Supplementary Information

One- and two-electron reductions of a bulky BODIPY compound

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Materials and Methods

Synthetic and characterising data for new compounds.

General considerations. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon. All glassware and cannulae were dried in a 140 °C oven for a minimum of 12 hours prior to use. All solvents, bar benzene, were collected from an MBraun solvent purification system, stored under argon in Teflon valved ampoules over a mirror of sodium metal or 4 Å molecular sieves where appropriate, and sparged with argon prior to use. Benzene and C_6D_6 were dried and distilled from molten potassium and stored in Teflon capped ampoule over molecular sieves. NMR samples were prepared under argon in 5 mm Norell Select Series NMR Tube fitted with J. Young Teflon valves. ^{1}H, $^{13}C\{^{1}H\}$, $^{11}B\{^{1}H\}$, and $^{19}F\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm). $^{11}B\{^{1}H\}$ and $^{19}F\{^{1}H\}$ were externally referenced to BF_3OEt_2 and CF_3CO_2H, respectively. Assignments were confirmed using two-dimensional ^{1}H-^{1}H and ^{13}C-^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Infrared spectra were obtained using a PerkinElmer Spectrum One with an attenuated total reflectance (ATR) accessory. Samples were suspended in Nujol oil prior to spectroscopic analysis. Peaks associated with the Nujol oil were removed post-collection via the Perkin Elmer Spectrum 10 STD software. Elemental analyses were carried out by the Elemental Analysis Service, Science Centre at London Metropolitan University, UK. H(^{Dipp}DPM),[S1] [(^{Mes}NacNac)Mg]$_2$[S2] and magnesium anthracene [Mg($C_{14}H_{10}$)(THF)$_3$][S3] were prepared by literature methods. All other reagents were purchased from chemical suppliers and used as received.

Synthesis of (^{Dipp}DPM)BF_2 (1-F): To a yellow solution of H(^{Dipp}DPM) (1.00 g, 1.71 mmol) in dichloromethane (100 mL), was added triethylamine (1.44 mL, 10.3 mmol) via syringe under argon and allowed to stir for two minutes at room temperature. With stirring, $BF_3{\cdot}OEt_2$ (1.90 mL, 15.4 mmol) was then added via syringe. The solution immediately turned bright red, which was left to stir at room temperature overnight. The reaction mixture was then washed three times with water, the organic layer separated, dried with magnesium sulphate, filtered, and the filtrate evaporated to dryness under reduced pressure. The resulting solid was dissolved in minimal dichloromethane (*ca.* 20 mL) to which methanol was added (*ca.* 50 mL). The dichloromethane was then removed under reduced pressure, yielding **1-F** as a bright orange precipitate, which was isolated by filtration (Yield: 1.07 g, 99%). X-ray quality crystals were isolated by dissolving **1-F** in hot benzene, which was left to slowly evaporate overnight. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = 1.12 (d, J_{HH} = 6.9 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 1.38 (d, J_{HH} = 6.7 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$)), 2.02 (s, 6H, Mes-*o*-C(C*H*$_3$)), 2.13 (s, 3H, Mes-*p*-C(C*H*$_3$)), 2.98 (h, J_{HH} = 3.9 Hz, 6.77 Hz, 4H, Dipp-C*H*), 6.18 (d, J_{HH} = 4.1 Hz, 2H, pyrrole-α-Dipp-C*H*), 6.49 (d, J_{HH} = 4.2 Hz, 2H, pyrrole-ß-Dipp-C*H*), 6.70 (s, 2H, Mes-C*H*), 7.09 (d, J_{HH} = 7.7 Hz, 4H, Dipp-*m*-C*H*), 7.21 (t, J_{HH} = 7.7 Hz, 2H, Dipp-*p*-CH); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 19.7 (Mes-*o*-C(*C*H$_3$)), 20.7 (Mes-p-C(*C*H$_3$)), 22.4, 25.8 (Dipp-*C*H$_3$),

31.5 (Dipp-*C*H), 122.2, 122.8, 130.1, 130.4, 130.9, 135.6, 136.9, 138.6, 144.9, 148.2, 159.2 (Ar-C); **^{11}B{^{1}H} NMR** (128 MHz, C_6D_6): δ = 1.0 (t, J_{FB} = 30 Hz); **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ = –143.8 (q, J_{BF} = 30 Hz); **IR**: cm^{-1} = 2958 (s), 2923 (m), 2865 (m), 1550 (s), 1261 (s), 1241 (m), 1130 (m), 1087 (s), 994 (s), 956 (s), 870 (m), 849 (w), 749 (m), 738 (s), 701 (s). **Elemental**: Found (%) C, 81.62; H, 7.54; N, 4.04. Calc(%) for **1-F**+C_6H_6 ($C_{48}H_{55}BF_2N_2$): C 81.34, H 7.82, N 3.95.

Synthesis of (^{Dipp}DPM)BBr$_2$ (1-Br): To a solution of **1-F** (500 mg, 0.795 mmol) in toluene (30 mL) was added BBr_3 (0.755 mL, 7.95 mmol) via syringe, under argon. This solution was stirred overnight at room temperature. The solvent was then removed *in vacuo* and the resulting solid was dried under vacuum until a pressure of <50 µbar had been reached. The resulting dark purple powder was redissolved in dry n-hexane (10 mL) and left to sit at room temperature overnight to give **1-Br** as deep red crystals suitable for X-ray crystallography. (Yield: 0.540 g, 90%). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): *δ* = 1.08 (d, J_{HH} = 6.8 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 1.41 (d, J_{HH} = 6.7 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 2.16 (s, 3H, Mes-p-C(C*H*$_3$)), 2.18 (s, 6H, Mes-*o*-C(C*H*$_3$)), 3.09 (h, J_{HH} = 6.9 Hz, 4H, Dipp-C*H*), 6.20 (d, J_{HH} = 4.2 Hz, 2H, pyrrole-α-Dipp-C*H*), 6.56 (d, J_{HH} = 4.2 Hz, 2H, pyrrole-ß-Dipp-C*H*), 6.73 (s, 2H, Mes-C*H*), 7.08 (d, J_{HH} = 7.8, 4H, Dipp-*m*-C*H*), 7.24 (t, J_{HH} = 7.8 Hz, 2H, Dipp-*p*-C*H*); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): *δ* = 20.3 (Mes-*o*-C(*C*H$_3$)), 21.1 (Mes-*p*-C(*C*H$_3$)), 23.3, 26.1 (Dipp-*C*H$_3$), 32.1 (Dipp-*C*H), 123.0, 124.9, 130.2, 131.5, 136.2, 137.1, 139.2, 145.6, 147.8, 161.8 (Ar-C); **^{11}B{^{1}H} NMR** (128 MHz, C_6D_6): *δ* = –3.8; **IR**: cm^{-1} = 2956 (m), 2922 (s), 2854 (m), 1557 (s), 1462 (s), 1264 (w), 1054 (w), 804 (s), 579 (s). **Elemental**: Found(%) C 66.67, H 6.83, N 3.12; Calc.(%) for **1-Br** ($C_{42}H_{49}BBr_2N_2$): C 67.04, H 6.56, N 3.72.

Synthesis of [(^{Dipp}DPM)BBr][BBr$_4$] (2): To a solution of **1-F** (60.0 mg, 0.096 mmol) in benzene (10 mL), was added BBr_3 (0.092 mL, 0.96 mmol) via syringe, under argon with stirring at room temperature. The solution immediately turned dark purple, with the fluorescence under ambient light being quenched. The solution was stirred at room temperature overnight, then was left to stand at room temperature for a second night yielding deep red crystals of **2** suitable for X-ray crystallography. (Yield: 36.6 mg, 38%). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): *δ* = 1.08 (d, J_{HH} = 6.8 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 1.41 (d, J_{HH} = 6.8 Hz, 12H, Dipp-CH(C*H*$_3$)$_2$), 2.13 (d, J_{HH} = 16.2 Hz, 6H, Mes-*o*-C(C*H*$_3$)), 2.18 (s, 3H, Mes-*p*-C(C*H*$_3$)), 3.09 (h, J_{HH} = 6.8 Hz, 4H, Dipp-C*H*), 6.19 (d, J_{HH} = 4.2 Hz, 2H, pyrrole-α-Dipp-C*H*), 6.55 (d, J_{HH} = 4.2 Hz, 2H, pyrrole-ß-Dipp-C*H*), 6.72 (s, 2H, Mes-C*H*), 7.08 (d, J_{HH} = 7.8 Hz, 4H, Dipp-*m*-C*H*), 7.24 (t, J_{HH} = 7.7 Hz, 2H, Dipp-p-C*H*); **^{11}B{^{1}H} NMR** (128 MHz, C_6D_6): *δ* = –2.48 ([BBr_4]$^-$), 28.50 ([(DPM)BBr]$^+$). **Elemental**: Found(%) C 53.48, H 5.25, N 3.10; Calc(%) for **2**+C_6H_6 ($C_{48}H_{55}B_2Br_5N_2$): C, 53.33; H, 5.13; N, 2.59.

Synthesis of [(^{Dipp}DPM)BF]$_2$ (3-F): To a 50 mL Schlenk flask containing a solution of **1-F** (250 mg, 0.332 mmol) and 0.5 eq of [(^{Mes}NacNac)Mg]$_2$ (118 mg, 0.166 mmol) was added dry n-hexane (10 mL) at room temperature. This quickly gave a deep dark blue solution (which fluoresced bright red in ambient light), which was stirred at room temperature for one day, resulting in a further colour change to green and a large amount of colourless precipitate forming. The reaction mixture was filtered, and the filtrate concentrated *in vacuo* and allowed to

sit for three days, yielding **3-F** as colourless crystals suitable for X-ray crystallography. (Yield (crystalline): 13.4 mg, 6%). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = 1.06 (m, 24H, Dipp-CH(CH_3)$_2$), 1.14 (d, J_{HH} = 6.9 Hz, 6H, Dipp-CH(CH_3)$_2$), 1.18 (d, J_{HH} = 6.9 Hz, 6H, Dipp-CH(CH_3)$_2$), 1.24 (d, J_{HH} = 6.8 Hz, 12H, Dipp-CH(CH_3)$_2$), 1.63 (s, 6H, Mes-*p*-C(CH_3)), 2.22 (s, 6H, Mes-*o*-C(CH_3)), 2.30 (s, 6H, Mes-*o*-C(CH_3)), 2.62 (h, J_{HH} = 6.9 Hz, 2H, Dipp-C*H*), 2.84 (h, J_{HH} = 6.8 Hz, 2H, Dipp-C*H*), 3.16 (h, J_{HH} = 6.8 Hz, 2H, Dipp-C*H*), 3.24 (h, J_{HH} = 6.8 Hz, 2H, Dipp-C*H*), 4.29 (d, J_{HH} = 1.5 Hz, 2H, pyrrole-α-dimer-Dipp-C*H*), 5.47 (d, J_{HH} = 1.5 Hz, 2H, pyrrole-α-Dipp-C*H*), 5.91 (d, J_{HH} = 3.3 Hz, 2H, pyrrole-β-dimer-Dipp-C*H*), 6.34 (d, J_{HH} = 3.3 Hz, 2H, pyrrole-β-Dipp-C*H*), 6.82 (s, 2H, Mes-*m*-C*H*), 6.88 (s, 2H, Mes-*m*-C*H*), 6.93 (d, J_{HH} = 7.7 Hz, 2H, Dipp-*m*-C*H*), 6.96 (d, J_{HH} = 7.7 Hz, 2H, Dipp-*m*-C*H*), 7.03 (dt, J_{HH} = 7.9, 1.6 Hz, 4H, Dipp-*m*-C*H*), 7.10 (t, J_{HH} = 7.9 Hz, 4H, Dipp-*p*-C*H*); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 19.2 (Mes-*p*-C(*C*H_3), 20.6, 20.3 (Mes-*o*-C(*C*H_3)), 24.5, 24.9 (Dipp-CH(*C*H_3)$_2$), 25.2 (Dipp-CH(*C*H_3)$_2$), 31.1, 31.2, 31.3, 31.3 (Dipp-*C*H), 49.5 (pyrrole-α-dimer-Dipp-*C*H), 105.2 (pyrrole-β-dimer-Dipp-*C*H), 114.7 (pyrrole-α-Dipp-*C*H), 117.8 (pyrrole-β-Dipp-*C*H), 23.1, 23.6, 23.7, 25.4, 25.8 (Alkyl-C), 122.4, 122.6, 123.1, 123.2, 131.7, 131.9, 136.3, 137.4, 137.6, 138.0, 142.0, 147.5, 147.8, 149.2, 149.5 (Ar-C); **^{11}B{^{1}H} NMR** (128 MHz, C_6D_6): δ = 22.0; **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ = -133.9; **IR**: cm^{-1} = 2921 (s), 2853 (m), 2730 (w), 1528 (s), 1456 (m), 1397 (m), 1257 (s), 1201 (s), 1016 (m), 854 (s), 539 (w). **Elemental**: a satisfactory elemental analysis could not be obtained for this compound, possibly due to decomposition during shipping.

Synthesis of [(^{Dipp}DPM)BBr]$_2$ (3-Br): To a solution of **1-F** (250 mg, 0.332 mmol) in n-hexane (15 mL), 0.5 eq of [(^{Mes}NacNac)Mg]$_2$ (119 mg, 0.166 mmol) was added at room temperature. The solution quickly changed from purple to dark blue and fluoresced brightly red in natural light. The solution was stirred for two days at room temperature, before being filtered. The filtrate was concentrated under reduced pressure and allowed to sit for three days, yielding **4** as colourless crystals suitable for X-ray crystallography. (Yield (crystalline): 21.8 mg, 9%). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = 1.05 (d, J_{HH} = 6.9 Hz, 6H, Dipp-CH(CH_3)$_2$), 1.07 (d, J_{HH} = 6.7 Hz, 6H, Dipp-CH(CH_3)$_2$), 1.16 (m, 24H, Dipp-CH(CH_3)$_2$), 1.35 (d, J_{HH} = 6.7 Hz, 6H, Dipp-CH(CH_3)$_2$), 1.74 (s, 6H, Mes-*p*-C(CH_3)), 2.21 (d, J_{HH} = 19.2 Hz, 12H, Mes-*o*-C(CH_3)), 2.61 (h, J_{HH} = 6.8 Hz, 2H, Dipp-C*H*), 2.71 (h, J_{HH} = 6.8 Hz, 2H, Dipp-C*H*), 2.83 (h, J_{HH} = 6.9 Hz, 2H, Dipp-C*H*), 3.29 (h, J_{HH} = 6.8 Hz, 2H, Dipp-C*H*), 3.95 (d, J_{HH} = 1.7 Hz, 2H, pyrrole-α-dimer-Dipp-C*H*), 5.62 (m, 2H, pyrrole-α-Dipp-C*H*), 6.02 (d, J_{HH} = 3.4 Hz, 2H, pyrrole-β-dimer-Dipp-C*H*), 6.45 (d, J_{HH} = 3.4 Hz, 2H, pyrrole-β-Dipp-C*H*), 6.77 (s, 2H, Mes-*m*-C*H*), 6.83 (s, 2H, Mes-*m*-C*H*), 7.04 (m, 8H, Dipp-*m*-C*H*), 7.20 (t, J_{HH} = 7.8 Hz, 2H, Dipp-*p*-C*H*), 7.25 (t, J_{HH} = 7.7 Hz, 2H, Dipp-*p*-C*H*); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 19.0 (Mes-*p*-C(*C*H_3)), 20.7, 21.3 (Mes-*o*-C(*C*H_3)), 22.9, 23.2 (Dipp-CH(*C*H_3)$_2$), 25.7 (Dipp-CH(*C*H_3)$_2$), 25.5 (Dipp-CH(*C*H_3)$_2$), 31.1, 31.5, 31.6, 32.0 (Dipp-*C*H), 48.8 (pyrrole-α-dimer-Dipp-*C*H), 104.8 (pyrrole-β-dimer-Dipp-*C*H), 118.1 (pyrrole-α-Dipp-*C*H), 119.0 (pyrrole-β-Dipp-*C*H), 122.4 (Dipp-*m*-*C*H), 128.7, 130.2 (Mes-*m*-*C*H), 129.3, 129.6 (Dipp-*p*-*C*H), 23.1, 23.3 (Alkyl-C); **^{11}B{^{1}H} NMR** (128 MHz, C_6D_6): δ = –2.1. **IR**: cm^{-1} = 2921 (s), 2854 (m), 1528 (s), 1456 (s), 1397 (s), 1376 (s), 1258 (m), 1201 (m), 1147 (w), 1016 (br), 854 (m), 540 (m). **Elemental**: a satisfactory elemental analysis could not be obtained for this compound, possibly due to decomposition during shipping.

Synthesis of $Mg(THF)_2[(^{Dipp}DPM)BF]_2$ (4): Under an atmosphere of argon, **1-F** (25.0 mg, 0.0790 mmol) and magnesium anthracene (33.1 mg, 0.158 mmol) were added to a J. Youngs NMR tube. C_6D_6 (0.5 mL) was added resulting in an orange solution. The Young's flask was shaken by hand causing the solution to change colour to dark blue within a few seconds and then to a dark red colour almost instantaneously. The solution was then sonicated for 30 minutes and left to stand at room temperature overnight, resulting in the crystallisation of anthracene. The mixture was then filtered under argon and volatiles from the filtrate removed *in vacuo*, resulting in a red powder. This powder was redissolved in minimal hot benzene and left to slowly cool overnight resulting in orange plate crystals suitable for X-ray diffraction. (Yield: 13.3 mg, 12%). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = 0.99 (d, J_{HH} = 6.9 Hz, 6H, Dipp-CH-(CH_3)$_2$), 1.12 (m, 26H, Dipp-CH-(CH_3)$_2$ and THF-βCH_2), 1.20 (d, J_{HH} = 6.9 Hz, 6H, Dipp-CH-(CH_3)$_2$)), 1.30 (d, J_{HH} = 6.9 Hz, 12H, Dipp-CH-(CH_3)$_2$), 1.42 (d, J_{HH} = 6.8 Hz, 6H, Dipp-CH-(CH_3)$_2$), 2.06 (s, 6H, Mes-*p*-CH_3), 2.25 (s, 6H, Mes-*o*-CH_3), 2.36 (s, 6H, Mes-*o*-CH_3), 2.81 (h, J_{HH} = 6.9 Hz, 2H, Dipp-C*H*), 2.99 (h, J_{HH} = 6.9 Hz, 2H, Dipp-C*H*), 3.00 (h, J_{HH} = 6.9 Hz, 2H, Dipp-C*H*), 3.12 (h, J_{HH} = 6.9 Hz, 2H, Dipp-C*H*), 3.28 (b, 4H, THF-αCH_2), 3.49 (b, 4H, THF-αCH_2), 3.63 (s, 2H, α-Mg-C*H*), 5.77 (d, J_{HH} = 2.5 Hz, 2H, pyrrole-β-Mg-C*H*), 5.88 (d, J_{HH} = 3.2 Hz, 2H, pyrrole-α-Dipp-C*H*), 6.52 (d, J_{HH} = 3.2 Hz, 2H, pyrrole-β-Dipp-C*H*), 7.07 (m, 16H, Ar-C*H*); **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 20.2 (Mes-*o*-CH_3), 20.5 (Mes-*p*-CH_3), 21.5 (Mes-*o*-CH_3), 24.4, 24.2, 25.1, 24.9, 25.5, 25.7 (Dipp-CH-(*C*H_3)$_2$), 24.9 (THF-βCH_2), 31.2, 31.3, 31.6 (Dipp-*C*H), 36.3 (α-Mg-*C*H), 70.3 (THF-α*C*H_2), 96.0 (pyrrole-α-Dipp-*C*H), 117.6 (pyrrole-β-Dipp-*C*H), 123.7 (pyrrole-β-Mg-*C*H), 122.6, 122.4, 122.8, 121.8, 123.4, 123.6, 125.6, 126.3, 126.4, 126.7, 127.7, 127.9, 128.2, 128.6, 128.9, 129.1, 129.4, 130.8, 132.24, 133.0, 134.0, 134.8, 136.2, 136.5, 137.0, 139.6, 140.2, 147.5, 149.3, 150.3, 150.7, 151.6 (Ar-*C*); **^{19}F{^{1}H} NMR** (376 MHz, C_6D_6): δ = –137.6. **Elemental**: Found(%) C 76.52, H 7.93, N 3.86; Calc(%) for **4**+5(THF) ($C_{112}H_{147}B_2F_2MgN_4O_8$): C 77.08, H 8.49, N 3.21.

^{1}H NMR spectra of new compounds

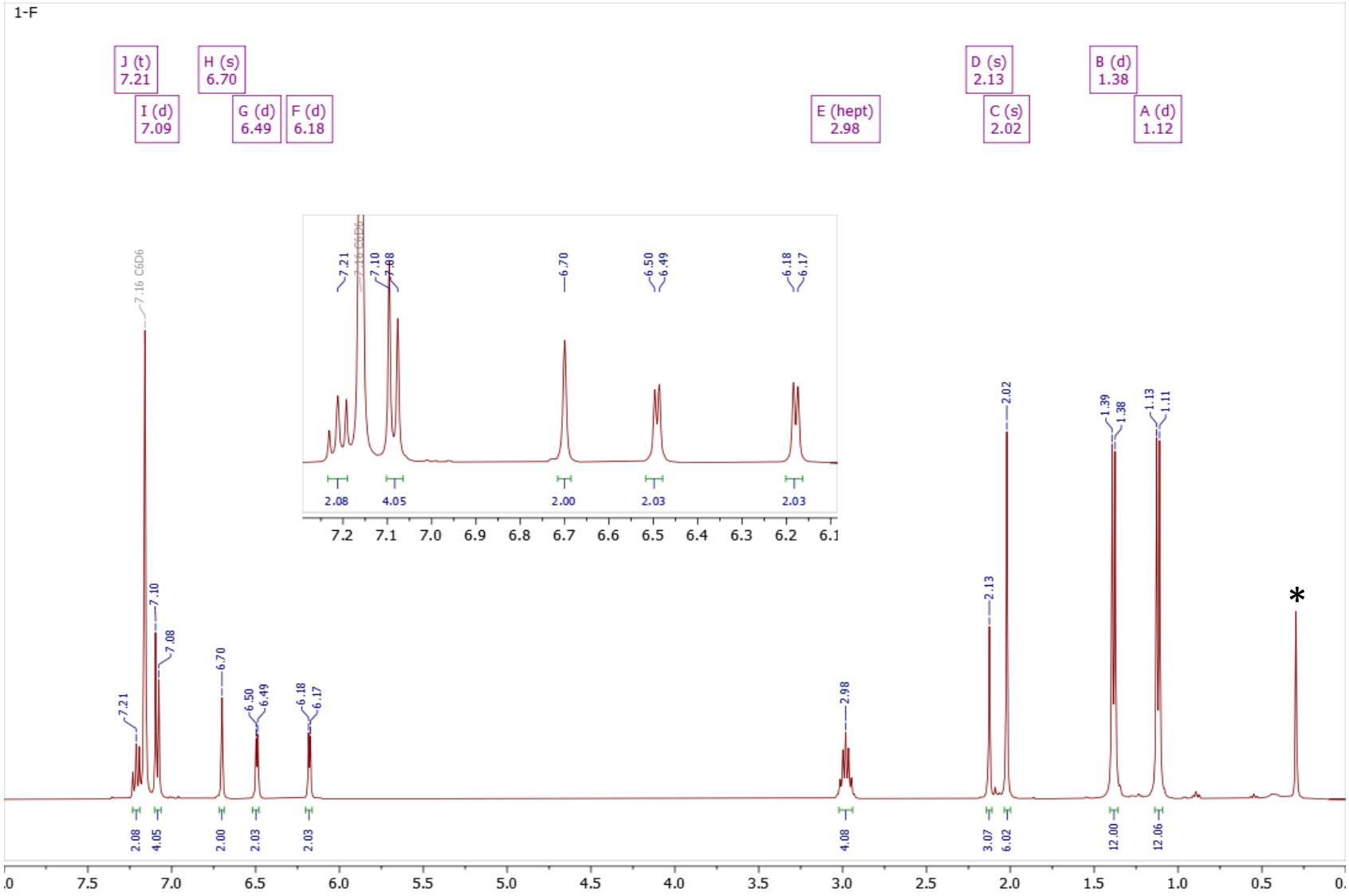

Figure S1: ^{1}H NMR spectrum of (^{Dipp}DPM)BF_2 (**1-F**) (400 MHz, C_6D_6, 298 K). (* indicates silicone grease)

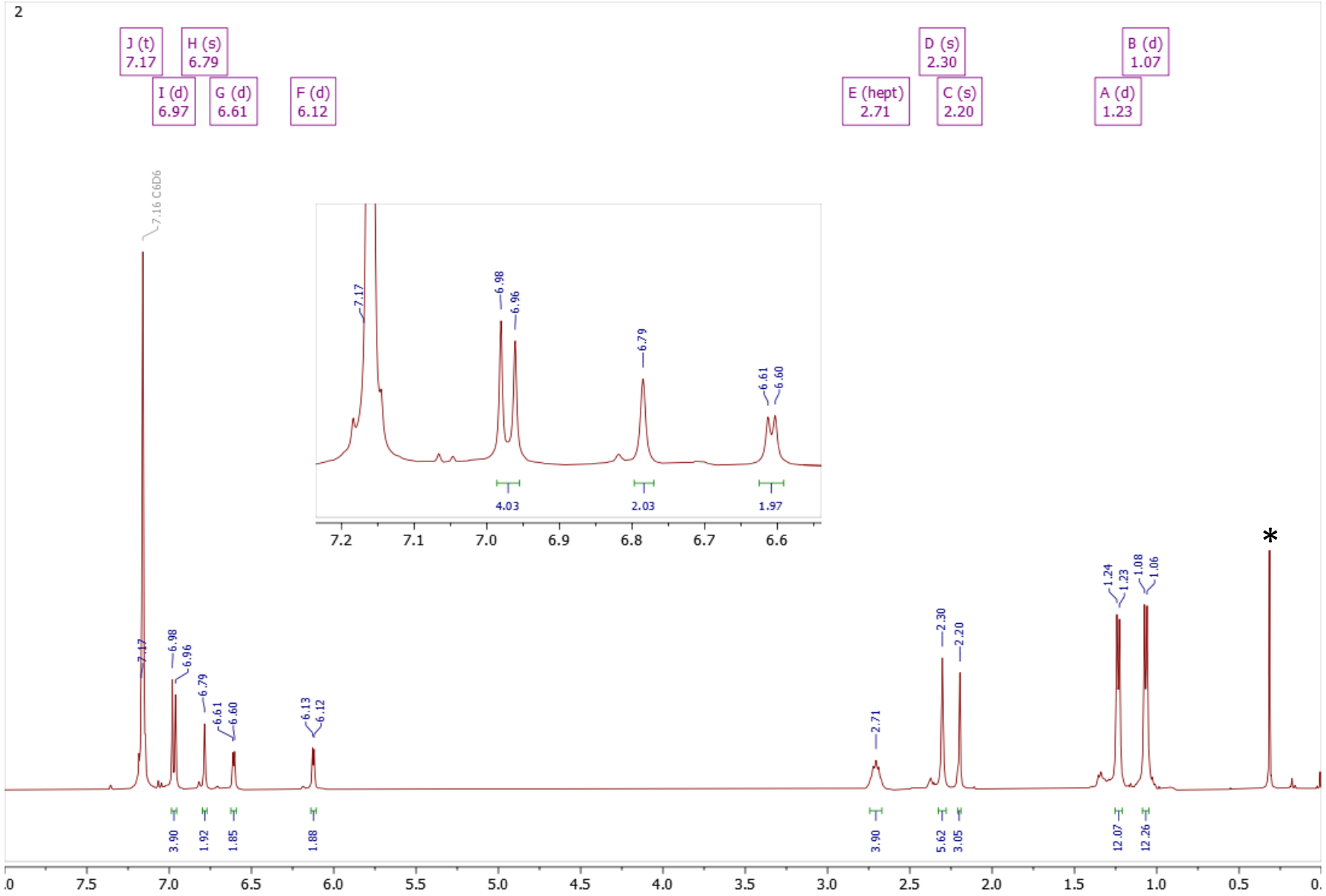

Figure S2: ^{1}H NMR spectrum of [(^{Dipp}DPM)BBr][BBr_4] (**2**) (400 MHz, C_6D_6, 298 K). (* indicates silicone grease)

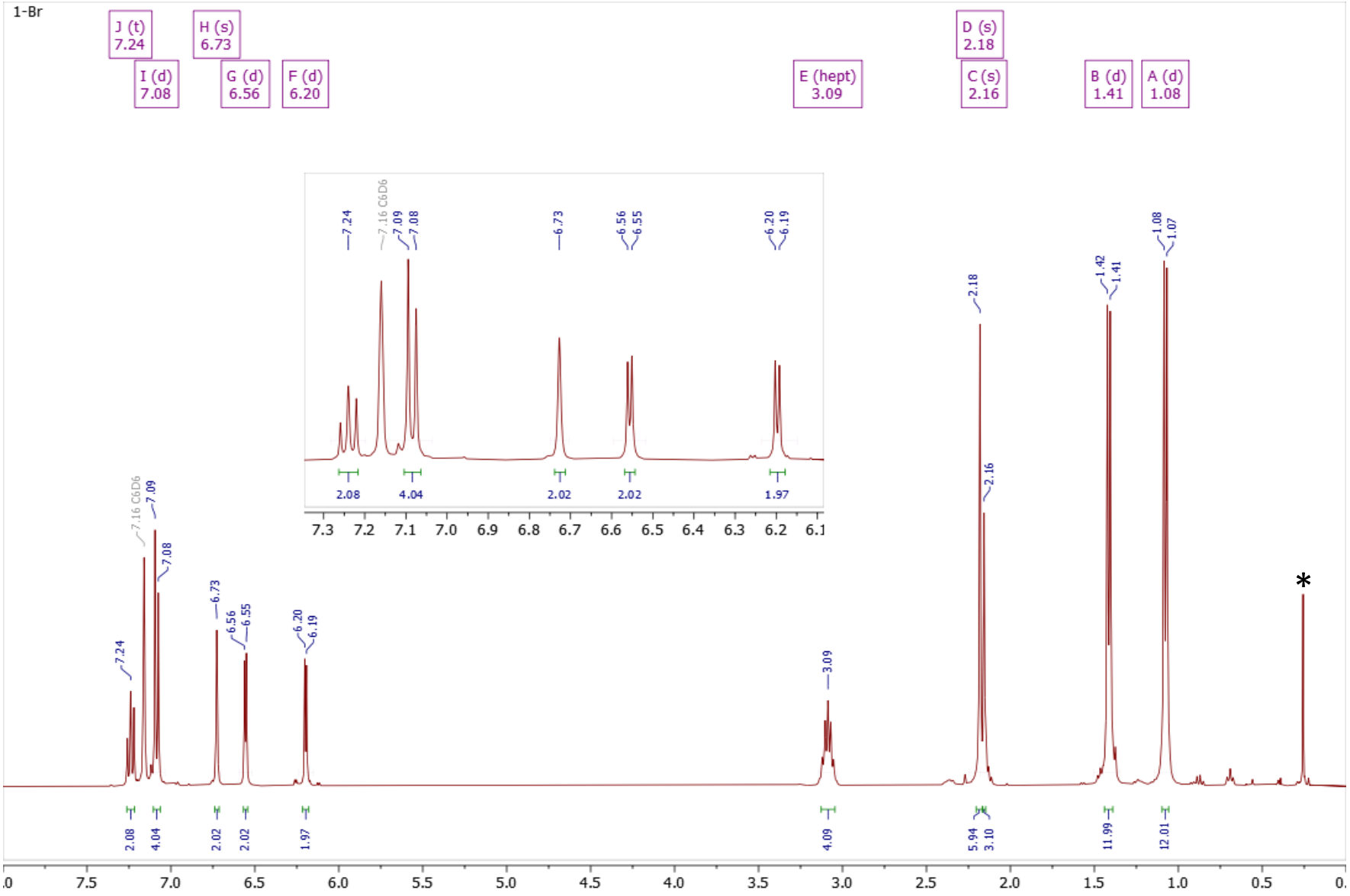

Figure S3: ^{1}H NMR spectrum of (^{Dipp}DPM)BBr_2 (**1-Br**) (400 MHz, C_6D_6, 298 K). (* indicates silicone grease)

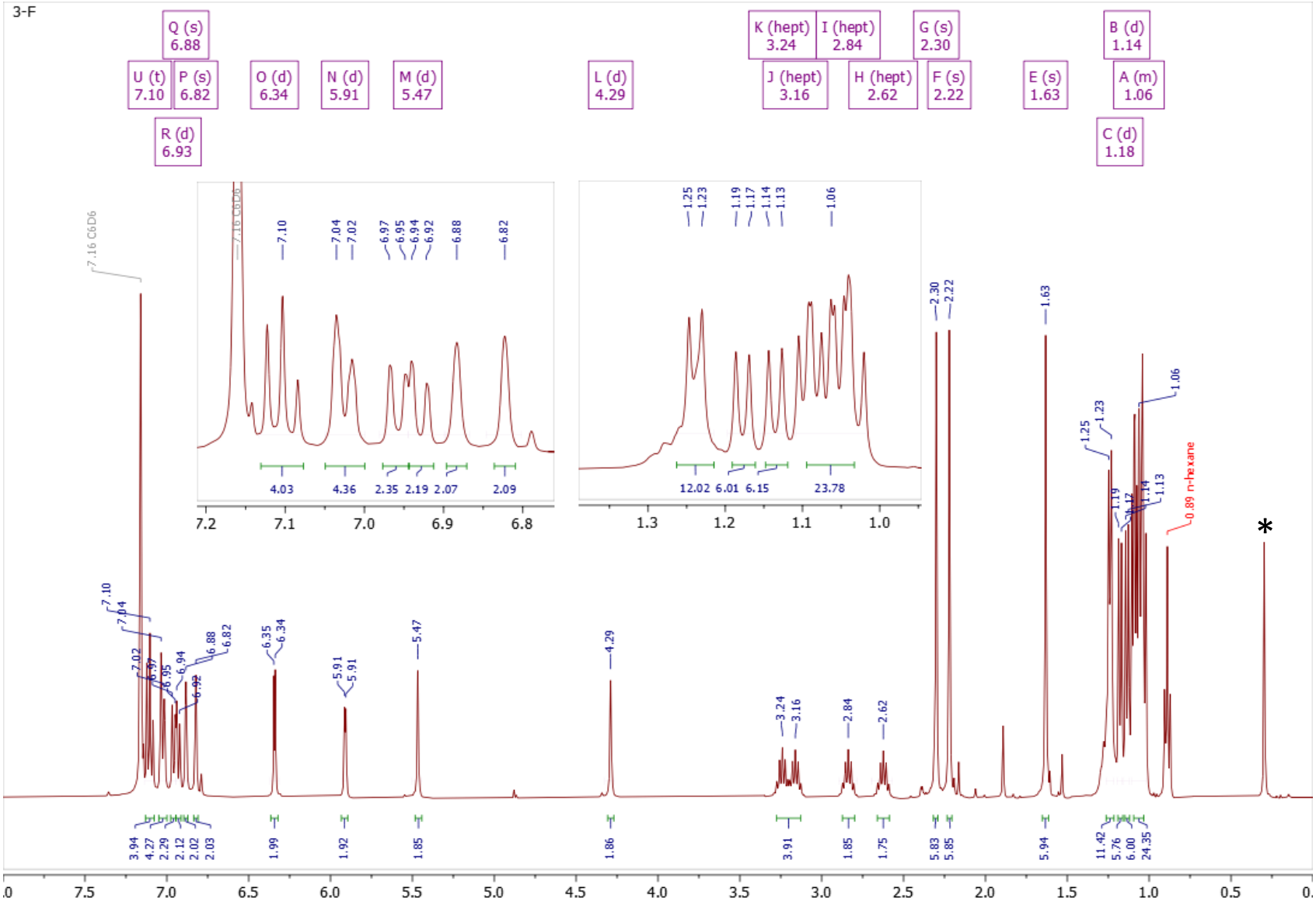

Figure S4: ^{1}H NMR spectrum of [(^{Dipp}DPM)BF]$_2$ (**3-F**) (400 MHz, C_6D_6, 298 K). (* indicates silicone grease)

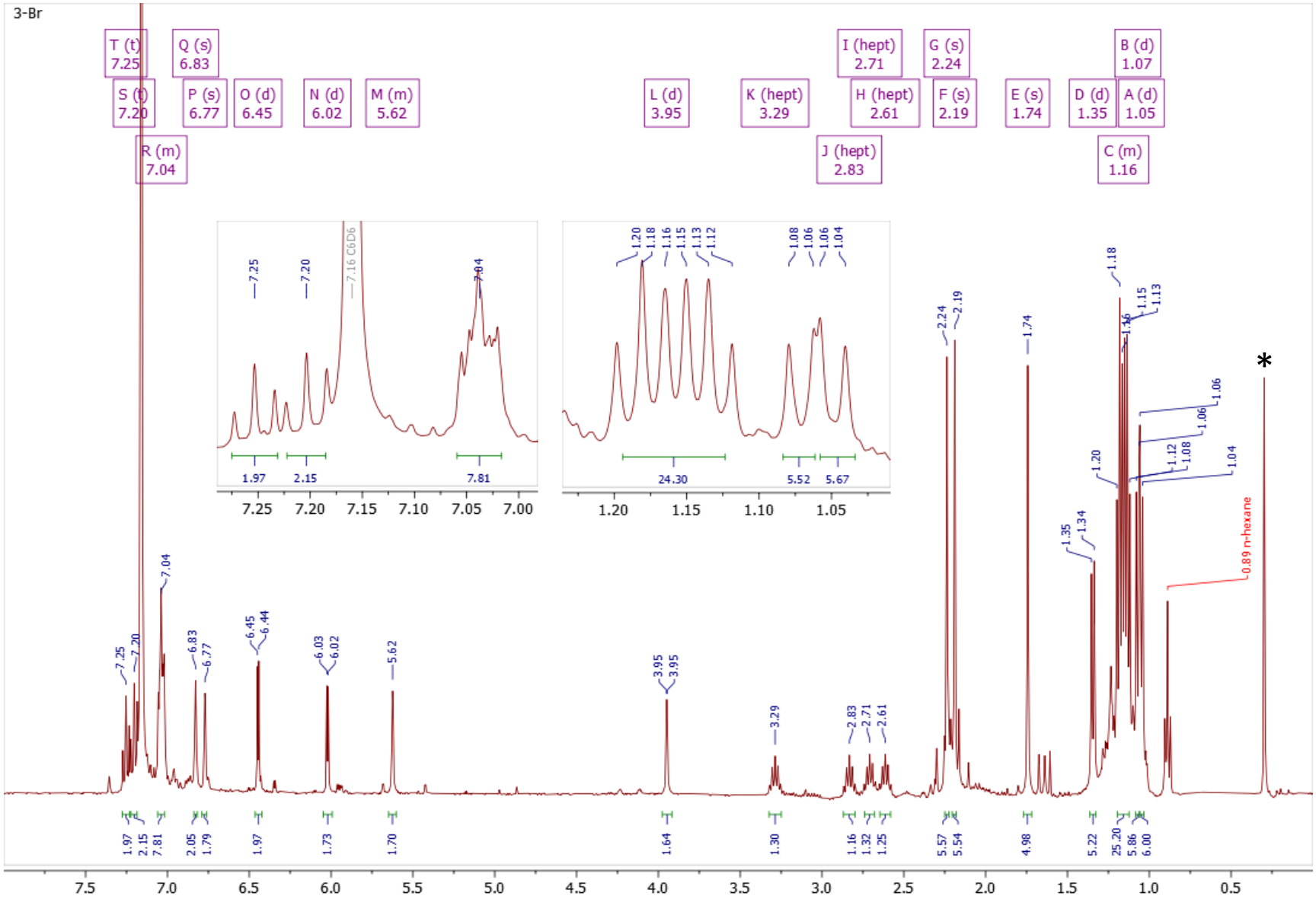

Figure S5: ^{1}H NMR spectrum of [(^{Dipp}DPM)BBr]$_2$ (**3-Br**) (400 MHz, C_6D_6, 298 K). (* indicates silicone grease)

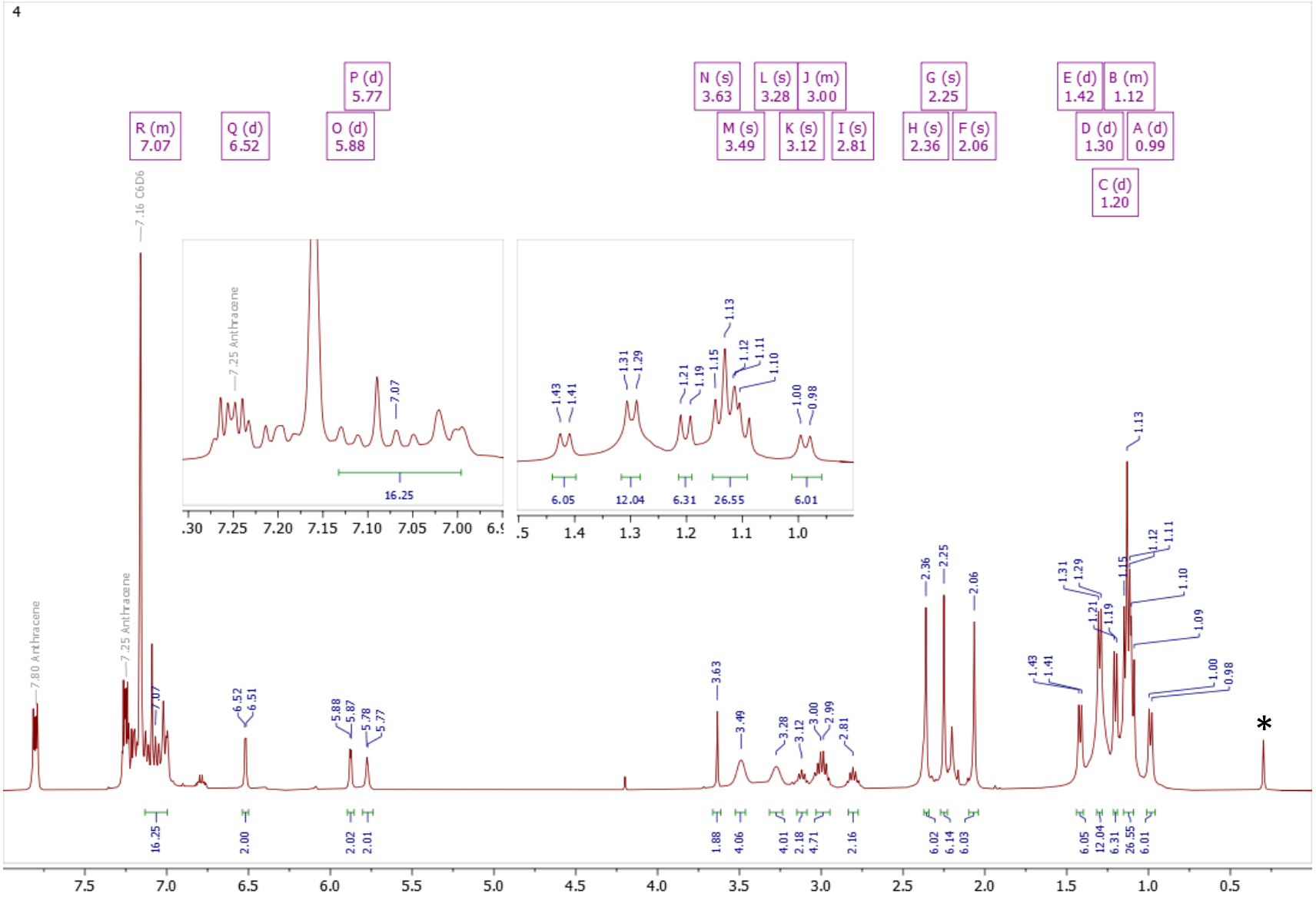

Figure S6: ^{1}H NMR spectrum of [Mg(THF)$_2${(^{Dipp}DPM)BF}$_2$] (**4**) (400 MHz, C_6D_6, 298 K). (* indicates silicone grease)

$^{13}C\{^{1}H\}$ NMR spectra of new compounds

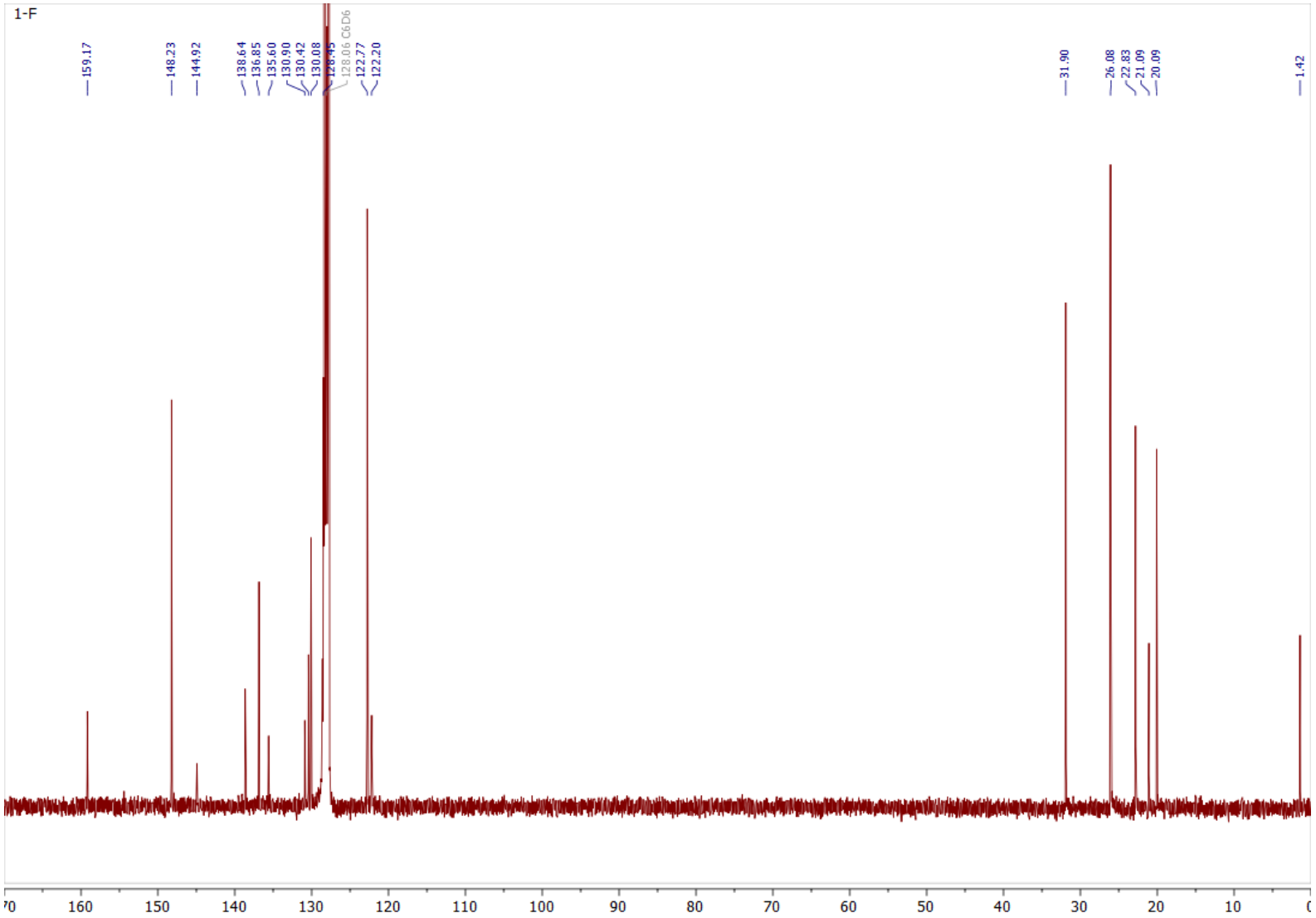

Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum of (^{Dipp}DPM)BF_2 (**1-F**) (101 MHz, C_6D_6, 298 K).

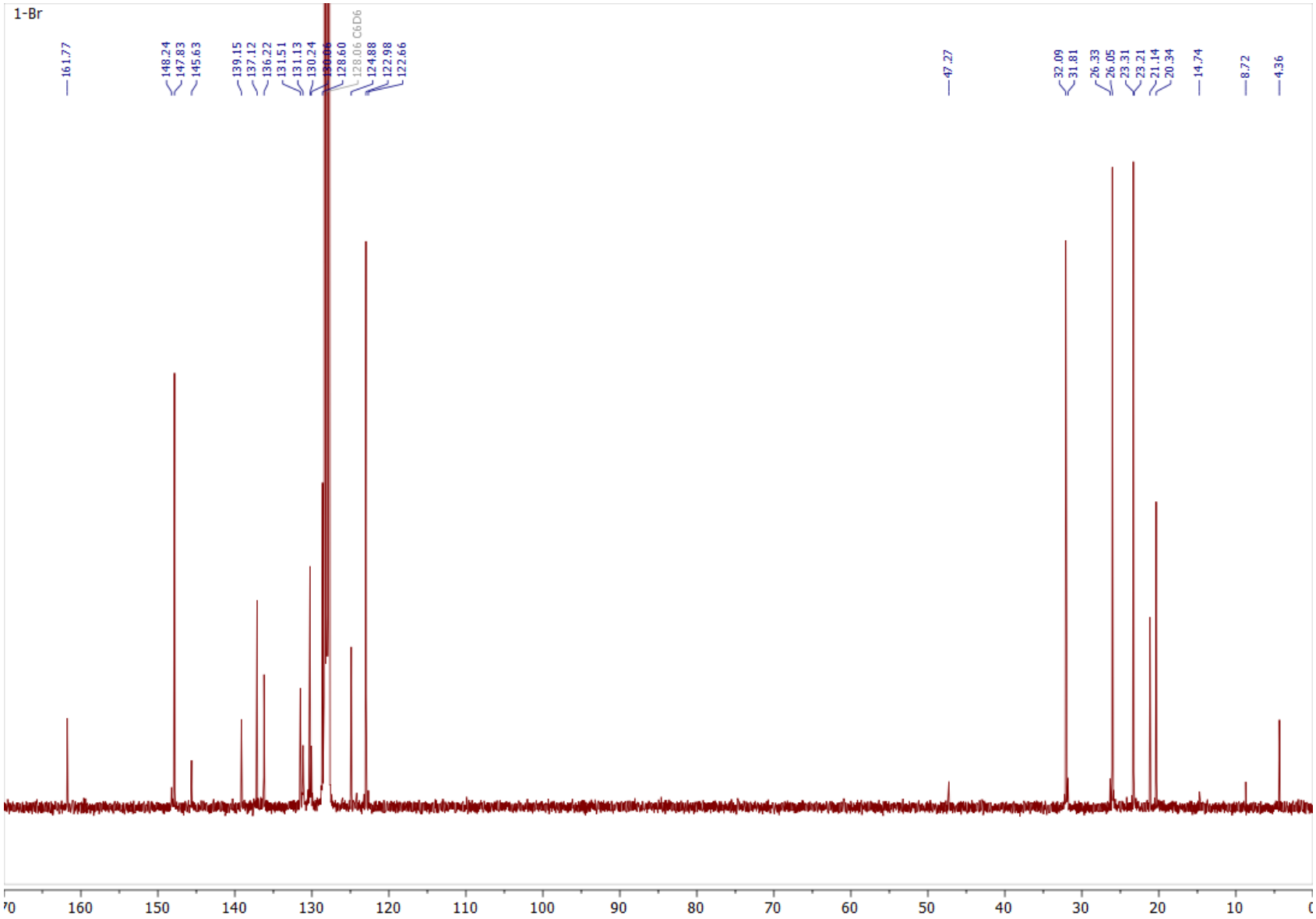

Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of (^{Dipp}DPM)BBr_2 (**1-Br**) (101 MHz, C_6D_6, 298 K).

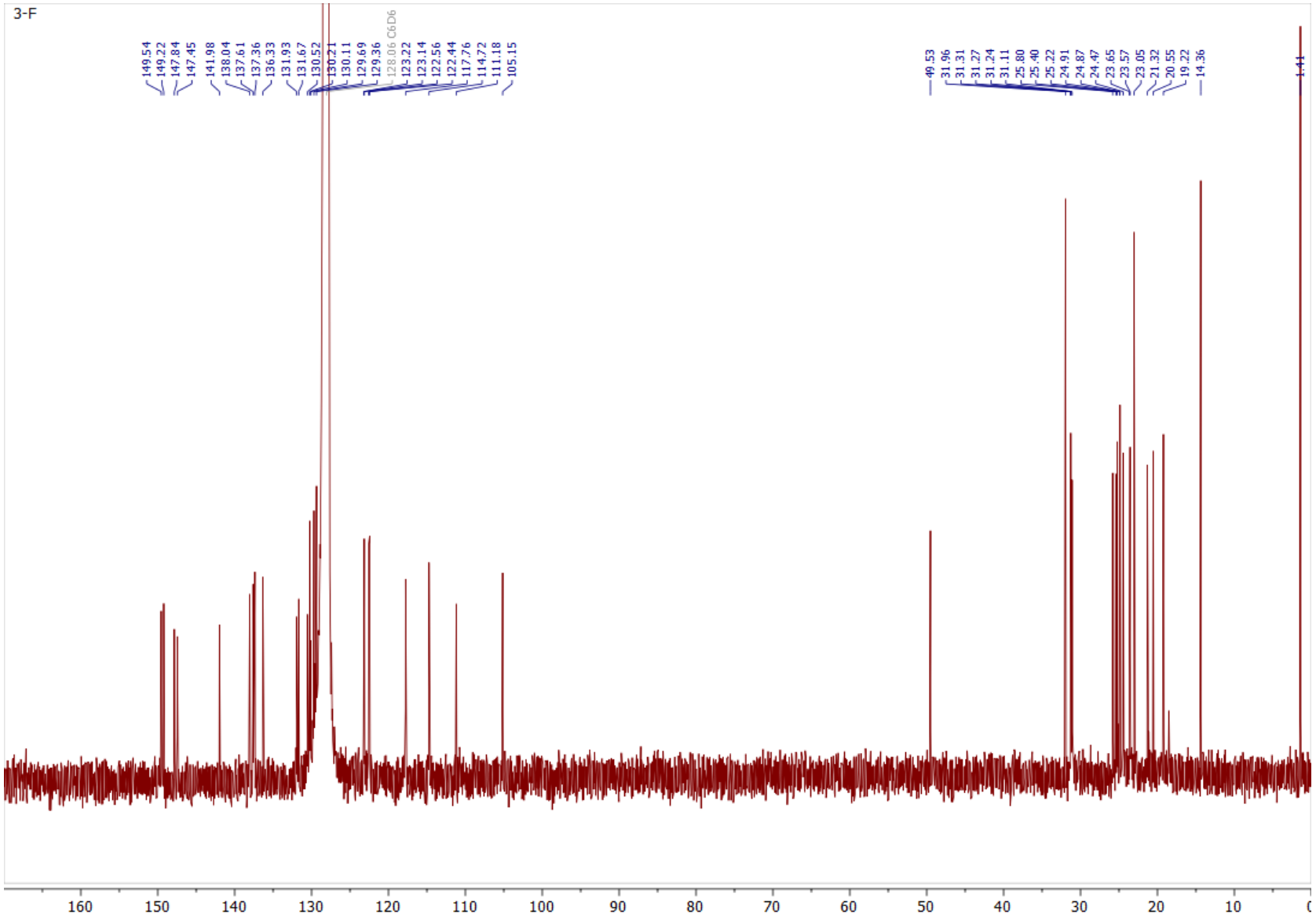

Figure S9: $^{13}C\{^{1}H\}$ NMR spectrum of $[(^{Dipp}DPM)BF]_2$ (**3-F**) (101 MHz, C_6D_6, 298 K).

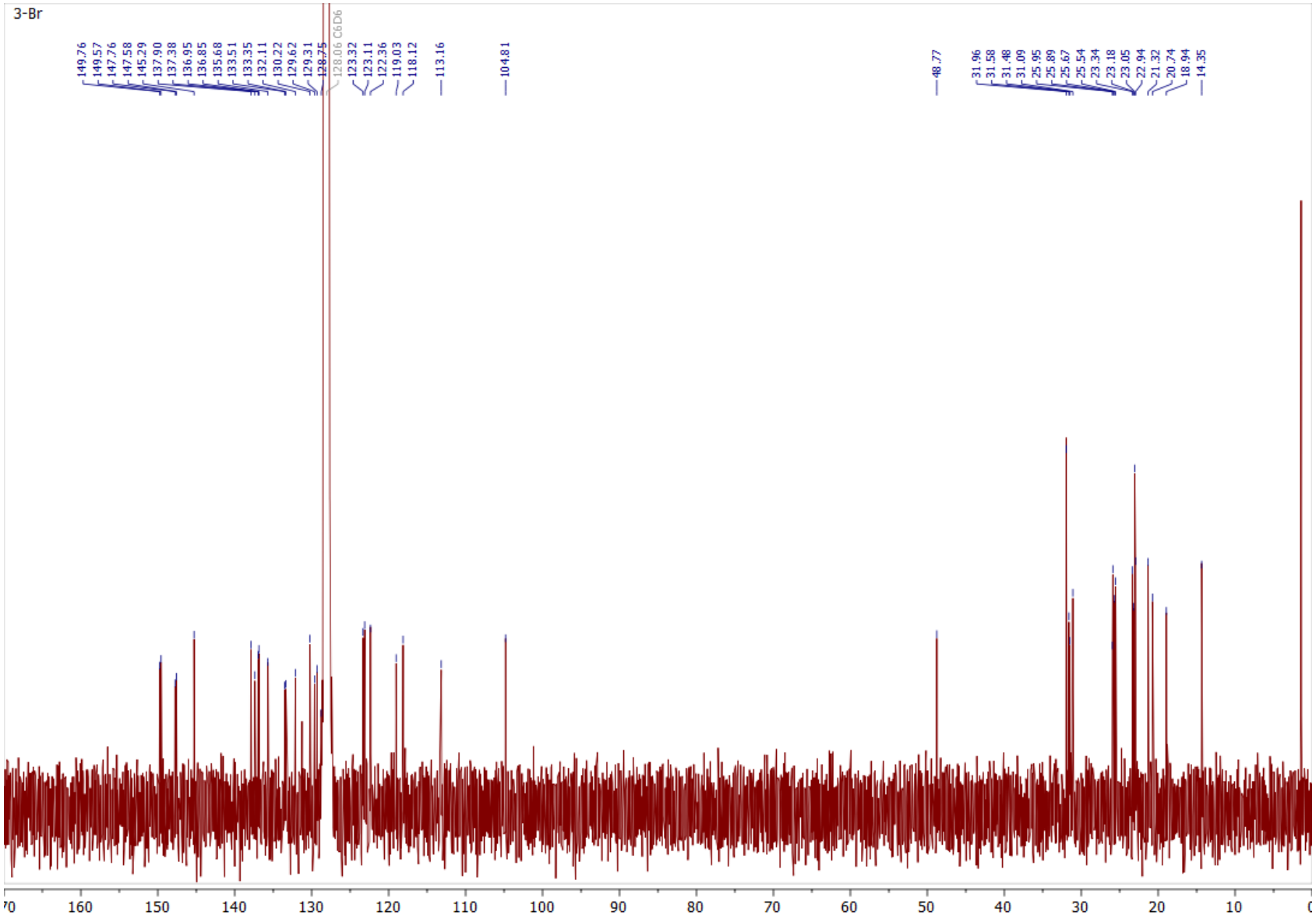

Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of [(^{Dipp}DPM)BBr]$_2$ (**3-Br**) (101 MHz, C_6D_6, 298 K).

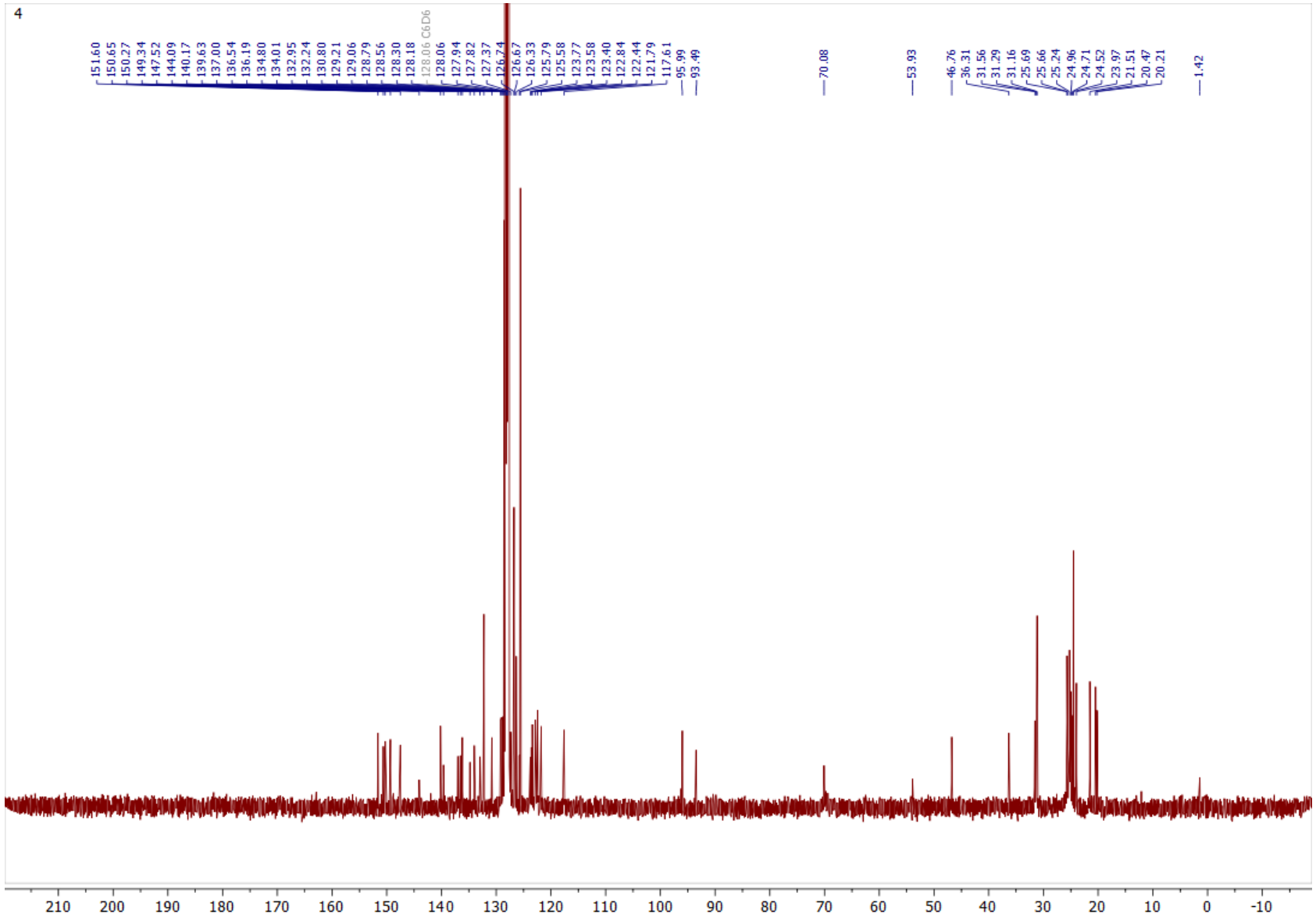

Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum of $[Mg(THF)_2\{(^{Dipp}DPM)BF\}_2]$ (**4**) (101 MHz, C_6D_6, 298 K).

^{11}B NMR spectra of new compounds

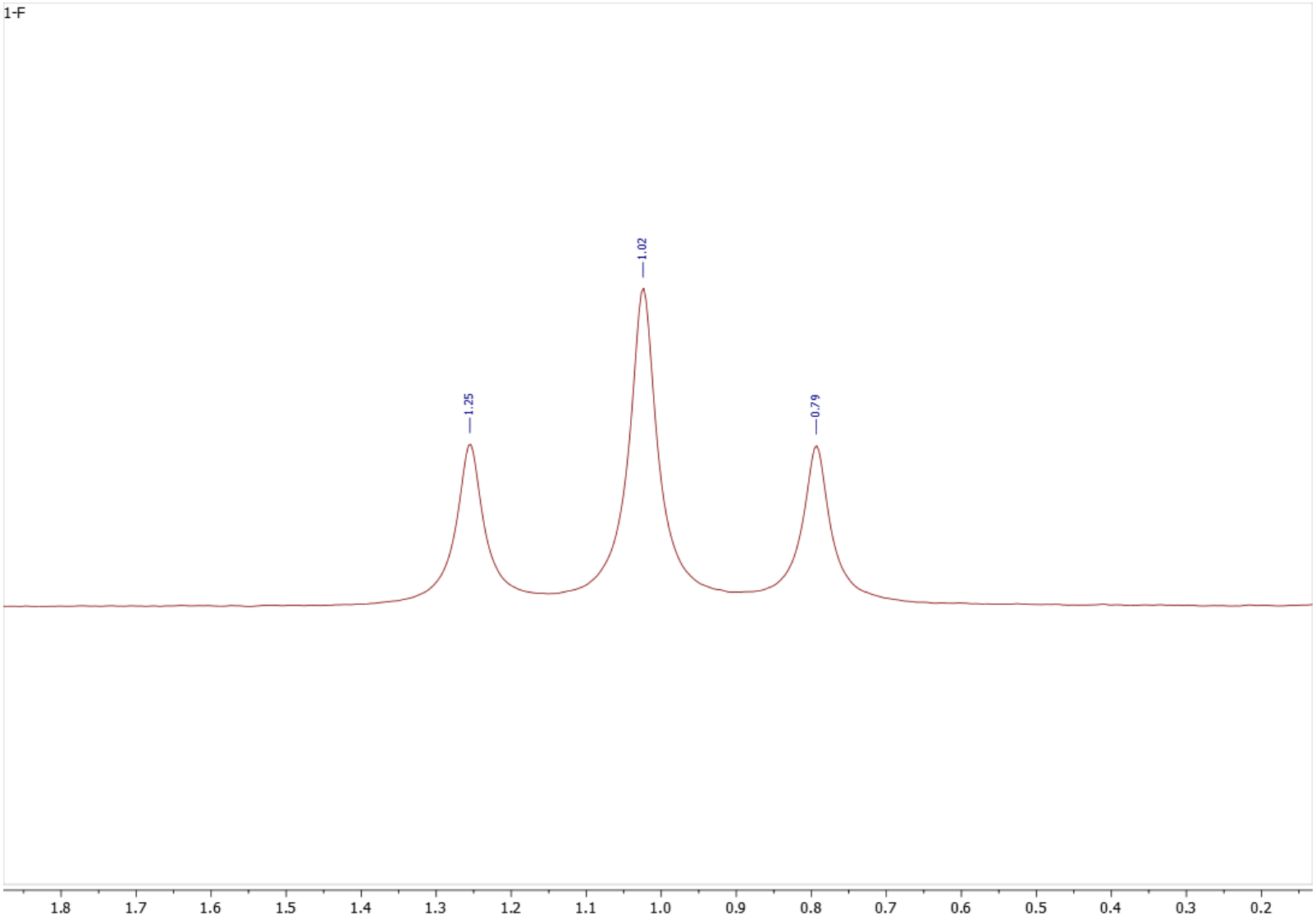

Figure S12: ^{11}B NMR spectrum of (^{Dipp}DPM)BF_2 (**1-F**) (128 MHz, C_6D_6, 298 K).

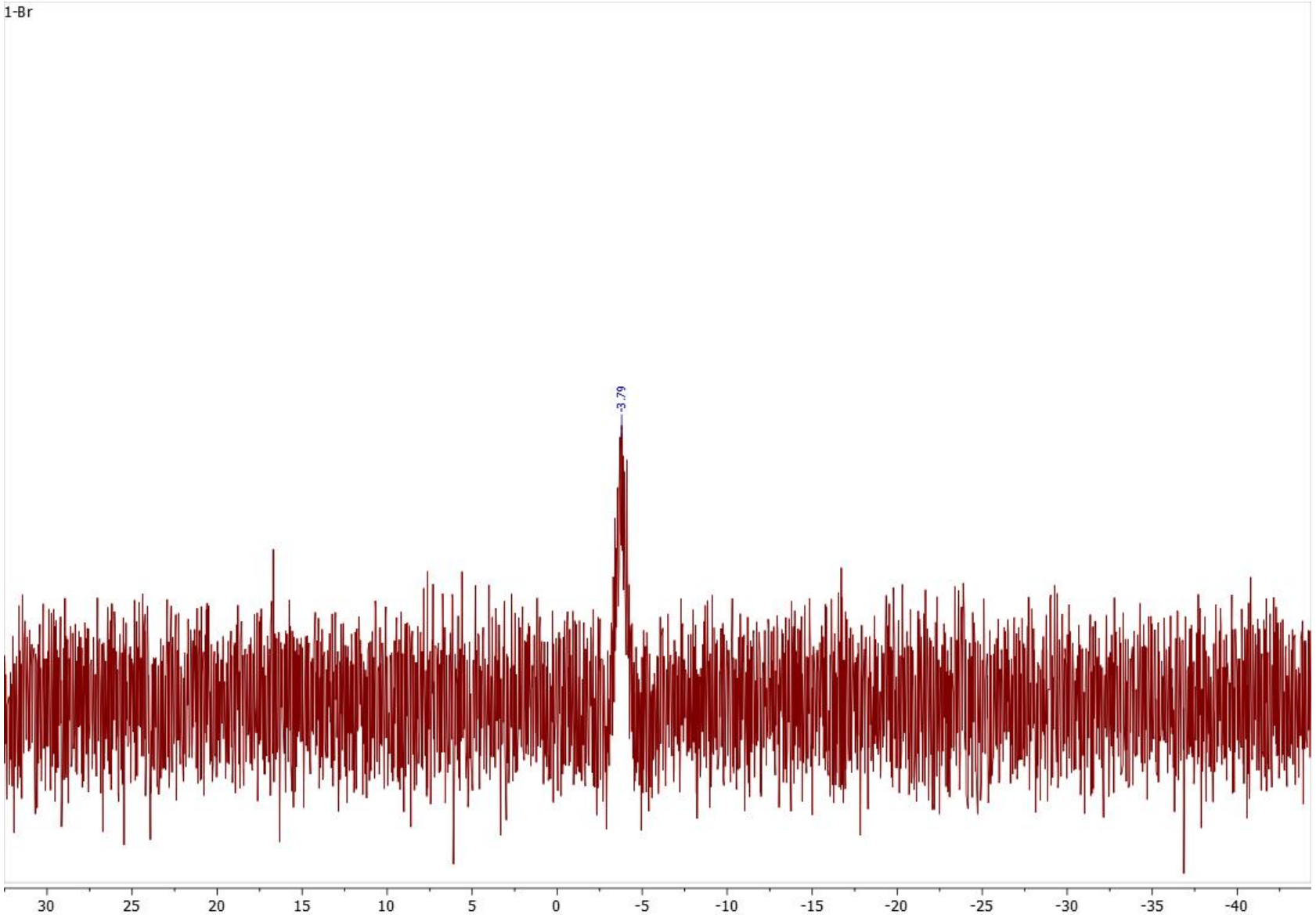

Figure S13: ^{11}B NMR spectrum of (^{Dipp}DPM)BBr_2 (**1-Br**) (128 MHz, C_6D_6, 298 K).

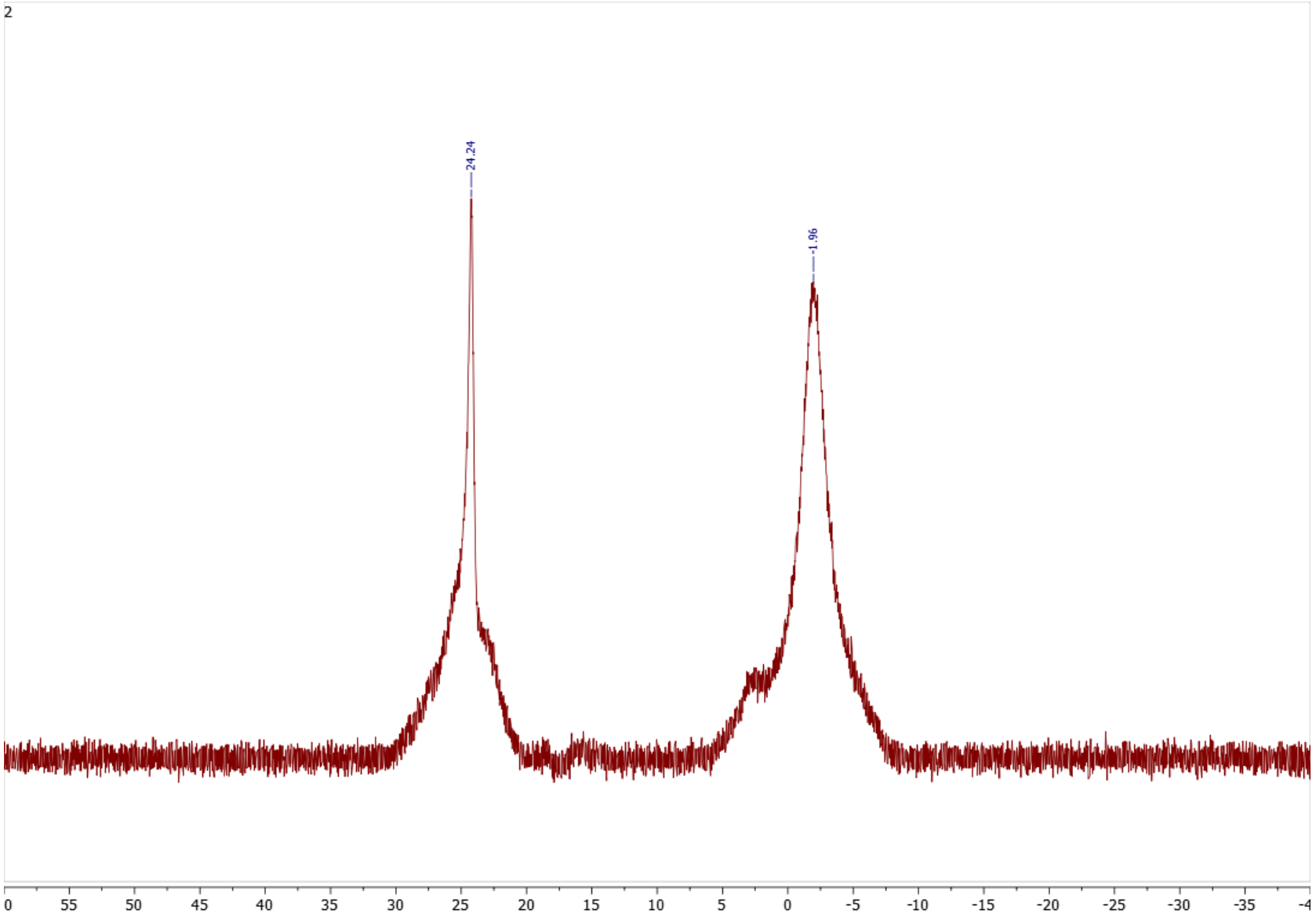

Figure S14: ^{11}B NMR spectrum of [(^{Dipp}DPM)BBr][BBr_4] (**2**) (128 MHz, C_6D_6, 298 K).

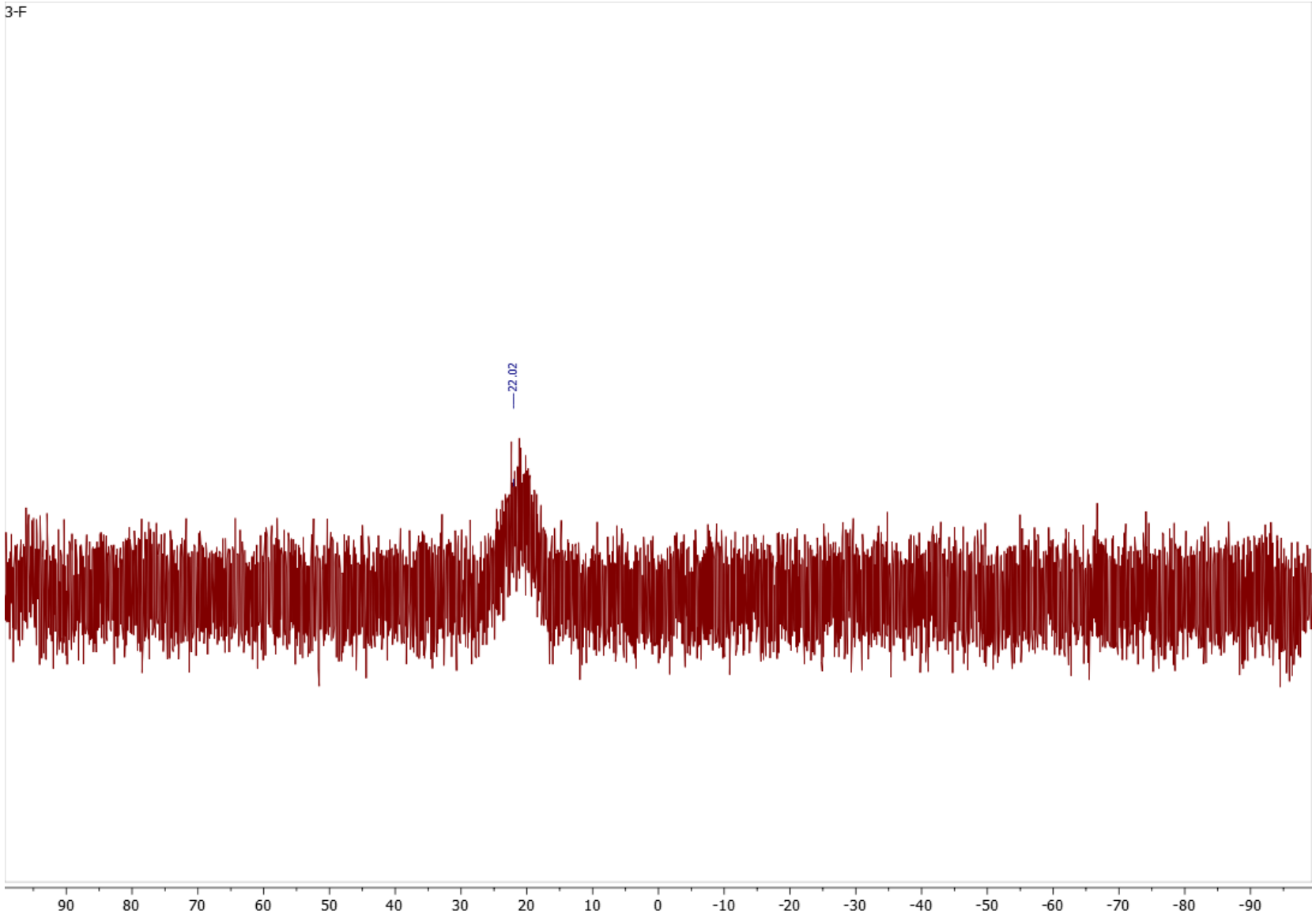

Figure S15: ^{11}B NMR spectrum of [(^{Dipp}DPM)BF]$_2$ (**3-F**) (128 MHz, C_6D_6, 298 K).

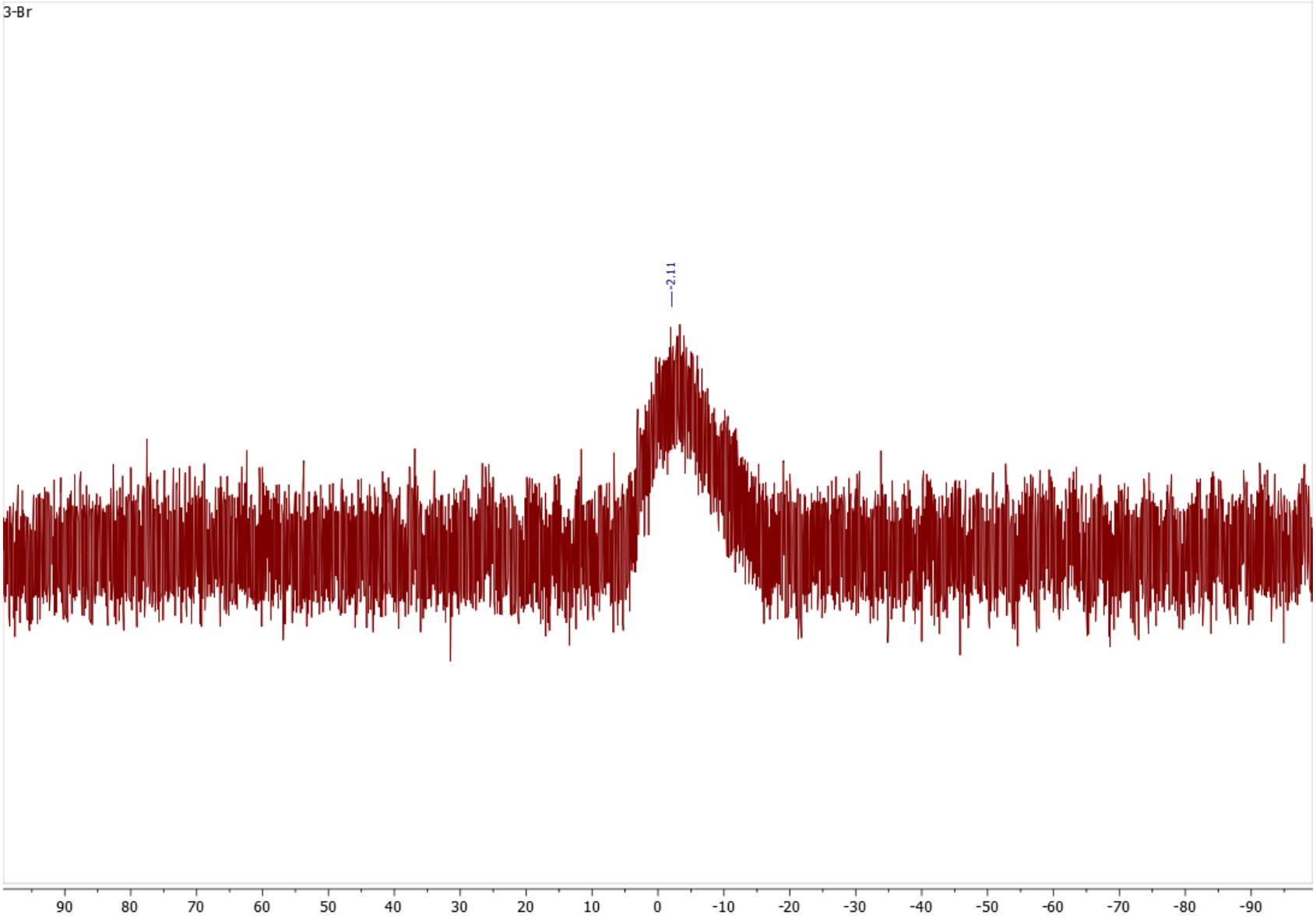

Figure S16: ^{11}B NMR spectrum of [(^{Dipp}DPM)BBr]$_2$ (**3-Br**) (128 MHz, C_6D_6, 298 K).

^{19}F NMR spectra of new compounds

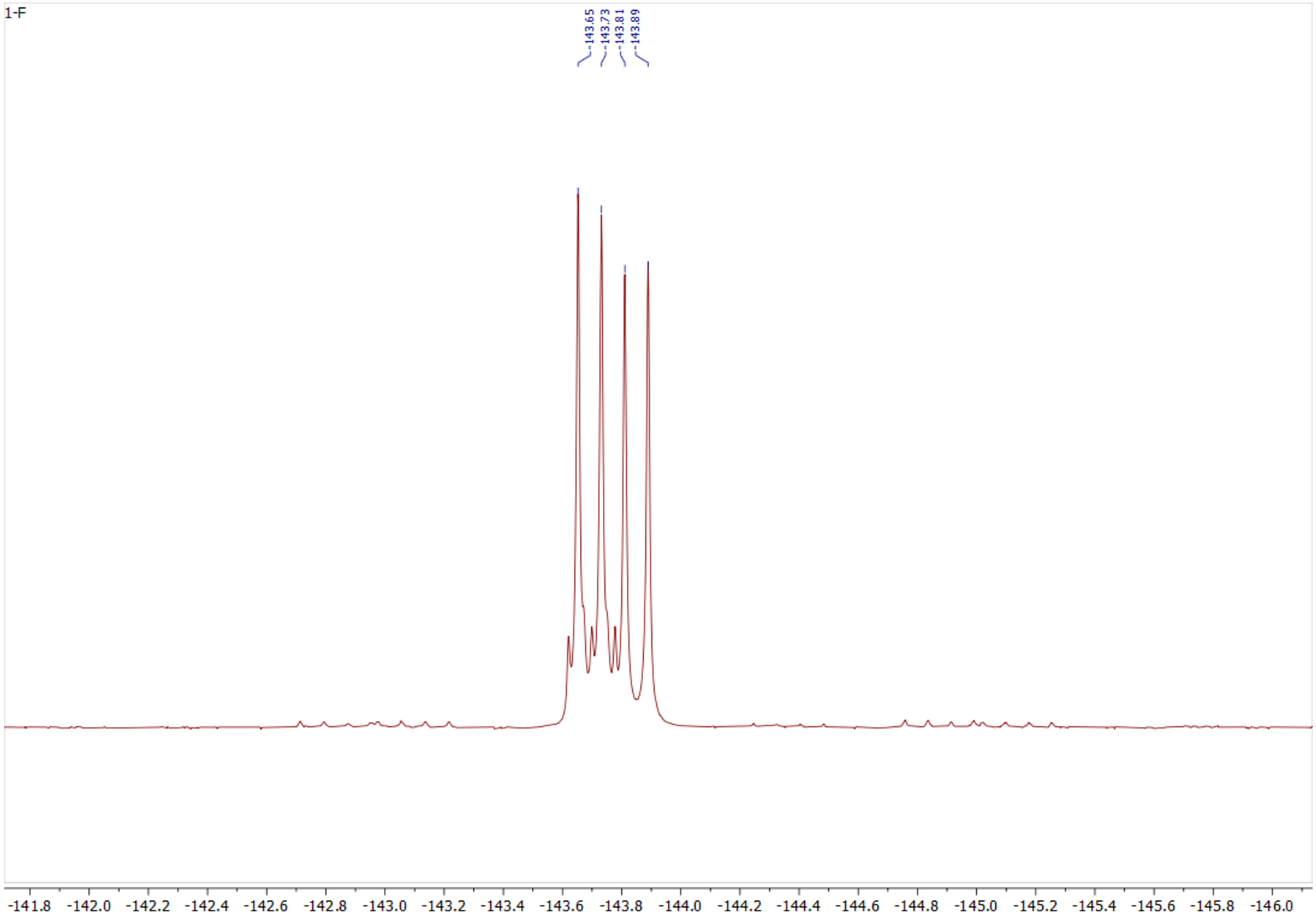

Figure S17: ^{19}F NMR spectrum of (^{Dipp}DPM)BF_2 (**1-F**) (376 MHz, C_6D_6, 298 K).

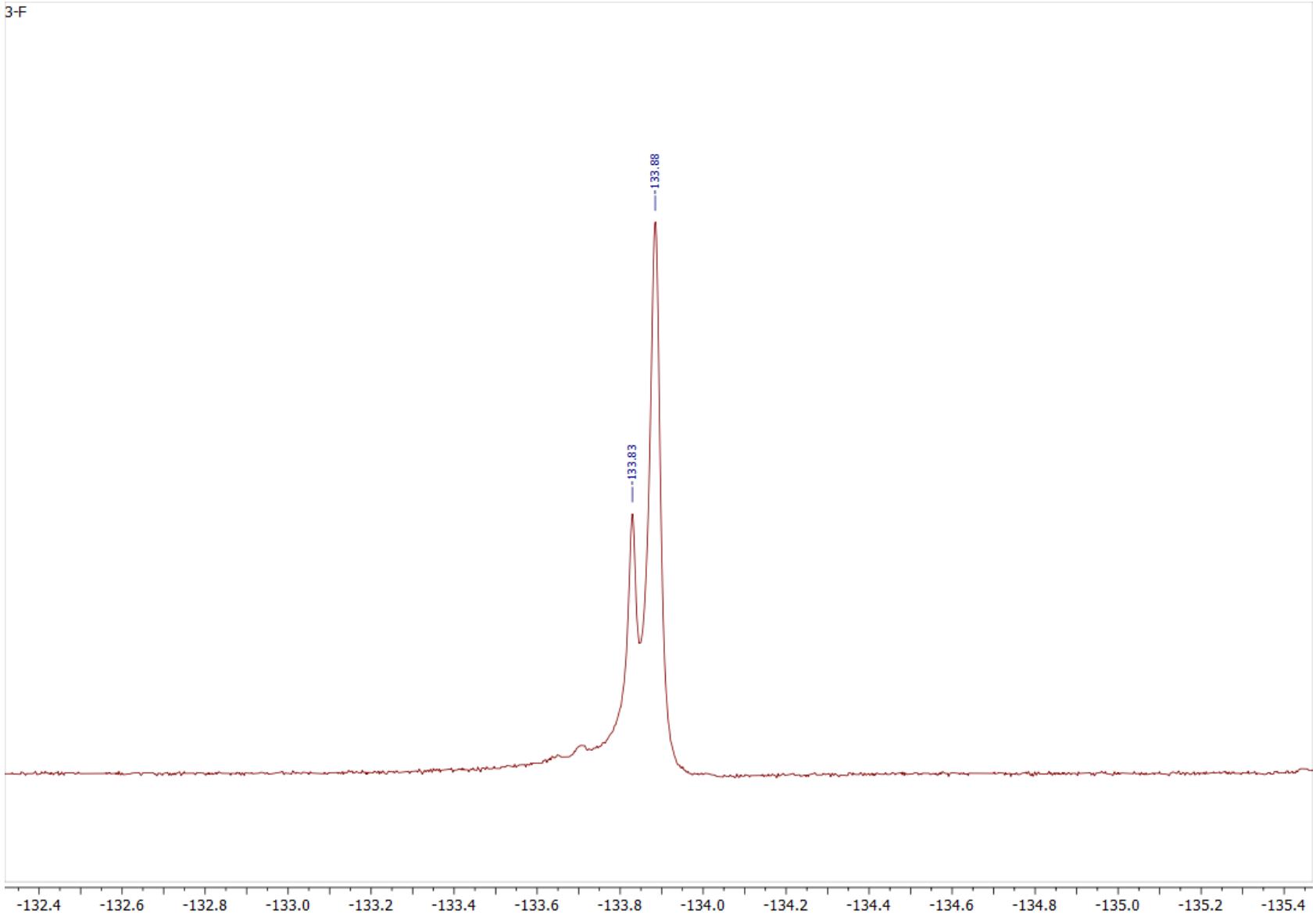

Figure S18: ^{19}F NMR spectrum of [(^{Dipp}DPM)BF]$_2$ (**3-F**) (376 MHz, C_6D_6, 298 K).

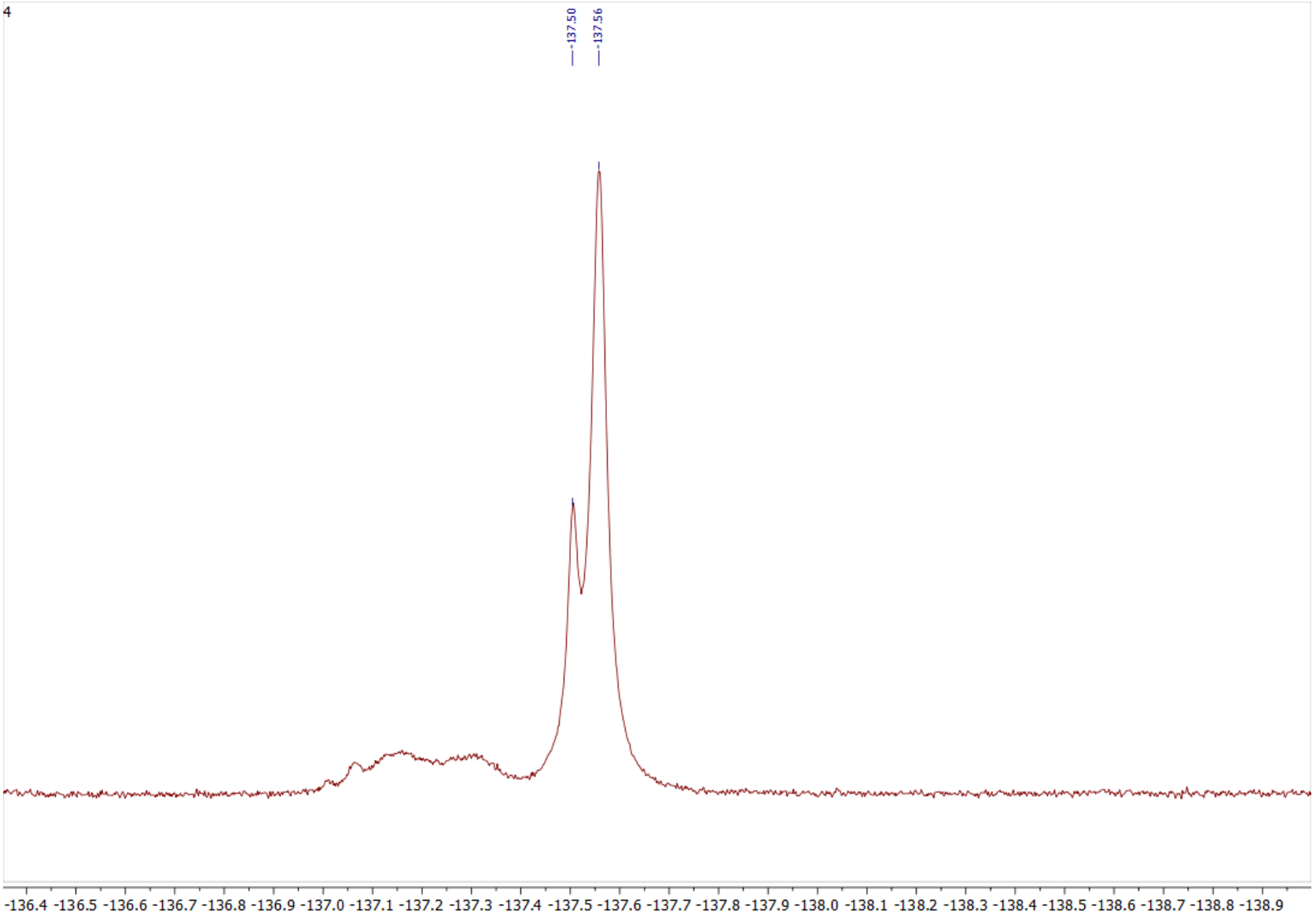

Figure S19: ^{19}F NMR spectrum of $[Mg(THF)_2\{(^{Dipp}DPM)BF\}_2]$ (**4**) (376 MHz, C_6D_6, 298 K).

X-ray crystallographic studies

Single-crystal X-ray diffraction data were collected using a Rigaku Supernova dual-source diffractometer. Crystals were selected under Paratone-N oil, mounted on Micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device.[S4] Data were collected at 150 K using mirror monochromated Cu K_α (λ = 1.5418 Å) radiation. Data collected were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[S5] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite.[S5] Structures were subsequently solved using SHELXT-2018 and refined on F^2 using the SHELXL 2018 package and the graphical interface Olex2.[S6-S8]

Finalised CIFs for all X-ray diffraction structures (2277691-2277696) have been deposited at the Cambridge Crystallographic Data Centre. These can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

The crystals of **3-Br** were found to be twinned (2-fold), therefore a twin integration was applied. Due to the large differences in the intensity of the two components, single and composite reflections from only one component were used to refine the model. **3-Br** was found to have crystallised with the hydrolysis product $[(^{Dipp}DPM)BOH]_2$, where the bromides have been substituted with hydroxides. This hydrolysed species has been modelled in the refinement and up approximately 27% of the crystal. There is no evidence for this hydrolysed compound in the NMR or IR spectra, therefore the hydrolysis is proposed to have occurred during crystallisation attempts.

Table S1: Crystallographic and refinement parameters for the structures of compounds **1-F**, **1-Br**, **2**, **3-F**, **3-Br** and **4**.

	1-F	**1-Br·C_6H_{14}**	**2·C_6H_6**	**3-F·C_6H_{14}**	**3-Br·0.5C_6H_{14}**	**4·5C_6H_6**
Formula	$C_{42}H_{49}BF_2N_2$	$C_{42}H_{49}BBr_2N_2$	$C_{48}H_{55}B_2Br_5N_2$	$C_{90}H_{112}B_2F_2N_4$	$C_{87}H_{105.5}B_2Br_{1.5}N_4O_{0.5}$	$C_{122}H_{144}B_2F_2MgN_4O_2$
M	630.64	838.63	1081.11	1309.45	1353.90	1782.33
Cell Setting	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space Group	$P2_1/n$	P–1	P–1	$P2_1/c$	P–1	$P2_1/n$
a/Å	21.4180(3)	10.3900(3)	11.5135(4)	10.86146(9)	11.6625(4)	11.2816(2)
b/Å	17.0027(2)	14.6043(3)	13.7856(5)	35.6092(3)	13.5508(5)	36.4512(8)
c/Å	22.8135(4)	15.6325(4)	16.3179(5)	21.07021(16)	25.3021(12)	26.0374(5)
α/°	90	81.880(2)	75.759(3)	90	82.352(3)	90
β/°	116.951(2)	73.939(2)	75.100(3)	99.2415(7)	77.952(4)	96.278(2)
γ/°	90	89.774(2)	83.917(3)	90	85.009(3)	90
V/Å^3	7405.6(2)	225.06(11)	2423.46(15)	8043.49(11)	3868.5(3)	10643.1(4)
Z	8	2	2	4	2	4
Unique/I > 2σI	14538/11608	8841/7958	9500/8208	15693/12694	18726/16107	20866/11002
R_{int}	0.0212	0.0189	0.0250	0.0229	-	0.0612
Parameters	869	547	576	907	950	1303
R_1 (all data/ I > 2σI)	0.0604/0.0467	0.0385/0.0341	0.0655/0.0582	0.0709/0.0561	0.0561/0.0486	0.1563/0.0925
wR_2 (all data/ I > 2σI)	0.1250/0.1172	0.0895/0.0861	0.1758/0.1675	0.1545/0.1430	0.1290/0.1260	0.2435/0.2897
GooF	1.025	1.054	1.034	1.044	1.029	1.005
Residual max/min	0.276/–0.259	0.668/–0.466	1.420/–2.414	0.485/–0.514	0.523/–0.350	0.710/–0.489
T/K	150.00(10)	150.01(10)	150.01(10)	150.01(10)	149.98(10)	150.01(10)
Radiation, λ (Å)	Cu Kα, (1.54184)	Cu Kα, (1.54184)	Cu Kα, (1.54184)	Cu Kα, (1.54184)	Cu Kα, (1.54184)	Cu Kα, (1.54184)
CCDC number	2277691	2277692	2277693	2277694	2277695	2277696

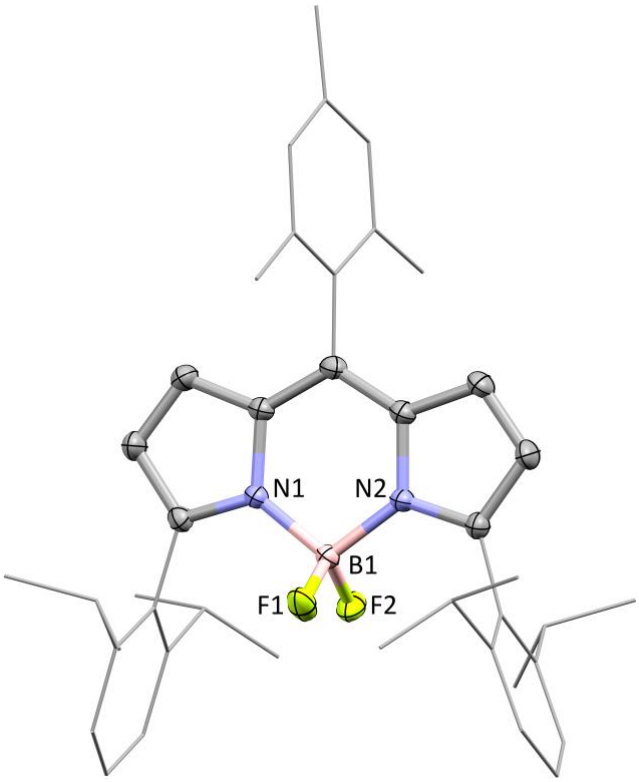

Figure S20: Molecular structure of **1-F** as determined by X-ray crystallography. Non-coordinating solvent molecules and hydrogen atoms have been removed, and Mes and Dipp groups have been displayed in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

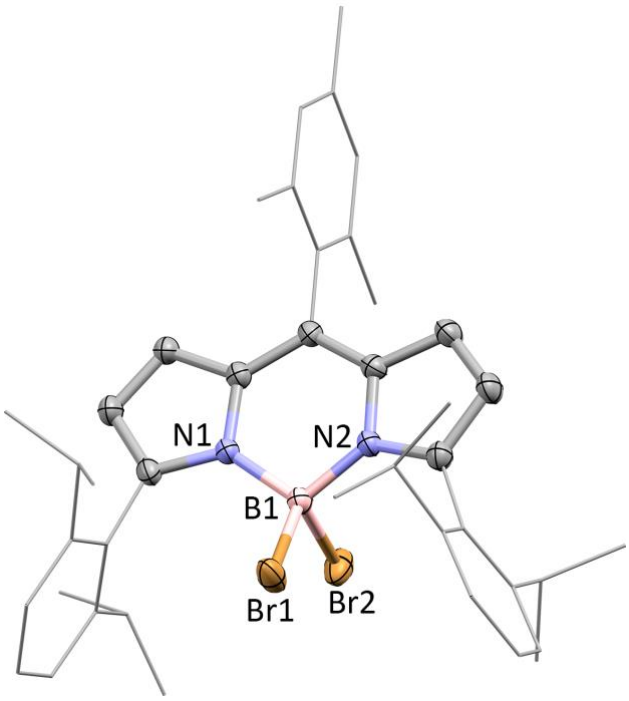

Figure S21: Molecular structure of **1-Br** as determined by X-ray crystallography. Non-coordinating solvent molecules and hydrogen atoms have been removed, and Mes and Dipp groups have been displayed in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

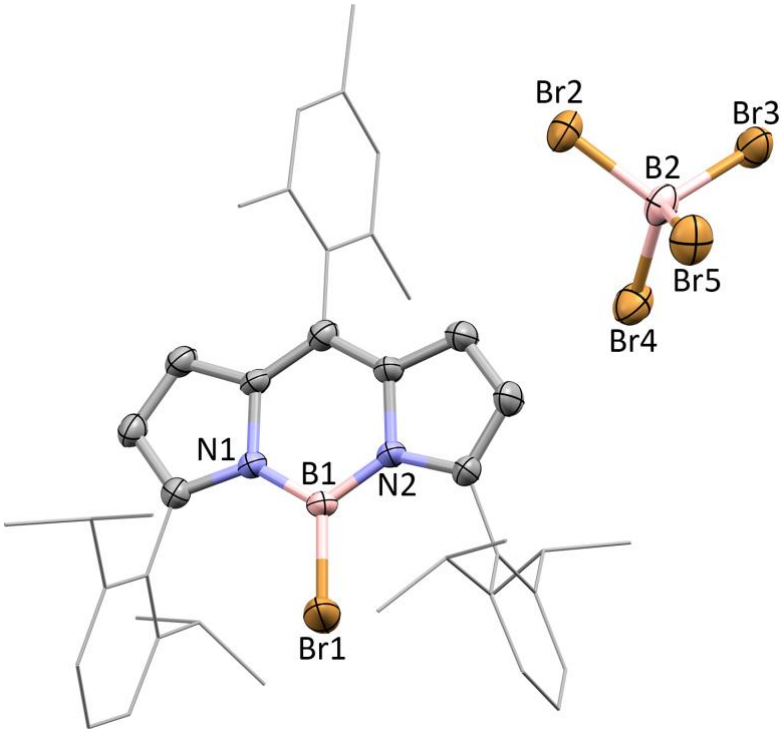

Figure S22: Molecular structure of **2** as determined by X-ray crystallography. Non-coordinating solvent molecules and hydrogen atoms have been removed, and Mes and Dipp groups have been displayed in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

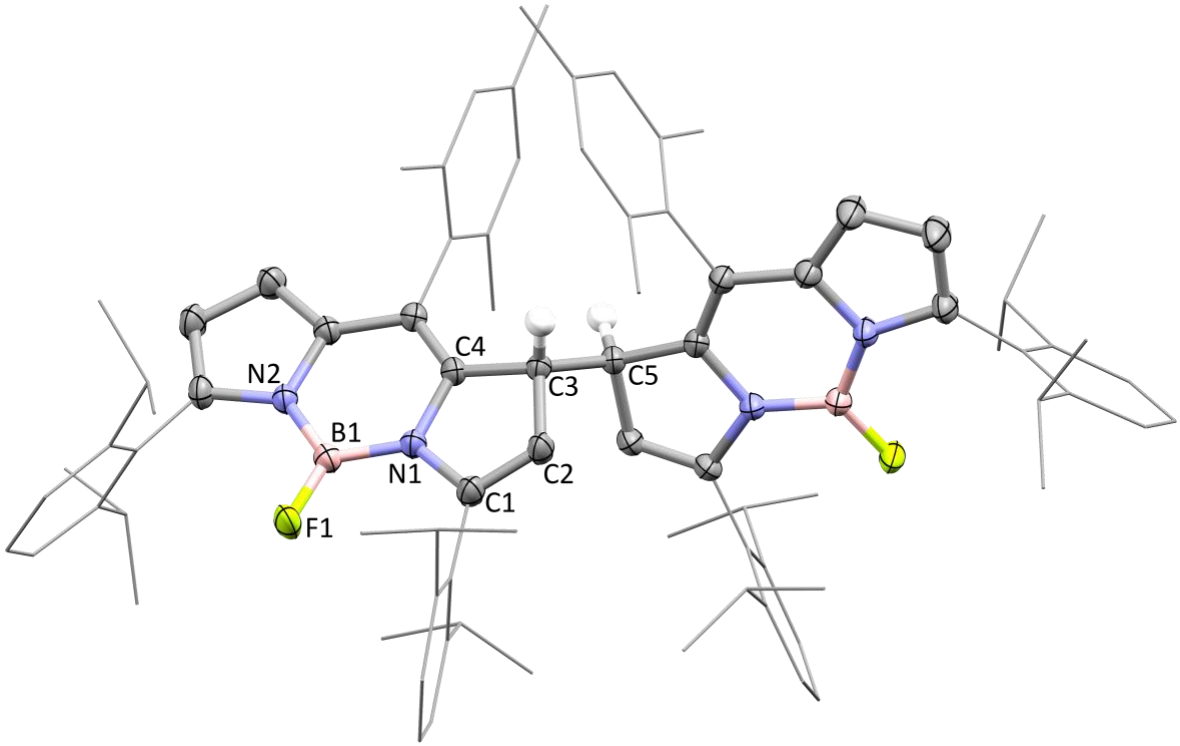

Figure S23: Molecular structure of **3-F** as determined by X-ray crystallography. Non-coordinating solvent molecules and most hydrogen atoms have been removed, and Mes and Dipp groups have been displayed in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

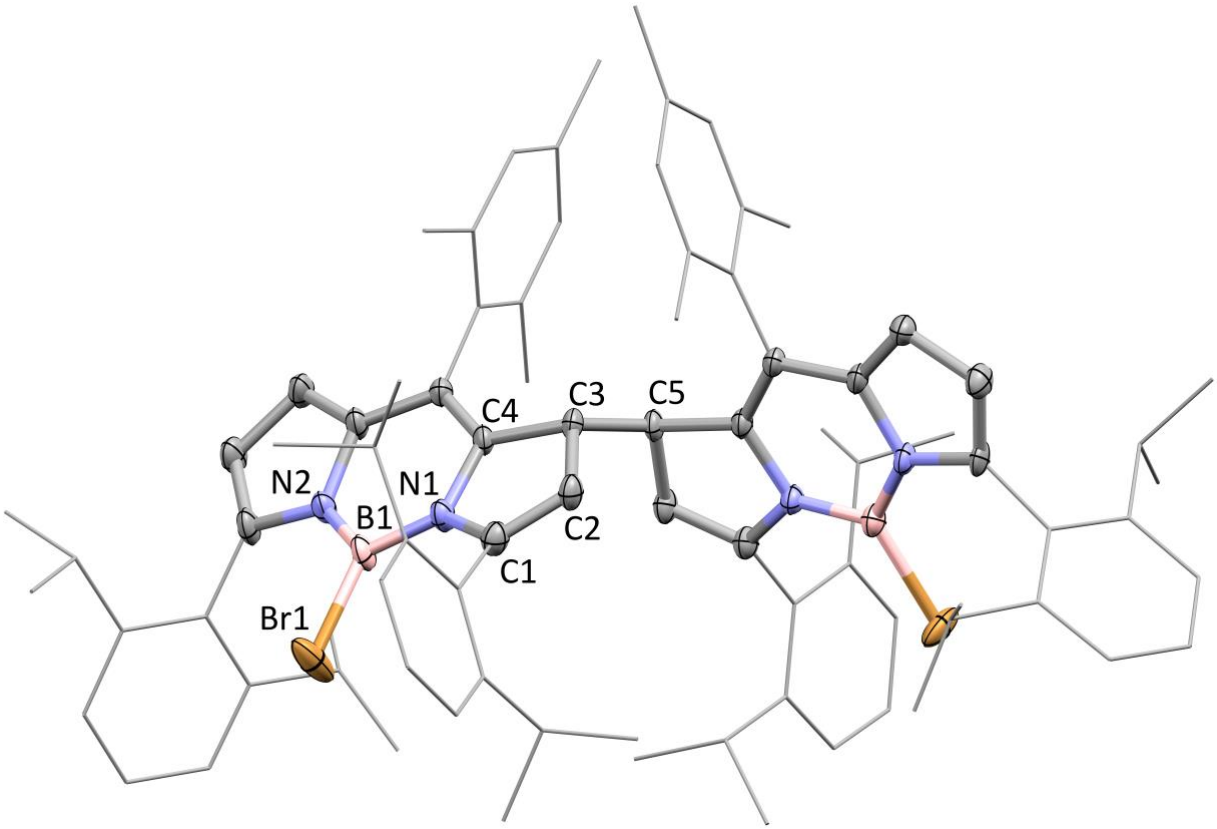

Figure S24: Molecular structure of **3-Br** as determined by X-ray crystallography. Non-coordinating solvent molecules and hydrogen atoms have been removed, and Mes and Dipp groups have been displayed in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

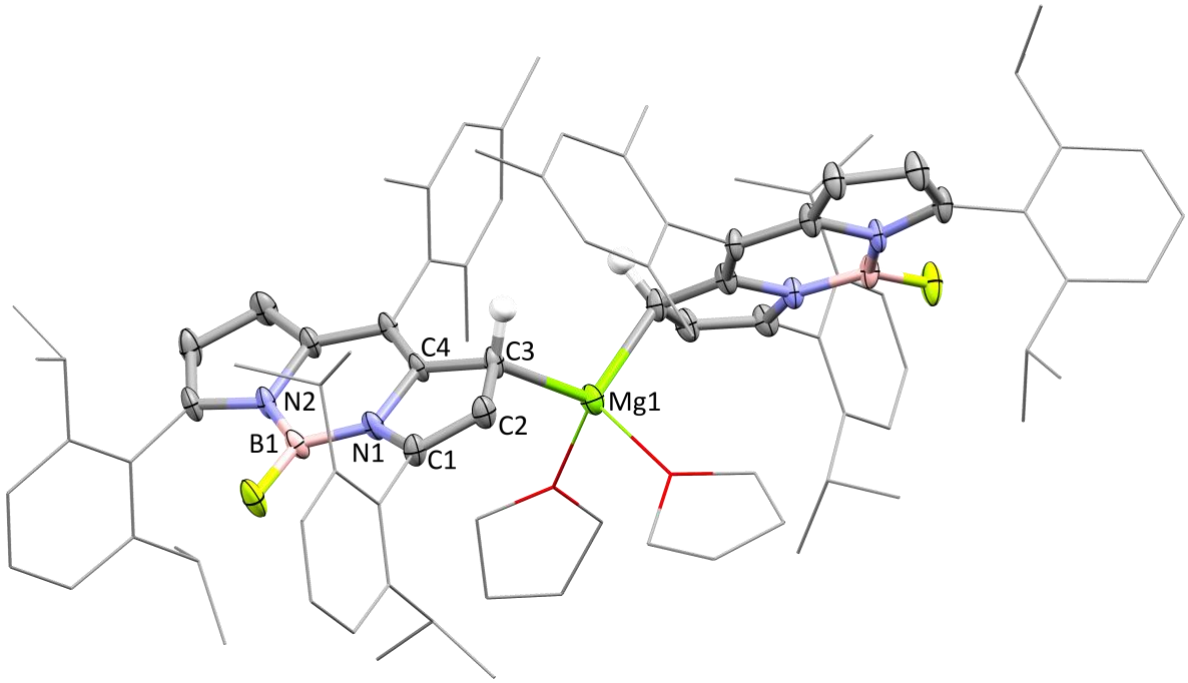

Figure S25: Molecular structure of **4** as determined by X-ray crystallography. Non-coordinating solvent molecules and hydrogen atoms have been removed, and Mes and Dipp groups have been displayed in wireframe for clarity. Displacement ellipsoids set at the 50% probability level.

EPR materials and methods

X-band EPR tubes equipped with J. Young's taps were used to collect the EPR data on the reaction between [(^{Mes}NacNac)Mg]$_2$ and **1-F**. These were custom-made by fusing a borosilicate J. Young's NMR tube cap to a quartz EPR tube via a seal comprising an increasing gradient of the borosilicate-to-quartz ratio.

CW X-band solution-phase EPR spectra were collected on a 9.4 GHz X-band Bruker Elexsys E580 spectrometer with an ER4112SHQE resonator. Reported spectra were recorded with a field modulation of 0.01 mT and a microwave power of 0.00006325 mW. Microwave saturation curves (not shown) were collected to ensure the signal was not saturated. Frozen solution spectra were also collected but were featureless. Simulations were performed using the fast-motion CW EPR program "garlic" in the EasySpin package in MATLAB.[S9]

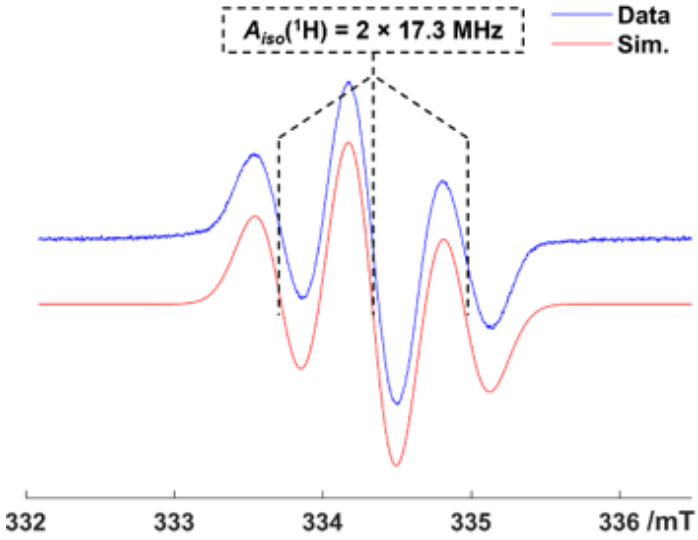

Figure S26: X-band CW EPR spectrum of the reaction between [(^{Mes}Nacnac)Mg]$_2$ and **1-F** at 291 K. The experimental spectrum is reflected in the blue trace, while the red trace shows the simulated spectrum with g_{iso} = 2.005 and A_{iso}(^{1}H) = 2 × 17.3 MHz, due to coupling with the two hydrogens on the γ-positions.

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