Tris(5,6,7,8-tetrafluoronaphthalen-2-yl)borane, a Partially Fluorinated Boron Lewis Acid with Fluorination Distal to the Boron Atom

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Supporting Information

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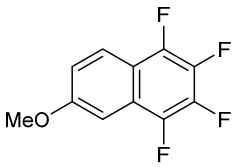
1 General Information

All reactions were performed in flame-dried glassware using an *MBraun* glove box (O_2 < 0.5 ppm, H_2O < 0.5 ppm) or conventional Schlenk techniques under a static pressure of nitrogen. Liquids and solutions were transferred with syringes. Solvents (1,2-$F_2C_6H_4$, *n*-hexane, *n*-pentane, diethyl ether, THF, CH_2Cl_2, 1,4-dioxane, toluene, and methanol) were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (diethyl ether, cyclohexane, ethyl acetate, *n*-pentane) were distilled prior to use. C_6F_5Br, *n*BuLi (solution in hexanes), 3-bromothiophene, C_6F_5Cl, 3-methoxythiophene, BBr_3 (1.0M in CH_2Cl_2), pyridine, Tf_2O, *N*-methylmorpholine, (dppf)$PdCl_2$, pinacolborane, $CuBr_2$, Me_3SnCl, BCl_3 (1.0M in heptane), Et_3PO, and Ph_3PO were purchased from commercial suppliers and used without further purification. Acetophenone (**16**) and 1-phenylethanol (**20**) were dried over $CaSO_4$ or molecular sieves and distilled prior to use. Me_2PhSiH (**15**) was dried over $LiAlH_4$ and distilled prior to use. (*E*)-*N*,1-Diphenylethan-1-imine (**18**),[S1] *i*PrMgCl·LiCl (solution in THF),[S2] and $B(C_6F_5)_3$ (**1**)[S3] were prepared according to reported procedures. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 glass plates by *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 µm, 230–400 mesh, ASTM) by *Merck* using the indicated solvents. ^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{29}Si, ^{119}Sn, and 2D NMR spectra were recorded in CD_2Cl_2, $CDCl_3$, or C_6D_6 on *Bruker* AV400, AV 500, DRX500, and AV700 instruments (Technische Universität Berlin, Germany). Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard (CD_2Cl_2: δ = 5.32 ppm for ^{1}H and 53.8 ppm for ^{13}C NMR; $CDCl_3$: δ = 7.26 ppm for ^{1}H and 77.2 ppm for ^{13}C NMR; C_6D_6: δ = 7.16 ppm for ^{1}H and 128.1 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, m = multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz), and integration. Gas liquid chromatography (GLC) was performed on an *Agilent Technologies* 7820A gas chromatograph equipped with a FS-SE-54 capillary column (30 m × 0.32 mm, 0.25 µm film thickness) by *CS-Chromatographie Service* using the following program: N_2 carrier gas, injection temperature 240 °C, detector temperature 300 °C, flow rate: 1.74 mL/min; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. Infrared (IR) spectra were recorded on an *Agilent Technologies* Cary 630 FT-IR spectrometer (Technische Universität Berlin, Germany) equipped with an ATR unit and the signals (w = weak, m = medium, s = strong) are reported in wavenumbers (cm^{-1}). Melting points (m.p.) were determined with a *Stuart Scientific* SMP20 melting point apparatus and are not corrected. Mass spectra (MS) were obtained from the Analytical Facility at the Institut für Chemie, Technische Universität Berlin.

2 Experimental Details for the Preparation of Tris(5,6,7,8-tetrafluoronaphthalen-2-yl)borane (5)

2.1 1,2,3,4-Tetrafluoro-6-methoxynaphthalene

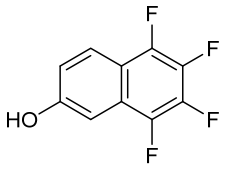


$C_{11}H_6F_4O$
M = 230.16 g/mol

To a solution of chloropentafluorobenzene (2.58 mL, 4.05 g, 20.0 mmol, 2.50 equiv) and 3-methoxythiophene (0.80 mL, 0.91 g, 8.0 mmol, 1.0 equiv) in *n*-hexane (40 mL) at –20 °C, *n*BuLi (1.5M in *n*-hexane, 10.7 mL, 16.0 mmol, 2.00 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature, diluted with diethyl ether (50 mL), and washed with aqueous HCl (2M, 20 mL), aqueous NaOCl (11–14%, 20 mL), aqueous NaOH (1M, 20 mL), and brine (40 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Flash column chromatography on silica gel using cyclohexane as eluent and subsequent sublimation at room temperature under full vacuum afforded the title compound (1.07 g, 58%) as a white solid.

m.p. = 69–70 °C (cyclohexane). $\boldsymbol{R_f}$ = 0.23 (cyclohexane). **GLC** (SE-54): t_R = 13.3 min. **IR** (ATR): $\tilde{\nu}$ = 3109 (w), 3063 (w), 3016 (w), 2979 (w), 1934 (w), 1793 (w), 1670 (m), 1621 (s), 1516 (s), 1495 (m), 1463 (m), 1444 (m), 1421 (s), 1364 (s), 1292 (m), 1259 (m), 1234 (s), 1182 (m), 1117 (m), 1023 (s), 980 (s), 912 (s), 830 (s), 781 (s), 677 (s) cm^{-1}. **HRMS** (EI) calculated for $C_{11}H_6F_4O$ $[M]^+$: 230.0349; found: 230.0349. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 3.94 (s, 3H), 7.15–7.22 (m, 2H), 7.81–7.90 (m, 1H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ = 55.7, 98.0 (m_c), 114.7 (m, *J* = 14.9 Hz), 120.7, 121.1 (m, *J* = 14.3 Hz), 121.9 (m_c), 136.2 (m, *J* = 248.6 Hz), 138.5 (m, *J* = 251.4 Hz), 141.5 (m, *J* = 248.2 Hz), 142.4 (m, *J* = 248.2 Hz), 159.0 ppm. **^{19}F NMR** (659 MHz, $CDCl_3$): δ = –163.6 (m_c), –159.1 (m_c), –152.1 (m_c), –150.7 (m_c) ppm. The analytical and spectroscopic data are in accordance with those reported.[S4]

2.2 5,6,7,8-Tetrafluoronaphthalen-2-ol (11)

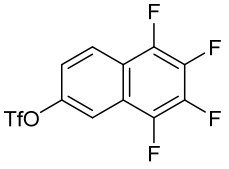


11
$C_{10}H_4F_4O$
M = 216.13 g/mol

BBr_3 (1M in CH_2Cl_2, 17.4 mL, 17.4 mmol, 4.00 equiv) was added dropwise to a solution of 1,2,3,4-tetrafluoro-6-methoxynaphthalene (1.00 g, 4.35 mmol, 1.00 equiv) in CH_2Cl_2 (60 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted with diethyl ether (100 mL) and washed with water. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Flash column chromatography on silica gel using cyclohexane/ethyl acetate (5:1) as eluent afforded the title compound **11** (0.86 g, 91%) as a white solid.

m.p. = 84–85 °C (cyclohexane/ethyl acetate). $\boldsymbol{R_f}$ = 0.24 (cyclohexane/ethyl acetate = 5:1). **GLC** (SE-54): t_R = 15.0 min. **IR** (ATR): $\tilde{\nu}$ = 3279 (s), 1669 (m), 1622 (m), 1521 (s), 1495 (m), 1426 (s), 1389 (s), 1303 (m), 1248 (w), 1198 (s), 1124 (m), 1029 (s), 992 (m), 919 (s), 866 (m), 839 (s), 820 (s), 799 (s), 751 (w), 699 (w), 677 (m) cm^{-1}. **HRMS** (EI) calculated for $C_{10}H_4F_4O$ $[M]^+$: 216.0193; found: 216.0195. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 5.65 (s, 1H), 7.20 (dd, *J* = 9.2 Hz, *J* = 2.3 Hz, 1H), 7.28 (m_c, 1H), 7.91 (d, *J* = 9.2, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 102.4 (m_c), 115.0 (m, *J* = 15.1 Hz), 119.5, 121.1 (m, *J* = 14.3 Hz), 122.7 (m), 136.3 (m, *J* = 249.6 Hz), 138.6 (m, *J* = 251.8 Hz), 141.2 (m, *J* = 248.4 Hz), 142.5 (m, *J* = 251.0 Hz), 154.7 ppm. **^{19}F NMR** (659 MHz, $CDCl_3$): δ = –163.2 (m_c), –158.5 (m_c), –151.9 (m_c), –150.4 (m_c) ppm. The analytical and spectroscopic data are in accordance with those reported.[S4]

2.3 5,6,7,8-Tetrafluoronaphthalen-2-yl Trifluoromethanesulfonate (12)

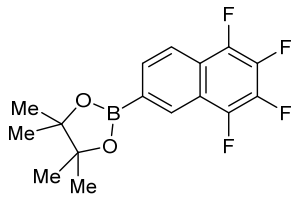


12
$C_{11}H_3F_7O_3S$
M = 348.19 g/mol

Tf_2O (0.81 mL, 1.4 g, 4.8 mmol, 1.3 equiv) was added dropwise to a solution of alcohol **11** (0.80 g, 3.7 mmol, 1.0 equiv) and pyridine (0.45 mL, 0.44 g, 5.6 mmol, 1.5 equiv) in CH_2Cl_2 (60 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. After addition of saturated aqueous $NaHCO_3$, the phases were separated, the aqueous phase was extracted with dichloromethane, and the combined organic phases were dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford the title compound **12** (1.08 g, 84%) as a colorless oil.

$\boldsymbol{R_f}$ = 0.16 (cyclohexane). **GLC** (SE-54): t_R = 13.1 min. **IR** (ATR): $\tilde{\nu}$ = 1670 (m), 1622 (m), 1520 (s), 1494 (s), 1468 (s), 1417 (s), 1371 (s), 1245 (w), 1208 (s), 1137 (s), 1037 (s), 995 (w), 918 (s), 881 (m), 854 (s), 820 (m), 778 (m), 747 (s), 664 (m) cm^{-1}. **HRMS** (EI) calculated for $C_{11}H_3F_7O_3S$ $[M]^+$: 347.9686; found: 347.9686. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.53 (dd, *J* = 9.3 Hz, *J* = 2.2 Hz, 1H), 7.97 (m_c, 1H), 8.19 (d, *J* = 9.3 Hz, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 112.8 (m), 117.7, 118.9 (m), 120.2 (m), 120.3, 121.8, 123.8 (m), 138.9 (m, *J* = 255.1 Hz), 139.4 (m, *J* = 255.9 Hz), 142.4 (m, *J* = 255.1 Hz), 148.5 (s) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –156.1 (m_c), –155.1 (m_c), –148.3 (m_c), –148.3 (m_c), –72.8 ppm.

2.4 4,4,5,5-Tetramethyl-2-(5,6,7,8-tetrafluoronaphthalen-2-yl)-1,3,2-dioxaborolane (13)



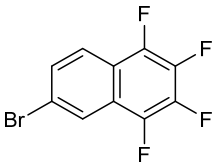
13
$C_{16}H_{15}BF_4O_2$
M = 326.10 g/mol

To a solution of (dppf)$PdCl_2$ (64 mg, 88 µmol, 3.0 mol %) in 1,4-dioxane (20 mL) was added a solution of triflate **12** (1.02 g, 2.93 mmol, 1.00 equiv) and *N*-methylmorpholine (0.97 mL, 0.89 g, 8.8 mmol, 3.0 equiv) in 1,4-dioxane (10 mL). After addition of pinacolborane (1.28 mL, 1.13 g, 8.79 mmol, 3.00 equiv) the reaction mixture was heated to reflux for 24 h. Water (30 mL) was added, the phases were separated, the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL), and the combined organic phases were dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the resulting residue was purified by flash column chromatography on

silica gel using cyclohexane/ethyl acetate (50:1) as eluent to afford the title compound **13** (0.56 g, 59%) as a white solid.

m.p. = 144–145 °C (cyclohexane/ethyl acetate). $\boldsymbol{R_f}$ = 0.61 (cyclohexane/ethyl acetate = 10:1). **GLC** (SE-54): t_R = 18.8 min. **IR** (ATR): $\tilde{\nu}$ = 2987 (m), 1665 (m), 1619 (m), 1594 (m), 1514 (m), 1494 (s), 1456 (m), 1363 (s), 1343 (s), 1327 (s), 1267 (w), 1248 (w), 1211 (m), 1167 (w), 1143 (m), 1124 (s), 1090 (s), 1035 (s), 958 (s), 907 (s), 852 (s), 823 (s), 695 (s), 663 (s) cm^{-1}. **HRMS** (EI) calculated for $C_{16}H_{15}BF_4O_2$ $[M]^+$: 326.1096; found: 326.1097. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.40 (s, 12H), 7.97 (m_c, 2H), 8.53 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 25.1, 84.6, 119.1 (m), 119.2 (m), 121.1 (m), 127.9 (m_c), 132.2, 137.8 (m, *J* = 251.3 Hz), 138.7 (m, *J* = 253.2 Hz), 142.2 (m, *J* = 251.7 Hz), 142.6 (m, *J* = 253.2 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –159.5 (m_c), –157.6 (m_c), –150.8 (m_c), –149.5 (m_c) ppm. **^{11}B NMR** (161 MHz, $CDCl_3$): δ = 31.2 ppm.

2.5 6-Bromo-1,2,3,4-tetrafluoronaphthalene (6)



6
$C_{10}H_3BrF_4$
M = 279.03 g/mol

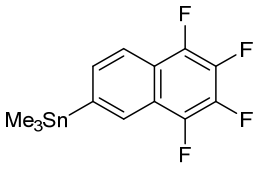
Approach A (Scheme 2): To a solution of boronate ester **13** (0.56 g, 1.7 mmol, 1.0 equiv) in MeOH/THF (3:1, 20 mL) was added dropwise a solution of $CuBr_2$ (1.2 g, 5.4 mmol, 3.1 equiv) in water (15 mL). The reaction mixture was heated to reflux for 20 h. The mixture was diluted with water (15 mL), the phases were separated, the aqueous phase was extracted with diethyl ether (3 × 30 mL), and the combined organic phases were dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel using *n*-pentane as eluent to afford the title compound **6** (0.36 g, 75%) as a white solid.

Approach B (Scheme 1): *n*BuLi (1.50M in hexanes, 37.2 mL, 55.8 mmol, 1.00 equiv) was added dropwise to a solution of bromopentafluorobenzene (7.10 mL, 13.8 g, 55.8 mmol, 1.00 equiv) in *n*-hexane (80 mL) at –78 °C. After stirring for 1 h, 3-bromothiophene (6.79 mL, 11.8 g, 72.5 mmol, 1.30 equiv) was added dropwise and the reaction mixture was allowed to warm to

room temperature over the course of 15 h. The reaction mixture was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using *n*-pentane as eluent and subsequent crystallization from methanol to afford the title compound **6** (2.30 g, 15%) as a white solid.

m.p. = 65–66 °C (*n*-pentane). $\boldsymbol{R_f}$ = 0.57 (cyclohexane). **GLC** (SE-54): t_R = 13.2 min. **IR** (ATR): $\tilde{\nu}$ = 3108 (w), 2124 (w), 1921 (w), 1753 (w), 1666 (m), 1635 (w), 1601 (s), 1509 (m), 1482 (m), 1452 (s), 1408 (s), 1362 (s), 1283 (w), 1248 (m), 1200 (w), 1125 (m), 1067 (m), 1029 (s), 962 (s), 879 (s), 815 (s), 751 (w), 716 (s), 669 (s) cm^{-1}. **HRMS** (EI) calculated for $C_{10}H_3BrF_4$ $[M]^+$: 277.9348; found: 277.9349. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 8.12 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 118.2 (m_c, *J* = 14.9 Hz), 120.7 (m_c, *J* = 14.4 Hz), 121.9 (m_c), 122.2, 122.4 (m), 131.2, 138.2 (m_c, *J* = 253.9 Hz), 138.7 (m_c, *J* = 254.2 Hz), 141.4 (m, *J* = 251.7 Hz), 142.4 (m, *J* = 251.3 Hz) ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –157.8 (m_c), –156.6 (m_c), –150.0 (m_c), –149.4 (m_c) ppm.

2.6 Trimethyl(5,6,7,8-tetrafluoronaphthalen-2-yl)stannane (14)



14
$C_{13}H_{12}F_4Sn$
M = 362.94 g/mol

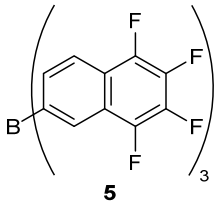
Metalation A: *n*BuLi (1.21M in hexanes, 3.35 mL, 4.05 mmol, 1.00 equiv) was added dropwise to a solution of bromide **6** (1.13 g, 4.05 mmol, 1.00 equiv) in *n*-pentane/diethyl ether (1:1, 40 mL) at –80 °C. After stirring at this temperature for 3 h, a solution of Me_3SnCl (1.06 g, 5.32 mmol, 1.31 equiv) in diethyl ether (5 mL) was added, and the reaction mixture was allowed to warm to room temperature overnight. The solvents were evaporated under reduced pressure, and the resulting residue was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford the title compound **14** (1.25 g, 85%) as a white solid.

Metalation B: To a solution of bromide **6** (1.98 g, 7.10 mmol, 1.00 equiv) in THF was added *i*PrMgCl·LiCl (0.380M in THF, 20.5 mL, 7.79 mmol, 1.10 equiv) at 0 °C. The mixture was stirred at room temperature for 3 h and cooled again to 0 °C before Me_3SnCl (1.84 g, 9.23 mmol, 1.30 equiv) in THF (5 mL) was added. The reaction mixture was allowed to warm to room tempera-

ture and stirred overnight. After addition of water (20 mL), the phases were separated, the aqueous phase was extracted with diethyl ether (2 × 20 mL), and the combined organic phases were dried over Na_2SO_4. After evaporation of the solvents under reduced pressure, the resulting residue was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford the title compound **14** (1.97 g, 76%) as a white solid.

m.p. = 80–82 °C (*n*-pentane). $\boldsymbol{R_f}$ = 0.59 (cyclohexane). **GLC** (SE-54): t_R = 16.5 min. **IR** (ATR): $\tilde{\nu}$ = 2984 (w), 2914 (w), 2365 (w), 1930 (w), 1777 (w), 1663 (m), 1587 (s), 1503 (m), 1481 (m), 1434 (s), 1411 (m), 1353 (s), 1290 (w), 1246 (m), 1193 (m), 1118 (m), 1076 (m), 1029 (s), 957 (s), 889 (s), 766 (s), 712 (w), 668 (s) cm^{-1}. **HRMS** (EI) calculated for $C_{13}H_{12}F_4Sn$ $[M]^+$: 363.9892; found: 363.9897. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.42 (s, 9H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 8.13 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$): δ = –9.3, 118.7 (m), 119.2 (m, *J* = 14.6 Hz), 119.6 (m, *J* = 14.6), 127.3 (m), 134.0, 137.7 (m, *J* = 253.5), 142 (m, *J* = 251.1), 143.0 ppm. **^{19}F NMR** (471 MHz, $CDCl_3$): δ = –159.6 (m_c), –159.5 (m_c), –151.6 (m_c), –151.4 (m_c) ppm. **^{119}Sn NMR** (187 MHz, $CDCl_3$): –19.9 ppm.

2.7 Tris(5,6,7,8-tetrafluoronaphthalen-2-yl)borane (5)



5

$C_{30}H_9BF_{12}$

M = 608.19 g/mol

A Schlenk tube was charged with stannane **14** (1.26 g, 3.47 mmol, 3.16 equiv) in *n*-hexane (5 mL). BCl_3 (1.00M in heptane, 1.10 mL, 1.10 mmol, 1.00 equiv.) was added, the tube was sealed, and the reaction mixture was heated to 100 °C for 14 h. Heating to 50 °C under full vacuum removed most of the solvent and volatile by-products. The resulting light yellow raw product was dissolved in 1,2-$F_2C_6H_4$. Precipitation at –35 °C and drying for several hours under full vacuum afforded the title compound **5** (457 mg, 68%) as a white solid.

Crystals of the water adduct suitable for X-ray diffraction were obtained by dissolving **5** in a mixture of THF and *n*-hexane and slow evaporation of the solvents at room temperature and ambient atmosphere.

HRMS (ESI) calculated for $C_{30}H_9BF_{12}$ $[M]^+$: 608.0600; found: 608.0570. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ = 7.87 (d, *J* = 8.5 Hz, 3H), 8.21 (d, *J* = 8.5 Hz, 3H), 8.37 (s, 3H) ppm. **^{13}C DEPT** (126 MHz, CD_2Cl_2): 119.4, 132.0, 135.2 ppm. **^{19}F/^{13}C HMQC** (659 MHz/176 MHz, CD_2Cl_2): δ = –159.6/138.1, –156.5/138.9, –150.9/142.2, –149.7/142.9 ppm. **^{19}F NMR** (471 MHz, CD_2Cl_2): δ = –159.3 (m_c), –156.4 (m_c), –150.9 (m_c), –149.6 (m_c) ppm. **^{11}B NMR** (161 MHz, CD_2Cl_2): δ = 71.0 ppm.

3 General Procedure for the Preparation of Triethylphosphine Oxide Adducts of Boranes

In a glove box, the indicated borane (20–25 µmol) in CD_2Cl_2 or C_6D_6 (0.5 mL), respectively was mixed with triethylphosphine oxide (1.0 equiv) in CD_2Cl_2 or C_6D_6 (0.5 mL), respectively. The sample was transferred to an NMR tube and directly subjected to NMR spectroscopic analysis.

3.1 Tris(5,6,7,8-tetrafluoronaphthalen-2-yl)borane Triethylphosphine Oxide Adduct (5·Et$_3$PO)

In C_6D_6: Prepared from borane **5** (15 mg, 25 µmol, 1.0 equiv) and triethylphosphine oxide (3.3 mg, 25 µmol, 1.0 equiv) according to the general procedure.

^{1}H NMR (500 MHz, C_6D_6): δ = 0.47 (m_c, 9H), 0.86 (m_c, 6H), 7.73 (d, *J* = 8.5 Hz, 3H), 7.88 (d, *J* = 8.5 Hz, 3H), 8.37 (s, 3H) ppm. **^{19}F NMR** (471 MHz, C_6D_6): δ = –161.8, –161.1, –153.4, –151.8 ppm. **^{11}B NMR** (161 MHz, C_6D_6): δ = 6.3 ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 74.7 ppm.

In CD_2Cl_2: Prepared from borane **5** (13 mg, 21 µmol, 1.0 equiv) and triethylphosphine oxide (2.9 mg, 22 µmol, 1.0 equiv) according to the general procedure.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.14 (m_c, 9H), 1.73 (m_c, 6H), 7.72 (d, *J* = 8.5 Hz, 3H), 7.90 (d, *J* = 8.6 Hz, 3H), 8.16 (s, 3H) ppm. **^{19}F NMR** (471 MHz, CD_2Cl_2): δ = –163.1, –162.4, –153.1, –152.8 ppm. **^{11}B NMR** (161 MHz, CD_2Cl_2): δ = 5.9 ppm. **^{31}P NMR** (203 MHz, CD_2Cl_2): δ = 76.6 ppm.

3.2 Tris(pentafluorophenyl)borane Triethylphosphine Oxide Adduct (1·Et$_3$PO)

In C_6D_6: Prepared from borane **1** (12 mg, 23 µmol, 1.0 equiv) and triethylphosphine oxide (3.1 mg, 23 µmol, 1.0 equiv) according to the general procedure.

^{1}H NMR (500 MHz, C_6D_6): δ = 0.27 (dt, *J* = 18.6 Hz, *J* = 7.7 Hz, 9H), 0.94 (dq, *J* = 12.3 Hz, *J* = 7.7 Hz, 6H). **^{19}F NMR** (471 MHz, C_6D_6): δ = –164.0, –157.4, –133.9 ppm. **^{11}B NMR** (161 MHz, C_6D_6): δ = –2.1 ppm. **^{31}P NMR** (203 MHz, C_6D_6): δ = 75.3 ppm.

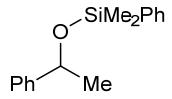
In CD_2Cl_2: Prepared from borane **1** (10 mg, 20 µmol, 1.0 equiv) and triethylphosphine oxide (2.7 mg, 20 µmol, 1.0 equiv) according to the general procedure.
^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.07 (dt, *J* = 18.6 Hz, *J* = 7.7 Hz, 9H), 1.92 (dq, *J* = 12.2 Hz, *J* = 7.7 Hz, 6H. **^{19}F NMR** (471 MHz, CD_2Cl_2): δ = –165.0, –159.1, –134.4 ppm. **^{11}B NMR** (161 MHz, CD_2Cl_2): δ = –2.4 ppm. **^{31}P NMR** (203 MHz, CD_2Cl_2): δ = 76.9 ppm.

3.3 Tris(5,6,7,8-tetrafluoronaphthalen-2-yl)borane Triphenylphosphine Oxide Adduct (5·Ph_3PO)

Prepared from equimolar amounts of borane **5** and triphenylphosphine oxide in a mixture of C_6D_6 and 1,2-$F_2C_6H_4$ in a glove box. Crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvents at room temperature in the glove box.

4 Experimental Details for Reactions Catalyzed by Tris(5,6,7,8-tetrafluoronaphthalen-2-yl)borane (5)

4.1 Dimethyl(phenyl)(1-phenylethoxy)silane (17)



17
$C_{16}H_{20}OSi$
M = 256.42 g/mol

from hydrosilylation

In a glove box, a 2-mL vial was charged with acetophenone (**16**, 77.9 mg, 0.648 mmol, 0.97 equiv), dimethylphenylsilane (**15**, 90.7 mg, 0.666 mmol, 1.0 equiv), and borane **5** (1.9 mg, 3.1 µmol, 0.48 mol % based on **16**) in toluene (0.5 mL). The reaction mixture was stirred at room temperature for 2 h and then subjected directly to flash column chromatography on silica gel using cyclohexane/ethyl acetate (30:1) as eluent, yielding the title compound **17** (150 mg, 90%) as a colorless oil.

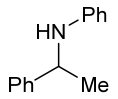
from dehydrogenative Si–O coupling

In a glove box, a 2-mL vial was charged with 1-phenylethanol (**20**, 77.9 mg, 0.504 mmol, 1.0 equiv), dimethylphenylsilane (**15**, 67.0 mg, 0.492 mmol, 1.0 equiv), and borane **5** (1.4 mg, 2.3 µmol, 0.47 mol %) in toluene (0.5 mL). The reaction mixture was stirred at room temperature for 2 h and then subjected directly to flash column chromatography on silica gel using cyclo-

hexane/ethyl acetate (30:1) as eluent, yielding the title compound **17** (101 mg, 80%) as a colorless oil.

***R*$_f$** = 0.68 (cyclohexane/ethyl acetate = 20:1). **GLC** (SE-54): t_R = 16.8 min. **IR** (ATR): $\tilde{\nu}$ = 2969 (w), 1491 (w), 1447 (w), 1367 (w), 1251 (m), 1085 (m), 1029 (m), 957 (m), 823 (s), 784 (s), 738 (m), 696 (s). **HRMS** (EI) calculated for $C_{16}H_{20}OSi$ $[M]^+$: 256.1278; found: 256.1269. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 0.33 (s, 3H), 0.37 (s, 3H), 1.44–1.48 (m, 3H), 4.89 (m_c, 1H), 7.21–7.44 (m, 8H), 7.57–7.61 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = –1.2, –0.7, 27.0, 71.2, 125.5, 127.0, 127.9, 128.3, 129.6, 133.7, 138.3, 146.4 ppm. **^{29}Si NMR** (99 MHz, $CDCl_3$): δ = 6.6 ppm. The analytical and spectroscopic data are in accordance with those reported.[S5]

4.2 *N*-(1-Phenylethyl)aniline (19)



19
$C_{14}H_{15}N$
M = 197.28

In a glove box, a 2-mL vial was charged with (*E*)-*N*,1-diphenylethan-1-imine (**18**, 39.7 mg, 0.203 mmol, 0.92 equiv), dimethylphenylsilane (**15**, 30.0 mg, 0.220 mmol, 1.0 equiv), and borane **5** (4.6 mg, 7.6 μmol, 3.7 mol % based on **18**) in toluene (0.5 mL). The reaction mixture was stirred at room temperature for 48 h and then subjected directly to flash column chromatography on silica gel using cyclohexane/ethyl acetate (50:1) as eluent, yielding the title compound **19** (34.4 mg, 86%) as a colorless oil.

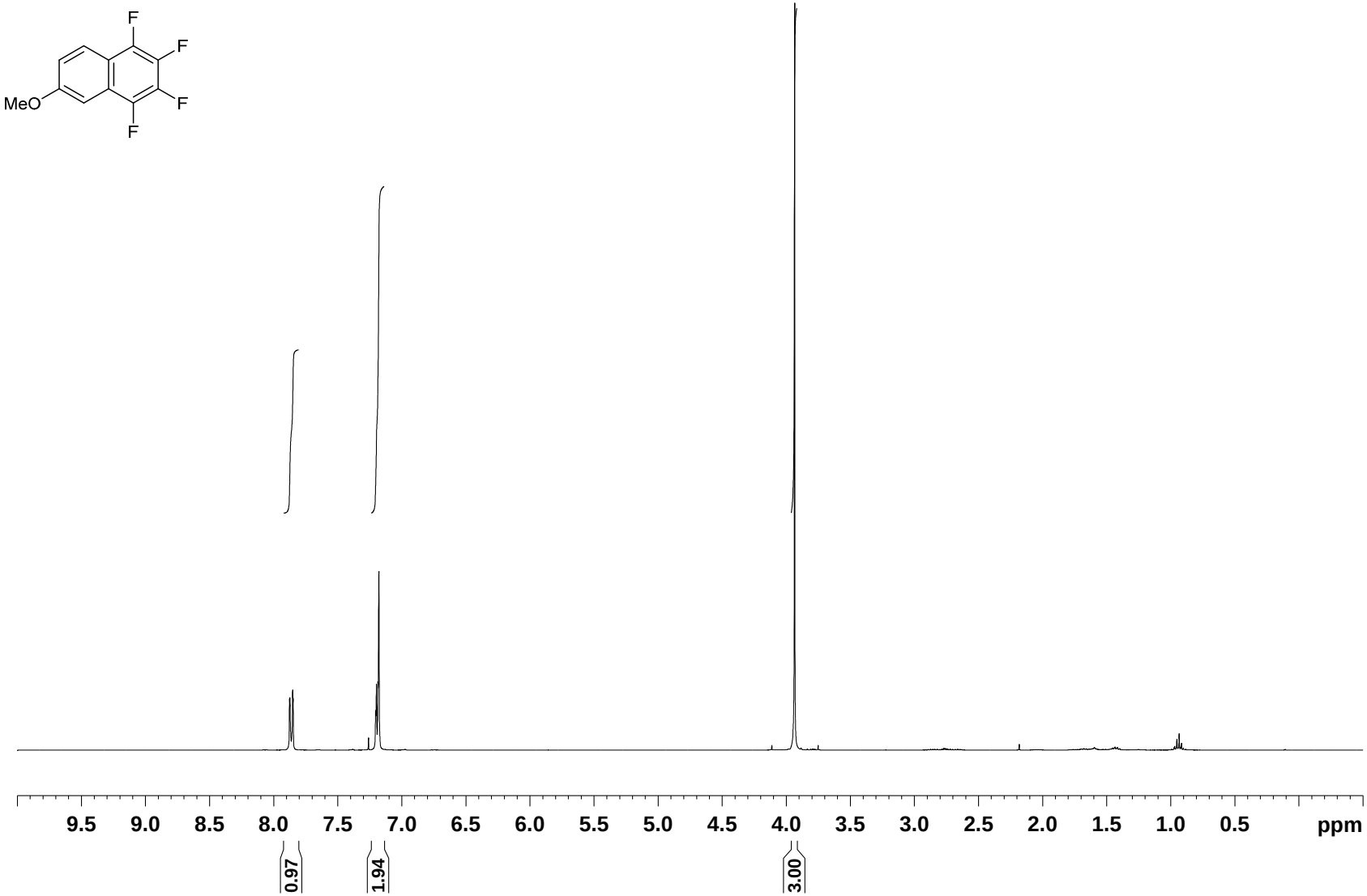
***R*$_f$** = 0.41 (cyclohexane/ethyl acetate = 20:1). **GLC** (SE-54): t_R = 17.2 min. **IR** (ATR): $\tilde{\nu}$ = 3406 (w), 3020 (w), 2964 (w), 2865 (w), 1598 (s), 1501 (s), 1447 (m), 1314 (m), 1255 (m), 1204 (w), 1138 (w), 867 (w), 754 (s), 690 (s) cm^{-1}. **HRMS** (ESI) calculated for $C_{14}H_{16}N$ $[M+H]^+$: 198.1277; found: 198.1276. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 1.53 (d, *J* = 6.8 Hz, 3H), 4.15 (br s, 1H), 4.49 (q, *J* = 6.8 Hz, 1H), 6.53 (m_c, 2H), 6.65 (tt, *J* = 7.3 Hz, *J* = 1.0 Hz, 1H), 7.10 (m_c, 2H), 7.23 (tt, *J* = 7.3 Hz, *J* = 1.4 Hz, 1H), 7.30–7.35 (m, 2H), 7.35–7.40 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ = 25.1, 53.7, 113.6, 117.5, 126.0, 127.0, 128.8, 129.2, 145.3, 147.3 ppm. The analytical and spectroscopic data are in accordance with those reported.[S6]

.

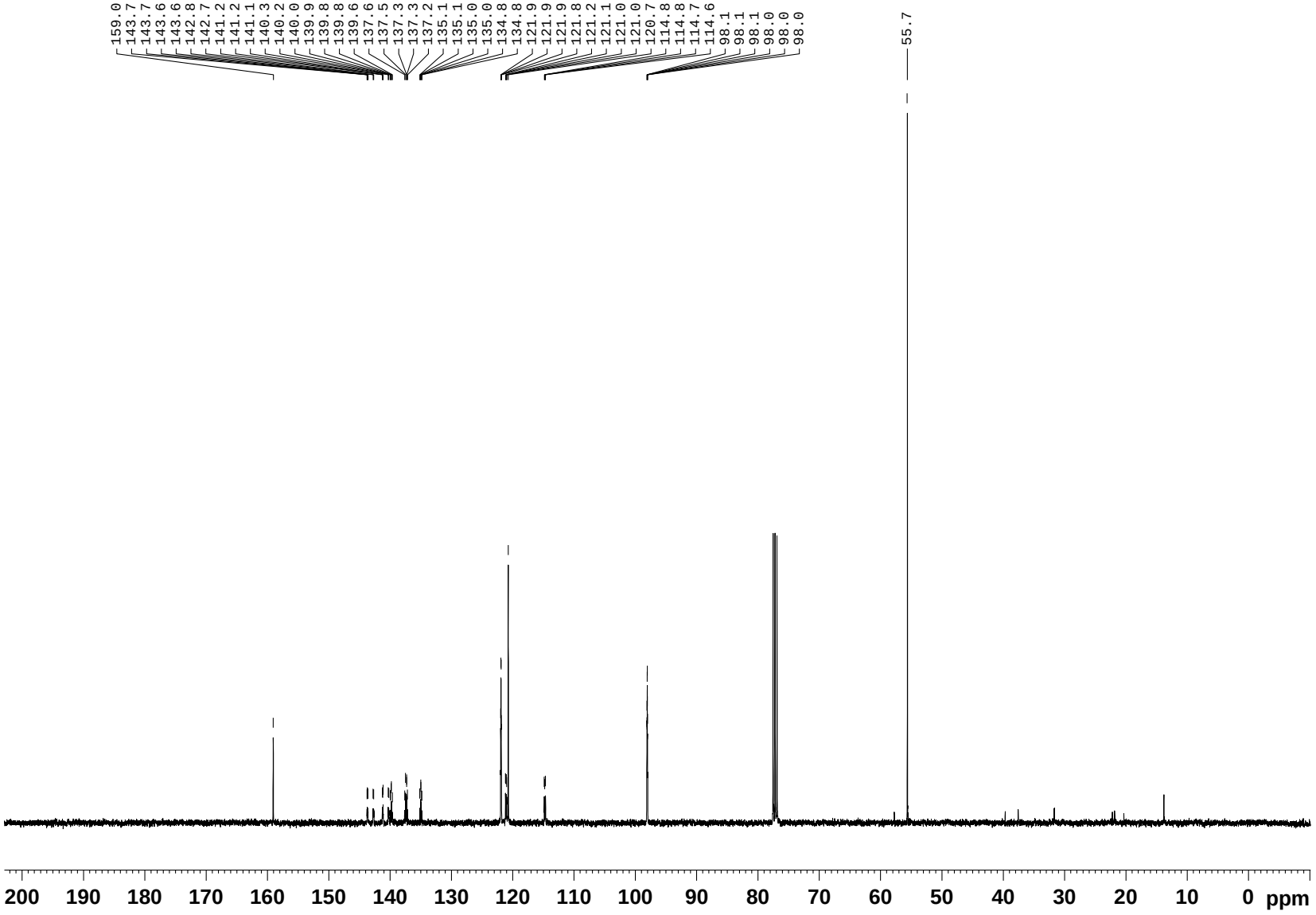
5 NMR Spectra

1,2,3,4-Tetrafluoro-6-methoxynaphthalene

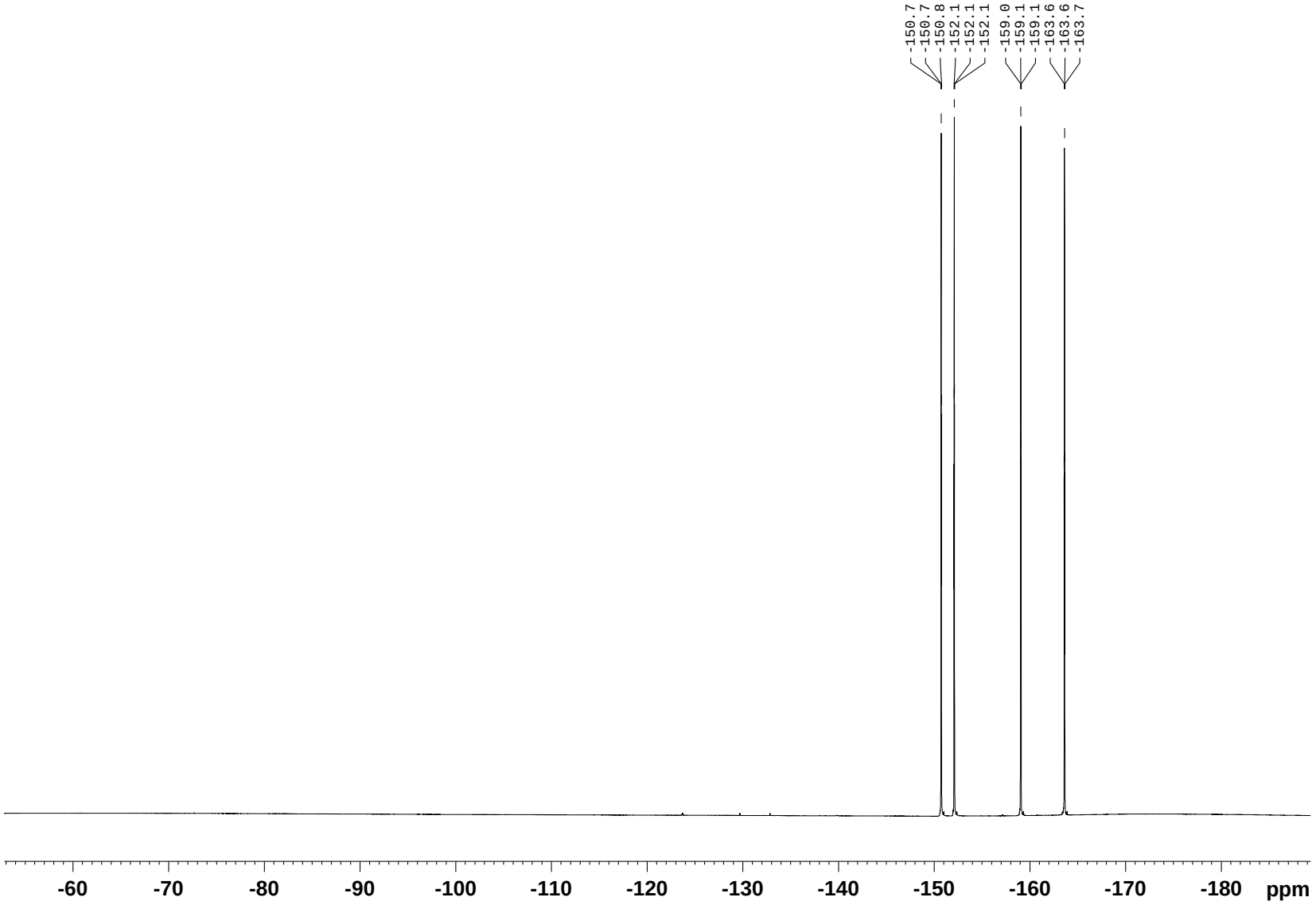
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

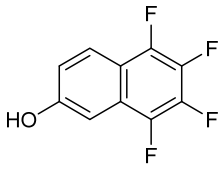


^{19}F NMR (659 MHz, $CDCl_3$)

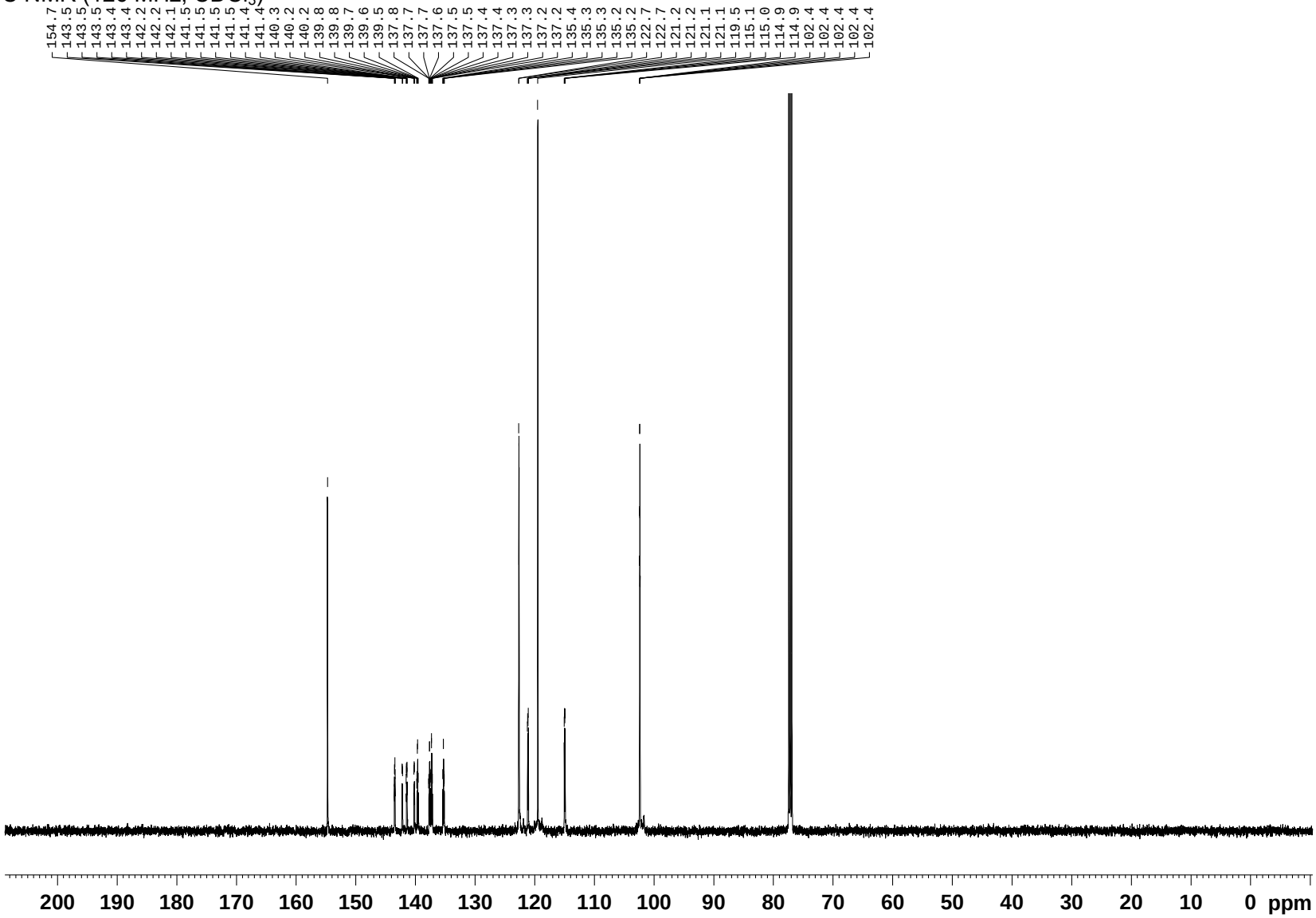


5,6,7,8-Tetrafluoronaphthalen-2-ol (11)

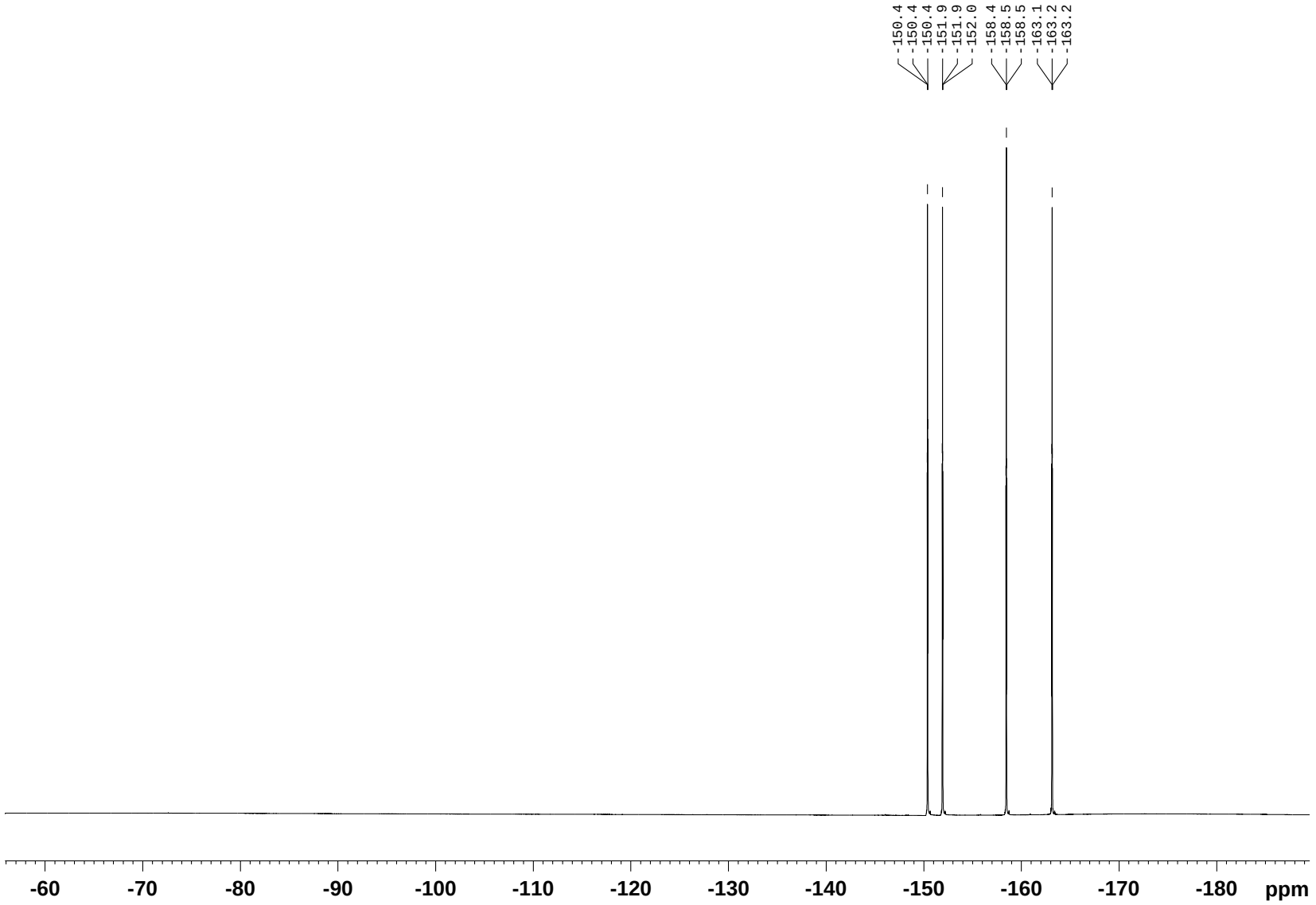
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

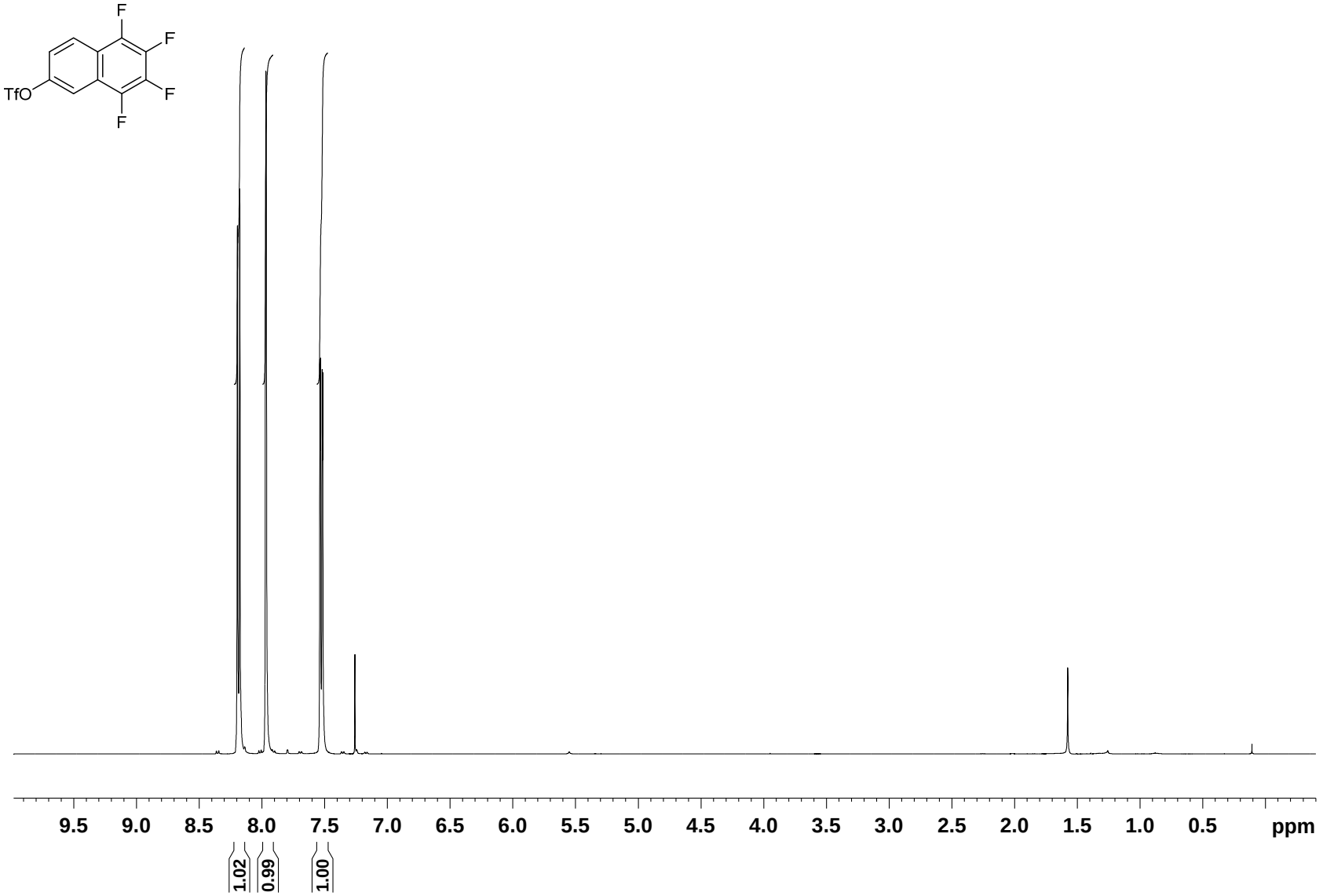


^{19}F NMR (659 MHz, $CDCl_3$)

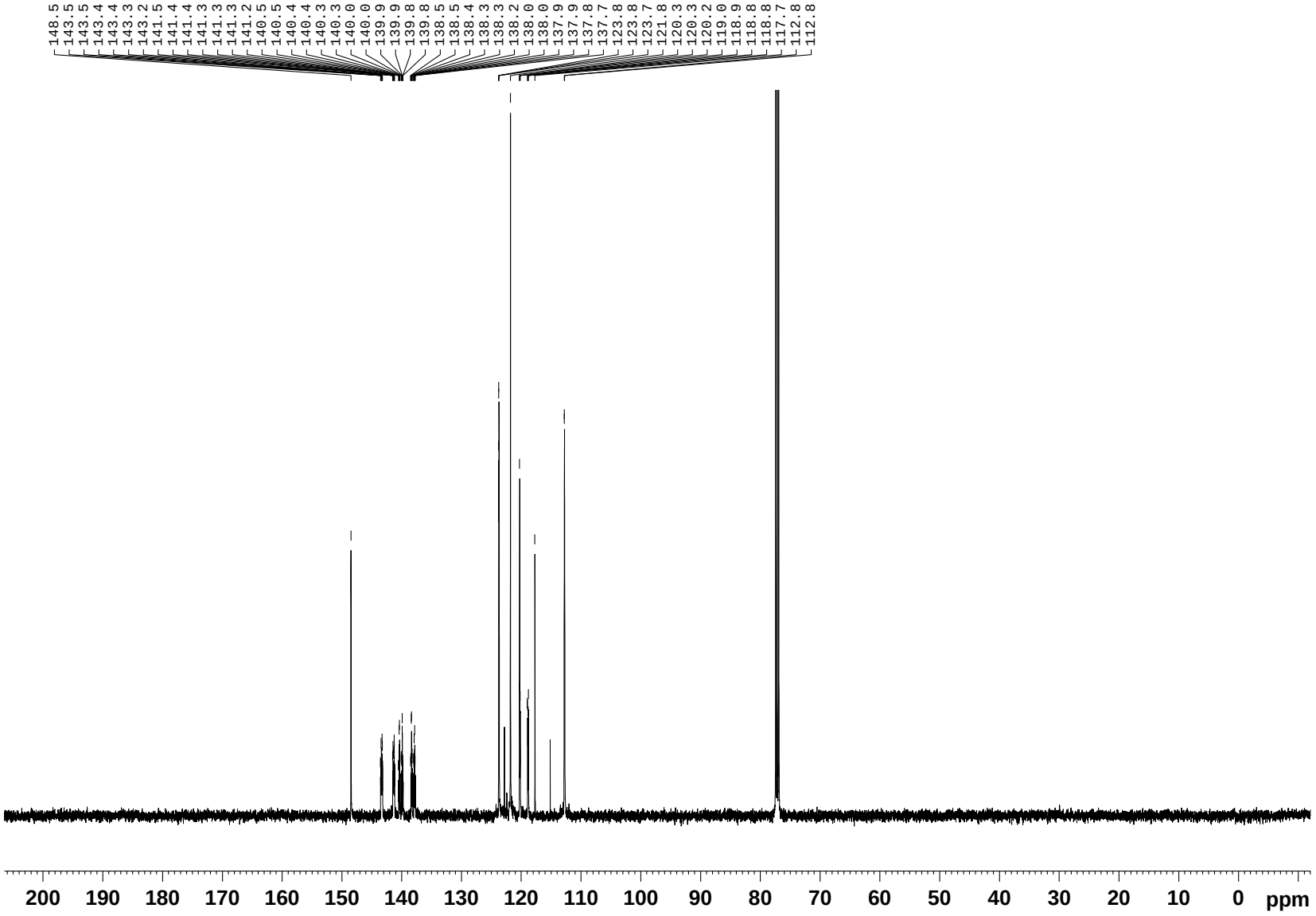


5,6,7,8-Tetrafluoronaphthalen-2-yl Trifluoromethanesulfonate (12)

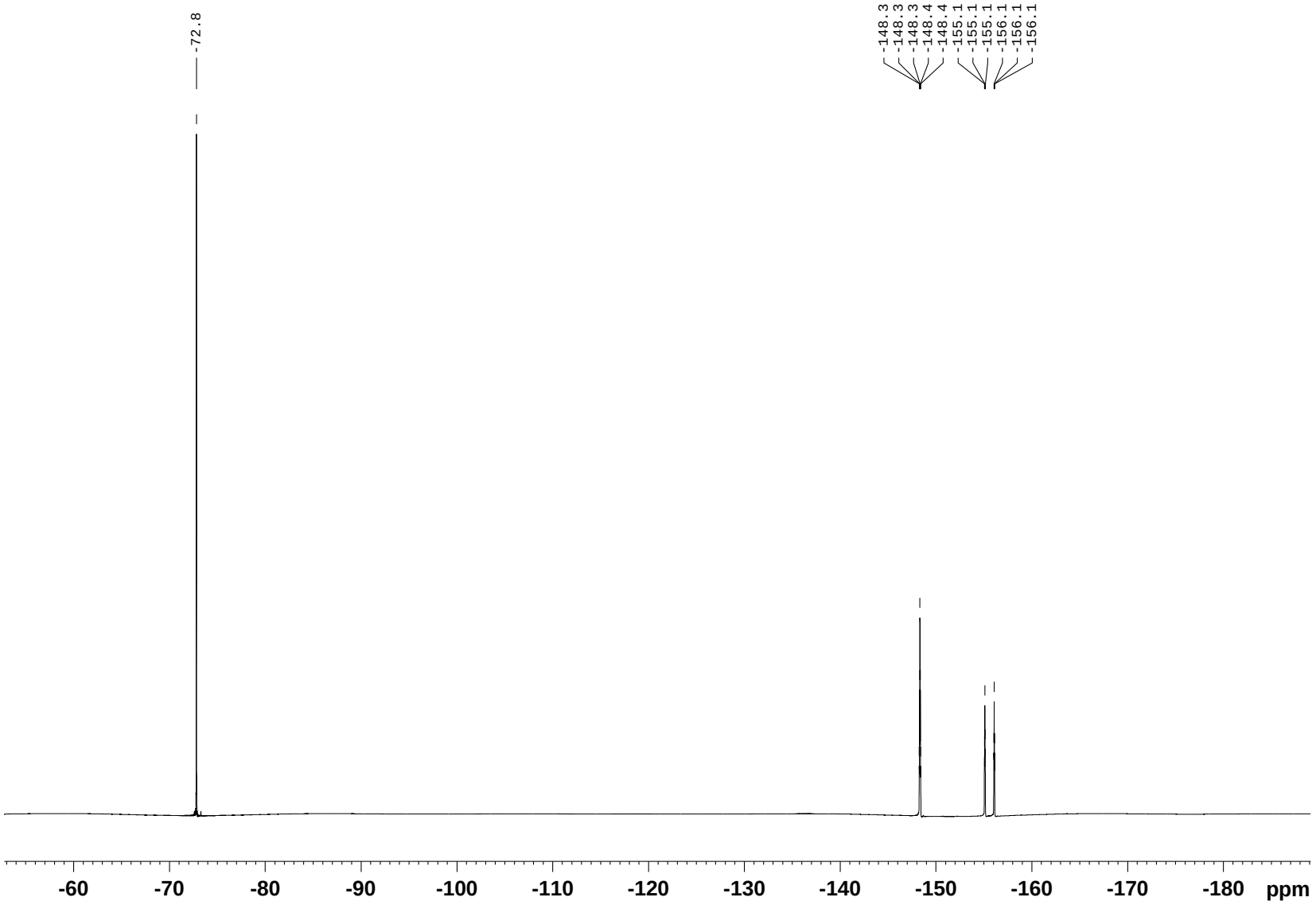
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

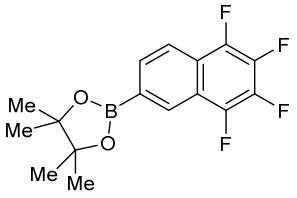


^{19}F NMR (471 MHz, $CDCl_3$)



4,4,5,5-Tetramethyl-2-(5,6,7,8-tetrafluoronaphthalen-2-yl)-1,3,2-dioxaborolane (13)

^{1}H NMR (500 MHz, $CDCl_3$)

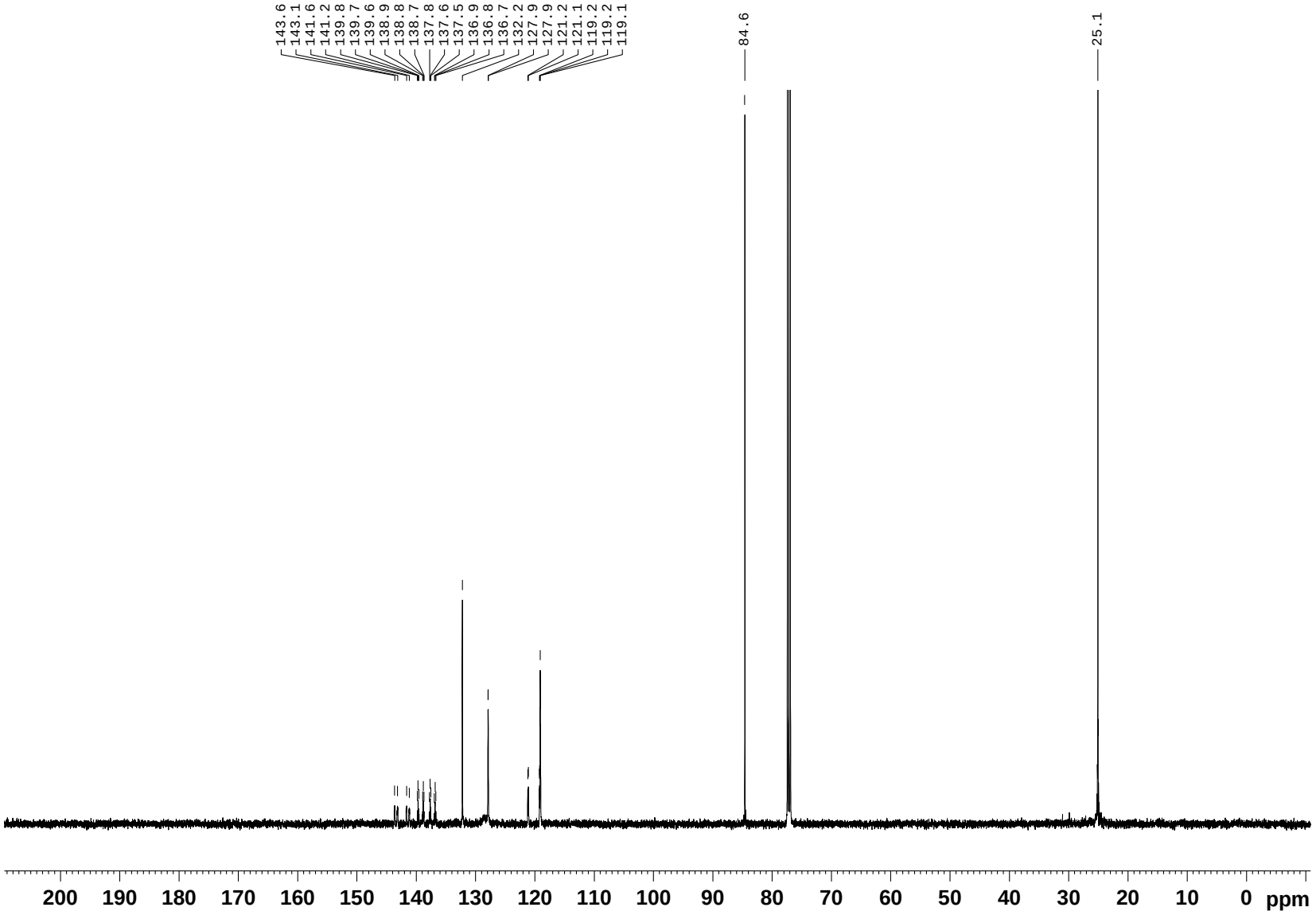


13

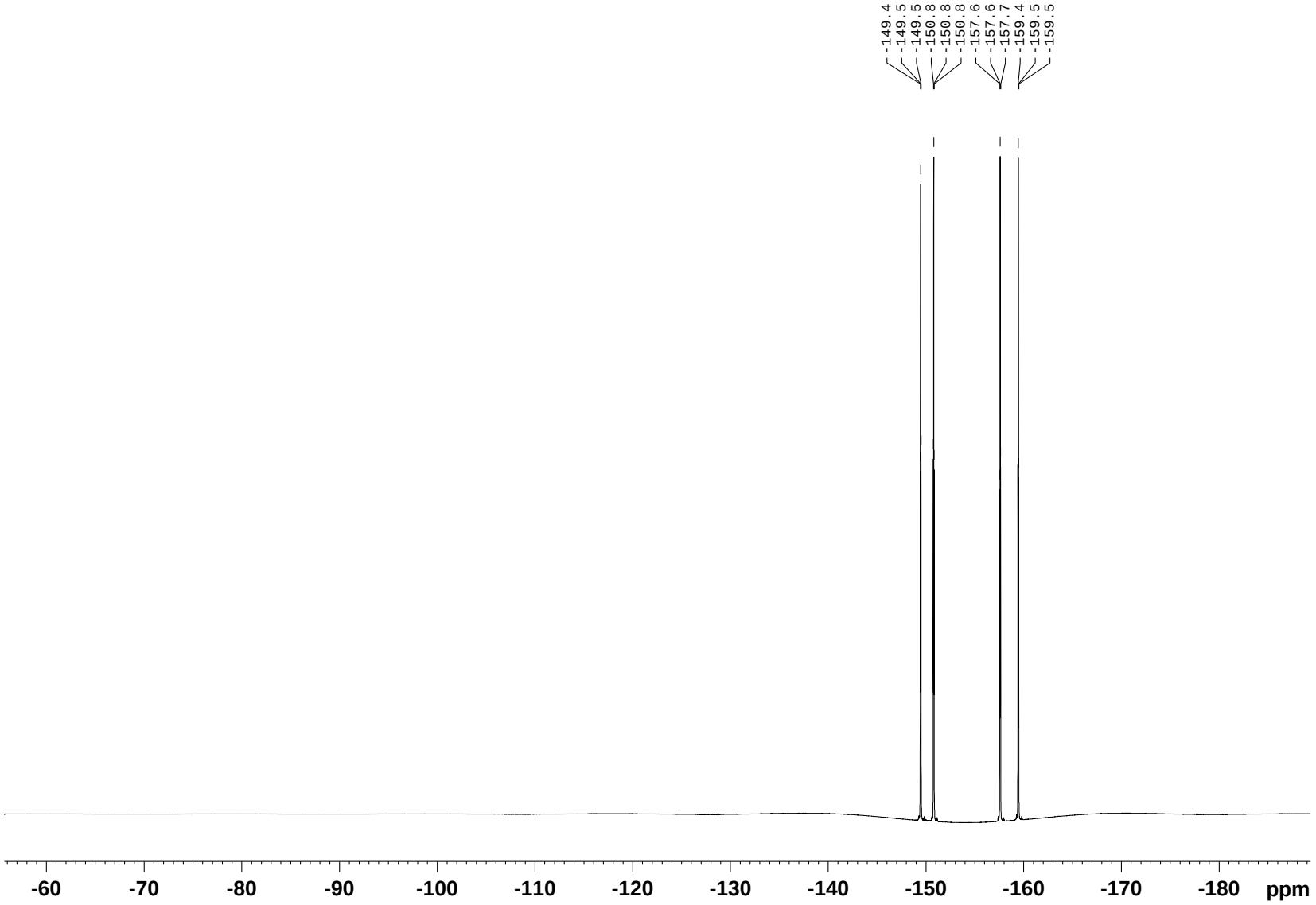
$C_{16}H_{15}BF_4O_2$

M = 326.10 g/mol

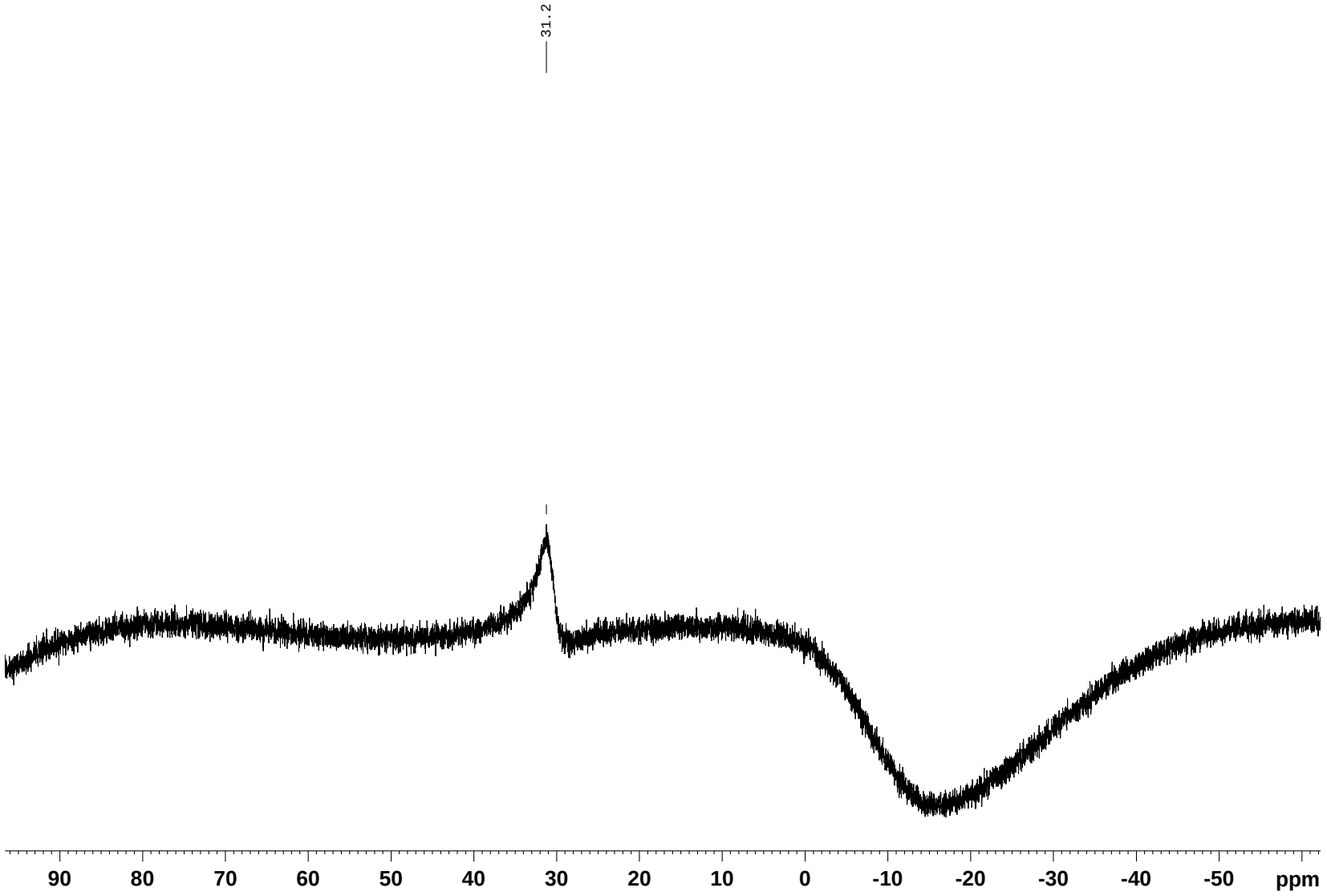
^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)

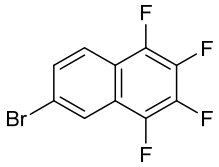


^{11}B NMR (160 MHz, $CDCl_3$)

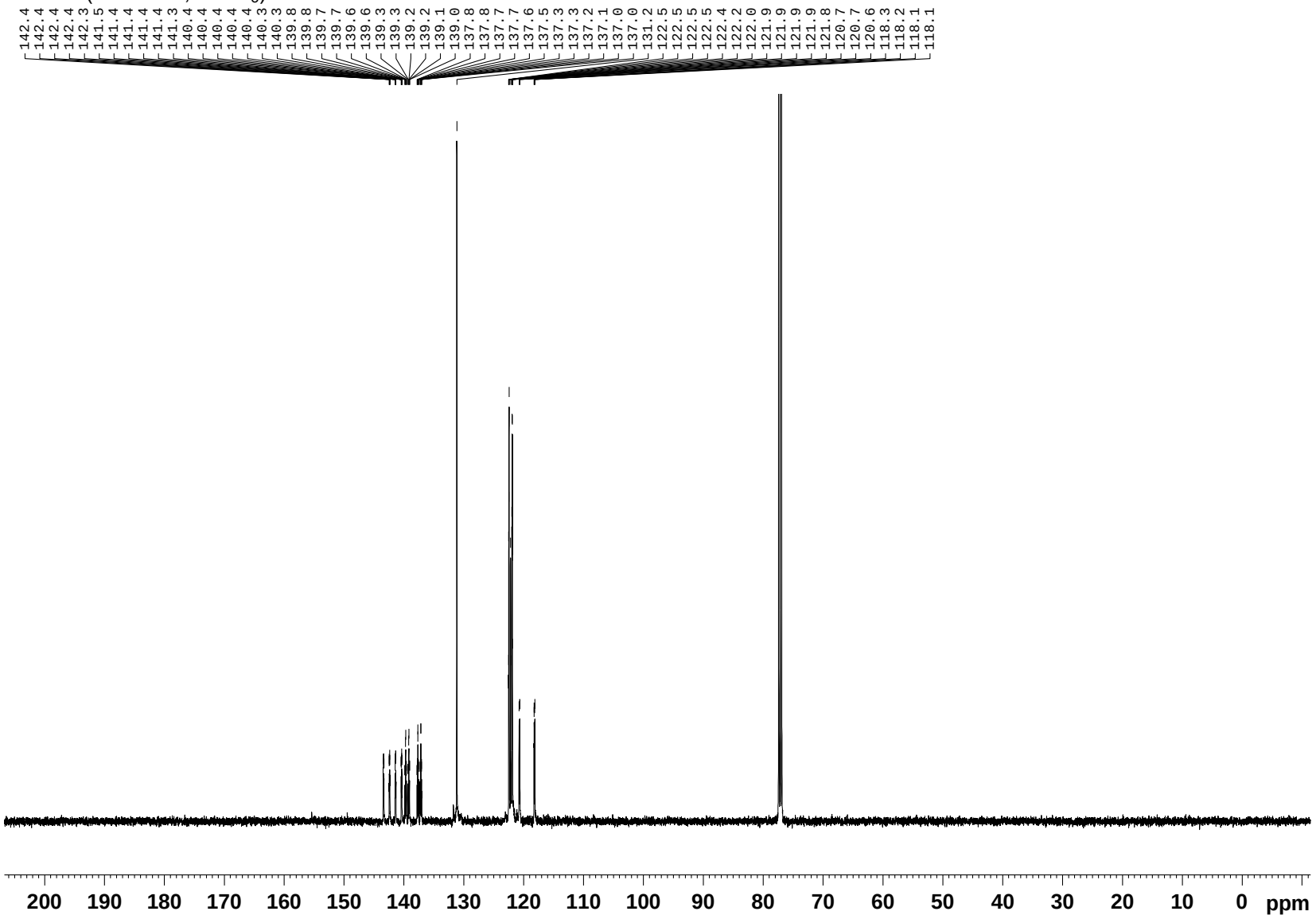


6-Bromo-1,2,3,4-tetrafluoronaphthalene (6)

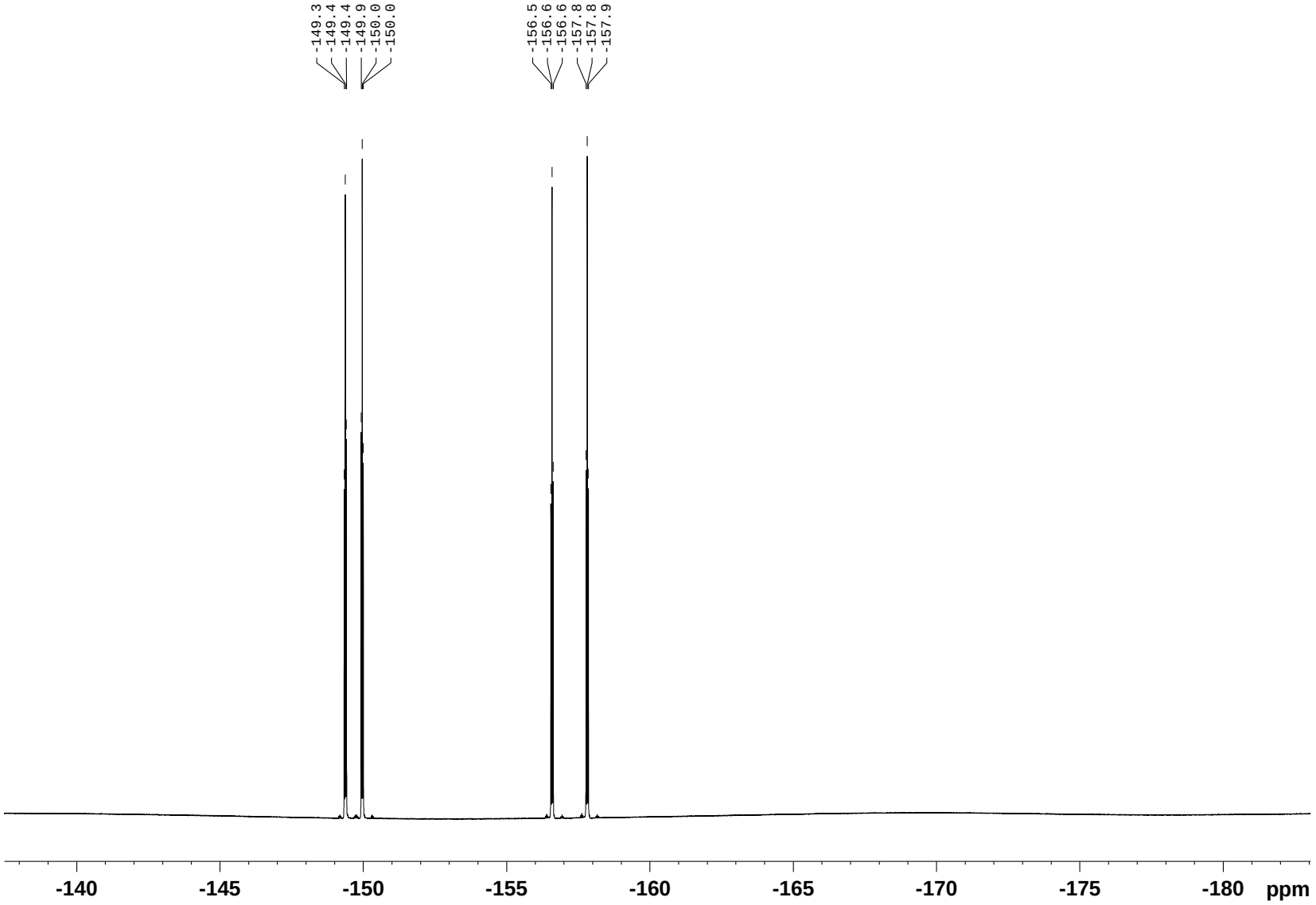
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

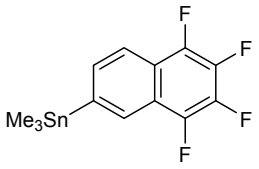


^{19}F NMR (471 MHz, $CDCl_3$)

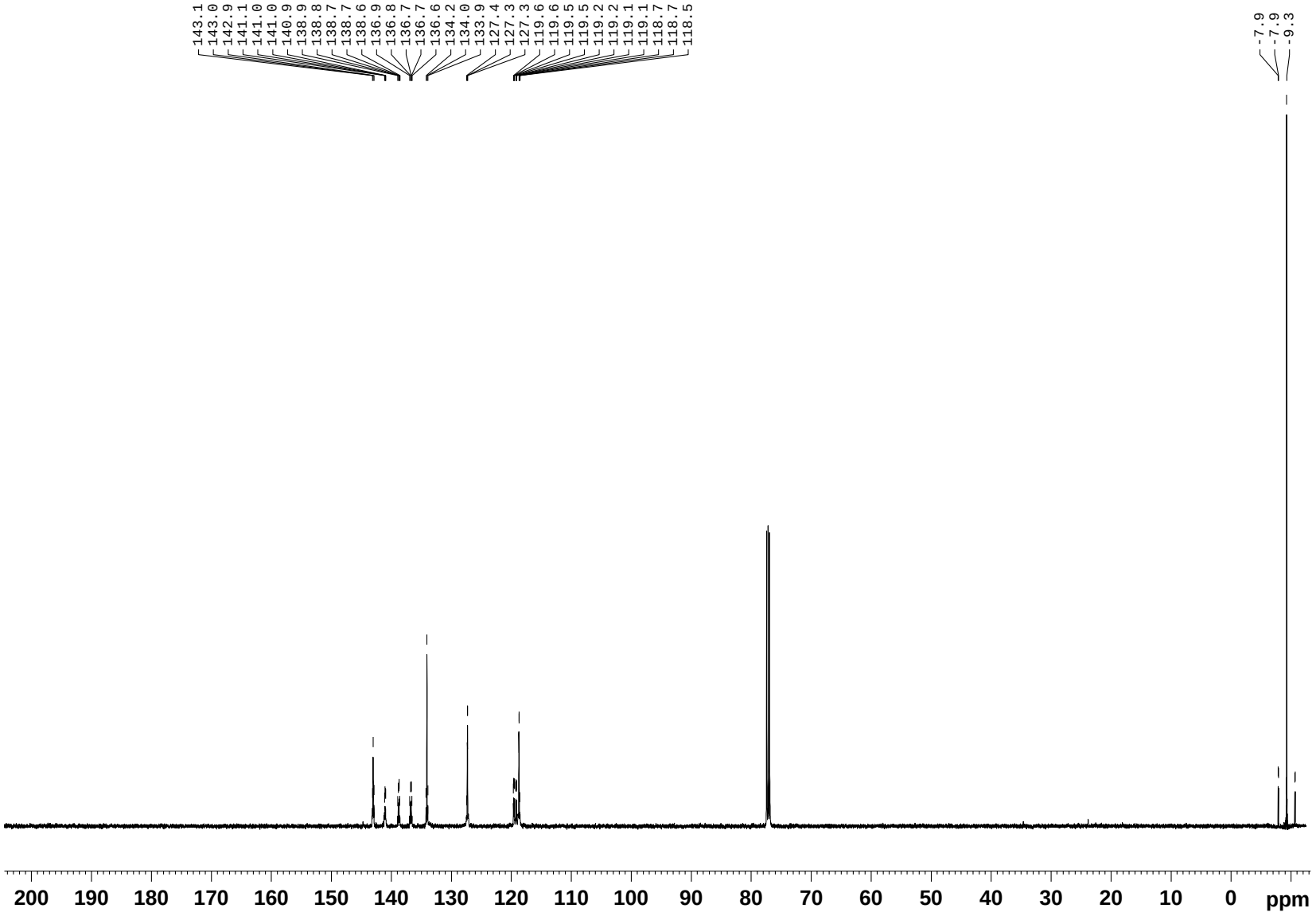


Trimethyl(5,6,7,8-tetrafluoronaphthalen-2-yl)stannane (14)

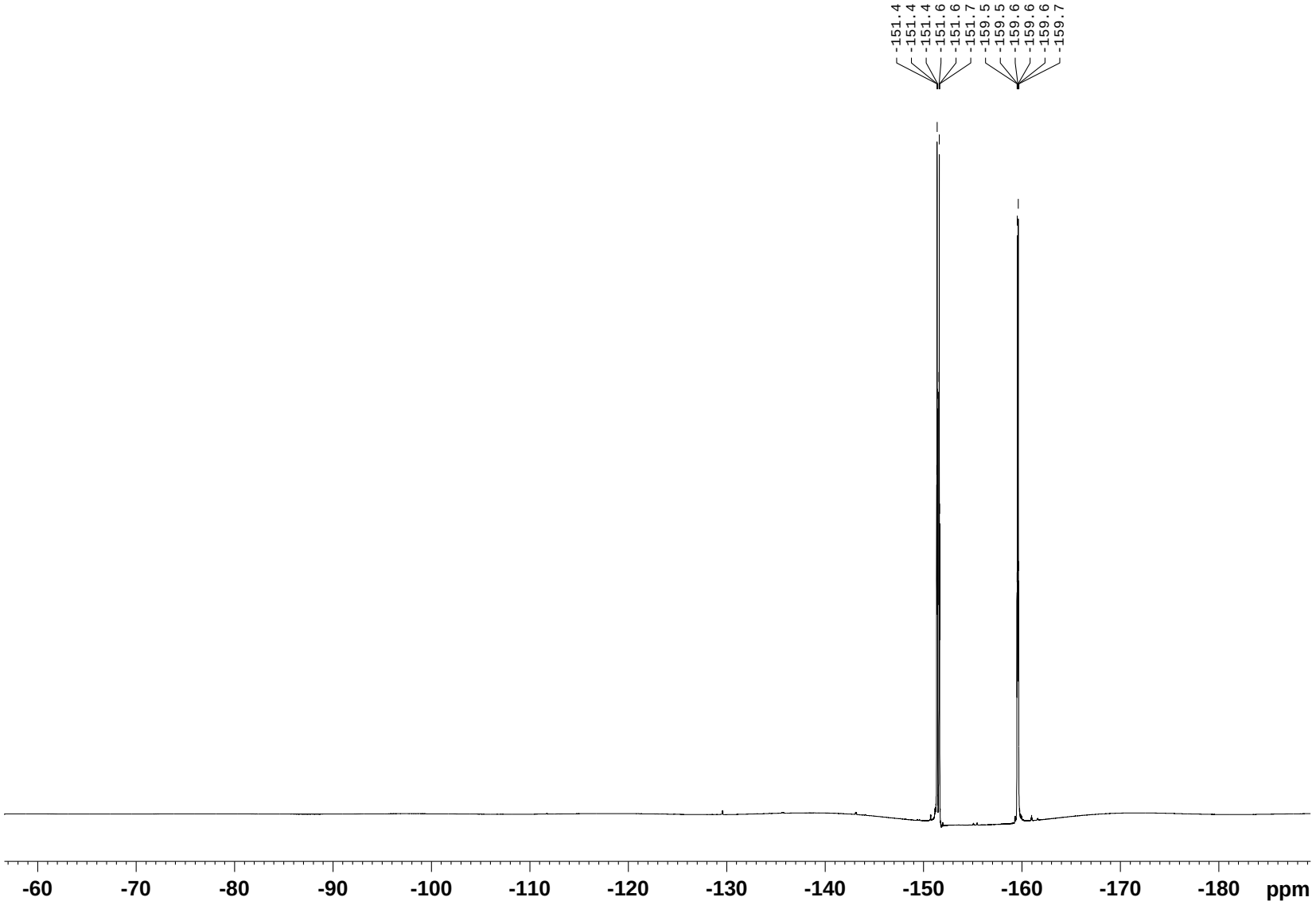
^{1}H NMR (500 MHz, $CDCl_3$)



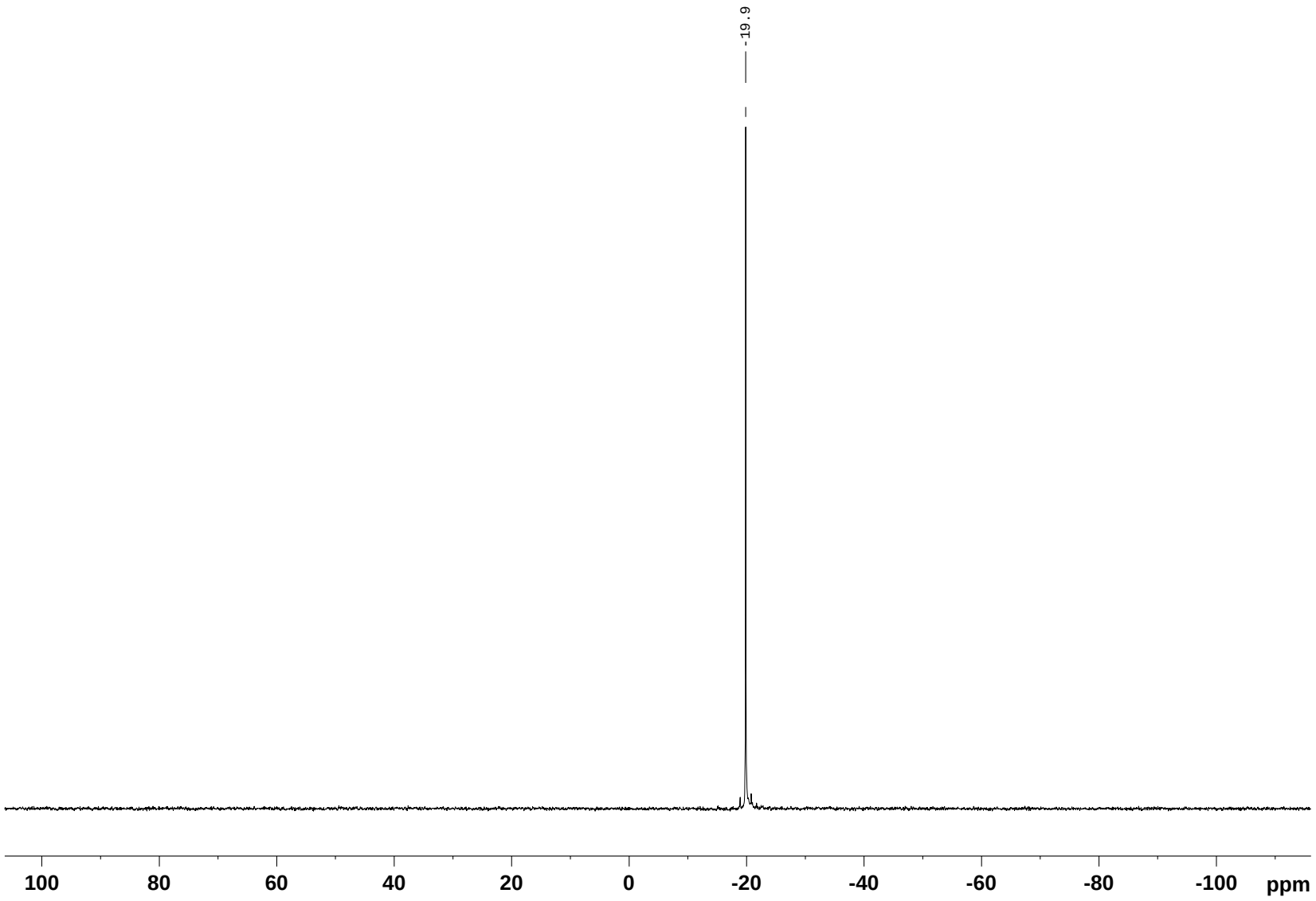
^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (471 MHz, $CDCl_3$)

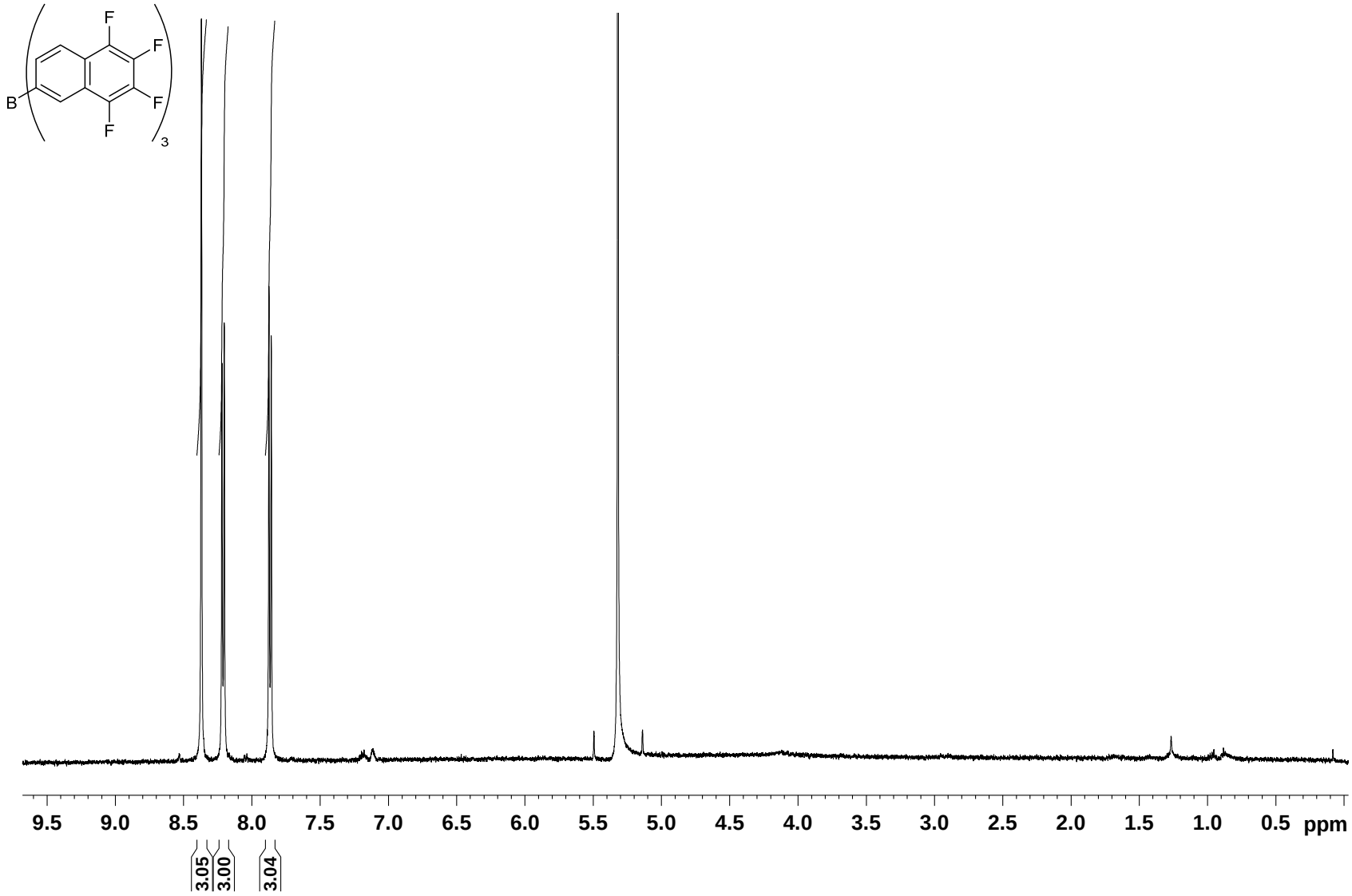


^{119}Sn NMR (187 MHz, $CDCl_3$)

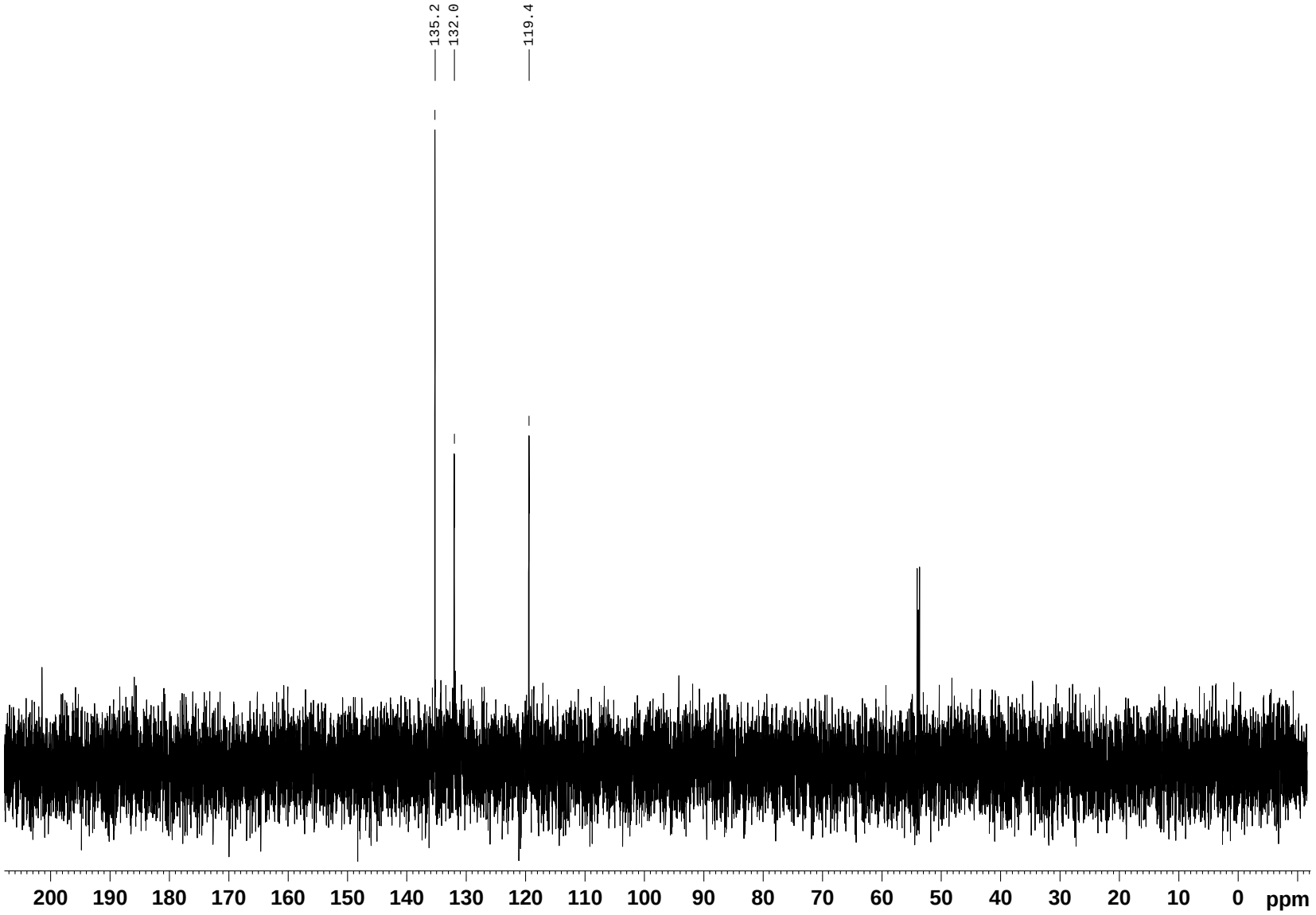


Tris(5,6,7,8-tetrafluoronaphthalen-2-yl)borane (5)

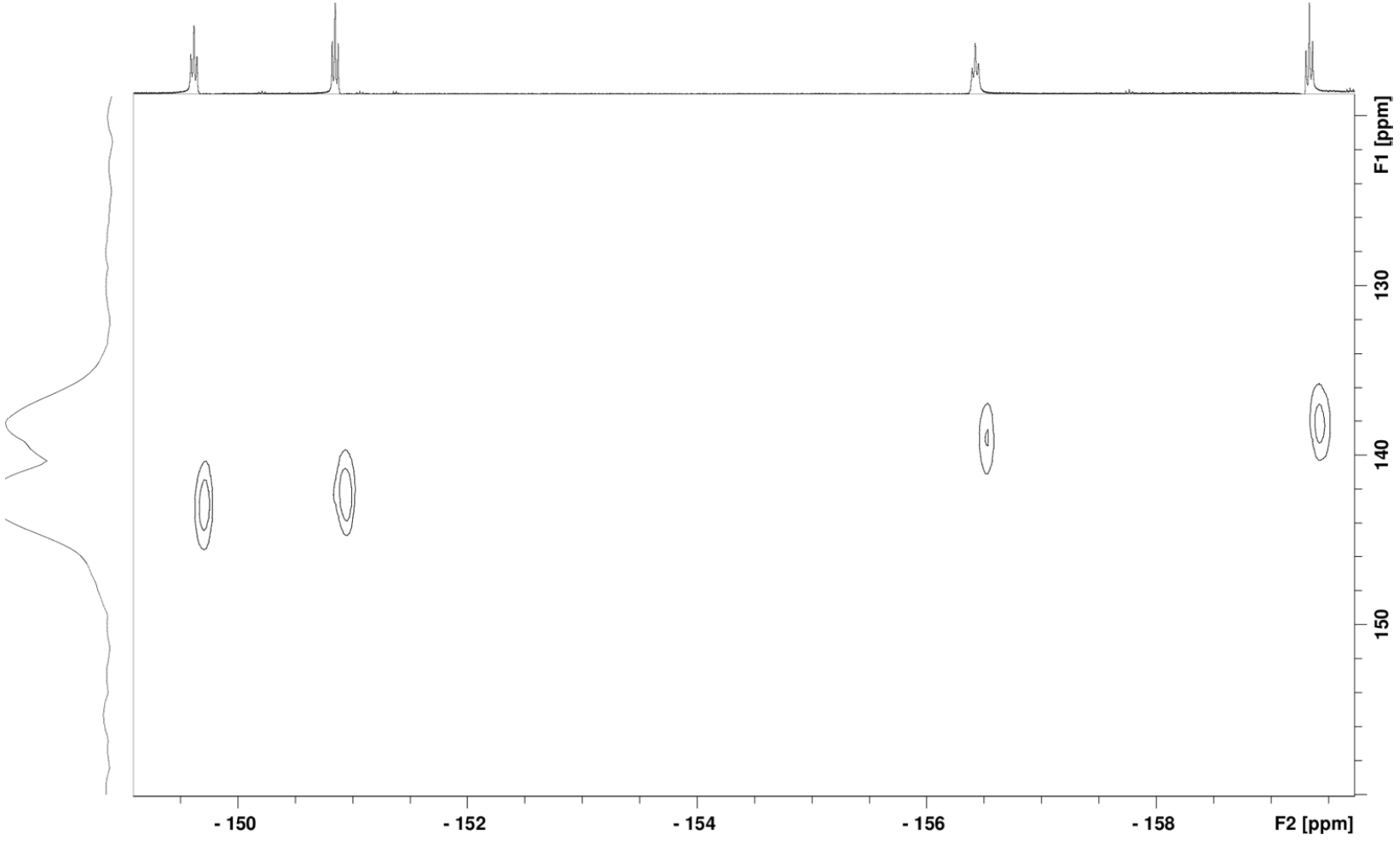
^{1}H NMR (500 MHz, CD_2Cl_2)



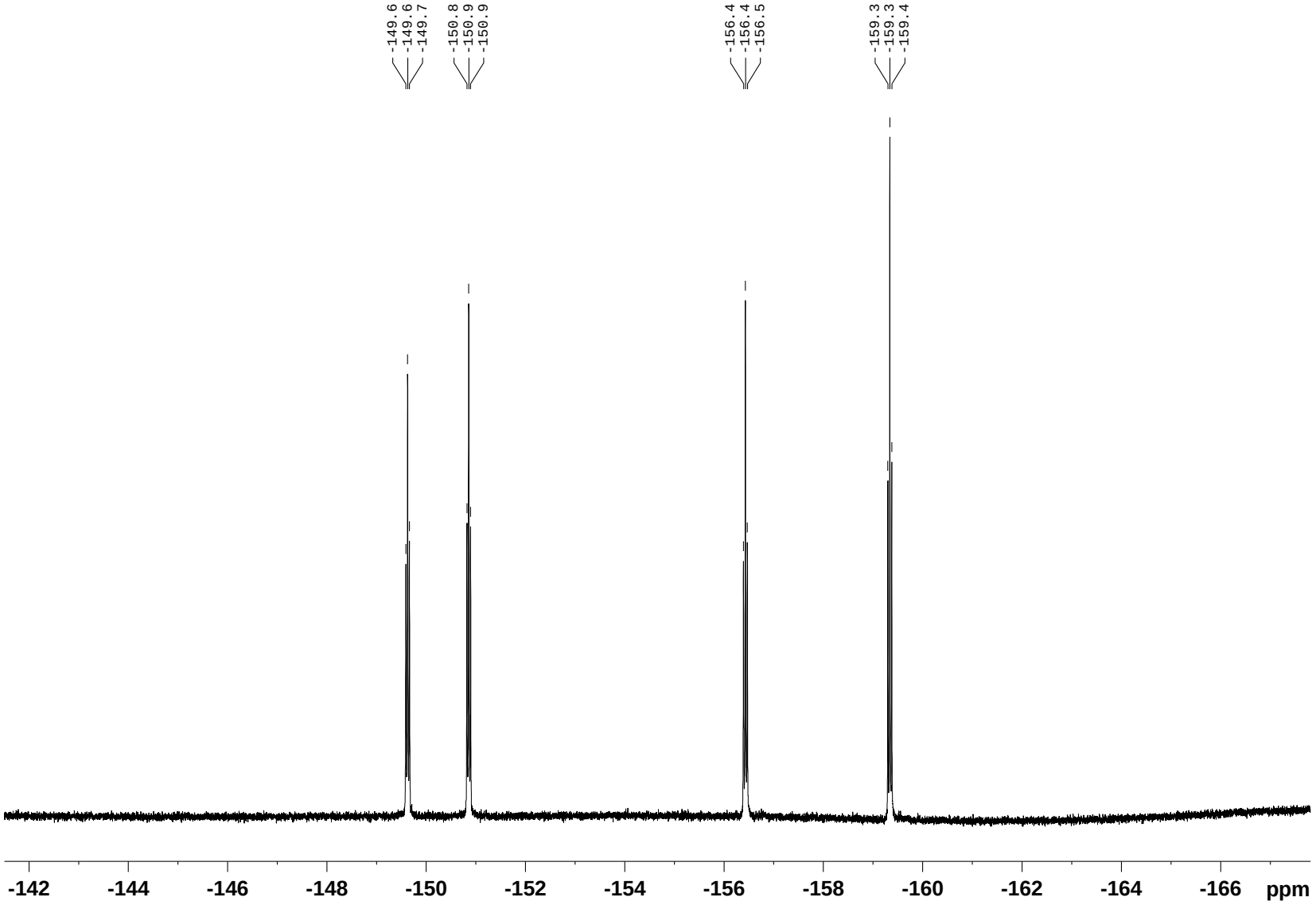
^{13}C DEPT (126 MHz, CD_2Cl_2)



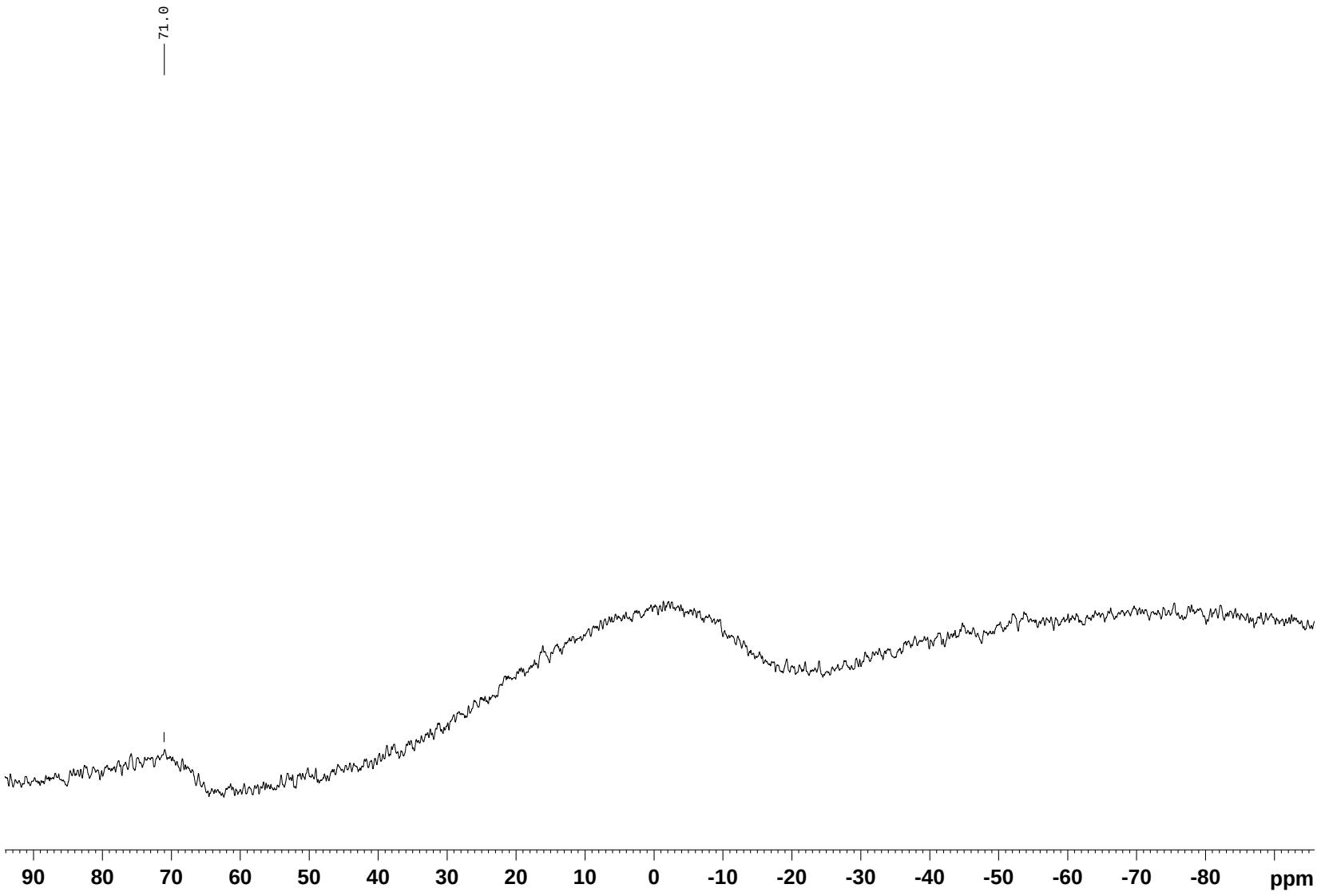
$^{19}F/^{13}C$ HMQC (659 MHz/176 MHz, CD_2Cl_2)



^{19}F NMR (471 MHz, CD_2Cl_2)

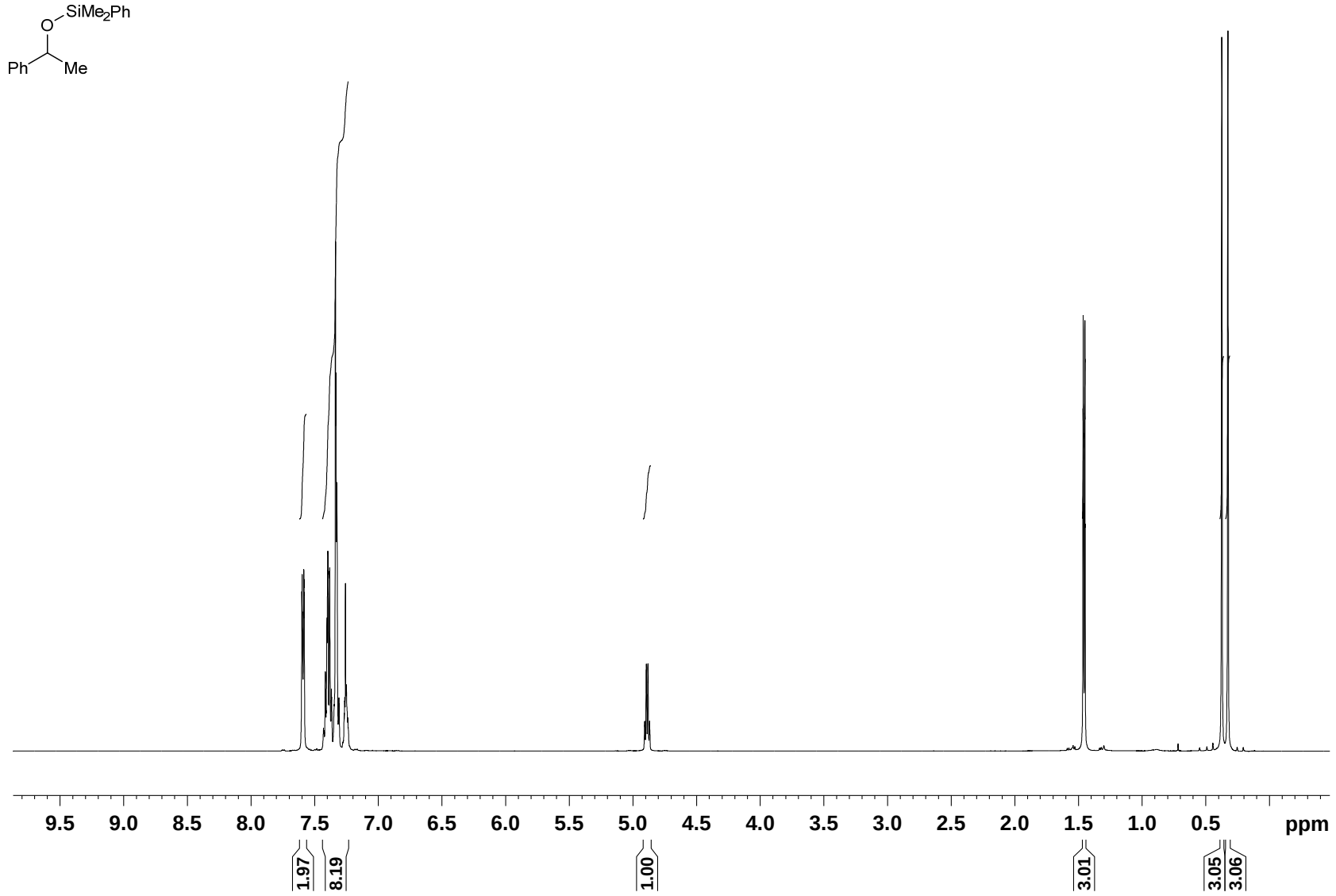


^{11}B NMR (161 MHz, CD_2Cl_2)

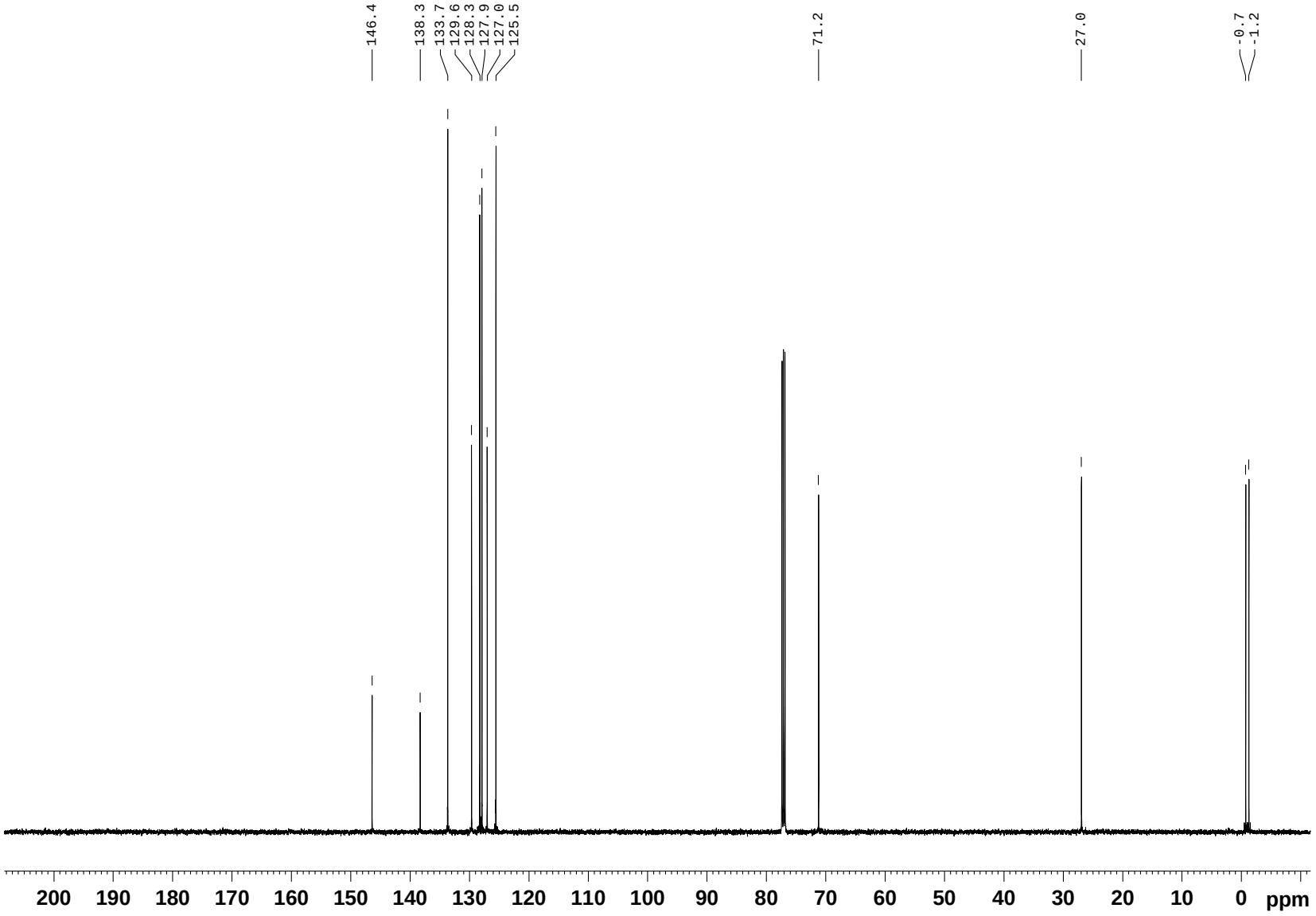


Dimethyl(phenyl)(1-phenylethoxy)silane (17)

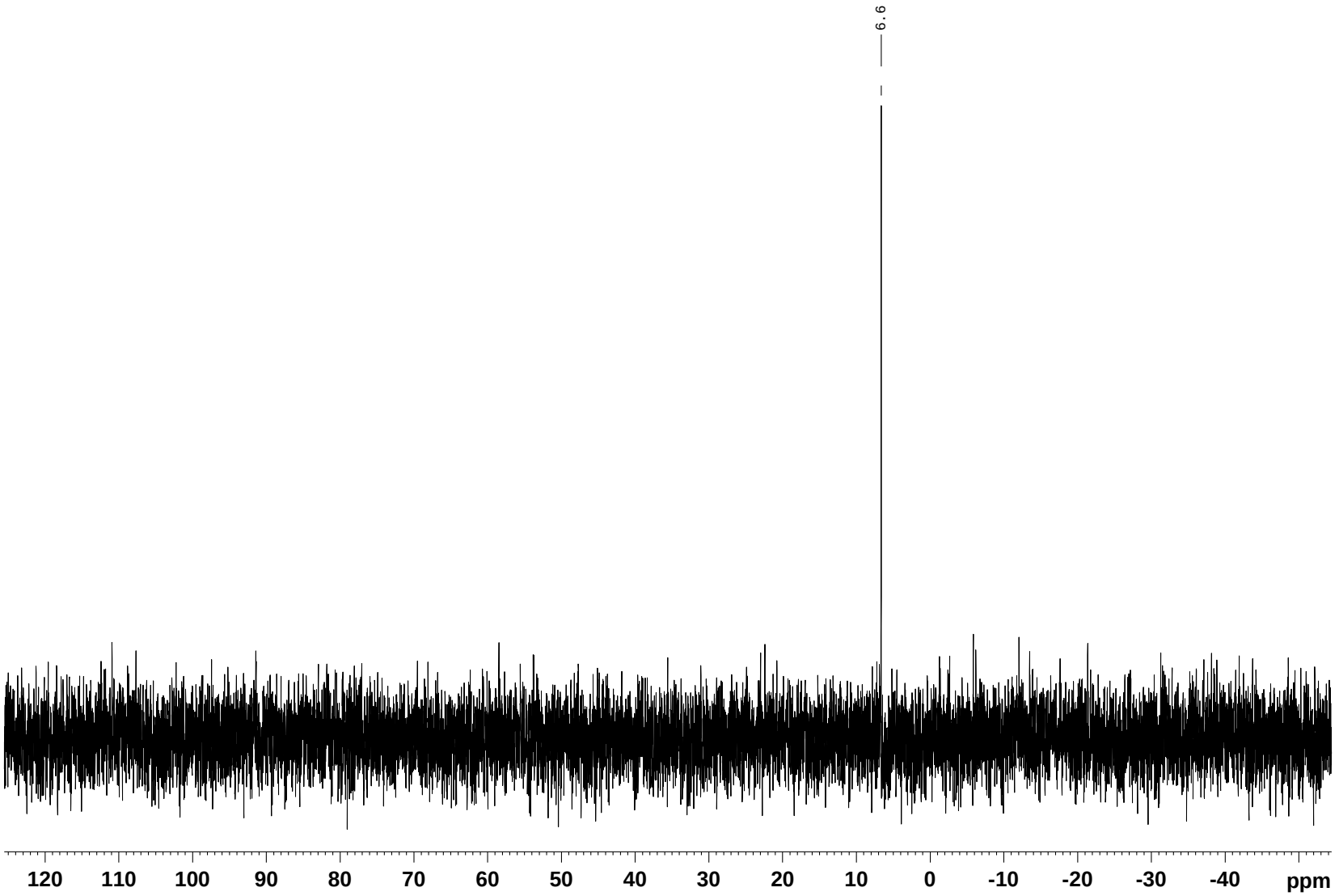
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

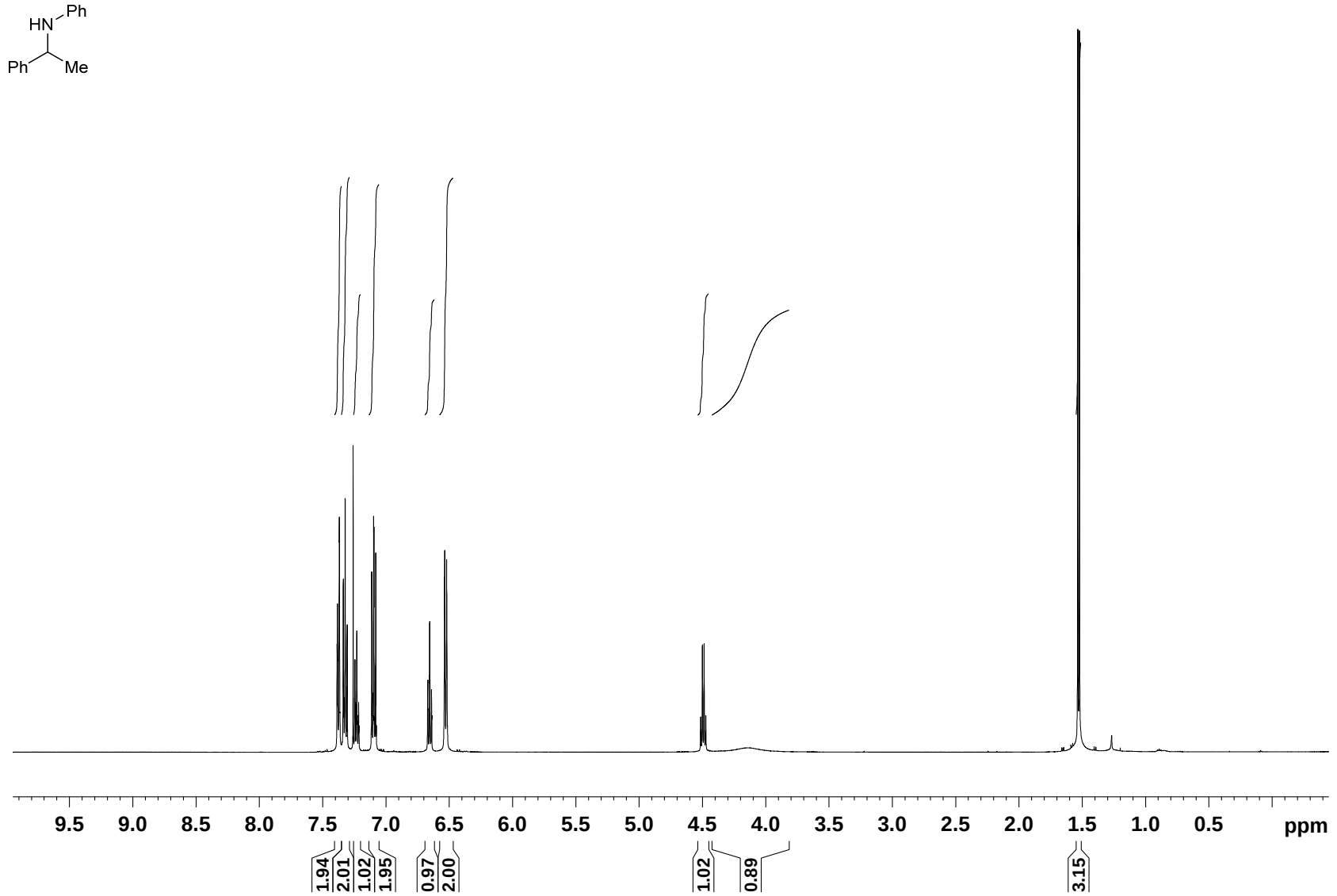


^{29}Si NMR (99 MHz, $CDCl_3$)

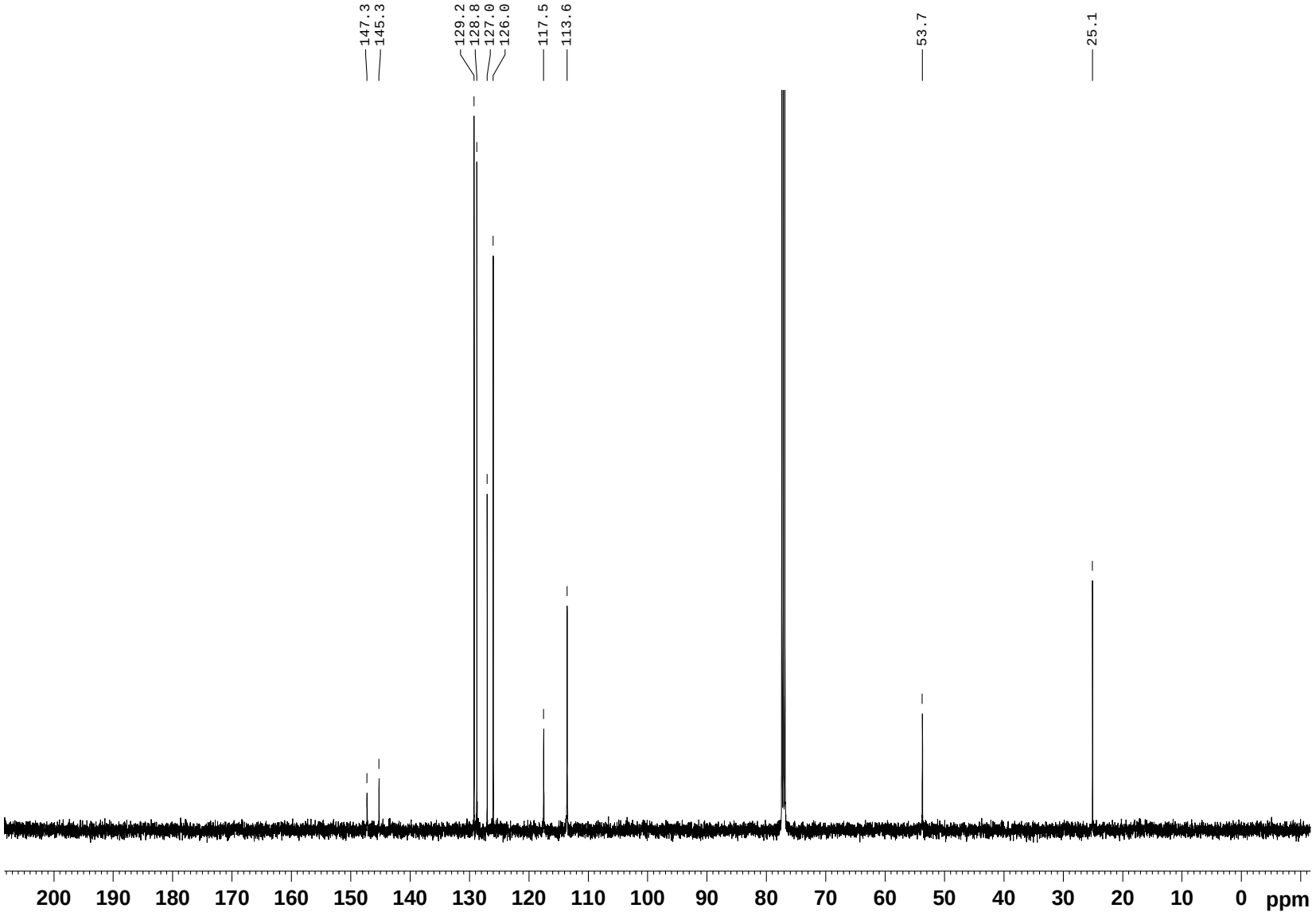


_N_-(1-Phenylethyl)aniline (19)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

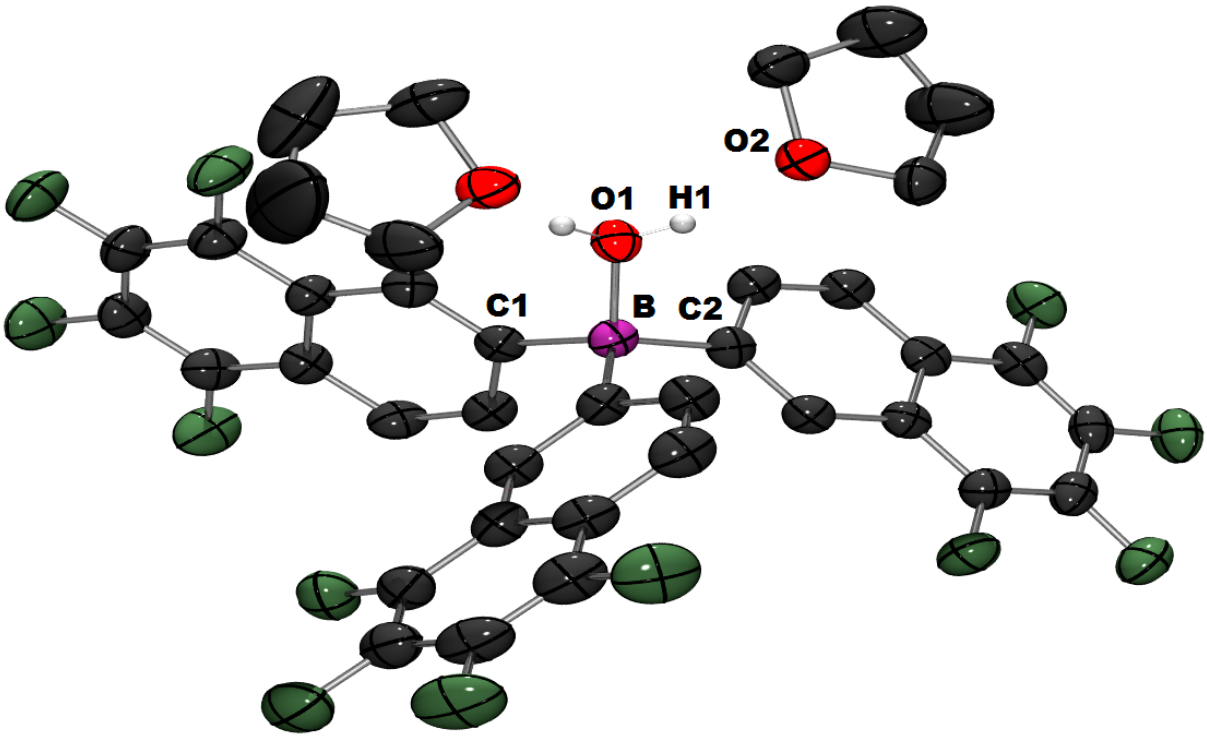


6 Molecular Structures and X-Ray Data

Data for the single-crystal structure determination were collected with an Agilent SuperNova diffractometer equipped with a CCD area Atlas detector and a mirror monochromator by utilizing Cu-K_α radiation (λ= 1.5418 Å). Software packages used: CrysAlis PRO for data collection, cell refinement, and data reduction,[S7] SHELXS-97 for structure solution,[S8] SHELXL-97 for structure refinement,[S9] Ortep-3[S10] and POV-Ray[S11] for graphics.

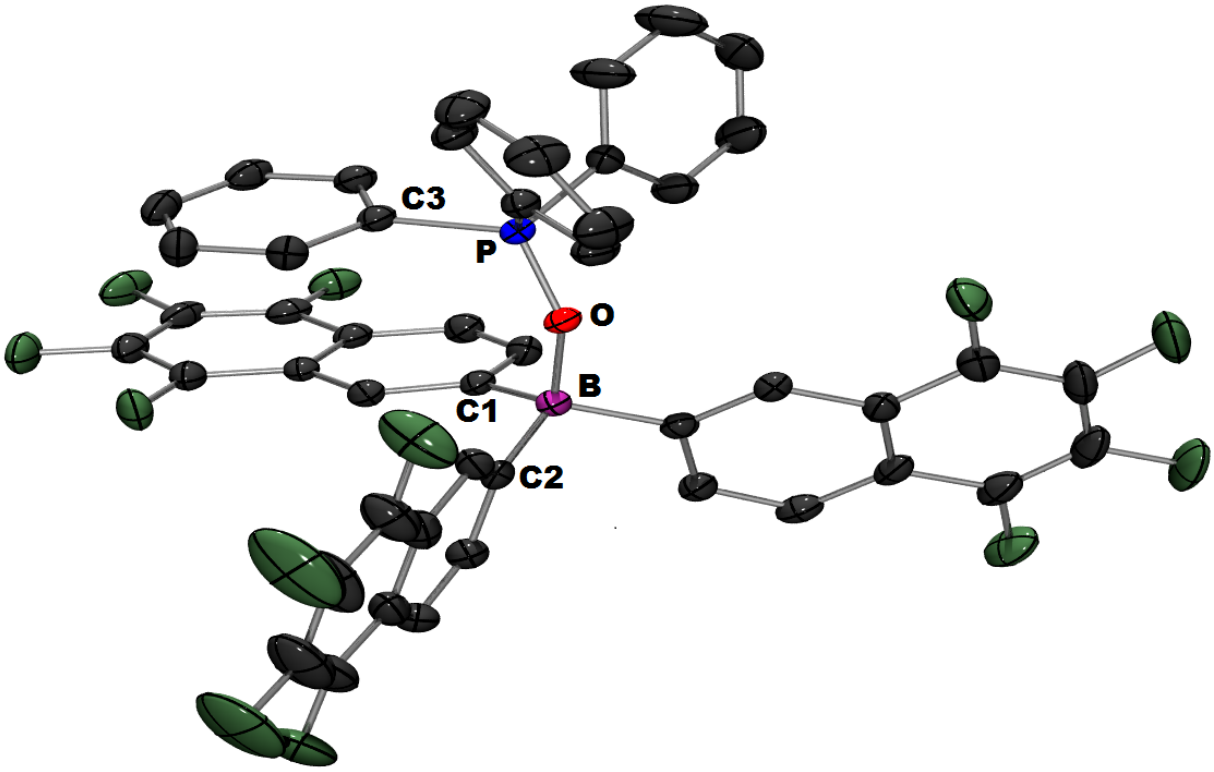
CCDC-985744 (for **5**·$OH_2(THF)_2$) and CCDC-985745 (for **5**·Ph_3PO) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

6.1 Molecular Structure of 5·$OH_2(THF)_2$



X-ray crystal structure analysis: formula $C_{38}H_{27}BF_{12}O_3$; M = 770.41, colourless block, 0.12 x 0.18 x 0.25 mm, a = 12.5486(5) Å, b = 13.7189(6) Å, c = 20.0521(8) Å, α = 97.612(3)°, β = 96.728(3)°, γ = 92.256(3)°, V = 3392.8(2) $Å^3$, ρ_{calc} = 1.508 g cm^{-3}, μ = 1.222 mm^{-1}, semi-empirical absorption correction from equivalents (0.7499 ≤ T ≤ 0.8672), Z = 4, triclinic, space group P-1, λ = 1.54184 Å, T = 150(2) K, 23231 reflections collected, 12217 independent (R_{int} = 0.0449) and 12217 observed reflections [$I \geq 2\ \sigma(I)$], 985 refined parameters, R = 0.0814, $wR2$ = 0.1891, GOF = 1.098, max. (min.) residual electron density 0.847 (–0.524) e $Å^{-3}$.

6.2 Molecular Structure of 5·Ph_3PO



X-ray crystal structure analysis: formula $C_{63}H_{39}BF_{12}OP$; M = 770.41, colourless rod, 0.08 x 0.12 x 0.30 mm, a = 9.9578(4) Å, b = 12.8785(3) Å, c = 20.3876(7) Å, α = 89.118(2)°, β = 89.773(3)°, γ = 83.346(3)°, V = 2596.60(15) $Å^3$, ρ_{calc} = 1.384 g cm^{-3}, μ = 1.224 mm^{-1}, semi-empirical absorption correction from equivalents (0.7103 ≤ T ≤ 0.9084), Z = 2, triclinic, space group P-1, λ = 1.54184 Å, T = 150(2) K, 19257 reflections collected, 9361 independent (R_{int} = 0.0300) and 9361 observed reflections [$I \geq 2\ \sigma(I)$], 813 refined parameters, R = 0.0468, $wR2$ = 0.1364, GOF = 1.036, max. (min.) residual electron density 0.590 (–0.350) e $Å^{-3}$.

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