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Diverse Reactivity of Borenium Cations with >N–H Compounds

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SUPPLEMENTARY INFORMATION

Contents

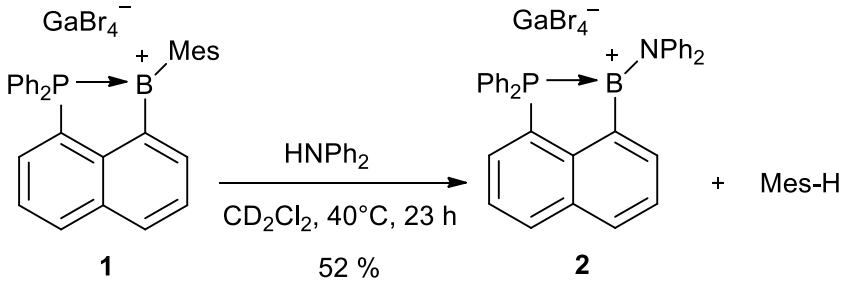
General experimental considerations

All reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques. All solvents were sparged with argon and dried using an MBRAUN Solvent Purification System (SPS). ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker Avance 500 or 300 spectrometers. Chemical shifts are expressed with a positive sign, in parts per million, calibrated to residual ^{1}H (7.24 ppm) and ^{13}C (77.16 ppm) solvent signals, external $BF_3.OEt_2$, $CFCl_3$ and 85% H_3PO_4 (0 ppm) respectively. Otherwise stated, NMR spectra were recorded at 293 K. Mass spectra were recorded on a Waters LCT mass spectrometer. Compound **1**,[1] dibromomesitylborane[1] and 1-iodo-8-diisopropylphosphinonaphtalene[2] was synthetized as previously reported.

[1] M. Devillard, R. Brousses, K. Miqueu, G. Bouhadir, D. Bourissou, *Angew. Chem. Int. Ed*. **2015**, *54*, 5722.
[2] S. Bontemps, M. Devillard, S. Mallet-Ladeira, G. Bouhadir, K. Miqueu, D. Bourissou, *Inorg. Chem.* **2013**, *52*, 4714.

Experimental procedures and analytical data

[Ph_2P-Naphth-$BNPh_2$][$GaBr_4$] 2



Diphenylamine (20.5 mg, 0.121 mmol, 1 eq.) was added to a solution of **1** (100.9 mg, 0.121 mmol) in CD_2Cl_2 (0.5 mL) and the solution was heated for 23 h at 40 °C. The mixture of the expected compound and of C_9H_{12} was fully characterized by NMR. Then, the product was precipitated as a white powder by addition of pentane and the mother liquor was removed via canula. The expected compound was obtained as colorless crystals from a saturated dichloromethane / pentane solution at -20 °C in 52 % yield. Single crystals suitable for X-Ray analysis were obtained from a saturated dichloromethane solution at room temperature. Anal. Calcd. For $C_{34}H_{26}BNPGaBr_4$; C, 46.42; H, 2.98; N, 1.59. Found: C, 46.15; H, 2.81; N, 1.60; m.p.: 239 – 244 °C.

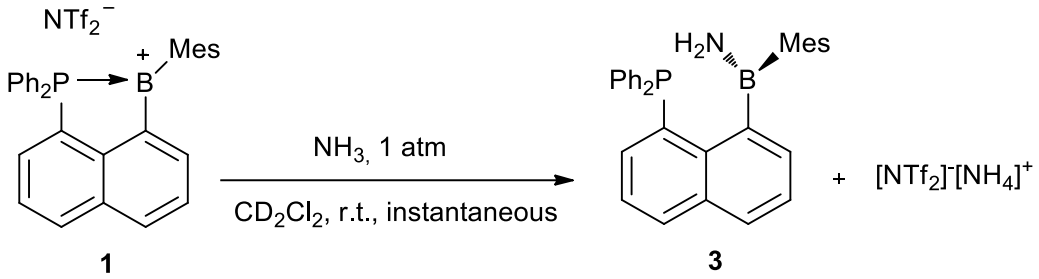
^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C, δ): 7.09 (m, 3H, $2H_{Ph}$ and $1H_{Naphth}$), 7.17 (m, 2H, H_{Ph}), 2.30- 7.40 (m, 5H, H_{Ph}), 7.48 (m, 2H, H_{Ph}), 7.54-7.64 (m, 8H, $7H_{Ph}$ and $1H_{Naphth}$), 7.78 (m, 2H, H_{Ph}), 7.86 (ddd, 1H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 7.1 Hz, J_{HP} = 3.2 Hz, H_{Naphth}), 7.98 (ddd, 1H, $^3J_{HP}$ = 10.5 Hz, $^3J_{HH}$ = 7.1.Hz, $^5J_{HH}$ = 1.1 Hz, H_{Naphth}), 8.24 (ddd, 1H, $^3J_{HH}$ = 8.3.Hz, $^5J_{HH}$ = 1.0 Hz, J_{HP} = 1.2 Hz, H_{Naphth}), 8.34 (ddd, 1H, $^3J_{HH}$ = 8.2.Hz, $^5J_{HH}$ = 1.1 Hz, J_{HP} = 1.3 Hz, H_{Naphth}).

^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 20 °C, δ): 118.7 (d, 2C, $^1J_{CP}$ = 72.5 Hz, P-C_{Ph}), 122.4 (d, $^1J_{CP}$ = 77.5 Hz, P-C_{Naphth}), 126.8 (s, 2C, CH_{NPh2}), 126.9 (s, 2C, CH_{NPh2}), 128.4 (d, J_{CP} = 11.1 Hz, CH_{Naphth}), 128.8 (d, J_{CP} = 2.4 Hz, CH_{Naphth}), 129.2 (s, CH_{NPh2}), 129.4 (s, CH_{NPh2}), 130.4 (s, 2C, CH_{NPh2}), 130.8 (d, 4C, J_{CP} = 12.7 Hz, CH_{PPh2}), 130.9 (s, 2C, CH_{NPh2}), 132.3 (d, J_{CP} = 4.2 Hz, CH_{Naphth}), 132.9 (d, J_{CP} = 9.1 Hz, $C_{quat.\ Naphth}$), 133.5 (d, 4C, J_{CP} = 11.2 Hz, CH_{PPh2}), 133.7 (d, J_{CP} = 1.5 Hz, CH_{Naphth}), 134.3 (d, J_{CP} = 2.7 Hz, CH_{Naphth}), 135.0 (d, 2C, J_{CP} = 3.2 Hz, CH_{PPh2}), 135.4 (d, J_{CP} = 10.4 Hz, CH_{Naphth}), 145.6 (d, J_{CP} = 10.5 Hz, N-C), 145.6 (d, J_{CP} = 10.5 Hz, N-C), 146.9 (d, J_{CP} = 5.1 Hz, N-C), 148.2 (d, J_{CP} = 21.3 Hz, $C_{quat.\ Naphth}$) the quaternary carbon in alpha position of boron is not observed.

^{11}B {^{1}H} NMR (96 MHz, CD_2Cl_2, 20 °C, δ) = 42.2.

^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2, 20 °C, δ): -9.0.

Ph_2P-Naphth-B(Mes)(NH_2) 3



An NMR tube containing a solution of **1 (X = NTf_2)** (124.6 mg, 0.173 mmol) in dichloromethane (0.5 mL) was layered with ammonia (1 atm) at room temperature leading to a colorless solution. After a few minutes at room temperature, colorless crystals appeared. The X-Ray analysis of the crystals revealed the formation of the ammonia N-H bond activation product **3**. The ^{31}P NMR of the mother liquor revealed the formation of **3** as the only phosphorus-containing product. The ^{1}H NMR analysis of the mother liquor showed the presence of $[NH_4][NTf_2]$ and ammonia in mixture with **3** (in situ complete NMR characterization of **3** was performed at this stage). Removing the ammonia pressure leads to the quantitative formation of **[Ph_2P-Naphth-B(Mes)(NH_3)][NTf_2] 4**.

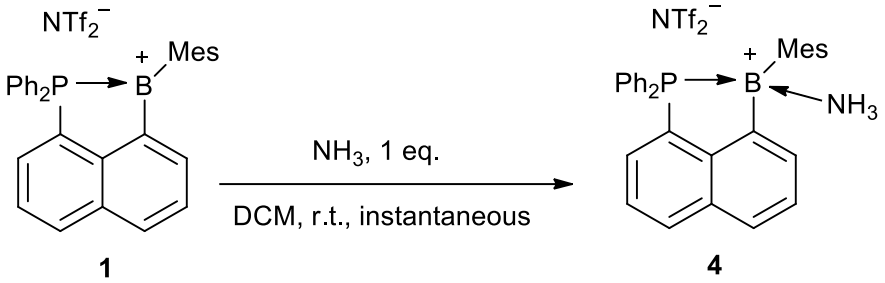
^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C, δ): 2.09 (s, 6H, $CH_{3o\text{-}Mes}$), 2.17 (s, 3H, $CH_{3p\text{-}Mes}$), 6.63 (s, 2H, CH_{Mes}), 6.96 (dd, 4H, J_{HP} = 6.9 Hz, $^{4}J_{HH}$ = 6.7 Hz, $H_{o\text{-}Ph}$), 7.13 – 7.25 (m, 6H, $H_{m\text{-}Ph}$ and $H_{p\text{-}Ph}$), 7.33 (m, 1H, H_{Naphth}), 7.37 (m, 1H, H_{Naphth}), 7.45 (m, 1H, H_{Naphth}), 7.70 (d, 1H, $^{3}J_{HH}$ = 6.7 Hz, H_{Naphth}), 7.83 (d, 1H, $^{3}J_{HH}$ = 8.01 Hz, H_{Naphth}), 7.89 (d, 1H, $^{3}J_{HH}$ = 7.8 Hz, H_{Naphth}). Due to fast exchange, amido protons couldn't be observed.

^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2, 20 °C, δ): 21.0 (s, $CH_{3p\text{-}Mes}$), 24.3 (d, 2C, J_{CP} = 7.2 Hz, $CH_{3p\text{-}Mes}$), 125.5 (s br., CH_{Naphth}), 126.2 (s, CH_{Naphth}), 128.4 (s, 2C, $CH_{p\text{-}Ph}$), 128.5 (d, 4C, J_{CP} = 6.4 Hz, $CH_{m\text{-}Ph}$), 129.2 (s, 2C, CH_{Mes}), 129.3 (d, J_{CP} = 3.1 Hz, CH_{Naphth}), 131.0 (s br., CH_{Naphth}), 133.1 (d, 4C, J_{CP} = 17.5 Hz, $CH_{o\text{-}Ph}$), 133.8 (d, , J_{CP} = 3.2 Hz, CH_{Naphth}), 134.3 (d, J_{CP} = 7.0 Hz, $C_{quat.Naphth}$), 135.6 (d, J_{CP} = 7.7 Hz, $C_{quat.Naphth}$), 135.7 (d, J_{CP} = 2.8 Hz, CH_{Naphth}), 137.7 (d, J_{CP} = 1.6 Hz, $C_{p\text{-}Mes}$), 138.1 (d, 2C, $^{1}J_{CP}$ = 11.2 Hz, P-C_{Ph}), 141.0 (d, $^{1}J_{CP}$ = 32.6 Hz, P-C_{Naphth}), 142.4 (d, 2C, J_{CP} = 2.9 Hz, $C_{o\text{-}Mes}$), 146.4 (br., B-C_{Naphth}). The quaternary carbon connected to boron in ipso position of the mesityl group was not observed).

^{11}B {^{1}H} NMR (96 MHz, CD_2Cl_2, 20 °C, δ) = 40.4.

^{31}P {^{1}H} NMR (203 MHz, CD_2Cl_2, 20 °C, δ): -12.6.

[Ph_2P-Naphth-B(Mes)(NH_3)][NTf_2] 4



1 **4**

Protocol A

A solution of **1** (27.7 mg, $3.84.10^{-2}$ mmol) in dichloromethane (0.4 mL) was treated with a solution of ammonia in dichloromethane ($4.25.10^{-2}$ mmol, 0.25 mL, 0.17 M, 1.1 eq.) at room temperature. After 5 minutes at room temperature, the slight excess of ammonia was removed by a few vacuum / argon cycles. The ammonia adduct **4** was the only product that could be detected by multinuclear NMR.

Protocol B

A solution of **1** (124.6 mg, 0.173 mmol) in dichloromethane (0.5 mL) was treated with 1 atmosphere of ammonia at room temperature leading to the crystallization of **3** after a few minutes. After solubilization of the crystals by addition of DCM, the reaction mixture was filtered under an argon atmosphere (leading to the immediate transformation of **3** to **4**) and layered with pentane at room temperature giving the ammonia-adduct **4** as colorless crystals in 48% yield. Single crystals suitable for X-Ray diffraction analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **4** at room temperature. m.p.; 139 – 145 °C.

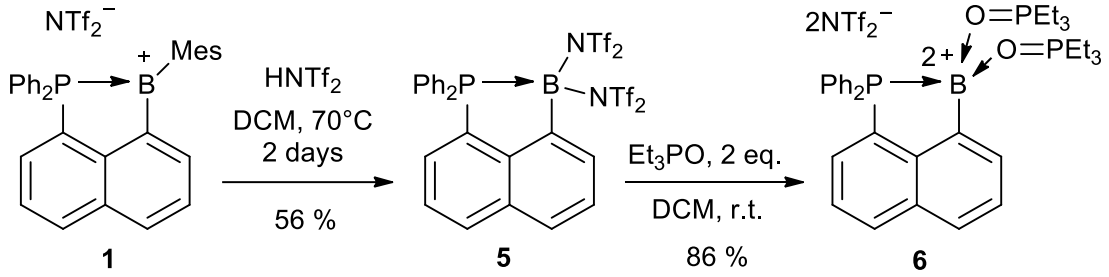
^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C, δ): 1.13 (s, 3H, CH_{3Mes}), 2.24 (d, 3H, J_{HP} = 1.9 Hz, CH_{3Mes}), 2.41 (s, 3H, CH_{3Mes}), 4.93 (s br., 3H, H_{NH3}), 6.63 (s, 1H, CH_{Mes}), 6.89 (s, 1H, CH_{Mes}), 7.21 (m, 2H, H_{Ph}), 7.30 (m, 2H, H_{Ph}), 7.35 (m, 2H, H_{Ph}), 7.53 (m, 1H, H_{Ph}), 7.58 (m, 2H, H_{Ph}), 7.67 (m, 1H, H_{Ph}), 7.71 – 7.77 (m, 2H, H_{Naphth}), 7.77 – 7.85 (m, 2H, H_{Naphth}), 8.03 (ddd, 1H, $^{3}J_{HH}$ = 7.5.Hz, $^{4}J_{HH}$ = 1.8 Hz, J_{HP} = 1.5 Hz, H_{Naphth}), 8.29 (ddd, 1H, $^{3}J_{HH}$ = 7.8.Hz, $^{4}J_{HH}$ = 1.4 Hz, J_{HP} = 1.7 Hz, H_{Naphth}).

^{13}C {^{1}H} NMR (126 MHz, CD_2Cl_2, 20 °C, δ): 20.9 (s br., CH_{3Mes}), 25.7 (s, CH_{3Mes}), 25.8 (s, CH_{3Mes}), 120.0 (d, 2C, $^{1}J_{CF}$ = 321.8 Hz, CF_3), 121.8 (d, $^{1}J_{CP}$ = 63.1 Hz, P-C_{Ph}), 122.5 (d, $^{1}J_{CP}$ = 50.9 Hz, P-C_{Ph}), 125.7 (d, $^{1}J_{CP}$ = 68.0 Hz, P-C_{Naphth}), 127.4 (d, J_{CP} = 1.7 Hz, $CH_{arom.}$), 127.6 (d, J_{CP} = 9.4 Hz, $CH_{arom.}$), 129.5 (d, J_{CP} = 2.0 Hz, $CH_{arom.}$), 129.6 (d, 2C, J_{CP} = 11.1 Hz, CH_{Ph}), 130.8 (d, J_{CP} = 2.3 Hz, CH_{Mes}), 131.1 (d, 2C, J_{CP} = 10.9 Hz, CH_{Ph}), 131.2 (s br., CH_{Mes}), 131.6 (d, J_{CP} = 13.8 Hz, $CH_{arom.}$), 131.9 (d, J_{CP} = 1.5 Hz, $CH_{arom.}$), 132.7 (d, 2C, J_{CP} = 10.0 Hz, CH_{Ph}), 133.2 (d, J_{CP} = 2.9 Hz, $CH_{arom.}$), 133.3 (d, J_{CP} = 10.3 Hz, $C_{quat.Naphth}$), 133.5 (d, 2C, J_{CP} = 8.5 Hz, CH_{Ph}), 133.6 (d, J_{CP} = 3.0 Hz, $CH_{arom.}$), 133.6 (d, J_{CP} = 2.6 Hz, $CH_{arom.}$), 138.6 (d, J_{CP} = 3.0 Hz, $C_{quat.Mes}$), 141.2 (d, J_{CP} = 3.4 Hz, $C_{quat.Mes}$), 143.7 (d, J_{CP} = 29.5 Hz, $C_{quat.Naphth}$), 144.0 (d, J_{CP} = 5.9 Hz, $C_{quat.Mes}$), 147.7 (br., B-C_{Naphth}). one quaternary carbon in alpha position of boron is not observed.

^{11}B {^{1}H} NMR (96 MHz, CD_2Cl_2, 20 °C, δ) = -2.1.

^{31}P {^{1}H} NMR (203 MHz, CD_2Cl_2, 20 °C, δ): 3.9.

[Ph$_2$P-Naphth-B(OPEt$_3$)$_2$][(NTf$_2$)$_2$] 6



Preparation of **5**: Acid bis(trifluoromethanesulfonyl)imidic (51.2 mg, 0.182 mmol, 0.95 eq.) was added on a solution of **1 (X = NTf$_2$)** (138.5 mg, 0.192 mmol) in dichloromethane (1.5 mL) at room temperature and the resulting yellow solution was heated at 70 °C for 2 days. Then the solution was concentrated and the colorless oil thus obtained was washed with pentane (3 times 1 mL). After removal of the volatiles under vaccum, the expected compound was obtained as a colorless oil with a yield of 56 %.

^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C, δ): 7.46 - 7.54 (m, 2H, $H_{arom.}$), 7.56 - 7.62 (m, 2H, $H_{arom.}$), 7.62 - 7.68 (m, 2H, $H_{arom.}$), 7.68 - 7.79 (m, 3H, $H_{arom.}$), 7.79 - 7.86 (m, 1H, $H_{arom.}$), 7.86 - 7.93 (m, 2H, $H_{arom.}$), 7.94 - 7.99 (m, 1H, $H_{arom.}$), 8.17 - 8.25 (m, 2H, $H_{arom.}$), 8.34 (m, 1H, $H_{arom.}$).

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 20 °C, δ): -3.3.

^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 20 °C, δ): = 9.3.

Preparation of **6**: Triethylphosphine oxide (36.3 mg, 0.271 mmol, 2.5 eq.) was added to a solution of **5** (95.6 mg, 0.108 mmol) in dichloromethane (2 mL) at room temperature under stirring. The product was precipitated as a colorless oil from the reaction mixture by adding pentane and the mother liquor was removed via syringe. The oil was dried under vacuum giving the expected compound in 86 % yield. HRMS (ESI): exact mass (monoisotopic) calcd for $[C_{34}H_{46}BO_2P_3]^{2+}$, $[M^{2+}/2]$, 294.6420; found, 294.6424.

^{1}H NMR (500 MHz, C_2DCl_2, 20 °C, δ): 0.87 (dt, 18H, $^3J_{HP}$ = 19.5 Hz, $^3J_{HH}$ = 7.7 Hz, CH_3), 1.79 (m, 12H, CH_2), 7.63 – 7.71 (m, 8H, H_{Ph}), 7.73 - 7.79 (m, 2H, H_{Ph}), 7.90 – 8.00 (m, 3H, H_{Naphth}), 8.17 – 8.27 (m, 2H, H_{Naphth}), 8.42 (d br., 1H, $^3J_{HH}$ = 8.4 Hz, H_{Naphth}).

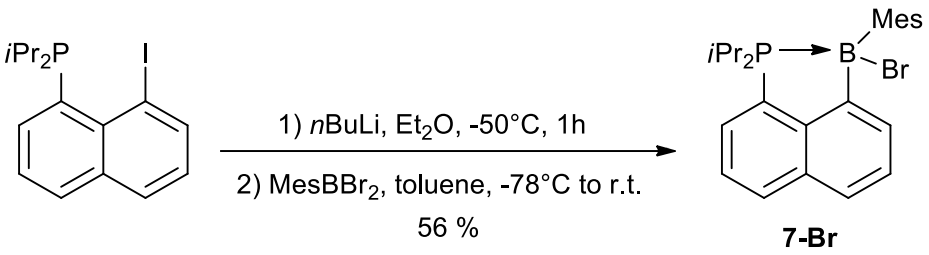
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 20 °C, δ): 15.3 (d, 6C, $^2J_{CP}$ = 4.8 Hz CH_3), 17.8 (d, 6C, $^1J_{CP}$ = 62.2 Hz CH_2), 120.4 (q, 4C, $^1J_{CF}$ = 321.9 Hz, CF_3), 120.9 (d, 2C, $^1J_{CP}$ = 69.2 Hz, P-C_{Ph}), 121.0 (d, $^1J_{CP}$ = 59.1 Hz, P-C_{Naphth}), 128.6 (d, J_{CP} = 9.3 Hz, CH_{Naphth}), 129.4 (d, J_{CP} = 3.0 Hz, CH_{Naphth}), 130.6 (d, J_{CP} = 1.6 Hz, CH_{Naphth}), 130.8 (d, J_{CP} = 11.8 Hz, CH_{Naphth}), 130.9 (d, 4C, J_{CP} = 11.2 Hz, CH_{Ph}), 133.3 (d, 4C, J_{CP} = 9.5 Hz, CH_{Ph}), 133.4 (d, J_{CP} = 8.7 Hz, $C_{quat.}$), 134.2 (s, J_{CP} = 11.5 Hz, CH_{Naphth}), 134.4 (d, 2C, $^4J_{CP}$ = 2.8 Hz, $CH_{p\text{-}Ph}$), 134.8 (d, J_{CP} = 2.6 Hz, CH_{Naphth}), 138.5 (br., B-C), 144.1 (d, J_{CP} = 24.3 Hz, $C_{quat.}$).

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 20 °C, δ): -8.7 (br., Ph_2P), 90.8 (d, $^3J_{PP}$ = 14.5 Hz, $OPEt_3$).

^{11}B{^{1}H} NMR (96 MHz, CD_2Cl_2, 20 °C, δ): = 8.6.

^{19}F{^{1}H} NMR (283 MHz, CD_2Cl_2, 20 °C, δ): -78.9.

Phosphino-bromoborane 7-Br



A *n*-BuLi solution (1.6 M in hexanes, 2.32 mL, 3.73 mmol) was added dropwise to a 1-iodo-8-diisopropylphosphinonaphtalene solution (1.38 g, 3.73 mmol) in diethylether (10 mL) at -50 °C. After stirring 1 h at this temperature, the solution was filtered off and the resulting yellow solid was dissolved in 10 mL of toluene. The solution was then cooled down to -78 °C and dibromomesitylborane (1.13 g, 3.91 mmol) in solution in toluene (10 mL) was added dropwise at the same temperature. The reaction mixture was allowed to warm to room temperature overnight. The resulting mixture was then filtered over celite and the volatiles were removed under vacuum. The residue was dissolved in dichloromethane and colorless crystals of the expected compound were obtained at -20 °C in 56% yield. HRMS (CI, CH_4): exact mass (monoisotopic) calcd for $[C_{25}H_{32}BPBr]^+$, $[M-H]^+$, 451.1362; found, 451.1355; m.p.: 184.5 – 197.6 °C.

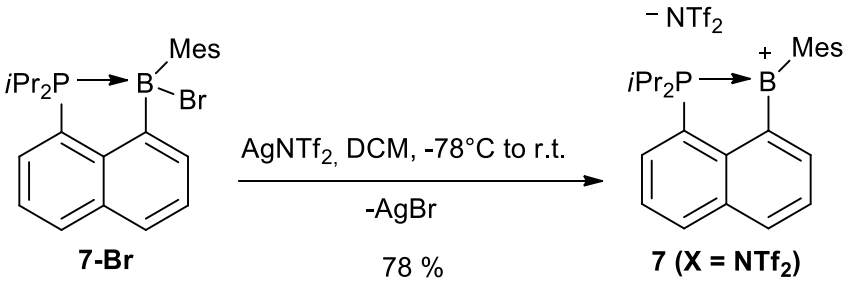
^{1}H NMR (500 MHz, $CDCl_3$, 20 °C, δ): 0.82 (dd, 3H, $^3J_{HP}$ = 16.2 Hz, $^3J_{HH}$ = 7.0 Hz, CH_{3iPr}), 1.14 (dd, 3H, $^3J_{HP}$ = 13.7 Hz, $^3J_{HH}$ = 7.2 Hz, CH_{3iPr}), 1.20 (dd, 3H, $^3J_{HP}$ = 14.4 Hz, $^3J_{HH}$ = 7.0 Hz, CH_{3iPr}), 1.23 (s, 3H, $CH_{3p\text{-}Mes}$), 1.45 (dd, 3H, $^3J_{HP}$ = 15.8 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{3iPr}), 2.21 (s, 3H, $CH_{3o\text{-}Mes}$), 2.53 (m, 1H, CH_{iPr}), 2.80 (m, 1H, CH_{iPr}), 2.83 (s, 3H, $CH_{3o\text{-}Mes}$), 6.52 (s, 1H, $H_{m\text{-}Mes}$), 6.91 (s, 1H, $H_{m\text{-}Mes}$), 7.54 (m, 1H, H_{Naphth}), 7.62 (m, 1H, H_{Naphth}), 7.66 (dd, 1H, J_{PH} = 7.8 Hz, $^3J_{HH}$ = 6.7 Hz, H_{Naphth}), 7.75 (d, 1H, $^3J_{HH}$ = 8.1 Hz, H_{Naphth}), 8.03 (d, 1H, $^3J_{HH}$ = 8.1 Hz, H_{Naphth}), 8.06 (d, 1H, $^3J_{HH}$ = 7.9 Hz, H_{Naphth}).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 20 °C, δ): 17.7 (d, $^2J_{CP}$ = 2.6 Hz, CH_{3iPr}), 17.7 (s, CH_{3iPr}), 18.2 (d, $^2J_{CP}$ = 4.2 Hz, CH_{3iPr}), 18.4 (s, CH_{3iPr}), 20.8 (s, $CH_{3o\text{-}Mes}$), 22.8 (d, $^1J_{CP}$ = 27.9 Hz, CH_{iPr}), 26.4 (d, $^1J_{CP}$ = 25.3 Hz, CH_{iPr}), 26.9 (s, $CH_{3p\text{-}Mes}$), 28.5 (s, $CH_{3o\text{-}Mes}$), 124.8 (d, J_{CP} = 1.2 Hz, CH_{Naphth}), 125.3 (d, J_{CP} = 7.8 Hz, CH_{Naphth}), 126.9 (d, $^1J_{CP}$ = 54.6 Hz, P-C_{Naphth}), 127.8 (s, CH_{Naphth}), 128.5 (d, J_{CP} = 2.0 Hz, CH_{Naphth}), 130.1 (s, $CH_{m\text{-}Mes}$), 130.2 (s, $CH_{m\text{-}Mes}$), 131.4 (d, J_{CP} = 2.3 Hz, CH_{Naphth}), 132.3 (d, J_{CP} = 8.7 Hz, $C_{quat.}$), 134.2 (d, J_{CP} = 13.2 Hz, CH_{Naphth}), 136.4 (d, J_{CP} = 2.8 Hz, $C_{quat.}$), 136.7 (br., $C_{quat.}$), 141.7 (d, J_{CP} = 8.0 Hz, $C_{quat.}$), 142.8 (d, J_{CP} = 24.8 Hz, $C_{quat.}$), 144.1 (s, $C_{quat.}$), 155.2 (br., $C_{quat.}$).

^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$, 20 °C, δ): -1.5.

^{31}P{^{1}H} NMR (203 MHz, $CDCl_3$,20 °C, δ): 14.1.

[*i*Pr$_2$P-Naphth-BMes][NTf$_2$] 7 (X = NTf$_2$)



7-Br **7 (X = NTf$_2$)**

Dichloromethane (2mL) was added at -78 °C on a neat mixture of **7-Br** (78.8 mg, 0.17 mmol) and silver bis(trifluoromethanesulfonyl)imide (67.5 mg, 0.17 mmol, 1 eq.) giving a bright yellow solution and a white precipitate. The reaction mixture was then allowed to warm up to room temperature. The solution was then filtered and the silver salt was washed with dichloromethane (0.5 mL). The volatiles were removed under reduced pressure at room temperature giving **7 (X = NTf$_2$)** as a yellow oil with a yield of 78 %. HRMS (CI, CH_4): exact mass (monoisotopic) calcd for [$C_{25}H_{31}BP^+$], $[M]^+$, 372.2293; found, 372.2285, exact mass (monoisotopic) calcd for [$C_2NO_4S_2F_6^-$], 279.9173; found 279.9186.

^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C, δ): 1.17 (dd, 6H, $^3J_{HP}$ = 18.7 Hz, $^3J_{HH}$ = 7.0 Hz, CH_{3iPr}), 1.37 (dd, 6H, $^3J_{HP}$ = 17.8 Hz, $^3J_{HH}$ = 7.0 Hz, CH_{3iPr}), 2.22 (s, 6H, $CH_{3o\text{-}Mes}$), 2.40 (s, 3H, $CH_{3p\text{-}Mes}$), 3.13 (dsept, 2H, $^3J_{HP}$ = 10.0 Hz, $^3J_{HH}$ = 7.0 Hz, CH_{iPr}), 7.06 (s, 2H, $H_{m\text{-}Mes}$), 7.95 (ddd, 1H, J_{HP} = 0.7 Hz, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.1 Hz, H_{Naphth}), 7.99 (ddd, 1H, J_{HP} = 3.2 Hz, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.1 Hz, H_{Naphth}), 8.23 (ddd, 1H, J_{HP} = 8.0 Hz, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 0.9 Hz, H_{Naphth}), 8.31 (dd, 1H, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.0 Hz, H_{Naphth}), 8.43 (ddd, 1H, J_{HP} = 1.0 Hz, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 0.9 Hz, H_{Naphth}), 8.57 (ddd, 1H, J_{HP} = 1.1 Hz, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.0 Hz, H_{Naphth}).

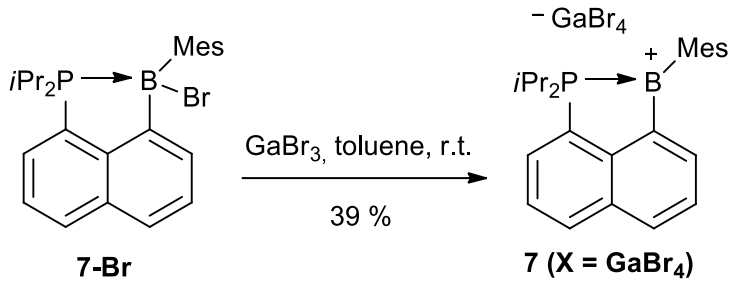
^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 20 °C, δ): 17.2 (s, 2C, CH_{3iPr}), 17.4 (d, 2C, J_{CP} = 3.1 Hz, CH_{3iPr}), 21.5 (s, $CH_{3p\text{-}Mes}$), 23.7 (d, 2C, J_{CP} = 31.3 Hz, CH_{iPr}), 24.6 (s, 2C, $CH_{3o\text{-}Mes}$), 119.1 (d, $^1J_{CP}$ = 66.0 Hz, P-C_{Naphth}), 120.3 (q, 2C, $^1J_{CF}$ = , CF_3), 128.7 (d, J_{CP} = 9.6 Hz, CH_{Naphth}), 129.2 (d, J_{CP} = 2.4 Hz, CH_{Naphth}), 129.7 (s, 2C, $CH_{m\text{-}Mes}$), 132.6 (d, J_{CP} = 2.9 Hz, CH_{Naphth}), 133.0 (d, J_{CP} = 8.6 Hz, $C_{quat.Naphth}$), 133.4 (br. s, B-C_{Mes}), 133.9 (d, J_{CP} = 2.6 Hz, CH_{Naphth}), 139.8 (s, CH_{Naphth}), 140.3 (d, 2C, J_{CP} = 3.5 Hz, $C_{o\text{-}Mes}$), 140.5 (d, J_{CP} = 11.6 Hz, CH_{Naphth}), 141.9 (br. s, B-C_{Naphth}), 143.8 (d, $^5J_{CP}$ = 1.6 Hz, $C_{p\text{-}Mes}$), 149.6 (d, J_{CP} = 19.4 Hz, $C_{quat.Naphth}$).

^{11}B{^{1}H} NMR (96 MHz, CD_2Cl_2, 20 °C, δ): 75.4.

^{31}P{^{1}H} (202 MHz, CD_2Cl_2, 20 °C, δ): 19.3.

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, 20 °C, δ): -78.8.

[*i*Pr$_2$P-Naphth-BMes][GaBr$_4$] 7 (X = GaBr$_4$)



7-Br **7 (X = GaBr$_4$)**

Toluene (1 mL) was added on a neat mixture of **7-Br** (20 mg, 4.4.10^{-2} mmol) and gallium tribromide (13.7 mg, 4.4.10^{-2} mmol, 1 eq.) at room temperature leading to the precipitation of a bright yellow oil. After 10 minutes of stirring at the same temperature, the mother liquor was removed via seringe and the oil was dried under vaccum giving the expected compound as a yellow solid with a yield of 39 %. Crystals suitable for X-Rays diffraction analysis were grown from a saturated solution in dichloromethane at -20 °C. HRMS (ESI): exact mass (monoisotopic) calcd for $[C_{25}H_{31}BP]^+$, $[M]^+$, 372.2293; found, 372.2290, exact mass (monoisotopic) calcd for $[GaBr_4]^-$, 384.5989; found 384.5981.

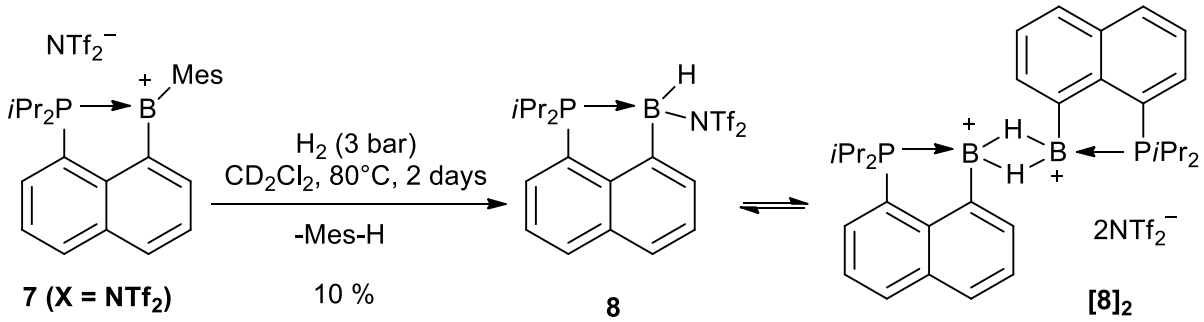
^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C, δ): 1.19 (dd, 6H, $^3J_{HP}$ = 18.6 Hz, $^3J_{HH}$ = 7.0 Hz, CH_{3iPr}), 1.40 (dd, 6H, $^3J_{HP}$ = 17.7 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{3iPr}), 2.23 (s, 6H, $CH_{3o\text{-}Mes}$), 2.40 (s, 3H, $CH_{3p\text{-}Mes}$), 3.13 (dsept, 2H, $^3J_{HP}$ = 9.3 Hz, $^3J_{HH}$ = 7.1 Hz, CH_{iPr}), 7.1 (s, 2H, $H_{m\text{-}Mes}$), 7.97 (m, 1H, H_{Naphth}), 8.00 (m, 1H, H_{Naphth}), 8.23 (dd, 1H, J_{HP} = 6.9 Hz, $^3J_{HH}$ = 7.1 Hz, H_{Naphth}), 8.32 (d, 1H, $^3J_{HH}$ = 6.9 Hz, H_{Naphth}), 8.45 (d, 1H, $^3J_{HH}$ = 8.3 Hz, H_{Naphth}), 8.58 (d, 1H, $^3J_{HH}$ = 8.2 Hz, H_{Naphth}).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 20 °C, δ): 17.4 (s, 2C, CH_{3iPr}), 17.7 (d, 2C, J_{CP} = 3.1 Hz, CH_{3iPr}), 21.6 (s, $CH_{3p\text{-}Mes}$), 23.9 (d, 2C, J_{CP} = 31.1 Hz, CH_{iPr}), 24.7 (s, 2C, $CH_{3o\text{-}Mes}$), 119.0 (d, $^1J_{CP}$ = 65.7 Hz, P-C_{Naphth}), 128.8 (d, J_{CP} = 9.6 Hz, CH_{Naphth}), 129.4 (d, J_{CP} = 2.5 Hz, CH_{Naphth}), 129.7 (s, 2C, $CH_{m\text{-}Mes}$), 132.6 (d, J_{CP} = 2.9 Hz, CH_{Naphth}), 133.0 (d, J_{CP} = 8.5 Hz, $C_{quat.}$), 133.3 (br. s, $C_{quat.}$), 134.0 (d, J_{CP} = 2.6 Hz, CH_{Naphth}), 139.9 (d, J_{CP} = 0.9 Hz, CH_{Naphth}), 140.3 (d, $^3J_{CP}$ = 3.3 Hz, $C_{o\text{-}Mes}$), 140.6 (d, J_{CP} = 11.6 Hz, CH_{Naphth}), 141.9 (br. s, $C_{quat.}$), 143.9 (d, $^5J_{CP}$ = 1.7 Hz, $C_{p\text{-}Mes}$), 149.6 (d, J_{CP} = 19.6 Hz, $C_{quat.}$).

^{11}B{^{1}H} NMR (96 MHz, CD_2Cl_2, 20 °C, δ): 77.9.

^{31}P{^{1}H} (202 MHz, CD_2Cl_2, 20 °C, δ): 19.2.

*i*Pr$_2$P-Naphth-B(H)(NTf$_2$) 8 and [8]$_2$



A NMR tube containing a solution of **7 (X = NTf$_2$)** (216 mg, 0.331 mmol) in CD_2Cl_2 (0.3 mL) was pressurized with H_2 (3 bars) and the solution was heated for 2 days at 80 °C leading to a colorless solution and a grey precipitate. ^{31}P NMR monitoring of the reaction showed the formation of a mixture of compound **8** and **[8]$_2$** (2.5 / 1). After filtration, the mixture of compounds was crystallized twice (to get rid of the mesitylene, the compound hydrolysing under prolonged vacuum) from a saturated solution of dichloromethane at room temperature (yield = 10 %).

8

^{1}H NMR (500 MHz, C_2DCl_2, 20 °C, δ): 0.85 (dd, $^3J_{HP}$ = 14.9 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, CH_{3iPr}), 1.24 (dd, $^3J_{HP}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, CH_{3iPr}), 1.59 (dd, $^3J_{HP}$ = 16.7 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, CH_{3iPr}), 1.67 (dd, $^3J_{HP}$ = 14.5 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, CH_{3iPr}), 2.55 (dsept, $^3J_{HP}$ = 12.2 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, CH_{iPr}), 3.04 (dsept, $^3J_{HP}$ = 10.6 Hz, $^3J_{HH}$ = 7.3 Hz, 1H, CH_{iPr}), 4.15 (br., 1H, B-H), 7.57 - 7.63 (m, 2H, H_{Naphth}), 7.74 (d br., 1H, $^3J_{HH}$ = 6.7 Hz, H_{Naphth}), 7.81 (d, 1H, $^3J_{HH}$ = 8.4 Hz, H_{Naphth}), 7.83 (m, 1H, H_{Naphth}), 8.06 (d br., 1H, J_{HH} = 8.2 Hz, H_{Naphth}).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 20 °C, δ): 17.6 (s, 2C, CH_{3iPr}), 18.7 (d, $^2J_{CP}$ = 3.6 Hz, CH_{3iPr}), 19.1 (s, CH_{3iPr}), 23.9 (d, $^1J_{CP}$ = 31.1 Hz,CH_{iPr}), 119.8 (q, 2C, $^1J_{CF}$ = 325.2 Hz, CF_3), 126.1 (d, J_{CP} = 8.9 Hz, CH_{Naphth}), 126.3 (s, CH_{Naphth}), 127.3 (d, $^1J_{CP}$ = 59.4 Hz, P-C_{Naphth}), 128.1 (s, CH_{Naphth}), 129.3 (s, CH_{Naphth}), 130.6 (d, J_{CP} = 14.5 Hz, CH_{Naphth}), 131.9 (s, CH_{Naphth}), 132.5 (d, J_{CP} = 9.2 Hz, $C_{quat.}$), 144.4 (d, J_{CP} = 23.1 Hz, $C_{quat.}$), the quaternary carbon in alpha position at boron is not observed.

^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 20 °C, δ): = -8.4.

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 20 °C, δ): 17.2.

^{19}F{^{1}H} NMR (283 MHz, CD_2Cl_2, 20 °C, δ): -78.2.

[8]$_2$

^{1}H NMR (500 MHz, C_2DCl_2, 20 °C, δ): 0.99 – 1.14 (m, 6H, CH_{3iPr}), 1.30 – 1.43 (m, 6H, CH_{3iPr}), 2.77 (m, 2H, CH_{iPr}), 4.57 (br., 1H, B-H), 7.63 – 7.68 (m, 2H, H_{Naphth}), 7.77 (m, 1H, H_{Naphth}), 7.87 (d, 1H, $^3J_{HH}$ = 8.2 Hz, H_{Naphth}), 8.12 (d, 1H, $^3J_{HH}$ = 8.1 Hz, H_{Naphth}), one naphthyl proton was not observed.

^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 20 °C, δ): = -1.2.

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 20 °C, δ): 20.6.

^{19}F{^{1}H} NMR (283 MHz, CD_2Cl_2, 20 °C, δ): -78.2.

NMR spectra

[Ph_2P-Naphth-$BNPh_2$][$GaBr_4$] 2

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of **2** (203 MHz, 20 °C) in CD_2Cl_2

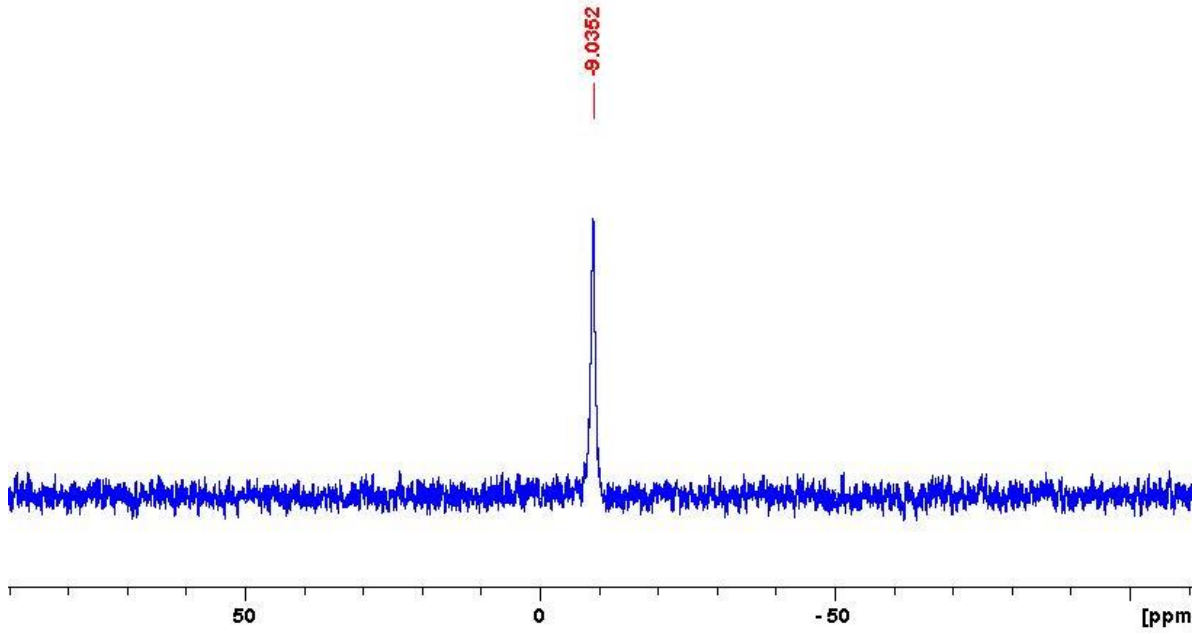


Figure 2. ^1H NMR spectrum of **2** (500 MHz, 20 °C) in CD_2Cl_2

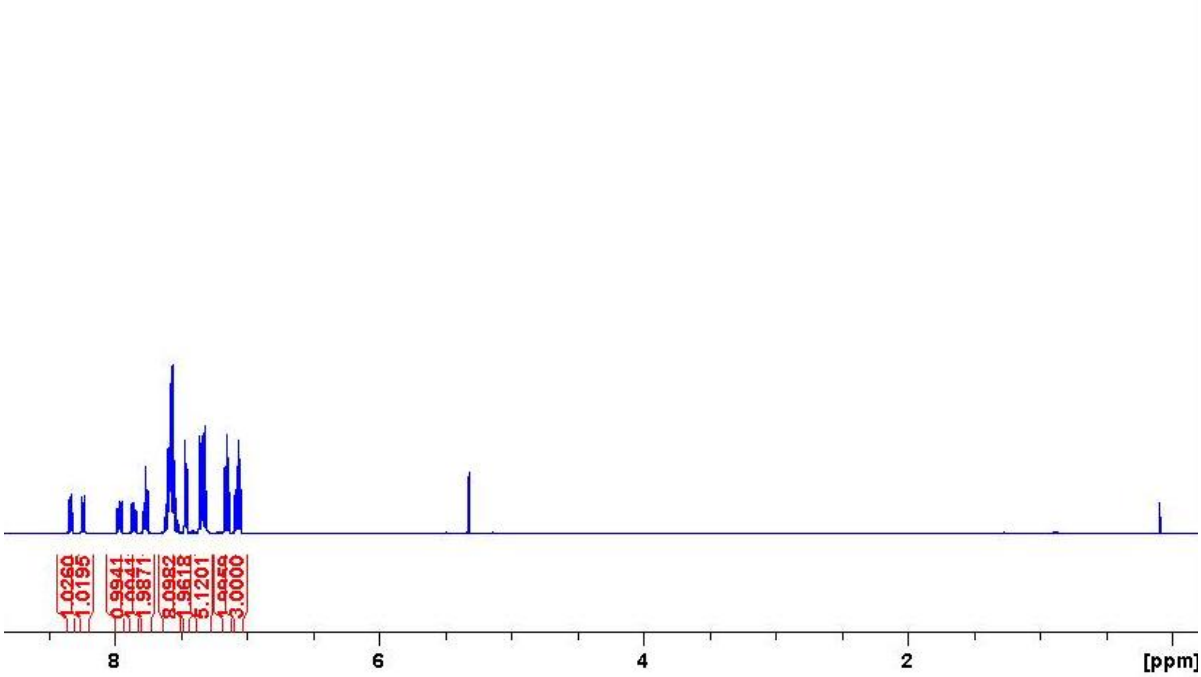


Figure 3. ^{1}H NMR spectrum of **2** (500 MHz, 20 °C) in CD_2Cl_2; aromatic region

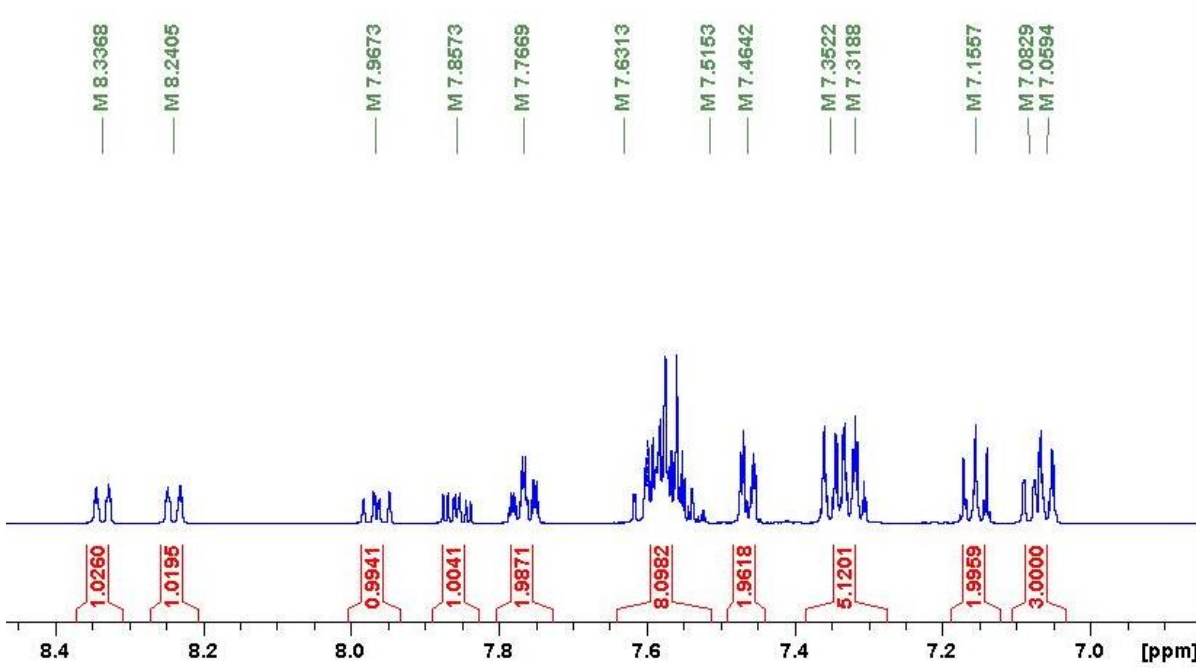


Figure 4. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (126 MHz, 20 °C) in CD_2Cl_2

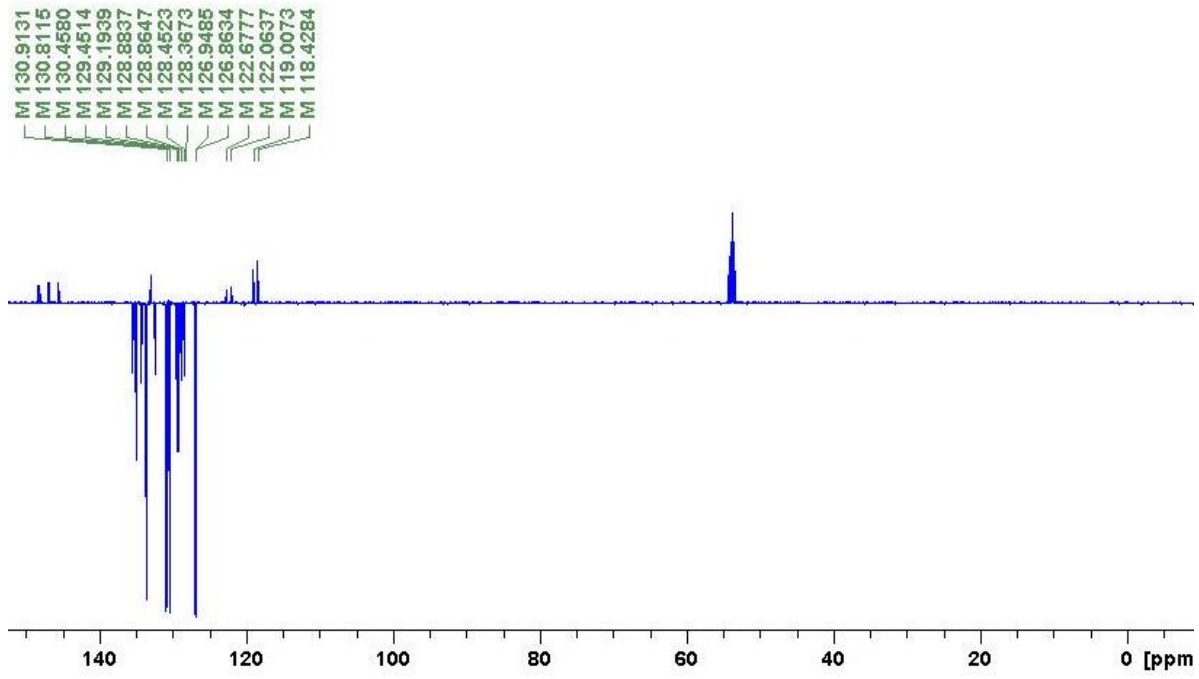


Figure 5. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 1

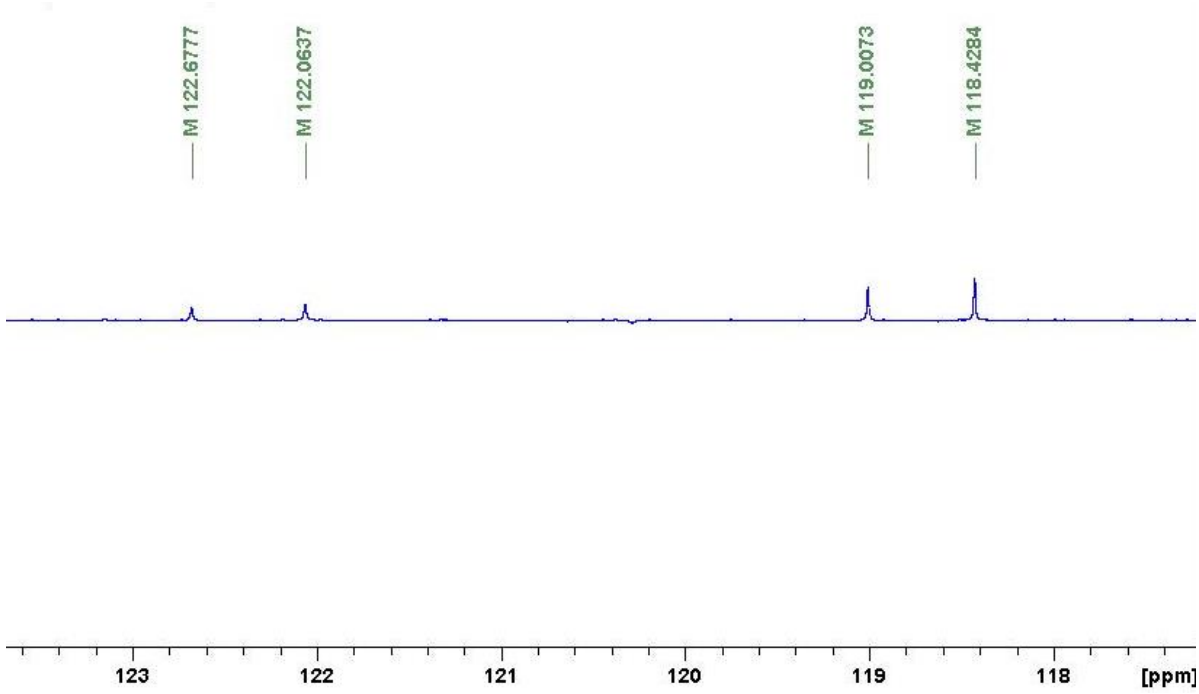


Figure 6. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 2

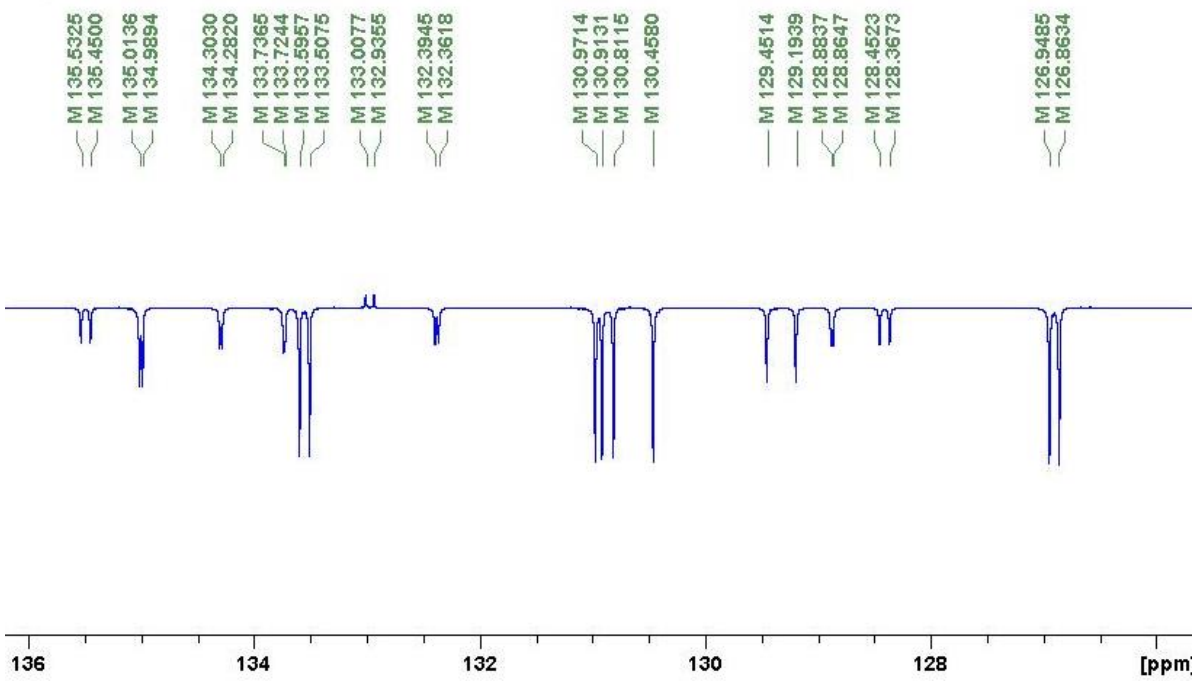


Figure 7. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 3

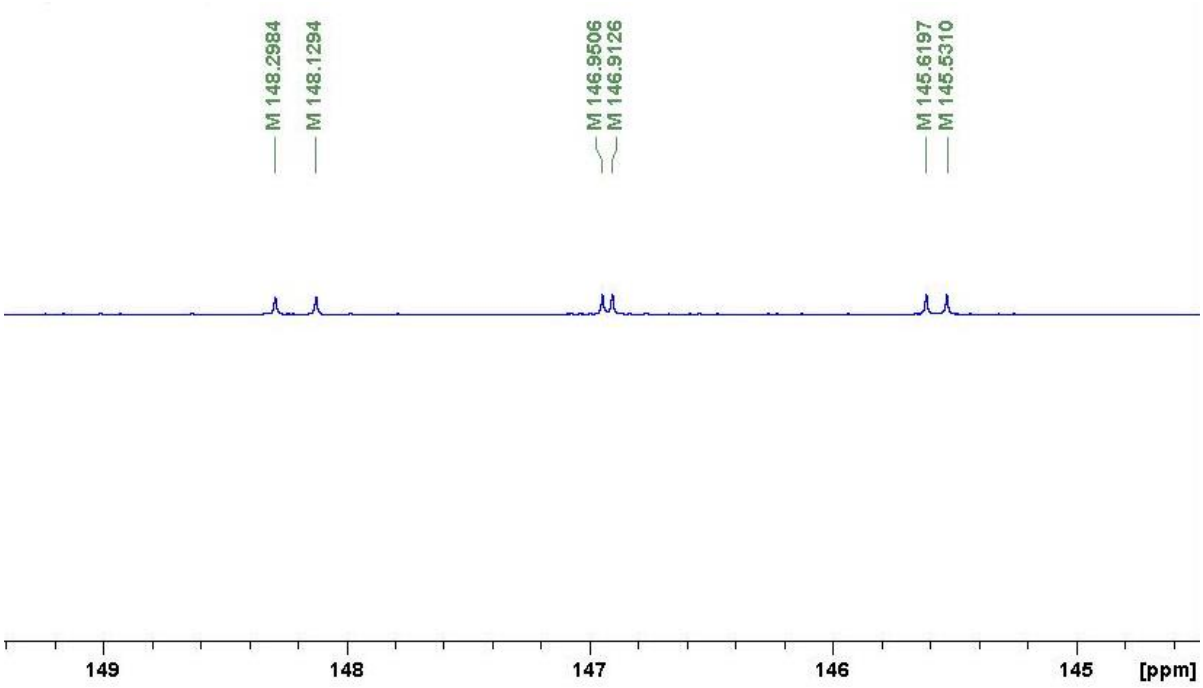
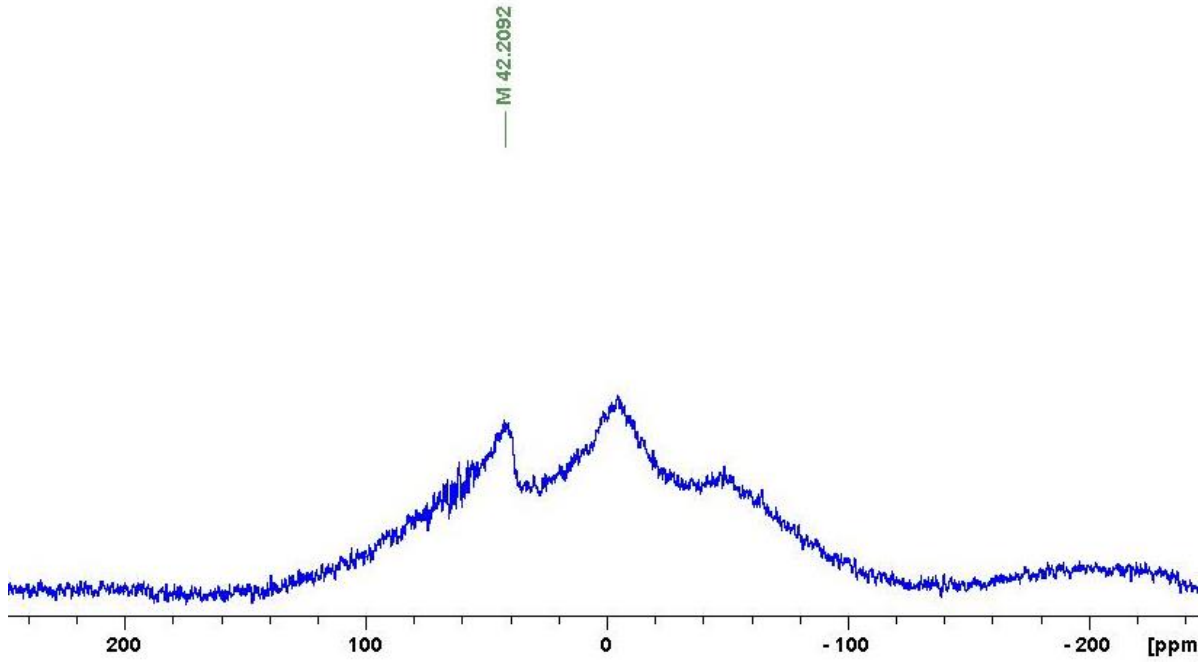


Figure 8. $^{11}B\{^{1}H\}$ NMR spectrum of **2** (96 MHz, 20 °C) in CD_2Cl_2



Ph_2P-Naphth-B(Mes)(NH_2) 3

Figure 9. $^{31}P\{^1H\}$ NMR spectrum of **3** (203 MHz, 20 °C) in CD_2Cl_2

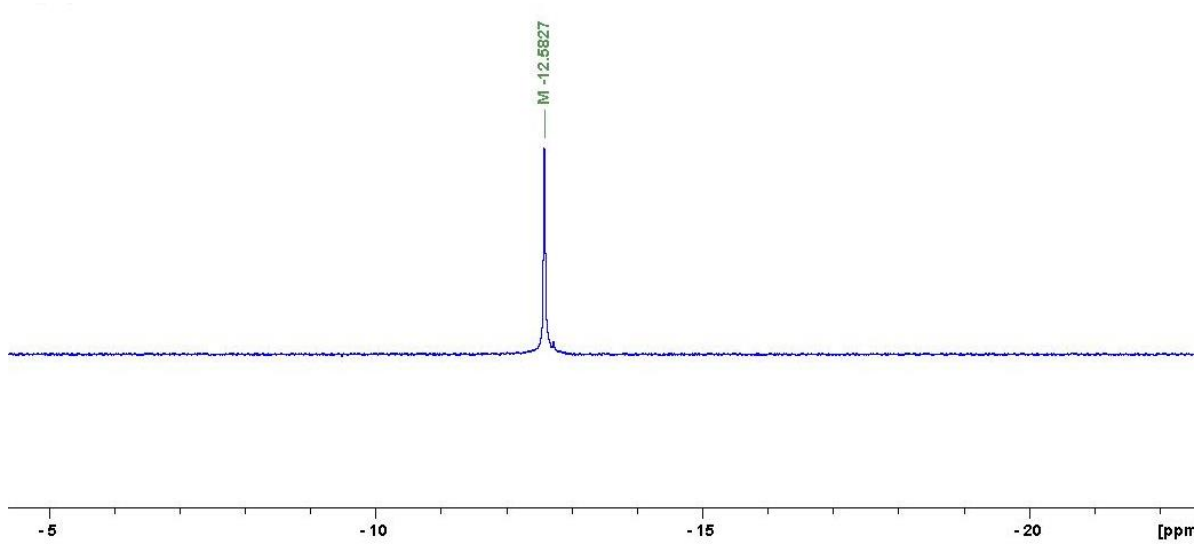


Figure 10. ^1H NMR spectrum of **3** (500 MHz, 20 °C) in CD_2Cl_2

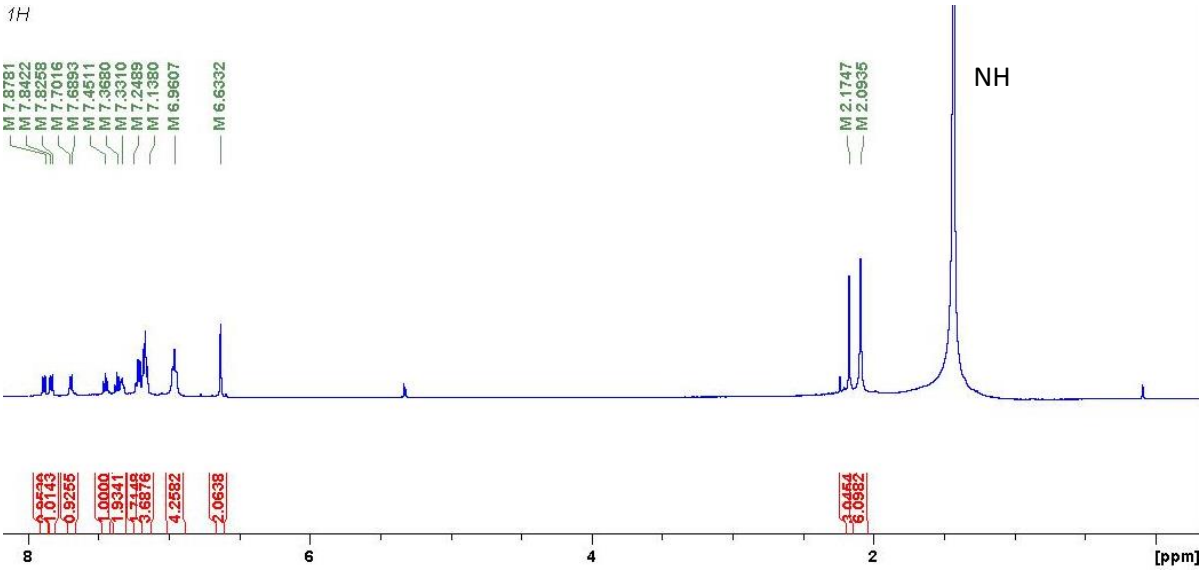


Figure 11. ^{1}H NMR spectrum of **3** (500 MHz, 20 °C) in CD_2Cl_2; aromatic region

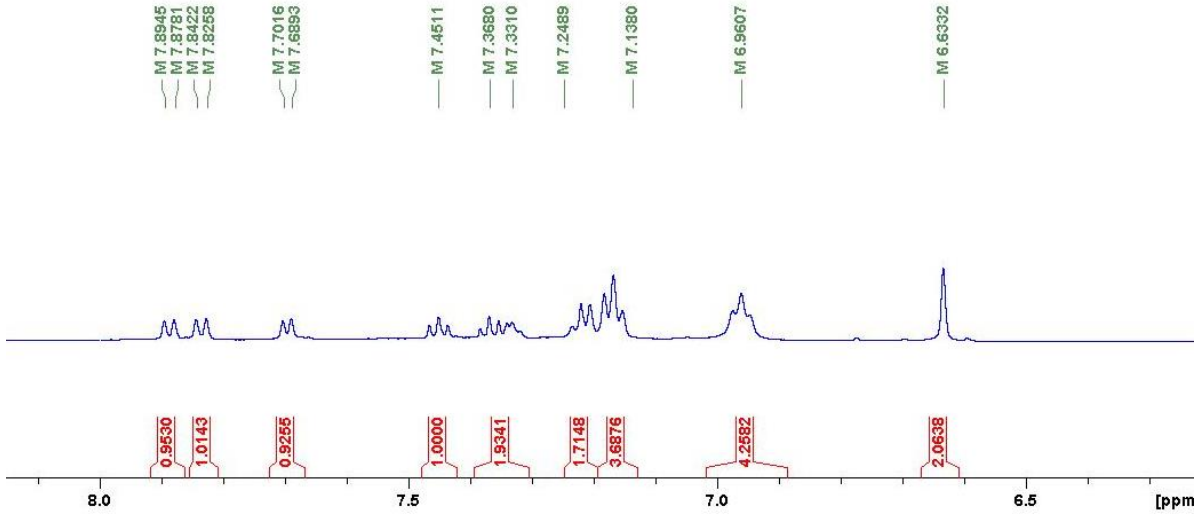


Figure 12. $^{11}B\{^{1}H\}$ NMR spectrum of **3** (96 MHz, 20 °C) in CD_2Cl_2

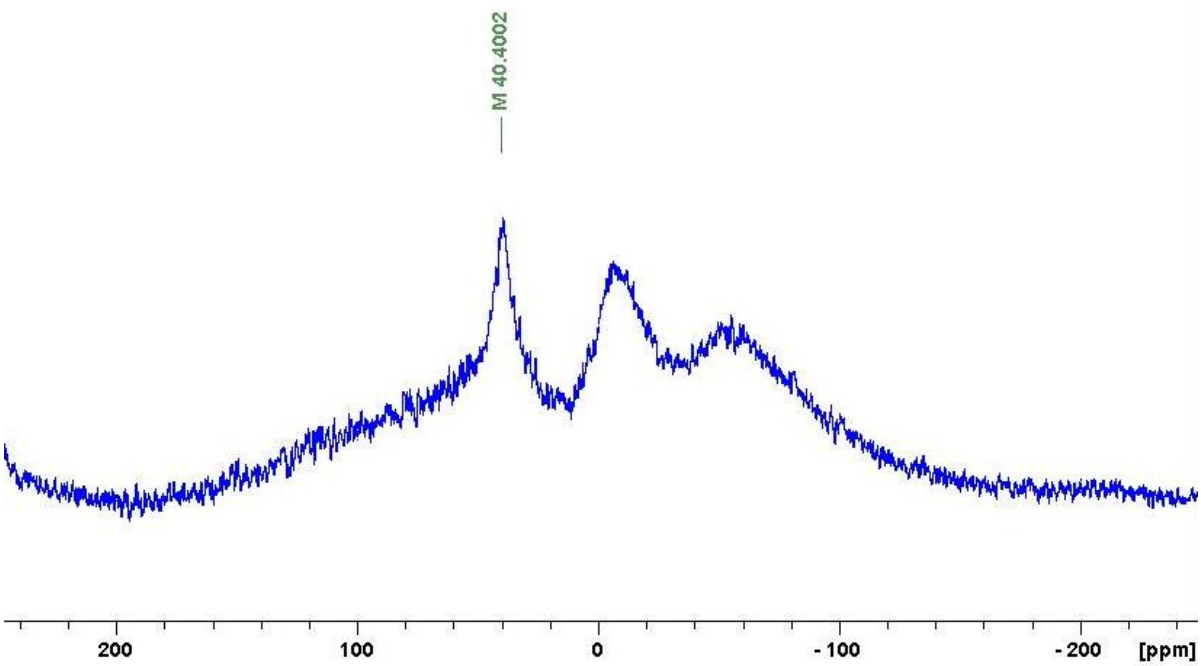


Figure 13. ^{13}C {^{1}H} NMR spectrum of **3** (126 MHz, 20 °C) in CD_2Cl_2

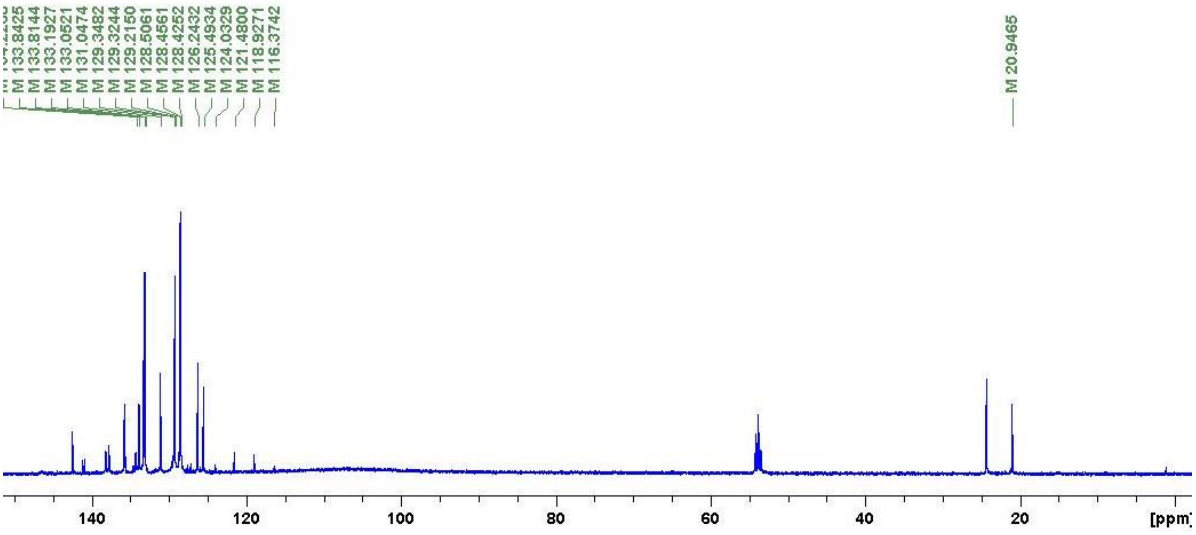


Figure 14. ^{13}C {^{1}H} NMR spectrum of **3** (126 MHz, 20 °C) in CD_2Cl_2: aliphatic region

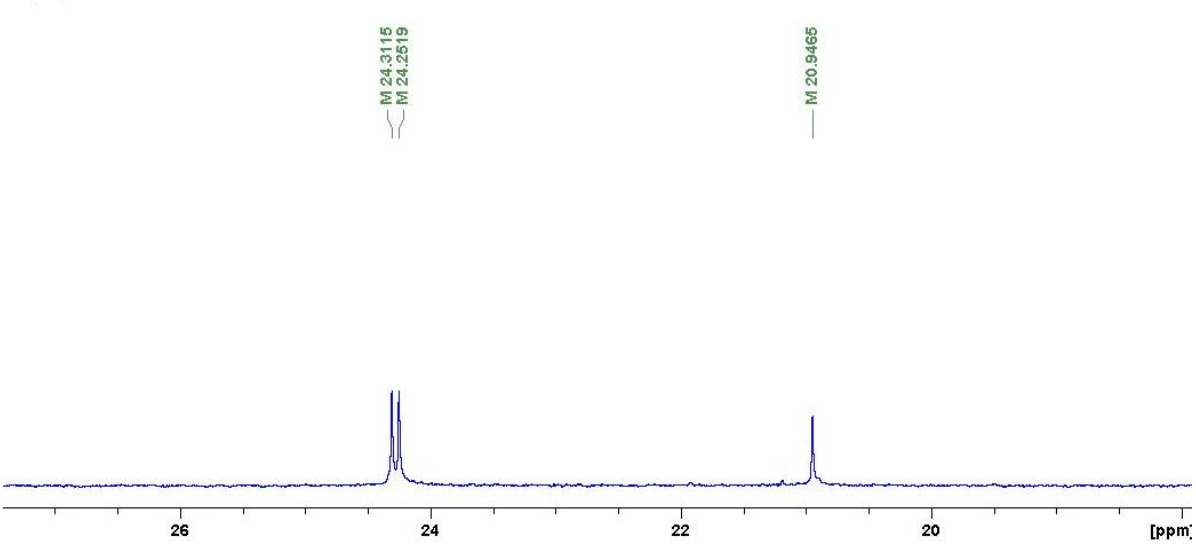


Figure 15. ^{13}C {^{1}H} NMR spectrum of **3** (126 MHz, 20 °C) in CD_2Cl_2: aromatic region 1

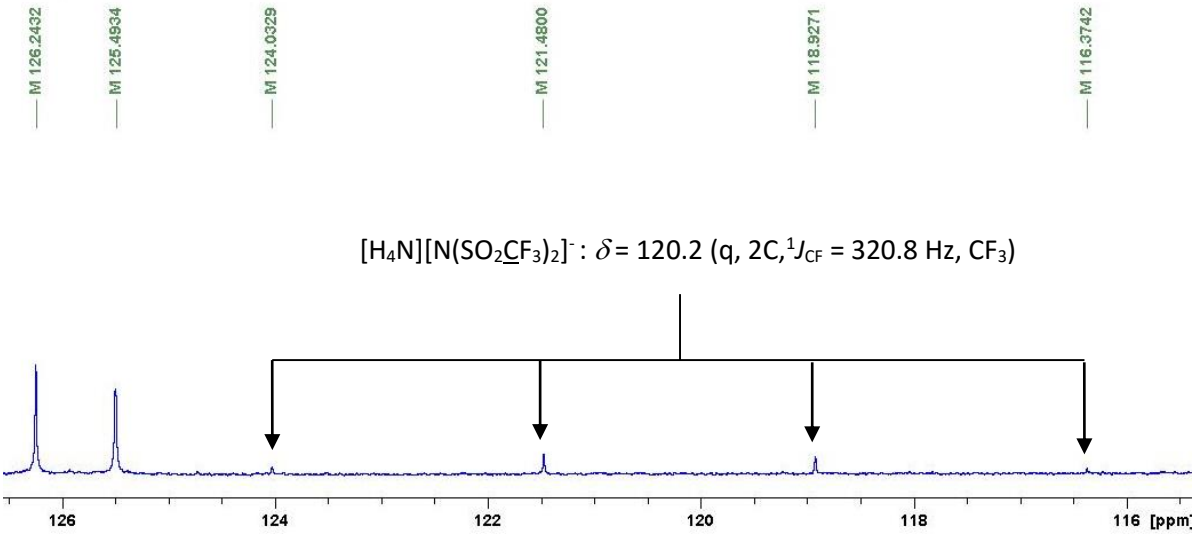


Figure 16. ^{13}C {^{1}H} NMR spectrum of **3** (126 MHz, 20 °C) in CD_2Cl_2: aromatic region 2

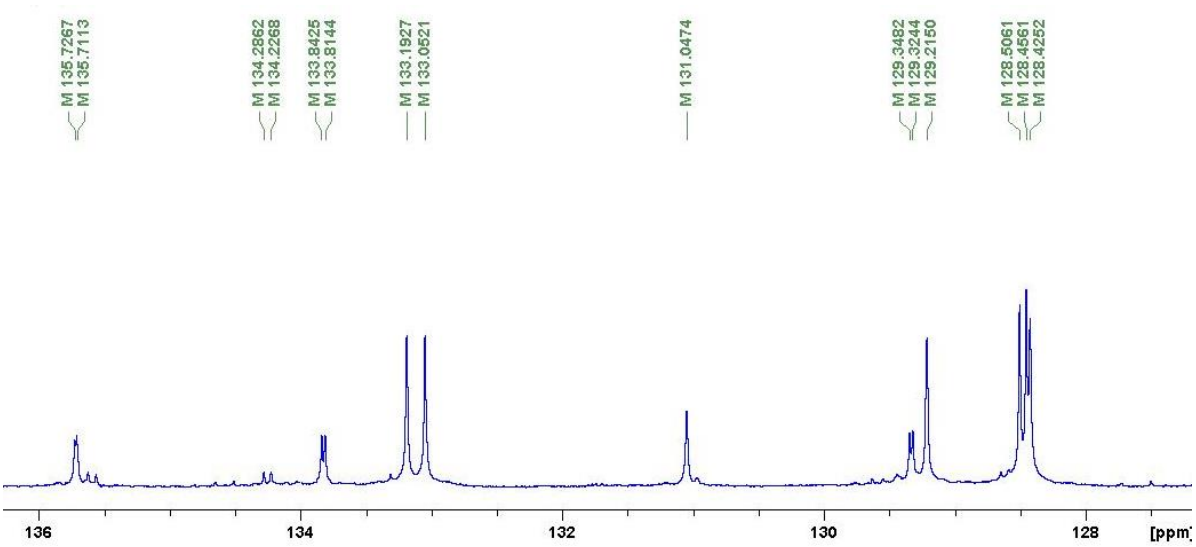
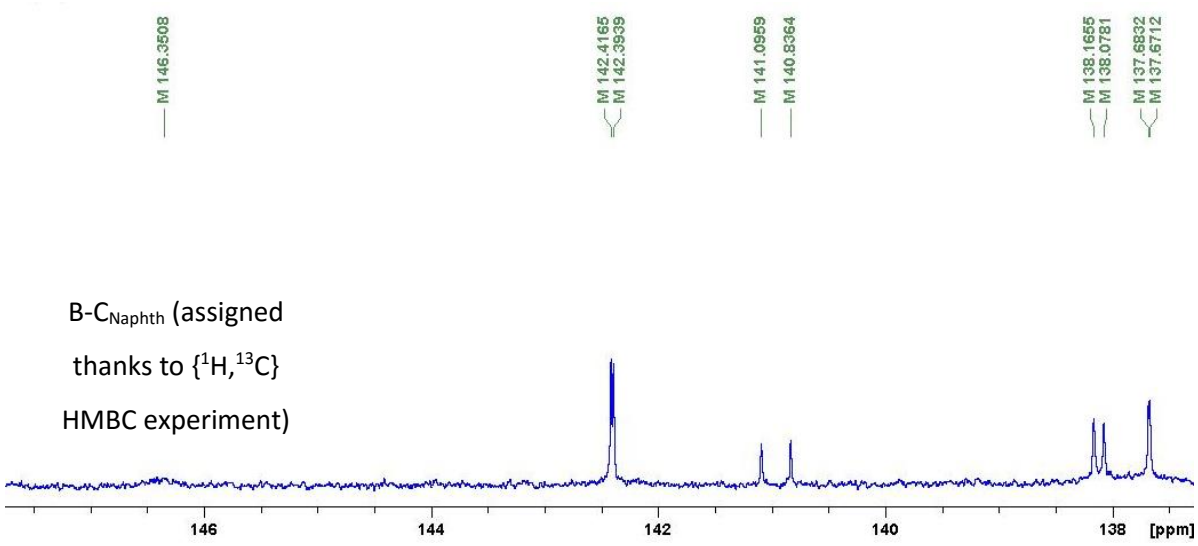


Figure 17. ^{13}C {^{1}H} NMR spectrum of **3** (126 MHz, 20 °C) in CD_2Cl_2: aromatic region 3



[Ph_2P-Naphth-B(Mes)(NH_3)][NTf_2] 4

Figure 18. $^{31}P\{^1H\}$ NMR spectrum of **4** (203 MHz, 20 °C) in CD_2Cl_2

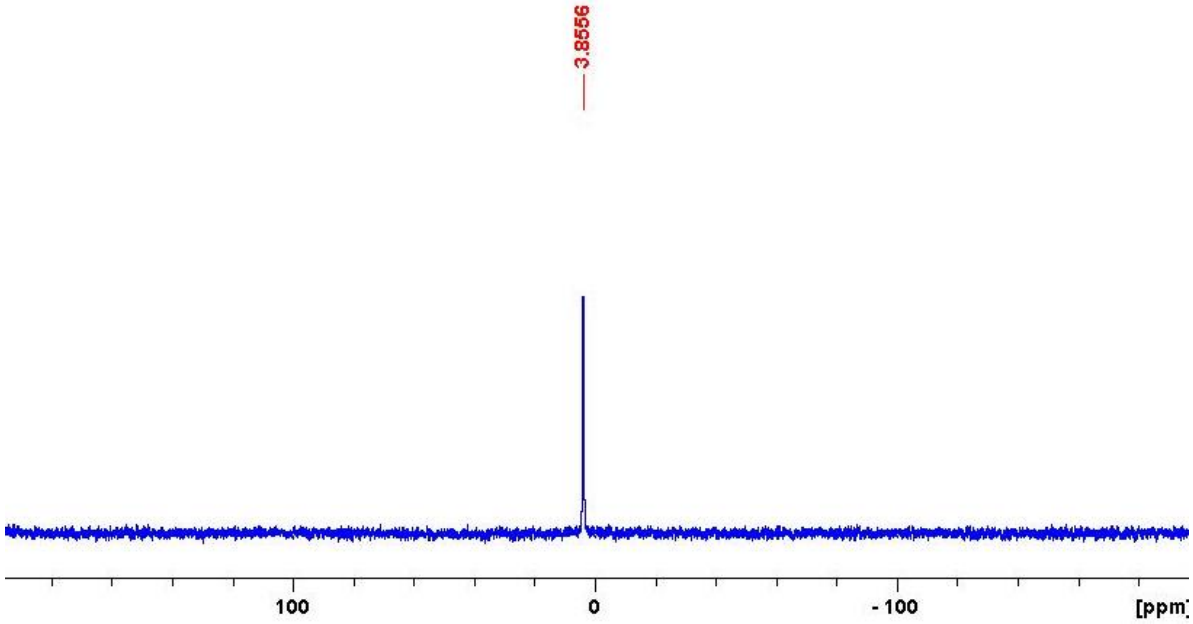


Figure 19. ^1H NMR spectrum of **4** (500 MHz, 20 °C) in CD_2Cl_2

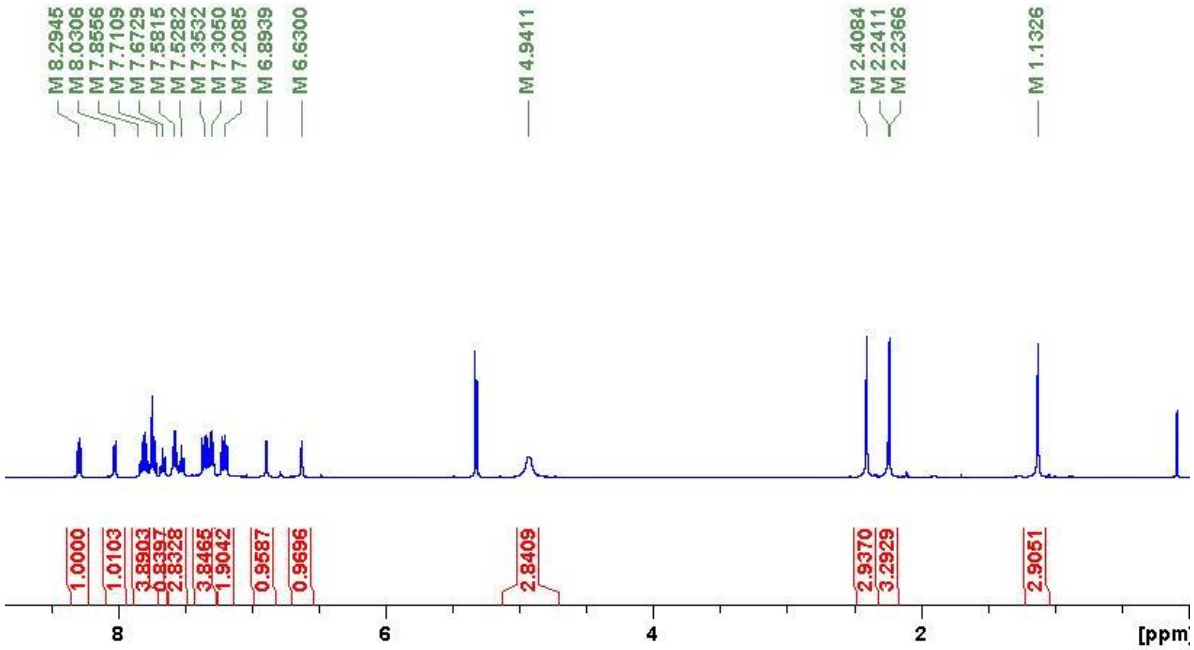


Figure 20. ^{1}H NMR spectrum of **4** (500 MHz, 20 °C) in CD_2Cl_2; aliphatic region

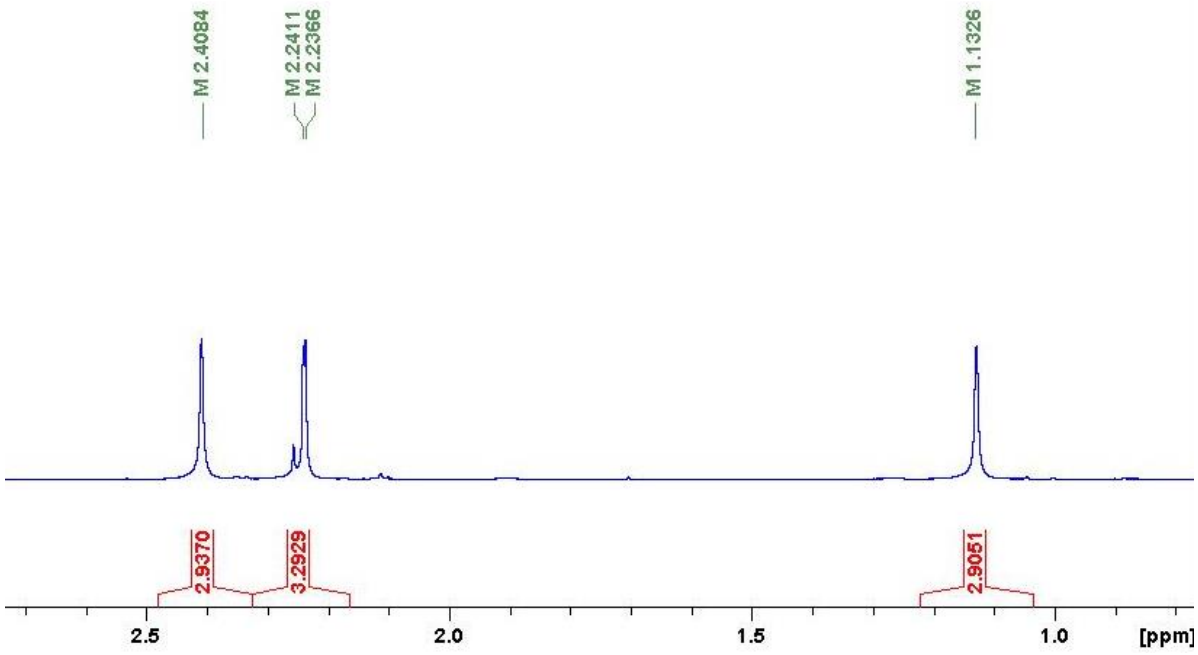


Figure 21. ^{1}H NMR spectrum of **4** (500 MHz, 20 °C) in CD_2Cl_2; aromatic region

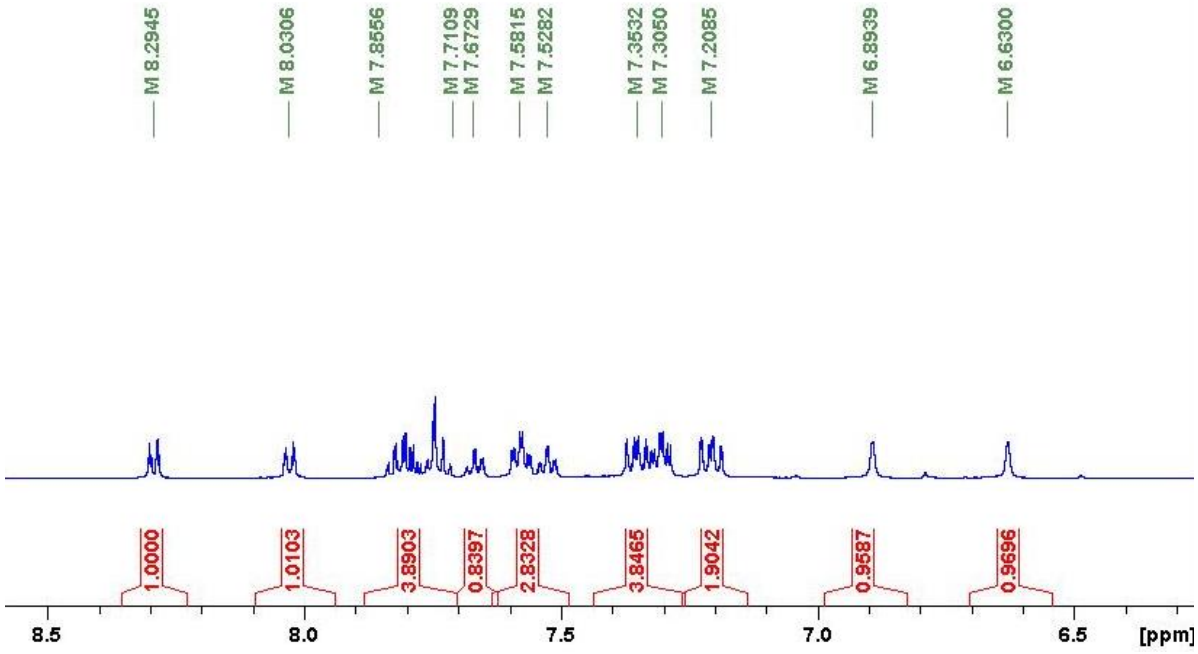


Figure 22. $^{13}C\{^{1}H\}$ NMR spectrum of **4** (126 MHz, 20 °C) in CD_2Cl_2

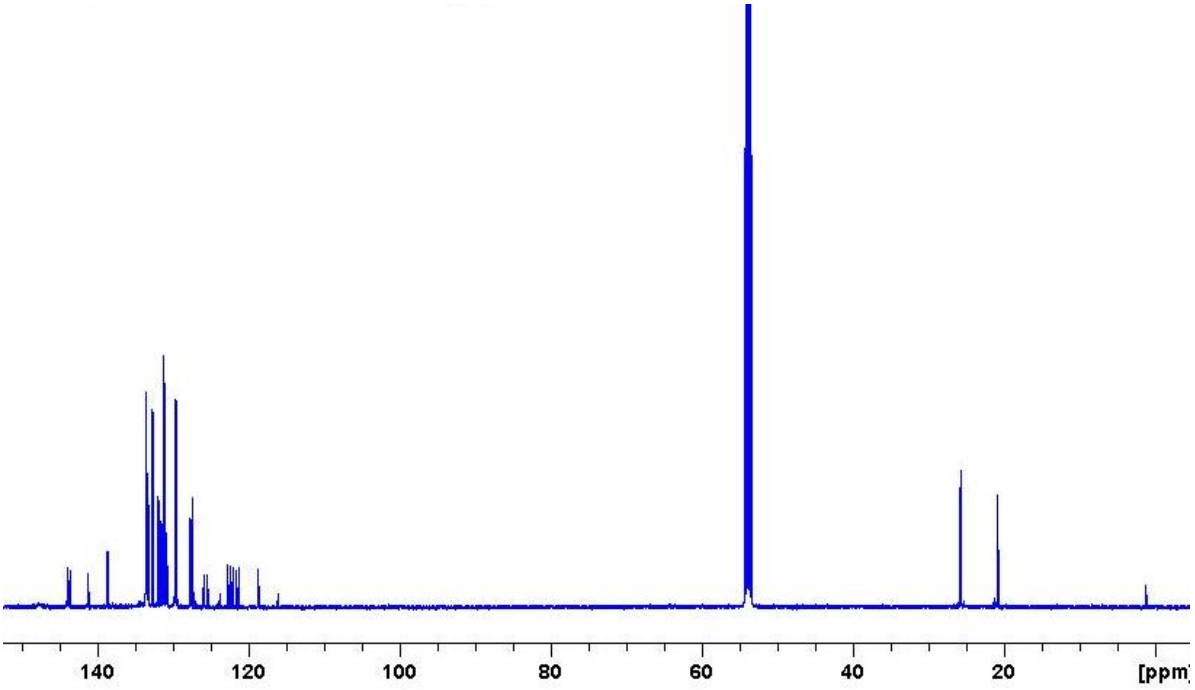


Figure 23. $^{13}C\{^{1}H\}$ NMR spectrum of **4** (126 MHz, 20 °C) in CD_2Cl_2; aliphatic region 1

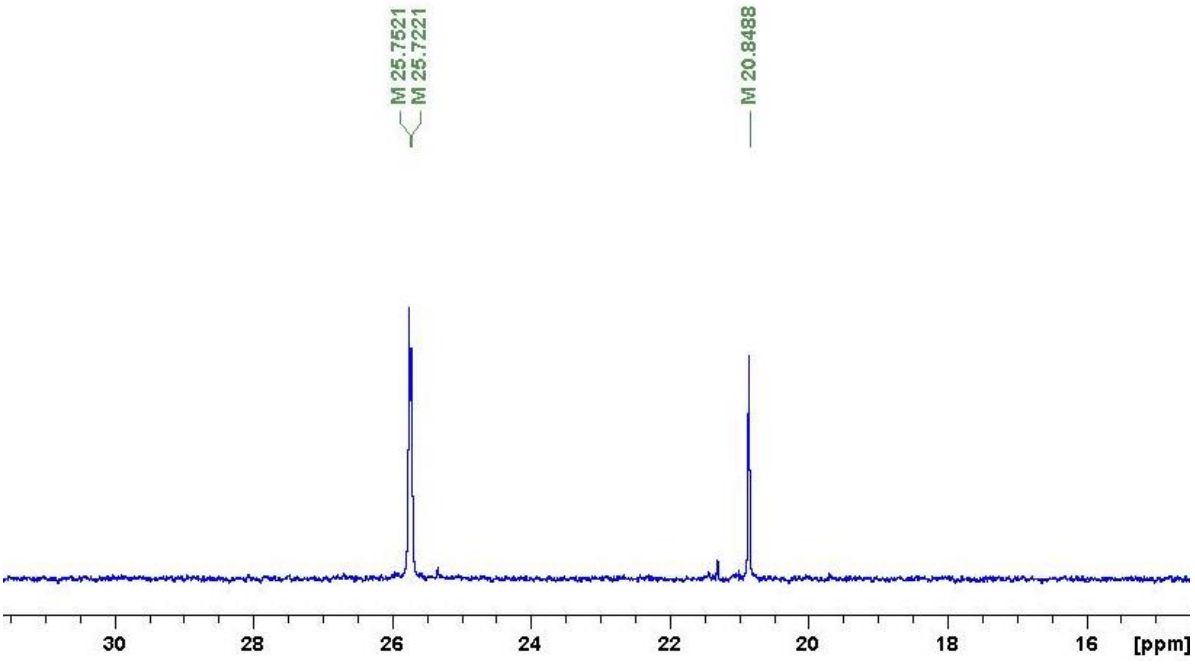


Figure 24. $^{13}C\{^{1}H\}$ NMR spectrum of **4** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 1

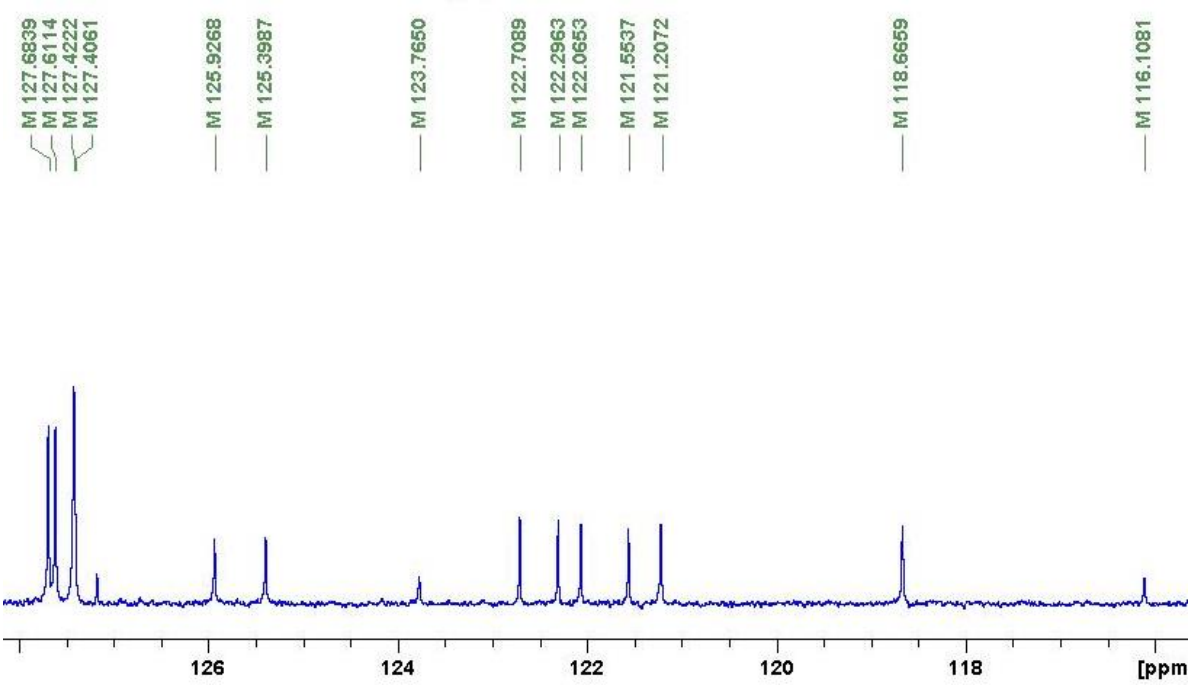


Figure 25. $^{13}C\{^{1}H\}$ NMR spectrum of **4** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 2

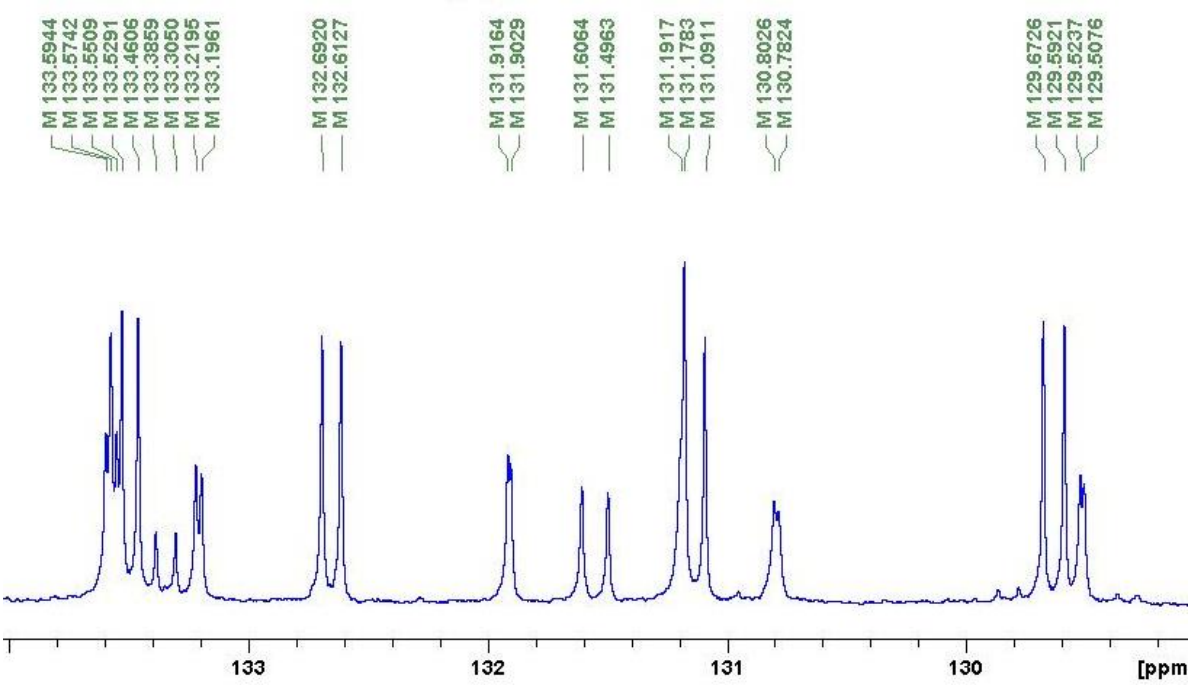


Figure 26. $^{13}C\{^{1}H\}$ NMR spectrum of **4** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 3

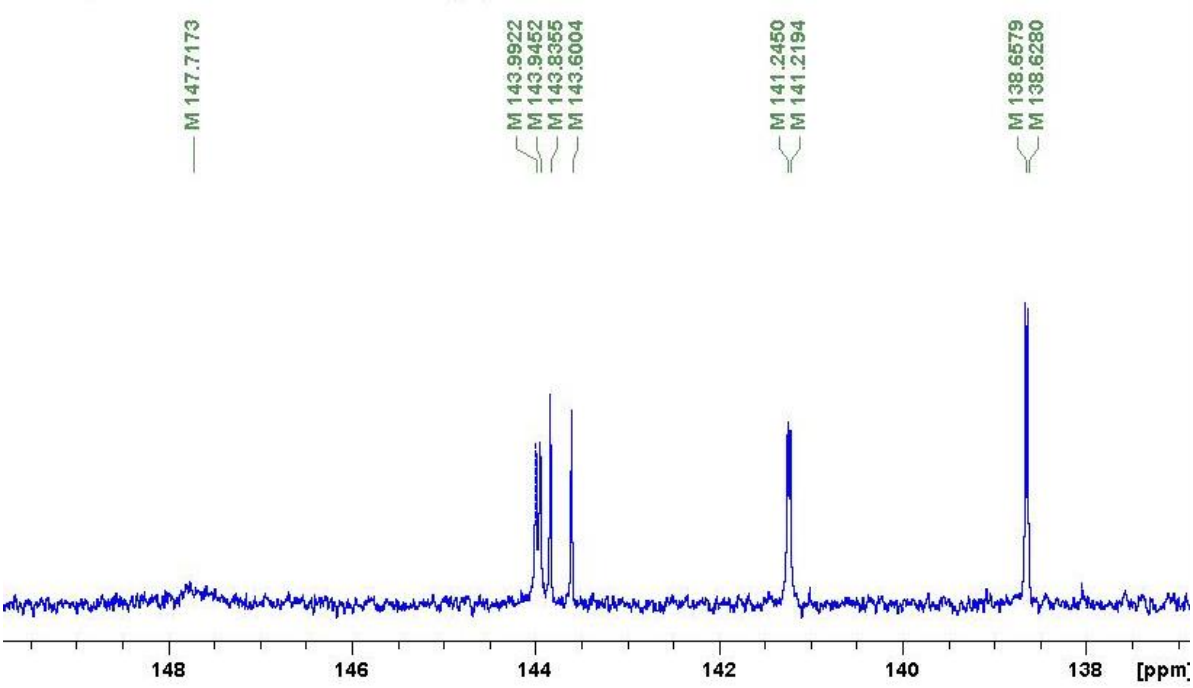
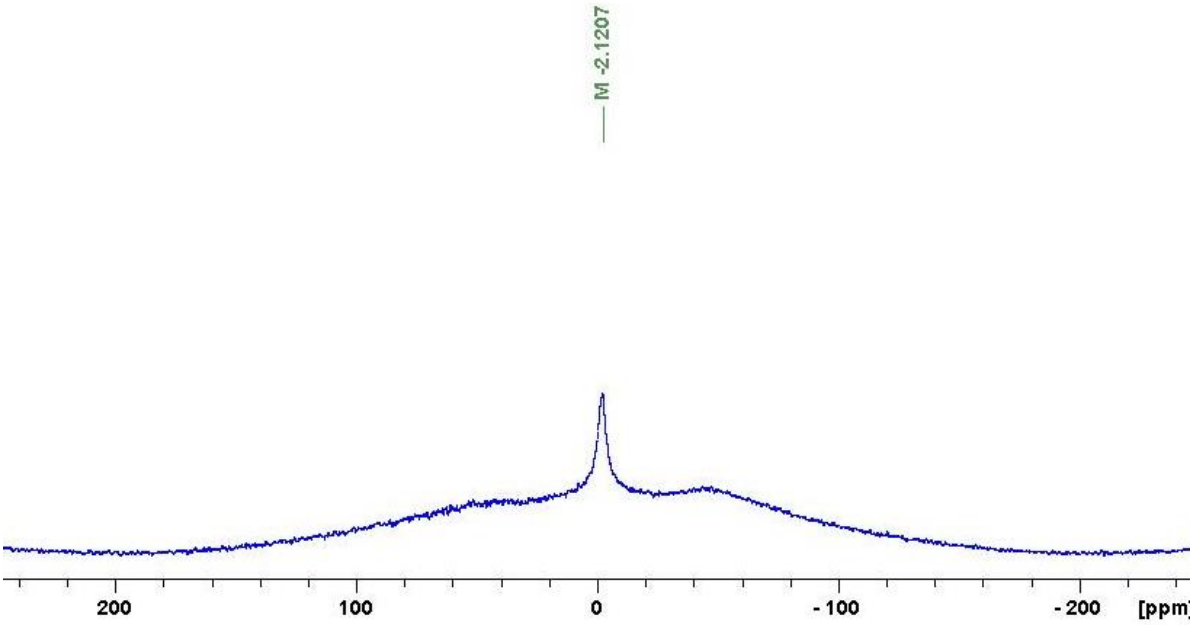


Figure 27. $^{11}B\{^{1}H\}$ NMR spectrum of **4** (96 MHz, 20 °C) in CD_2Cl_2



Ph_2P-Naphth-$B(NTf_2)_2$ 5

Figure 28. $^{31}P\{^1H\}$ NMR spectrum of **5** (203 MHz, 20 °C) in CD_2Cl_2

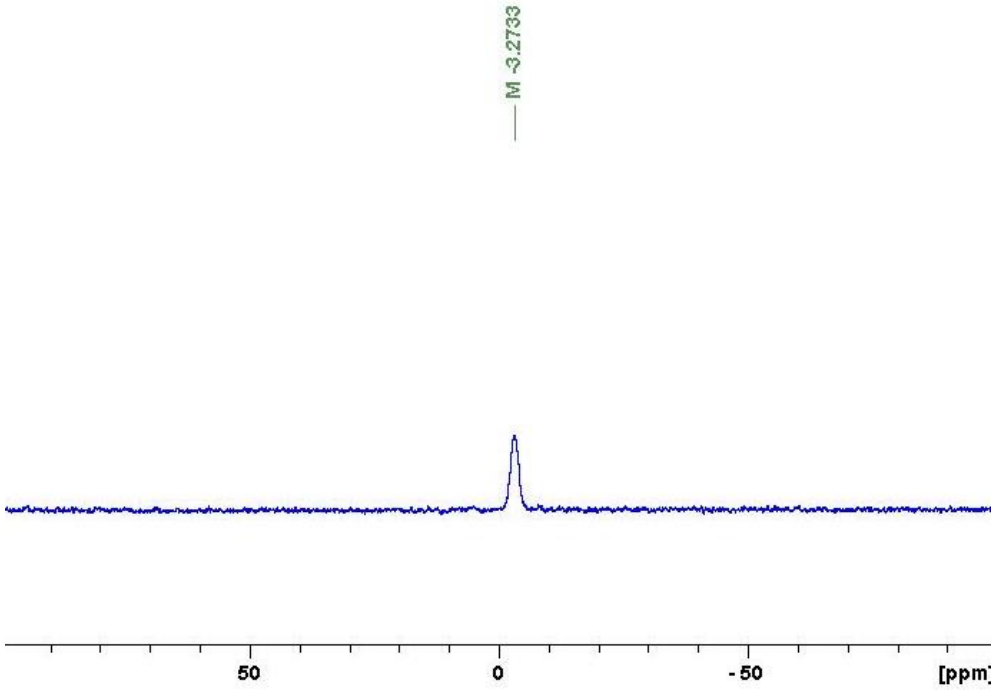
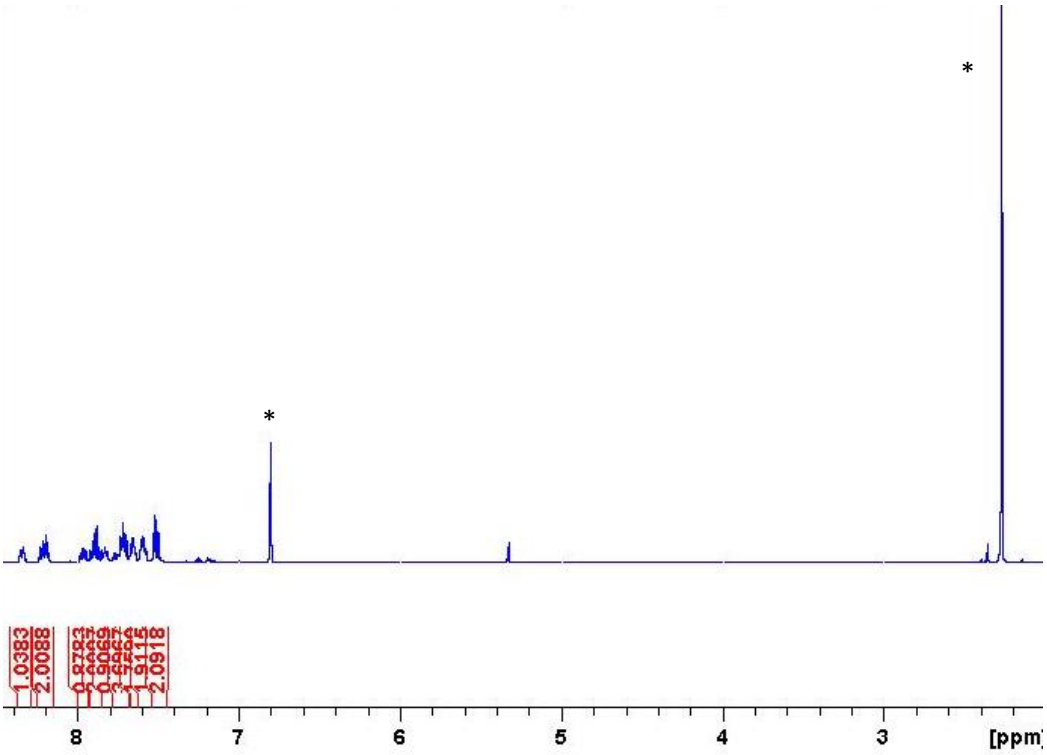


Figure 29. ^1H NMR spectrum of **5** (500 MHz, 20 °C) in CD_2Cl_2



*Signals attributed to Mes-H

Figure 30. ^{1}H NMR spectrum of **5** (500 MHz, 20 °C) in CD_2Cl_2; aromatic region

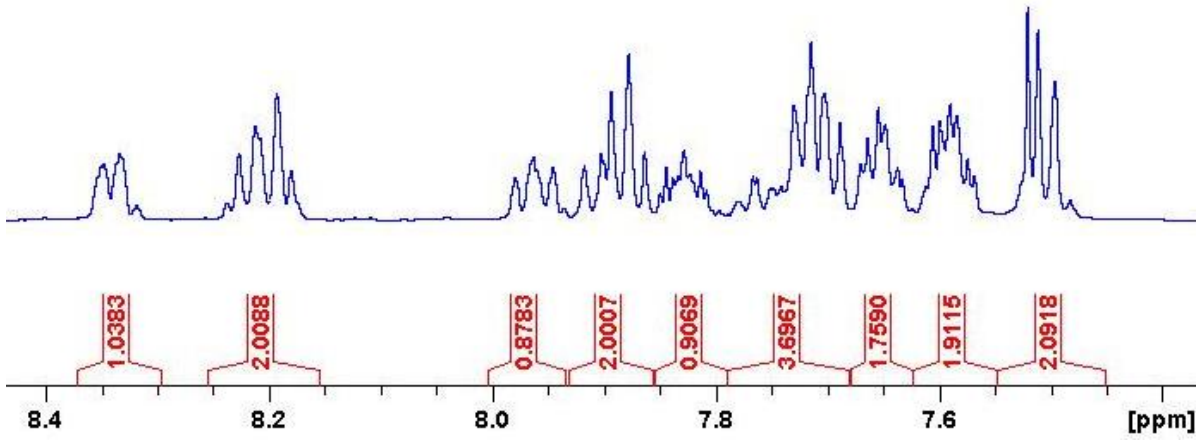


Figure 31. $^{11}B\{^{1}H\}$ NMR spectrum of **5** (160 MHz, 20 °C) in CD_2Cl_2

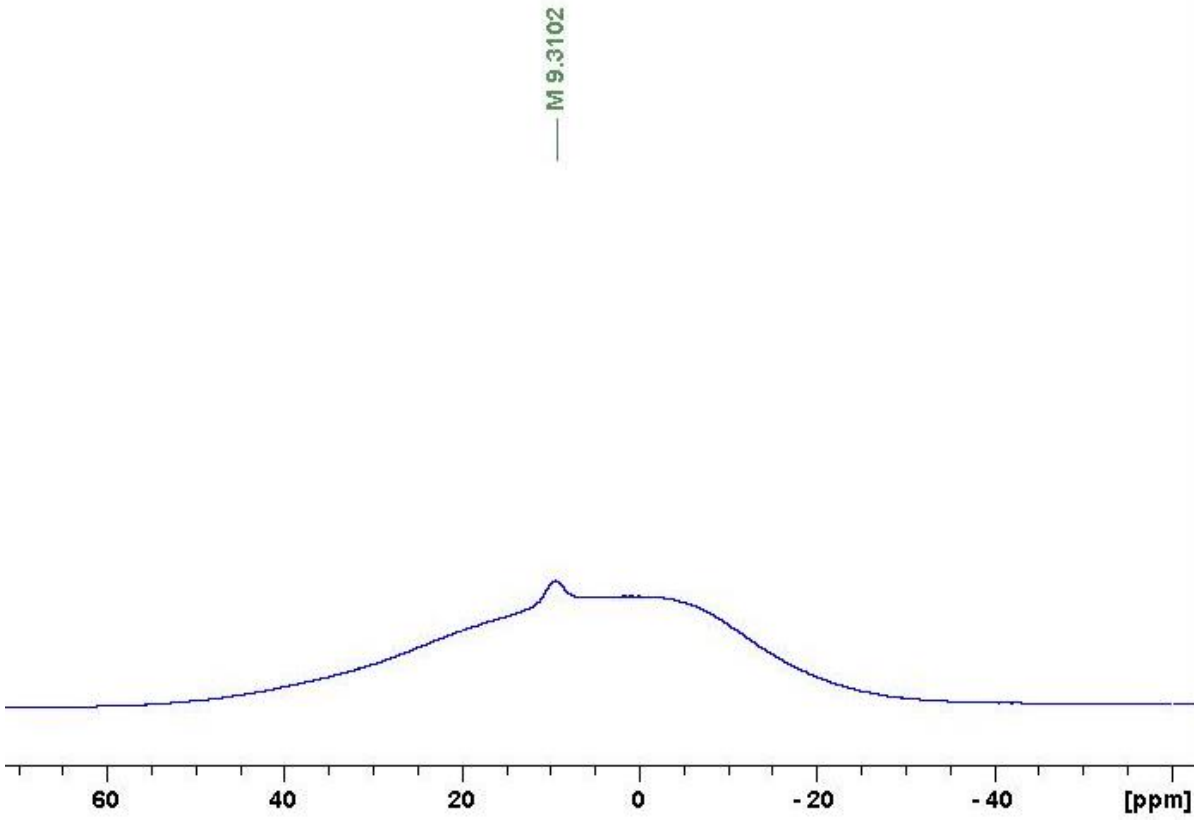
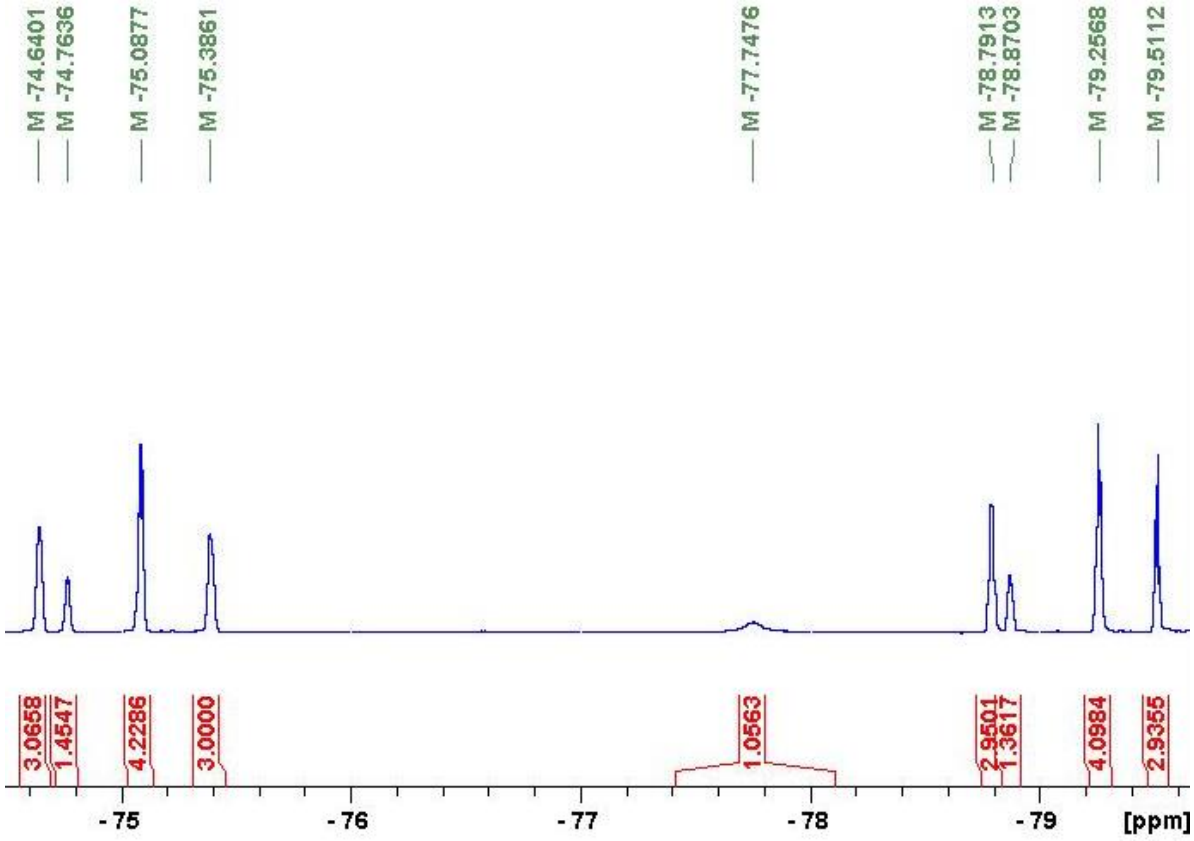


Figure 32. $^{19}F\{^{1}H\}$ NMR spectrum of **5** (282 MHz, 20 °C) in CD_2Cl_2



[Ph_2P-Naphth-$B(OPEt_3)_2$][$(NTf_2)_2$] 6

Figure 33. $^{31}P\{^1H\}$ NMR spectrum of **6** (203 MHz, 20 °C) in CD_2Cl_2

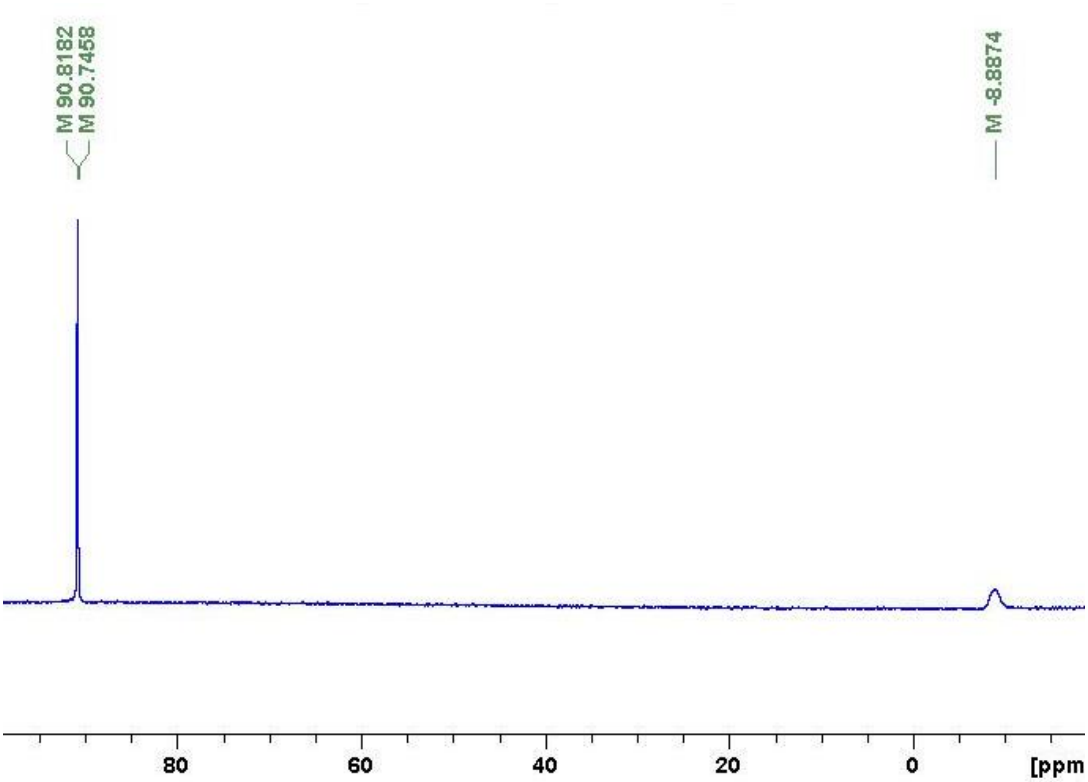


Figure 34. $^{31}P\{^1H\}$ NMR spectrum of **6** (203 MHz, 20 °C) in CD_2Cl_2; low fields

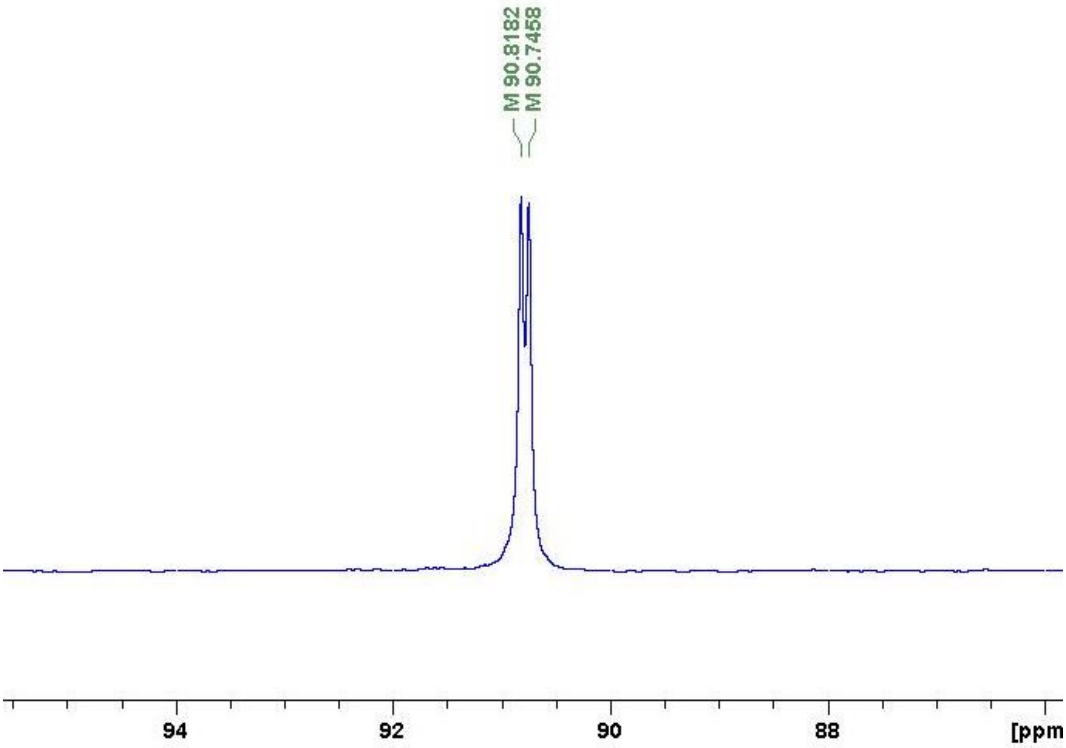


Figure 35. ^{1}H NMR spectrum of **6** (500 MHz, 20 °C) in CD_2Cl_2

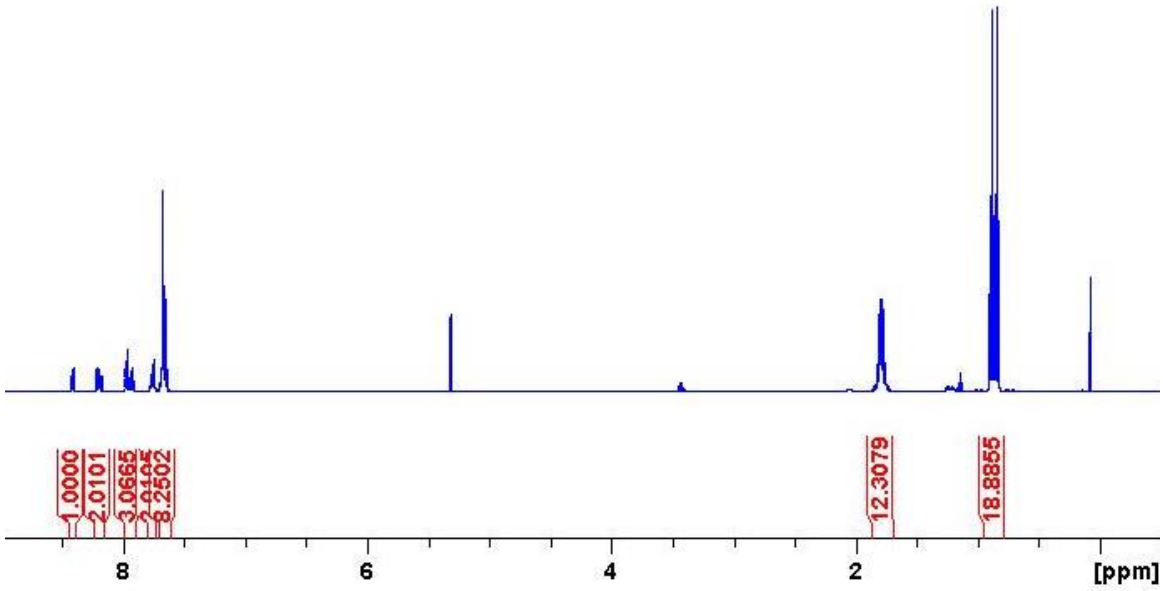


Figure 36. ^{1}H NMR spectrum of **6** (500 MHz, 20 °C) in CD_2Cl_2; aliphatic region

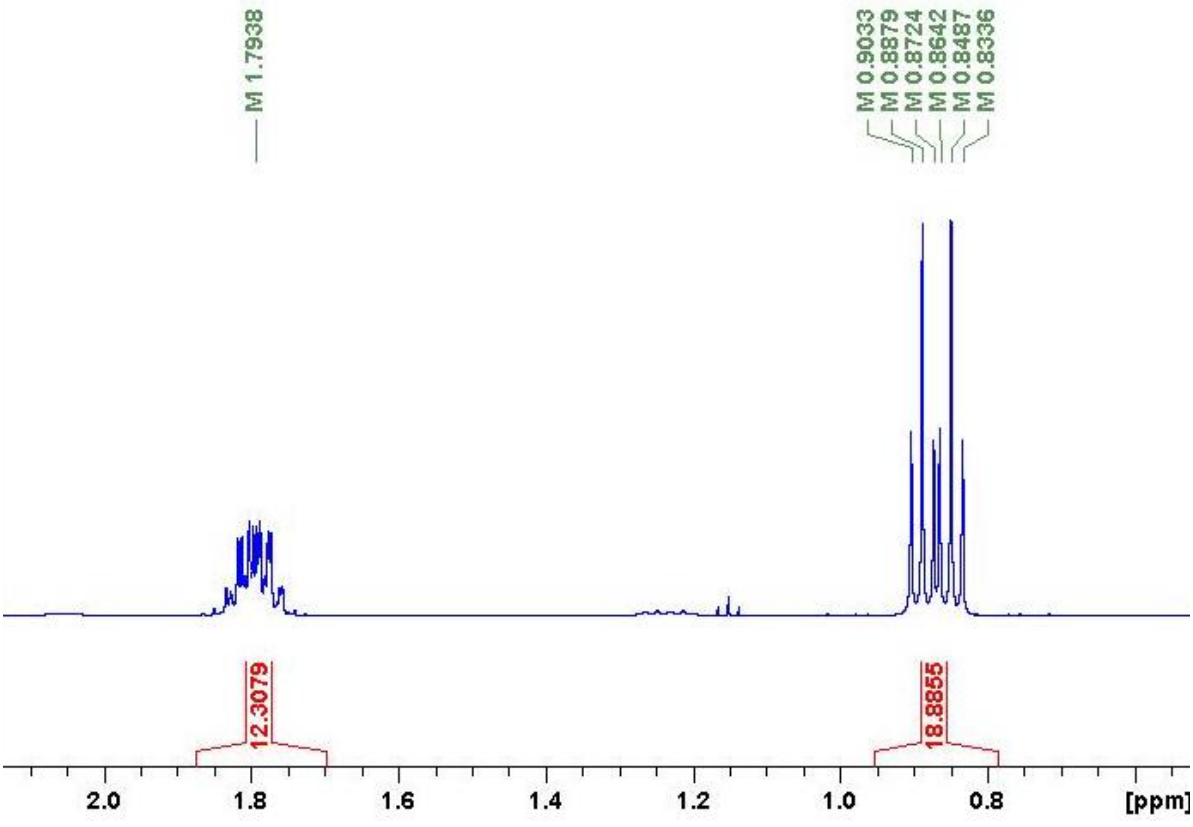


Figure 37. ^{1}H NMR spectrum of **6** (500 MHz, 20 °C) in CD_2Cl_2; aromatic region

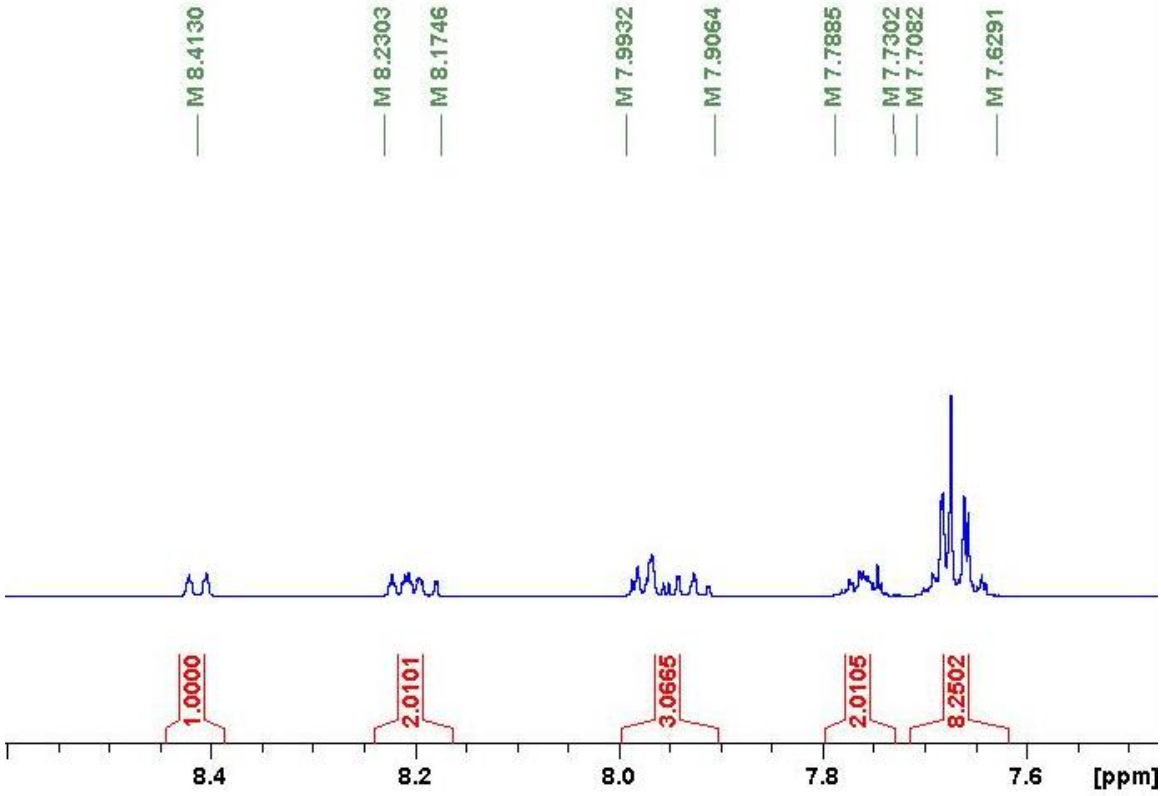


Figure 38. $^{13}C\{^{1}H\}$ NMR spectrum of **6** (126 MHz, 20 °C) in CD_2Cl_2

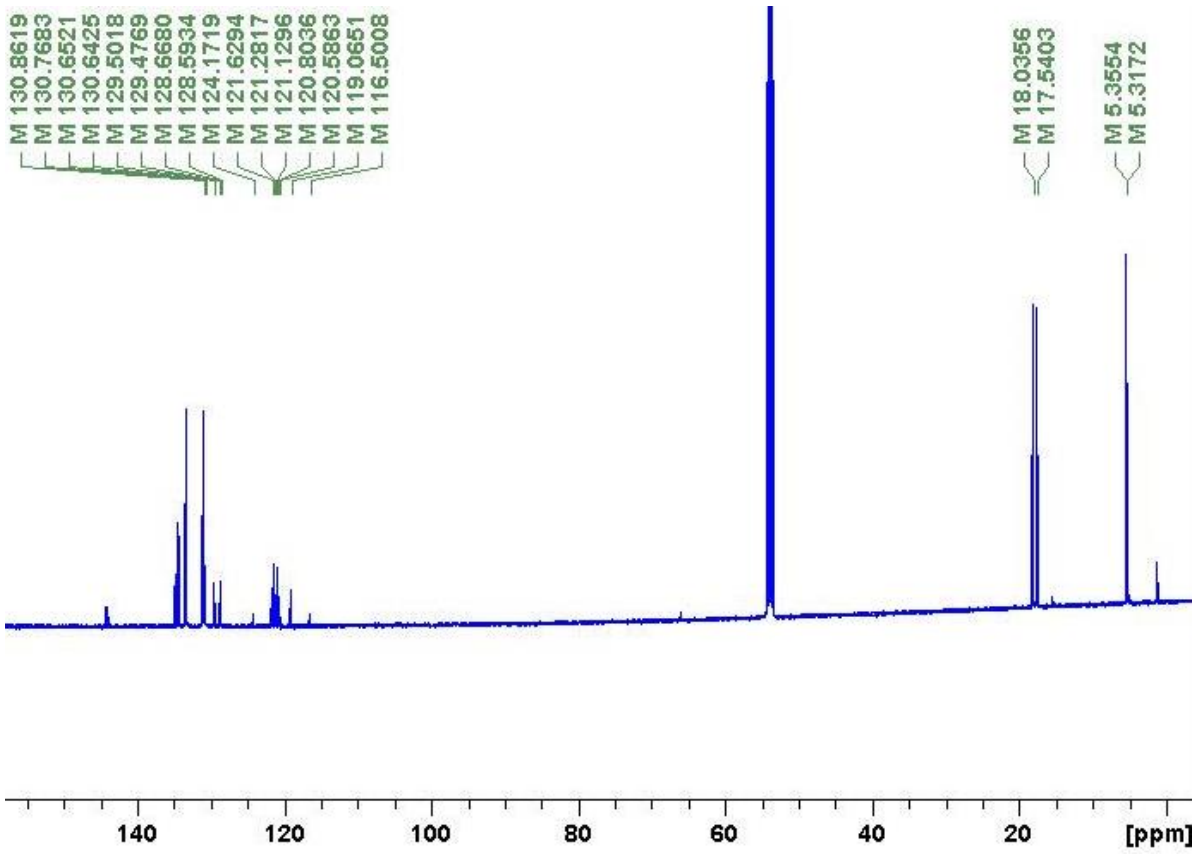


Figure 39. $^{13}C\{^{1}H\}$ NMR spectrum of **6** (126 MHz, 20 °C) in CD_2Cl_2; aliphatic region

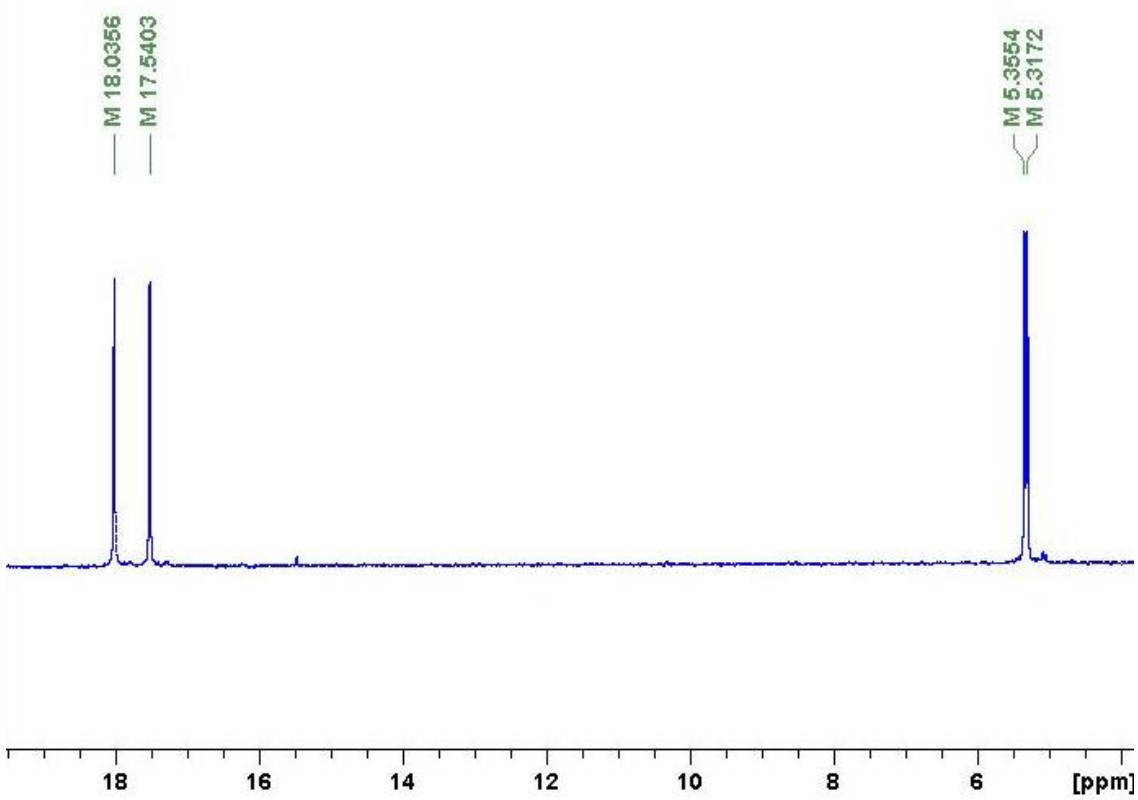


Figure 40. $^{13}C\{^{1}H\}$ NMR spectrum of **6** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 1

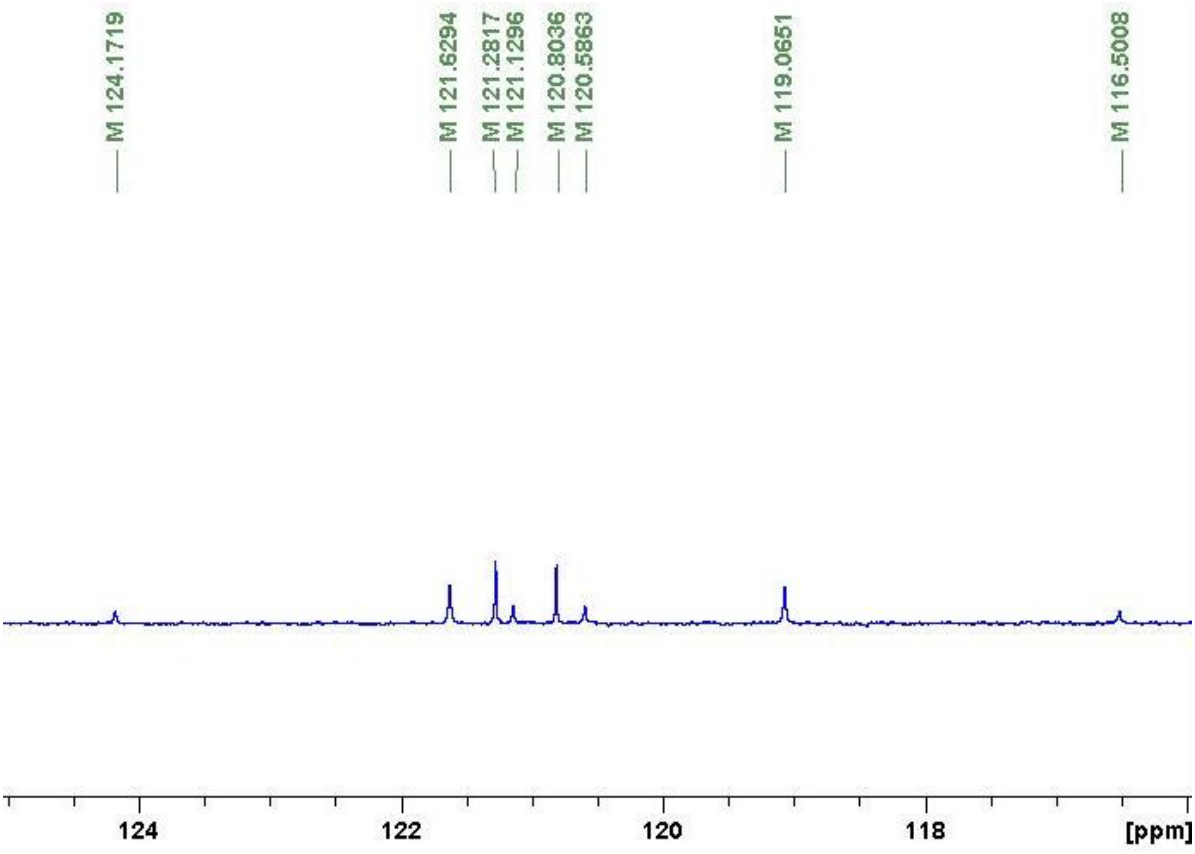


Figure 41. $^{13}C\{^{1}H\}$ NMR spectrum of **6** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 2

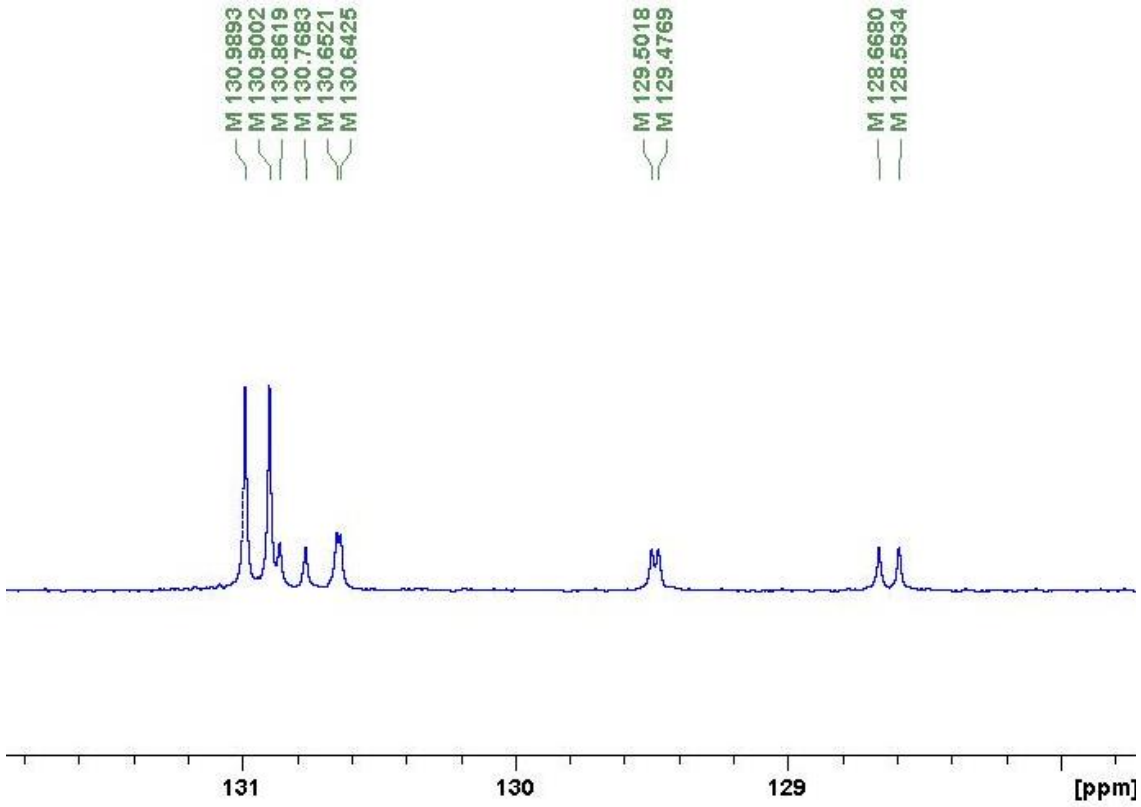


Figure 42. $^{13}C\{^{1}H\}$ NMR spectrum of **6** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 3

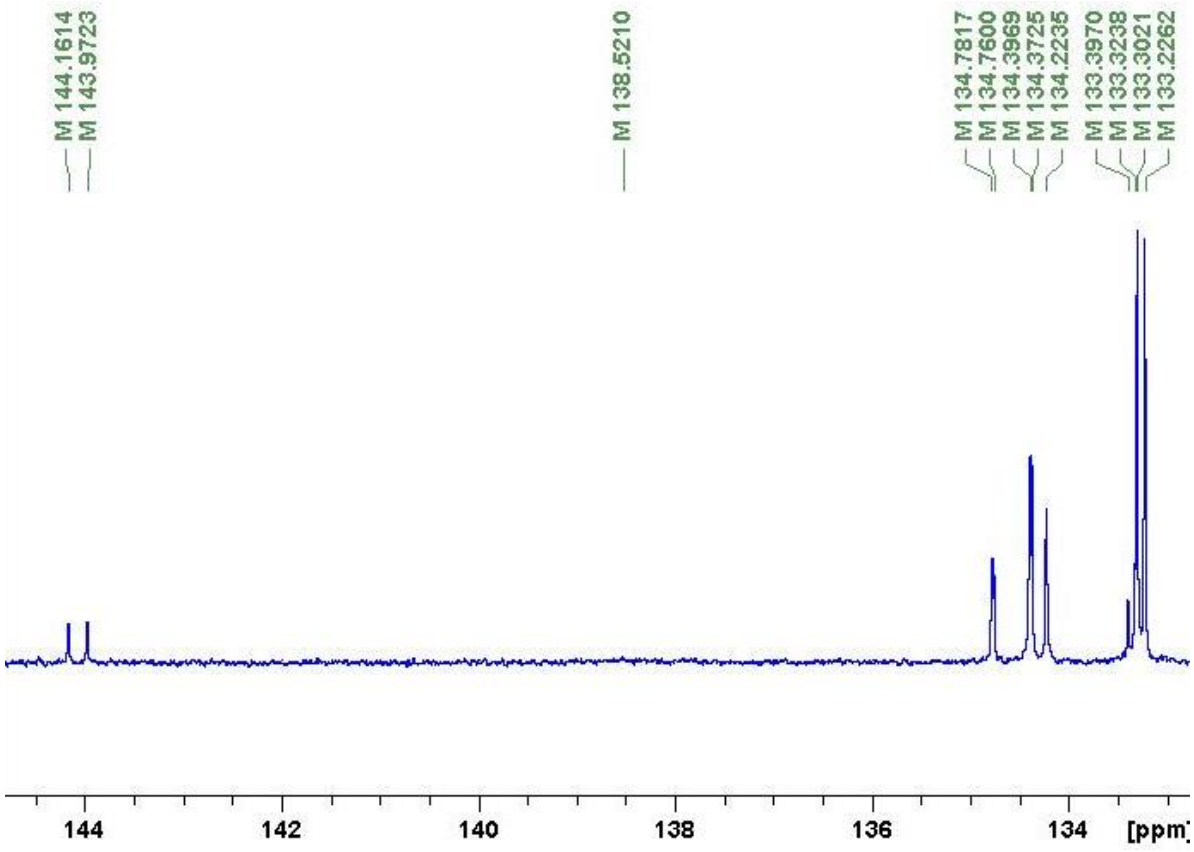


Figure 43. $^{11}B\{^{1}H\}$ NMR spectrum of **6** (96 MHz, 20 °C) in CD_2Cl_2

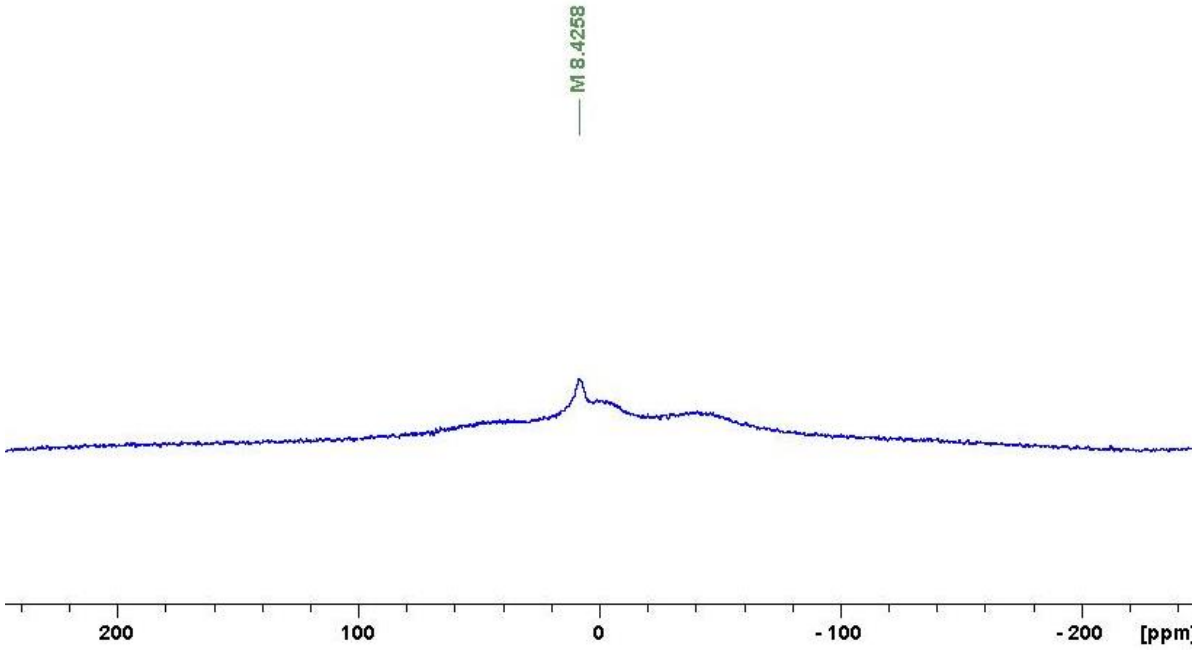
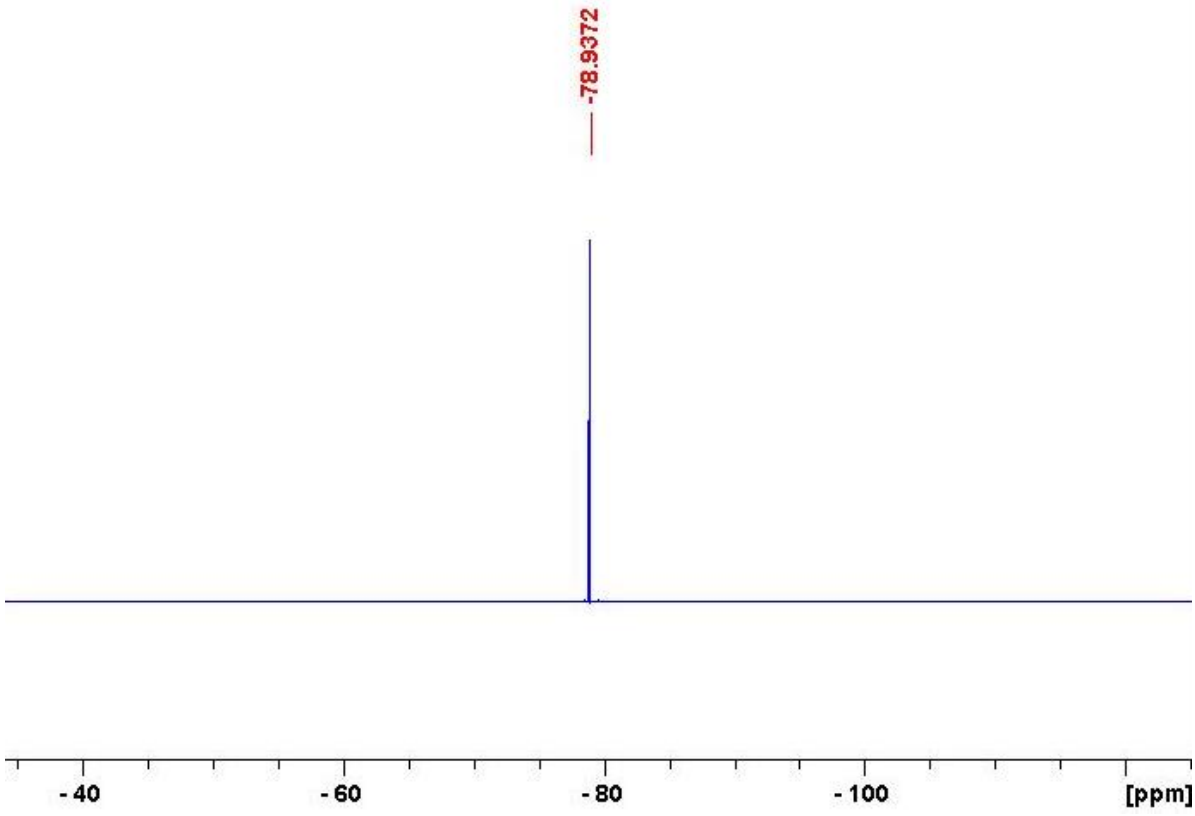


Figure 44. $^{19}F\{^{1}H\}$ NMR spectrum of **6** (282 MHz, 20 °C) in CD_2Cl_2



*i*Pr$_2$P-Naphth-B(Mes)(Br) 7-Br

Figure 45. $^{31}P\{^1H\}$ NMR spectrum of **7-Br** (203 MHz, 20 °C) in $CDCl_3$

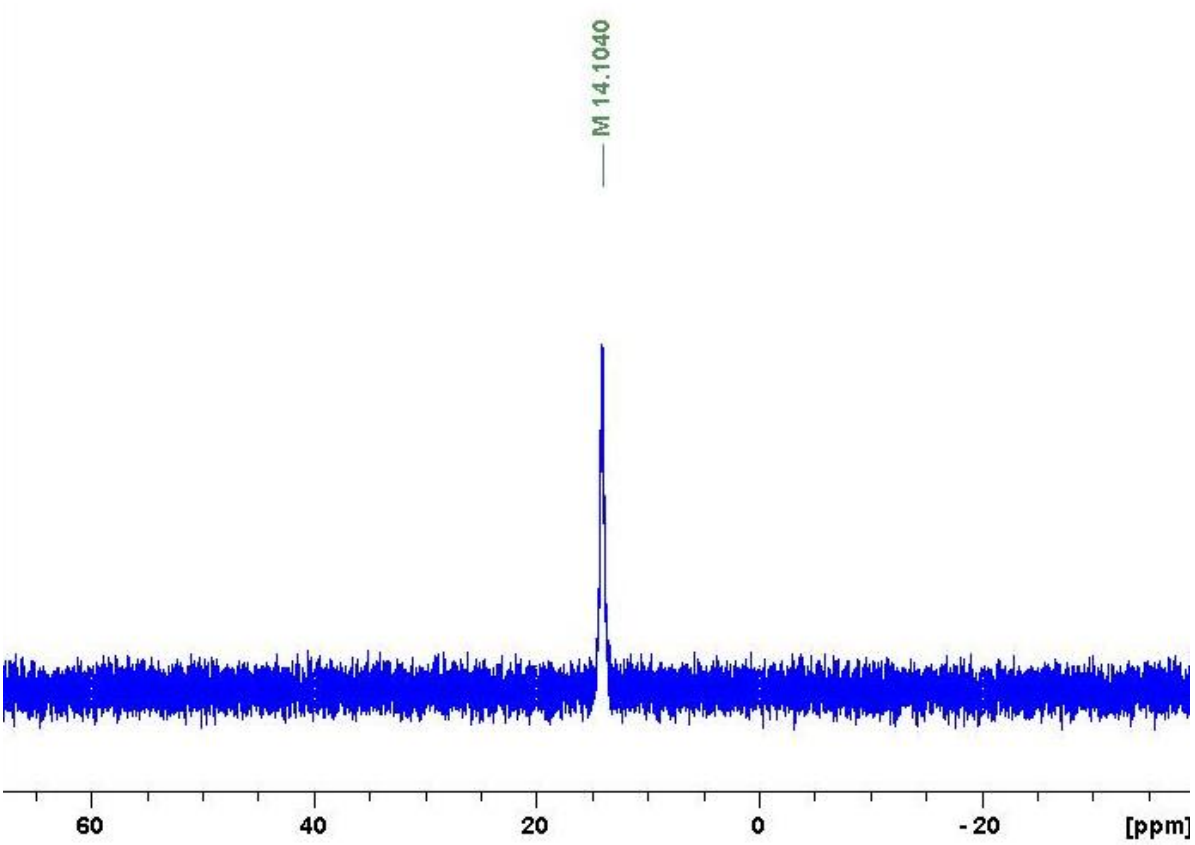


Figure 46. ^1H NMR spectrum of **7-Br** (500 MHz, 20 °C) in $CDCl_3$

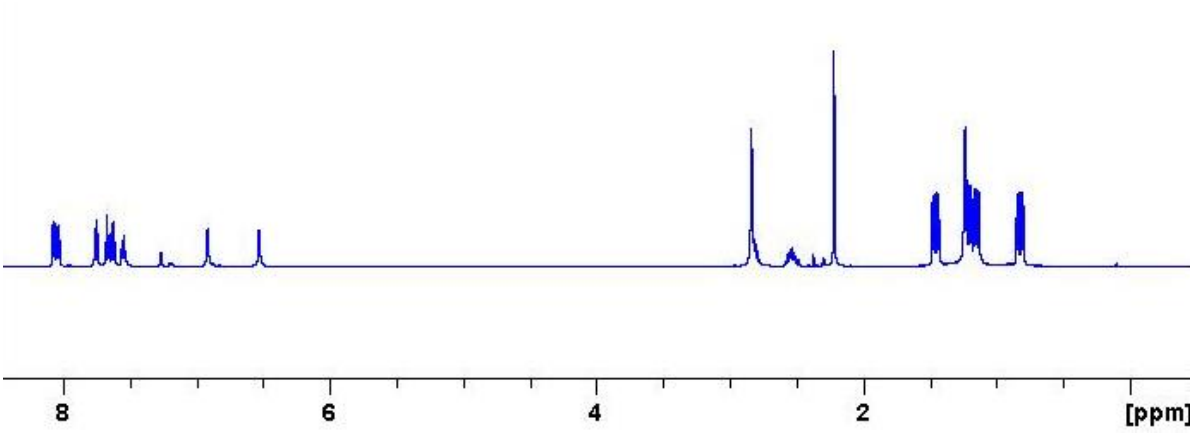


Figure 47. ^{1}H NMR spectrum of **7-Br** (500 MHz, 20 °C) in $CDCl_3$; aliphatic region

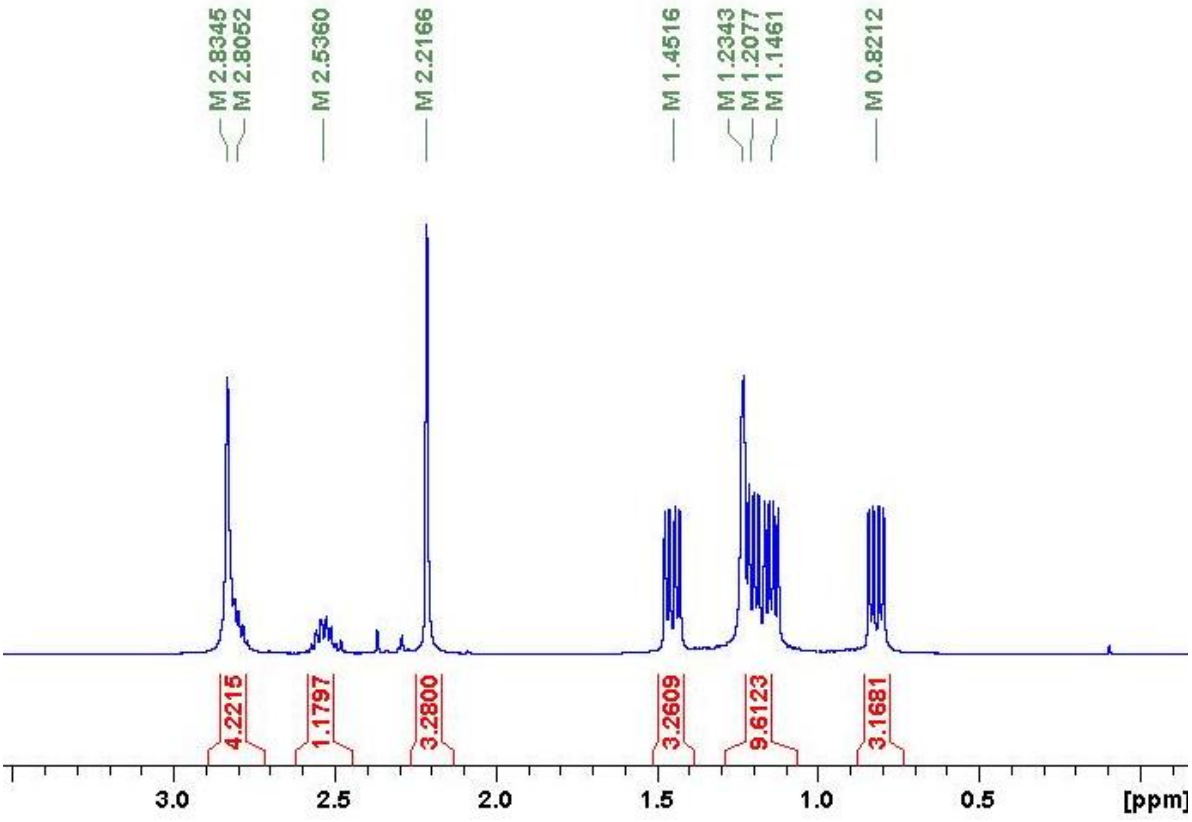


Figure 48. ^{1}H NMR spectrum of **7-Br** (500 MHz, 20 °C) in $CDCl_3$; aromatic region

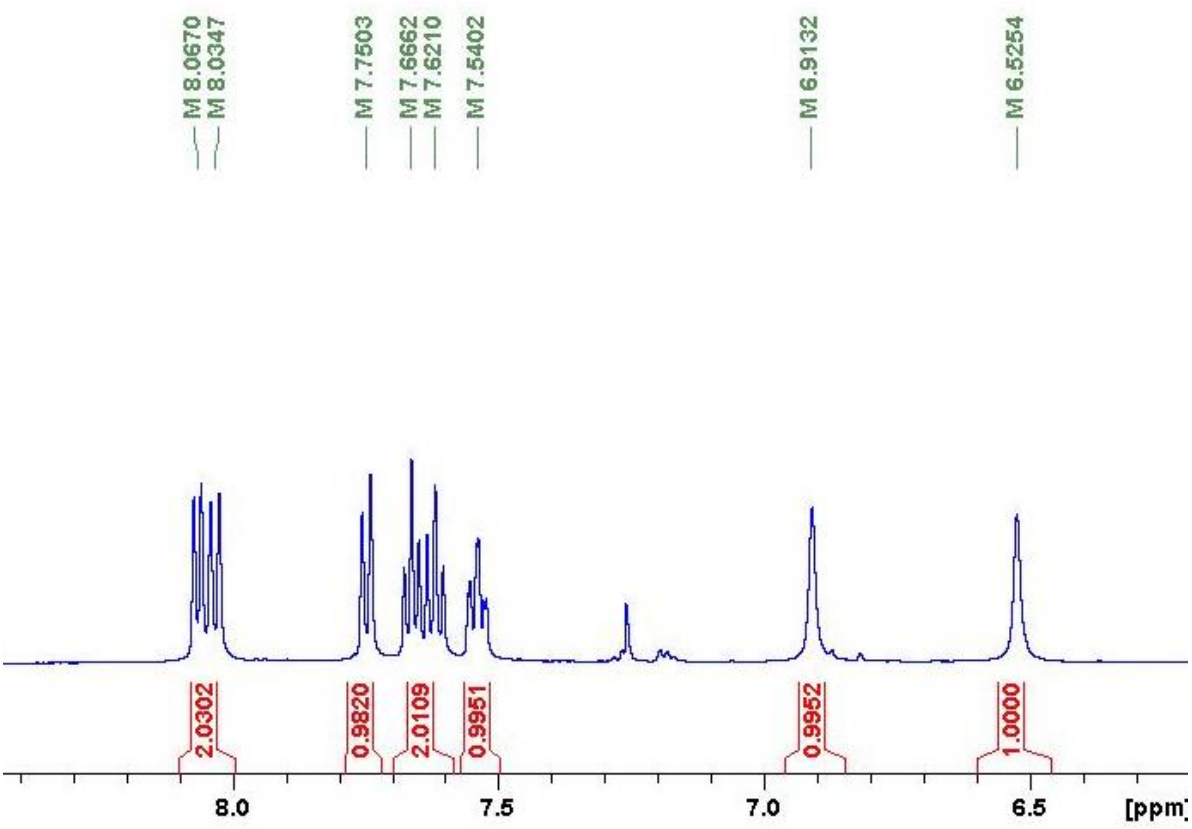


Figure 49. $^{13}C\{^{1}H\}$ NMR spectrum of **7-Br** (126 MHz, 20 °C) in $CDCl_3$

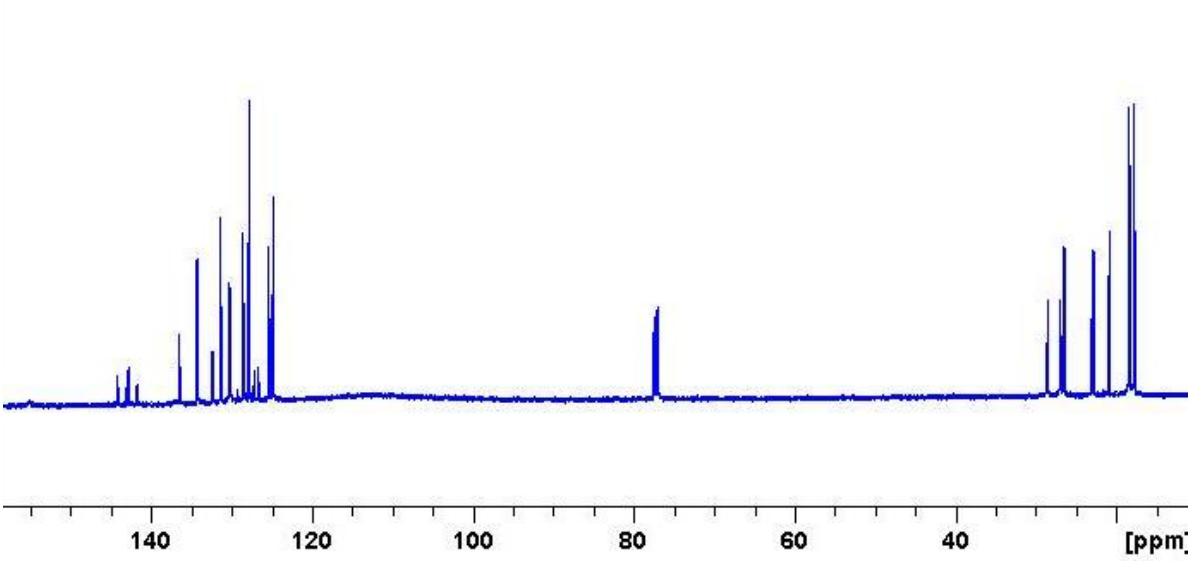


Figure 50. $^{13}C\{^{1}H\}$ NMR spectrum of **7-Br** (126 MHz, 20 °C) in $CDCl_3$; aliphatic region

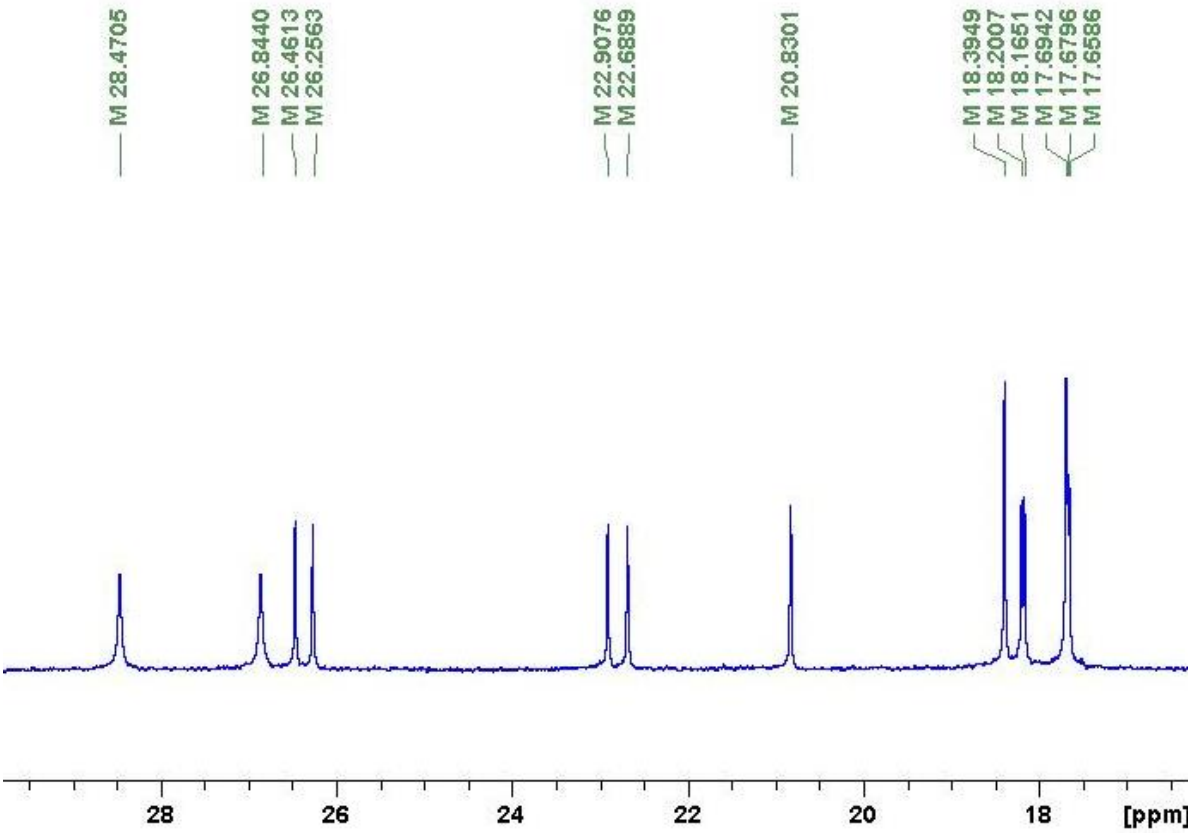


Figure 51. $^{13}C\{^{1}H\}$ NMR spectrum of **7-Br** (126 MHz, 20 °C) in $CDCl_3$; aromatic region

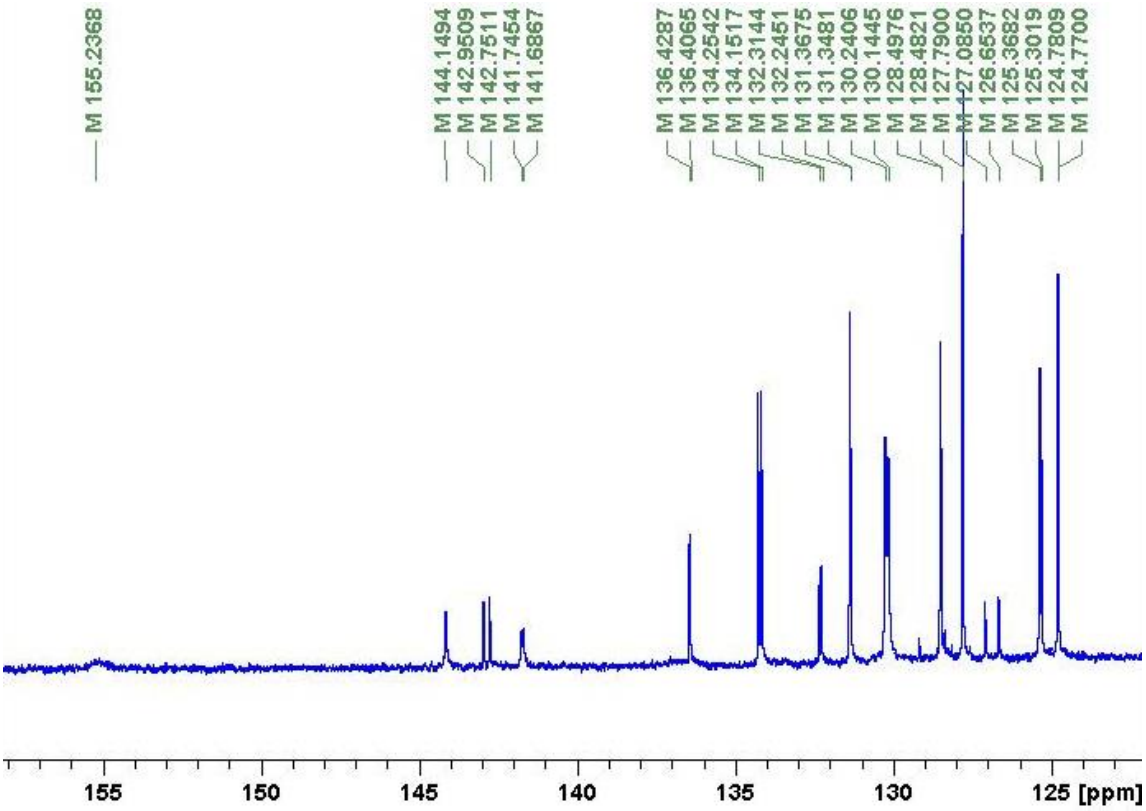
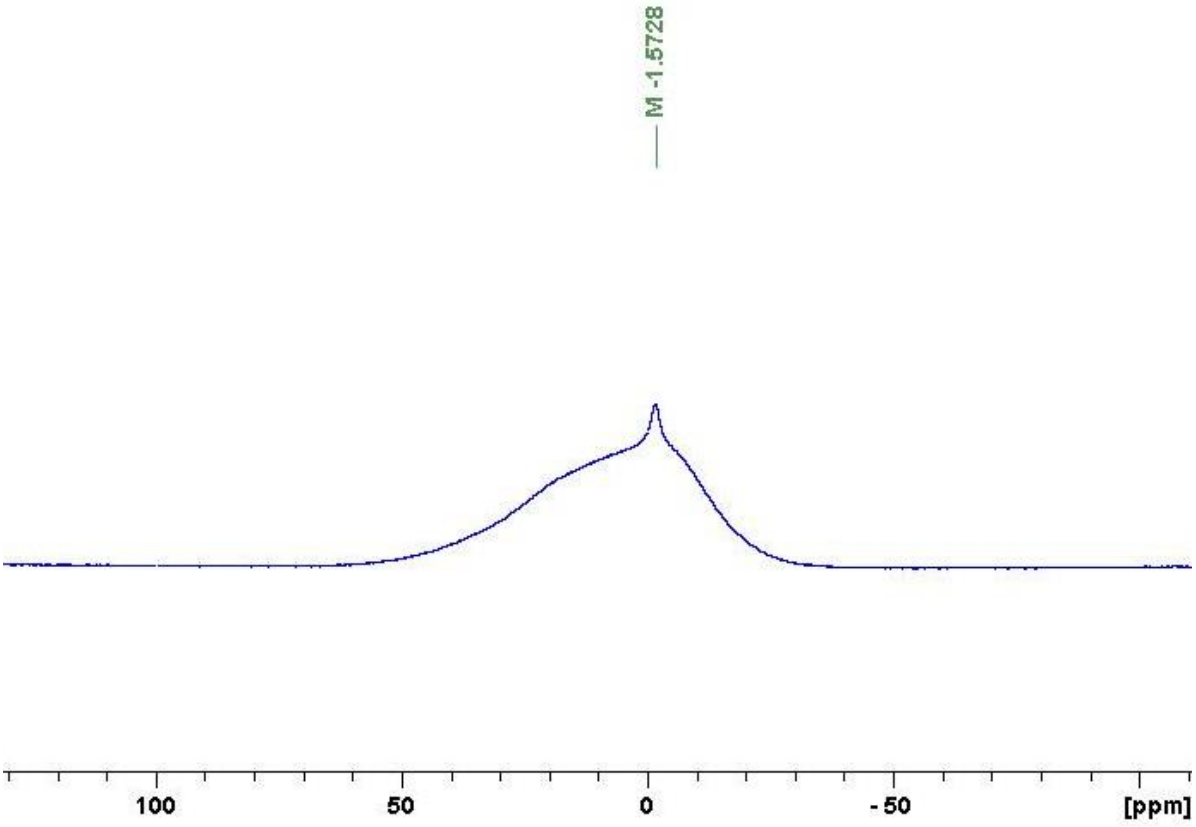


Figure 52. $^{11}B\{^{1}H\}$ NMR spectrum of **7-Br** (160 MHz, 20 °C) in $CDCl_3$



[*i*Pr$_2$P-Naphth-BMes][NTf$_2$] 7 (X = NTf$_2$)

Figure 53. $^{31}P\{^1H\}$ NMR spectrum of **7 (X = NTf$_2$)** (203 MHz, 20 °C) in CD_2Cl_2

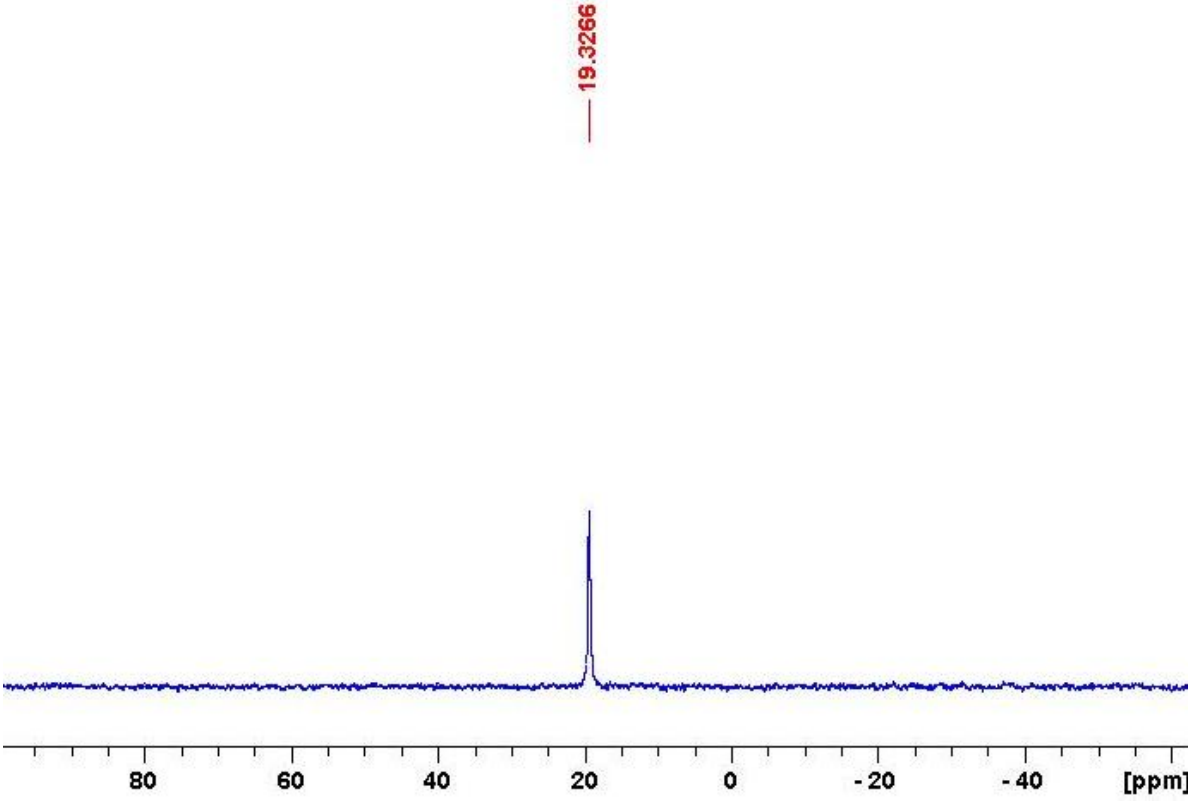


Figure 54. ^1H NMR spectrum of **7 (X = NTf$_2$)** (500 MHz, 20 °C) in CD_2Cl_2

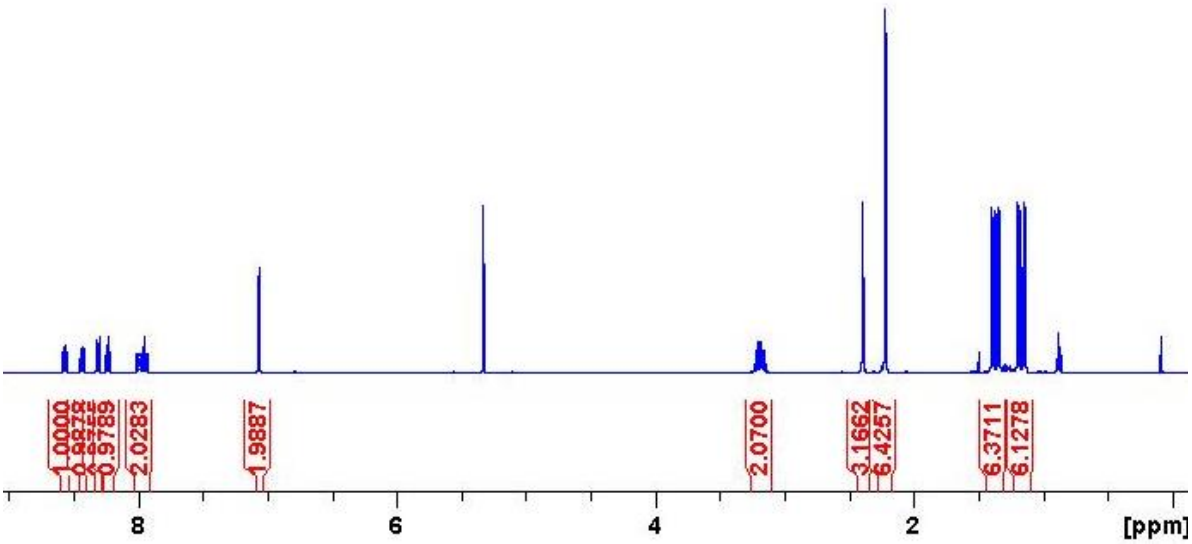


Figure 55. ^{1}H NMR spectrum of **7 (X = NTf_2)** (500 MHz, 20 °C) in CD_2Cl_2; aliphatic region

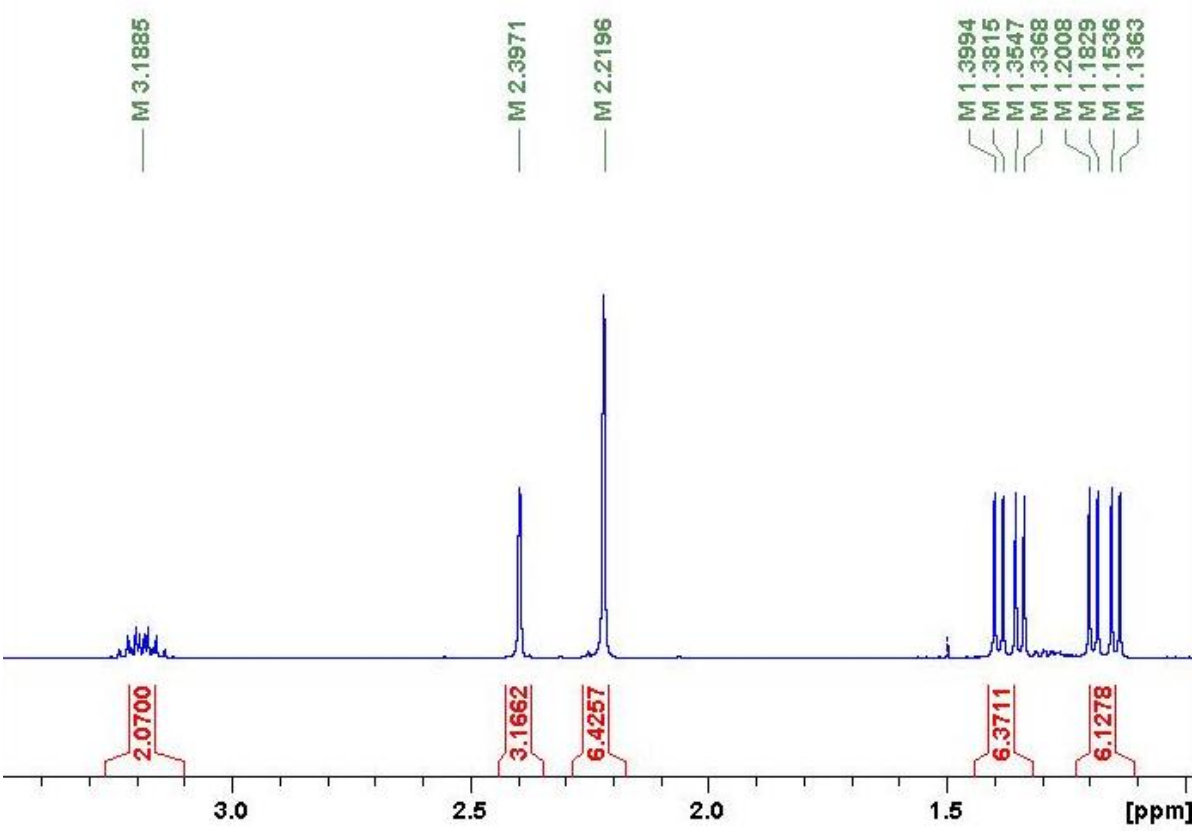


Figure 56. ^{1}H NMR spectrum of **7 (X = NTf_2)** (500 MHz, 20 °C) in CD_2Cl_2; aromatic region

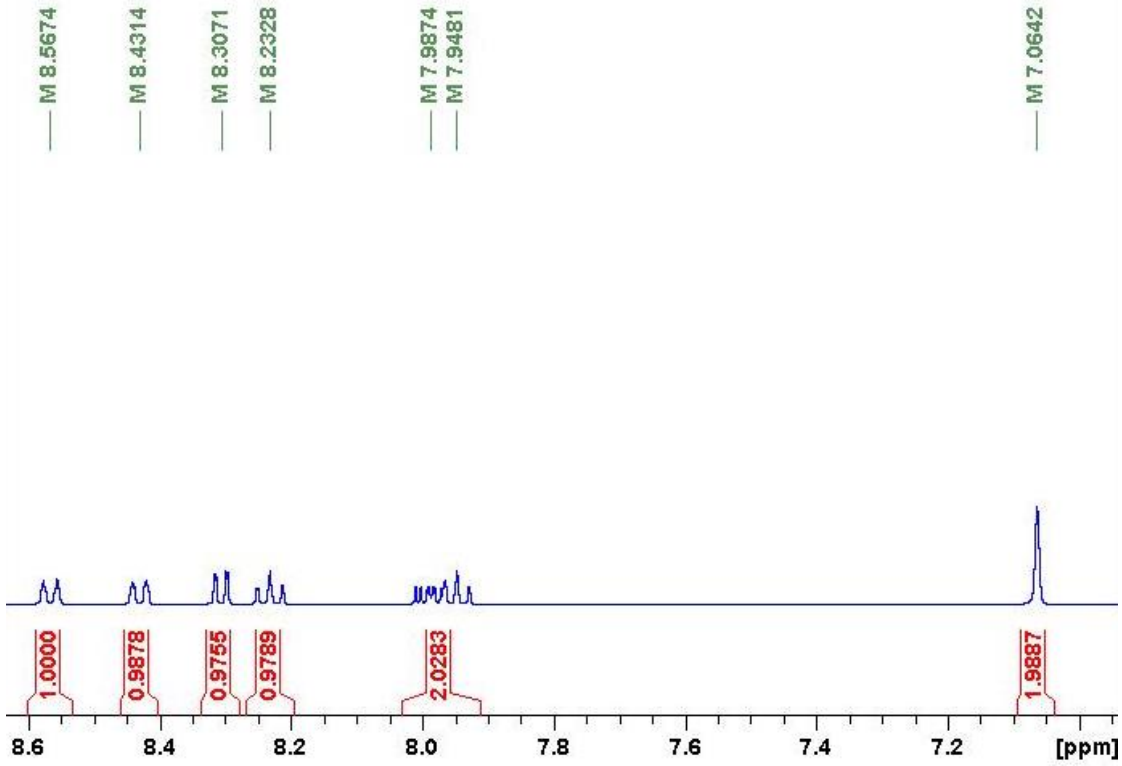


Figure 57. $^{13}C\{^{1}H\}$ NMR spectrum of **7 (X = NTf_2)** (126 MHz, 20 °C) in CD_2Cl_2

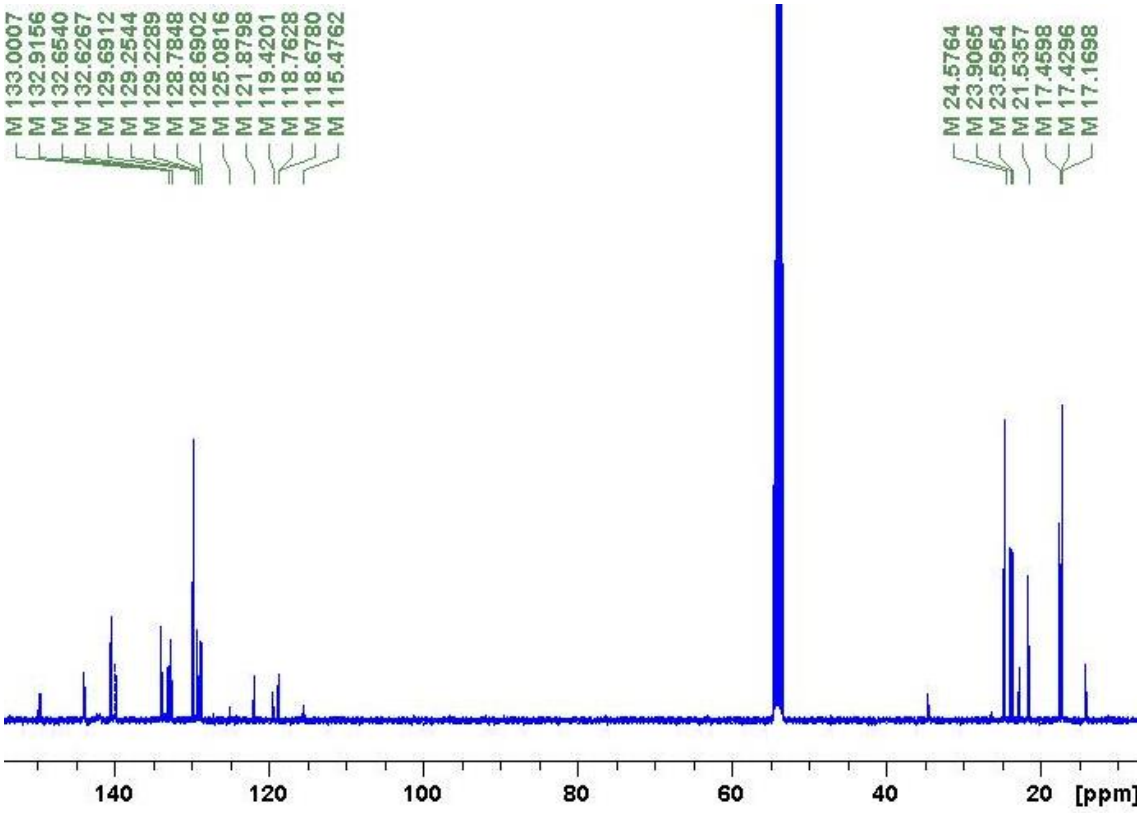


Figure 58. $^{13}C\{^{1}H\}$ NMR spectrum of **7 (X = NTf_2)** (126 MHz, 20 °C) in CD_2Cl_2; aliphatic region

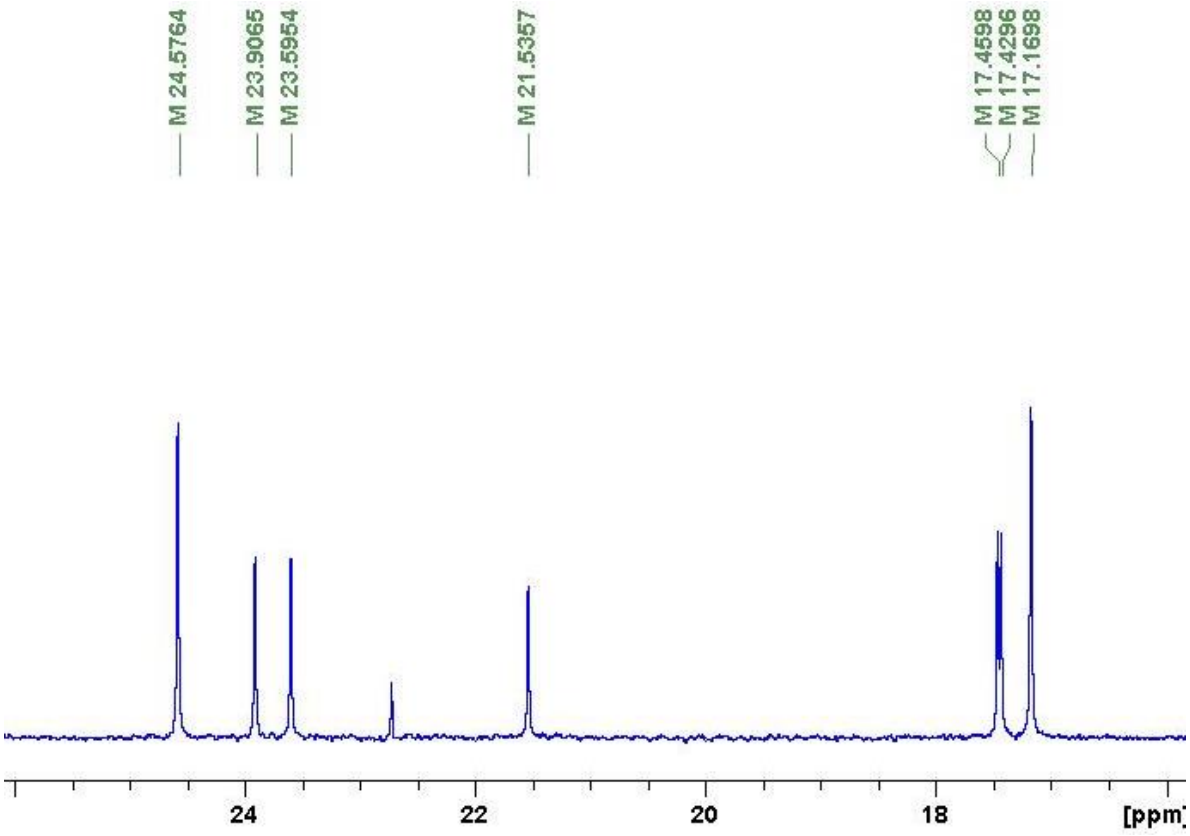


Figure 59. $^{13}C\{^{1}H\}$ NMR spectrum of **7 (X = NTf_2)** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 1

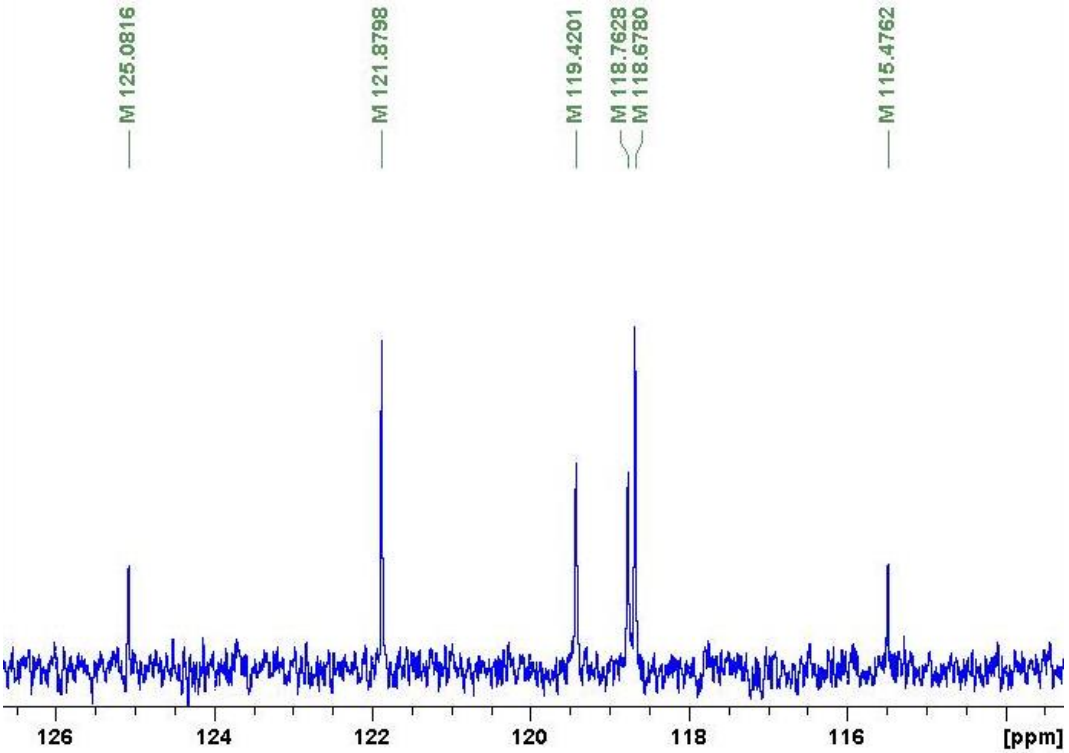


Figure 60. $^{13}C\{^{1}H\}$ NMR spectrum of **7 (X = NTf_2)** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 2

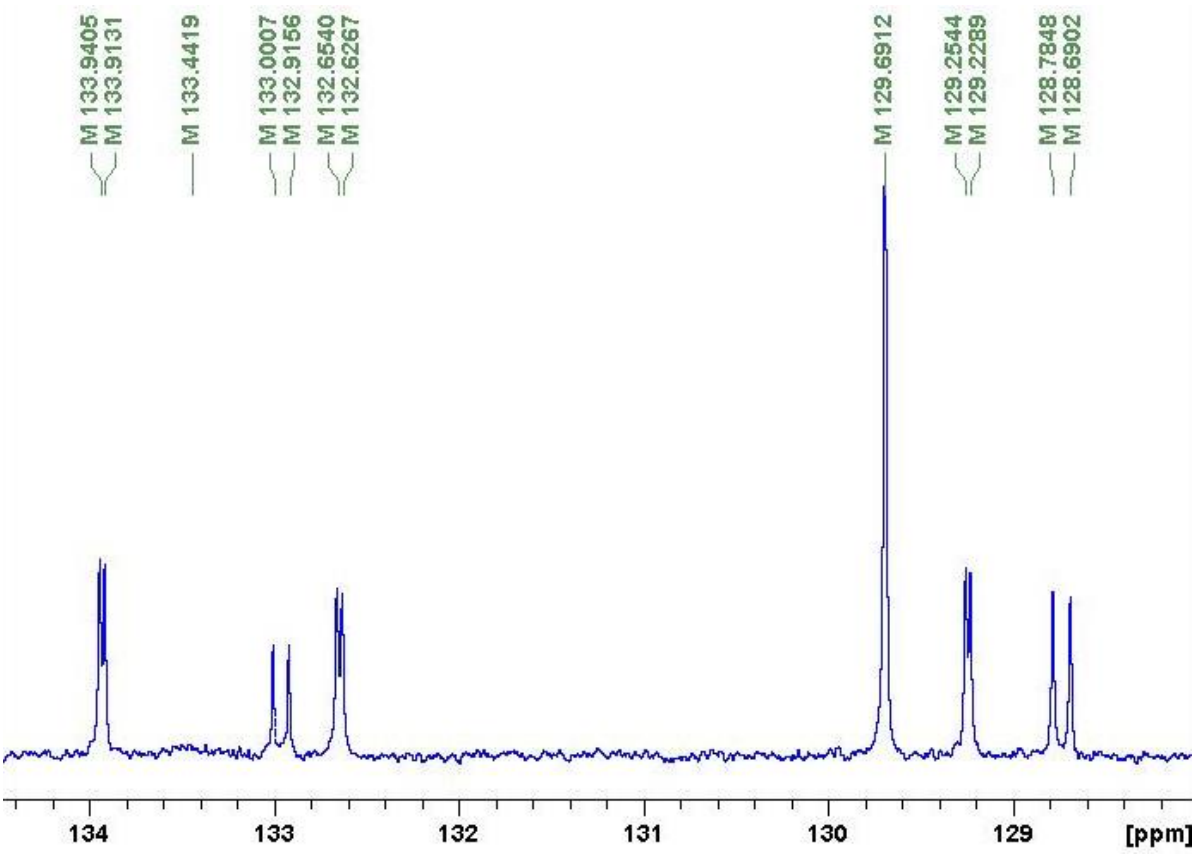


Figure 61. $^{13}C\{^{1}H\}$ NMR spectrum of **7 (X = NTf_2)** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 3

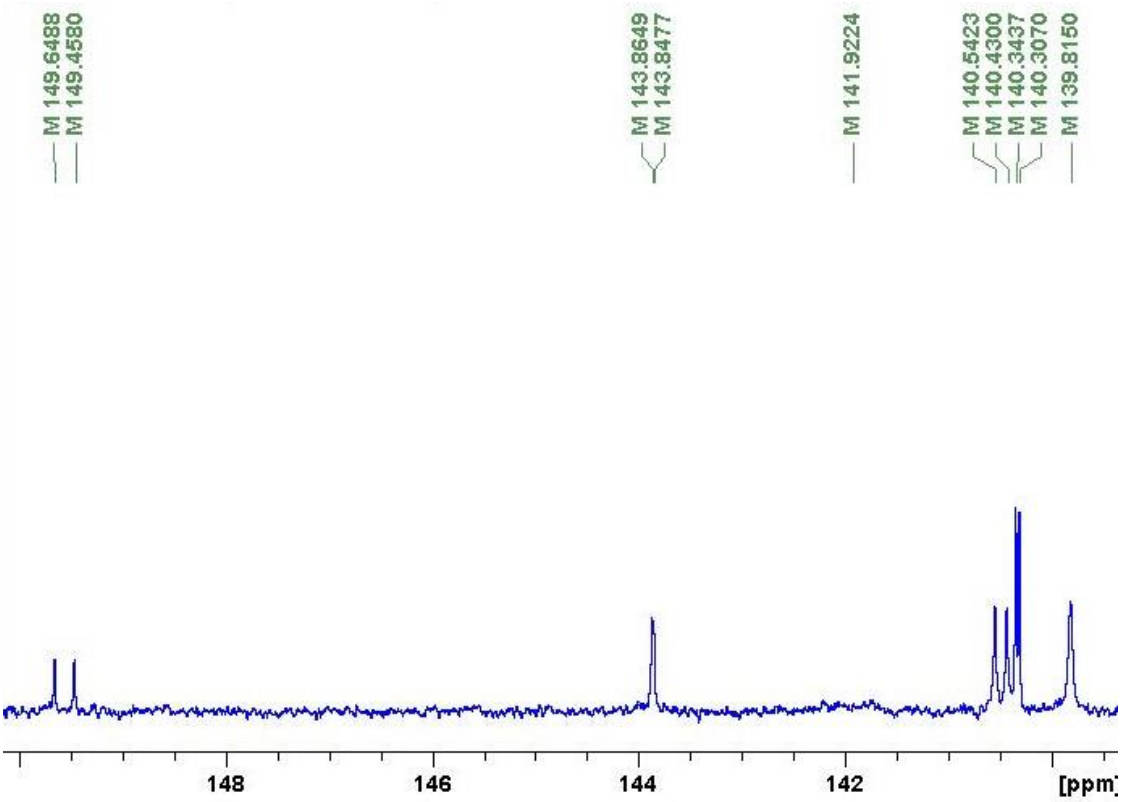


Figure 62. $^{11}B\{^{1}H\}$ NMR spectrum of **7 (X = NTf_2)** (96 MHz, 20 °C) in CD_2Cl_2

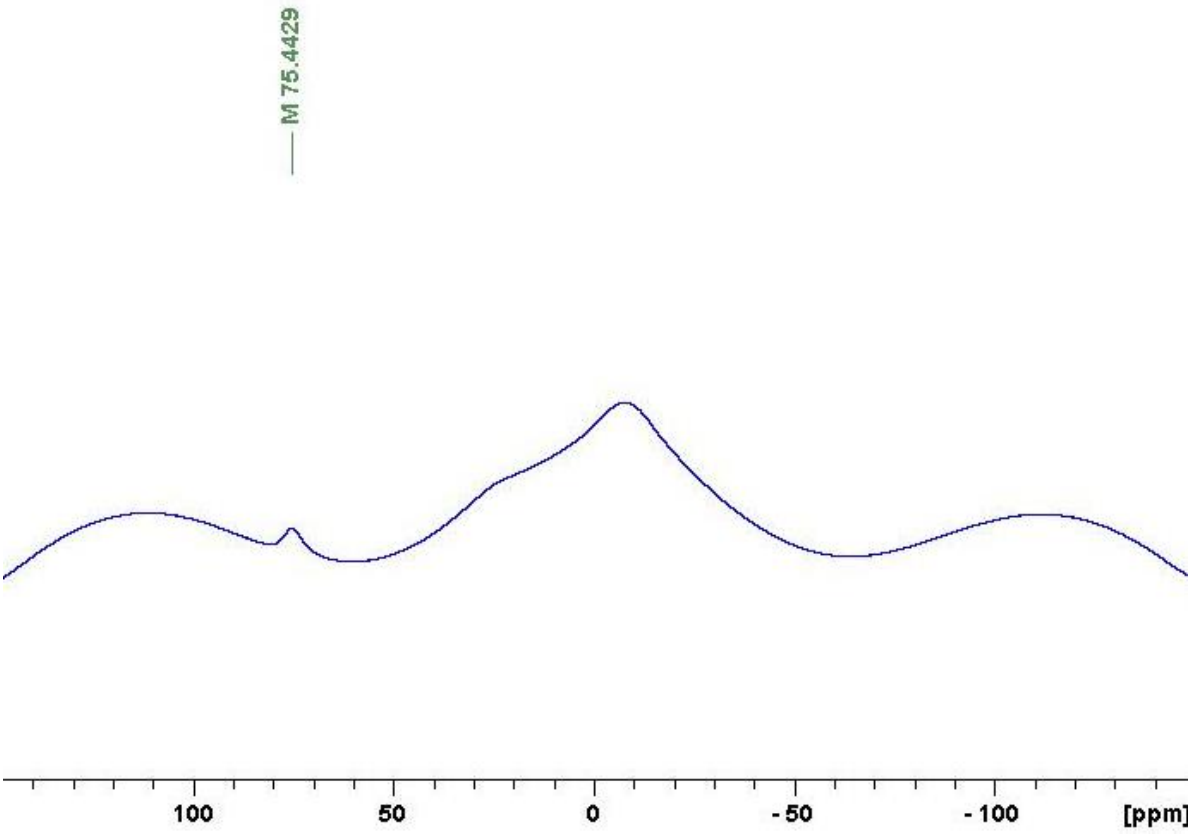
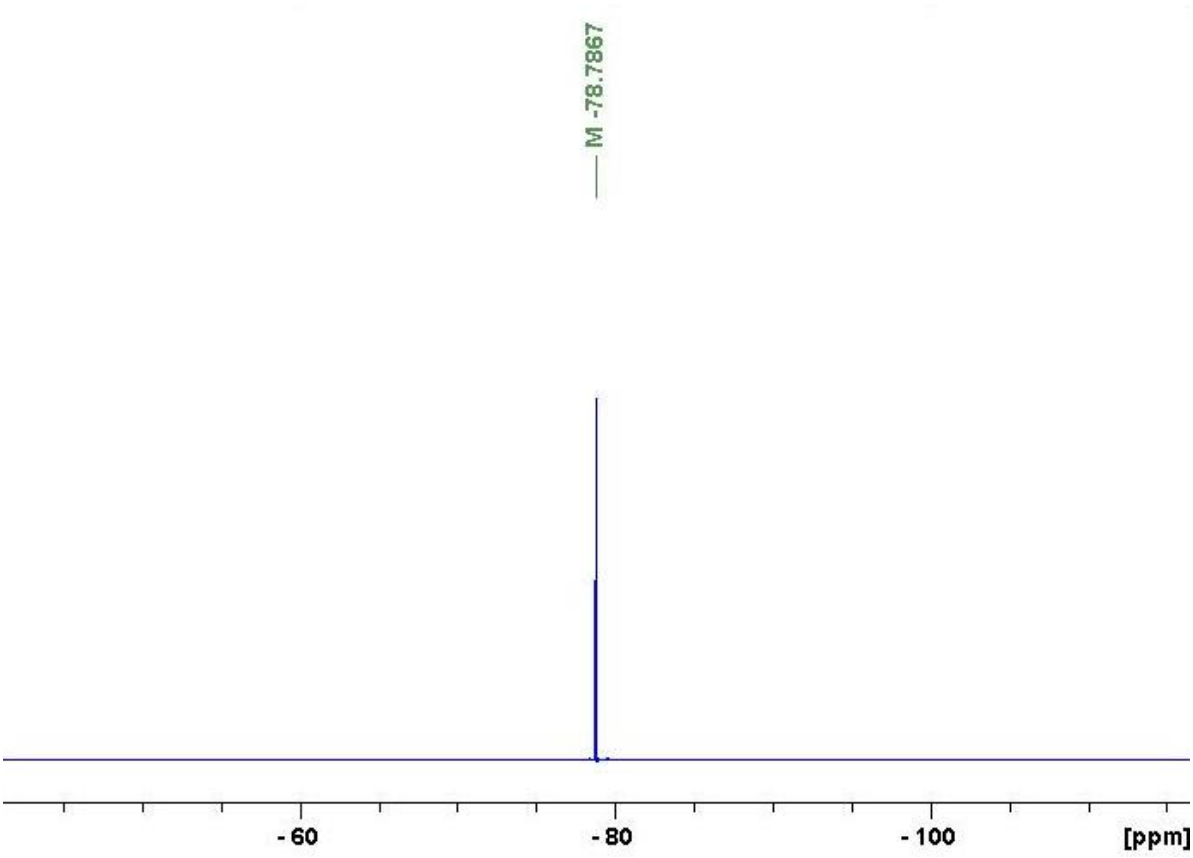


Figure 63. $^{19}F\{^{1}H\}$ NMR spectrum of **7 (X = NTf_2)** (282 MHz, 20 °C) in $CDCl_3$



[*i*Pr$_2$P-Naphth-BMes][GaBr$_4$] 7 (X = GaBr$_4$)

Figure 64. $^{31}P\{^1H\}$ NMR spectrum of **7 (X = GaBr$_4$)** (203 MHz, 20 °C) in CD_2Cl_2

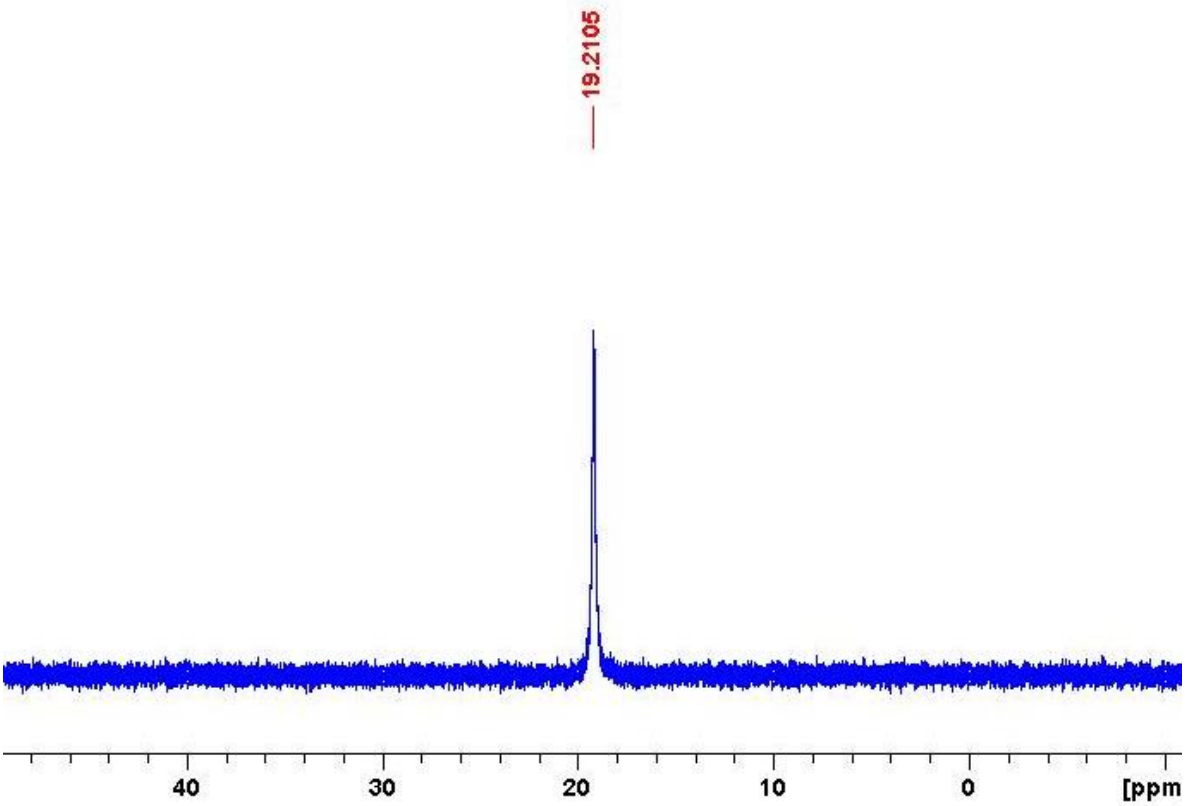


Figure 65. ^1H NMR spectrum of **7 (X = GaBr$_4$)** (500 MHz, 20 °C) in CD_2Cl_2

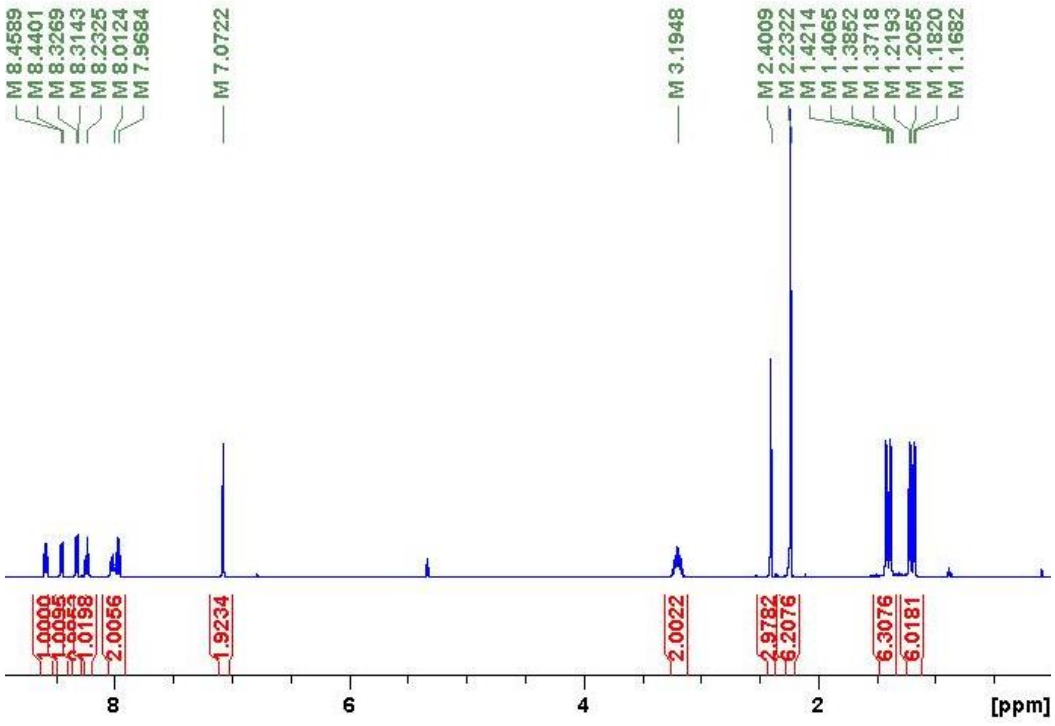


Figure 66. ^{1}H NMR spectrum of **7 (X = $GaBr_4$)** (500 MHz, 20 °C) in CD_2Cl_2; aliphatic region

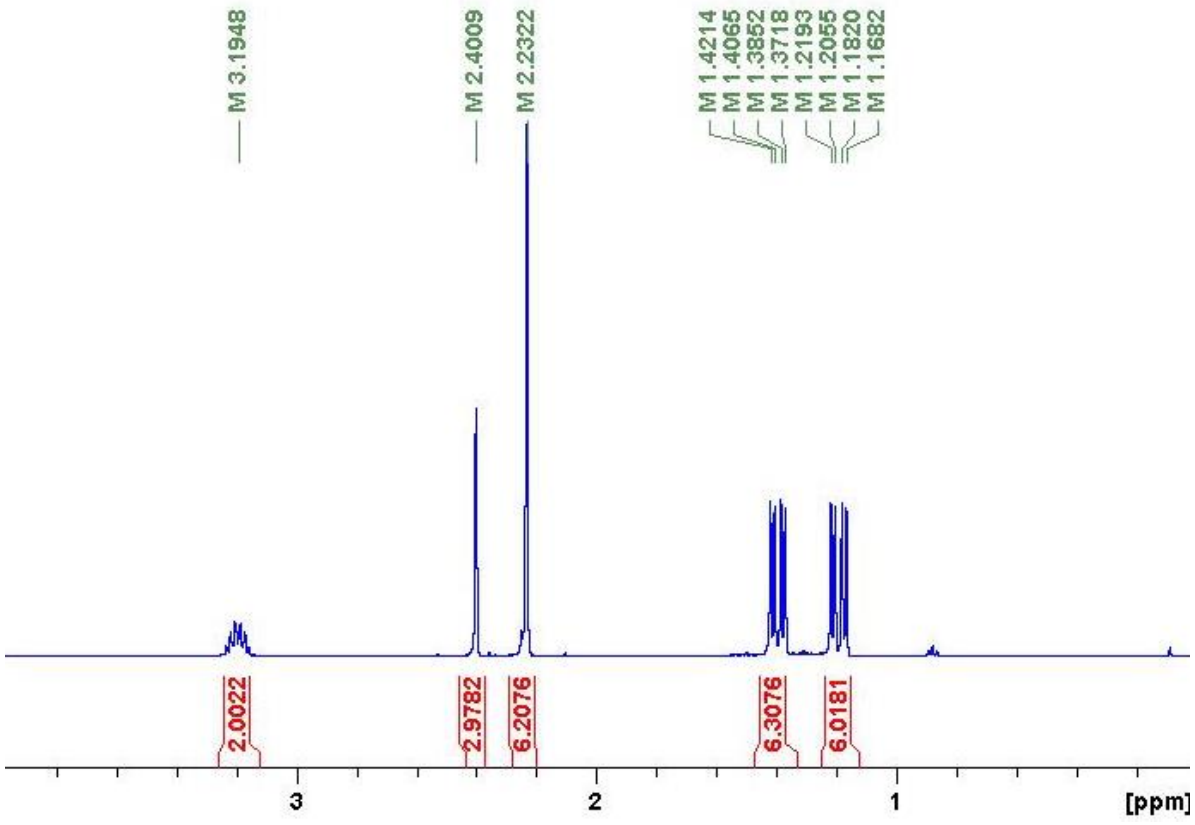


Figure 67. ^{1}H NMR spectrum of **7 (X = $GaBr_4$)** (500 MHz, 20 °C) in CD_2Cl_2; aromatic region

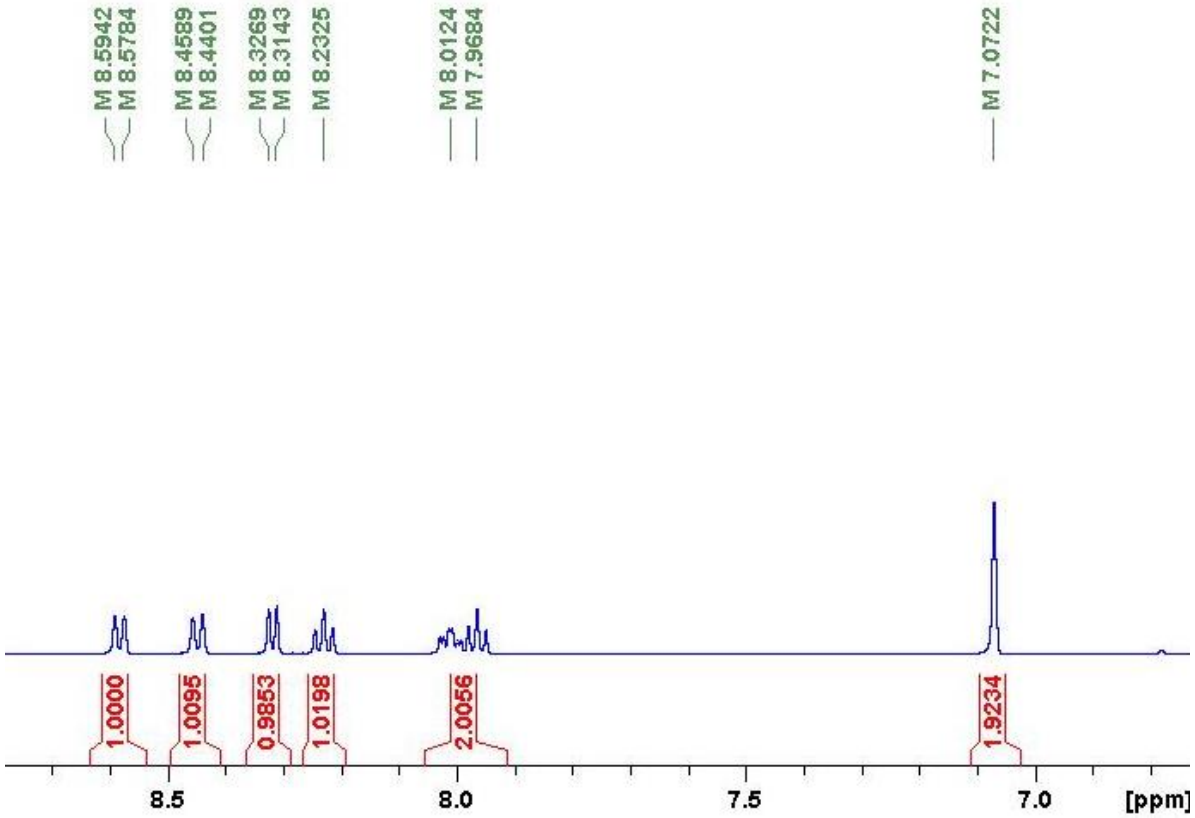


Figure 68. $^{13}C\{^{1}H\}$ NMR spectrum of **7 (X = $GaBr_4$)** (126 MHz, 20 °C) in CD_2Cl_2

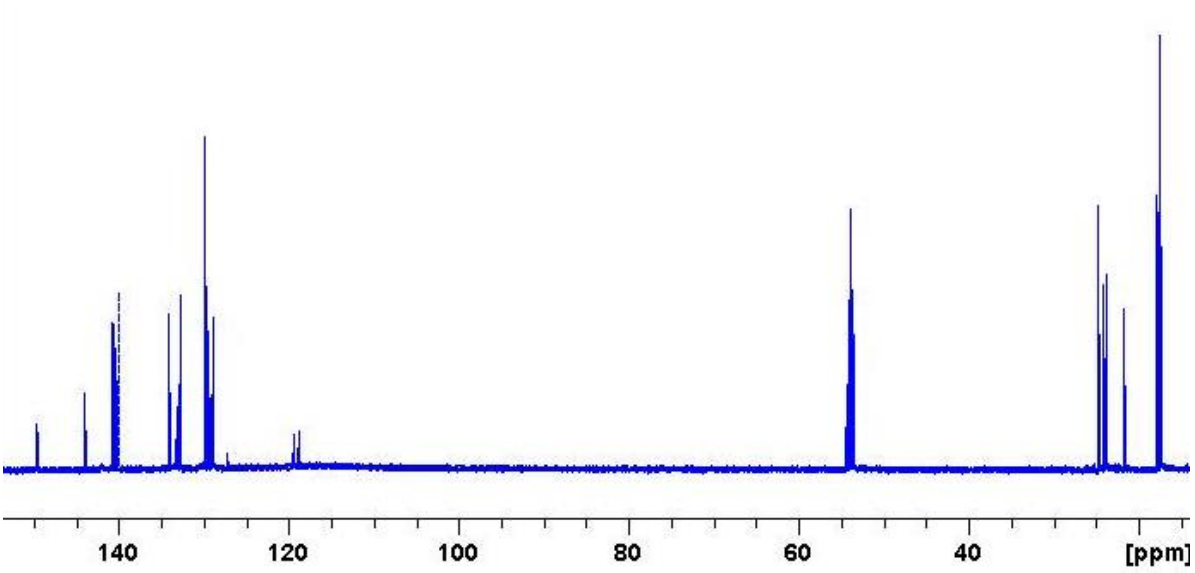


Figure 69. $^{13}C\{^{1}H\}$ NMR spectrum of **7 (X = $GaBr_4$)** (126 MHz, 20 °C) in CD_2Cl_2; aliphatic region

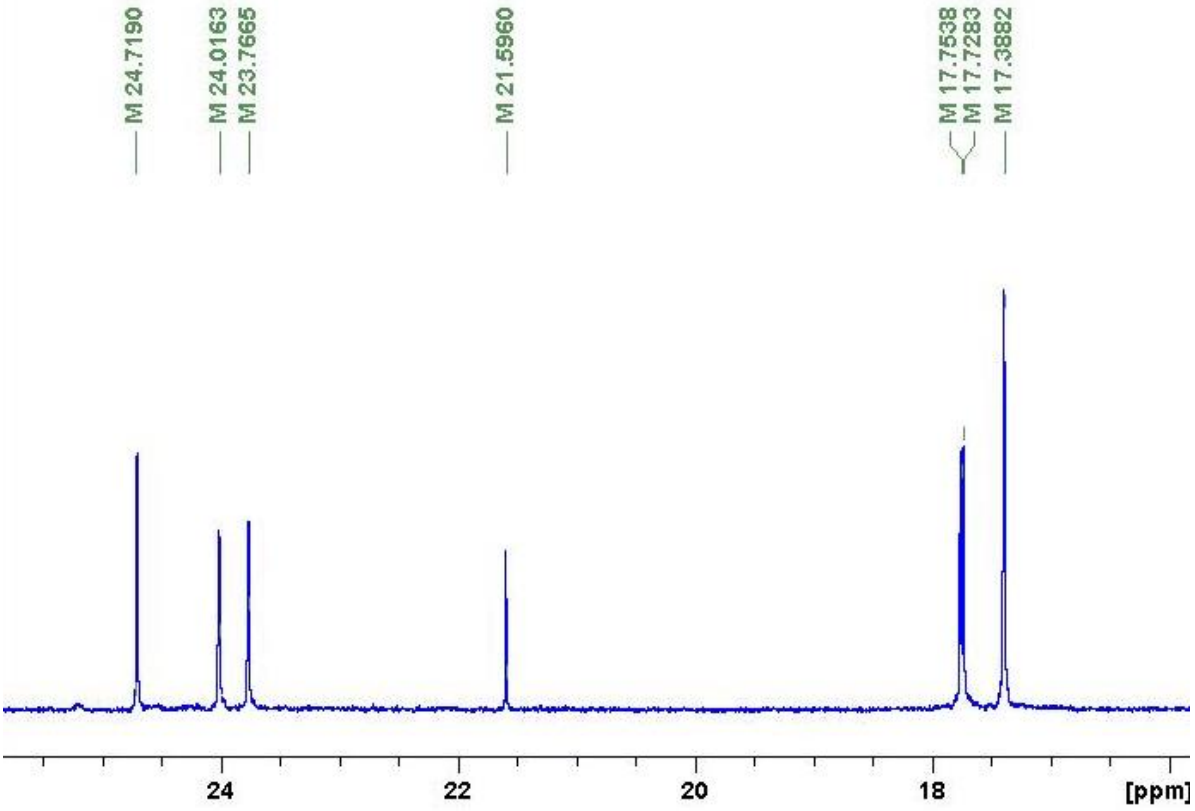


Figure 70. $^{13}C\{^{1}H\}$ NMR spectrum of **7 (X = $GaBr_4$)** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 1

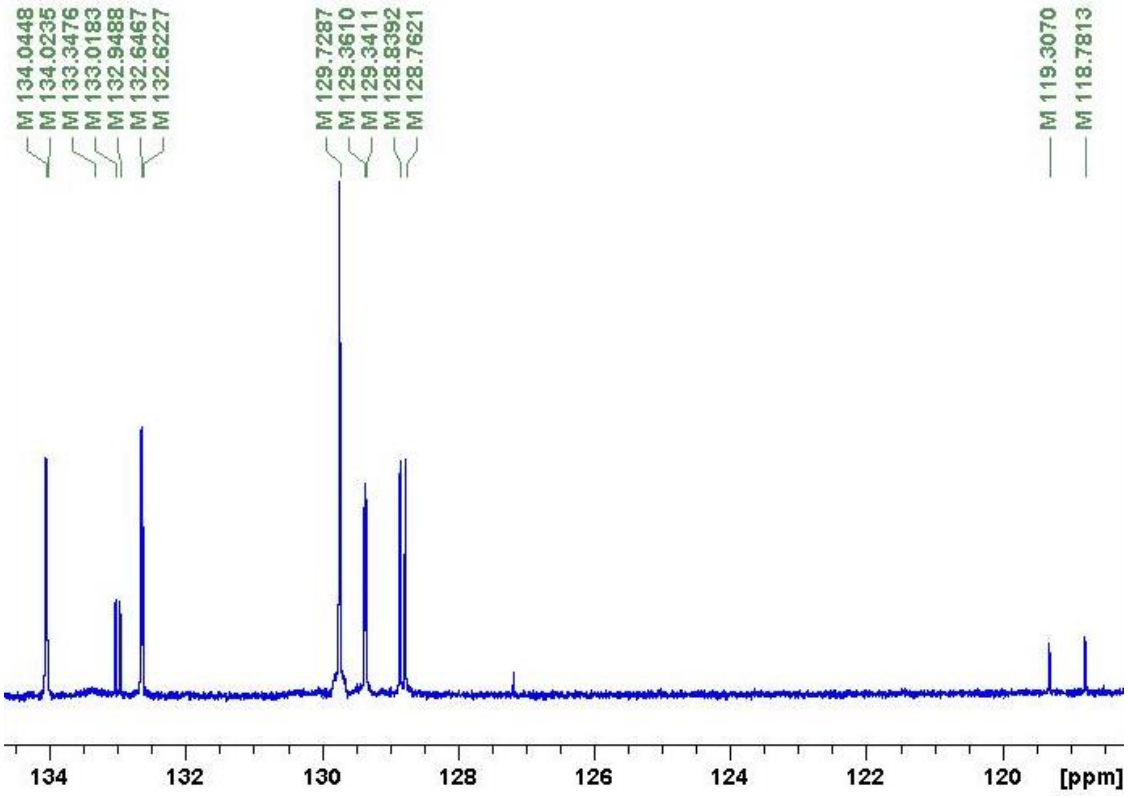


Figure 71. $^{13}C\{^{1}H\}$ NMR spectrum of **7 (X = $GaBr_4$)** (126 MHz, 20 °C) in CD_2Cl_2; aromatic region 2

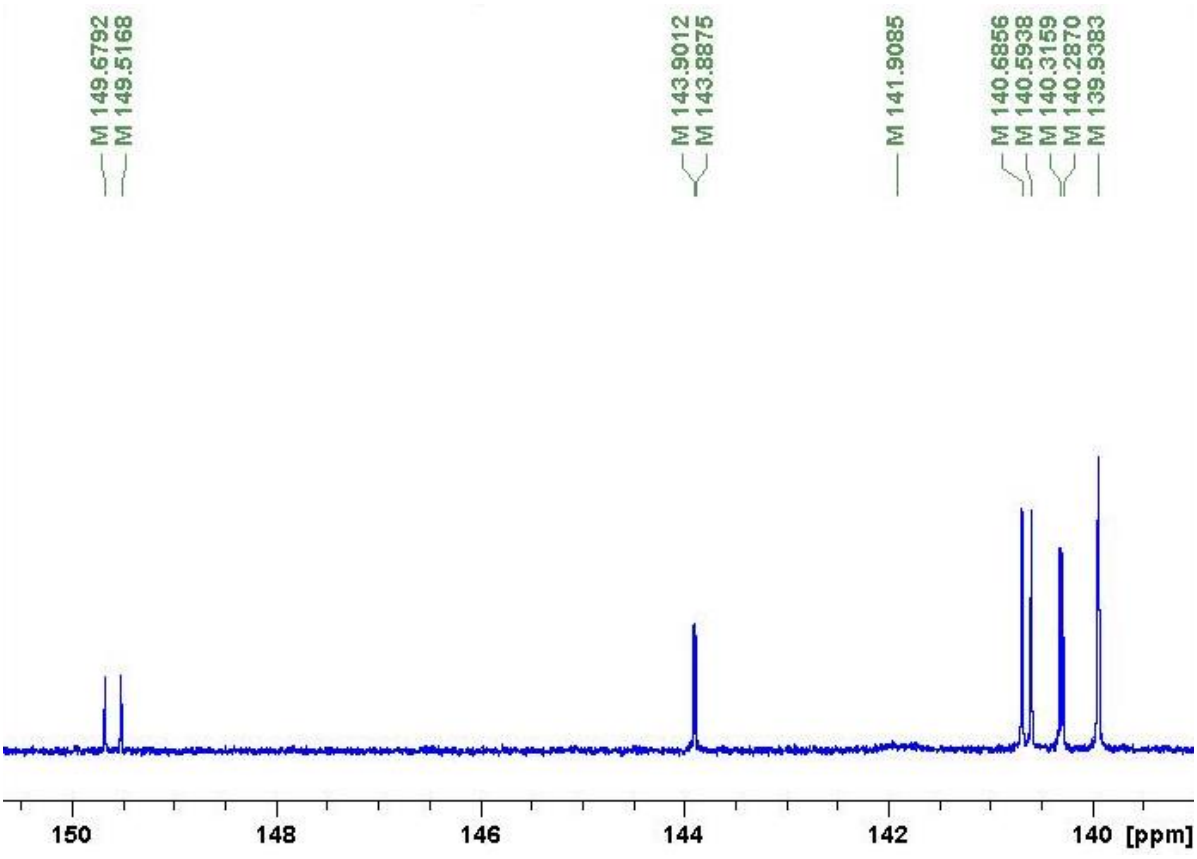
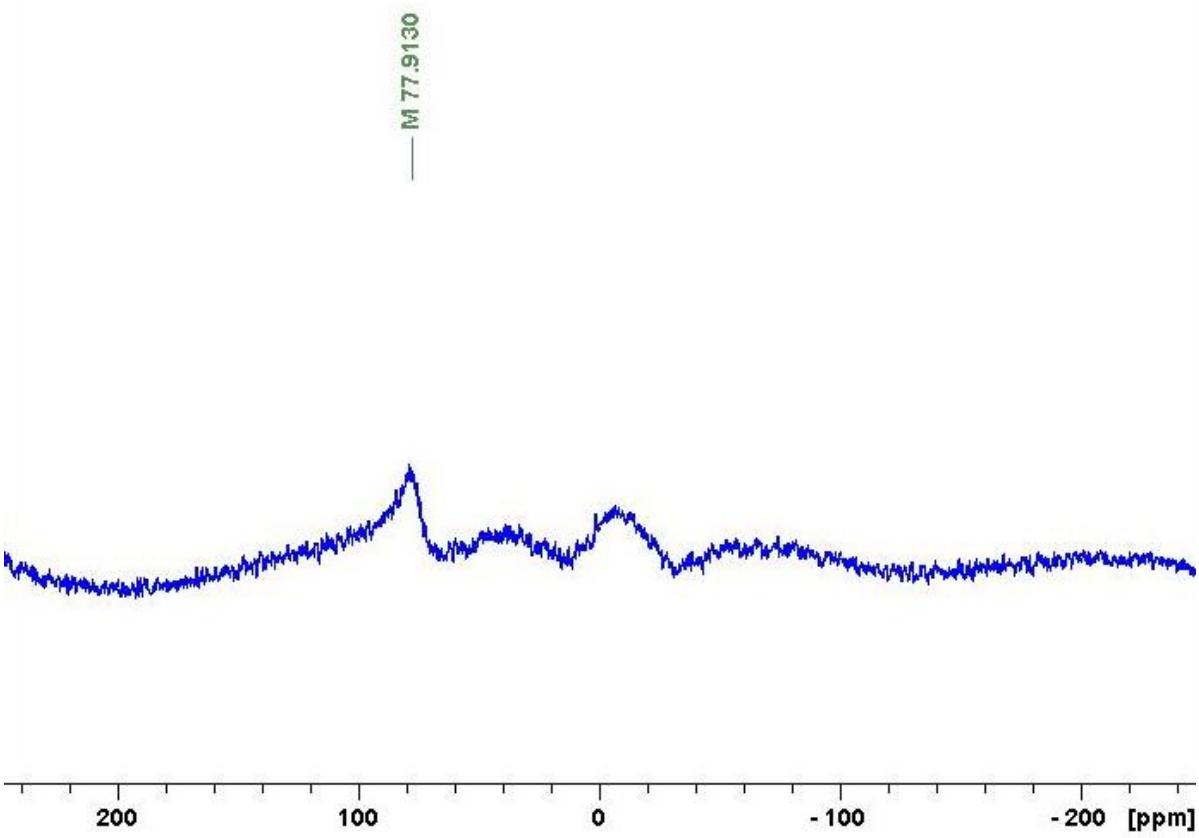
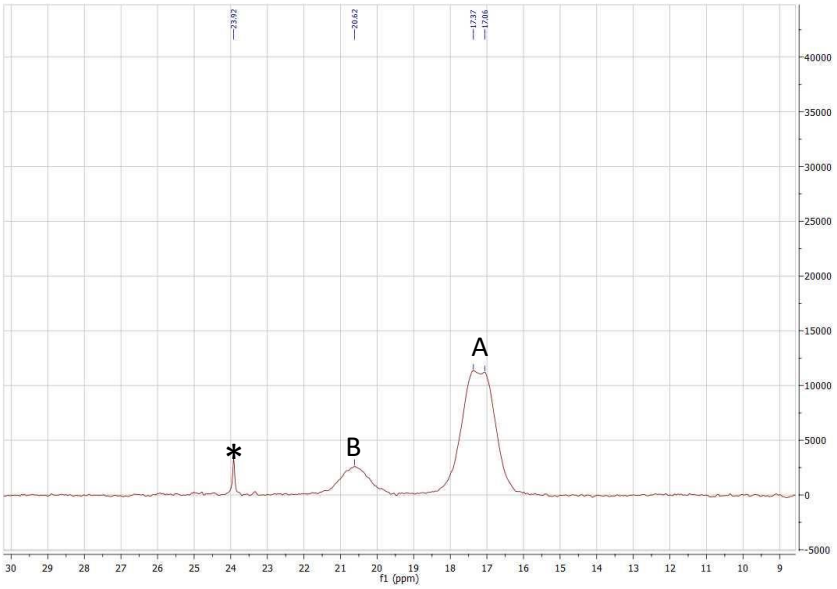


Figure 72. $^{11}B\{^{1}H\}$ NMR spectrum of **7 (X = $GaBr_4$)** (96 MHz, 20 °C) in CD_2Cl_2



*i*Pr$_2$P-Naphth-B(H)(NTf$_2$) 8 and [8]$_2$

Figure 73. $^{31}P\{^1H\}$ NMR spectrum of compound **8** and **[8]$_2$** (202 MHz, 20 °C) in CD_2Cl_2

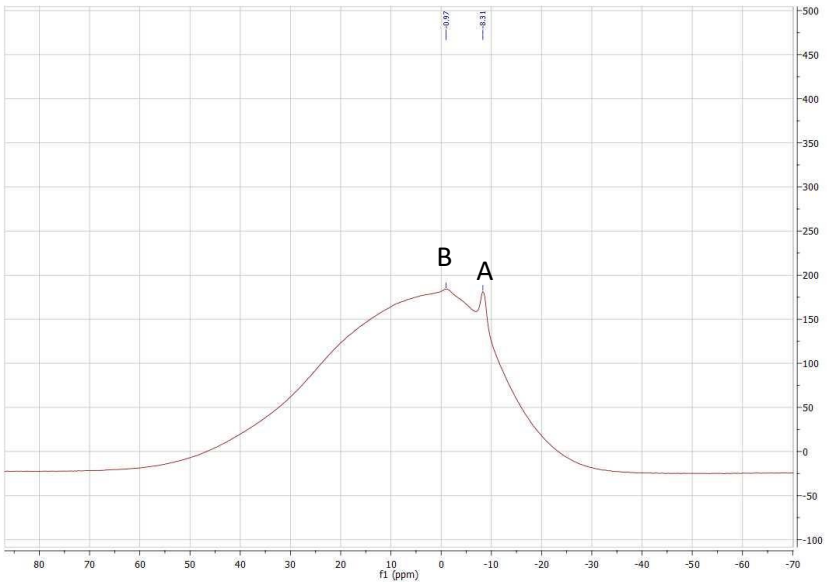


[A]Signal attributed to **8**

[B]Signal attributed to **[8]$_2$**

*Non-attributed impurity

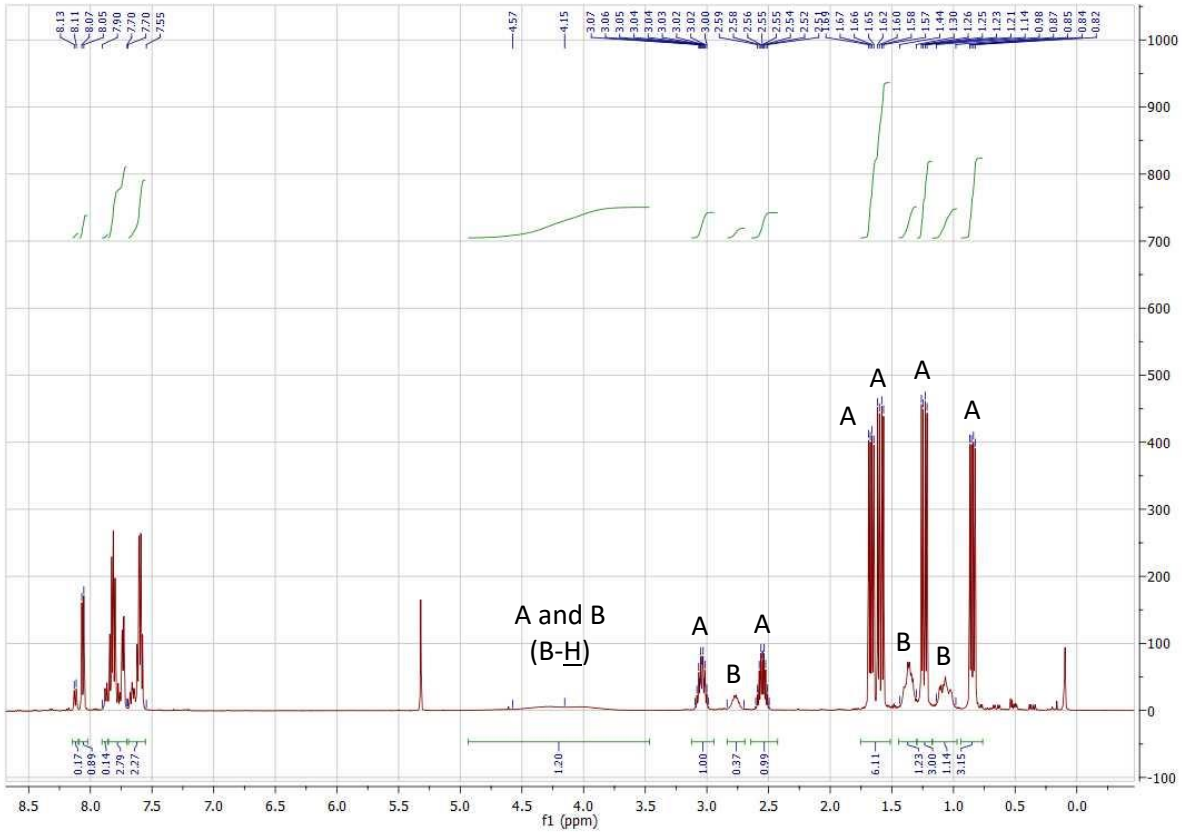
Figure 74. $^{11}B\{^1H\}$ NMR spectrum of compound **8** and **[8]$_2$** (160 MHz, 20 °C) in CD_2Cl_2



[A]Signal attributed to **8**

[B]Signal attributed to **[8]$_2$**

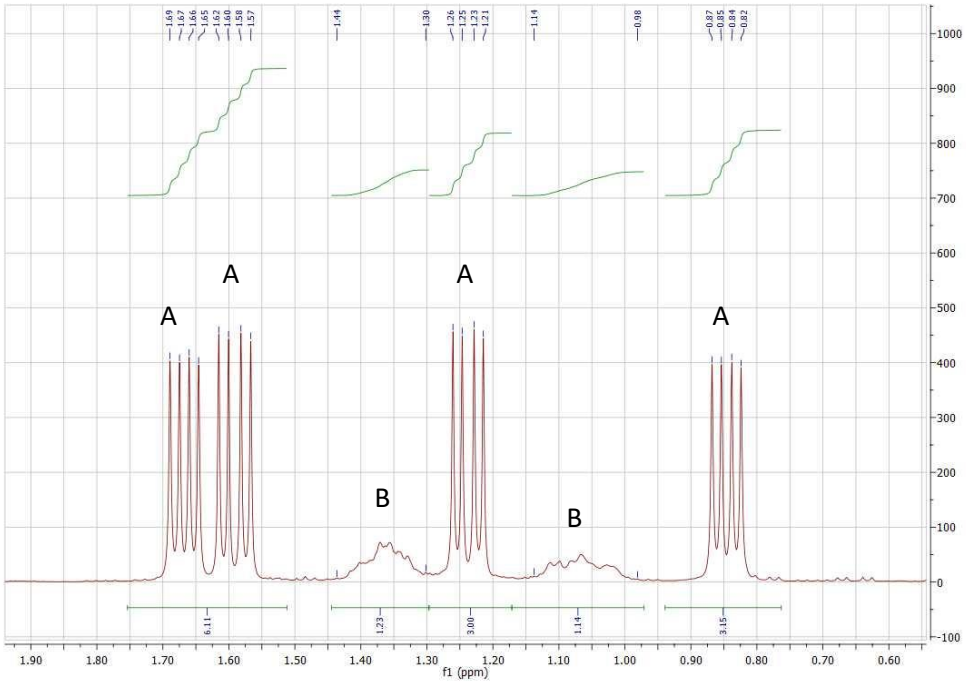
Figure 75. ^{1}H NMR spectrum of compound **8** and **[8]$_2$** (500 MHz, 20 °C) in CD_2Cl_2



[A]Signal attributed to **8**

[B]Signal attributed to **[8]$_2$**

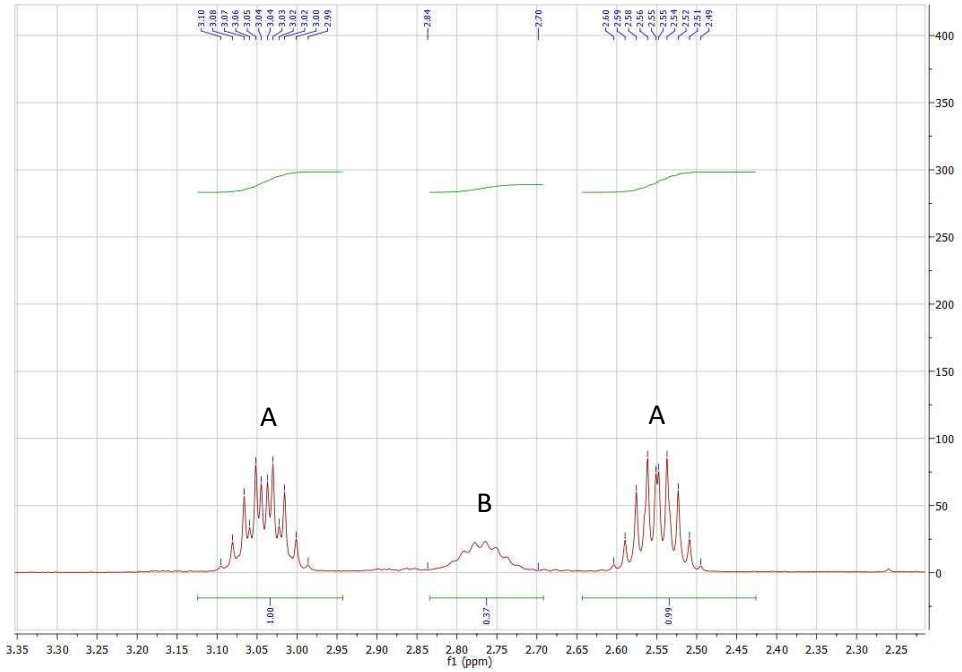
Figure 76. ^{1}H NMR spectrum of compound **8** and **[8]$_2$** (500 MHz, 20 °C) in CD_2Cl_2: zoom 1



[A]Signal attributed to **8:** CH_{3iPr}

[B]Signal attributed to **[8]$_2$:** CH_{3iPr}

Figure 77. ^{1}H NMR spectrum of compound **8** and **[8]$_2$** (500 MHz, 20 °C) in CD_2Cl_2: zoom 2



[A]Signal attributed to **8:** CH_{iPr}

[B]Signal attributed to **[8]$_2$:** CH_{iPr}

Figure 78. ^{1}H NMR spectrum of compound **8** and **[8]$_2$** (500 MHz, 20 °C) in CD_2Cl_2: zoom 3; B-H signals

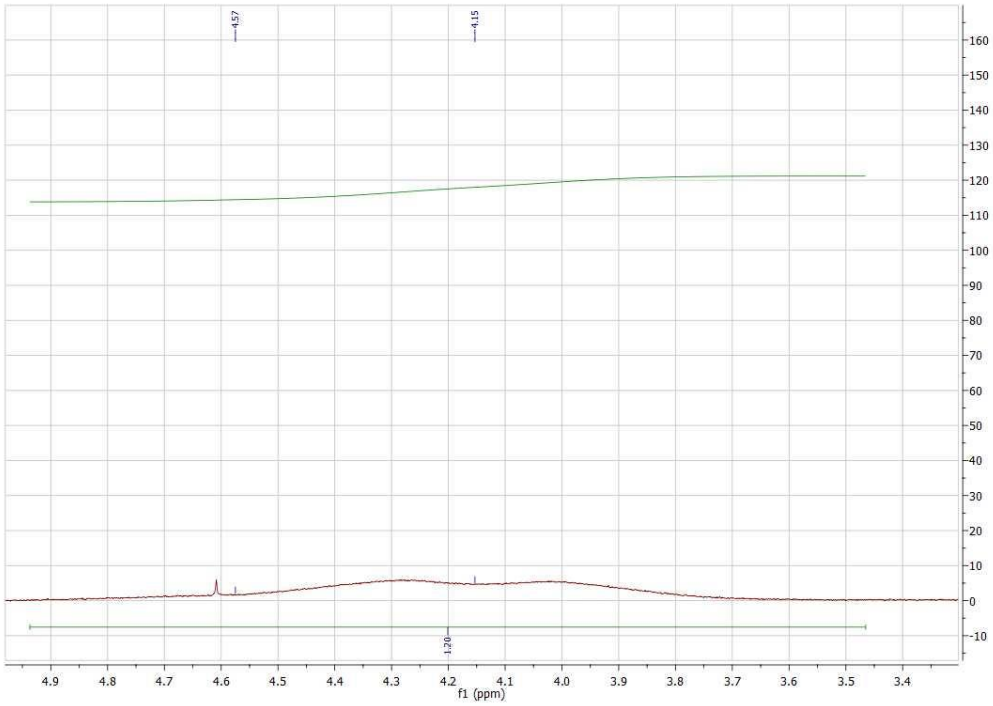
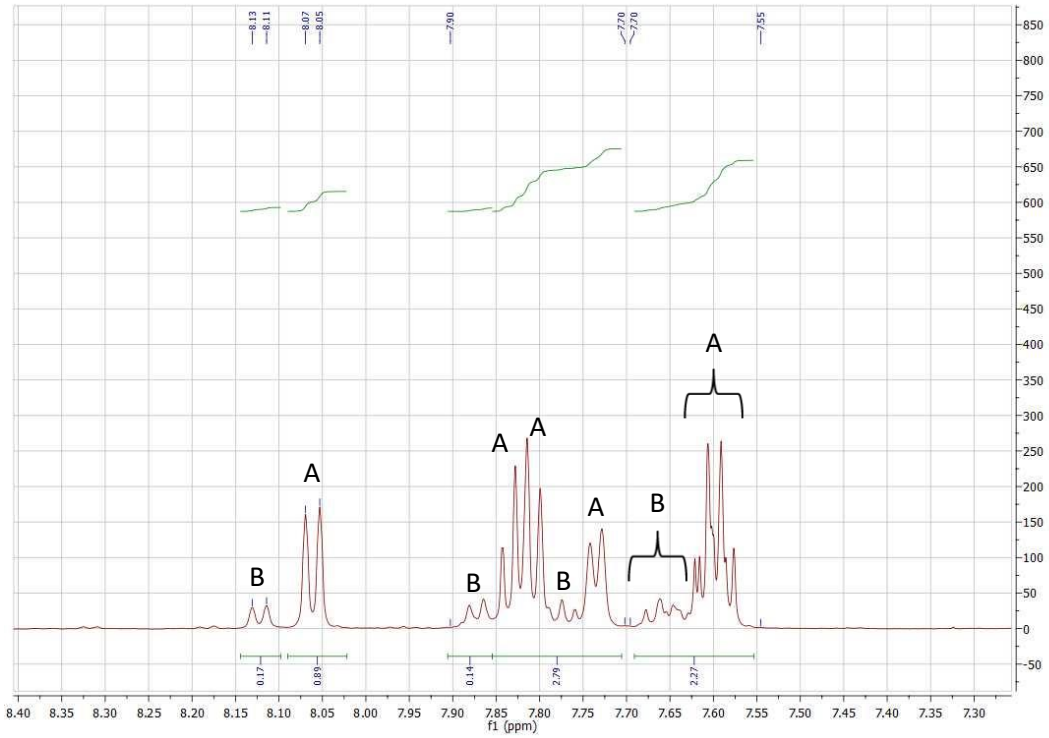


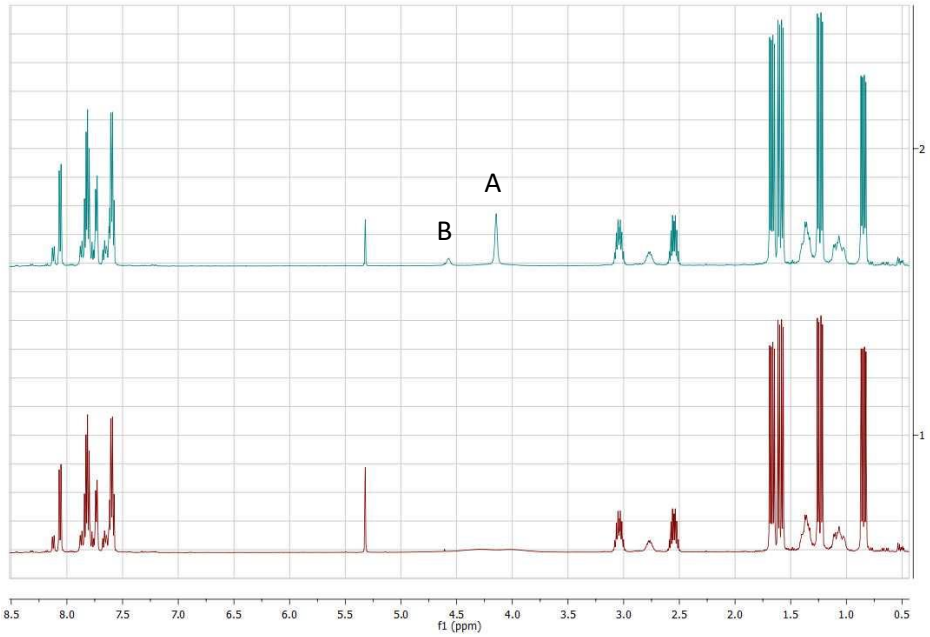
Figure 79. ^{1}H NMR spectrum of compound **8** and **[8]$_2$** (500 MHz, 20 °C) in CD_2Cl_2: zoom 4



[A]Signal attributed to **8:** CH_{Naphth}

[B]Signal attributed to **[8]$_2$:** CH_{Naphth}

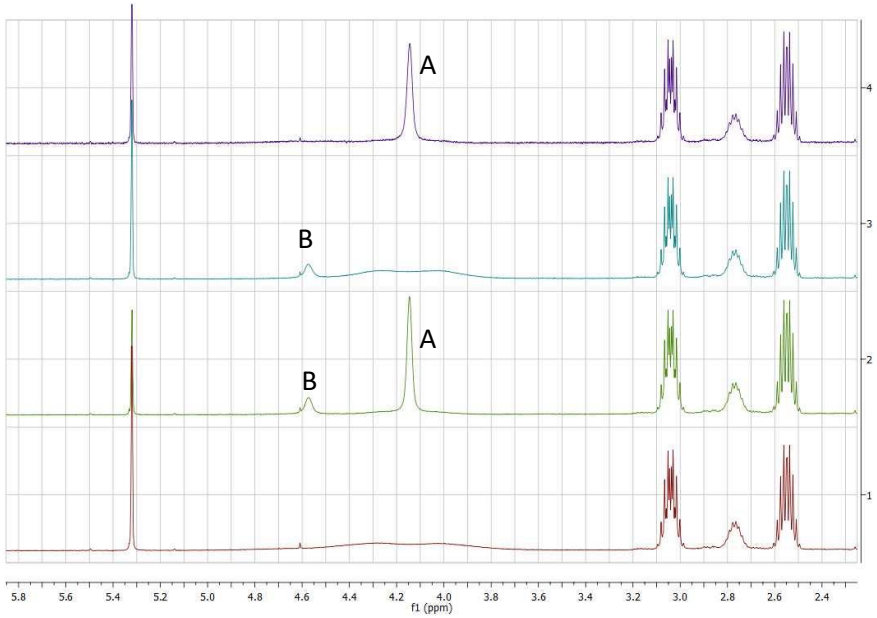
Figure 80. Stacked ^{1}H (bottom) and $^{1}H\{^{11}B\}$ (top) NMR spectra of compound **8** and **[8]$_2$** (500 MHz, 20 °C) in CD_2Cl_2



[A]Signal attributed to **8:** B-H signal

[B]Signal attributed to **[8]$_2$:** B-H signal

Figure 81. From bottom to top: ^{1}H, $^{1}H\{^{11}B\}$ bb, $^{1}H\{^{11}B\}$ -1.2 ppm, $^{1}H\{^{11}B\}$ -8.4 ppm, NMR spectra of compound **8** and **[8]$_2$** (500 MHz, 20 °C) in CD_2Cl_2



[A]Signal attributed to **8:** B-H signal

[B]Signal attributed to **[8]$_2$:** B-H signal

Figure 82. [1H, 1H] ROESY NMR spectrum of compound **8** and **[8]$_2$** (500 MHz, 20 °C) in CD_2Cl_2

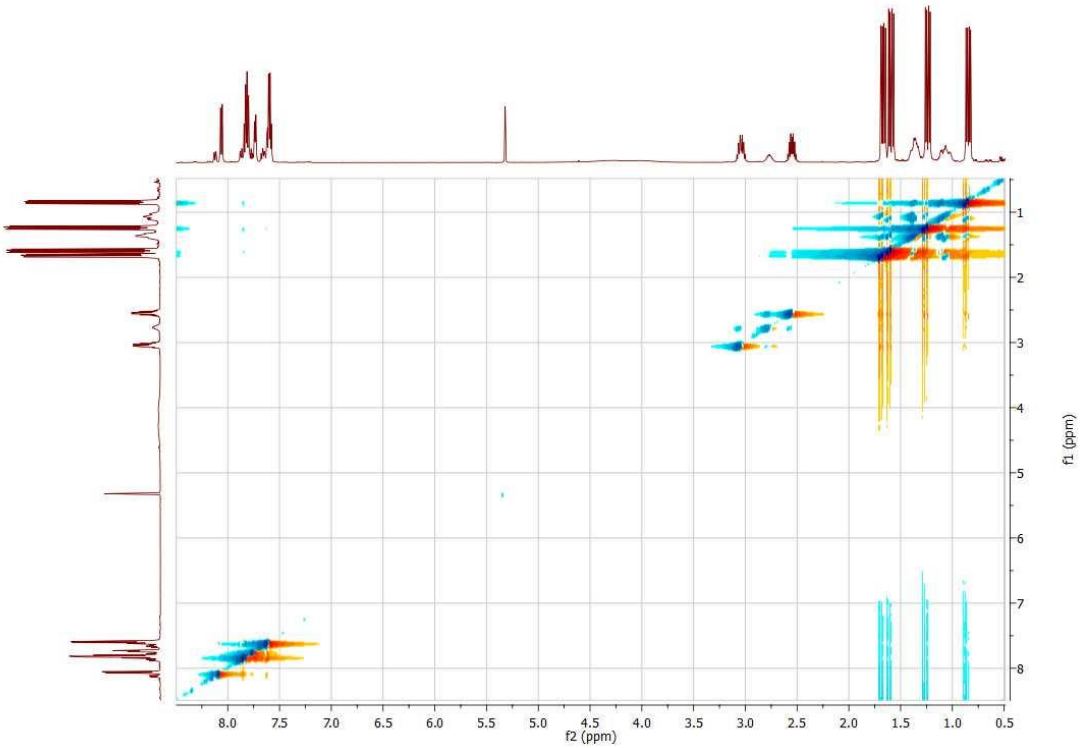
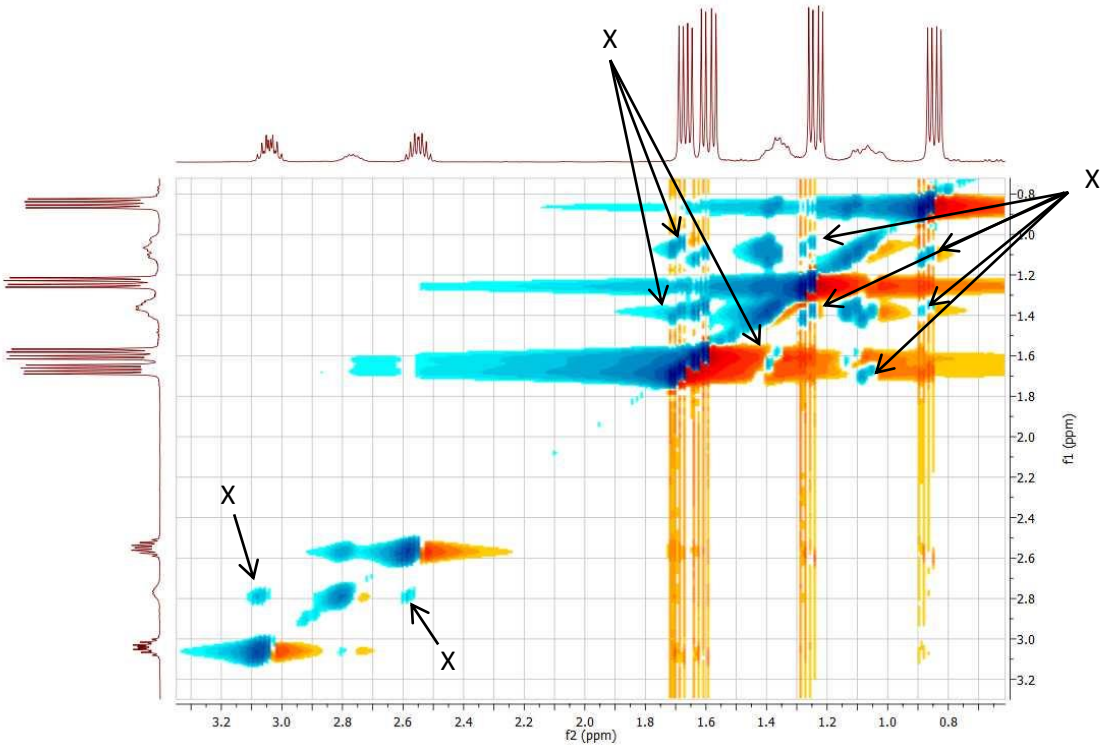


Figure 83. [1H, 1H] ROESY NMR spectrum of compound **8** and **[8]$_2$** (500 MHz, 20 °C) in CD_2Cl_2: zoom



[X]Exchange correlation spot between **8** and **[8]$_2$**

Figure 84. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8** and **[8]$_2$** (126 MHz, 20 °C) in CD_2Cl_2

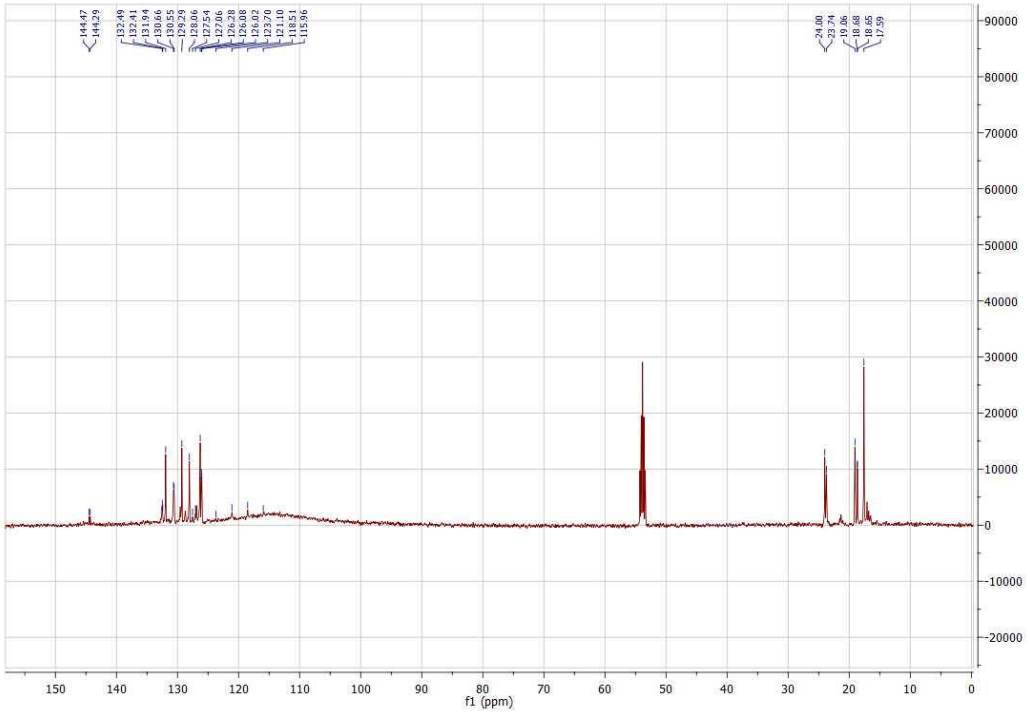
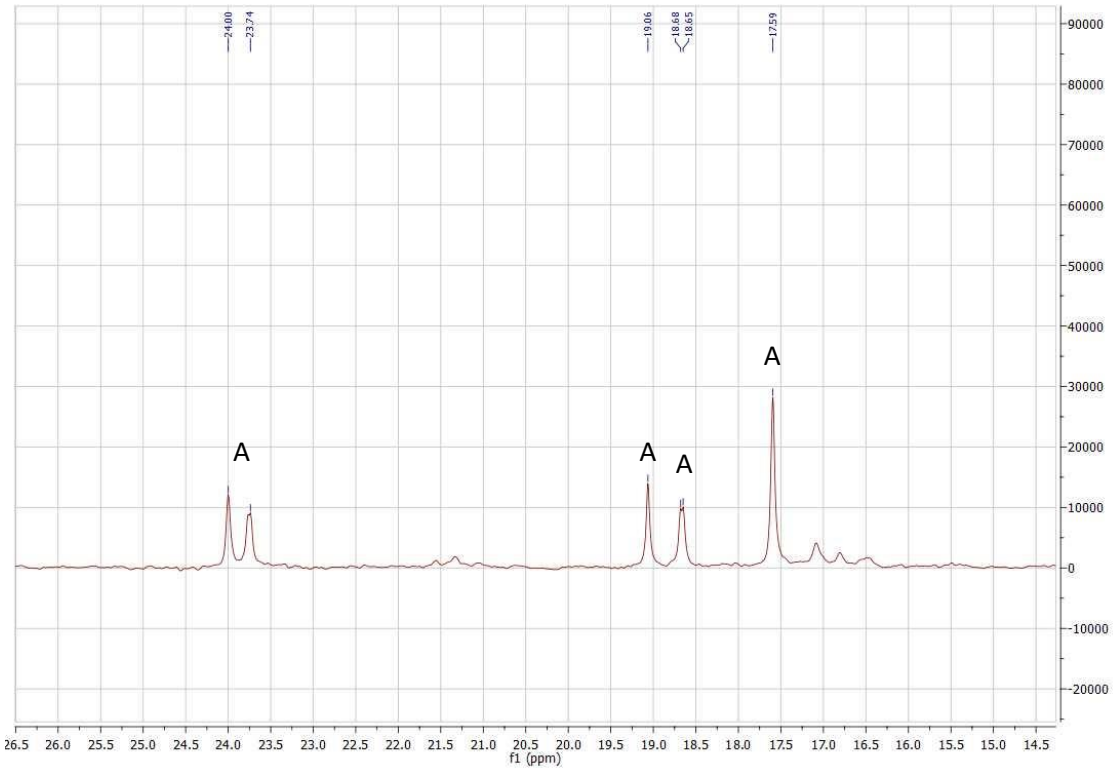
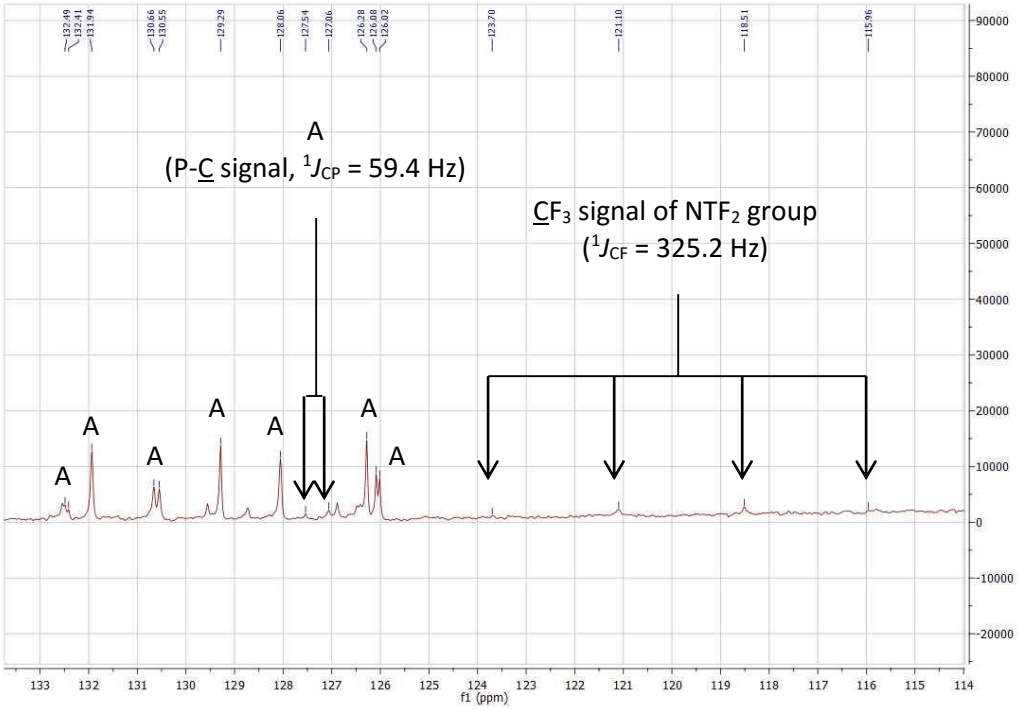


Figure 85. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8** and **[8]$_2$** (126 MHz, 20 °C) in CD_2Cl_2: zoom 1



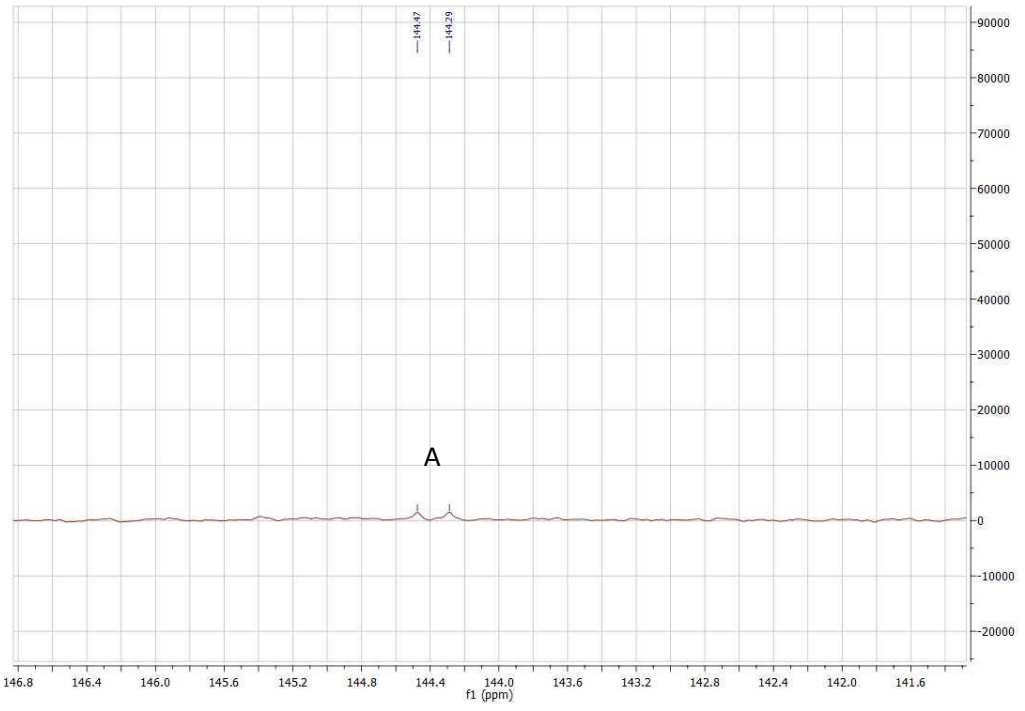
[A]Signal attributed to **8**

Figure 86. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8** and **[8]$_2$** (126 MHz, 20 °C) in CD_2Cl_2: zoom 2



[A]Signal attributed to **8**

Figure 87. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8** and **[8]$_2$** (126 MHz, 20 °C) in CD_2Cl_2: zoom 3



[A]Signal attributed to **8**

Figure 88. Stacked $^{13}C\{^{1}H\}$ (bottom) and $^{13}C\{^{1}H,^{31}P\}$ (top) NMR spectra of compound **8** and **[8]$_2$** (126 MHz, 20 °C) in CD_2Cl_2: zoom 1

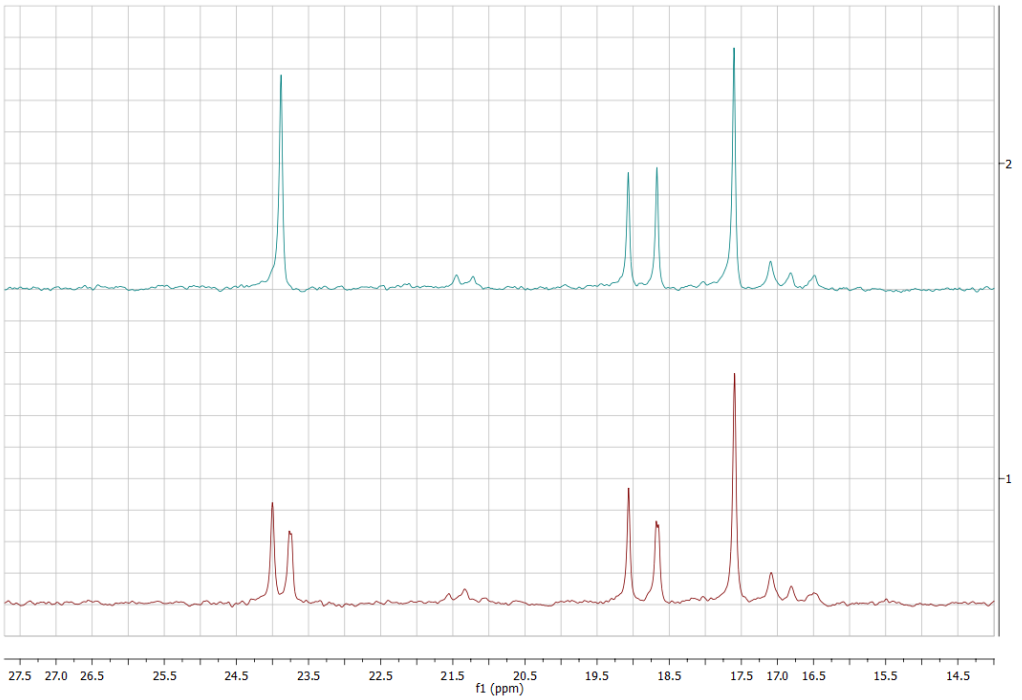


Figure 89. Stacked $^{13}C\{^{1}H\}$ (bottom) and $^{13}C\{^{1}H,^{31}P\}$ (top) NMR spectra of compound **8** and **[8]$_2$** (126 MHz, 20 °C) in CD_2Cl_2: zoom 2

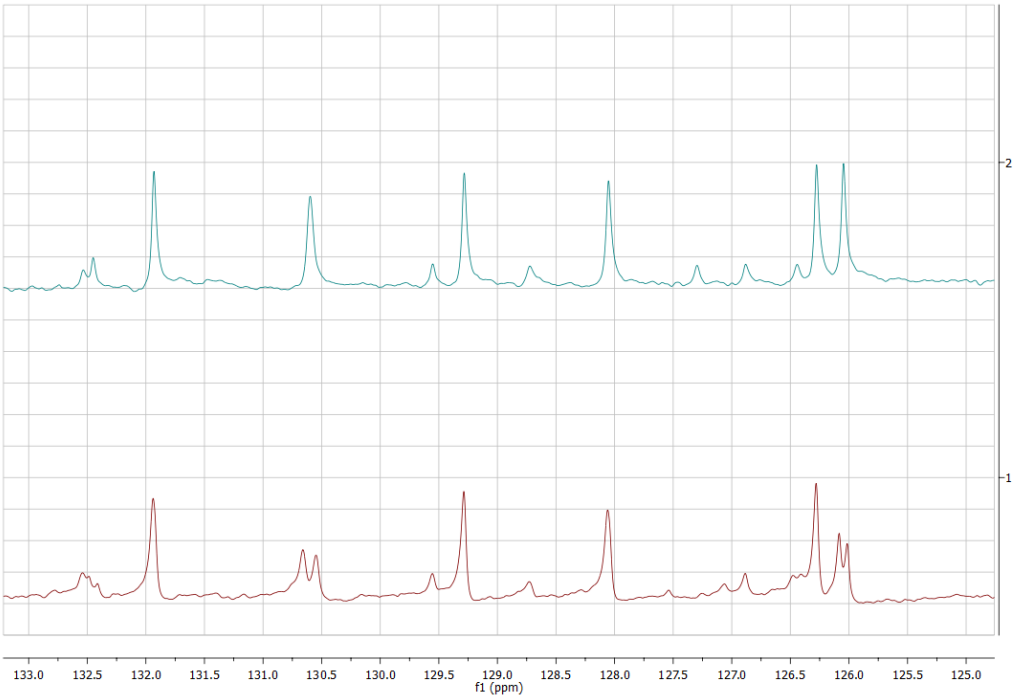


Figure 90. Stacked $^{13}C\{^{1}H\}$ (bottom) and $^{13}C\{^{1}H,^{31}P\}$ (top) NMR spectra of compound **8** and **[8]$_2$** (126 MHz, 20 °C) in CD_2Cl_2: zoom 3

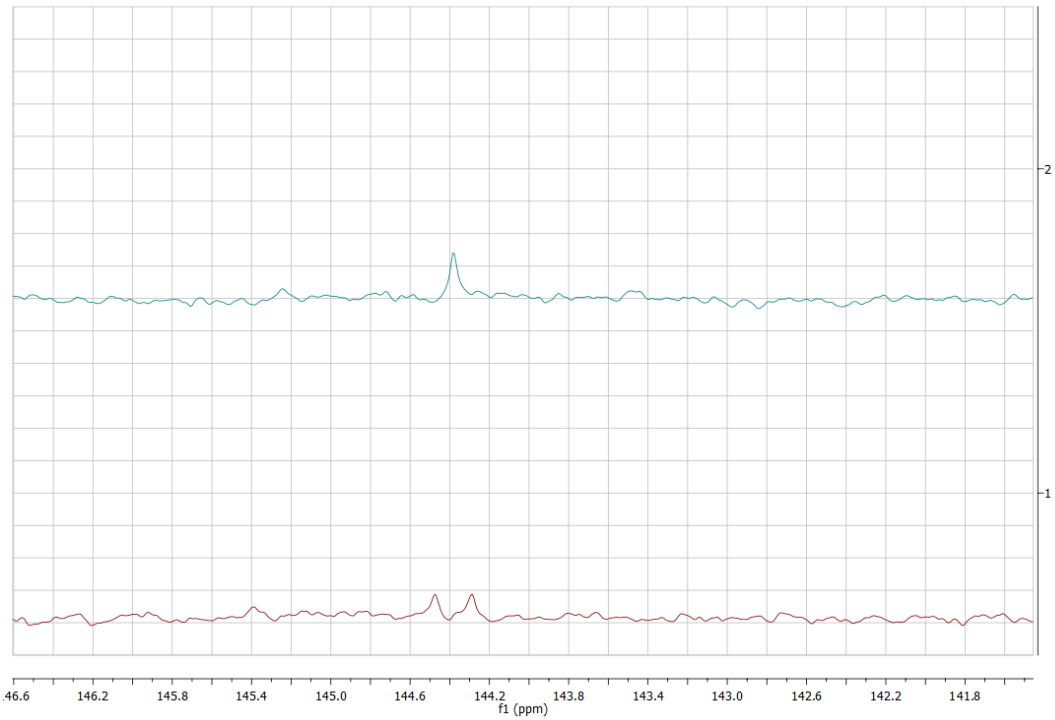


Figure 91. 2D [^{1}H, ^{13}C] HSQC NMR spectrum of compound **8** and **[8]$_2$** in CD_2Cl_2

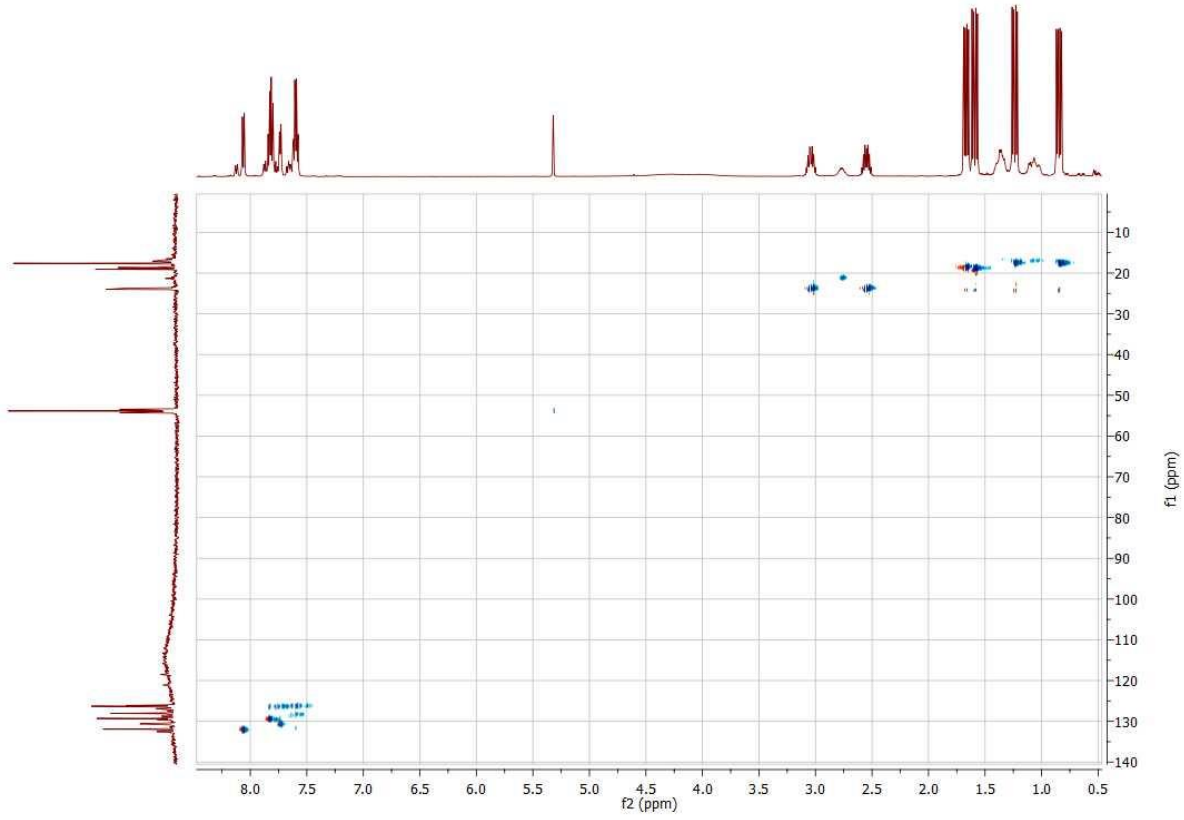


Figure 92. 2D [^{1}H, ^{13}C] HSQC NMR spectrum of compound **8** and **[8]$_2$** in CD_2Cl_2: zoom1

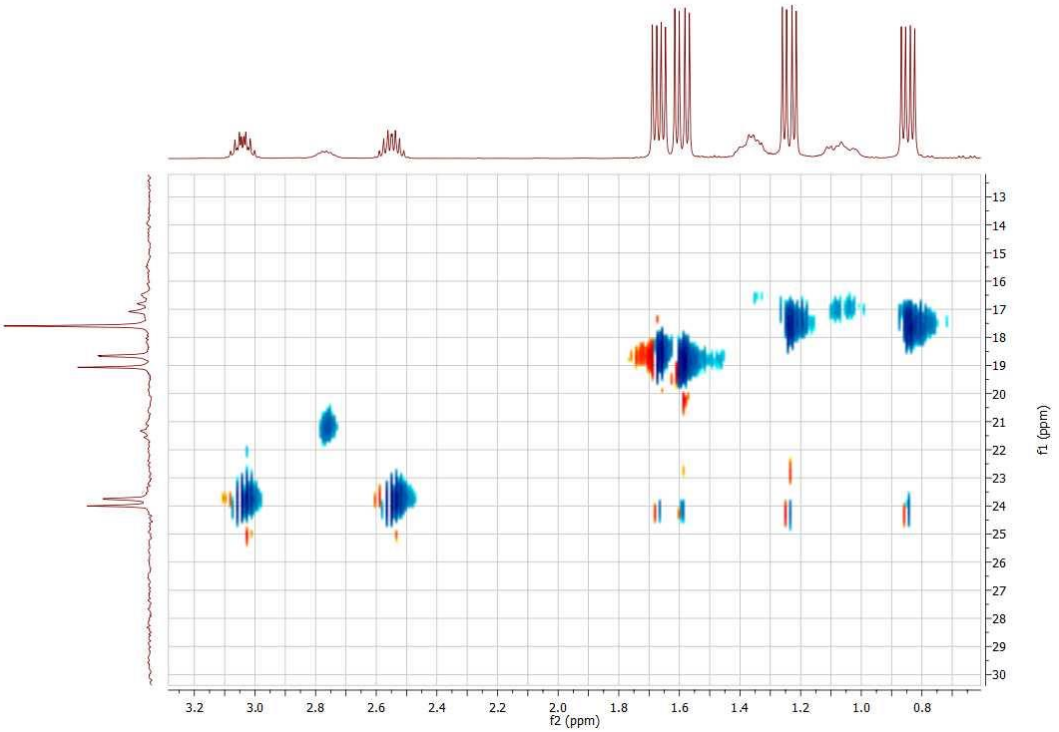


Figure 93. 2D [^{1}H, ^{13}C] HSQC NMR spectrum of compound **8** and **[8]$_2$** in CD_2Cl_2: zoom2

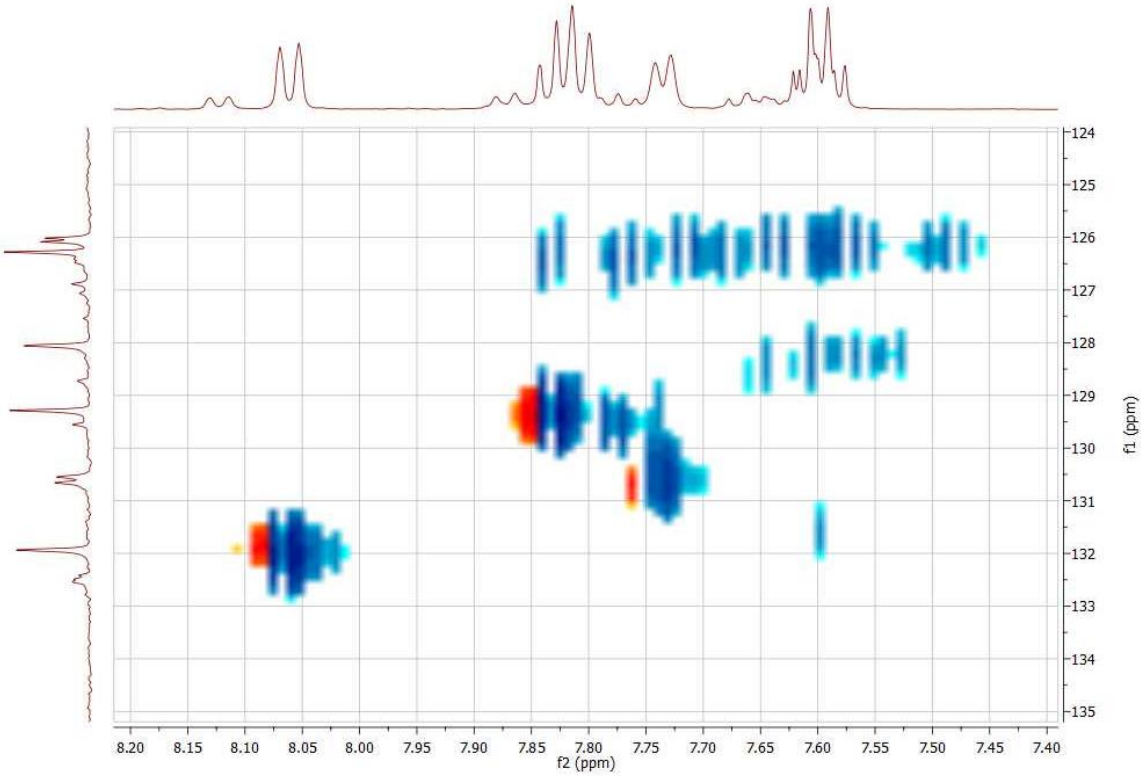


Figure 94. 2D [^{1}H, ^{13}C] HMBC NMR spectrum of compound **8** and **[8]$_2$** in CD_2Cl_2

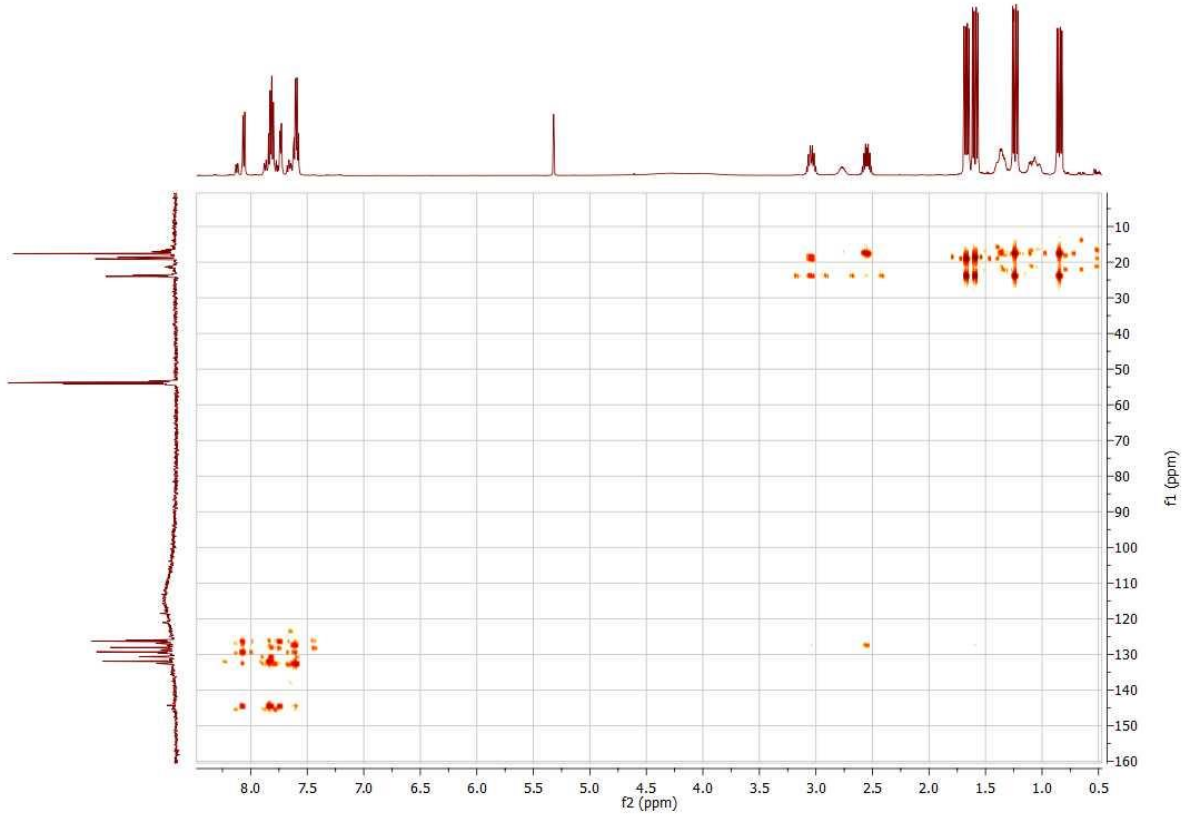


Figure 95. 2D [^{1}H, ^{13}C] HMBC NMR spectrum of compound **8** and **[8]$_2$** in CD_2Cl_2: zoom1

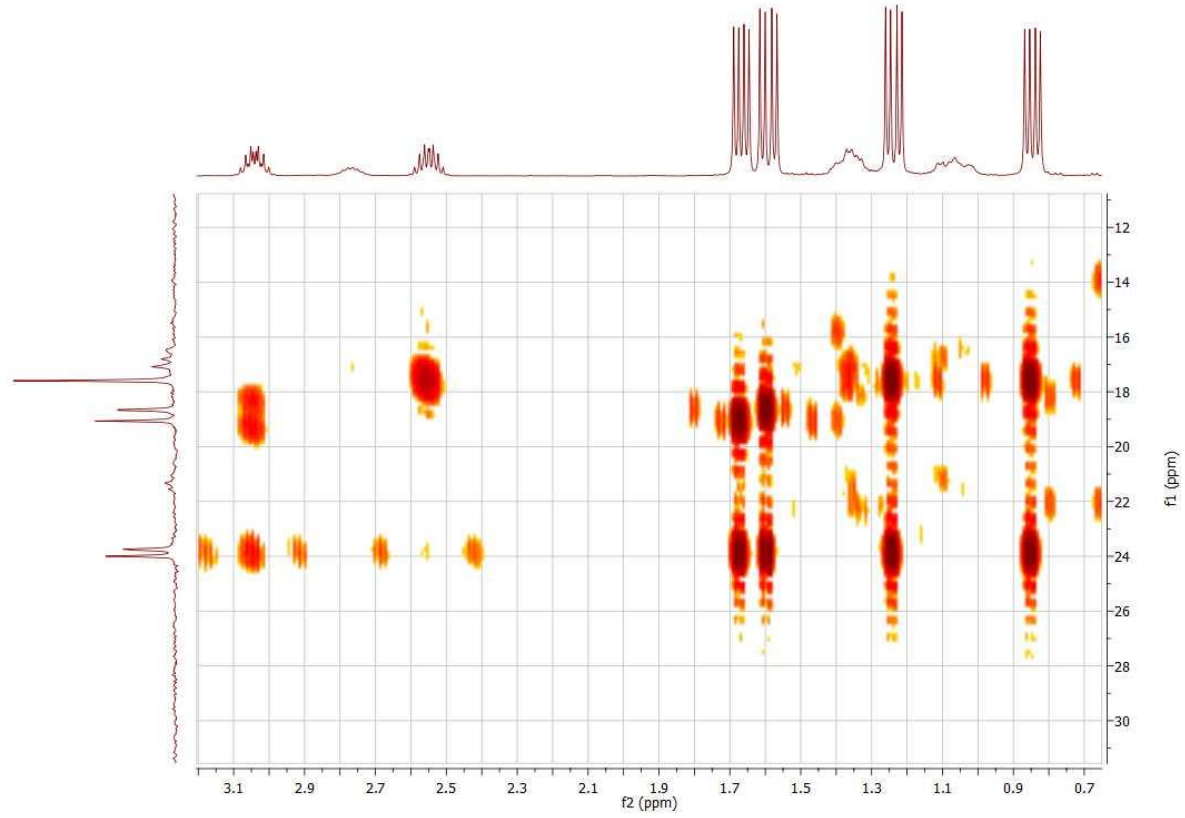
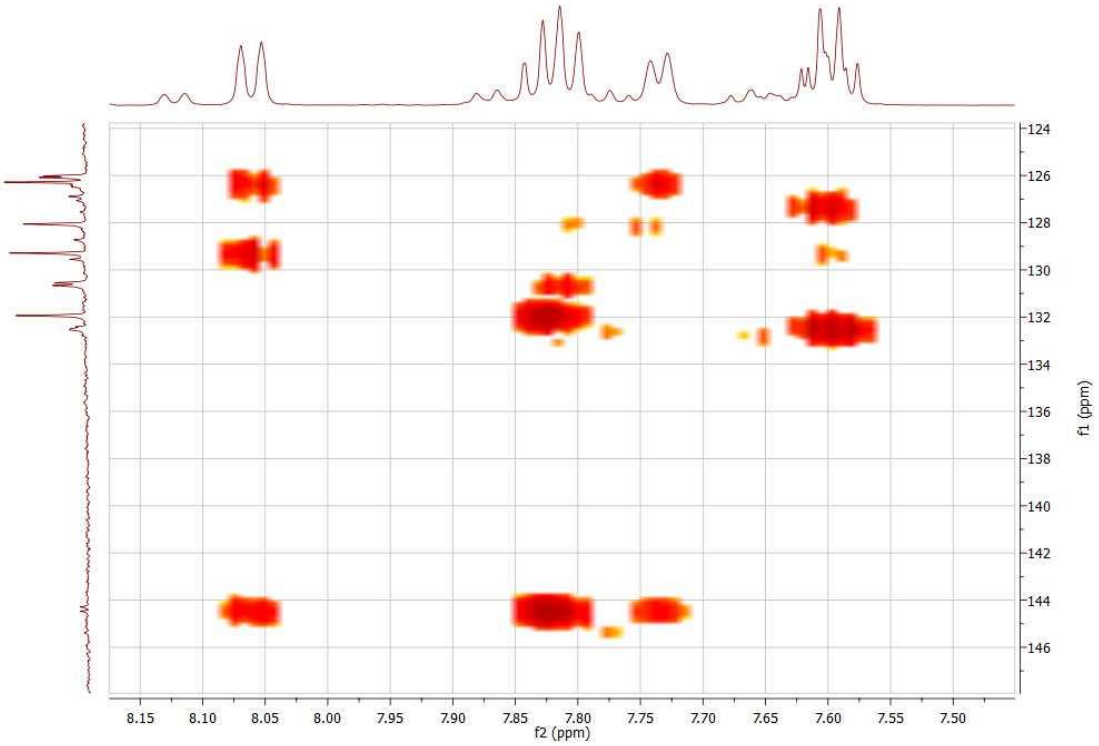


Figure 96. 2D [^{1}H, ^{13}C] HMBC NMR spectrum of compound **8** and **[8]$_2$** in CD_2Cl_2: zoom2



Crystallographic data

The data were collected at low temperature (173(2)K or 193(2)K) on a Bruker-AXS APEX II QUAZAR diffractometer equipped with a 30W air-cooled microfocus source (**3**, **7** and **8**) or on a Bruker-AXS PHOTON100 D8 VENTURE diffractometer (**2** and **4**), using MoKα radiation (λ = 0.71073Å). Phi- and omega- scans were used. An empirical absorption correction with SADABS was applied.[3] The structures were solved by direct methods (SHELXS-97)[4] and refined using the least-squares method on F^2[2]. All non-H atoms were refined with anisotropic displacement parameters. The H atoms on carbon atoms were refined isotropically at calculated positions using a riding model. For **3, 4** and **8**, the N-bound and B-bound H atoms were located in a difference Fourier maps and the H atom bonded to B atom was refined freely. The standard N-H distances in **3** and **4** were fixed accordingly.

2 : $C_{34}H_{26}BBr_4GaNP$, M = 879.66, monoclinic, $P2_1/n$, a = 12.5932(11) Å, b = 14.1435(11) Å, c = 19.2716(16) Å, α = 90°, β = 107.068(3)°, γ = 90°, V = 3281.3(5) Å^3, Z = 4, crystal size 0.40 x 0.40 x 0.32 mm^3, 136889 reflections collected (6435 independent, R_{int} = 0.0355), 380 parameters, $R1$ [I>2σ(I)] = 0.080, $wR2$ [all data] = 0.248, largest diff. peak and hole: 2.98 and -3.172 eÅ^{-3}.

3 : $C_{31}H_{29}BNP$, M = 457.33, monoclinic, $P2_1/n$, a = 6.9184(3) Å, b = 22.8078(12) Å, c = 16.1979(8) Å, α = 90°, β = 101.927(2)°, γ = 90°, V = 2500.7(2) Å^3, Z = 4, crystal size 0.18 x 0.04 x 0.02 mm^3, 38483 reflections collected (5074 independent, R_{int} = 0.0384), 318 parameters, $R1$ [I>2σ(I)] = 0.0399, $wR2$ [all data] = 0.1028, largest diff. peak and hole: 0.287 and -0.270 eÅ^{-3}.

4 : $C_{33}H_{30}BF_6N_2O_4PS_2$, M = 738.49, triclinic, $P\bar{1}$, a = 8.9898(4) Å, b = 12.2194(6) Å, c = 15.5624(8) Å, α = 91.453(2)°, β = 91.387(2)°, γ = 106.552(2)°, V = 1637.28(14) Å^3, Z = 2, crystal size 0.55 x 0.04 x 0.04 mm^3, 20842 reflections collected (6352 independent, R_{int} = 0.0775), 455 parameters, $R1$ [I>2σ(I)] = 0.0818, $wR2$ [all data] = 0.2558, largest diff. peak and hole: 0.571 and -0.551 eÅ^{-3}.

7 : $C_{25}H_{31}BBr_4Ga$ P, M = 762.60, monoclinic, $P2_1/n$, a = 12.2483(4) Å, b = 15.5100(5) Å, c = 15.3013(5) Å, α = 90°, β = 90.0940(10)°, γ = 90°, V = 2906.80(16) Å^3, Z = 4, crystal size 0.18 x 0.10 x 0.08 mm^3, 28885 reflections collected (5108 independent, R_{int} = 0.0462), 296 parameters, $R1$ [I>2σ(I)] = 0.0382, $wR2$ [all data] = 0.0972, largest diff. peak and hole: 1.845 and -1.392 eÅ^{-3}.

8 : $C_{18}H_{21}BF_6NO_4PS_2$, M = 535.26, orthorhombic, $Pbcn$, a = 30.337(3) Å, b = 7.7017(6) Å, c = 19.3533(17) Å, α = 90°, β = 90°, γ = 90°, V = 4521.8(7) Å^3, Z = 8, crystal size 0.20 x 0.04 x 0.04 mm^3, 39674 reflections collected (4797 independent, R_{int} = 0.1124), 307 parameters, $R1$ [I>2σ(I)] = 0.0517, $wR2$ [all data] = 0.1524, largest diff. peak and hole: 0.431 and -0.439eÅ^{-3}.

[3] SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
[4] Sheldrick, G. M., **2008**, *Acta Cryst*. A64, 112.

Computational details

Calculations were carried out with the Gaussian09[5] program at the DFT level of theory using the hybrid functional B3PW91.[6] B3PW91 is Becke's 3 parameter functional, with the non-local correlation provided by the Perdew 91 expression. All the atoms have been described with a 6-31G(d,p) double-ζ basis set.[7,] Geometry optimizations were carried out in gas phase on the cationic complexes (without taking into account counter-anion, experimentally : ion-pair without any interaction cation/counter-anion) without any symmetry restriction. The nature of the *minima* was verified with analytical frequency calculations. All total energies (in kcal/mol), ΔE, and Gibbs Free energies, ΔG, have been zero-point energy (ZPE) and temperature corrected using unscaled density functional frequencies.

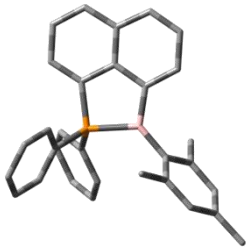
[5] Gaussian 09, Revision **D.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, 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, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[6] a) A. D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648-5652; b) K. Burke, J. P. Perdew, Y. Wang, *Electronic Density Functional Theory: Recent Progress and New Directions*, Eds.: J. F. Dobson, G. Vignale, M. P. Das, Plenum Press, New York, **1998**.

[7] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta*, **1973**, *28*, 213-222.

Z-matrices and energies (in au)

Initial reactant [Ph_2P-naphthyl-BMes]$^+$ (1)



C	1.38033000	-0.27747000	-0.00502600
P	0.85943700	-0.55064300	0.09403600
C	1.73662800	1.93513300	-0.14345700
C	2.22951500	0.62569600	0.10550100
C	2.64161700	3.02819300	-0.19645700
C	0.33003900	2.11654100	-0.35839500
C	-2.90113400	1.16767900	0.60430500
C	-2.05266500	0.65030100	-0.41020800
B	-0.52502700	0.84163800	-0.31916700
C	-4.86695100	0.35606400	-0.59968100
C	-2.63853800	-0.01418300	-1.51994900
C	-6.35939200	0.22533000	-0.71916300
H	-6.76473500	1.00958000	-1.36966600
H	-6.64306900	-0.73561500	-1.15800700
H	-6.85189000	0.31846100	0.25194800
C	-2.35964300	1.80908300	1.85811900
H	-2.12611500	1.05012000	2.61461300
H	-1.44328000	2.37761700	1.68204000
H	-3.09465800	2.48757400	2.29872700
C	-1.79288800	-0.50148700	-2.66780100
H	-1.47749400	0.33224100	-3.30691400
H	-0.88566300	-1.01316400	-2.33074100
H	-2.34524200	-1.20194500	-3.29910200
C	-4.02210500	-0.14549400	-1.59476300
C	-4.28248900	1.00317200	0.48987000
H	-4.45676900	-0.64308700	-2.45909400
H	-4.92156200	1.38955600	1.28096500
C	-0.13344800	3.40113600	-0.63241500
C	0.75312200	4.49369400	-0.68188200
C	2.10630300	4.31397300	-0.46687400
C	4.02206200	2.77205700	0.00499200
C	4.47842700	1.49048900	0.22864000
C	3.58138400	0.39927100	0.27207300
H	5.53949400	1.30984000	0.36782000
H	3.96606000	-0.60515400	0.42476800
H	4.72404200	3.60068700	-0.03018600
H	2.78085100	5.16503900	-0.51320800
H	0.36981600	5.48626800	-0.89652900
H	-1.19298800	3.56000800	-0.81383400
C	0.50196800	-1.19215300	1.75130400
C	1.48211000	-1.21673000	2.75217100
C	-0.78704600	-1.68330500	2.01346900
C	1.17433200	-1.74078300	4.00438600
H	2.47453400	-0.82154700	2.56141400
C	-1.08027900	-2.21264800	3.26779100
H	-1.55869500	-1.64348200	1.24952100
C	-0.10191300	-2.24076400	4.26108400
H	1.93273400	-1.75701100	4.78088400
H	-2.07587800	-2.59518700	3.47006200
H	-0.33621200	-2.64823800	5.23984300
C	1.25589100	-1.92692600	-1.02080800
C	1.92099500	-1.65377000	-2.22629700
C	0.88690000	-3.23914300	-0.70133900
C	2.21332700	-2.69407900	-3.10177700
H	2.21711500	-0.63887500	-2.47591100
C	1.18565300	-4.27251200	-1.58638500
H	0.38207500	-3.45714900	0.23433800
C	1.84573500	-4.00200700	-2.78322100
H	2.73251500	-2.48400000	-4.03171700
H	0.90538700	-5.29070500	-1.33512800
H	2.07811300	-4.81134500	-3.46860600

Sum of electronic and zero-point Energies= -1562.652351
Sum of electronic and thermal Free Energies= -1562.715296

Ph_2NH

C	-1.26039000	-0.44365000	0.01897700
C	-1.48862300	0.84502800	0.52745900
H	-0.66226800	1.42214300	0.92725800
C	-2.77780000	1.36882600	0.54957000
H	-2.93249600	2.36790300	0.94839300
C	-3.86438600	0.62675600	0.09041100
H	-4.86672100	1.04295100	0.11469200
C	-3.64356800	-0.66161600	-0.39500700
H	-4.47660200	-1.26000800	-0.75390100
C	-2.35915200	-1.18994500	-0.43891400
H	-2.19418000	-2.18848200	-0.83767100
C	1.26038800	-0.44361900	-0.01919700
C	1.48872700	0.84505500	-0.52755200
H	0.66239600	1.42231200	-0.92724800
C	2.77794800	1.36880000	-0.54952600
H	2.93264200	2.36791800	-0.94827500
C	3.86444000	0.62663300	-0.09035100
H	4.86682600	1.04267600	-0.11458000
C	3.64347100	-0.66168700	0.39517700
H	4.47644400	-1.26008900	0.75421700
C	2.35900100	-1.18991900	0.43899500
H	2.19391100	-2.18834100	0.83808600
N	-0.00003300	-1.03815500	-0.00013300
H	-0.00006100	-2.04588300	-0.00029300

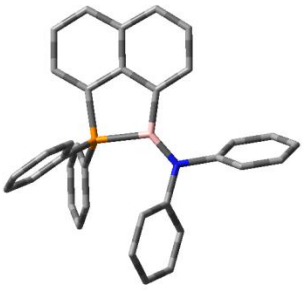
Sum of electronic and zero-point Energies= -518.274451
Sum of electronic and thermal Free Energies= -518.311315

Mes-H

C	0.91333500	1.04323100	-0.00590600
C	-0.93013700	-1.05658900	-0.00704800
C	-0.44992800	1.33389200	-0.00592000
C	-1.91776600	-2.19435600	0.00871300
H	-1.94971400	-2.67785700	0.99262200
H	-2.92975600	-1.84989400	-0.22142600
H	-1.65056400	-2.96680900	-0.72007000
C	2.85958200	-0.56326000	0.00728300
H	3.38495000	0.01327800	-0.76164600
H	3.30754000	-0.29563500	0.97178300
H	3.06434900	-1.62285800	-0.16870300
C	-0.94177300	2.75793600	0.00790300
H	-1.37554000	3.01824100	0.98090400
H	-0.13073400	3.46391600	-0.19086400
H	-1.72091600	2.91955200	-0.74459400
C	-1.36049900	0.26928000	-0.00869300
C	0.44700400	-1.31289400	-0.00753400
H	-2.42816000	0.48214800	-0.01588200
H	0.79602500	-2.34412500	-0.01391100
H	1.63162700	1.86142500	-0.01084900

Sum of electronic and zero-point Energies= -349.905363
Sum of electronic and thermal Free Energies= -349.943466

Final compound $[Ph_2P\text{-naphthyl-}BNPh_2]^+$ (2)



C	-1.43996700	2.00292900	-0.33551800
C	-0.23891800	2.71447400	-0.05791800
C	0.95164900	1.98273800	0.26452300
C	2.09110500	2.71166700	0.57974700
H	3.01088300	2.19933500	0.84021700
C	2.08137800	4.12242900	0.56675800
H	2.98945000	4.66055600	0.82069900
C	0.94240600	4.82226300	0.23199200
H	0.94990500	5.90886100	0.21776500
C	-0.25685400	4.13698900	-0.08645300
C	-1.47053400	4.79329000	-0.41301800
H	-1.48818800	5.87942600	-0.44301500
C	-2.61884600	4.07794200	-0.67682800
H	-3.54072000	4.59877500	-0.91518500
C	-2.61488400	2.66715500	-0.62496900
H	-3.53530900	2.11999500	-0.80798700
C	-2.28945700	-0.33477100	1.20787600
C	-3.41009600	-1.12996900	0.94709400
H	-3.61767300	-1.47668700	-0.06004100
C	-4.26507600	-1.47866500	1.99176400
H	-5.13403900	-2.09700900	1.78873300
C	-4.00866700	-1.03503300	3.28678100
H	-4.67772700	-1.30989300	4.09651400
C	-2.89564000	-0.23336600	3.54568000
H	-2.69855500	0.11887100	4.55347200
C	-2.03622300	0.11947200	2.51113500
H	-1.17778500	0.75408600	2.71804100
C	-1.54404300	-0.67234700	-1.65908200
C	-1.49240000	-2.07567100	-1.67582700
H	-1.27116300	-2.63326300	-0.77071800
C	-1.73078400	-2.75791900	-2.86499000
H	-1.69619900	-3.84284700	-2.87494900
C	-2.00864500	-2.05404200	-4.03662300
H	-2.19331000	-2.59255900	-4.96125000
C	-2.04837100	-0.66132700	-4.02307500
H	-2.26267400	-0.11164300	-4.93432900
C	-1.81682400	0.03375200	-2.83883000
H	-1.84910800	1.11833000	-2.83350900
C	1.29982200	-1.99285800	0.43530500
C	1.80096300	-2.93652700	-0.46802000
H	2.46777500	-2.61896000	-1.26315100
C	1.43597100	-4.27231600	-0.34191800
H	1.82454700	-5.00132400	-1.04658400
C	0.57668800	-4.67727900	0.68190600
H	0.30102600	-5.72280500	0.77972800
C	0.09379000	-3.73871100	1.59070500
H	-0.55293000	-4.04834100	2.40599200
C	0.46211300	-2.39765200	1.47660900
H	0.12443100	-1.67236100	2.20944700
C	3.08808700	-0.37188200	0.19947600
C	3.92269300	-0.68718000	1.27360100
H	3.49827600	-1.10422400	2.18184600
C	5.29242100	-0.46077900	1.16735900
H	5.94197100	-0.70057100	2.00364100
C	5.82860500	0.07003100	-0.00610900
H	6.89767100	0.24125700	-0.08565400
C	4.99168000	0.37228400	-1.07891000
H	5.40576900	0.77577900	-1.99793300
C	3.61948200	0.14969700	-0.98104200
H	2.95891800	0.37751800	-1.81222800
N	1.66749100	-0.61173200	0.30253400
P	-1.19063000	0.22672200	-0.12510600
B	0.75120600	0.44161800	0.24283700

Sum of electronic and zero-point Energies= -1731.062561
Sum of electronic and thermal Free Energies= -1731.125613