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Supporting Information

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A Boronium Ion with Exceptional Electrophilicity**

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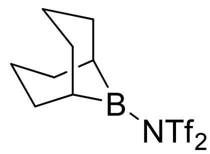
All reactions were performed at room temperature (unless otherwise stated), under an atmosphere of dry nitrogen, either in a glovebox, or using standard Schlenk techniques. Nuclear magnetic resonance experiments were performed on Varian Inova 500 and Inova 400 spectrometers at the following frequencies: ^{1}H 500 MHz or 400 MHz; $^{13}C\{^{1}H\}$ 101 MHz; ^{11}B and $^{11}B\{^{1}H\}$ 128 MHz; ^{19}F 377 MHz. All spectra were recorded in CD_2Cl_2 and referenced to the ^{1}H signal of internal Me_4Si according to IUPAC recommendations,[33] using a Ξ of 25.145020 for Me_4Si (^{13}C), a Ξ of 32.083974 for BF_3-OEt_2 (^{11}B), and a Ξ of 94.094011 for CCl_3F (^{19}F). IR spectra were acquired in CCl_4 or CD_2Cl_2 solutions using a CaF_2 cell. UV spectra were acquired using a Shimadzu UV-1601 spectrophotometer. Toluene and NEt_3 were distilled over CaH_2; CH_2Cl_2 and hexanes were dried by passing through a column of activated alumina. Then, the solvents and NEt_3 were dried by storing over activated 3Å molecular sieves in the glovebox. Commercially available CD_2Cl_2 (Cambridge Isotope Laboratories) was not distilled; instead it was simply dried over a large amount of activated 3Å molecular sieves in the glovebox. Bis(trifluoromethanesulfonyl)imide was purchased from Sigma-Aldrich.

Reference:

[33] R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem.* **2001**, *73*, 1795-1818.

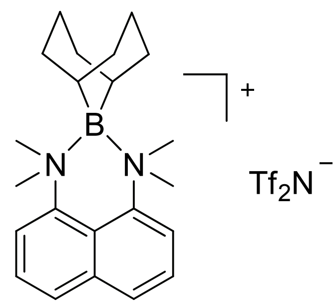
N-(Borabicyclo[3.3.1]nonan-9-yl)-1,1,1-trifluoro-N-(trifluoromethanesulfonyl)methanesulfonamide (5a)



A suspension of 9-borabicyclo[3.3.1]nonane dimer (0.868 g, 7.11 mmol of the monomer) and bis(trifluoromethanesulfonyl)imide (2.00 g, 7.11 mmol) in 1 mL of dry toluene was carefully heated under a dry N_2 atmosphere at 90 °C for 40 minutes. Intensive gas liberation was observed while heating, and a clear solution was formed. The resulting solution was distilled in vacuum, and a fraction boiling at 108 °C (1.5 Torr) was collected. Boron bistriflimide **5a** is a very dense (d = 1.49 g/cm^3), viscous liquid and is highly air-sensitive.

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ = 2.07-1.81 (m, 10H), 1.59-1.52 (m, 2H), 1.52-1.42 ppm (m, 2H). ^{11}B NMR (128 MHz, CD_2Cl_2, Et_2O-BF_3): δ = 59.2 ppm (s). ^{13}C NMR (101 MHz, CD_2Cl_2, TMS): δ = 119.4 (q, ^1J(C-F) = 325 Hz), 33.6, 29.6-28.0 (m), 22.9 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, $CFCl_3$): δ = -70.0 ppm (br s). HRMS (EI+ 70 eV): *m/z*: calculated 401.0362, found 401.0347 (-4 ppm). IR (CCl_4, CaF_2): 1437, 1417, 1359, 1325, 1121 cm^{-1}.

Preparation of Boronium Salt 8a

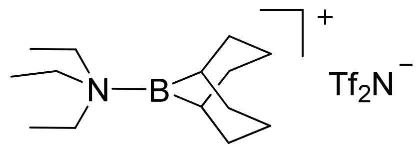


Method A. A mixture of 9-borabicyclo[3.3.1]nonane dimer (0.461 g, 3.78 mmol of the monomer) and bis(trifluoromethanesulfonyl)imide (0.966 g, 3.44 mmol) in 5 mL of dry toluene was refluxed for 1 hour under nitrogen. Intensive gas liberation was observed while heating, and a clear solution was formed. The resulting solution along with 2x1 mL of dry toluene was slowly added at room temperature to a solution of 1,8-bis(dimethylamino)naphthalene (0.737 g, 3.44 mmol) in 3 mL of dry toluene. Upon mixing the reagents the reaction mixture developed a striking red color that persisted for a few seconds. A small exotherm was observed, and precipitation of a pale yellow oil began immediately. The oil crystallized within a few minutes of stirring at room temperature, the resulting crystals were isolated by filtration under nitrogen, and then washed with 2x1 mL of dry toluene followed by 2 mL of dry hexanes. Drying the resulting solid in the glovebox yielded 2.04 g (96%) of the desired product. The resulting crystals of **8a** are very stable in dry air, although solutions of the product are very sensitive.

Method B. Alternatively, the boronium salt **8a** can be prepared by mixing equimolar amounts of the boron bis-triflimide reagent **5a** and 1,8-bis(dimethylamino)-naphthalene in dry CH_2Cl_2 followed by evaporation of the solvent. The reaction was essentially instantaneous, but the product prepared in this manner was contaminated with the bis(trifluoromethanesulfonyl)imide salt of 1,8-bis(dimethylamino)naphthalene due to impurities in the boron reagent **5a**.

8a: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 ^{o}C, TMS): δ = 8.01 (dd, *J* = 8.3 Hz, 0.5 Hz, 2H), 7.90 (dd, *J* = 8.0 Hz, 0.5 Hz, 2H), 7.74 (t, *J* = 8.0 Hz, 2H), 3.48 (s, 12H), 2.31-2.13 (m, 4H), 2.19-2.05 (m, 2H), 1.81-1.67 (m, 6H), 1.02-0.91 ppm (br s, 2H). ^{11}B NMR (128 MHz, CD_2Cl_2, Et_2O-BF_3): δ = 16.2 ppm (s). ^{13}C NMR (101 MHz, CD_2Cl_2, TMS): δ = 142.9, 135.0, 129.5, 127.7, 120.3 (q, ^{1}J(C-F) = 322 Hz), 120.1, 119.7, 57.1, 34.6, 21.0-19.9 (m), 20.3 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, $CFCl_3$): δ = -79.4 ppm (s). HRMS (ES+): *m/z*: calculated 335.2653, found 355.3655 (+1 ppm). IR(CD_2Cl_2, CaF_2): 2874, 1603, 1576, 1492, 1435, 1342, 1142 cm^{-1}. m.p. 128 °C (sealed capillary); decomposition begins ca. 100 °C.

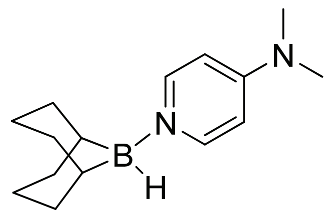
Generation of Borenium Salt 10



A dry J. Young NMR tube was charged with a solution of boron bis-triflimide **5a** (30.0 μL, 44.7 mg, 0.111 mmol) in 0.6 mL of dry CD_2Cl_2. Neat triethylamine (15.5 μL, 11.3 mg, 0.112 mmol) was added, and the mixture was shaken vigorously. NMR analysis indicated clean formation of borenium salt **10**.

10: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ = 3.51 (q, J = 7.4 Hz, 6H), 2.35-2.26 (m, 4H), 2.25-2.12 (m, 2H), 2.07-1.94 (m, 4H), 1.87-1.80 (m, 2H), 1.66-1.56 (m, 2H), 1.35 ppm (t, J = 7.4 Hz, 9H). ^{11}B NMR (128 MHz, CD_2Cl_2, Et_2O-BF_3): δ = 85.1 ppm (s). ^{13}C NMR (101 MHz, CD_2Cl_2, TMS): δ = 120.4 (q, ^1J(C-F) = 322 Hz), 50.0, 36.3, 30.4-29.1 (m), 22.5, 9.6 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, $CFCl_3$): δ = -79.5 ppm (s).

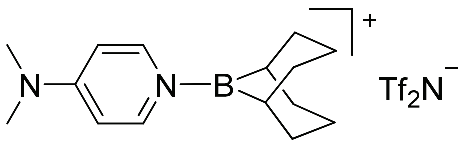
Preparation of Amine-Borane Complex 12



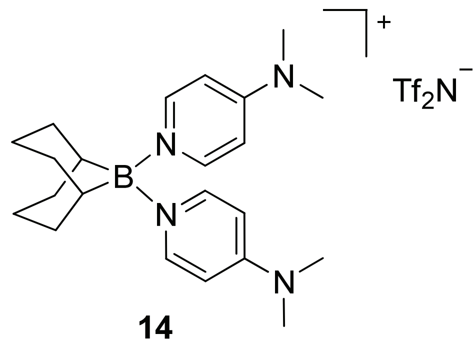
A mixture of solid 9-borabicyclo[3.3.1]nonane dimer (82.2 mg, 0.674 mmol of the monomer) and 4-(dimethylamino)pyridine (82.3 mg, 0.674 mmol) was dissolved in 1 mL of dry CH_2Cl_2, and the resulting clear solution was stirred at room temperature overnight. A white precipitate appeared on stirring, and the slurry was concentrated to afford **12** as a white solid in quantitative yield.

12: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS): δ = 8.11-8.06 (m, 2H), 6.62-6.58 (m, 2H), 3.09 (s, 6H), 2.77-2.00 (m, 1H), 1.96-1.72 (m, 6H), 1.56-1.48 (m, 3H), 1.48-1.39 (m, 2H), 1.29-1.21 (m, 1H), 1.13-1.04 ppm (m, 2H). ^{11}B NMR (128 MHz, CD_2Cl_2, Et_2O-BF_3): δ = -3.2 ppm (d, ^1J(B-H) = 60 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2, TMS): δ = 155.1, 144.8, 106.9, 39.6, 35.4, 29.5, 25.9, 25.5, 24.6-23.0 ppm (m). IR(CD_2Cl_2, CaF_2): 2269, 2239, 1635, 1547, 1444, 1344, 1229, 1202 cm^{-1}. The compound has no distinct melting point; partial melting ca. 163 °C (sealed capillary) with decomposition.

Generation of Borenium Salt 13 and Boronium Salt 14



13



14

Solid bis(trifluoromethanesulfonyl)imide (23.8 mg, 84.8 μmol) was added in small portions to a stirred solution of amine-borane complex **12** (20.7 mg, 84.8 μmol) in 1 mL of dry CD_2Cl_2. Intensive gas liberation was observed. NMR assay of the resulting clear solution showed formation of borenium salt **13**, along with minor amounts of the boronium salt **14** and DMAP·$HNTf_2$ (typically 7-11:1 **13**:**14**). Addition of an extra equivalent of 4-(dimethylamino)pyridine (10.4 mg, 84.8 μmol) cleanly produced boronium salt **14**, as evidenced by NMR spectroscopy.

Alternatively, complex **14** was prepared by carefully treating a solution of 4-(dimethylamino)pyridine (27.1 mg, 0.222 mmol) in 0.5 mL of anhydrous CH_2Cl_2 with neat boron bis-triflimide **5a** (30.0 μL, 44.7 mg, 0.111 mmol). Concentration of the resulting solution afforded a white crystalline solid in quantitative yield.

13: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS): δ = 8.37-8.33 (m, 2H), 6.99-6.95 (m, 2H), 3.37 (s, 6H), 2.14-1.98 (m, 8H), 1.93-1.84 (m, 4H), 1.45-1.37 ppm (m, 2H). ^{11}B NMR (128 MHz, CD_2Cl_2, Et_2O-BF_3): δ = 66.5 ppm (s). ^{13}C NMR (101 MHz, CD_2Cl_2, TMS): δ = 159.2, 142.6, 120.3 (q, ^{1}J(C-F) = 322 Hz), 108.8, 41.2, 34.4, 28.0-26.2 (m), 23.2 ppm. ^{19}F NMR (377 MHz, CD_2Cl_2, $CFCl_3$): δ = -79.4 ppm (s).

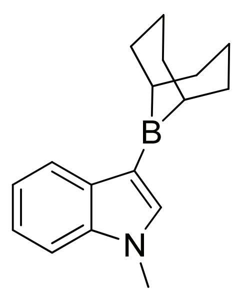
14: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS): δ = 8.07-8.03 (m, 4H), 6.69-6.65 (m, 4H), 3.11 (s, 12H), 1.97-1.85 (m, 2H), 1.85-1.78 (m, 4H), 1.62-1.58 (m, 2H), 1.58-1.48 (m, 4H), 1.38-1.31 ppm (m, 2H). ^{11}B NMR (128 MHz, CD_2Cl_2, Et_2O-BF_3): δ = 3.0 ppm (s). ^{13}C NMR (101 MHz, CD_2Cl_2, TMS): δ = 156.3, 142.8, 120.4 (q, ^{1}J(C-F) = 322 Hz), 108.1, 39.9, 30.4, 23.7, 21.5-20.5 ppm (m). ^{19}F NMR (377 MHz, CD_2Cl_2, $CFCl_3$):

δ = -79.5 ppm (s). HRMS (ES+): *m/z*: calculated 365.2871, found 365.2873 (+1 ppm). IR(CD_2Cl_2, CaF_2): 2891, 2851, 1635, 1557, 1444, 1350, 1138 cm^{-1}. The compound has no distinct melting point; partial melting ca. 208 °C (sealed capillary) with decomposition. UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon)$ = 295 (24000), 283 nm (21000).

Representative Procedure for Indole and Pyrrole Borylation

A dry 4 mL scintillation vial was charged with a solution of the desired substrate (0.16-0.17 mmol) and boronium salt **8a** (1.05 equivalents per each 9-BBN unit introduced) in dry CH_2Cl_2 (0.5 mL per each 9-BBN unit introduced). The reaction vessel was sealed, heated at 50 ^oC for the indicated amount of time, and the reaction mixture was then diluted with dry hexanes (1 mL per each 9-BBN unit introduced) and left at room temperature for 1-2 hours to allow the byproduct to precipitate. Following decantation of supernatant, the solids were washed with 4x0.5 mL of dry hexanes, and the combined extracts were evaporated to dryness to give crude material. The pure product was obtained by extracting the crude material with 4x0.5 mL of dry hexanes followed by concentration of the extracts. All of the resulting borylated heterocycles were found to be extremely sensitive to water and were protected from exposure to air by working under dry nitrogen. UV spectra of the borylated heterocycles were acquired in 0.83% (v/v) solution of NEt_3 in hexanes. Very rapid protodeboronation precludes acquisition of UV spectra in the absence of NEt_3.

3-(9-Borabicyclo[3.3.1]nonan-9-yl)-1-methyl-1*H*-indole (16a)



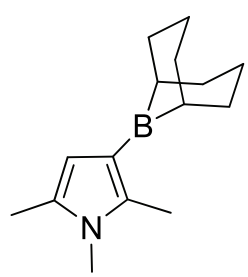
Reaction time 1.5 hours, 96% yield of a colorless crystalline solid.

^1H NMR (500 MHz, CD_2Cl_2, 25 ^oC, TMS): δ = 8.04 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.20-7.16 (m, 1H), 3.83 (s, 3H), 2.38-2.29 (m, 2H), 2.07-1.95 (m, 6H), 1.94-1.82 (m, 4H), 1.40-1.31 ppm (m, 2H). ^{11}B NMR (128 MHz, CD_2Cl_2, Et_2O-BF_3): δ = 72.6 ppm (s). ^{13}C NMR (101 MHz, CD_2Cl_2, TMS): δ =

141.7, 139.8, 133.5, 122.9, 122.2, 121.2, 116.2-114.9 (m), 110.0, 34.3, 33.5, 30.0-28.8 (m), 24.0 ppm. HRMS (EI+ 70 eV): *m/z*: calculated 251.1845, found 251.1850 (+2 ppm). IR(CCl_4, CaF_2): 1675, 1511, 1465, 1421, 1364, 1333, 1159, 1132, 1109 cm^{-1}. m.p. 106-108 °C (sealed capillary). UV/Vis (0.83% v/v NEt_3 in hexanes): $\lambda_{max}(\varepsilon)$ = 291 nm (15000).

Compound **16a** was also prepared on a larger scale using a modified procedure. A dry 12 mL thick-walled Schlenk tube fitted with a teflon stopper was charged with a mixture of N-methylindole (206 µL, 0.218 g, 1.66 mmol) and boronium salt **8a** (1.07 g, 1.74 mmol) in 3 mL of dry CH_2Cl_2. The reaction vessel was sealed and then heated at 50 °C for 2 h. The reaction mixture was then diluted with 5 mL of dry hexanes and left at room temperature for 1-2 hours to allow the byproduct to precipitate. Following decantation of supernatant, the solids were washed with 3x1 mL of dry hexanes, and the combined extracts were evaporated to dryness to give crude material. The pure product (0.415 g) was obtained in essentially quantitative yield by extracting the crude material with 5 portions of dry hexanes (total solvent volume 12 mL) followed by concentration of the extracts.

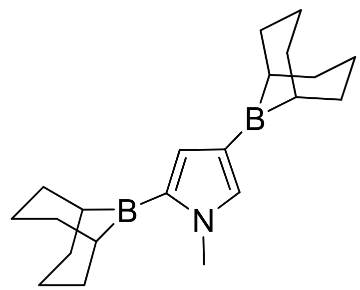
3-(9-Borabicyclo[3.3.1]nonan-9-yl)-1,2,5-trimethyl-1*H*-pyrrole (16b)



Reaction time 1.5 hours, 98% yield of a colorless crystalline solid.
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS): δ = 6.21 (q, *J* = 0.9 Hz, 1H), 3.41 (s, 3H), 2.43 (s, 3H), 2.20 (s, 3H), 2.11-2.05 (m, 2H), 2.01-1.86 (m, 6H), 1.82-1.73 (m, 4H), 1.35-1.25 ppm (m, 2H). ^{11}B NMR (128 MHz, CD_2Cl_2, Et_2O-BF_3): δ = 72.2 ppm (s). ^{13}C NMR (101 MHz, CD_2Cl_2, TMS): δ = 140.5, 129.0, 120.0-118.3 (m), 112.7, 34.2, 30.6, 29.8-

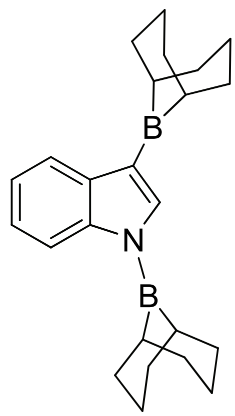
29.0 (m), 24.0, 13.4, 12.6 ppm. HRMS (EI+ 70 eV): *m/z*: calculated 229.2002, found 229.2002 (0 ppm). IR(CCl_4, CaF_2): 2915, 2837, 1503, 1433, 1405, 1372, 1350, 1172, 1115 cm^{-1}. m.p. 120 °C (sealed capillary). UV/Vis (0.83% v/v NEt_3 in hexanes): $\lambda_{max}(\varepsilon)$ = 286 nm (6100).

2,4-Di(9-borabicyclo[3.3.1]nonan-9-yl)-1-methyl-1*H*-pyrrole (16c)



Reaction time 3.5 hours, 97% yield of a colorless crystalline solid.
^{1}H NMR (500 MHz, CD_2Cl_2, 25 ^{o}C, TMS): δ = 7.60 (d, *J* = 1.6 Hz, 1H), 7.55 (dd, *J* = 1.6 Hz, 0.4 Hz, 1H), 3.92 (t, *J* =0.4 Hz, 3H), 2.23-2.18 (m, 2H), 2.08-1.90 (m, 14H), 1.90-1.73 (m, 8H), 1.41-1.25 ppm (m, 4H). ^{11}B NMR (128 MHz, CD_2Cl_2, Et_2O-BF_3): δ = 73.0 (s), 70.2 ppm (s). ^{13}C NMR (101 MHz, CD_2Cl_2, TMS): δ = 142.8, 141.2-140.0 (m), 134.4, 124.0-123.1 (m), 38.4, 34.4, 34.3, 29.9-29.1(m), 29.1-28.3 (m), 24.0, 23.8 ppm. HRMS (EI+ 70 eV): *m/z*: calculated 321.2799, found 321.2811 (+4 ppm). IR(CCl_4, CaF_2): 1656, 1486, 1450, 1422, 1362, 1325, 1150, 1112 cm^{-1}. m.p. 133-135 °C (sealed capillary). UV/Vis (0.83% v/v NEt_3 in hexanes): $\lambda_{max}(\varepsilon)$ = 290 nm (22000).

1,3-Di(9-borabicyclo[3.3.1]nonan-9-yl)-1*H*-indole (16d)



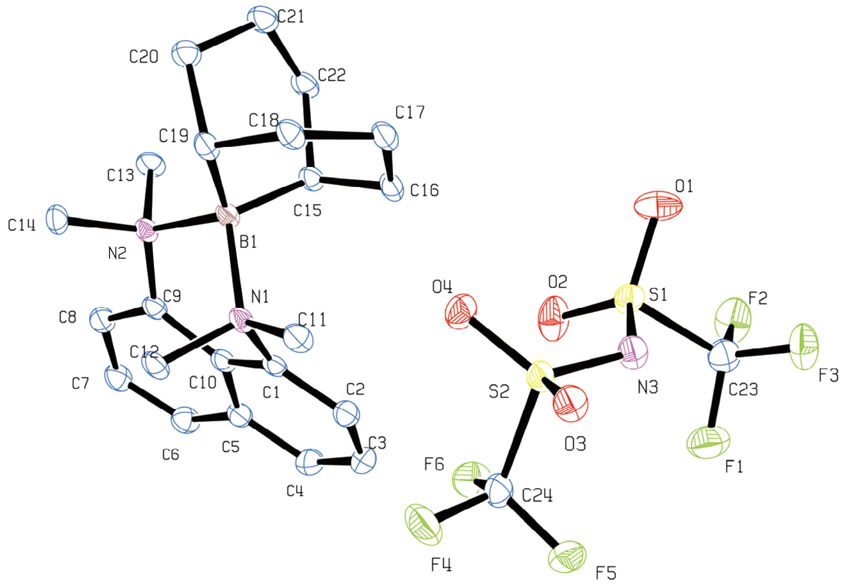
Reaction time 5.5 days, 97% yield of a colorless crystalline solid.

^{1}H NMR (500 MHz, CD_2Cl_2, 25 ^{o}C, TMS): δ = 8.22 (s, 1H), 8.03-7.99 (m, 1H), 7.93-7.88 (m, 1H), 7.28-7.23 (m, 2H), 2.70-2.21 (m, 4H), 2.16-1.83 (m, 20H), 1.50-1.41 (m, 2H), 1.41-1.32 ppm (m, 2H). ^{11}B NMR (128 MHz, CD_2Cl_2, Et_2O-BF_3): δ = 75.7 (s), 62.0 ppm (s). ^{13}C NMR (101 MHz, CD_2Cl_2, TMS): δ = 143.5, 143.3, 137.4, 123.5, 123.2, 122.9, 122.7-122.0 (m), 116.0, 34.3, 34.1, 30.7-29.6 (m), 28.2-26.3 (m), 23.9, 23.5 ppm. HRMS (EI+ 70 eV): *m/z*: calculated 357.2799, found 357.2814 (+4 ppm). IR(CCl_4, CaF_2): 1694, 1487, 1471, 1449, 1405, 1334, 1292, 1135, 1108 cm^{-1}. m.p. 204-206 °C (sealed capillary).

X-ray Crystallography Details of 8a

Colorless plates of **8a** were grown from a hexanes/dichloromethane solution by slow cooling to ambient temperature. A crystal of dimensions 0.37x0.37x0.025 mm was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 Å) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 2790 frames were collected with a scan width of 0.5° in ω and 0.45° in φ with an exposure time of 25 s/frame. The integration of the data yielded a total of 61663 reflections to a maximum 2θ value of 56.58° of which 6437 were independent and 5096 were greater than 2σ(I). The final cell constants (monoclinic, a = 12.0734(12) Å; α = 90°; b = 26.951(3) Å; β = 100.946(2)°; c = 8.1362(8) Å; γ = 90°; V = 2599.2(4) $Å^3$) were based on the xyz centroids of 9873 reflections above 10σ(I). Linear absorption coefficient μ = 0.287 mm^{-1}. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/3) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{24}H_{32}BF_6N_3O_4S_2$ (M_r 615.46 g/mol, ρ_{calcd} = 1.573 g/cm^3). All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0493 and wR2 = 0.1158 [based on I > 2σ(I)], R1 = 0.0671 and wR2 = 0.1255 for all data. **CCDC-791459** contains the supplementary crystallographic data for **8a**. The cif file can be obtained free of charge from Cambridge Crystallographic Data Center (http://www.ccdc.cam.ac.uk/products/csd/request/).

Sheldrick, G.M. SHELXTL, v. 2008/3, Bruker Analytical X-ray, Madison, WI, 2008; Sheldrick, G.M. SADABS, v. 2008/1, Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen, Gottingen, Germany, 2008; Saint Plus, v. 7.53a, Bruker Analytical X-ray, Madison, WI, 2008



Bond lengths, Å:

B(1)-C(19)	1.612(3)	C(3)-C(4)	1.362(3)	C(21)-C(22)	1.543(3)
B(1)-C(15)	1.631(3)	C(4)-C(5)	1.421(3)	C(23)-F(1)	1.328(3)
B(1)-N(1)	1.724(3)	C(5)-C(6)	1.419(3)	C(23)-F(3)	1.331(2)
B(1)-N(2)	1.732(3)	C(5)-C(10)	1.429(3)	C(23)-F(2)	1.337(2)
N(1)-C(1)	1.477(3)	C(6)-C(7)	1.368(3)	C(23)-S(1)	1.831(2)
N(1)-C(11)	1.513(2)	C(7)-C(8)	1.408(3)	C(24)-F(6)	1.328(2)
N(1)-C(12)	1.523(2)	C(8)-C(9)	1.376(3)	C(24)-F(5)	1.333(2)
N(2)-C(9)	1.511(3)	C(9)-C(10)	1.426(3)	C(24)-F(4)	1.336(2)
N(2)-C(14)	1.522(2)	C(15)-C(16)	1.542(3)	C(24)-S(2)	1.844(2)
N(2)-C(13)	1.525(2)	C(15)-C(22)	1.565(3)	S(1)-O(1)	1.4311(17)
N(3)-S(2)	1.5690(18)	C(16)-C(17)	1.543(3)	S(1)-O(2)	1.4319(16)
N(3)-S(1)	1.5923(18)	C(17)-C(18)	1.556(3)	S(2)-O(4)	1.4357(15)
C(1)-C(2)	1.370(3)	C(18)-C(19)	1.570(3)	S(2)-O(3)	1.4384(15)
C(1)-C(10)	1.423(3)	C(19)-C(20)	1.555(3)		
C(2)-C(3)	1.413(3)	C(20)-C(21)	1.537(3)		

Bond angles, deg.:

C(19)-B(1)-C(15)	106.00(15)	C(16)-C(15)-C(22)	106.72(16)
C(19)-B(1)-N(1)	112.06(16)	C(16)-C(15)-B(1)	109.06(16)
C(15)-B(1)-N(1)	112.40(16)	C(22)-C(15)-B(1)	114.17(16)
C(19)-B(1)-N(2)	115.36(16)	C(15)-C(16)-C(17)	113.07(17)
C(15)-B(1)-N(2)	111.28(15)	C(16)-C(17)-C(18)	117.65(16)
N(1)-B(1)-N(2)	99.91(13)	C(17)-C(18)-C(19)	118.33(16)
C(1)-N(1)-C(11)	111.39(15)	C(20)-C(19)-C(18)	106.63(15)
C(1)-N(1)-C(12)	106.81(15)	C(20)-C(19)-B(1)	110.84(16)
C(11)-N(1)-C(12)	100.32(14)	C(18)-C(19)-B(1)	111.40(16)
C(1)-N(1)-B(1)	106.55(14)	C(21)-C(20)-C(19)	112.51(17)
C(11)-N(1)-B(1)	118.00(15)	C(20)-C(21)-C(22)	116.00(17)
C(12)-N(1)-B(1)	113.31(14)	C(21)-C(22)-C(15)	117.23(17)
C(9)-N(2)-C(14)	111.87(15)	F(1)-C(23)-F(3)	108.08(18)
C(9)-N(2)-C(13)	102.43(15)	F(1)-C(23)-F(2)	108.12(19)
C(14)-N(2)-C(13)	103.89(15)	F(3)-C(23)-F(2)	108.31(18)
C(9)-N(2)-B(1)	114.19(14)	F(1)-C(23)-S(1)	111.61(15)
C(14)-N(2)-B(1)	112.98(15)	F(3)-C(23)-S(1)	111.86(16)
C(13)-N(2)-B(1)	110.42(14)	F(2)-C(23)-S(1)	108.74(15)
S(2)-N(3)-S(1)	123.98(11)	F(6)-C(24)-F(5)	108.09(18)
C(2)-C(1)-C(10)	121.05(19)	F(6)-C(24)-F(4)	108.31(17)
C(2)-C(1)-N(1)	123.71(18)	F(5)-C(24)-F(4)	107.72(17)
C(10)-C(1)-N(1)	115.07(17)	F(6)-C(24)-S(2)	112.58(15)
C(1)-C(2)-C(3)	119.97(19)	F(5)-C(24)-S(2)	110.91(14)
C(4)-C(3)-C(2)	120.4(2)	F(4)-C(24)-S(2)	109.10(15)
C(3)-C(4)-C(5)	120.9(2)	O(1)-S(1)-O(2)	118.22(11)
C(6)-C(5)-C(4)	121.9(2)	O(1)-S(1)-N(3)	112.11(10)
C(6)-C(5)-C(10)	119.30(19)	O(2)-S(1)-N(3)	115.72(10)
C(4)-C(5)-C(10)	118.82(19)	O(1)-S(1)-C(23)	104.34(11)
C(7)-C(6)-C(5)	120.4(2)	O(2)-S(1)-C(23)	105.43(10)

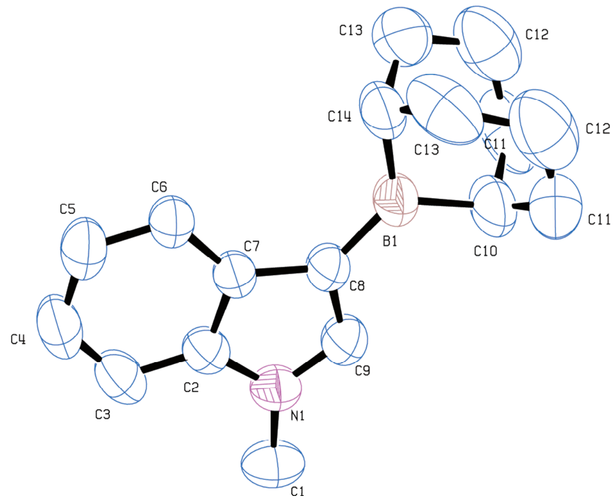
C(6)-C(7)-C(8)	120.33(19)
C(9)-C(8)-C(7)	120.78(19)
C(8)-C(9)-C(10)	120.02(18)
C(8)-C(9)-N(2)	119.42(17)
C(10)-C(9)-N(2)	120.08(16)
C(1)-C(10)-C(9)	123.64(19)
C(1)-C(10)-C(5)	117.95(18)
C(9)-C(10)-C(5)	118.29(18)

N(3)-S(1)-C(23)	97.78(10)
O(4)-S(2)-O(3)	118.77(9)
O(4)-S(2)-N(3)	115.79(9)
O(3)-S(2)-N(3)	108.08(9)
O(4)-S(2)-C(24)	104.77(9)
O(3)-S(2)-C(24)	102.18(9)
N(3)-S(2)-C(24)	105.42(10)

X-ray Crystallography Details of 16a

Colorless needles of **16a** were grown from a hexanes solution by slow evaporation at ambient temperature. A crystal of dimensions 0.37x0.24x0.24 mm was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 Å) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(2) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 2333 frames were collected with a scan width of 0.5° in ω and 0.45° in φ with an exposure time of 25 s/frame. The frames were integrated with the Bruker SAINT software package with a narrow frame algorithm. The integration of the data yielded a total of 19089 reflections to a maximum 2θ value of 48.34° of which 2510 were independent and 2007 were greater than 2σ(I). The final cell constants (monoclinic, a = 20.122(2) Å; α = 90°; b = 7.1578(8) Å; β = 115.372(6)°; c = 22.560(2) Å; γ = 90°; V = 2935.9(5) $Å^3$) were based on the xyz centroids of 7767 reflections above 10σ(I). Linear absorption coefficient μ = 0.064mm^{-1}. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group C2/m with Z = 8 for the formula $C_{17}H_{22}BN$ (M_r 251.17 g/mol, ρ_{calcd} = 1.136 g/cm^3). All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. There are two crystallographically independent molecules in the asymmetric unit, each lying on a mirror plane. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0579 and wR2 = 0.1697 [based on I > 2σ(I)], R1 = 0.0705 and wR2 = 0.1822 for all data. **CCDC-791460** contains the supplementary crystallographic data for **16a**. The cif file can be obtained free of charge from Cambridge Crystallographic Data Center (http://www.ccdc.cam.ac.uk/products/csd/request/).

Sheldrick, G.M. SHELXTL, v. 2008/4, Bruker Analytical X-ray, Madison, WI, 2008; Sheldrick, G.M. SADABS, v. 2008/1, Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen, Gottingen, Germany, 2008; Saint Plus, v. 7.60a, Bruker Analytical X-ray, Madison, WI, 2008.



Bond lengths, Å:

N(1)-C(9)	1.345(4)	C(8)-B(1)	1.516(4)	C(20)-C(21)	1.390(4)
N(1)-C(2)	1.388(4)	C(10)-C(11)#1	1.539(4)	C(21)-C(22)	1.466(3)
N(1)-C(1)	1.460(3)	C(10)-C(11)	1.539(4)	C(22)-C(23)	1.387(4)
N(2)-C(23)	1.343(4)	C(10)-B(1)	1.583(5)	C(22)-B(2)	1.518(4)
N(2)-C(16)	1.386(3)	C(11)-C(12)	1.501(4)	C(24)-C(25)#2	1.528(4)
N(2)-C(15)	1.462(3)	C(12)-C(13)	1.499(4)	C(24)-C(25)	1.528(4)
C(2)-C(3)	1.391(4)	C(13)-C(14)	1.539(3)	C(24)-B(2)	1.564(4)
C(2)-C(7)	1.401(4)	C(14)-C(13)#1	1.539(3)	C(25)-C(26)	1.500(4)
C(3)-C(4)	1.366(5)	C(14)-B(1)	1.566(5)	C(26)-C(27)	1.513(4)
C(4)-C(5)	1.393(5)	C(16)-C(17)	1.391(4)	C(27)-C(28)	1.539(3)
C(5)-C(6)	1.378(4)	C(16)-C(21)	1.414(4)	C(28)-C(27)#2	1.539(3)
C(6)-C(7)	1.403(4)	C(17)-C(18)	1.375(4)	C(28)-B(2)	1.576(4)
C(7)-C(8)	1.467(4)	C(18)-C(19)	1.376(4)		
C(8)-C(9)	1.384(4)	C(19)-C(20)	1.390(4)		

Bond angles, deg.:

C(9)-N(1)-C(2)	107.9(2)	N(2)-C(16)-C(17)	129.2(3)
C(9)-N(1)-C(1)	126.6(3)	N(2)-C(16)-C(21)	108.1(2)
C(2)-N(1)-C(1)	125.5(2)	C(17)-C(16)-C(21)	122.7(3)
C(23)-N(2)-C(16)	107.8(2)	C(18)-C(17)-C(16)	117.4(3)
C(23)-N(2)-C(15)	127.0(3)	C(17)-C(18)-C(19)	121.3(3)
C(16)-N(2)-C(15)	125.2(3)	C(18)-C(19)-C(20)	121.5(3)
N(1)-C(2)-C(3)	129.1(3)	C(21)-C(20)-C(19)	119.3(3)
N(1)-C(2)-C(7)	108.0(2)	C(20)-C(21)-C(16)	117.9(2)
C(3)-C(2)-C(7)	122.9(3)	C(20)-C(21)-C(22)	134.8(2)
C(4)-C(3)-C(2)	117.7(3)	C(16)-C(21)-C(22)	107.3(2)
C(3)-C(4)-C(5)	121.1(3)	C(23)-C(22)-C(21)	103.2(2)
C(6)-C(5)-C(4)	121.2(3)	C(23)-C(22)-B(2)	124.1(2)
C(5)-C(6)-C(7)	119.3(3)	C(21)-C(22)-B(2)	132.6(2)
C(2)-C(7)-C(6)	117.8(2)	N(2)-C(23)-C(22)	113.5(2)
C(2)-C(7)-C(8)	107.8(2)	C(25)#2-C(24)-C(25)	114.0(3)
C(6)-C(7)-C(8)	134.4(2)	C(25)#2-C(24)-B(2)	108.83(18)
C(9)-C(8)-C(7)	103.2(2)	C(25)-C(24)-B(2)	108.83(18)
C(9)-C(8)-B(1)	124.4(3)	C(26)-C(25)-C(24)	114.9(2)
C(7)-C(8)-B(1)	132.4(2)	C(25)-C(26)-C(27)	114.0(2)
N(1)-C(9)-C(8)	113.2(3)	C(26)-C(27)-C(28)	115.2(2)
C(11)#1-C(10)-C(11)	113.4(3)	C(27)-C(28)-C(27)#2	113.7(3)
C(11)#1-C(10)-B(1)	107.6(2)	C(27)-C(28)-B(2)	107.84(17)
C(11)-C(10)-B(1)	107.6(2)	C(27)#2-C(28)-B(2)	107.84(17)
C(12)-C(11)-C(10)	115.7(3)	C(8)-B(1)-C(14)	127.3(3)
C(13)-C(12)-C(11)	114.3(2)	C(8)-B(1)-C(10)	123.9(3)
C(12)-C(13)-C(14)	115.1(3)	C(14)-B(1)-C(10)	108.8(3)
C(13)#1-C(14)-C(13)	113.8(3)	C(22)-B(2)-C(24)	126.7(2)
C(13)#1-C(14)-B(1)	108.26(19)	C(22)-B(2)-C(28)	124.9(3)
C(13)-C(14)-B(1)	108.26(19)	C(24)-B(2)-C(28)	108.4(3)

Computational Details

All calculations were performed using Gaussian 09, Revision A.02 suite of computational programs. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

NBO analysis was performed using NBO Version 3.1 (E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold), as implemented in Gaussian.

All calculations were performed in gas phase. Ultrafine integration grids (**int=ultrafine**) and very tight optimization criterion (**opt=verytight**) were used. The optimized structure was confirmed to be the local minimum by performing a frequency calculation. In addition, the wavefunction was tested for stability at the local minimum, confirming the closed-shell nature of the cation of **8a**.

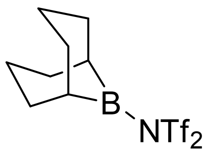
Cation of 8a

M06-2X/6-31G(d,p):

E(M06-2X) = -991.365691904

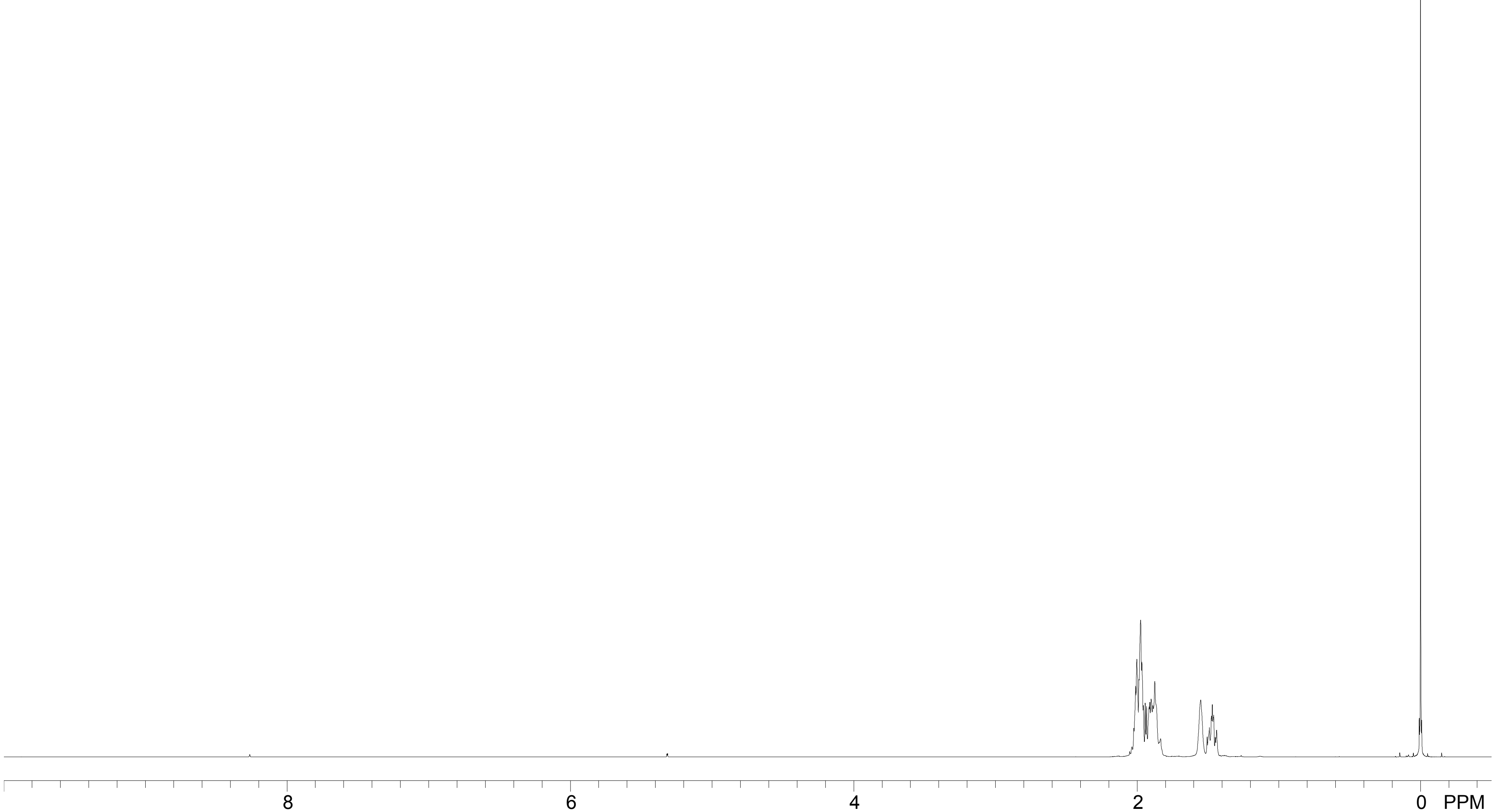
1	B	-0.988854	-0.154085	0.256678
2	N	-0.033213	0.988445	1.125664
3	N	0.053602	-1.546720	0.369601
4	C	1.147787	1.254147	0.290508
5	C	1.546464	2.509758	-0.082125
6	H	0.939664	3.380894	0.129490
7	C	2.792394	2.694813	-0.731627
8	H	3.085645	3.694515	-1.030252
9	C	3.638453	1.637532	-0.911660
10	H	4.626753	1.783112	-1.335508
11	C	3.243723	0.323855	-0.539811
12	C	4.140024	-0.768247	-0.643619
13	H	5.140822	-0.589514	-1.023379
14	C	3.755065	-2.019383	-0.242524
15	H	4.448677	-2.851308	-0.279789
16	C	2.422069	-2.253333	0.158851
17	H	2.127563	-3.274823	0.371864
18	C	1.509163	-1.226708	0.216832
19	C	1.933659	0.110114	-0.026706
20	C	-0.734129	2.248018	1.546753
21	H	0.011916	2.931937	1.953509
22	H	-1.426851	1.983656	2.340168
23	H	-1.271942	2.721473	0.737397
24	C	0.465433	0.483026	2.460704
25	H	1.220864	-0.284371	2.339102
26	H	-0.388269	0.110803	3.027646
27	H	0.921581	1.319961	2.991396
28	C	-0.236194	-2.452140	-0.803680
29	H	0.081741	-1.954956	-1.715405
30	H	-1.295991	-2.677506	-0.838277
31	H	0.323427	-3.378230	-0.683765
32	C	-0.206941	-2.391224	1.587989
33	H	0.286542	-3.356832	1.474657
34	H	-1.278911	-2.550849	1.675225
35	H	0.160522	-1.917830	2.489928
36	C	-1.229562	0.265979	-1.299409
37	H	-0.300517	0.288792	-1.887581
38	C	-1.826456	1.686083	-1.348722
39	H	-2.021171	1.948993	-2.394169
40	H	-1.085817	2.420946	-1.023156
41	C	-3.159048	1.792209	-0.575503
42	H	-3.951223	1.496101	-1.266659
43	H	-3.367692	2.844375	-0.350208
44	C	-3.314961	0.966676	0.735336
45	H	-4.366390	0.664624	0.807440
46	H	-3.173341	1.624192	1.592518
47	C	-2.452068	-0.329637	0.917457
48	H	-2.433166	-0.545786	1.997036
49	C	-3.223737	-1.479314	0.226178
50	H	-2.740756	-2.449684	0.379644
51	H	-4.203032	-1.581466	0.707339
52	C	-3.448578	-1.210934	-1.270657
53	H	-4.282115	-0.509910	-1.355466
54	H	-3.799959	-2.128364	-1.754370
55	C	-2.236849	-0.660227	-2.062227
56	H	-2.630531	-0.081607	-2.905958
57	H	-1.710776	-1.489355	-2.534675

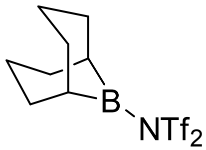
NMR Spectra



5a

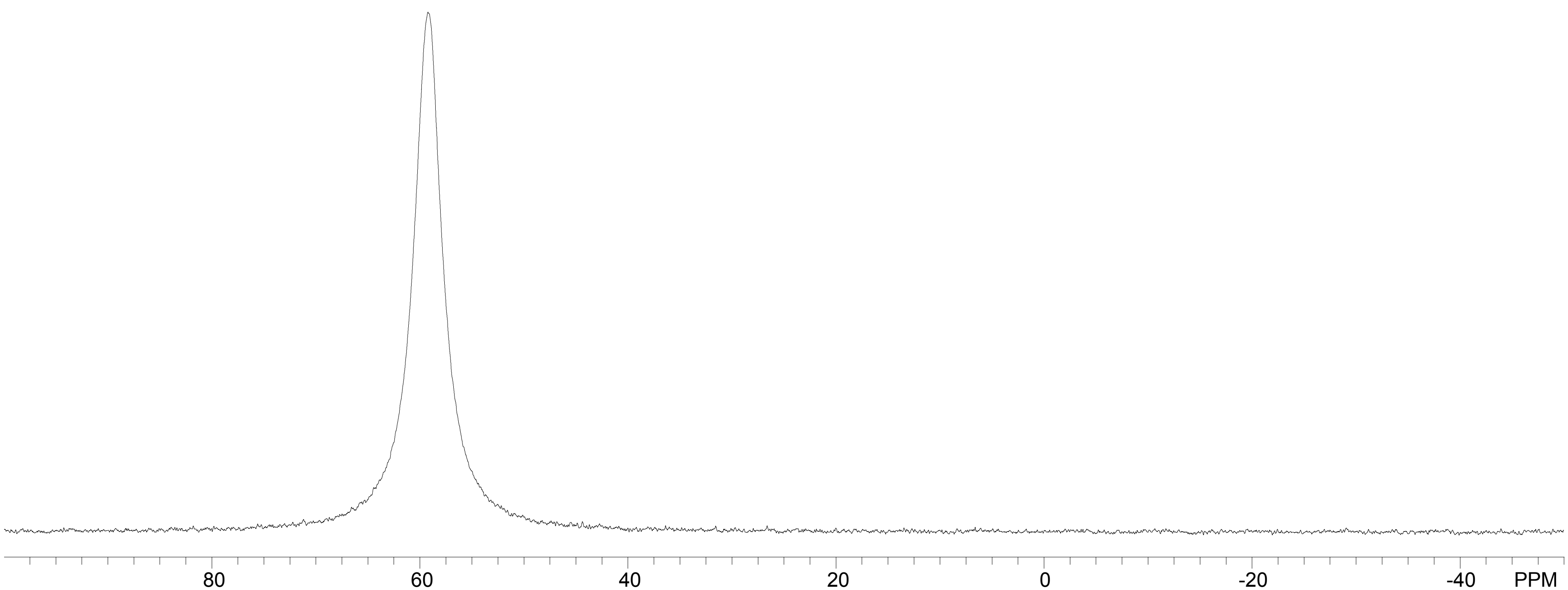
^{1}H NMR (400 MHz),
CD_2Cl_2

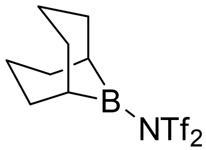




5a

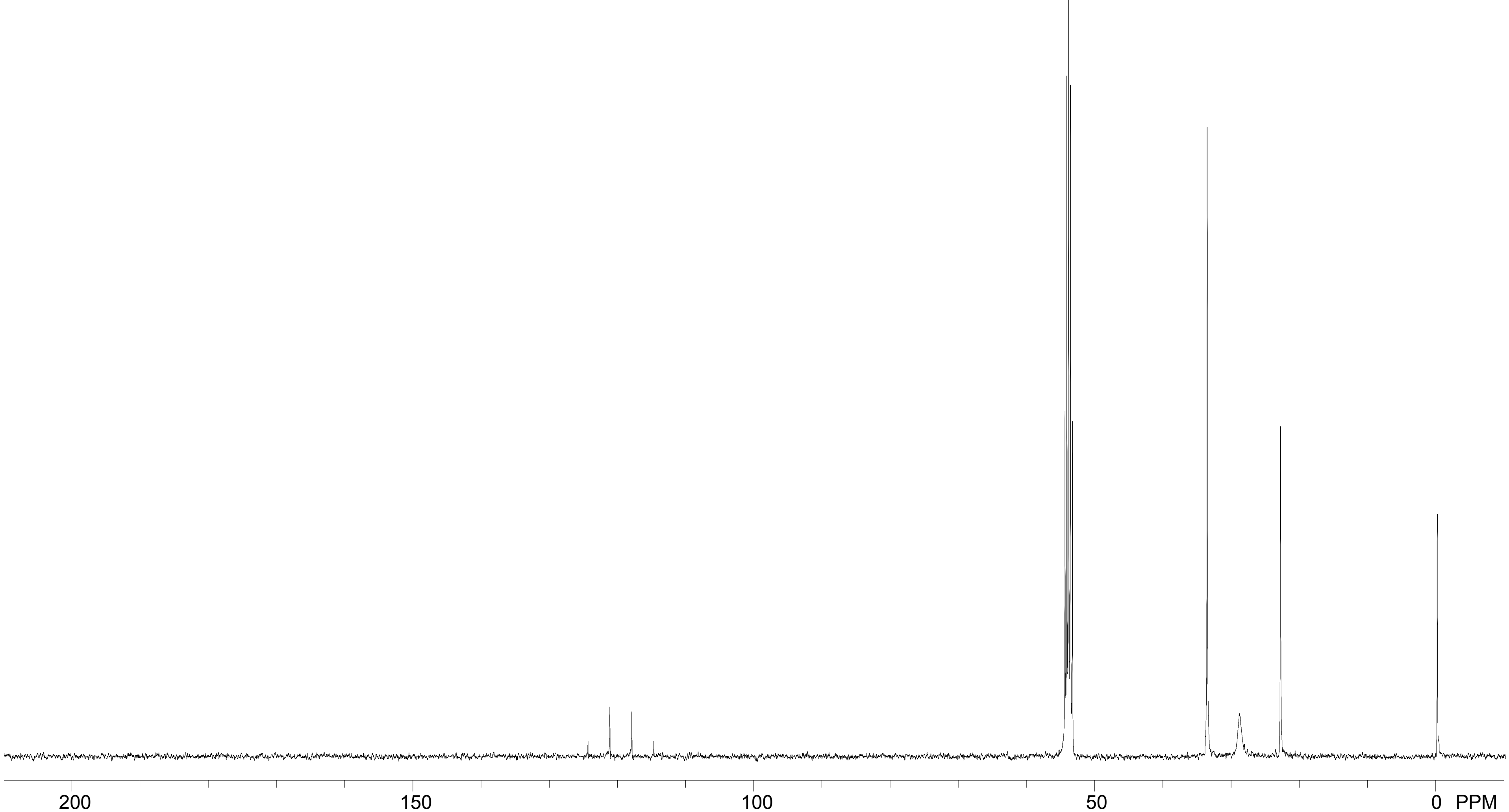
^{11}B NMR (128 MHz),
CD_2Cl_2

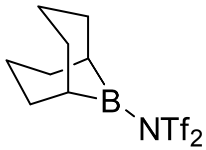




5a

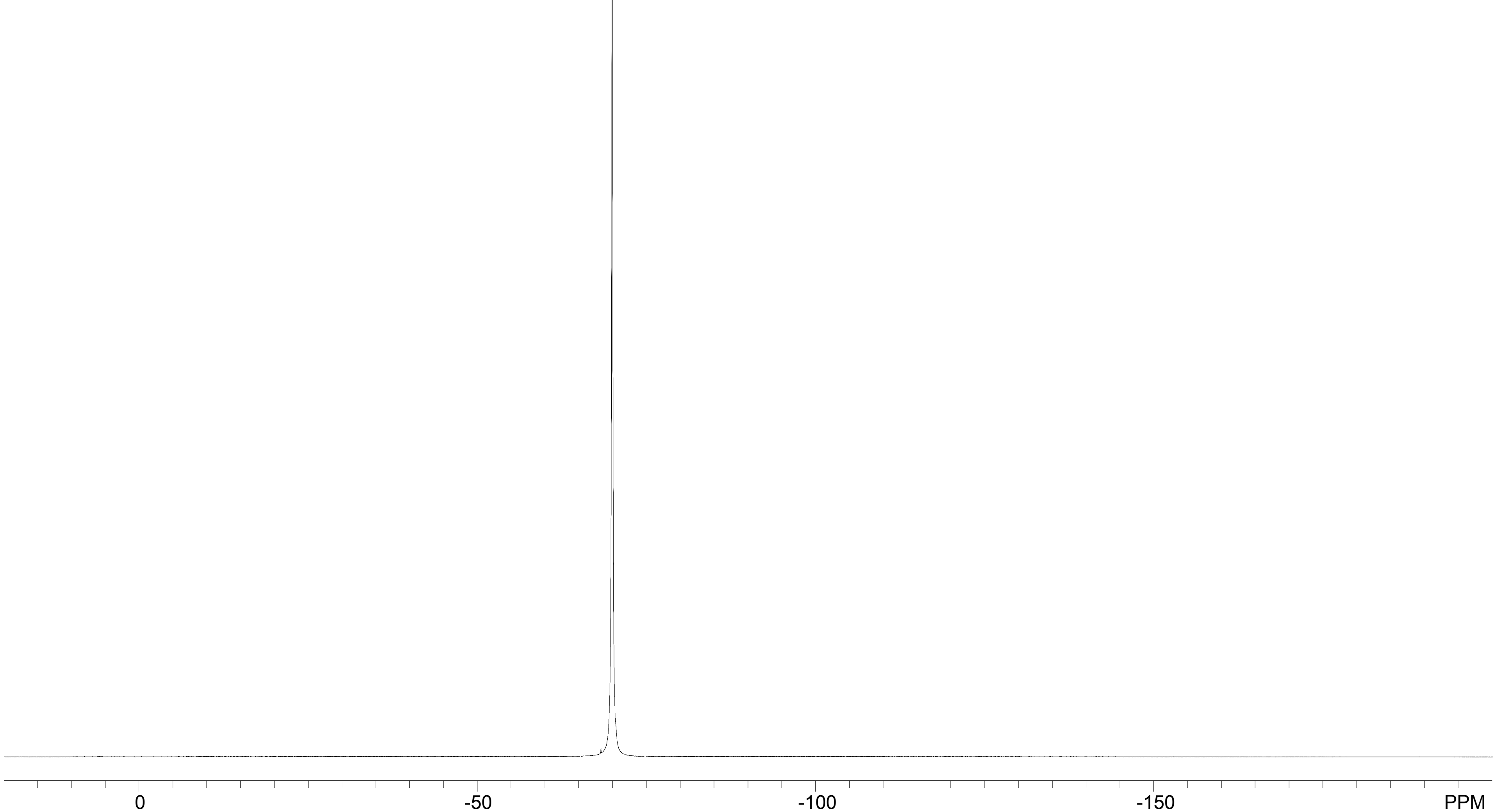
$^{13}C\{^{1}H\}$ NMR (101 MHz), CD_2Cl_2

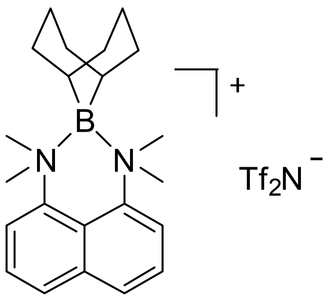




5a

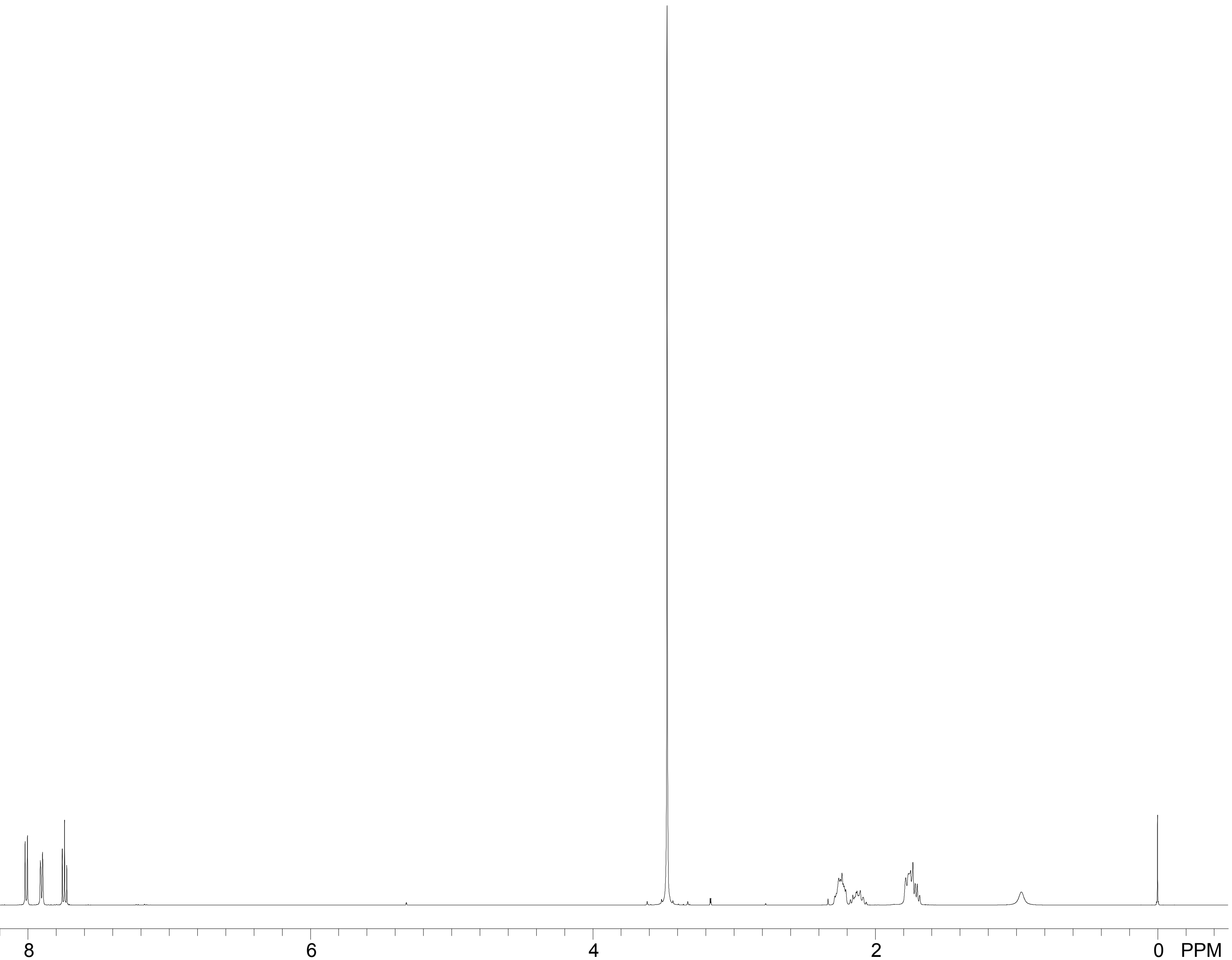
^{19}F NMR (377 MHz), CD_2Cl_2

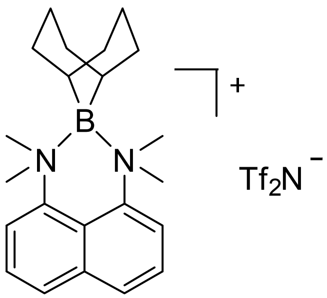




8a

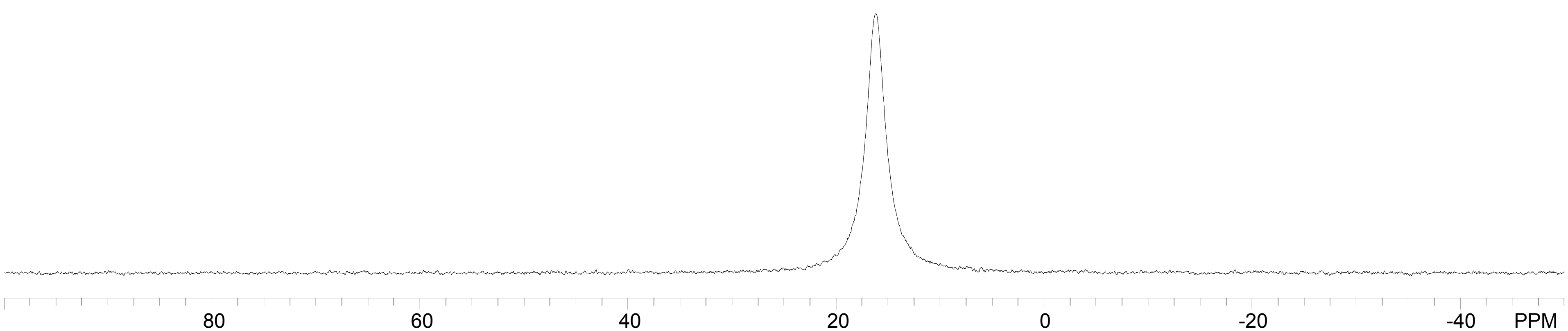
^{1}H NMR (500 MHz),
CD_2Cl_2

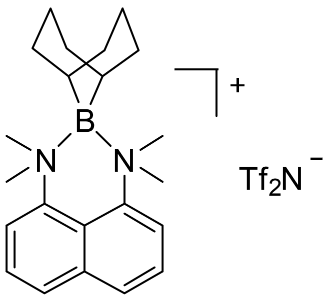




8a

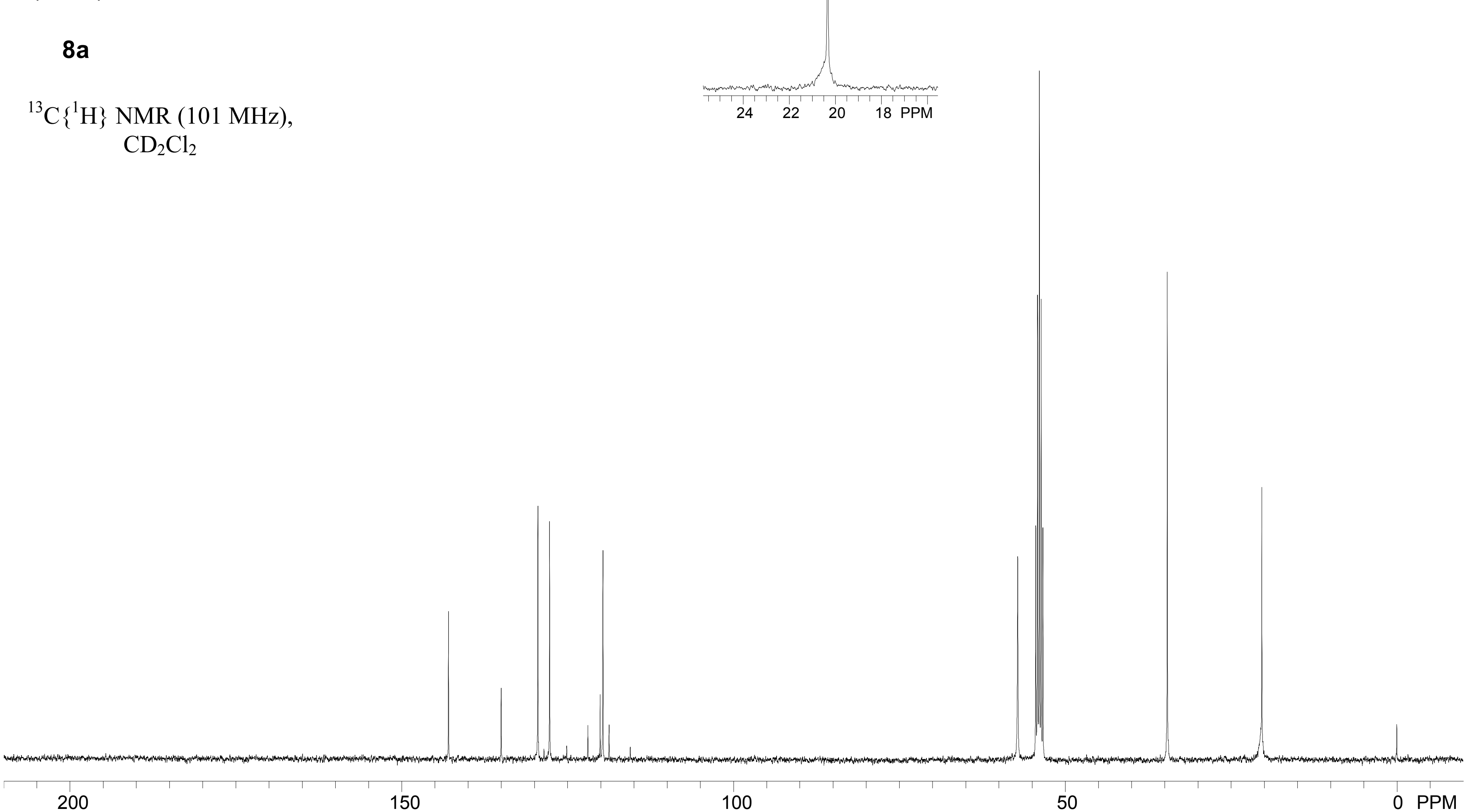
^{11}B NMR (128 MHz), CD_2Cl_2

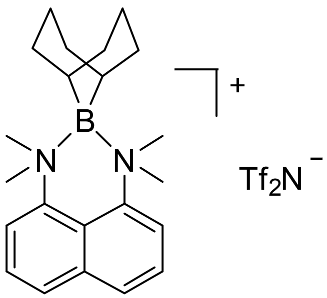




8a

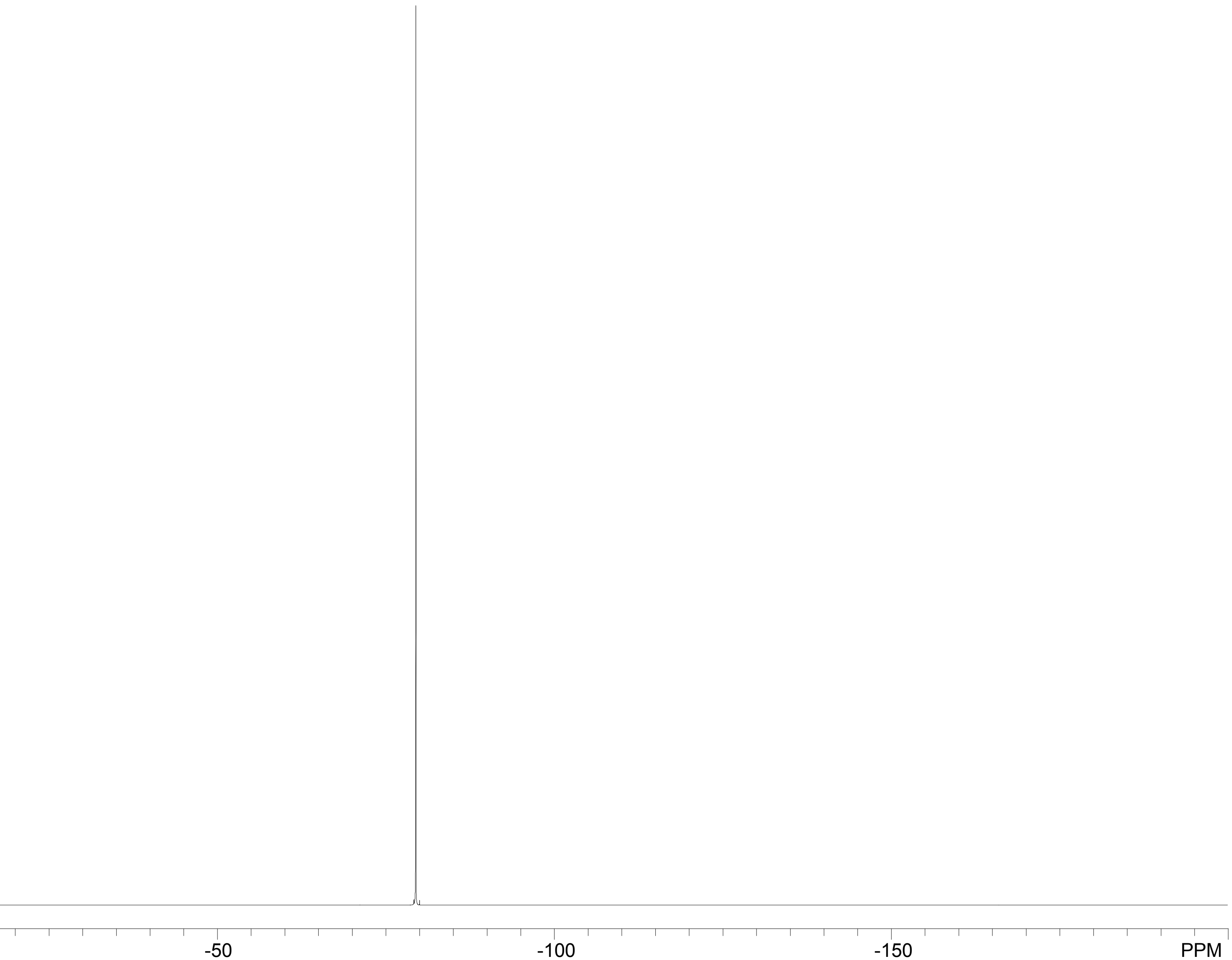
$^{13}C\{^1H\}$ NMR (101 MHz), CD_2Cl_2

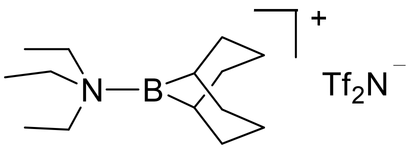




8a

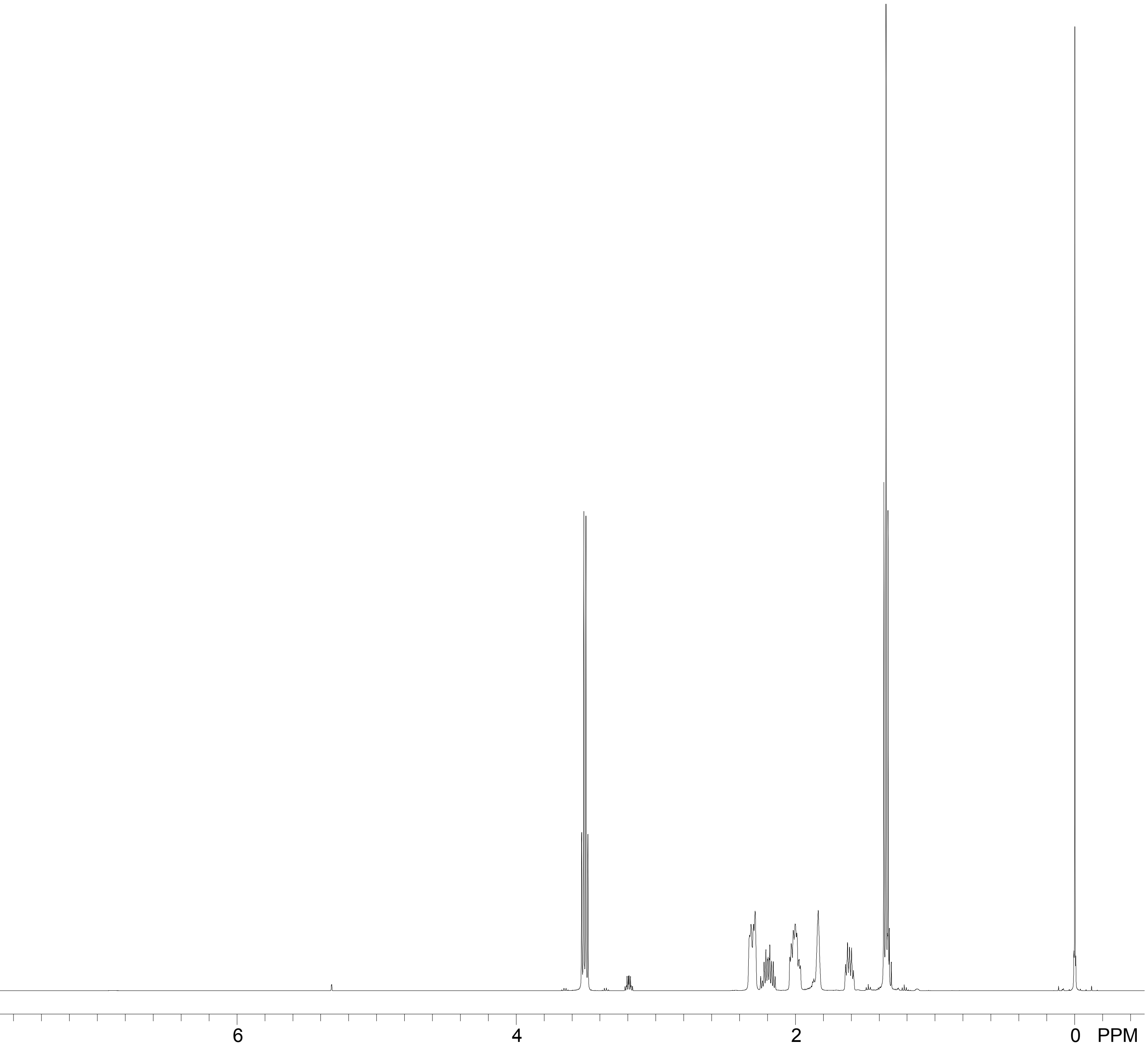
^{19}F NMR (377 MHz),
CD_2Cl_2

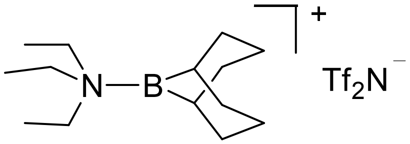




10

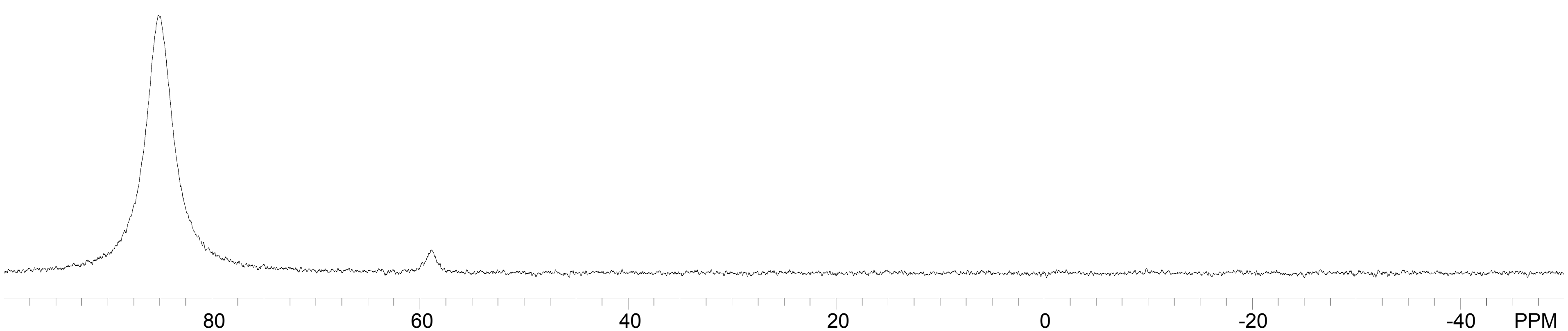
^{1}H NMR (400 MHz),
CD_2Cl_2

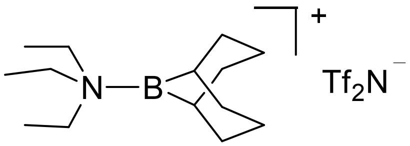




10

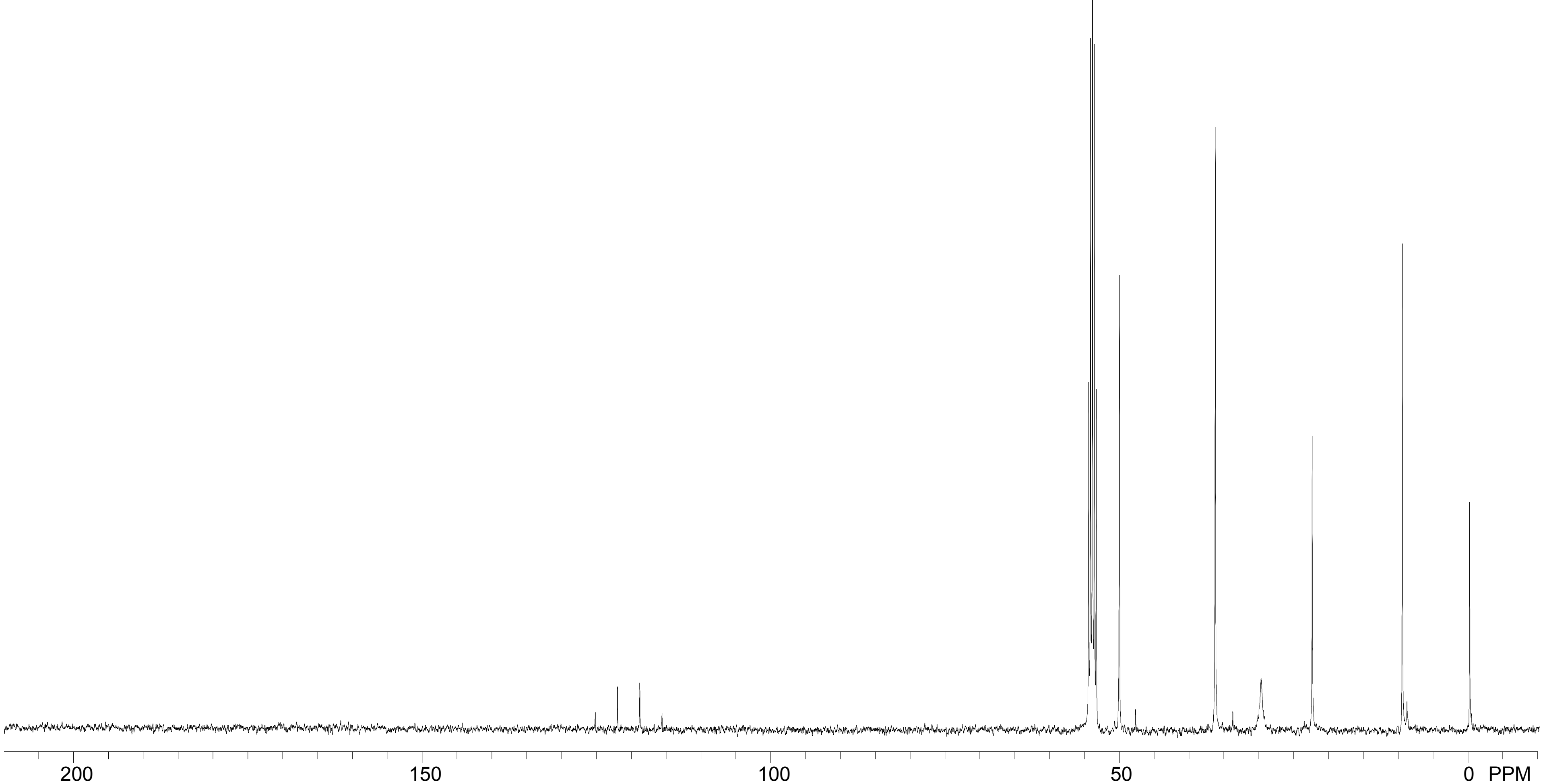
^{11}B NMR (128 MHz),
CD_2Cl_2

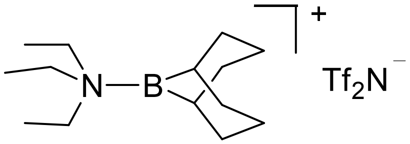




10

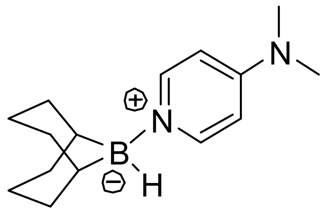
$^{13}C\{^1H\}$ NMR (101 MHz),
CD_2Cl_2





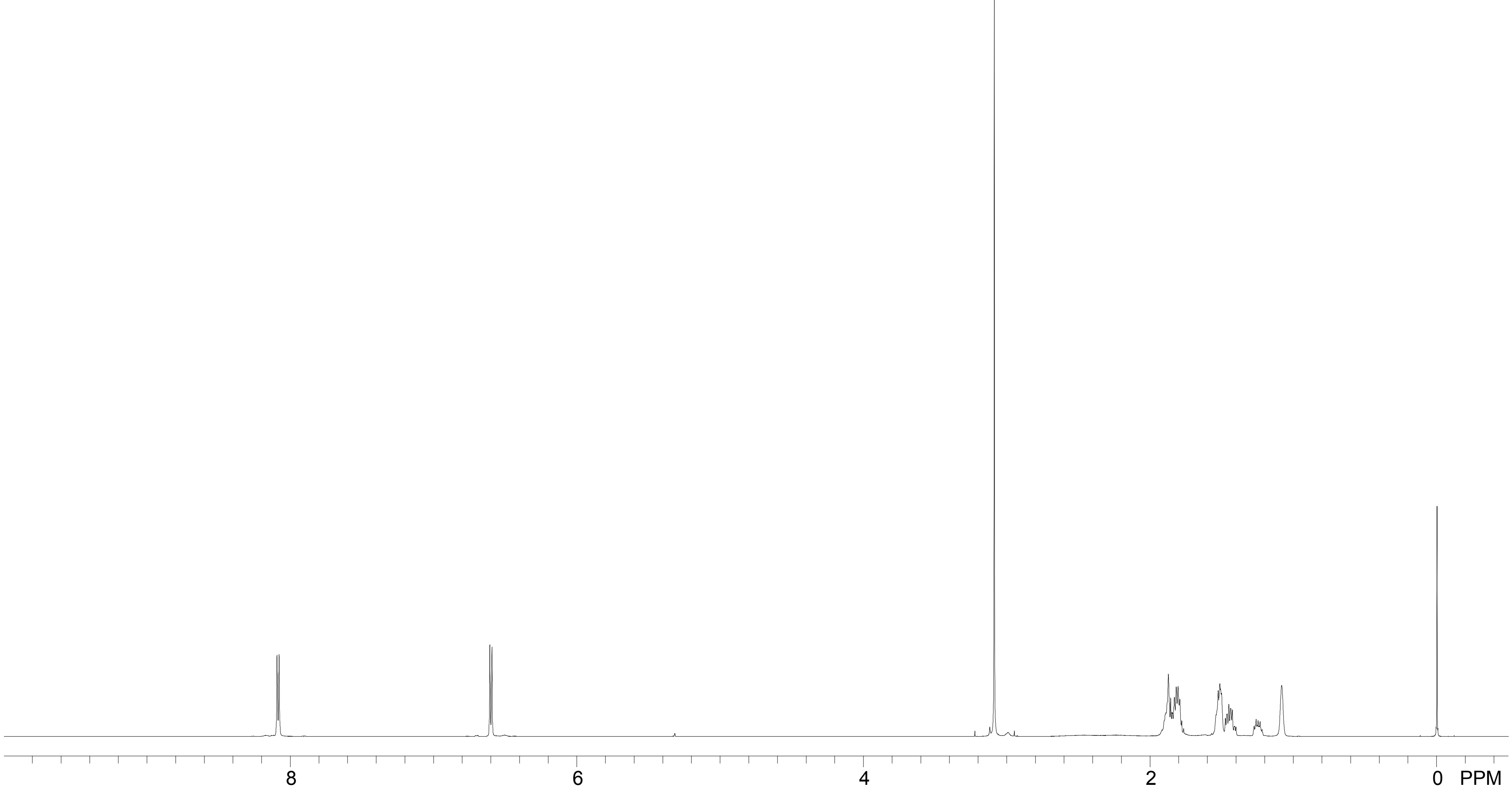
10

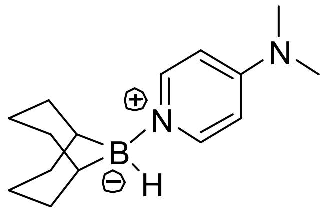
^{19}F NMR (377 MHz), CD_2Cl_2



12

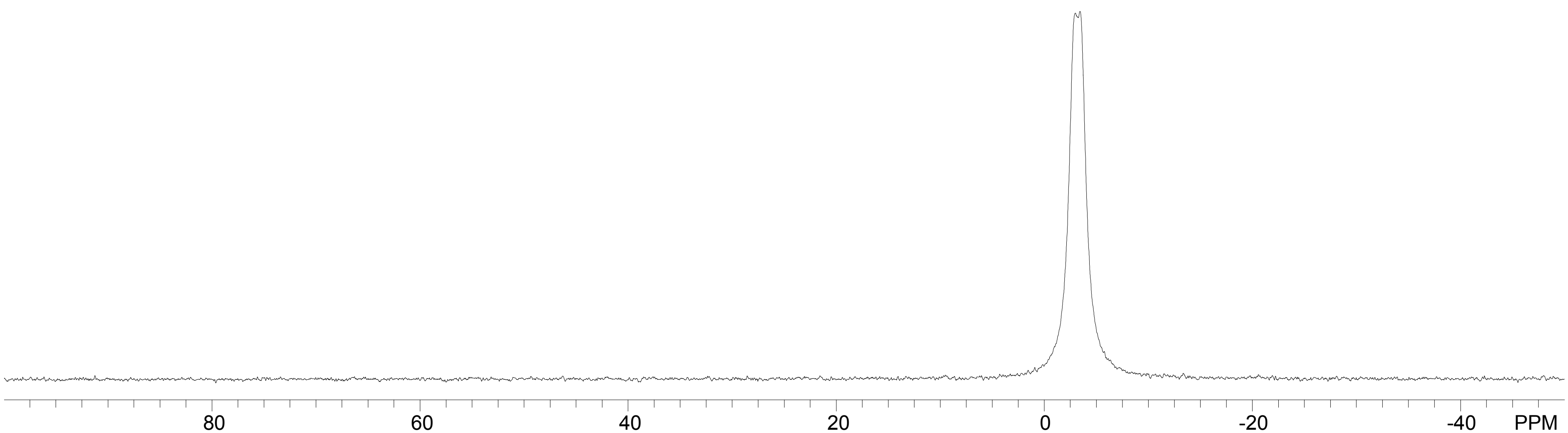
^{1}H NMR (500 MHz), CD_2Cl_2

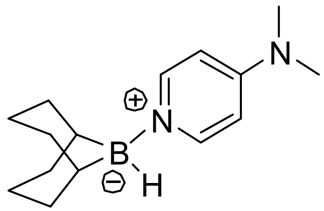




12

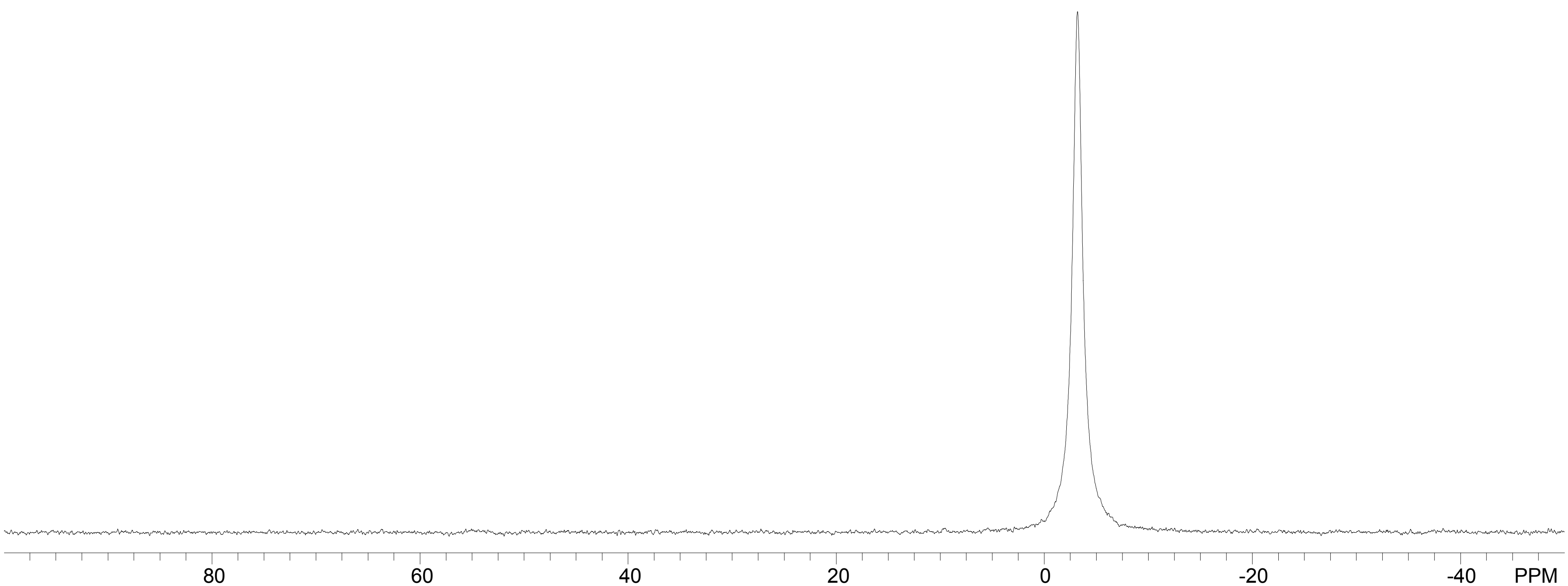
^{11}B NMR (128 MHz), CD_2Cl_2

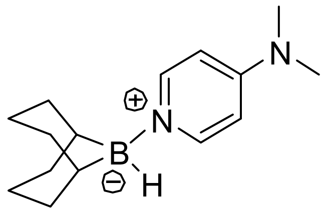




12

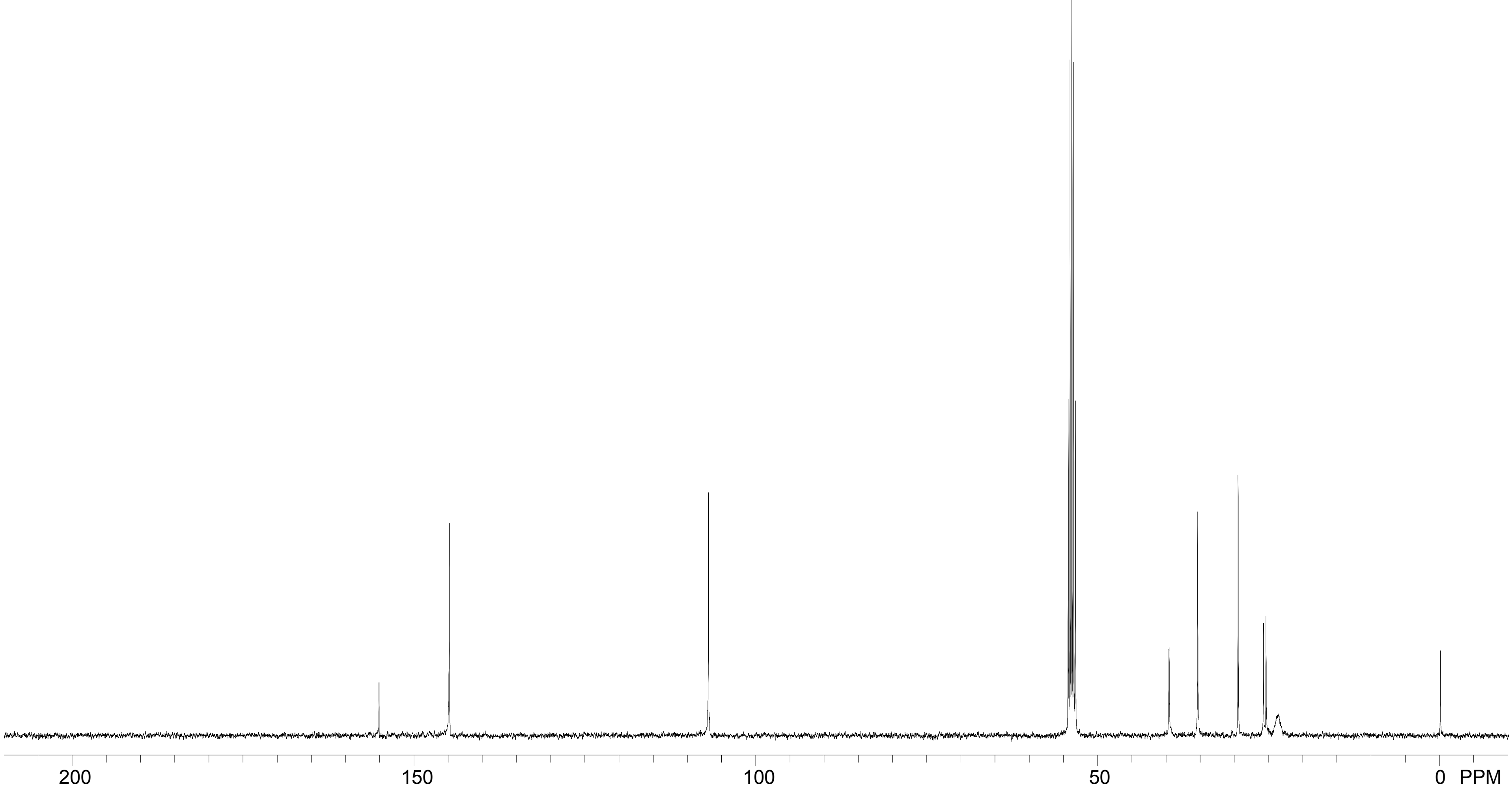
$^{11}B\{^{1}H\}$ NMR (128 MHz), CD_2Cl_2

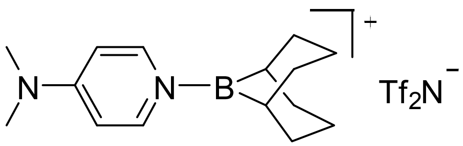




12

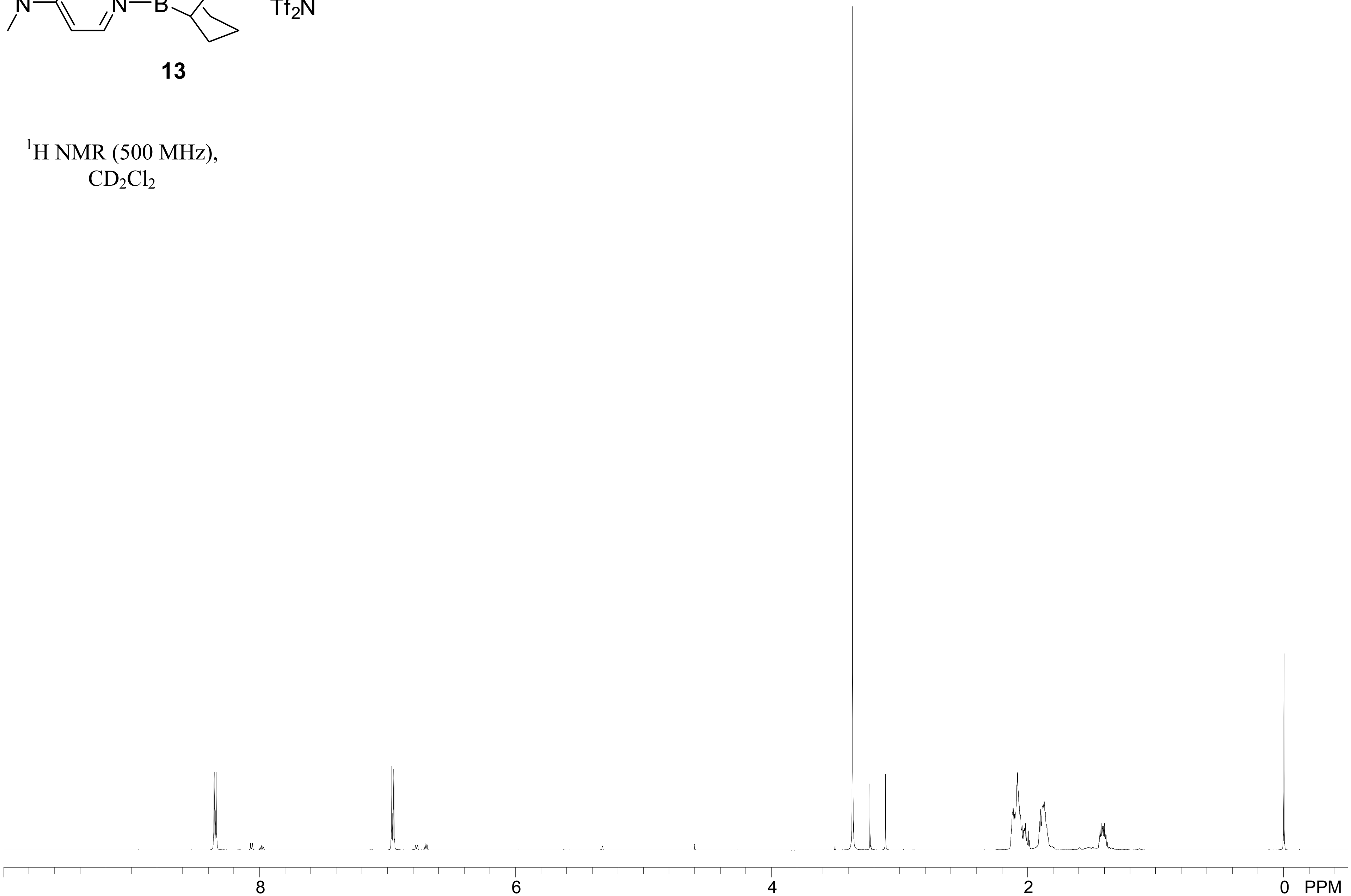
$^{13}C\{^{1}H\}$ NMR (101 MHz), CD_2Cl_2

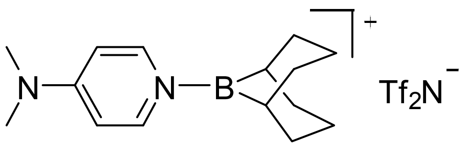




13

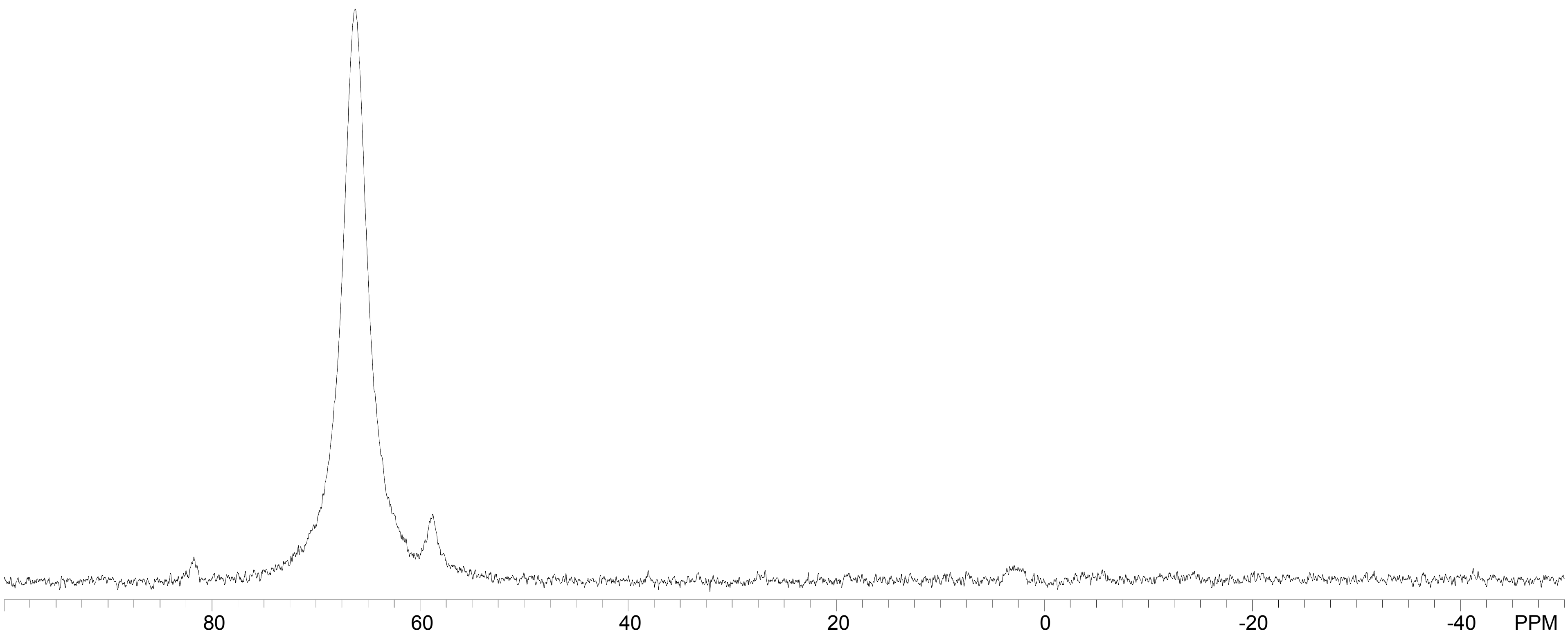
[1]H NMR (500 MHz),
CD_2Cl_2

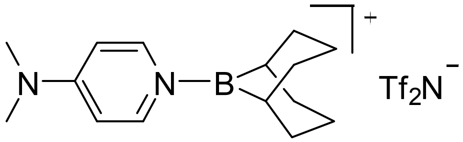




13

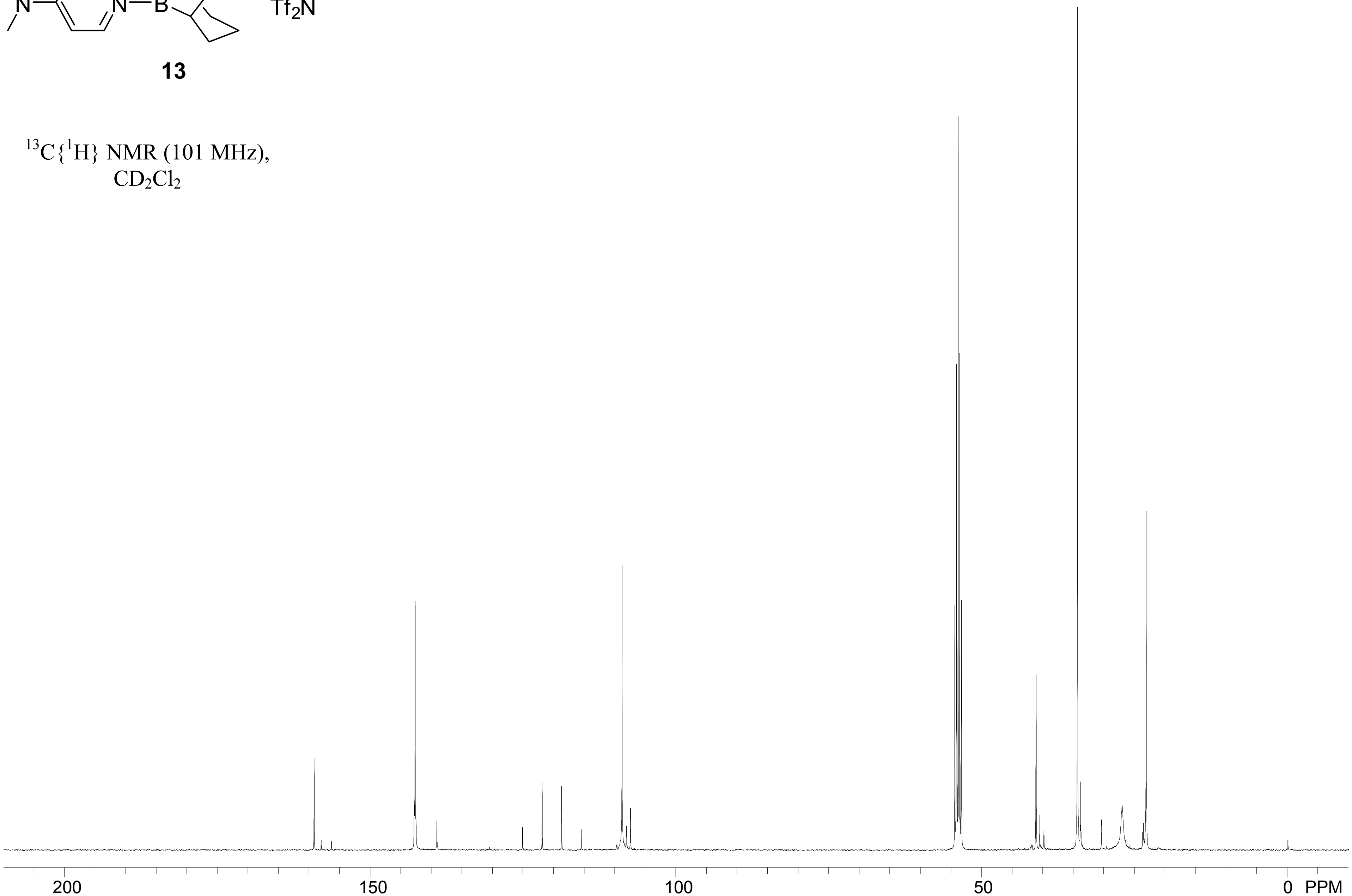
^{11}B NMR (128 MHz),
CD_2Cl_2

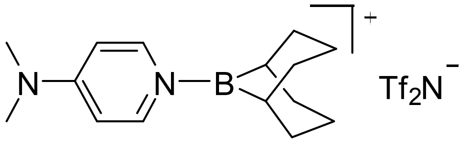




13

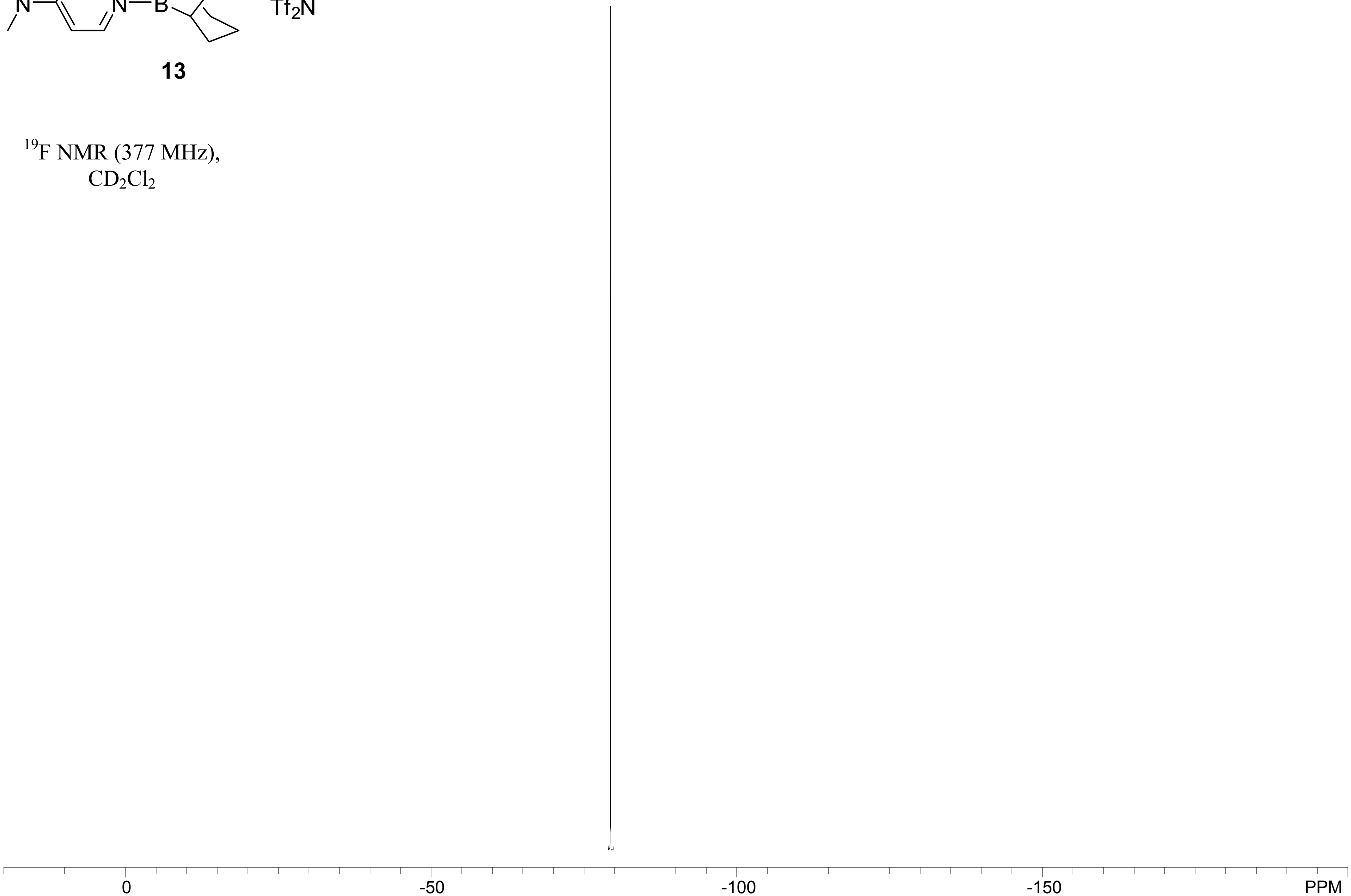
$^{13}C\{^{1}H\}$ NMR (101 MHz), CD_2Cl_2

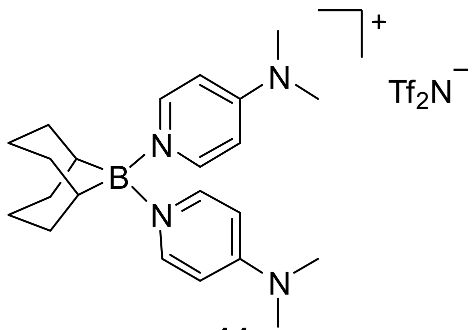




13

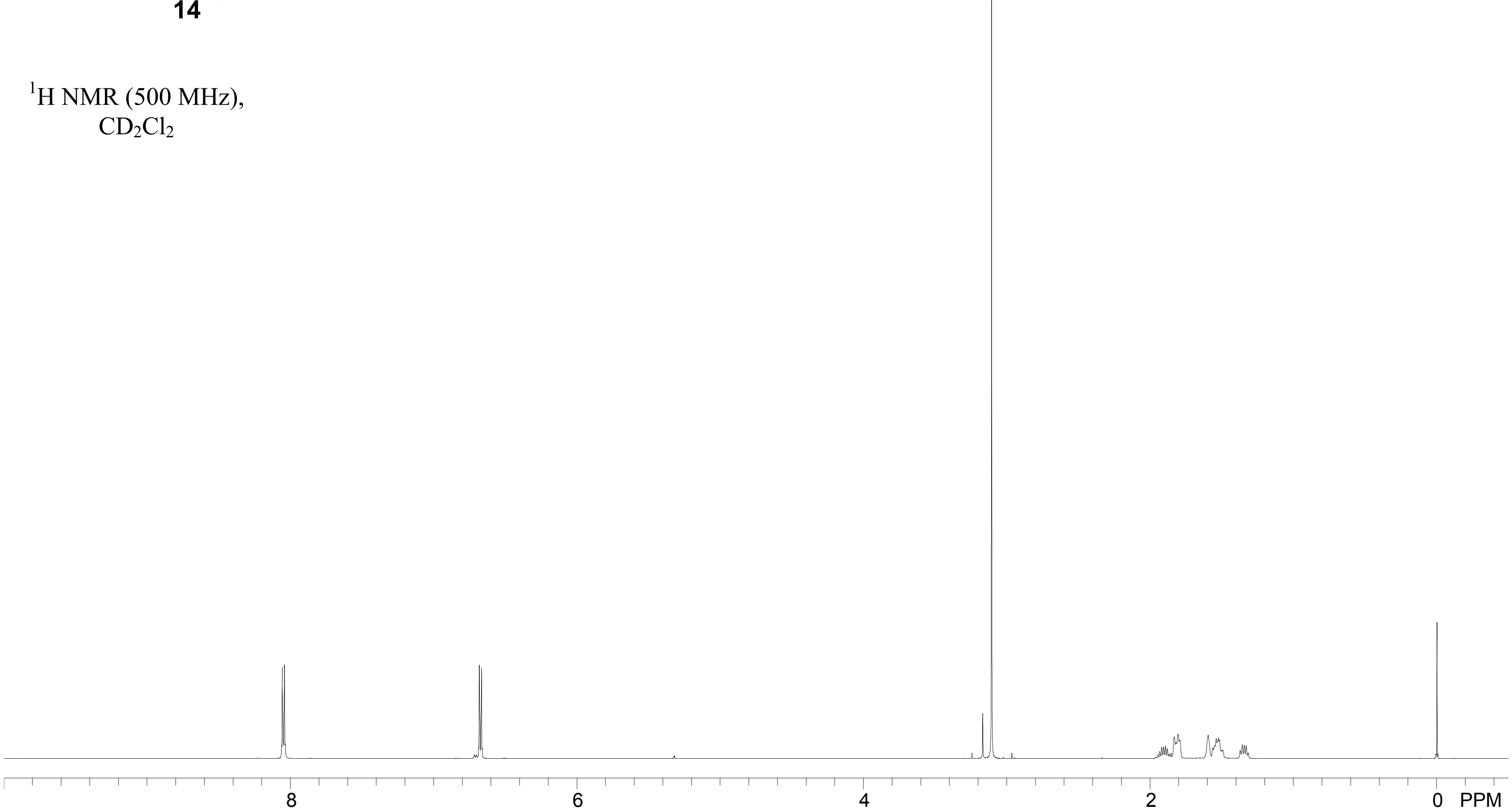
^{19}F NMR (377 MHz),
CD_2Cl_2

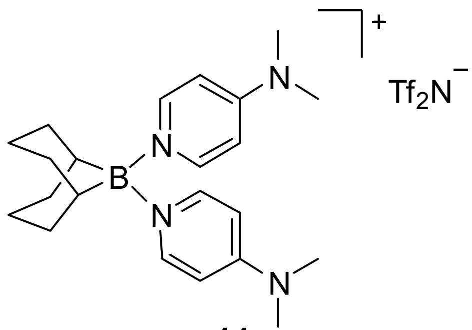




14

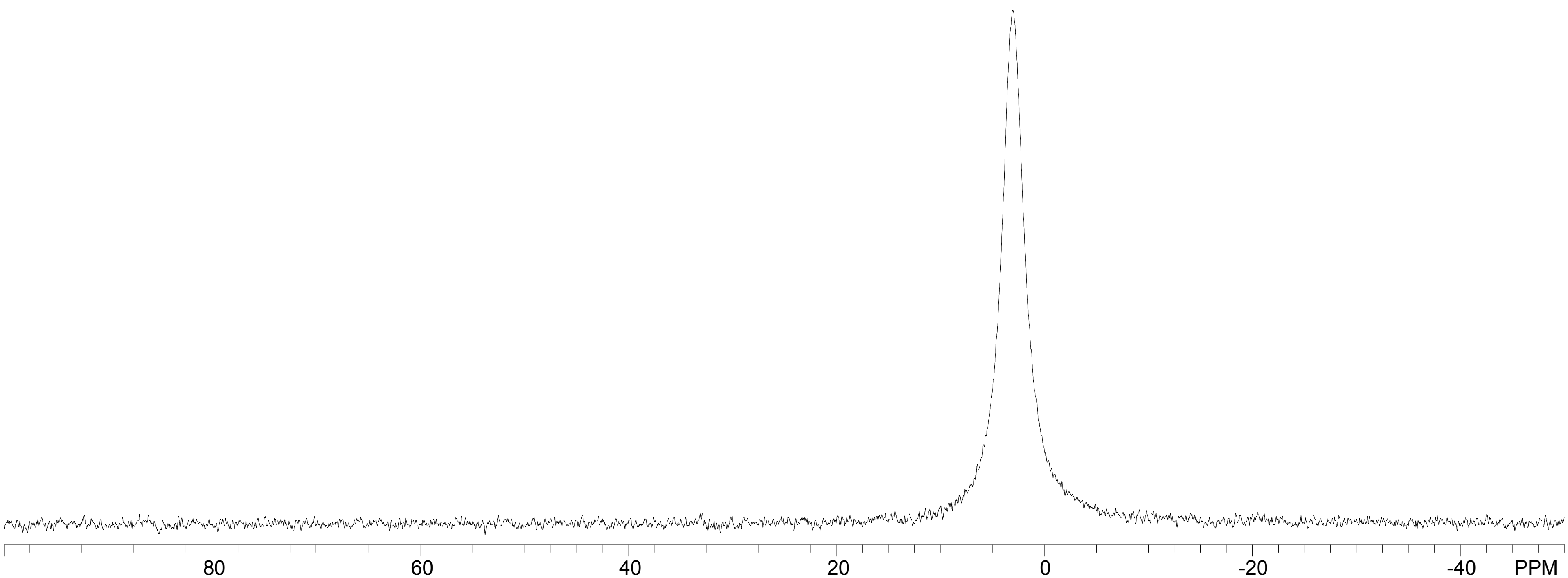
^{1}H NMR (500 MHz),
CD_2Cl_2

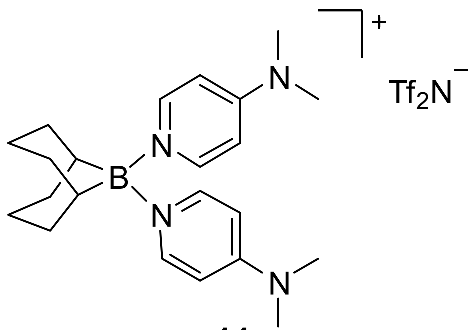




14

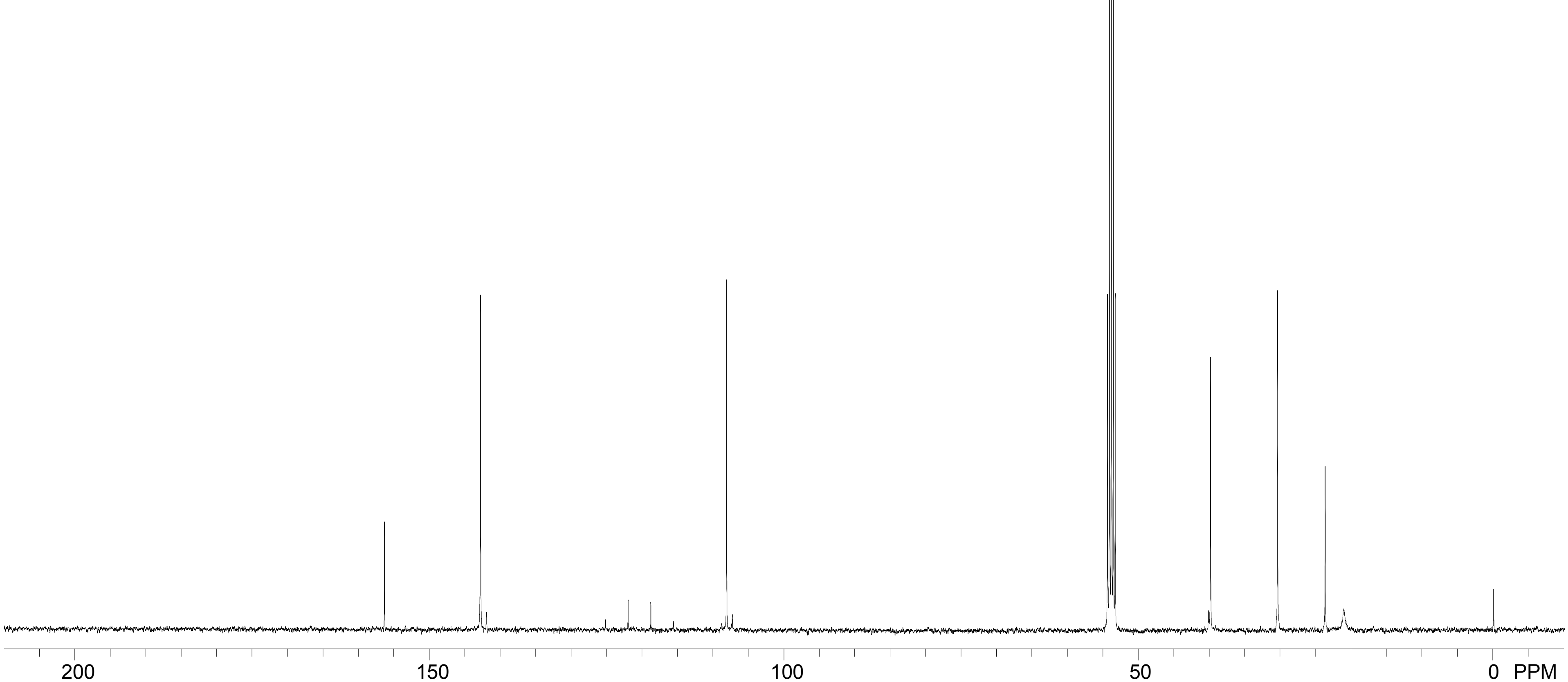
^{11}B NMR (128 MHz), CD_2Cl_2

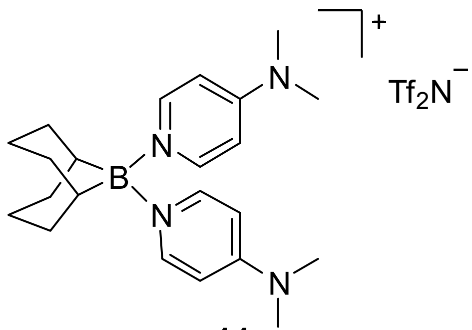




14

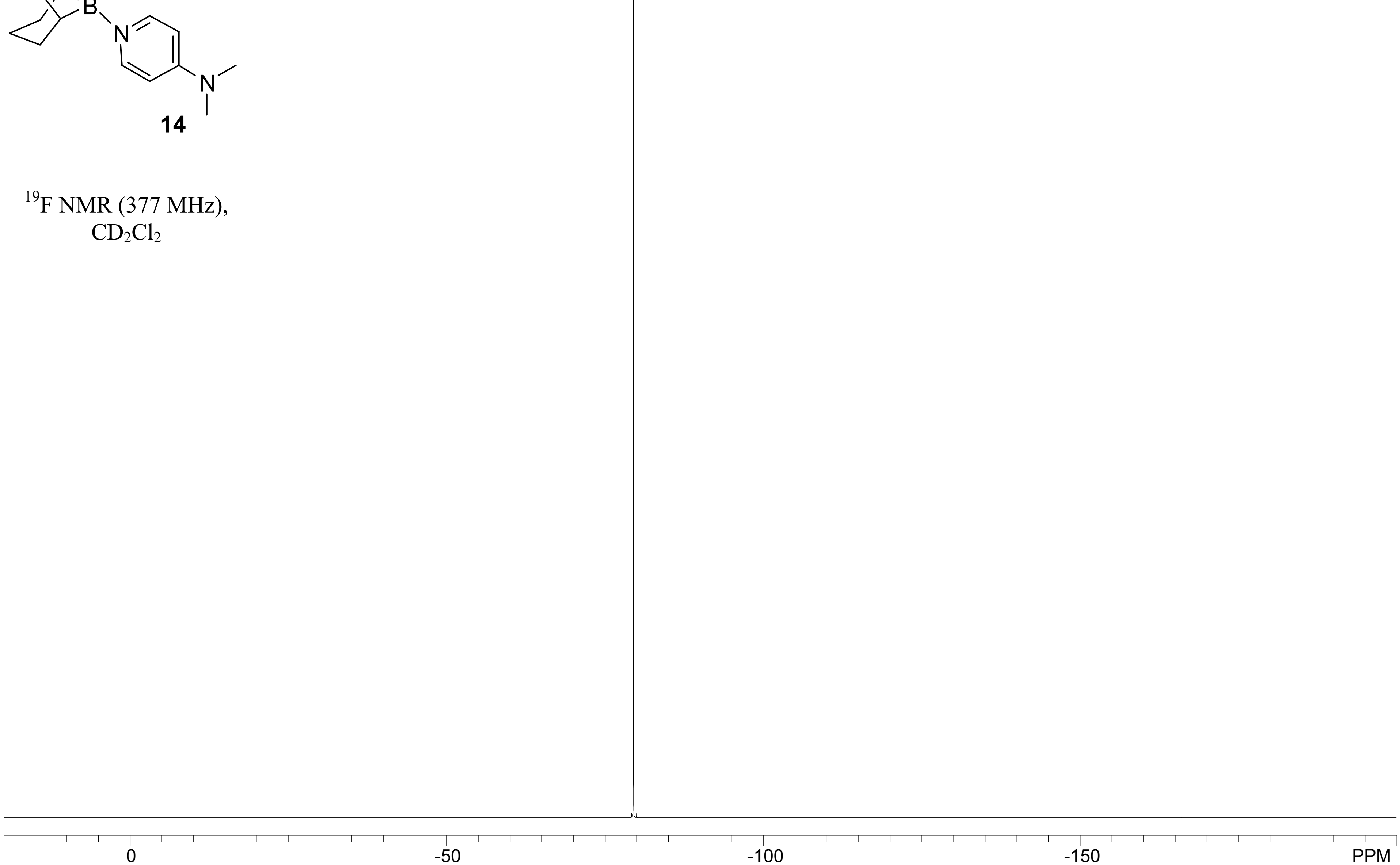
$^{13}C\{^{1}H\}$ NMR (101 MHz), CD_2Cl_2

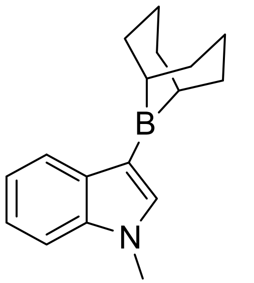




14

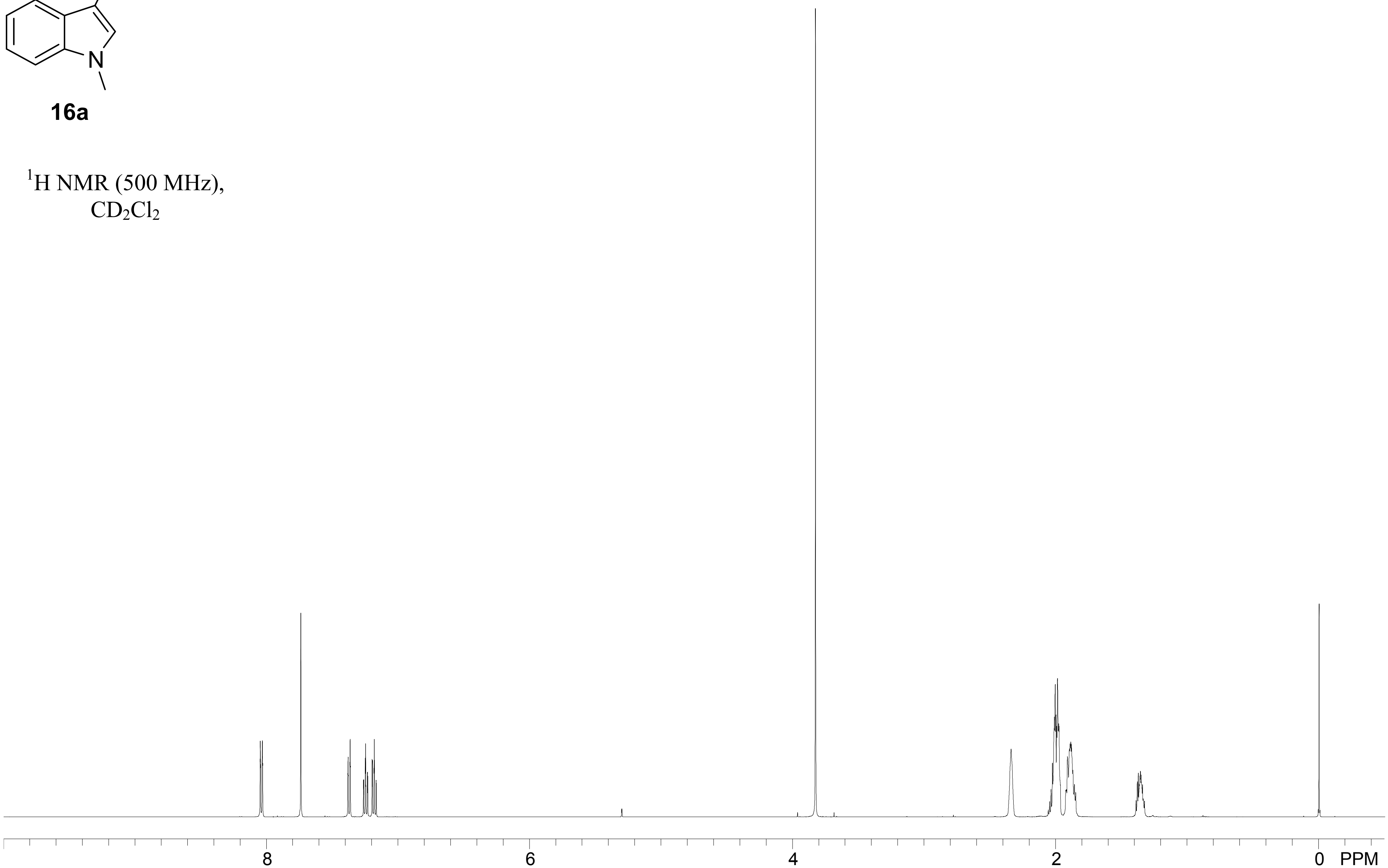
^{19}F NMR (377 MHz), CD_2Cl_2

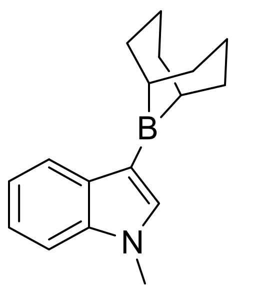




16a

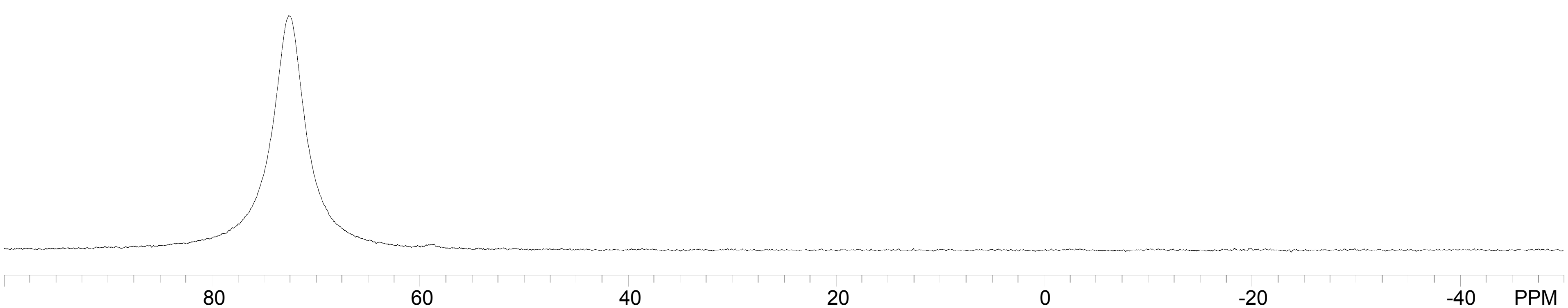
^{1}H NMR (500 MHz),
CD_2Cl_2

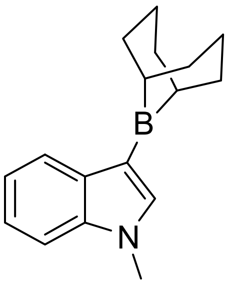




16a

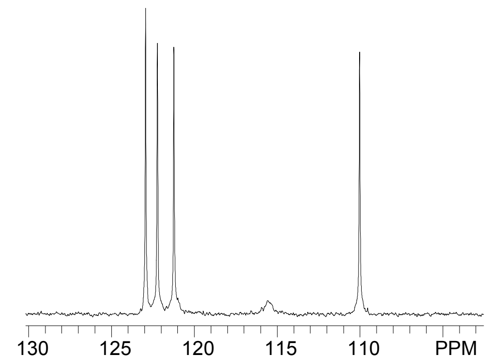
^{11}B NMR (128 MHz), CD_2Cl_2

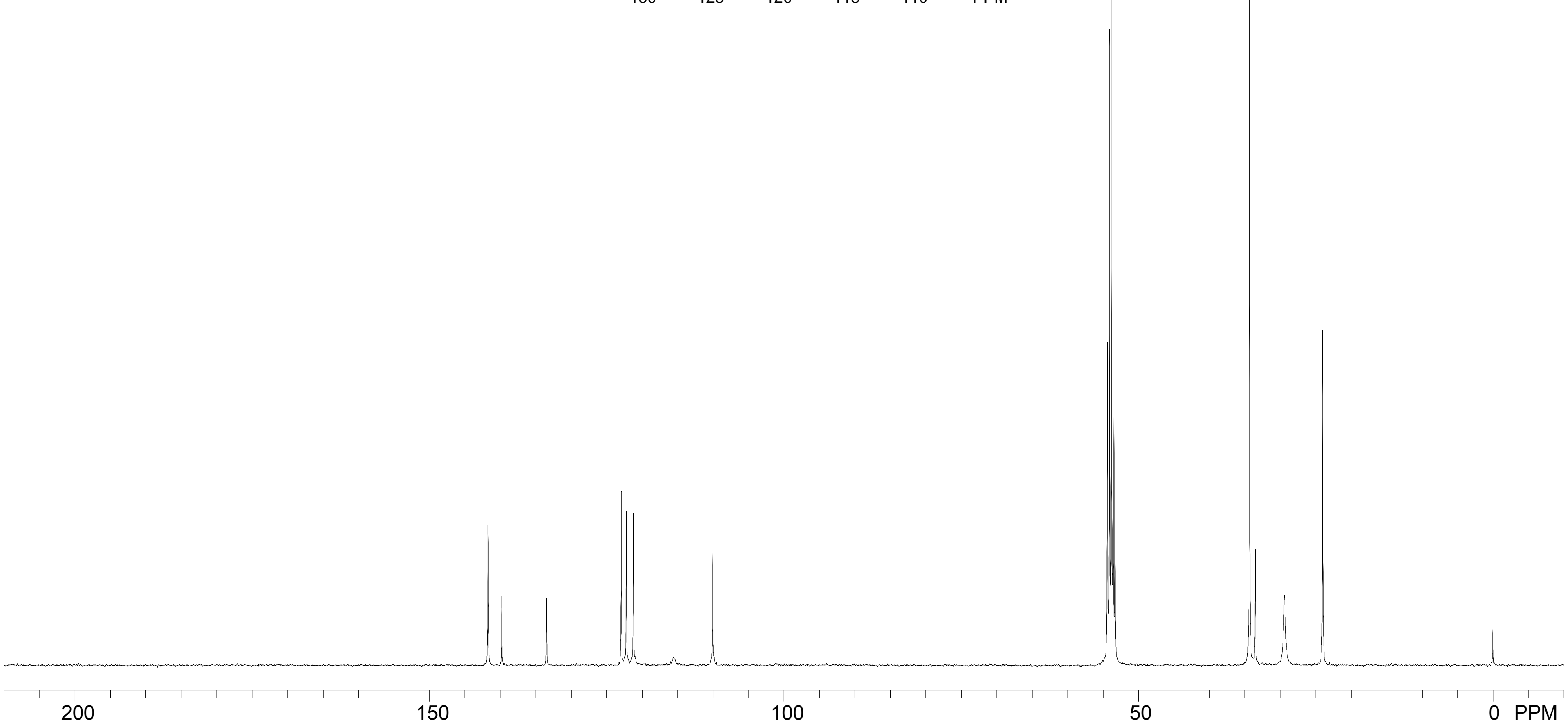


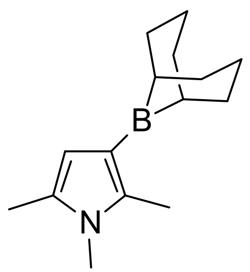


16a

$^{13}C\{^{1}H\}$ NMR (101 MHz), CD_2Cl_2

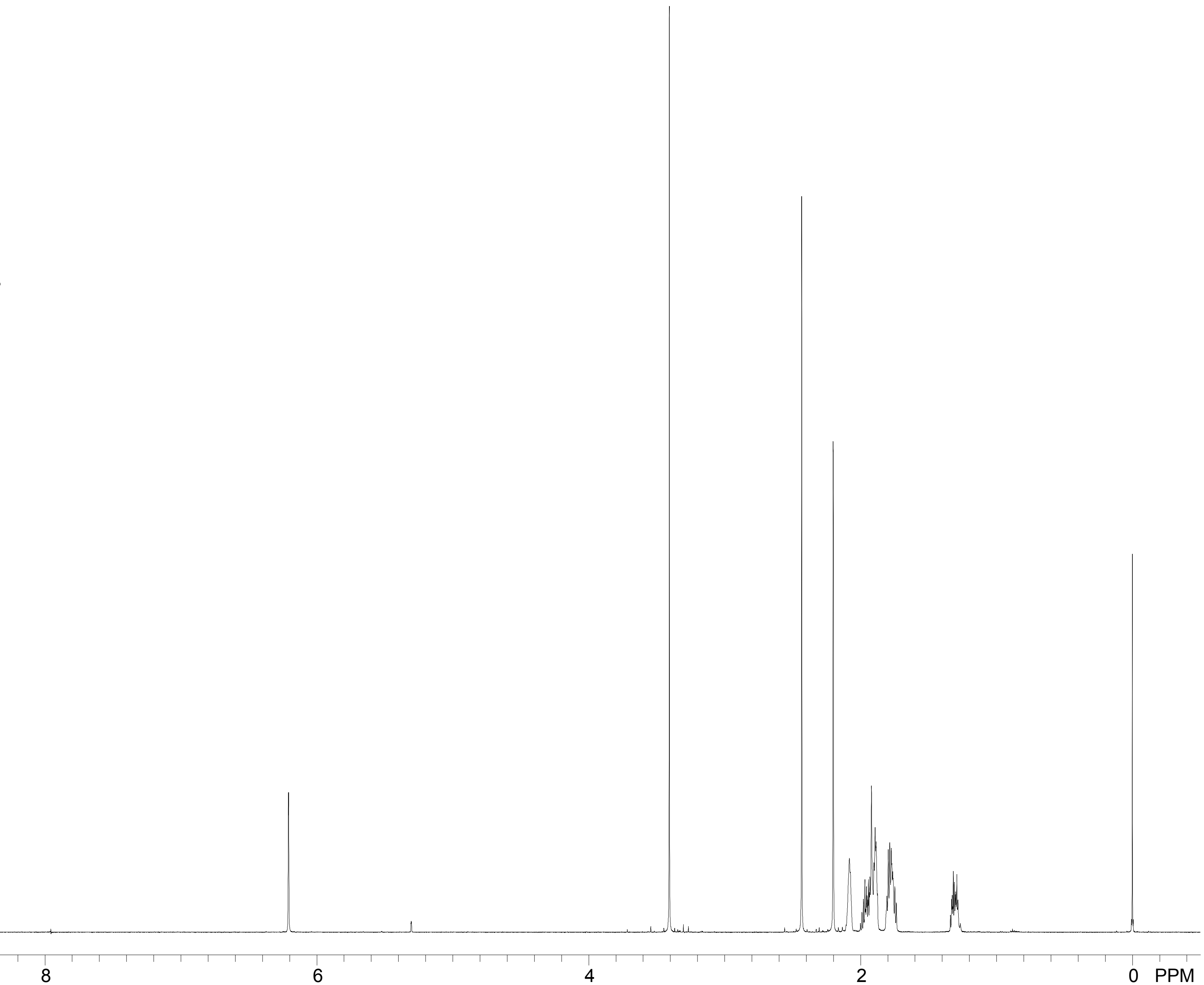


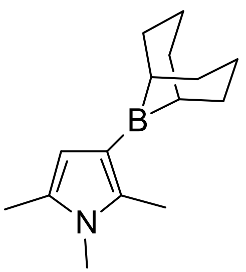




16b

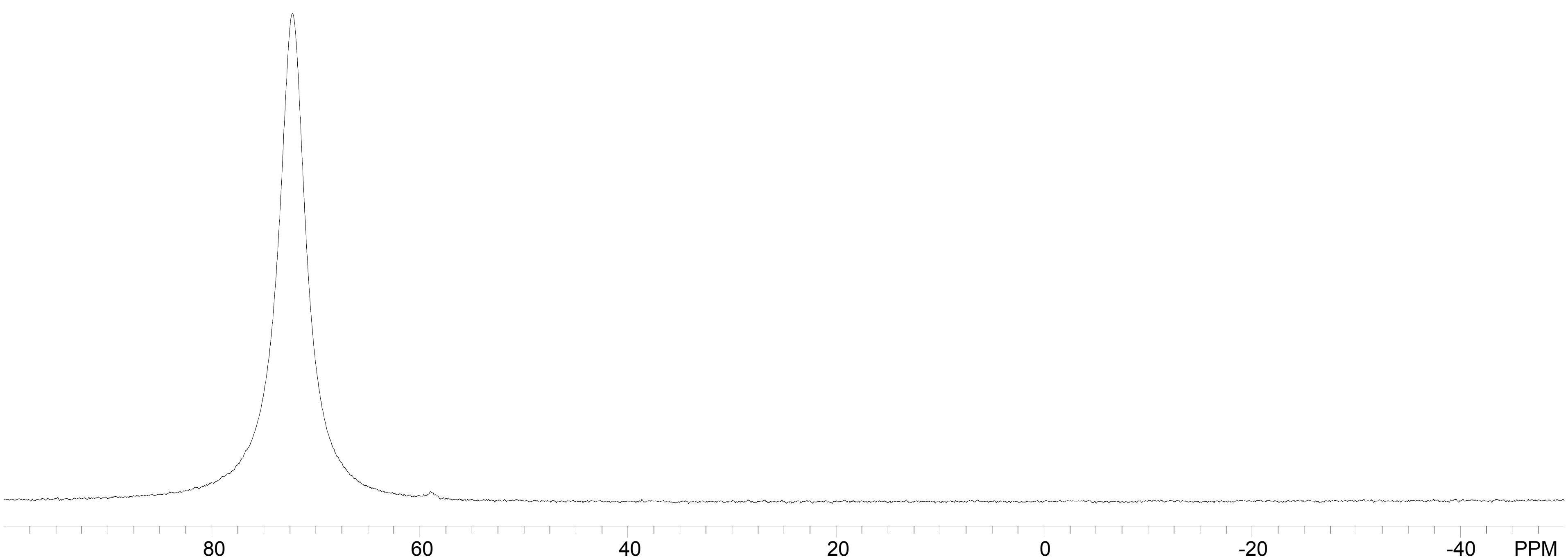
^{1}H NMR (500 MHz),
CD_2Cl_2

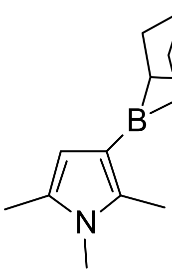




16b

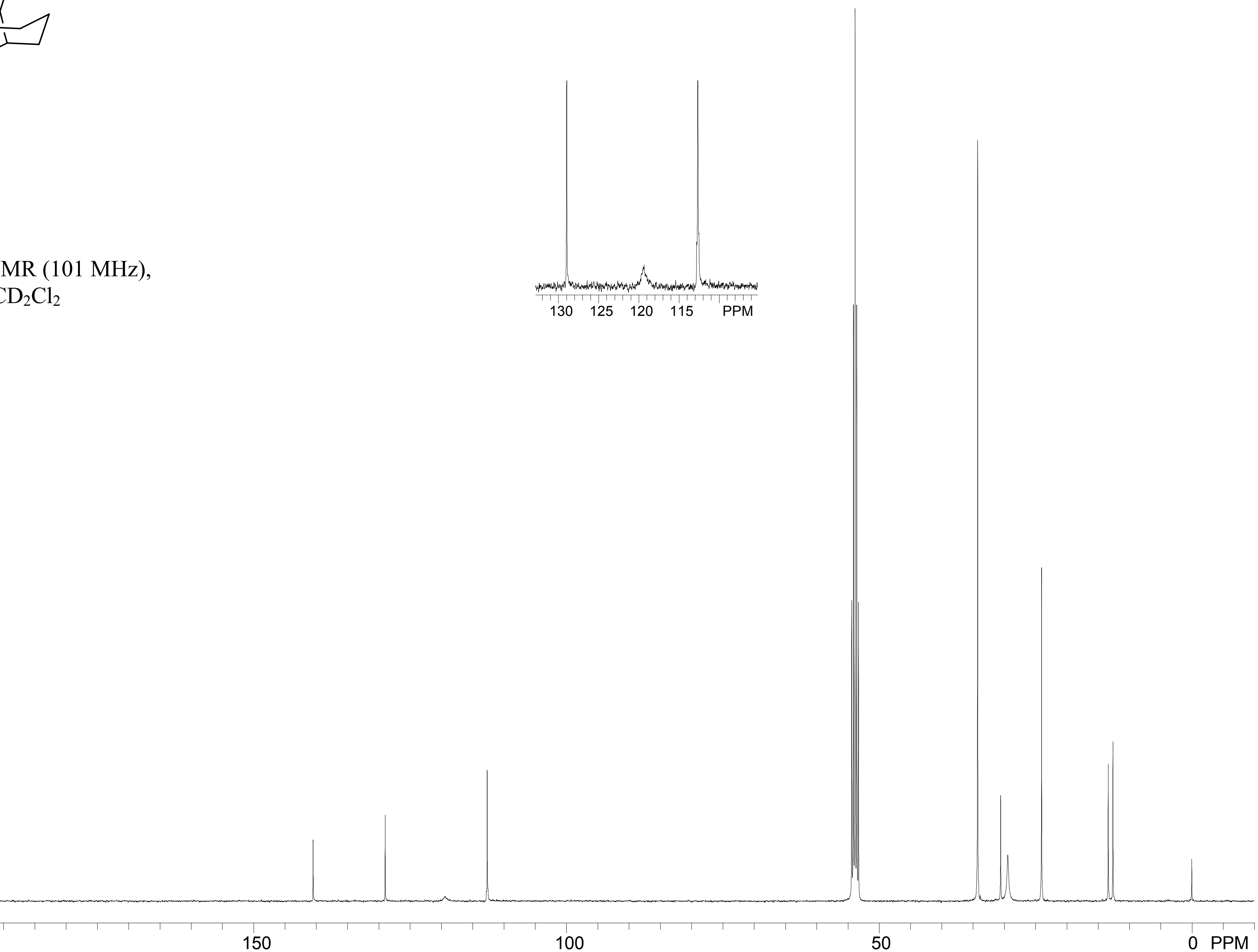
^{11}B NMR (128 MHz),
CD_2Cl_2

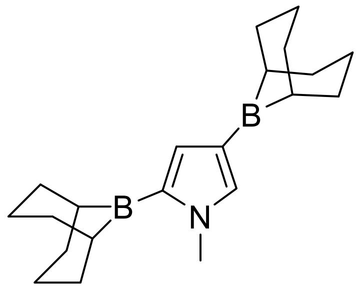




16b

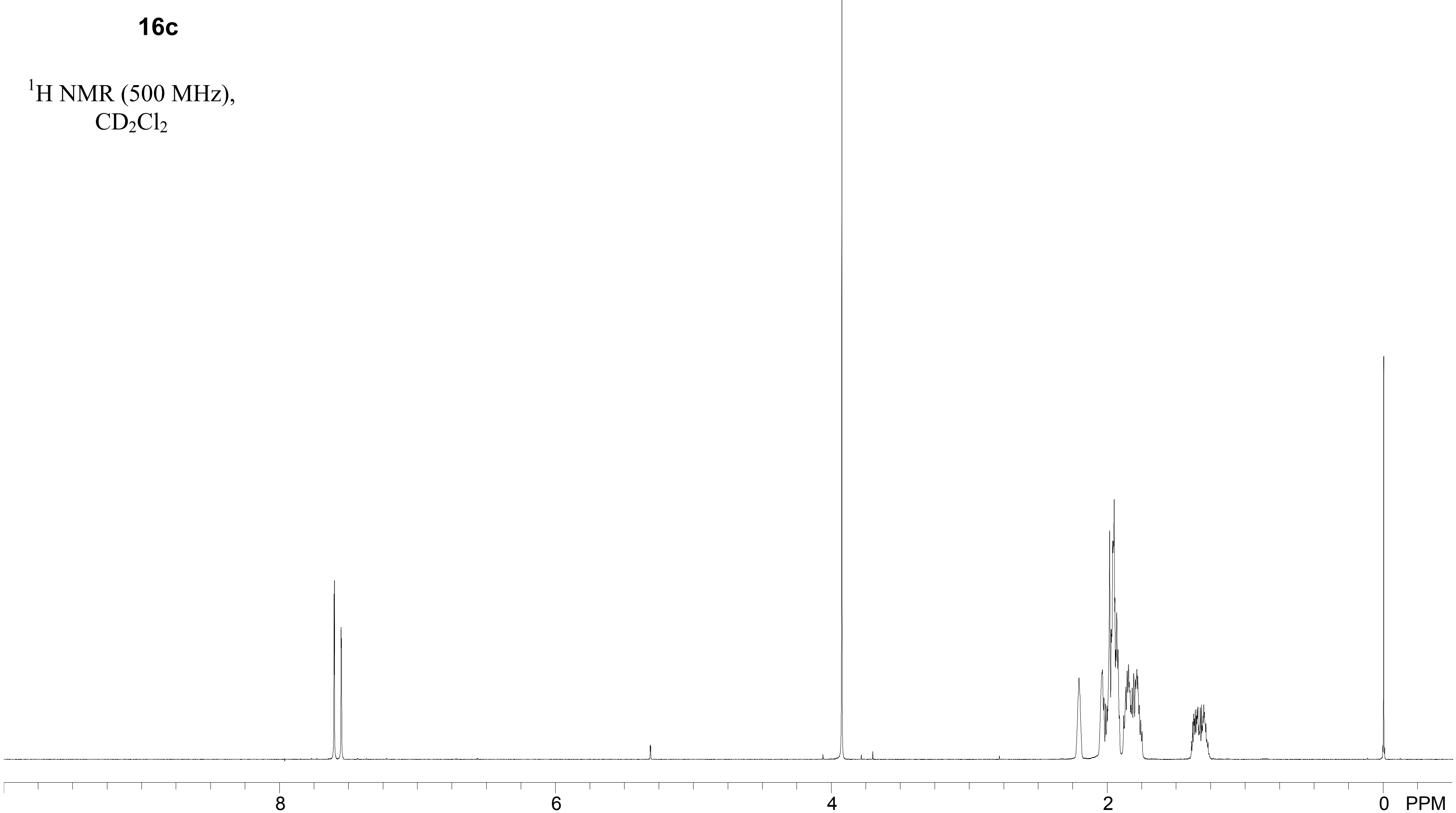
$^{13}C\{^{1}H\}$ NMR (101 MHz), CD_2Cl_2

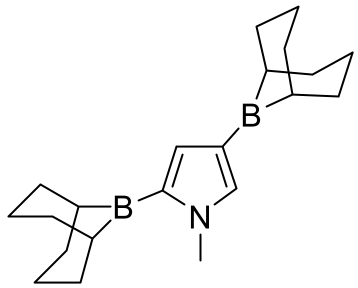




16c

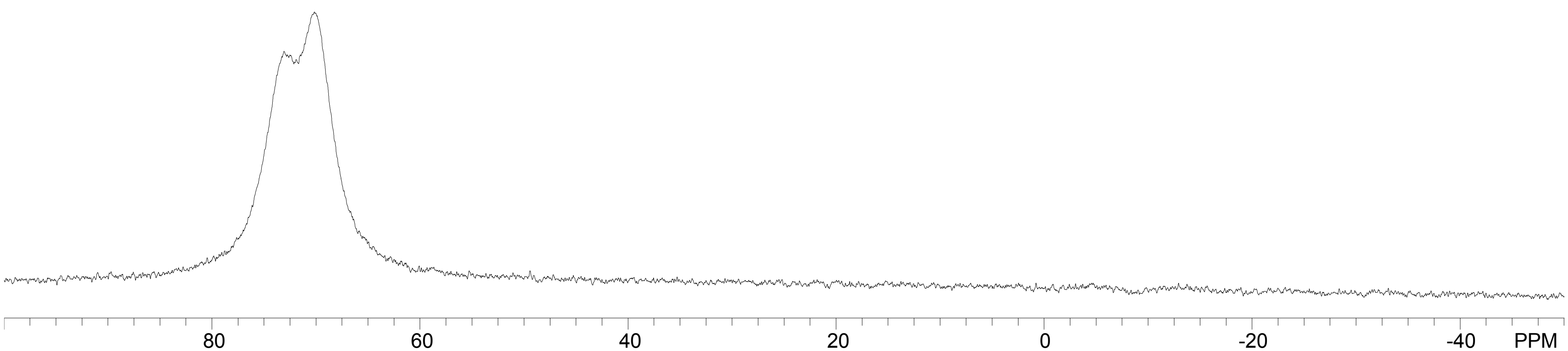
^{1}H NMR (500 MHz), CD_2Cl_2

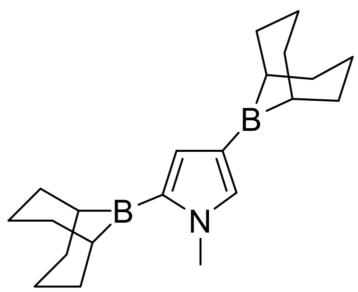




16c

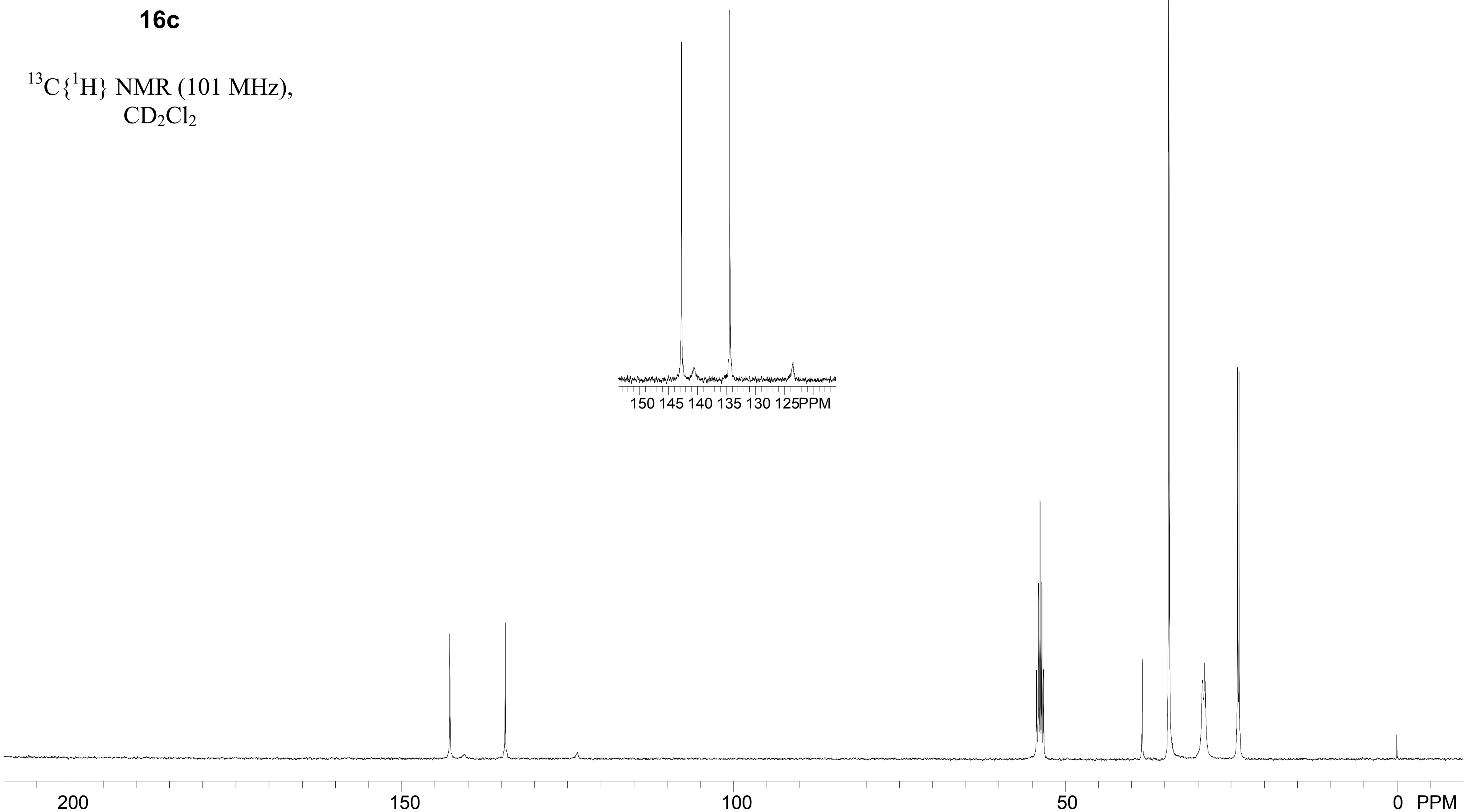
^{11}B NMR (128 MHz),
CD_2Cl_2

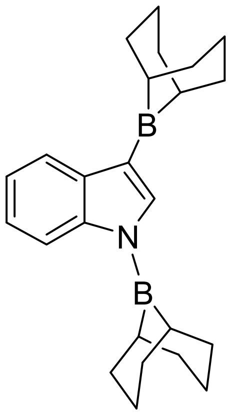




16c

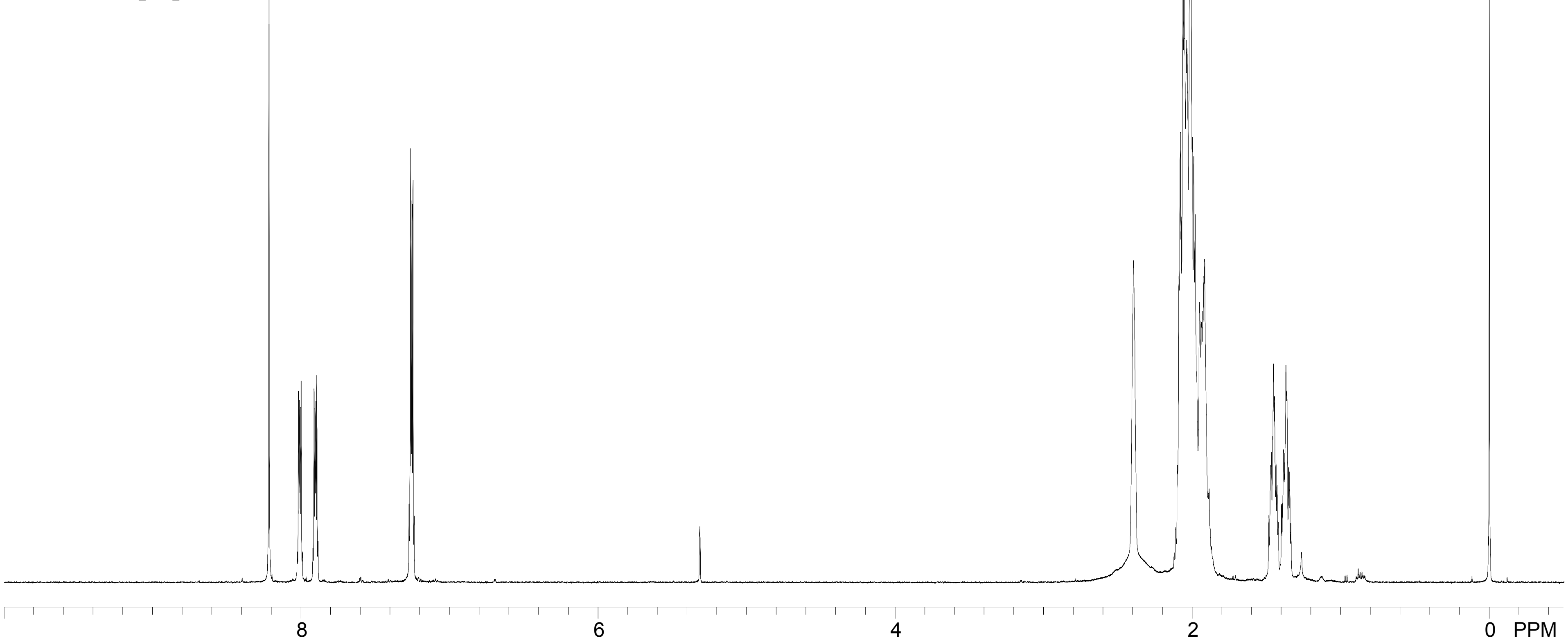
$^{13}C\{^{1}H\}$ NMR (101 MHz), CD_2Cl_2

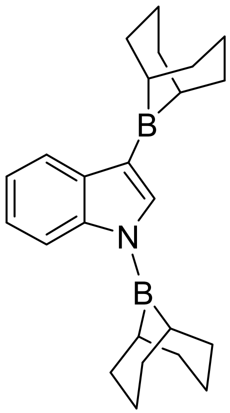




16d

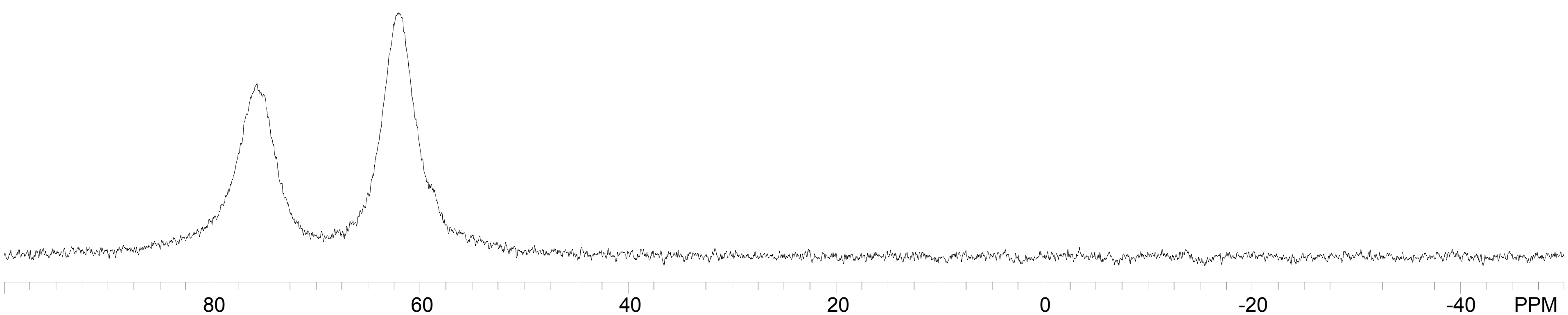
^{1}H NMR (500 MHz), CD_2Cl_2

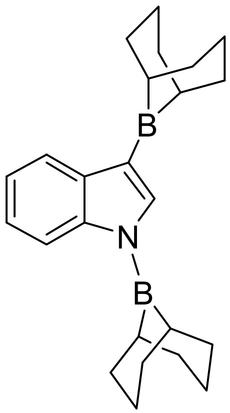




16d

^{11}B NMR (128 MHz), CD_2Cl_2





16d

$^{13}C\{^{1}H\}$ NMR (101 MHz), CD_2Cl_2