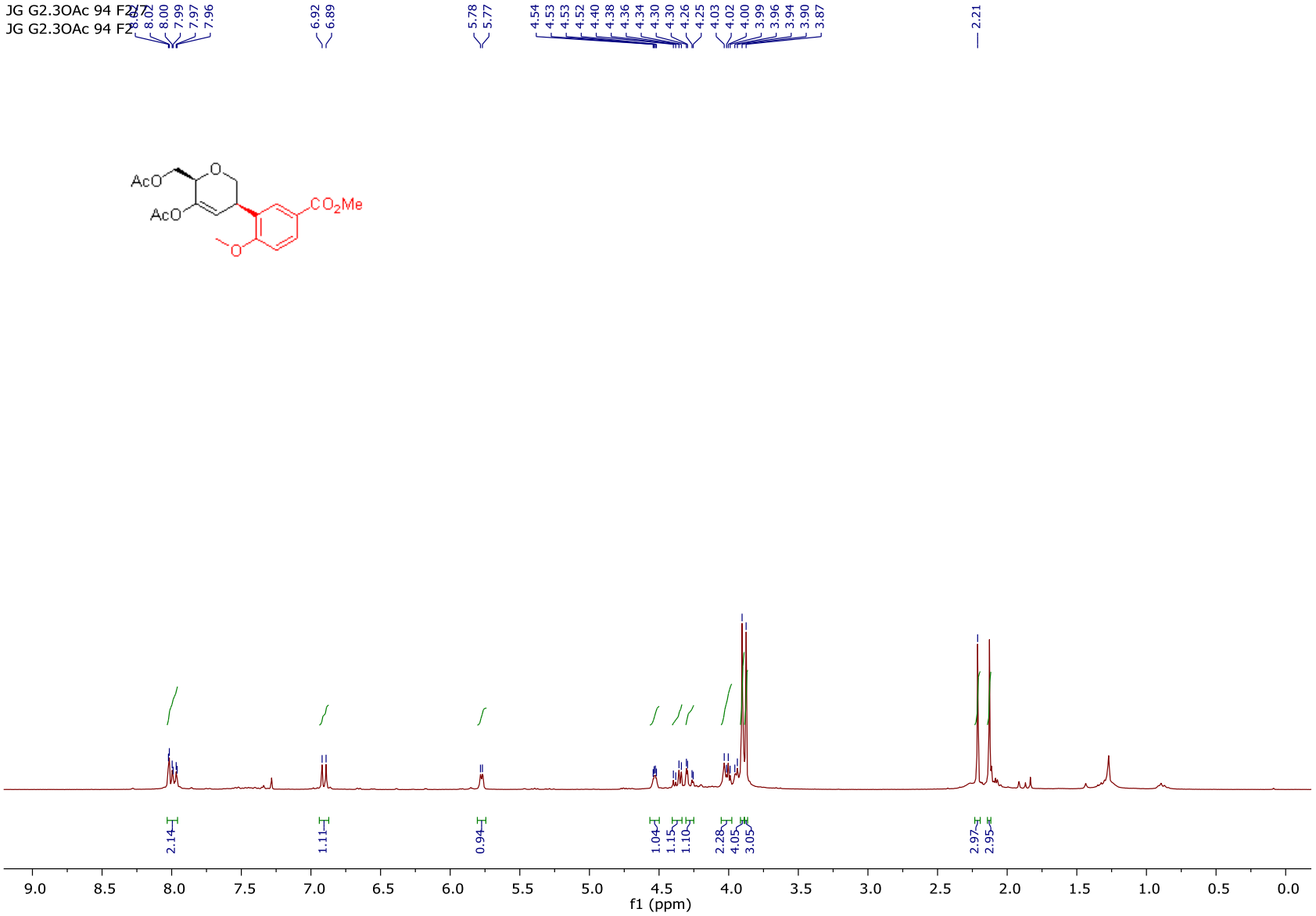
^{13}C NMR spectrum of **3r** (75 MHz, $CDCl_3$)



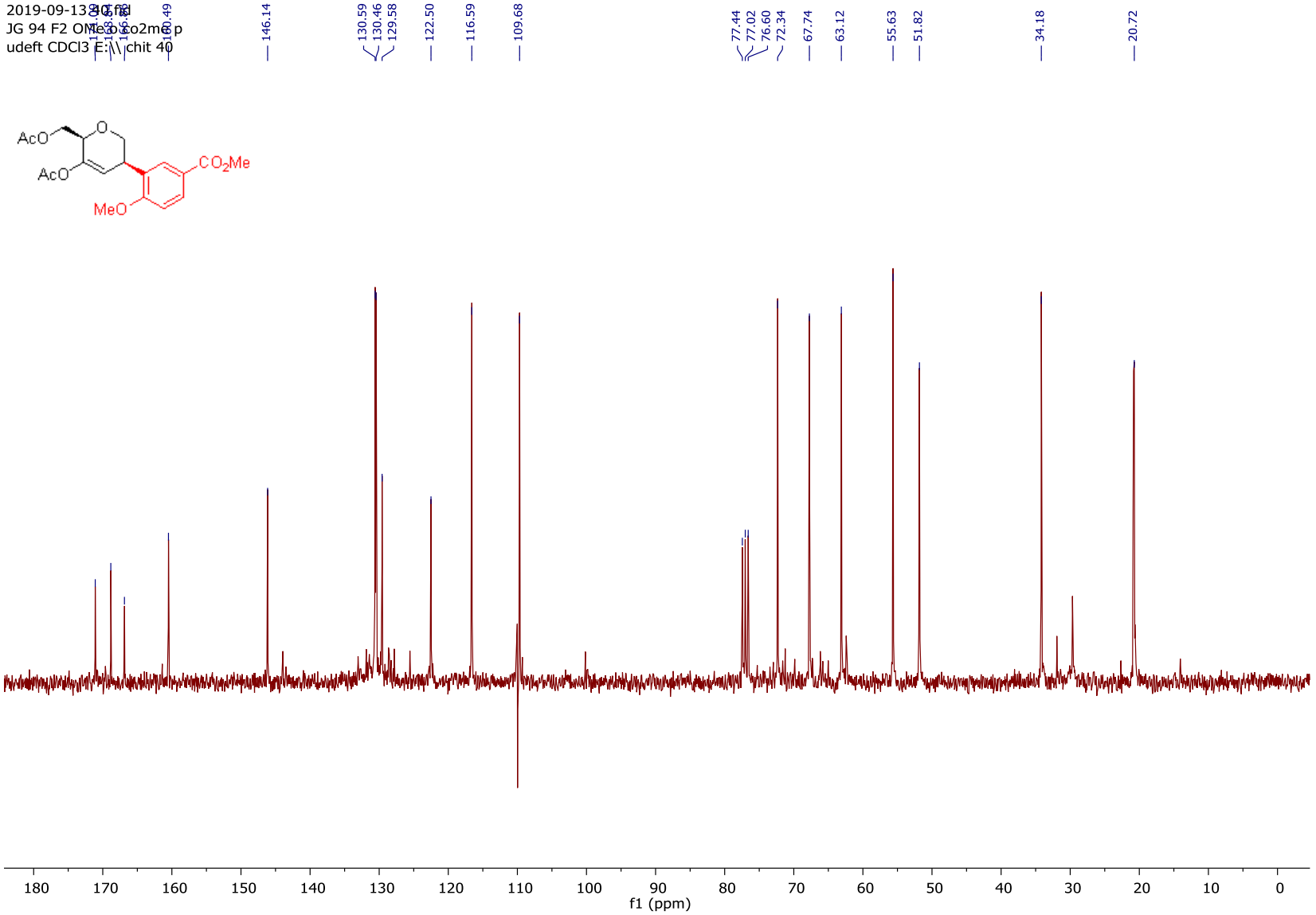
^{1}H NMR spectrum of **3s** (300 MHz, $CDCl_3$)



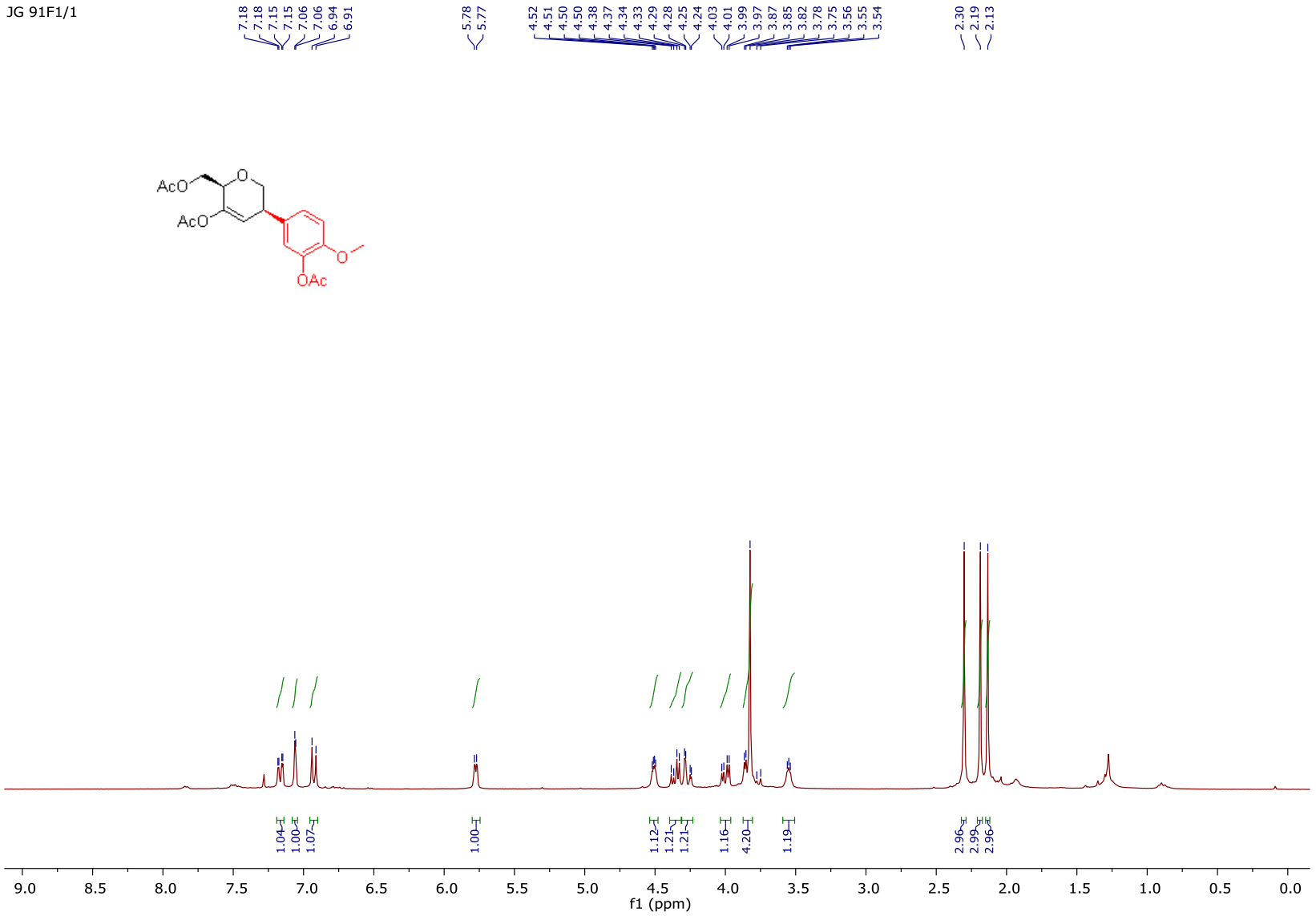
^{13}C NMR spectrum of **3s** (75 MHz, $CDCl_3$)



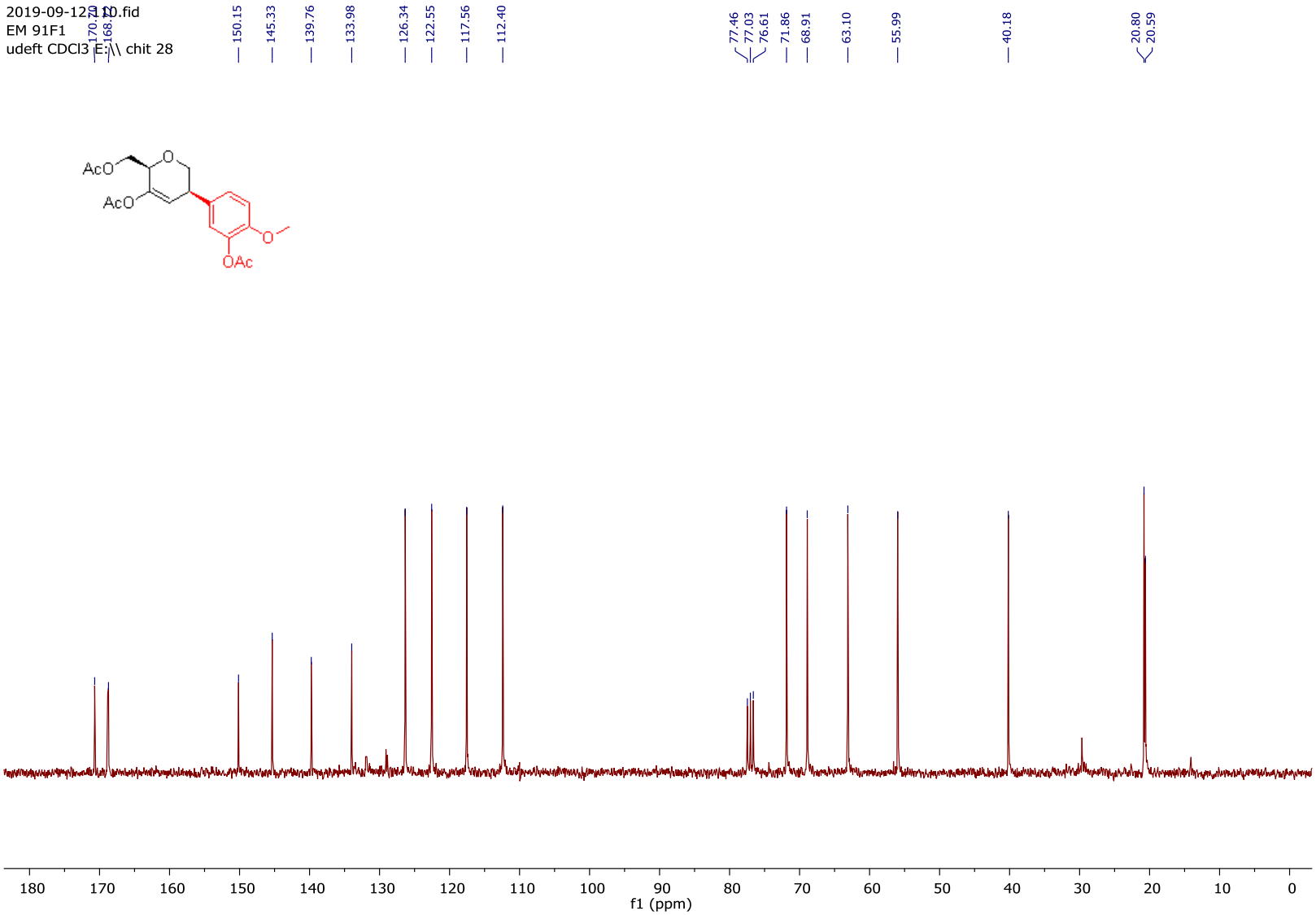
^{1}H NMR spectrum of **3t** (300 MHz, $CDCl_3$)



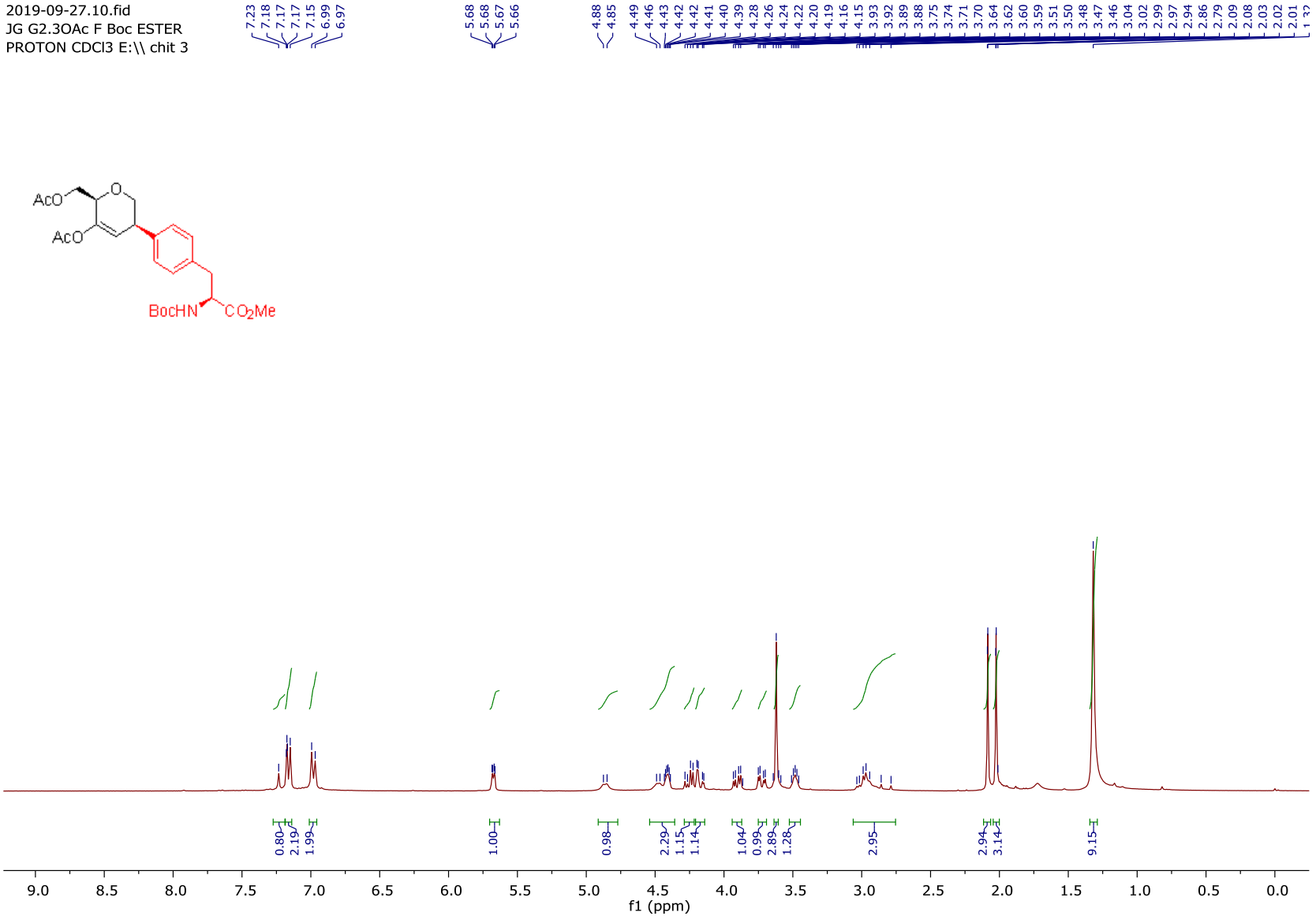
^{13}C NMR spectrum of **3t** (75 MHz, $CDCl_3$)



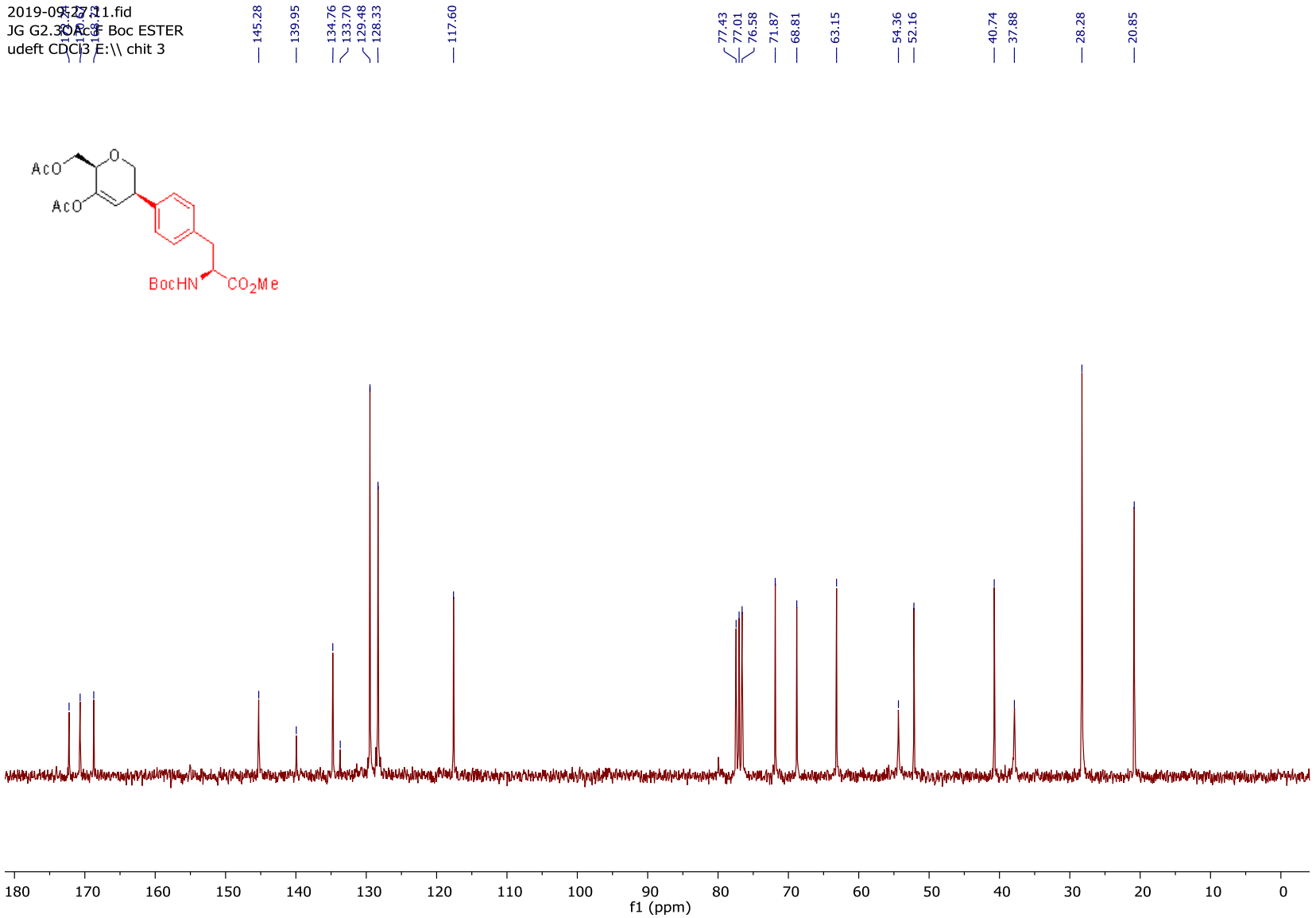
^{1}H NMR spectrum of **3u** (300 MHz, $CDCl_3$)



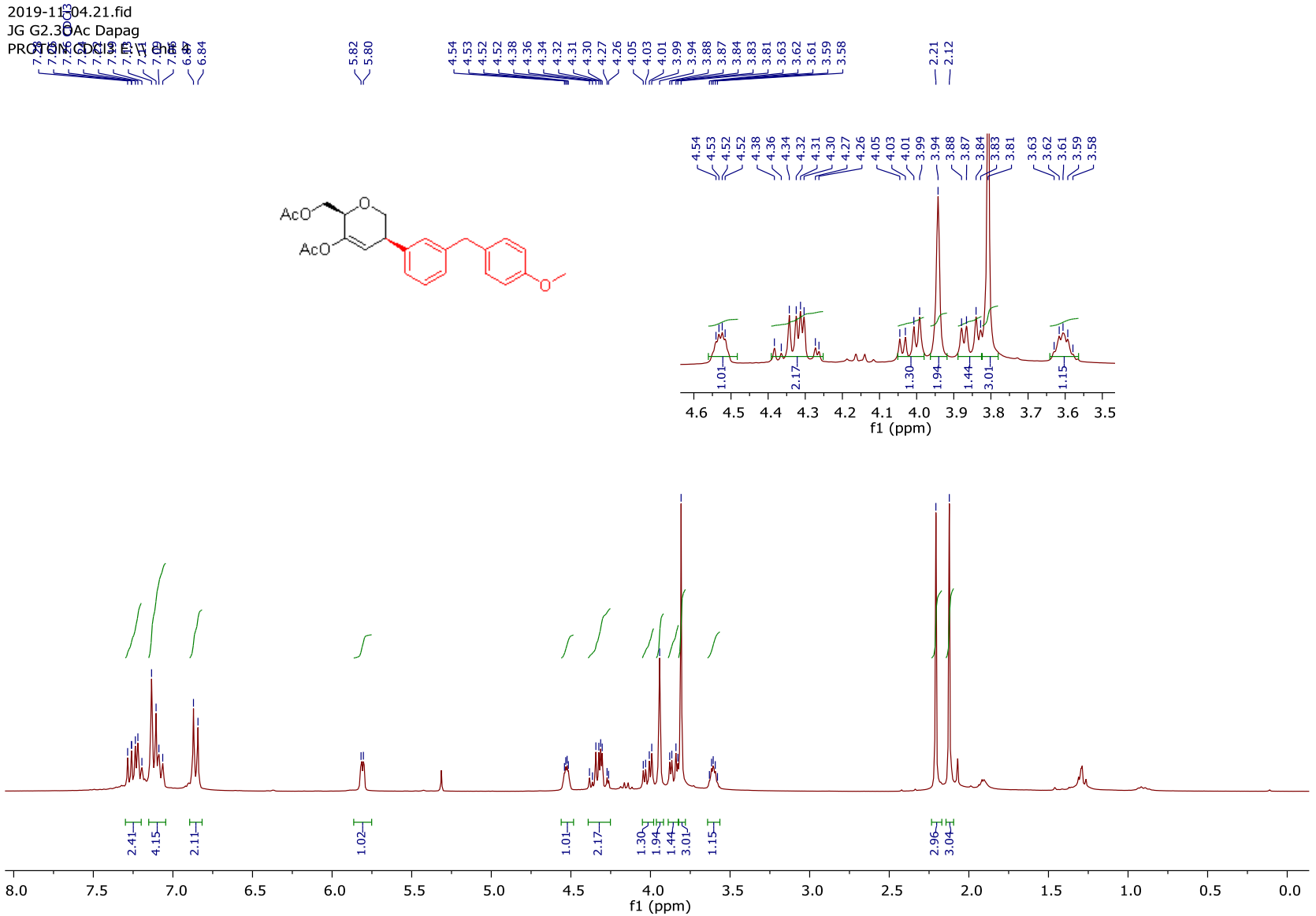
^{13}C NMR spectrum of **3u** (75 MHz, $CDCl_3$)



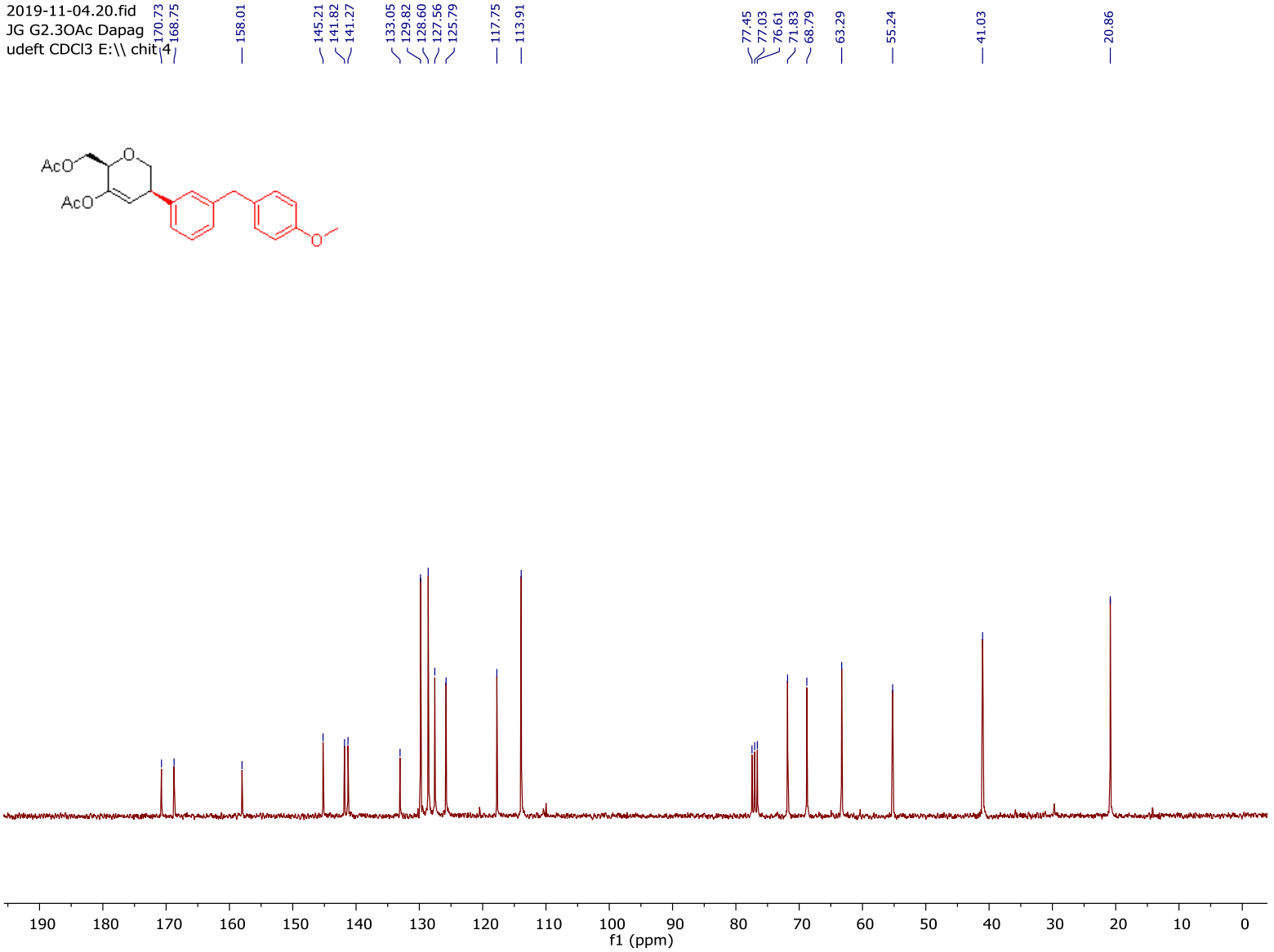
^{1}H NMR spectrum of **3v** (300 MHz, $CDCl_3$)



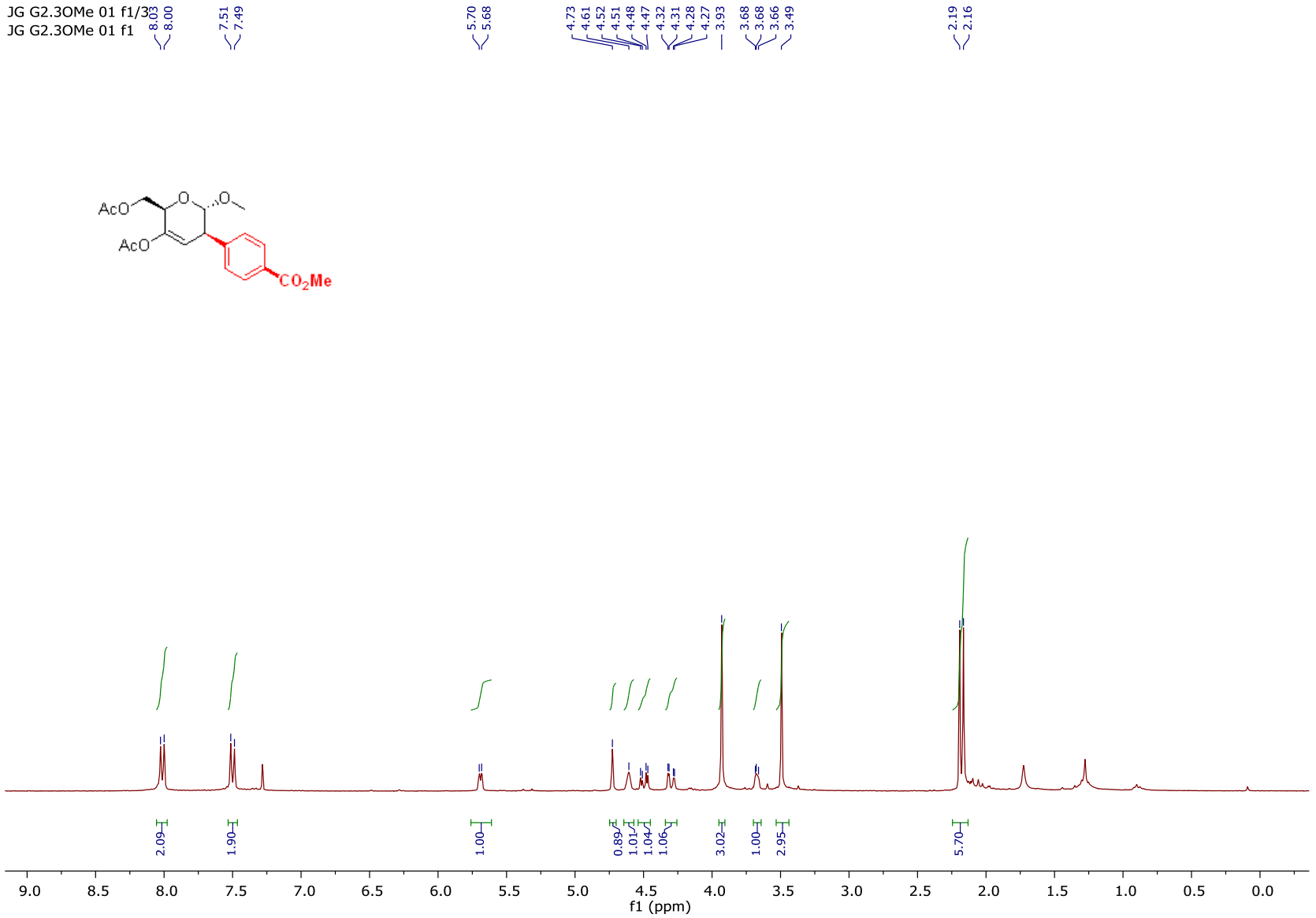
^{13}C NMR spectrum of **3v** (75 MHz, $CDCl_3$)



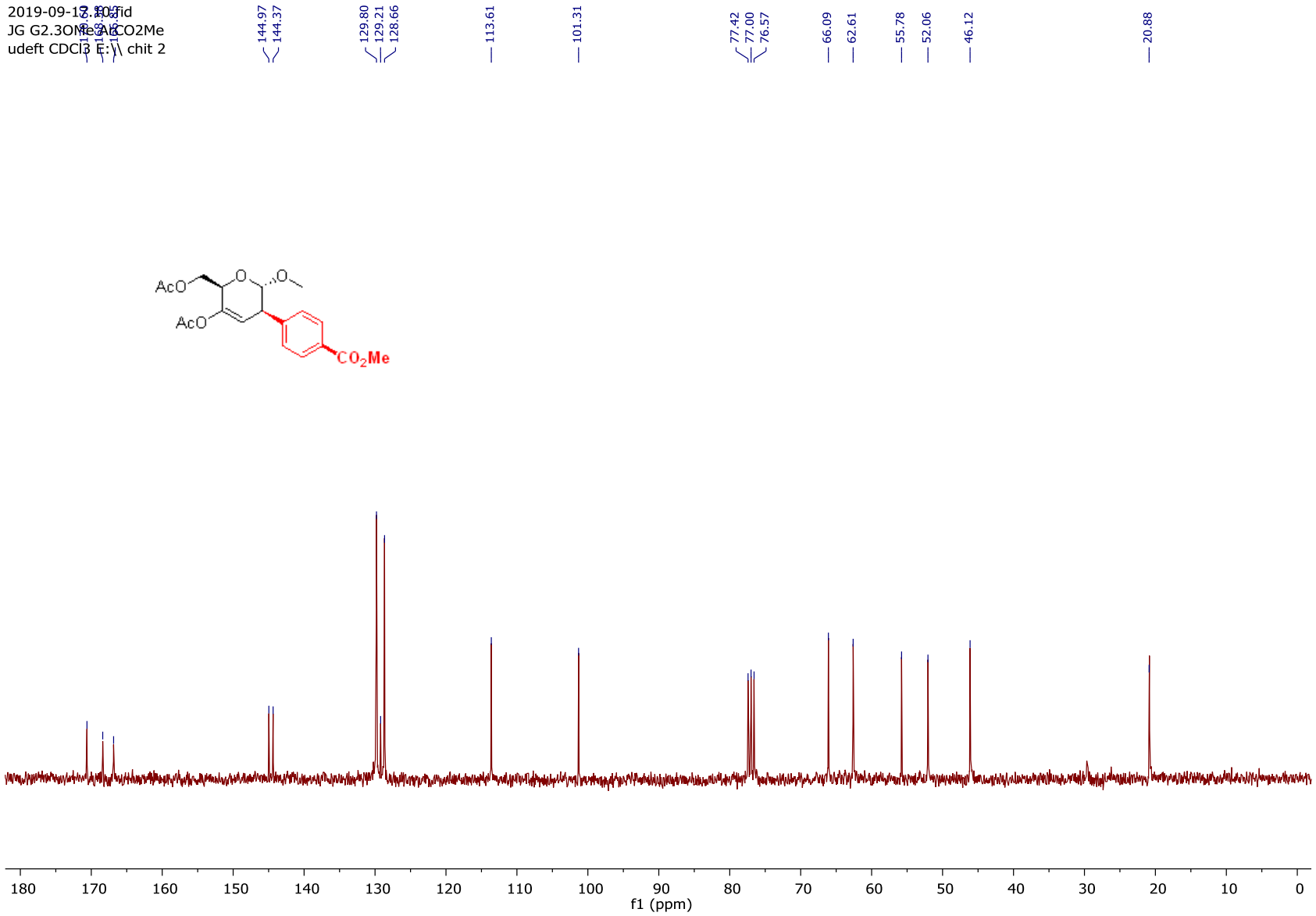
^{1}H NMR spectrum of **3w** (300 MHz, $CDCl_3$)



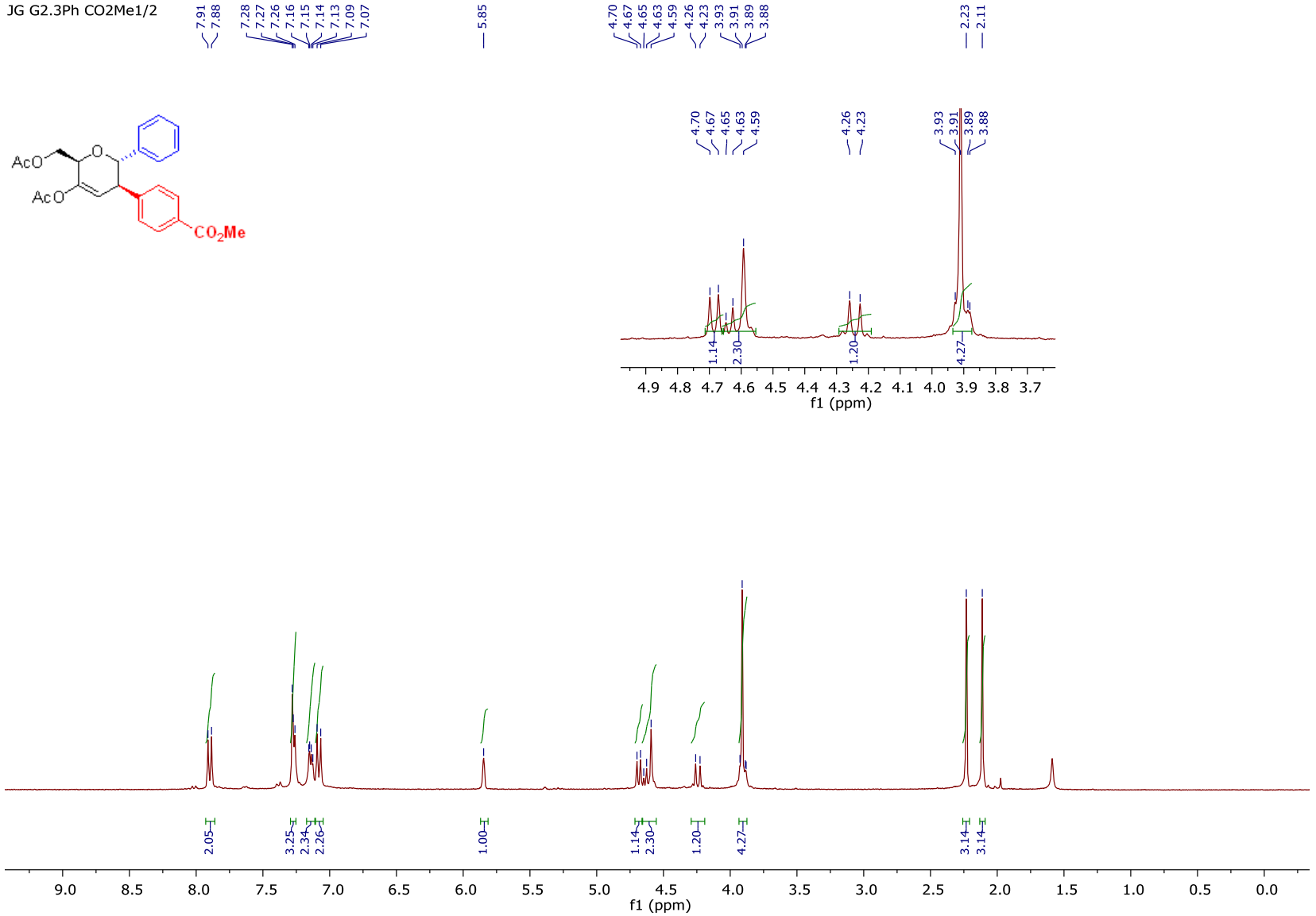
^{13}C NMR spectrum of **3w** (75 MHz, $CDCl_3$)



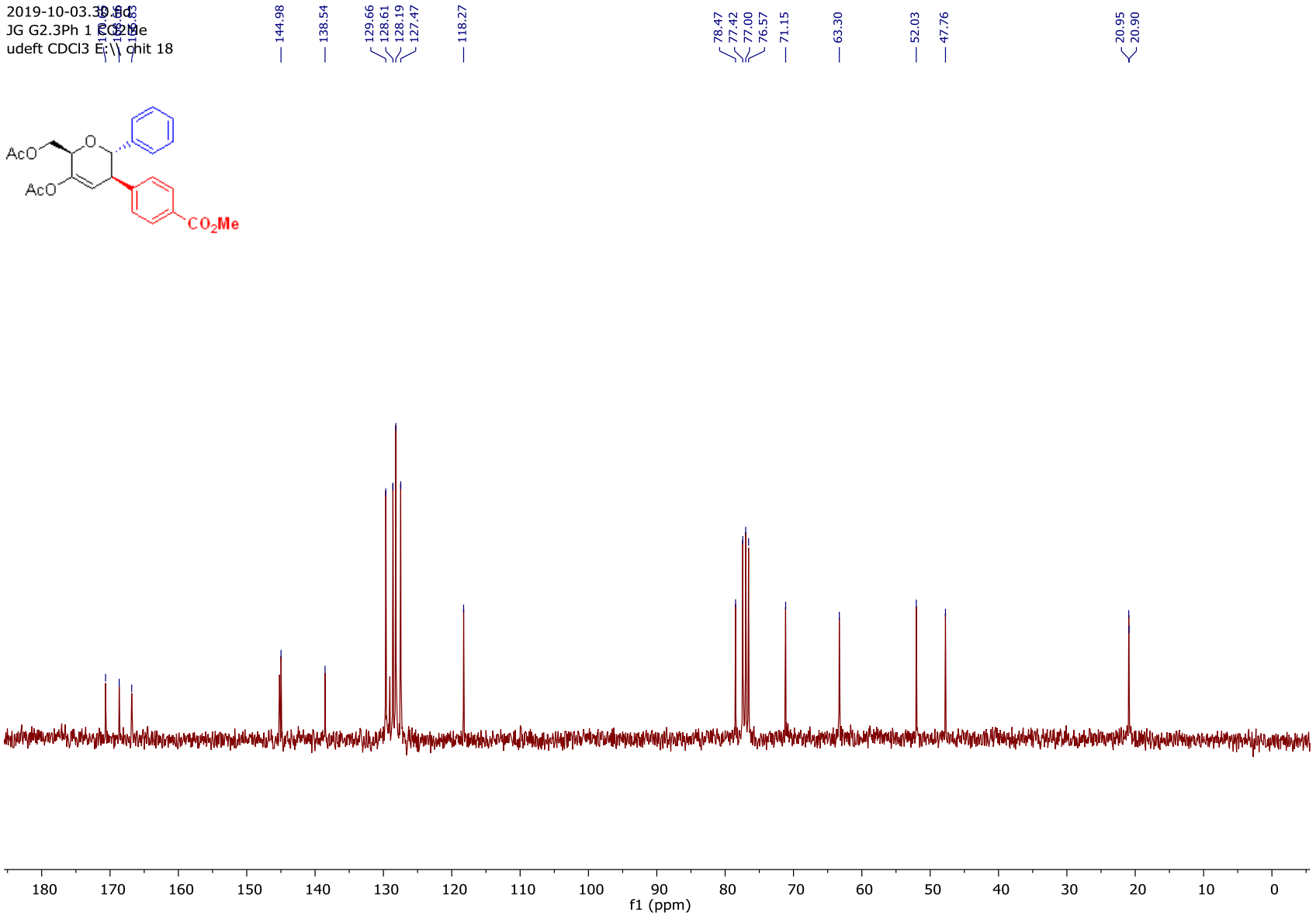
^{1}H NMR spectrum of **4a** (300 MHz, $CDCl_3$)



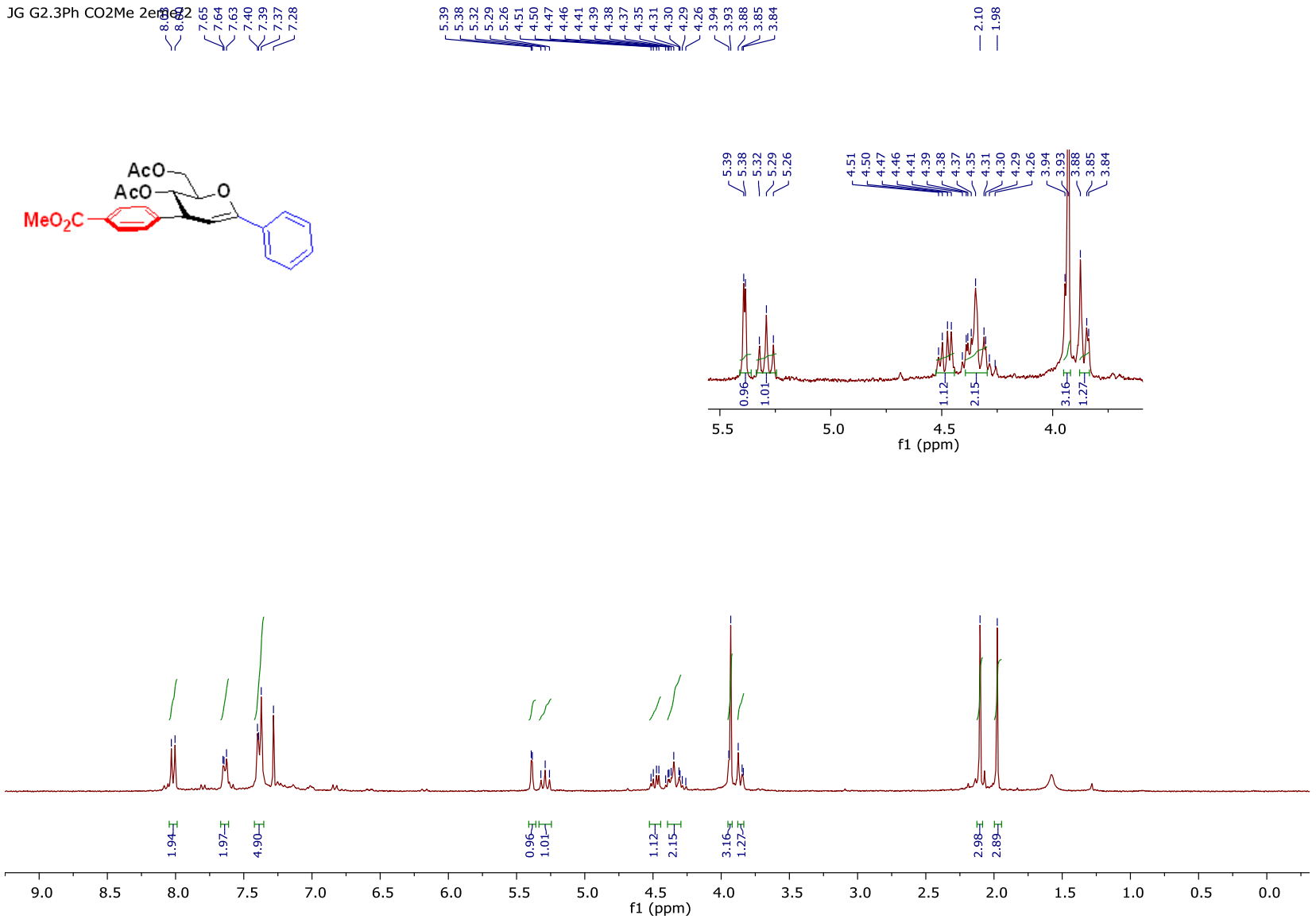
^{13}C NMR spectrum of **4a** (75 MHz, $CDCl_3$)



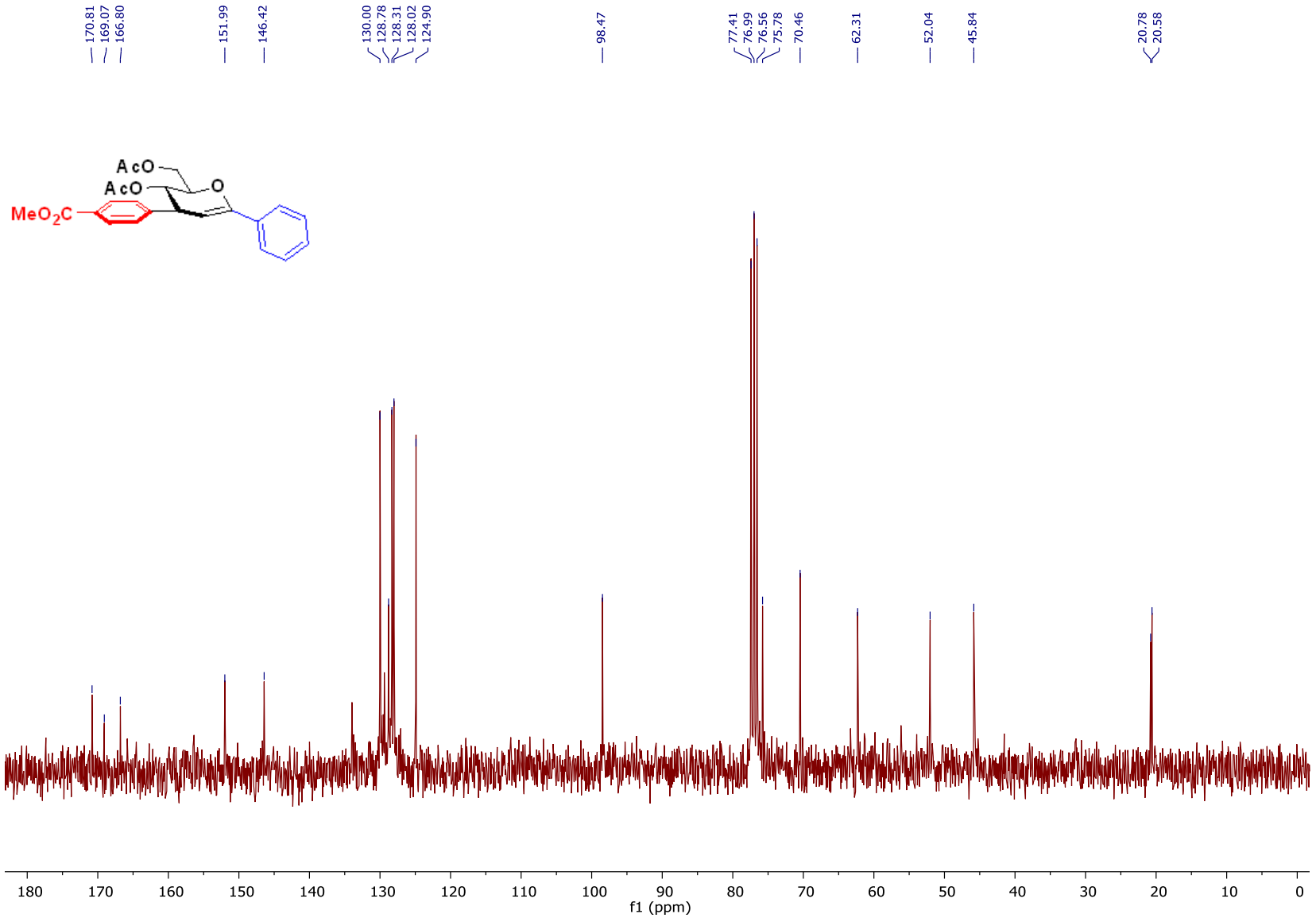
^{1}H NMR spectrum of **4b** (300 MHz, $CDCl_3$)



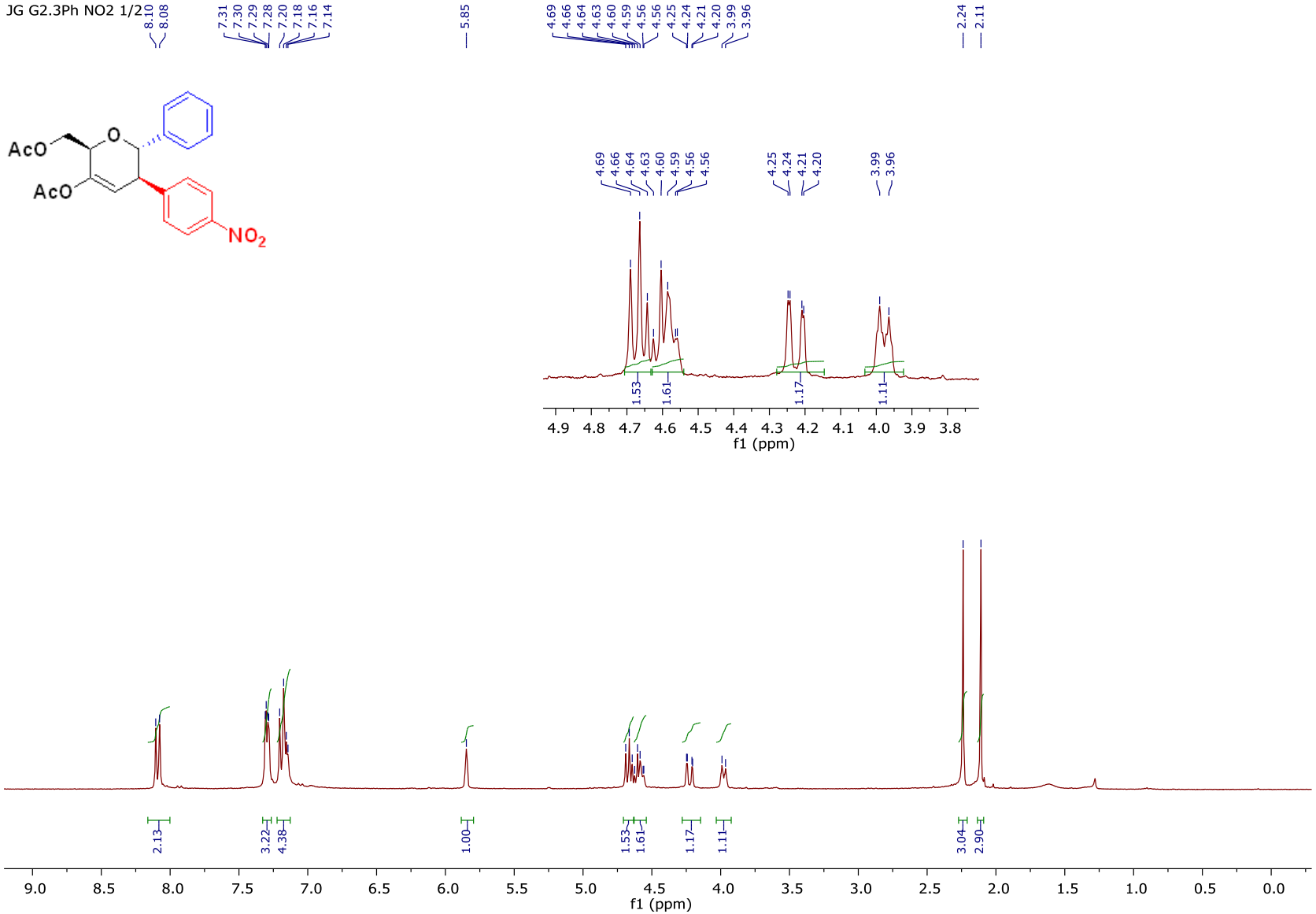
^{13}C NMR spectrum of **4b** (75 MHz, $CDCl_3$)



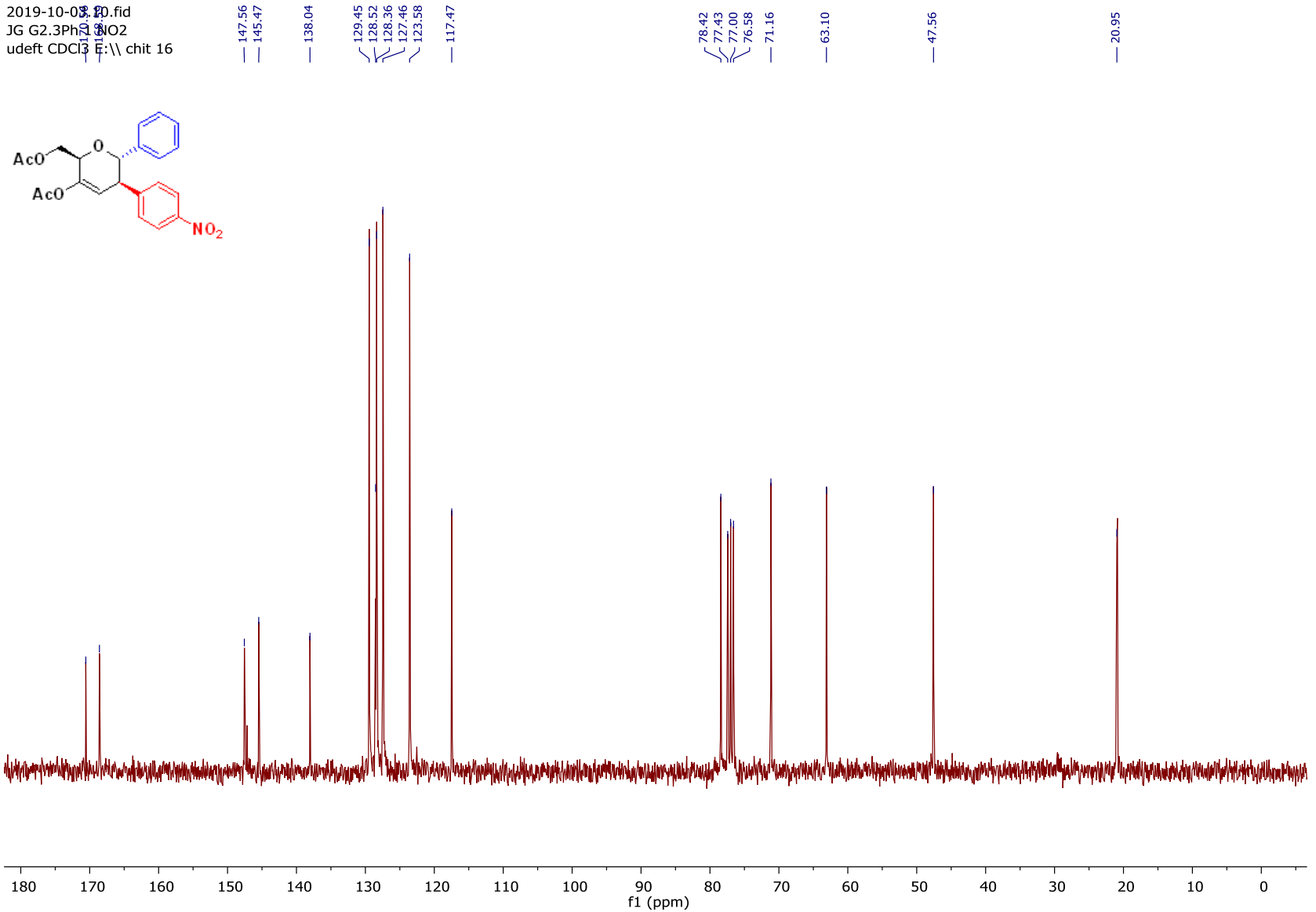
^{1}H NMR spectrum of **4b'** (300 MHz, $CDCl_3$)



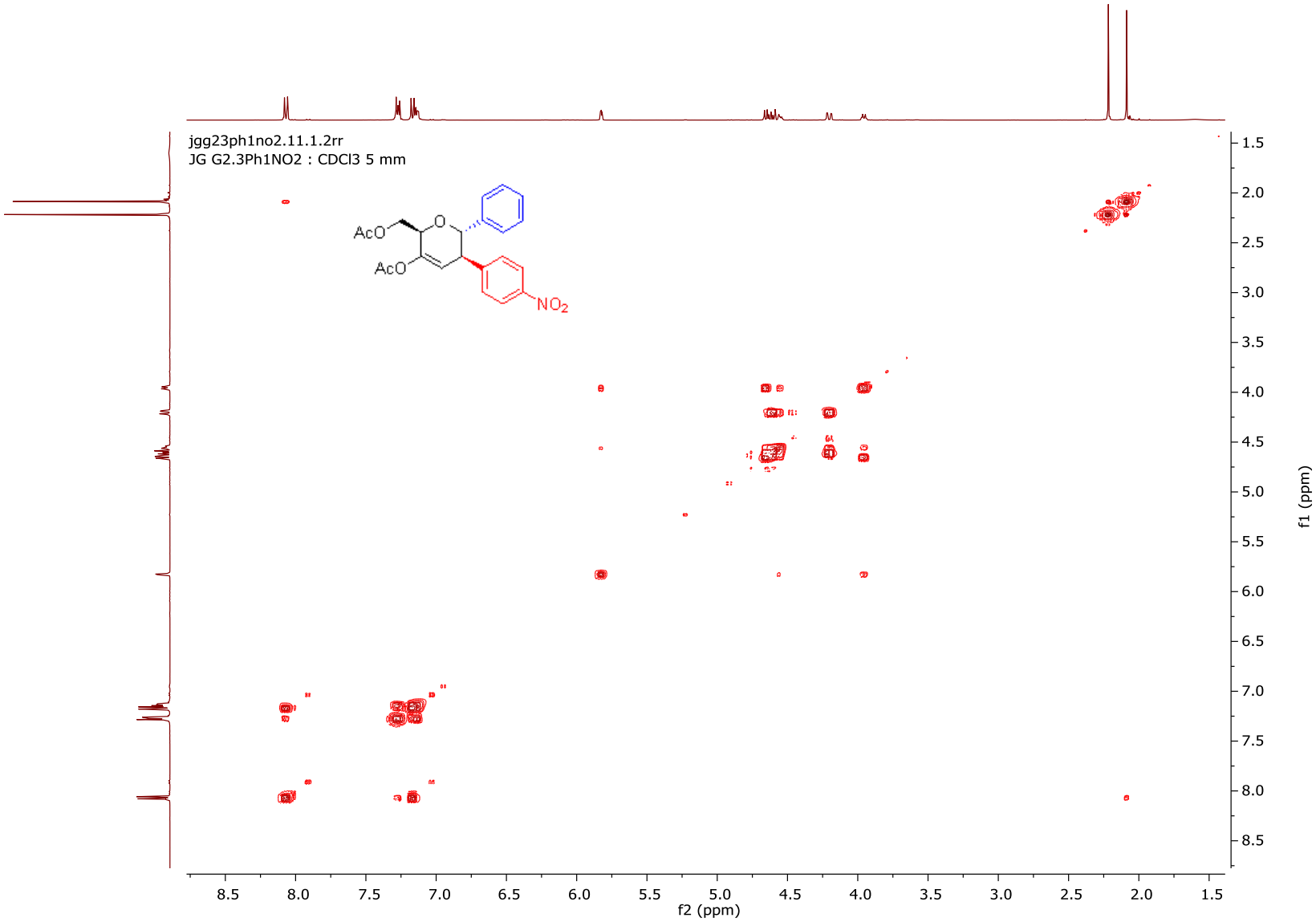
^{13}C NMR spectrum of **4b'** (75 MHz, $CDCl_3$)

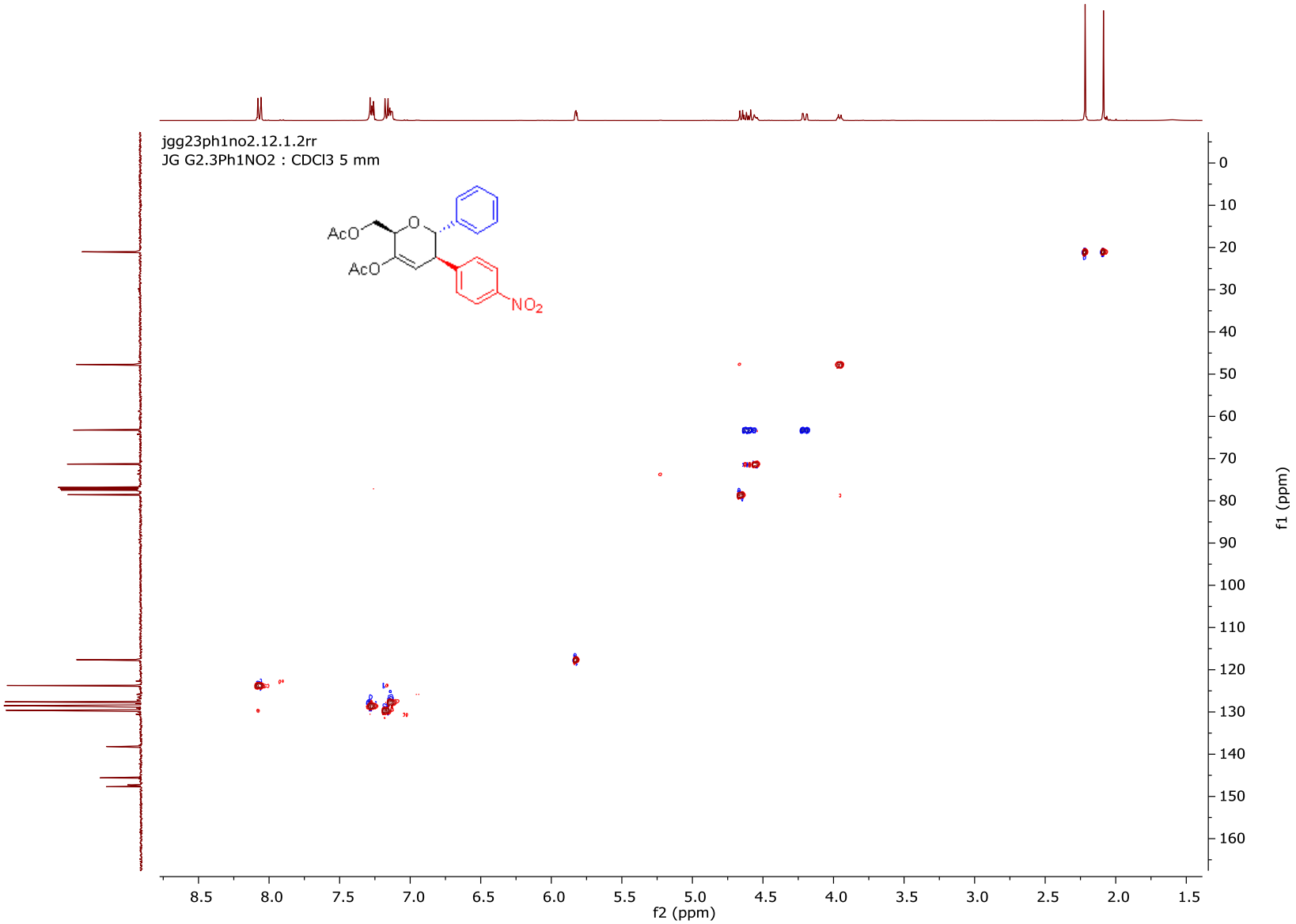


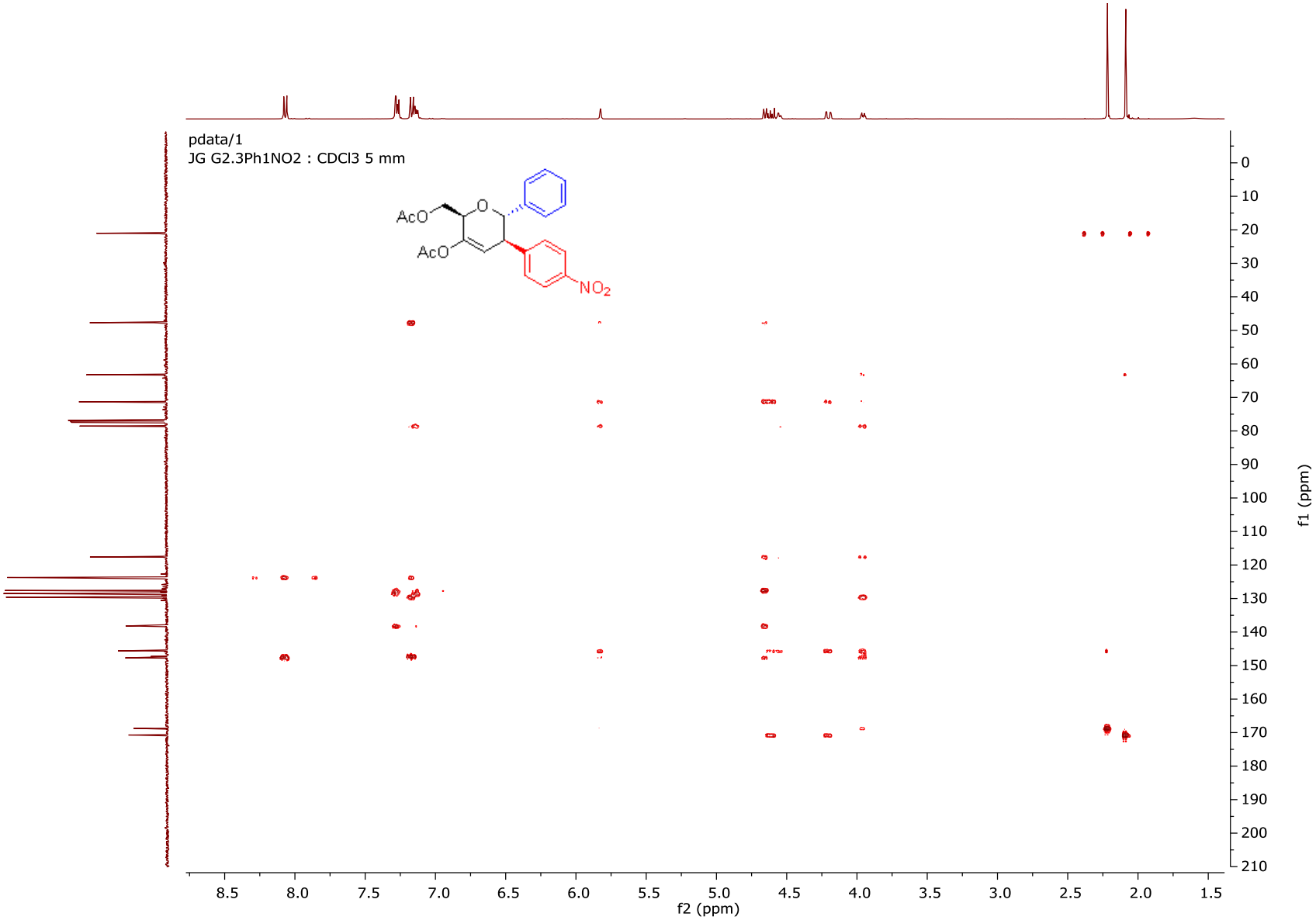
^{1}H NMR spectrum of **4c** (300 MHz, $CDCl_3$)

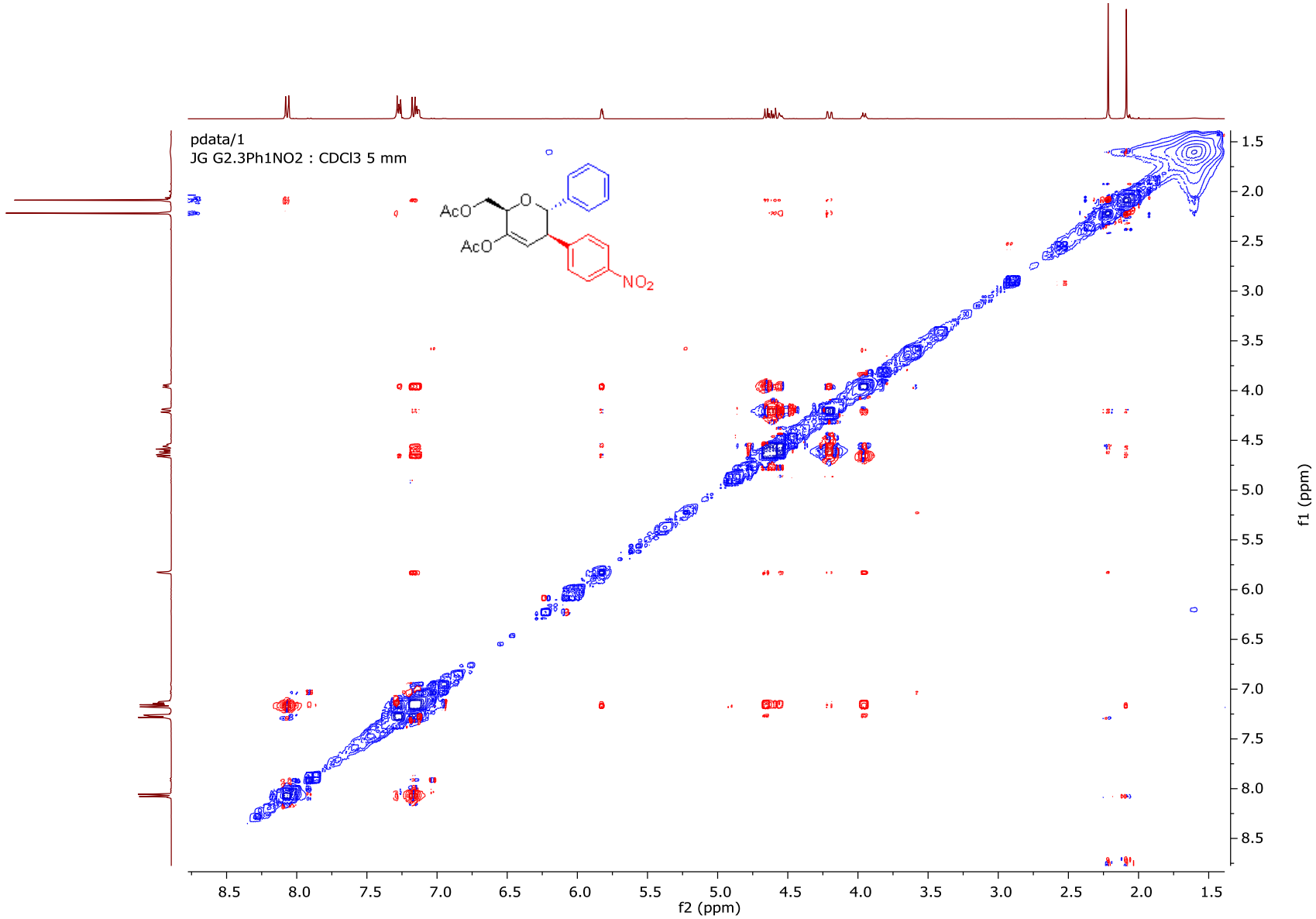


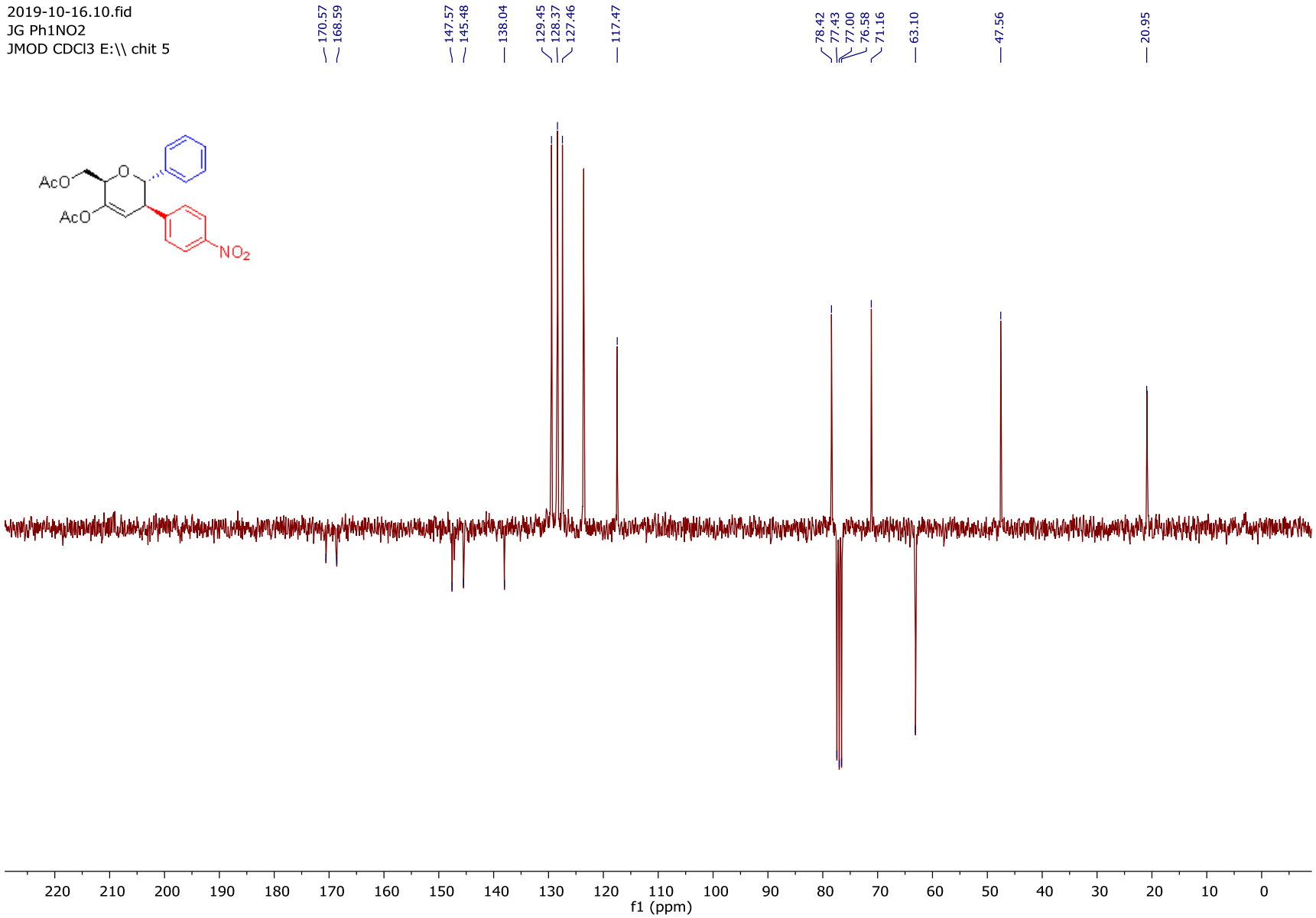
^{13}C NMR spectrum of **4c** (75 MHz, $CDCl_3$)

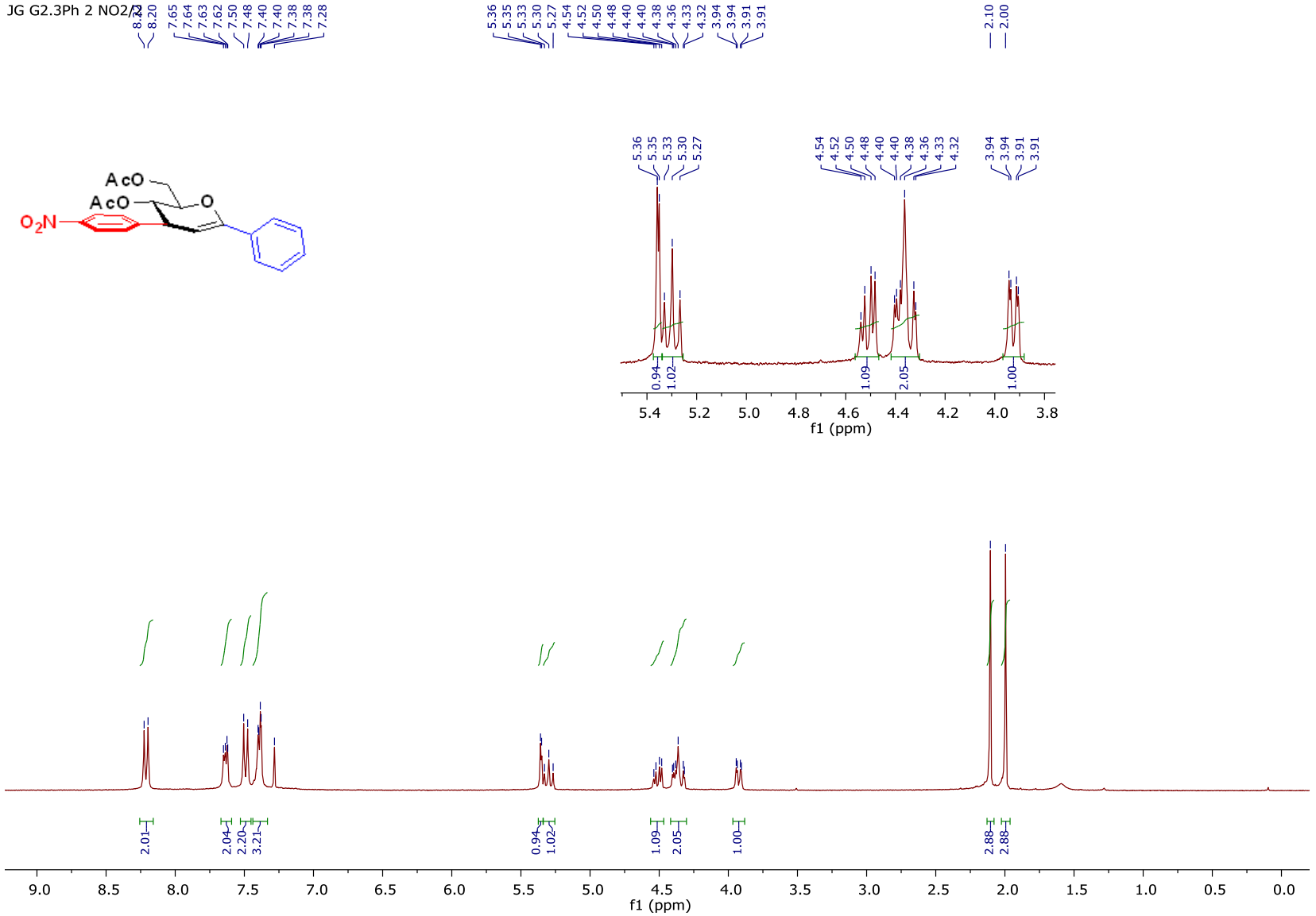

jgg23ph1no2.11.1.2rr
JG G2.3Ph1NO2 : CDCl3 5 mm
AcO
AcO
O
NO2
f2 (ppm)
f1 (ppm)


jgg23ph1no2.12.1.2rr
JG G2.3Ph1NO2 : CDCl3 5 mm
AcO
AcO
O
NO2
f2 (ppm)
f1 (ppm)

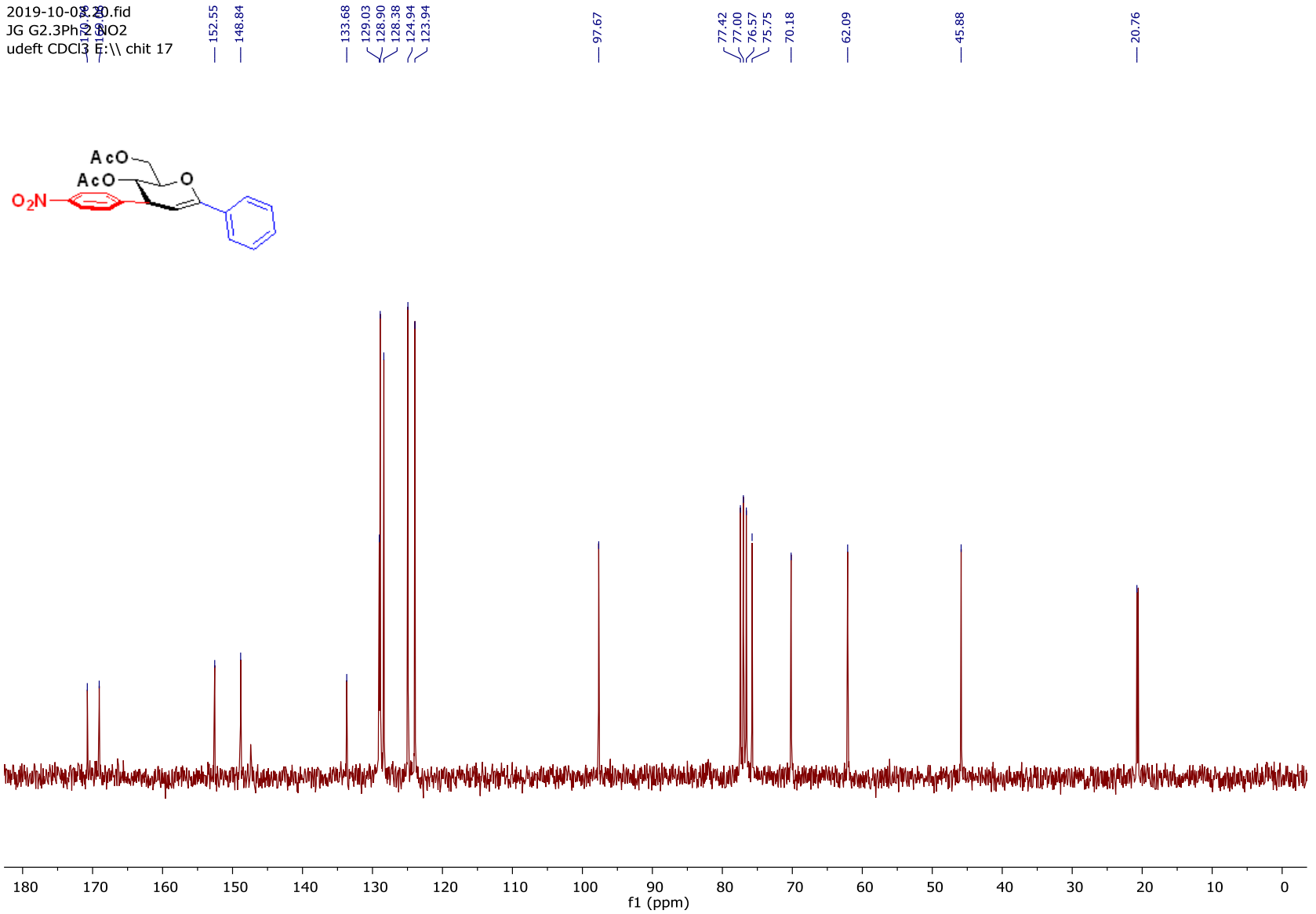

pdata/1
JG G2.3Ph1NO2 : CDCl3 5 mm
AcO
AcO
O
NO2
f2 (ppm)
f1 (ppm)


pdata/1
JG G2.3Ph1NO2 : CDCl3 5 mm
AcO
AcO
O
NO2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
f1 (ppm)

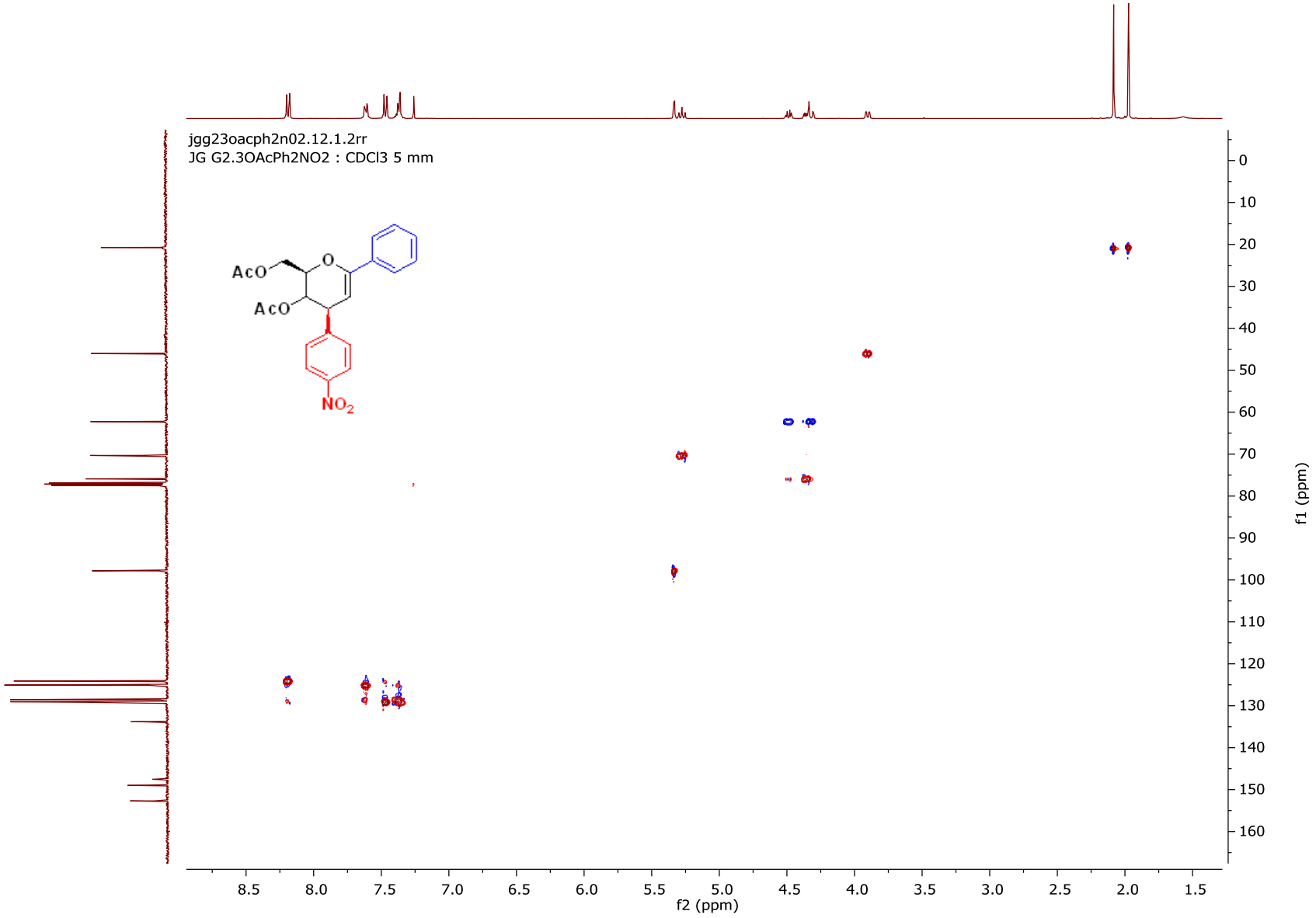

2019-10-16.10.fid
JG Ph1NO2
JMOD CDCl3 E:\\ chit 5
170.57
168.59
147.57
145.48
138.04
129.45
128.37
127.46
117.47
78.42
77.43
77.00
76.58
71.16
63.10
47.56
20.95
AcO
AcO
O
NO2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

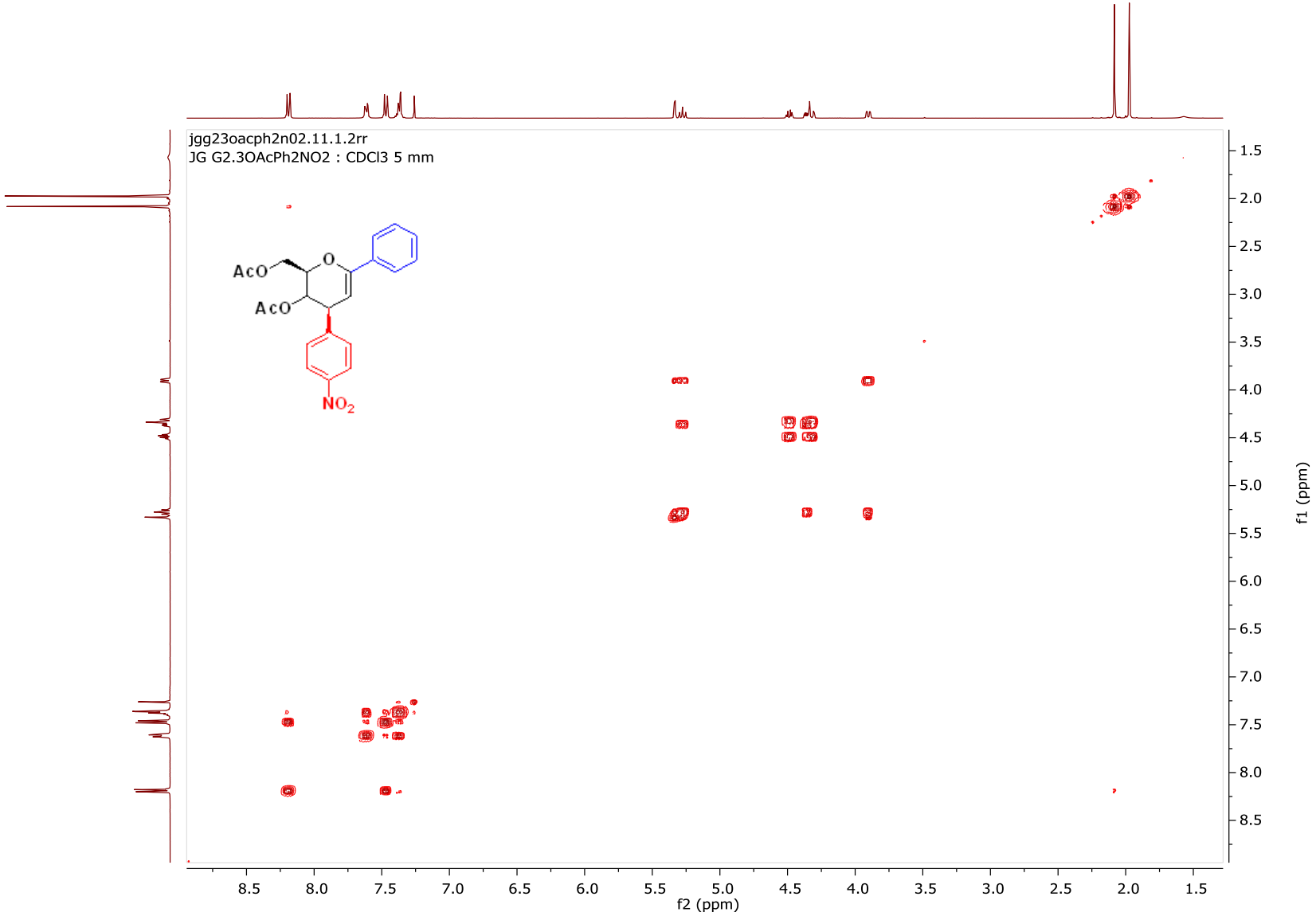


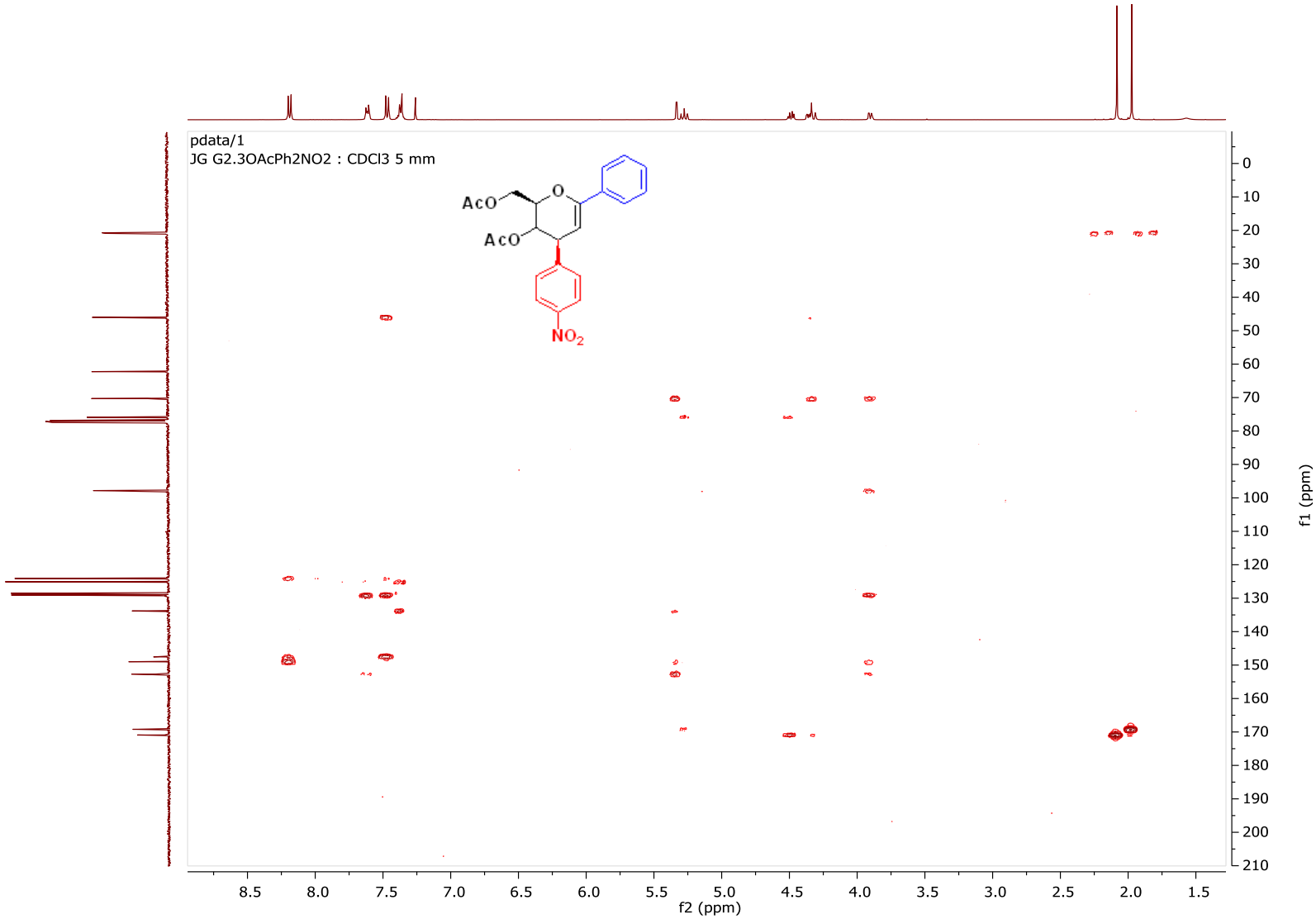
^{1}H NMR spectrum of **4c'** (300 MHz, $CDCl_3$)

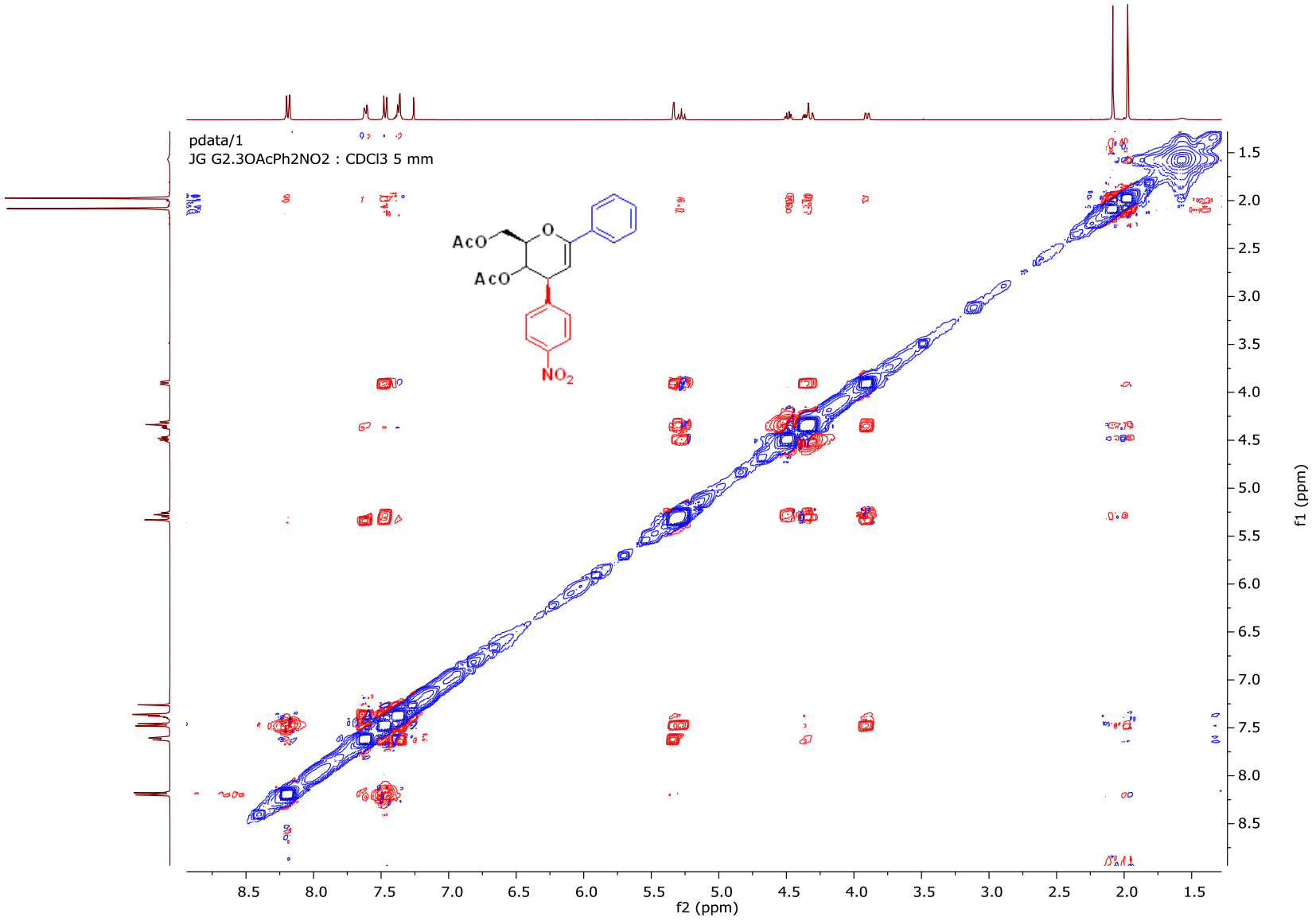


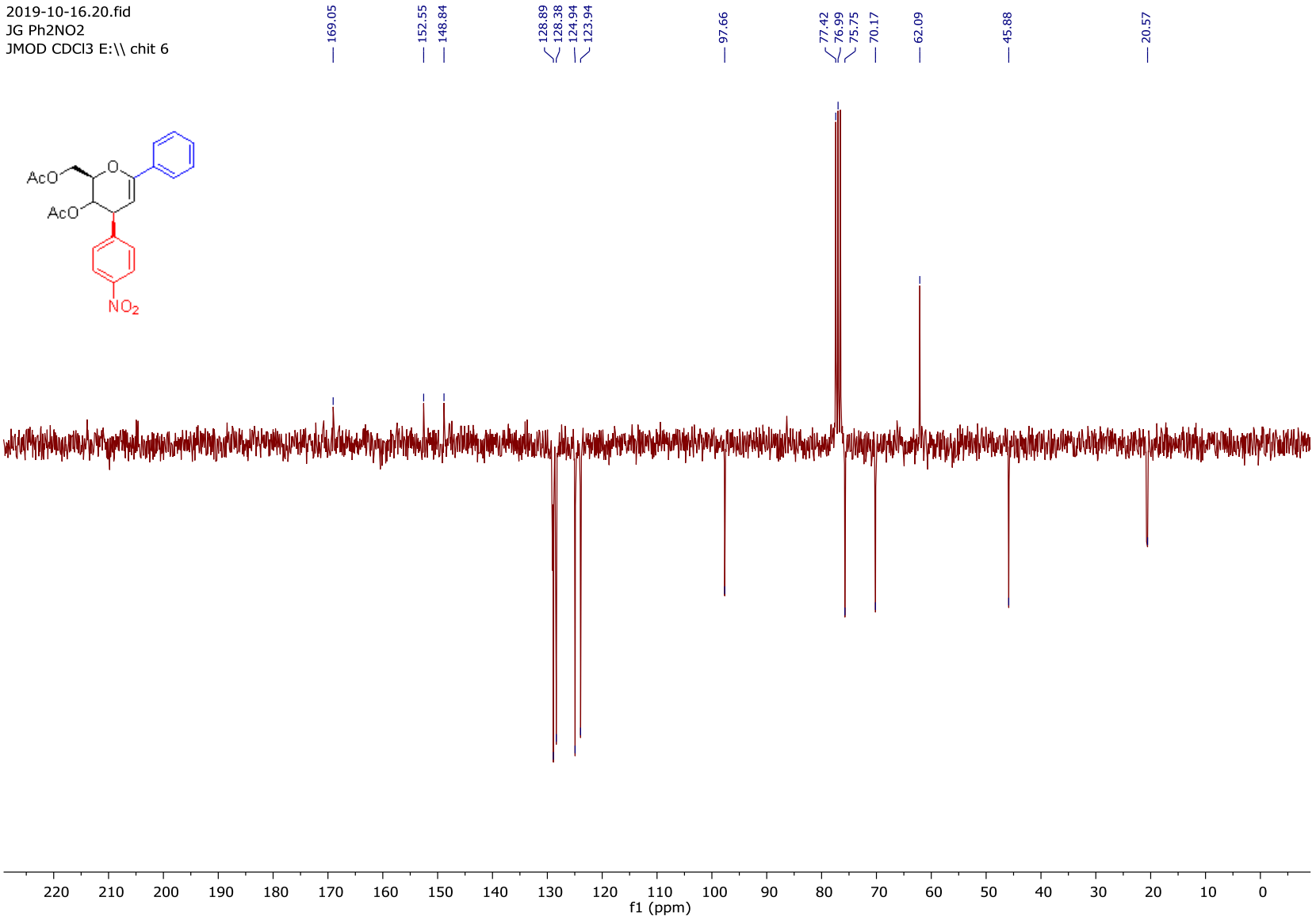
^{13}C NMR spectrum of **4c'** (75 MHz, $CDCl_3$)

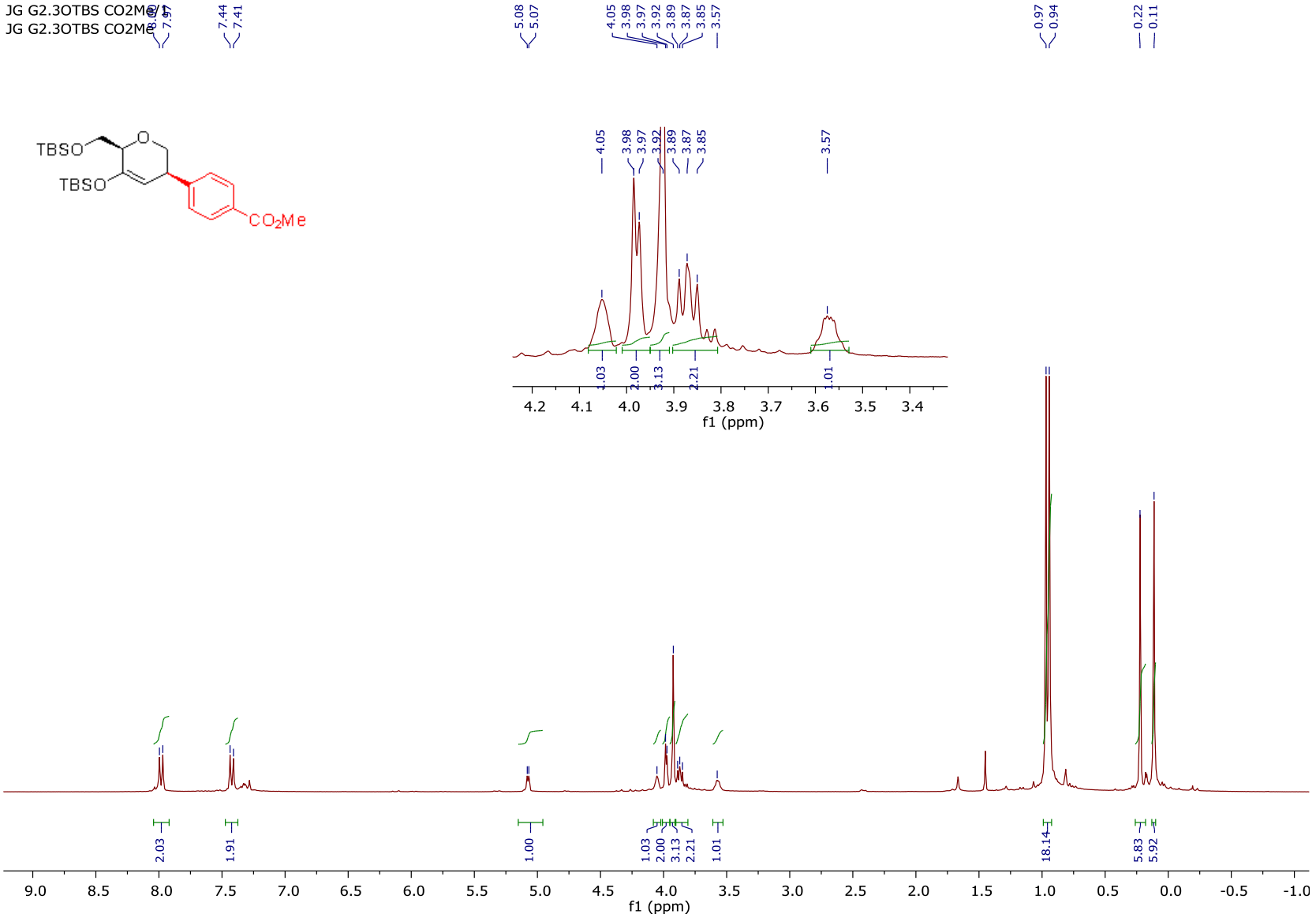

jgg23oacph2n02.12.1.2rr
JG G2.3OAcPh2NO2 : CDCl3 5 mm
AcO
AcO
O
NO2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)


jgg23oacph2n02.11.1.2rr
JG G2.3OAcPh2NO2 : CDCl3 5 mm
AcO
AcO
O
NO2
f2 (ppm)
f1 (ppm)

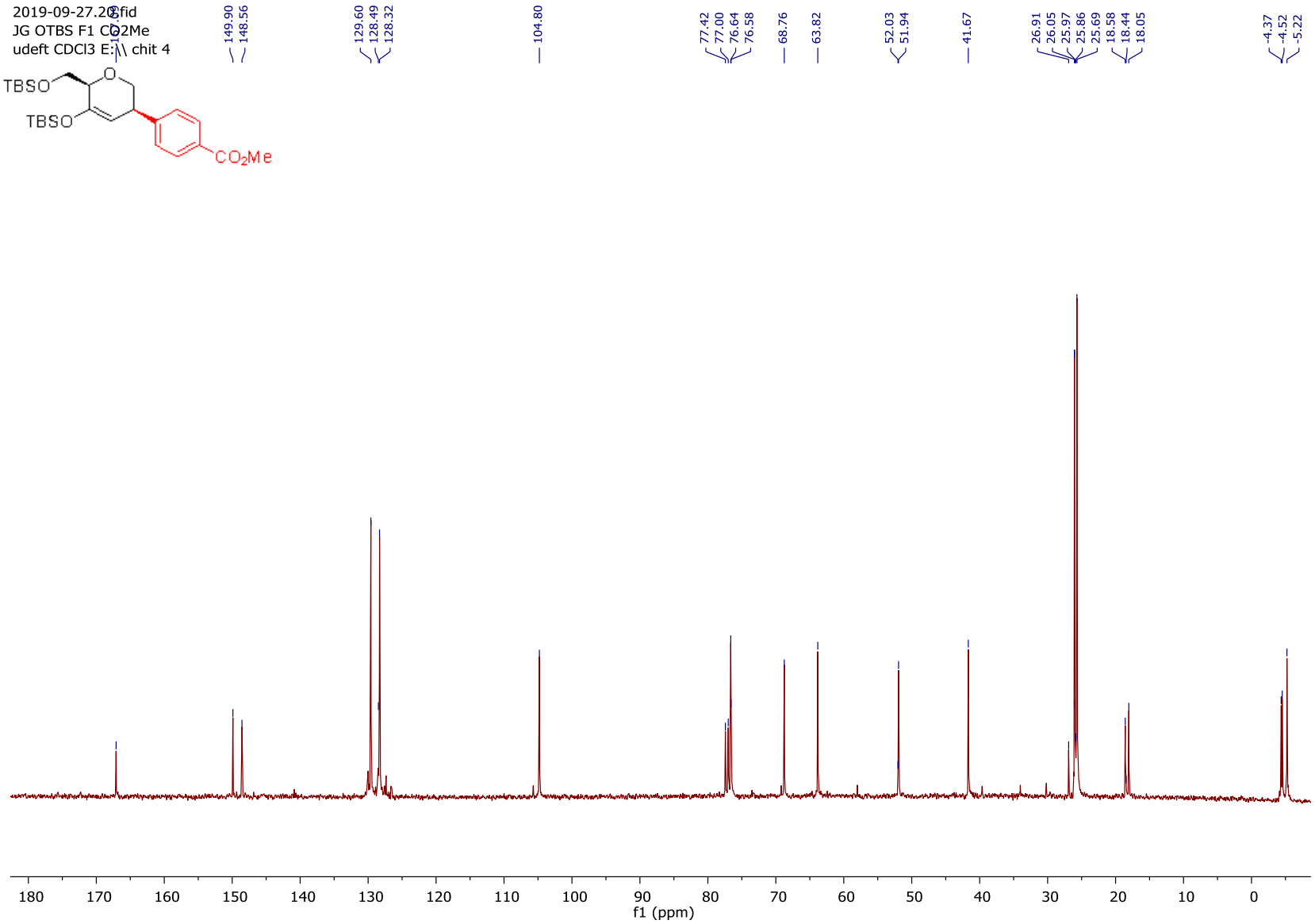

pdata/1
JG G2.3OAcPh2NO2 : CDCl3 5 mm
AcO
AcO
O
NO2
f2 (ppm)
f1 (ppm)


pdata/1
JG G2.3OAcPh2NO2 : CDCl3 5 mm
AcO
AcO
O
NO2
f2 (ppm)
f1 (ppm)

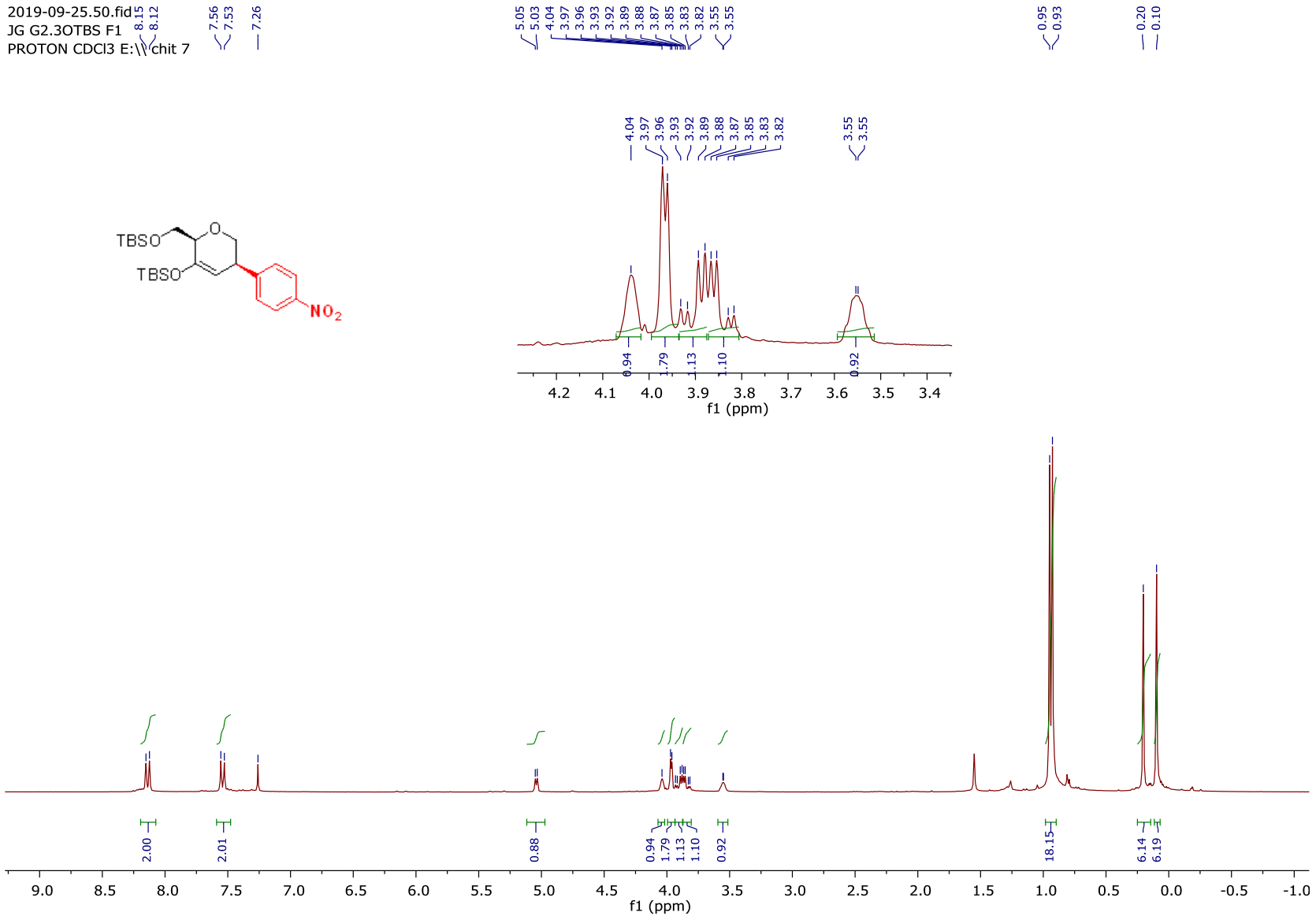

2019-10-16.20.fid
JG Ph2NO2
JMOD CDCl3 E:\\ chit 6
169.05
152.55
148.84
128.89
128.38
124.94
123.94
97.66
77.42
76.99
75.75
70.17
62.09
45.88
20.57
AcO
AcO
O
NO2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



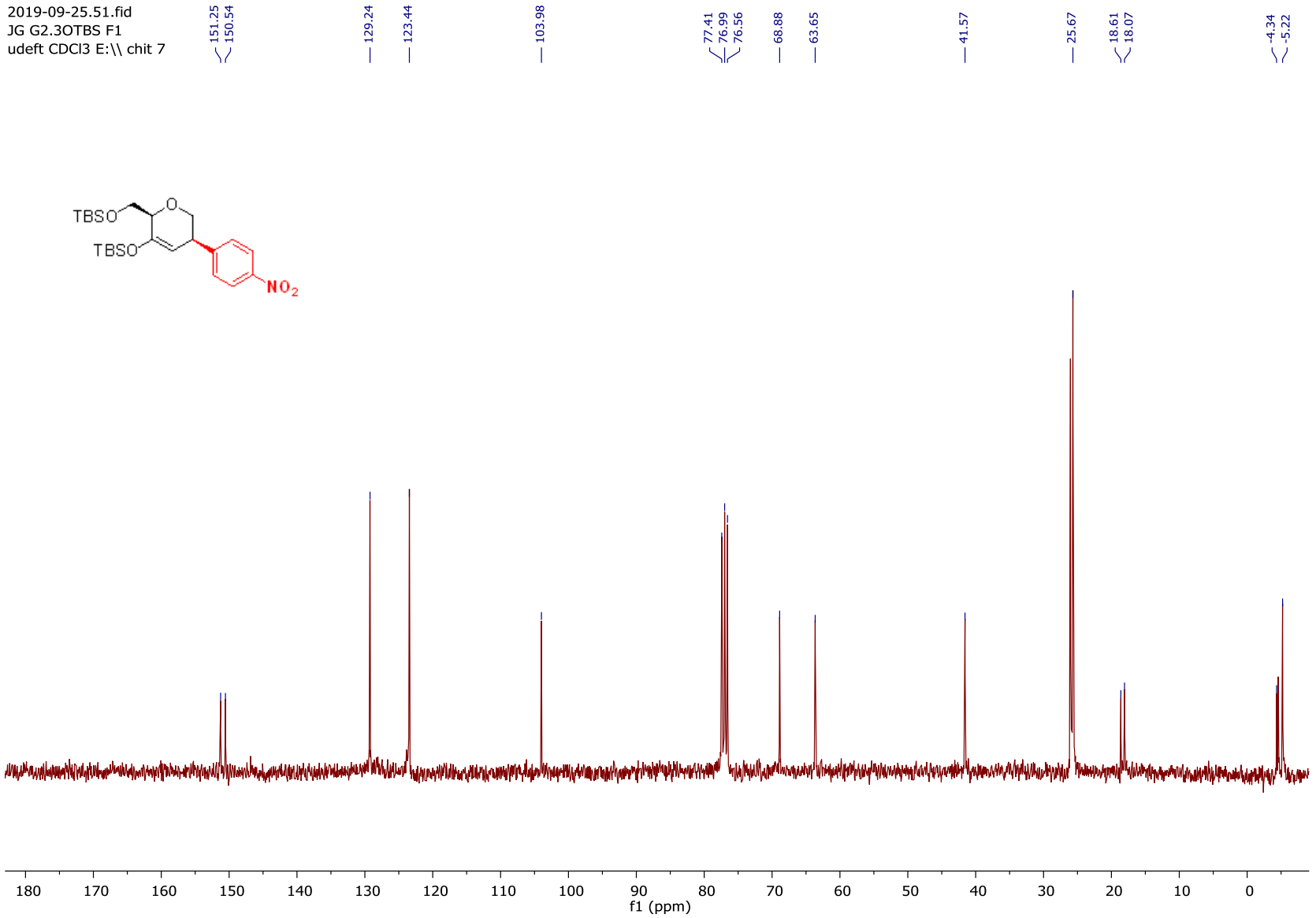
^{1}H NMR spectrum of **4d** (300 MHz, $CDCl_3$)



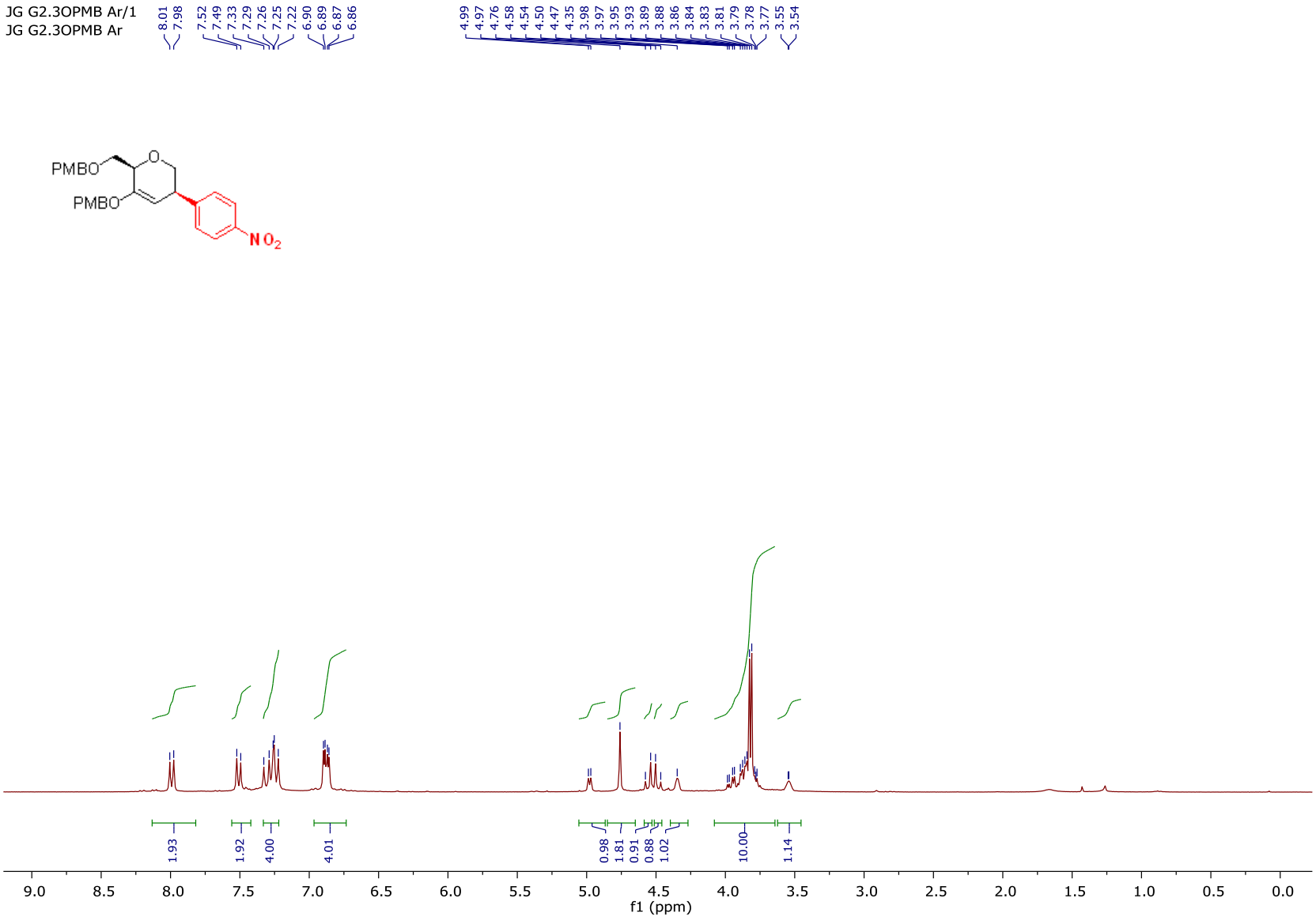
^{13}C NMR spectrum of **4d** (75 MHz, $CDCl_3$



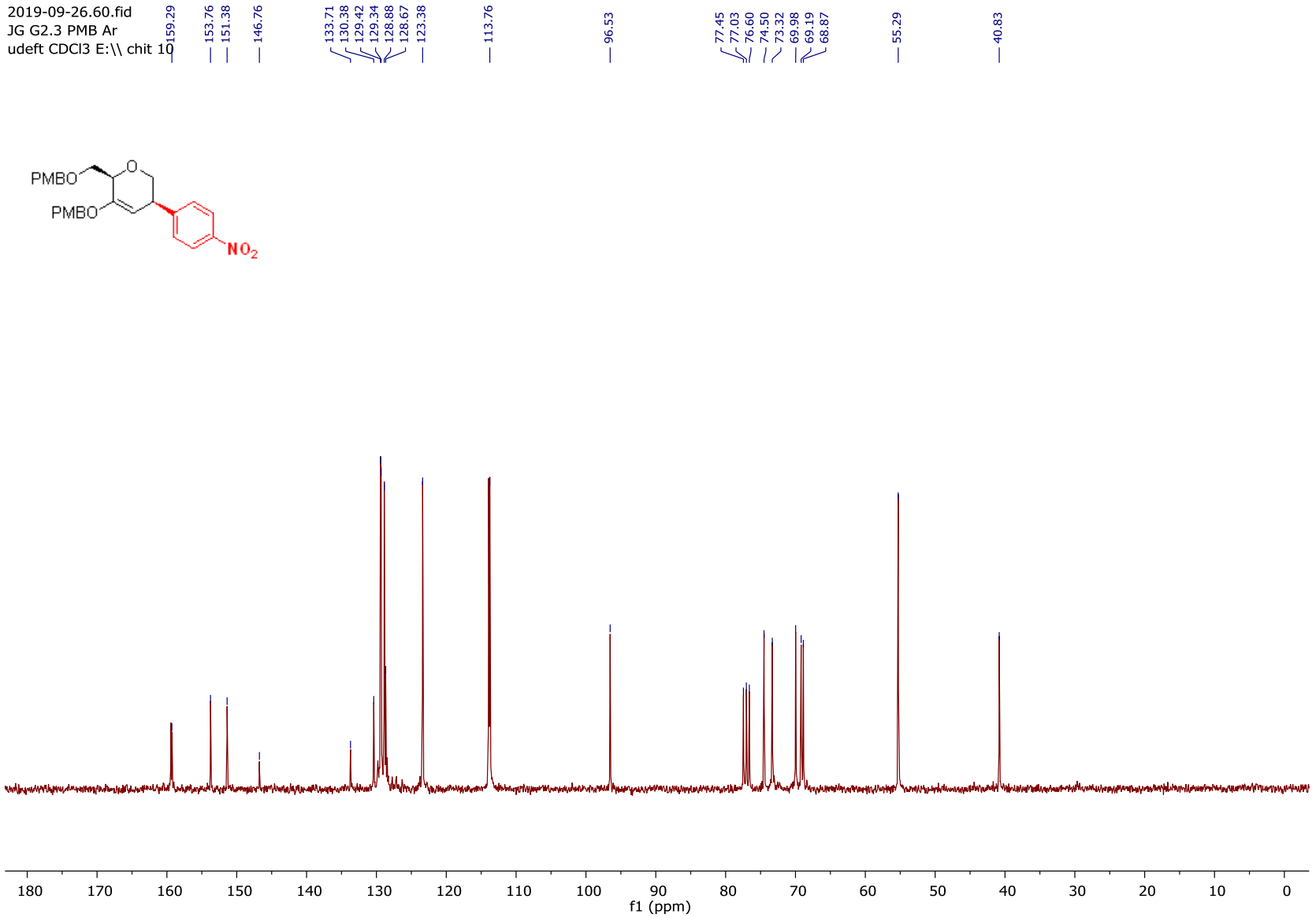
^{1}H NMR spectrum of **4e** (300 MHz, $CDCl_3$)



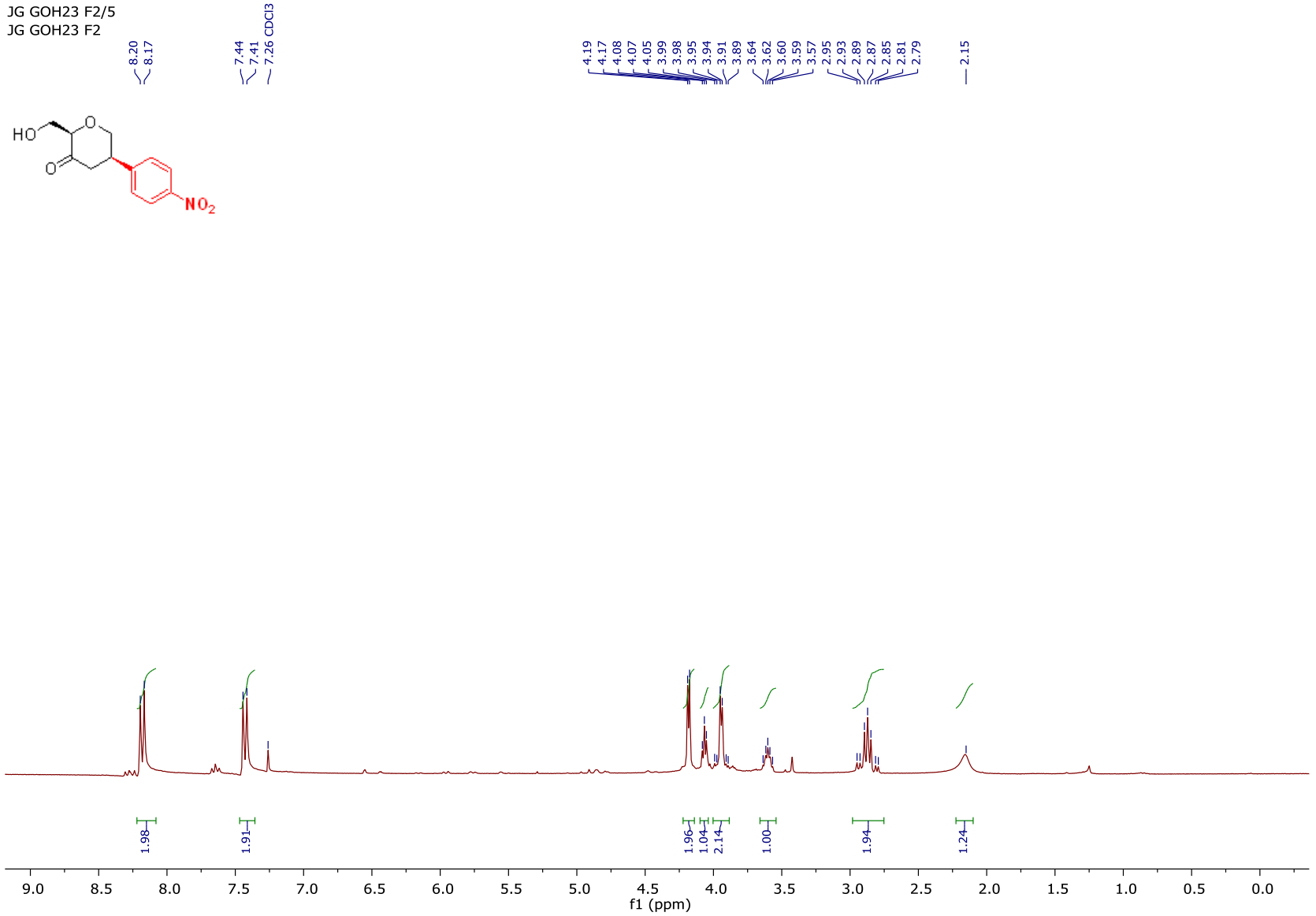
^{13}C NMR spectrum of **4e** (75 MHz, $CDCl_3$)



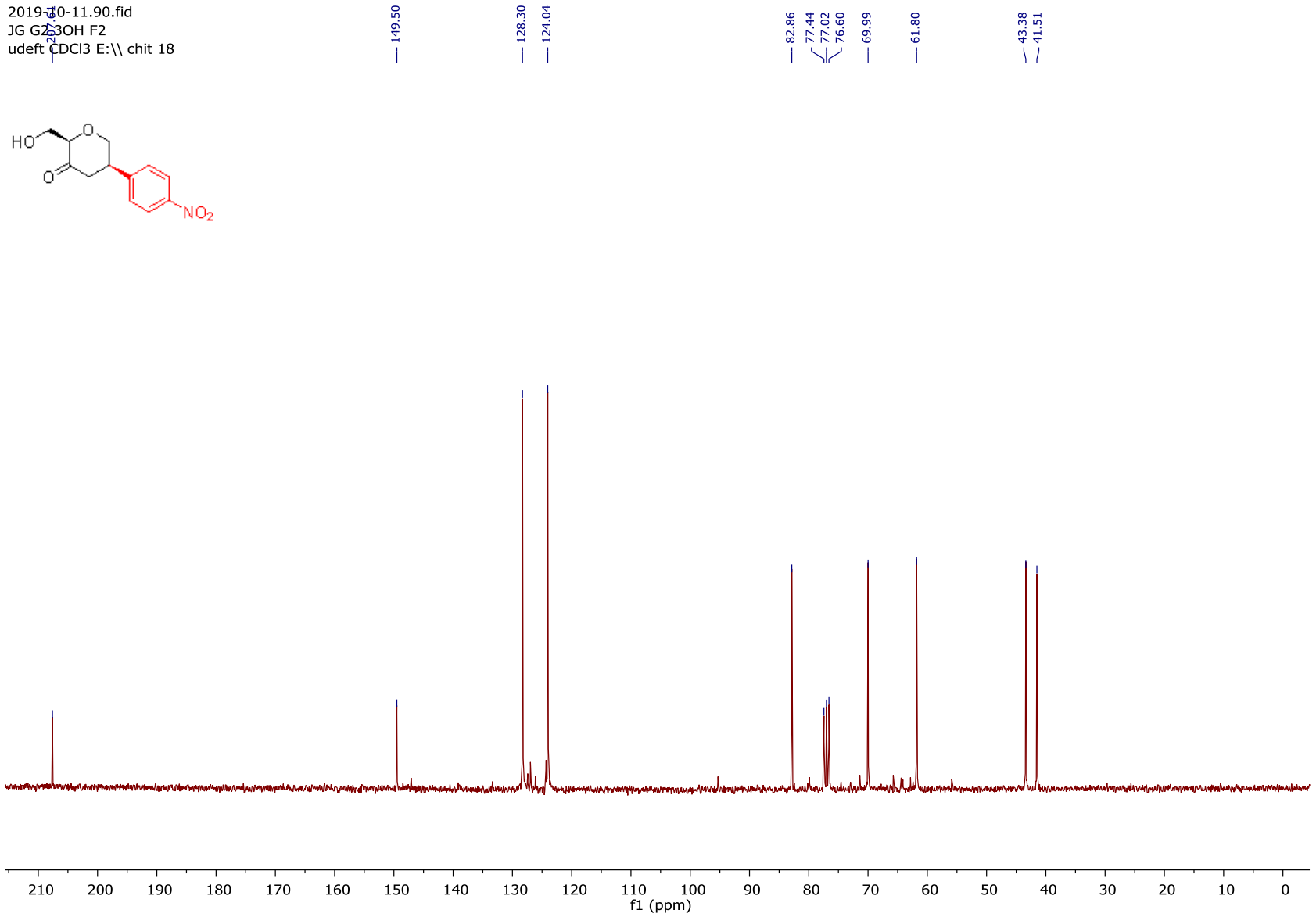
^{1}H NMR spectrum of **4f** (300 MHz, $CDCl_3$)



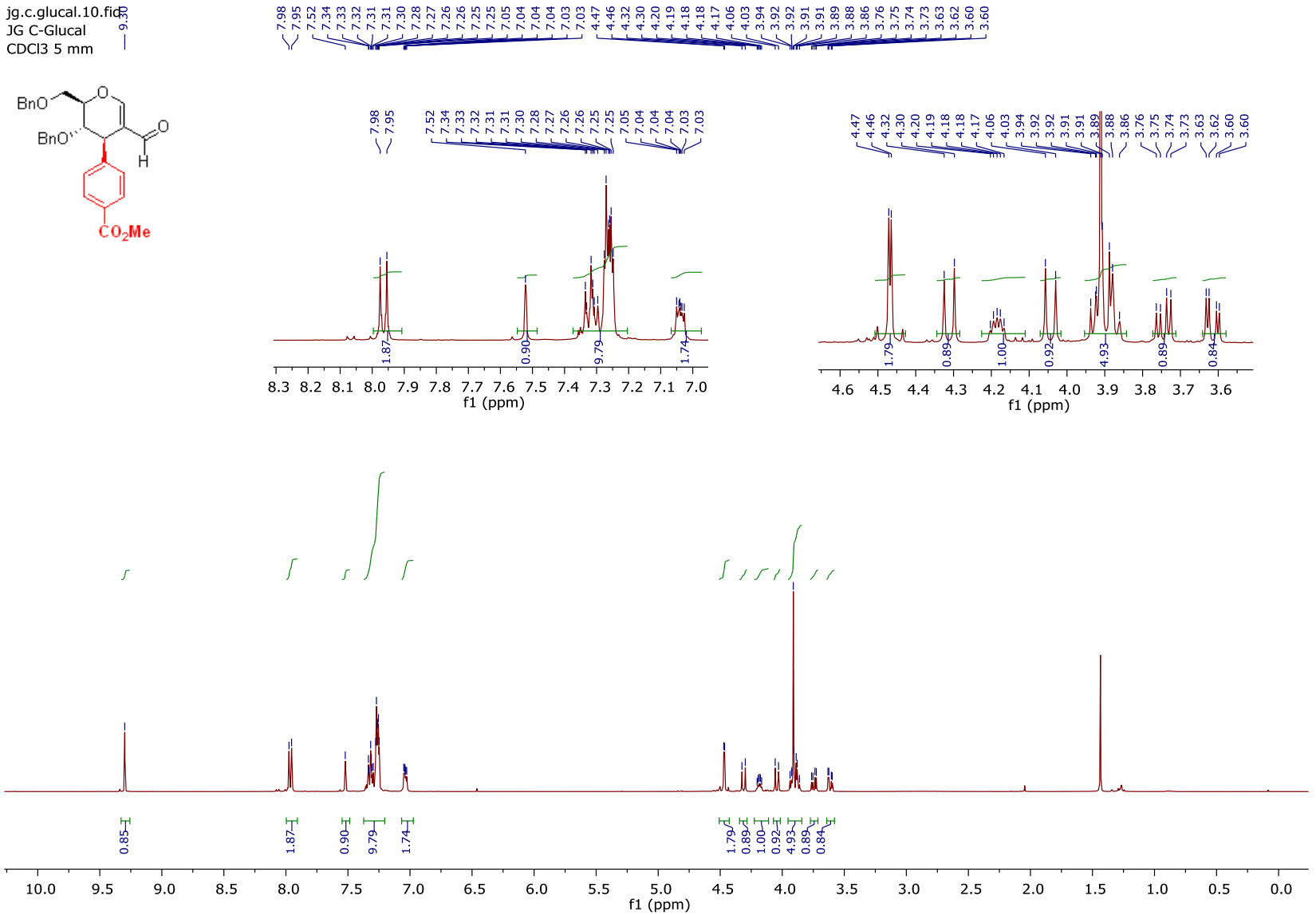
^{13}C NMR spectrum of **4f** (75 MHz, $CDCl_3$)



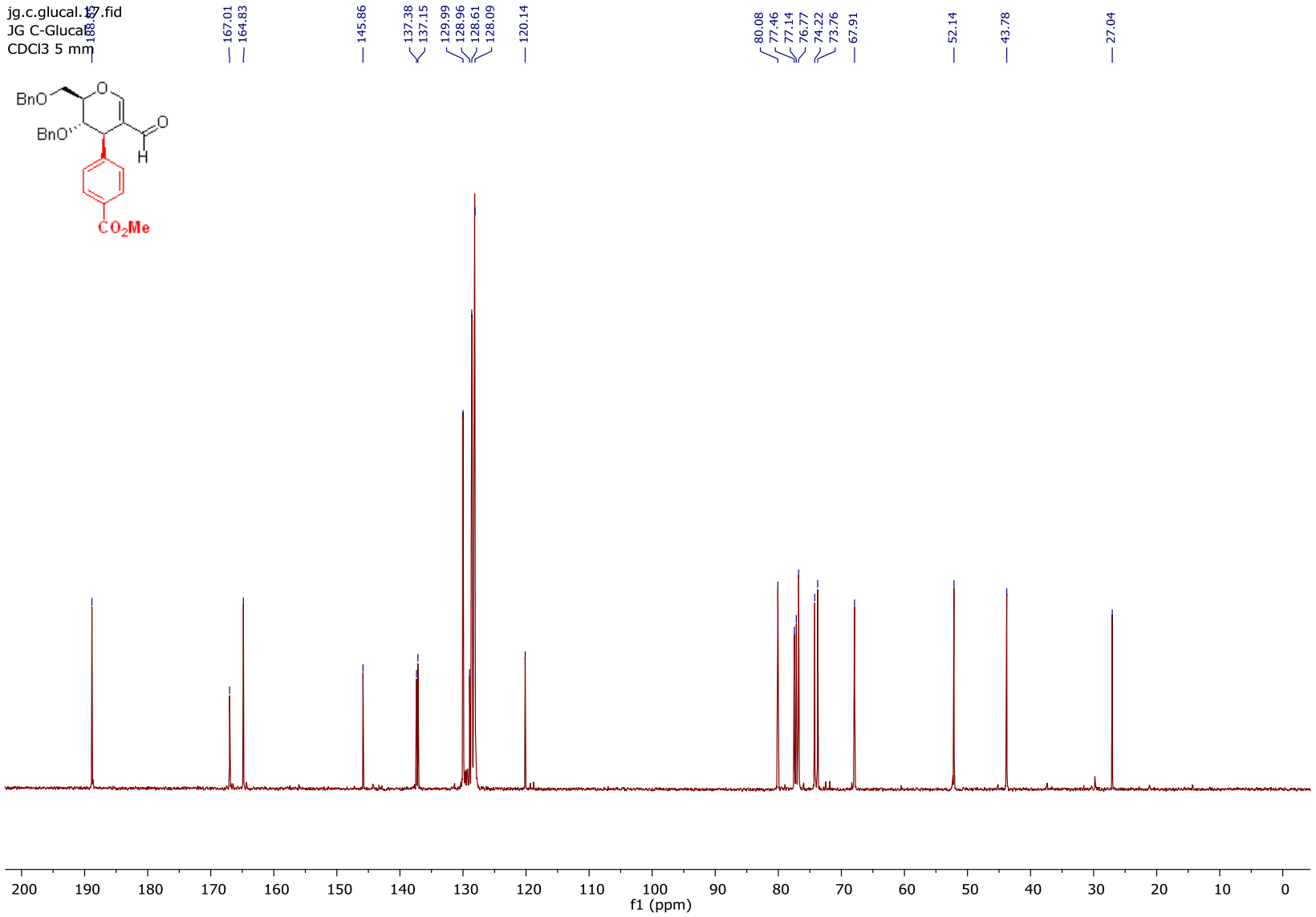
^{1}H NMR spectrum of **4g** (300 MHz, $CDCl_3$)



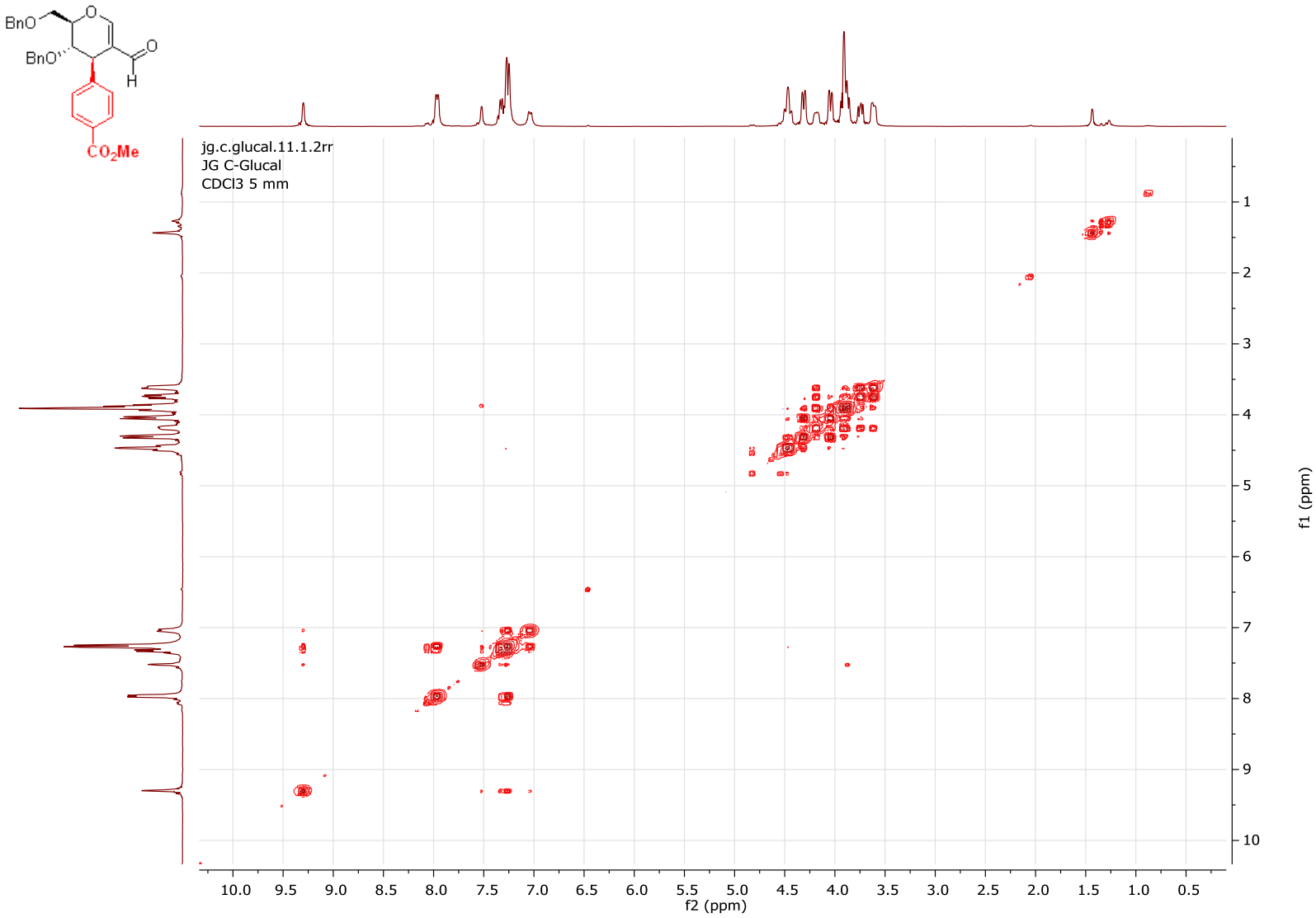
^{13}C NMR spectrum of **4g** (75 MHz, $CDCl_3$)

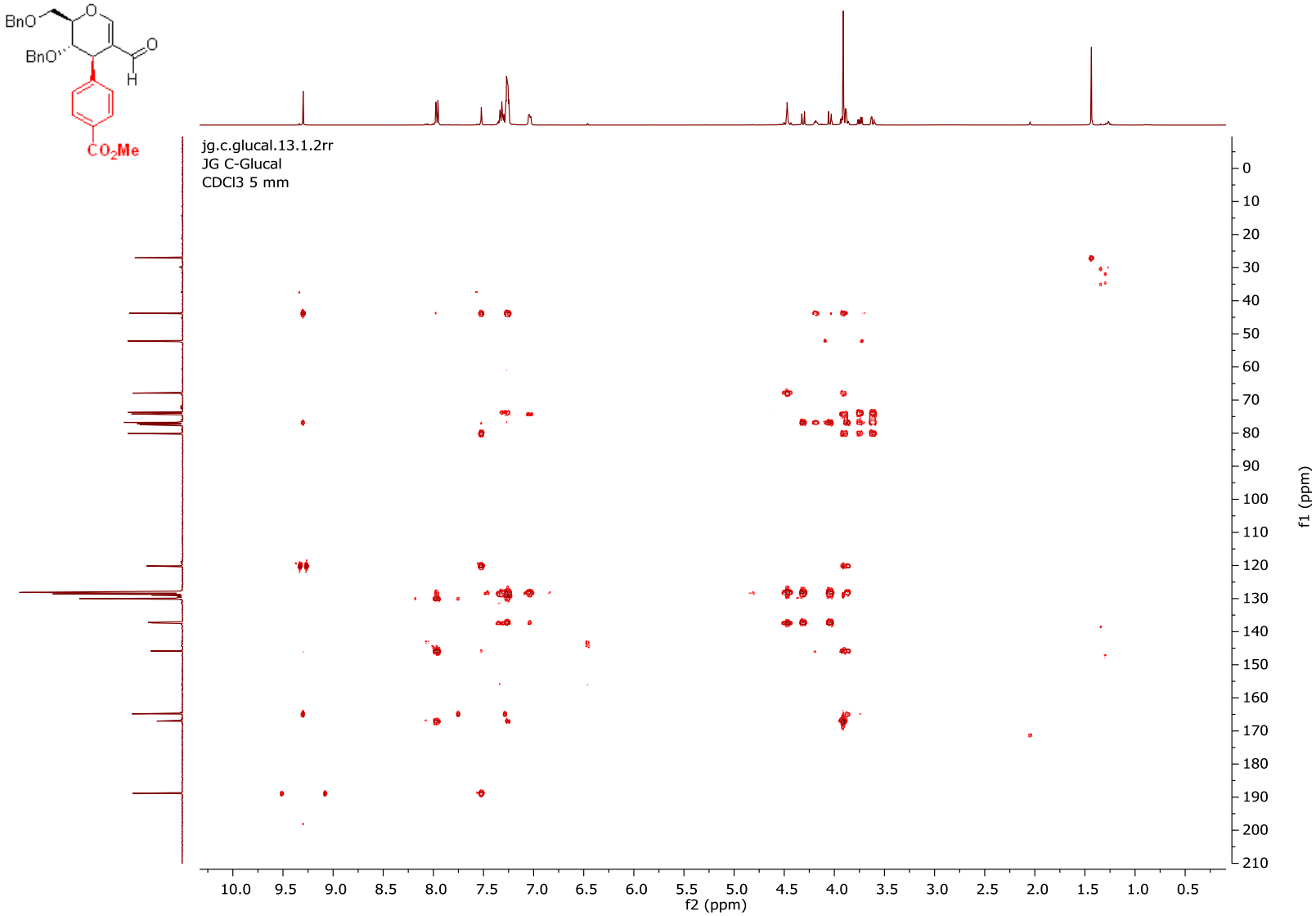


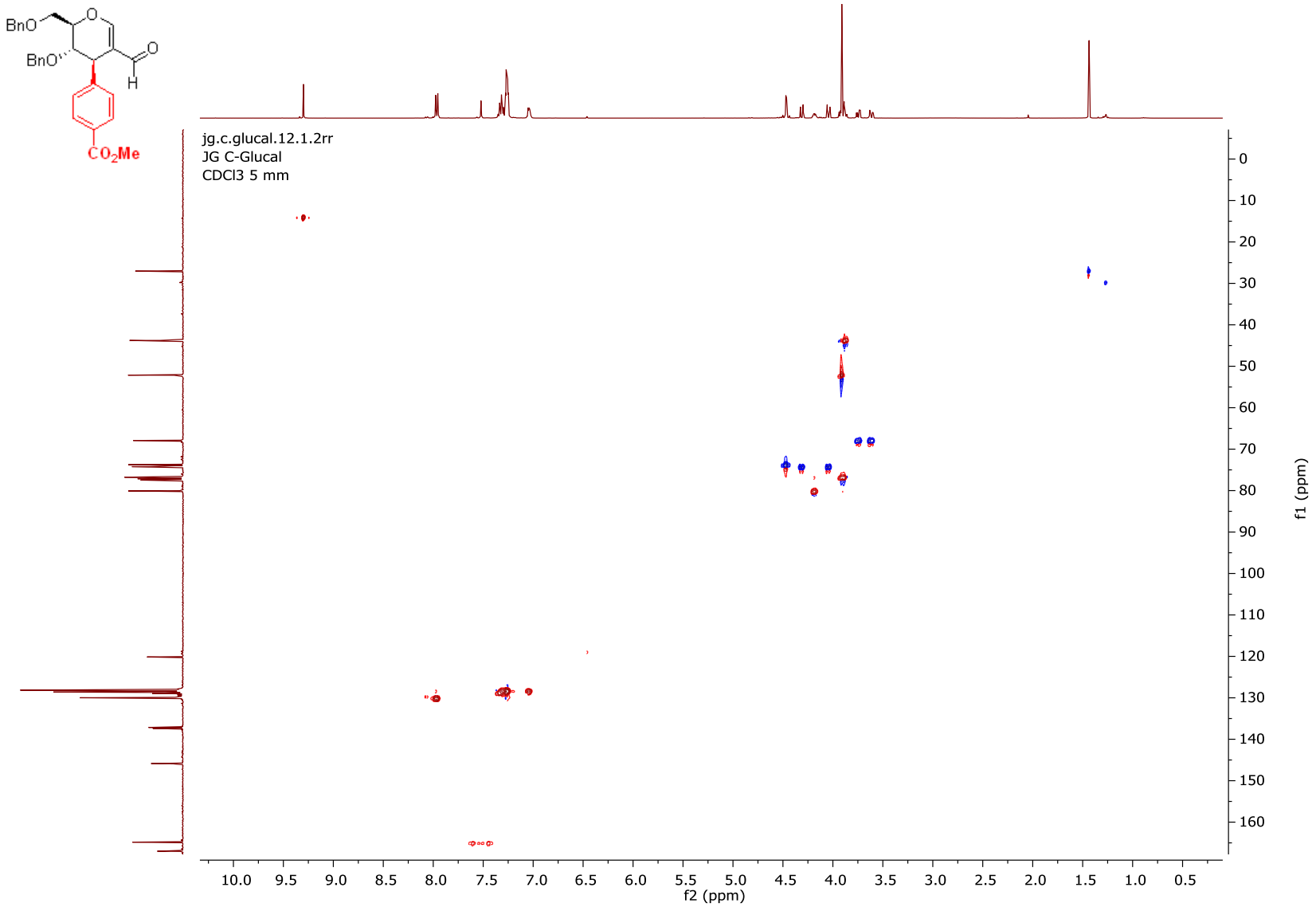
^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$)

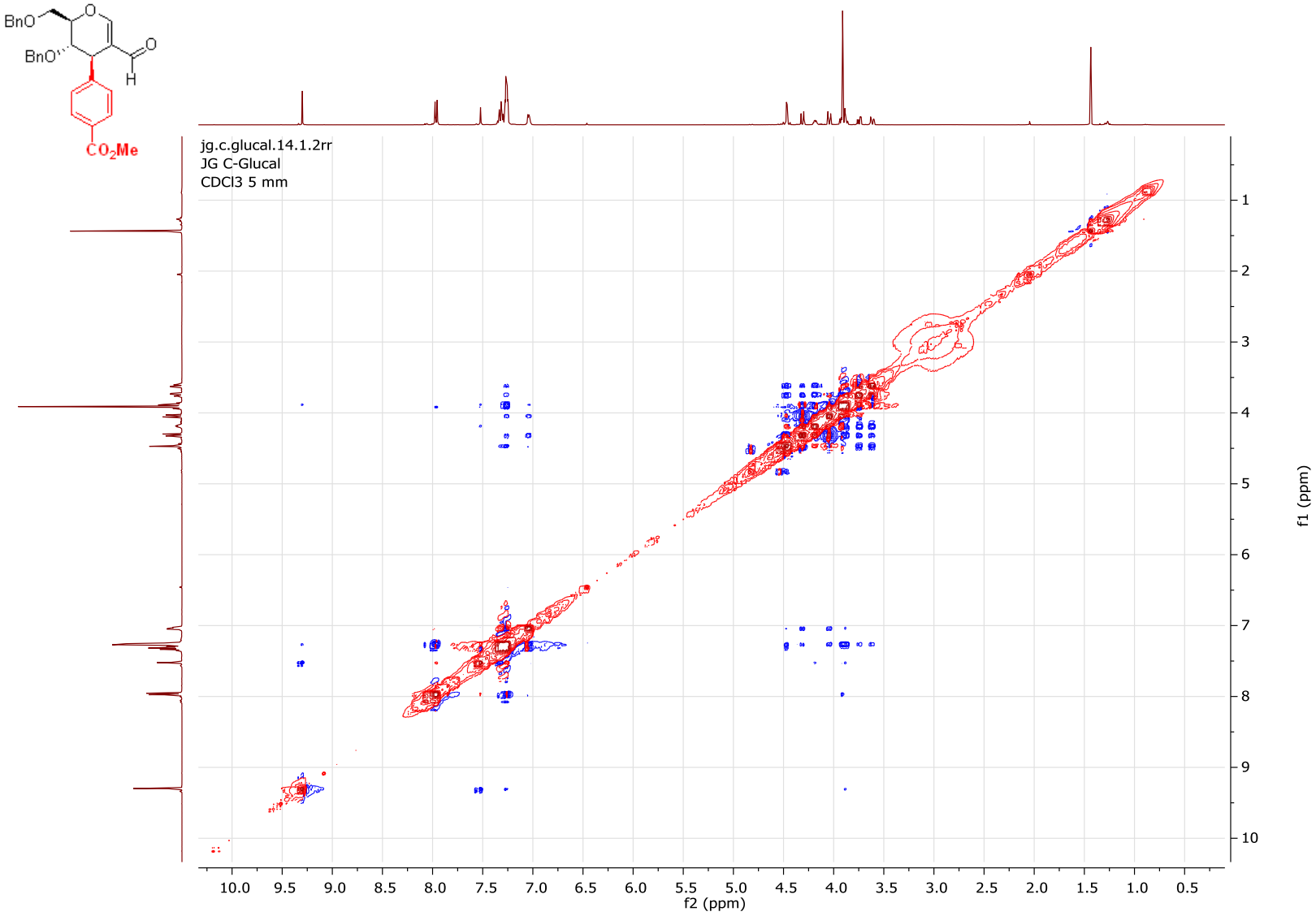


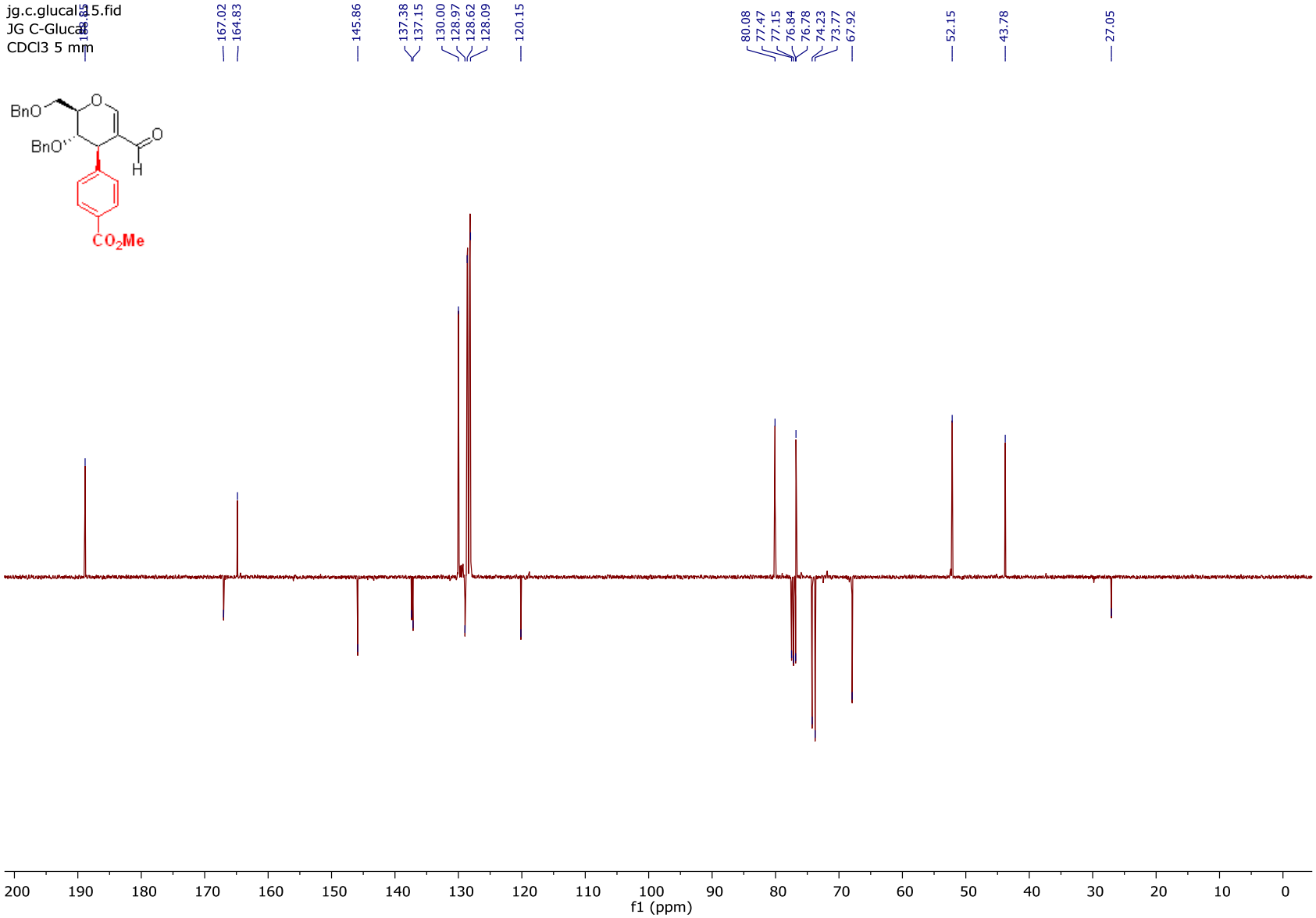
^{13}C NMR spectrum of **4h** (101 MHz, $CDCl_3$)

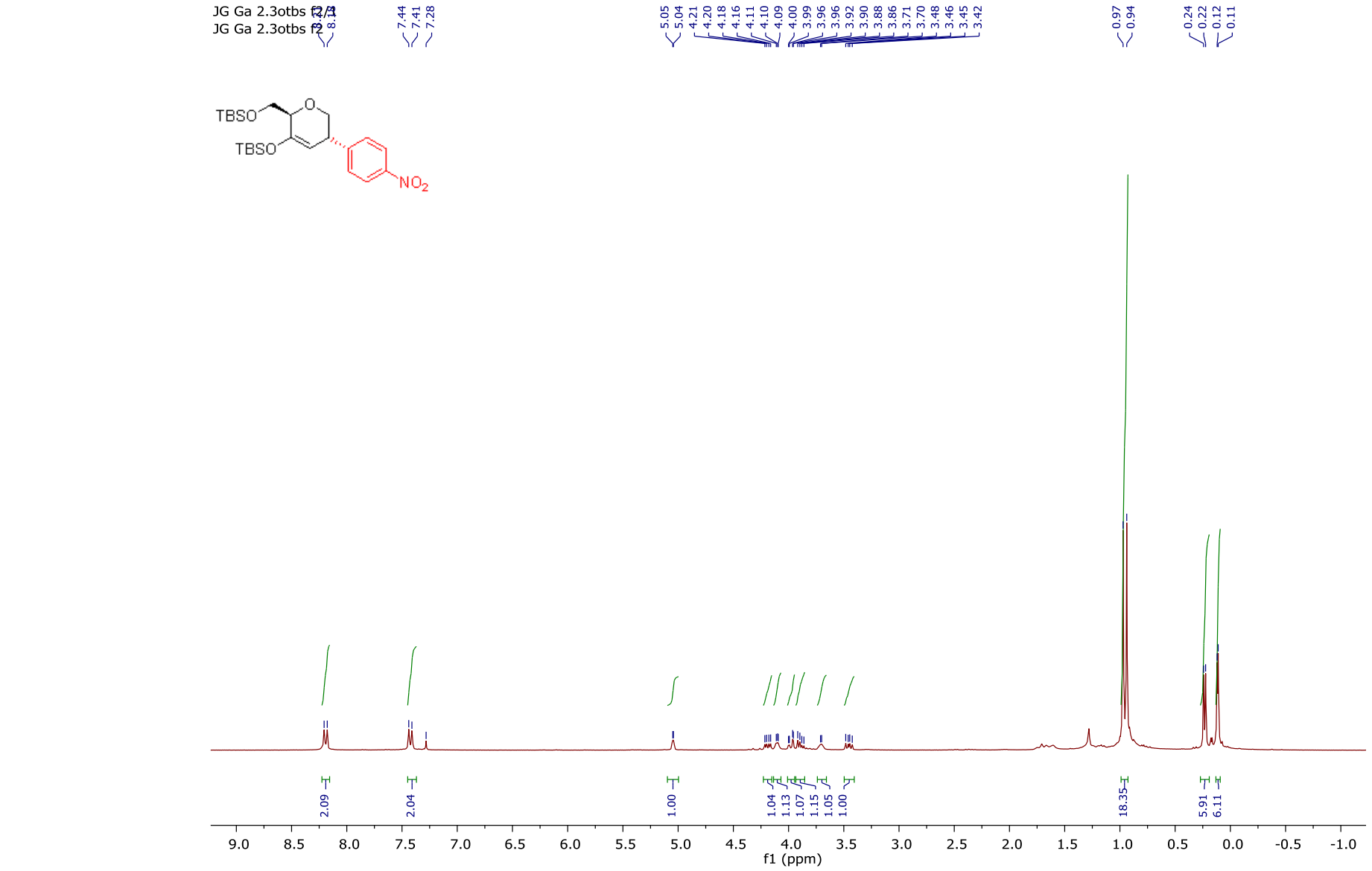

BnO
BnO
O
O
H
CO2Me
jg.c.glucal.11.1.2rr
JG C-Glucal
CDCl3 5 mm
f2 (ppm)
f1 (ppm)


BnO
BnO
O
O
H
CO2Me
jg.c.glucal.13.1.2rr
JG C-Glucal
CDCl3 5 mm
f2 (ppm)
f1 (ppm)

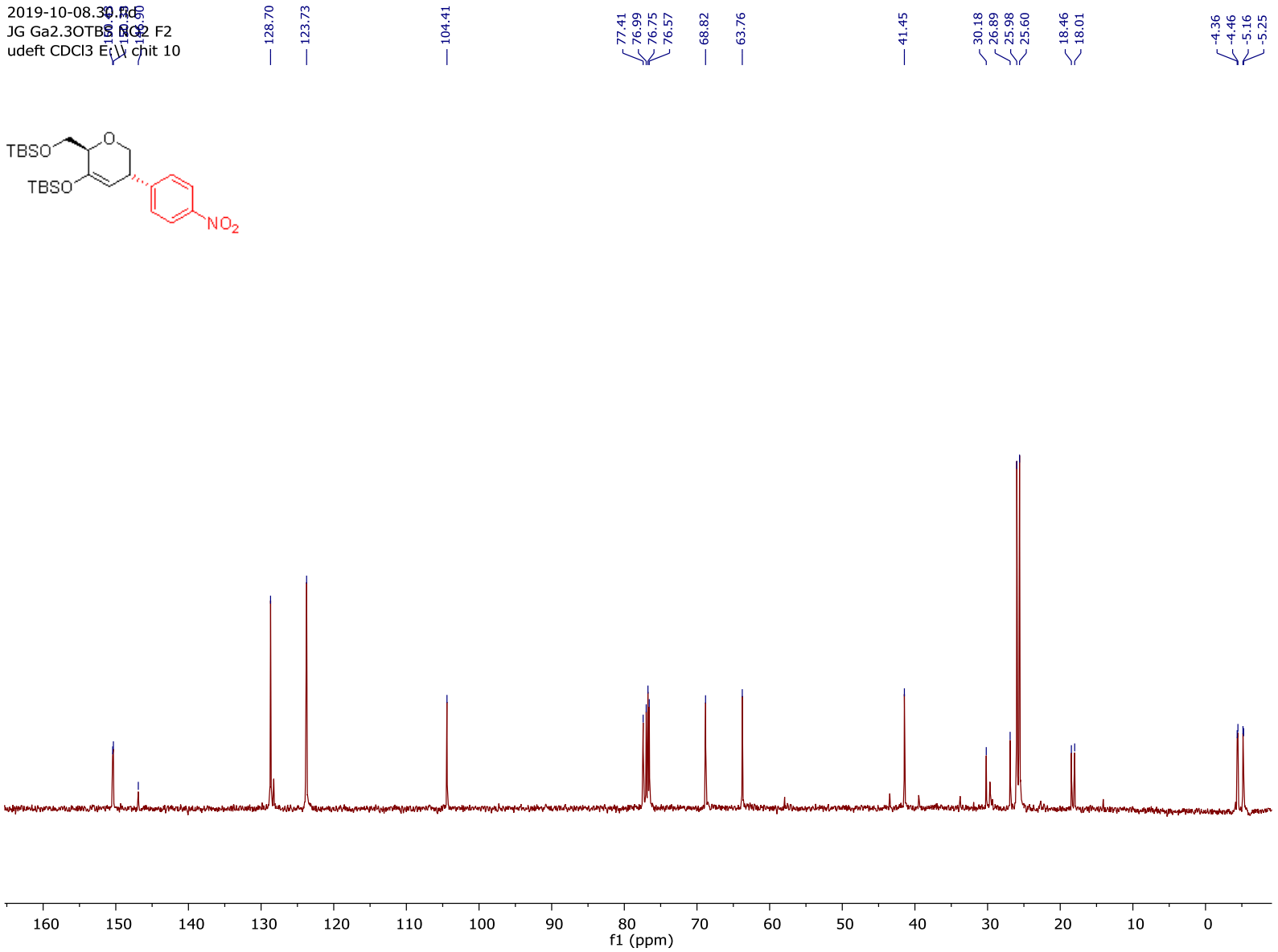

BnO
BnO
O
O
H
CO2Me
jg.c.glucal.12.1.2rr
JG C-Glucal
CDCl3 5 mm
f2 (ppm)
f1 (ppm)


BnO
BnO
O
H
CO2Me
jg.c.glucal.14.1.2rr
JG C-Glucal
CDCl3 5 mm
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f2 (ppm)
1 2 3 4 5 6 7 8 9 10
f1 (ppm)

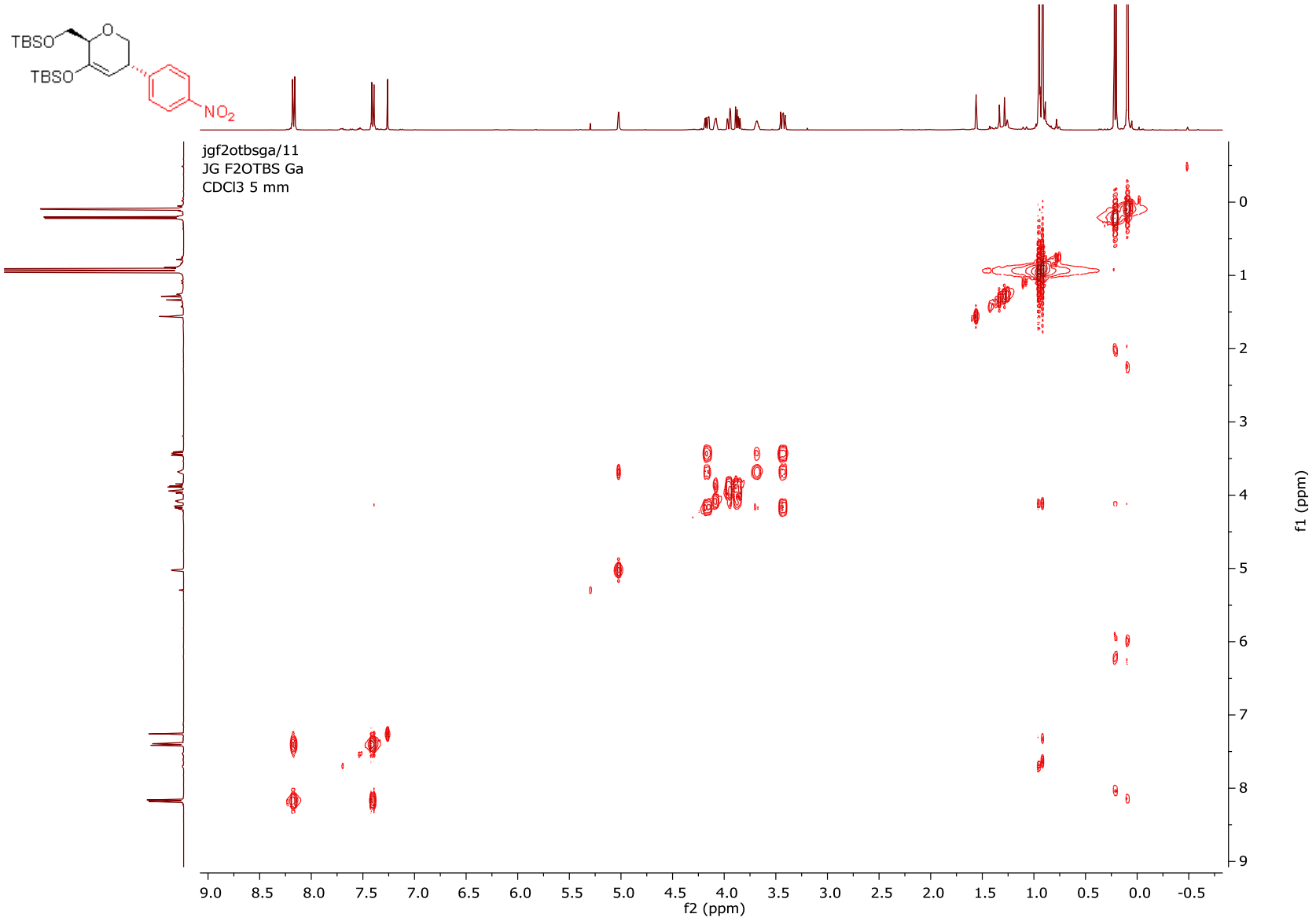

jg.c.glucal-15.fid
JG C-Glucal
CDCl3 5 mm
167.02
164.83
145.86
137.38
137.15
130.00
128.97
128.62
128.09
120.15
80.08
77.47
77.15
76.84
76.78
74.23
73.77
67.92
52.15
43.78
27.05
BnO
BnO
O
O
H
CO2Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

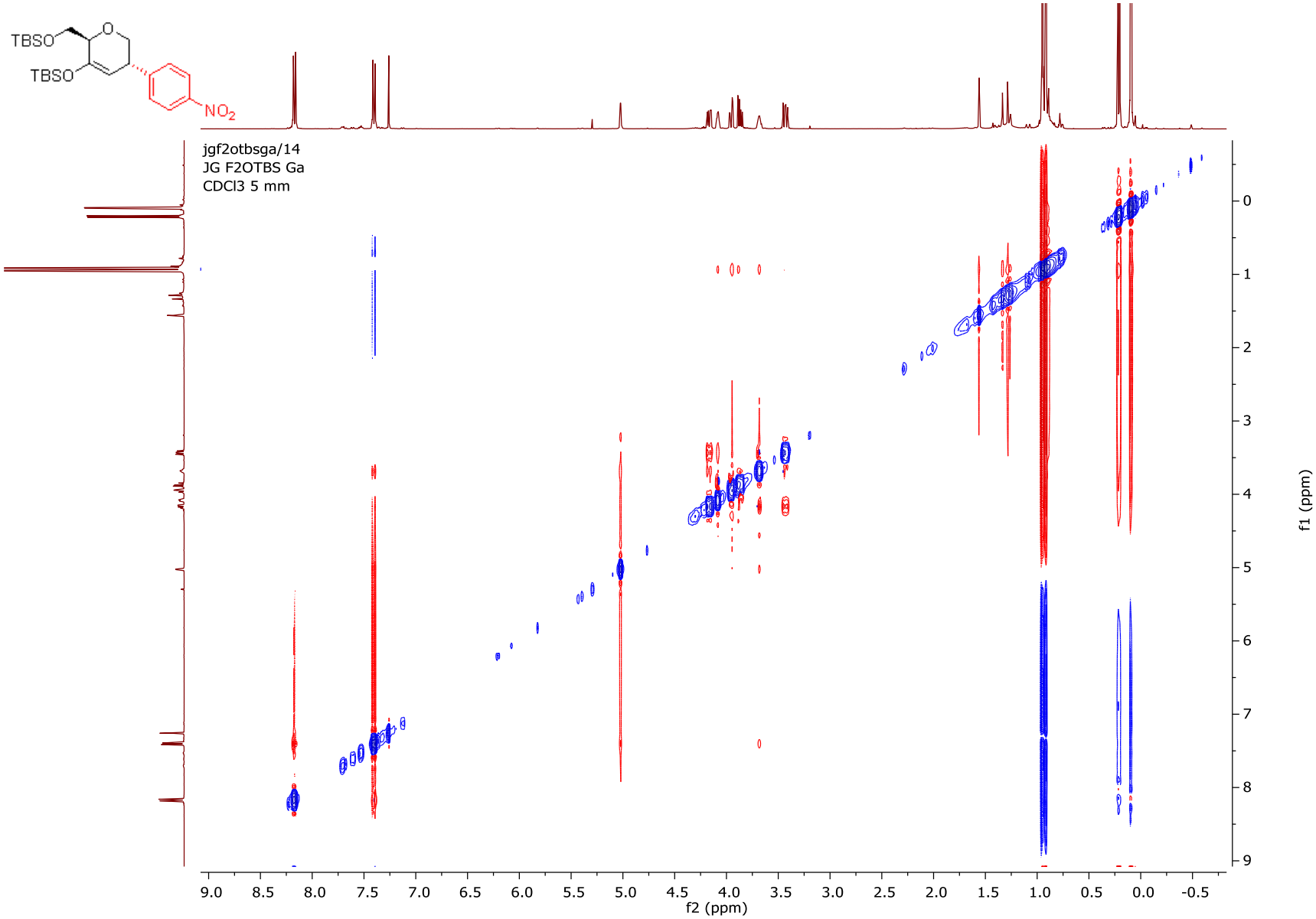


^{1}H NMR spectrum of **4i** (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of **4i** (75 MHz, $CDCl_3$)


TBSO
TBSO
O
NO2
jgf2otbsga/11
JG F2OTBS Ga
CDCl3 5 mm
f2 (ppm)
f1 (ppm)


TBSO
TBSO
O
NO2
jgf2otbsga/14
JG F2OTBS Ga
CDCl3 5 mm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)