Electronic Supplementary Information

for

Stimuli Responsive Asymmetric Catalysis by Triggered Pseudo-Enantiomeric Proligand Release

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General information:

Proton and carbon nuclear magnetic resonance (NMR) spectra were recorded on an Agilent Technologies 500 MHz spectrometer (^{1}H NMR at 500 MHz, ^{13}C NMR at 126 MHz, ^{19}F NMR at 470 MHz, ^{31}P NMR at 202.5 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the solvent (^{1}H NMR: $CHCl_3$ at 7.26 ppm, and D_2O at 4.90 ppm). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and, where available, are referenced to the carbon resonances of the deuterated solvent peak (^{13}C NMR: $CDCl_3$ at 77.0 ppm). Chemical shifts for fluorines are reported in parts per million downfield from trichlorofluoromethane. Chemical shifts for phosphorus' are reported in parts per million downfield from 85% H_3PO_4. NMR data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, dt = doublet of triplets, dq = double of quartets, ddt = doublet of doublet of triplets, m = multiplet), coupling constants (Hz), integration. IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrophotometer, with absorbencies quoted as ν in cm^{-1}. High resolution mass spectrometry was performed on an Agilent 6545 quadrupole time-of-flight (QTOF) mass spectrometer. Melting points were obtained on an OptiMelt MPA100 automated melting point system. Electrochemical analysis was performed on a Metrohm Autolab PGSTAT30 potentiostat. Analytical thin layer chromatography (TLC) were performed using aluminium-backed plates coated with Alugram® SIL G/UV254 purchased from Macherey-Nagel and visualised by UV light (254 nm). Silica gel column chromatography was carried out using 60 Å, 200-400 mesh particle size silica gel purchased from Sigma-Aldrich. Analytical high performance liquid chromatography was performed on an Agilent 1260 Infinity Binary LC using a Chiralcel OJ, OD or OB-H column. Preparative flash chromatography was performed on a CombiFlash NextGen 300+ using RediSep® Rf preparative columns.

Materials:

All reactions were carried out under an ambient atmosphere, in oven-dried glassware unless otherwise stated. Dichloromethane (DCM), tetrahydrofuran (THF), and toluene were dried and degassed by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system and stored under an atmosphere of nitrogen prior to use. All substrates and reagents were used as received from commercial suppliers or prepared according to published procedures, respectively, unless otherwise stated. Manganese dioxide was activated before use by stirring in concentrated nitric acid, before filtering, washing and drying.

Desktop Electrochemical analysis:

Electrochemical analysis was performed by applying a 20 µL sample to screen-printed electrochemical cell equipped with carbon working and counter electrodes and a silver (pseudo Ag/AgCl) reference electrode. The potential across the cell was powered by a Metrohm Autolab PGSTAT30 potentiostat controlled by a laptop running General Purpose Electrochemical System (GPES) software in differential pulse mode (modulation = 0.04 s, interval = 0.1 s, initial voltage = −300 mV, end voltage = 700 mV, step potential = 3 mV, modulation amplitude 49.95 mV). Post-scan, a baseline correction (moving average: peak width = 0.03) was erformed. Peak integrals were obtained using the 'peak search' function.

Phosgene Reactions

The reactions were carried out in a two-necked flask complete with magnetic stirrer bar, and nitrogen line at 0 °C. The output line was bubbled through a 1M NaOH (aq.) trap to quench any phosgene vapour, and the reaction conducted at 0 °C to prevent phosgene evaporation. After use glassware was washed with sat. $NaHCO_3$ (aq.) to remove any residual phosgene.

Calibration Curve

Due to the activated nature of the ketone with the strongly electron withdrawing trifluoromethyl group, the voltammogram exhibited two peaks. This was proposed to be hemiacetal formation in the nucleophilic solvent system. Comparative ^{19}F NMR spectra in a non-nucleophilic ($CDCl_3$) solvent and in nucleophilic solvent (MeOD-d_4) showed the formation of a second fluorine peak. To account for this a calibration curve was recorded and trendline fitted. Conversions were obtained using equation **1**.

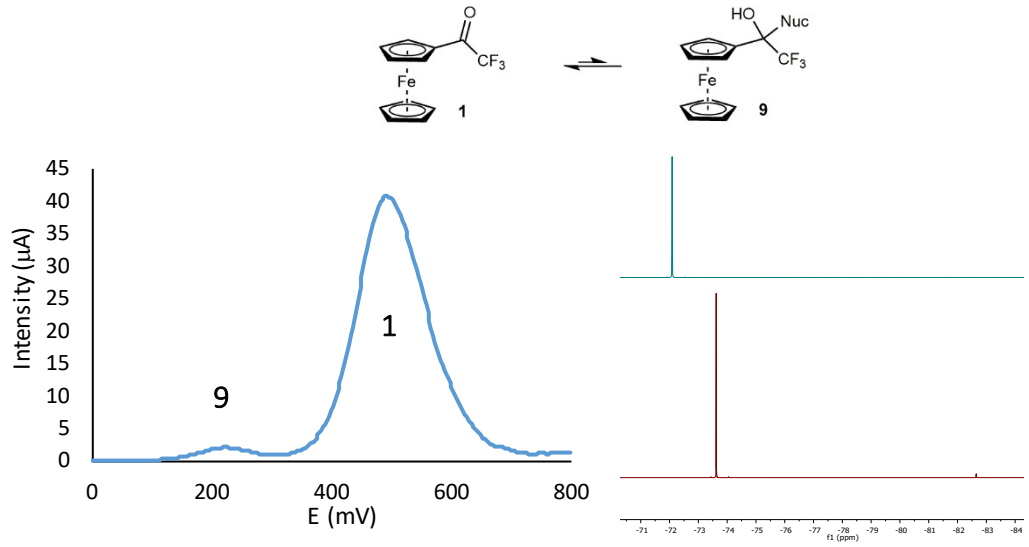

Figure **S1**– (a) Voltammogram of trifluoroacetyl ferrocene **1** (0.1 mM) in 1:1 mix of MeOH (0.05 mL) and tris buffer (pH 7, 50 mM, 0.05 mL); (b) top: ^{19}F NMR of **1** in $CDCl_3$; bottom: ^{19}F NMR of **1** in MeOD-d_4.

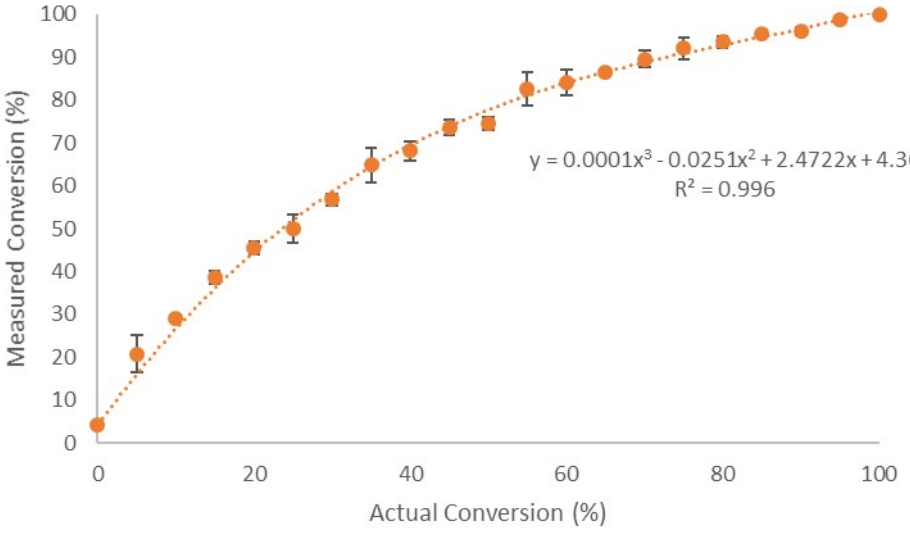

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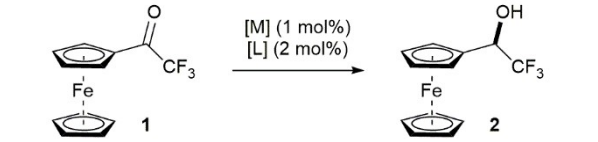
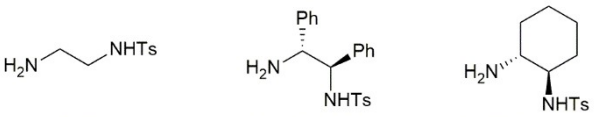
Figure **S2** – Calibration curve calculated for trifluoroacetyl ferrocene **1** (125 µM) and 1-ferrocenyl-2,2,2-trifluoroethanol **2** (125 µM) in 50 mM pH 7.8 tris buffer. Error bars represent the standard deviation where n = 3.

$Eqn.\ 1: y = 0.0001\,x^3 - 0.0251\,x^2 + 2.4722\,x + 4.36$

Initial Catalyst Optimisation

To a medium screw-top vial equipped with a magnetic flea was added metal catalyst (1 mol %), ligand (2 mol %) and sodium formate (170 mg, 2.5 mmol, 5 eq.) and dissolved in water (1 mL). Trifluoroacetyl ferrocene **1** (141mg, 0.5 mmol, 1 eq.) in ethanol (1 mL) was then added. The reaction was stirred at 1000 rpm for 2-16 h. The reaction mixture was poured onto water (20 mL) and EtOAc (20 mL). The organic layer was separated, and the aqueous layer extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with water (20 mL), brine (20 mL), then dried over $MgSO_4$ and concentrated under reduced pressure. Purification via silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc) afforded the title compound as an orange solid. Enantiomeric ratios were measured *via* HPLC.



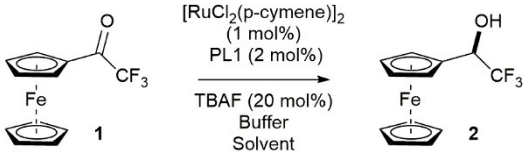


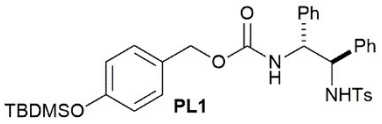
	CATALYST	LIGAND	YIELD (%)	e.r.
1	$[IrCl_2Cp^*]_2$	Ts-EN	94	-
2	$[IrCl_2Cp^*]_2$	(*R*,*R*)-Ts-DPEN	94	72:28
3	$[IrCl_2Cp^*]_2$	(*R*,*R*)-Ts-CYDN	84	78:22
4	$[RhCl_2Cp^*]_2$	Ts-EN	91	-
5	$[RhCl_2Cp^*]_2$	(*R*,*R*)-Ts-DPEN	96	67:33
6	$[RuCl_2(p\text{-cymene})]_2$	Ts-EN	NR	-
7	$[RuCl_2(p\text{-cymene})]_2$	(*R*,*R*)-Ts-DPEN	84	87:13
8	$[RuCl_2(p\text{-cymene})]_2$	(*R*,*R*)-Ts-CYDN	<5[b]	88:12
9	$[RuCl_2(p\text{-cymene})]_2$	-	1	N/A
10	-	(*R*,*R*)-Ts-DPEN	NR	N/A

Table **S1** – **1** (0.5 mmol), [M] (1 mol %), [L] (2 mol %), NaOOCH (5 equiv.), water (1 mL), ethanol (1 mL), 25 °C, air, 4–16h.

Initial Reaction Optimisation

To a medium screw-top vial equipped with a magnetic flea was added dichloro(cyclopentadienyl)ruthenium(II) dimer (1 mg, 1.25 μmol, 1 mol %), sodium formate (42 mg, 625 μmol, 5 eq.), 4-((*tert*-butyldimethylsilyl)oxy)benzyl (2-((4-methylphenyl)sulfonamido)-1,2-diphenylethyl)carbamate (1.6 mg, 2.5 μmol, 2 mol %), and trifluoroacetyl ferrocene (35 mg, 125 μmol, 1 eq.) were dissolved in solvent (0.5 mL) and buffer (0.5 mL). Tetrabutylammonium fluoride (1 M in THF, 25 μL, 25 μmol, 20 mol %) was added, and the reaction was stirred at 1000 rpm at room temperature for 16 h. A 5 μL sample was taken after 16h and diluted in MeOH 1:1 water (95 μL) and shaken. A 5 μl sample was diluted in tris buffer (pH 7, 50 mM, 95 μL) and subjected to electrochemical analysis.





	SOLVENT	BUFFER	PH	CONVERSION (%)[A]	BACKGROUND (%)[A]
1	MeOH	Water	-	100	15
2	EtOH	Water	-	43	30
3	*i*-PrOH	Water	-	48	16
4	MeCN	Water	-	44	-
5	THF	Water	-	21	-
6	DMSO	Water	-	45	-
7	DMF	Water	-	49	42
8	Dioxane	Water	-	29	-
9	*i*-PrOH	Tris	9	26	13
10	*i*-PrOH	Borate	9	100	39
11	*i*-PrOH	CO_3^{2-}	9.8	33	18
12	*i*-PrOH	CO_3^{2-}	9.2	100	7
13	*i*-PrOH	CO_3^{2-}	9.5	40	-
14	*i*-PrOH	CO_3^{2-}	10.1	100	33
15	*i*-PrOH	CO_3^{2-}	10.4	100	37
16	*i*-PrOH	CO_3^{2-}	10.7	24	-

Table **S2** – Reaction conditions: **1** (0.125 mmol), $[RuCl_2(p\text{-cymene}]_2$ (1 mol %), **PL1** (2 mol %), NaOOCH (5 equiv.), buffer (50 mM, 0.5 mL), solvent (0.5 mL), TBAF in THF (1 M, 20 mol %), 25 °C, air, 16h; [a]Determined *via* DPV.

Stability of Proligand

Stability of PL1

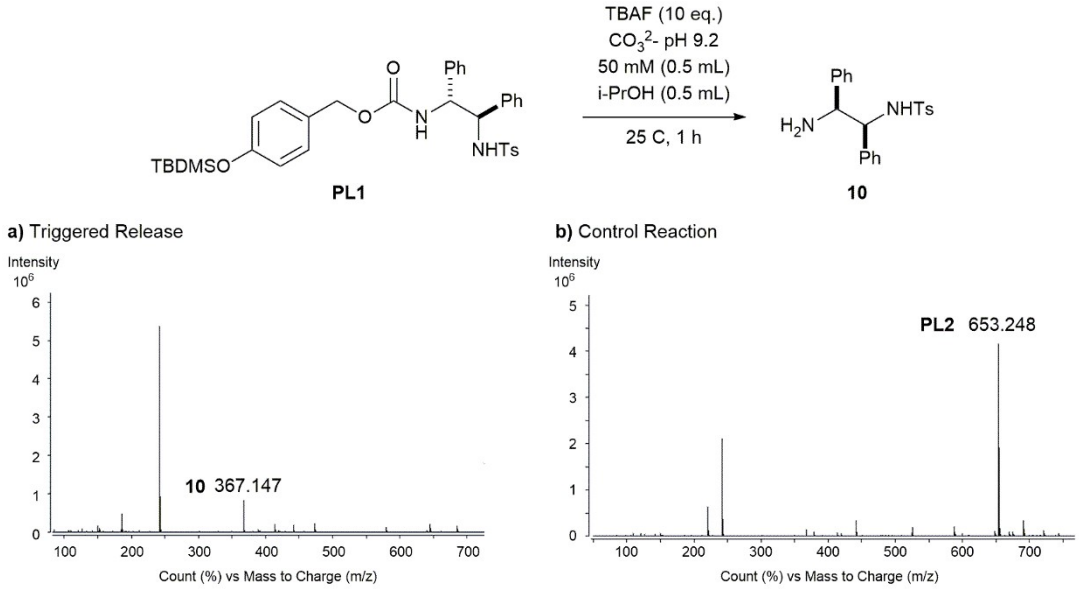


Figure **S3** – a) Triggered release of **PL1** with TBAF, ESI-MS obtained after 1 h; b) control reaction of **PL1** without TBAF, ESI-MS obtained after 1 h.

Stability of *S*-PL2

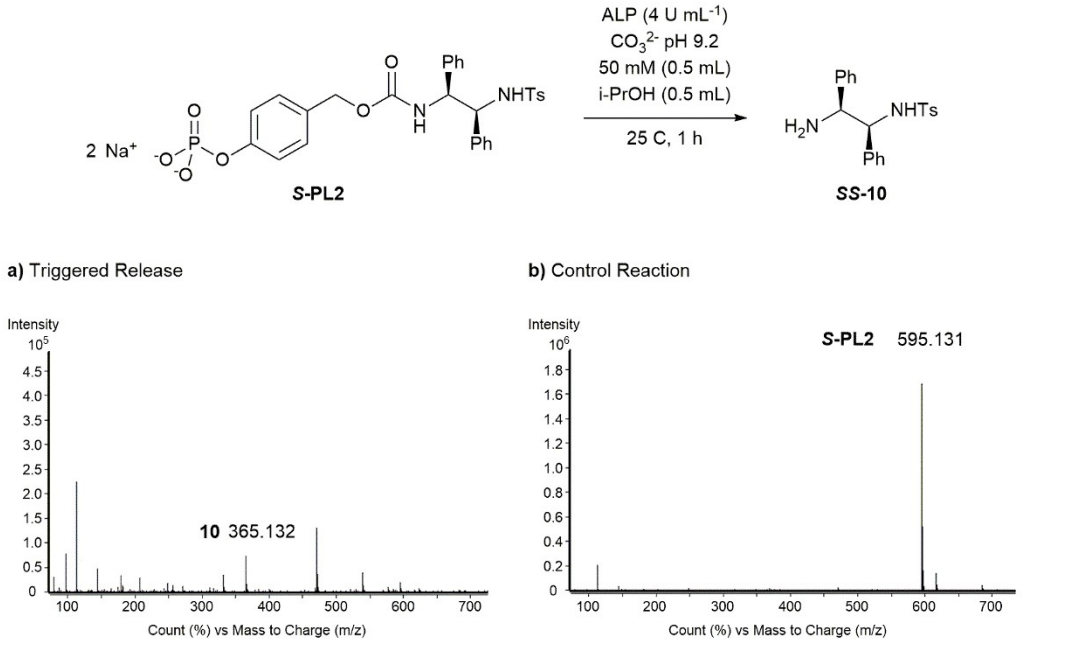
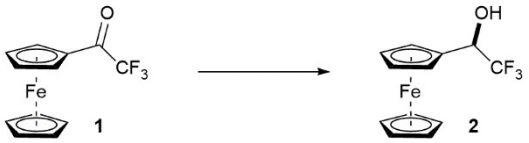


Figure **S4** – a) Triggered release of ***S*-PL2** with ALP, ESI-MS obtained after 1 h; b) control reaction of ***S*-PL2** without ALP, ESI-MS obtained after 1 h.

Catalytic Systems

Single Pseudo-enantiomeric Proligand System – *R*-PL1

1-ferrocenyl-2,2,2-trifluoroethanol 2

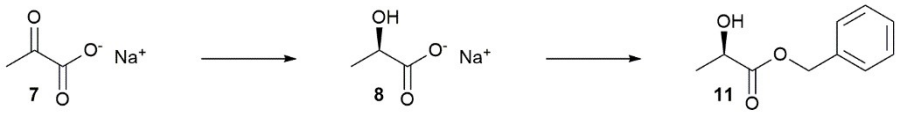


To a medium screw-top vial equipped with a magnetic flea was added dichloro(*p*-cymene)ruthenium(II) dimer (1 mg, 1.25 μmol, 1 mol %), sodium formate (42 mg, 625 μmol, 5 eq.), 4-((*tert*-butyldimethylsilyl)oxy)benzyl (2-((4-methylphenyl)sulfonamido)-*R*,*R*-1,2-diphenylethyl) carbamate ***R*-PL1** (1.6 mg, 2.5 μmol, 2 mol %), and trifluoroacetyl ferrocene **1** (35 mg, 125 μmol, 1 eq.) were dissolved in *i*-PrOH (0.5 mL) and carbonate buffer (pH 9.2, 50 mM, 0.5 mL). Tetrabutylammonium fluoride (1 M in THF, 25 μL, 25 μmol, 20 mol %) was added, and the reaction was stirred at 1000 rpm at room temperature for 16 h. A 5 μL sample was taken after 16h and diluted in MeOH 1:1 water (95 μL) and shaken. A 5 μl sample was diluted in tris buffer (pH 7, 50 mM, 95 μL) and subjected to electrochemical analysis. The reaction mixture was poured onto water (10 mL) and EtOAc (10 mL). The organic layer was separated, and the aqueous layer extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), then dried over $MgSO_4$ and concentrated under reduced pressure. Purification via silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc) gave the title compound **2** as an orange solid. Enantiomeric ratio determined by HPLC analysis (Chiracel OJ: hexane/*i*-PrOH = 100:0 → 95:5 ramp 35 min, 95/5 constant 5 min, 95:5 → 100:0 ramp 5 min, 0 → 0.8 mL/min, 250 nm, 20 °C). Retention time: t_1 = 29.4 min, t_2 = 33.4 min.

1-phenylethanol 6

To a medium screw-top vial equipped with a magnetic flea was added dichloro(*p*-cymene)ruthenium(II) dimer (3.1 mg, 5 μmol, 2 mol %), sodium formate (85 mg, 1.25 mmol, 5 eq.), 4-((*tert*-butyldimethylsilyl)oxy)benzyl (2-((4-methylphenyl)sulfonamido)-*R*,*R*-1,2-diphenylethyl) carbamate ***R*-PL1** (6.3 mg, 10 μmol, 4 mol %) and acetophenone **5** (29 μl, 250 μmol, 1 eq.) were dissolved in *i*-PrOH (1 mL) and carbonate buffer (pH 9.2, 50 mM, 1 mL). Tetrabutylammonium fluoride (1 M in THF, 100 μL, 100 μmol, 40 mol %) was added and the reaction was stirred at 1000 rpm at 25 °C for 24 h. The reaction mixture was poured onto water (10 mL) and EtOAc (10 mL). The organic layer was separated, and the aqueous layer extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), then dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was then analysed by ^{1}H NMR to obtain conversions. Purification via silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc) gave the title compound **6** as a colourless oil. Enantiomeric ratio determined by HPLC analysis (Chiracel OD: hexane/*i*-PrOH = 95:5 25 min, 0.5 mL/min, 254 nm, 20 °C). Retention time: t_1 = 15.8 min, t_2 = 19.9 min.

Benzyl 2-hydroxypropanoate 11



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dissolved in *i*-PrOH (1 mL) and carbonate buffer (pH 9.2, 50 mM, 1 mL). Tetrabutylammonium fluoride (1 M in THF, 100 µL, 100 µmol, 40 mol %) was added and the reaction was stirred at 1000 rpm at 25 °C for 24 h. The reaction mixture was poured onto water (10 mL) and EtOAc (10 mL). The aqueous layer was separated, and the organic layer extracted with water (2 × 10 mL). The combined aqueous layers were concentrated under reduced pressure, and the crude residue of **8** analysed by ^{1}H NMR to obtain conversions. The residue was dissolved in DMF (0.5 mL) and cooled to 0 °C. Benzyl bromide (0.06 mL, 0.5 mmol, 1 eq.) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 18 h, after which Et_2O (10 mL) was added. Sat. LiCl (10 mL) was added and the organic layer separated. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organic layers were washed with sat. $NaHCO_3$ (10 mL), brine (10 mL), then dried over $MgSO_4$ and the solvent was removed *in vacuo*. Purification *via* silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc) afforded the title compound **11** as a colourless oil. Enantiomeric ratio determined by HPLC analysis (Chiracel OB-H: hexane/*i*-PrOH = 95:5 40 min, 0.5 mL/min, 254 nm, 20 °C). Retention time: t_1 = 29.0 min, t_2 = 30.1 min.

Single Pseudo-enantiomeric Proligand System – PL2

1-ferrocenyl-2,2,2-trifluoroethanol 2

To a medium screw-top vial equipped with a magnetic flea was added dichloro(*p*-cymene)ruthenium(II) dimer (1 mg, 1.25 µmol, 1 mol %), sodium formate (42 mg, 625 µmol, 5 eq.), disodium 4-(((((1*S*,2*S*)-2-((4-methylphenyl)sulfonamido)-1,2-diphenylethyl)carbamoyl)oxy) methyl)phenyl phosphate ***S*-PL2** (1.6 mg, 2.5 µmol, 2 mol %), and trifluoroacetyl ferrocene (35 mg, 125 µmol, 1 eq.) were dissolved in *i*-PrOH (0.5 mL) and carbonate buffer (pH 9.2, 50 mM, 0.5 mL). Alkaline phosphatase ALP (1 mg, 10 units mg^{-1}) was added, and the reaction was stirred at 1000 rpm at room temperature for 16 h. A 5 µL sample was taken after 16h and diluted in MeOH 1:1 water (95 µL) and shaken. A 5 µl sample was diluted in tris buffer (pH 7, 50 mM, 95 µL) and subjected to electrochemical analysis. The reaction mixture was poured onto water (10 mL) and EtOAc (10 mL). The organic layer was separated, and the aqueous layer extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), then dried over $MgSO_4$ and concentrated under reduced pressure. Purification via silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc) afforded the title compound **2** as an orange solid. Enantiomeric ratio determined by HPLC analysis (Chiracel OJ: hexane/*i*-PrOH = 100:0 → 95:5 ramp 35 min, 95/5 constant 5 min, 95:5 → 100:0 ramp 5 min, 0 → 0.8 mL/min, 250 nm, 20 °C). Retention time: t_1 = 29.4 min, t_2 = 33.4 min.

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1-phenylethanol 6

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Benzyl 2-hydroxypropanoate 11

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Triggered Release of *R*-PL1 and *S*-PL2

Release profile of *R*-PL1 and *S*-PL2

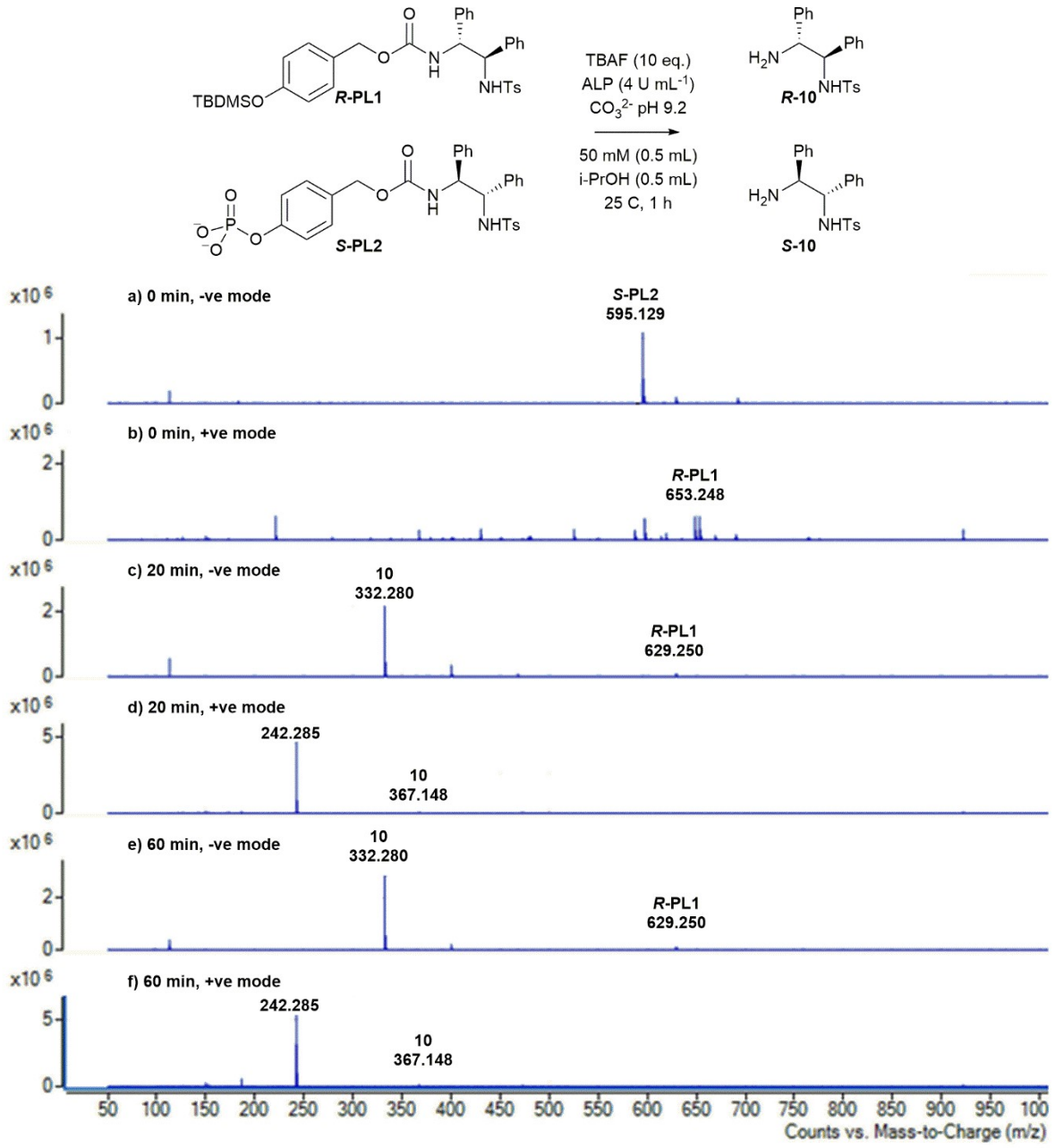
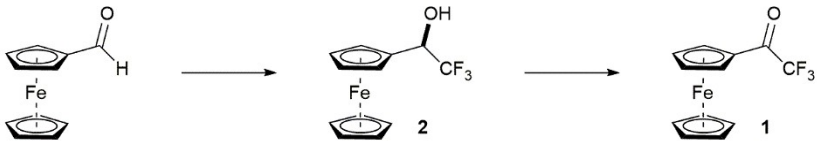


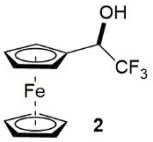
Figure **S5** – Triggered release of ***R*-PL1** and ***S*-PL2** with TBAF and ALP. a) -ve ESI-MS at 0 min; b) +ve ESI-MS at 0 min; c) -ve ESI-MS at 20 min; d) +ve ESI-MS at 20 min; e) -ve ESI-MS at 60 min; f) +ve ESI-MS at 60 min.

Compound Data

Synthetic route to trifluoroacetyl ferrocene



1-ferrocenyl-2,2,2-trifluoroethanol 2



Ferrocene carboxaldehyde (1.0 g, 4.67 mmol, 1 eq.) and caesium fluoride (0.14 g, 0.93 mmol, 0.2 eq.) were suspended in anhydrous THF (50 mL) under N_2 and cooled to 0 °C. $TMSCF_3$ (0.83 mL, 5.60 mmol, 1.2 eq) was then added dropwise and stirred for 30 min. The solvent was removed under reduced pressure and the crude product was passed through a silica plug (DCM 95:5 MeOH). The crude product was taken up in dry THF (25 mL) under N_2 and cooled to 0 °C. TBAF (5.6 mL, 1 M in THF, 1.2 eq.) was then added dropwise, and the reaction was stirred for 1 h after which water (15 mL) and Et_2O (10 mL) were added. The organic layer was separated and the aqueous layer extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with brine (10 mL), then dried over $MgSO_4$ and the solvent removed *in vacuo*. Purification *via* silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc (R_f = 0.46)) gave the title compound as an orange crystalline solid (1.27 g, 97%).

Mp; 79-82 °C (lit.[1] 73–74 °C).

^{1}H NMR (500 MHz, $CDCl_3$); 4.63 (p, *J* 6.2, 1 H), 4.41 (s, 1 H), 4.37 – 4.24 (m, 7 H), 2.43 (d, *J* 4.8, 1 H).

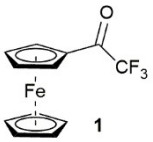
^{13}C NMR (126 MHz, $CDCl_3$); 124.0 (m), 83.8, 69.4, 69.2, 69.0, 66.3.

^{19}F NMR (470 MHz, $CDCl_3$); -78.12 (d, *J* 6.5).

IR (solid, cm^{-1}); ν_{max} 3458, 3101, 2922, 2103, 1655, 1410.

Data in accordance with literature precedent.[1]

Trifluoroacetyl ferrocene 1



1-ferrocenyl-2,2,2-trifluoroethanol 2 (1.02 g, 3.59 mmol, 1 eq.) was added to toluene (40 mL). Activated MnO_2 (3.13 g, 36 mmol, 10 eq.) was added in one portion and the reaction was stirred at 60 °C for 24 h. The reaction mixture was filtered and the precipitate was washed with EtOAc (20 mL) and water (50 mL). The filtrate and washings were combined and the organic layer separated. The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers washed with brine (10 mL), then dried over $MgSO_4$ and the solvent removed *in vacuo.* Purification *via* silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc (R_f = 0.69)) gave the title compound as a red solid (1.05 g, 94%).

Mp; 40-42 °C.

^{1}H NMR (500 MHz, $CDCl_3$); 4.99–4.97 (m, 2 H), 4.78–4.73 (m, 2 H), 4.30 (s, 5 H).

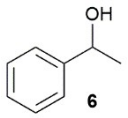
^{13}C NMR (126 MHz, $CDCl_3$); 116.8 (m), 74.7, 70.9 (m).

^{19}F NMR (470 MHz, $CDCl_3$); -72.09.

IR (film, cm^{-1}); ν_{max} 3112, 2160, 1682.

HRMS (ESI); calc'd for $C_{12}H_9F_3FeO$ $[M+H_2O]^+$: *m/z* 300.0010, found 300.010.

1-phenylethanol 6



6

Dichloro(*p*-cymene)ruthenium(II) dimer (4 mg, 0.005 mmol, 1 mol %), *N*-tosyl ethylenediamine (2 mg, 0.01 mmol, 2 mol %) and sodium formate (170 mg, 2.5 mmol) were dissolved in water (0.5 mL) and heated to 80 °C. Acetophenone (0.06 mL, 0.5 mmol, 1 eq.) in ethanol (0.5 mL) was then added. The reaction was stirred for 1 h after which the reaction mixture was poured onto water (20 mL) and ethyl acetate (20 mL). The organics were extracted and the aqueous layer was extracted further with ethyl acetate (2 × 20 mL). The combined organic layers were washed with water (20 mL), brine (20 mL) then dried over $MgSO_4$, and then the solvent was removed *in vacuo*. Purification *via* silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc (R_f = 0.31)) gave the title compound as a pale yellow oil (87 mg, 99%).

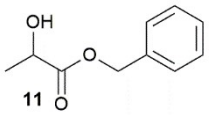
^{1}H NMR (500 MHz, $CDCl_3$); 7.40–7.33 (m, 4 H), 7.30–7.25 (m, 1 H), 4.90 (q, *J* 6.5, 1 H), 1.91 (s, 1 H), 1.50 (d, *J* 6.5, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$); 145.9, 128.6, 127.6, 125.5, 70.5, 25.3.

IR (film, cm^{-1}); ν_{max} 3350, 3063, 3028, 2973, 2927, 2874, 2160, 2031, 1602, 1450, 1368, 1283.

Data in accordance with literature precedent.[2]

Benzyl 2-hydroxypropanoate 11



11

Dichloro(*p*-cymene)ruthenium(II) dimer (6.1 mg, 0.01 mmol, 2 mol %), sodium formate (170 mg, 2.5 mmol, 5 eq), (±)-(*N*)-*p*-Tosyl-1,2-diphenylethylenmediamine (3.7 mg, 0.01 mmol, 4 mol %) and sodium pyruvate (55 mg, 0.5 mmol, 1 eq.) were dissolved in *i*-PrOH (2 mL) and carbonate buffer (pH 9.2, 50 mM, 2 mL). The reaction was stirred at room temperature for 24 h. The solvent was removed *in vacuo* to give sodium lactate. Sodium lactate was dissolved in DMF (0.5 mL) and cooled to 0 °C. Benzyl bromide (0.06 mL, 0.5 mmol, 1 eq.) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 18 h, after which Et_2O (10 mL) was added. Sat. LiCl (10 mL) was added and the organic layer separated. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organic layers were washed with sat. $NaHCO_3$ (10 mL), brine (10 mL), then dried over $MgSO_4$ and the solvent was removed *in vacuo*. Purification *via* silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc) afforded the title compound as a colourless oil (50.4 mg, 65 %).

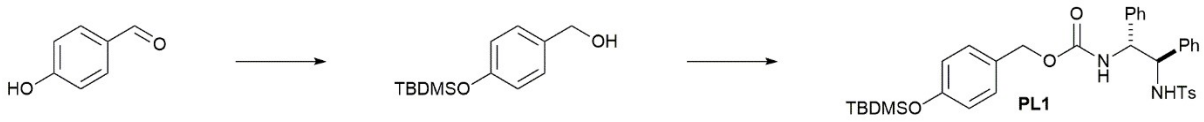
^{1}H NMR (500 MHz, $CDCl_3$); 7.41 – 7.32 (m, 5 H), 5.21 (s, 2 H), 4.32 (dt, *J* 11.3, 5.7, 1 H), 2.99 (d, *J* 5.2, 1 H), 1.43 (d, *J* 6.9, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$); 175.6, 141.0, 135.3, 128.7, 128.6, 128.3, 127.7, 127.0, 67.4, 66.9, 65.3, 20.4.

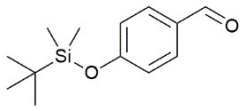
IR (film, cm^{-1}); ν_{max} 3413, 2981, 1733, 1203, 1124.

Data in accordance with literature precedent. [3]

Synthesis of PL1



4-((tert-butyldimethylsilyl)oxy)benzaldehyde



4-hydroxybenzaldehyde (3.66 g, 30 mmol, 1 eq.) and triethylamine (6.3 mL, 45 mmol, 1.5 eq.) were suspended in anhydrous DCM (50 mL) under N_2. A solution of *tert*-butyldimethylsilyl chloride (6.76 g, 45 mmol, 1.5 eq.) in anhydrous DCM (50 mL) was added dropwise over 30 min. The reaction was stirred at room temperature for 2 h, after which the reaction was quenched with water (100 mL). The organic layer was separated and the aqueous layer extracted with DCM (3 × 100 mL). The combined organic layers were washed with water (150 mL), brine (100 mL), then dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification *via* silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc (R_f =)) gave the title compound as a colourless oil (6.14 g, 87%).

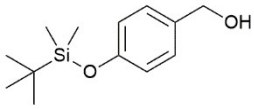
^{1}H NMR (300 MHz, $CDCl_3$); 9.85 (s, 1 H), 7.79 – 7.68 (m, 2 H), 6.94 – 6.87 (m, 2 H), 0.96 (s, 9 H), 0.22 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$); 190.7, 161.4, 131.8, 130.4, 120.4, 25.5, 18.2, -4.4.

IR (film cm^{-1}); ν_{max} 2956, 2931, 2859, 1697, 1596, 1507, 1271, 1257, 1155.

Data in accordance with literature precedent.[4]

(4-((tert-butyldimethylsilyl)oxy)phenyl)methanol



4-((tert-butyldimethylsilyl)oxy)benzaldehyde (6.00 g, 25.4 mmol, 1 eq.) was suspended in MeOH (125 mL) and cooled to 0 °C. Sodium borohydride (0.96 g, 25.4 mmol, 1 eq.) was added portionwise. The reaction was stirred at room temperature for 30 min, after which the reaction was cooled to 0 °C. The reaction was quenched with HCl (1 M) and extracted with DCM (3 × 100 mL). The combined the organic layer were washed with brine (100 mL), then dried over $MgSO_4$, and the solvent was removed *in vacuo*. Purification *via* silica gel column chromatography (Pet. 40–60 °C 4:1 EtOAc (R_f = 0.37)) gave the title compound as colourless oil (5.54 g, 92%).

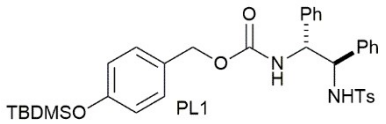
^{1}H NMR (300 MHz, $CDCl_3$); 7.23 – 7.20 (m, 2 H), 6.84 – 6.80 (m, 2 H), 4.58 (s, 2 H), 0.99 (s, 9 H), 0.20 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$); 155.2, 133.7, 128.5, 120.1, 65.0, 25.7, 18.2, -4.4.

IR (film cm^{-1}); ν_{max} 3352 br, 2956, 2950, 2858, 1610, 1510, 1253, 915.

Data in accordance with literature precedent.[4]

4-((tert-butyldimethylsilyl)oxy)benzyl (2-((4-methylphenyl)sulfonamido)-1,2-diphenylethyl)carbamate PL1



Phosgene (2.6 mL, 20 wt % in toluene) was stirred under N_2 and cooled to 0 °C. *tert*-butyldimethylsilyloxy benzyl alcohol (119 mg, 0.5 mmol, 1 eq.) was dissolved in toluene (2.5 mL) and added dropwise and then stirred for 2 h. The reaction was concentrated, and the residue taken up in anhydrous THF (4 mL) under N_2 and cooled to 0 °C. (*N*)-tosyl-(±)-diphenylethylenediamine (183 mg,

0.5 mmol, 1 eq.) was added and the reaction allowed to warm to room temperature. The reaction was stirred for 16 h, and then sat. $NaHCO_3$ (20 mL) was added, followed by EtOAc (20 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with water (20 mL), brine (10 mL), dried over $MgSO_4$, and then the solvent was removed in vacuo. Purification via silica gel column chromatography (Pet. 40–60 °C 3:2 EtOAc (R_f = 0.20) gave the title compound as a white solid (56 mg, 18%).

Mp; 97-103 °C.

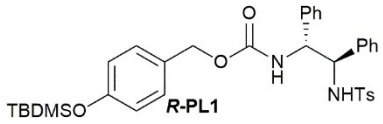
^{1}H NMR (500 MHz, $CDCl_3$); 7.44 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.17 – 7.12 (m, 3H), 7.06 – 7.00 (m, 3H), 7.00 – 6.95 (m, 2H), 6.92 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 7.4 Hz, 2H), 5.89 (d, *J* = 7.2 Hz, 1H), 5.46 (d, *J* = 7.9 Hz, 1H), 5.04 (s, 2H), 4.86 (dd, *J* = 9.6, 7.9 Hz, 1H), 4.57 (dd, *J* = 9.6, 7.4 Hz, 1H), 2.30 (s, 3H), 0.98 (s, 9H), 0.19 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$); 157.3, 156.0, 143.0, 138.0, 137.7, 137.6 130.1, 129.4, 128.9, 128.7, 128.2, 128.2, 127.7, 127.6, 127.5, 127.0, 120.3, 67.4, 63.6, 60.5, 25.8, 21.5, 18.4, -4.3.

IR (solid cm^{-1}); ν_{max} 3288, 2954, 2931, 2858, 1683, 1511, 1251, 1155.

HRMS (ESI); calc'd $C_{35}H_{42}N_2NaO_5SSi$ $[M+Na]^+$: m/z: 653.247, found: 653.247.

4-((tert-butyldimethylsilyl)oxy)benzyl (2-((4-methylphenyl)sulfonamido)-*R*,*R*-1,2-diphenylethyl)carbamate *R*-PL1



Phosgene (2 mL, 15 % in toluene) was suspended in toluene (2.5 mL) under N_2 and cooled to 0 °C. (4-((*tert*-butyldimethylsilyl)oxy)phenyl)methanol (262 mg, 1.1 mmol, 1.1 eq.) was dissolved in toluene (2.5 mL) and added dropwise. The reaction was allowed to warm to room temperature and then stirred for 2 h. The reaction was concentrated, and the residue taken up in anhydrous THF (8 mL) under N_2 and cooled to 0 °C. (*N*)-tosyl-(*R*,*R*)-diphenylethylenediamine (366 mg, 1 mmol, 1 eq.) and triethylamine (0.1 mL) were added and the reaction allowed to warm to room temperature. The reaction was stirred for 16 h, then sat. $NaHCO_3$ (20 mL) was added, followed by EtOAc (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with water (20 mL), brine (10 mL), dried over $MgSO_4$ and then the solvent was removed *in vacuo*. Purification *via* silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc (R_f = 0.07)) gave the title compound as a white solid (240 mg, 38 %).

Mp; 97-103 °C.

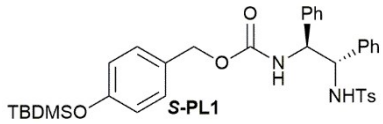
^{1}H NMR (500 MHz, $CDCl_3$); 7.43 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.17 – 7.12 (m, 3H), 7.05 – 6.91 (m, 7H), 6.82 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 2H), 6.16 (d, *J* = 7.6 Hz, 1H), 5.69 (d, *J* = 7.7 Hz, 1H), 5.03 (s, 2H), 4.93 – 4.87 (m, 1H), 4.58 (dd, *J* = 9.6, 7.7 Hz, 1H), 2.28 (s, 3H), 0.99 (s, 9H), 0.20 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$); 157.2, 155.9, 142.9, 138.3, 137.8, 137.6, 130.0, 129.3, 128.9, 128.6, 128.2, 128.0, 127.6, 127.6, 127.5, 127.0, 120.2, 67.4, 63.5, 60.5, 25.8, 21.5, 18.3, -4.3.

IR (solid, cm^{-1}); ν_{max} 3295, 3032, 2955, 2931, 2858, 1689, 1610, 1511, 1456, 1288, 1251, 1156, 1089, 1037.

HRMS (ESI); calc'd $C_{35}H_{42}N_2NaO_5SSi$ $[M+Na]^+$: m/z: 653.247, found: 653.247.

4-((tert-butyldimethylsilyl)oxy)benzyl (2-((4-methylphenyl)sulfonamido)-*S*,*S*-1,2-diphenylethyl)carbamate *S*-PL1



Phosgene (2 mL, 15 % in toluene) was suspended in toluene (2.5 mL) under N_2 and cooled to 0 °C. (4-((*tert*-butyldimethylsilyl)oxy)phenyl)methanol (262 mg, 1.1 mmol, 1.1 eq.) was dissolved in toluene (2.5 mL) and added dropwise. The reaction was allowed to warm to room temperature and then stirred for 2 h. The reaction was concentrated, and the residue taken up in anhydrous THF (8 mL) under N_2 and cooled to 0 °C. (*N*)-tosyl-(*S*,*S*)-diphenylethylenediamine (366 mg, 1 mmol, 1 eq.) and triethylamine (0.1 mL) were added and the reaction allowed to warm to room temperature. The reaction was stirred for 16 h, then sat. $NaHCO_3$ (20 mL) was added, followed by EtOAc (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 $\times$ 20 mL). The combined organic layers were washed with water (20 mL), brine (10 mL), dried over $MgSO_4$ and then the solvent was removed *in vacuo*. Purification *via* silica gel column chromatography (Pet. 40–60 °C 9:1 EtOAc (R_f = 0.07)) gave the title compound as a white solid (260 mg, 41 %).

Mp; 97-103 °C.

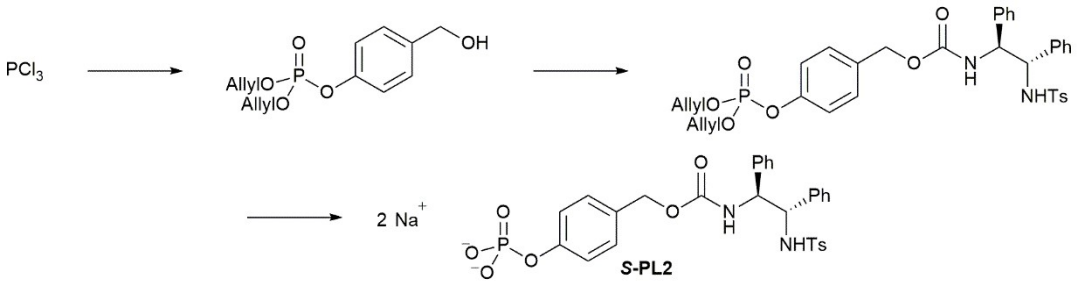
^{1}H NMR (500 MHz, $CDCl_3$); 7.43 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.17 – 7.12 (m, 3H), 7.05 – 6.91 (m, 7H), 6.82 (d, *J* = 7.9 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 2H), 6.16 (d, *J* = 7.6 Hz, 1H), 5.69 (d, *J* = 7.7 Hz, 1H), 5.03 (s, 2H), 4.93 – 4.87 (m, 1H), 4.58 (dd, *J* = 9.6, 7.7 Hz, 1H), 2.28 (s, 3H), 0.99 (s, 9H), 0.20 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$); 157.2, 155.9, 142.9, 138.3, 137.8, 137.6, 130.0, 129.3, 128.9, 128.6, 128.2, 128.0, 127.6, 127.6, 127.5, 127.0, 120.2, 67.4, 63.5, 60.5, 25.8, 21.5, 18.3, -4.3.

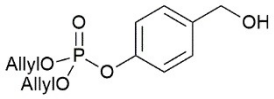
IR (solid, cm^{-1}); ν_{max} 3296, 3031, 2931, 2859, 1687, 1611, 1536, 1511, 1456, 1331, 1288, 1251, 1155, 1089, 1037.

HRMS (ESI); calc'd $C_{35}H_{42}N_2NaO_5SSi$ $[M+Na]^+$: m/z: 653.247, found: 653.247.

Synthesis of *S*-PL2



diallyl (4-(hydroxymethyl)phenyl) phosphate



Phosphorus trichloride (8.7 mL, 100 mmol, 2 eq.) was added to anhydrous THF (75 mL) and cooled to 0 °C. A solution of allyl alcohol (13.6 mL, 200 mmol, 4 eq.) and anhydrous TEA (31 mL, 220 mmol, 4.4 eq.) in anhydrous THF (25 mL) was then added dropwise. The reaction mixture was then allowed to warm to room temperature and stirred for 1 h, after which the reaction was cooled to 0 °C. Water (50 mL) was then added slowly and the reaction mixture allowed to warm to room temperature, and stirred for 30 min. The organics were removed *in vacuo*, and the aqueous layer extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, and the solvent removed *in vacuo*. The residue was then dissolved in anhydrous toluene (75 ml) and added dropwise to a stirring solution of *N*-chlorosuccinimide (11.7 g, 87.5 mmol, 1.75 eq.) in anhydrous toluene (75 mL) under argon at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 16 h, after which the reaction was filtered *via* gravity filtration. The filtrate was then concentrated *in vacuo*. The residue was then taken up in anhydrous THF (50 mL) and added slowly to a stirring solution of 4-hydroxybenzaldehyde (6.1 g, 50 mmol, 1 eq.) and anhydrous TEA (10.5 mL, 75 mmol, 1.5 eq.) in anhydrous THF (50 mL) at 0 °C under N_2. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. After which the reaction was filtered, and the filtrate concentrated *in vacuo*, then taken up in EtOAc (50 mL). The organic layer was washed with sat. $NaHCO_3$ (50 mL) and the organic layer separated. The aqueous layer was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with water (3 × 50 mL), dried over Na_2SO_4, and then the solvent was removed *in vacuo*. The residue was then taken up in anhydrous THF (50 mL) and cooled to 0 °C before sodium borohydride (3.8 g, 100 mmol, 2 eq.) was added portion-wise. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction mixture was then cooled to 0 °C and quenched with sat. $NaHCO_3$ (50 mL). The reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with 1 M NaOH (2 × 50 mL), water (2 × 50 mL), dried over Na_2SO_4, and then the solvent was removed *in vacuo*. Purification via silica gel column chromatography (EtOAc 1:1 Pet. 40–60 °C (R_f = 0.20)) gave the title compound as a colourless liquid (2.63 g, 19%).

^{1}H NMR (500 MHz, $CDCl_3$); 7.30 (d, *J* 8.4, 2 H), 7.19 – 7.14 (m, 2 H), 5.97 – 5.87 (m, 2 H), 5.35 (dq, *J* 17.1, 1.4, 2 H), 5.25 (dq, *J* 10.4, 1.4, 2 H), 4.65 – 4.58 (m, 6 H).

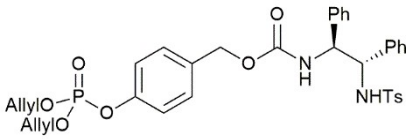
^{13}C NMR (126 MHz, $CDCl_3$); 149.9 (d, *J* 7.1), 138.2 (d, *J* 1.4), 132.1 (d, *J* 7.1), 128.4, 120.1 (d, *J* 4.8), 118.8, 69.0 (d, *J* 5.7), 64.5.

^{31}P NMR (202 MHz, $CDCl_3$); -6.24.

IR (solid, cm^{-1}); ν_{max} 3418, 2880, 1608, 1506, 1267, 1210, 1164, 1097, 1013.

Data in accordance with literature precedent.[5]

4-((bis(allyloxy)phosphoryl)oxy)benzyl ((1S,2S)-2-((4-methylphenyl)sulfonamido)-1,2-diphenylethyl)carbamate



Phosgene (2 mL, 15% in toluene) was suspended in anhydrous THF (2 mL) under N_2 and cooled to 0 °C. A solution of diallyl (4-(hydroxymethyl)phenyl) phosphate (370 mg, 1.3 mmol, 1.3 eq.) in anhydrous THF (3 mL) was added dropwise, and the reaction stirred at 0 °C for 3 h. After which the reaction was concentrated, and the residue was then taken up in anhydrous THF (8 mL). (*N*)-tosyl-(*S*,*S*)-diphenylethylenediamine (366 mg, 1 mmol, 1 eq.) and triethylamine (0.2 mL) were added, and the reaction was stirred at room temperature for 16 h. After which the solvent was removed *in vacuo*, and the residue was taken up in EtOAc (20 mL), then washed with 1M HCl (20 mL). The organic layer was separated, and the aqueous layer extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and then the solvent was removed *in vacuo*. Purification *via* silica gel column chromatography (Pet. 40–60 °C 1:1 EtOAc (R_f = 0.6) to give the title compound as an amorphous white solid (460 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$); 7.42 (d, *J* 7.9, 2 H), 7.32 (d, *J* 8.1, 2 H), 7.20 (d, *J* 8.1, 2 H), 7.17 – 7.13 (m, 3 H), 7.07 – 6.92 (m, 8 H), 6.77 (d, *J* 7.5, 2 H), 6.00 (d, *J* 7.8, 1 H), 5.93 (ddt, *J* 16.3, 10.8, 5.6, 2 H), 5.74 (d, *J* 8.0, 1 H), 5.37 (dq, *J* 17.1, 1.4, 2 H), 5.26 (dq, *J* 10.4, 1.4, 2 H), 5.07 (s, 2 H), 4.89 (t, *J* 8.8,1 H), 4.67 – 4.60 (m, 4 H), 4.57 (t, *J* 8.6, 1 H), 2.28 (s, 3 H).

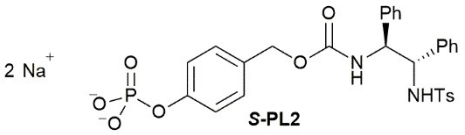
^{13}C NMR (126 MHz, $CDCl_3$); 157.0, 150.6, 143.0, 138.1, 137.8, 137.6, 133.2, 132.2 (d, *J* 6.8), 129.8, 129.3, 128.7, 128.3, 128.1, 127.7, 127.5, 127.5, 127.0, 120.3 (d, *J* 5.0), 118.9, 69.0 (d, *J* 5.7), 66.7, 63.5, 60.5, 21.5.

^{31}P NMR (162 MHz, $CDCl_3$); -6.32.

IR (solid, cm^{-1}); ν_{max} 3233, 3064, 2981, 1693, 1538, 1508, 1328, 1263, 1219, 1157, 1091, 1016.

HRMS (ESI); calc'd $C_{35}H_{37}N_2NaO_8PS$ $[M+Na]^+$: m/z: 699.191, found: 699.199.

dIsodium 4-(((((1*S*,2*S*)-2-((4-methylphenyl)sulfonamido)-1,2-diphenylethyl)carbamoyl)oxy)methyl)phenyl phosphate



S-PL2

4-((bis(allyloxy)phosphoryl)oxy)benzyl ((1S,2S)-2-((4-methylphenyl)sulfonamido)-1,2-diphenylethyl)carbamate (460 mg, 0.68 mmol, 1 eq.) was suspended in MeOH (70 mL) and cooled to 0 °C. Tetrakis(triphenylphosphine)palladium(0) (8 mg, 0.01 mmol, 0.01 eq.) and sodium borohydride (51 mg, 1.36 mmol, 2 eq.) was added portionwise . The reaction was stirred at room temperature for 20 h, after which the reaction was filtered through Celite, and then the solvent was removed *in vacuo*. The residue was taken up in water (10 mL), and then 1 M NaOH (1.4 mL, 2 eq.) was added. The reaction was stirred at room temperature for 1 h, after which the reaction was washed with EtOAc (2 × 20 mL), and then the solvent was removed in vacuo. Purification via reversed-phase flash column chromatography on C18 silica gel (50 g, 20 mm Ø) (water 1:0 MeOH → water 0:1 MeOH) to give the title compound as a white solid (252 mg, 58%).

Mp; >170 °C (decomposition)

^{1}H NMR (500 MHz, D_2O); 7.28 (d, *J* 8.0, 2 H), 7.15 (s, 2 H), 7.11 – 7.04 (m, 5 H), 7.04 – 6.97 (m, 5 H), 6.95 (t, *J* 7.4, 2 H), 6.90 – 6.83 (m, 2 H), 4.90 – 4.79 (m, 3 H), 4.51 (d, *J* 8.5, 1 H), 2.18 (s, 3 H).

^{13}C NMR (126 MHz, D_2O); 153.8, 144.3, 135.7, 129.6, 128.9, 128.4, 128.2, 127.7, 127.5, 127.3, 127.2, 126.4, 120.4 (d, *J* 4.5), 66.9, 62.1, 48.8, 20.5.

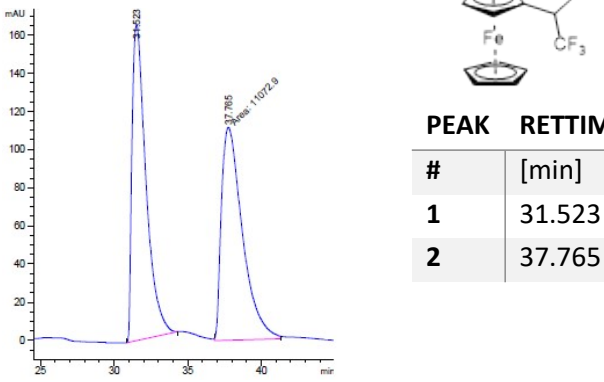
^{31}P NMR (202 MHz, D_2O); 0.04.

IR (solid, cm^{-1}); ν_{max} 3279, 1684, 1612, 1510, 1455, 1240, 1152, 1091.

HRMS (ESI); calc'd $C_{29}H_{28}N_2O_8PS$ $[M+H]^-$: m/z: 595.130, found: 593.130.

HPLC Traces

1-ferrocenyl-2,2,2-trifluoroethanol 2



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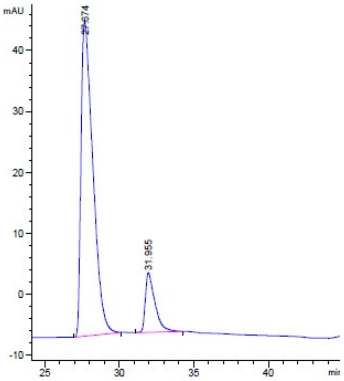

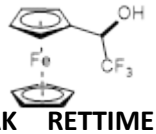

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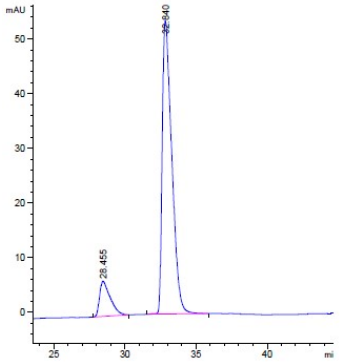

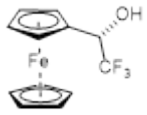

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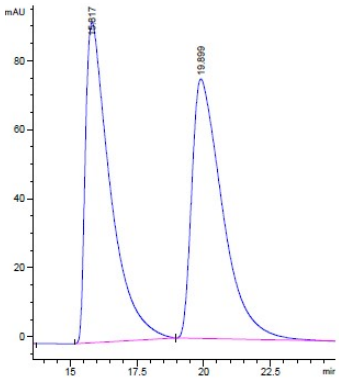
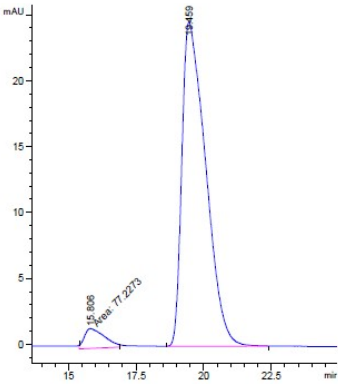
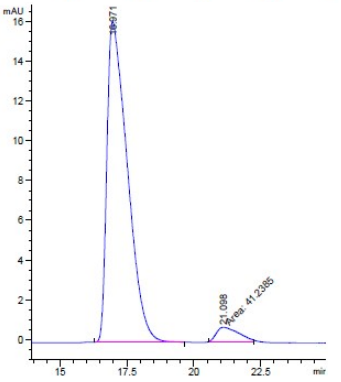
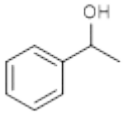
1-phenylethanol 6









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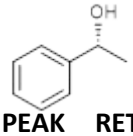

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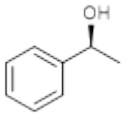

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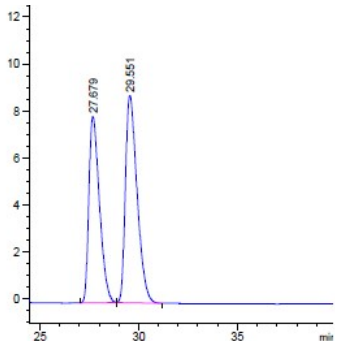
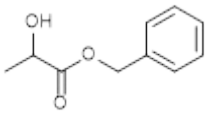
Benzyl 2-hydroxypropanoate 11





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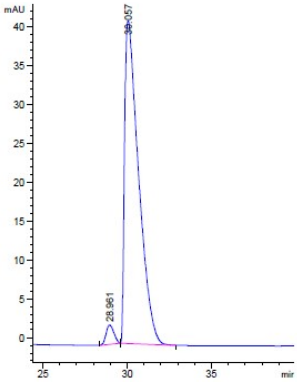

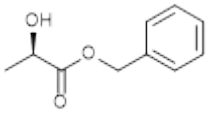

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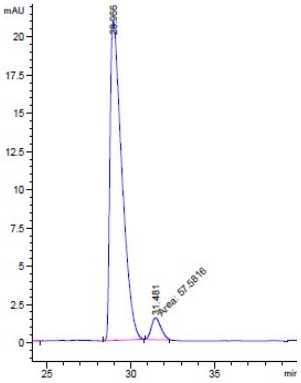

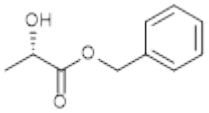

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2	31.481	0.6735	5.76E+01	1.42E+00	5.3106

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NMR Traces

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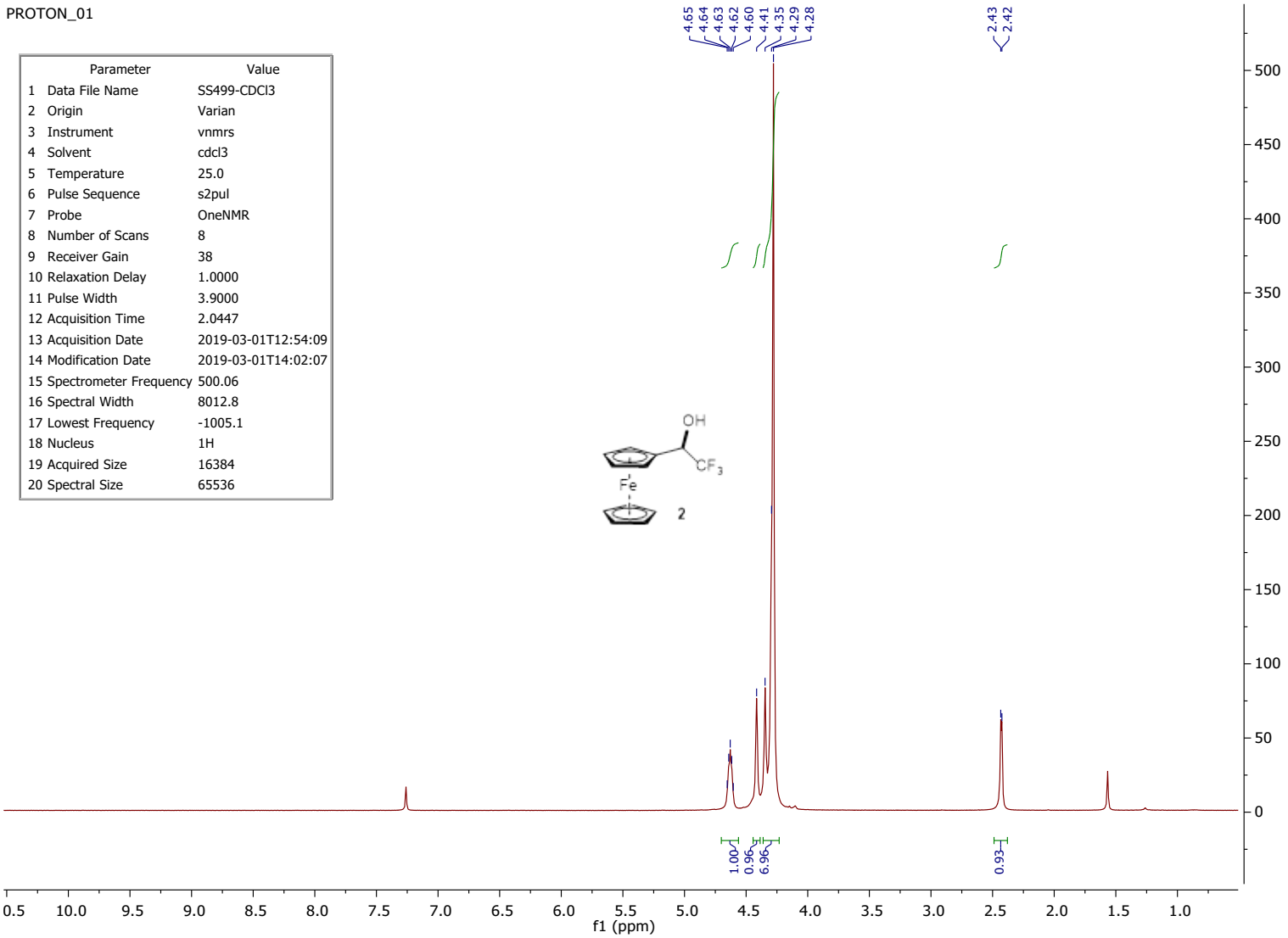

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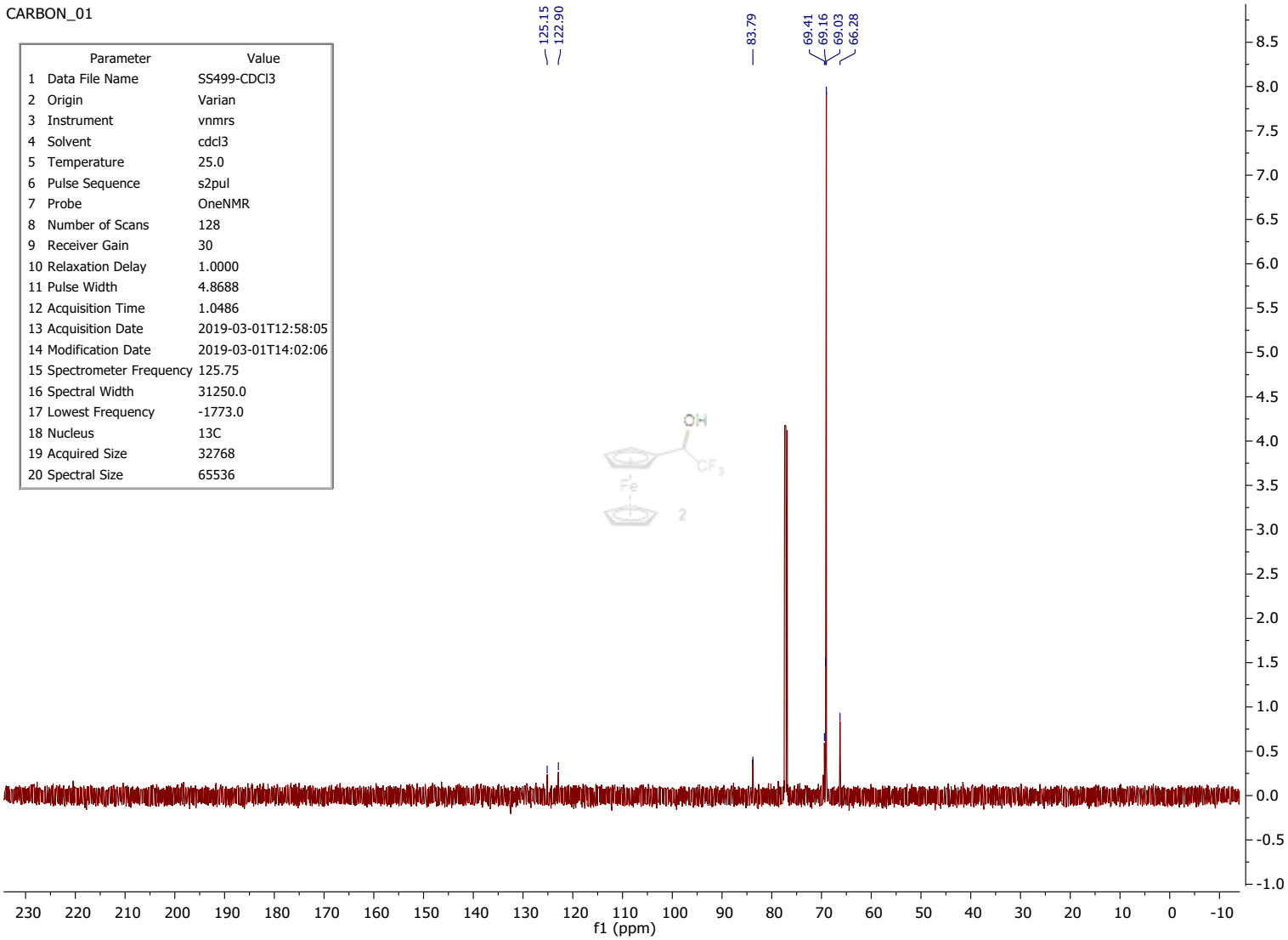

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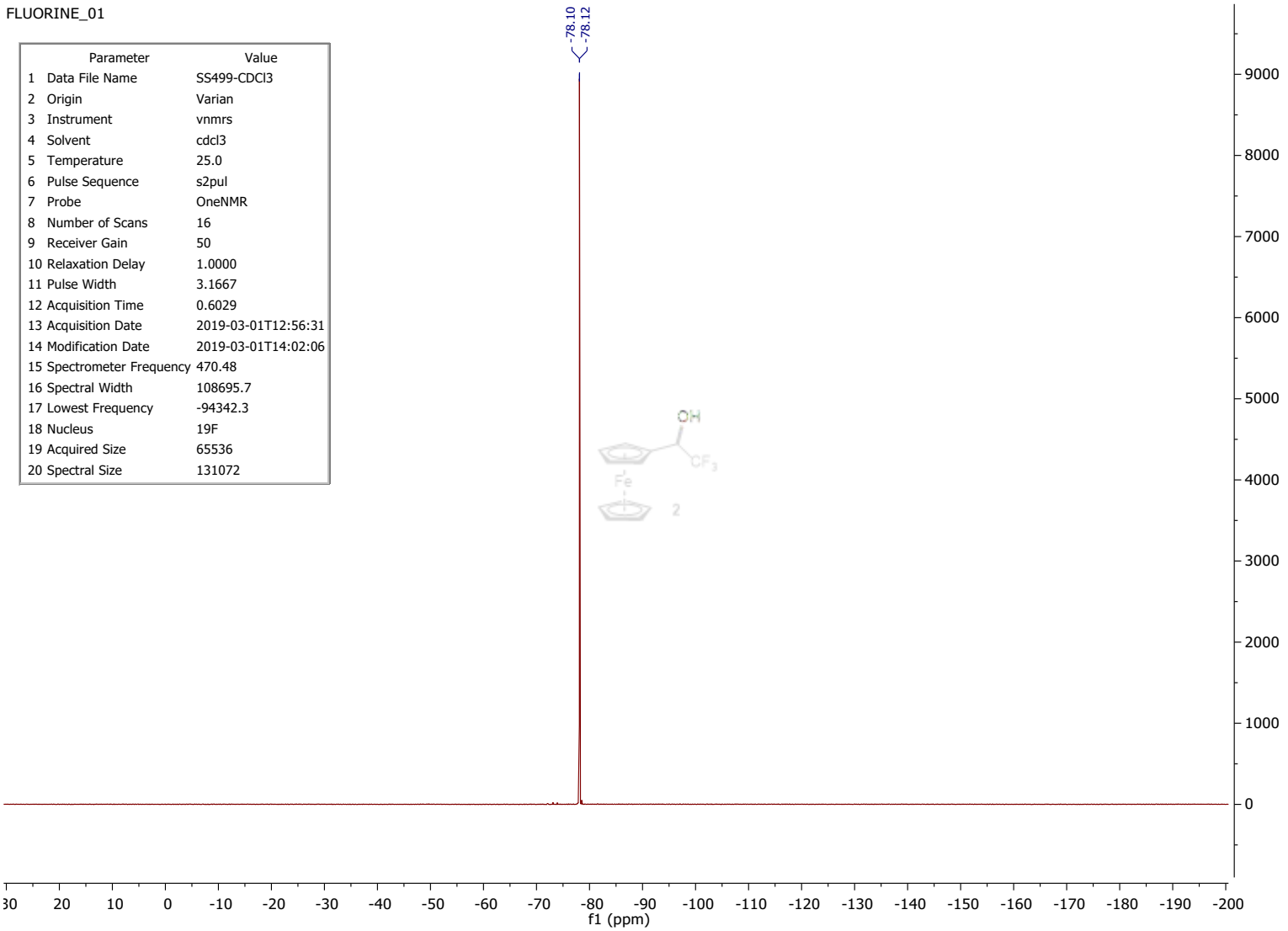

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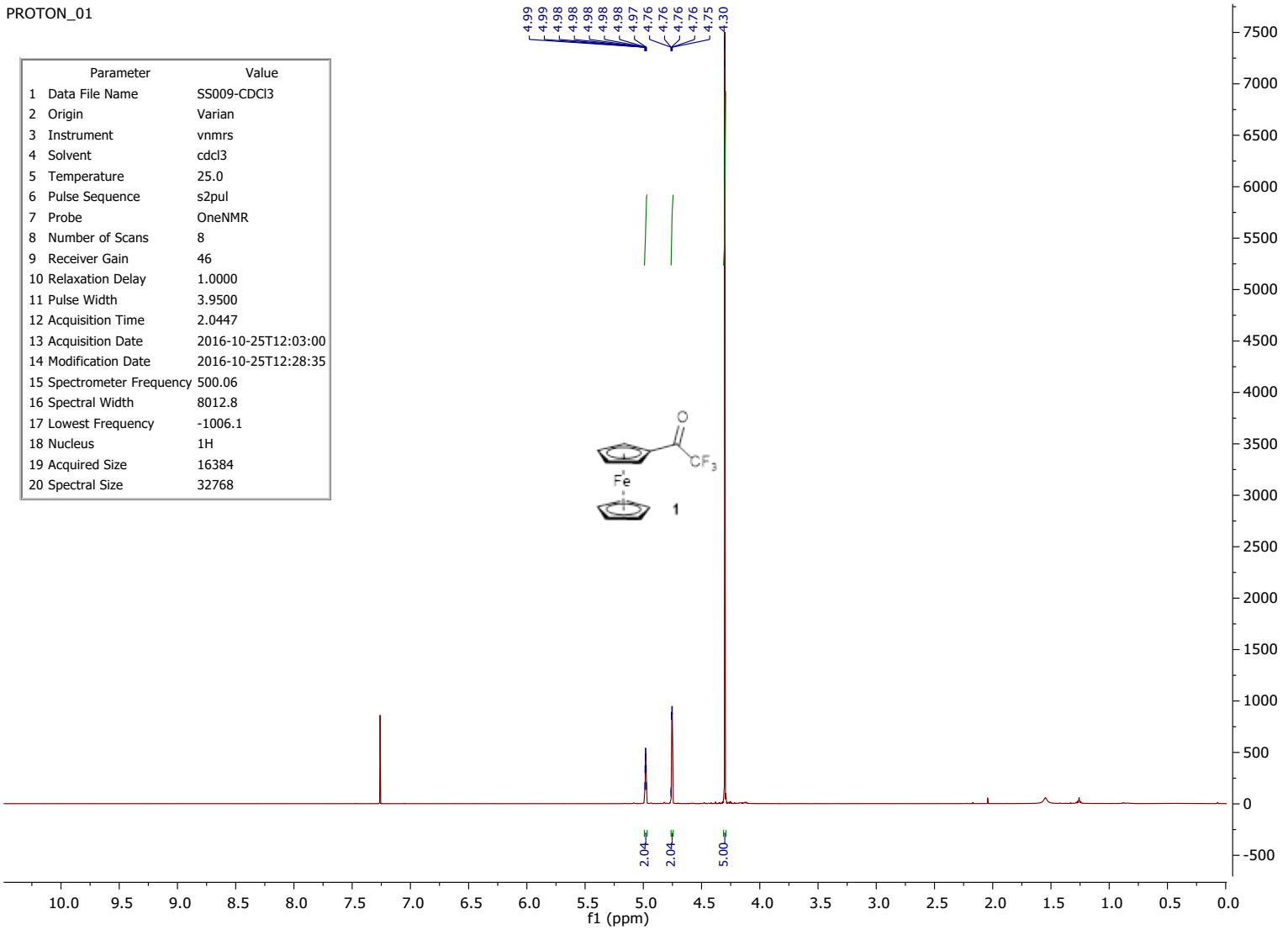
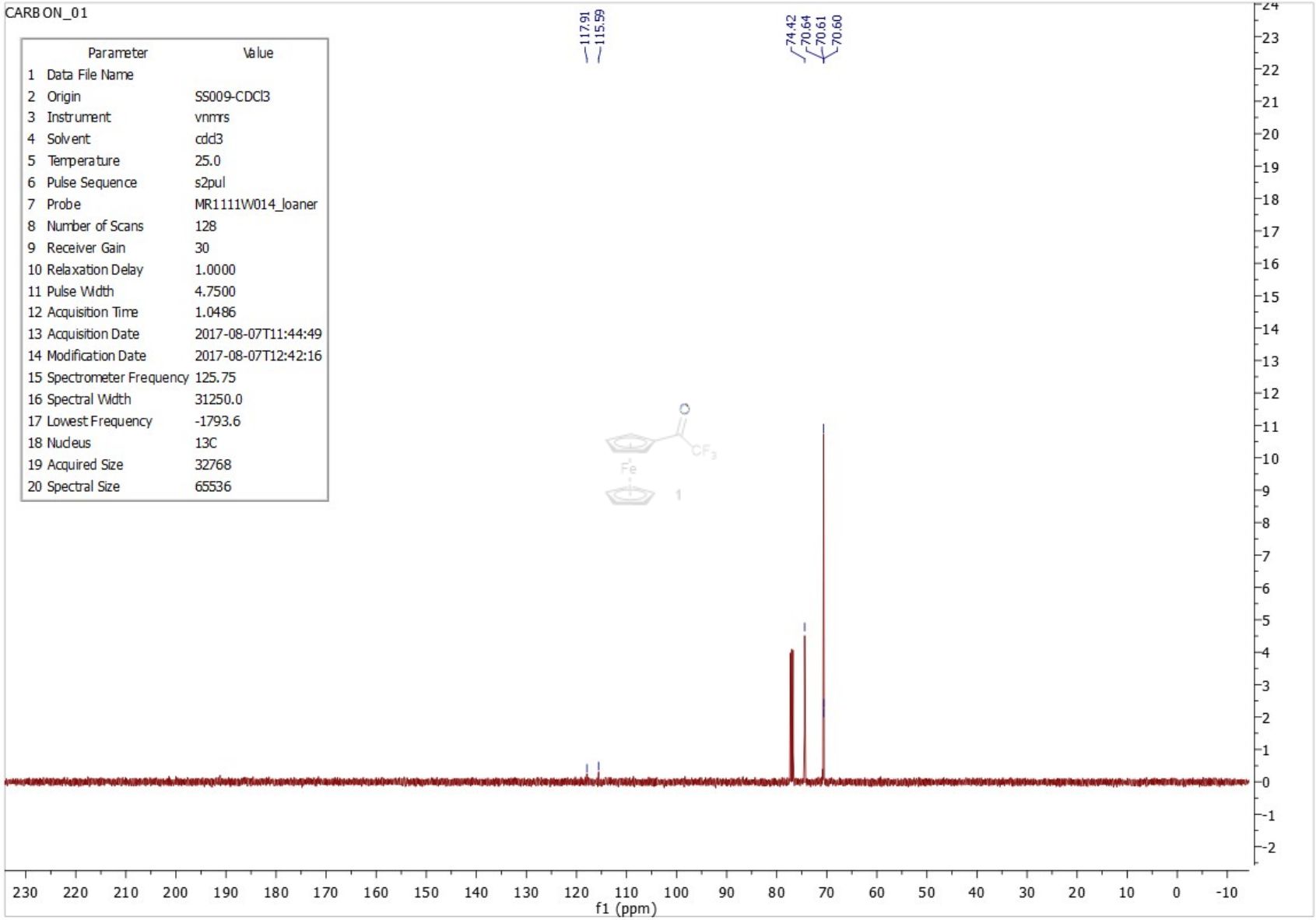
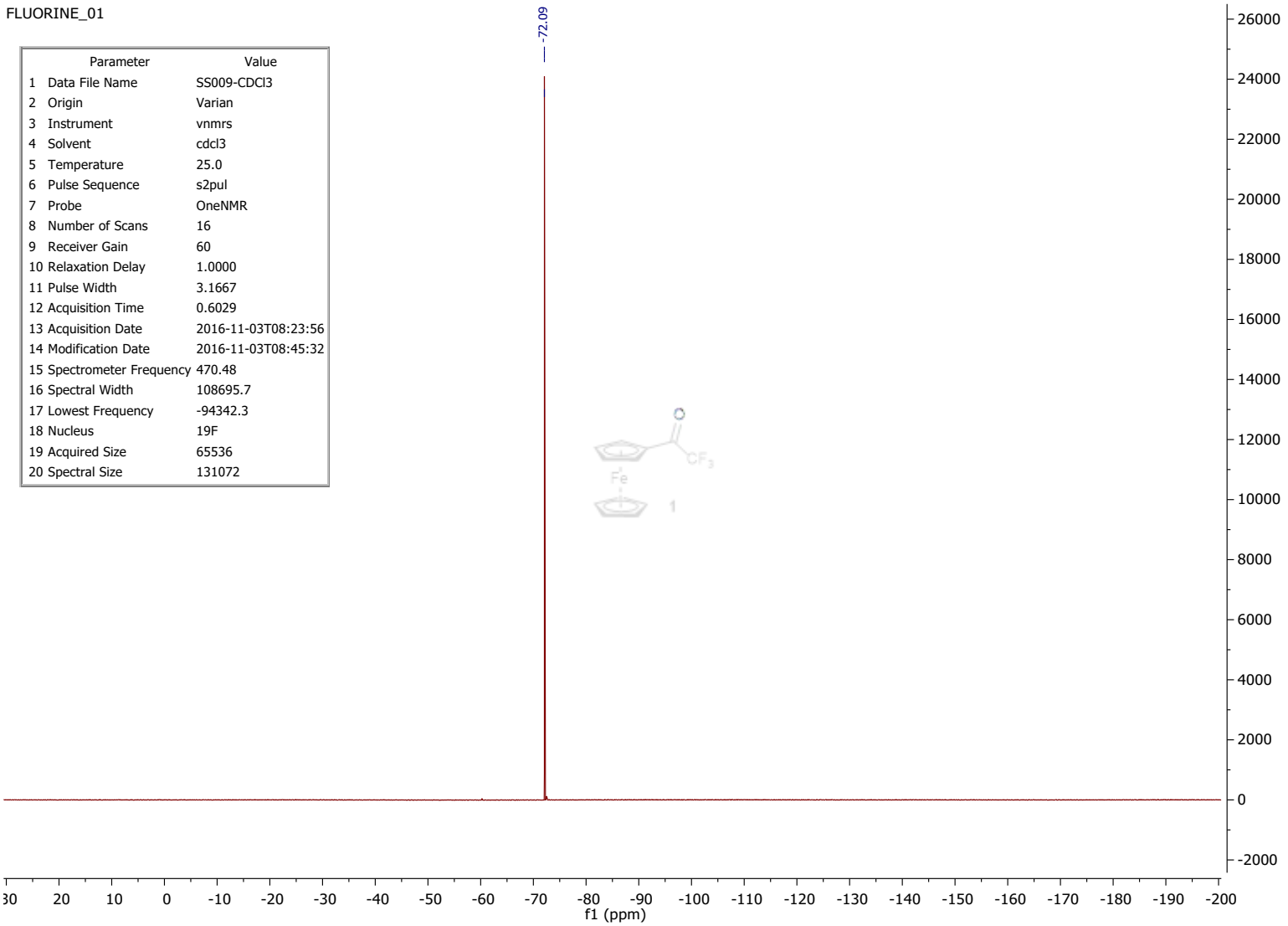
19	Acquired Size	16384
20	Spectral Size	32768



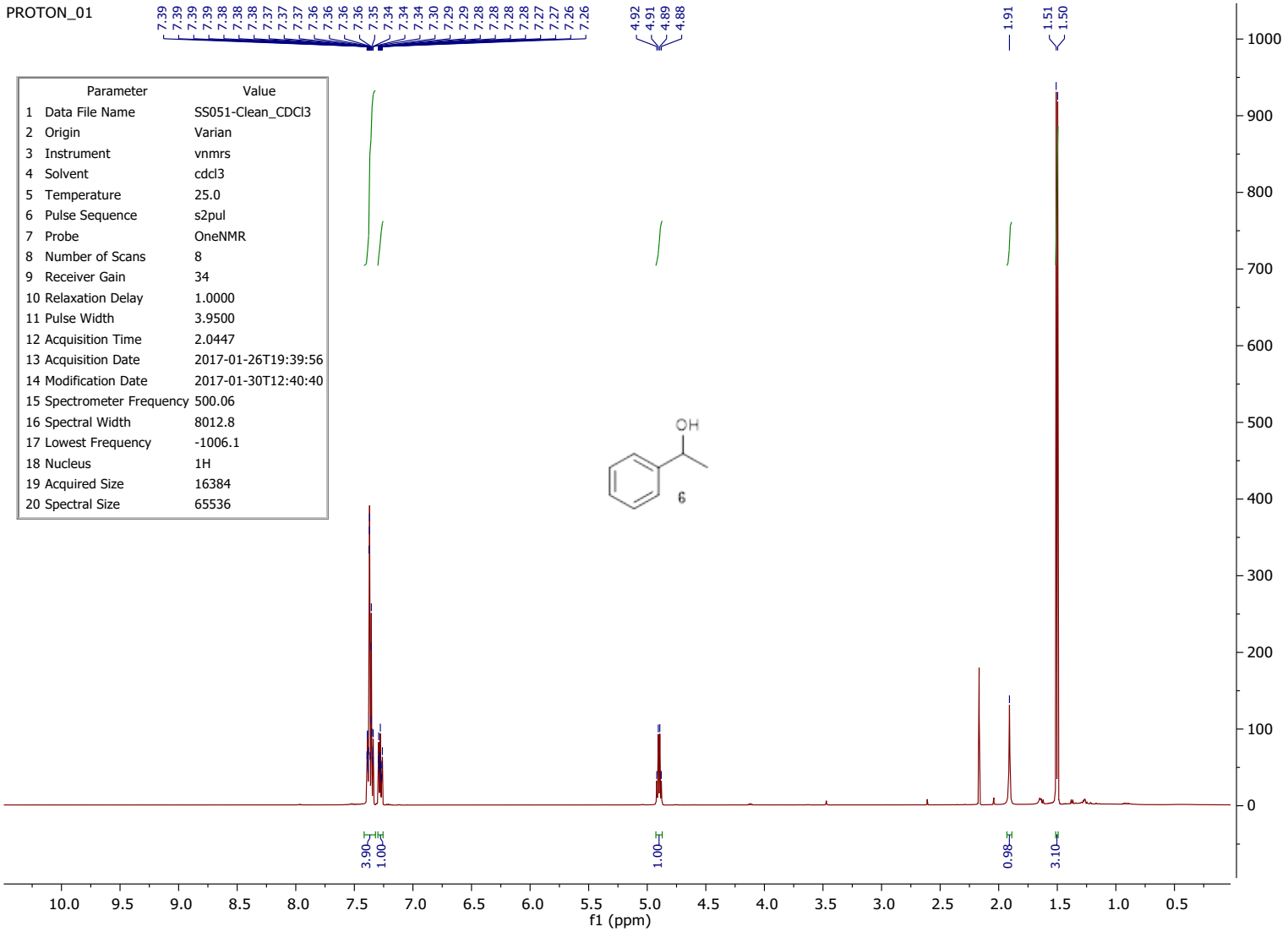

CARBON_01
Parameter Value
1 Data File Name
2 Origin SS009-CDCl3
3 Instrument vnmrs
4 Solvent cdcl3
5 Temperature 25.0
6 Pulse Sequence s2pul
7 Probe MR1111W014_loaner
8 Number of Scans 128
9 Receiver Gain 30
10 Relaxation Delay 1.0000
11 Pulse Width 4.7500
12 Acquisition Time 1.0486
13 Acquisition Date 2017-08-07T11:44:49
14 Modification Date 2017-08-07T12:42:16
15 Spectrometer Frequency 125.75
16 Spectral Width 31250.0
17 Lowest Frequency -1793.6
18 Nucleus 13C
19 Acquired Size 32768
20 Spectral Size 65536
117.91
115.59
74.42
70.64
70.61
70.60
O
CF3
Fe
1
f1 (ppm)

FLUORINE_01

	Parameter	Value
1	Data File Name	SS009-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	16
9	Receiver Gain	60
10	Relaxation Delay	1.0000
11	Pulse Width	3.1667
12	Acquisition Time	0.6029
13	Acquisition Date	2016-11-03T08:23:56
14	Modification Date	2016-11-03T08:45:32
15	Spectrometer Frequency	470.48
16	Spectral Width	108695.7
17	Lowest Frequency	-94342.3
18	Nucleus	19F
19	Acquired Size	65536
20	Spectral Size	131072



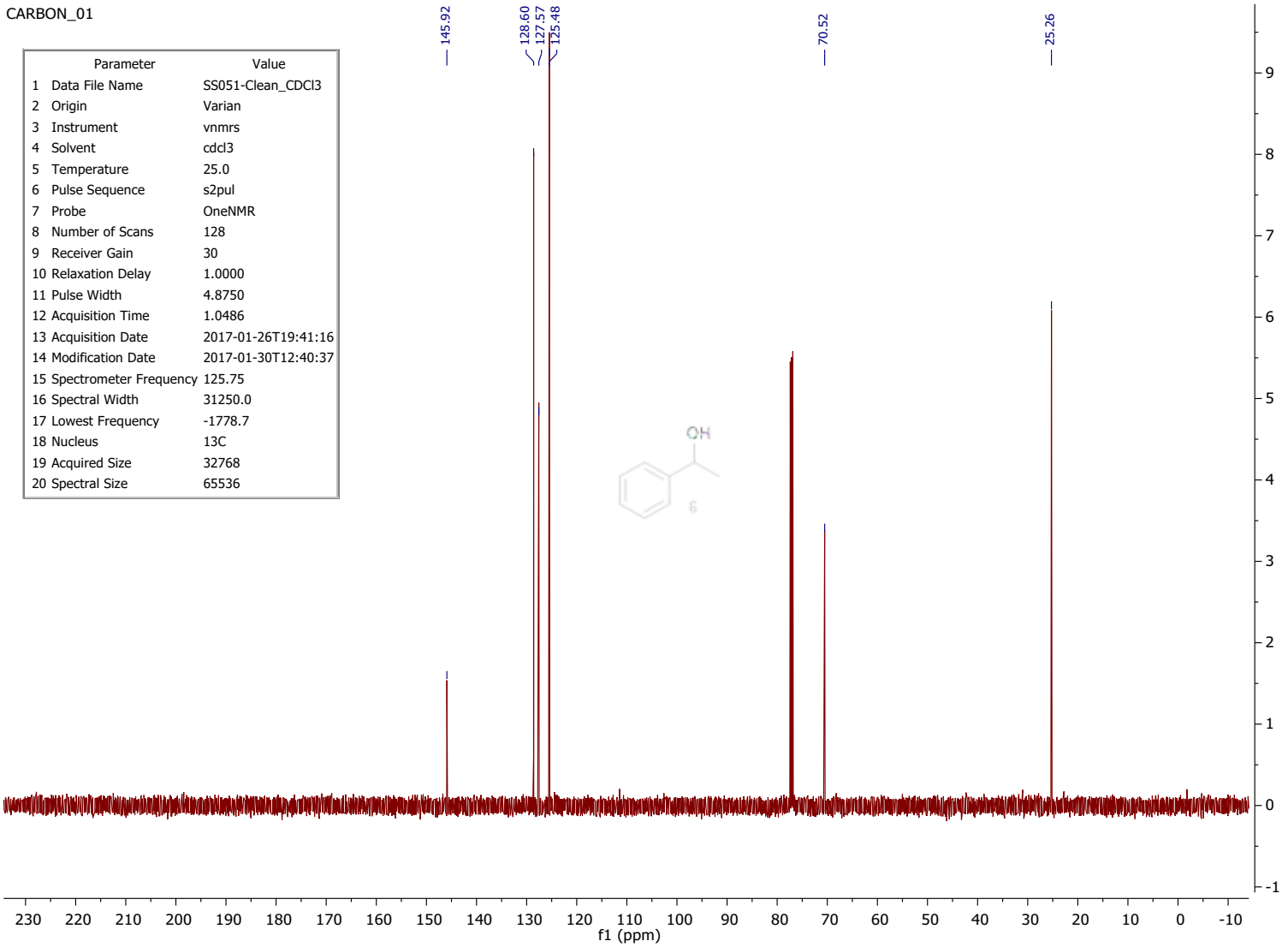
PROTON_01



	Parameter	Value
1	Data File Name	SS051-Clean_CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	8
9	Receiver Gain	34
10	Relaxation Delay	1.0000
11	Pulse Width	3.9500
12	Acquisition Time	2.0447
13	Acquisition Date	2017-01-26T19:39:56
14	Modification Date	2017-01-30T12:40:40
15	Spectrometer Frequency	500.06
16	Spectral Width	8012.8
17	Lowest Frequency	-1006.1
18	Nucleus	1H
19	Acquired Size	16384
20	Spectral Size	65536

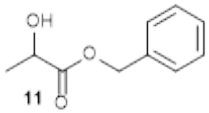
CARBON_01

	Parameter	Value
1	Data File Name	SS051-Clean_CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	128
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	4.8750
12	Acquisition Time	1.0486
13	Acquisition Date	2017-01-26T19:41:16
14	Modification Date	2017-01-30T12:40:37
15	Spectrometer Frequency	125.75
16	Spectral Width	31250.0
17	Lowest Frequency	-1778.7
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



PROTON_01

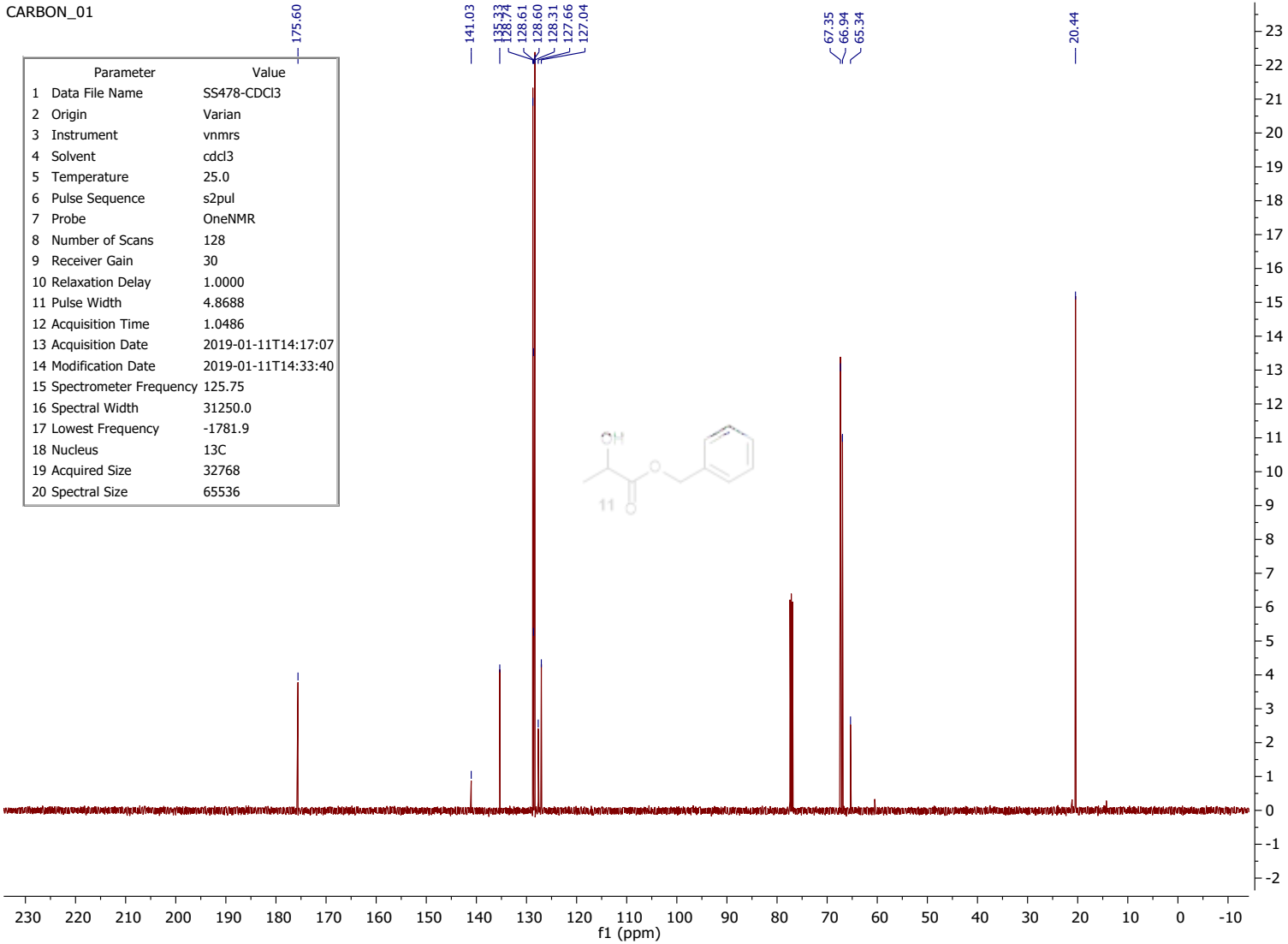
	Parameter	Value
1	Data File Name	SS478-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	8
9	Receiver Gain	26
10	Relaxation Delay	1.0000
11	Pulse Width	3.9000
12	Acquisition Time	2.0447
13	Acquisition Date	2019-01-11T12:11:02
14	Modification Date	2019-01-11T13:35:53
15	Spectrometer Frequency	500.06
16	Spectral Width	8012.8
17	Lowest Frequency	-1005.1
18	Nucleus	1H
19	Acquired Size	16384
20	Spectral Size	65536

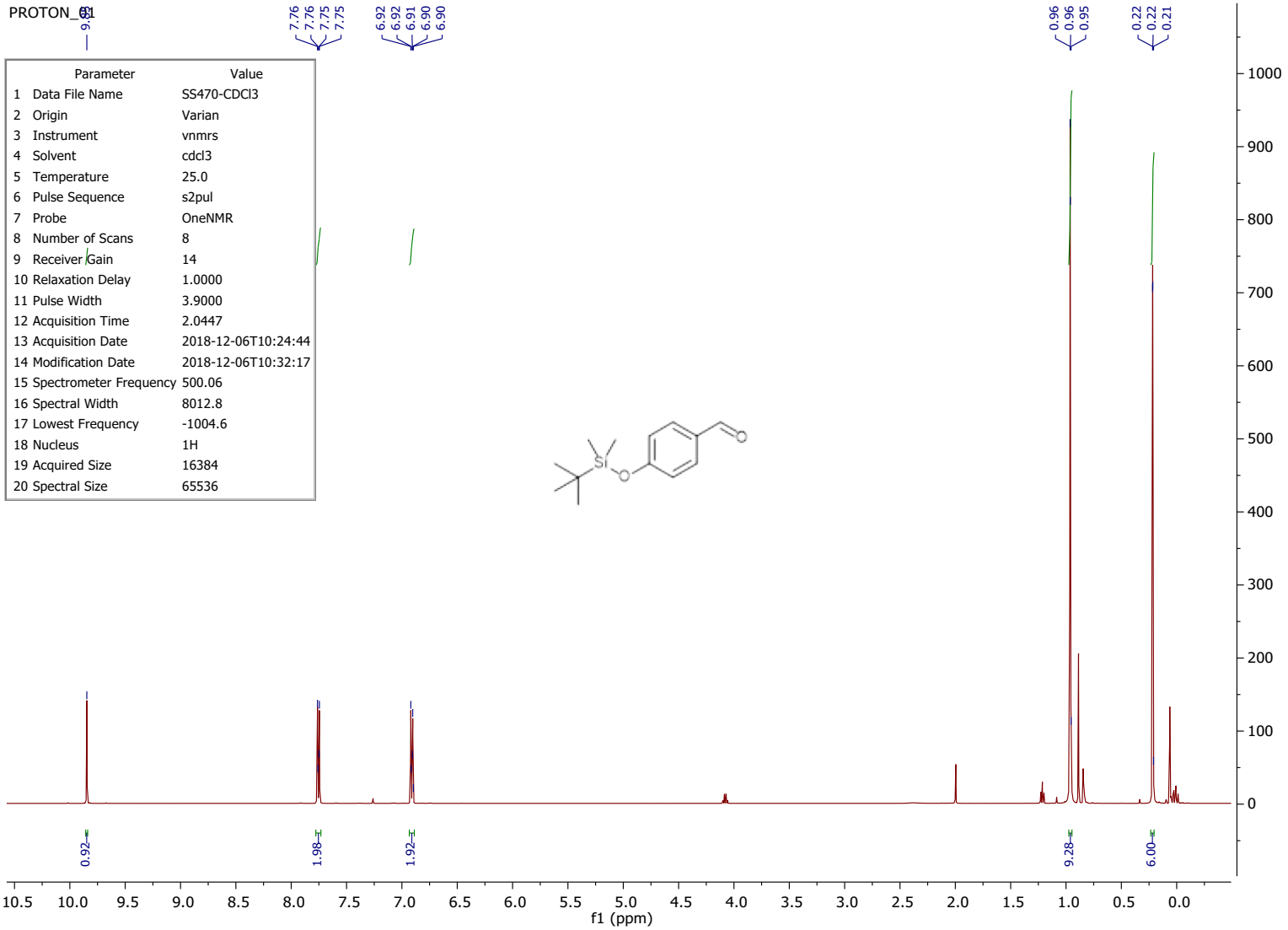


f1 (ppm)

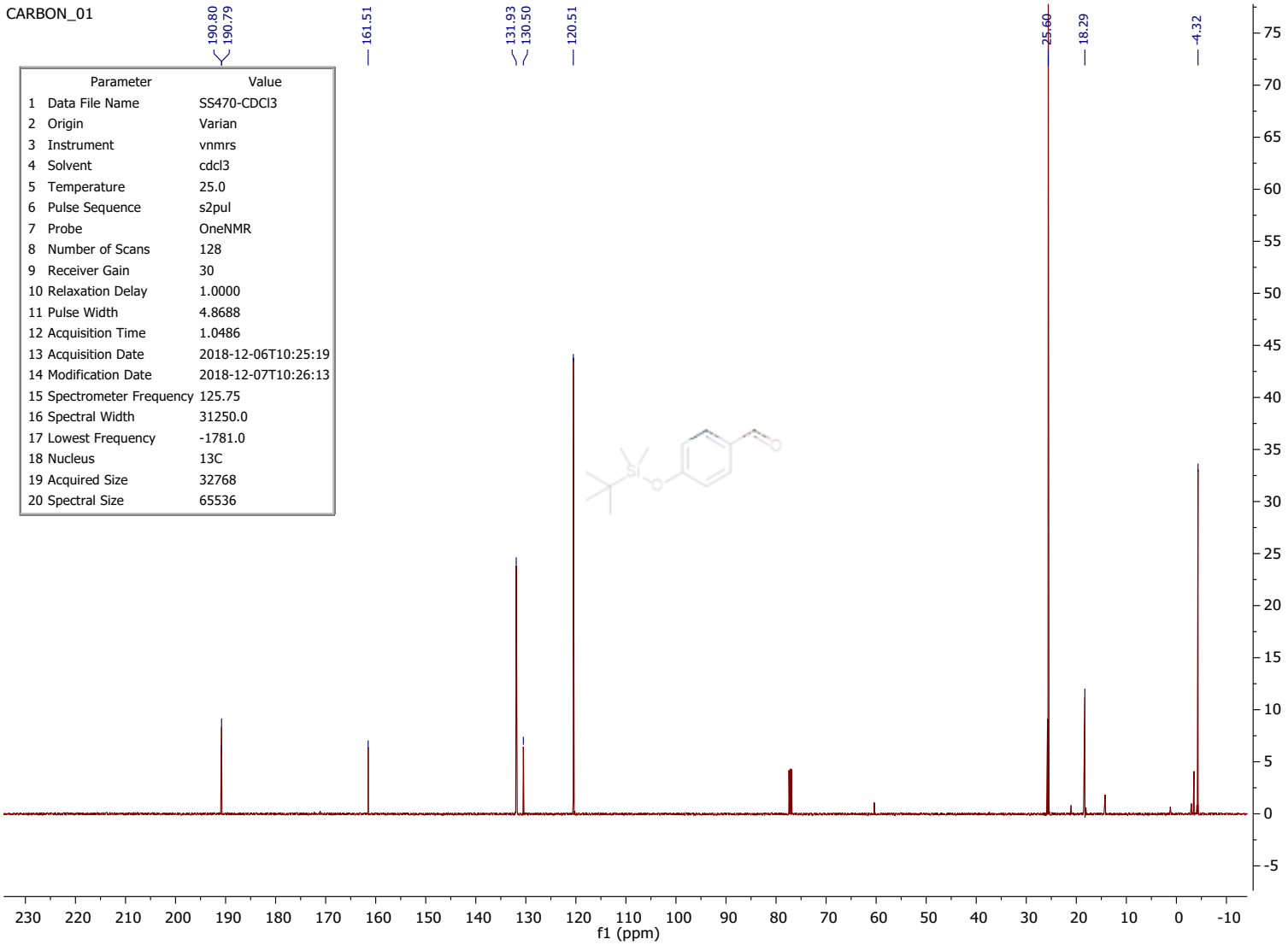
CARBON_01

	Parameter	Value
1	Data File Name	SS478-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	128
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	4.8688
12	Acquisition Time	1.0486
13	Acquisition Date	2019-01-11T14:17:07
14	Modification Date	2019-01-11T14:33:40
15	Spectrometer Frequency	125.75
16	Spectral Width	31250.0
17	Lowest Frequency	-1781.9
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536




PROTON_01
9.81
7.76
7.76
7.75
7.75
6.92
6.92
6.91
6.90
6.90
0.96
0.96
0.95
0.22
0.22
0.21
Parameter Value
1 Data File Name SS470-CDCl3
2 Origin Varian
3 Instrument vnmrs
4 Solvent cdcl3
5 Temperature 25.0
6 Pulse Sequence s2pul
7 Probe OneNMR
8 Number of Scans 8
9 Receiver Gain 14
10 Relaxation Delay 1.0000
11 Pulse Width 3.9000
12 Acquisition Time 2.0447
13 Acquisition Date 2018-12-06T10:24:44
14 Modification Date 2018-12-06T10:32:17
15 Spectrometer Frequency 500.06
16 Spectral Width 8012.8
17 Lowest Frequency -1004.6
18 Nucleus 1H
19 Acquired Size 16384
20 Spectral Size 65536
Si
O
0.92
1.98
1.92
9.28
6.00
1000
900
800
700
600
500
400
300
200
100
0
10.5 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 0.0
f1 (ppm)

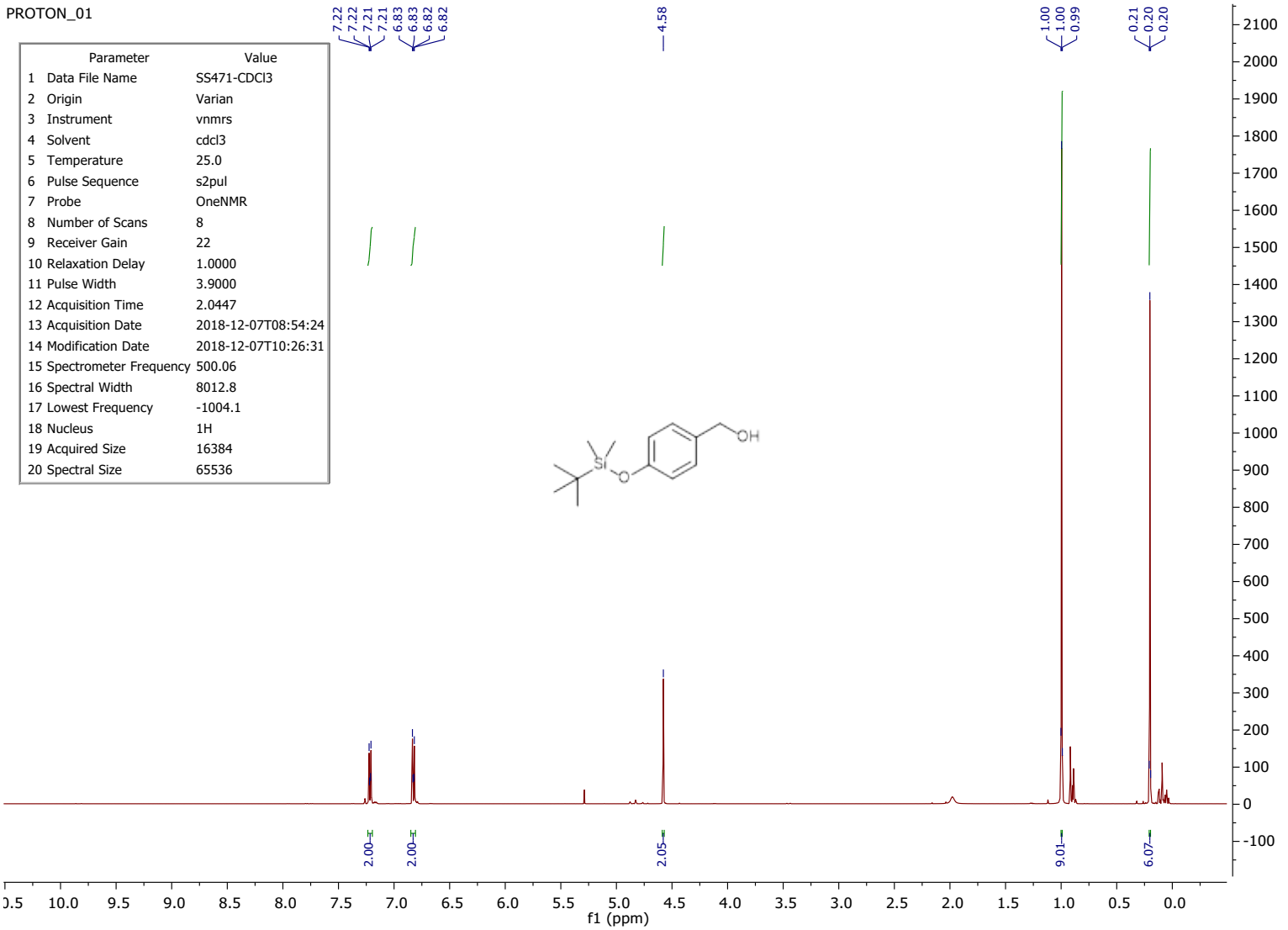
CARBON_01



	Parameter	Value
1	Data File Name	SS470-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	128
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	4.8688
12	Acquisition Time	1.0486
13	Acquisition Date	2018-12-06T10:25:19
14	Modification Date	2018-12-07T10:26:13
15	Spectrometer Frequency	125.75
16	Spectral Width	31250.0
17	Lowest Frequency	-1781.0
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536

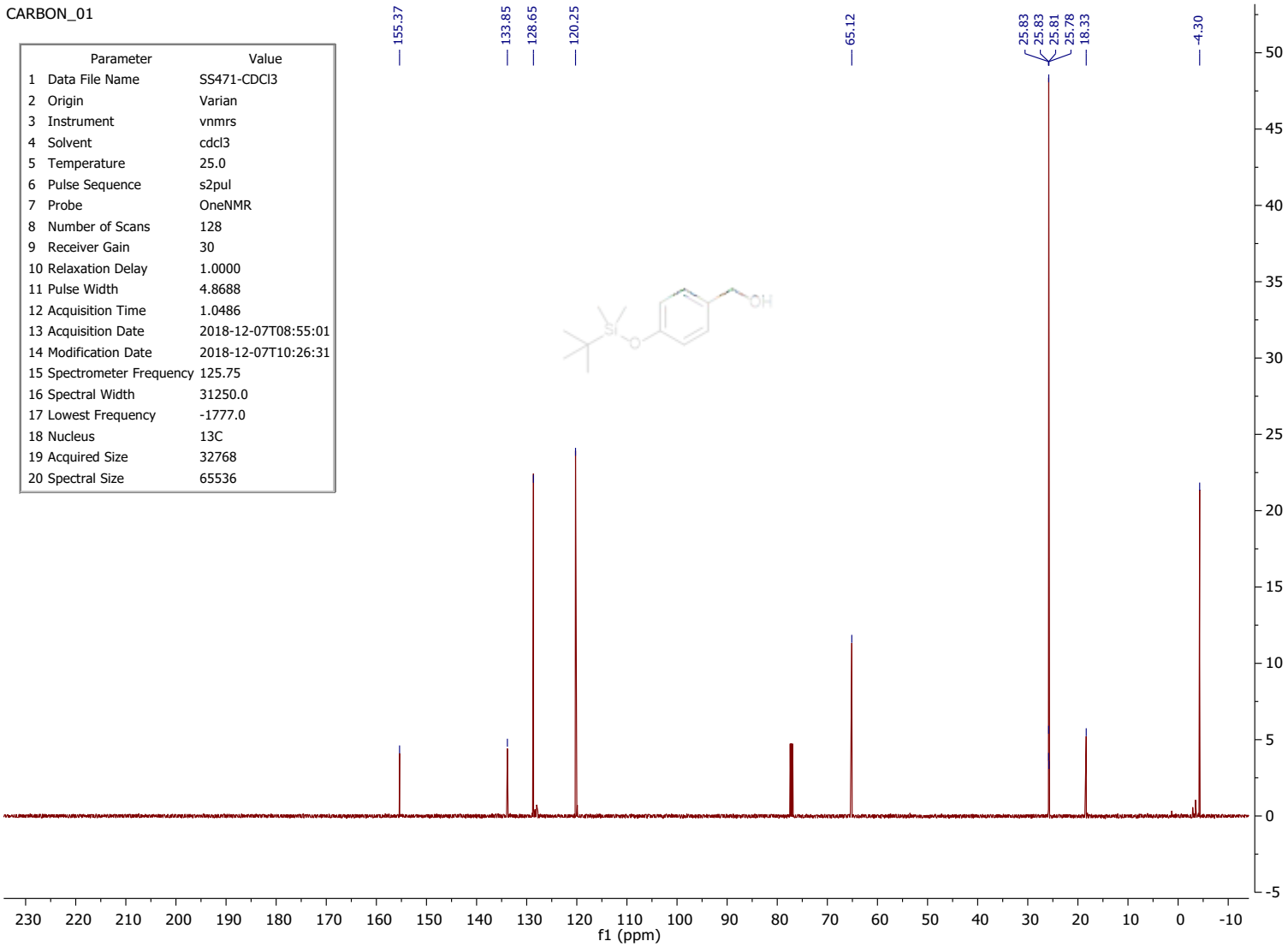
PROTON_01

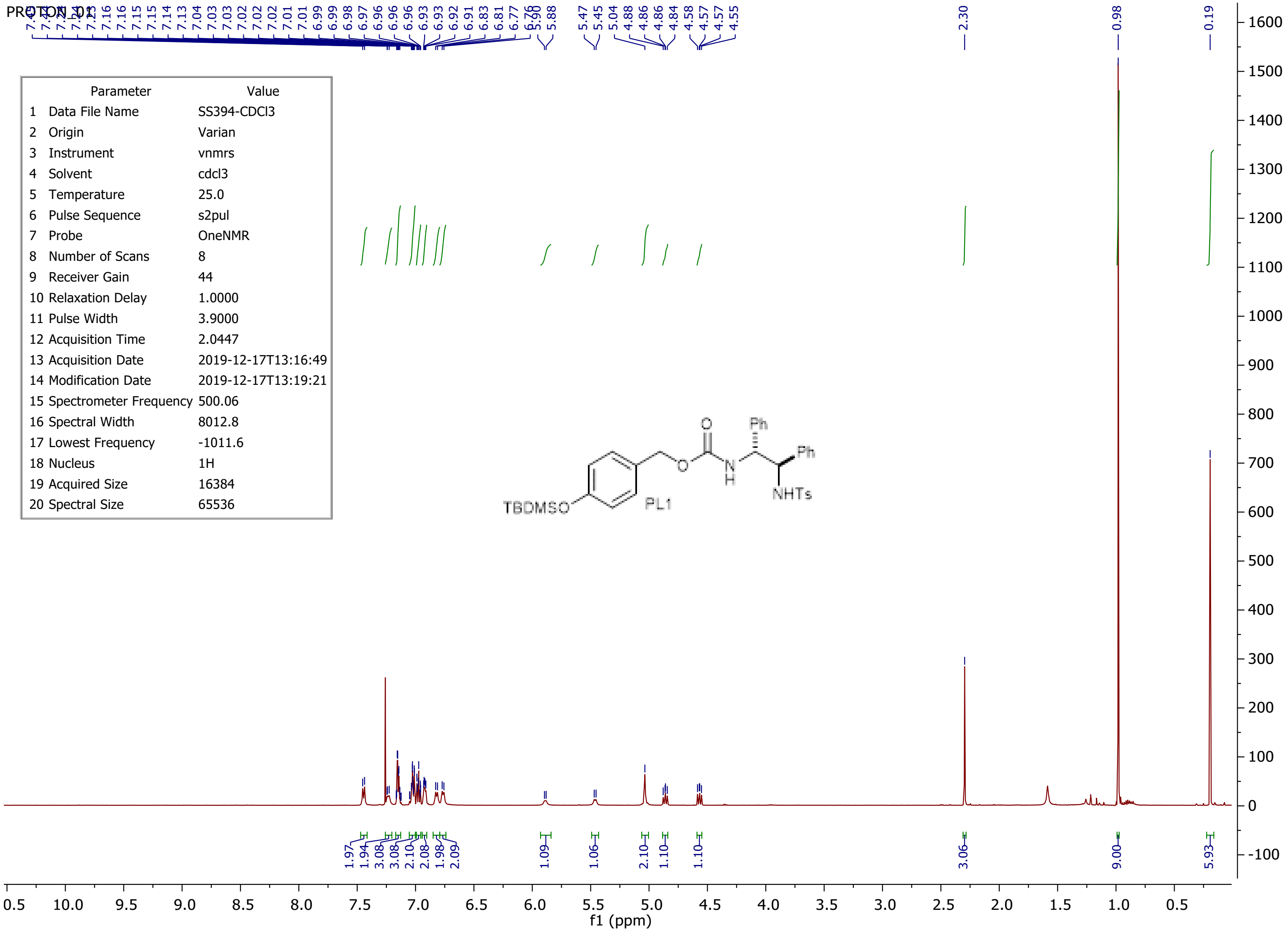
	Parameter	Value
1	Data File Name	SS471-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	8
9	Receiver Gain	22
10	Relaxation Delay	1.0000
11	Pulse Width	3.9000
12	Acquisition Time	2.0447
13	Acquisition Date	2018-12-07T08:54:24
14	Modification Date	2018-12-07T10:26:31
15	Spectrometer Frequency	500.06
16	Spectral Width	8012.8
17	Lowest Frequency	-1004.1
18	Nucleus	1H
19	Acquired Size	16384
20	Spectral Size	65536



CARBON_01

	Parameter	Value
1	Data File Name	SS471-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	128
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	4.8688
12	Acquisition Time	1.0486
13	Acquisition Date	2018-12-07T08:55:01
14	Modification Date	2018-12-07T10:26:31
15	Spectrometer Frequency	125.75
16	Spectral Width	31250.0
17	Lowest Frequency	-1777.0
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536

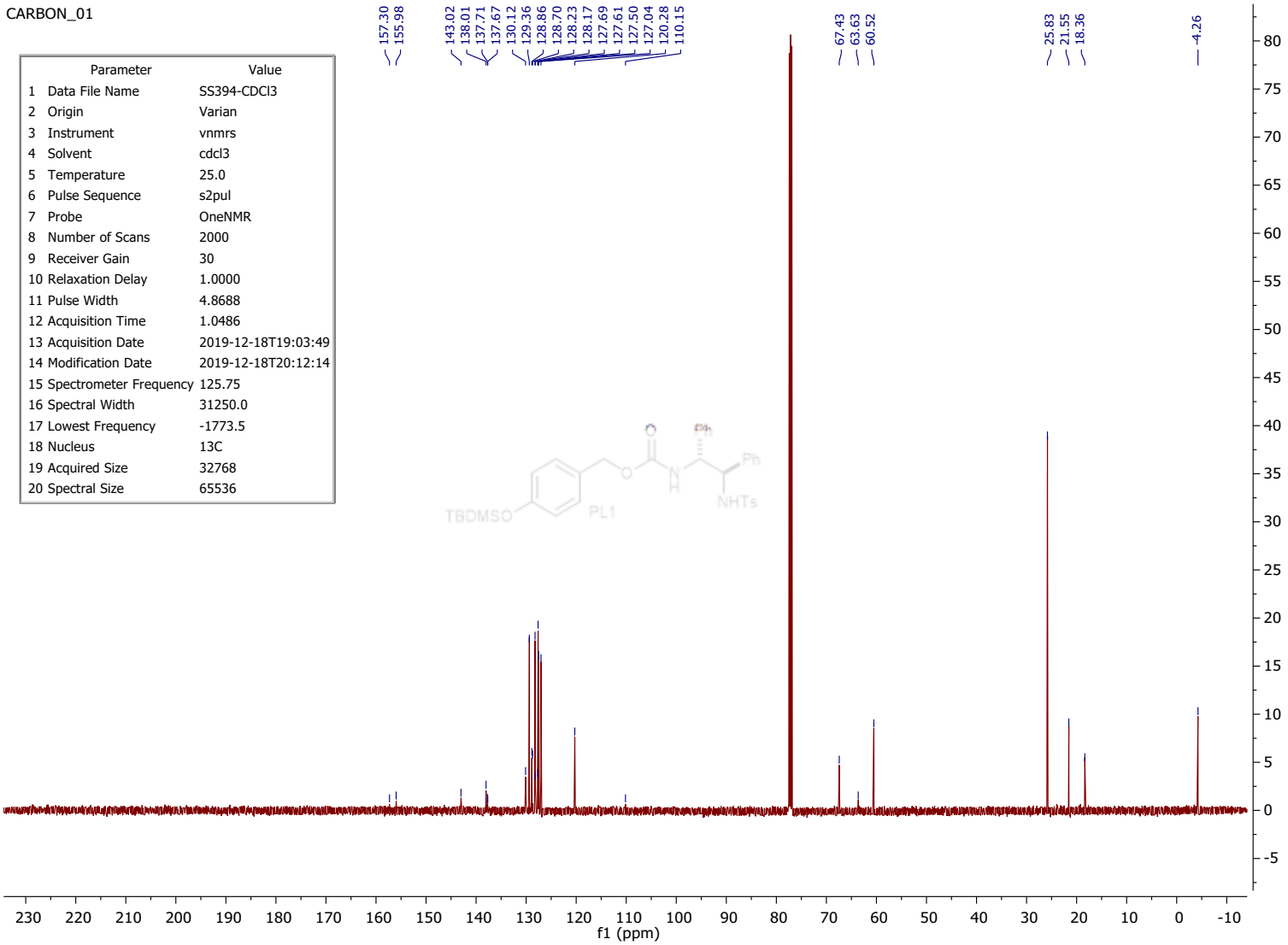


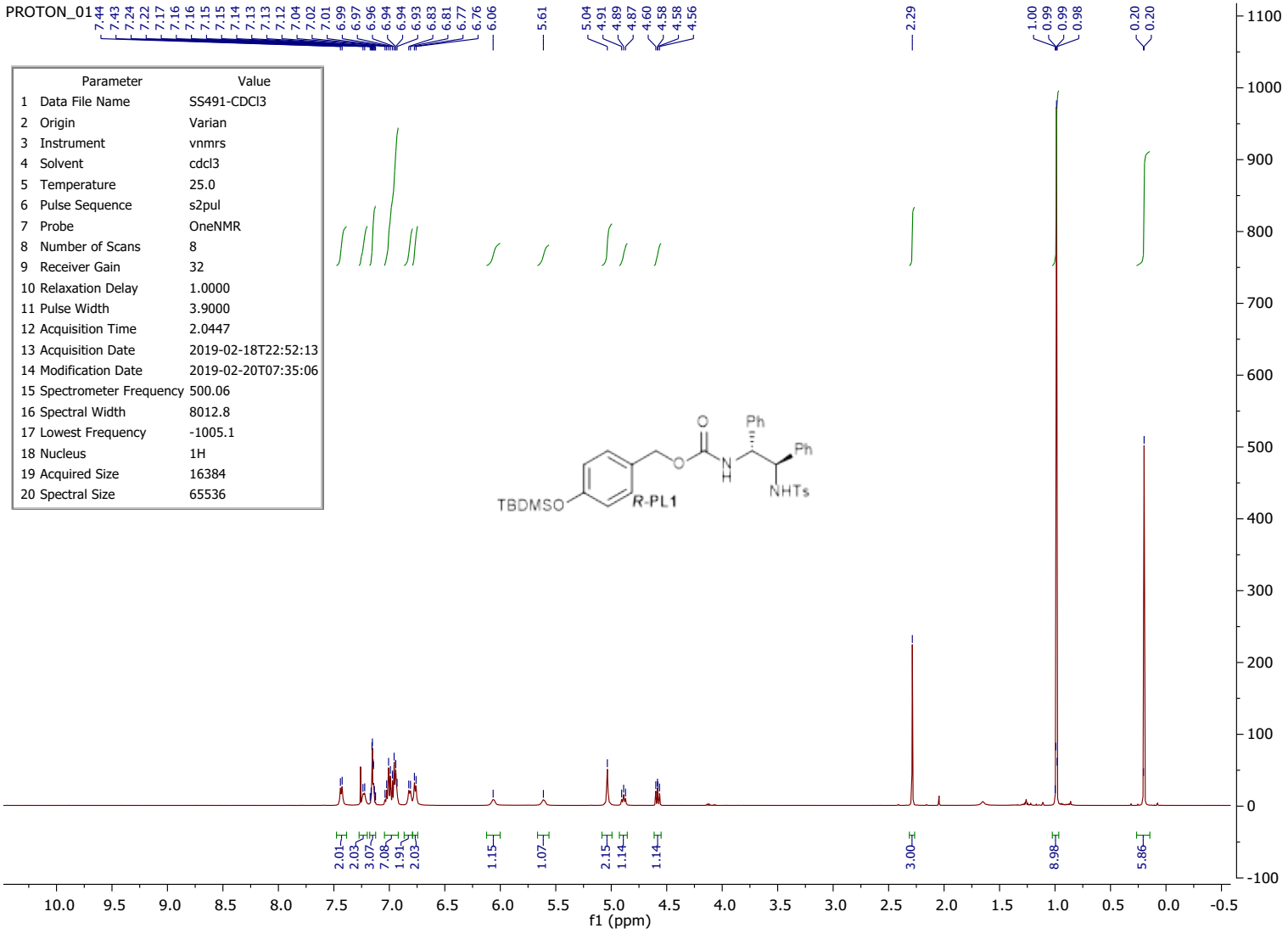


	Parameter	Value
1	Data File Name	SS394-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	8
9	Receiver Gain	44
10	Relaxation Delay	1.0000
11	Pulse Width	3.9000
12	Acquisition Time	2.0447
13	Acquisition Date	2019-12-17T13:16:49
14	Modification Date	2019-12-17T13:19:21
15	Spectrometer Frequency	500.06
16	Spectral Width	8012.8
17	Lowest Frequency	-1011.6
18	Nucleus	1H
19	Acquired Size	16384
20	Spectral Size	65536

CARBON_01

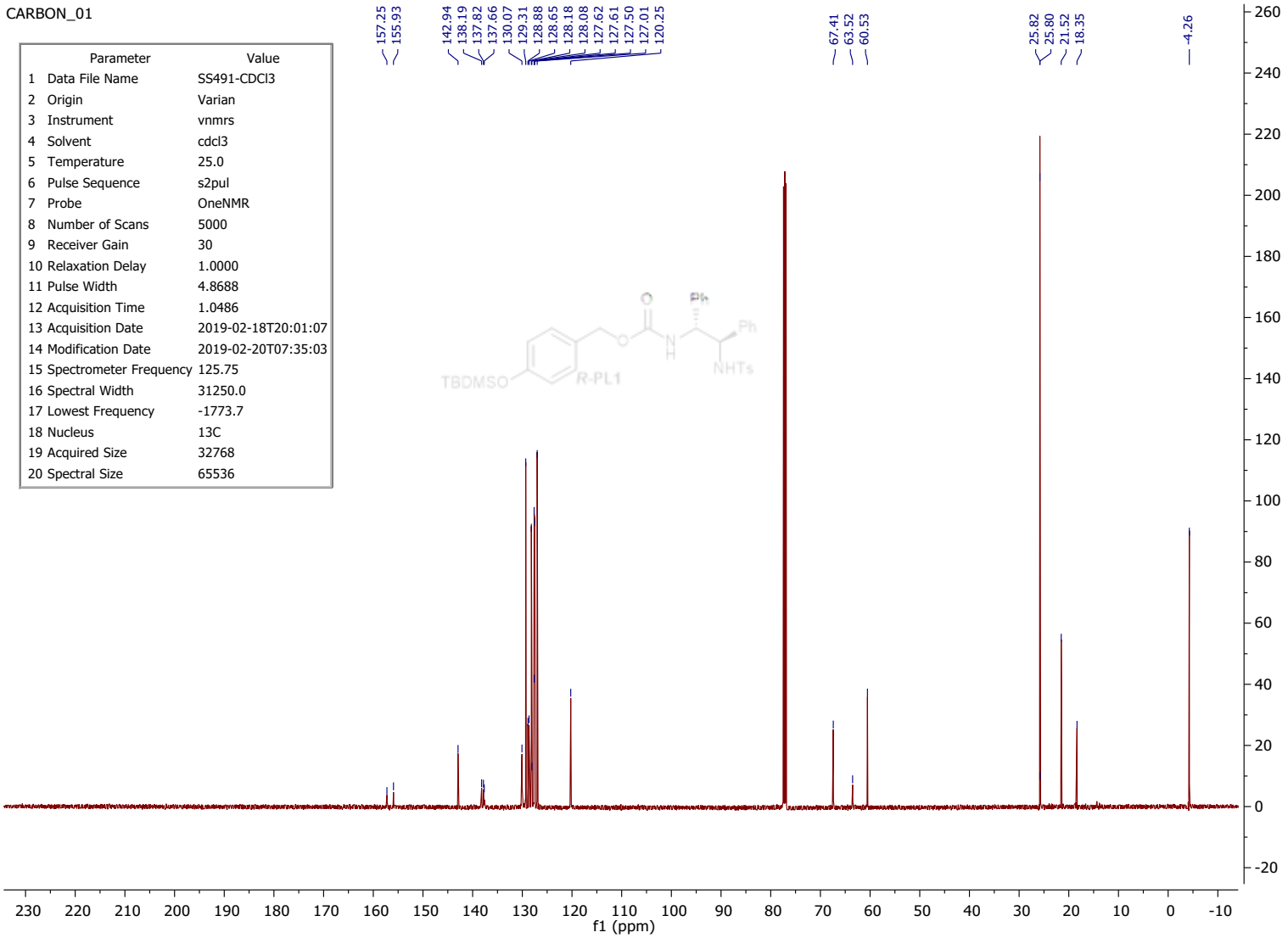
	Parameter	Value
1	Data File Name	SS394-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	2000
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	4.8688
12	Acquisition Time	1.0486
13	Acquisition Date	2019-12-18T19:03:49
14	Modification Date	2019-12-18T20:12:14
15	Spectrometer Frequency	125.75
16	Spectral Width	31250.0
17	Lowest Frequency	-1773.5
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536

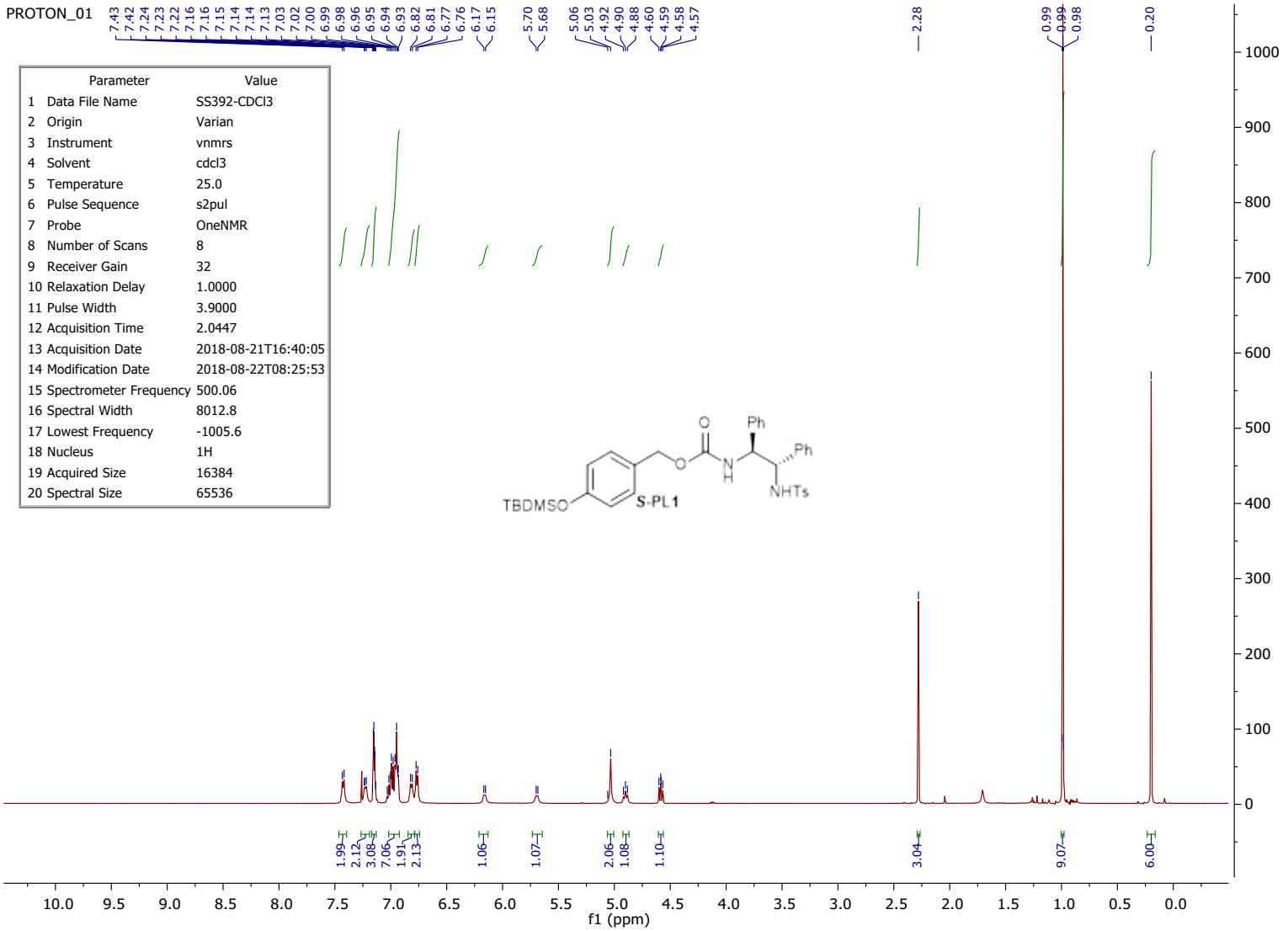



PROTON_01
7.44 7.43 7.24 7.22 7.17 7.16 7.16 7.15 7.15 7.14 7.13 7.13 7.12 7.04 7.02 7.01 6.99 6.97 6.96 6.94 6.94 6.93 6.83 6.81 6.77 6.76 6.06
5.61
5.04 4.91 4.89 4.87 4.60 4.58 4.58 4.56
2.29
1.00 0.99 0.99 0.98
0.20 0.20
Parameter Value
1 Data File Name SS491-CDCl3
2 Origin Varian
3 Instrument vnmrs
4 Solvent cdcl3
5 Temperature 25.0
6 Pulse Sequence s2pul
7 Probe OneNMR
8 Number of Scans 8
9 Receiver Gain 32
10 Relaxation Delay 1.0000
11 Pulse Width 3.9000
12 Acquisition Time 2.0447
13 Acquisition Date 2019-02-18T22:52:13
14 Modification Date 2019-02-20T07:35:06
15 Spectrometer Frequency 500.06
16 Spectral Width 8012.8
17 Lowest Frequency -1005.1
18 Nucleus 1H
19 Acquired Size 16384
20 Spectral Size 65536
TBDMSO
R-PL1
O
N
H
Ph
Ph
NHTs
2.01 2.03 3.07 7.08 1.91 2.03
1.15
1.07
2.15 1.14
1.14
3.00
8.98
5.86
f1 (ppm)

CARBON_01

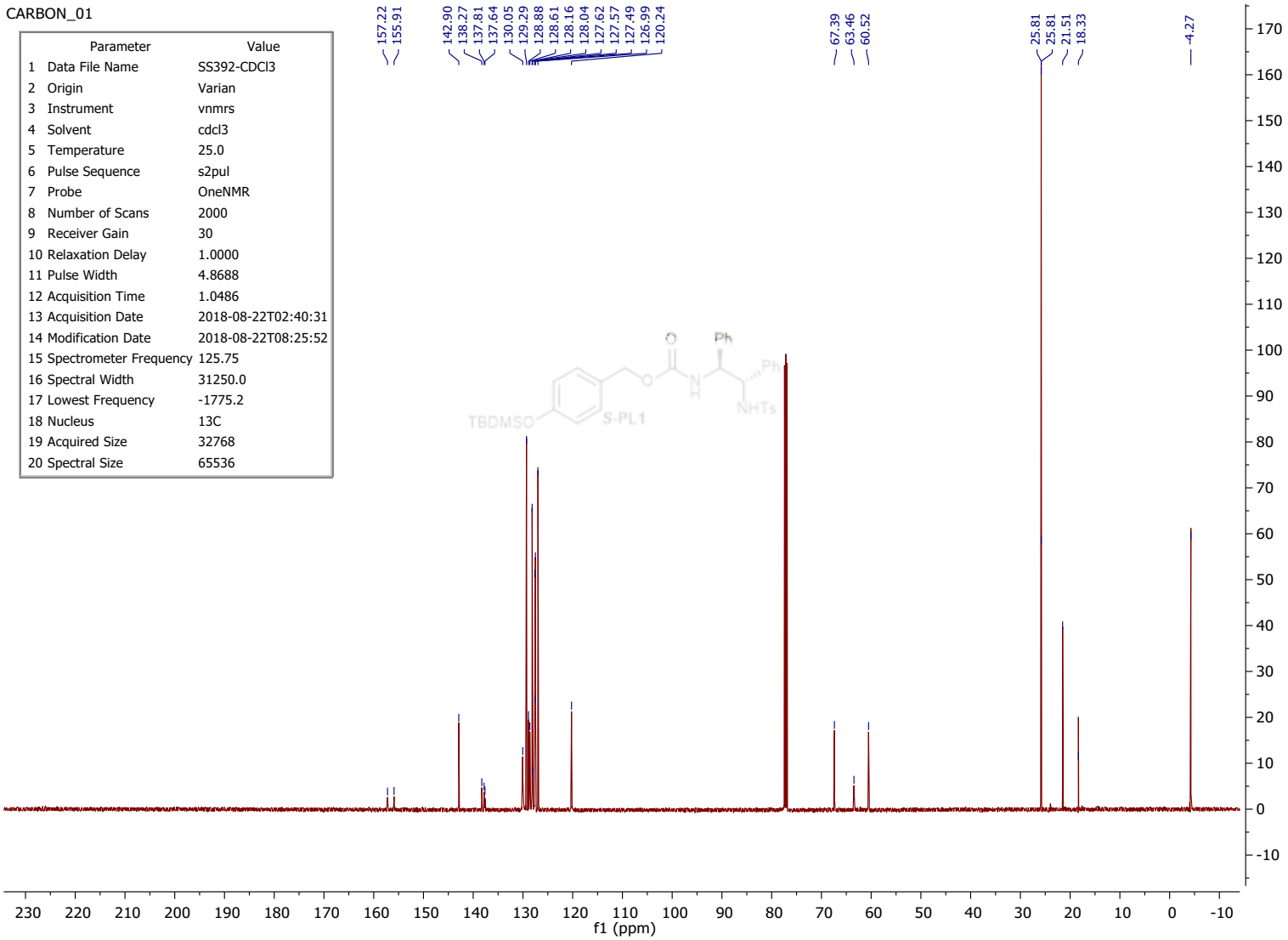
	Parameter	Value
1	Data File Name	SS491-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	5000
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	4.8688
12	Acquisition Time	1.0486
13	Acquisition Date	2019-02-18T20:01:07
14	Modification Date	2019-02-20T07:35:03
15	Spectrometer Frequency	125.75
16	Spectral Width	31250.0
17	Lowest Frequency	-1773.7
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536




PROTON_01
7.43 7.42 7.24 7.23 7.22 7.16 7.16 7.15 7.14 7.14 7.13 7.03 7.02 7.00 6.99 6.98 6.96 6.95 6.94 6.93 6.82 6.81 6.77 6.76 6.17 6.15 5.70 5.68 5.06 5.03 4.92 4.90 4.88 4.60 4.59 4.58 4.57 2.28 0.99 0.99 0.98 0.20
Parameter Value
1 Data File Name SS392-CDCl3
2 Origin Varian
3 Instrument vnmrs
4 Solvent cdcl3
5 Temperature 25.0
6 Pulse Sequence s2pul
7 Probe OneNMR
8 Number of Scans 8
9 Receiver Gain 32
10 Relaxation Delay 1.0000
11 Pulse Width 3.9000
12 Acquisition Time 2.0447
13 Acquisition Date 2018-08-21T16:40:05
14 Modification Date 2018-08-22T08:25:53
15 Spectrometer Frequency 500.06
16 Spectral Width 8012.8
17 Lowest Frequency -1005.6
18 Nucleus 1H
19 Acquired Size 16384
20 Spectral Size 65536
TBDMSO
S-PL1
O
N
H
Ph
Ph
NHTs
1000
900
800
700
600
500
400
300
200
100
0
1.99 2.12 3.08 7.06 1.91 2.13 1.06 1.07 2.06 1.08 1.10 3.04 9.07 6.00
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 0.0
f1 (ppm)

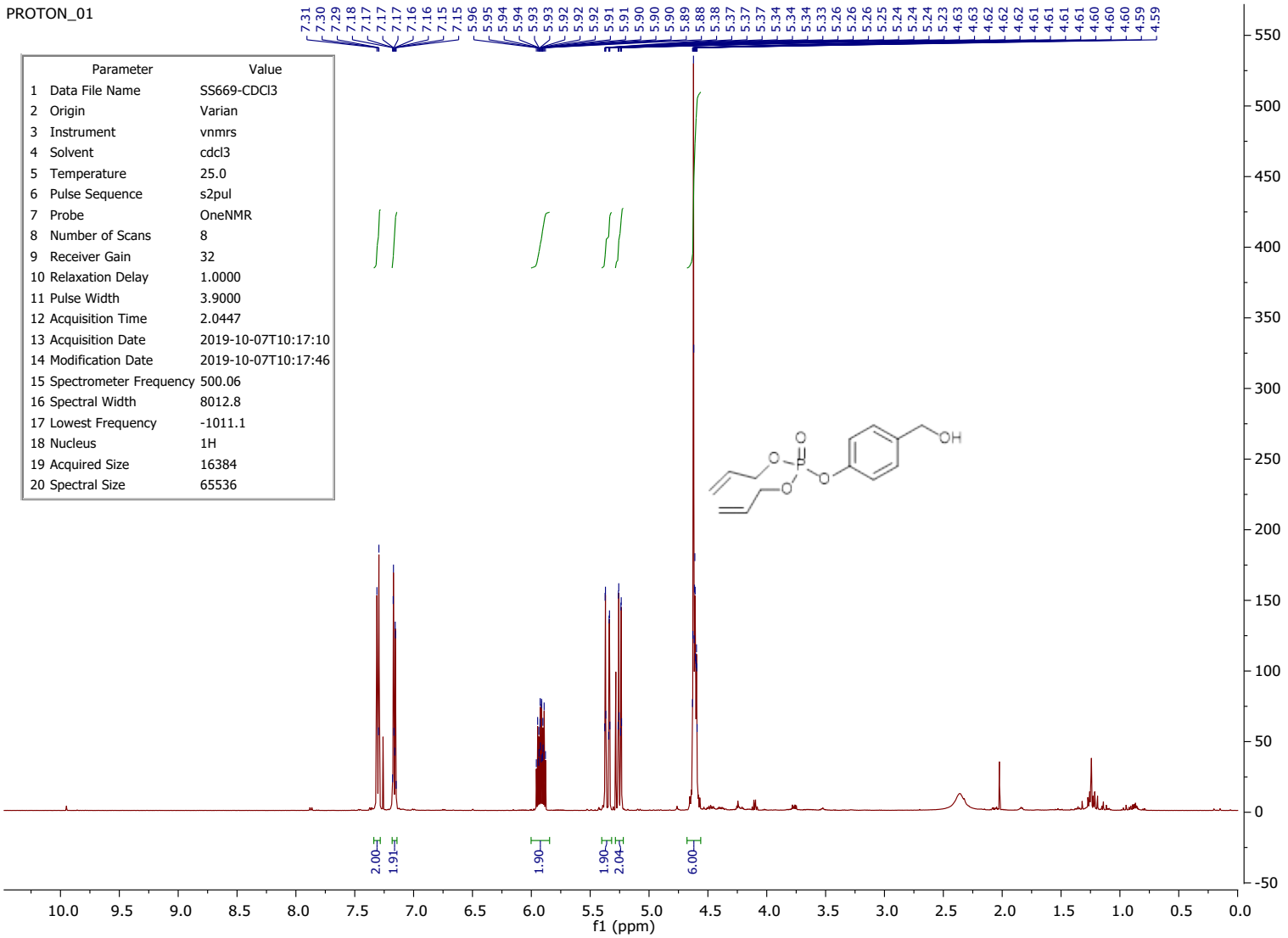
CARBON_01

	Parameter	Value
1	Data File Name	SS392-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	2000
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	4.8688
12	Acquisition Time	1.0486
13	Acquisition Date	2018-08-22T02:40:31
14	Modification Date	2018-08-22T08:25:52
15	Spectrometer Frequency	125.75
16	Spectral Width	31250.0
17	Lowest Frequency	-1775.2
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



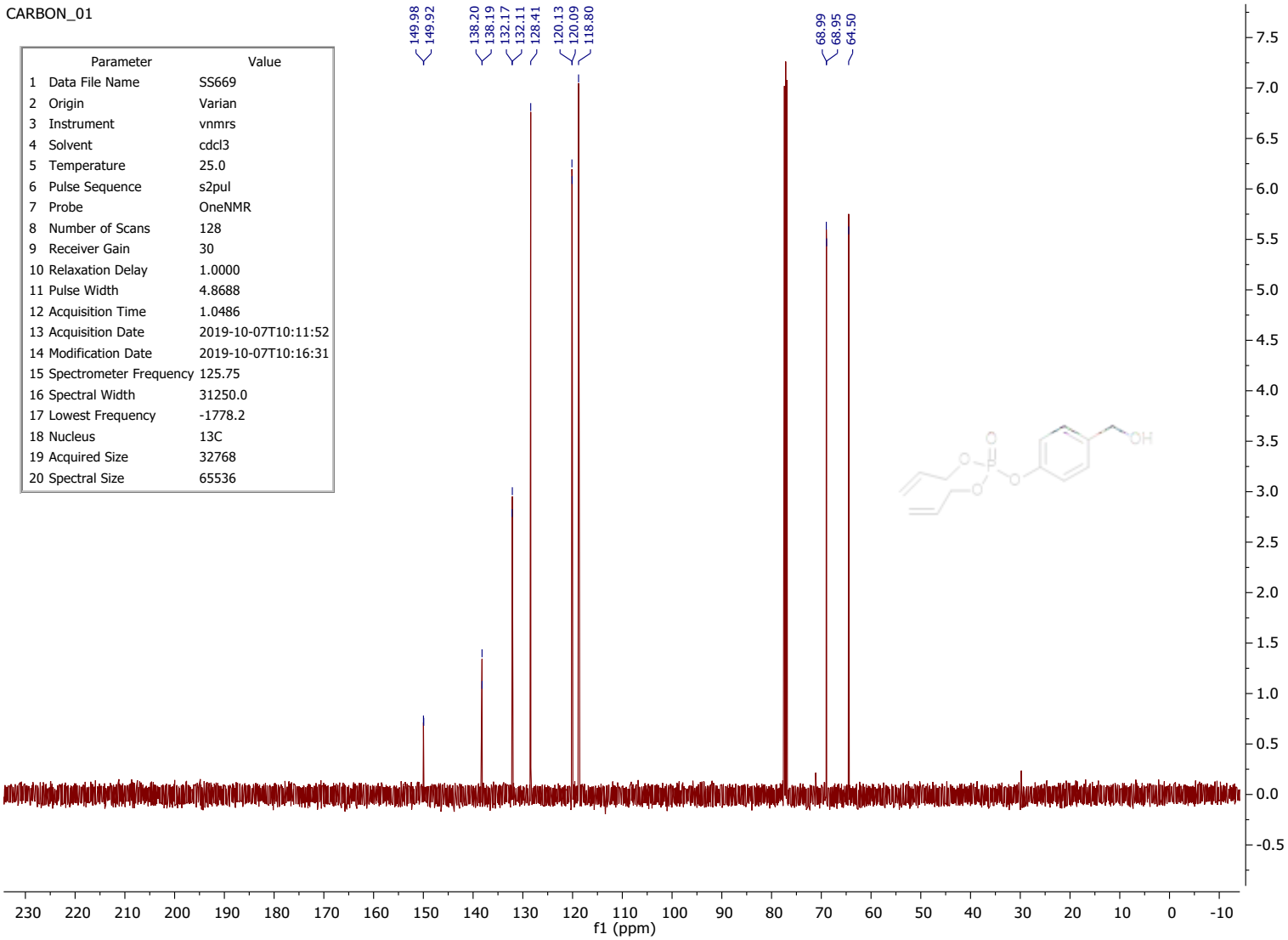
PROTON_01

	Parameter	Value
1	Data File Name	SS669-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	8
9	Receiver Gain	32
10	Relaxation Delay	1.0000
11	Pulse Width	3.9000
12	Acquisition Time	2.0447
13	Acquisition Date	2019-10-07T10:17:10
14	Modification Date	2019-10-07T10:17:46
15	Spectrometer Frequency	500.06
16	Spectral Width	8012.8
17	Lowest Frequency	-1011.1
18	Nucleus	1H
19	Acquired Size	16384
20	Spectral Size	65536



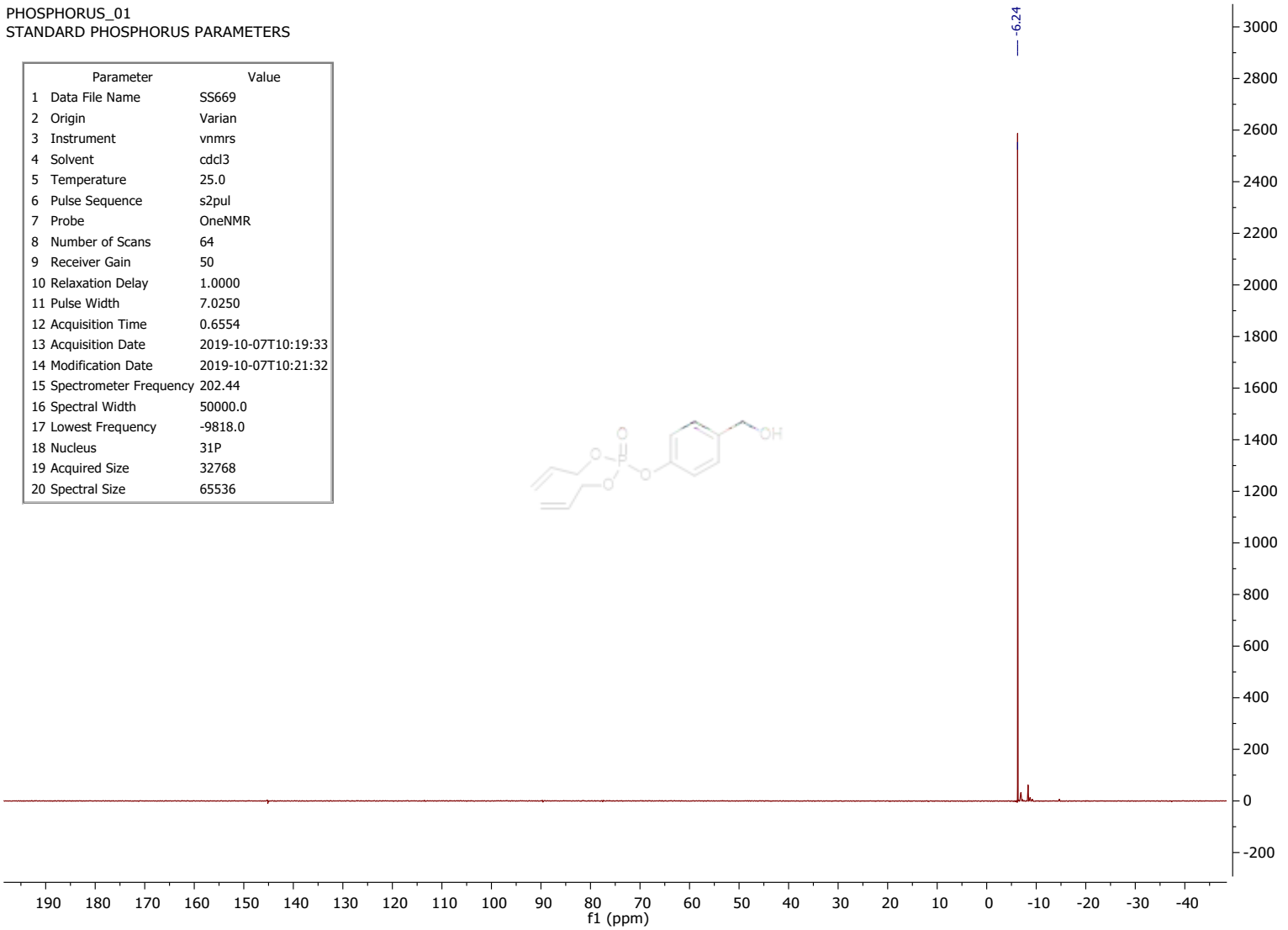
CARBON_01

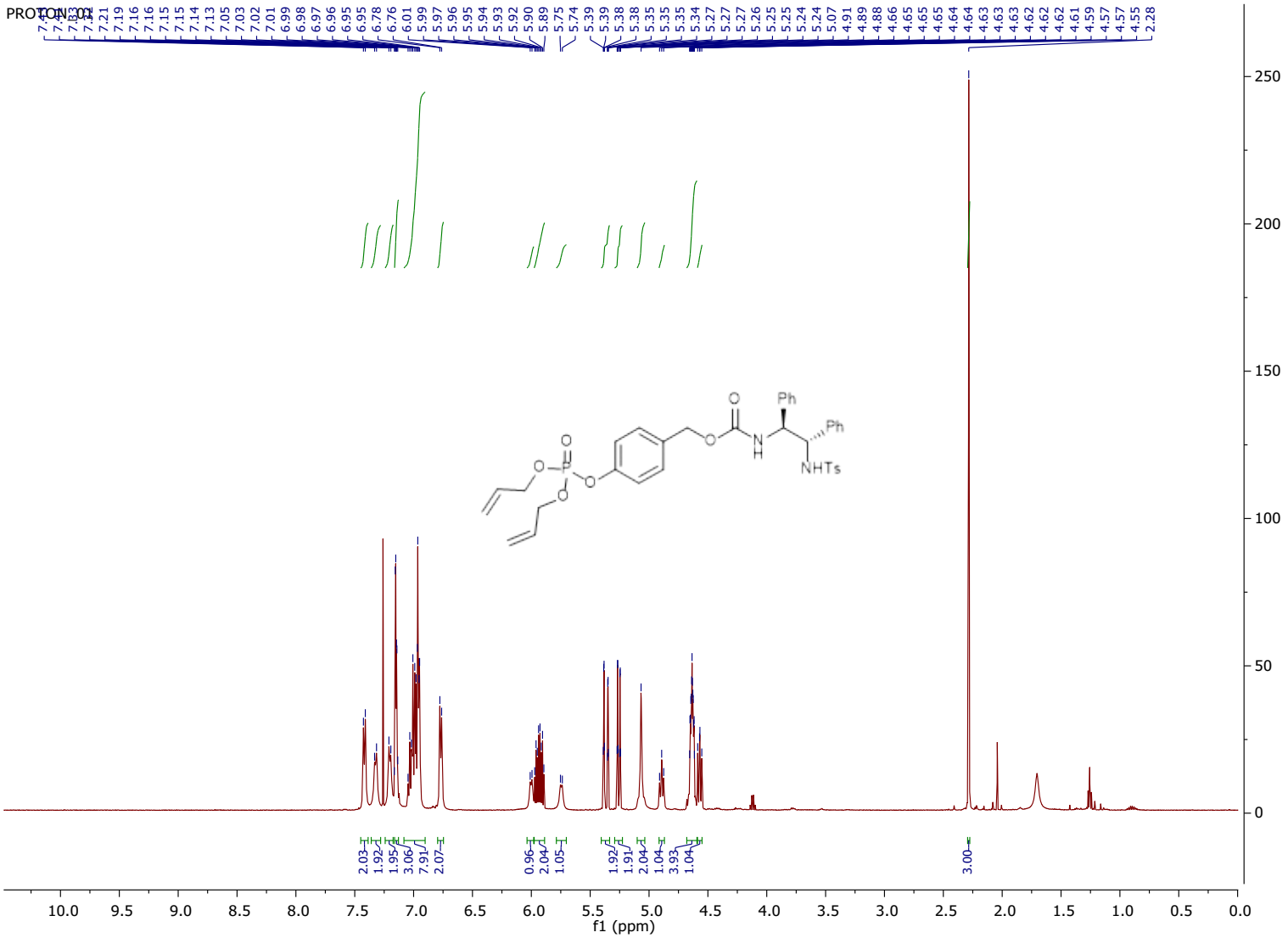
	Parameter	Value
1	Data File Name	SS669
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	128
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	4.8688
12	Acquisition Time	1.0486
13	Acquisition Date	2019-10-07T10:11:52
14	Modification Date	2019-10-07T10:16:31
15	Spectrometer Frequency	125.75
16	Spectral Width	31250.0
17	Lowest Frequency	-1778.2
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



PHOSPHORUS_01
STANDARD PHOSPHORUS PARAMETERS

	Parameter	Value
1	Data File Name	SS669
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	64
9	Receiver Gain	50
10	Relaxation Delay	1.0000
11	Pulse Width	7.0250
12	Acquisition Time	0.6554
13	Acquisition Date	2019-10-07T10:19:33
14	Modification Date	2019-10-07T10:21:32
15	Spectrometer Frequency	202.44
16	Spectral Width	50000.0
17	Lowest Frequency	-9818.0
18	Nucleus	31P
19	Acquired Size	32768
20	Spectral Size	65536




PROTON_01
f1 (ppm)
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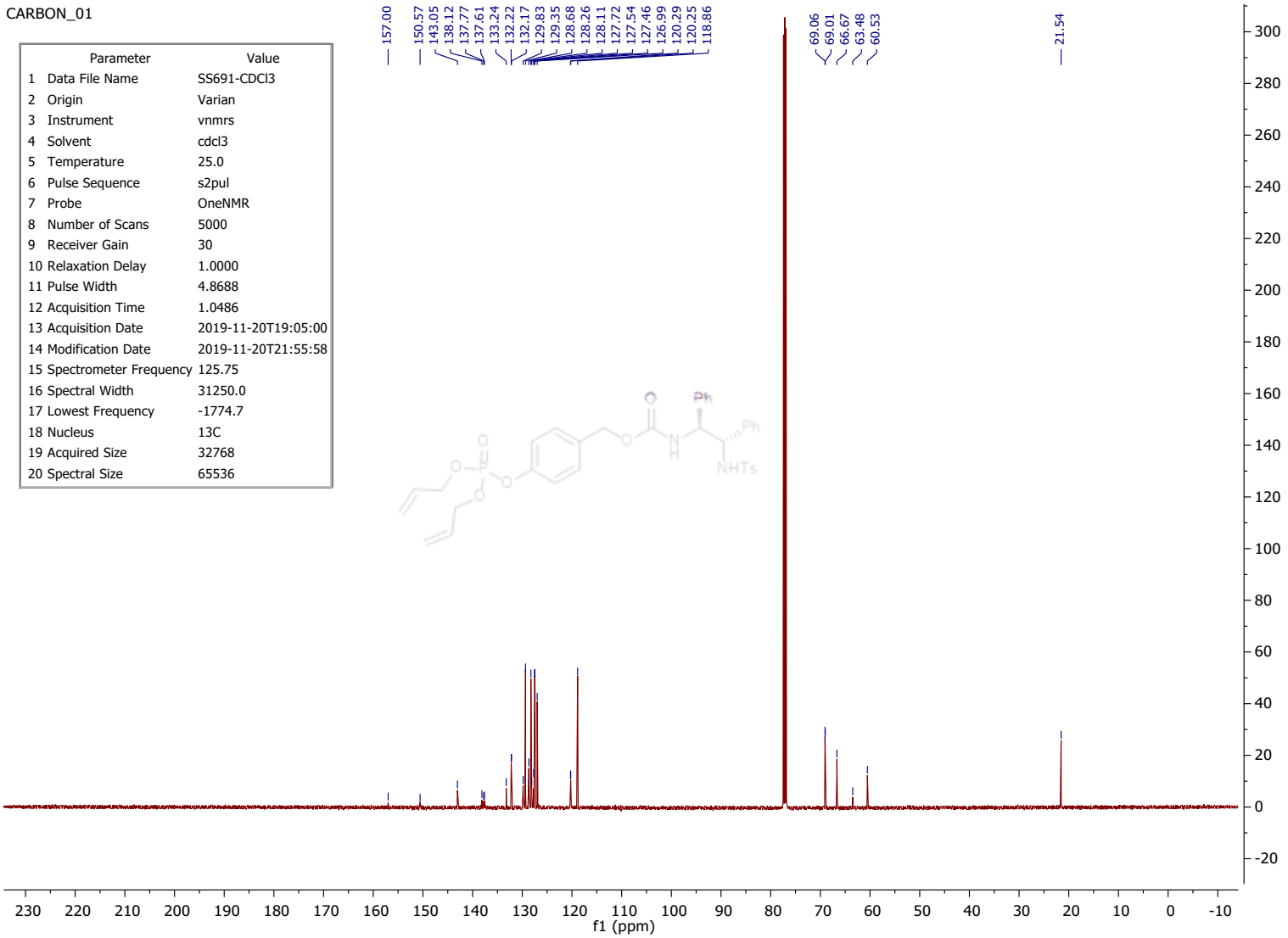
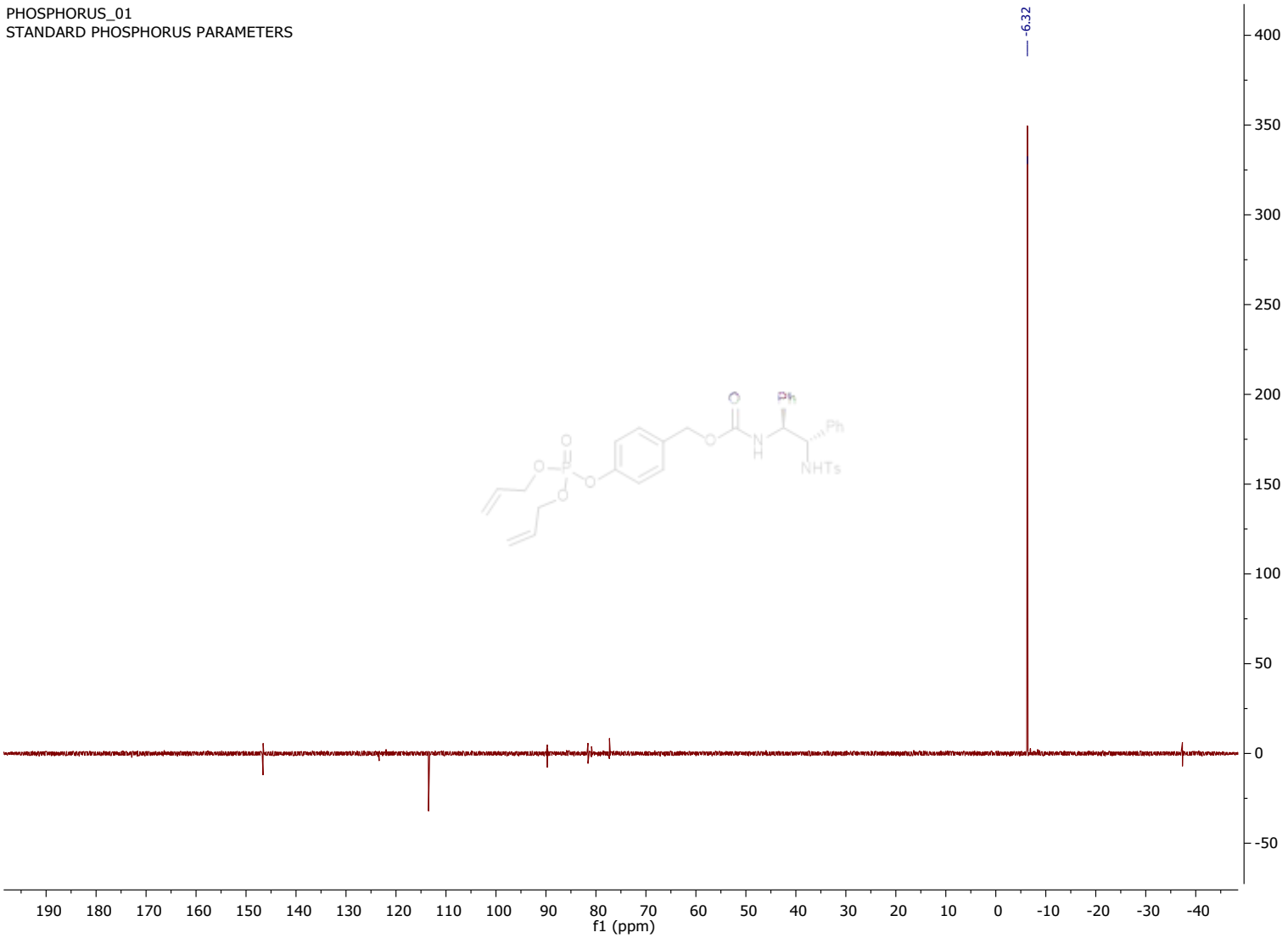
CARBON_01

	Parameter	Value
1	Data File Name	SS691-CDCl3
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	5000
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	4.8688
12	Acquisition Time	1.0486
13	Acquisition Date	2019-11-20T19:05:00
14	Modification Date	2019-11-20T21:55:58
15	Spectrometer Frequency	125.75
16	Spectral Width	31250.0
17	Lowest Frequency	-1774.7
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536

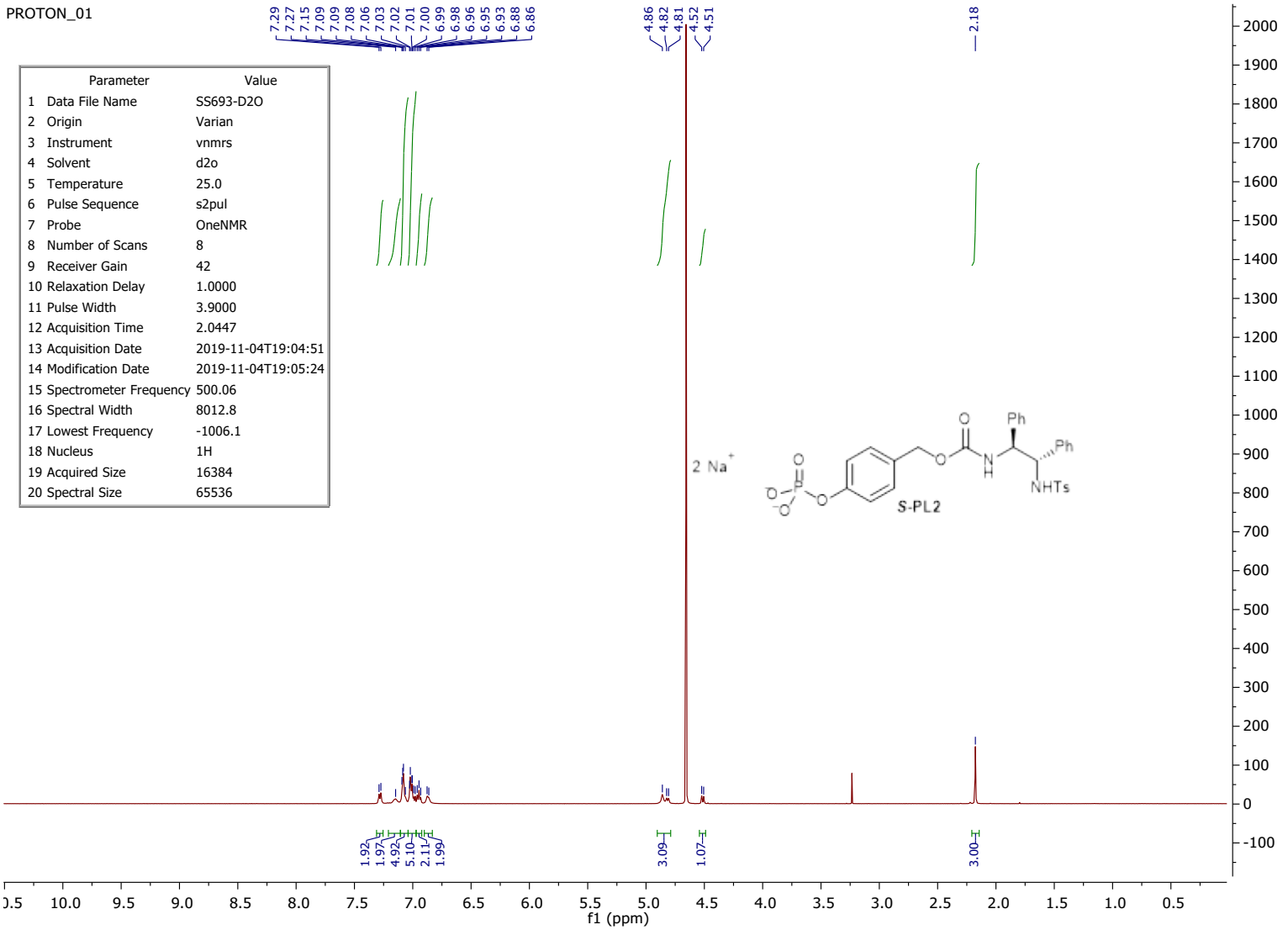


PHOSPHORUS_01
STANDARD PHOSPHORUS PARAMETERS



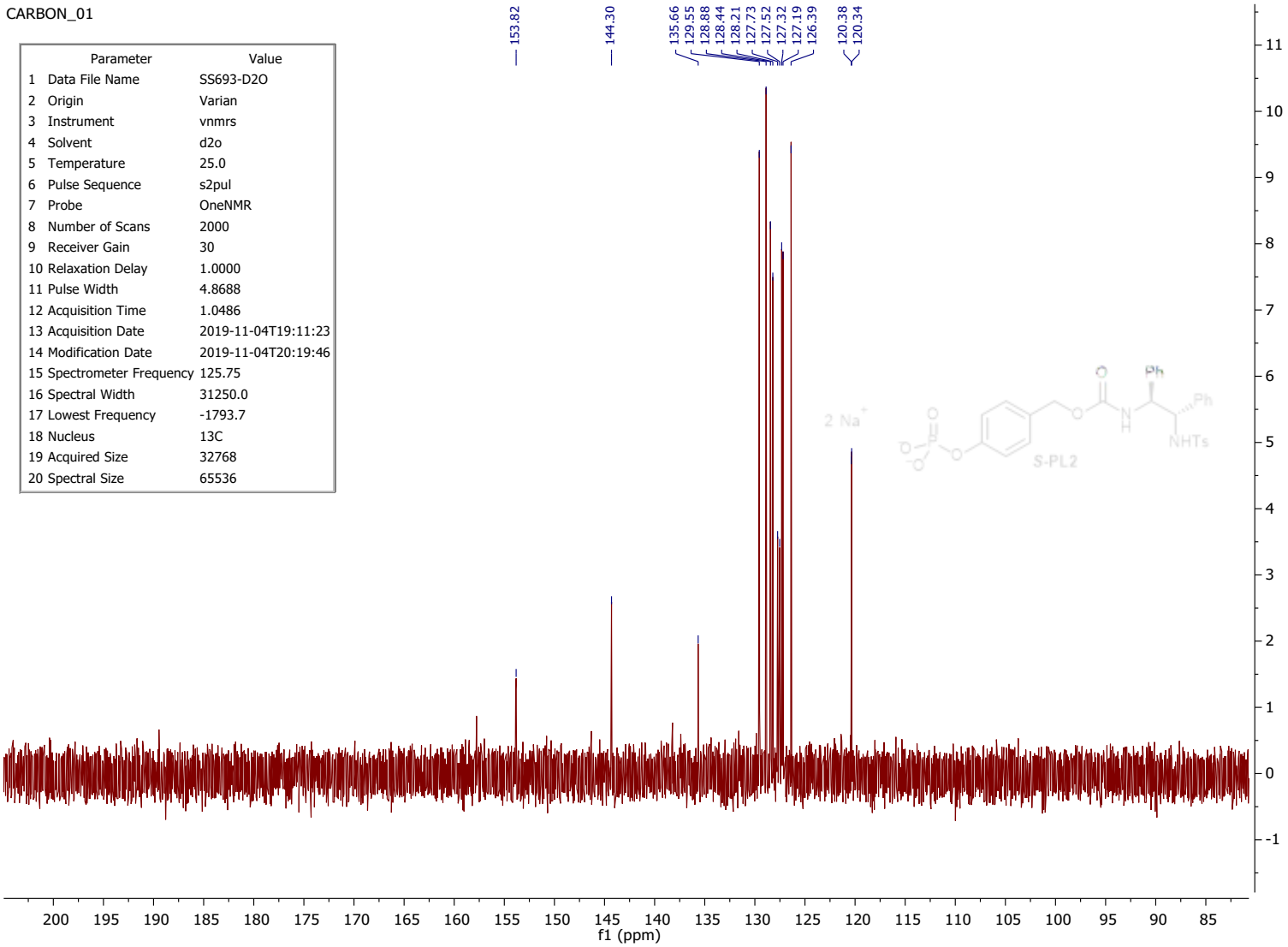
PROTON_01

	Parameter	Value
1	Data File Name	SS693-D2O
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	d2o
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	8
9	Receiver Gain	42
10	Relaxation Delay	1.0000
11	Pulse Width	3.9000
12	Acquisition Time	2.0447
13	Acquisition Date	2019-11-04T19:04:51
14	Modification Date	2019-11-04T19:05:24
15	Spectrometer Frequency	500.06
16	Spectral Width	8012.8
17	Lowest Frequency	-1006.1
18	Nucleus	1H
19	Acquired Size	16384
20	Spectral Size	65536



CARBON_01

	Parameter	Value
1	Data File Name	SS693-D2O
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	d2o
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	2000
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	4.8688
12	Acquisition Time	1.0486
13	Acquisition Date	2019-11-04T19:11:23
14	Modification Date	2019-11-04T20:19:46
15	Spectrometer Frequency	125.75
16	Spectral Width	31250.0
17	Lowest Frequency	-1793.7
18	Nucleus	13C
19	Acquired Size	32768
20	Spectral Size	65536



PHOSPHORUS_01
STANDARD PHOSPHORUS PARAMETERS

	Parameter	Value
1	Data File Name	SS693-D2O
2	Origin	Varian
3	Instrument	vnmrs
4	Solvent	d2o
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	OneNMR
8	Number of Scans	64
9	Receiver Gain	50
10	Relaxation Delay	1.0000
11	Pulse Width	7.0250
12	Acquisition Time	0.6554
13	Acquisition Date	2019-11-04T19:06:56
14	Modification Date	2019-11-04T19:08:48
15	Spectrometer Frequency	202.44
16	Spectral Width	50000.0
17	Lowest Frequency	-9818.0
18	Nucleus	31P
19	Acquired Size	32768
20	Spectral Size	65536