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Supporting Information

Design, Synthesis, and Application of Chiral C_2-Symmetric Spiroketal-Containing Ligands in Transition-Metal Catalysis

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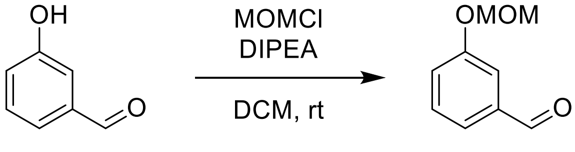
General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring, unless otherwise noted. Air-sensitive reagents and solutions were transferred *via* syringe or cannula and were introduced to the apparatus through rubber septa. Reactions were cooled via external cooling baths: ice water (0°C), dry ice-acetone (-78°C), or Neslab CB 80 immersion cooler (0 to -60°C). Heating was achieved using a silicone bath with regulated by an electronic contact thermometer. Deionized water was used in the preparation of all aqueous solutions and for all aqueous extractions. Solvents used for extraction and column chromatography were ACS or HPLC grade. Dry tetrahydrofuran (THF), dichloromethane (DCM), toluene (PhMe), and diethyl ether (Et_2O) was prepared by filtration through a column (Innovative Technologies) of activated alumina under nitrogen atmosphere. Reactions were monitored by nuclear magnetic resonance (NMR, see below) or thin layer chromatography (TLC) on silica gel precoated glass plates (0.25 mm, SiliCycle, SiliaPlate). TLC plate visualization was accomplished by irradiation with UV light at 254 nm or by staining with a potassium permanganate ($KMnO_4$) or cerium ammonium molybdate (CAM) solution. Flash chromatography was performed using SiliCycle SiliaFlash P60 (230-400 mesh) silica gel. Powdered 4 Å molecular sieves were pre-activated by flame-drying under vacuum before use.

Proton (^1H), deuterium (D), carbon (^{13}C), fluorine (^{19}F), and phosphorus (^{31}P) NMR spectra were recorded on Varian VNMRS-700 (700 MHz), Varian VNMRS-500 (500 MHz), Varian INOVA 500 (500 MHz), or Varian MR400 (400 MHz). ^1H , ^{13}C, ^{19}F, and ^{31}P NMR spectra are referenced on a unified scale, where the single reference is the frequency of the residual solvent peak in the ^1H NMR spectrum. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane for ^1H and ^{13}C NMR, fluorotrichloromethane for ^{19}F, 85% phosphoric acid for ^{31}P. Data is reported as (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration). Slight shape deformation of the peaks in some cases due to weak coupling (e.g. aromatic protons) is not explicitly mentioned. High resolution mass spectra (HRMS) were recorded on Micromass AutoSpec Ultima or VG (Micromass) 70-250-S Magnetic sector mass. IR spectra were collected using a Nicolet iS10 spectrometer equipped with a diamond attenuated total reflectance (ATR) accessory. IR absorption peaks were reported in wavenumbers (cm^{-1}). The enantiomeric excesses were determined by GC, SFC, or HPLC analysis employing a chiral stationary phase column and conditions specified in the individual experiment. SFC analysis was carried out in a Waters Investigator SFC instrument. HPLC experiments were performed using a Waters Alliance e2695 Separations Module instrument. GC analysis was done in a Shimadzu GC-2010 Plus instrument. Optical rotations were measured at room temperature in a solvent of choice on a JASCO P-2000 digital polarimeter at 589 nm (D-line).

Synthesis of diphosphine (*S,S,S*)-SPIRAP and Pd(II) complex

3-(methoxymethoxy)benzaldehyde (1a)



1a

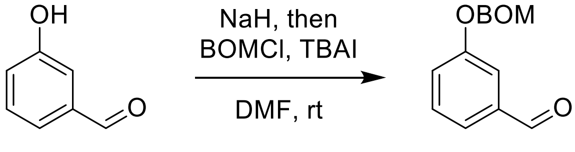
3-hydroxybenzaldehyde (24.0g, 196.5mmol), DCM (500mL), and N,N-diisopropylethylamine (100mL, 574mmol) were cooled to 0°C before adding chloromethyl methyl ether (23mL, 302.8mmol) over 2h with a venting needle to handle the fumes. Reaction mixture was then warmed to room temperature. After 17h at room temperature, reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (500 mL). After separating the phases, the aqueous layer was extracted DCM twice. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, 20% EtOAc in hexanes) to obtain the desired product **1a** as pale yellow liquid (31.94g, 97.8% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.57 – 7.51 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.32 – 7.28 (m, 1H), 5.24 (s, 2H), 3.49 (s, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 191.96, 157.76, 137.82, 130.11, 123.81, 122.83, 115.93, 94.39, 56.16.

IR (film): ν_{max} = 2956, 2923, 2849, 2730, 1699, 1585, 1463, 1454, 1389, 1248, 1152, 1077, 1008, 789 cm^{-1}

3-((benzyloxy)methoxy)benzaldehyde (1b)



1b

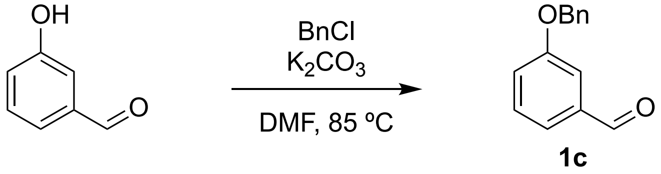
NaH (60% suspension) (2.47g, 60.25mmol) was added to a solution of 3-hydroxybenzaldehyde (5.00g, 40.94 mmol) in DMF (120mL) at 0°C. After 15min, benzyl chloromethyl ether (8.54mL, 61.42mmol) was added dropwise followed by the addition of tetrabutylammonium iodide (826mg, 2.24mmol). After overnight stirring at 0°C, reaction mixture was quenched with water (80mL), and the product was extracted with DCM (4 x 70mL). Combined organic was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, 5% EtOAc in hexanes) to afford aldehyde **1b** as clear oil (9.62g, 97% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.60 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.39 – 7.28 (m, 6H), 5.36 (s, 2H), 4.74 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.93, 157.83, 137.86, 136.96, 130.14, 128.49, 128.00, 127.98, 123.74, 122.76, 116.16, 92.24, 70.22.

IR (film): ν_{max} = 2904, 2729, 1699, 1585, 1483, 1454, 1383, 1242, 1157, 1144, 1076, 1013, 989, 736 cm^{-1}

3-(benzyloxy)benzaldehyde (1c)



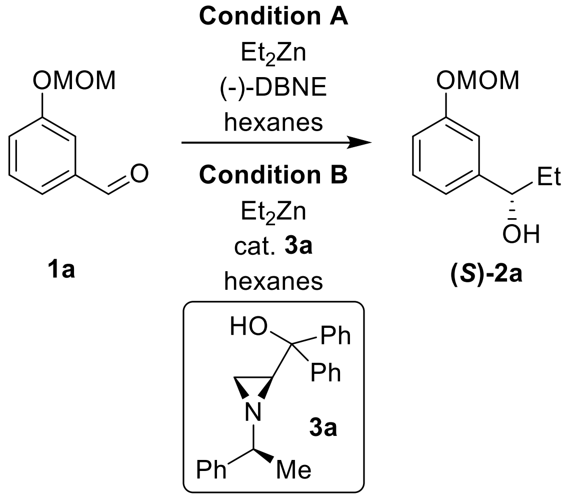
A solution of 3-hydroxybenzaldehyde (13.50g, 110.54mmol) and potassium carbonate (22.90g, 165.7mmol) in DMF (225mL) was treated dropwise with solution of benzylchloride (19mL, 165.1mmol) in DMF (160mL). After 15min at 50°C, reaction mixture was heated to 85°C for 24h. Reaction mixture was cooled to room temperature, diluted with DCM (150mL), and quenched with water (300mL). After separating the phases, the aqueous layer was extracted with DCM (3 x 200mL). Combined organic was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, 5% EtOAc in hexanes) to yield aldehyde **1c** as a white solid (18.77g, 80% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.51-7.43 (m, 5H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.37-7.32 (m, 1H), 7.27-7.23 (m, 1H), 5.13 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.02, 159.30, 137.82, 136.30, 130.10, 128.66, 128.19, 127.53, 123.65, 122.17, 113.27, 70.22.

IR (film): ν_{max} = 2811, 2727, 1693, 1594, 1480, 1443, 1383, 1325, 1255, 1146, 1016, 990, 794, 741, 697 cm^{-1}

(*S*)-1-(3-(methoxymethoxy)phenyl)propan-1-ol (2a)



Alkylations using DBNE as a catalyst were based on a reported procedure.[1] Those using aziridine catalyst **3a** or **3b** were based on another report.[2]

a) Using (-)-DBNE

Aldehyde **1a** (31.92g, 192.1mmol), hexanes (370mL), and N,N-dibutyl-D-(−)-norephedrine (3.8mL, 13.6mmol) were cooled to 0°C before adding a 1M solution of diethylzinc in hexanes (430mL, 430mmol) portionwise over 2h. After 27h at 0°C, reaction mixture was quenched with an aqueous solution of HCl 1M (150mL) and then filtered with DCM washings. Water (400mL) was added to the filtrate. After separating the layers, the aqueous fraction was with DCM twice. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, 30% EtOAc in hexanes) to obtain **(*S*)-2a** as pale yellow oil (36.5g, 96.8% yield, 94% *ee*).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 7.03 (t, *J* = 2.0 Hz, 1H), 6.99 (dt, *J* = 7.4, 1.2 Hz, 1H), 6.96 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 5.19 (s, 2H), 4.60 – 4.55 (m, 1H), 3.49 (s, 3H), 1.85 – 1.71 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 157.36, 146.44, 129.44, 119.47, 115.15, 113.91, 94.44, 75.83, 56.01, 31.84, 10.15.

IR (film): ν_{max} = 3411 (br), 2961, 2932, 1586, 1486, 1451, 1242, 1149, 1077, 1011, 993, 923 cm^{-1}

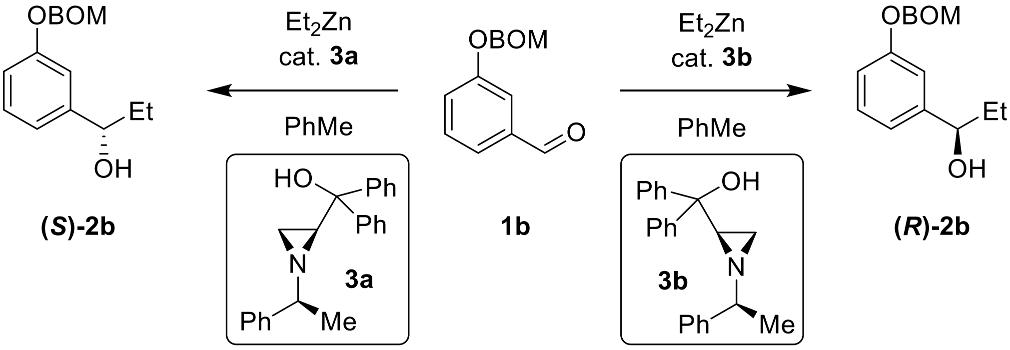
HPLC (Chiralpak IA column, 96:4 hexanes/isopropanol, 1.0 ml/min), t_r = 15.4 min (minor, *R*), 17.0 min (major, *S*)

b) Using aziridine organocatalyst 3a:

Hexanes (20mL), and diphenyl((*R*)-1-((*S*)-1-phenylethyl)aziridin-2-yl)methanol **3a** (100.0mg, 0.30mmol) were cooled to 0°C before adding a 1 M solution of diethylzinc in hexanes (13.3mL, 13.3mmol) dropwise. Reaction mixture was stirred at 0°C before the addition of aldehyde **1a** (1.00g, 6.0mmol) dropwise. After 20h at 0°C and 20h at room temperature, action mixture was quenched with a saturated solution of NH_4Cl (20mL). After separating the layers, the aqueous fraction was with EtOAc three times. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, 20% EtOAc in hexanes) to obtain **(*S*)-2a** (1.14g, 96.5% yield, >99% *ee*) as pale yellow oil.

Identical spectral properties as above.

(*R*)-1-(3-((benzyloxy)methoxy)phenyl)propan-1-ol (2b)



Using aziridine organocatalyst 3a:

A solution of Et_2Zn (1M in hexanes) (2.7mL, 2.7mmol) was added dropwise to a cooled (0°C) solution of diphenyl((*S*)-1-((*S*)-1-phenylethyl)aziridin-2-yl)methanol **3a** (20mg , 0.06mmol) in toluene (0.5mL). After 30min at 0°C, a solution of aldehyde **1b** (300mg, 1.24mmol) in toluene (1.5mL) was added dropwise, and the reaction mixture was allowed to slowly warm to room temperature. After 24h, reaction mixture was quenched with a saturated solution of NH_4Cl (8mL), the solid was filtered, and filtrate was extracted with Et_2O (3 x 8mL). Combined organic was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, 10% EtOAc in hexanes) to alcohol **(*S*)-2b** as a clear oil (307mg, 91.0% yield, 99% e.e.)

Using aziridine organocatalyst 3b:

A solution of Et_2Zn (1M in hexanes) (6mL, 6mmol) was added dropwise to a cooled (0°C) solution of diphenyl((*R*)-1-((*S*)-1-phenylethyl)aziridin-2-yl)methanol **3b** (50mg, 0.15mmol) in toluene (0.5mL). After 30min at 0°C, a solution of aldehyde **1b** (658mg, 2.72mmol) in toluene (4.5mL) was added dropwise, and the reaction mixture was allowed to slowly warm to room temperature. After 24h, reaction mixture was quenched with a saturated solution of NH_4Cl (8mL), the solid was filtered, and filtrate was extracted with Et_2O (3 x 8mL). Combined organic was washed with brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, 10% EtOAc in hexanes) to alcohol **(*R*)-2b** as a clear oil (548mg, 74.1% yield, 99% *ee*).

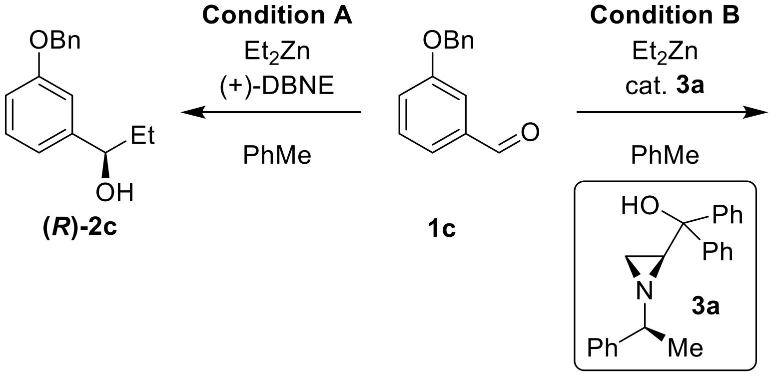
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 6H), 7.08 (s, 1H), 7.00 (t, *J* = 7.6 Hz, 2H), 5.30 (s, 2H), 4.73 (s, 2H), 4.57 (td, *J* = 6.6, 3.4 Hz, 1H), 1.96 (d, *J* = 3.4 Hz, 1H), 1.87 – 1.70 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.42, 146.43, 137.26, 129.46, 128.43, 128.01, 127.85, 119.51, 115.22, 113.99, 92.30, 75.81, 69.93, 31.84, 10.13.

IR (film): ν_{max} = 3406 (br), 2962, 2932, 2875, 1585, 1486, 1453, 1237, 1157, 1075, 1015, 993, 785, 736, 696 cm^{-1}

HPLC (Chiralpak IA column, 96:4 hexanes/isopropanol, 1.0 ml/min), t_r = 22.6 min (major, *R*), 24.2 min (minor, *S*)

1-(3-(benzyloxy)phenyl)propan-1-ol (2c)



a) Using (+)-DBNE

Aldehyde **1c** (50mg, 0.24mmol), toluene (3mL), and N,N-dibutyl-D-(+)-norephedrine (4μL, 0.014mmol) were cooled to 0°C before adding a 1M solution of diethylzinc in hexanes (0.5mL, 0.5mmol) dropwise over 20min. After 20h from 0°C to room temperature, reaction mixture was quenched with a saturated solution of NH_4Cl (5mL). After separating the layers, the aqueous fraction was with EtOAc three times. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, 20% EtOAc in hexanes) to obtain **(*R*)-2c** (47mg, 82% yield, 95% BRSM, 91% *ee*) as pale yellow oil.

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.04 (s, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.93 (dd, *J* = 8.1, 2.3 Hz, 1H), 5.09 (s, 2H), 4.56 (t, *J* = 6.6 Hz, 1H), 2.44 (d, *J* = 9.4 Hz, 1H), 1.87 – 1.80 (m, 1H), 1.80 – 1.73 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (176 MHz, CDCl3) δ 158.93, 146.52, 137.08, 129.44, 128.61, 127.99, 127.58, 118.71, 113.80, 112.55, 75.81, 69.99, 31.88, 10.21.

IR (film): ν_{max} = 3366 (br), 3032, 2962, 2929. 2873, 1583, 1485, 1446, 1250, 1154, 1025, 994, 779 cm^{-1}

HPLC (Chiralpak IA column, 95:5 hexanes/isopropanol, 1.0 ml/min), t_r = 21.2 min (*R*), 24.5 min (*S*)

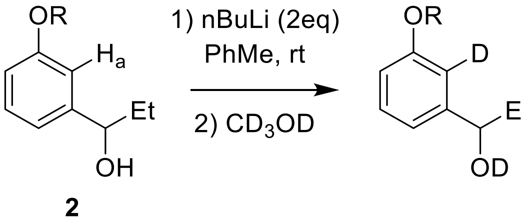
b) Using aziridine organocatalyst 3a

Aldehyde **1c** (14.2g, 66.9mmol), toluene (35mL), and diphenyl((*S*)-1-((*S*)-1-phenylethyl)aziridin-2-yl)methanol **3a** (1.32g, 4.0mmol) were cooled to 0°C before adding a 1M solution of diethylzinc in toluene (148mL, 148mmol) dropwise over 6h. Reaction mixture was allowed to warm to room temperature slowly. After 30h, reaction mixture was quenched with a saturated solution of NH_4Cl (150mL). After separating the layers, the aqueous fraction was with EtOAc three times. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, 20% EtOAc in hexanes) to obtain **(*S*)-2c** (16.2g, quant. yield, 98% *ee*) as pale yellow oil.

Identical spectral properties as above.

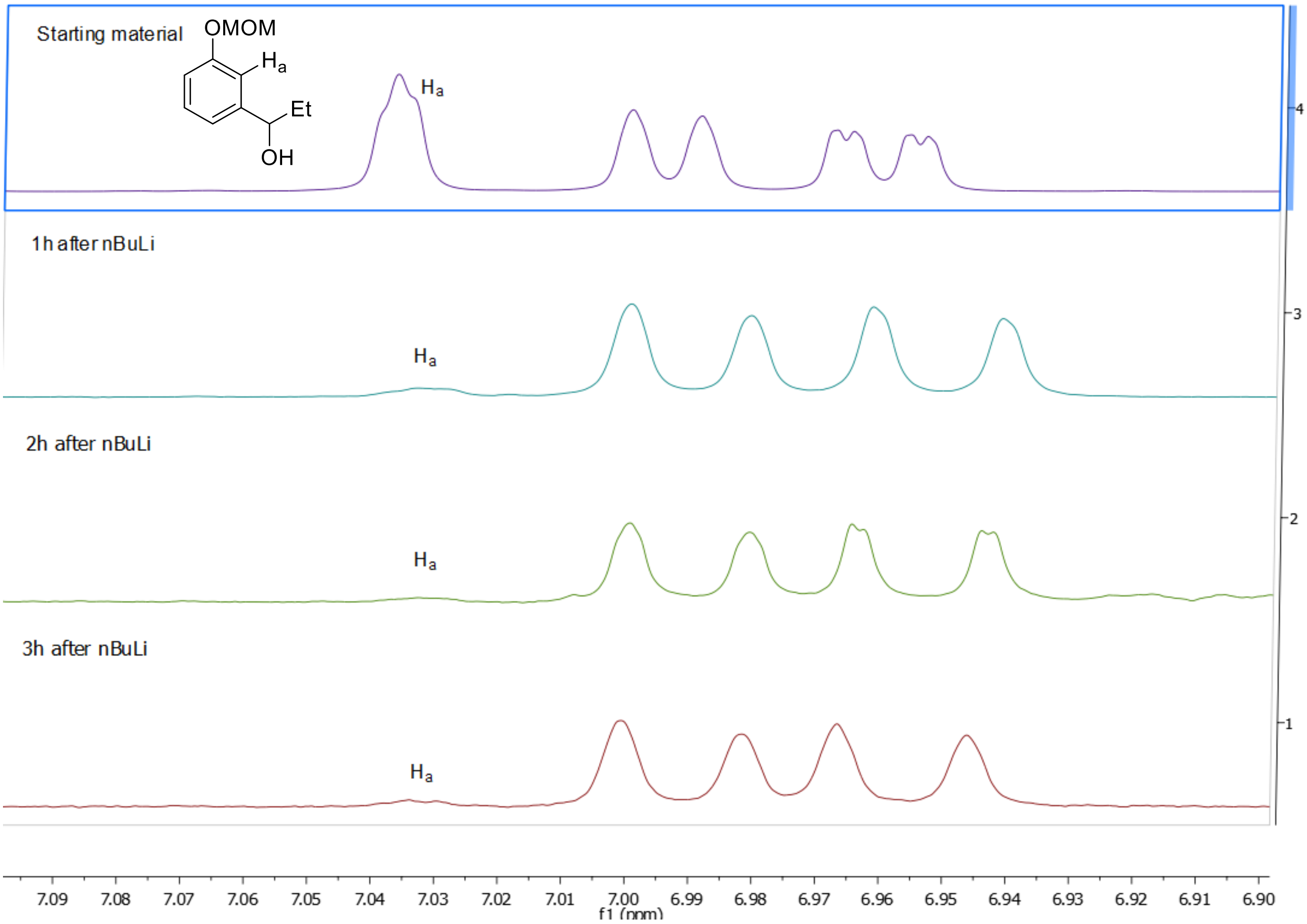
Using organocatalyst **3b**, **(*R*)-2c** obtained in 97.8% *ee*.

Lithiation studies



2

Before optimizing the spiroketalization reaction, we decided to study the selectivity of the *ortho*-lithiation of alcohols **2**. After treating **2** with 2 equivalents of *n*-butyllithium, aliquots were extracted at time points and then quenched with CD_3OD. After removing the volatiles, the deuterated material was analyzed by NMR. We found that selective and almost quantitative lithiation at the desired position occurred for **2a** and **2b,** and **2c** at around 2-3h in toluene. For example, for **2a**:


Starting material
OMOM
Ha
Et
OH
Ha
1h after nBuLi
Ha
2h after nBuLi
Ha
3h after nBuLi
Ha
4
3
2
1
7.09
7.08
7.07
7.06
7.05
7.04
7.03
7.02
7.01
7.00
6.99
6.98
6.97
6.96
6.95
6.94
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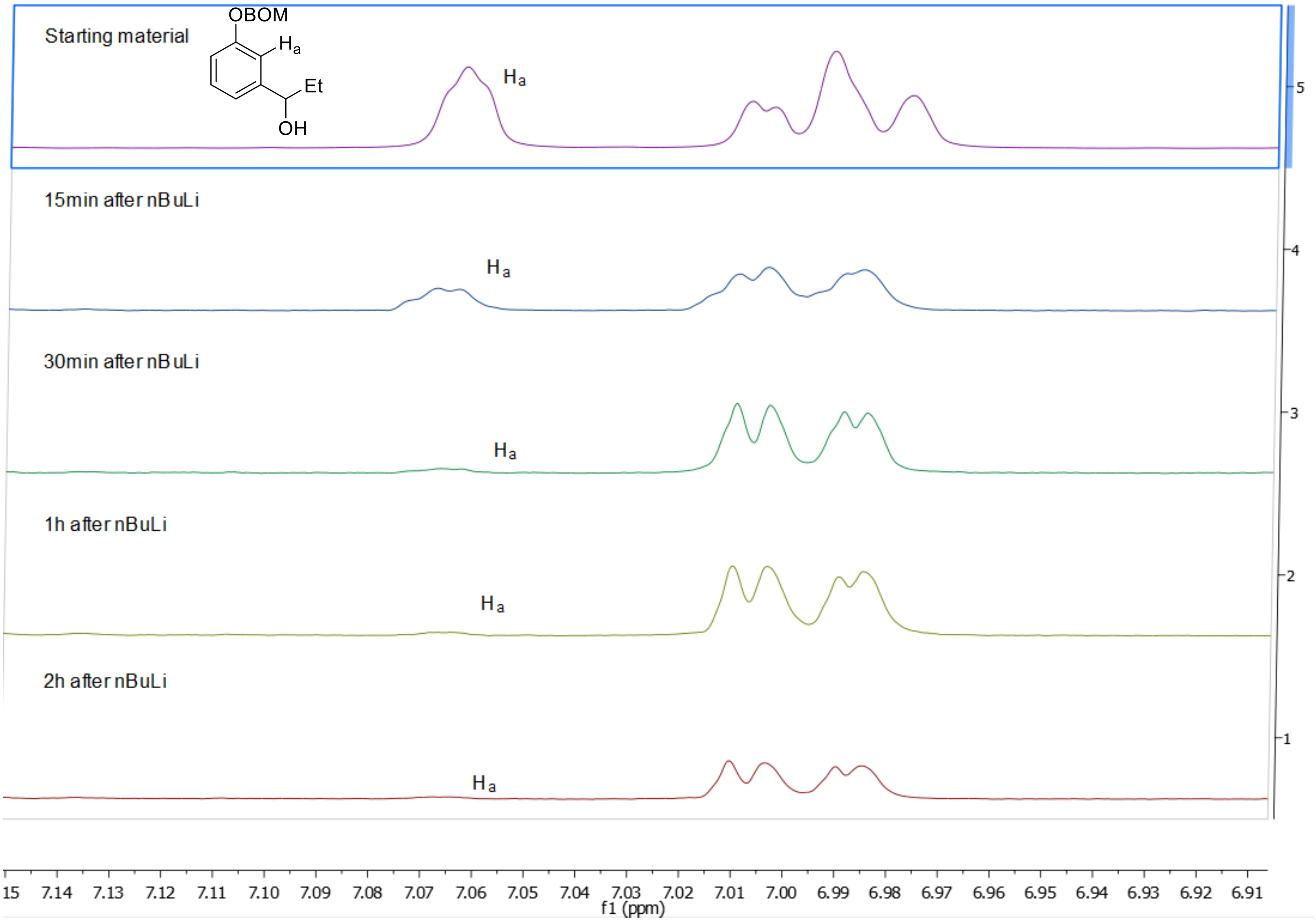
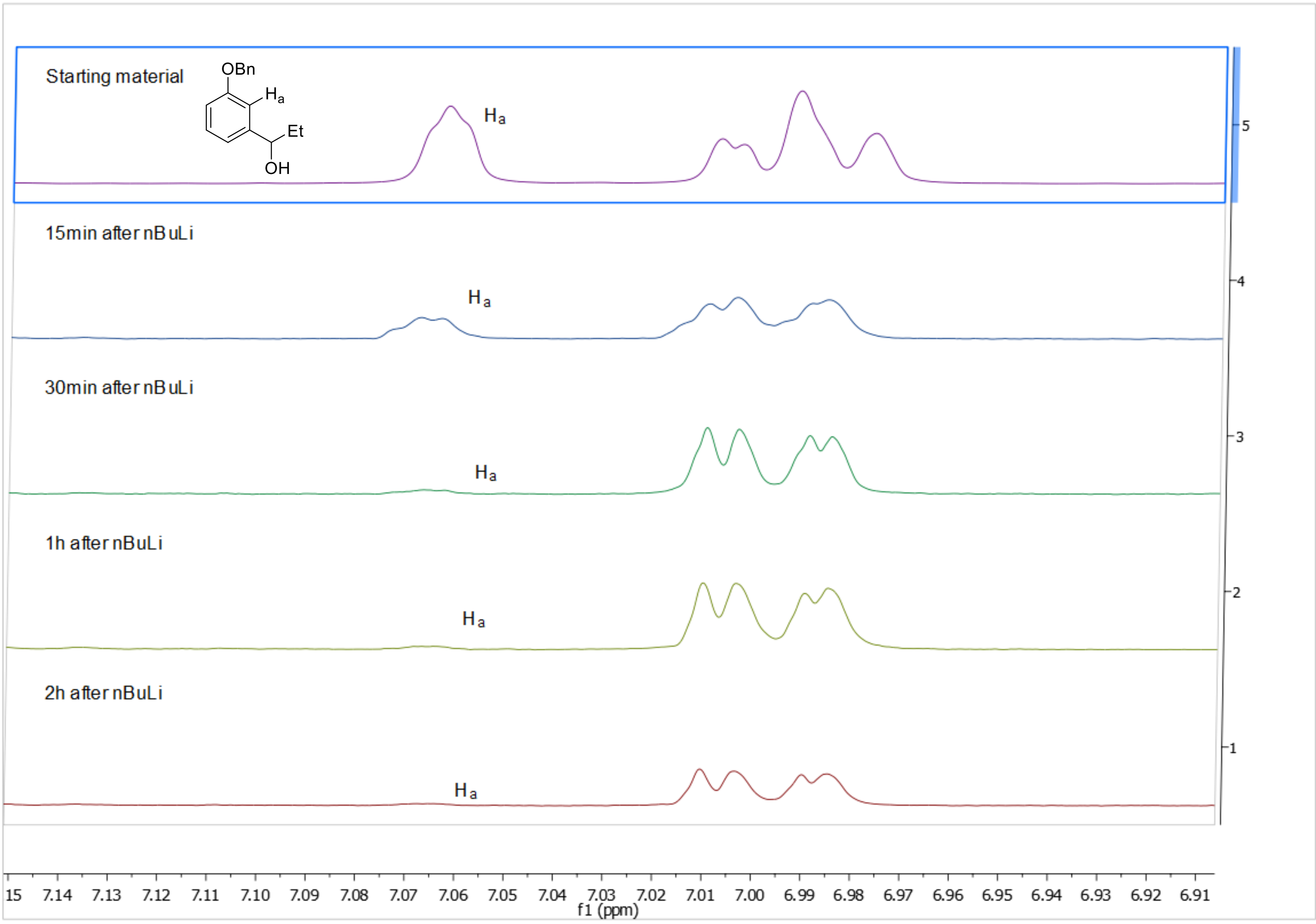
6.92
6.91
6.90
f1 (ppm)

For **2b**:

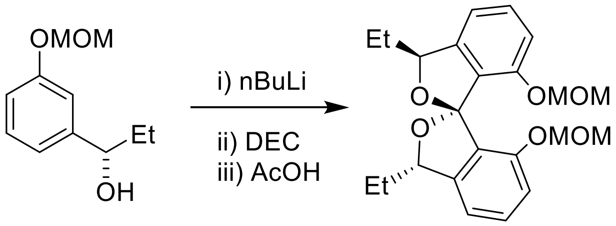

Starting material
OBOM
Ha
Et
OH
Ha
15min after nBuLi
Ha
30min after nBuLi
Ha
1h after nBuLi
Ha
2h after nBuLi
Ha
5
4
3
2
1
15
7.14
7.13
7.12
7.11
7.10
7.09
7.08
7.07
7.06
7.05
7.04
7.03
7.02
7.01
7.00
6.99
6.98
6.97
6.96
6.95
6.94
6.93
6.92
6.91
f1 (ppm)

For **2c**:



Additionally, using THF as solvent, or TMEDA as additive gave unselective lithiations.

(*1R,3S,3'S*)-3,3'-diethyl-7,7'-bis(methoxymethoxy)-3H,3'H-1,1'-spirobi[isobenzofuran] ((*R,S,S*)-6a)



(*S*)-2a **(*R,S,S*)-6a**

Alcohol **(*S*)-2a** (22.84g, 116.4mmol) and PhMe (330mL) were cooled to 0°C before addition of a 2.5M solution *n*-Butyllithium in hexanes (44mL over 15min, then 50 mL over 1h, 235.0mmol). Reaction mixture was then warmed to room temperature. After 3h, the resulting suspension was dissolved using 12mL of THF and cooled again to 0°C. Diethyl carbonate (7.7mL, 63.5mmol) was incorporated over 2h at 0°C. Reaction mixture was allowed to warm slowly to room temperature overnight (12h). Glacial acetic acid (100mL) was then added slowly at room temperature. After 4h at room temperature, reaction mixture was quenched with 500mL of water, followed by careful addition of 100g of $NaHCO_3$. After separating the layers, the aqueous fraction was with DCM three times. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The mixture components were purified by FCC (SiO_2): 3.34g of starting material **2a** (14.6% recovery) were obtained at 15% EtOAc in hexanes, while 15.65g of desired product

6a (67.2% yield, 78.7% BRSM) were isolated at 25% EtOAc in hexanes as pale yellow oil. Additionally, some intermediate isobenzofuranone **4a** (2.43g, 9.4% yield) was obtained at 35% EtOAc in hexanes as pale yellow oil.

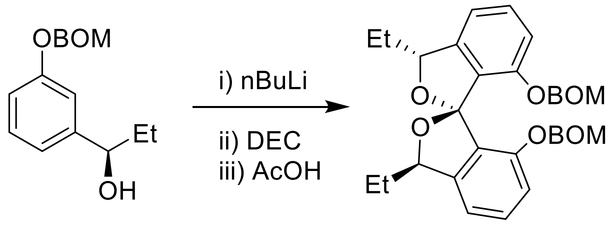
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.8 Hz, 2H), 6.88 (dd, *J* = 7.9, 3.6 Hz, 4H), 5.40 (dd, *J* = 7.4, 3.9 Hz, 2H), 4.95 (d, *J* = 6.6 Hz, 2H), 4.82 (d, *J* = 6.6 Hz, 2H), 3.07 (s, 6H), 1.98 (dtd, *J* = 14.8, 7.3, 3.9 Hz, 2H), 1.86 (dq, *J* = 14.3, 7.3 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.44, 145.61, 130.58, 127.76, 113.99, 112.15, 93.29, 83.15, 55.60, 28.06, 9.74.

ESI-HRMS Calcd. for $C_{23}H_{29}O_6^+$ 401.1964 $[M+H]^+$, found 401.1958.

IR (film): ν_{max} = 2962, 2934, 1614, 1599, 1479, 1256, 1152, 1002, 960, 928, 734 cm^{-1}

(*1S,3R,3'R*)-7,7'-bis((benzyloxy)methoxy)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran] ((*S,R,R*)-6b)



(***R***)-**2b** (***S,R,R***)-**6b**

Alcohol **(*S*)-2b** (210mg, 0.77mmol) and PhMe (4.6mL) were cooled to 0°C before dropwise addition of a 2.5M solution *n*-Butyllithium in hexanes (690µL, 1.73mmol). Reaction mixture was stirred at room temperature for 90min. Diethyl carbonate (50µL, 0.41mmol) was incorporated over 20min at 0°C. Reaction mixture was allowed to warm slowly to room temperature overnight. After 24h, glacial acetic acid (1mL) was then added slowly at room temperature. After 5h at room temperature, reaction mixture was treated with a saturated solution of $NaHCO_3$ (8mL). After separating the layers, the aqueous fraction was washed with DCM three times. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The mixture components were purified by FCC (SiO_2, 5% EtOAc in hexanes) to obtain **(*S,R,R*)-6b** (126mg, 59% yield, 64% BRSM) as pale yellow oil.

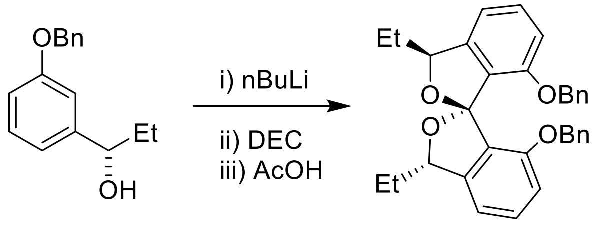
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.9 Hz, 2H), 7.28 – 7.20 (m, 6H), 7.03 (dd, *J* = 6.5, 2.8 Hz, 4H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 7.5 Hz, 2H), 5.42 (dd, *J* = 7.4, 4.0 Hz, 2H), 5.04 (d, *J* = 6.7 Hz, 2H), 4.87 (d, *J* = 6.8 Hz, 2H), 4.27 – 4.11 (m, 4H), 1.98 (m, 2H), 1.87 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.53, 145.77, 136.67, 130.73, 128.28, 128.25, 128.16, 127.81, 127.78, 115.94, 114.04, 112.11, 90.33, 83.28, 69.03, 28.13, 9.85.

ESI-HRMS Calcd. for $C_{35}H_{37}O_6^+$ 553.2584 $[M+H]^+$, found 553.2580.

IR (film): ν_{max} = 2964, 2874, 1599, 1479, 1250, 1155, 1093, 1065, 1002, 958, 734, 697 cm^{-1}

(*1R,3S,3'S*)-7,7'-bis(benzyloxy)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran] ((*R,S,S*)-6c)



(*S*)-2c **(*R,S,S*)-6c**

Alcohol **(*S*)-2c** (200mg, 0.83mmol) and PhMe (2.4mL) were cooled to 0°C before addition of a 2.5M solution *n*-Butyllithium in hexanes (300µL dropwise, then 370µL over 30min, 1.68mmol). Reaction mixture was stirred at 0°C for 3h. Dimethyl carbonate (38µL, 0.45mmol) was incorporated over 30min 0°C. Reaction mixture was allowed to warm slowly to room temperature overnight (12h). Glacial acetic acid (1.2mL) was then added slowly at room temperature. After 6h at room temperature, reaction mixture was diluted with water (20mL) and then neutralized carefully with solid $NaHCO_3$. The product was extracted with DCM three times. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The mixture components were purified by FCC (SiO_2, 10% EtOAc in hexanes) to obtain **(*R,S,S*)-6c** (84.8mg, 42% yield, 66% BRSM) as white solid, as well as 74.1mg of **(*S*)-2c**.

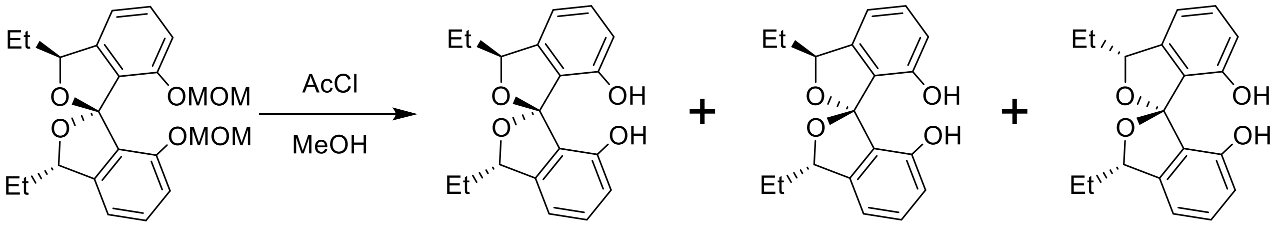
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.8 Hz, 2H), 7.19 – 7.02 (m, 6H), 6.83 (dd, *J* = 14.9, 7.8 Hz, 4H), 6.75 – 6.62 (m, 4H), 5.39 (dd, *J* = 7.2, 4.3 Hz, 2H), 5.00 – 4.80 (m, 4H), 1.87 – 1.59 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.21, 145.84, 136.62, 130.52, 127.97, 127.50, 127.15, 126.42, 115.83, 113.51, 110.36, 83.14, 68.86, 27.79, 9.64.

ESI-HRMS Calcd. for $C_{33}H_{33}O_4^+$ 493.2373 $[M+H]^+$, found 493.2370.

IR (powder): v_{max} = 3030, 2963, 2933, 2872. 1735, 1612, 1597, 1480, 1451, 1284, 1267, 1027, 930 cm^{-1}

(*1R,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diol ((*R,S,S*)-7) and (*S,S,S*)-7 diastereomer from 6a



(*R,S,S*)-6a **(*R,S,S*)-7** **(*S,S,S*)-7** **(*S,R,S*)-7**

The deprotection of the MOM group using AcCl in MeOH was mild enough that after 6h at room temperature the less thermodynamically stable diol **(*R,S,S*)-7** is the major compound. However, SiO_2 and other acidic conditions epimerize it into **(*S,S,S*)-7**. These results agree with the calculated ΔG of 1.0 kcal/mol favoring **(*R,S,S*)-7**. Consequently, neutralizing the acidic conditions after 6h of reaction yields **(*R,S,S*)-7** selectively, while performing chromatography after the reaction time gives **(*S,S,S*)-7** enriched material, as exemplified below. In addition, acidic deprotection led to partial epimerization of **(*R,S,S*)-6a** and **(*R,S,S*)-6b** leading to formation of undesired **(*S,R,S*)-7** diastereomer. This side reaction could be avoided by using non-acidic deprotection methods such as hydrogenolysis of **(*R,S,S*)-6c**.

(***R,S,S***)-selective deprotection

Spiroketal **(*R,S,S*)-6a** (21.9mg, 0.055mmol) and MeOH (0.5mL) were added to a vial. Solution was cooled to 0°C, and then acetyl chloride (8.0µL, 0.11mmol) was added slowly. Reaction mixture was warmed to room temperature. After 6h, reaction mixture was quenched with a saturated solution of NaHCO$_3$. Extracted three times with DCM, and then combined organic was dried with Na$_2$SO$_4$, and concentrated *in vacuo* to afford a mixture of diols **7** (17.0mg, 93% yield, d.r. 1:3.8 **(*S,S,S*)-7:(*R,S,S*)-7** with 6% of undesired **(*S,R,S*)-7**).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34 (t, *J* = 7.7 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.41 (dd, *J* = 6.7, 4.1 Hz, 1H), 4.73 (s, 1H), 2.07 (m, 1H), 1.83 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 151.86, 145.37, 132.30, 123.26, 115.49, 113.62, 83.07, 27.76, 9.18.

ESI-HRMS Calcd. for $C_{19}H_{21}O_4^+$ 314.1440 [M+H]$^+$, found 314.1435.

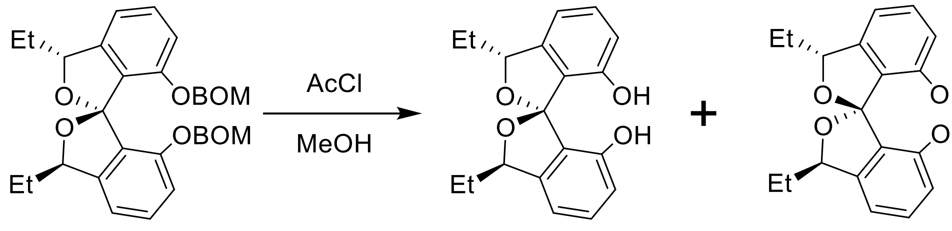
(S,***S,S***)-selective deprotection

Spiroketal **(*R,S,S*)-6a** (2.82g, 7.04mmol) and MeOH (35mL) were added to a round bottom flask. Solution was cooled to 0°C, and then acetyl chloride (1.0mL, 14.1mmol) was added slowly. Reaction mixture was warmed to room temperature. After 6h, reaction mixture was concentrated *in vacuo*, and purified by FCC (SiO$_2$, 30%→40% EtOAc in hexanes) to obtain a mixture of diols **7** (2.15g, 92.1% yield 1:1.9 d.r. **(*R,S,S*)-7:(*S,S,S*)-7** with 5.6% of undesired **(*S,R,S*)-7**).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.27 (dd, *J* = 7.6, 4.4 Hz, 1H), 4.60 (s, 1H), 1.99 – 1.85 (m, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 151.65, 145.24, 131.99, 123.37, 115.46, 113.84, 84.89, 30.61, 9.74.

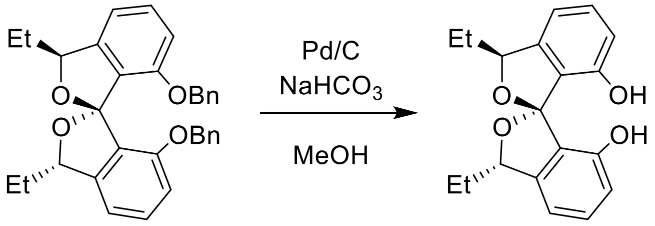
(*1S,3R,3'R*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diol ((*S,R,R*)-7) from 6b



(*S,R,R*)-6b **(*S,R,R*)-7** **(*R,R,R*)-7**

Spiroketal **(*S,R,R*)-6b** (20.9mg, 0.04mmol) and MeOH (200µL) were added to a vial. Solution was cooled to 0°C, and then acetyl chloride (8.0µL, 0.11mmol) was added slowly. Reaction mixture was warmed to room temperature. After 3h, reaction mixture was diluted with EtOAc, and treated with a saturated solution of NaHCO$_3$ (1 mL). After separating layers, the aqueous fraction was extracted three times with EtOAc. Combined organic was washed with brine, dried with Na$_2$SO$_4$, and purified by FCC (SiO$_2$, 5%→40% EtOAc in hexanes) to obtain a mixture of diols **7** (11.6mg, 87% yield 1:1.3 d.r. **(*S,R,R*)-7:(*R,R,R*)-7** with 11% of undesired **(*R,S,R*)-7**).

(*1R,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diol (*R*,*S*,*S*-7) from 6c



(*R,S,S*)-6c **(*R,S,S*)-7**

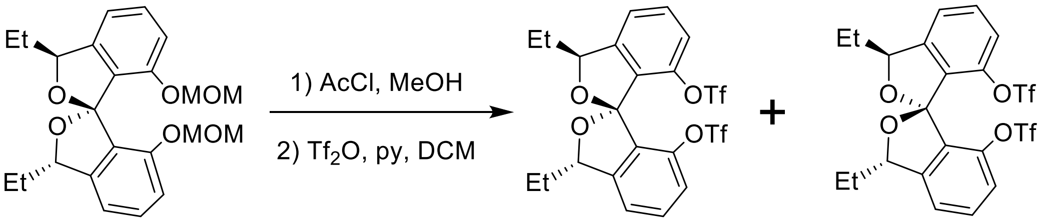
Spiroketal **(*R,S,S*)-6c** (54mg, 0.11mmol), Pd/C (22mg, 0.022mmol), $NaHCO_3$ (84mg, 1mmol) and methanol (2mL) were added to a round bottom flask charged with nitrogen before purging with hydrogen balloon twice. After 2h at room temperature, reaction mixture was filtered through syringe filter and concentrated *in vacuo* to obtain a mixture of diols **7** (32 mg, 94% yield, dr =1:6.9 **(*S,S,S*)-7:(*R,S,S*)-7**, no undesired **(*S,R,S*)-7** was observed) as white solid. Spectral properties described above.

Diol equilibration studies

The isomeric ratio of the diols was variable, because epimerization happens in silica-containing solutions and the dr is dependent on the solvent. Most solvents, such as EtOAc/Hexanes mixtures slightly favor the **(*S,S,S*)-7** isomer. Curiously, SiO_2 in PhMe lightly favors equilibration towards the **(*R,S,S*)-7** isomer, this is not unreasonable given that the gas phase free energy difference between diastereomers is small.

A vial was charged with a 2.9:1 **(*S,S,S*)-7:(*R,S,S*)-7** mixture (300mg), PhMe (3mL), and SiO_2 (3.0g). After stirring at room temperature for 4 days, the diol mixture was recovered quantitatively by filtration and concentration *in vacuo*, with a 1:2.4 **(*S,S,S*)-7:(*R,S,S*)-7** d.r.. Similarly, a vial was charged with a 1:2.4 **(*S,S,S*)-7:(*R,S,S*)-7** mixture (100mg), EtOAc (0.5mL), hexanes (0.5mL), and SiO_2 (1.0g). After stirring at room temperature for 2 days, the diol mixture was recovered quantitatively by filtration and concentration *in vacuo*, with a 1.2:1 **(*S,S,S*)-7:(*R,S,S*)-7** d.r..

(*1S,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl bis(trifluoromethanesulfonate) ((*S,S,S*)-8) from (*R,S,S*)-6a



(*R,S,S*)-6a **(*R,S,S*)-8** **(*S,S,S*)-8**

The **(*R,S,S*)-8:(*S,S,S*)-8** ratio was mostly conserved during the triflation, so the product ratio depended on the d.r. of the diol used. An **(*S,S,S*)-8**-selective preparation is shown below.

Spiroketal **(*R,S,S*)-6a** (12.57g, 31.4mmol) and methanol (160mL) were cooled to 0°C before dropwise addition of acetyl chloride (4.5mL, 63.3mmol). Reaction mixture was then warmed to room temperature. After for 6h, the volatiles were removed *in vacuo*, and the crude was purified by FCC (SiO_2, 30%→40% EtOAc in hexanes). Purified diol, DCM (150mL), and pyridine (12.5mL, 155.2mmol) were cooled to 0°C before addition of trifluoromethanesulfonic anhydride (12.0mL, 71.5mmol) over 30min. Reaction mixture was then warmed to room temperature. After 1h, a saturated aqueous solution of $NaHCO_3$ (150mL) was added. After separating the layers, the aqueous phase extracted with DCM twice. Combined organic was dried over Na_2SO_4 and concentrated *in vacuo*. Crude was purified by a short column (SiO_2, 10% EtOAc in hexanes) to afford a mixture of triflates as an oil which solidified on cooling (17.55g, 91% yield 1:1.9 d.r. **(*R,S,S*)-7:(*S,S,S*)-7** with 6% of undesired **(*R,S,R*)-7**).

The ditriflates can be separated by FCC (SiO_2, 4% EtOAc in hexanes), but for convenience we chose to do a chemical resolution (*vide infra*). The spectral characteristics of the isolated ditriflates are shown below:

(*1R,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl bis(trifluoromethanesulfonate) ((*R,S,S*)-8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 4H), 5.36 (dd, *J* = 8.5, 4.0 Hz, 2H), 2.05 (m, *J* = 15.0, 7.5, 4.0 Hz, 2H), 1.97 – 1.82 (m, 2H), 1.11 (t, *J* = 7.4 Hz, 6H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -74.57.

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.80, 144.92, 132.21, 129.82, 122.91, 120.81, 119.72, 119.13, 116.54, 113.33, 83.64, 27.39, 10.05.

ESI-HRMS Calcd. for $C_{21}H_{19}F_6O_8S_2^+$ 577.0426 $[M+H]^+$, found 577.0415.

IR (powder): ν_{max} = 2975, 2878, 1470, 1419, 1204, 1137, 936, 896, 848 cm^{-1}

(1*S*,3*S*,3'*S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl bis(trifluoromethanesulfonate) ((*S*,*S*,*S*)-8)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 5.38 (dd, *J* = 7.2, 4.5 Hz, 2H), 2.07 – 1.81 (m, 4H), 1.06 (t, *J* = 7.4 Hz, 6H)

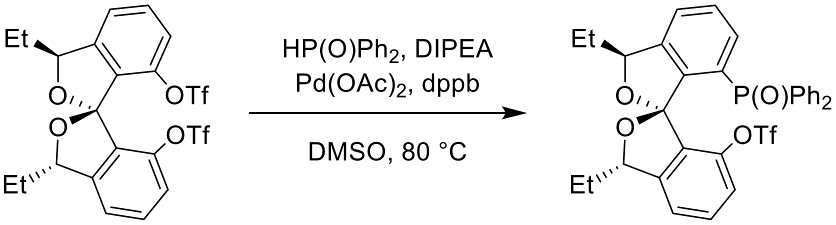
^{19}F NMR (376 MHz, $CDCl_3$) δ -74.58.

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.33, 144.73, 132.07, 130.30, 122.92, 121.21, 119.74, 119.62, 119.60, 116.55, 114.51, 113.37, 84.77, 30.09, 9.45.

ESI-HRMS Calcd. for $C_{21}H_{19}F_6O_8S_2^+$ 577.0426 $[M+H]^+$, found 577.0418.

IR (powder): ν_{max} = 2973, 2880, 1470, 1422, 1207, 1137, 935, 852, 749 cm^{-1}

(*1S,3S,3'S*)-7'-(diphenylphosphoryl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl trifluoromethanesulfonate ((*S,S,S*)-9)



(*S,S,S*)-8
+(*R,S,S*)-8
+(*S,R,S*)-8

(*S,S,S*)-9

A flask in the glovebox was charged with a mixture of ditriflates (12.624g, 21.89mmol, 1:1.9 d.r. **(*R,S,S*)-7:(*S,S,S*)-7** with 6% of undesired **(*R,S,R*)-7**), palladium(II) acetate (245mg, 1.09mmol), 1,4-Bis(diphenylphosphino)butane (466mg, 1.09mmol), and diphenylphosphine oxide (4.861g, 24.04mmol). The flask was taken outside the glovebox, and DMSO (85mL) and N,N-diisopropylethylamine (9.5mL, 54.5mmol) were added. Reaction mixture was then stirred at room temperature for 1h, before being heated to 80°C. After 8h, reaction mixture was cooled to room temperature and partitioned between EtOAc (260mL) and a half saturated aqueous solution of $NaHCO_3$ (260mL). After separating the layers, the aqueous phase was extracted with EtOAc twice. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo.* Crude was purified by FCC (SiO_2, 10 → 50% EtOAc in hexanes) to yield two fractions. At 10% EtOAc in hexanes, a **(*R,S,S*)-8** was obtained (4.82g total, 31% recovery of **(*R,S,S*)-8** with 4% undesired **(*S,R,S*)-8**) At 50% EtOAc in hexanes, the desired phosphine oxide **(*S,S,S*)-9** was obtained (7.71g, 54% yield of **(*S,S,S*)-9** with 2% undesired **(*S,R,S*)-9**).

The desired product was further purified by two recrystallizations from cyclohexane with excellent recovery. The first recrystallization of 5.71g of the product mixture gave 5.33g of a 1:26 mixture of epimeric product **(*S,R,S*)-8** and desired phosphine oxide **(*S,S,S*)-8**, respectively (97% recovery of product). A second recrystallization of 5.02g of this mixture produced 4.58g of almost pure **(*S,S,S*)-8** (1:65 with respect to **(*S,R,S*)-8**) (93% recovery of product), as a white foam.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 4H), 7.42 – 7.31 (m, 4H), 7.27 – 7.21 (m, 2H), 7.21 – 7.10 (m, 4H), 7.02 (dd, *J* = 13.9, 7.5 Hz, 1H), 6.41 (dd, *J* = 7.1, 1.5 Hz, 1H), 5.56 (dd, *J* = 7.1, 4.7 Hz, 1H), 5.28 (dd, *J* = 7.2, 5.0 Hz, 1H), 1.92 (m, *J* = 13.5, 6.3 Hz, 3H), 1.83 (m, *J* = 14.3, 7.2 Hz, 1H), 1.06 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.85, 146.47, 146.40, 144.19, 141.69, 141.64, 133.80, 133.77, 133.70, 132.93, 132.51, 132.14, 132.07, 131.68, 131.55, 131.53, 131.31, 131.25, 131.20, 131.18, 131.01, 130.94, 128.59, 128.49, 128.22, 128.19, 128.12, 128.09, 127.40, 125.38, 125.36, 121.89, 120.41, 119.34, 118.47, 116.80, 116.25, 85.27, 83.49, 30.60, 29.71, 26.90, 9.88, 9.66.

^{19}F NMR (471 MHz, $CDCl_3$) δ -75.05.

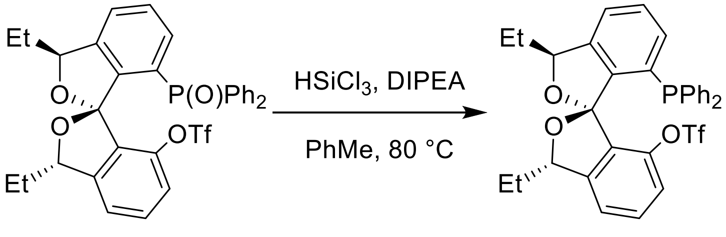
^{31}P NMR (202 MHz, $CDCl_3$) δ 28.57.

ESI-HRMS Calcd. for $C_{32}H_{29}F_3O_6PS^+$ 629.1375 $[M+H]^+$, found 629.1366.

IR (powder): ν_{max} = 2934, 1419, 1210, 1194, 1140, 931 cm^{-1}

[α]$_D$: -70.8 (c = 1.0 in DCM)

(*1S,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl trifluoromethanesulfonate ((*S,S,S*)-10)



(*S*,*S*,*S*)-9 **(*S*,*S*,*S*)-10**

Phosphine oxide **(*S*,*S*,*S*)-9** (4.95g, 7.88mmol), PhMe (80mL), and Diisopropylethylamine (55mL, 315.7mmol) were cooled to 0°C before addition of trichlorosilane (12.5mL, 125.7mmol) over 10min. The flask was sealed with a glass stopped and heated to 80°C. After 20h, the mixture was cooled to room temperature and quenched carefully by transferring it to a flask containing a saturated aqueous solution of $NaHCO_3$ (120mL) at 0°C, with diethyl ether washings. Crude was filtered through Celite with diethyl ether washings, and the filtrate was dried over Na_2SO_4 and concentrated *in vacuo.* Crude was purified by FCC (SiO_2, 5% EtOAc in hexanes) to afford **(*S*,*S*,*S*)-10** (3.89g, 80.6% yield) as white foam.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.20 (m, 6H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.13 (td, *J* = 7.5, 1.5 Hz, 2H), 7.07 (td, *J* = 7.5, 2.0 Hz, 2H), 6.89 (dd, *J* = 7.4, 4.6 Hz, 1H), 6.85 (td, *J* = 7.9, 1.4 Hz, 2H), 6.62 (d, *J* = 8.1 Hz, 1H), 5.35 (td, *J* = 6.8, 4.6 Hz, 2H), 1.96 (m, *J* = 16.9, 14.0, 5.9 Hz, 2H), 1.87 (m, *J* = 14.2, 7.2, 4.6 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.39, 147.37, 144.53, 143.68, 143.62, 142.55, 142.35, 137.03, 136.93, 135.49, 135.41, 133.96, 133.94, 133.63, 133.49, 133.46, 133.33, 132.58, 132.56, 132.42, 131.46, 129.59, 128.42, 128.20, 128.17, 128.12, 128.00, 127.95, 122.04, 120.56, 119.35, 118.87, 116.81, 116.51, 116.49, 84.66, 84.61, 84.05, 30.47, 29.70, 9.64, 9.43.

^{19}F NMR (471 MHz, $CDCl_3$) δ -74.90.

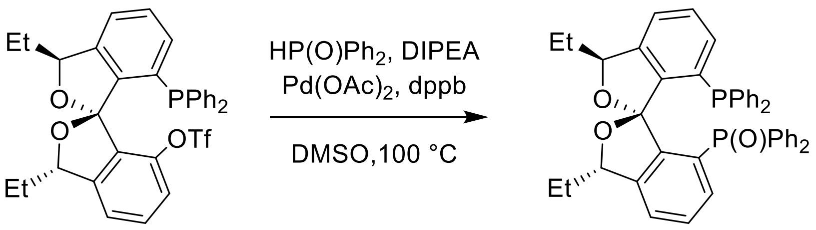
^{31}P NMR (202 MHz, $CDCl_3$) δ -18.88.

ESI-HRMS Calcd. for $C_{32}H_{29}F_3O_5PS^+$ 613.1425 $[M+H]^+$, found 613.1419.

IR (powder): ν_{max} = 2970, 1738, 1421, 1211, 1140, 943 cm^{-1}

$[\alpha]_D$: -44.0 (c = 1.0 in DCM)

((*1S,3S,3′S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl)diphenylphosphine oxide ((*S,S,S*)-SPIRAP(O))



(*S,S,S*)-10 **(*S,S,S*)-SPIRAP(O)**

A flask in the glovebox was charged with phosphine **(*S,S,S*)-10** (3.89g, 6.35mmol), palladium(II) acetate (71.3mg, 0.32mmol), 1,4-Bis(diphenylphosphino)butane (135.4mg, 0.32mmol), and diphenylphosphine oxide (2.57g, 12.7mmol). The flask was taken outside the glovebox, and DMSO (25 mL) and N,N-diisopropylethylamine (5.5mL, 31.6mmol) were added. Reaction mixture was then stirred at room temperature for 1h before being then heated to 100°C. After 2h, reaction mixture was cooled down to room temperature and partitioned between EtOAc (160mL) and a half saturated aqueous solution of $NaHCO_3$ (160mL). After separating the layers, the aqueous phase was extracted with EtOAc twice. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo.* Crude was purified by FCC (SiO_2, 20 → 30% EtOAc in hexanes) to yield **(*S,S,S*)-SPIRAP(O)** (3.95g, 93.6% yield) as white foam.

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.45 (td, *J* = 6.3, 2.6 Hz, 1H), 7.41 – 7.29 (m, 6H), 7.29 – 7.13 (m, 13H), 7.07 (td, *J* = 7.3, 2.1 Hz, 2H), 7.02 (td, *J* = 7.7, 1.7 Hz, 2H), 6.87 (dd, *J* = 7.5, 4.8 Hz, 1H), 6.71 (dd, *J* = 13.9, 7.5 Hz, 1H), 5.35 (t, *J* = 5.2 Hz, 1H), 4.71 (dd, *J* = 8.2, 3.8 Hz, 1H), 1.93 (m, *J* = 14.8, 7.5, 3.8 Hz, 1H), 1.79 (m, *J* = 14.0, 6.9 Hz, 1H), 1.72 (m, *J* = 11.4, 3.4 Hz, 1H), 1.64 (m, *J* = 14.3, 7.4 Hz, 1H), 0.86 (t, *J* = 7.3 Hz, 3H), 0.75 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 146.70, 146.55, 146.26, 146.24, 146.21, 146.19, 144.53, 144.51, 144.50, 143.64, 143.60, 138.60, 138.53, 136.55, 136.48, 134.76, 134.17, 134.16, 134.06, 133.46, 133.42, 133.40, 133.24, 133.13, 133.05, 132.87, 132.36, 132.31, 131.56, 131.51, 131.08, 131.07, 131.03, 131.01, 130.99, 130.93, 128.79, 128.29, 128.22, 127.95, 127.93, 127.89, 127.86, 127.81, 127.76, 127.74, 127.72, 127.65, 127.27, 124.65, 124.64, 121.46, 118.68, 84.29, 83.26, 83.21, 29.93, 29.54, 9.85, 8.82.

^{31}P NMR (283 MHz, $CDCl_3$) δ 28.63, -18.52.

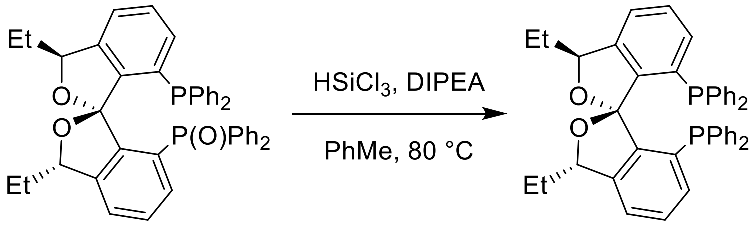
ESI-HRMS Calcd. for $C_{43}H_{39}O_3P_2^+$ 665.2374 $[M+H]^+$, found 665.2366.

IR (powder): ν_{max} = 2964, 1434, 1336, 1214, 998, 915, 696 cm^{-1}

[α]$_D$: -93.3 (c = 1.0 in $CHCl_3$)

Crystallographic data: CCDC **1812181** contains the supplementary crystallographic data of **(*S,S,S*)-SPIRAP(O)**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

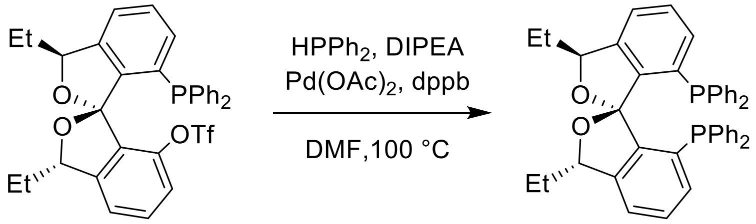
((*1S,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(diphenylphosphane) ((*S,S,S*)-SPIRAP) from phosphine oxide (*S,S,S*)-SPIRAP(O)



(*S,S,S*)-SPIRAP(O) **(*S,S,S*)-SPIRAP**

Phosphine oxide **(*S,S,S*)-SPIRAP(O)** (106mg, 0.159 mmol), PhMe (1.6mL), and diisopropylethylamine (1.1mL, 6.3mmol) were cooled to 0°C before dropwise addition of trichlorosilane (0.25mL, 2.5mmol). The flask was sealed with a glass stopped and heated to 80°C. After 20h, reaction mixture was cooled to room temperature and quenched carefully by transferring it to a flask containing a saturated aqueous solution of $NaHCO_3$ (5mL) at 0°C, with diethyl ether washings. Crude was filtered through Celite with diethyl ether washings, and the filtrate was dried over Na_2SO_4, and concentrated *in vacuo.* Crude mixture was purified by FCC (SiO_2, 5% EtOAc in hexanes) to afford **(*S,S,S*)-SPIRAP** (58.2mg, 56% yield) as white foam. The yield for this reaction was variable, with a 2.9g scale giving 35% yield due to the formation of an epimeric trichlorosilane adduct as the major component of the mixture, which can be cleanly converted to its free phosphine by stirring in isopropanol with traces of acetyl chloride. For this reason, we developed a direct method of obtaining **(*S,S,S*)-SPIRAP** from monophosphine **(*S,S,S*)-10**. Spectral properties described below.

((*1S,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(diphenylphosphane) ((*S,S,S*)-SPIRAP) from phosphine (*S,S,S*)-10



(*S,S,S*)-10 **(*S,S,S*)-SPIRAP**

A Schlenk flask was charged with palladium(II) acetate (36.6mg, 0.163mmol) and 1,4-Bis(diphenylphosphino)butane (76.6mg, 0.180mmol). DMF (3.0mL) and diisopropylethylamine (1.8mL, 10.3mmol) were added. Solution was stirred at room temperature. After 1h, diphenyl phosphine (850µL, 4.89mmol) was added. After 5min, phosphine **(*S,S,S*)-10** (1.000g, 1.632mmol) was added as a solution in DMF (3.5mL, including washings). The sealed flask was heated to 100°C. After 24h, volatiles were removed under N_2 flow. Crude was purified by FCC (SiO_2, 0 → 15% → 30% DCM in hexanes), and the product was then washed with hexanes to yield **(*S,S,S*)-SPIRAP** (977mg, 92.3% yield) as white solid.

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (tq, *J* = 13.7, 7.6 Hz, 10H), 7.17 – 7.10 (m, 4H), 7.06 (td, *J* = 7.5, 1.8 Hz, 4H), 6.89 (dd, *J* = 7.5, 4.5 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 4H), 4.96 (dd, *J* = 6.8, 4.3 Hz, 2H), 1.86 (m, *J* = 14.6, 7.3, 4.1 Hz, 2H), 1.76 (m, *J* = 14.3, 7.2 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 145.51, 145.49, 145.36, 145.34, 144.09, 144.07, 144.05, 144.03, 138.22, 138.15, 136.81, 136.74, 134.11, 133.99, 133.72, 133.71, 133.13, 133.02, 132.59, 132.48, 129.12, 128.23, 128.02, 127.98, 127.93, 127.85, 127.82, 127.76, 121.54, 118.55, 83.29, 83.25, 29.76, 9.32.

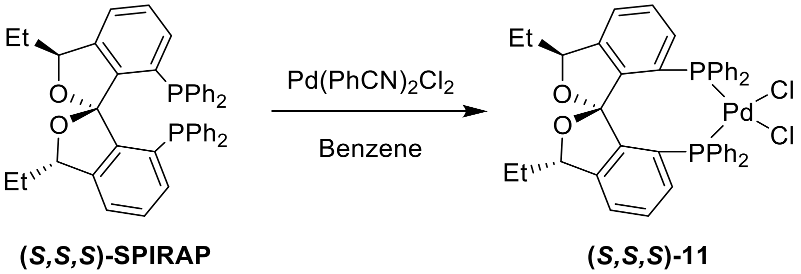
^{31}P NMR (283 MHz, $CDCl_3$) δ -18.71.

ESI-HRMS Calcd. for $C_{43}H_{39}O_2P_2^+$ 649.2425 $[M+H]^+$, found 649.2417.

IR (powder): ν_{max} = 2970, 1739, 1433, 1365, 1217, 696 cm^{-1}

[α]$_D$: -227.4 (c = 1.0 in $CHCl_3$)

[((*1S,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(diphenylphosphane)]palladium(II) chloride ((*S,S,S*)-11)



Diphosphine **(*S,S,S*)-SPIRAP** (8.0mg, 0.012mmol), bis(benzonitrile)palladium(II) chloride (4.7mg, 0.012mmol), and benzene (0.82mL) were stirred at room temperature. After 6h, the complex was precipitated upon addition of hexanes as an orange solid, which was collected by filtration and washed with hexanes. The solid was redissolved in DCM for collection, and the volatiles were evaporated *in vacuo* to yield pure complex **(*S,S,S*)-11** as a yellow-orange solid (9.9mg, 97% yield).

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 12.3, 7.4 Hz, 4H), 7.57 (s, 4H), 7.48 – 7.40 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 6H), 7.24 – 7.17 (m, 4H), 7.09 (d, *J* = 7.8 Hz, 4H), 6.88 (d, *J* = 7.5 Hz, 2H), 3.75 (dd, *J* = 9.9, 4.3 Hz, 2H), 1.80 (m, 2H), 1.72 – 1.62 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (176 MHz, $CDCl_3$) δ 147.30, 147.26, 137.91, 137.87, 135.23, 135.16, 134.24, 134.18, 133.99, 133.93, 131.75, 131.39, 130.52, 130.30, 129.46, 129.41, 128.02, 127.95, 126.64, 126.33, 125.54, 125.42, 125.31, 116.26, 83.57, 30.49, 11.27.

^{31}P NMR (283 MHz, $CDCl_3$) δ 32.83.

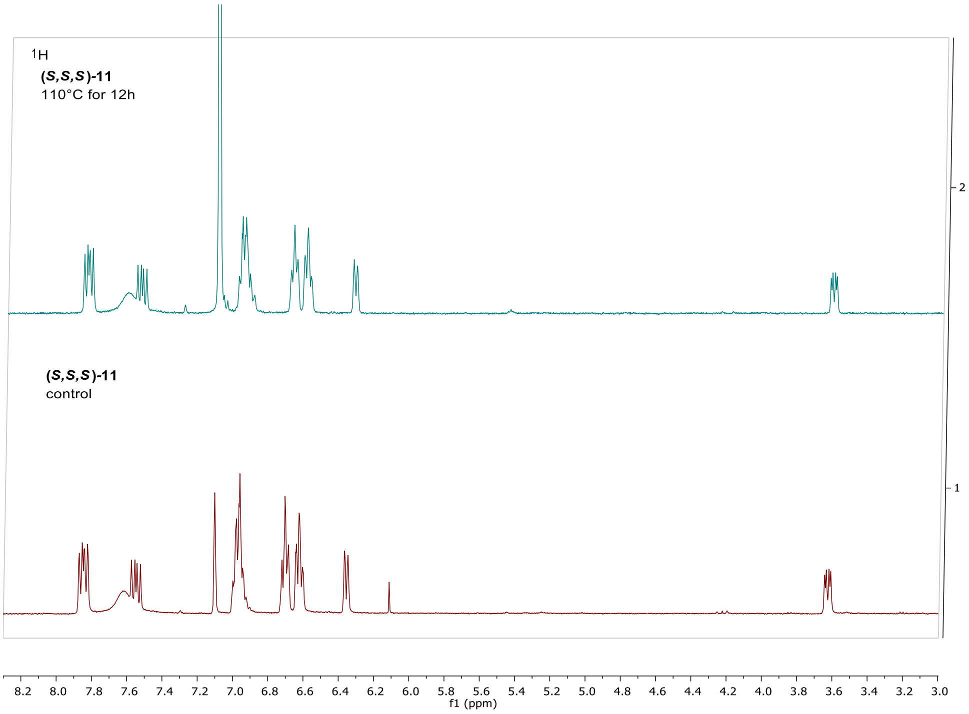
ESI-HRMS Calcd. for $C_{43}H_{38}ClO_2P_2Pd^+$ 789.1070 $[M-Cl]^+$, found 789.1076.

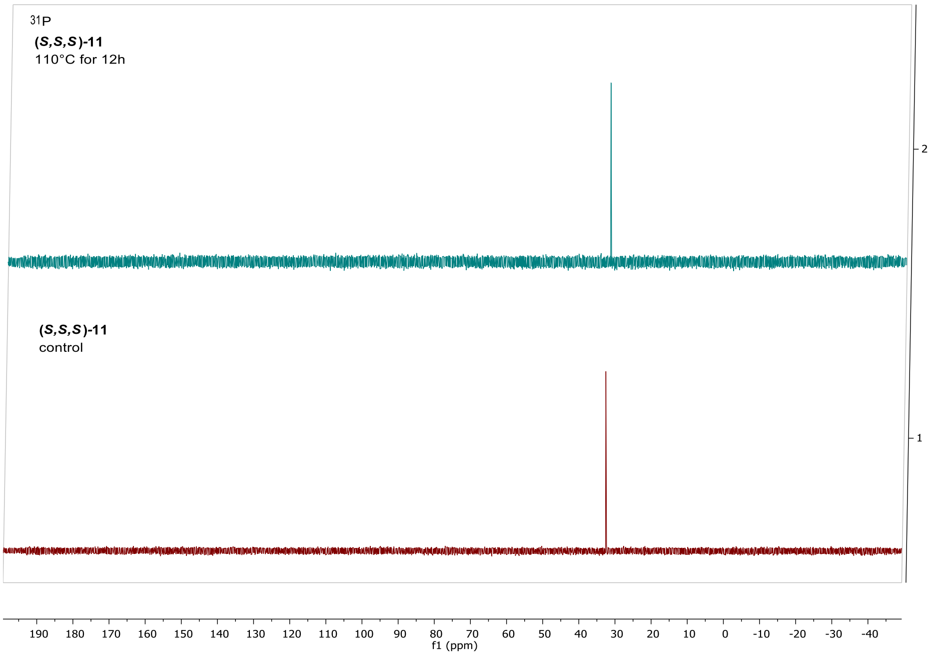
IR (powder): ν_{max} = 2225, 1435, 1095, 998, 921 727, 688 cm^{-1}

[α]$_D$: +10.9 (c = 0.5 in $CHCl_3$)

Thermal stability study

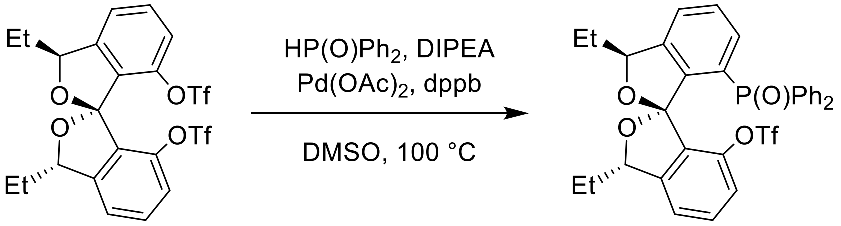
Complex **(*S,S,S*)-11** (8.0mg) was dissolved in PhMe and heated to 110°C for 12h. The material was recovered quantitatively and was unchanged by NMR analysis.





Synthesis of diphosphine (*R,S,S*)-SPIRAP and Pd(II) complex

(*1R,3S,3'S*)-7'-(diphenylphosphoryl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl trifluoromethanesulfonate ((*R,S,S*)-9)



(*R,S,S*)-8 **(*R,S,S*)-9**

Recovered **(*R,S,S*)-8** (from the coupling of **(*S,S,S*)-8** to diphenylphosphine oxide) was recrystallized from cyclohexane. A flask in the glovebox was charged with ditriflate (3.946g, 6.84mmol), palladium(II) acetate (154mg, 0.69mmol), 1,4-Bis(diphenylphosphino)butane (321mg, 0.75mmol), and diphenylphosphine oxide (2.768g, 13.69mmol). The flask was taken outside the glovebox, and DMSO (27mL) and N,N-diisopropylethylamine (4.8mL, 27.6mmol) were added. Reaction mixture was then stirred at room temperature for 1h, before being heated to 100°C. After 24h, reaction mixture was cooled to room temperature and partitioned between EtOAc (60mL) and a half saturated aqueous solution of $NaHCO_3$ (60mL). After separating the layers, the aqueous phase was extracted with EtOAc twice. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo.* Crude was purified by FCC (SiO_2, 5 → 40% EtOAc in hexanes). At 5% EtOAc in hexanes, some impure starting material was recovered (100.9mg). At 40% EtOAc in hexanes, the desired product **(*R,S,S*)-9** was obtained as white foam (4.081g, 94.8% yield).

^{1}H NMR (401 MHz, $CDCl_3$) δ 7.51 – 7.28 (m, 13H), 7.15 (dd, *J* = 10.0, 8.0 Hz, 2H), 7.06 (dd, *J* = 13.8, 7.5 Hz, 1H), 5.33 (dd, *J* = 8.2, 4.0 Hz, 1H), 5.14 (dd, *J* = 10.0, 3.5 Hz, 1H), 2.03 (m, *J* = 14.9, 7.4, 4.1 Hz, 1H), 1.88 (m, *J* = 14.4, 7.3 Hz, 1H), 1.70 (m, *J* = 15.0, 7.5, 3.7 Hz, 1H), 1.60 – 1.44 (m, 1H), 1.08 (t, *J* = 7.4 Hz, 3H), 0.53 (t, *J* = 7.4 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.90.

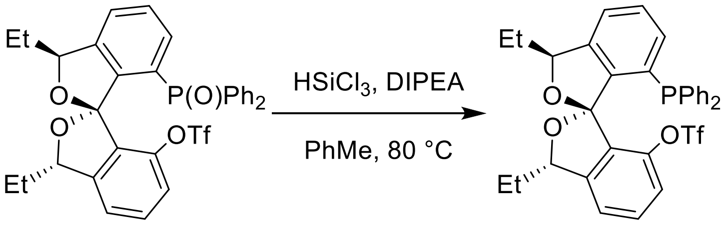
^{19}F NMR (377 MHz, $CDCl_3$) δ -75.08.

ESI-HRMS Calcd. for $C_{32}H_{29}F_3O_6PS^+$ 629.1375 $[M+H]^+$, found 629.1372.

IR (powder): ν_{max} = 2970, 1738, 1419, 1214, 1141, 930, 695 cm^{-1}

[α]$_D$: -46.3 (c = 1.0 in $CHCl_3$)

(*1R,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl trifluoromethanesulfonate ((*R,S,S*)-10)



(*R,S,S*)-9 **(*R,S,S*)-10**

Phosphine oxide **(*R,S,S*)-8** (2.00g, 3.18mmol), PhMe (32mL), and Diisopropylethylamine (22.2mL, 127.5mmol) were cooled to 0°C before addition of trichlorosilane (6.80mL, 68.4mmol) over 10min. The flask was sealed with a glass stopped and heated to 80°C. After 16h, the mixture was cooled to room temperature and quenched carefully by transferring it to a flask containing a saturated aqueous solution of $NaHCO_3$ (70mL) at 0°C, with diethyl ether washings. Crude was filtered through Celite with diethyl ether washings, and the filtrate was dried over Na_2SO_4 and concentrated *in vacuo.* Crude was purified by FCC (SiO_2, 5% EtOAc in hexanes) to afford **(*R,S,S*)-10** (870mg, 44.6% yield, 66.1% BRSM) as white foam. Starting material was recovered at 50% EtOAc in hexanes (311mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.20 (m, 6H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.13 (td, *J* = 7.5, 1.5 Hz, 2H), 7.07 (td, *J* = 7.5, 2.0 Hz, 2H), 6.89 (dd, *J* = 7.4, 4.6 Hz, 1H), 6.85 (td, *J* = 7.9, 1.4 Hz, 2H), 6.62 (d, *J* = 8.1 Hz, 1H), 5.35 (td, *J* = 6.8, 4.6 Hz, 2H), 1.96 (m, *J* = 16.9, 14.0, 5.9 Hz, 2H), 1.87 (m, *J* = 14.2, 7.2, 4.6 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.39, 147.37, 144.53, 143.68, 143.62, 142.55, 142.35, 137.03, 136.93, 135.49, 135.41, 133.96, 133.94, 133.63, 133.49, 133.46, 133.33, 132.58, 132.56, 132.42, 131.46, 129.59, 128.42, 128.20, 128.17, 128.12, 128.00, 127.95, 122.04, 120.56, 119.35, 118.87, 116.81, 116.51, 116.49, 84.66, 84.61, 84.05, 30.47, 29.70, 9.64, 9.43.

^{19}F NMR (471 MHz, $CDCl_3$) δ -74.90.

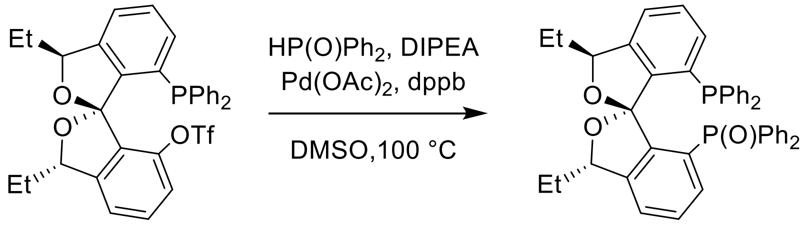
^{31}P NMR (202 MHz, $CDCl_3$) δ -18.88.

ESI-HRMS Calcd. for $C_{32}H_{29}F_3O_5PS^+$ 613.1425 $[M+H]^+$, found 613.1419.

IR (powder): ν_{max} = 2968, 1469, 1421, 1211, 1140, 1009, 962, 926, 848, 743 cm^{-1}

$[\alpha]_D$: +47.6 (c = 1.0 in $CHCl_3$)

((*1R,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl)diphenylphosphine oxide ((*R,S,S*)-SPIRAP(O)



(*R,S,S*)-10 **(*R,S,S*)-SPIRAP(O)**

A flask in the glovebox was charged with phosphine **(*R,S,S*)-10** (83mg, 0.14mmol), palladium(II) acetate (1.52mg, 0.007mmol), 1,4-Bis(diphenylphosphino)butane (2.89mg, 0.007mmol), and diphenylphosphine oxide (54.8mg, 0.271mmol). The flask was taken outside the glovebox, and DMSO (540µL) and N,N-diisopropylethylamine (100µL, 0.57mmol) were added. Reaction mixture was then stirred at room temperature for 1h before being then heated to 100°C. After 3h, reaction mixture was cooled down to room temperature and partitioned between EtOAc (1mL) and a half saturated aqueous solution of $NaHCO_3$ (1mL). After separating the layers, the aqueous phase was extracted with EtOAc twice. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo.* Crude was purified by FCC (SiO_2, 35% EtOAc in hexanes) to yield **(*R,S,S*)-SPIRAP(O)** (84.8mg, 94% yield) as white foam.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.16 (m, 20H), 7.16 – 7.00 (m, 5H), 6.95 (dd, *J* = 13.9, 7.5 Hz, 1H), 5.19 (dd, *J* = 9.9, 3.5 Hz, 1H), 5.11 (dd, *J* = 10.1, 3.5 Hz, 1H), 1.81 (m, 1H), 1.73 – 1.62 (m, 1H), 1.55 (m, 1H), 1.40 (m, 1H), 0.83 (t, *J* = 7.4 Hz, 3H), 0.45 (t, *J* = 7.4 Hz, 3H).

^{31}P NMR (202 MHz, $CDCl_3$) δ 29.82, -22.07.

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.72, 148.49, 147.11, 147.09, 147.04, 147.02, 144.48, 142.80, 142.74, 138.82, 138.71, 137.86, 137.75, 135.25, 135.22, 135.04, 134.93, 134.21, 134.10, 133.59, 133.55, 133.44, 132.83, 132.68, 132.59, 132.52, 131.97, 131.89, 131.16, 131.13, 131.10, 131.08, 130.47, 130.33, 128.67, 128.21, 128.11, 128.08, 128.03, 128.01, 127.97, 127.90, 127.81, 127.45, 126.62, 124.66, 124.64, 121.61, 110.00, 83.37, 82.38, 28.03, 28.00, 27.32, 10.88, 10.59.

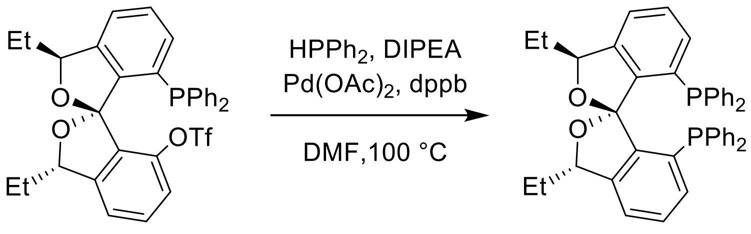
ESI-HRMS Calcd. for $C_{43}H_{39}O_3P_2^+$ 665.2374 $[M+H]^+$, found 665.2370.

IR (powder): ν_{max} = 2969, 2842, 1435, 1217, 1007, 973, 917, 741, 694 cm^{-1}

$[\alpha]_D$: -45.8 (c = 1.0 in $CHCl_3$)

Crystallographic data: CCDC **1812182** contains the supplementary crystallographic data of **(*S,R,R*)-SPIRAP(O)** made by using **(*R*)-2a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

((*1R,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(diphenylphosphane) ((*R,S,S*)-SPIRAP) from phosphine (*R,S,S*)-10



(*R,S,S*)-10 **(*R,S,S*)-SPIRAP**

A Schlenk flask was charged with palladium(II) acetate (21.9mg, 0.097mmol) and 1,4-Bis(diphenylphosphino)butane (46.0mg, 0.107mmol). DMF (1.9mL) and diisopropylethylamine (1.04mL, 5.97mmol) were added. Solution was stirred at room temperature. After 1h, diphenyl phosphine (510µL, 2.92mmol) was added. After 5min, phosphine **(*R,S,S*)-10** (596mg, 0.97mmol) was added as a solution in DMF (2.0mL, including washings). The sealed flask was heated to 100°C. After 16h, volatiles were removed under N_2 flow. Crude was purified by FCC (SiO_2, 30% → 40% DCM in hexanes) and the product was washed in hexanes to yield **(*R,S,S*)-SPIRAP** (551mg, 87% yield) as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.14 (m, 14H), 7.06 – 6.92 (m, 10H), 5.15 (dd, *J* = 10.1, 3.5 Hz, 2H), 1.70 (m, 2H), 1.30 (m, 2H), 0.66 (t, *J* = 7.3 Hz, 6H).

^{31}P NMR (202 MHz, $CDCl_3$) δ -20.99.

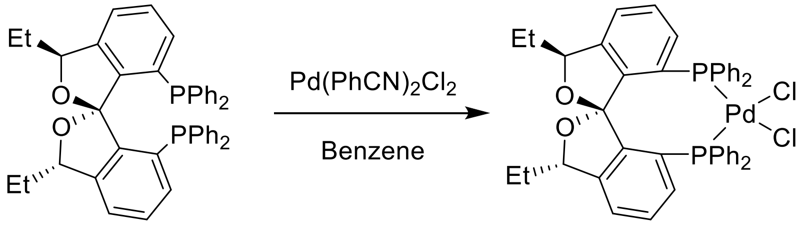
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.38, 145.15, 144.72, 144.69, 144.65, 138.28, 138.18, 137.55, 137.44, 134.73, 134.14, 134.05, 133.97, 132.98, 132.90, 132.83, 132.15, 132.12, 131.98, 131.95, 129.28, 128.22, 128.19, 128.17, 128.14, 128.11, 128.09, 128.04, 128.02, 128.00, 127.97, 127.95, 127.57, 121.73, 117.51, 82.84, 27.88, 10.77.

ESI-HRMS Calcd. for $C_{43}H_{39}O_2P_2^+$ 649.2425 $[M+H]^+$, found 649.2421.

IR (powder): ν_{max} = 3067, 2969, 2845, 1434, 1274 , 1005, 969, 917, 741, 694 cm^{-1}

$[\alpha]_D$: +203.8 (c = 1.0 in $CHCl_3$)

[((*1R,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(diphenylphosphane)]palladium(II) chloride ((*R,S,S*)-11)



(*R,S,S*)-SPIRAP **(*R,S,S*)-11**

Diphosphine **(*R,S,S*)-SPIRAP** (12.0mg, 0.018mmol), bis(benzonitrile)palladium(II) chloride (7.1mg, 0.018mmol), and benzene (1.2mL) were stirred at room temperature. After 16h, the complex was precipitated upon addition of hexanes as an orange solid, which was collected by filtration and washed with hexanes. The solid was redissolved in DCM for collection, and the volatiles were evaporated *in vacuo* to yield pure complex **(*R,S,S*)-11** as a yellow-orange solid (14.0mg, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (ddd, *J* = 12.3, 6.6, 2.7 Hz, 4H), 7.65 – 7.51 (m, 4H), 7.41 (dd, *J* = 12.8, 7.9 Hz, 2H), 7.36 (d, *J* = 2.6 Hz, 6H), 7.24 (t, *J* = 7.8 Hz, 2H), 7.21 – 7.14 (m, 2H), 7.05 (ddd, *J* = 18.8, 9.1, 4.8 Hz, 6H), 4.71 (dd, *J* = 9.8, 4.0 Hz, 2H), 1.50 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 6H), 0.84 (m, 2H).

^{31}P NMR (202 MHz, $CDCl_3$) δ 33.38.

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.22, 148.16, 140.26, 140.19, 135.74, 135.64, 134.11, 134.03, 133.87, 133.78, 132.70, 132.19, 130.83, 130.25, 129.57, 129.50, 128.23, 128.13, 128.08, 128.03, 127.88, 127.46, 125.78, 125.42, 124.17, 113.55, 80.36, 24.97, 10.80.

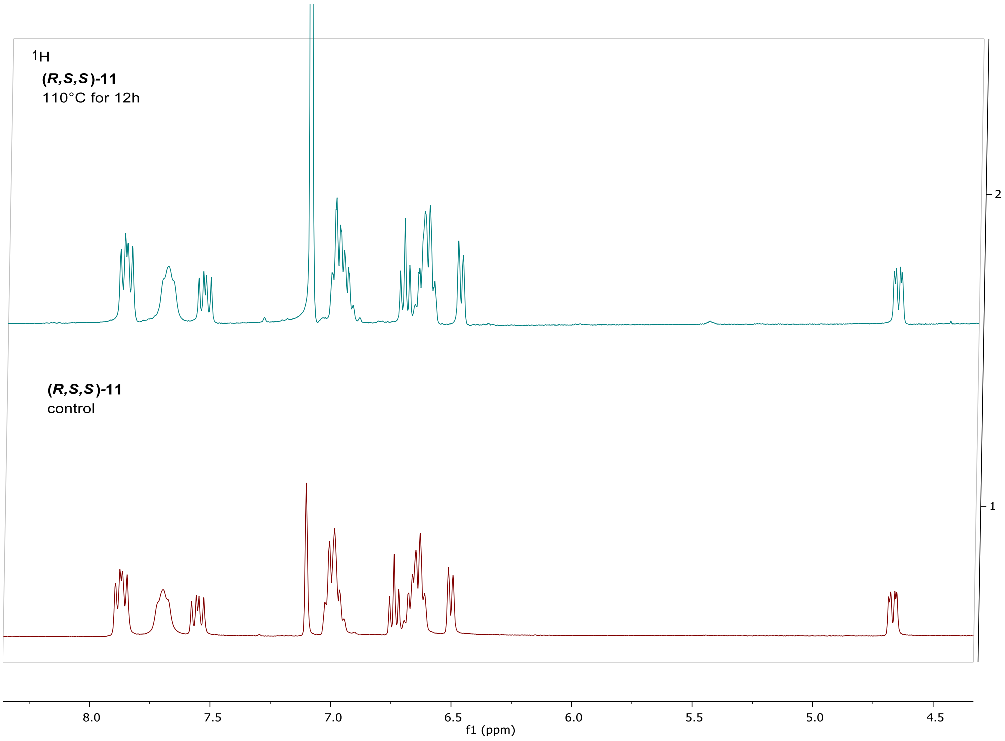
ESI-HRMS Calcd. for $C_{43}H_{39}O_2P_2Pd^+$ 755.1460 $[M-2Cl+H]^+$, found 755.1438.

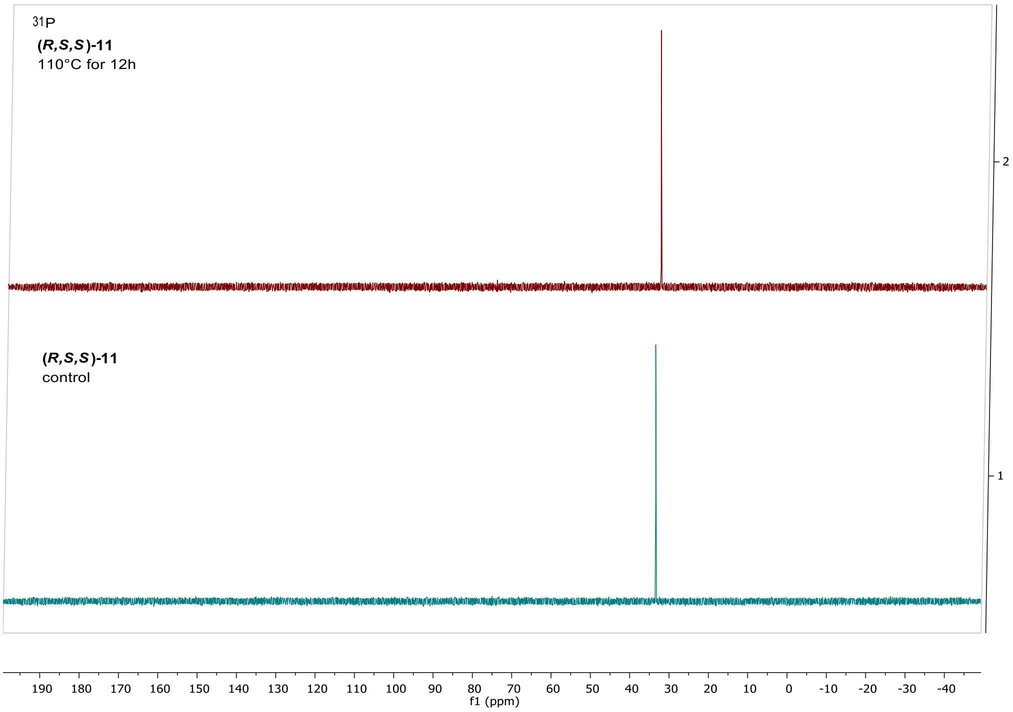
IR (powder): ν_{max} = 2970, 1738, 1435, 1092, 998, 969, 912, 740, 688 cm^{-1}

$[\alpha]_D$: +27.1 (c = 1.0 in $CHCl_3$)

Thermal stability study

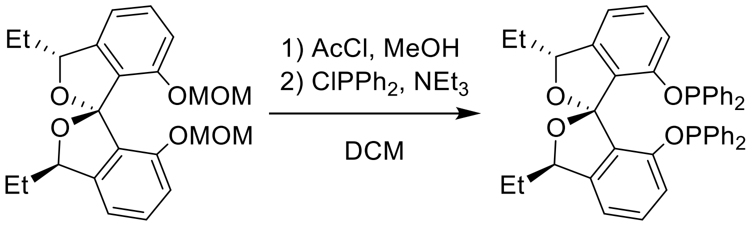
Complex **(*R,S,S*)-11** (10.0mg) was dissolved in PhMe and heated to 110°C for 12h. The material was recovered quantitatively and was unchanged by NMR analysis.





Synthesis of diphosphinite (*S,R,R*)-SPIRAPO

(((*1S,3R,3'R*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(oxy))bis(diphenylphosphane) ((*S,R,R*)-SPIRAPO)



(*S,R,R*)-6a **(*S,R,R*)-SPIRAPO**

Spiroketal **(*S,R,R*)-6a** (40mg, 0.10mmol) and methanol (1.0mL) were cooled to 0°C before dropwise addition of acetyl chloride (14μL, 0.20mmol). Reaction mixture was then warmed to room temperature. After for 6h, the volatiles were removed in vacuo. The crude diol and 4-Dimethylaminopyridine (1.2mg, 0.01mmol) were dissolved into DCM (1.0mL) at room temperature before addition of triethylamine (0.13mL, 1.0mmol) and chlorodiphenylphosphine (46μL, 0.25mmol) over 30min. After 12h, volatiles were removed *in vacuo*, and the crude was purified by FCC (SiO_2 treated with 5% TEA, 4%→ 9% EtOAc in hexanes) to afford **(*S,R,R*)-SPIRAPO** (34mg, 56% yield) and **(*R,R,R*)-SPIRAPO** (17mg, 26% yield) as white foams.

For purified **(*S,R,R*)-12**

^{1}H NMR (399.54 MHz, $CDCl_3$) *δ* 7.31-7.21 (m, 12H), 7.14 (t, *J* = 7.4 Hz, 2H), 7.06 (m, 6H), 6.97 – 6.90 (m, 4H), 6.86 – 6.81 (m, 2H), 5.26 (dd, *J* = 8.2, 4.2 Hz, 2H), 1.57 (m, 2H), 1.41 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.36, 152.27, 146.31, 140.11, 139.92, 139.88, 139.72, 130.73, 130.59, 130.49, 129.74, 129.63, 129.52, 128.89, 128.39, 128.31, 128.25, 128.18, 115.33, 115.17, 115.09, 114.69, 82.94, 28.02, 10.25

^{31}P NMR (161.75 MHz, $CDCl_3$) *δ* 105.24

ESI-HRMS Calcd. for $C_{43}H_{39}O_4P_2^+$ 681.2317 $[M+H]^+$, found 681.2316.

[α]$_D$: -80.7 (c = 1.25 in THF)

For purified **(*R,R,R*)-12**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 12H), 7.15 (t, *J* = 7.7 Hz, 2H), 7.13 – 6.99 (m, 6H), 6.97 (t, *J* = 7.4 Hz, 4H), 6.71 (d, *J* = 7.5 Hz, 2H), 4.78 (dd, *J* = 7.2, 4.5 Hz, 2H), 1.89 – 1.72 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 6H).

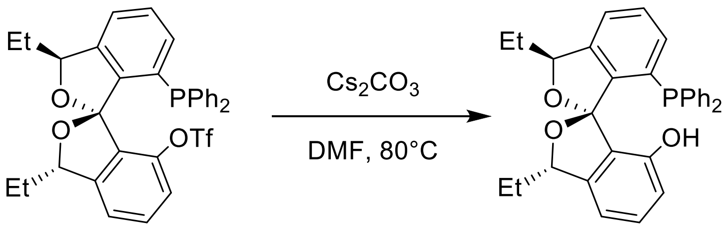
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.83, 130.82, 130.63, 130.47, 130.46, 129.75, 129.61, 129.57, 129.06, 128.23, 128.17, 115.11, 114.72, 84.21, 30.06, 9.74.

^{31}P NMR (202 MHz, $CDCl_3$) δ 104.37.

[α]$_D$: -14.8 (c = 5.25 in THF)

Synthesis of monophosphine (*R,S,S*)-SPIROMP and (*S,S,S*)-SPIROMP

(*1S,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-ol ((*S,S,S*)-SPIROMP)



(*S,S,S*)-10 **(*S,S,S*)-SPIROMP**

Hydrolysis based on a modified reported procedure.[3] Triflate **(*S,S,S*)-10** (300mg, 0.49mmol), wet Cs_2CO_3 (800mg, 2.45mmol), and DMF (8.0mL) were added to a flask. Reaction mixture was heated to 80°C. After 8h, reaction mixture was filtered through Celite and then purified by FCC (SiO_2, 20% → 25% EtOAc in hexanes) to obtain **(*S,S,S*)-SPIROMP** (224mg, 95% yield) as white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.5 Hz, 1H), 7.26 (m, 5H), 7.16 – 7.06 (m, 4H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.93 (dd, *J* = 7.3, 4.4 Hz, 1H), 6.86 (t, *J* = 7.7 Hz, 2H), 6.73 (d, *J* = 7.4 Hz, 1H), 6.10 (d, *J* = 7.9 Hz, 1H), 5.42 (t, *J* = 5.4 Hz, 1H), 5.24 (dd, *J* = 7.9, 4.3 Hz, 1H), 4.13 (s, 1H), 2.04 – 1.77 (m, 4H), 1.11 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{31}P NMR (202 MHz, $CDCl_3$) δ -18.74.

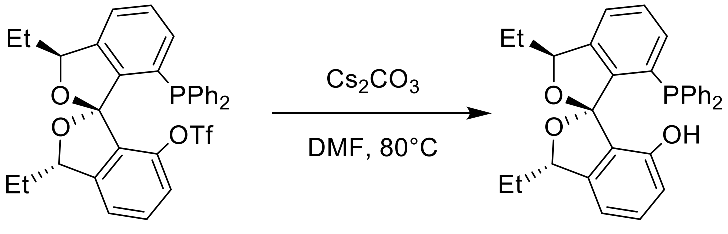
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.04, 145.19, 145.17, 143.40, 143.35, 142.91, 142.71, 137.32, 137.22, 135.46, 135.38, 134.29, 134.27, 133.86, 133.68, 133.63, 133.53, 133.46, 133.38, 131.46, 129.56, 128.40, 128.16, 128.11, 127.88, 127.82, 126.08, 126.05, 122.12, 116.75, 116.73, 114.46, 113.09, 85.38, 85.32, 83.73, 30.96, 29.54, 10.04, 9.14.

ESI-HRMS Calcd. for $C_{31}H_{30}O_3P^+$ 481.1933 $[M+H]^+$, found 481.1934.

IR (powder): ν_{max} = 3306, 2962, 1606, 1474, 1297, 1005, 927, 741, 692 cm^{-1}

[α]$_D$: -3.7 (c = 1.0 in $CHCl_3$)

(*1R,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-ol ((*R,S,S*)-SPIROMP)



(*R,S,S*)-10 **(*R,S,S*)-SPIROMP**

Triflate **(*R,S,S*)-10** (112mg, 0.18mmol), wet Cs_2CO_3 (300mg, 0.92mmol), and DMF (3.0mL) were added to a flask. Reaction mixture was heated to 80°C. After 8h, reaction mixture was filtered through Celite and then purified by FCC (SiO_2, 20% EtOAc in hexanes) to obtain **(*R,S,S*)-SPIROMP** together with an impurity (90.1mg, 1:11.6 impurity:product). The product was further purified by recrystallization from cyclohexane (35mg, 40% yield).

^{1}H NMR (401 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.16 (m, 8H), 7.02 (m, 5H), 6.79 (d, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 8.0 Hz, 1H), 5.41 (dd, *J* = 6.7, 4.0 Hz, 1H), 5.24 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.24 (s, 1H), 2.07 (m, 1H), 1.90 – 1.77 (m, 2H), 1.77 – 1.66 (m, 1H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H).

^{31}P NMR (162 MHz, $CDCl_3$) δ -23.06.

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.95, 145.81, 143.90, 143.84, 142.99, 142.72, 137.33, 137.20, 136.59, 136.45, 135.30, 134.12, 133.91, 133.70, 132.98, 132.80, 131.38, 130.09, 128.51, 128.18, 128.11, 127.81, 125.98, 125.95, 122.30, 115.57, 114.87, 113.10, 84.39, 84.34, 81.67, 81.63, 27.94, 27.64, 27.59, 10.70, 9.24

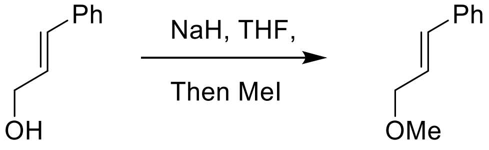
ESI-HRMS Calcd. for $C_{31}H_{30}O_3P^+$ 481.1933 $[M+H]^+$, found 481.1929.

IR (powder): ν_{max} = 3326 (br), 2959, 2853, 1604, 1473, 1295, 1005, 922, 740, 696 cm^{-1}

$[\alpha]_D$: +13.2 (c = 1.0 in $CHCl_3$)

Asymmetric hydroarylation of methylated cinnamyl alcohol

Preparation of substrate - (*E*)-(3-methoxyprop-1-en-1-yl)benzene



12

Alkenyl ether (**15**) was prepared according a reported procedure.[4] A flask was charged with a suspension of NaH (60%, prewashed with hexanes, 520mg, 21.7mmol) and THF (30mL) before addition of cinnamyl alcohol (1.4mL, 10.87mmol). After stirring at room temperature for 100min, methyl iodide (2.0mL, 32.6mmol) was added at room temperature. After 3h, reaction mixture was filtered through a SiO$_2$ pad, with 50% EtOAc in hexanes elution. The filtrate was concentrated *in vacuo* and purified by FCC (SiO$_2$, 5% EtOAc in hexanes) to afford the desired product (1.52g, 94.4% yield) as a colorless oil. Spectral properties match those reported in literature.

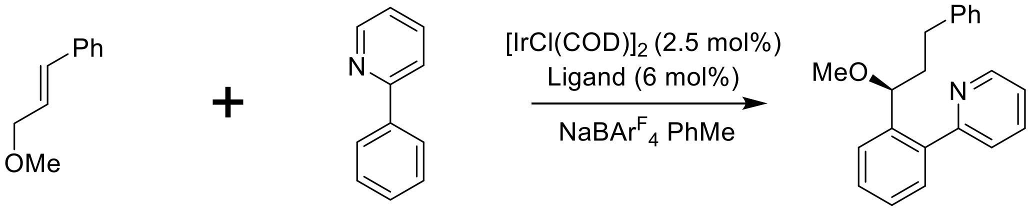
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.31 (dd, *J* = 8.4, 6.7 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.28 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.09 (dd, *J* = 6.0, 1.5 Hz, 1H), 3.38 (d, *J* = 0.5 Hz, 2H).

^{13}C NMR (100 MHz, cdcl$_3$) δ 136.70, 132.40, 128.52, 127.63, 126.44, 125.94, 73.07, 57.96.

IR (film): v_{max} = 3026, 2924, 2820, 1494, 1449, 1379, 1190, 1119, 965, 734, 691 cm^{-1}

Hydroarylation procedure

(*S*)-2-(2-(1-methoxy-3-phenylpropyl)phenyl)pyridine



12 **13** **14**

Hydroarylations were carried out according to a recently reported procedure.[5] Bis(1,5-cyclooctadiene)diiridium(I) dichloride (3.3mg, 0.0049 mmol) and **(*S,S,S*)-SPIRAP** (7.6mg, 0.012mmol) were added to a Schlenk tube strictly under nitrogen. PhMe (330μL) was added and the mixture was stirred at room temperature. After 20min, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (18.1mg, 0.0196mmol) was added. After 15min, 2-phenylpyridine **13** (30μL, 0.21mmol) and cinnamyl ether **12** (30μL, 0.196mmol) were added. Reaction mixture was then heated to 70°C. After 24h, reaction mixture was cooled to room temperature. Volatiles were removed *in vacuo* and the crude was purified by FCC (10% EtOAc in hexanes) to obtain pure product **14** (56.9mg, 96% yield, 95.4% *ee*) as colorless oil that solidifies on cooling.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.59 – 8.51 (m, 1H), 7.63 (td, *J* = 7.7, 5.3 Hz, 2H), 7.46 (dt, *J* = 8.2, 4.3 Hz, 1H), 7.35 (d, *J* = 4.3 Hz, 2H), 7.19 (ddt, *J* = 26.8, 14.7, 7.7 Hz, 5H), 7.11 – 7.04 (m, 2H), 4.45 (dd, *J* = 8.4, 4.2 Hz, 1H), 3.17 (s, 3H), 2.75 (m, 1H), 2.65 (m, 1H), 2.02 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.28, 149.05, 142.02, 140.75, 140.19, 136.06, 129.41, 128.73, 128.52, 128.18, 127.06, 126.16, 125.50, 123.99, 121.63, 78.18, 56.57, 39.61, 32.20.

ESI-HRMS Calcd. for $C_{21}H_{22}NO^+$ 304.1701 $[M+H]^+$, found 304.1696.

IR (film): ν_{max} = 2924, 1585, 1425, 1100, 1022, 747, 698 cm^{-1}

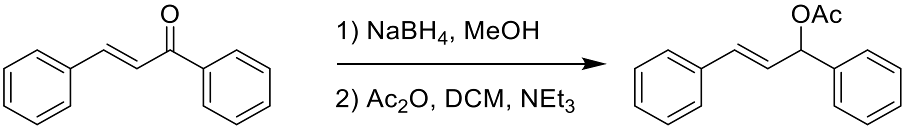
SFC (Chiralpak OD-H, 92:8 CO_2/isopropanol, 3.5 ml/min, 40°C, 120 bar back pressure), t_r = 7.4 min (minor, *R*), 7.9 min (major, *S*)

For **(*S,R,R*)-SPIRAP** – No product observed.

For **(*R*)-SDP** – 82% yield, 94.9% *ee*.

Asymmetric allylic alkylation of chalcone derivatives

Preparation of substrate - (*E*)-1,3-diphenylallyl acetate



15

(E)-1,3-diphenylallyl acetate was synthesized following a slightly modified reported procedure.[6] (E)-chalcone (988mg, 4.74mmol) and methanol (12mL) were cooled to 0°C before portionwise addition of sodium borohydride (365mg, 9.66mmol). Reaction mixture was then warmed to room temperature. After 1h, reaction mixture was partitioned between EtOAc (30mL) and water (30mL). After separating the layers, the aqueous solution was extracted with EtOAc twice. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. The allylic alcohol was acetylated without further purification as follows. 4-Dimethylaminopyridine (58.8mg, 48.1mmol), DCM (30mL), and triethylamine (1.7mL, 12.2mmol) were added to the crude. Reaction mixture was cooled to 0°C before dropwise addition of acetic anhydride (1.1mL, 11.6mmol). Reaction mixture was warmed to room temperature and stirred overnight. Water (30mL) was added, and after separating the layers, the aqueous solution was extracted with DCM twice. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Pure product **15** (841.2mg, 70.3% yield) was obtained after purification by FCC (SiO_2, 10 → 20% EtOAc in hexanes). Spectral properties match those reported in literature.

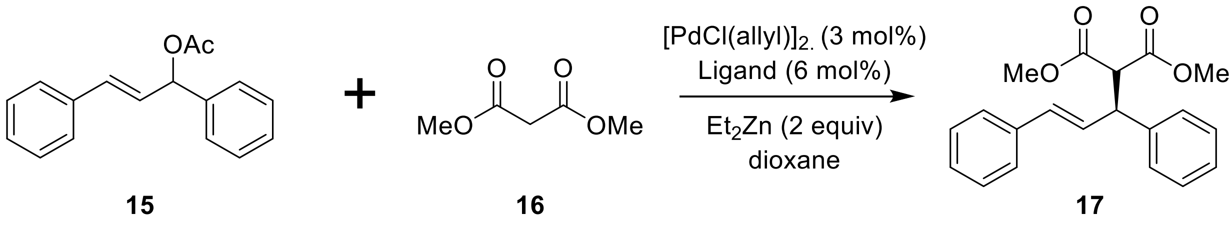
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.13 (m, 10H), 6.65 (d, *J* = 15.8 Hz, 1H), 6.46 (d, *J* = 6.9 Hz, 1H), 6.36 (dd, *J* = 15.7, 6.8 Hz, 1H), 2.15 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.97, 139.20, 136.14, 132.56, 128.59, 128.54, 128.45, 128.39, 128.29, 128.13, 128.02, 127.47, 127.01, 126.66, 76.10, 21.32.

IR (film): ν_{max} = 3029, 1734, 1495, 1370, 1227, 1017, 962, 743, 694 cm^{-1}

Asymmetric allylic alkylation procedure

Dimethyl (*S,E*)-2-(1,3-diphenylallyl)malonate



The asymmetric alkylation was performed following a modified reported procedure.[7] (E)-1,3-diphenylallyl acetate (49.3mg, 0.195mmol) **15** and 1,4-dioxane (1mL) were stirred at room temperature. In a separate flask, allylpalladium(II) chloride dimer (1.8mg, 0.0049mmol), **(*S,S,S*)-SPIRAP** (7.6mg, 0.012mmol), and 1,4-dioxane (1mL) were stirred for 1h at room temperature. The catalyst solution was transferred to the substrate flask by syringe with dioxane washings (1mL). In another flask, dimethyl malonate **16** (45μL, 0.39mmol) and 1,4-dioxane (1mL) were cooled to 0°C, and then treated with a 1 M solution of diethylzinc in hexanes (390μL, 0.39mmol). The substrate flask was cooled with an ice bath while the reagent solution was slowly transferred via syringe with dioxane washings (1mL). Reaction mixture was then warmed to room temperature. After 90min, reaction mixture was diluted with EtOAc (5mL) and quenched with a saturated aqueous solution of NH_4Cl (5mL). After separating the layers, the aqueous solution was extracted with EtOAc twice. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, gradient 0 → 10% EtOAc in hexanes) to afford pure product **17** (59.8mg, 94% yield, 96.6% *ee*) as colorless oil. Spectral properties match those reported in literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.18 (m, 10H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.37 (dd, *J* = 15.7, 8.6 Hz, 1H), 4.30 (dd, *J* = 10.9, 8.5 Hz, 1H), 3.99 (d, *J* = 10.8 Hz, 1H), 3.73 (s, 3H), 3.54 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.20, 167.78, 140.20, 136.84, 131.85, 129.14, 128.74, 128.49, 127.89, 127.59, 127.18, 126.40, 57.67, 52.63, 52.46, 49.22.

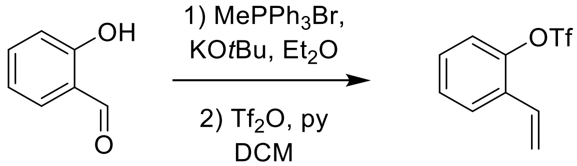
IR (film): ν_{max} = 3316 (br), 3026, 2861, 1494, 1091, 945, 733, 691 cm^{-1}

HPLC (Chiralpak AD column, 95:5 hexanes/isopropanol, 1.0 ml/min), t_r = 12.6 min (minor, *R*), 17.1 min (major, *S*)

For **(*R,S,S*)-SPIRAP** – 98% yield, 86% *ee*

Asymmetric Heck reaction of 2-vinylphenyl triflate with norbornene

Substrate synthesis



18

2-vinylphenyl trifluoromethanesulfonate was synthesized following a two-step procedure reported elsewhere.[8] Methyltriphenylphosphonium bromide (3.52g, 9.85mmol) and diethyl ether (60mL) were cooled to 0°C before the addition of KO*t*-Bu (2.16g, 19.25mmol). After 15min, a solution of salicylaldehyde (1mL, 9.38mmol) in diethyl ether (30mL) was added. Reaction mixture was then warmed to room temperature. After 16h, a saturated aqueous solution of NH_4Cl (30mL) was added. After separating the layers, the aqueous solution was extracted with diethyl ether twice. Combined organic was washed with brine, dried over Na_2SO_4, and concentrated *in vacuo*. Crude was purified by FCC (SiO_2, gradient 5 → 15% EtOAc in hexanes) to afford unreacted starting material (141mg, 12% recovery) and pure 2-vinylphenol (942 mg, 84% yield) as light yellow liquid.

Vinylphenol (767mg, 6.38mmol), DCM (18mL), and pyridine (1mL, 12.77mmol) were cooled to 0°C before the dropwise addition of trifluoromethanesulfonic anhydride (1.3mL, 7.66mmol). Reaction mixture was then warmed to room temperature. After 13h, reaction mixture was filtered with DCM washings, concentrated *in vacuo*, and purified by FCC (SiO_2, hexanes) to afford 2-vinyltriflate (1.427g, 89% yield) as colorless liquid.

^{1}H NMR (401 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 1H), 7.39 – 7.15 (m, 3H), 6.92 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.84 (d, *J* = 17.5 Hz, 1H), 5.48 (d, *J* = 11.0 Hz, 1H).

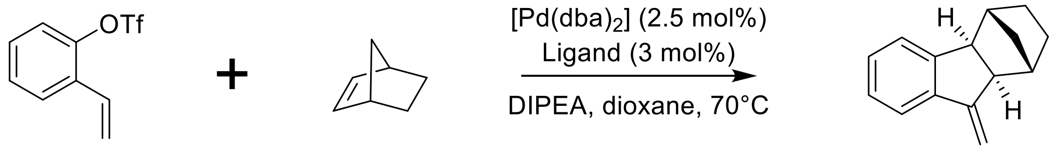
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.82, 131.01, 129.23, 128.81, 128.35, 127.21, 121.62, 120.15, 118.58, 116.97.

^{19}F NMR (377 MHz, $CDCl_3$) δ -73.64.

IR (film): ν_{max} = 1419, 1207, 1137, 1077, 886, 792, 760 cm^{-1}

Asymmetric Heck reaction

(*1S,4R,4aS,9aR*)-9-methylene-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene



18 **19** **20**

The asymmetric Heck reaction was performed following a modified reported procedure.**Error! Bookmark not defined.** Bis(dibenzylideneacetone)palladium(0) (4.7mg, 0.0082mmol), **(*S,S,S*)-SPIRAP(O)** (6.5mg, 0.0098mmol) were added to a Schlenk tube strictly under nitrogen. 1,4-dioxane (320µL) was added, and the mixture was stirred at room temperature. After 30min, 2-vinyltriflate **18** (60µL, 0.32mmol), norbornene (122.1mg, 1.30mmol), and diisopropylethylamine (110µL, 0.63mmol) were added and then the mixture was heated to 70°C. After 20h, reaction mixture was concentrated *in vacuo* and purified through a short pipette column (SiO_2) with hexanes elution to afford pure product **20** (63.7mg, 99% yield, 95% *ee*)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 1H), 7.29 – 7.12 (m, 3H), 5.51 (d, *J* = 2.4 Hz, 1H), 5.03 (d, *J* = 2.0 Hz, 1H), 3.06 (d, *J* = 7.0 Hz, 1H), 2.83 (d, *J* = 7.0 Hz, 1H), 2.36 – 2.20 (m, 2H), 1.61 (m, *J* = 18.4, 15.4, 11.6, 5.7 Hz, 2H), 1.41 (m, *J* = 18.9, 9.0, 2.4 Hz, 2H), 1.09 – 0.92 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.44, 148.89, 142.58, 128.54, 126.57, 125.09, 119.95, 102.93, 52.20, 52.01, 44.59, 42.49, 32.33, 29.36, 28.62.

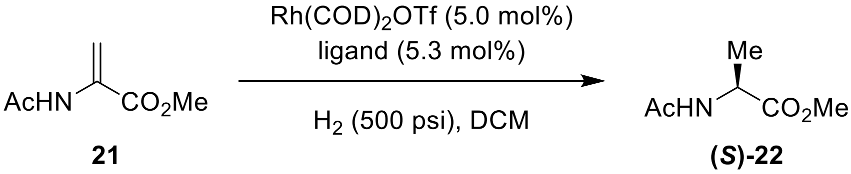
IR (film): ν_{max} = 2948, 2868, 1635, 1471, 868, 782, 756, 730 cm^{-1}

SFC (Chiralpak OJ-H, 99:1 CO_2/isopropanol, 3.5 ml/min, 40°C, 120 bar back pressure), t_r = 3.5 min (minor, (*1R,4S,4aR,9aS*)), 3.8 min (major, (*1S,4R,4aS,9aR*))

For **(*R,S,S*)-SPIRAP(O)** – 96% yield, -86% *ee* (enantiomer of **20**)

Asymmetric hydrogenation of acrylate derivatives

Methyl acetyl-*L*-alaninate



The asymmetric hydrogenation of acetamidoacryllic esters was based on a reported procedure.[9] **(*S,R,R*)-SPIRAPO** (11.2mg, 0.016mmol) and Rh(COD)$_2$OTf (7.0mg, 0.015mmol) were measured and packed into a Schlenk tube in the glovebox before the addition of dry DCM (3.0mL) to make a stock solution. Methyl 2-acetamidoacrylate (28.6mg, 0.20mmol) was added to the flask before addition of the stock solution (2.0mL). The reaction flask was placed into the hydrogenation apparatus before purging with N_2 and H_2, and the reaction was stirred under 500 psi H_2 for 3h. Volatiles were removed *in vacuo*, and the crude was purified by FCC (SiO_2, 20% EtOAc in hexanes) to afford methyl acetyl-L-alaninate **(*S*)-22** (25.3mg, 87% yield, 91% *ee*) as clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (s, 1H), 4.58 (p, *J* = 7.3 Hz, 1H), 3.74 (s, 3H), 2.00 (s, 3H), 1.38 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.62, 169.52, 52.46, 48.00, 23.15, 18.55.

IR (film): ν_{max} = 3282, 2955, 1739, 1652, 1533, 1436, 1372, 1207, 1160, 1058, 733, 607 cm^{-1}

GC conditions 1:

Rt- bDExsm column (df = 0.25 µm, 0.25 mm i.d. × 30 m, fused silica capillary column); carrier gas, He (flow 1.5 mL/min); injection temp, 230 °C; initial column temperature, 70 °C; progress rate, 2 °C /min; final column temperature, 90 °C); t_r = 28.9 min (minor, *R*), 29.3 min (major, *S*)

GC conditions 2

Rt- bDExsm column (df = 0.25 µm, 0.25 mm i.d. × 30 m, fused silica capillary column); carrier gas, He (flow 1.5 mL/min); injection temp, 230 °C; initial column temperature, 70 °C; progress rate, 2 °C /min; final column temperature, 110 °C); t_r = 48.7 min (major, *R*), 51.2 min (minor, *S*)

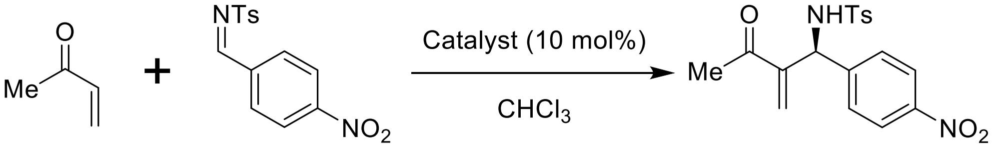
For **(*S*)-SDPO** – 85% yield, 94% *ee* **(*S*)-22**

For **(*S*)-BINAPO** – 84% yield, -91% *ee* **(*R*)-22**

For **(*R,R,R*)-SPIRAPO** – 85% yield, -93% *ee* **(*R*)-22**

Asymmetric Baylis-Hillman reaction of methyl vinyl ketone and an aromatic tosylimine

(*S*)-4-methyl-N-(2-methylene-1-(4-nitrophenyl)-3-oxobutyl)benzenesulfonamide



SI-1 **(*S*)-SI-2**

The asymmetric Baylis-Hillman reaction was performed following a reported procedure.[10] Imine **SI-1** (48mg, 0.16mmol), catalyst **(*S,S,S*)-SPIROMP** (7.9mg. 0.02mmol)**,** activated 3Å MS, and $CHCl_3$ (820µL) were added to a Schlenk tube. Mixture was cooled to -78°C, then 3-Buten-2-one (41µL, 0.50mmol) was added before warming the reaction to -10°C. After 5 days, volatiles were removed *in vacuo*, and the crude was purified by FCC (SiO_2, 20→40% EtOAc in hexanes) to afford sulfonamide **(*S*)-SI-2** (50.2mg, 85% yield, 83% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.01 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.13 (s, 1H), 6.08 (s, 1H), 5.93 (d, *J* = 9.3 Hz, 1H), 5.32 (d, *J* = 9.4 Hz, 1H), 2.41 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.72, 147.18, 146.15, 145.42, 143.81, 137.36, 129.63, 127.23, 127.17, 123.61, 58.95, 26.17, 21.51.

SFC (Chiralpak IA, 70:30 CO_2/isopropanol, 3.5 ml/min, 40°C, 120 bar back pressure), t_r = 4.0 min (major *S*), 4.6 min (minor, *R*)

For **(*R,S,S*)-SPIROMP** – 6.8% yield, -71.8% *ee* **(*R*)-SI-2**

Computational models and analysis

Quantum chemical calculations were performed using the Q-Chem 4.3 package.[11] Geometry optimizations were evaluated using the B97-D density functional.[12] For compounds not containing transition metals, double-ζ- quality basis set with polarization functions was used on all atoms, 6-31G**.[13] For Pd-complexes, the LANL2DZ basis set[14] was used of Pd, P, and Cl atoms, while 6-31G** was used on all other atoms. Pictorial representations of we made in Discovery Studio 4.1 Visualizer.[15] The electronic Gibbs free energy values were obtained from single point calculatings using the ωB97X-D exchange functional.[16] The final Gibbs free energy values were obtained by correcting the electronic free energy with the enthalpic and entropic contributions from vibrations, rotations, and translations at 298 K. These frequency computations were performed using the B97-D functional. For the enthalpic and entropic corrections to the free energies from the harmonic oscillator approximation, all frequencies below 50 cm^{-1} were treated as if they were 50 cm^{-1} .

Cartesian coordinates for starting geometries, transition states, and products are described below.

Diol (*S*,*S*,*S*)-7

43

C	-3.16660418	2.51676888	1.21187067
C	-3.47220673	1.73275471	0.08830678
C	-2.53030555	0.80808774	-0.40577742
C	-1.30924670	0.68440827	0.27839571
C	-1.01430839	1.47044495	1.39556754
C	-1.93172027	2.40595904	1.88125011
C	-0.12997580	-0.19398482	-0.05346636
O	0.70580487	-0.09105548	1.11598208
C	0.39861682	1.13963116	1.82881223
C	-0.37560667	-1.64951697	-0.36454275
C	0.38034724	-2.02588796	-1.47838614
C	1.15869767	-0.80975373	-1.93518700
O	0.51272696	0.29807553	-1.24524866
C	-1.16867638	-2.57630232	0.33225338
C	-1.19723175	-3.90426804	-0.13963789
C	-0.43227714	-4.27249729	-1.25731951
C	0.37379853	-3.34325761	-1.94429854
O	-1.91800076	-2.25264222	1.42462945
O	-2.84906405	0.06926319	-1.50667348
C	3.41783300	0.38462186	-1.92406340
C	2.65144451	-0.89646971	-1.56304832
C	2.84936369	1.86763352	1.78200466
C	1.39725415	2.25469900	1.46328589
H	-3.91142875	3.22728152	1.57364590
H	-4.43155190	1.82694792	-0.41941506
H	-1.70717902	3.02792390	2.74812206
H	0.47683546	0.90246922	2.90277633
H	1.05154092	-0.60576479	-3.01314195
H	-1.82004054	-4.63174383	0.37983659
H	-0.47177422	-5.30695997	-1.60170327
H	0.96516968	-3.64555388	-2.80885692
H	-1.80138354	-1.30443316	1.61090982
H	-2.08996952	-0.49764490	-1.72910958
H	4.47230619	0.31117324	-1.62012042
H	3.38544103	0.57146204	-3.00921822
H	2.96579672	1.24714660	-1.41595888
H	2.71218848	-1.09304024	-0.48259783
H	3.08175872	-1.76942095	-2.08222447
H	3.54273745	2.67255686	1.49694678
H	2.97854259	1.66895187	2.85785605
H	3.12365368	0.95793215	1.23163953
H	1.28101785	2.46614191	0.38996576
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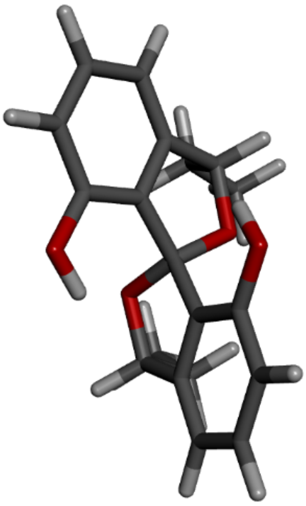

Diol (*R*,*S*,*S*)-7

43

C	-3.76748275	-3.51818612	3.74134222
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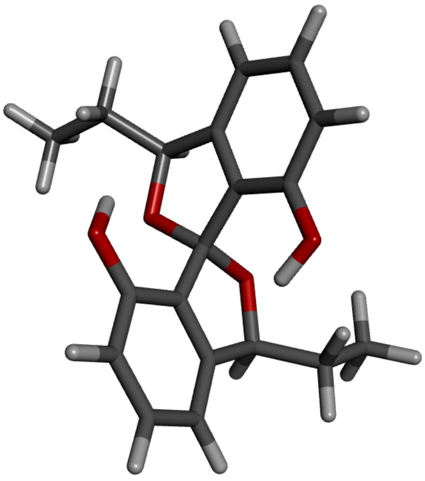
C	-3.45630547	-4.03988022	1.37903507
C	-2.58731767	-2.93968672	1.29453362
C	-2.33080690	-2.13637533	2.40609471
C	-2.90764851	-2.40726314	3.65048742
C	-1.75263192	-2.46918854	0.12313126
O	-1.33419260	-1.15283165	0.52609458
C	-1.39749492	-1.02425722	1.97727821
C	-2.41852000	-2.41568750	-1.22378468
C	-1.76340458	-3.25381099	-2.12681959
C	-0.58568313	-3.88561829	-1.41845772
O	-0.63347975	-3.35355276	-0.06748417
C	-3.54783541	-1.66657797	-1.59694885
C	-4.04281795	-1.82777312	-2.90574637
C	-3.39386045	-2.69531117	-3.79983007
C	-2.24066834	-3.41529605	-3.43270641
O	-4.17439363	-0.80788731	-0.74398872
O	-3.76646128	-4.84404146	0.31544995
C	0.53095627	-6.03436956	-0.60243733
C	-0.65273218	-5.42162842	-1.36568745
C	-0.95554273	1.48604679	1.79257206
C	-1.88902753	0.38542121	2.32117428
H	-4.24178652	-3.75594205	4.69457540
H	-4.73073494	-5.16856809	2.70062728
H	-2.70758831	-1.77956704	4.51933719
H	-0.38105357	-1.17187408	2.38584392
H	0.37166407	-3.57603345	-1.87653534
H	-4.92315513	-1.26253861	-3.20950163
H	-3.79409634	-2.80270317	-4.80896192
H	-1.74017002	-4.07168318	-4.14457134
H	-3.59982713	-0.69337294	0.03439360
H	-3.42615899	-4.43070991	-0.49806151
H	0.44644039	-7.12979398	-0.55685303
H	1.48529960	-5.78251220	-1.09156344
H	0.55748647	-5.64086814	0.42266486
H	-1.60205125	-5.70440808	-0.88514505
H	-0.68313979	-5.79451996	-2.40318202
H	-1.34103428	2.48445362	2.04502104
H	0.05015853	1.38430648	2.22935637
H	-0.86048987	1.41117827	0.70081747
H	-2.90513296	0.50713752	1.90944932
H	-1.98200101	0.45008968	3.41754948



Diphosphine (*S*,*S*,*S*)-SPIRAP

85

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C	-8.19982073	1.57815228	-0.84935829
C	-6.79307735	1.47712345	-0.87837356
C	-5.96971226	2.60520309	-0.86840526
C	-6.51019265	3.89422007	-0.85036631
C	-5.90792373	0.25061771	-0.97713722
O	-4.59106596	0.73441794	-0.67744595
C	-4.52621460	2.16693643	-0.88023199
C	-6.17256176	-0.96590450	-0.11275732
C	-6.08335956	-2.10139521	-0.92085989
C	-5.80582018	-1.68030128	-2.34138947
O	-5.97863626	-0.24283852	-2.32359121
C	-6.42856914	-1.05256265	1.27216854
C	-6.58147584	-2.35190383	1.80273633
C	-6.48332319	-3.49521836	0.98946764
C	-6.23375823	-3.38431127	-0.38623589
P	-6.78078390	0.48213066	2.26531693
C	-6.98264883	-0.23098775	3.97005112
C	-5.93078373	-0.39357444	4.89360778
C	-6.17654444	-0.95213631	6.15720737
C	-7.47150586	-1.36450667	6.50908669
C	-8.52607438	-1.20765798	5.59522774
C	-8.28407762	-0.63542328	4.33831026
C	-5.11365286	1.28903301	2.37946729
C	-3.89754775	0.59604254	2.21516053
C	-2.67533597	1.27755487	2.29588594
C	-2.65390580	2.66017617	2.54586685
C	-3.85990152	3.35978388	2.70811059
C	-5.08302591	2.67798932	2.61664993
P	-9.24673037	0.05359405	-0.62106436
C	-10.95981583	0.77002223	-0.64094337
C	-11.42747123	1.34630849	0.56147976
C	-12.71456381	1.89554698	0.63696180
C	-13.56372506	1.85516235	-0.48138255
C	-13.11358046	1.27113343	-1.67522810
C	-11.81748872	0.73823713	-1.75841582
C	-9.13924589	-0.77089700	-2.27768337
C	-9.37509966	-2.15997856	-2.32426442
C	-9.29822771	-2.85484377	-3.54094681
C	-8.96937924	-2.16851902	-4.72072830
C	-8.72122194	-0.78601403	-4.68035743
C	-8.80806051	-0.09071416	-3.46615752
C	-4.09030743	-1.53863732	-4.22412336
C	-4.38555316	-2.04782917	-2.80522051
C	-2.36275746	1.96149457	-2.21138747
C	-3.80347831	2.49280888	-2.20007364
H	-8.36371906	5.01127638	-0.81735828
H	-9.81679996	3.01756759	-0.79335127
H	-5.86560702	4.77455090	-0.83789391
H	-3.96614341	2.57700505	-0.02528605
H	-6.55538974	-2.07544920	-3.04544850
H	-6.79072764	-2.47799627	2.86382364
H	-6.60982679	-4.48034059	1.44186675
H	-6.17110686	-4.26957097	-1.02086764
H	-4.92247659	-0.08204485	4.62077012
H	-5.35450550	-1.07121192	6.86539243
H	-7.65843792	-1.80122674	7.49143592
H	-9.53596752	-1.52224537	5.86359684
H	-9.10645234	-0.50624819	3.63096079
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H	-6.02140882	3.22693431	2.71661133
H	-10.77256313	1.37381334	1.43531412
H	-13.05766320	2.34635264	1.56983298
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H	-11.46941555	0.29827418	-2.69309161
H	-9.59714548	-2.69919218	-1.40145400
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H	-3.07018880	-1.80464183	-4.53924995
H	-4.19382515	-0.44556076	-4.25707290
H	-4.79867957	-1.96941946	-4.94991582
H	-4.27968607	-3.14500505	-2.75648042
H	-3.67935161	-1.61255768	-2.08224141
H	-1.86467047	2.17860027	-3.16798376
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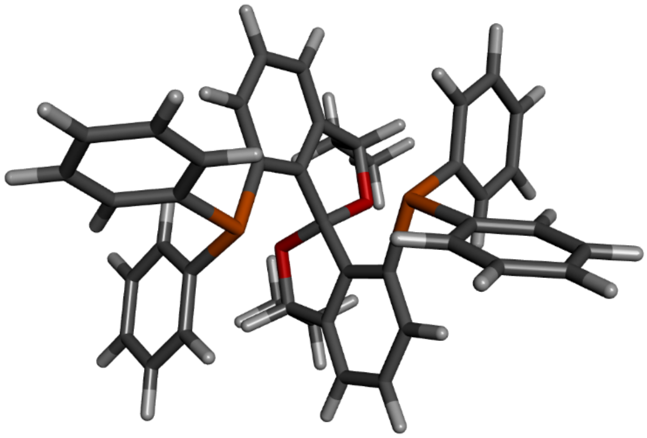

Diphosphine (*S*,*R*,*R*)-SPIRAP

85

P	-0.78415159	20.90796583	8.41079710
P	1.44835665	20.43430813	5.41165053
O	-1.04984959	17.26105507	7.80678199
O	-0.30266885	17.20831307	5.55590269
C	-1.66600258	20.13399215	9.84495430
C	-1.09623503	20.30205435	11.12593669
H	-0.18905620	20.89924711	11.23977342
C	-1.68127432	19.70405196	12.25082947
H	-1.23242863	19.84458927	13.23547462
C	-2.83319146	18.91319687	12.10660070
H	-3.28284917	18.43739840	12.97944197
C	-3.39766703	18.73140872	10.83504215
H	-4.28555929	18.10901962	10.71593561
C	-2.81978708	19.33731675	9.71008592
H	-3.24943097	19.17805742	8.72261144
C	-1.31874942	22.68327129	8.50317996
C	-2.15880668	23.20666114	9.50525908
H	-2.57059359	22.54357470	10.26624302
C	-2.46775272	24.57630343	9.52951042
H	-3.11890619	24.96770466	10.31330913
C	-1.95381877	25.43645292	8.54770159
H	-2.19874538	26.49952954	8.56664662
C	-1.12030554	24.92154126	7.54042534
H	-0.71441795	25.58191739	6.77222087
C	-0.79722161	23.55870422	7.52324894
H	-0.14376871	23.16803974	6.74064575
C	-1.77123850	20.30637233	6.95544366
C	-2.80272911	21.06589082	6.36246850
H	-3.08520489	22.01858200	6.80791271
C	-3.46127534	20.62695103	5.20081197
H	-4.25336544	21.24283339	4.77186890
C	-3.10603661	19.41576269	4.58694232
H	-3.60632120	19.08016497	3.67733792
C	-2.08213158	18.66129965	5.16631175
C	-1.43572263	19.09156420	6.32870521
C	-0.45011830	18.01137998	6.73664555

C	-0.01387803	16.65003924	8.61711635
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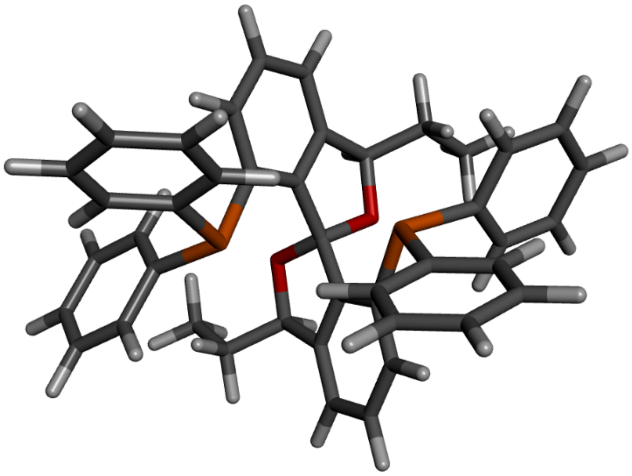
C	-0.45802469	16.64005166	10.08296308
H	0.37627309	16.23896695	10.68282052
H	-0.62826443	17.67615770	10.40413394
C	-1.72308853	15.79686732	10.30075393
H	-2.53627035	16.17476779	9.66774796
H	-2.05086861	15.85060209	11.34866297
H	-1.54480759	14.74088983	10.04150267
C	-1.47175595	17.35675891	4.71104185
H	-2.16325425	16.51494294	4.91083434
C	-1.03798088	17.32672629	3.24210820
H	-0.32112489	18.14124582	3.07505656
H	-1.92853948	17.53369087	2.62476451
C	-0.41765011	15.97954802	2.84489722
H	0.44671025	15.76284502	3.48662920
H	-0.07162089	16.00354784	1.80182159
H	-1.14707909	15.16104056	2.95664787
C	0.94298216	18.32973076	7.24450786
C	1.21184547	17.48143543	8.32188346
C	2.45775386	17.49231728	8.95504196
H	2.66414729	16.83238112	9.79920224
C	3.43127793	18.38740700	8.48397498
H	4.41276123	18.42395247	8.95938475
C	3.15621713	19.24681701	7.40628079
H	3.92190114	19.94425583	7.06981299
C	1.90162380	19.23810159	6.76101811
C	2.81885080	21.67689055	5.55692059
C	2.79328531	22.52623338	6.68689579
H	2.02042159	22.38908734	7.44513480
C	3.76034101	23.52640402	6.84830858
H	3.73045732	24.16933122	7.72956545
C	4.75869560	23.70602320	5.87560954
H	5.50681619	24.49082982	5.99685308
C	4.78771088	22.87115013	4.74871476
H	5.56366650	23.00082813	3.99221152
C	3.82783956	21.85817009	4.59107684
H	3.86448584	21.20608385	3.71875756
C	1.88737349	19.49699309	3.87551629
C	1.54939669	20.08168870	2.63484725
H	1.08602933	21.07010352	2.61118928
C	1.78783169	19.39689245	1.43513121
H	1.52278789	19.86110757	0.48379392
C	2.34942177	18.10985989	1.45932229
H	2.52195944	17.57094257	0.52651538
C	2.67936470	17.51833252	2.68790860
H	3.10922365	16.51603927	2.71429402
C	2.45247597	18.20612908	3.88879625
H	2.69521526	17.73460756	4.83950101

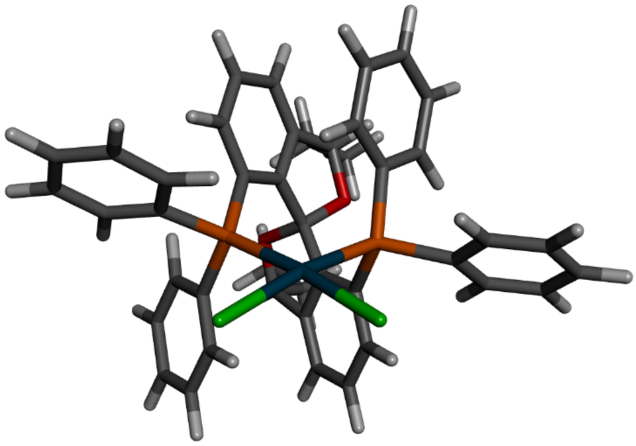


Pd(II) complex (*S*,*S*,*S*)-11

88

C	-7.31325408	4.25310845	-0.85667450
C	-8.28059072	3.24108705	-0.78570509
C	-7.93246512	1.87306479	-0.83350841
C	-6.56592680	1.55823475	-0.95121539
C	-5.60241497	2.57883528	-0.94677030
C	-5.95192899	3.92821540	-0.91974585
C	-5.80235929	0.25904828	-1.18699475
O	-4.46953808	0.56102088	-0.74196306
C	-4.22397977	1.97335870	-0.96471382
C	-6.20460791	-1.08161074	-0.61060131
C	-6.05771916	-2.04471358	-1.61904520
C	-5.60278464	-1.37020693	-2.88440487
O	-5.81246810	0.03811196	-2.61280113
C	-6.63842165	-1.45885458	0.66281852
C	-6.96377874	-2.81704924	0.88649366
C	-6.79154084	-3.77349867	-0.12268943
C	-6.32587692	-3.39353971	-1.39253495
P	-7.16546413	-0.32380265	2.05888680
C	-6.38682904	-1.09286747	3.59038195
C	-5.26550328	-1.93255208	3.47963304
C	-4.61203625	-2.37426697	4.64162253
C	-5.07302815	-1.97280590	5.90407583
C	-6.19098177	-1.12829268	6.00673118
C	-6.85107267	-0.68525327	4.85272282
C	-6.31391949	1.34702163	2.09853202
C	-4.91584006	1.43367961	2.21162113
C	-4.32023188	2.68131853	2.44001535
C	-5.11800771	3.83205463	2.56350910
C	-6.51389486	3.73556724	2.46194299
C	-7.11631737	2.48903229	2.23762135
P	-9.32435365	0.62351327	-0.51425630
C	-10.85596410	1.64584230	-0.88476260
C	-11.49617429	2.29316183	0.18570072
C	-12.57591914	3.14907211	-0.06982510
C	-13.02373340	3.34333004	-1.38745467
C	-12.39005938	2.68140842	-2.45046109
C	-11.29882039	1.83342641	-2.20215958
C	-9.21260266	-0.65364489	-1.87287261
C	-9.67151795	-1.95567625	-1.61016789
C	-9.64592498	-2.90995223	-2.63764062
C	-9.18516828	-2.56198054	-3.91757950
C	-8.73835520	-1.25492923	-4.17440044
C	-8.73901121	-0.29827514	-3.14835466
C	-3.68605429	-0.95947120	-4.51823506
C	-4.13283724	-1.66674286	-3.23085743
C	-2.09229412	1.54184743	-2.30938289
C	-3.46371114	2.23190164	-2.27740697
H	-7.63113301	5.29610331	-0.82964156
H	-9.32554374	3.52692046	-0.68616545
H	-5.18618099	4.70481481	-0.92297706
H	-3.62679775	2.32103147	-0.10691819
H	-6.25369424	-1.62320374	-3.73470222
H	-7.37771482	-3.11556068	1.84997212
H	-7.05021874	-4.81325055	0.07980392
H	-6.21410856	-4.12622044	-2.19246212
H	-4.90604542	-2.24554626	2.49992378
H	-3.74420512	-3.02994199	4.55429657
H	-4.56605695	-2.31945358	6.80584430
H	-6.55951071	-0.82137195	6.98620323
H	-7.73243805	-0.05189617	4.93020940
H	-4.30415581	0.53726095	2.12415480
H	-3.23524151	2.75288559	2.53166522
H	-4.65058437	4.80083117	2.74651897
H	-7.13567811	4.62582302	2.56091574
H	-8.20055590	2.39269092	2.17264325
H	-11.16611965	2.10027636	1.20617408
H	-13.07863312	3.64599650	0.76096440
H	-13.87133813	4.00200992	-1.58288924
H	-12.74445882	2.81979047	-3.47295034
H	-10.80667392	1.31362397	-3.02367618
H	-10.05101401	-2.20698801	-0.62018825

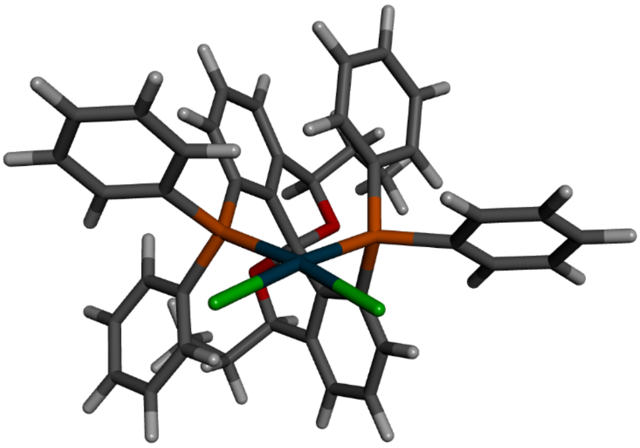
H	-9.99229999	-3.92407491	-2.43553562
H	-9.17475736	-3.30658540	-4.71542256
H	-8.37837332	-0.98053258	-5.16723401
H	-8.34911614	0.70243305	-3.32788003
H	-2.62954037	-1.16867867	-4.74107223
H	-3.81063922	0.12672242	-4.41717802
H	-4.29200442	-1.29308113	-5.37578636
H	-4.02572267	-2.75960897	-3.33513720
H	-3.51816056	-1.35346984	-2.37499949
H	-1.57366928	1.73804862	-3.25933052
H	-2.21227782	0.45618507	-2.19819514
H	-1.45092205	1.89990159	-1.48809403
H	-3.34567476	3.32363939	-2.38362073
H	-4.09554755	1.88395096	-3.10589737
Pd	-9.49227147	-0.41132773	1.63300775
Cl	-9.77093887	-1.66774910	3.69369728
Cl	-11.80753886	-0.89597443	1.04150558



Pd(II) complex (*S*,*R*,*R*)-11

88

P	-0.90564579	21.52013263	8.07779970
P	2.16806278	20.99025472	6.47176278
O	-0.95078418	17.50092404	7.78344443
O	0.26231649	17.41601059	5.76324743
C	-1.35079455	20.49334597	9.58341307
C	-0.57239852	20.59778059	10.74756900
H	0.32824982	21.20966943	10.74427984
C	-1.00182537	19.95375836	11.91884091
H	-0.40280373	20.03804863	12.82624115
C	-2.20318614	19.22714287	11.92942193
H	-2.54124877	18.74478364	12.84790900
C	-2.96190689	19.10416717	10.75368338
H	-3.87973749	18.51560037	10.75070386
C	-2.52681182	19.72004304	9.57191755
H	-3.09627699	19.60549305	8.65032876
C	-2.07811039	22.99178613	8.10870204
C	-3.31591521	22.94245564	8.76589386
H	-3.59917440	22.05709976	9.33400277
C	-4.17452960	24.05232766	8.71015458
H	-5.13153366	24.01991386	9.23297052
C	-3.79997274	25.19919794	7.99340370
H	-4.46757351	26.06118174	7.95464202
C	-2.55672563	25.24404137	7.34024500
H	-2.25008198	26.14192128	6.80217674
C	-1.69126862	24.14455192	7.40367756
H	-0.70195011	24.18974647	6.94644487
C	-1.57184049	20.51924643	6.61029570
C	-2.57753439	21.10411717	5.80966925
H	-2.97380301	22.08201989	6.07103630
C	-3.07103039	20.46494859	4.66402478
H	-3.84502743	20.95527900	4.07220695
C	-2.56317241	19.21849103	4.27200935
H	-2.92556535	18.71775093	3.37372654
C	-1.57076247	18.63761675	5.06063761
C	-1.07849215	19.26307605	6.21933342
C	-0.13644549	18.24956101	6.86830331
C	-0.07712602	16.73118240	8.64616236
H	0.10333090	15.74710319	8.17271379
C	-0.73048509	16.54030308	10.01427912
H	-0.04073392	15.93589047	10.62676931
H	-0.82197094	17.52233748	10.49259318
C	-2.10007994	15.85181375	9.91914806
H	-2.78224143	16.45923472	9.30961356
H	-2.54365684	15.72250480	10.91712146
H	-2.00967130	14.85971302	9.44853023
C	-0.88281105	17.30245735	4.88677719
H	-1.54157975	16.50154626	5.27534765
C	-0.42867905	16.94448117	3.47329937
H	0.18390921	17.76809073	3.08736338
H	-1.32969555	16.88069572	2.84074421
C	0.34796931	15.61851467	3.43331392
H	1.24046857	15.68523157	4.07080849
H	0.66520449	15.37840211	2.40785480
H	-0.27268430	14.78792381	3.80501582
C	1.13189910	18.52477805	7.66037711
C	1.19002909	17.54924819	8.66917596
C	2.27780561	17.44768145	9.53640179
H	2.29901847	16.68787867	10.31862176
C	3.32751412	18.37020794	9.39845726
H	4.17769098	18.34332250	10.08059748
C	3.27809876	19.35584370	8.40480813
H	4.06599659	20.10605994	8.34966042
C	2.19103983	19.42625597	7.50254438
C	3.92621206	21.18316787	5.83375426
C	4.73532032	20.05528789	5.61476928
H	4.40086149	19.06761642	5.93196298
C	5.98559189	20.21054947	4.99472612
H	6.61778244	19.33673683	4.82913123
C	6.41732724	21.48311330	4.59112502
H	7.39053821	21.60109094	4.11210904
C	5.60085671	22.60498736	4.81000651
H	5.93869160	23.59742811	4.50950412
C	4.35332156	22.45948237	5.43211456
H	3.72870756	23.32718987	5.63638208
C	1.27434986	20.86034865	4.82956477
C	0.32560267	21.84322627	4.51388123
H	0.02905756	22.56109464	5.27864226
C	-0.22383937	21.89327637	3.22490956
H	-0.97091852	22.65059116	2.98586328
C	0.19392073	20.97612557	2.24997567
H	-0.22438864	21.02116090	1.24349056
C	1.16460265	20.01004349	2.56315947
H	1.50269242	19.30654444	1.80090692
C	1.70385045	19.94474043	3.85490949
H	2.45924527	19.19958720	4.09994906
Pd	1.30592700	22.42607994	8.12900717
Cl	3.54114409	23.30447829	8.48135910
Cl	0.51438352	23.78480381	9.99552640



Pd(II) complex of SDP 23

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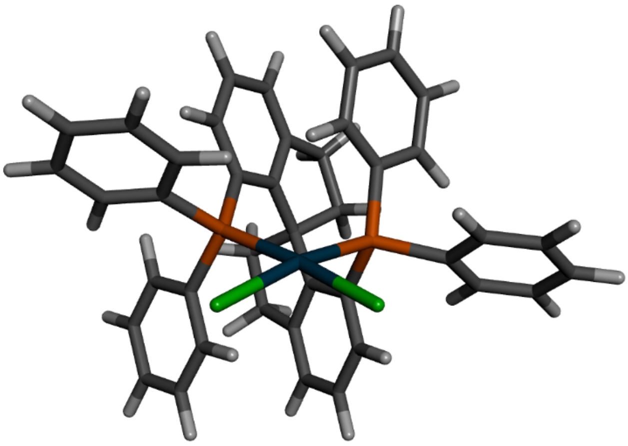
P	-1.03083899	21.55173105	7.79536988
P	2.06039684	20.97466813	6.28960293
C	-0.98767733	17.27059421	7.80515386
C	0.48969899	17.27541403	5.72945301
C	-1.17251147	20.64137704	9.42161851
C	-0.19336920	20.85507908	10.40490781
H	0.61803050	21.55401082	10.21023899
C	-0.28099594	20.16741362	11.62413992
H	0.48626648	20.32328689	12.38278033
C	-1.34406614	19.28218619	11.86419547
H	-1.40668141	18.74883844	12.81411744
C	-2.33370203	19.08793244	10.88660721
H	-3.16603158	18.40732435	11.07224498
C	-2.24948386	19.76984386	9.66351473
H	-3.00405613	19.60940129	8.89232618
C	-2.37400534	22.87238890	7.79650815
C	-3.56310989	22.72329959	8.52344495
H	-3.71042163	21.85588468	9.16493512
C	-4.55644256	23.71238959	8.43701482
H	-5.47684825	23.60433495	9.01278008
C	-4.36292258	24.83628667	7.61966909
H	-5.13549755	25.60405963	7.55576632
C	-3.16798370	24.98138634	6.89472715
H	-3.00368192	25.86401401	6.27527072
C	-2.16904360	24.00423565	6.98807280
H	-1.21825627	24.12638373	6.46826680
C	-1.62995039	20.35434238	6.43789451
C	-2.64632130	20.85252935	5.59049559
H	-3.12033800	21.80180167	5.82533229
C	-3.04515981	20.17503217	4.43248802
H	-3.83436917	20.59829226	3.80963759
C	-2.40782050	18.98468165	4.06529556
H	-2.67452727	18.46637950	3.14288064
C	-1.41241163	18.47079658	4.89864663
C	-1.03002399	19.11722531	6.09778147
C	-0.10218013	18.16784479	6.86441945
C	-0.05474690	16.79733495	8.94048947
H	0.37345269	15.80353583	8.72388060
H	-0.57529273	16.72957884	9.90688781
C	-0.63511182	17.19009738	4.67484001
H	-1.27933528	16.31149857	4.84780952
H	-0.24920012	17.11921210	3.64696471
C	1.00587261	18.64190236	7.78981086
C	1.03784974	17.84420493	8.95626251
C	1.99605847	18.04206580	9.95188413
H	1.98724353	17.42729632	10.85311158
C	2.95104882	19.05776303	9.78535274
H	3.69259476	19.25349626	10.56049546
C	2.94764391	19.84151370	8.62623437
H	3.66787028	20.65294431	8.51999286
C	1.99414993	19.62085026	7.60270120
C	3.86625655	20.99920877	5.76514979
C	4.66533426	19.85186794	5.90938651
H	4.28271740	18.98077970	6.44009574
C	5.96281023	19.83578595	5.37245063
H	6.58357362	18.94597223	5.48890700
C	6.45521834	20.95915690	4.69154949
H	7.46505963	20.94742688	4.27859857
C	5.64944659	22.10042277	4.54584606
H	6.03219412	22.97969317	4.02645439
C	4.35337044	22.12513843	5.07908614
H	3.73494920	23.01604166	4.99246844
C	1.26700022	20.62682274	4.62312530
C	0.22470765	21.47042040	4.21311281
H	-0.15955015	22.21140280	4.91352790
C	-0.31141761	21.34152882	2.92477727
H	-1.13177921	21.98861599	2.61432776
C	0.20582017	20.38124490	2.04238014
H	-0.21157895	20.28179575	1.03935322
C	1.27360231	19.55993966	2.44232346
H	1.69727208	18.83230403	1.74860401
C	1.81829993	19.69351626	3.72706708
H	2.68292733	19.09902480	4.02175109
Pd	1.08559651	22.67095635	7.60769297
Cl	3.20684563	23.84515231	7.63532991
Cl	0.23715372	24.18187929	9.32889567
H	1.36983928	17.77012854	5.30232504
H	0.80322027	16.29761799	6.12167921
H	-1.44210045	16.44644670	7.23832794
H	-1.79714027	17.87613280	8.22169960



Energy values and geometric parameters are described in the following tables.

	$G_{el}{}^{a}$ (kcal/mol)	$H_{vib}{}^{b}$ (kcal/mol)	$S_{vib}{}^{b}$ (kcal/mol)	$G_{corr}{}^{c}$ (kcal/mol)
Diol (*S,S,S*)-7	-650274.0	230.2	148.1	-650088.0
Diol (*R,S,S*)-7	-650273.2	230.1	147.5	-650087.0
Diphosphine (*S,S,S*)-SPIRAP	-1565059.2	450.3	245.8	-1564682.1
Diphosphine (*S,R,R*)-SPIRAP	-1565058.5	449.8	238.7	-1564679.8
Pd(II) complex ((*S,S,S*)-11)	-1243189.9			
Pd(II) complex ((*S,R,R*)-11)	-1243184.6			
Pd(II) complex of SDP (23)	-1099473.7			

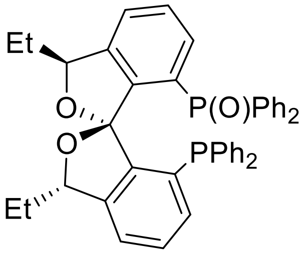
Table SI-1. Calculated values for optimized geometries. **a:** Gas-phase electronic energy (ωB97X-D/SMD/6-31G**). **b:** Vibrational, rotational, and translational entropic and enthalpic contributions (B97-D/6-31G**) at 298K. **c:** Corrected free energy values at 298K. Pd(II) complexes vibrational, rotational, and translational contributions to the total free energy were not calculated.

	α (°)^{a}	β (°)^{a}	$\tau_4{}^{b}$	$\tau_4{}'^{c}$	**Bite angle (°)^{d}**
(*S,S,S*)-11	173.8	169.9	0.11	0.13	94.4
(*S,R,R*)-11	174.8	172.8	0.09	0.09	95.3
23	174.7	169.2	0.11	0.13	94.2

Table SI-2. Geometric parameters of Pd(II) complexes. **a:** Largest angles at Pd. **b:** geometry index parameter, calculated from $\tau_4 = -0.00709\alpha - 0.00709\beta + 2.55$;[17] **c:** geometry index parameter, calculated from $\tau_4' = -0.00399\alpha - 0.01019\beta + 2.55$;[18] **d:** P-Pd-P angle.

X-Ray crystallography studies

(*S*,*S*,*S*)-SPIRAP(O) – CCDC Number: 1812181



(*S*,*S*,*S*)-SPIRAP(O)

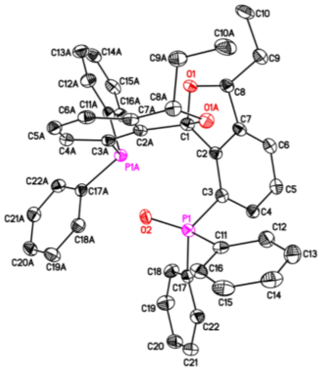
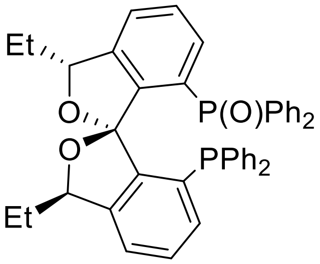


Table SI-3. Crystal data and structure refinement for aa1711.	
Identification code	aa1711
Empirical formula	C43 H38 O3 P2
Formula weight	664.67
Temperature	85(2) K
Wavelength	1.54184 A
Crystal system, space group	Hexagonal, P6(4)
Unit cell dimensions	a = 15.22339(13) A alpha = 90 deg.
	b = 15.22339(13) A beta = 90 deg.
	c = 12.75692(12) A gamma = 120 deg.
Volume	2560.35(5) A^3
Z, Calculated density	3, 1.295 Mg/m^3
Absorption coefficient	1.472 mm^-1
F(000)	1053
Crystal size	0.190 x 0.150 x 0.100 mm
Theta range for data collection	3.352 to 69.236 deg.
Limiting indices	-18<=h<=17, -18<=k<=18, -15<=l<=15
Reflections collected / unique	39371 / 3173 [R(int) = 0.0574]
Completeness to theta = 67.684	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.82517
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3173 / 1 / 224
Goodness-of-fit on F^2	1.109
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0865
R indices (all data)	R1 = 0.0343, wR2 = 0.0866
Absolute structure parameter	-0.130(18)
Extinction coefficient	0.0089(6)
Largest diff. peak and hole	0.191 and -0.227 e.A^-3

(*S*,*R*,*R*)-SPIRAP(O) – CCDC: 1812182



(*S*,*R*,*R*)-SPIRAP(O)

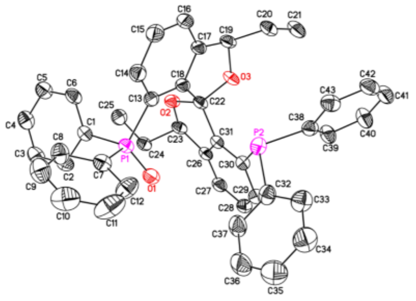


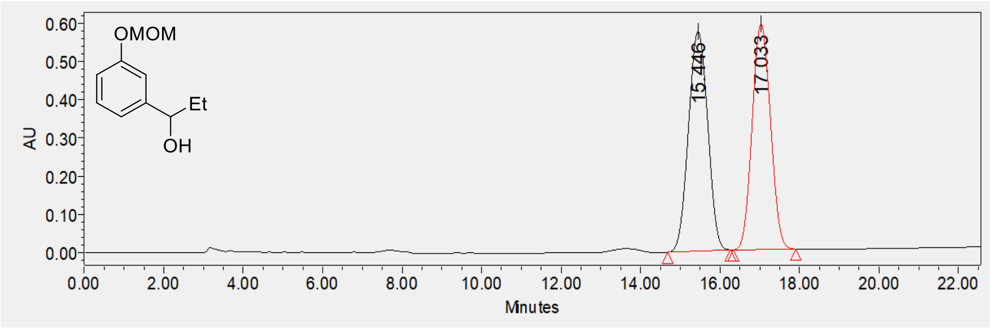
Table SI-4. Crystal data and structure refinement for aa2393.

Identification code	aa2393
Empirical formula	C43 H38 O3 P2
Formula weight	664.67
Temperature	225(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimension	a = 10.01060(10) A alpha = 90 deg.
	b = 31.3874(3) A beta = 90.2490(10) deg.
	c = 11.24650(10) A gamma = 90 deg.
Volume	3533.69(6) A^3
Z, Calculated density	4, 1.249 Mg/m^3
Absorption coefficient	1.422 mm^-1
F(000)	1400
Crystal size	0.12 x 0.04 x 0.04 mm
Theta range for data collection	2.816 to 69.327 deg.
Limiting indices	-12<=h<=11, -37<=k<=38, -13<=l<=13
Reflections collected / unique	54487 / 12761 [R(int) = 0.0529]
Completeness to theta = 67.679	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.59423
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12761 / 1 / 870
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0481, wR2 = 0.1318
R indices (all data)	R1 = 0.0509, wR2 = 0.1375
Absolute structure parameter	0.048(15)
Extinction coefficient	n/a
Largest diff. peak and hole	0.776 and -0.350 e.A^-3

HPLC, SFC, and GC traces

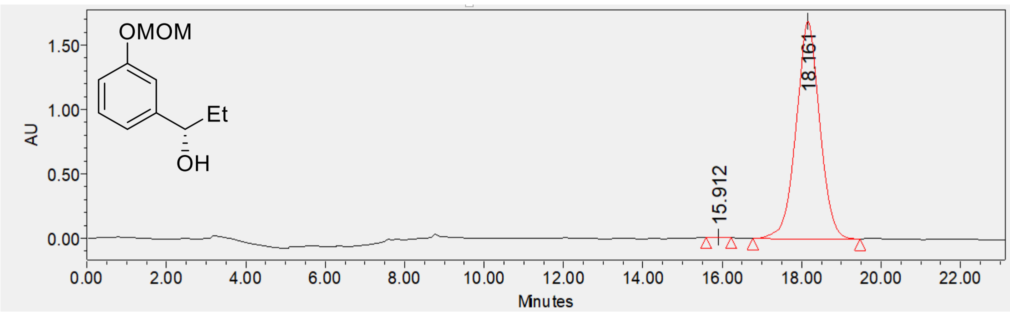
1-(3-(methoxymethoxy)phenyl)propan-1-ol (2a)

Racemic



Retention Time	% Area
15.446	50.56
17.033	49.44

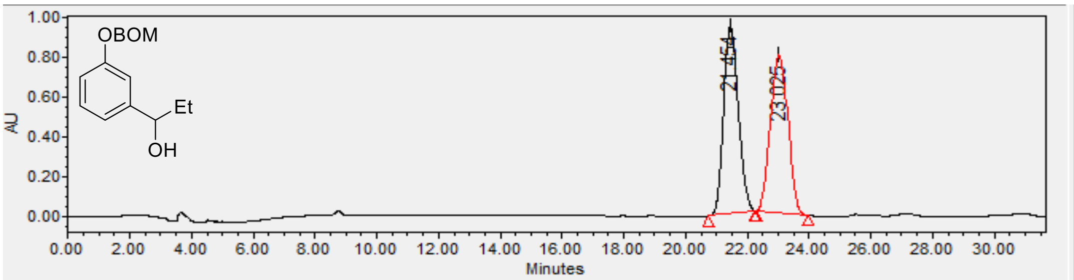
(*S*)-2a – Using diphenyl((*S*)-1-((*S*)-1-phenylethyl)aziridin-2-yl)methanol



Retention Time	% Area
15.912	0.09
18.161	99.91

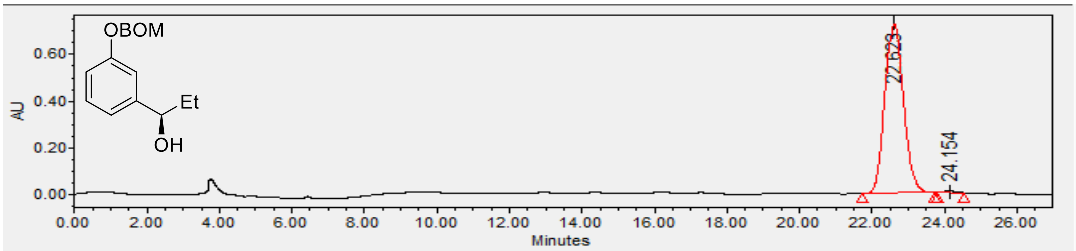
1-(3-((benzyloxy)methoxy)phenyl)propan-1-ol (2b)

Racemic



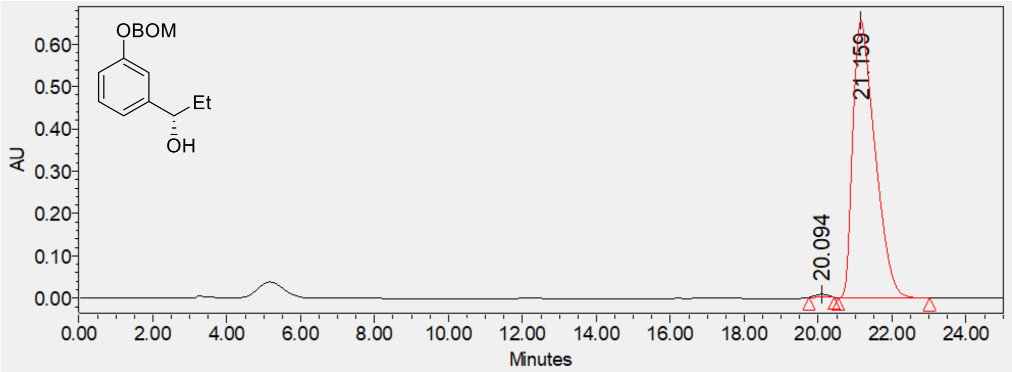
Retention Time (min)	% Area
21.454	49.87
23.025	50.13

(*R*)-2b – Using diphenyl((*R*)-1-((*S*)-1-phenylethyl)aziridin-2-yl)methanol



Retention Time (min)	% Area
22.623	99.43
24.154	0.57

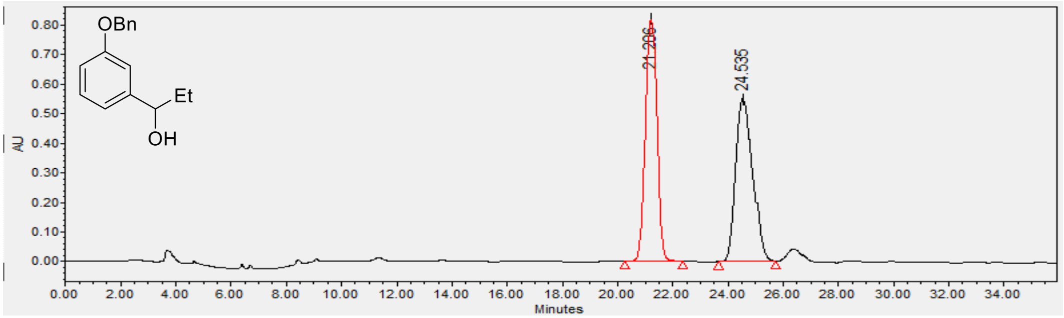
(*S*)-2b – Using diphenyl((*S*)-1-((*S*)-1-phenylethyl)aziridin-2-yl)methanol



Retention Time (min)	% Area
20.094	0.63
21.159	99.37

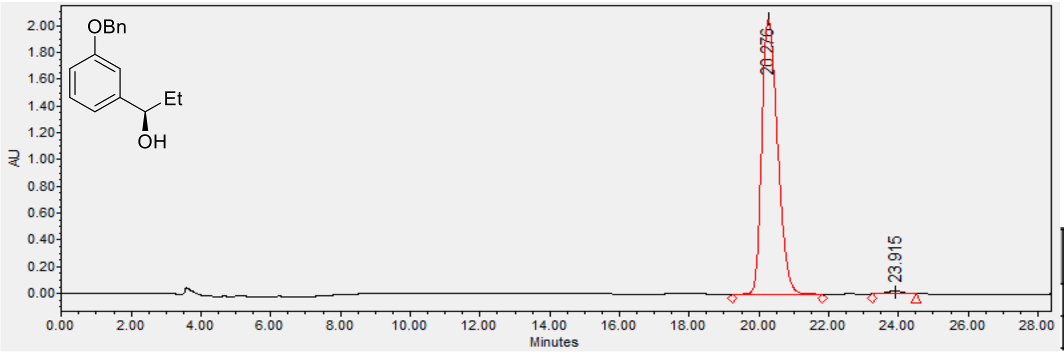
1-(3-(benzyloxy)phenyl)propan-1-ol (2c)

Racemic



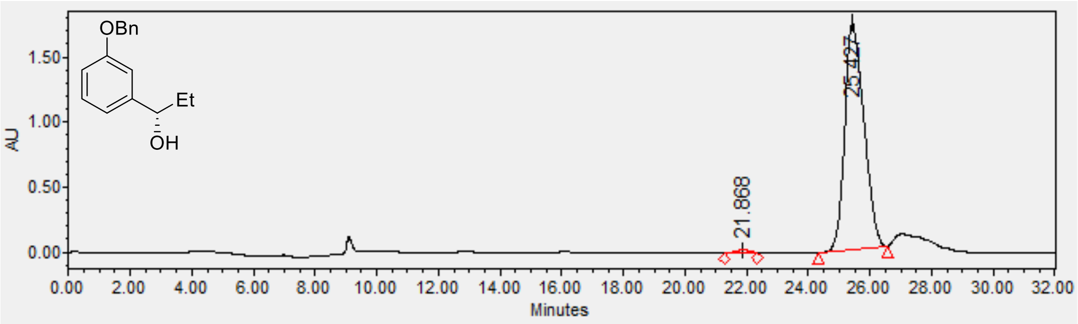
Retention Time (min)	% Area
21.206	50.43
24.535	49.57

(*R*)-2b – Using diphenyl((*R*)-1-((*S*)-1-phenylethyl)aziridin-2-yl)methanol



Retention Time (min)	% Area
20.276	98.91
23.915	1.09

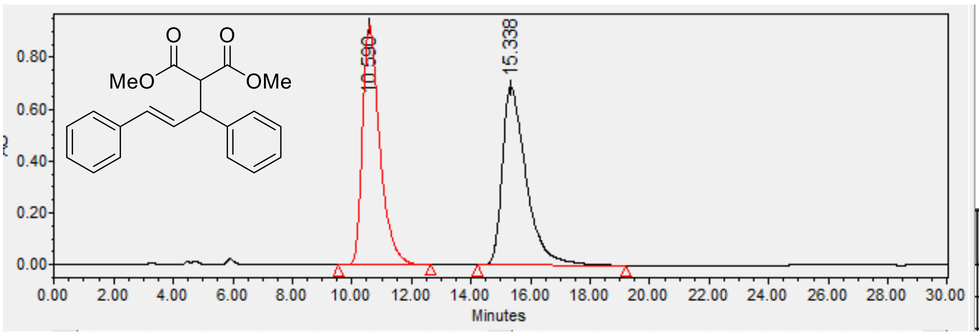
(*S*)-2b – Using diphenyl((*S*)-1-((*S*)-1-phenylethyl)aziridin-2-yl)methanol



Retention Time (min)	% Area
21.868	0.86
25.427	99.14

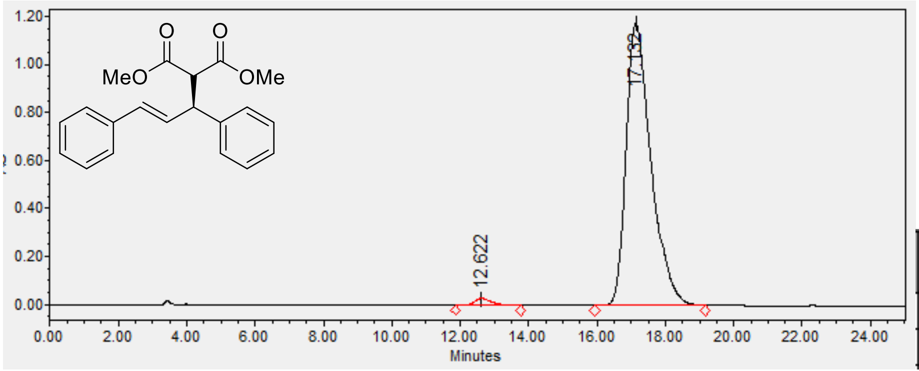
Dimethyl (*E*)-2-(1,3-diphenylallyl)malonate (17)

Racemic



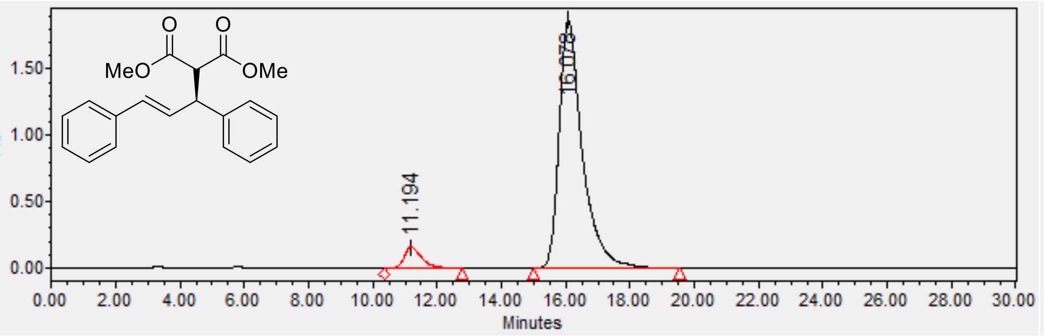
Retention Time (min)	% Area
10.590	49.39
15.338	50.61

Using (***S*,*S*,*S***)-**SPIRAP**



Retention Time (min)	% Area
12.622	1.71
17.132	98.29

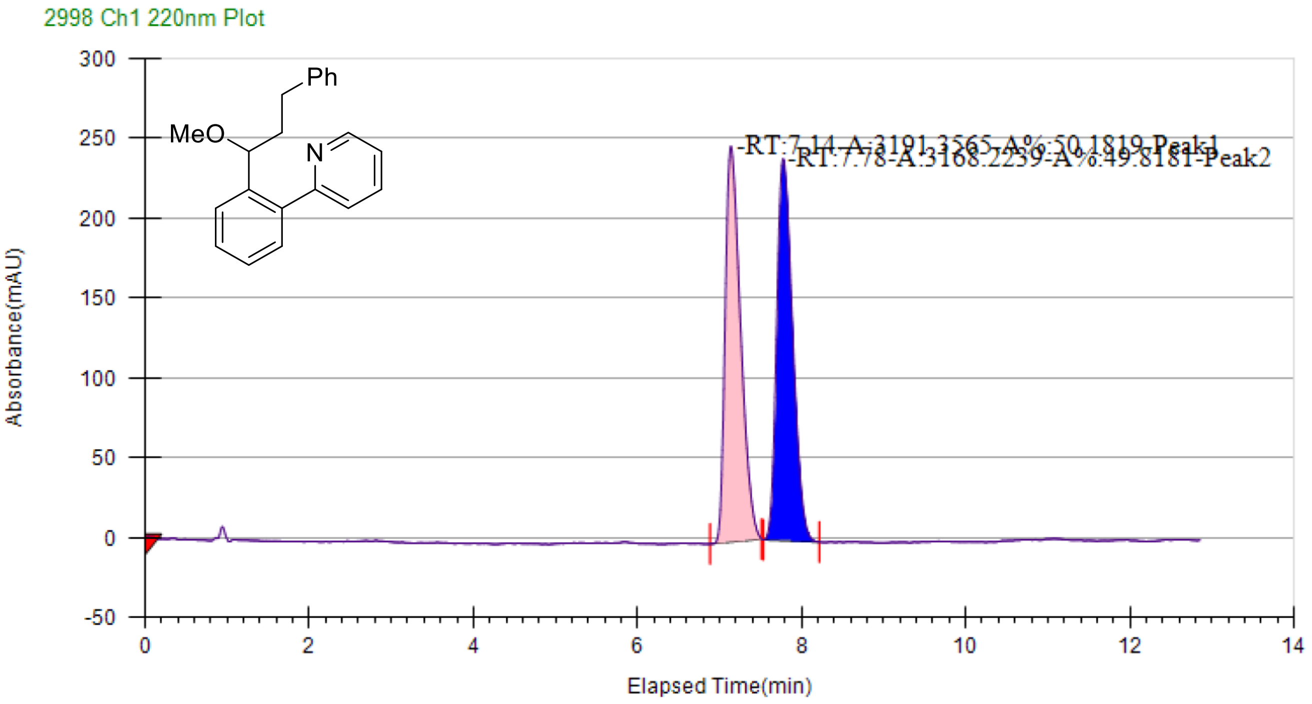
Using (***S*,*R*,*R***)-**SPIRAP**



Retention Time (min)	% Area
11.194	5.84
16.078	94.16

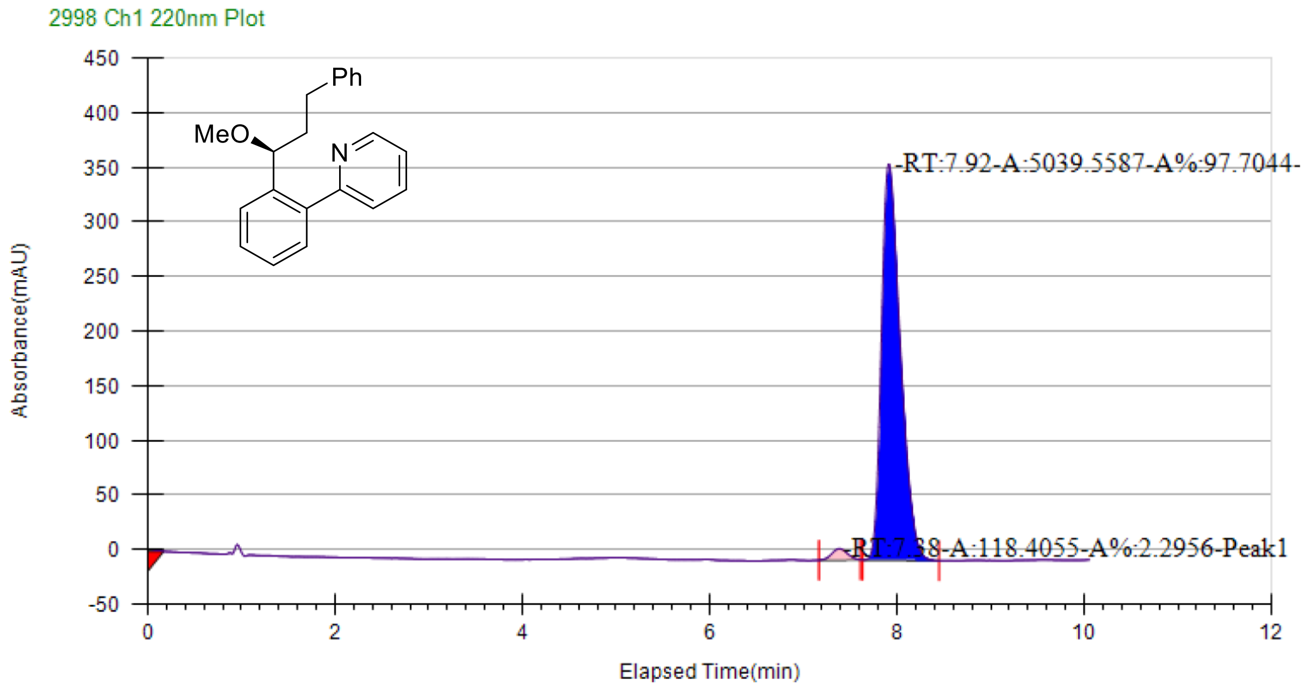
2-(2-(1-methoxy-3-phenylpropyl)phenyl)pyridine (14)

Racemic



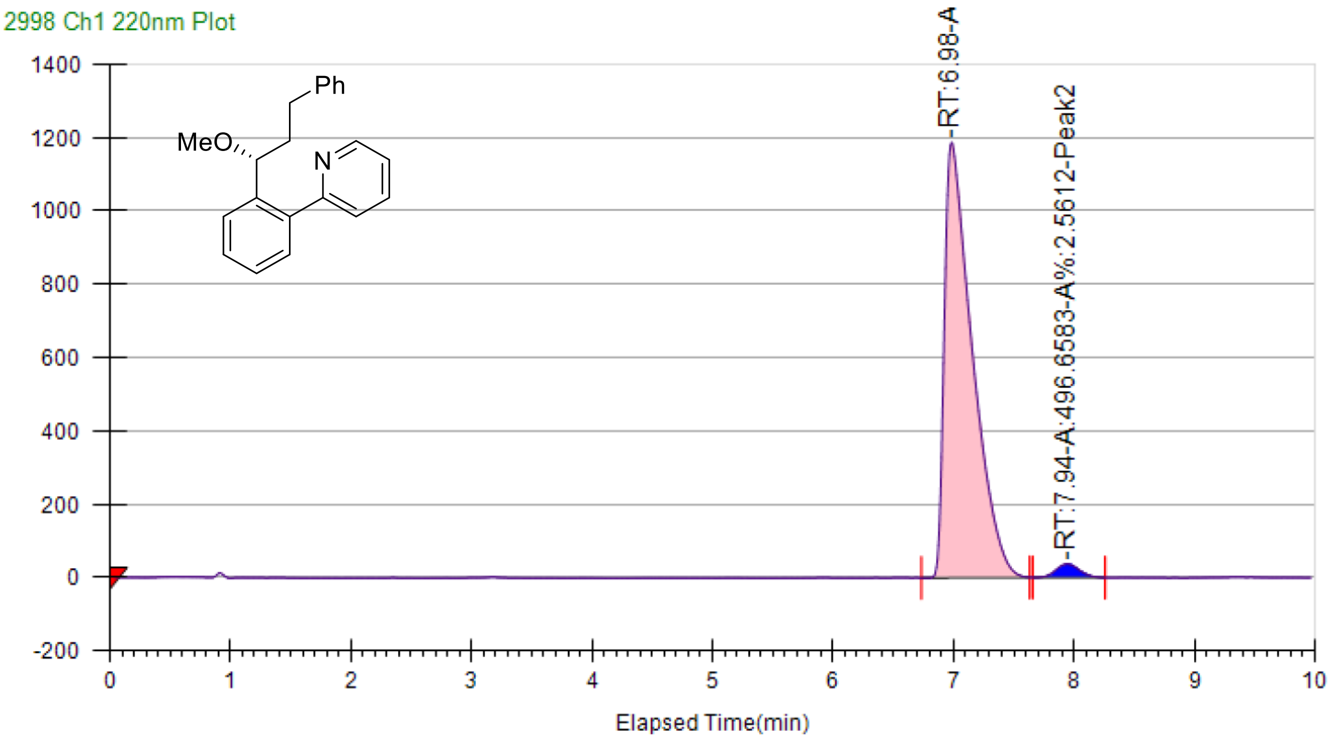
Peak No	% Area	Area	Ret. Time
1	50.1819	3191.3565	7.14 min
2	49.8181	3168.2239	7.78 min

Using **(*S*,*S*,*S*)-SPIRAP**



Peak No	% Area	Area	Ret. Time
1	2.2956	118.4055	7.38 min
2	97.7044	5039.5587	7.92 min

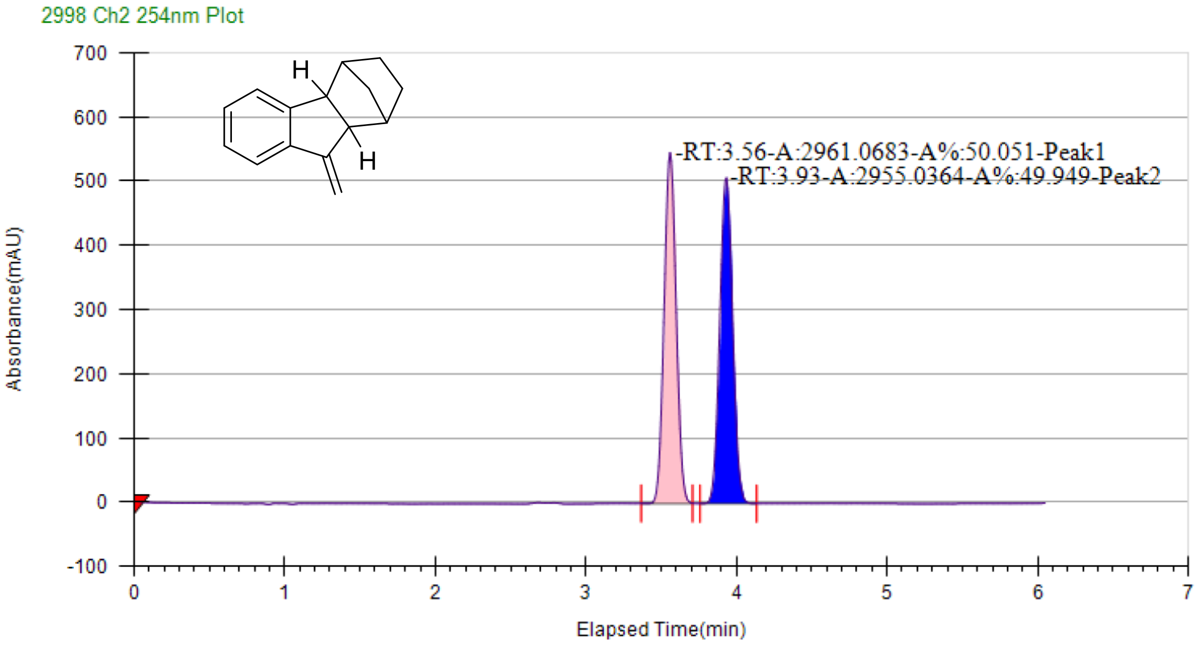
Using **(*R*)-SDP**



Peak No	% Area	Area	Ret. Time
1	97.4388	18894.892 9	6.98 min
2	2.5612	496.6583	7.94 min

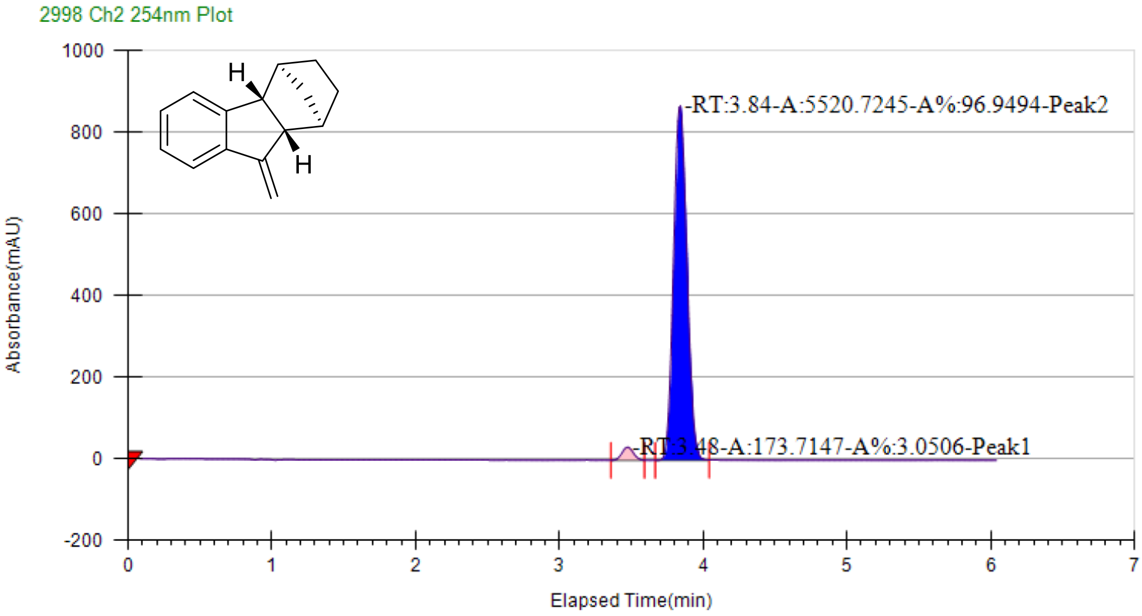
9-methylene-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (20)

Racemic



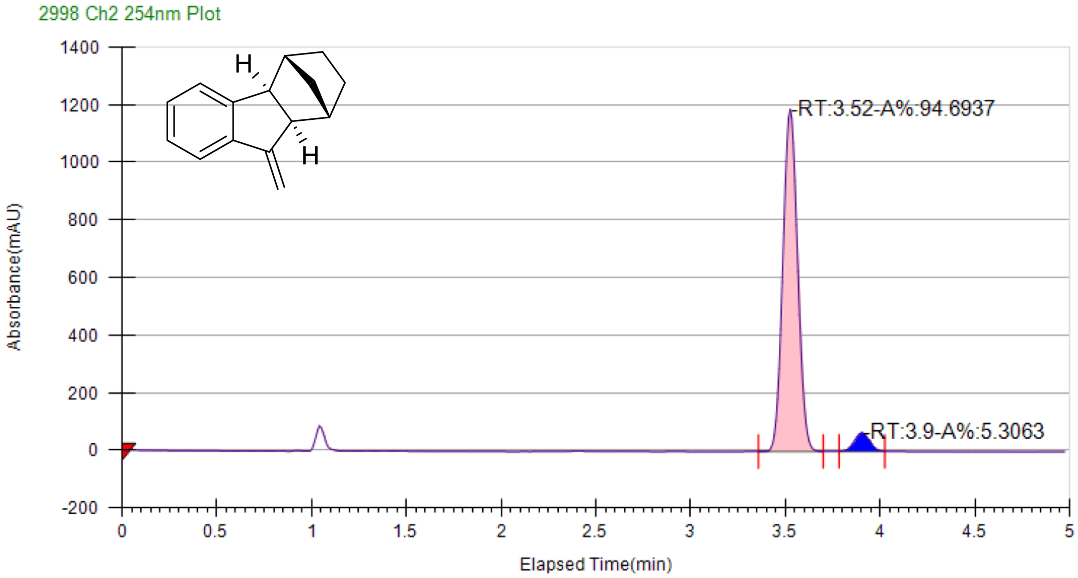
Peak No	% Area	Area	Ret. Time
1	50.051	2961.0683	3.56 min
2	49.949	2955.0364	3.93 min

Using **(*S*,*S*,*S*)-SPIRAP(O)**



Peak No	% Area	Area	Ret. Time
1	3.0506	173.7147	3.48 min
2	96.9494	5520.7245	3.84 min

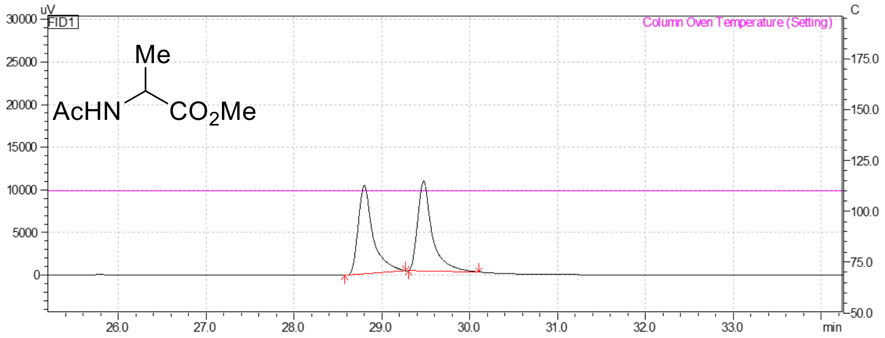
Using **(*R*,*S*,*S*)-SPIRAP(O)**



Peak No	% Area	Area	Ret. Time
1	94.6937	6277.2086	3.52 min
2	5.3063	351.7551	3.9 min

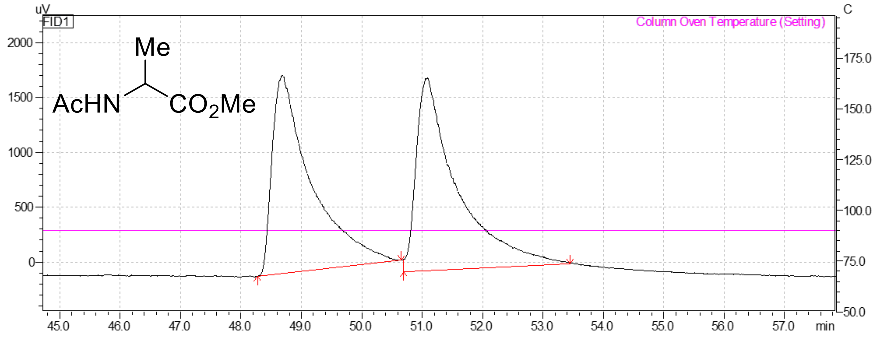
Methyl acetylalaninate (22)

Racemic (GC conditions 1)



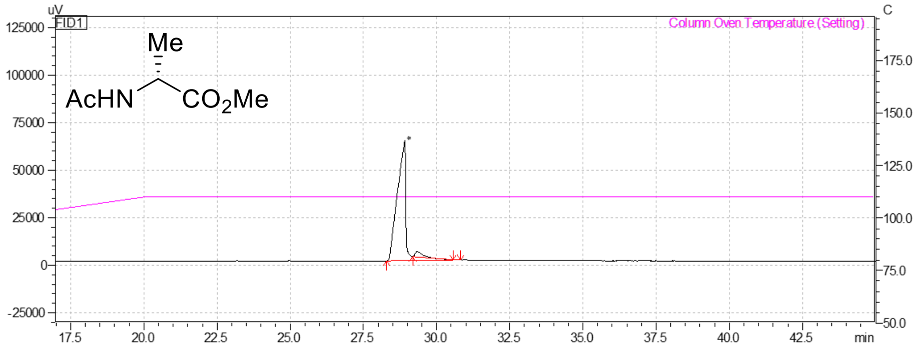
Retention Time	% Area
28.800	50.176
29.476	49.824

Racemic (GC conditions 2)



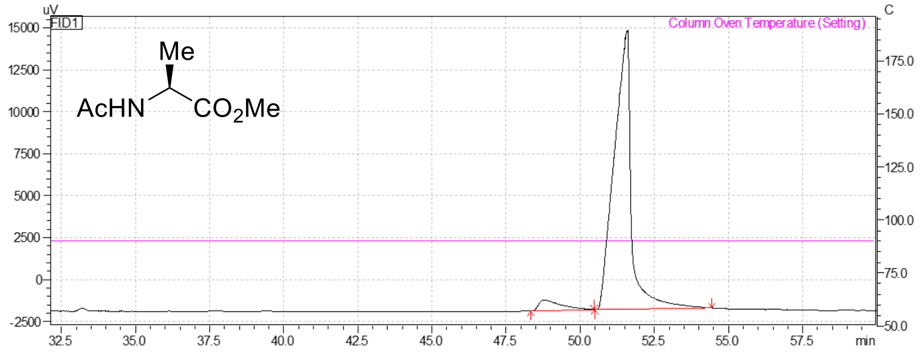
Retention Time	% Area
48.687	49.415
51.078	50.585

With ***(R,R,R)*-SPIRAPO** (GC conditions 1)



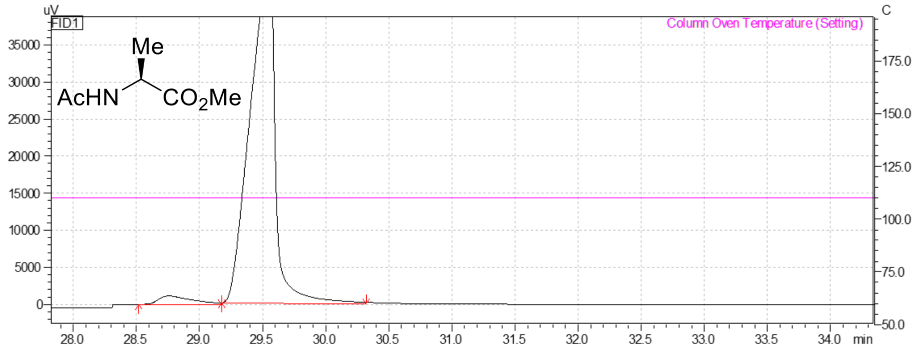
Retention Time	% Area
28.914	96.449
29.344	3.551

With ***(S,R,R)*-SPIRAPO** (GC conditions 2)



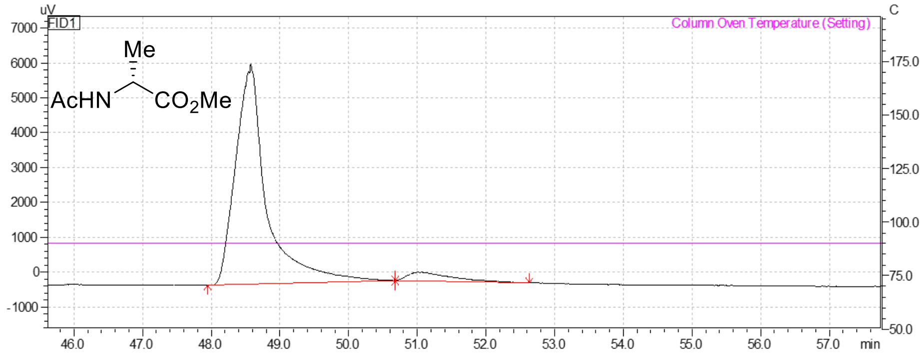
Retention Time	% Area
48.776	4.785
51.595	95.215

With ***(S)*-SDPO** (GC conditions 1)



Retention Time	% Area
28.753	3.256
29.553	96.744

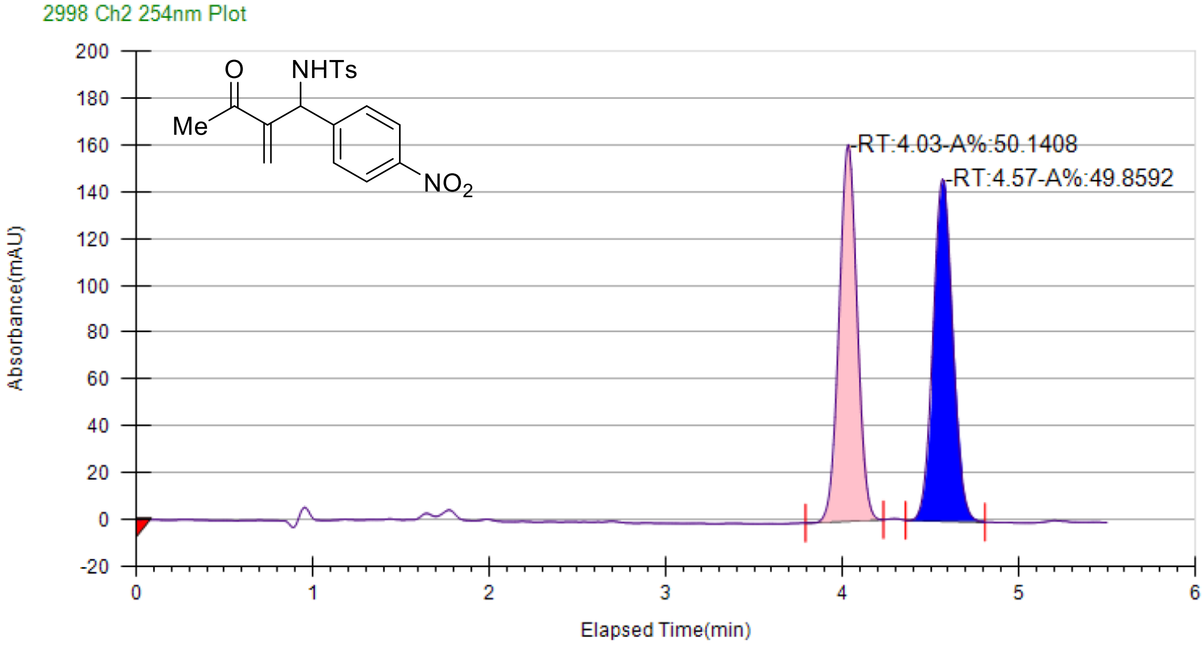
With **(*S*)-BINAPO** (GC conditions 2)



Retention Time	% Area
48.576	94.717
51.020	5.283

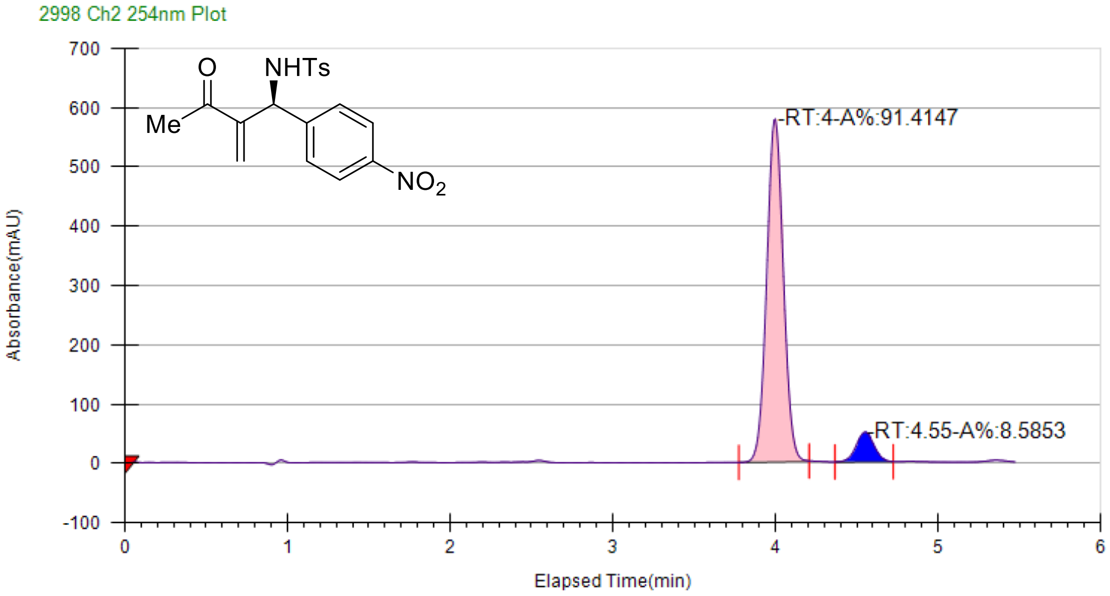
4-methyl-N-(2-methylene-1-(4-nitrophenyl)-3-oxobutyl)benzenesulfonamide (SI-2)

Racemic



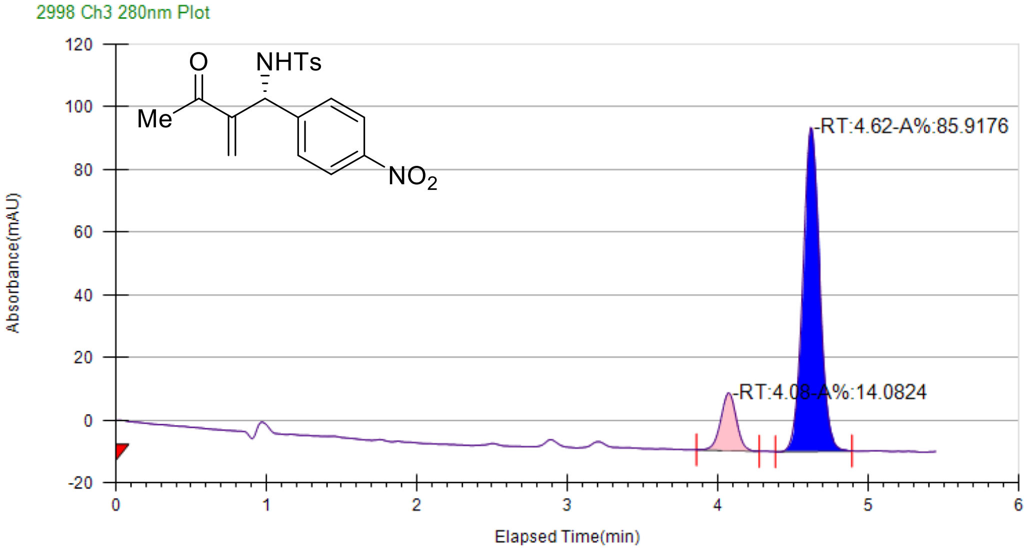
Peak No	% Area	Area	Ret. Time
1	50.1408	1123.648	4.03 min
2	49.8592	1117.336	4.57 min

Using (***S***,***S***,***S***)**-SPIROMP**



Peak No	% Area	Area	Ret. Time
1	91.4147	4028.0775	4 min
2	8.5853	378.2998	4.55 min

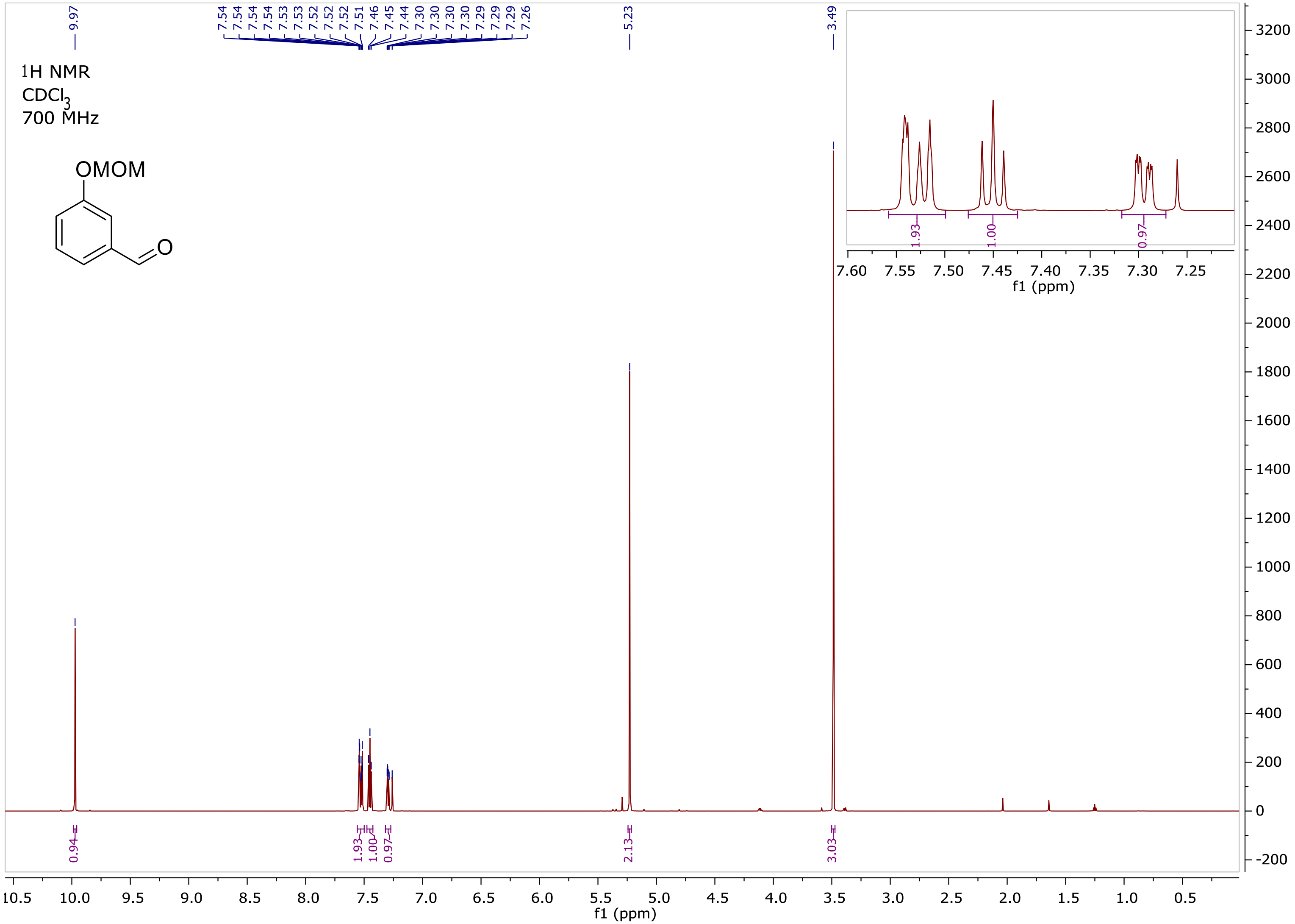
Using (***R*****,*****S*****,*****S***)**-SPIROMP**

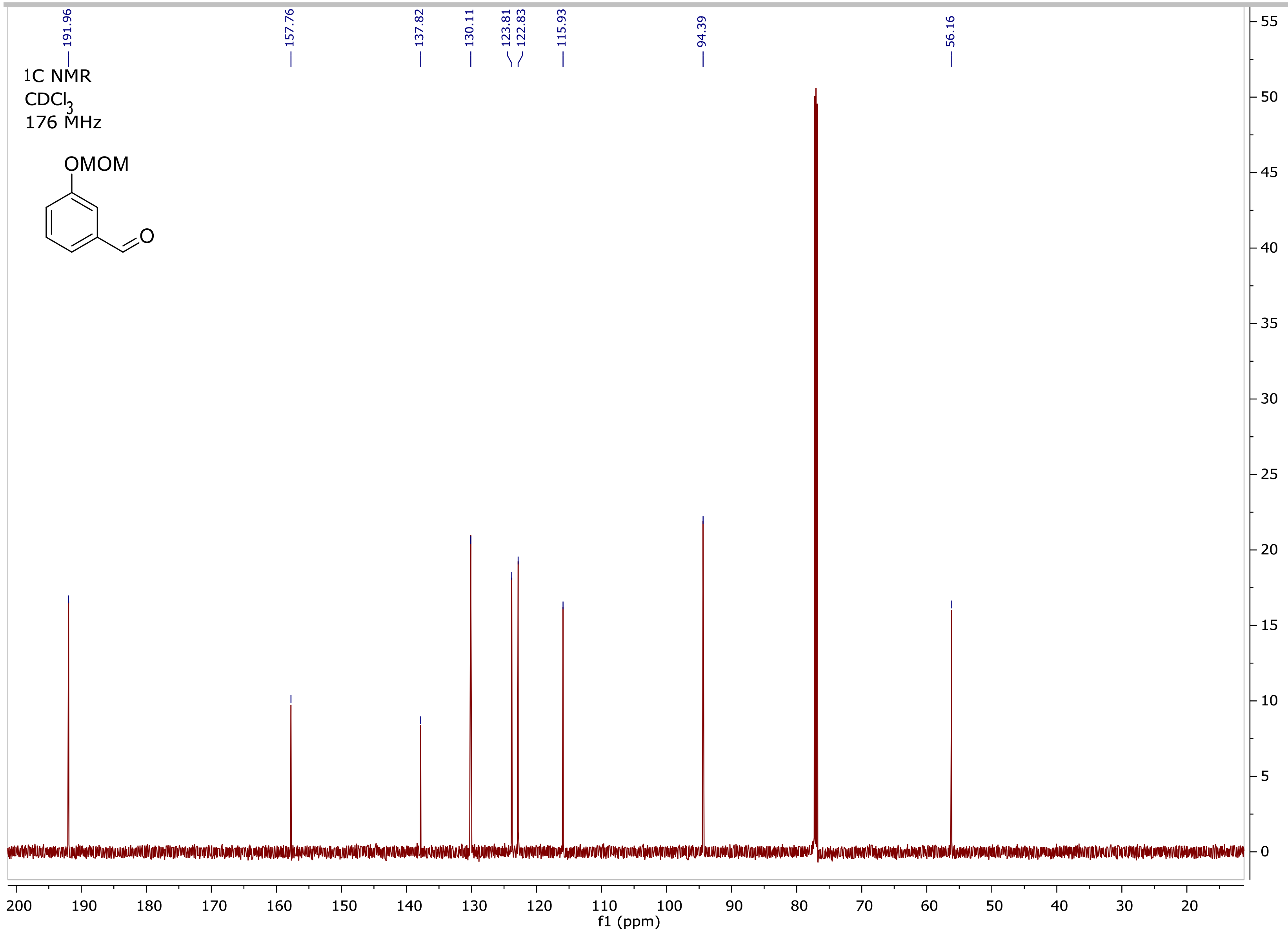


Peak No	% Area	Area	Ret. Time
1	14.0824	129.629	4.08 min
2	85.9176	790.8726	4.62 min

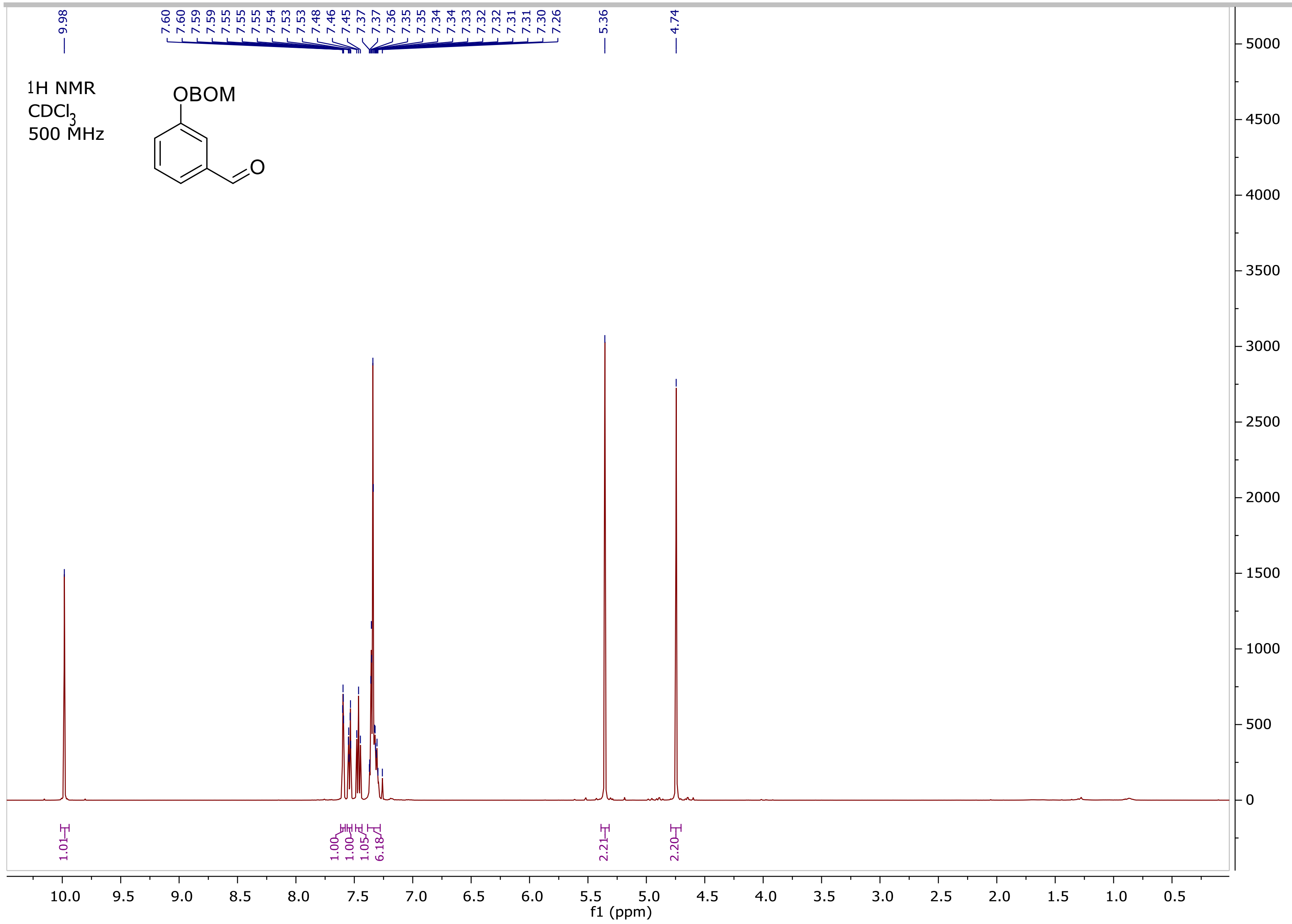
NMR spectra

3-(methoxymethoxy)benzaldehyde (1a)





3-((benzyloxy)methoxy)benzaldehyde (1b)


1H NMR
CDCl3
500 MHz
OBOM
O
9.98
7.60
7.60
7.59
7.59
7.55
7.55
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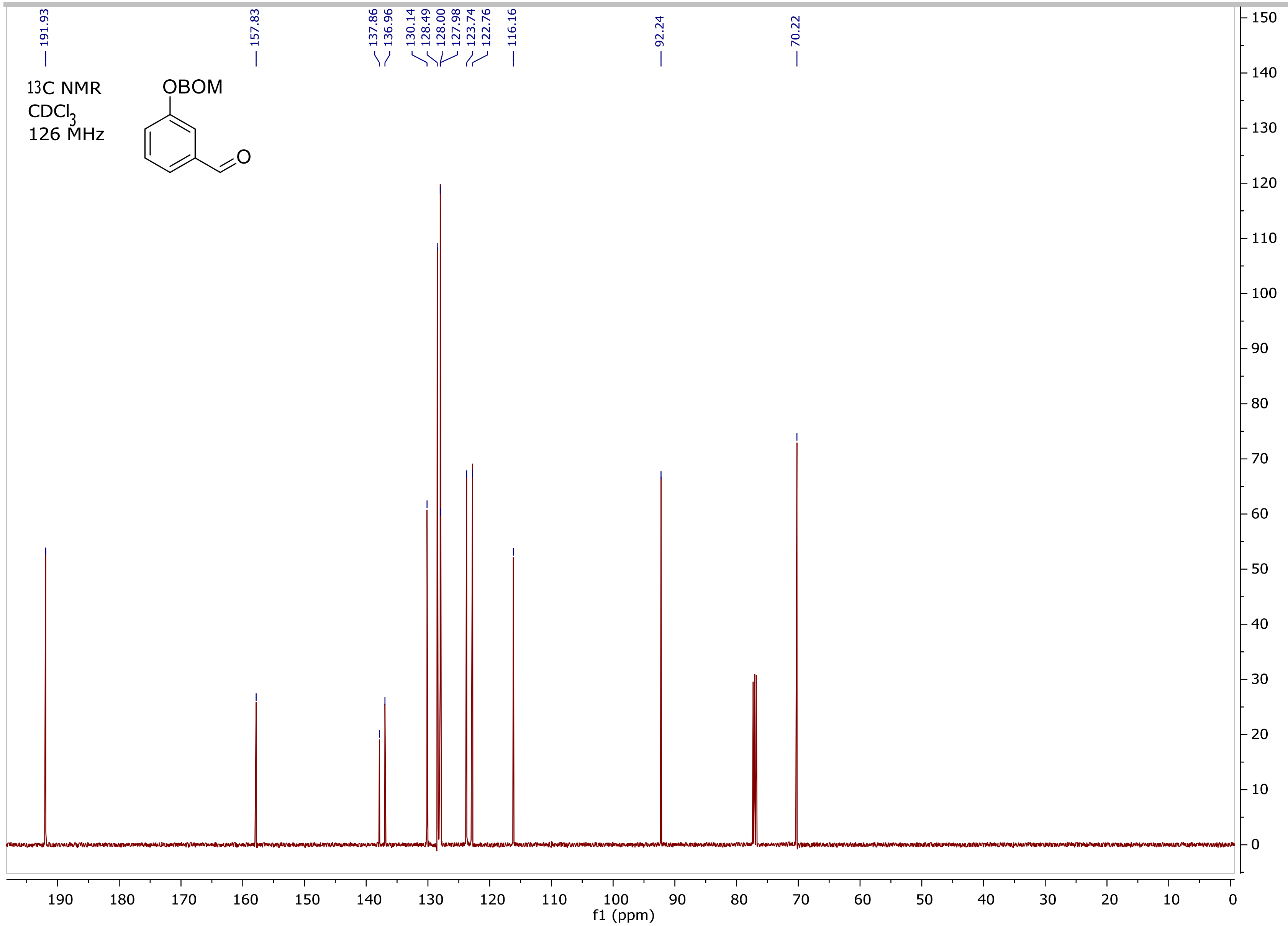
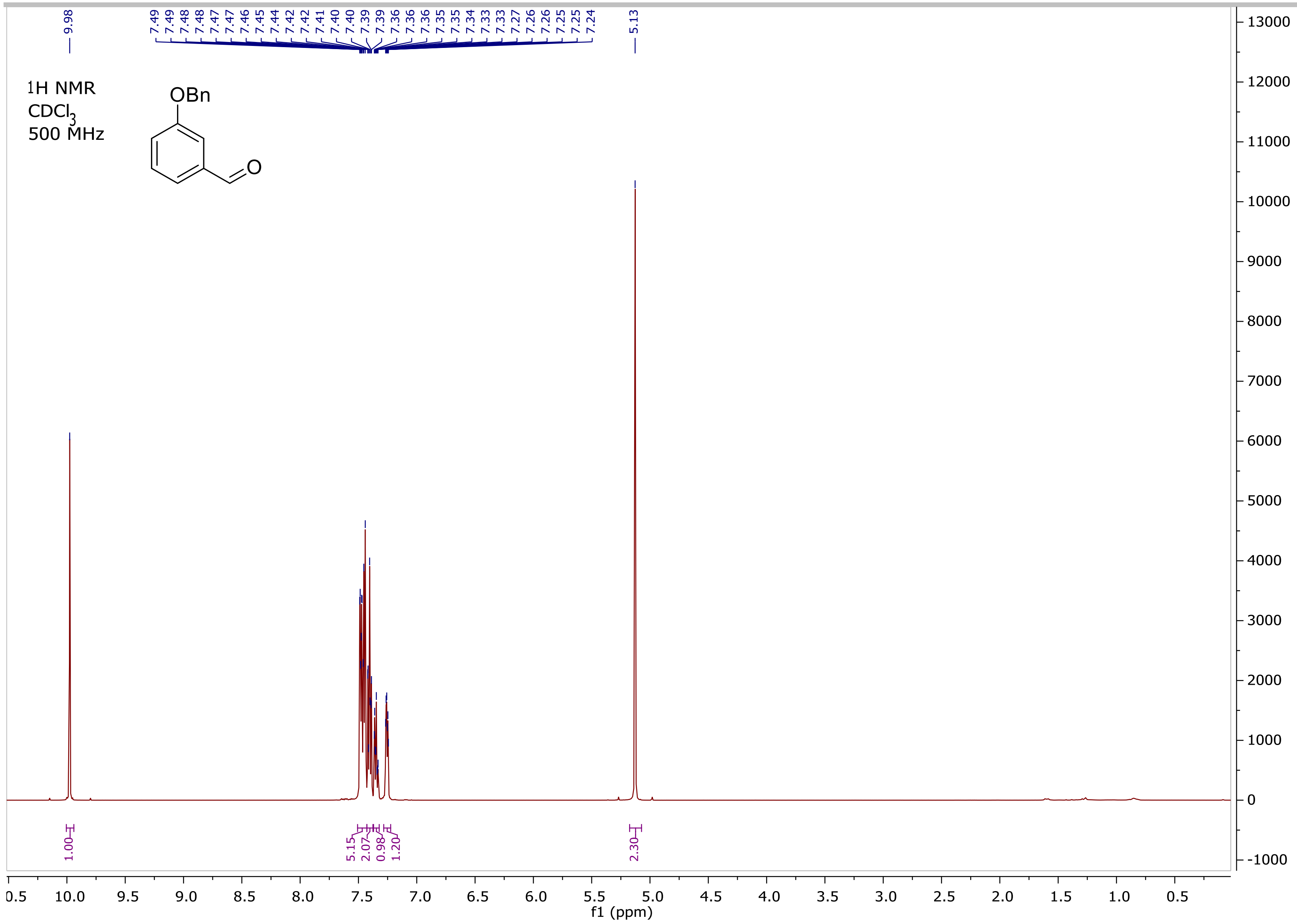
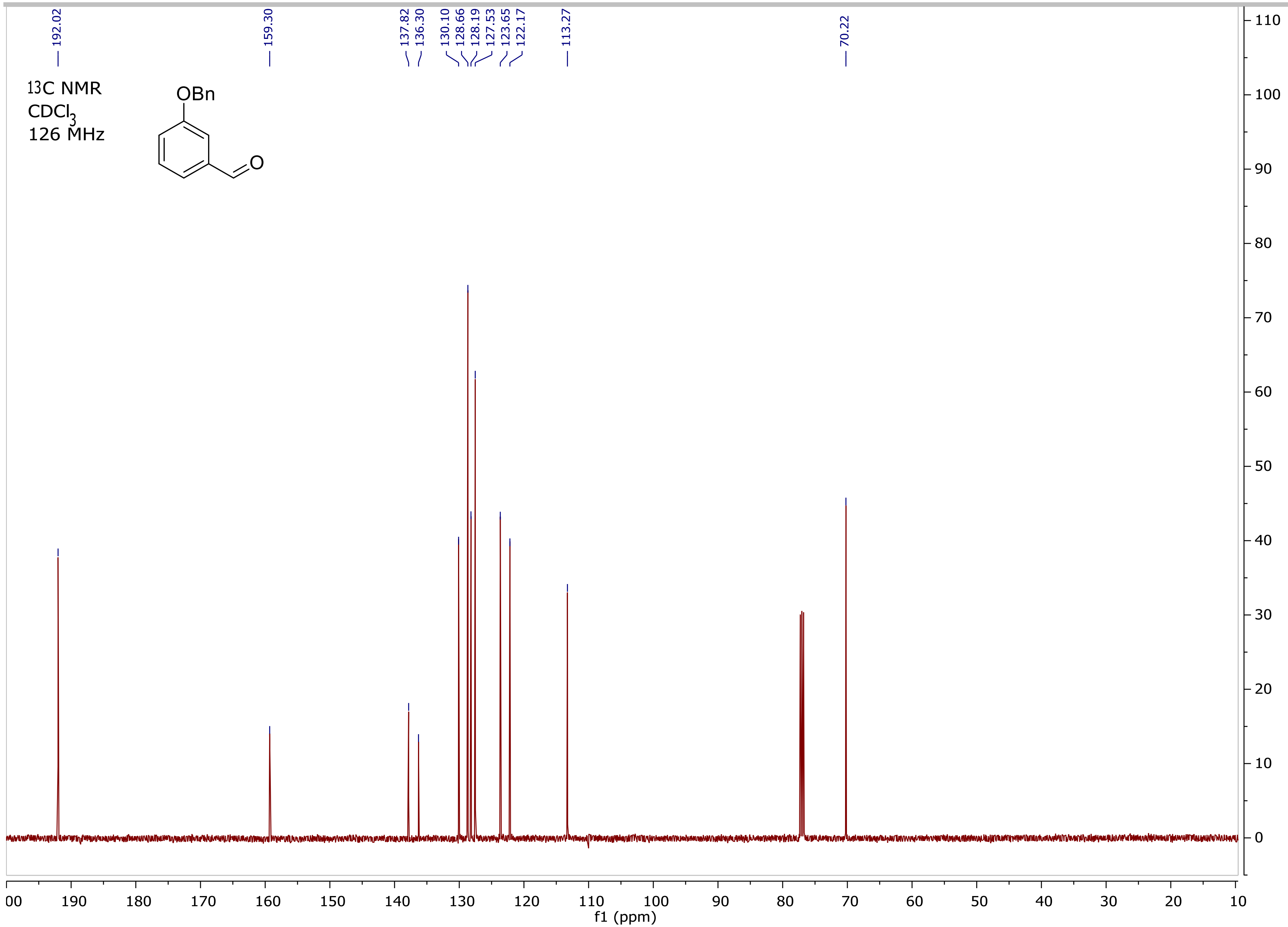
7.54
7.53
7.53
7.48
7.46
7.45
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.26
5.36
4.74
1.01
1.00
1.00
1.05
6.18
2.21
2.20
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

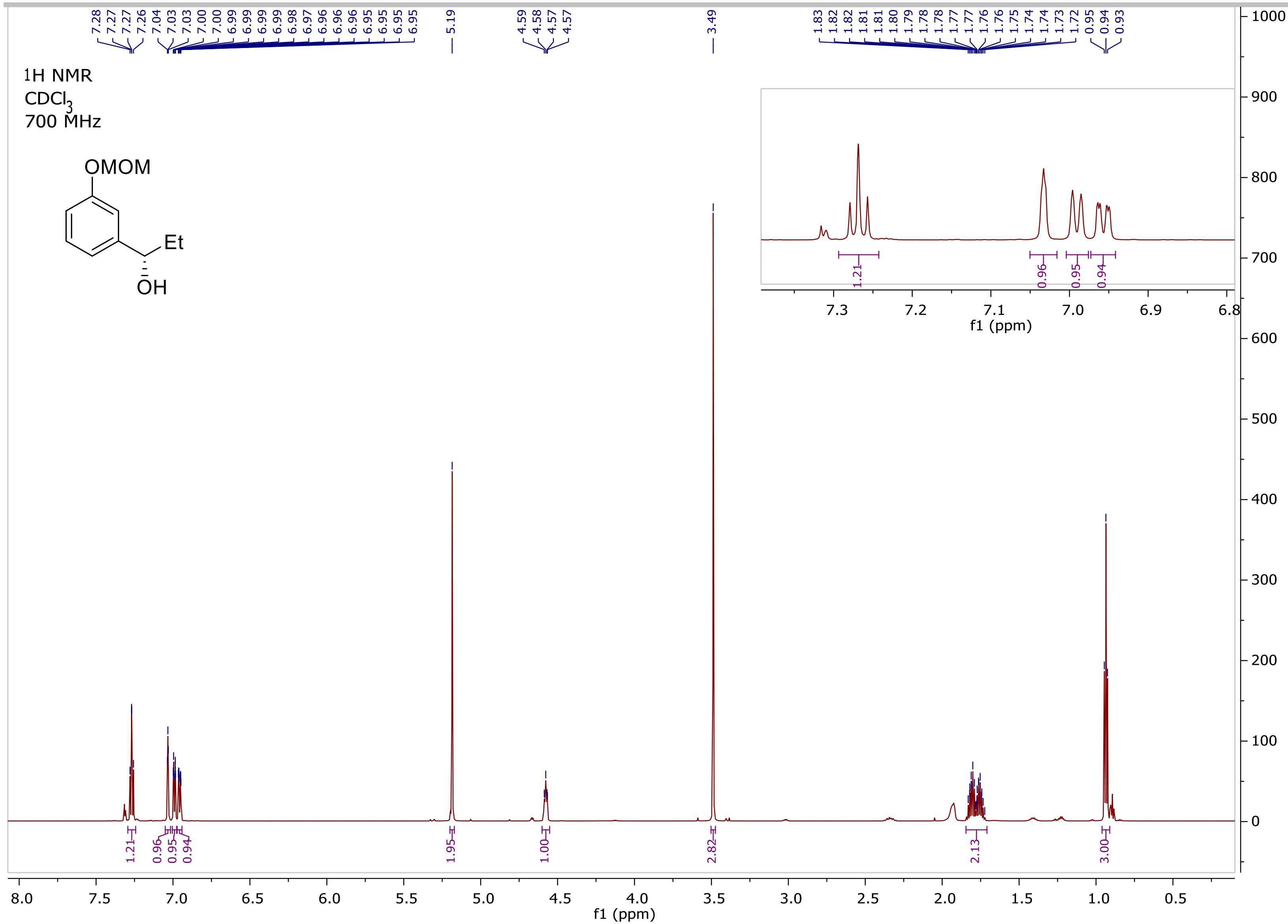


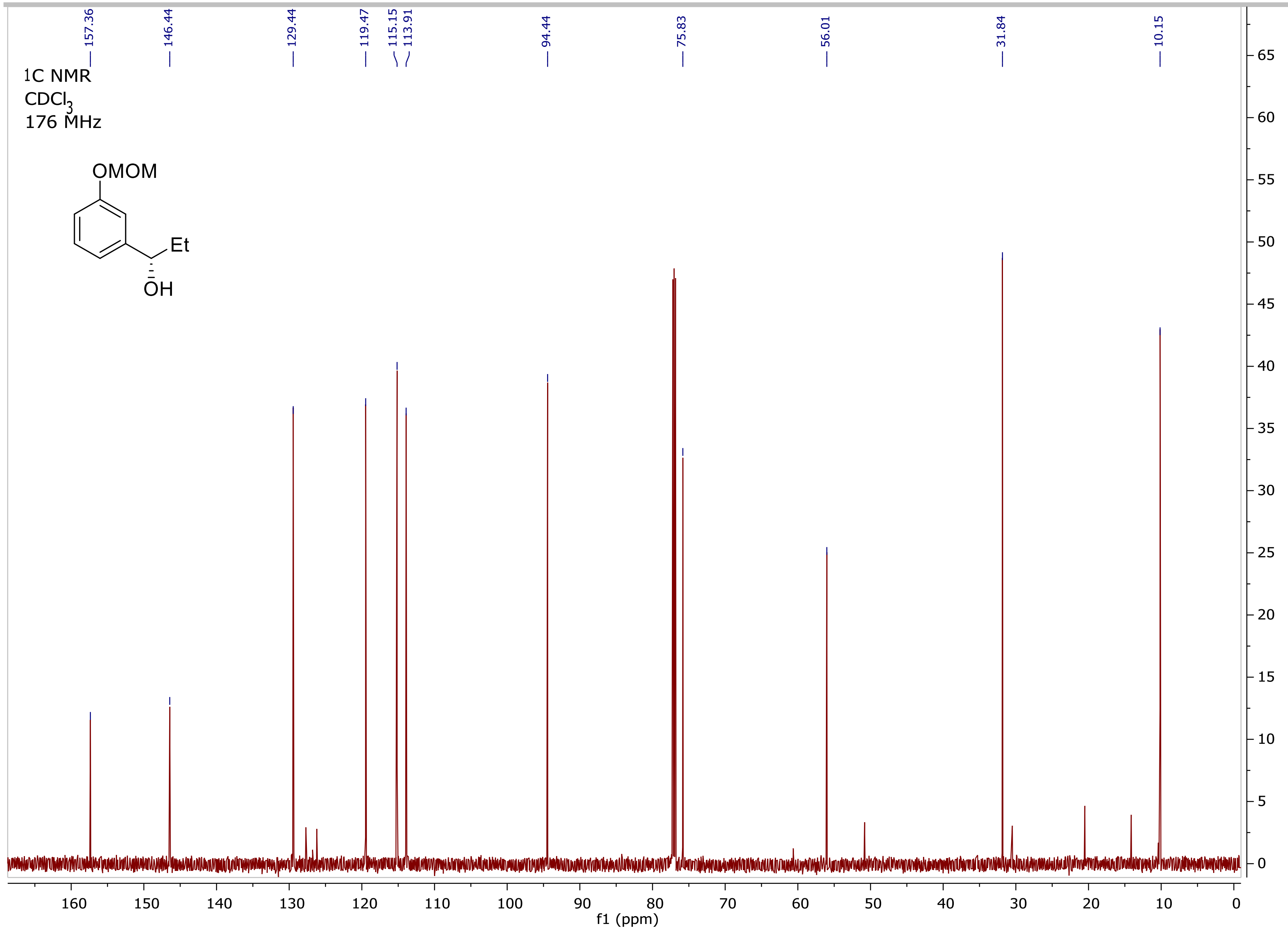
3-(benzyloxy)benzaldehyde (1c)


9.98
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.44
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.36
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.27
7.26
7.26
7.25
7.25
7.24
5.13
1H NMR
CDCl3
500 MHz
OBn
O
1.00
5.15
2.07
0.98
1.20
2.30
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
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

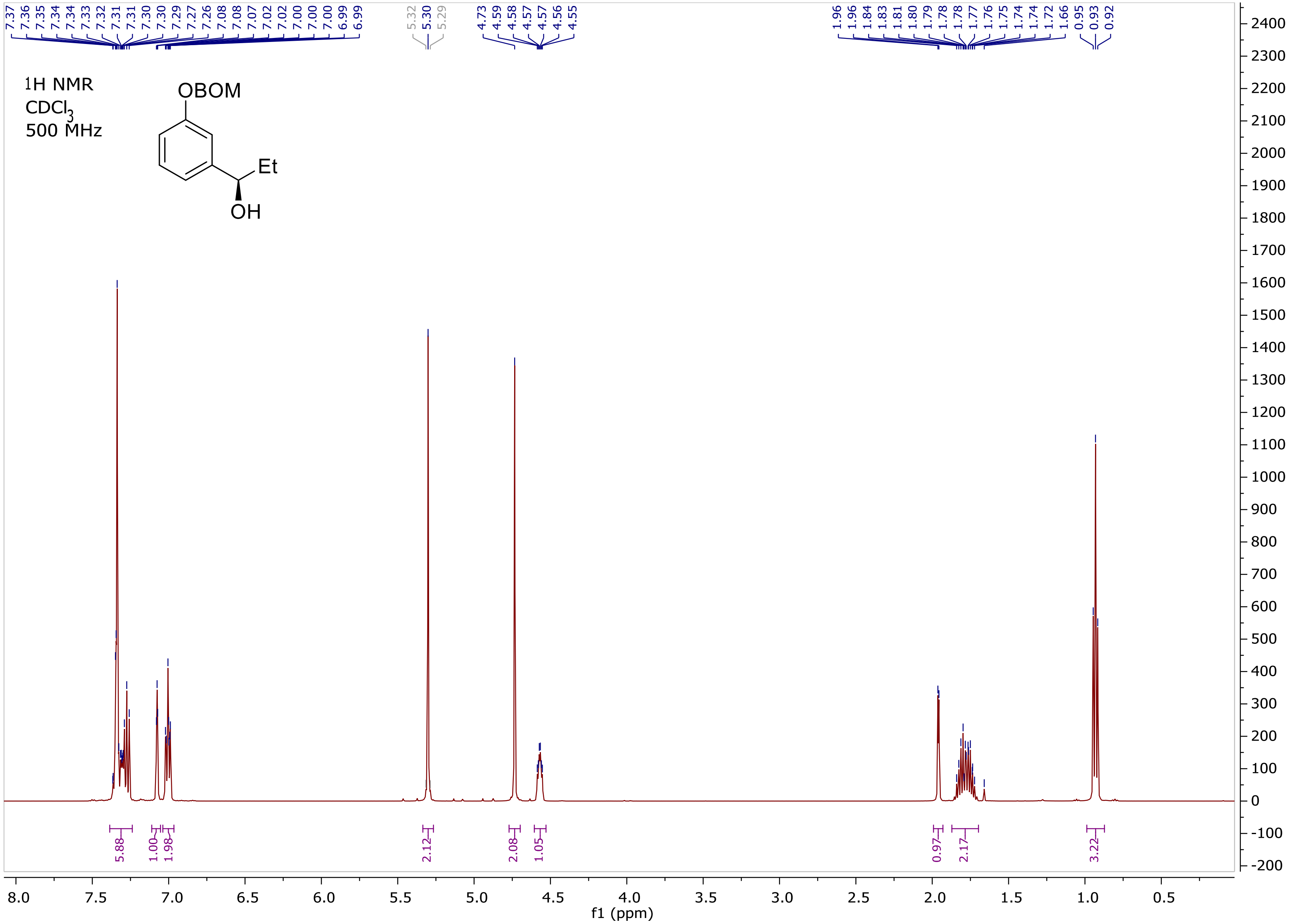


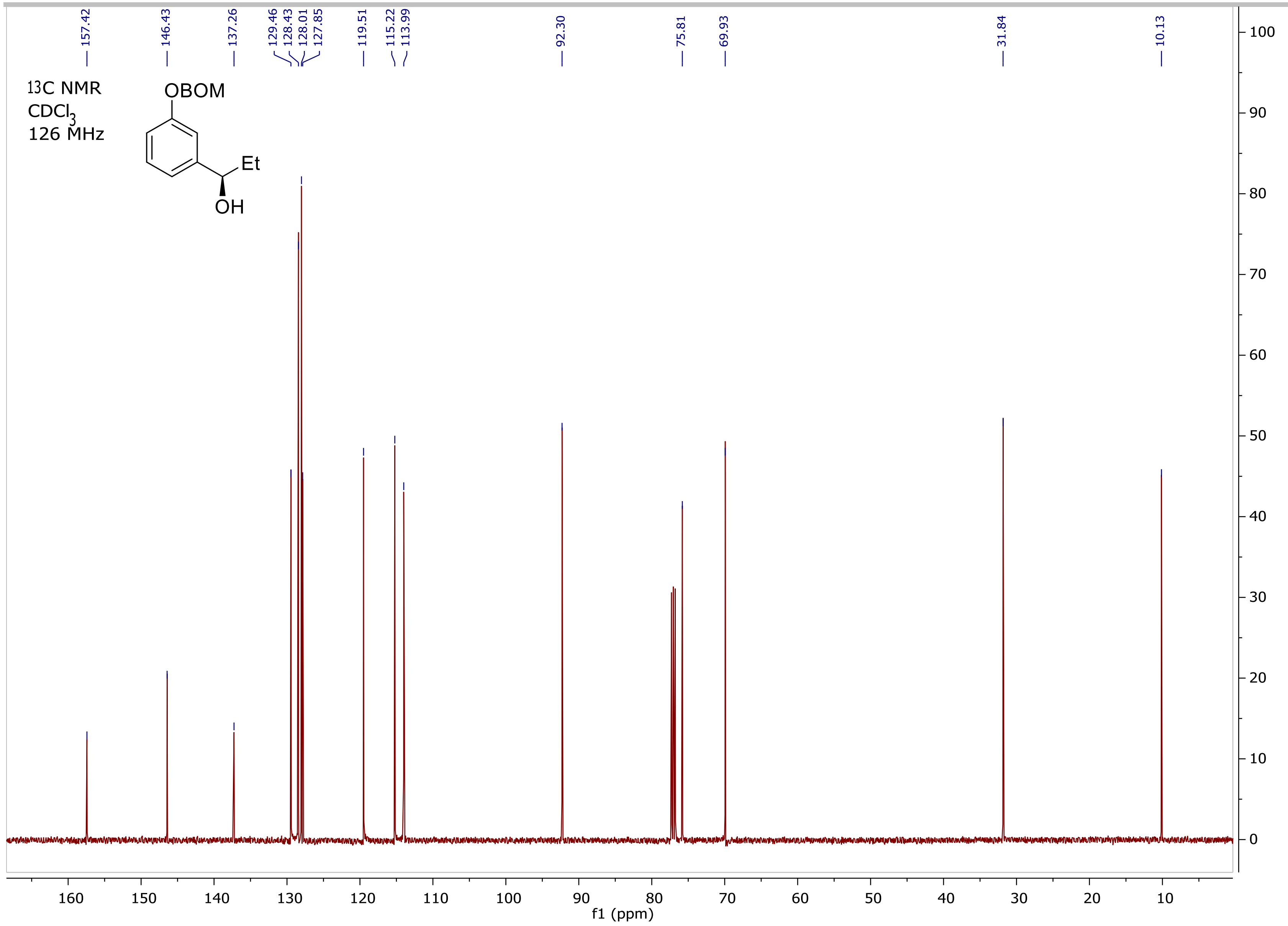
(*S*)-1-(3-(methoxymethoxy)phenyl)propan-1-ol ((*S*)-2a)


1H NMR
CDCl3
700 MHz
OMOM
Et
OH
7.28 7.27 7.27 7.26 7.04 7.03 7.03 7.00 7.00 6.99 6.99 6.99 6.98 6.97 6.96 6.96 6.96 6.95 6.95 6.95 6.95
5.19
4.59 4.58 4.57 4.57
3.49
1.83 1.82 1.82 1.81 1.81 1.80 1.79 1.78 1.78 1.77 1.77 1.76 1.76 1.75 1.74 1.74 1.73 1.72 0.95 0.94 0.93
1.21 0.96 0.95 0.94 1.95 1.00 2.82 2.13 3.00
f1 (ppm)
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
1000 900 800 700 600 500 400 300 200 100 0
7.3 7.2 7.1 7.0 6.9 6.8

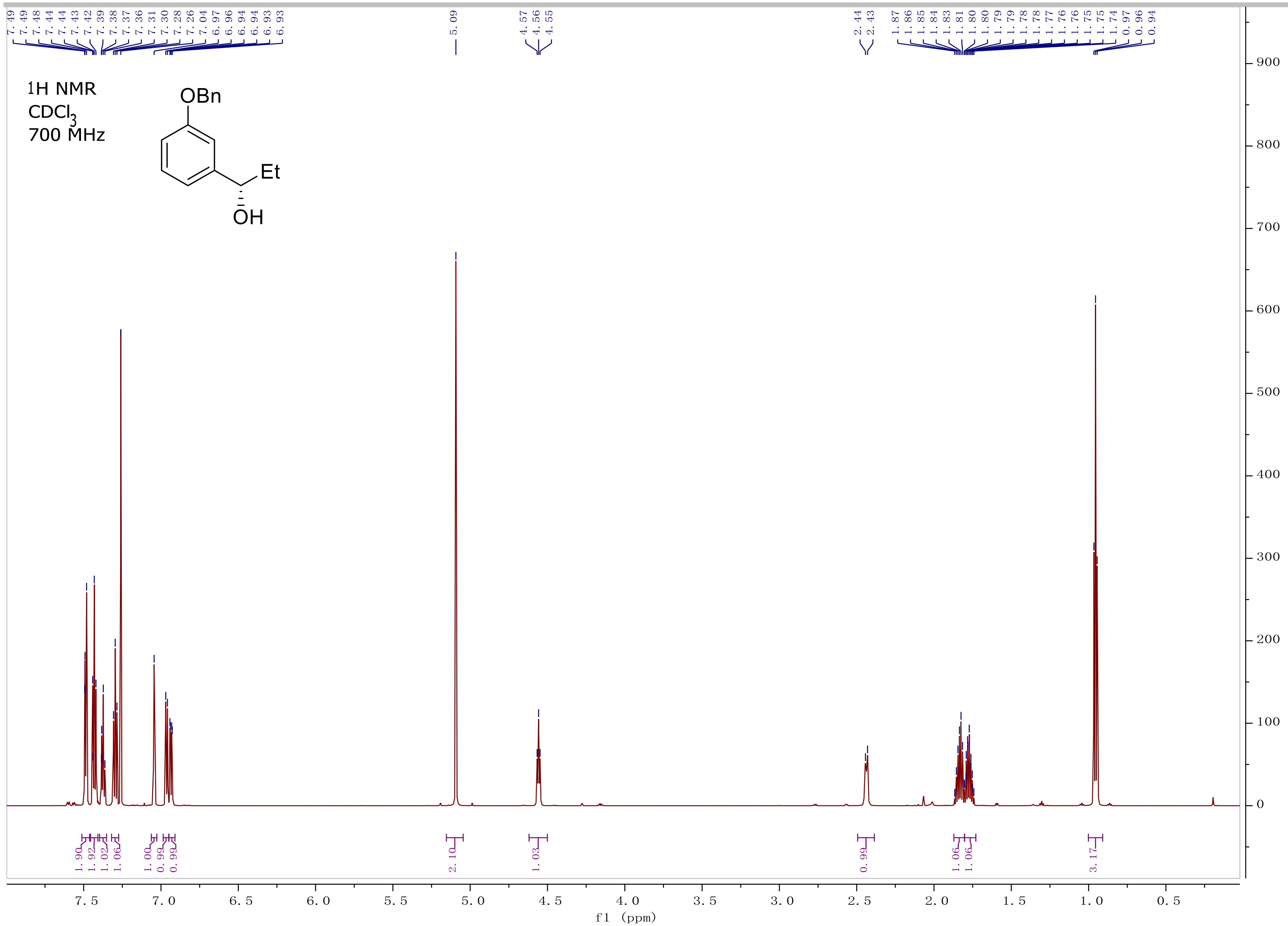

157.36
146.44
129.44
119.47
115.15
113.91
94.44
75.83
56.01
31.84
10.15
1C NMR
CDCl3
176 MHz
OMOM
Et
OH
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
65 60 55 50 45 40 35 30 25 20 15 10 5 0

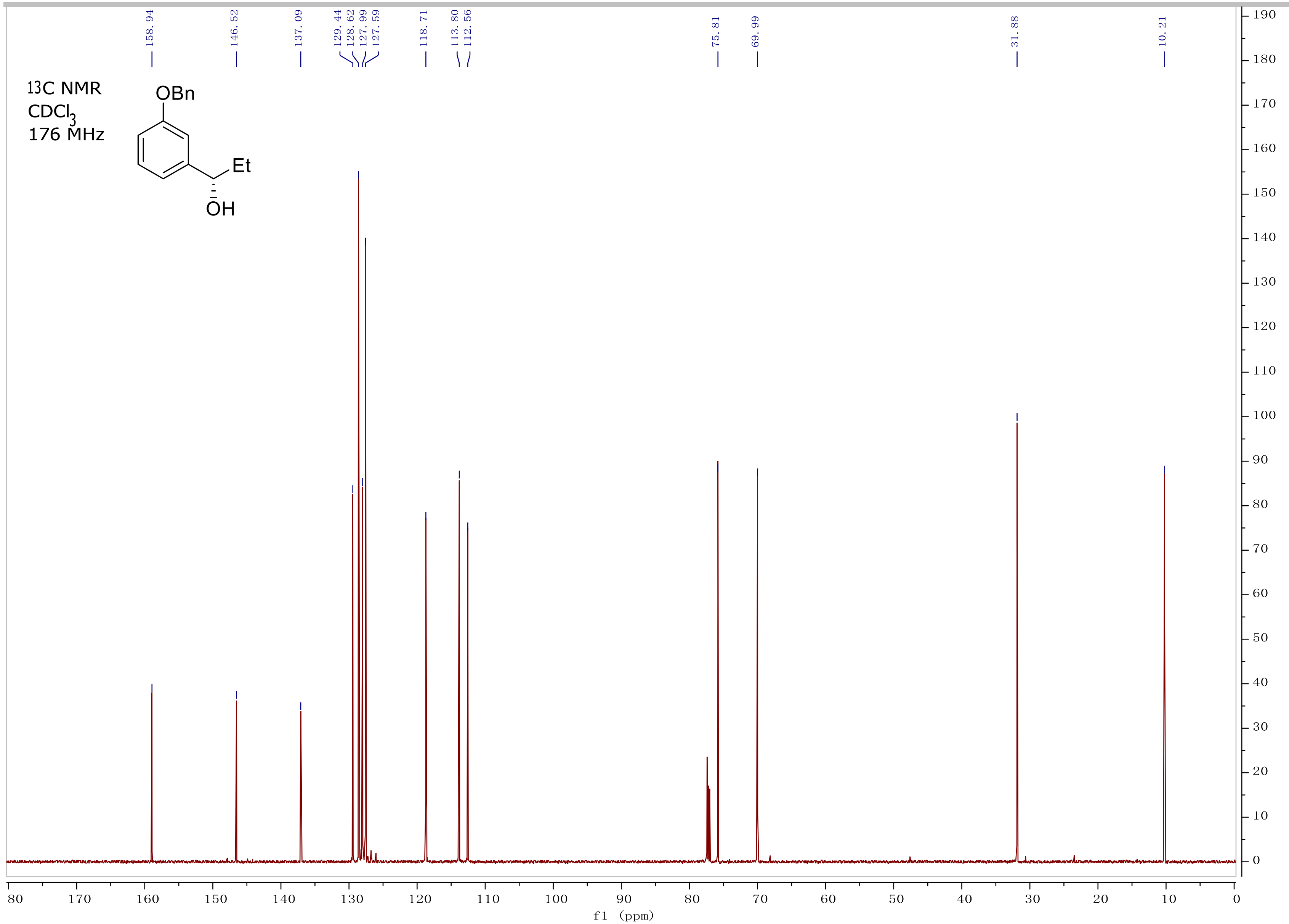
(*R*)-1-(3-((benzyloxy)methoxy)phenyl)propan-1-ol ((*R*)-2b)



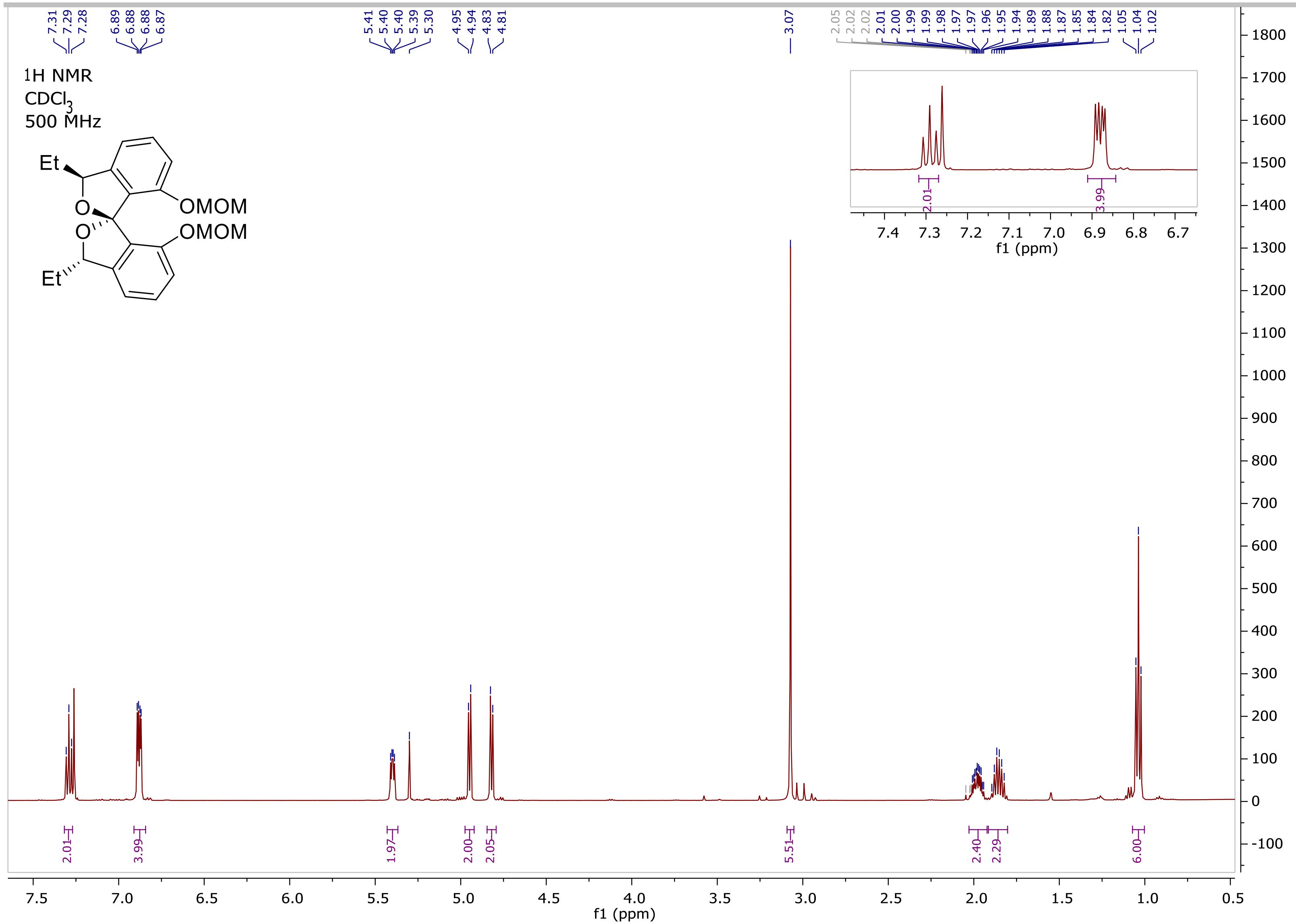


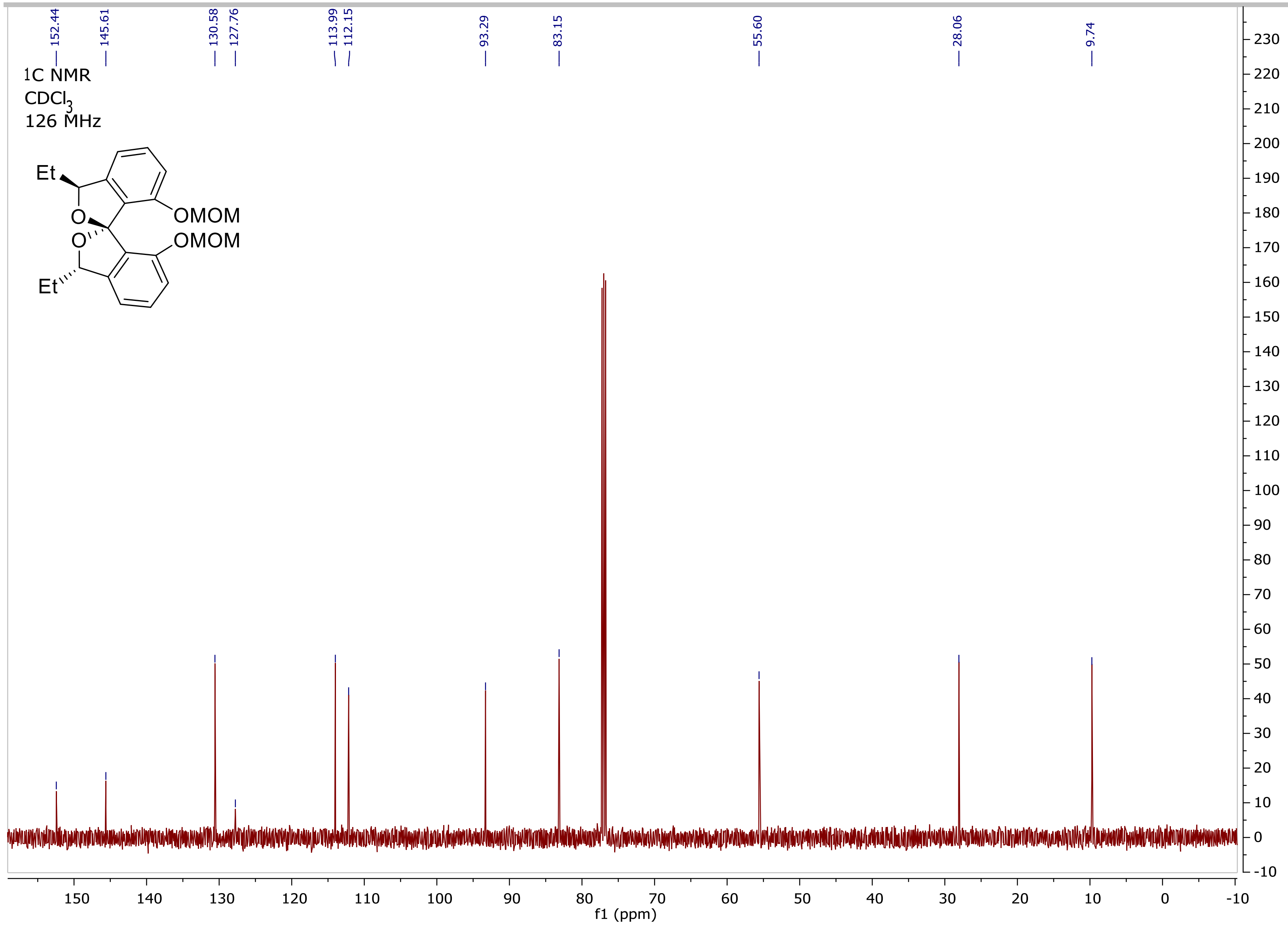
(*S*)-1-(3-(benzyloxy)phenyl)propan-1-ol ((*S*)-2c)


7.49
7.49
7.48
7.44
7.44
7.43
7.42
7.39
7.38
7.37
7.36
7.31
7.30
7.28
7.26
7.04
6.97
6.96
6.94
6.94
6.93
6.93
5.09
4.57
4.56
4.55
2.44
2.43
1.87
1.86
1.85
1.84
1.83
1.81
1.80
1.80
1.79
1.79
1.78
1.78
1.77
1.76
1.76
1.75
1.75
1.74
0.97
0.96
0.94
1H NMR
CDCl3
700 MHz
OBn
Et
OH
1.90
1.92
1.02
1.06
1.00
0.99
0.99
2.10
1.03
0.99
1.06
1.06
3.17
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
f1 (ppm)
900
800
700
600
500
400
300
200
100
0

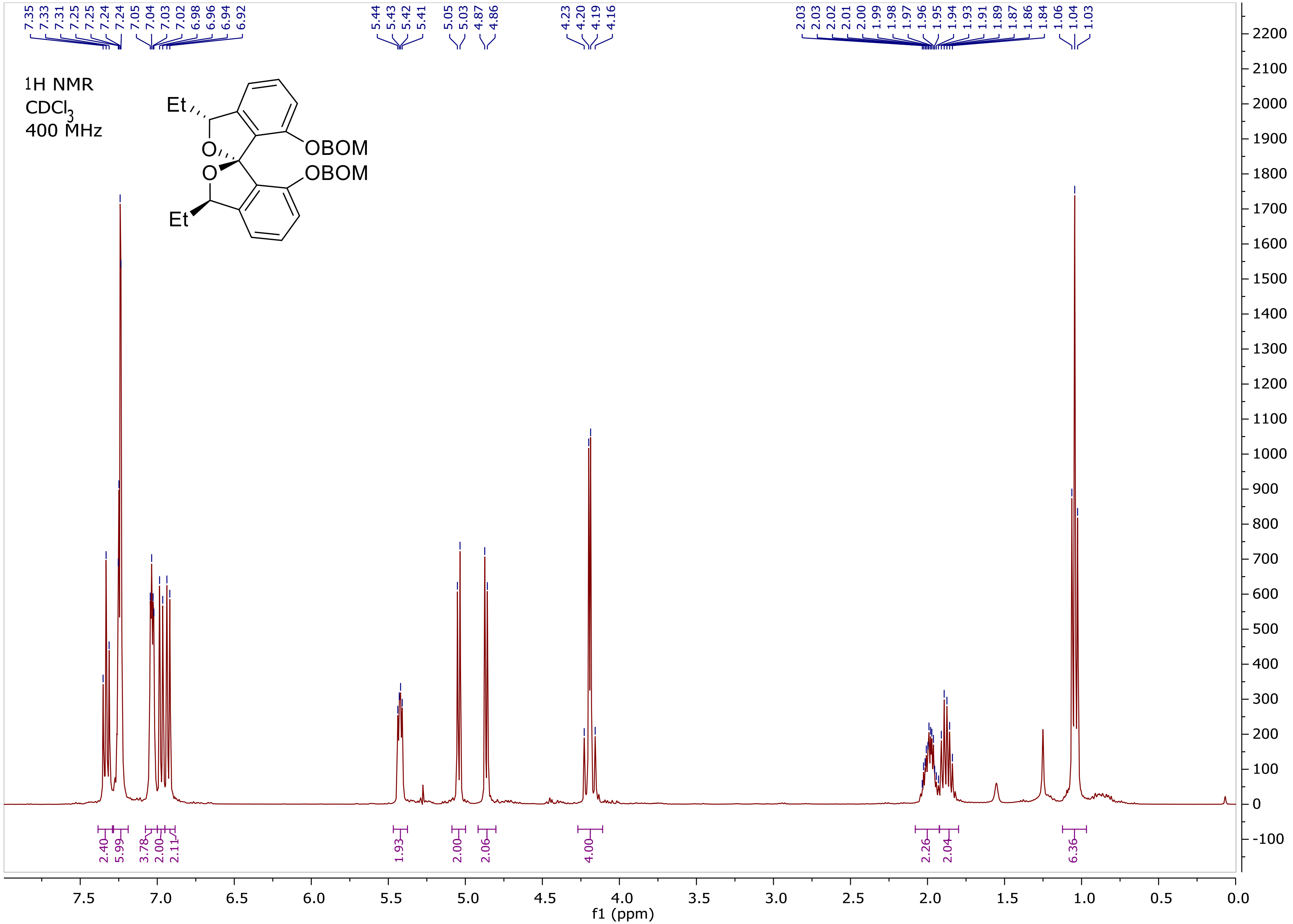


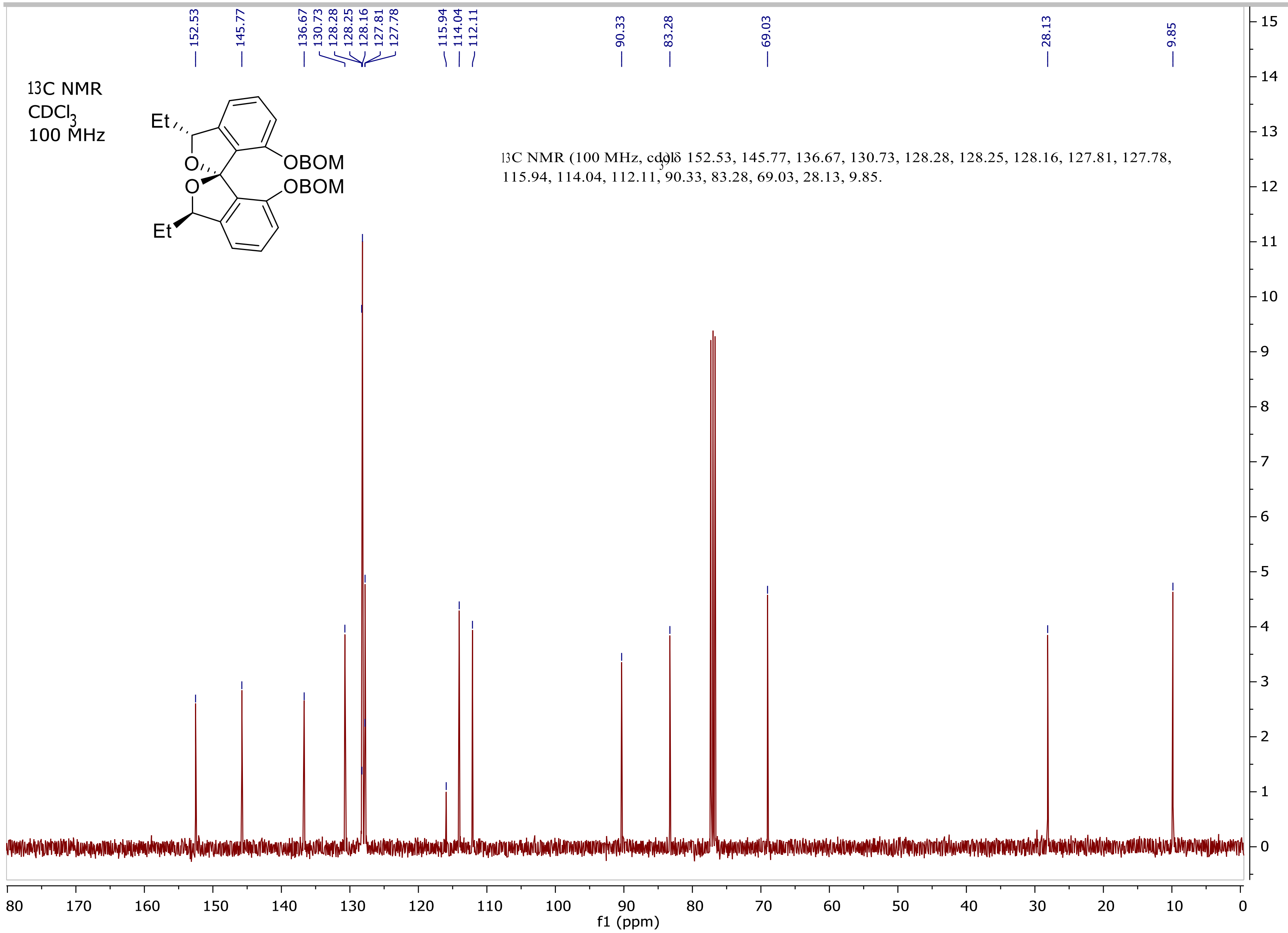
(*1R,3S,3'S*)-3,3'-diethyl-7,7'-bis(methoxymethoxy)-3H,3'H-1,1'-spirobi[isobenzofuran] ((*R,S,S*)-6a)


7.31
7.29
7.28
6.89
6.88
6.88
6.87
5.41
5.40
5.40
5.39
5.30
4.95
4.94
4.83
4.81
3.07
2.05
2.02
2.02
2.01
2.00
1.99
1.99
1.98
1.97
1.97
1.96
1.95
1.94
1.89
1.88
1.87
1.85
1.84
1.82
1.05
1.04
1.02
1H NMR
CDCl3
500 MHz
Et
O
O
OMOM
OMOM
Et
2.01
3.99
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
2.01
3.99
1.97
2.00
2.05
5.51
2.40
2.29
6.00
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
f1 (ppm)
1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100


152.44
145.61
130.58
127.76
113.99
112.15
93.29
83.15
55.60
28.06
9.74
1C NMR
CDCl3
126 MHz
Et
O
O
OMOM
OMOM
Et
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

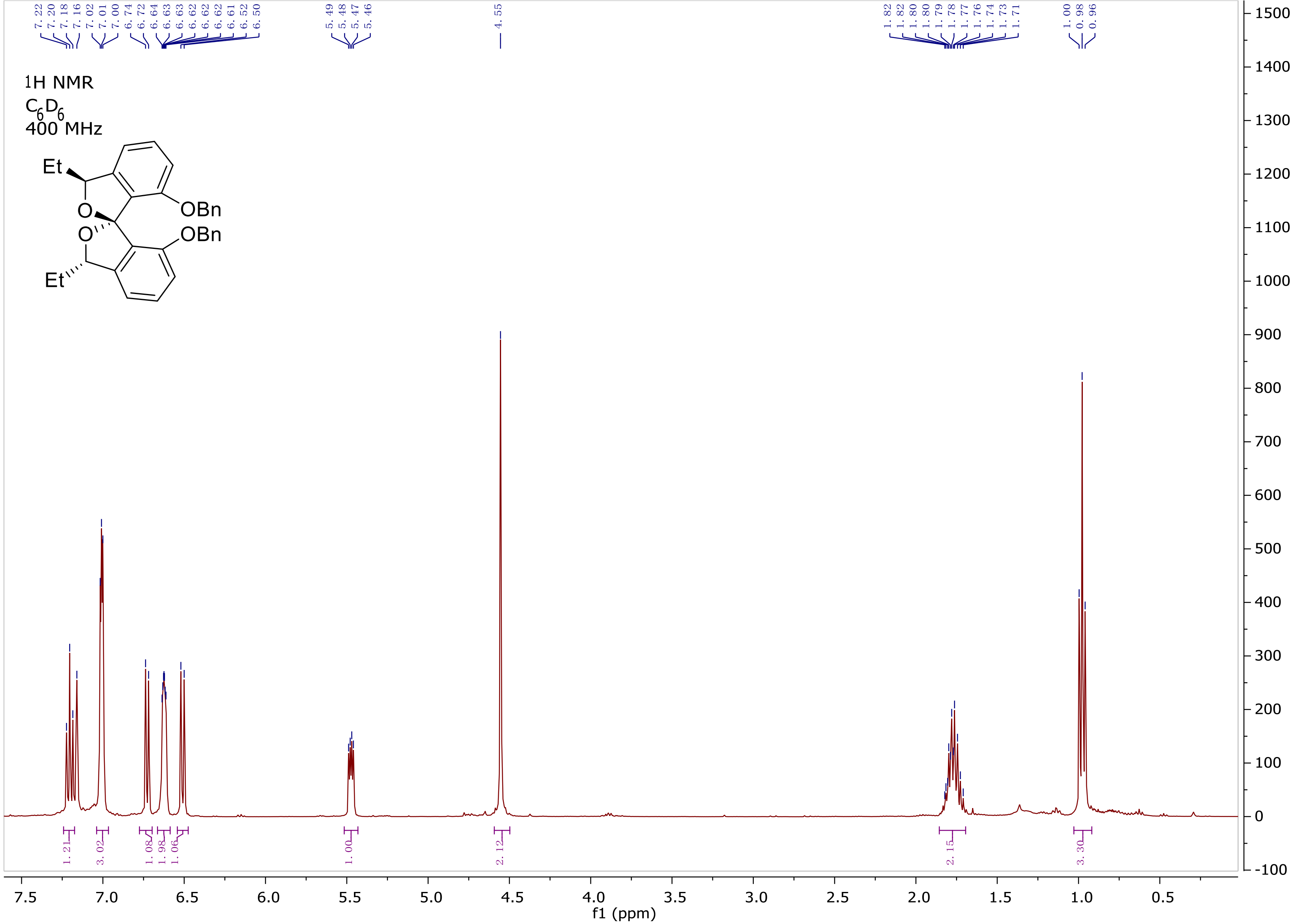
(*1S,3R,3'R*)-7,7'-bis((benzyloxy)methoxy)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran] ((*S,R,R*)-6b)

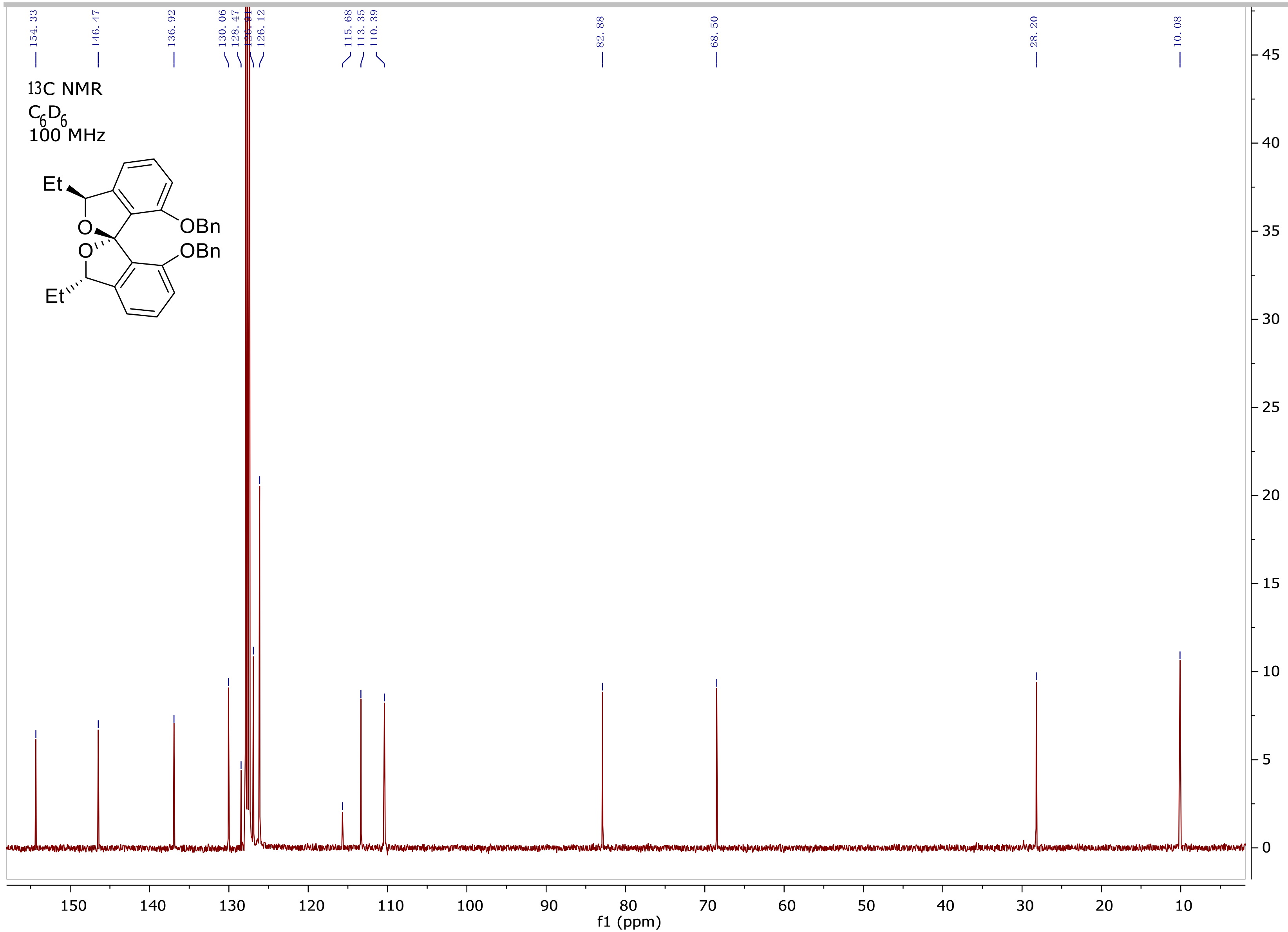




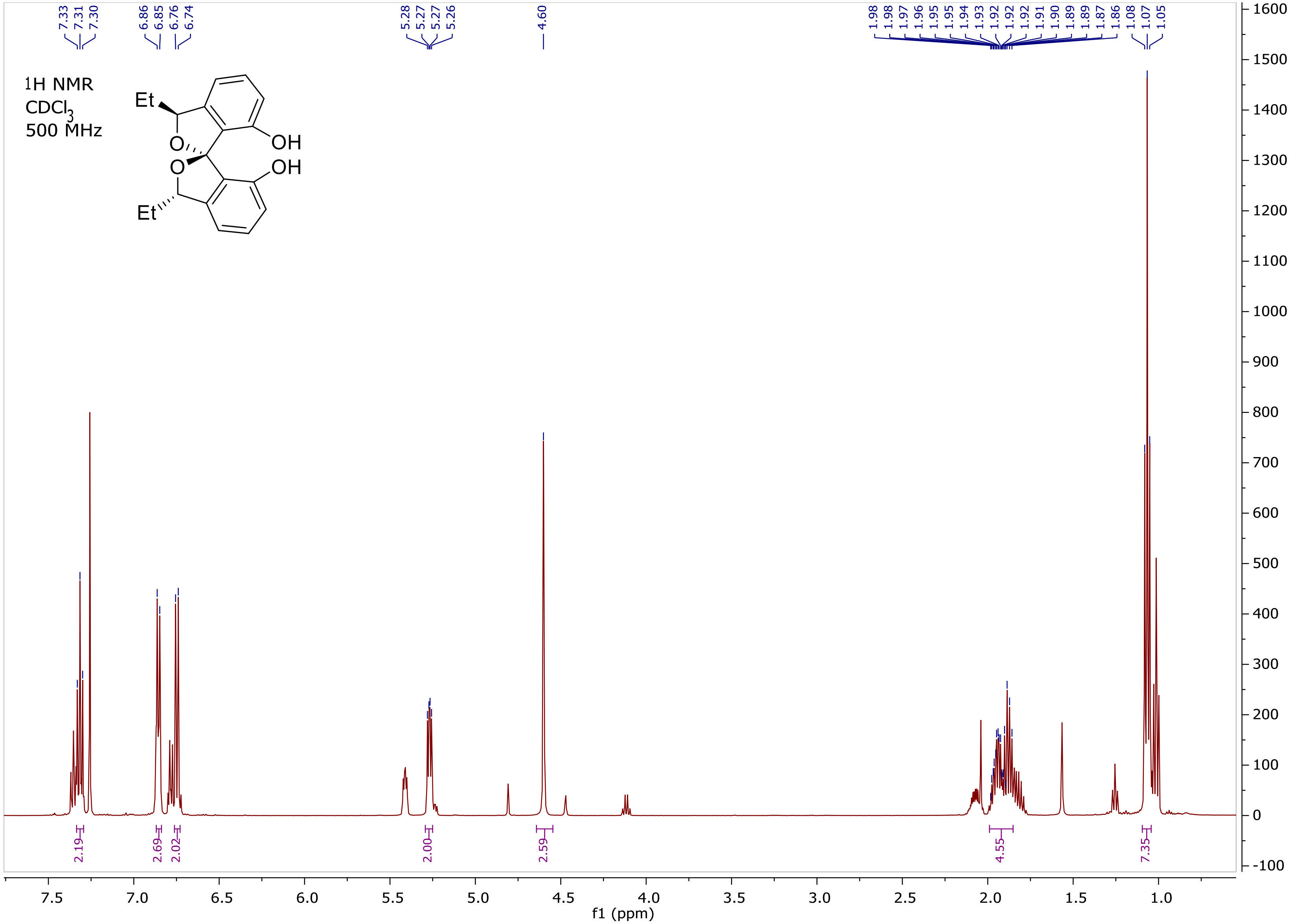
13C NMR (100 MHz, $cdcl_3$) δ 152.53, 145.77, 136.67, 130.73, 128.28, 128.25, 128.16, 127.81, 127.78, 115.94, 114.04, 112.11, 90.33, 83.28, 69.03, 28.13, 9.85.

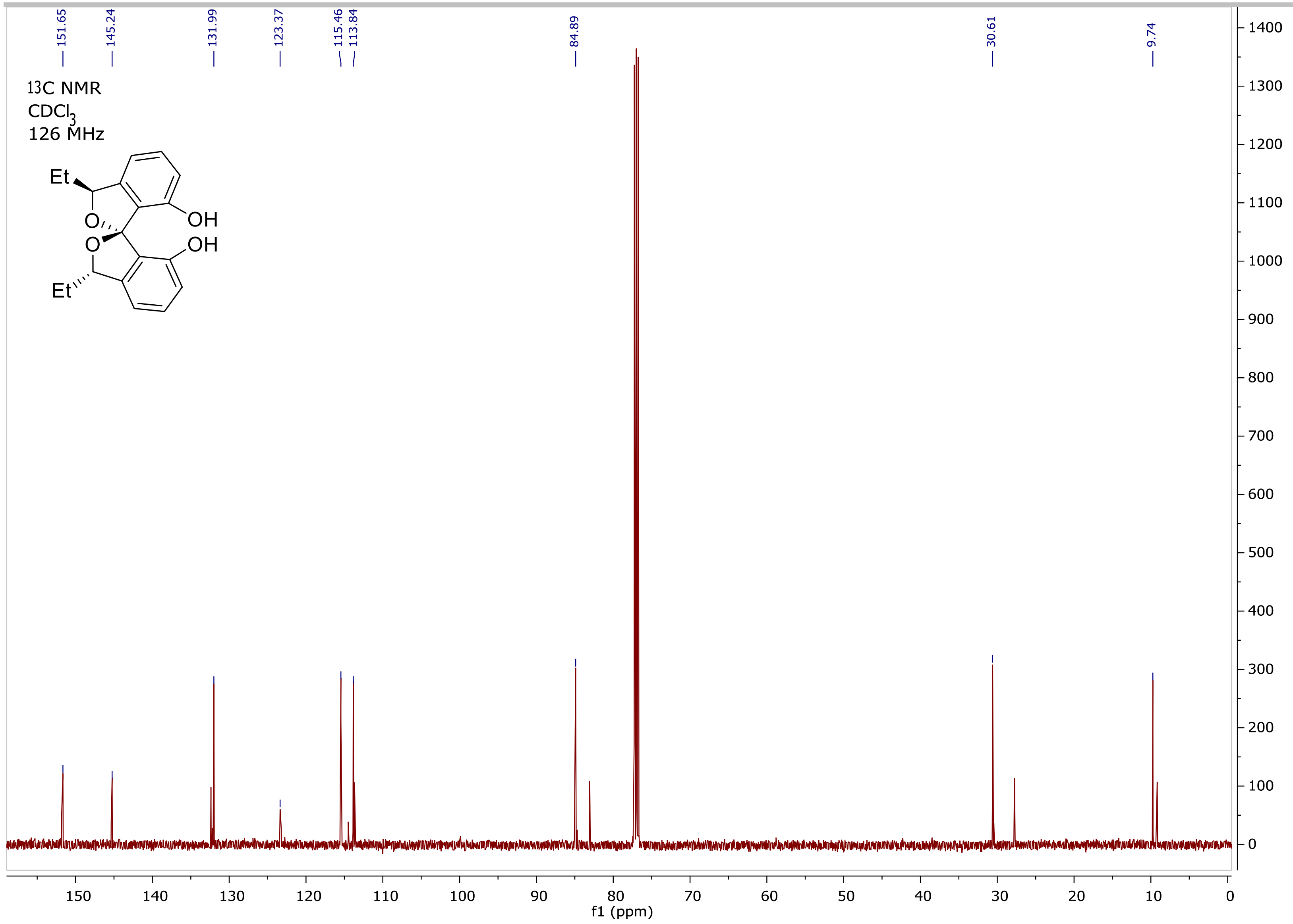
(*1R,3S,3'S*)-7,7'-bis(benzyloxy)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran] ((*R,S,S*)-6c)



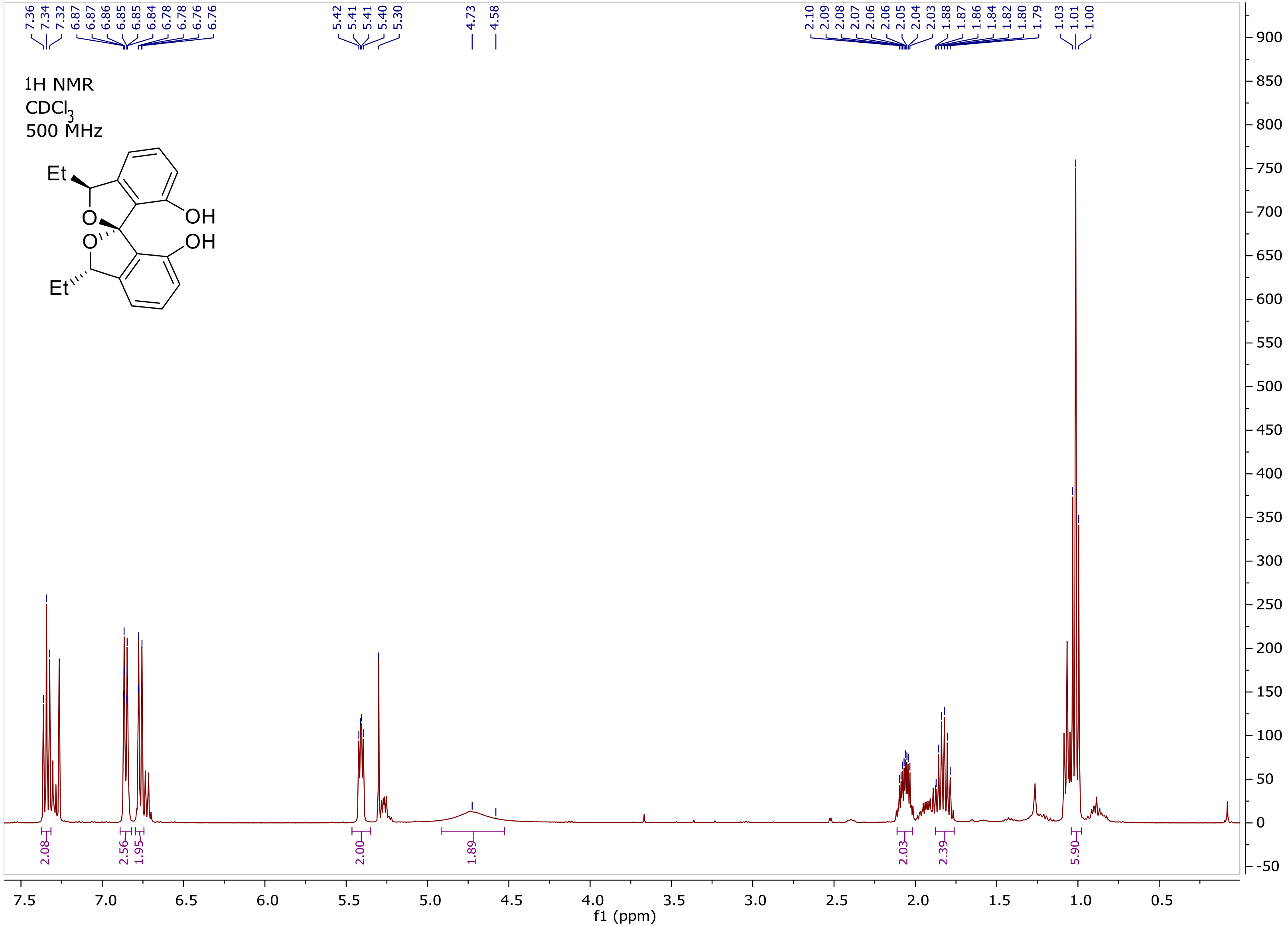

154.33
146.47
136.92
130.06
128.47
126.91
126.12
115.68
113.35
110.39
82.88
68.50
28.20
10.08
^{13}C NMR
C_6D_6
100 MHz
Et
O
O
OBn
OBn
Et
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
45
40
35
30
25
20
15
10
5
0

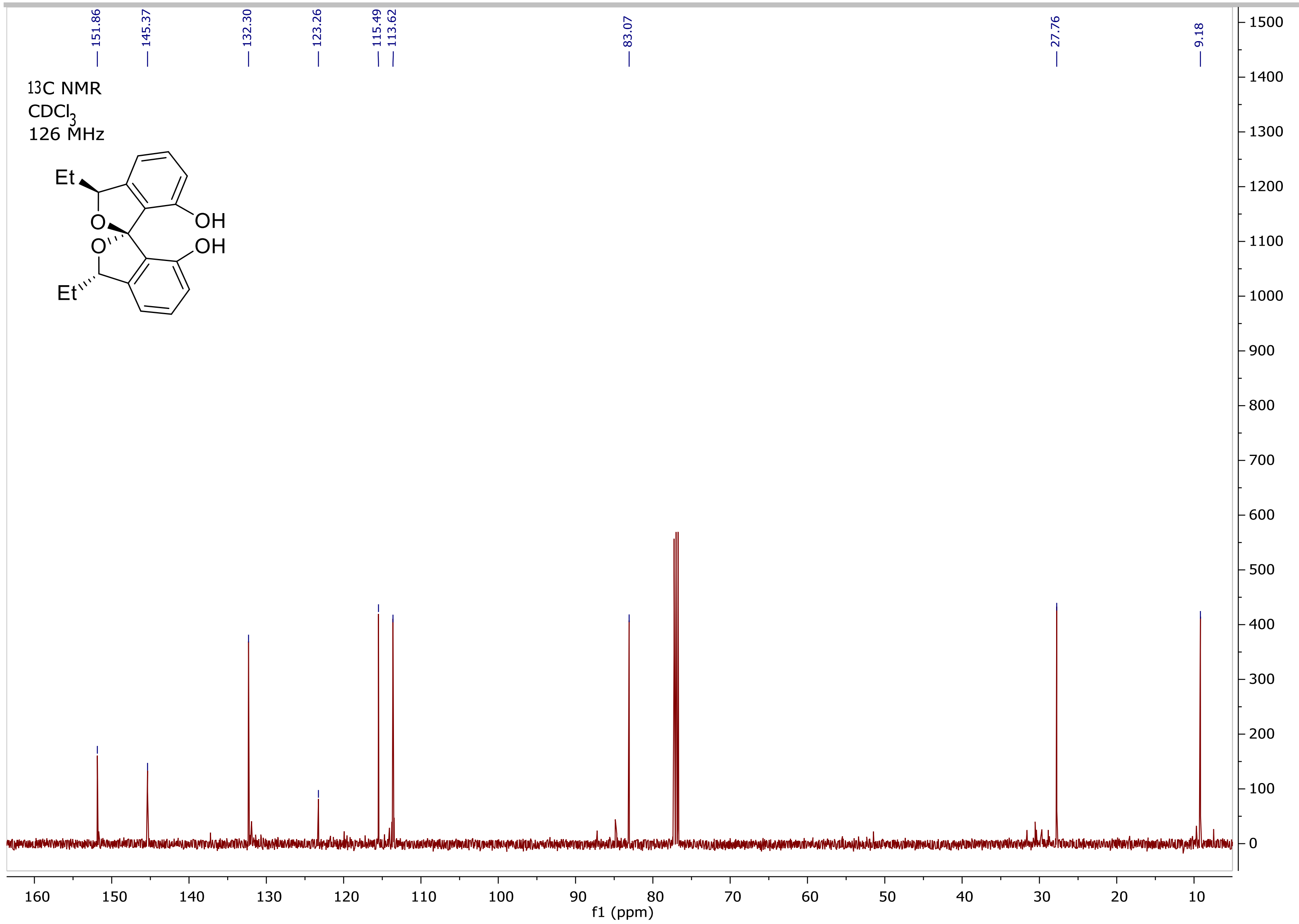
(*1S,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diol ((*S,S,S*)-7) – ~2:1 d.r. (*S,S,S*)-7:(*R,S,S*)-7



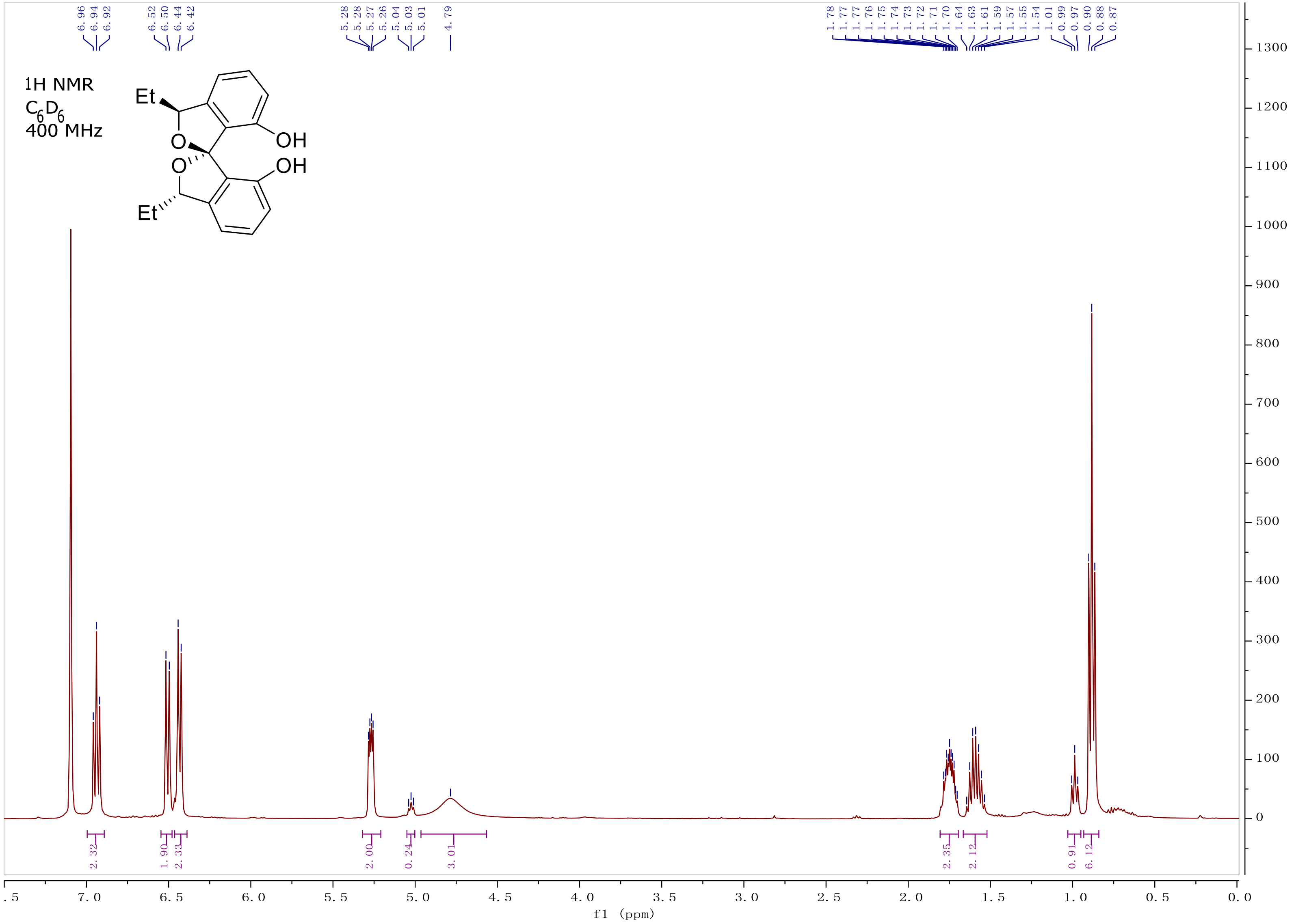

151.65
145.24
131.99
123.37
115.46
113.84
84.89
30.61
9.74
13C NMR
CDCl3
126 MHz
Et
O
O
OH
OH
Et
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

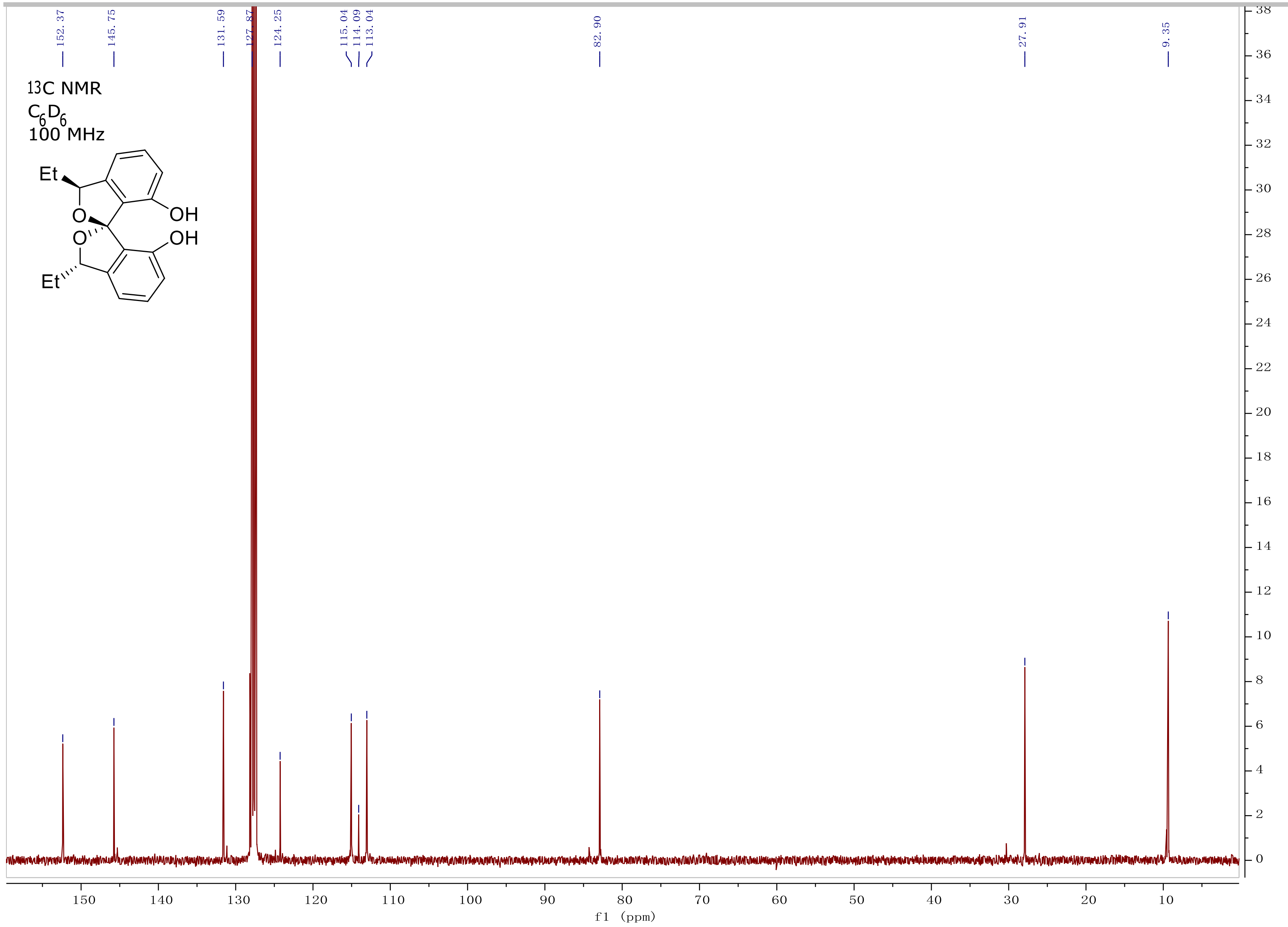
(*1R*,*3S*,*3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diol ((*R*,*S*,*S*)-7) – ~4:1 d.r. (*R*,*S*,*S*)-7:(*S*,*S*,*S*)-7



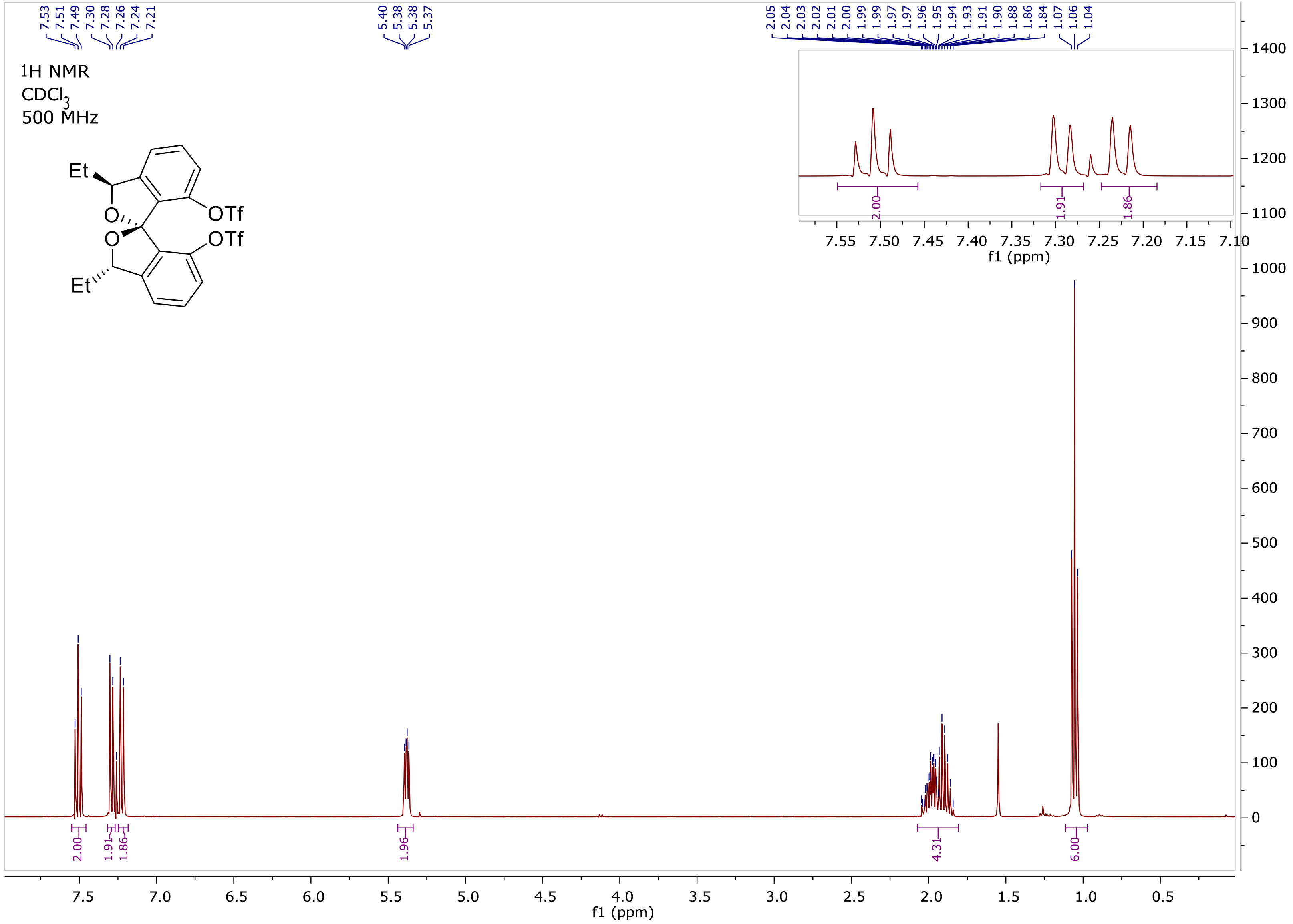

151.86
145.37
132.30
123.26
115.49
113.62
83.07
27.76
9.18
13C NMR
CDCl3
126 MHz
Et
O
O
OH
OH
Et
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

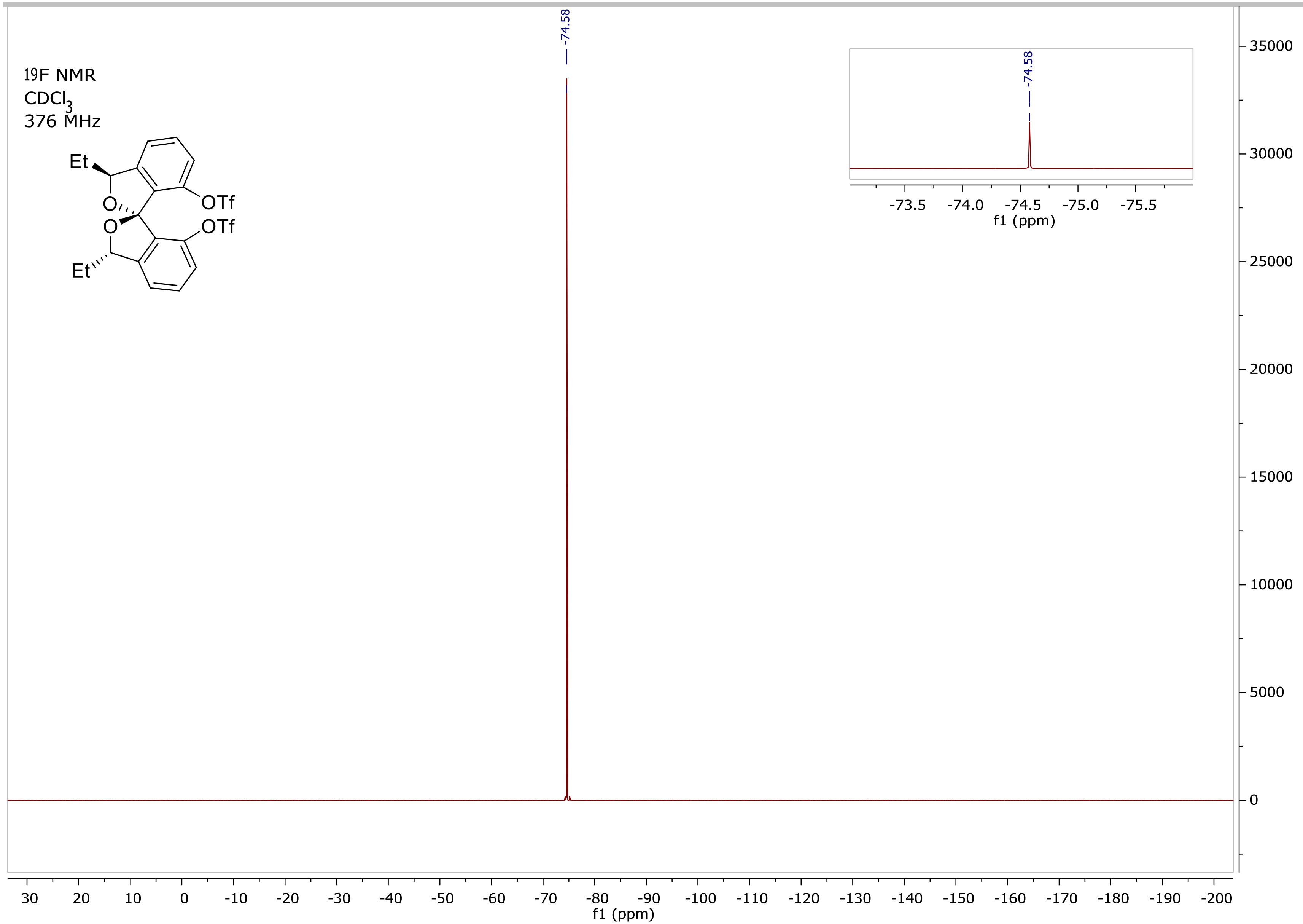
(*1R*,*3S*,*3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diol ((*R*,*S*,*S*)-7) – ~7:1 d.r. (*R*,*S*,*S*)-7:(*S*,*S*,*S*)-7 in C_6D_6

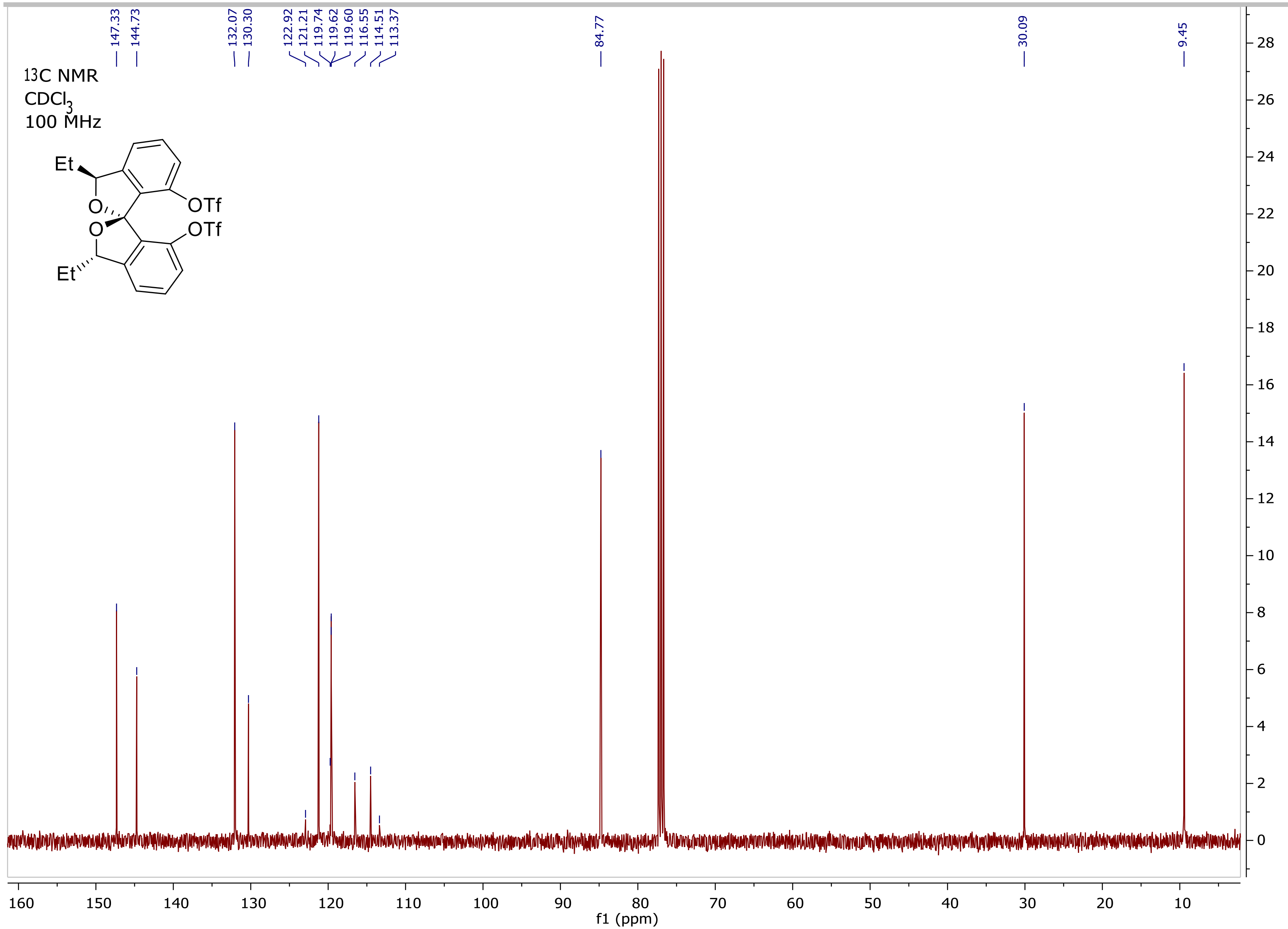



152.37
145.75
131.59
127.87
124.25
115.04
114.09
113.04
82.90
27.91
9.35
13C NMR
C6D6
100 MHz
Et
O
O
OH
OH
Et
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0

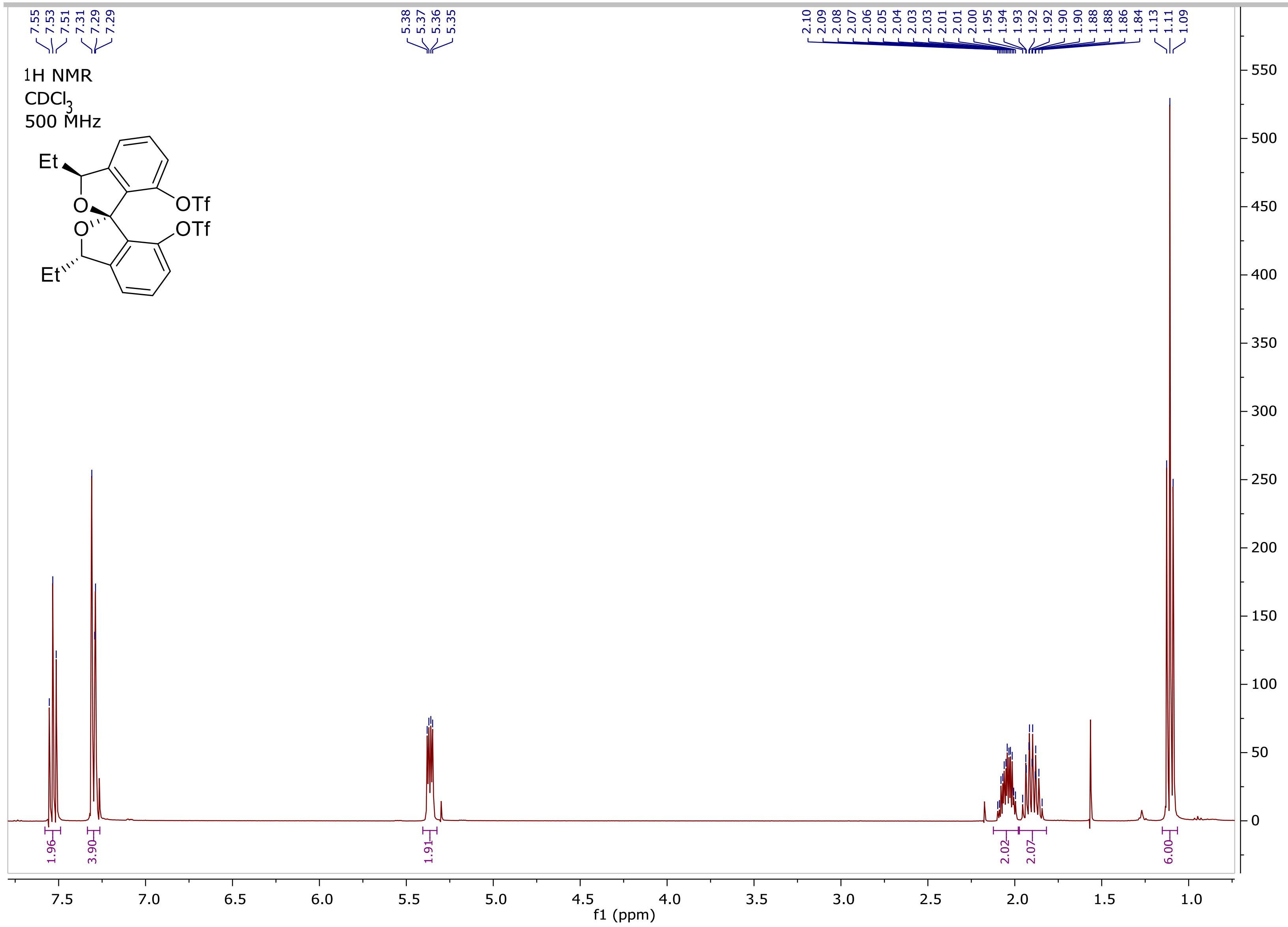
(1*S*,3*S*,3′*S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl bis(trifluoromethanesulfonate) ((*S*,*S*,*S*)-8)

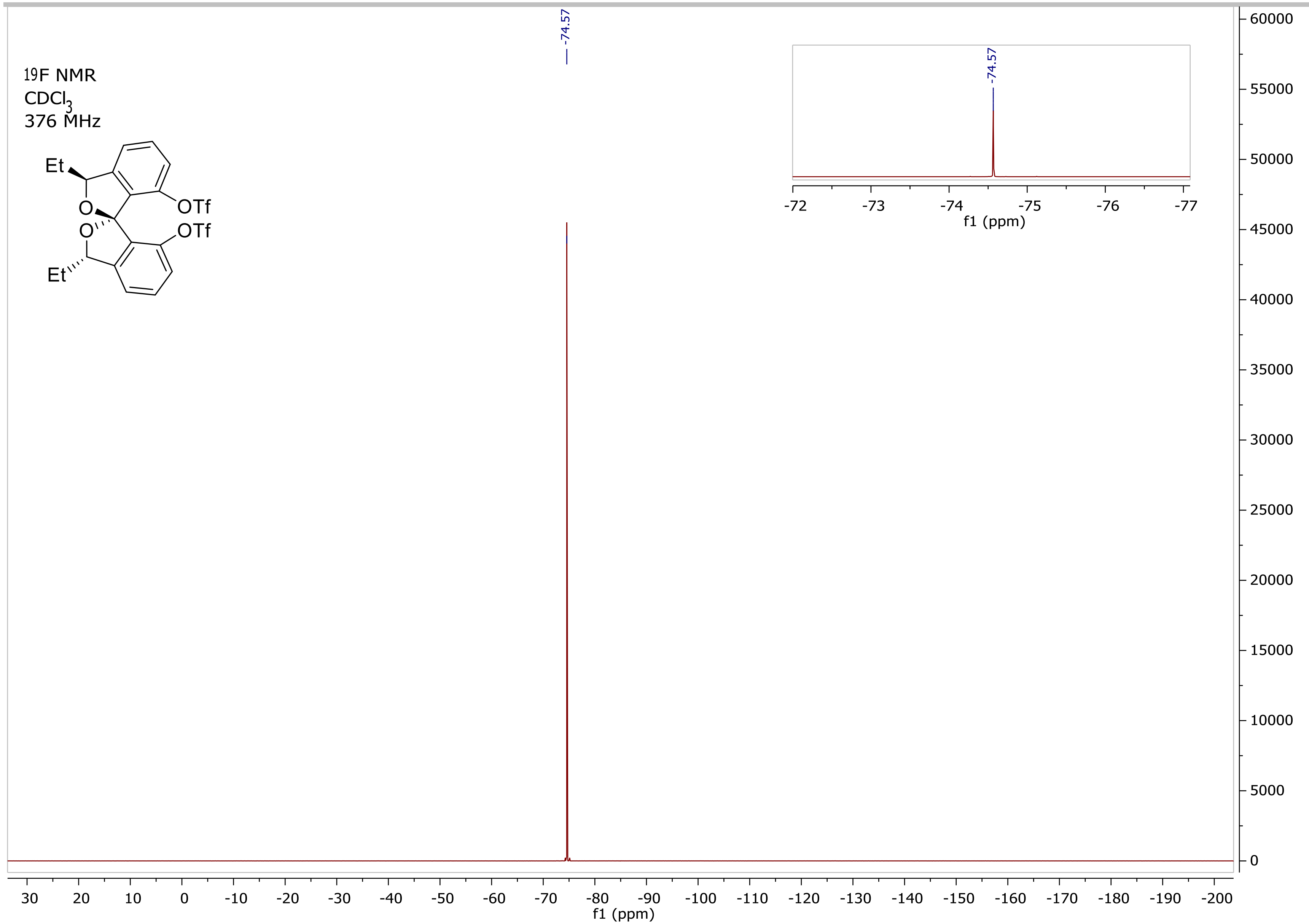


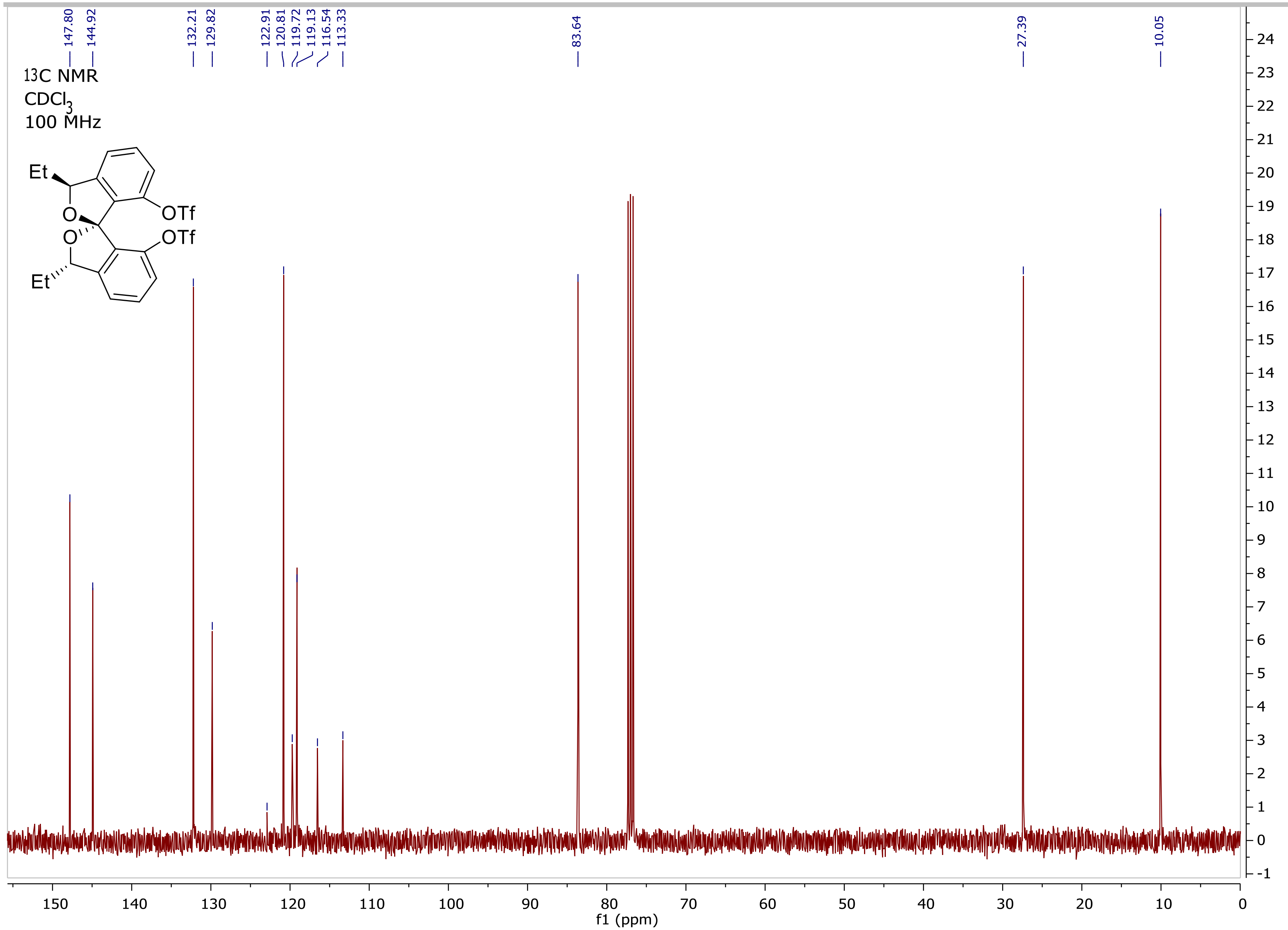

-74.58
19F NMR
CDCl3
376 MHz
Et
O
OTf
O
OTf
Et
-74.58
-73.5
-74.0
-74.5
-75.0
-75.5
f1 (ppm)
35000
30000
25000
20000
15000
10000
5000
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)



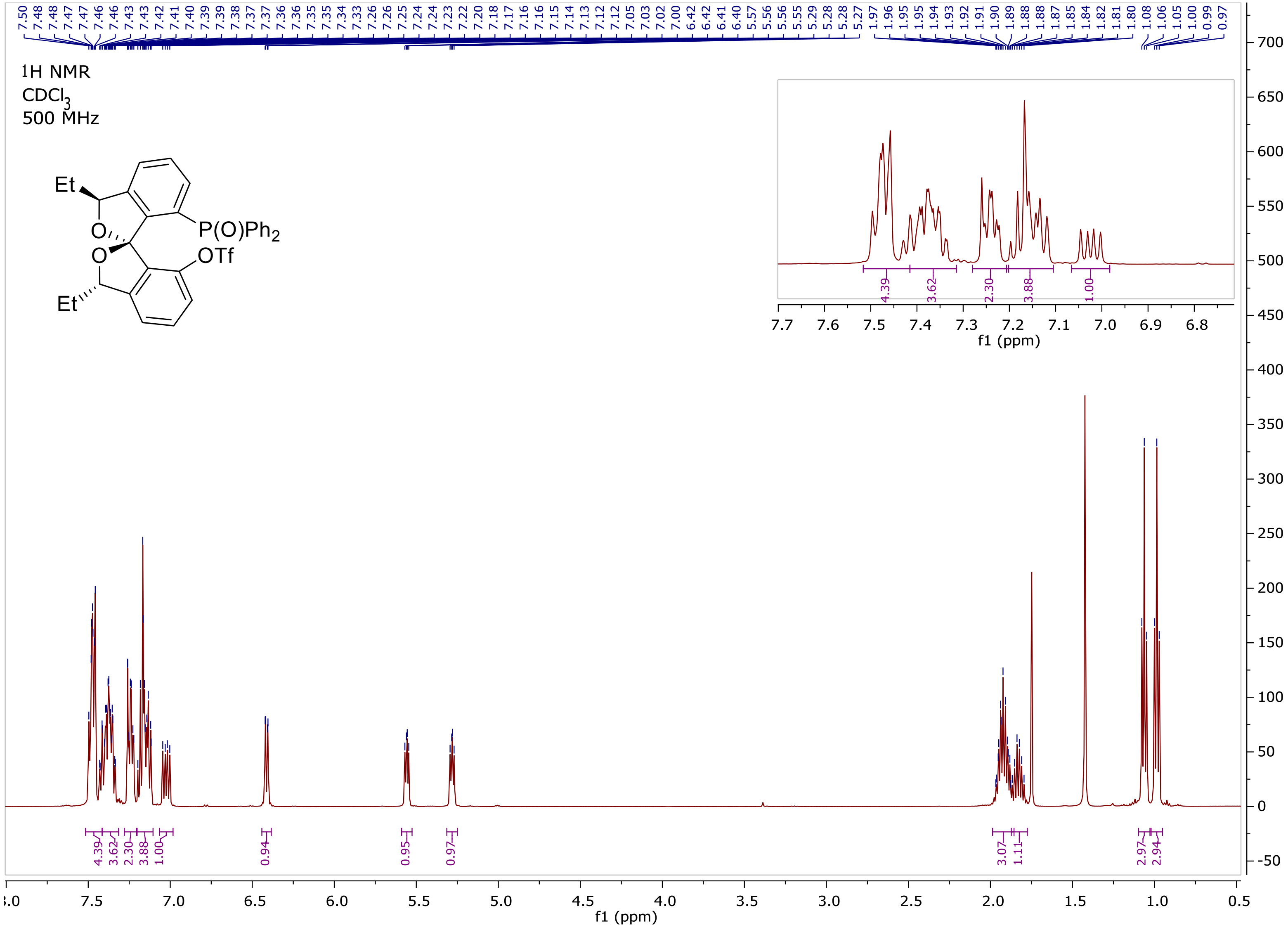
(*1R*,*3S*,*3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl bis(trifluoromethanesulfonate) ((*R*,*S*,*S*)-8)

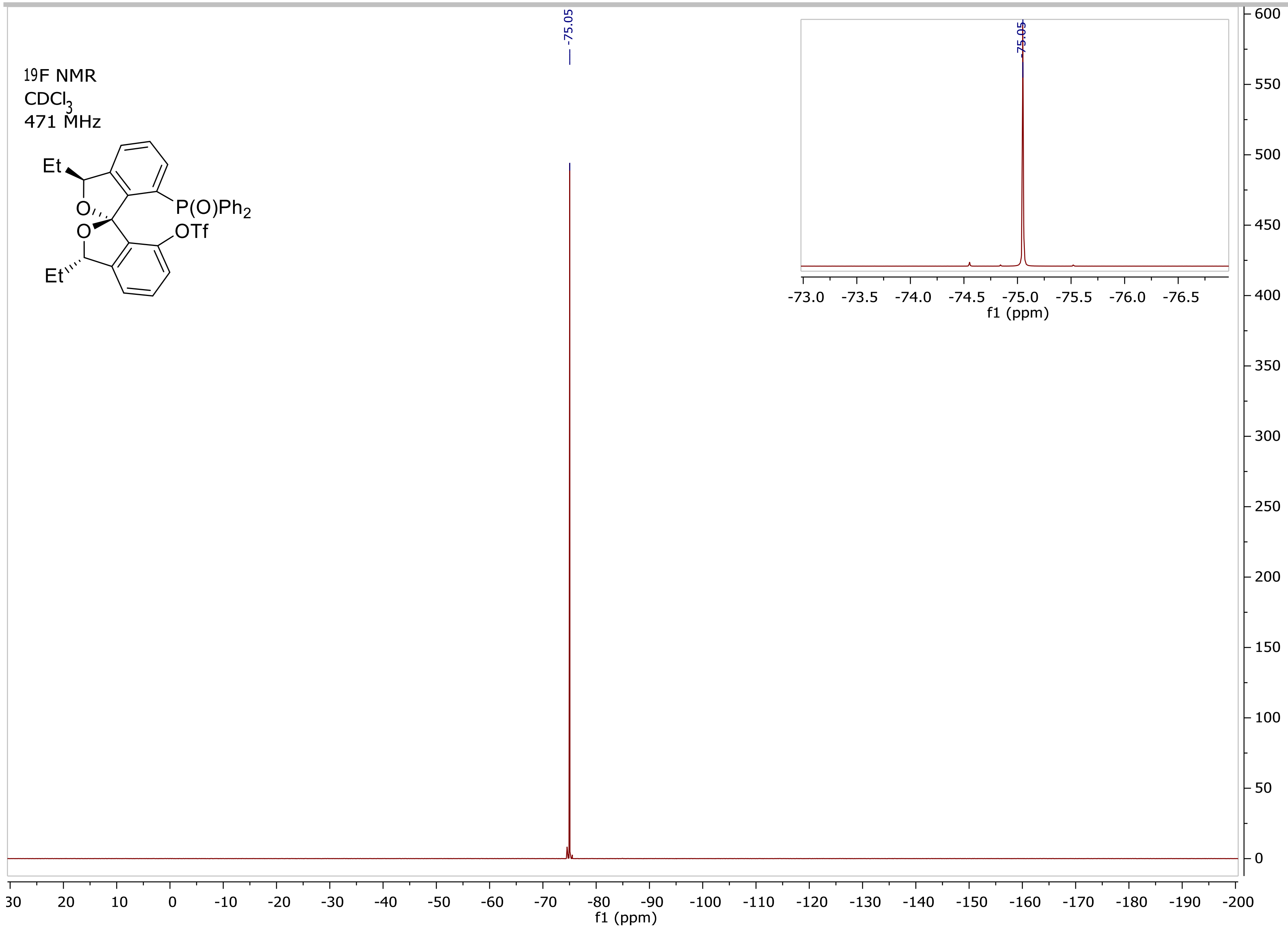

7.55
7.53
7.51
7.31
7.29
7.29
5.38
5.37
5.36
5.35
2.10
2.09
2.08
2.07
2.06
2.05
2.04
2.03
2.03
2.01
2.01
2.00
1.95
1.94
1.93
1.92
1.92
1.90
1.90
1.88
1.88
1.86
1.84
1.13
1.11
1.09
1H NMR
CDCl3
500 MHz
Et
O
OTf
O
OTf
Et
1.96
3.90
1.91
2.02
2.07
6.00
550
500
450
400
350
300
250
200
150
100
50
0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

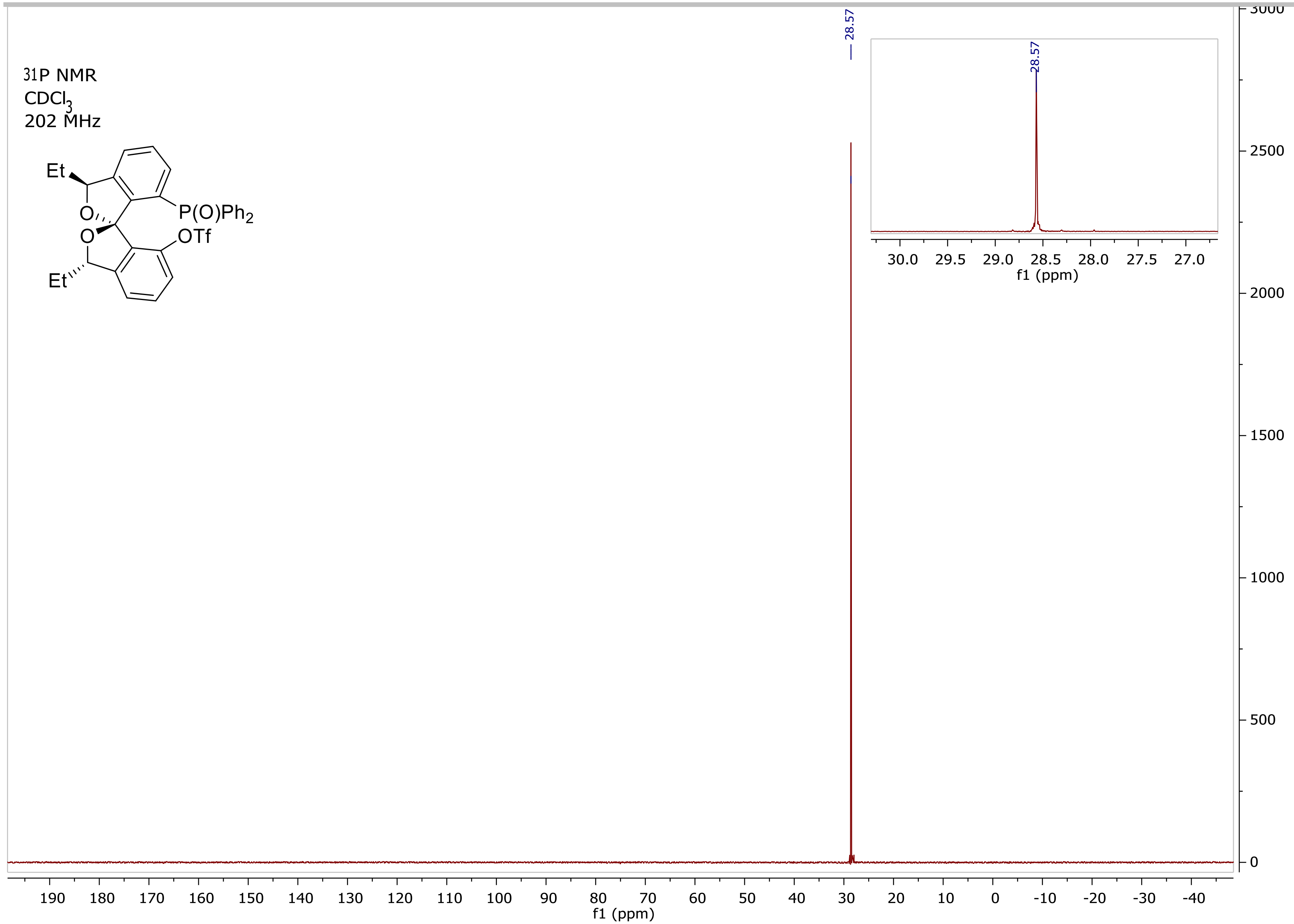

19F NMR
CDCl3
376 MHz
Et
O
O
OTf
OTf
Et
-74.57
-74.57
-72
-73
-74
-75
-76
-77
f1 (ppm)
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

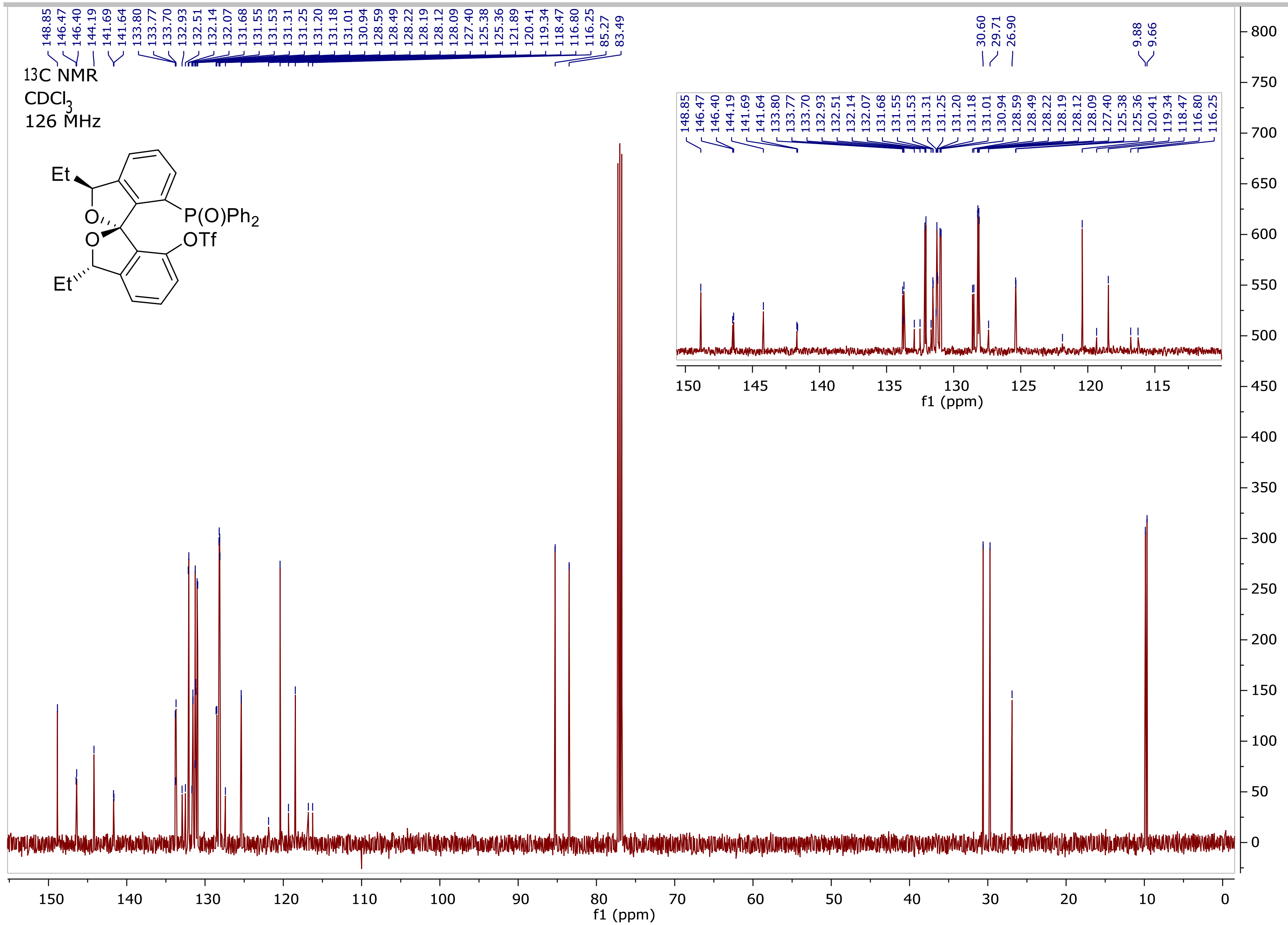

147.80
144.92
132.21
129.82
122.91
120.81
119.72
119.13
116.54
113.33
83.64
27.39
10.05
13C NMR
CDCl3
100 MHz
Et
O
O
OTf
OTf
Et
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(*1S,3S,3'S*)-7'-(diphenylphosphoryl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl trifluoromethanesulfonate ((*S,S,S*)-9)

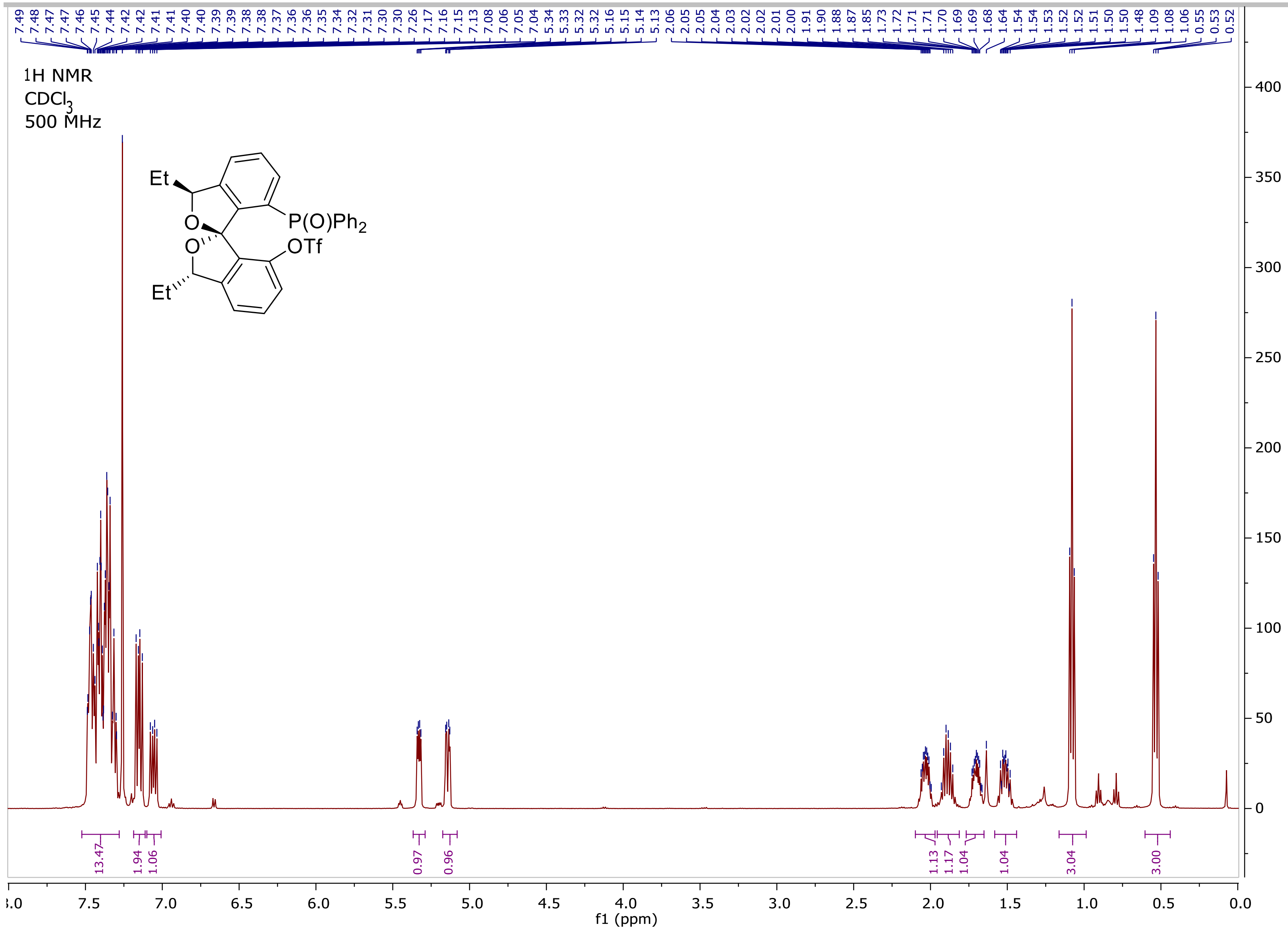


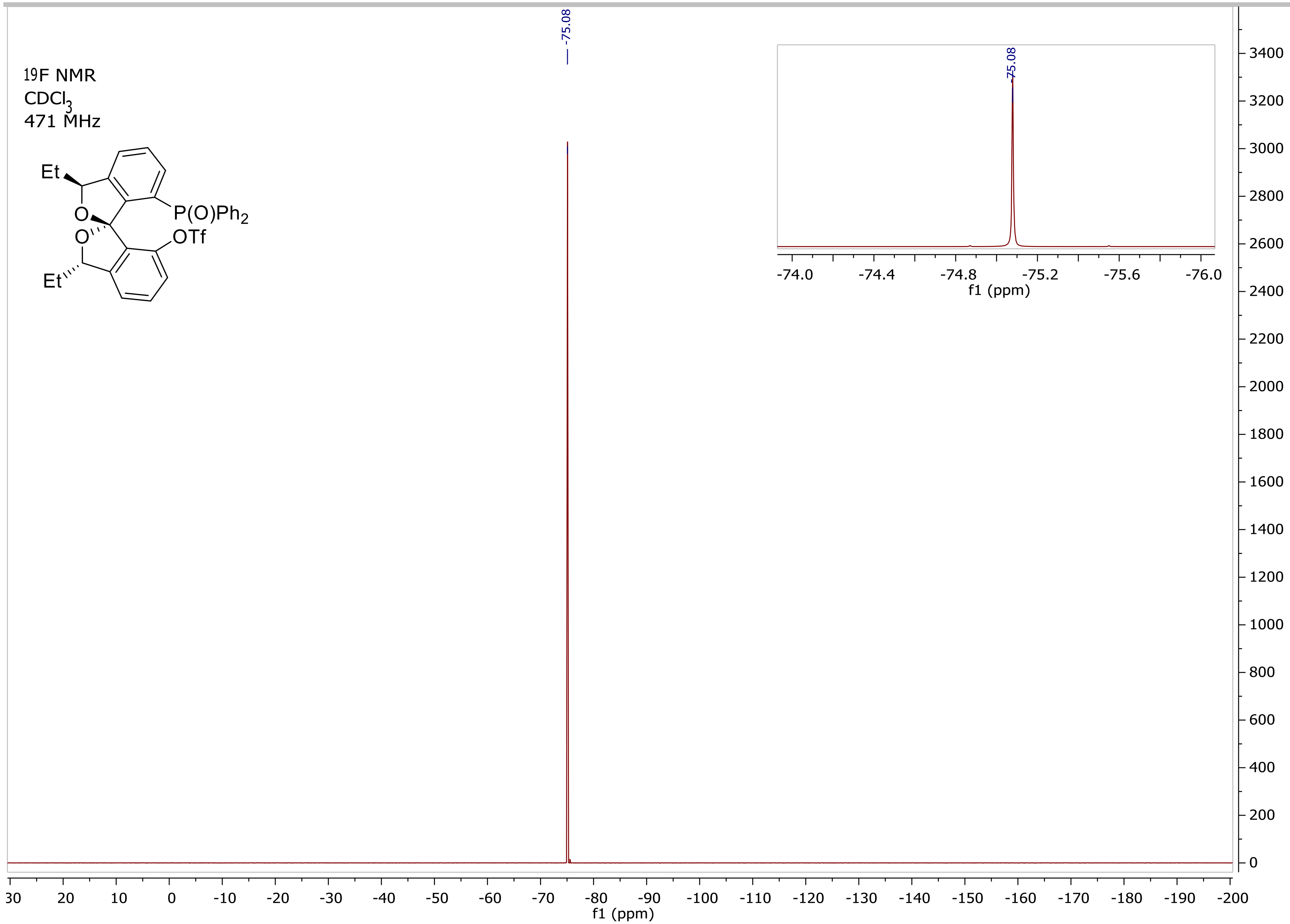

19F NMR
CDCl3
471 MHz
Et
O
O
P(O)Ph2
OTf
Et
-75.05
-75.05
-73.0
-73.5
-74.0
-74.5
-75.0
-75.5
-76.0
-76.5
f1 (ppm)
600
550
500
450
400
350
300
250
200
150
100
50
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

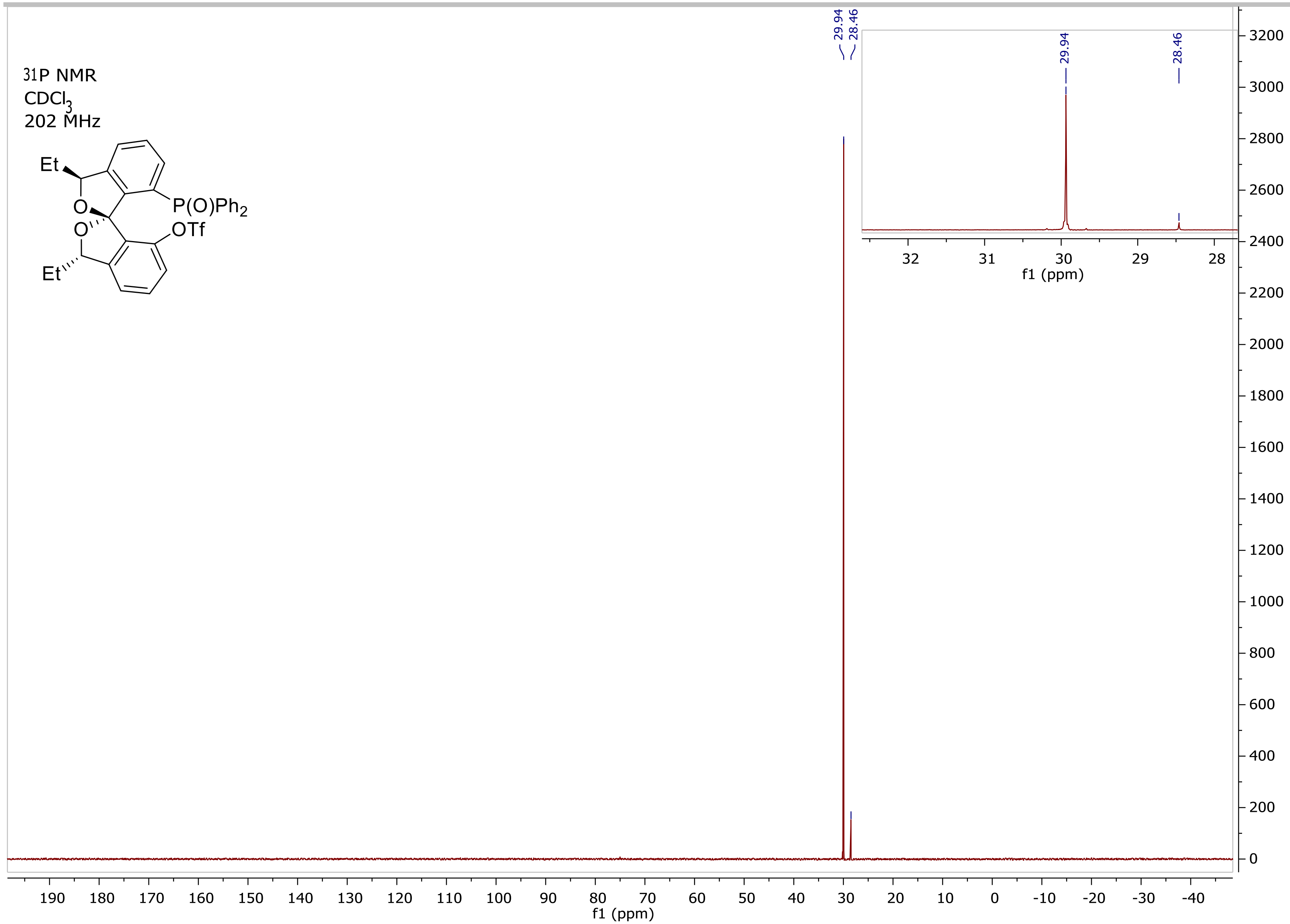

31P NMR
CDCl3
202 MHz
Et
O
O
Et
P(O)Ph2
OTf
28.57
28.57
30.0
29.5
29.0
28.5
28.0
27.5
27.0
f1 (ppm)
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

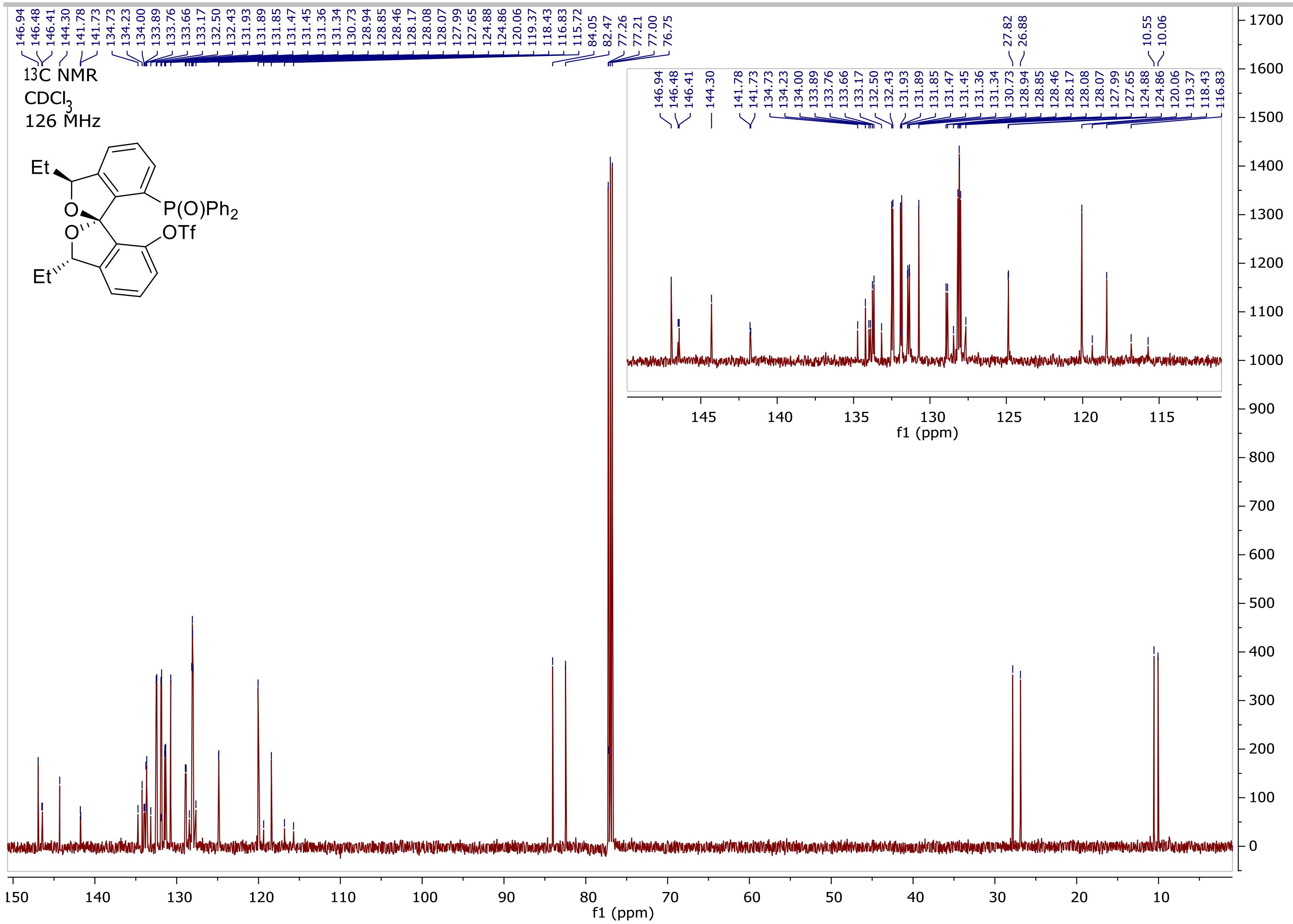


(*1R,3S,3'S*)-7'-(diphenylphosphoryl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl trifluoromethanesulfonate ((*R,S,S*)-9)

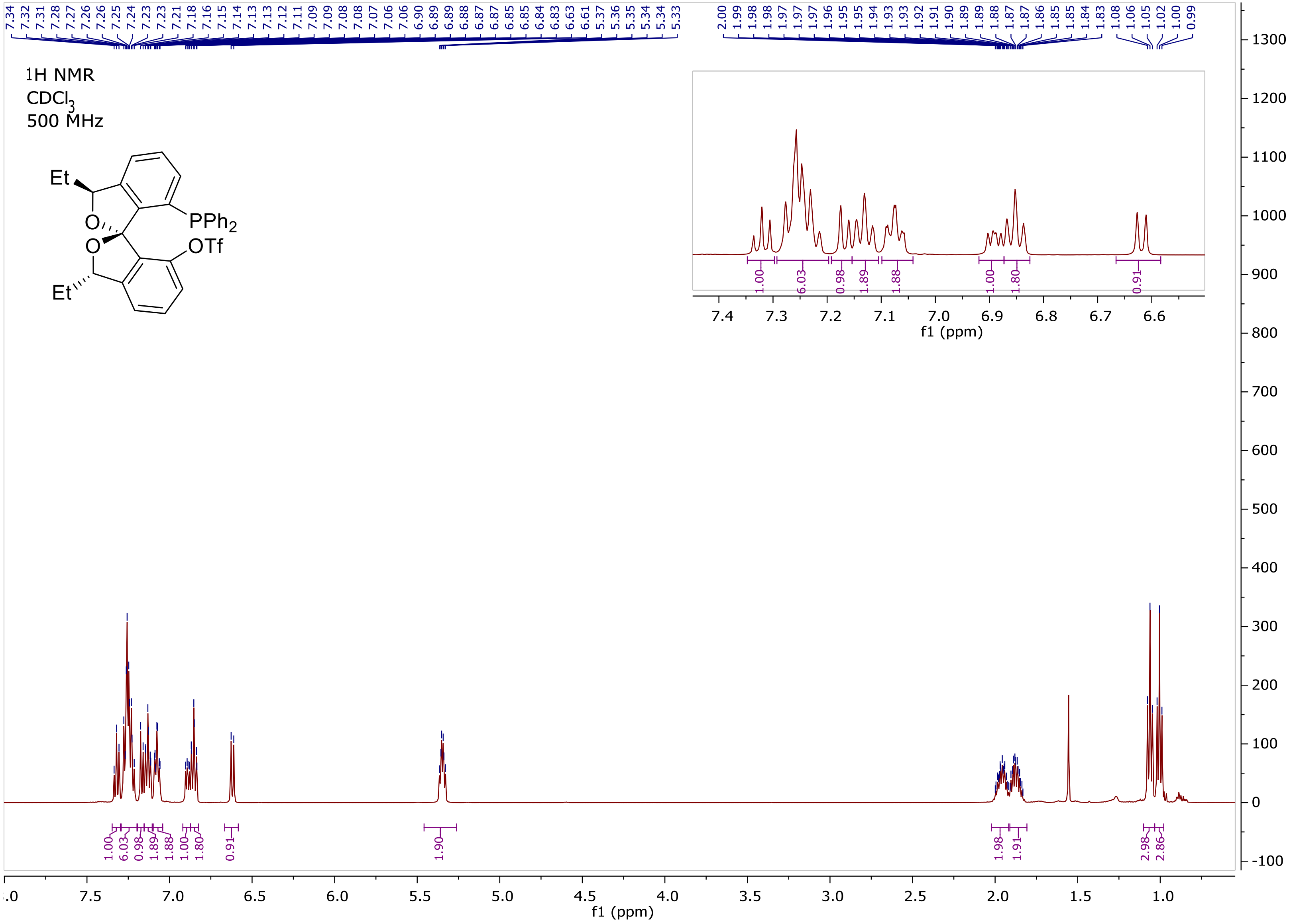

7.49
7.48
7.47
7.47
7.46
7.45
7.44
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.32
7.31
7.30
7.30
7.26
7.17
7.16
7.15
7.13
7.08
7.06
7.05
7.04
5.34
5.33
5.32
5.32
5.16
5.15
5.14
5.13
2.06
2.05
2.05
2.04
2.03
2.02
2.02
2.01
2.00
1.91
1.90
1.88
1.87
1.85
1.73
1.72
1.71
1.71
1.70
1.69
1.69
1.68
1.64
1.54
1.54
1.53
1.52
1.52
1.51
1.50
1.50
1.48
1.09
1.08
1.06
0.55
0.53
0.52
1H NMR
CDCl3
500 MHz
Et
O
O
Et
P(O)Ph2
OTf
13.47
1.94
1.06
0.97
0.96
1.13
1.17
1.04
1.04
3.04
3.00
.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)
400
350
300
250
200
150
100
50
0

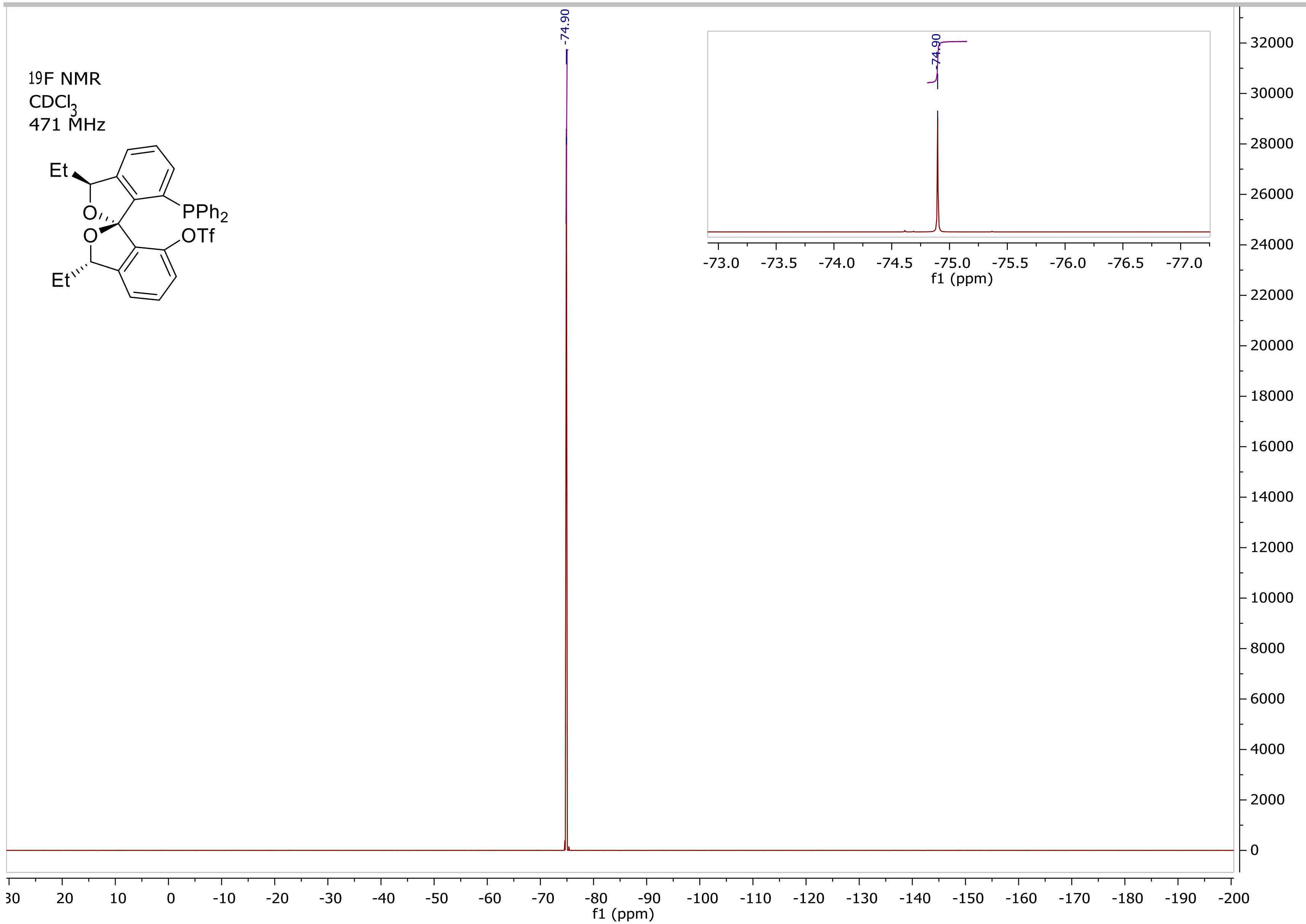

19F NMR
CDCl3
471 MHz
Et
O
O
Et
P(O)Ph2
OTf
-75.08
-75.08
-74.0
-74.4
-74.8
-75.2
-75.6
-76.0
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

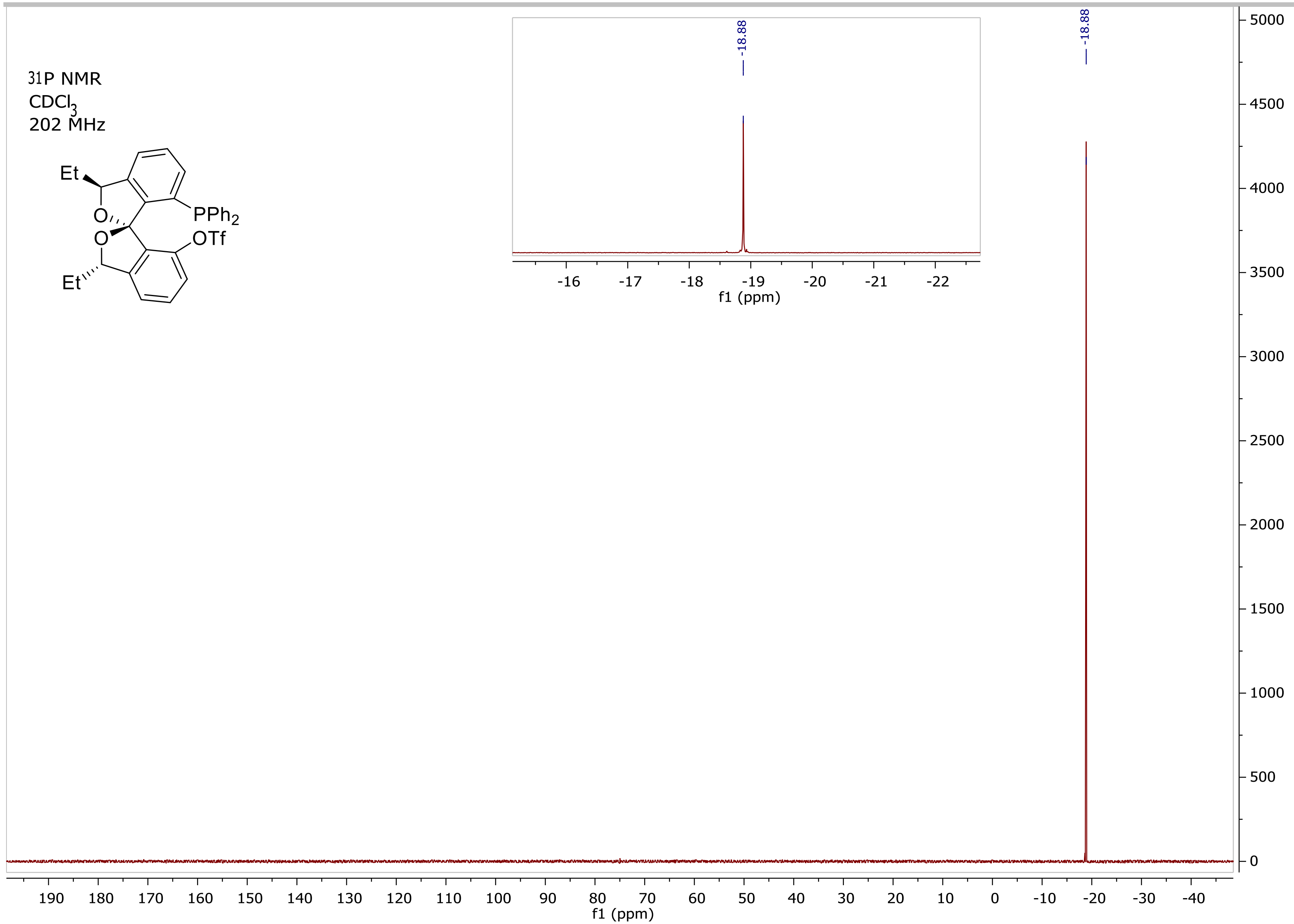

31P NMR
CDCl3
202 MHz
Et
O
O
Et
P(O)Ph2
OTf
29.94
28.46
29.94
28.46
32
31
30
29
28
f1 (ppm)
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

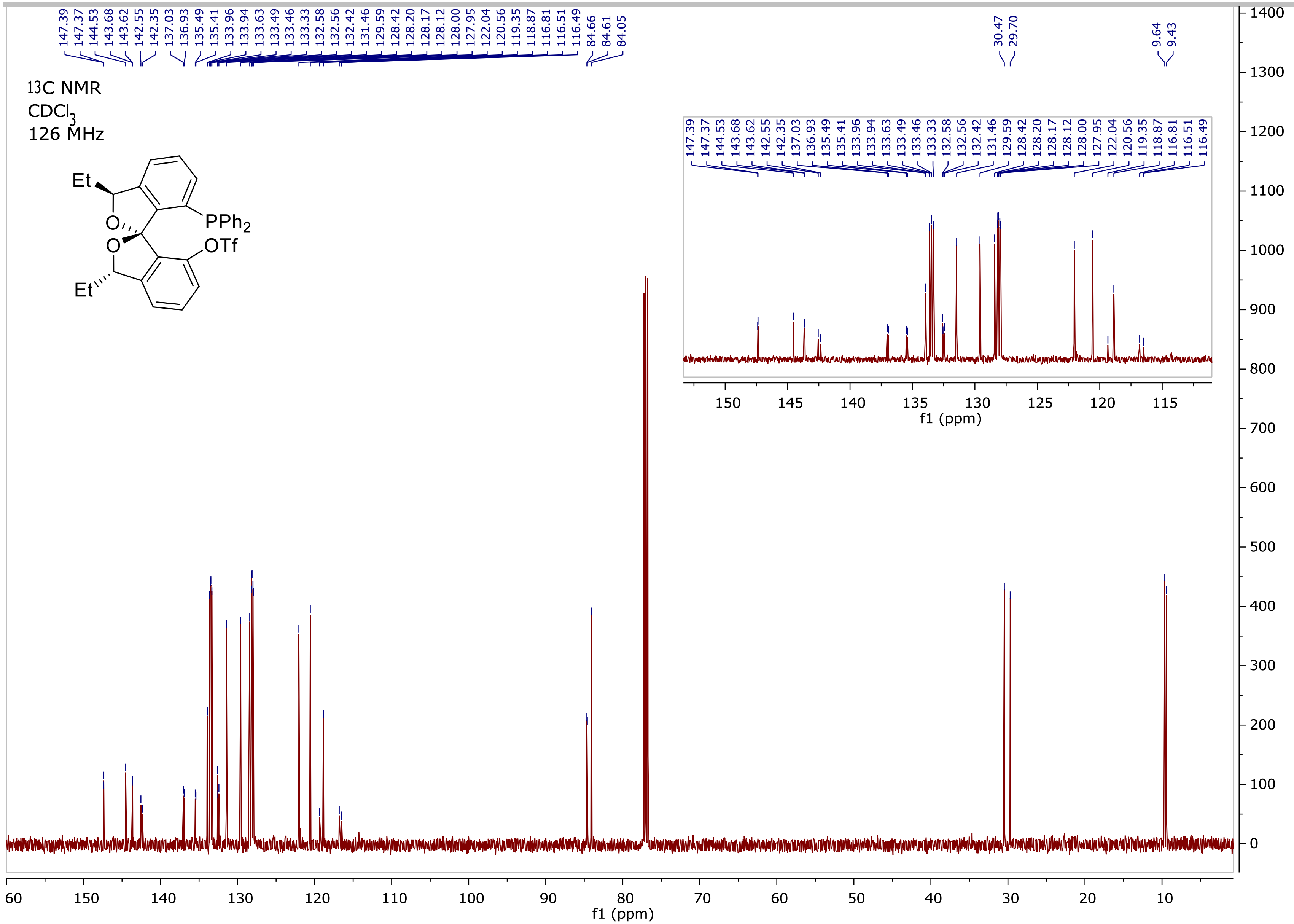

146.94
146.48
146.41
144.30
141.78
141.73
134.73
134.23
134.00
133.89
133.76
133.66
133.17
132.50
132.43
131.93
131.89
131.85
131.47
131.45
131.36
131.34
130.73
128.94
128.85
128.46
128.17
128.08
128.07
127.99
127.65
124.88
124.86
120.06
119.37
118.43
116.83
115.72
84.05
82.47
77.26
77.21
77.00
76.75
27.82
26.88
10.55
10.06
13C NMR
CDCl3
126 MHz
Et
O
O
Et
P(O)Ph2
OTf
145
140
135
130
125
120
115
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0

(*1S,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl trifluoromethanesulfonate ((*S,S,S*)-10)

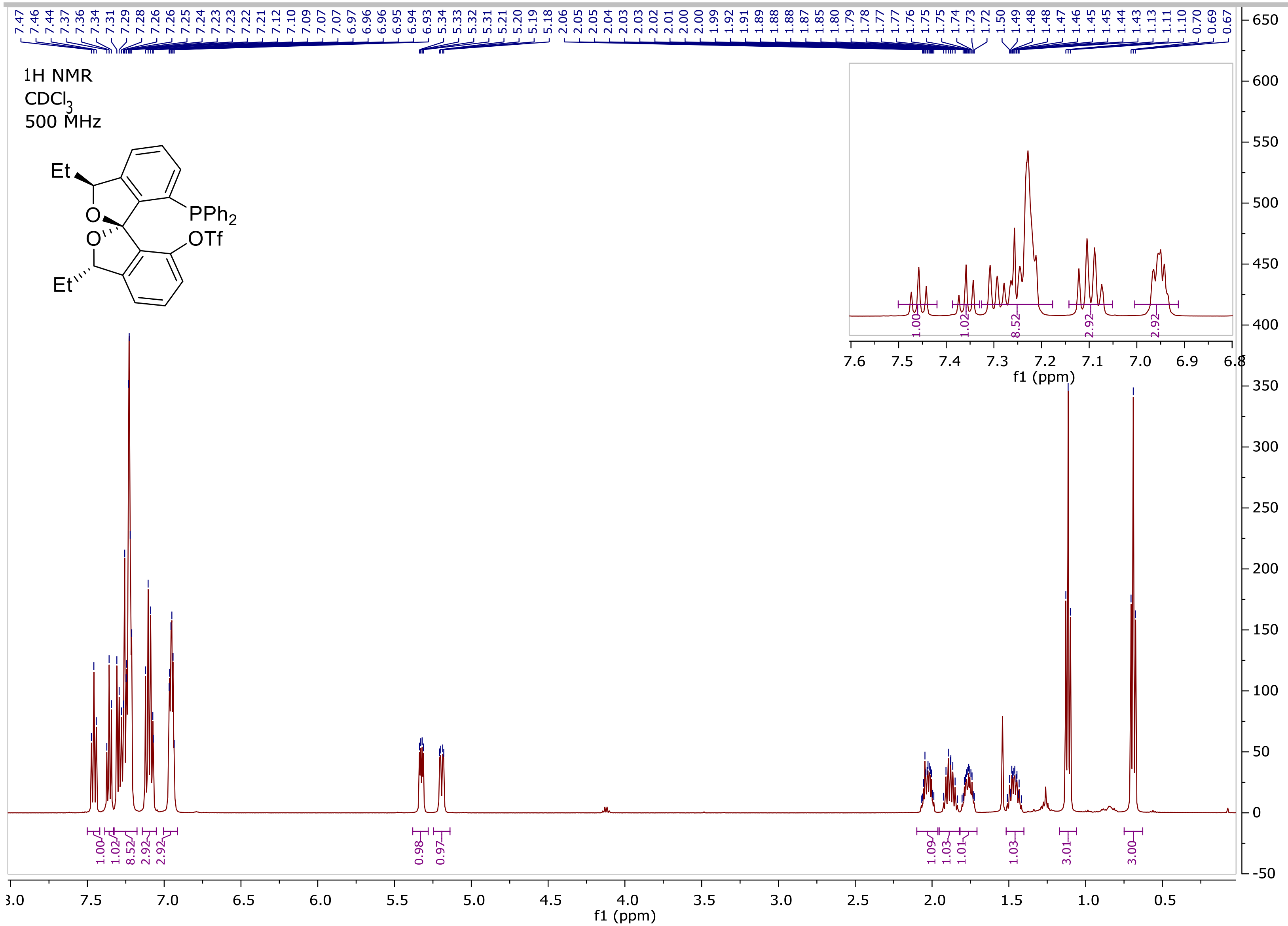


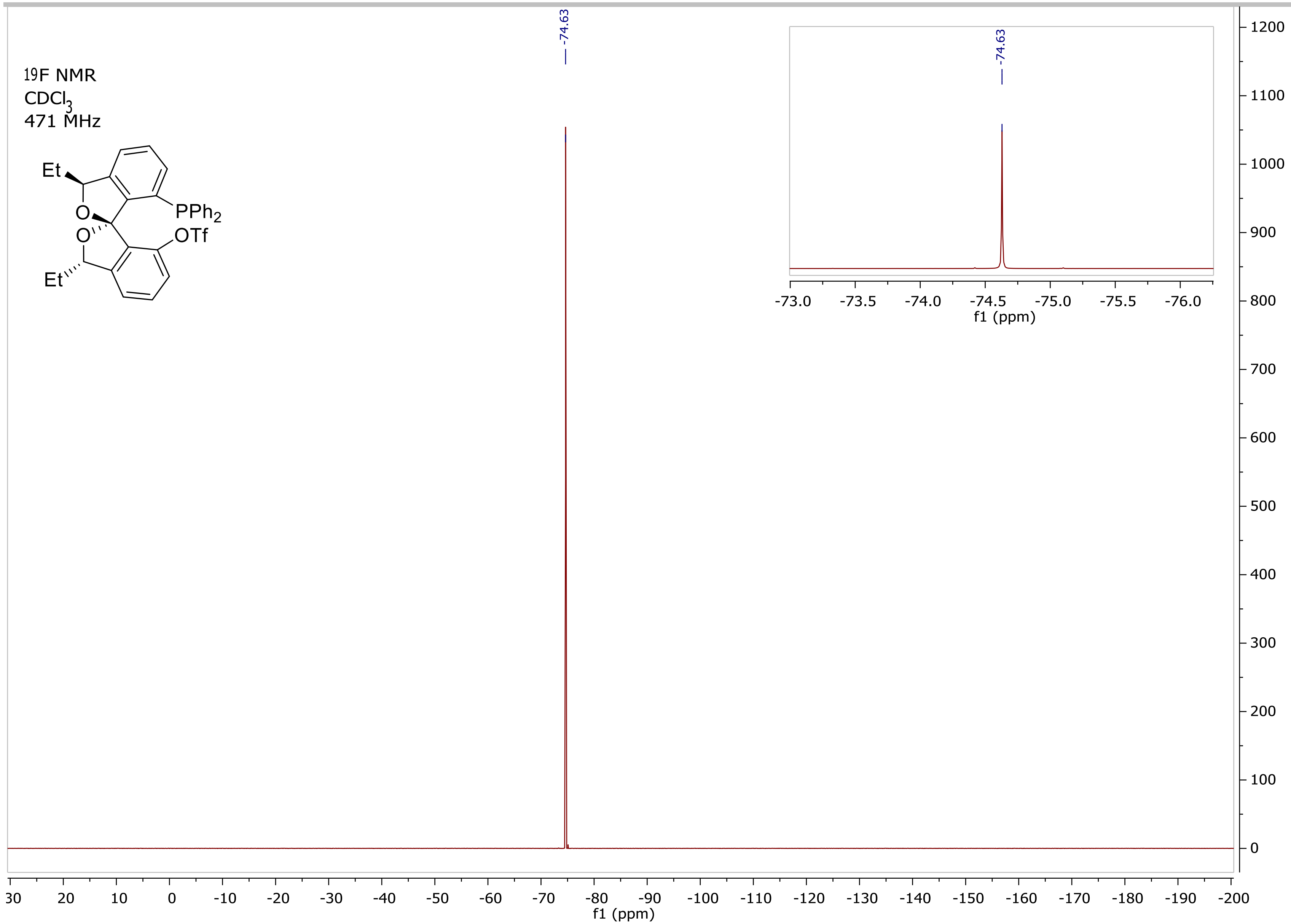

19F NMR
CDCl3
471 MHz
Et
O
O
PPh2
OTf
Et
-74.90
-74.90
-73.0
-73.5
-74.0
-74.5
-75.0
-75.5
-76.0
-76.5
-77.0
f1 (ppm)
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

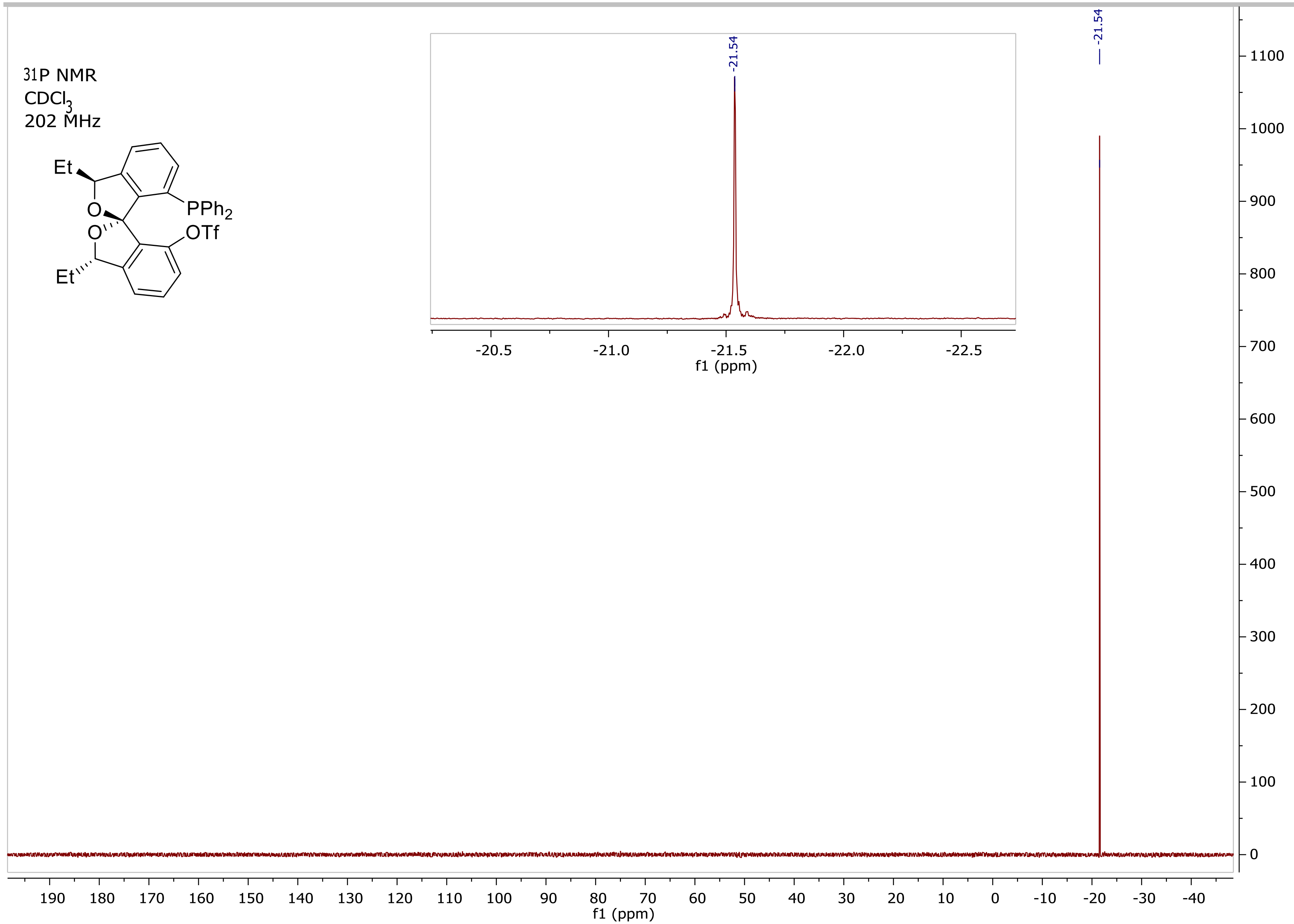

31P NMR
CDCl3
202 MHz
Et
O
O
PPh2
OTf
Et
-18.88
-16
-17
-18
-19
-20
-21
-22
f1 (ppm)
-18.88
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

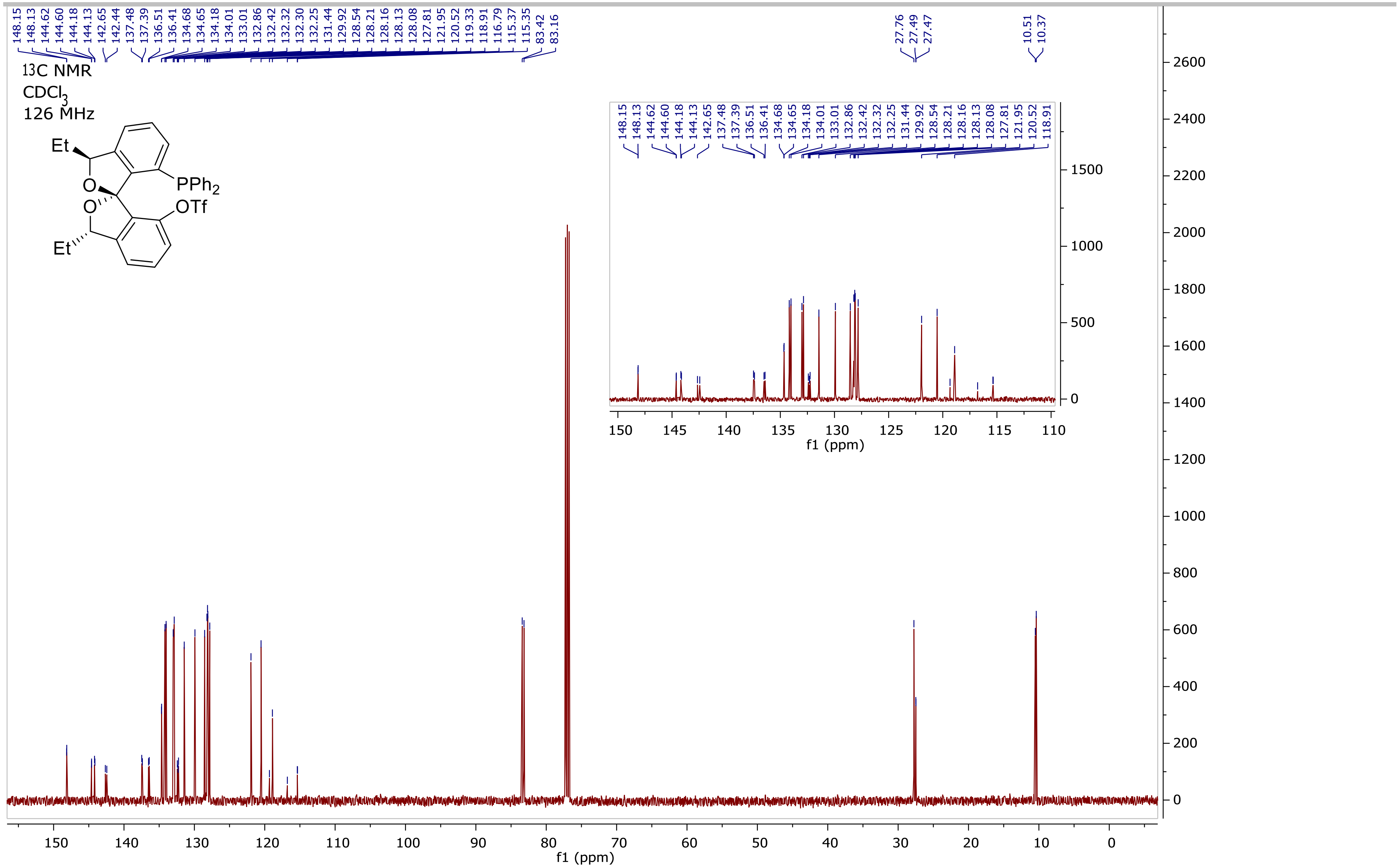


(*1R,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl trifluoromethanesulfonate ((*R,S,S*)-10)

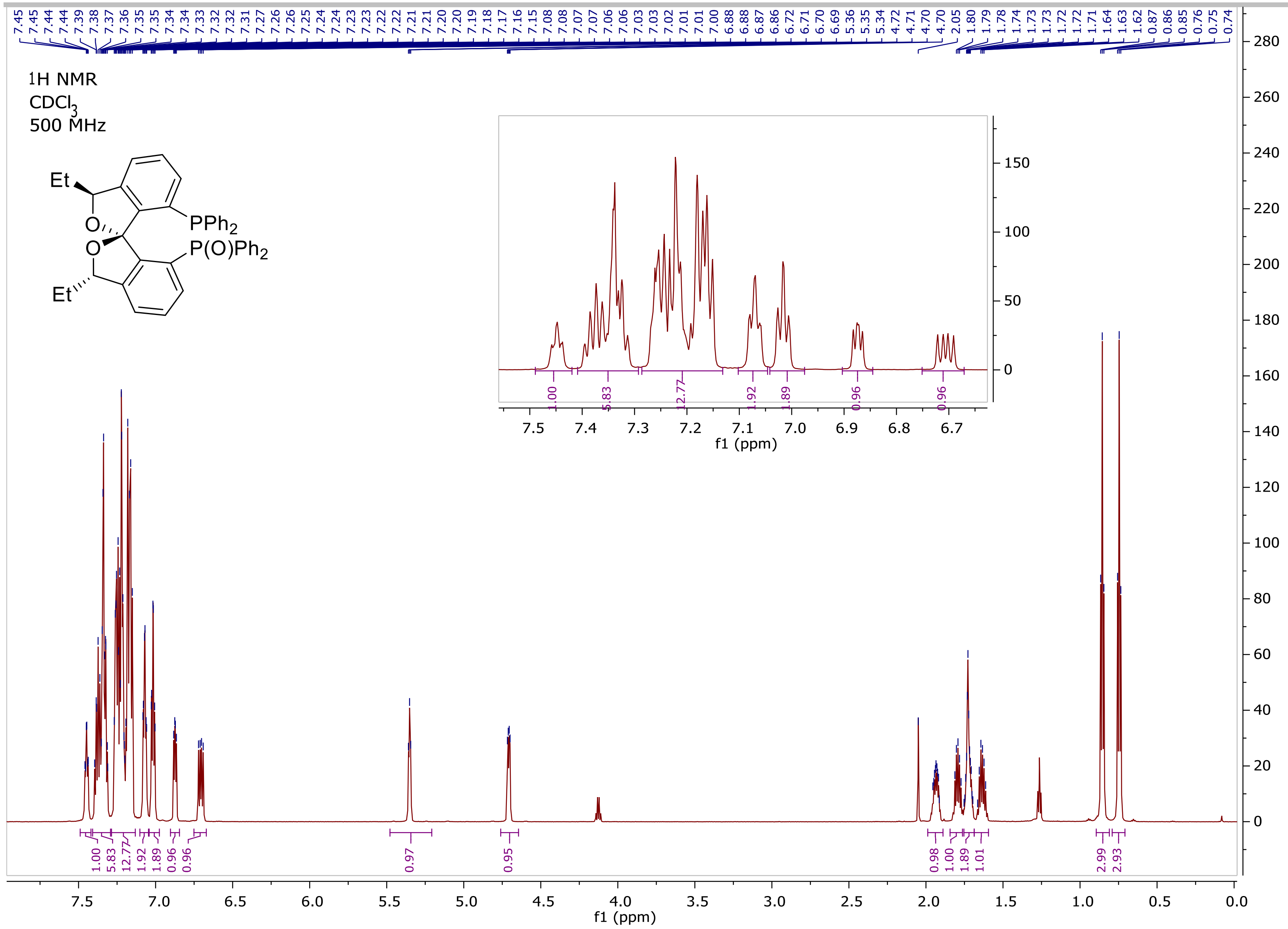

7.47 7.46 7.44 7.37 7.36 7.34 7.31 7.29 7.28 7.26 7.26 7.25 7.24 7.23 7.22 7.21 7.12 7.10 7.09 7.07 7.07 6.97 6.96 6.96 6.95 6.94 6.93 5.34 5.33 5.32 5.31 5.21 5.20 5.19 5.18 2.06 2.05 2.05 2.04 2.03 2.03 2.02 2.01 2.00 2.00 1.99 1.92 1.91 1.89 1.88 1.88 1.87 1.85 1.80 1.79 1.78 1.77 1.76 1.75 1.75 1.74 1.73 1.72 1.50 1.49 1.48 1.47 1.46 1.45 1.45 1.44 1.43 1.13 1.11 1.10 0.70 0.69 0.67
1H NMR
CDCl3
500 MHz
Et
O
O
PPh2
OTf
Et
1.00 1.02 8.52 2.92 2.92
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.00 1.02 8.52 2.92 2.92 0.98 0.97 1.09 1.03 1.01 1.03 3.01 3.00
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
f1 (ppm)
650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50

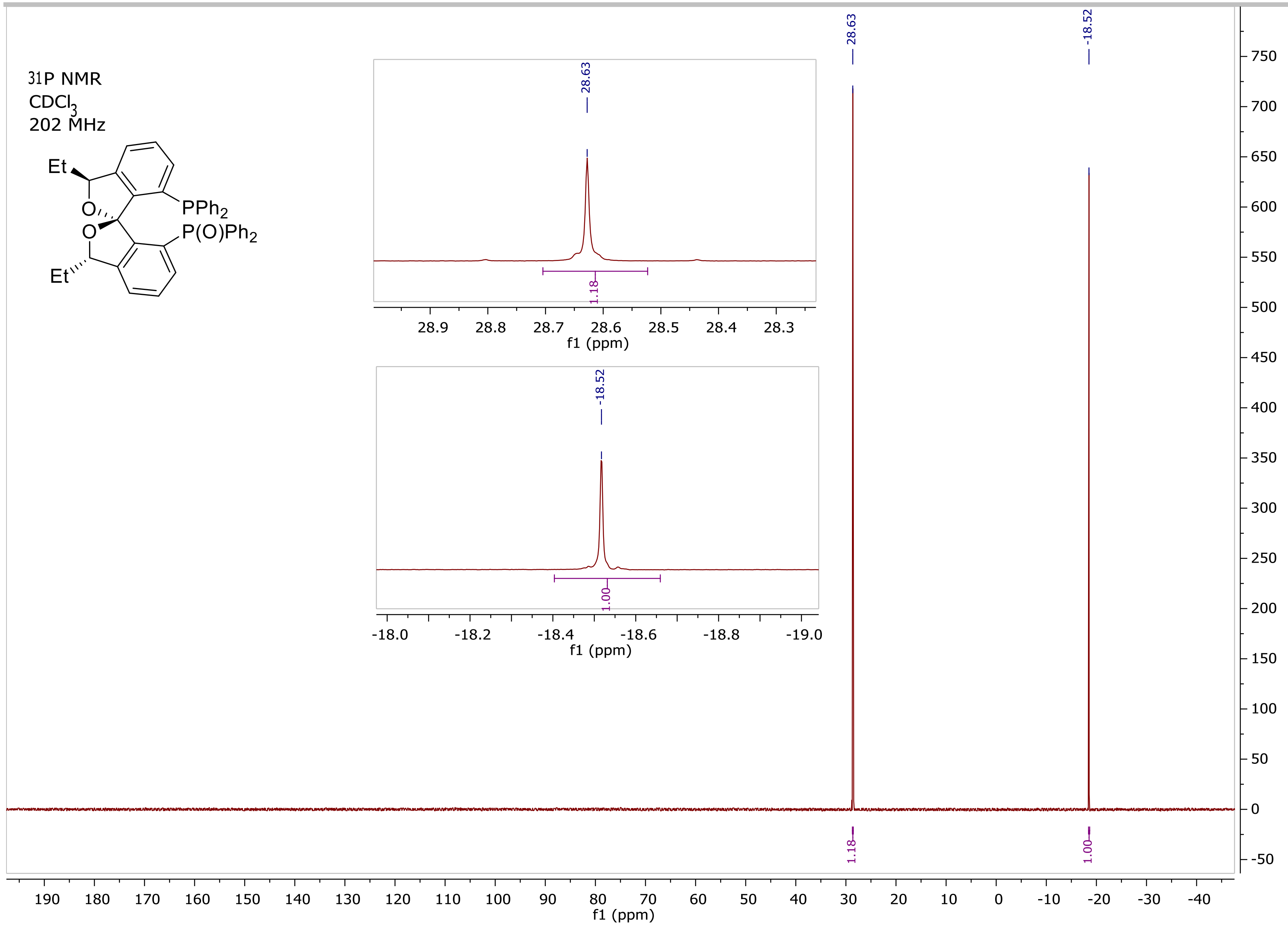

19F NMR
CDCl3
471 MHz
Et
O
O
Et
PPh2
OTf
-74.63
-74.63
-73.0
-73.5
-74.0
-74.5
-75.0
-75.5
-76.0
f1 (ppm)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

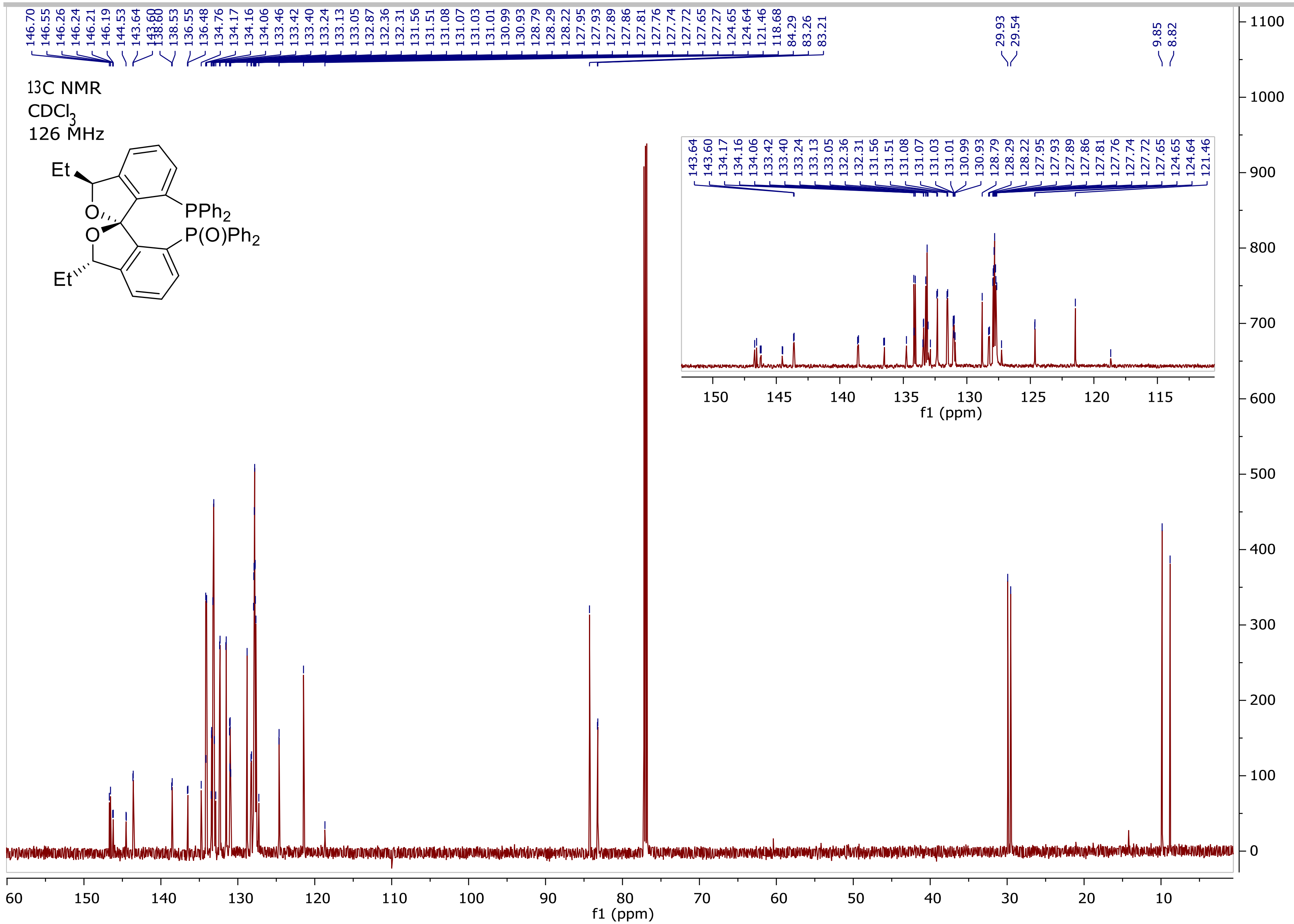

31P NMR
CDCl3
202 MHz
Et
O
O
PPh2
OTf
Et
-21.54
-20.5
-21.0
-21.5
-22.0
-22.5
f1 (ppm)
-21.54
1100
1000
900
800
700
600
500
400
300
200
100
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)



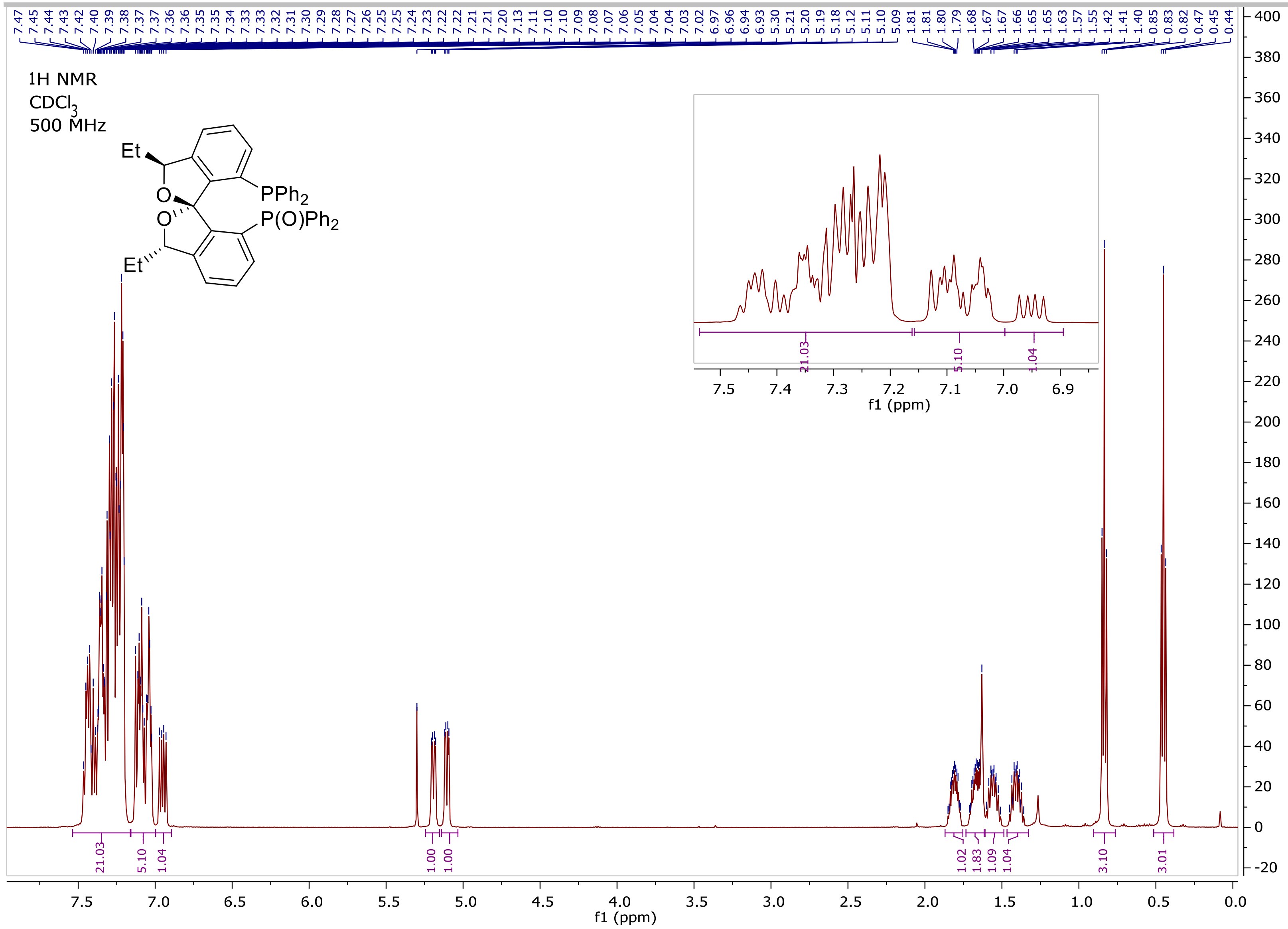
((*1S,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl)diphenylphosphine oxide ((*S,S,S*)-SPIRAP(O))

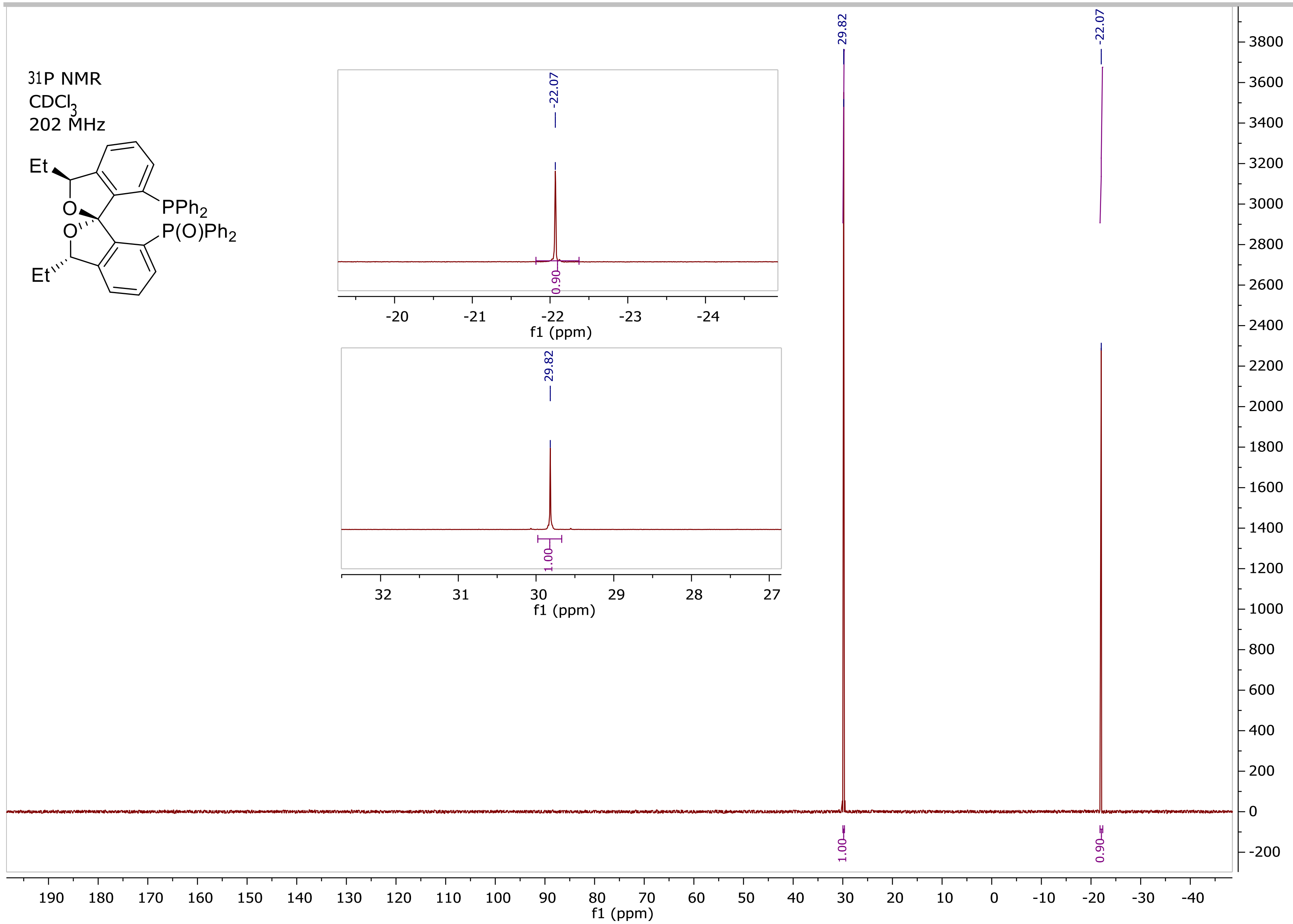

7.45 7.45 7.44 7.44 7.39 7.38 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.27 7.26 7.26 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.17 7.16 7.15 7.08 7.08 7.07 7.07 7.06 7.06 7.03 7.03 7.02 7.01 7.01 7.00 6.88 6.88 6.87 6.86 6.72 6.71 6.70 6.69 5.36 5.35 5.34 4.72 4.71 4.70 4.70 2.05 1.80 1.79 1.78 1.74 1.73 1.73 1.72 1.72 1.71 1.64 1.63 1.62 0.87 0.86 0.85 0.76 0.75 0.74
1H NMR
CDCl3
500 MHz
Et
O
O
PPh2
P(O)Ph2
Et
1.00 5.83 12.77 1.92 1.89 0.96 0.96
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
0 50 100 150
1.00 5.83 12.77 1.92 1.89 0.96 0.96 0.97 0.95 0.98 1.00 1.89 1.01 2.99 2.93
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)
280 260 240 220 200 180 160 140 120 100 80 60 40 20 0

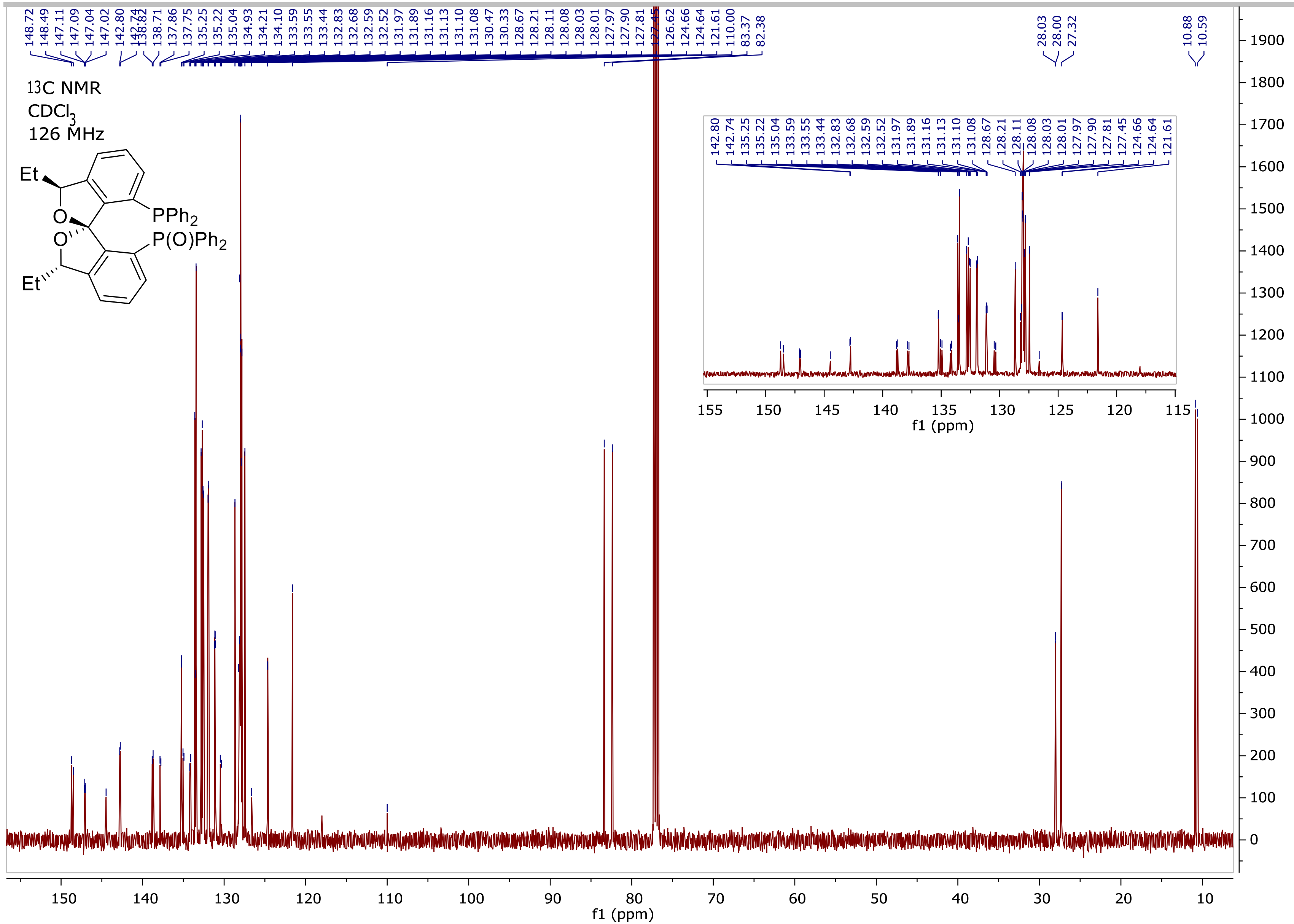

31P NMR
CDCl3
202 MHz
Et
O
O
Et
PPh2
P(O)Ph2
28.63
1.18
28.9
28.8
28.7
28.6
28.5
28.4
28.3
f1 (ppm)
-18.52
1.00
-18.0
-18.2
-18.4
-18.6
-18.8
-19.0
f1 (ppm)
28.63
-18.52
1.18
1.00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50



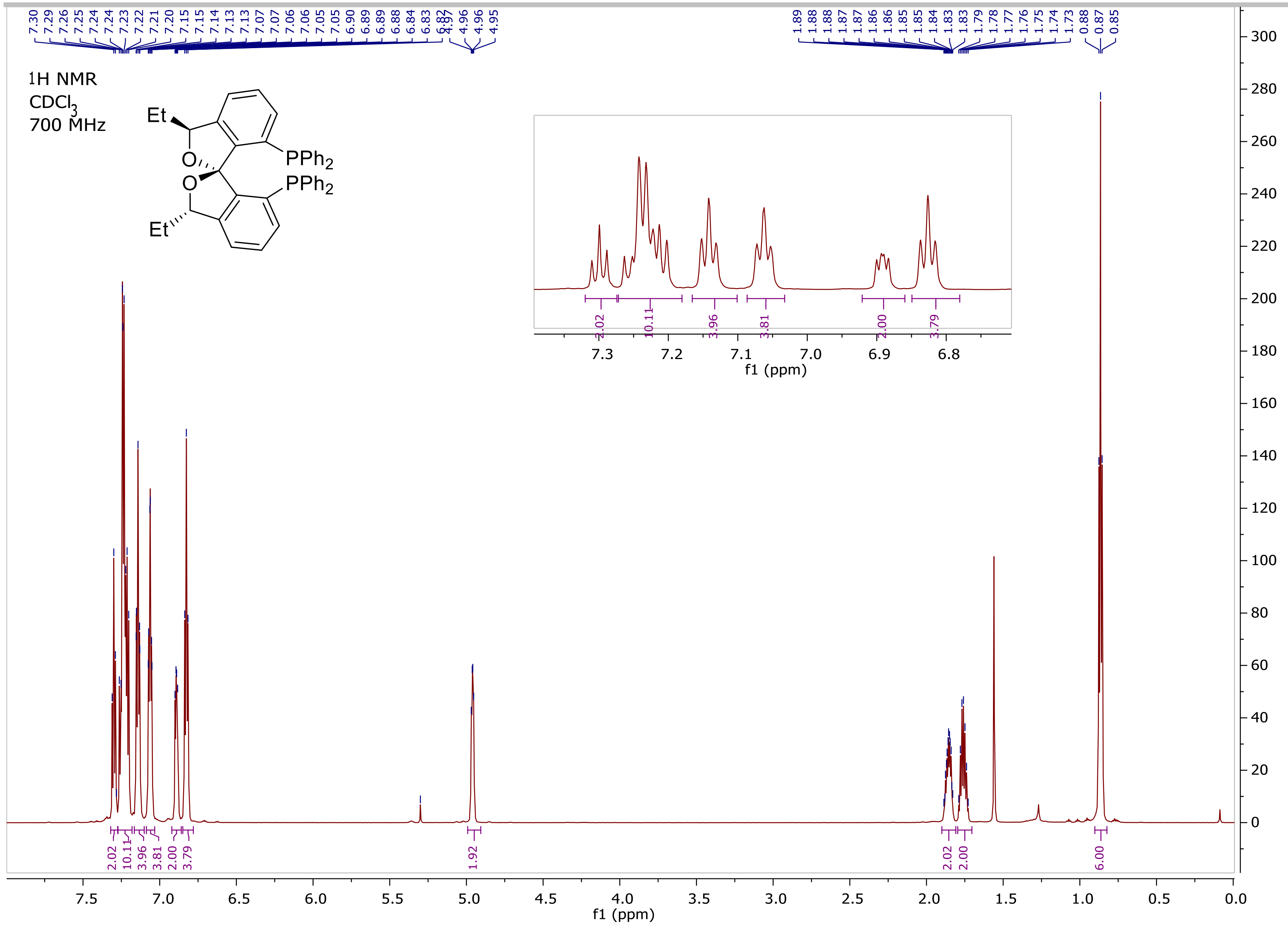
((*1R,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-yl)diphenylphosphine oxide ((*R,S,S*)-SPIRAP(O)

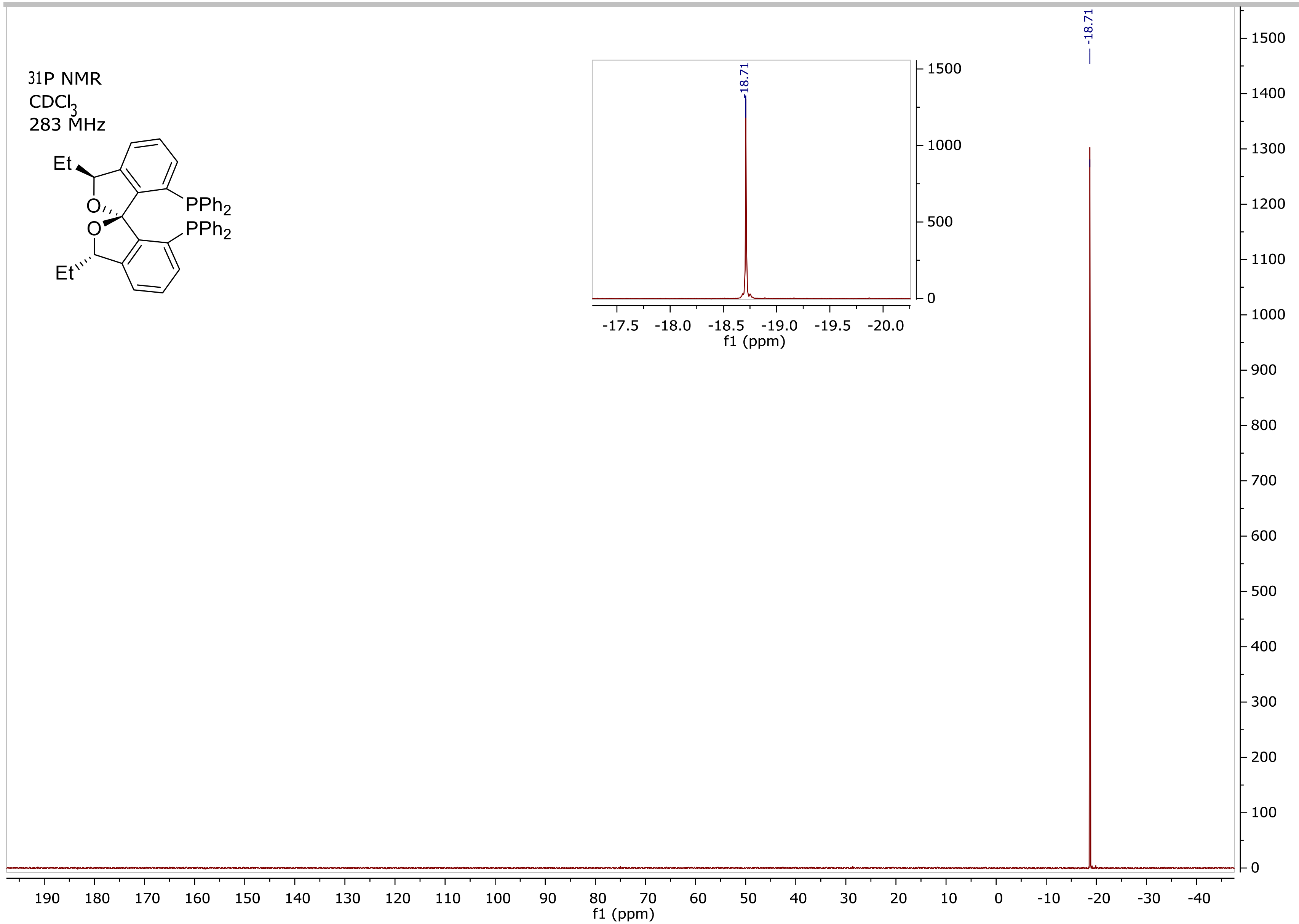

1H NMR
CDCl3
500 MHz
Et
O
O
Et
PPh2
P(O)Ph2
7.47
7.45
7.44
7.43
7.42
7.40
7.39
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.21
7.21
7.20
7.13
7.11
7.10
7.10
7.09
7.08
7.07
7.06
7.05
7.04
7.04
7.03
7.02
6.97
6.96
6.94
6.93
5.30
5.21
5.20
5.19
5.18
5.12
5.11
5.10
5.09
1.81
1.81
1.80
1.79
1.68
1.67
1.67
1.66
1.65
1.65
1.63
1.57
1.55
1.42
1.41
1.40
0.85
0.83
0.82
0.47
0.45
0.44
21.03
5.10
1.04
1.00
1.00
1.02
1.83
1.09
1.04
3.10
3.01
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
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)
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

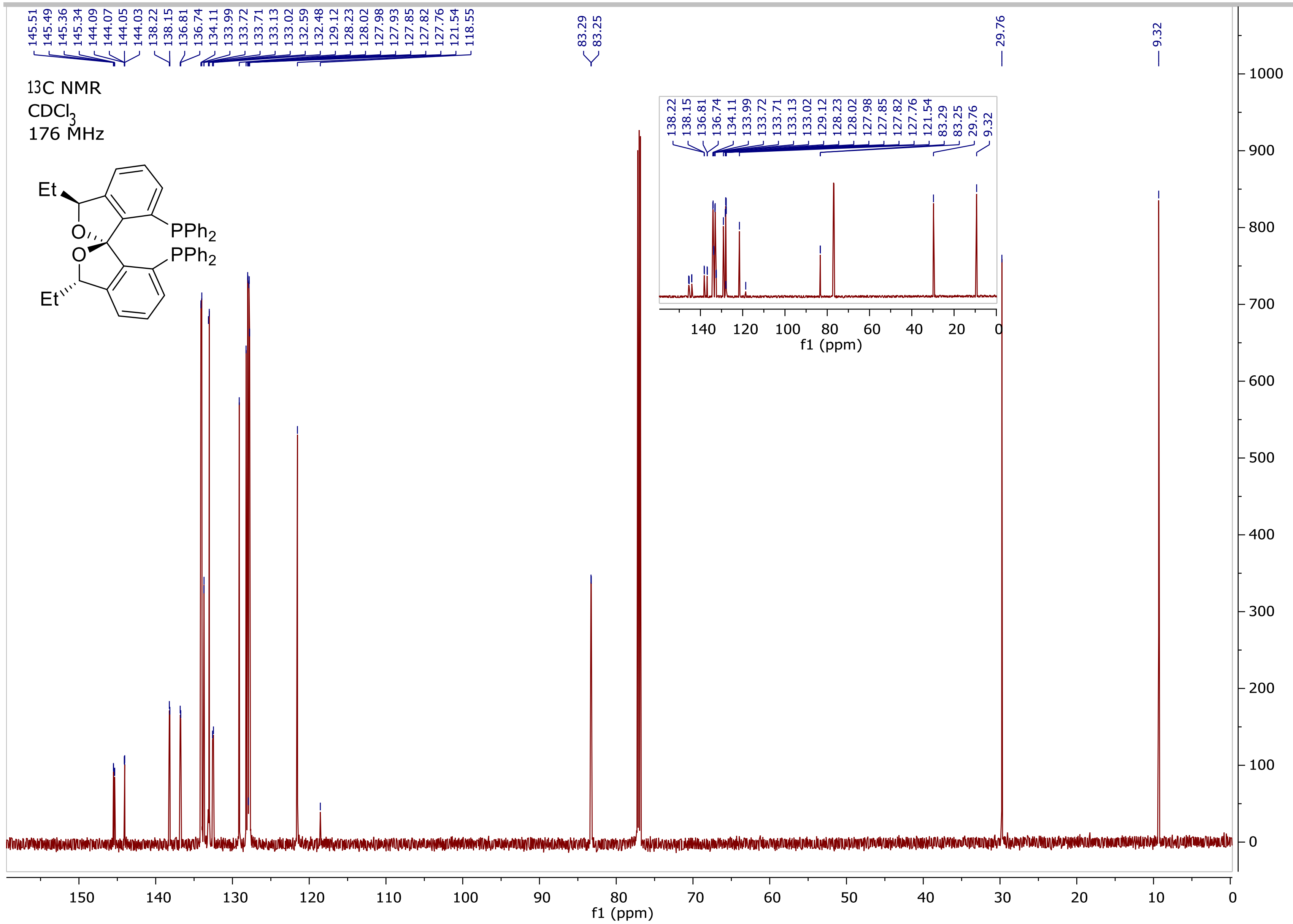

31P NMR
CDCl3
202 MHz
Et
O
O
PPh2
P(O)Ph2
Et
-22.07
0.90
-20
-21
-22
-23
-24
f1 (ppm)
29.82
1.00
32
31
30
29
28
27
f1 (ppm)
29.82
-22.07
1.00
0.90
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)



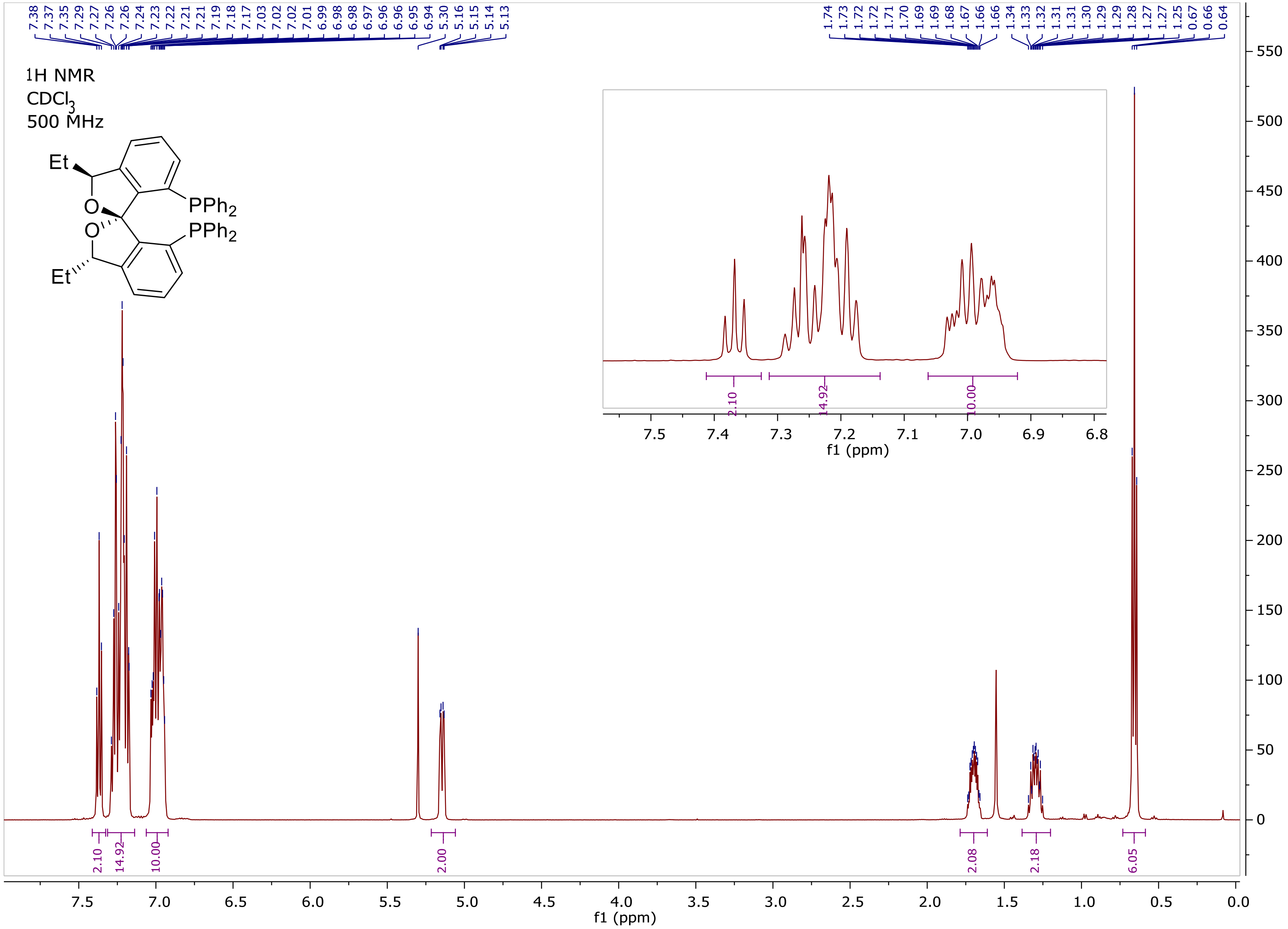
((*1S,3S,3′S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(diphenylphosphane) ((*S,S,S*)-SPIRAP)

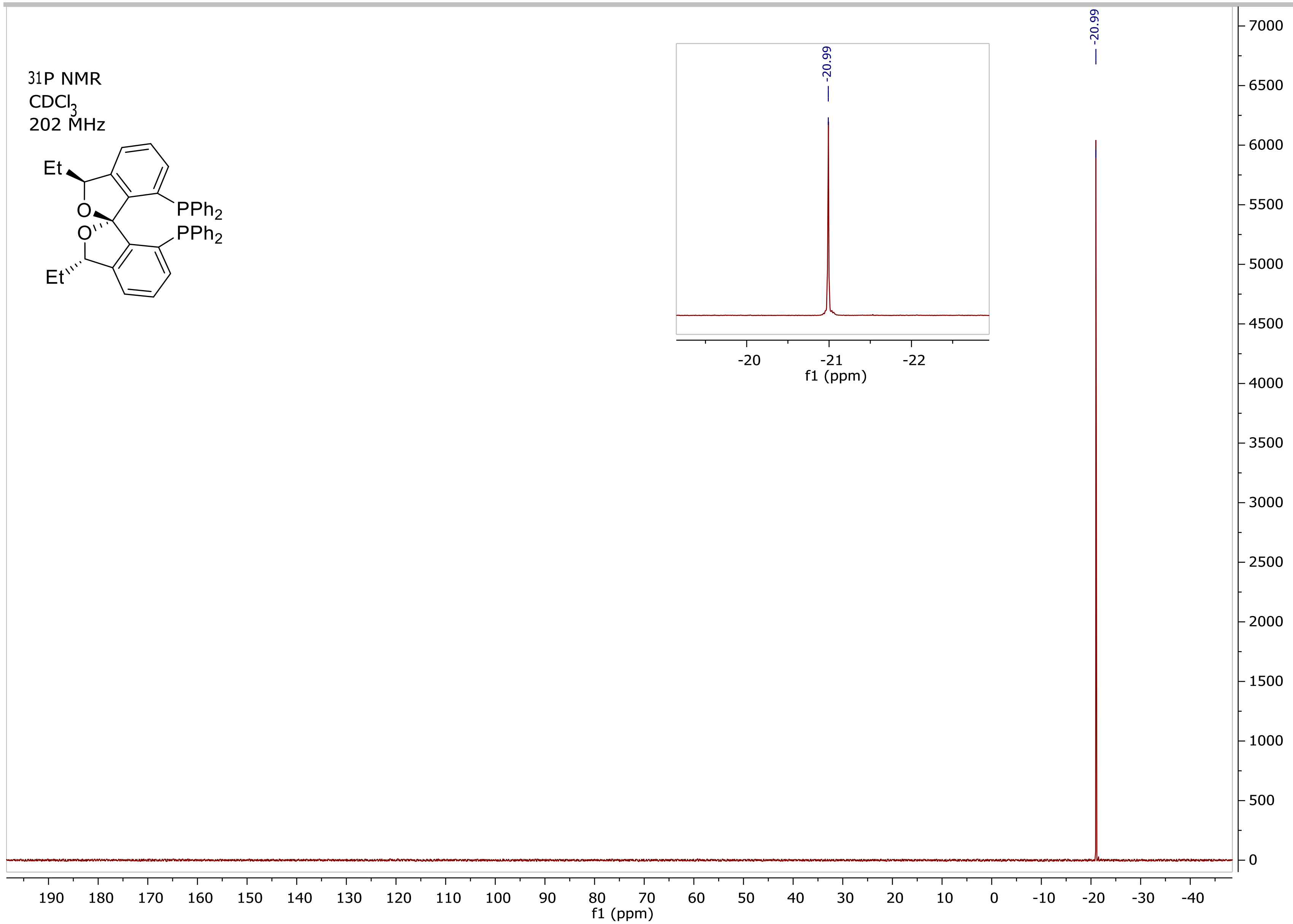

7.30 7.29 7.26 7.25 7.24 7.24 7.23 7.22 7.21 7.20 7.15 7.15 7.14 7.13 7.13 7.07 7.07 7.06 7.06 7.05 6.90 6.89 6.89 6.88 6.84 6.83 6.82 4.97 4.96 4.96 4.95
1.89 1.88 1.88 1.87 1.87 1.86 1.86 1.85 1.85 1.84 1.83 1.83 1.79 1.78 1.77 1.76 1.75 1.74 1.73 0.88 0.87 0.85
1H NMR
CDCl3
700 MHz
Et
O
O
PPh2
PPh2
Et
2.02
10.11
3.96
3.81
2.00
3.79
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
1.92
2.02
2.00
6.00
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
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)

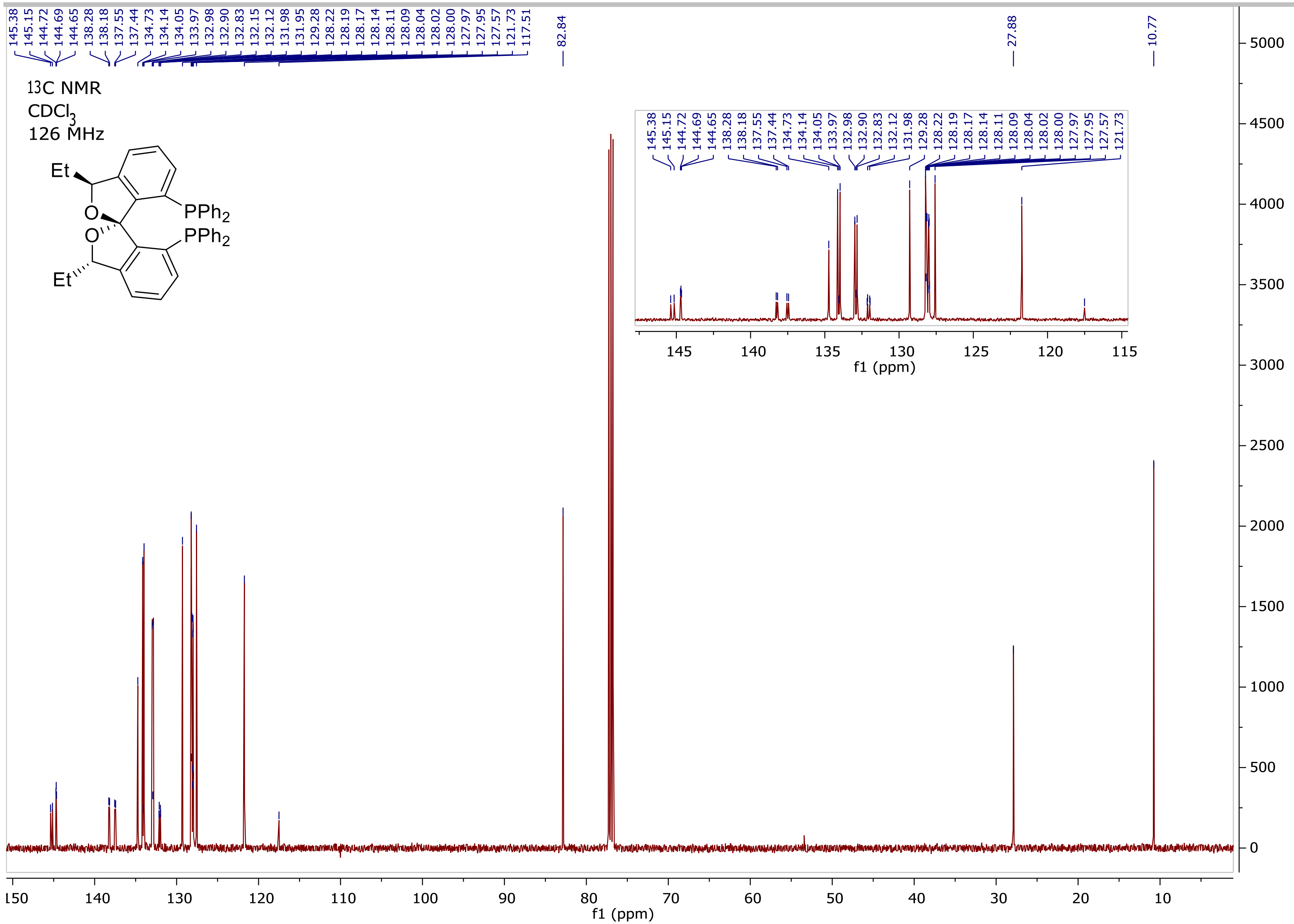

31P NMR
CDCl3
283 MHz
Et
O
O
Et
PPh2
PPh2
-18.71
-18.71
-17.5 -18.0 -18.5 -19.0 -19.5 -20.0
f1 (ppm)
0
500
1000
1500
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500


145.51
145.49
145.36
145.34
144.09
144.07
144.05
144.03
138.22
138.15
136.81
136.74
134.11
133.99
133.72
133.71
133.13
133.02
132.59
132.48
129.12
128.23
128.02
127.98
127.93
127.85
127.82
127.76
121.54
118.55
83.29
83.25
29.76
9.32
13C NMR
CDCl3
176 MHz
Et
O
O
PPh2
PPh2
Et
138.22
138.15
136.81
136.74
134.11
133.99
133.72
133.71
133.13
133.02
129.12
128.23
128.02
127.98
127.85
127.82
127.76
121.54
83.29
83.25
29.76
9.32
140 120 100 80 60 40 20 0
f1 (ppm)
1000
900
800
700
600
500
400
300
200
100
0
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

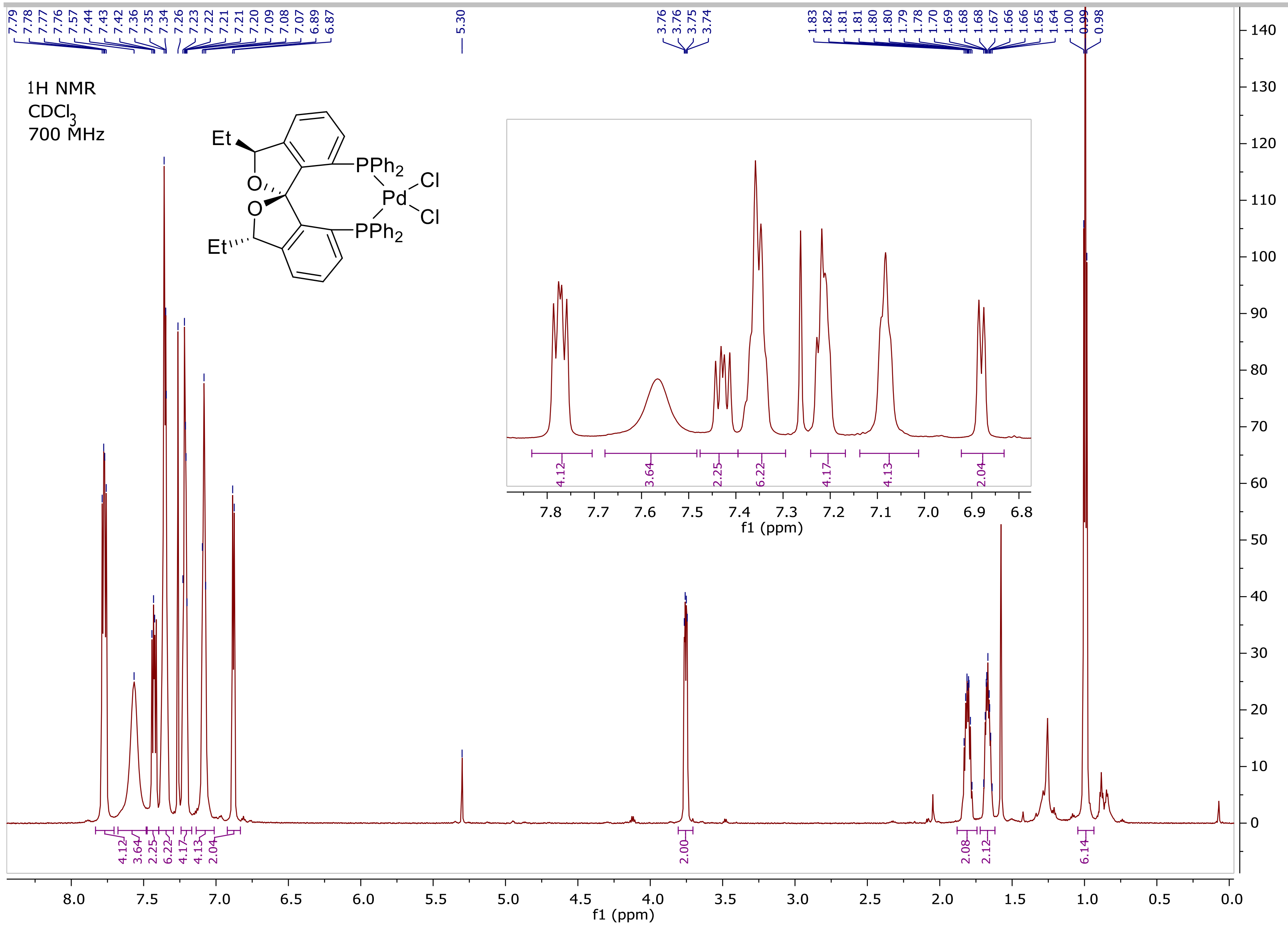
((*1R,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(diphenylphosphane) ((*R,S,S*)-SPIRAP)

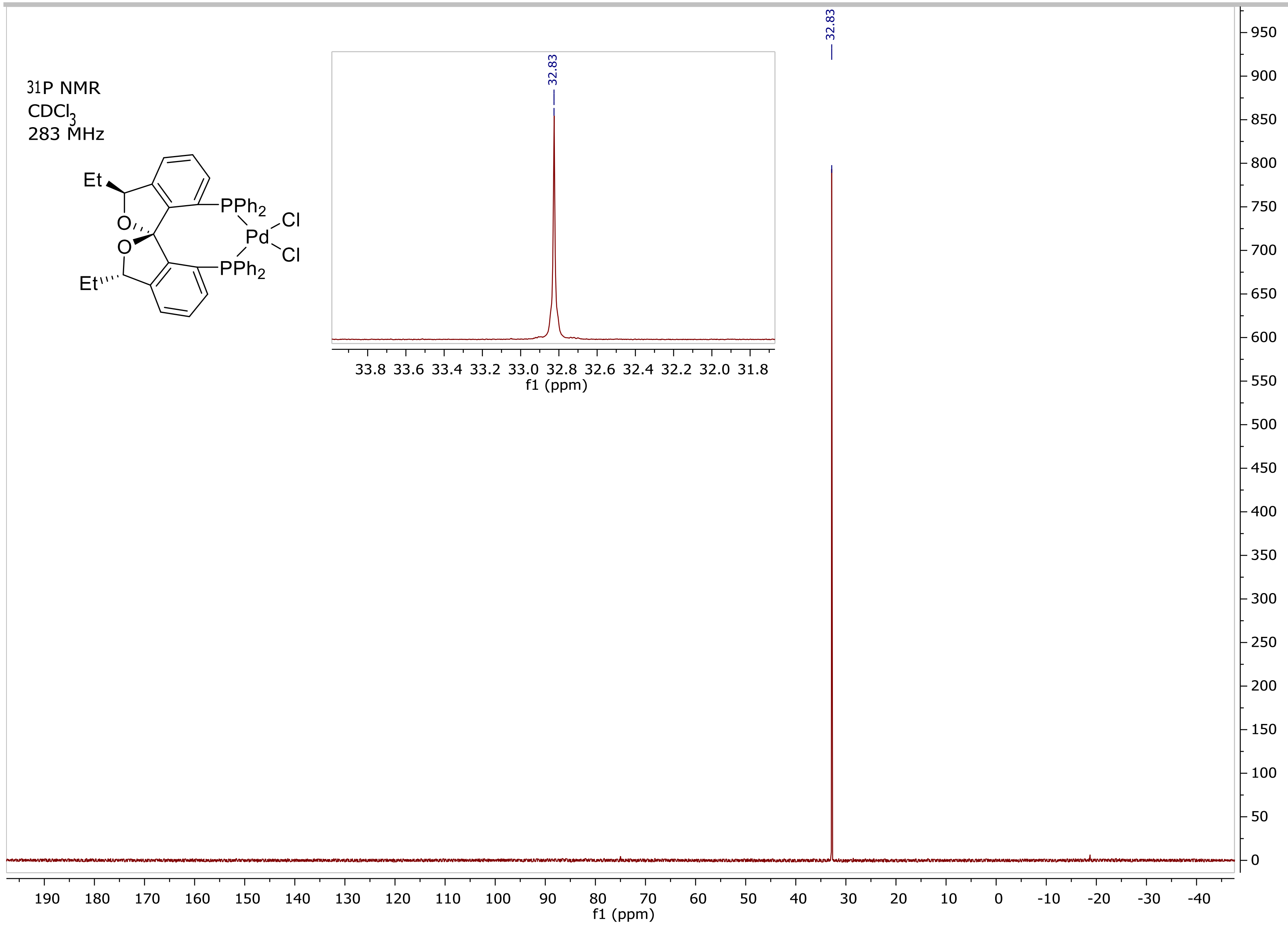


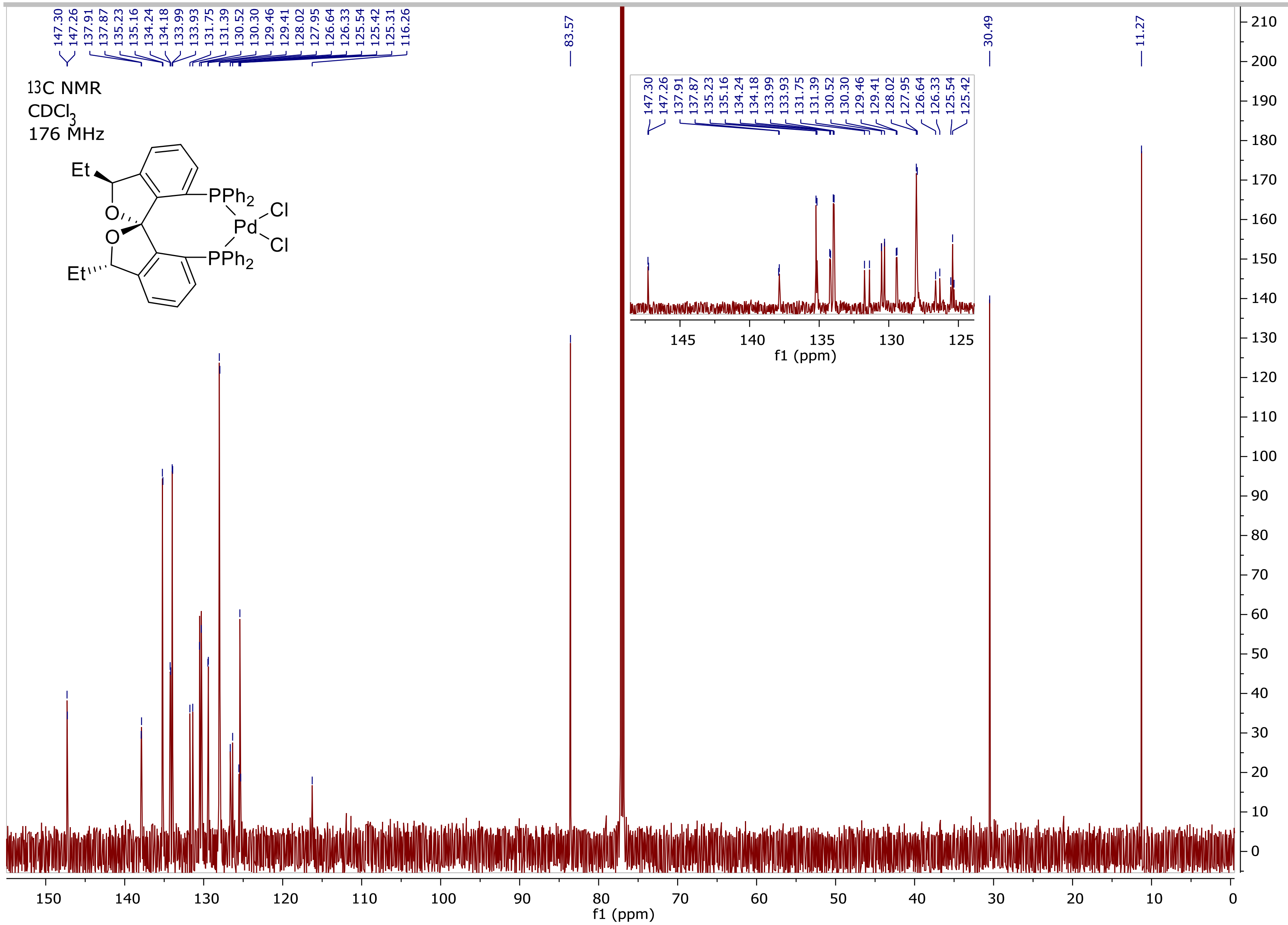

31P NMR
CDCl3
202 MHz
Et
O
O
PPh2
PPh2
Et
-20.99
-20.99
-20
-21
-22
f1 (ppm)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)



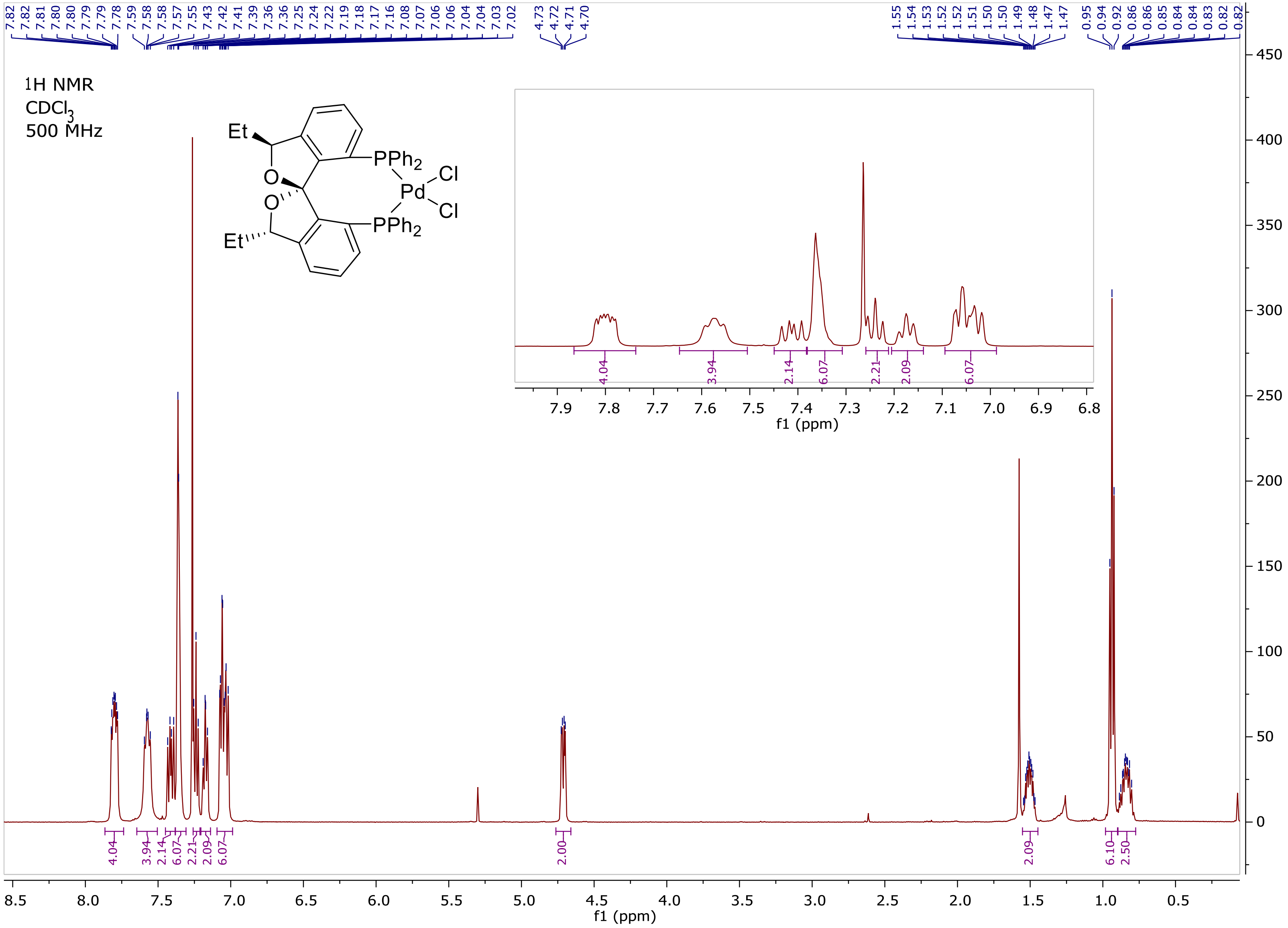
[((1*S*,3*S*,3'*S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(diphenylphosphane)]palladium(II) chloride ((*S*,*S*,*S*)-11)

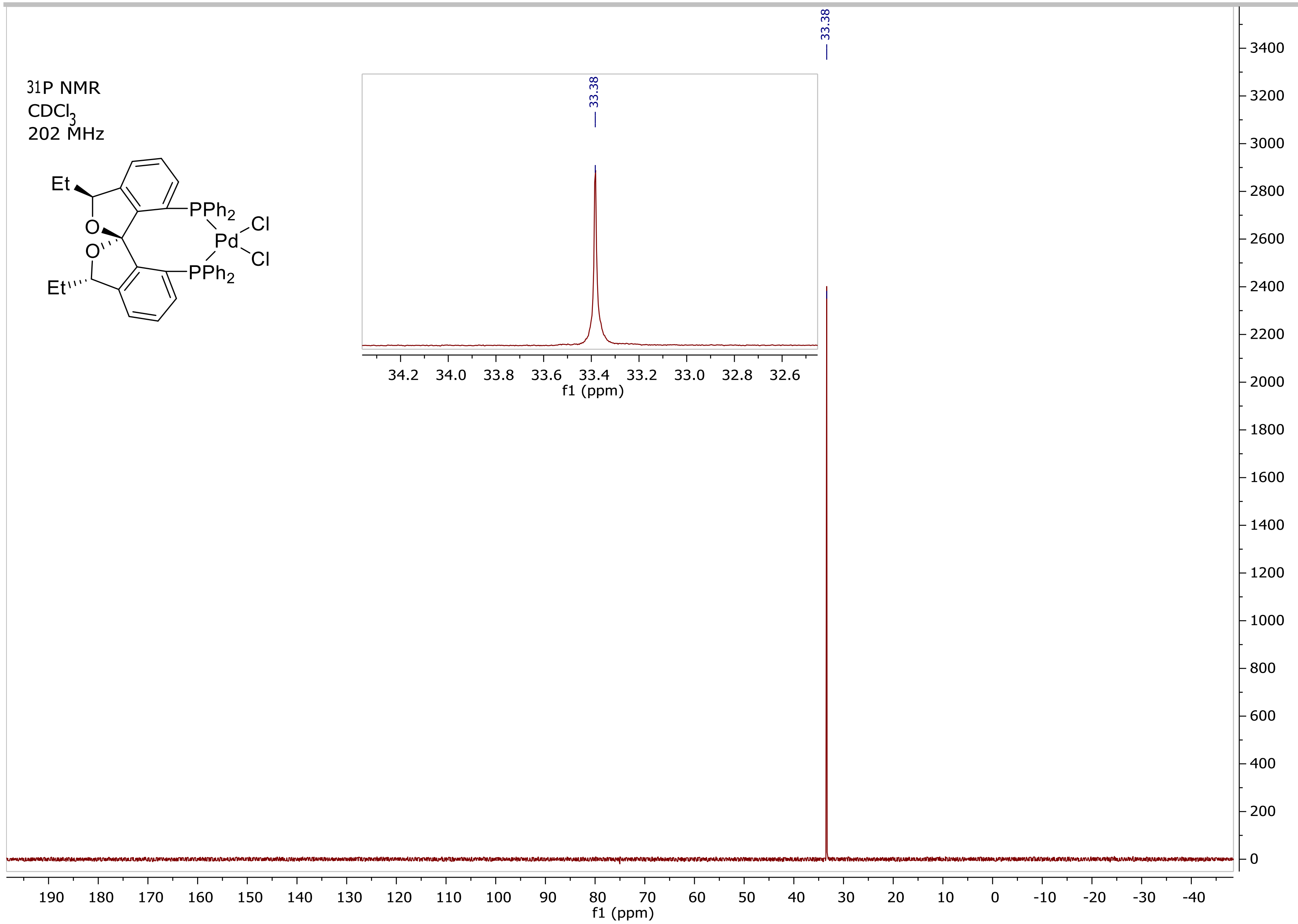

7.79
7.78
7.77
7.76
7.57
7.44
7.43
7.42
7.36
7.35
7.34
7.26
7.23
7.22
7.21
7.21
7.20
7.09
7.08
7.07
6.89
6.87
5.30
3.76
3.76
3.75
3.74
1.83
1.82
1.81
1.81
1.80
1.80
1.79
1.78
1.70
1.69
1.68
1.68
1.67
1.66
1.66
1.65
1.64
1.00
0.99
0.98
1H NMR
CDCl3
700 MHz
Et
O
O
Et
PPh2
PPh2
Pd
Cl
Cl
4.12
3.64
2.25
6.22
4.17
4.13
2.04
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
2.00
2.08
2.12
6.14
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)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

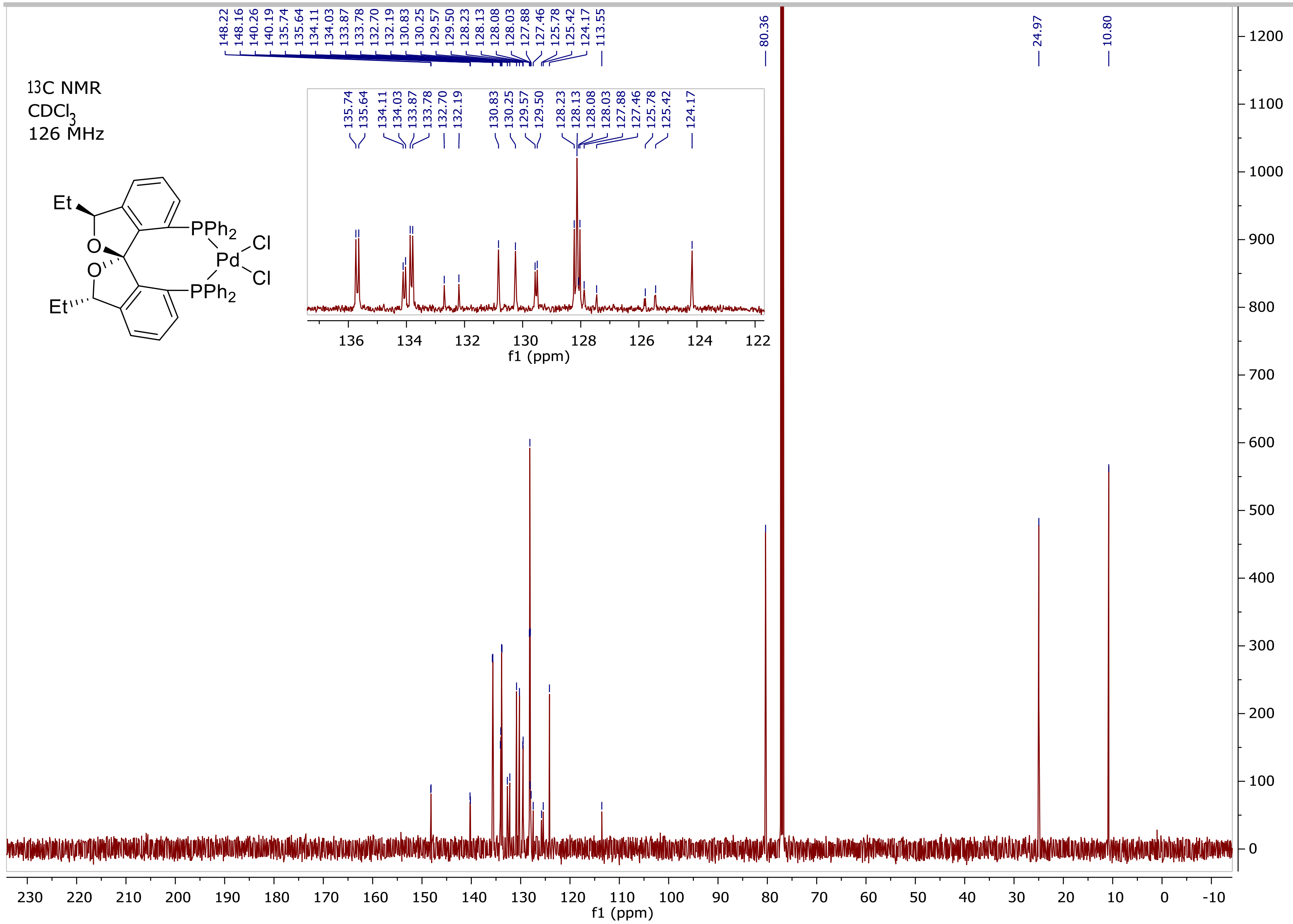

31P NMR
$CDCl_3$
283 MHz
Et
Et
O
O
PPh_2
PPh_2
Pd
Cl
Cl
32.83
32.83
33.8 33.6 33.4 33.2 33.0 32.8 32.6 32.4 32.2 32.0 31.8
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)
950 900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0


147.30
147.26
137.91
137.87
135.23
135.16
134.24
134.18
133.99
133.93
131.75
131.39
130.52
130.30
129.46
129.41
128.02
127.95
126.64
126.33
125.54
125.42
125.31
116.26
83.57
30.49
11.27
13C NMR
CDCl3
176 MHz
Et
O
O
Et
PPh2
PPh2
Pd
Cl
Cl
145
140
135
130
125
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

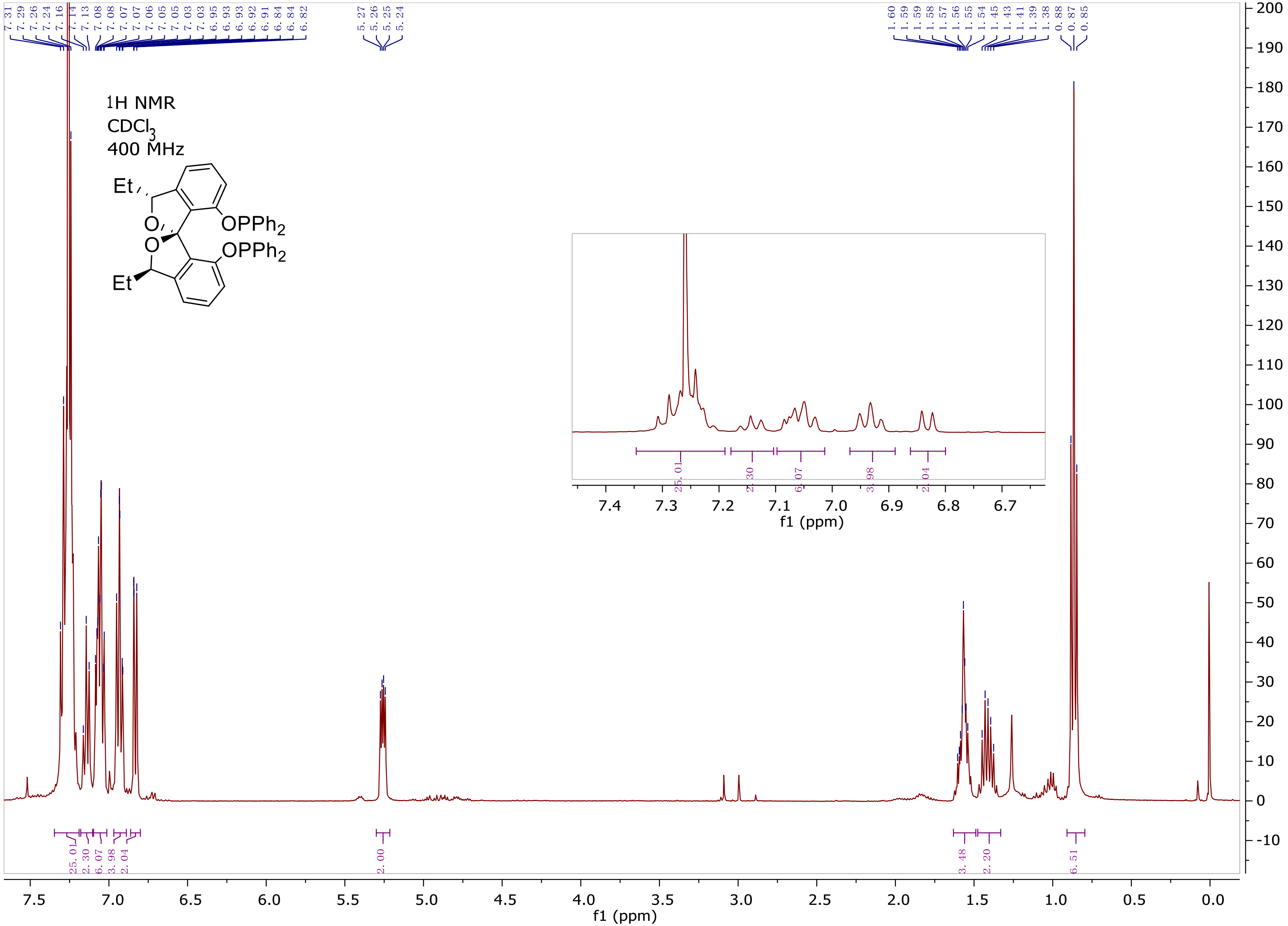
[((*1R,3S,3'S*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(diphenylphosphane)]palladium(II) chloride ((*R,S,S*)-11)

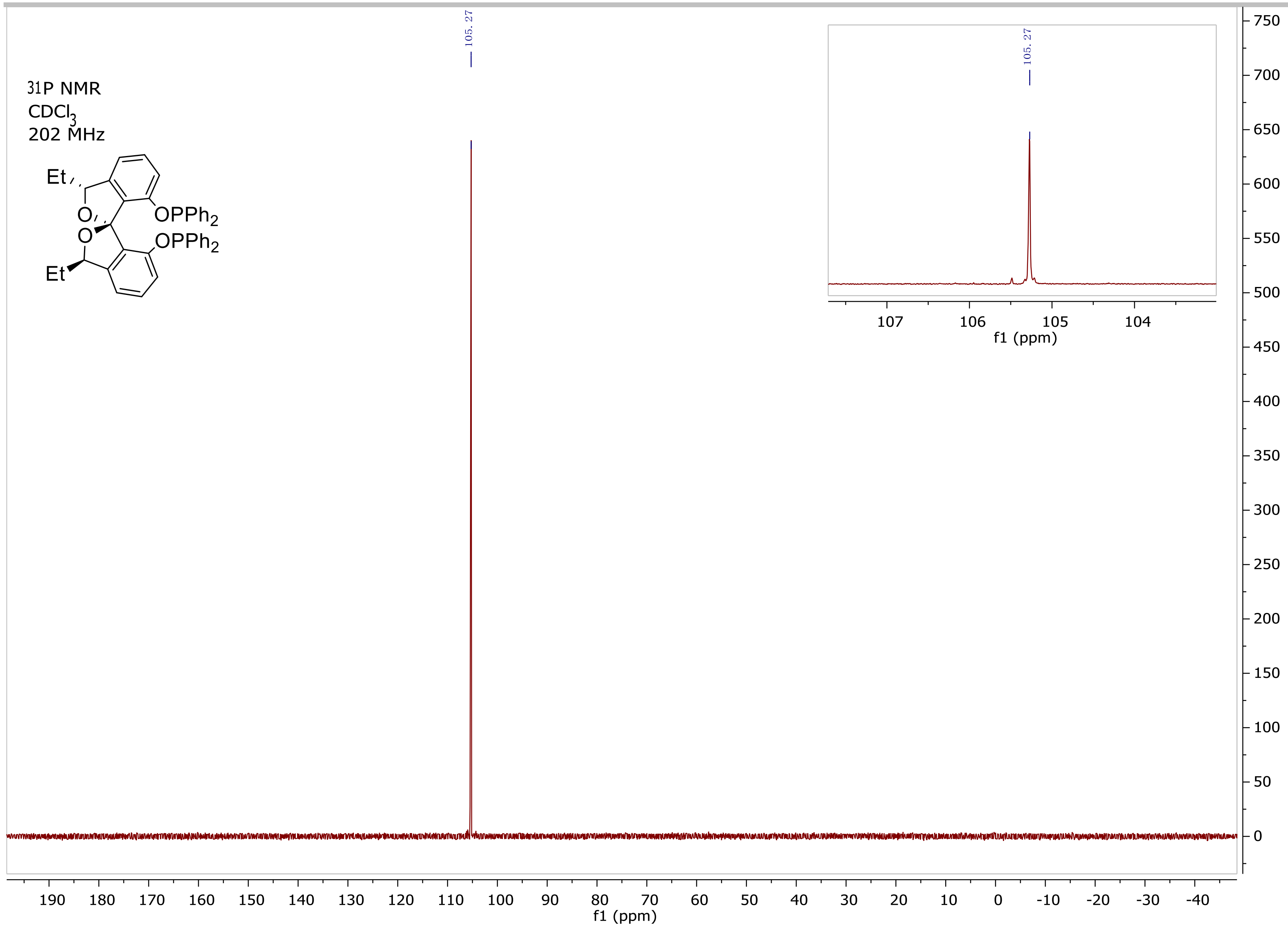


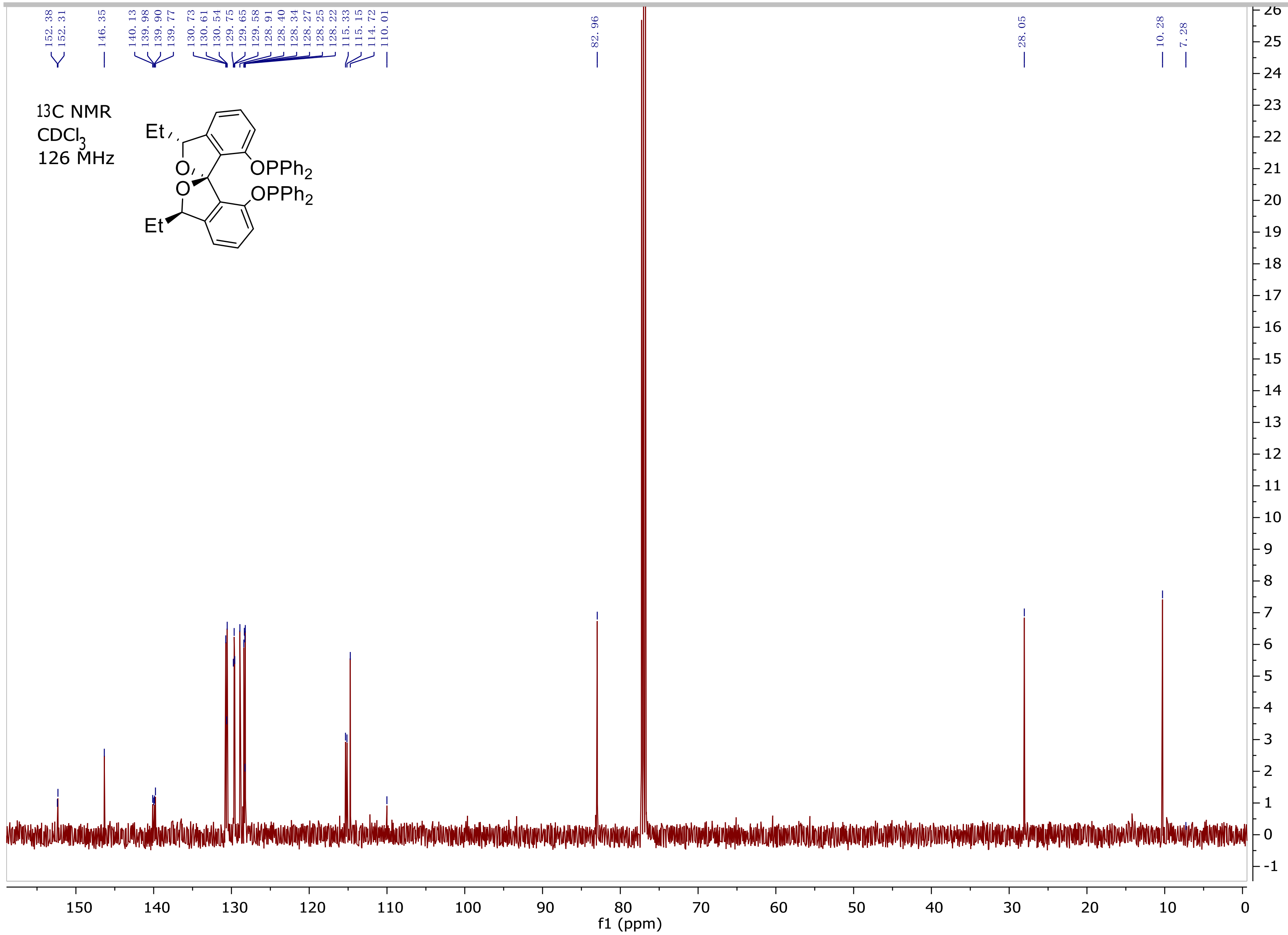

31P NMR
CDCl3
202 MHz
Et
O
O
Et
PPh2
PPh2
Pd
Cl
Cl
33.38
33.38
34.2
34.0
33.8
33.6
33.4
33.2
33.0
32.8
32.6
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


13C NMR
CDCl3
126 MHz
Et
O
O
Et
PPh2
PPh2
Pd
Cl
Cl
148.22
148.16
140.26
140.19
135.74
135.64
134.11
134.03
133.87
133.78
132.70
132.19
130.83
130.25
129.57
129.50
128.23
128.13
128.08
128.03
127.88
127.46
125.78
125.42
124.17
113.55
80.36
24.97
10.80
136
134
132
130
128
126
124
122
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0

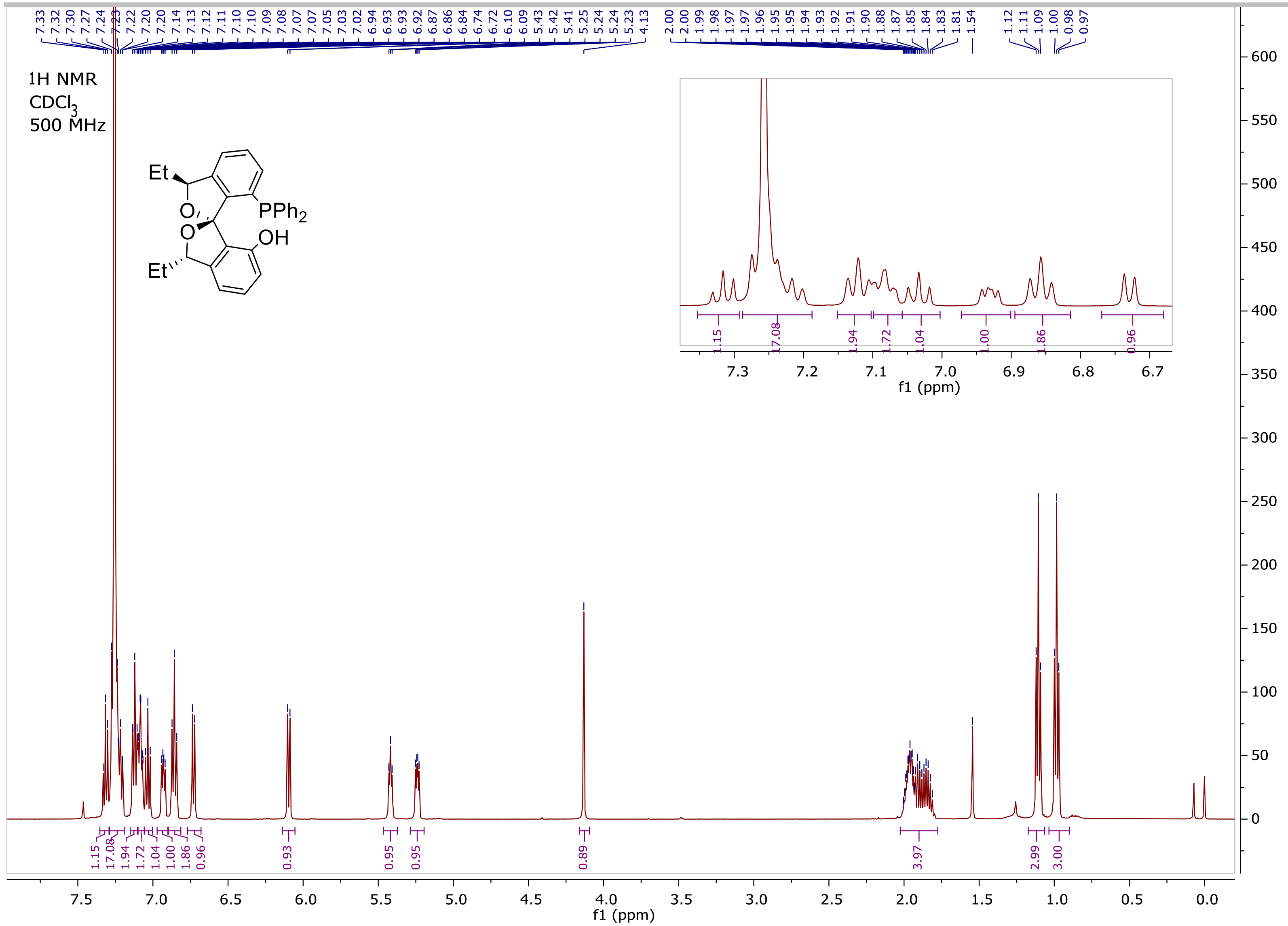
(((*1S,3R,3'R*)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7,7'-diyl)bis(oxy))bis(diphenylphosphane) ((*S,R,R*)-SPIRAPO)

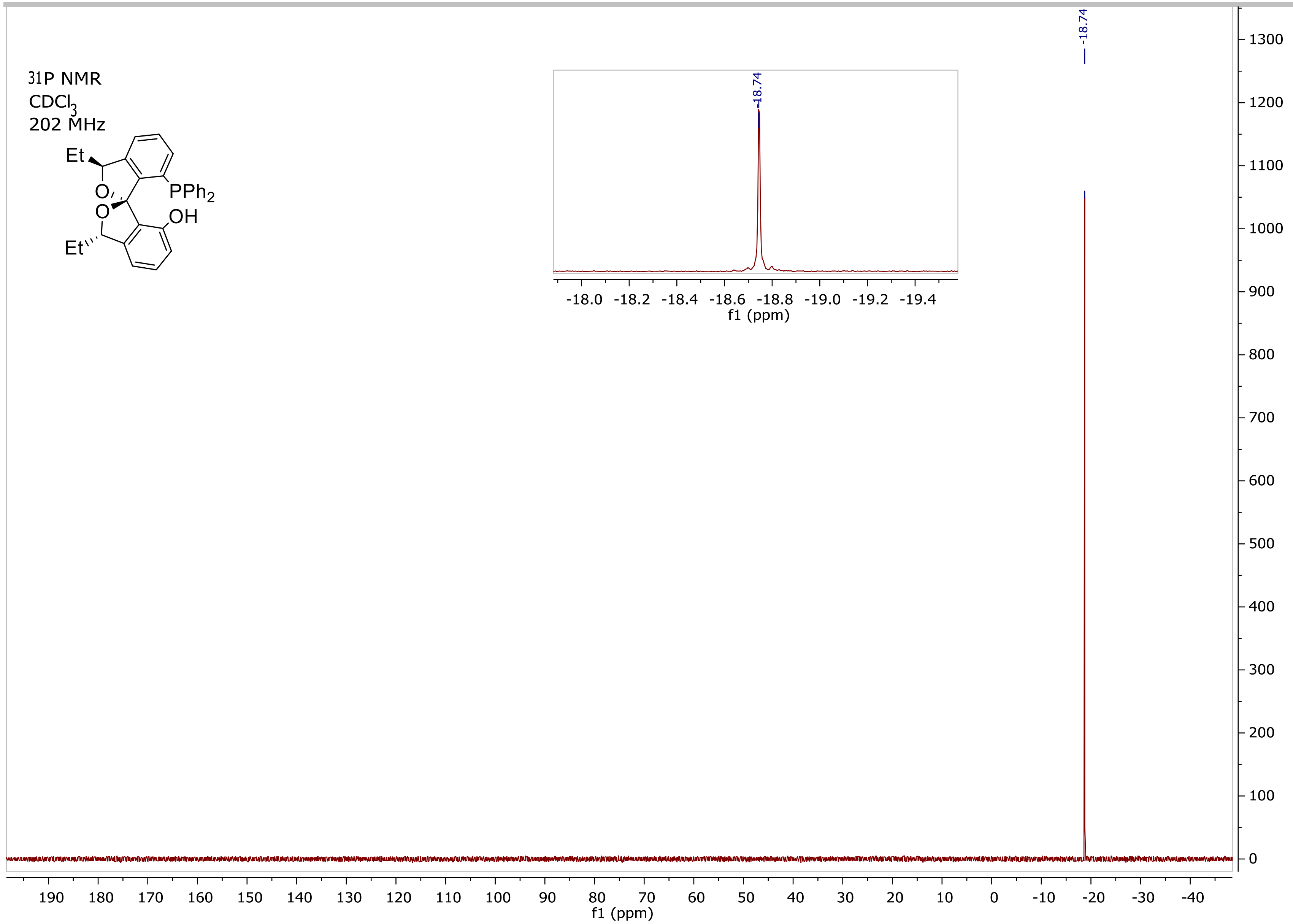


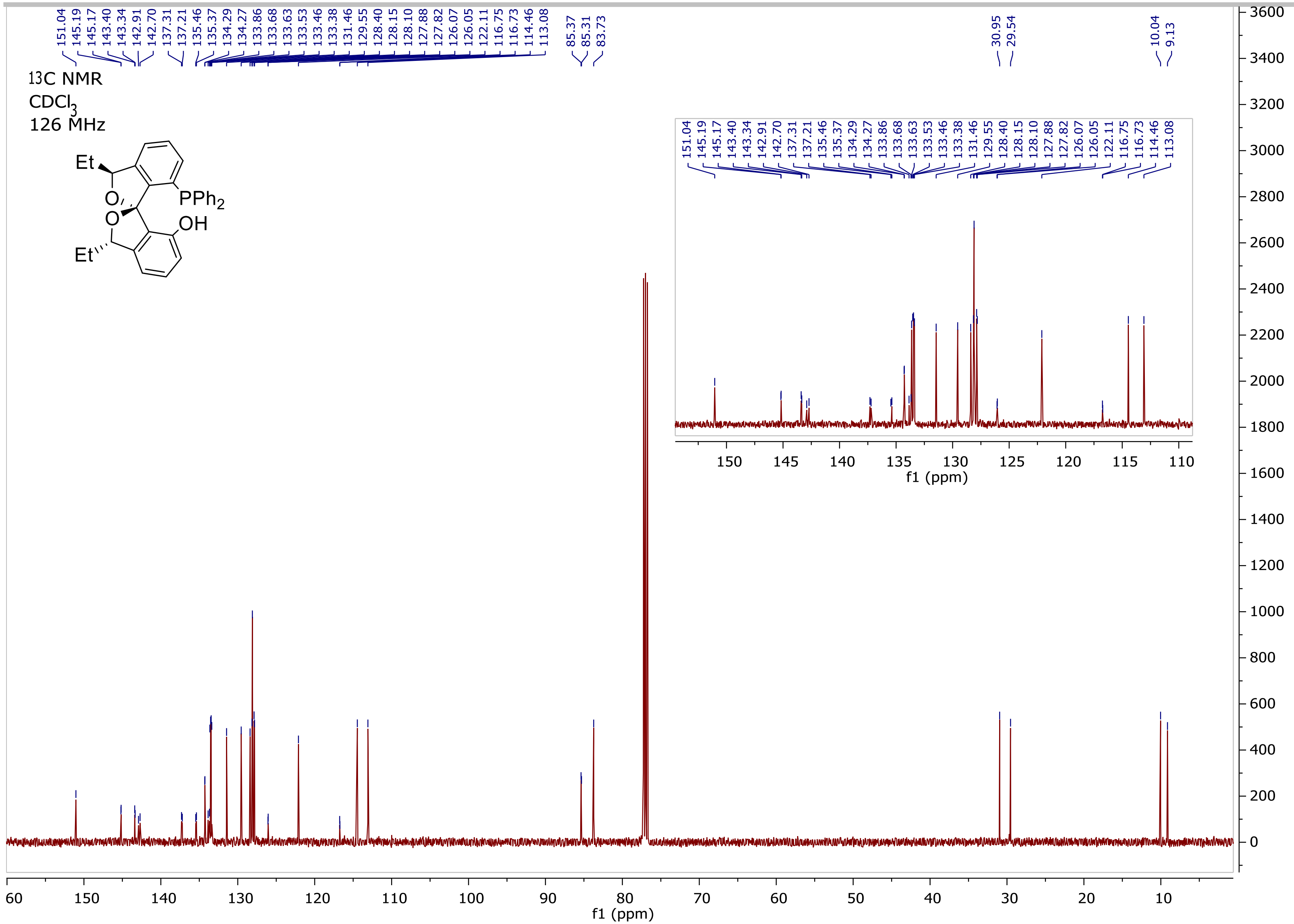

31P NMR
CDCl3
202 MHz
Et
O
O
Et
OPPh2
OPPh2
105.27
105.27
107
106
105
104
f1 (ppm)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)



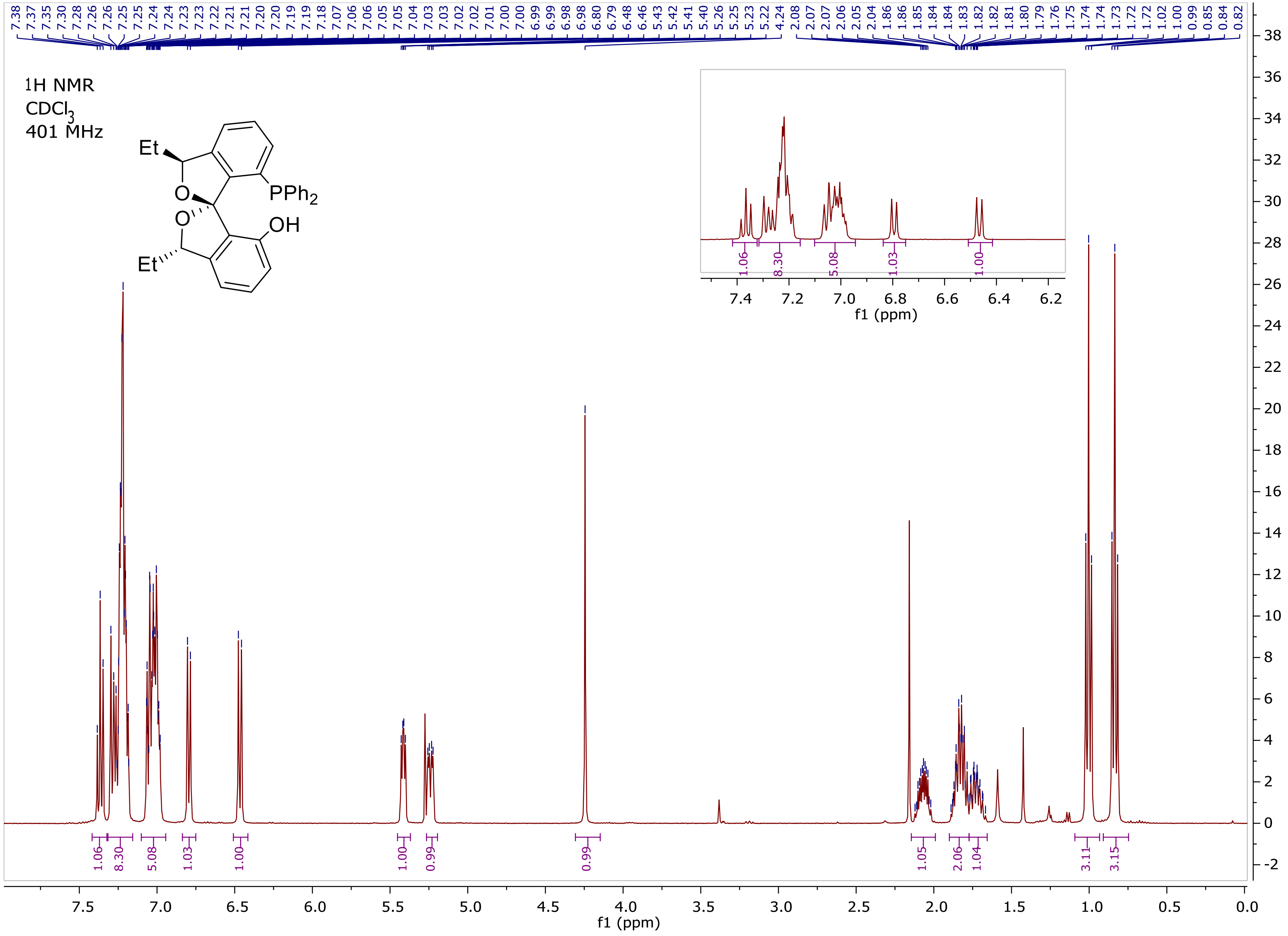
(*1S,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-ol ((*S,S,S*)-SPIROMP)

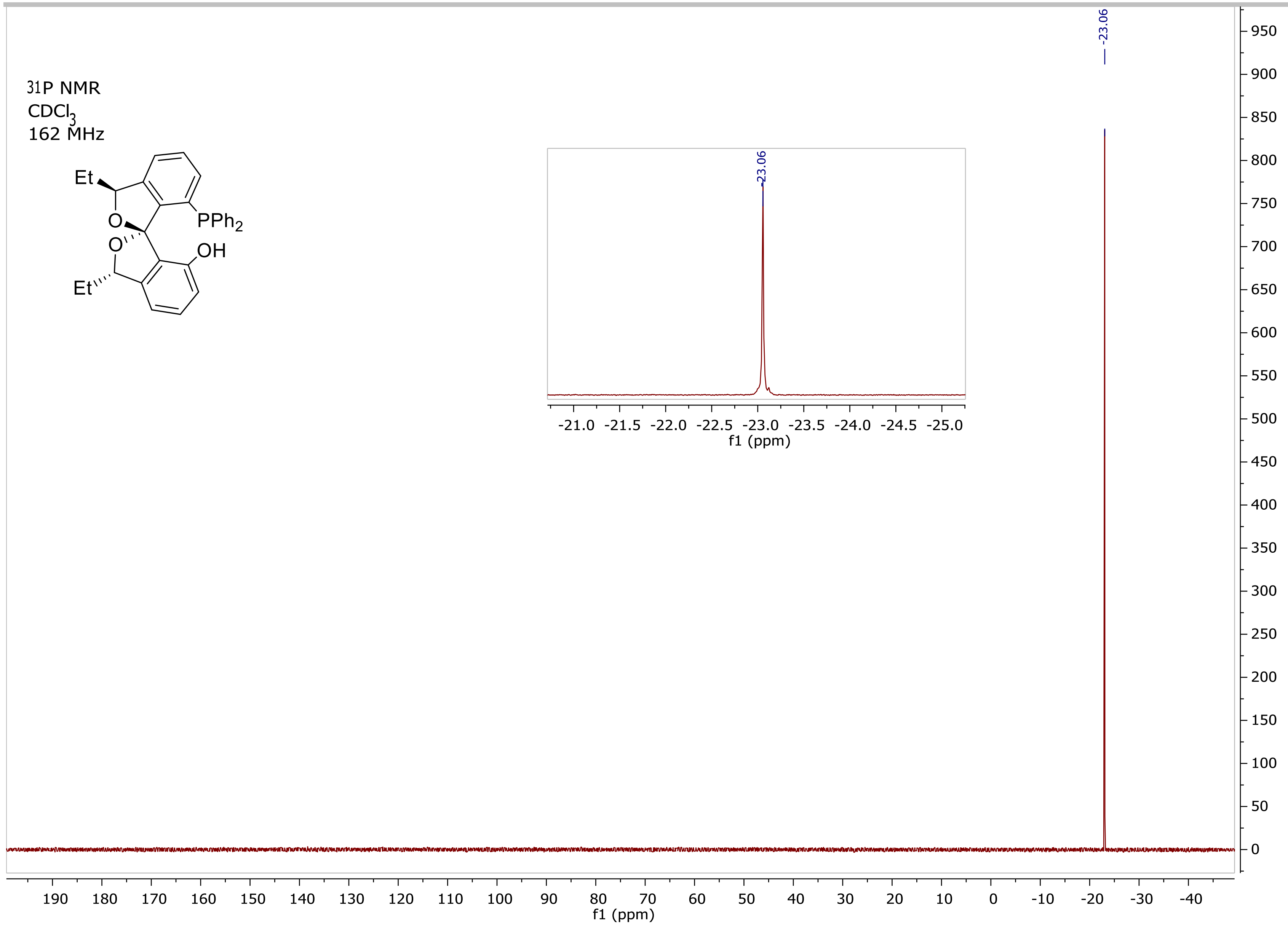

7.33
7.32
7.30
7.27
7.24
7.23
7.22
7.20
7.20
7.14
7.13
7.12
7.11
7.10
7.10
7.09
7.08
7.07
7.07
7.05
7.03
7.02
6.94
6.93
6.93
6.92
6.87
6.86
6.84
6.74
6.72
6.10
6.09
5.43
5.42
5.41
5.25
5.24
5.24
5.23
4.13
2.00
2.00
1.99
1.98
1.97
1.97
1.96
1.95
1.95
1.94
1.93
1.92
1.91
1.90
1.88
1.87
1.85
1.84
1.83
1.81
1.54
1.12
1.11
1.09
1.00
0.98
0.97
1H NMR
CDCl3
500 MHz
Et
O
PPh2
O
OH
Et
1.15
17.08
1.94
1.72
1.04
1.00
1.86
0.96
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
1.15
17.08
1.94
1.72
1.04
1.00
1.86
0.96
0.93
0.95
0.95
0.89
3.97
2.99
3.00
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)
600
550
500
450
400
350
300
250
200
150
100
50
0

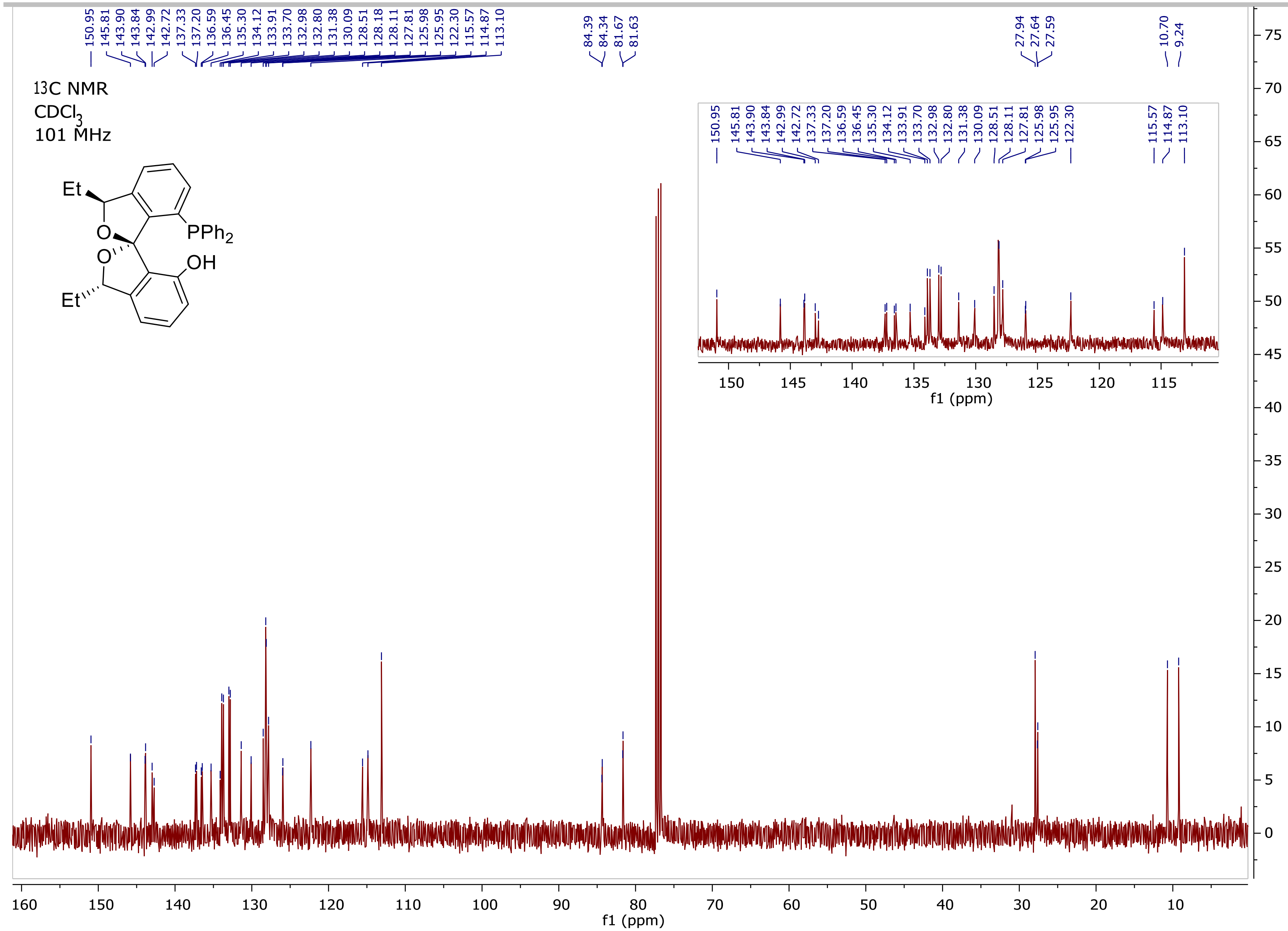

31P NMR
CDCl3
202 MHz
Et
O
O
PPh2
OH
Et
-18.74
-18.74
-18.0 -18.2 -18.4 -18.6 -18.8 -19.0 -19.2 -19.4
f1 (ppm)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)


151.04
145.19
145.17
143.40
143.34
142.91
142.70
137.31
137.21
135.46
135.37
134.29
134.27
133.86
133.68
133.63
133.53
133.46
133.38
131.46
129.55
128.40
128.15
128.10
127.88
127.82
126.07
126.05
122.11
116.75
116.73
114.46
113.08
85.37
85.31
83.73
30.95
29.54
10.04
9.13
13C NMR
CDCl3
126 MHz
Et
O
O
Et
PPh2
OH
150
145
140
135
130
125
120
115
110
f1 (ppm)
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

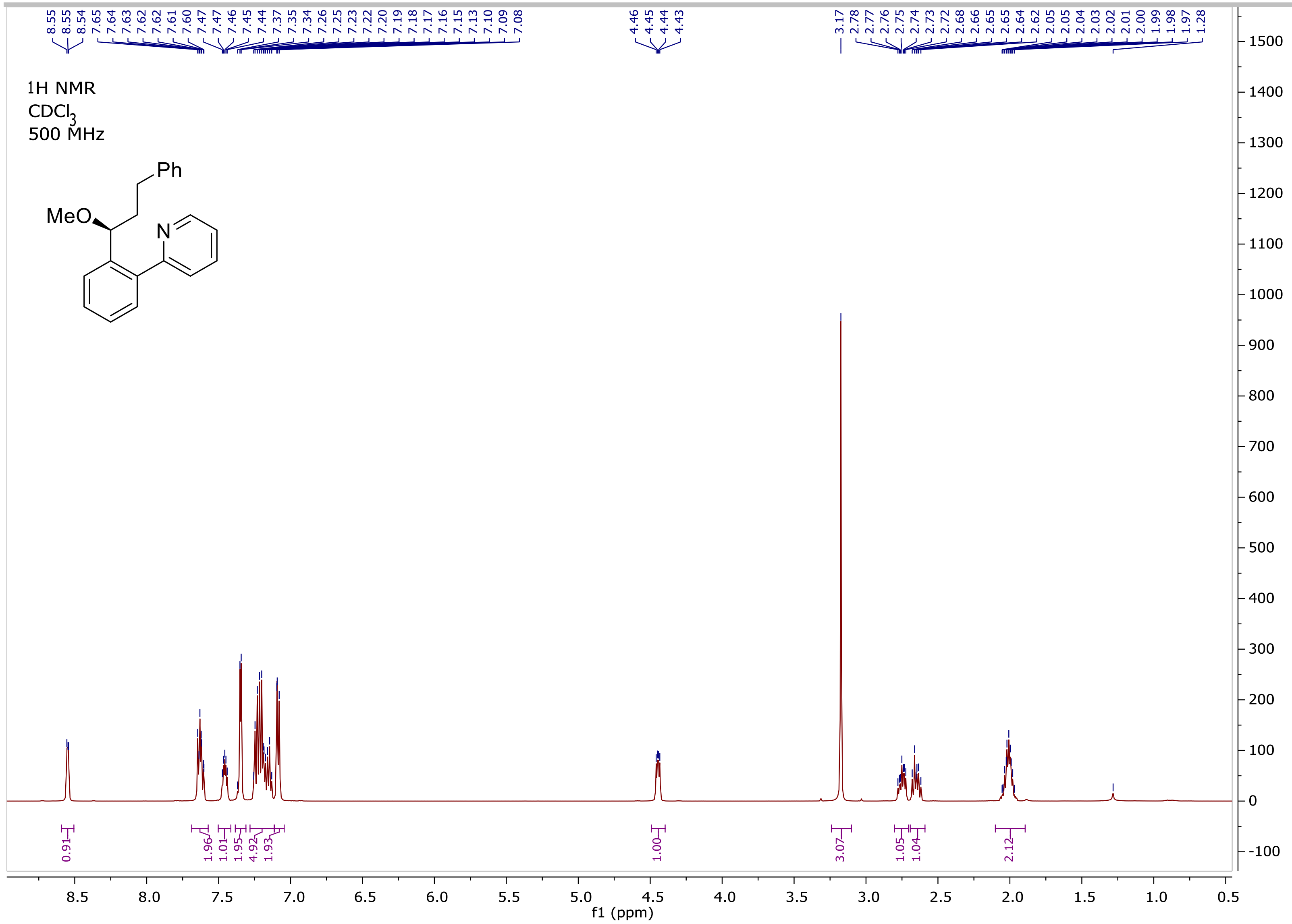
(*1R,3S,3'S*)-7'-(diphenylphosphanyl)-3,3'-diethyl-3H,3'H-1,1'-spirobi[isobenzofuran]-7-ol ((*R,S,S*)-SPIROMP)

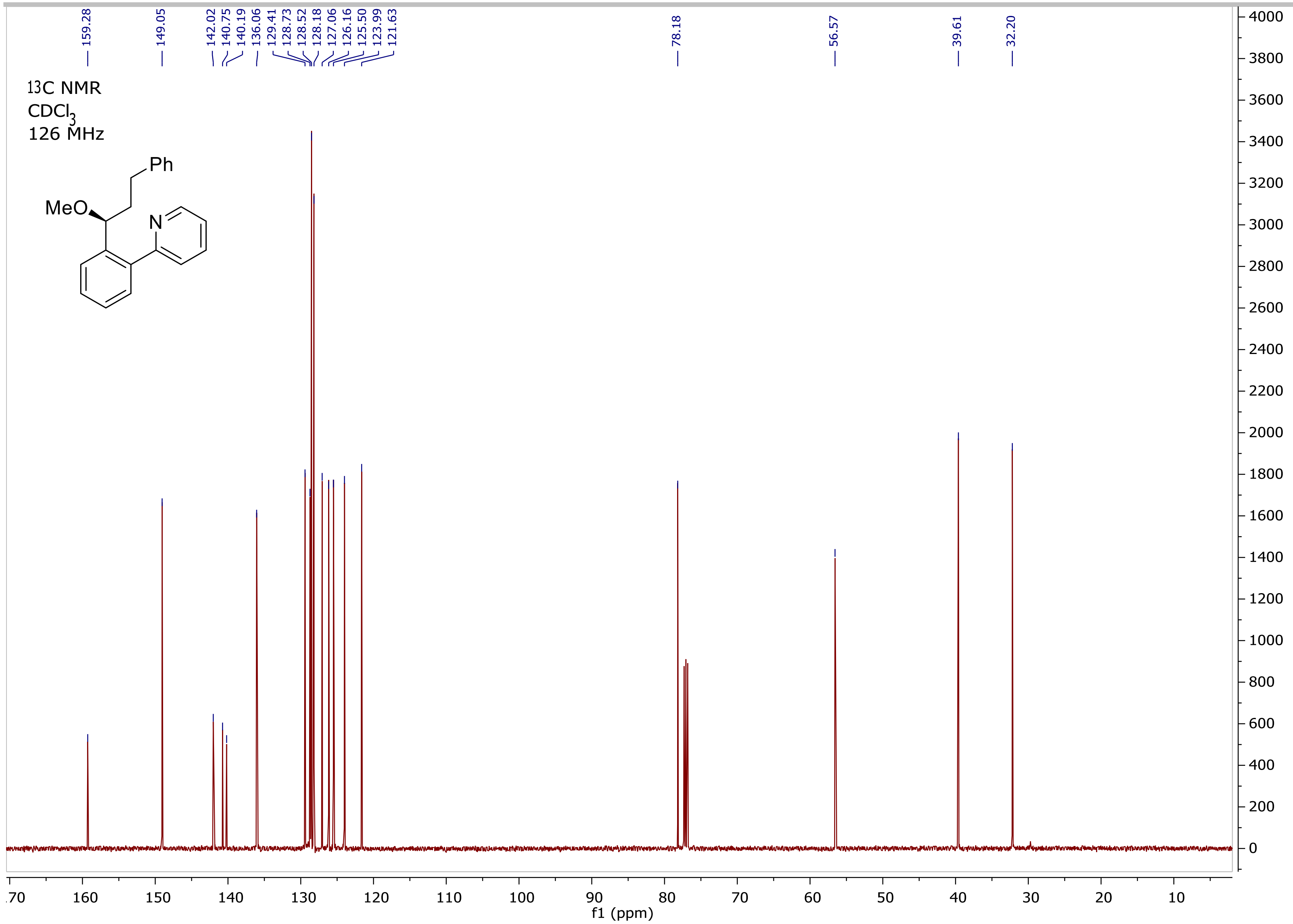



-23.06
31P NMR
CDCl3
162 MHz
Et
O
O
Et
PPh2
OH
-23.06
-21.0 -21.5 -22.0 -22.5 -23.0 -23.5 -24.0 -24.5 -25.0
f1 (ppm)
950
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

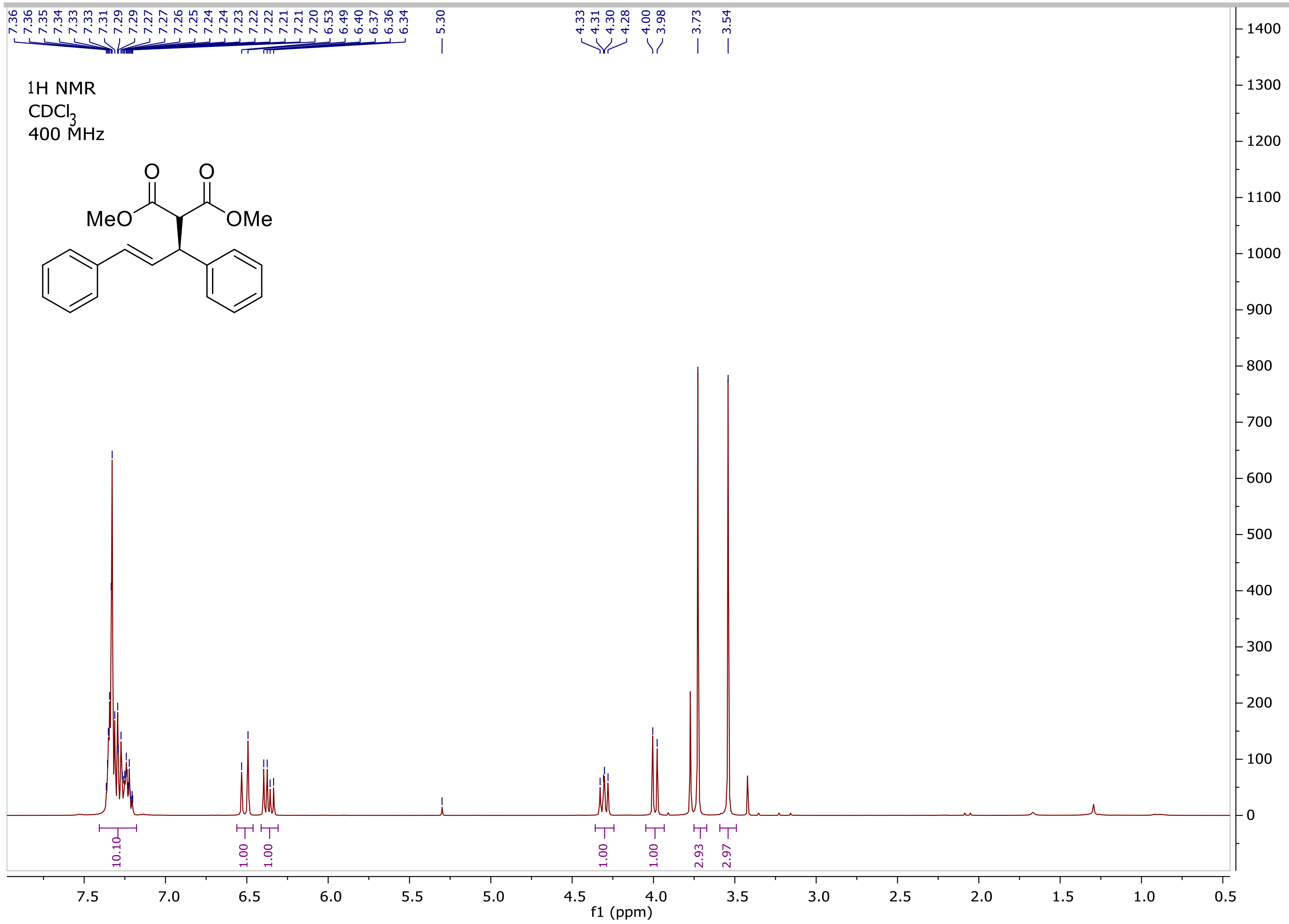


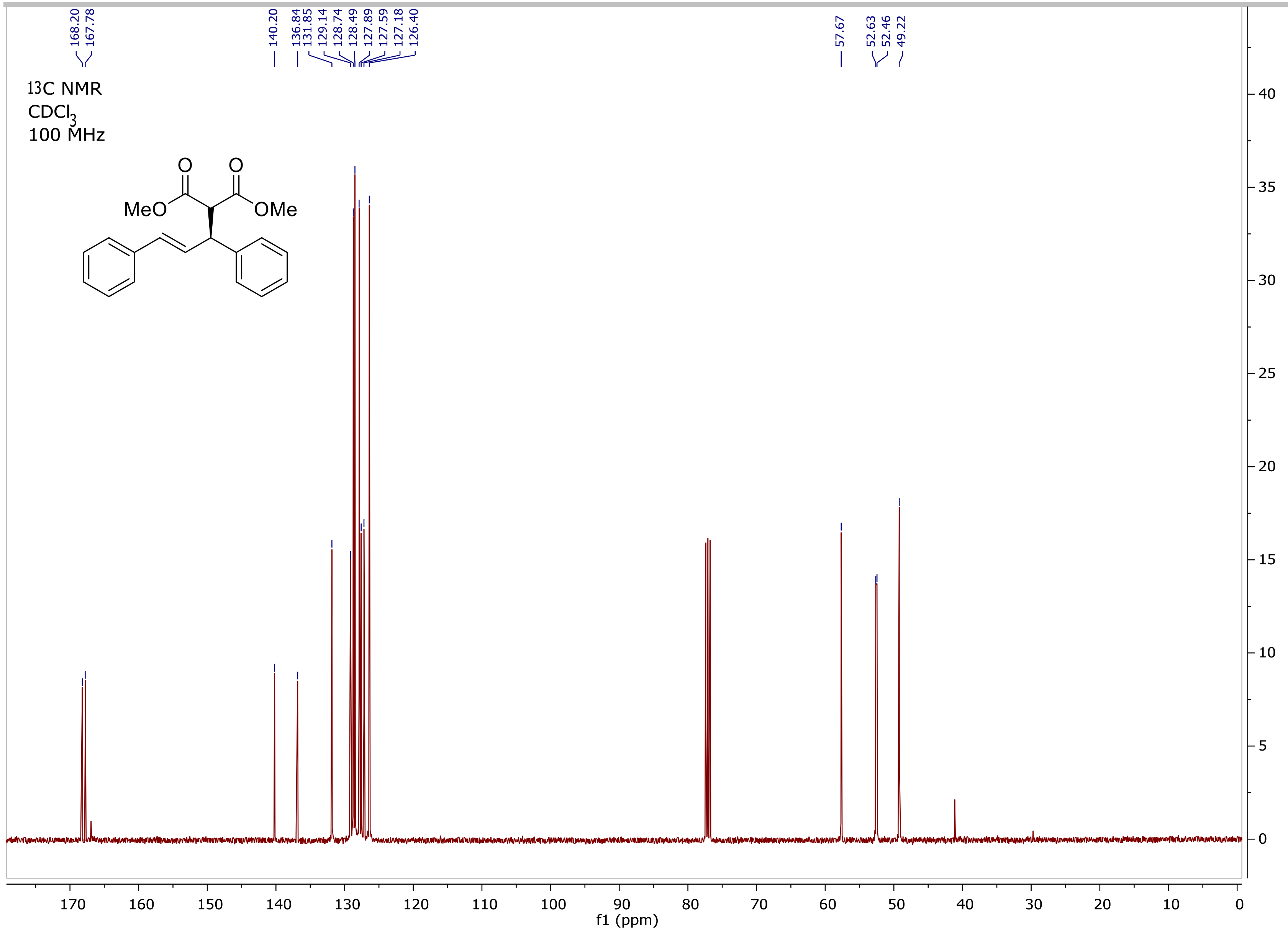
(*S*)-2-(2-(1-methoxy-3-phenylpropyl)phenyl)pyridine (14)


8.55 8.55 8.54 7.65 7.64 7.63 7.62 7.62 7.61 7.60 7.47 7.47 7.46 7.45 7.44 7.37 7.35 7.34 7.26 7.25 7.23 7.22 7.20 7.19 7.18 7.17 7.16 7.15 7.13 7.10 7.09 7.08
4.46 4.45 4.44 4.43
3.17 2.78 2.77 2.76 2.75 2.74 2.73 2.72 2.68 2.66 2.65 2.65 2.64 2.62 2.05 2.05 2.04 2.03 2.02 2.01 2.00 1.99 1.98 1.97 1.28
1H NMR
CDCl3
500 MHz
Ph
MeO
N
0.91 1.96 1.01 1.95 4.92 1.93 1.00 3.07 1.05 1.04 2.12
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
f1 (ppm)
1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

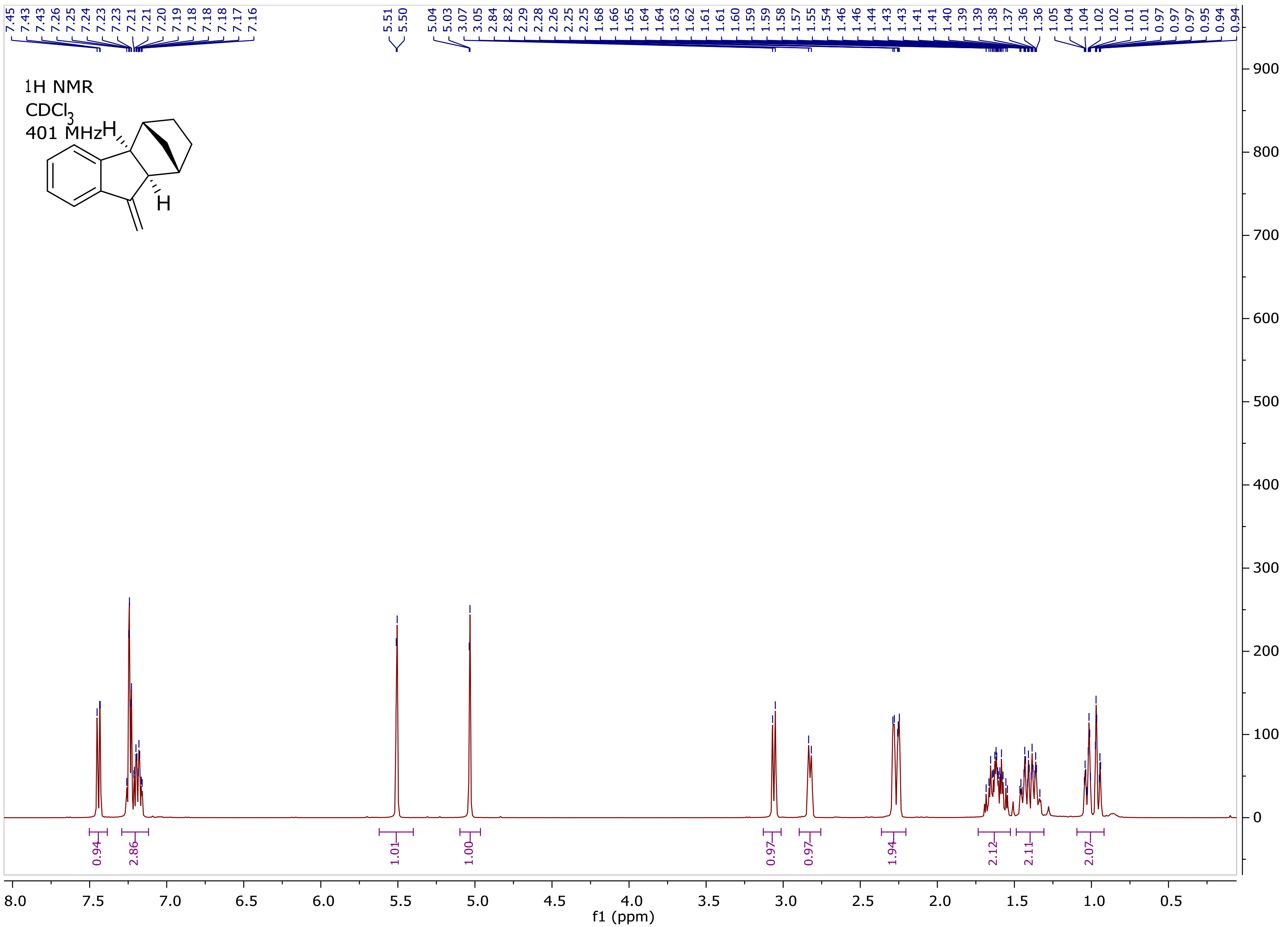


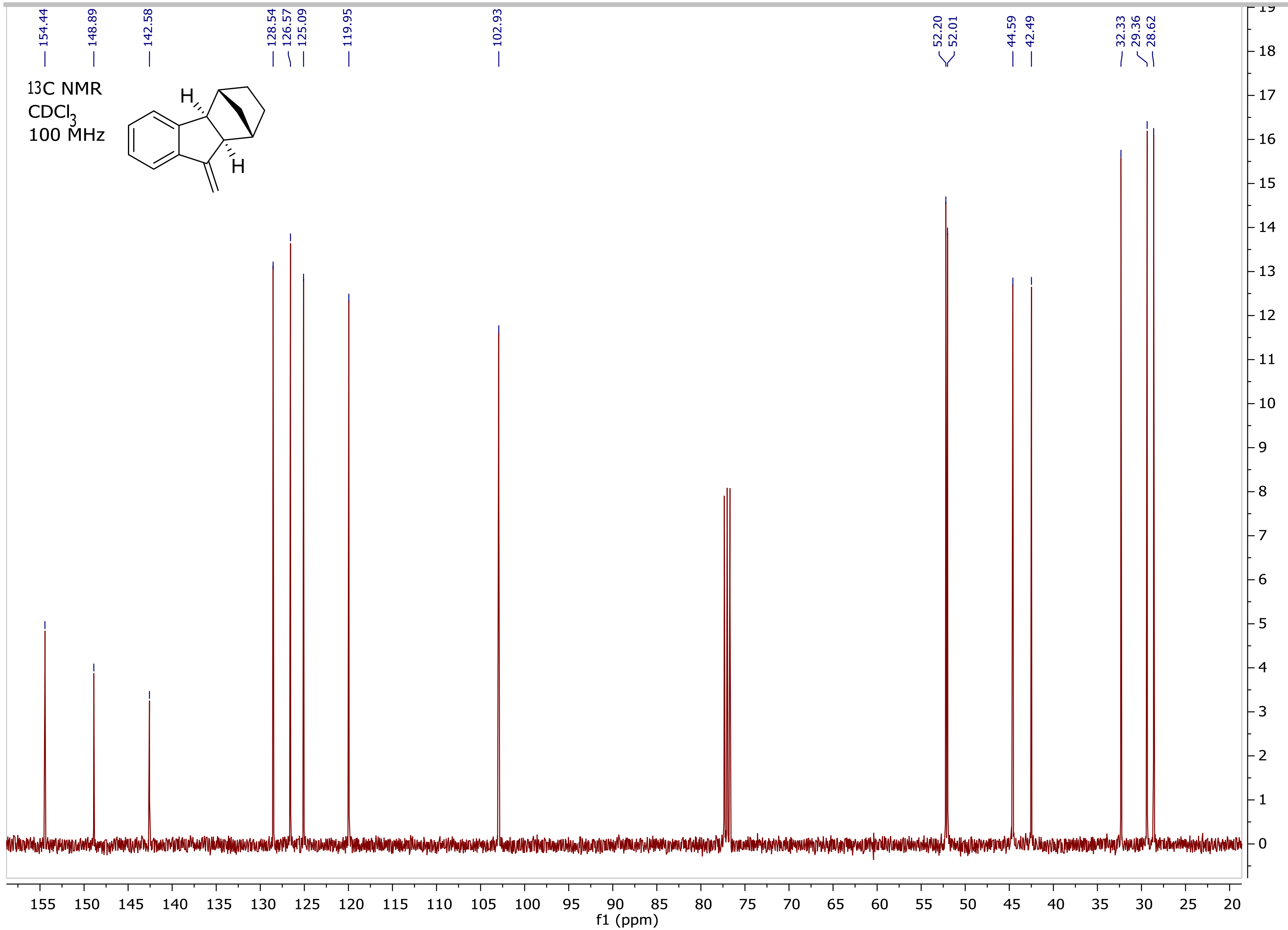
Dimethyl (*S*,*E*)-2-(1,3-diphenylallyl)malonate (17)


7.36
7.36
7.35
7.34
7.33
7.33
7.31
7.29
7.29
7.27
7.27
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.21
7.20
6.53
6.49
6.40
6.37
6.36
6.34
5.30
4.33
4.31
4.30
4.28
4.00
3.98
3.73
3.54
1H NMR
CDCl3
400 MHz
O
O
MeO
OMe
10.10
1.00
1.00
1.00
1.00
2.93
2.97
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
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0

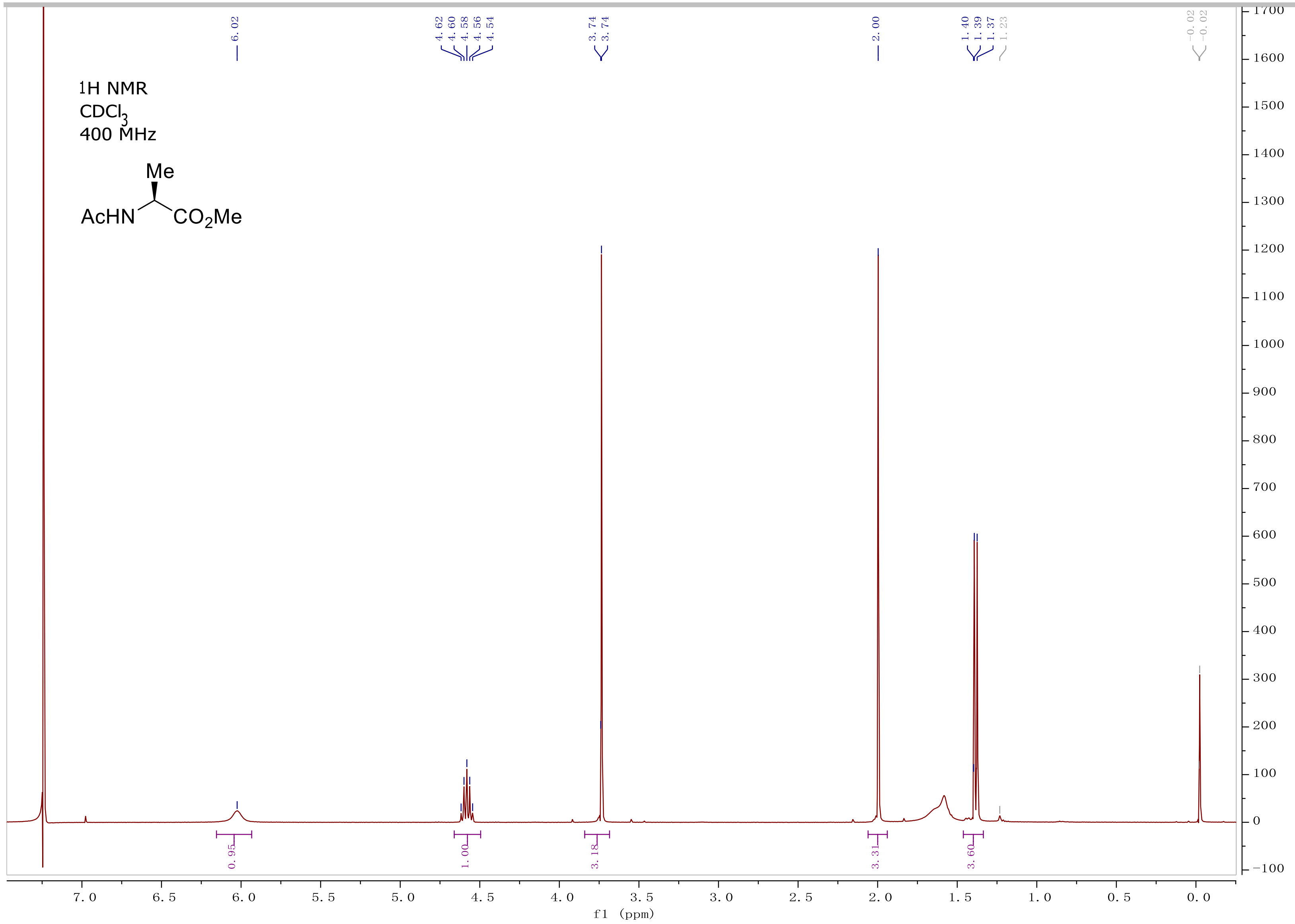

168.20
167.78
140.20
136.84
131.85
129.14
128.74
128.49
127.89
127.59
127.18
126.40
57.67
52.63
52.46
49.22
13C NMR
CDCl3
100 MHz
O
O
MeO
OMe
40
35
30
25
20
15
10
5
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

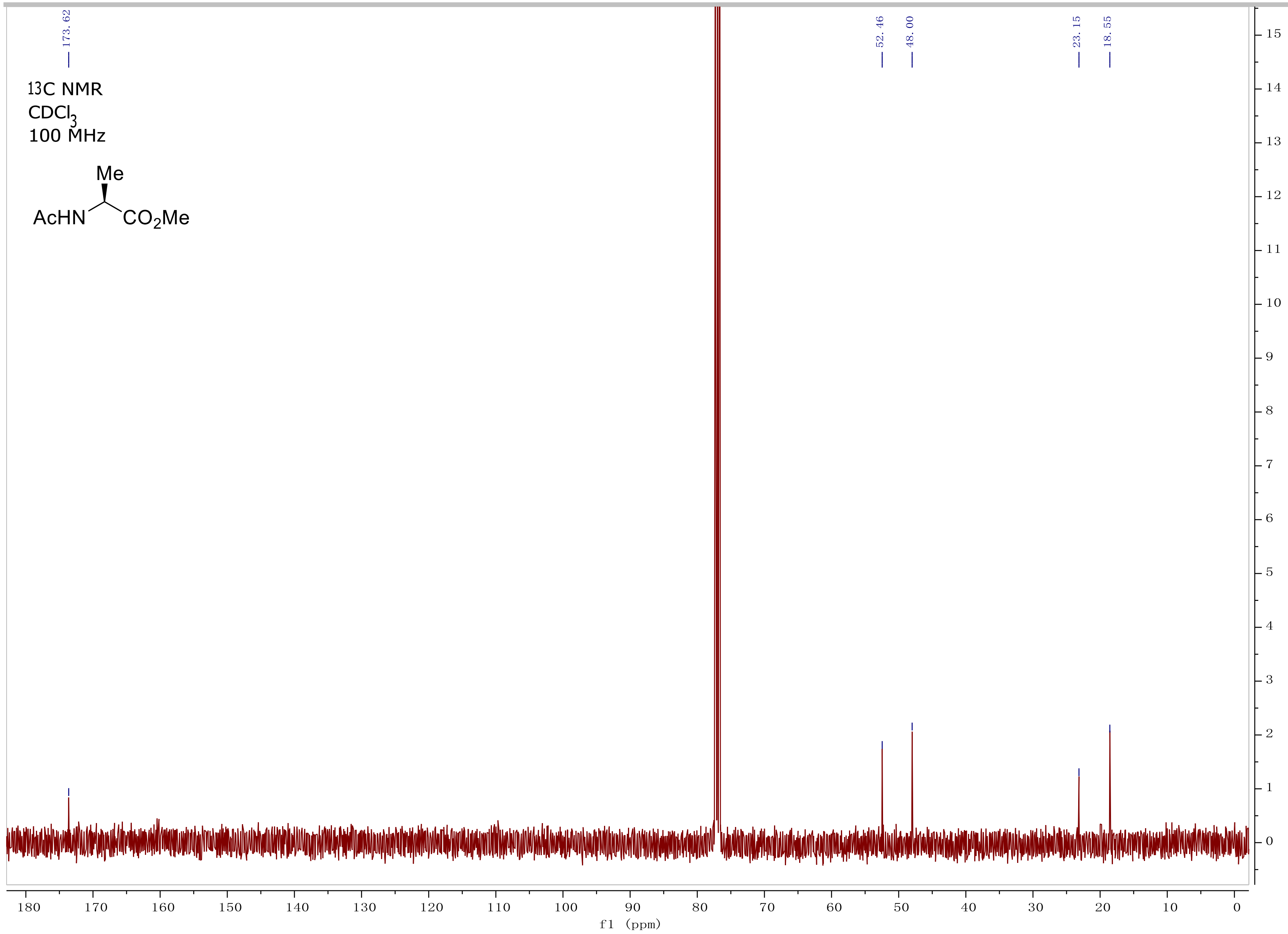
(*1S,4R,4aS,9aR*)-9-methylene-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanofluorene (20)



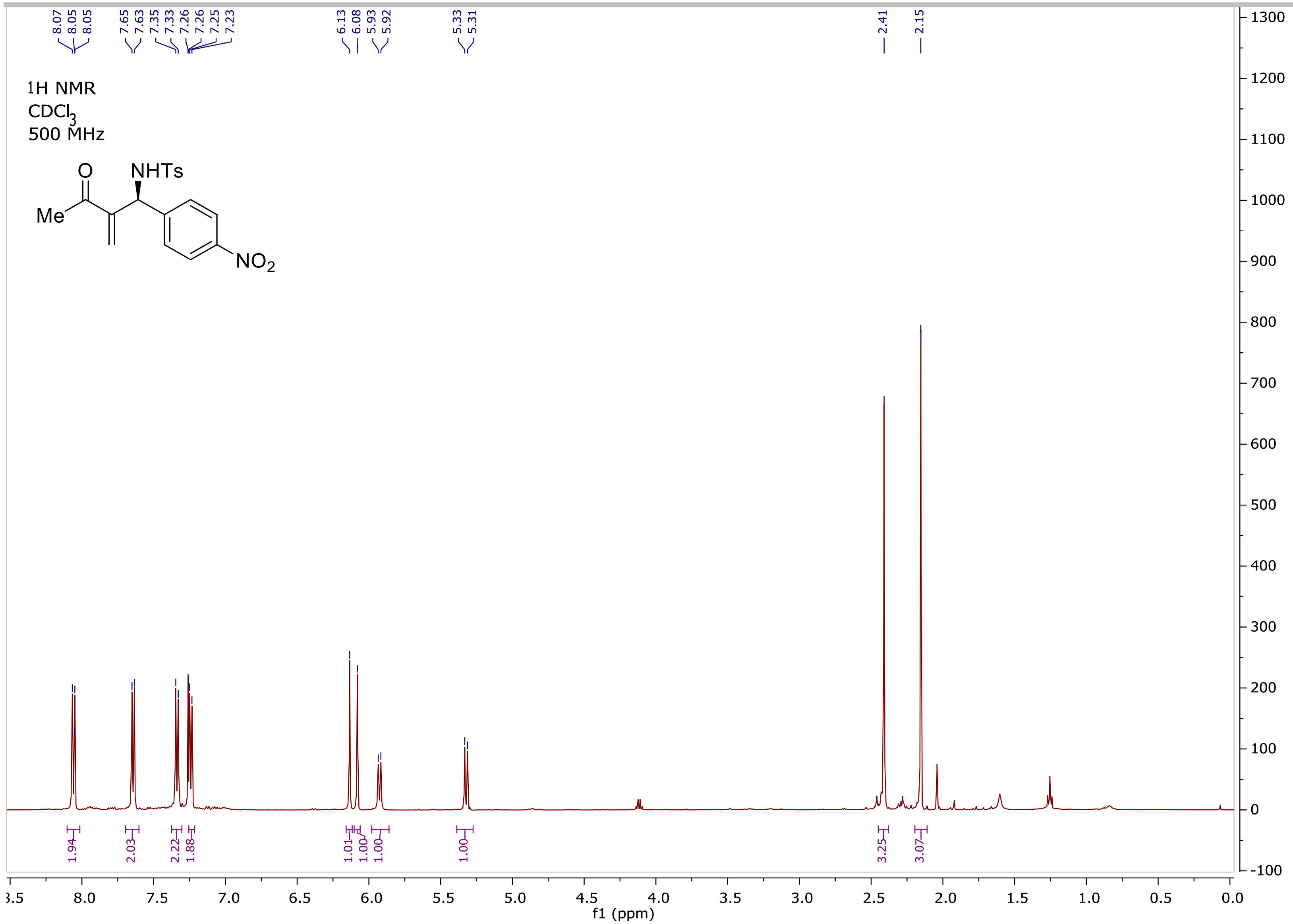


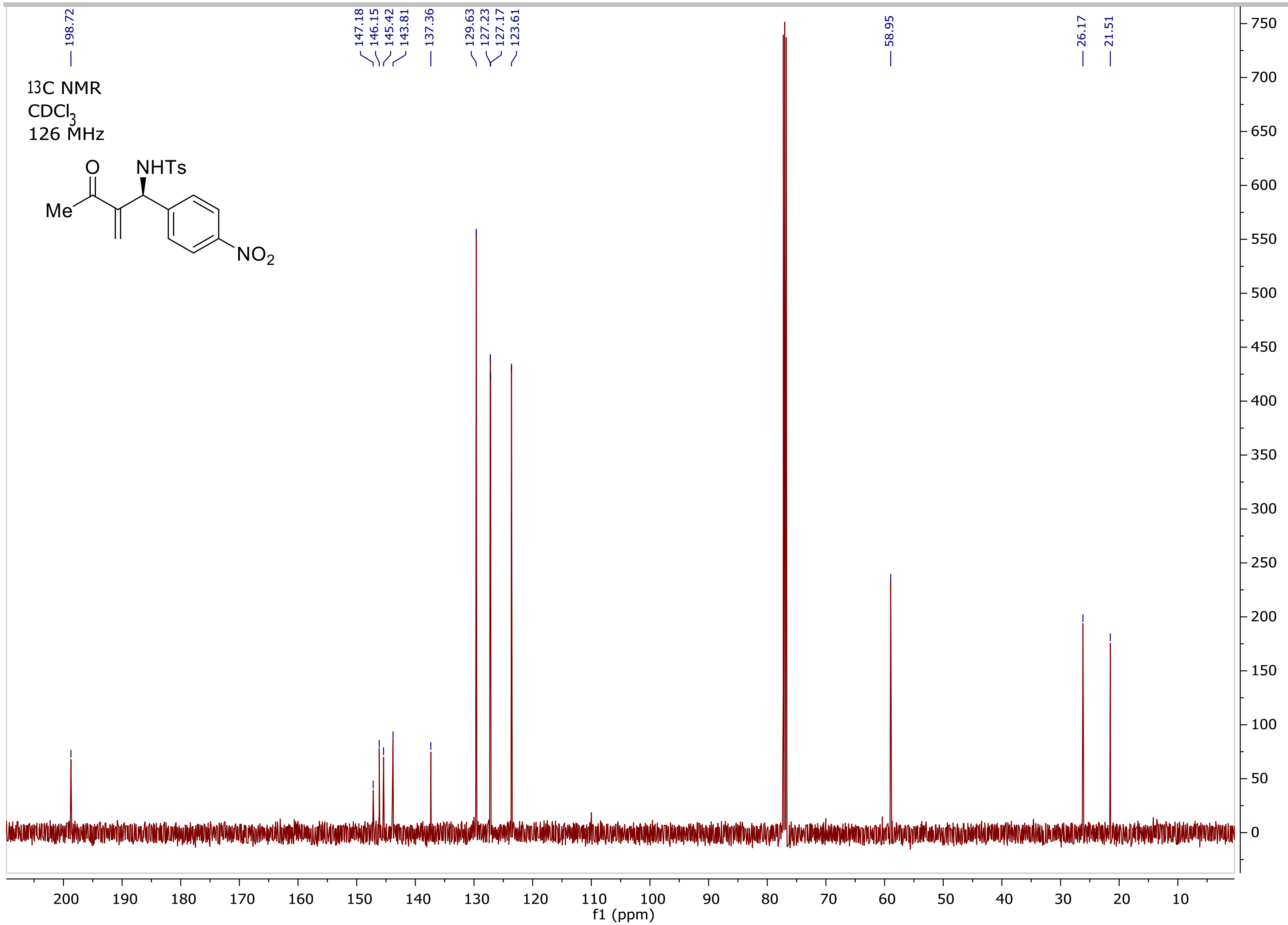
Methyl acetyl-*L*-alaninate (22)


1H NMR
CDCl3
400 MHz
Me
AcHN
CO2Me
6.02
4.62
4.60
4.58
4.56
4.54
3.74
3.74
2.00
1.40
1.39
1.37
1.23
-0.02
-0.02
0.95
1.00
3.18
3.31
3.60
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)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100



(*S*)-4-methyl-N-(2-methylene-1-(4-nitrophenyl)-3-oxobutyl)benzenesulfonamide (SI-2)


8.07
8.05
8.05
7.65
7.63
7.35
7.33
7.26
7.26
7.25
7.23
6.13
6.08
5.93
5.92
5.33
5.31
2.41
2.15
1H NMR
CDCl3
500 MHz
O
NHTs
Me
NO2
1.94
2.03
2.22
1.88
1.01
1.00
1.00
1.00
3.25
3.07
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)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100


198.72
147.18
146.15
145.42
143.81
137.36
129.63
127.23
127.17
123.61
58.95
26.17
21.51
13C NMR
CDCl3
126 MHz
O
NHTs
Me
NO2
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

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