Electronic Supporting information for:

Synthesis of Polyheterocyclic 1,1-Diboryltriazenes by *γ*-Nitrogen Insertion of Azides into Activated B–B Single Bonds

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General experimental details

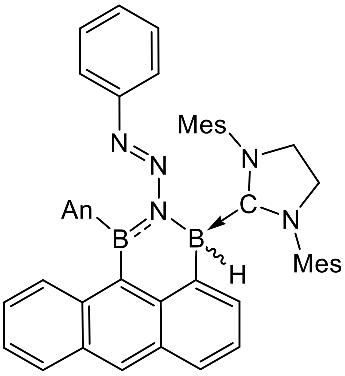
All reactions were performed under an atmosphere of dry argon using standard Schlenk line or glovebox techniques. Deuterated benzene was degassed by three freeze-pump-thaw cycles and dried over molecular sieves. All other solvents were distilled and degassed from appropriate drying agents. The solvents, both deuterated and non-deuterated, were then stored under argon over activated 4 Å molecular sieves. NMR spectra were obtained from a Bruker Avance 500 NMR spectrometer (^{1}H and $^{1}H\{^{11}B\}$: 500.1 MHz, $^{13}C\{^{1}H\}$: 125.8 MHz; ^{11}B: 160.5 MHz, ^{19}F: 470.6 MHz) or a Bruker Avance 400 (^{1}H and $^{1}H\{^{11}B\}$: 400.1 MHz, $^{13}C\{^{1}H\}$: 100.6 MHz; ^{11}B: 128.4 MHz, ^{19}F: 376.5 MHz) at 298 K. Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei ($^{13}C\{^{1}H\}$) or residual protons (^{1}H) of the solvent. ^{11}B and ^{19}F NMR spectra were referenced to external standard [$BF_3{\cdot}OEt_2$] or $CFCl_3$, respectively. UV-vis spectra were measured on a JASCO V-660 UV-vis spectrometer. High-resolution mass spectrometry was obtained from a Thermo Scientific Exactive Plus spectrometer. IR spectra were recorded with a Bruker Alpha spectrometer with an apodised resolution of 1 cm^{-1} in the attenuated total reflection (ATR) mode in the region of 4000−400 cm^{-1} using a setup with a diamond crystal.

Diboranes(5) **1a**[1] and **1b**,[2] PhN_3,[3] *p*-NMe_2-$C_6H_4N_3$[4] and *p*-CF_3-$C_6H_4N_3$[5] were synthesised according to literature procedures. All other chemicals were purchased from either Sigma-Aldrich, Acros Organics or TCI Chemical Co. and used as received unless otherwise specified.

Note on ^{11}B NMR spectra: The ^{11}B NMR resonances of some of the compounds presented herein are extremely broad. This is a common feature owed to quadrupolar coupling between the two boron atoms through the inserted nitrogen. Usually, a high temperature ^{11}B NMR spectrum (ca 80 °C) could offer a better resolution but this was not an option because of the thermal instability of these compounds. The assignments were conducted by picking the centre of the broad resonances in accordance with the sign change observed in the derivatives of the spectra.

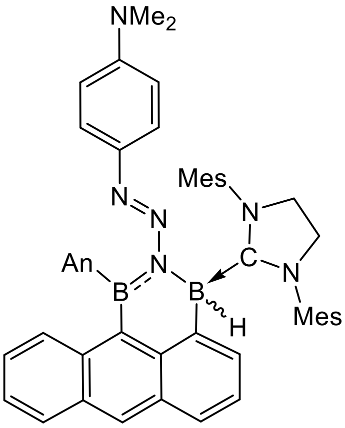
Synthetic procedures

Synthesis of $2b^H$



Diborane(5) **1b** (20.0 mg, 0.03 mmol) was suspended in benzene (0.6 mL) and PhN_3 (7.6 mg, 0.06 mmol, 2.2 equiv) was added. Heating at 60 °C for four days afforded a yellow suspension, which was dried *in vacuo*, washed with hexane (3 x 1.0 mL) and once with benzene (0.5 mL) to yield $\mathbf{2b^H}$ as a yellow solid (12.6 mg, 0.01 mmol, 54%). Crystals suitable for single-crystal X-ray diffraction were obtained during the reaction by cooling the reaction mixture from 60 °C to room temperature. $^1H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6): δ = 8.36 (s, 1H, Ar-C*H*), 8.18 (s, 1H, Ar-C*H*), 8.14 (br d, $^3J_{HH}$ = 8.3 Hz, 1H, Ar-C*H*), 8.11 (br d, $^3J_{HH}$ = 9.0 Hz, 1H, Ar-C*H*), 8.05 (br d, $^3J_{HH}$ = 8.3 Hz, 1H, Ar-C*H*), 7.86 (br d, $^3J_{HH}$ = 8.4Hz, 1H, Ar-C*H*), 7.71 (br d, $^3J_{HH}$ = 8.4Hz, 1H, Ar-C*H*), 7.59 – 7.55 (m, 1H, Ar-C*H*), 7.54 – 7.51 (m, 2H, Ar-C*H*), 7.43 (dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, Ar-C*H*), 7.31 – 7.28 (m, 2H, Ar-C*H*), 7.07 – 7.05 (m, 4H, Ar-C*H*), 6.97 – 6.93 (m, 2H, Ar-C*H*), 6.88 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar-C*H*), 6.85 – 6.82 (m, 1H, Ar-C*H*), 6.67 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar-C*H*), 6.48 (ddd, $^3J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, Ar-C*H*), 6.21 – 6.16 (m, 3H, Ar-C*H*), 4.38 (s, 1H, B*H*), 3.08 – 2.93 (m, 4H, NCH_2CH_2N), 2.17 (s, 6H, CH_3), 2.04 (s, 6H, CH_3), 1.75 (br s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ = 190.3 (br, $C_{Carbene}$, *observed by HMBC*), 151.8 (C_q), 146.9 (br, C_q), 140.5 (C_q), 139.7 (br, C_q), 138.7 (C_q), 137.3 (C_q), 137.1 (C_q), 136.1 (C_q), 135.2 (C_q), 134.8 (C_q), 133.8 (Ar-*C*H), 133.6 (C_q), 132.4 (Ar-*C*H), 132.1 (Ar-*C*H), 131.8 (C_q), 131.5 (C_q), 131.5 (C_q), 130.6 (Ar-*C*H), 130.3 (Ar-*C*H), 130.1 (Ar-*C*H), 129.5 (Ar-*C*H), 129.3 (Ar-*C*H), 128.6 (Ar-*C*H), 128.6 (Ar-*C*H), 128.6 (Ar-*C*H), 128.6 (Ar-*C*H), 127.0 (Ar-*C*H), 126.4 (Ar-*C*H), 126.1 (Ar-*C*H), 125.4 (Ar-*C*H), 124.7 (Ar-*C*H), 124.5 (Ar-*C*H), 124.4 (Ar-*C*H), 124.3 (Ar-*C*H), 123.3 (Ar-*C*H), 122.3 (Ar-*C*H), 50.6 (CH_2), 21.1 (CH_3), 19.1 (CH_3), 18.7 (CH_3) ppm. ^{11}B NMR (160.5 MHz, C_6D_6): δ = 50.4 (br), –12.0 (s, NHC-*B*) ppm. HRMS (LIFDI) for $[C_{55}H_{49}B_2N_5]$ calcd.: 801.4169; found: 801.4160. FT-IR (solid state): $\tilde{\nu}$ = 2384 cm^{-1} (B–H stretch). *Note: In solution* ***$2b^H$*** *slowly decomposed to the diborylaniline product* ***$5b^H$*** *through loss of N_2. The extremely slow rate of conversion to* ***$5b^H$*** *at rt and the fact that heating or irradiation resulted in decomposition to complex mixtures of products prevented the isolation of* ***$5b^H$****. The latter was, however, detected by HRMS. HRMS (LIFDI) for [$C_{55}H_{49}B_2N_3$] calcd.: 773.4113; found: 773.4089.*

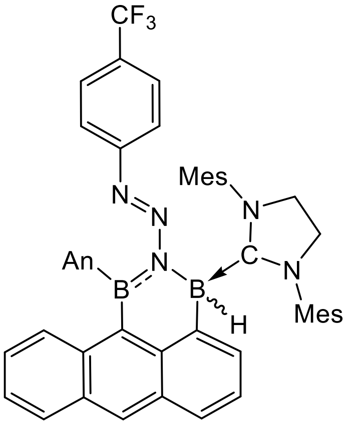
Synthesis of $\mathbf{2b^{NMe2}}$



Diborane(5) **1b** (22.8 mg, 0.03 mmol) was suspended in benzene (0.6 mL) and *p*-NMe$_2$-C$_6$H$_4$N$_3$ (11.9 mg, 0.07 mmol, 2.2 equiv) was added in one portion. The reaction mixture was heated at 60 °C for seven days prior to removal of all volatiles *in vacuo*. A solid precipitated upon addition of a mixture of benzene (0.2 mL) and hexane (0.6 mL) to the residual dark red oil, which was isolated and washed with hexane (3 x 0.8 mL) and benzene (1 x 0.6 mL) to afford $\mathbf{2b^{NMe2}}$ as an orange-brown solid (18.2 mg, 0.02 mmol, 65%). $^1H\{^{11}B\}$ NMR (400.6 MHz, C_6D_6): δ = 8.36 (br, 1H, Ar-C*H*), 8.22 – 8.20 (m, 2H, Ar-C*H*), 8.11 – 8.09 (m, 2H, Ar-C*H*), 7.88 (br d, $^3J_{HH}$ = 7.9 Hz, 1H, Ar-C*H*), 7.72 (br d, $^3J_{HH}$ = 8.2 Hz, 1H, Ar-C*H*), 7.61 – 7.56 (m, 3H, Ar-C*H*), 7.45 – 7.42 (m, 1H, Ar-C*H*), 7.37 (br d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar-C*H*), 7.29 (br d, $^3J_{HH}$ =6.7 Hz, 1H, Ar-C*H*), 7.11 – 7.07 (m, 4H, Ar-C*H*), 6.91 – 6.87 (m, 1H, Ar-C*H*), 6.71 – 6.69 (m, 1H, Ar-C*H*), 6.49 – 6.46 (m, 1H, Ar-C*H*), 6.32 (br d, $^3J_{HH}$ = 8.2 Hz, 2H, Ar-C*H*), 6.20 (m, 3H, Ar-C*H*), 4.41 (br s, 1H, B*H*), 3.10 – 3.04 (m, 4H, NC*H*$_2$C*H*$_2$N), 2.33 (s, 6H, C*H*$_3$), 2.23 (s, 6H, C*H*$_3$), 2.05 (s, 6H, C*H*$_3$), 1.82 (s, 6H, C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ = 150.0 (*C*$_q$), 148.6 (*C*$_q$), 142.4 (*C*$_q$), 140.5 (*C*$_q$), 139.9 (*C*$_q$), 138.8 (*C*$_q$), 138.6 (*C*$_q$), 137.7 (*C*$_q$), 137.2 (*C*$_q$), 137.0 (*C*$_q$), 136.2 (*C*$_q$), 135.6 (br *C*$_q$), 135.3 (*C*$_q$), 135.0 (*C*$_q$), 134.9 (*C*$_q$), 134.7 (*C*$_q$), 134.5 (*C*$_q$), 132.1 (Ar-*C*H), 130.3 (Ar-*C*H), 129.6 (Ar-*C*H), 129.6 (Ar-*C*H), 129.4 (Ar-*C*H), 129.0 (Ar-*C*H), 126.7 (Ar-*C*H), 125.8 (Ar-*C*H), 125.4 (Ar-*C*H), 124.5 (Ar-*C*H), 124.3 (Ar-*C*H), 124.2 (Ar-*C*H), 123.3 (Ar-*C*H), 112.5

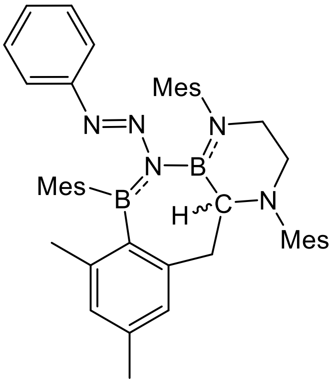
(Ar-*C*H), 50.4 (*C*H$_2$), 40.1 (*C*H$_3$), 21.1 (*C*H$_3$), 19.2 (*C*H$_3$), 18.9 (*C*H$_3$) ppm. *Two resonances are overlaid by the solvent signal at 128.5 ppm.* ^{11}B NMR (160.5 MHz, C$_6$D$_6$): δ = 50.8 (br), –11.9 (s, NHC-B) ppm. HRMS (LIFDI) for [C$_{57}$H$_{54}$B$_2$N$_6$] calcd.: 844.4591; found: 844.4576. FT-IR (solid state): $\tilde{\nu}$ = 2360 cm $^{-1}$ (B–H stretch). *Note: In solution* ***2b***^{NMe2} *slowly decomposed to the diborylaniline product* ***5b***^{NMe2} *through loss of N$_2$. The extremely slow rate of conversion to* ***5b***^{NMe2} *at rt and the fact that heating or irradiation resulted in decomposition to complex mixtures of products prevented the isolation of* ***5b***^{NMe2}*. The latter was, however, detected by HRMS. HRMS (LIFDI) for [C$_{57}$H$_{54}$B$_2$N$_4$] calcd.: 816.4535; found: 816.4510.*

Synthesis of 2b^{CF3}



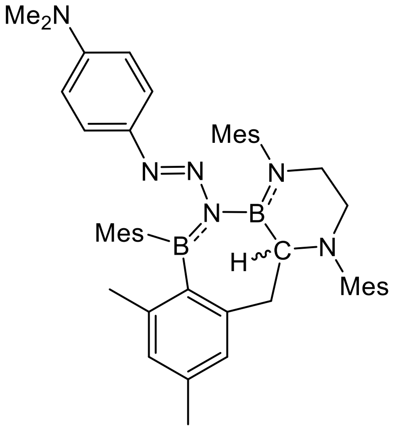
Diborane(5) **1b** (20.9 mg, 0.03 mmol) was suspended in benzene (0.6 mL) and *p*-CF$_3$-C$_6$H$_4$N$_3$ (12.6 mg, 0.07 mmol, 2.2 equiv) was added in one portion. The reaction mixture was heated at 60 °C for six days prior to removal of all volatiles *in vacuo*. The orange residue was washed once with toluene at –30 °C (0.4 mL) and with hexane at room temperature (3 x 0.8 mL) to afford **2b^{CF3}** as a yellow solid (16.8 mg, 0.02 mmol, 63%). Crystals suitable for single-crystal X-ray diffraction were obtained during the reaction by cooling the reaction mixture from 60 °C to room temperature. ^{1}H{^{11}B} NMR (500.1 MHz, C$_6$D$_6$): δ = 8.36 (s, 1H, Ar-C*H*), 8.20 (s, 1H, Ar-C*H*), 8.11 (d, $^3J_{HH}$ = 8.9 Hz, 1H, Ar-C*H*), 8.05 (t, $^3J_{HH}$ = 8.1 Hz, 2H, Ar-C*H*), 7.87 (br d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar-C*H*), 7.71 (br d, $^3J_{HH}$ = 8.4Hz, 1H, Ar-C*H*), 7.56 – 7.53 (m, 2H, Ar-C*H*), 7.50 – 7.47 (m, 1H, Ar-C*H*), 7.44 – 7.41 (m, 1H, Ar-C*H*), 7.29 (br d, $^3J_{HH}$ = 6.4Hz, 1H, Ar-C*H*), 7.25 (br d, $^3J_{HH}$ = 8.8 Hz, 1H, Ar-C*H*), 7.04 (m, 2H, Ar-C*H*), 6.91 – 6.88 (m, 3H, Ar-C*H*), 6.69 – 6.66 (m, 1H, Ar-C*H*), 6.50 – 6.47 (m, 1H, Ar-C*H*), 6.22 – 6.19 (m, 3H, Ar-C*H*), 4.36 (br s, 1H, B*H*), 3.06 – 2.93 (m, 4H, NC*H*$_2$C*H*$_2$N), 2.12 (s, 6H, C*H*$_3$), 2.05 (s, 6H, C*H*$_3$), 1.71 (s, 6H, C*H*$_3$) ppm. *Note: Two* Ar-*CH signals are overlaid by the solvent resonance, but were detected by HSQC experiments and found to correlate with a ^{13}C NMR resonance at 126.2 ppm.* ^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$): δ = 190.1 (br *C*$_{Carbene}$), 154.3 (C_q), 154.3 (C_q), 146.5 (br C_q), 145.6 (br C_q), 140.6 (C_q), 139.2 (br C_q), 138.8 (C_q), 137.4 (C_q), 136.9 (C_q), 136.1 (C_q), 135.1 (C_q), 134.6 (C_q), 133.5 (C_q), 133.4 (Ar-*C*H), 132.6 (Ar-*C*H), 132.1 (C_q), 131.7 (C_q), 131.5 (s. C_q), 131.1 (Ar-*C*H), 130.3 (Ar-*C*H), 130.0 (Ar-*C*H), 129.6 (Ar-*C*H), 129.4 (Ar-*C*H), 128.6 (Ar-*C*H), 128.6 (Ar-*C*H), 126.6 (Ar-*C*H), 126.2 (Ar-*C*H), 125.8 (q, $^1J_{CF}$ = 3.8 Hz, CF_3), 125.4 (Ar-*C*H), 124.8 (Ar-*C*H), 124.7 (Ar-*C*H), 124.6 (Ar-*C*H), 124.6 (Ar-*C*H), 124.5 (Ar-*C*H), 123.5 (Ar-*C*H), 122.2 (Ar-*C*H), 50.6 (s, NCH_2CH_2N), 21.1 (CH_3), 19.0 (CH_3), 18.6 (CH_3) ppm. ^{11}B NMR (160.5 MHz, C_6D_6): δ = 49.9 (br), –12.3 (s, NHC-*B*) ppm. ^{19}F{^{1}H} NMR (376.9 MHz, C_6D_6): δ = –61.7 ppm. HRMS (LIFDI) for [$C_{56}H_{48}B_2F_3N_5$] calcd.: 869.4042; found: 869.4030. FT-IR (solid state): $\tilde{\nu}$ = 2386 cm^{-1} (B–H stretch). *Note: In solution* ***2b***^{CF3} *slowly decomposed to the diborylaniline product* ***5b***^{CF3} *through loss of* N_2*. The extremely slow rate of conversion to* ***5b***^{CF3} *at rt and the fact that heating or irradiation resulted in decomposition to complex mixtures of products prevented the isolation of* ***5b***^{CF3}*. The latter was, however, detected by HRMS. HRMS (LIFDI) for [*$C_{56}H_{48}B_2F_3N_3$*] calcd.: 841.3986; found: 841.3965.*

Synthesis of 3a^{H}



Diborane(5) **1a** (50.0 mg, 0.09 mmol) was dissolved in benzene (0.6 mL) and PhN_3 (12.6 mg, 0.11 mmol, 1.2 equiv) was added. Heating at 60 °C for four days afforded a yellow solution containing **2a^{H}** and **3a^{H}** in a 1:2 ratio as determined by NMR spectroscopic analysis. An increase of the temperature to 80 °C for three days resulted in almost quantitative conversion of **2a^{H}** into **3a^{H}**. Upon concentration of the reaction mixture to 0.1 mL pale yellow crystals formed. The supernatant solution was removed and the crystals were washed once with benzene to yield **3a^{H}** as an off-white solid in 45% yield (27.2 mg, 0.04 mmol). Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated hexane solution at room temperature. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.54 – 7.52 (m, 2H, Ar-C*H*), 7.05 (br, 1H, Ar-C*H*), 6.97 – 6.94 (m, 2H, Ar-C*H*), 6.90 – 6.87 (m, 2H, Ar-C*H*), 6.82 (br, 1H, Ar-C*H*), 6.76 (s, 1H, Ar-C*H*), 6.71 (br, 1H, Ar-C*H*), 6.67 (s, 1H, Ar-C*H*), 6.56 (s, 1H, Ar-C*H*), 6.45 (s, 1H, Ar-C*H*), 4.41 (br t, $^{3}J_{\mathrm{HH}}$ = 3.4Hz, 1H, BC*H*), 3.64 (ddd, $^{3}J_{\mathrm{HH}}$ = 12.9 Hz, $^{3}J_{\mathrm{HH}}$ = 10.7 Hz, $^{2}J_{\mathrm{HH}}$ = 3.5 Hz, 1H, C*H*$_2$), 3.34 – 3.29 (m, 2H, C*H*$_2$), 2.92 (ddd, $^{3}J_{\mathrm{HH}}$ = 12.9 Hz, $^{2}J_{\mathrm{HH}}$ = 4.0 Hz, $^{2}J_{\mathrm{HH}}$ = 1.9 Hz, 1H, C*H*$_2$), 2.68 (br d, $^{3}J_{\mathrm{HH}}$ = 11.7 Hz, 1H, C*H*$_2$), 2.62 (dd, $^{3}J_{\mathrm{HH}}$ = 14.0 Hz, $^{2}J_{\mathrm{HH}}$ = 2.8 Hz, 1H, C*H*$_2$), 2.42 (s, 3H, C*H*$_3$), 2.31 (s, 3H, C*H*$_3$), 2.27 (s, 3H, C*H*$_3$), 2.23 (s, 3H, C*H*$_3$), 2.21 (s, 3H, C*H*$_3$), 2.16 (s, 6H, C*H*$_3$), 2.09 (s, 3H, C*H*$_3$), 1.99 (s, 3H, C*H*$_3$), 1.95 (s, 3H, C*H*$_3$), 1.90 (s, 3H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 149.9 (*C*$_q$), 145.8 (*C*$_q$), 144.9 (*C*$_q$), 144.6 (*C*$_q$), 140.9 (*C*$_q$), 140.8 (*C*$_q$), 140.1 (*C*$_q$), 139.1 (br, *C*$_q$), 139.0 (*C*$_q$), 138.4 (*C*$_q$), 137.3 (*C*$_q$), 136.5 (*C*$_q$), 136.2 (br, *C*$_q$), 135.8 (*C*$_q$), 135.3 (*C*$_q$), 135.2 (*C*$_q$), 134.4 (*C*$_q$), 130.8 (Ar-*C*H), 129.9 (Ar-*C*H), 129.8 (Ar-*C*H), 129.8 (Ar-*C*H), 129.7 (Ar-*C*H), 129.2 (Ar-*C*H), 129.1 (Ar-*C*H), 128.7 (Ar-*C*H), 122.3 (Ar-*C*H), 58.1 (B-*C*H), 51.6 (*C*H$_2$), 50.5 (*C*H$_2$), 37.5 (*C*H$_2$), 22.9 (*C*H$_3$), 22.8 (*C*H$_3$), 22.4 (*C*H$_3$), 21.4 (*C*H$_3$), 21.4 (*C*H$_3$), 21.0 (*C*H$_3$), 20.8 (*C*H$_3$), 20.5 (*C*H$_3$), 19.8 (*C*H$_3$), 18.4 (*C*H$_3$), 17.6 (*C*H$_3$) ppm. *Two* Ar-C*H signals are overlaid by the solvent signal.* ^{11}B NMR (160.5 MHz, C_6D_6): δ = 51.4 (br), 39.6 (br) ppm. HRMS (LIFDI) for [$C_{54}H_{53}B_2N_5$] calcd.: 685.4482; found: 685.4471.

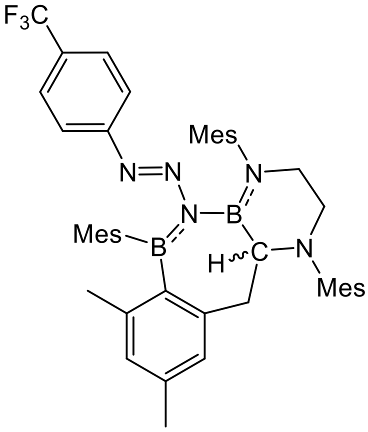
Synthesis of 3a$^{\mathbf{NMe2}}$



Diborane(5) **1a** (50.0 mg, 0.09 mmol) was dissolved in benzene (5 mL) and *p*-Me$_2$N-$C_6H_4N_3$ (47.2 mg, 0.29 mmol, 3.2 equiv) was added. Heating at 80 °C for two days afforded a red solution, which was dried *in vacuo* and washed with hexane (3 x 2 mL). The resulting solid was washed with hot hexane once to afford **3a$^{\mathbf{NMe2}}$** as a pale yellow solid in 53% yield (34.0 mg, 0.05 mmol). Single crystals suitable for X-ray diffraction were grown by slow evaporation of a saturated benzene/hexane solution (1:1) at room temperature. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.58 (m, 2H, Ar-C*H*), 7.05 (s, 1H, Ar-C*H*), 6.98 (s, 1H, Ar-C*H*), 6.81 (s, 1H, Ar-C*H*), 6.78 (s, 1H, Ar-C*H*), 6.75 (s, 1H, Ar-C*H*), 6.72 (s, 1H, Ar-C*H*), 6.61 (s, 1H, Ar-C*H*), 6.46 (s, 1H, Ar-C*H*), 6.27 (m, 2H, Ar-C*H*), 4.46 (br t, $^{3}J_{\mathrm{HH}}$ = 3.3 Hz, 1H, BC*H*), 3.72 (ddd, $^{3}J_{\mathrm{HH}}$ = 13.9 Hz, $^{3}J_{\mathrm{HH}}$ = 10.7 Hz, $^{2}J_{\mathrm{HH}}$ = 3.3 Hz, 1H, C*H*$_2$), 3.41–3.33 (m, 2H, C*H*$_2$), 2.95

(ddd, $^{3}J_{HH}$ = 12.9 Hz, $^{2}J_{HH}$ = 4.0 Hz, $^{2}J_{HH}$ = 1.9 Hz, 1H, CH_2), 2.74 (br d, $^{3}J_{HH}$ = 11.7 Hz, 1H, CH_2), 2.62 (dd, $^{3}J_{HH}$ =14.1 Hz, $^{2}J_{HH}$ = 2.8 Hz, 1H, CH_2), 2.44 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.33 (s, 6H, CH_3), 2.32 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.95 (s, 3H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6): δ = 150.9 (Ar-C_q), 145.9 (Ar-C_q), 145.0 (Ar-C_q), 144.4 (Ar-C_q), 141.2 (Ar-C_q), 141.0 (Ar-C_q), 140.2 (Ar-C_q), 140.1 (Ar-C_q), 138.5 (Ar-C_q), 138.5 (Ar-C_q), 136.9 (Ar-C_q), 136.6 (Ar-C_q), 135.6 (Ar-C_q), 135.4 (Ar-C_q), 134.3 (Ar-C_q), 134.2 (Ar-C_q), 130.8 (Ar-*C*H), 129.8 (Ar-*C*H), 129.7 (Ar-*C*H), 129.7 (Ar-*C*H), 129.7 (Ar-*C*H), 129.0 (Ar-*C*H), 128.0 (Ar-*C*H), 127.8 (Ar-*C*H), 123.6 (Ar-*C*H), 112.4 (Ar-*C*H), 58.8 (*C*H), 51.7 (*C*H_2), 50.5 (*C*H_2), 39.9 (N(*C*$H_3)_2$), 37.7 (*C*H_2), 23.0 (*C*H_3), 22.8 (*C*H_3), 22.4 (*C*H_3), 21.5 (*C*H_3), 21.4 (*C*H_3), 21.0 (*C*H_3), 20.8 (*C*H_3), 20.6 (*C*H_3), 19.8 (*C*H_3), 18.6 (*C*H_3), 17.7 (*C*H_3) ppm. ^{11}B NMR (160.5 MHz, C_6D_6): δ = *too broad to be observed.* HRMS (LIFDI) for [$C_{47}H_{58}B_2N_6$] calcd.: 728.4904; found: 728.4891.

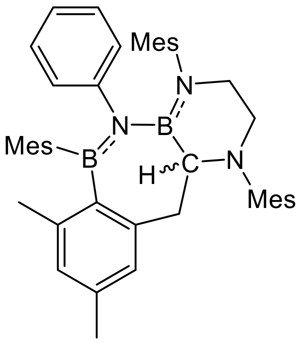
Synthesis of 3a^{CF3}



Diborane(5) **1a** (41.0 mg, 0.07 mmol) was dissolved in benzene (0.6 mL) and *p*-CF_3-$C_6H_4N_3$ (16.3 mg, 0.09 mmol, 1.2 equiv) was added. Heating at 60 °C for three days afforded a yellow solution, which was analyzed by multinuclear NMR spectroscopy and found to contain **2a^{CF3}** and **3a^{CF3}** in a 2:1 ratio. An increase of the temperature to 80 °C for four days resulted in a ca. 70% conversion of **2a^{CF3}** into **3a^{CF3}**. Pale yellow crystals formed upon concentration of the reaction mixture to 0.1 mL. The supernatant solution was removed and the crystals were washed once with benzene to yield **3a^{CF3}** as an off-white solid in 39% yield (21.1 mg, 0.03 mmol). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.29 (br d, $^{3}J_{HH}$ = 8.3 Hz, 2H, Ar-C*H*), 7.08 (s, 1H, Ar-C*H*), 7.05 (br s, 2H, Ar-C*H*), 6.92 (s, 1H, Ar-C*H*), 6.83 (s, 1H, Ar-C*H*), 6.76 (s, 1H, Ar-C*H*), 6.71 (s, 1H, Ar-C*H*), 6.69 (s, 1H, Ar-C*H*), 6.57 (s, 1H, Ar-C*H*), 6.43 (s, 1H, Ar-C*H*), 4.36 (br, 1H, BC*H*), 3.63 (ddd, $^{3}J_{HH}$ = 14.5 Hz, $^{3}J_{HH}$ = 10.9 Hz, $^{2}J_{HH}$ = 3.4Hz, 1H, CH_2), 3.29

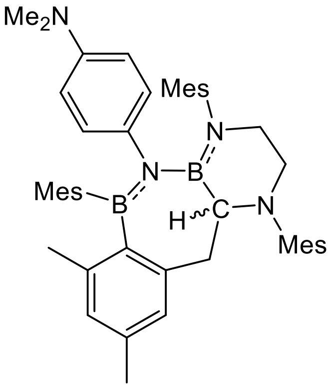
(m, 2H, CH_2), 2.93 – 2.89 (m, 1H, CH_2), 2.67 – 2.60 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.90 (s, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 152.1 (C_q), 145.7 (C_q), 144.7 (C_q), 144.6 (C_q), 140.7 (C_q), 140.6 (C_q), 140.1 (C_q), 139.4 (C_q), 138.4 (C_q), 137.6 (C_q), 136.4 (C_q), 136.0 (C_q), 135.2 (C_q), 135.0 (C_q), 134.5 (C_q), 130.9 (Ar-CH), 130.0 (Ar-CH), 129.9 (Ar-CH), 129.9 (Ar-CH), 129.7 (Ar-CH), 129.2 (Ar-CH), 126.4 (q, $^{1}J_{CF}$ = 3.7 Hz, CF_3), 122.3 (Ar-CH), 57.7 (br, B-CH), 51.5 (CH$_2$), 50.4 (CH$_2$), 37.6 (CH$_2$), 22.9 (CH$_3$), 22.7 (CH$_3$), 22.3 (CH$_3$), 21.4 (CH$_3$), 21.4 (CH$_3$), 21.0 (CH$_3$), 20.8 (CH$_3$), 20.5 (CH$_3$), 19.8 (CH$_3$), 18.2 (CH$_3$), 17.5 (CH$_3$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6): δ = 50.8 (br), 38.8 (br) ppm. ^{19}F{^{1}H} NMR (376.6 MHz, C_6D_6): δ = –62.2 ppm. HRMS (LIFDI) for [$C_{46}H_{52}B_2F_3N_5$] calcd.: 753.4355; found: 753.4346.

Synthesis of $\mathbf{4a^H}$



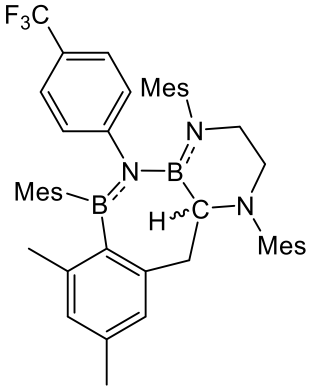
In a J.-Young NMR tube **3a$^{\mathbf{H}}$** (20 mg, 0.03 mmol) was dissolved in C_6D_6 (0.6 mL) and heated at 100 °C for 15 days, after which the ^{1}H NMR spectrum of the reaction mixture showed clean conversion to **4a$^{\mathbf{H}}$**. After removal of all volatiles *in vacuo* and washing with hexane (1 x 0.1 mL) **4a$^{\mathbf{H}}$** was isolated as a colourless solid in 97% yield (18.5 mg, 0.03 mmol). Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated hexane solution at room temperature. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.05 (s, 1H, Ar-CH), 6.87-6.83 (m, 4H, Ar-CH), 6.79 (s, 1H, Ar-CH), 6.78-6.70 (m, 5H, Ar-CH), 6.63 (s, 1H, Ar-CH), 6.45 (s, 1H, Ar-CH), 6.44 (s, 1H, Ar-CH), 4.23 (dd, $^{3}J_{HH}$ = 4.5 Hz, $^{3}J_{HH}$ = 2.7 Hz, 1H, BCH), 3.83 (dd, $^{3}J_{HH}$ = 13.7 Hz, $^{2}J_{HH}$ = 5.1 Hz, 1H, CH_2), 3.37-3.30 (m, 1H, CH_2), 3.22 (dt, $^{3}J_{HH}$ = 11.2 Hz, $^{2}J_{HH}$ = 3.9 Hz, 1H, CH_2), 2.84 (ddd, $^{3}J_{HH}$ = 12.6 Hz, $^{2}J_{HH}$ = 4.0 Hz, $^{2}J_{HH}$ = 2.2 Hz, 1H, CH_2), 2.80 (dd, $^{3}J_{HH}$ = 13.9 Hz, $^{2}J_{HH}$ = 2.8 Hz, 1H, CH_2), 2.46-2.43 (m, 1H, CH_2), 2.36 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.52 (s, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 146.0 (s, C_q), 145.7 (s, C_q), 144.8 (s, *C*$_q$), 144.1 (s, *C*$_q$), 142.3 (s, *C*$_q$), 139.1 (s, *C*$_q$), 139.1 (s, *C*$_q$), 138.9 (s, *C*$_q$), 137.7 (s, *C*$_q$), 136.7 (s, *C*$_q$), 136.1 (s, *C*$_q$), 136.0 (s, *C*$_q$), 136.0 (s, *C*$_q$), 135.2 (s, *C*$_q$), 134.5 (s, *C*$_q$), 130.6 (s, Ar-*C*H), 130.3 (s, Ar-*C*H), 129.8 (s, Ar-*C*H), 129.5 (s, Ar-*C*H), 129.4 (s, Ar-*C*H), 129.3 (s, Ar-*C*H), 127.6 (s, Ar-*C*H), 127.3 (s, Ar-*C*H), 125.2 (s, Ar-*C*H), 60.4 (br, B-*C*H), 52.0 (s, *C*H$_2$), 51.0 (s, *C*H$_2$), 37.2 (s, *C*H$_2$), 25.2 (s, *C*H$_3$), 23.0 (s, *C*H$_3$), 22.4 (s, *C*H$_3$), 21.2 (s, *C*H$_3$), 21.1 (s, *C*H$_3$), 21.0 (s, *C*H$_3$), 20.4 (s, *C*H$_3$), 19.8 (s, *C*H$_3$), 17.9 (s, *C*H$_3$), 17.5 (s, *C*H$_3$) ppm. ^{11}B NMR (128.4 MHz, C_6D_6): δ = *too broad to be observed*. HRMS (LIFDI) for [$C_{45}H_{53}B_2N_3$] calcd.: 657.4420; found: 657.4397.

Synthesis of 4a$^{\mathbf{NMe2}}$



In a J.-Young NMR tube **3a$^{\mathbf{NMe2}}$** (20 mg, 0.03 mmol) was dissolved in C_6D_6 (0.6 mL) and heated at 100 °C for 20 days, after which the ^{1}H NMR spectrum of the reaction mixture showed clean conversion to **4a$^{\mathbf{NMe2}}$**. After removal of all volatiles *in vacuo* the orange residue was extracted with hexane. Slow evaporation of the hexane solution yielded **4a$^{\mathbf{NMe2}}$** as yellow crystals in 74% yield (14.2 mg, 0.02 mmol). ^{1}H NMR (400.3 MHz, C_6D_6): δ = 7.06 (s, 1H, Ar-C*H*), 6.89 (s, 1H, Ar-C*H*), 6.86 (s, 1H, Ar-C*H*), 6.85 (s, 1H, Ar-C*H*), 6.80 (s, 1H, Ar-C*H*), 6.75-6.72 (m, 2H, Ar-C*H*), 6.66 (s, 1H, Ar-C*H*), 6.49 (s, 1H, Ar-C*H*), 6.46 (s, 1H, Ar-C*H*), 6.29-6.27 (m, 2H, Ar-C*H*), 4.31 (br, 1H, BC*H*), 3.90 (dd, $^3J_{HH}$ = 13.9 Hz, $^2J_{HH}$ = 5.1 Hz, 1H, C*H*$_2$), 3.42-3.35 (m, 1H, C*H*$_2$), 3.26 (td, $^3J_{HH}$ = 11.0 Hz, $^2J_{HH}$ = 4.1 Hz, 1H, C*H*$_2$), 2.89-2.86 (br m, 1H, C*H*$_2$), 2.82 (dd, $^3J_{HH}$ = 13.9 Hz, $^2J_{HH}$ = 2.6 Hz, 1H, C*H*$_2$), 2.49 (br d, $^3J_{HH}$ = 11.8 Hz, 1H, C*H*$_2$), 2.41 (s, 3H, C*H*$_3$), 2.38 (s, 3H, C*H*$_3$), 2.36 (s, 3H, C*H*$_3$), 2.30 (s, 6H, C*H*$_3$), 2.29 (s, 3H, C*H*$_3$), 2.28 (s, 3H, C*H*$_3$), 2.25 (s, 3H, C*H*$_3$), 2.20 (s, 9H, C*H*$_3$), 1.92 (s, 3H, C*H*$_3$), 1.69 (s, 3H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 148.2 (s, *C*$_q$), 145.9 (s, *C*$_q$), 145.0 (s, *C*$_q$), 143.9 (s, *C*$_q$), 142.6 (s, *C*$_q$), 139.2 (s, *C*$_q$), 138.9 (s, *C*$_q$), 137.5 (s, *C*$_q$), 136.7 (s, *C*$_q$), 136.3 (s, *C*$_q$), 135.9 (s, *C*$_q$), 135.8 (s, *C*$_q$), 135.4 (s, *C*$_q$), 135.2 (s, *C*$_q$), 134.4 (s, *C*$_q$), 130.6 (s, Ar-*C*H), 130.2 (s, Ar-*C*H), 129.8 (s, Ar-*C*H), 129.5 (s, Ar-*C*H), 129.4 (s, Ar-*C*H), 129.3 (s, Ar-*C*H), 127.4 (s, Ar-*C*H), 112.3 (s, Ar-*C*H), 60.3 (br, B-*C*H), 52.0 (s, *C*H$_2$), 51.0 (s, *C*H$_2$), 40.1 (s, $C\mathrm{H}_3$), 37.3 (s, $C\mathrm{H}_2$), 25.0 (s, $C\mathrm{H}_3$), 23.0 (s, $C\mathrm{H}_3$), 22.5 (s, $C\mathrm{H}_3$), 21.2 (s, $C\mathrm{H}_3$), 21.1 (s, $C\mathrm{H}_3$), 21.1 (s, $C\mathrm{H}_3$), 21.0 (s, $C\mathrm{H}_3$), 20.5 (s, $C\mathrm{H}_3$), 19.8 (s, $C\mathrm{H}_3$), 17.9 (s, $C\mathrm{H}_3$), 17.9 (s, $C\mathrm{H}_3$) ppm. ^{11}B NMR (128.4 MHz, C_6D_6): δ = 45.3 (br), 30.2 (br) ppm. HRMS (LIFDI) for [$C_{47}H_{58}B_2N_4$] calcd.: 700.4842; found: 700.4833.

Synthesis of 4a$^{\mathbf{CF3}}$



In a J.-Young NMR tube **3a$^{\mathbf{CF3}}$** (30 mg, 0.04 mmol) was dissolved in C_6D_6 (0.6 mL) and heated at 80 °C for 12 days and finally at 100 °C for one day, after which the ^{1}H and ^{19}F NMR spectra of the reaction mixture showed clean conversion to **4a$^{\mathbf{CF3}}$**. After removal of all volatiles *in vacuo* and washing with hexane (2 x 0.2 mL) **4a$^{\mathbf{CF3}}$** was isolated as a pale yellow solid in 95% yield (27.4 mg, 0.04 mmol). Crystals suitable for single-crystal X-ray diffraction were obtained by evaporation of a saturated hexane solution at room temperature. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 7.10 (s, 1H, Ar-$\mathrm{C}H$), 7.09 (s, 1H, Ar-$\mathrm{C}H$), 7.05 (s, 1H, Ar-$\mathrm{C}H$), 6.88 (s, 1H, Ar-$\mathrm{C}H$), 6.81 (s, 1H, Ar-$\mathrm{C}H$), 6.77 (s, 1H, Ar-$\mathrm{C}H$), 6.73 (s, 1H, Ar-$\mathrm{C}H$), 6.71 (s, 1H, Ar-$\mathrm{C}H$), 6.64 (s, 1H, Ar-$\mathrm{C}H$), 6.60 (s, 1H, Ar-$\mathrm{C}H$), 6.42 (s, 2H, Ar-$\mathrm{C}H$), 4.15 (br, 1H, B$\mathrm{C}H$), 3.74 – 3.70 (dd, $^3J_{\mathrm{HH}}$ = 13.8 Hz, $^2J_{\mathrm{HH}}$ = 4.9 Hz, 1H, $\mathrm{C}H_2$), 3.34 – 3.29 (br m, 1H, N-$\mathrm{C}H_2$), 3.18 (dt, $^3J_{\mathrm{HH}}$ = 11.4Hz, $^2J_{\mathrm{HH}}$ = 4.2 Hz, 1H, N-$\mathrm{C}H_2$), 2.82 (br m, 1H, $\mathrm{C}H_2$), 2.78 (dd, $^3J_{\mathrm{HH}}$ = 14.2 Hz, $^2J_{\mathrm{HH}}$ = 2.4Hz, 1H, $\mathrm{C}H_2$), 2.40 (s, 3H, $\mathrm{C}H_3$), 2.37 (br d, $^3J_{\mathrm{HH}}$ = 12.0 Hz, 1H, N-$\mathrm{C}H_2$), 2.31 (s, 3H, $\mathrm{C}H_3$), 2.30 (s, 3H, $\mathrm{C}H_3$), 2.22 (s, 3H, $\mathrm{C}H_3$), 2.21 (s, 3H, $\mathrm{C}H_3$), 2.19 (s, 3H, $\mathrm{C}H_3$), 2.17 (s, 3H, $\mathrm{C}H_3$), 2.11 (s, 3H, $\mathrm{C}H_3$), 2.06 (s, 3H, $\mathrm{C}H_3$), 1.92 (s, 3H, $\mathrm{C}H_3$), 1.37 (s, 3H, $\mathrm{C}H_3$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 149.5 (C_q), 149.5 (C_q), 145.6 (C_q), 144.6 (C_q), 144.2 (C_q), 141.8 (C_q), 139.5 (br C_q), 138.9 (C_q), 138.9 (C_q), 138.9 (C_q), 138.1 (C_q), 136.6 (C_q), 136.6 (C_q), 136.3 (C_q), 136.1 (br C_q), 135.7 (C_q), 135.1 (C_q), 134.7 (C_q), 130.6 (Ar-$C\mathrm{H}$), 130.5 (Ar-$C\mathrm{H}$), 129.9 (Ar-$C\mathrm{H}$), 129.6 (Ar-$C\mathrm{H}$), 129.5 (Ar-$C\mathrm{H}$), 129.4 (Ar-$C\mathrm{H}$), 127.4 (Ar-$C\mathrm{H}$), 125.3 (q, $^1J_{\mathrm{CF}}$ = 3.7 Hz, $C\mathrm{F}_3$), 60.3 (br, B-$C\mathrm{H}$), 51.9 ($C\mathrm{H}_2$), 50.9 ($C\mathrm{H}_2$), 37.0 ($C\mathrm{H}_2$), 25.1 ($C\mathrm{H}_3$), 23.0 ($C\mathrm{H}_3$), 22.3 ($C\mathrm{H}_3$), 21.2 ($C\mathrm{H}_3$), 21.0 ($C\mathrm{H}_3$), 21.0 ($C\mathrm{H}_3$), 21.0 ($C\mathrm{H}_3$), 20.4 ($C\mathrm{H}_3$), 19.7 ($C\mathrm{H}_3$), 17.8 ($C\mathrm{H}_3$), 17.2 ($C\mathrm{H}_3$) ppm. ^{11}B NMR (160.5 MHz, C_6D_6): δ = 45.9

(br), 36.2 (br) ppm. $^{19}F\{^{1}H\}$ NMR (376.6 MHz, C_6D_6): δ = −61.9 ppm. HRMS (LIFDI) for [$C_{46}H_{52}B_2F_3N_3$] calcd.: 725.4294; found: 725.4278.

NMR spectra of isolated compounds

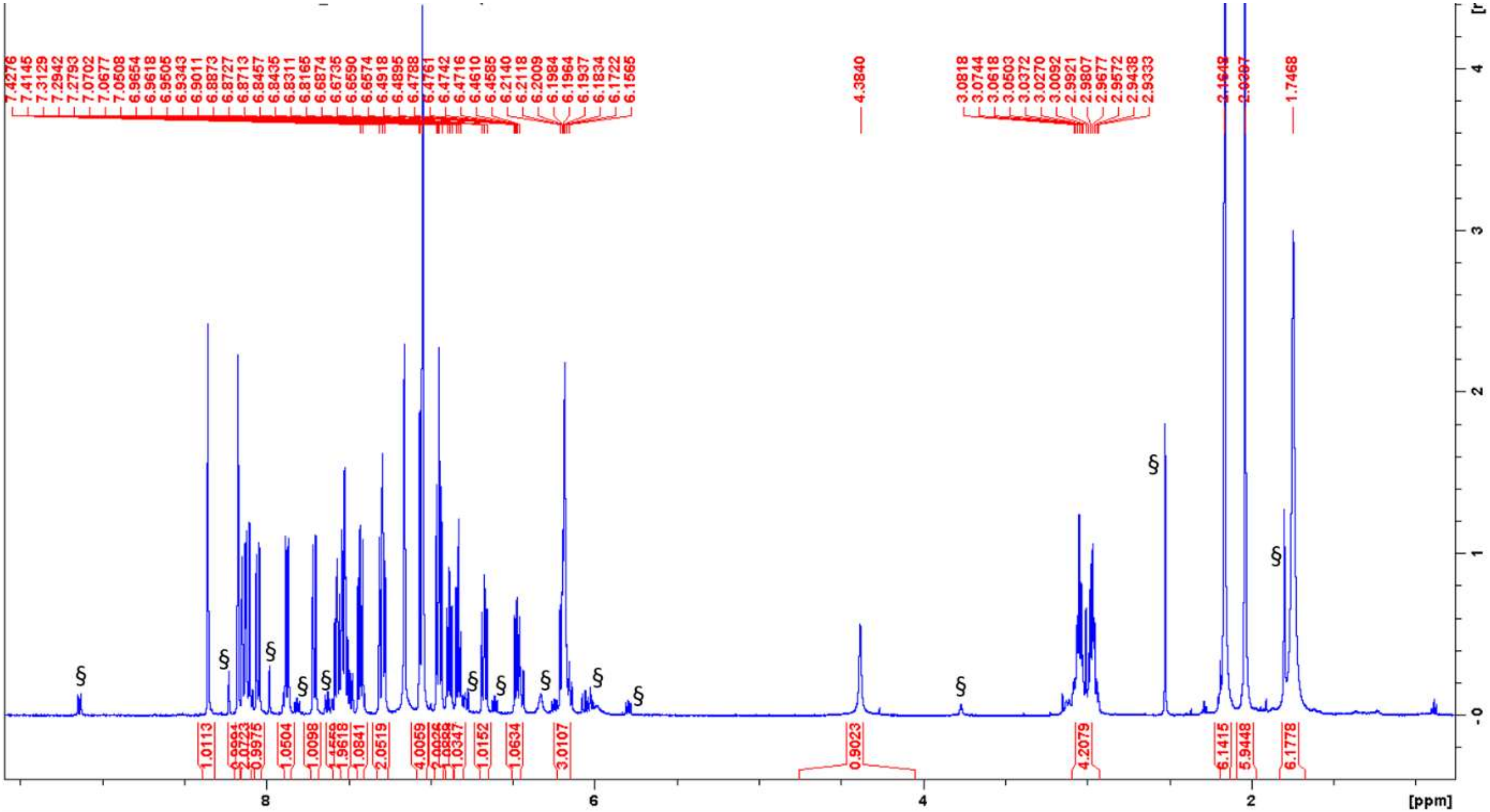


Figure S1. $^1H\{^{11}B\}$ NMR spectrum of **2b^H** in C_6D_6. Resonances marked with § correspond to the diborylaniline decomposition product **5b^H**.

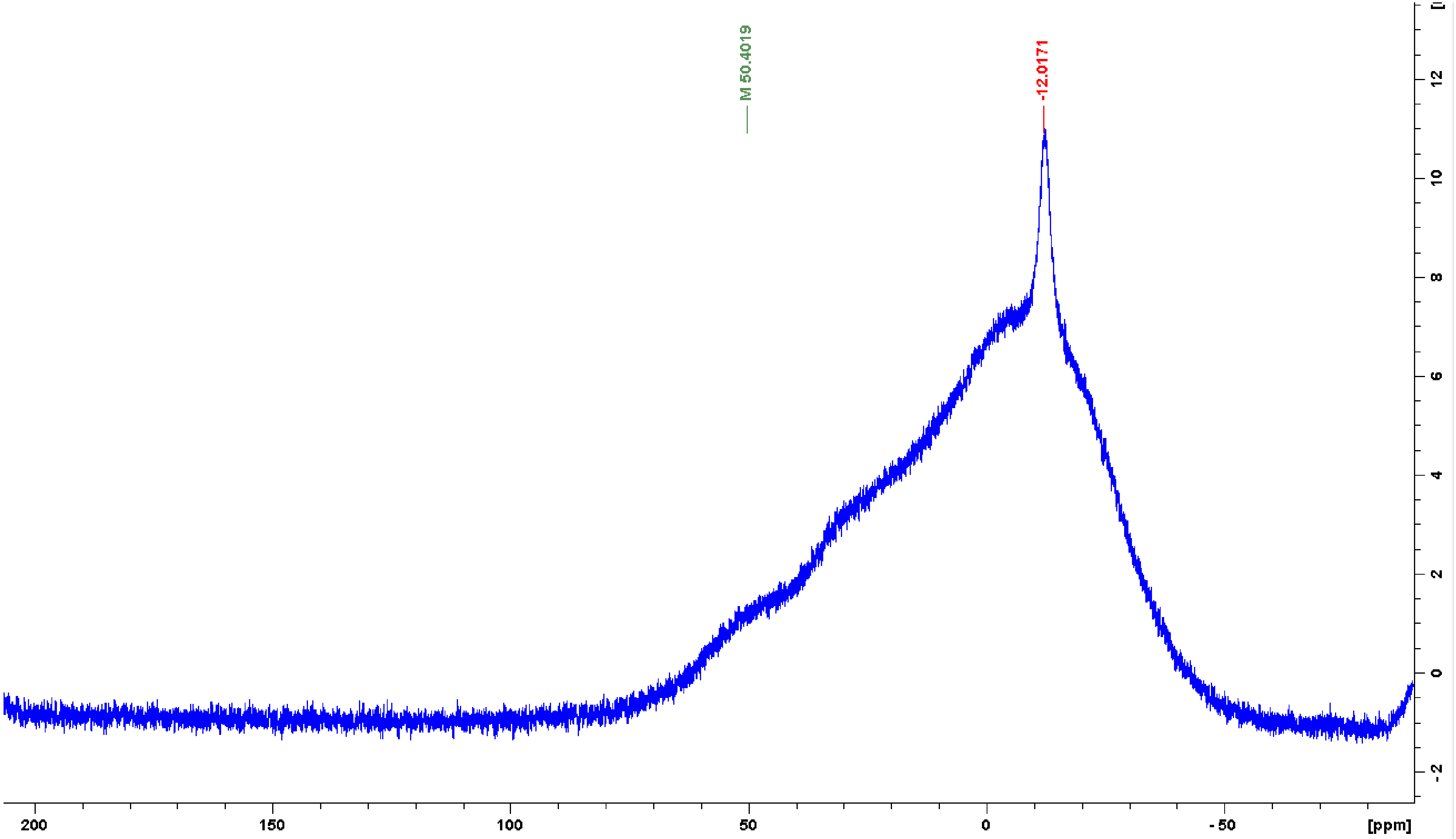


Figure S2. ^{11}B NMR spectrum of **2b^{H}** in C_6D_6.

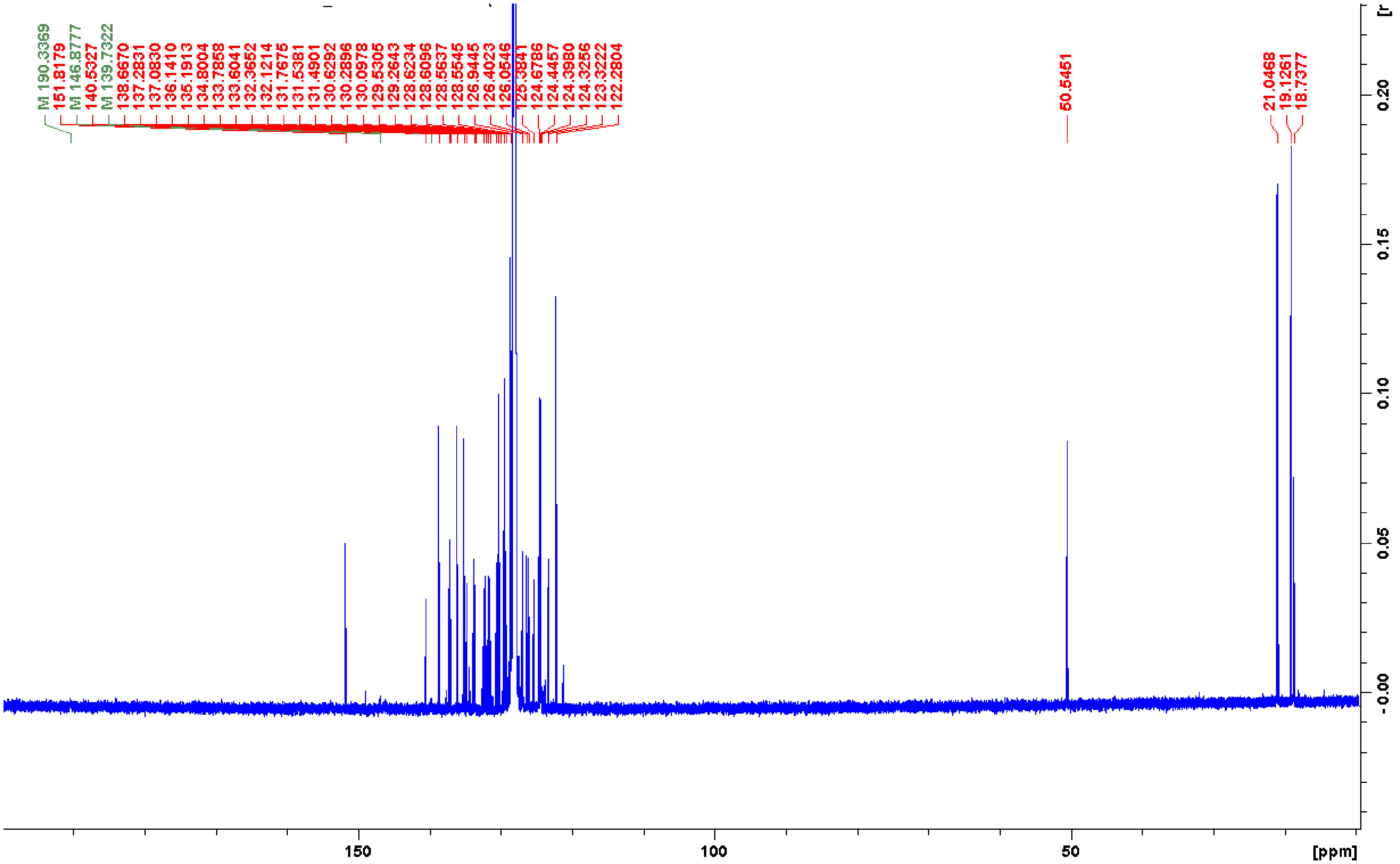


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{2b^{H}}$ in C_6D_6.

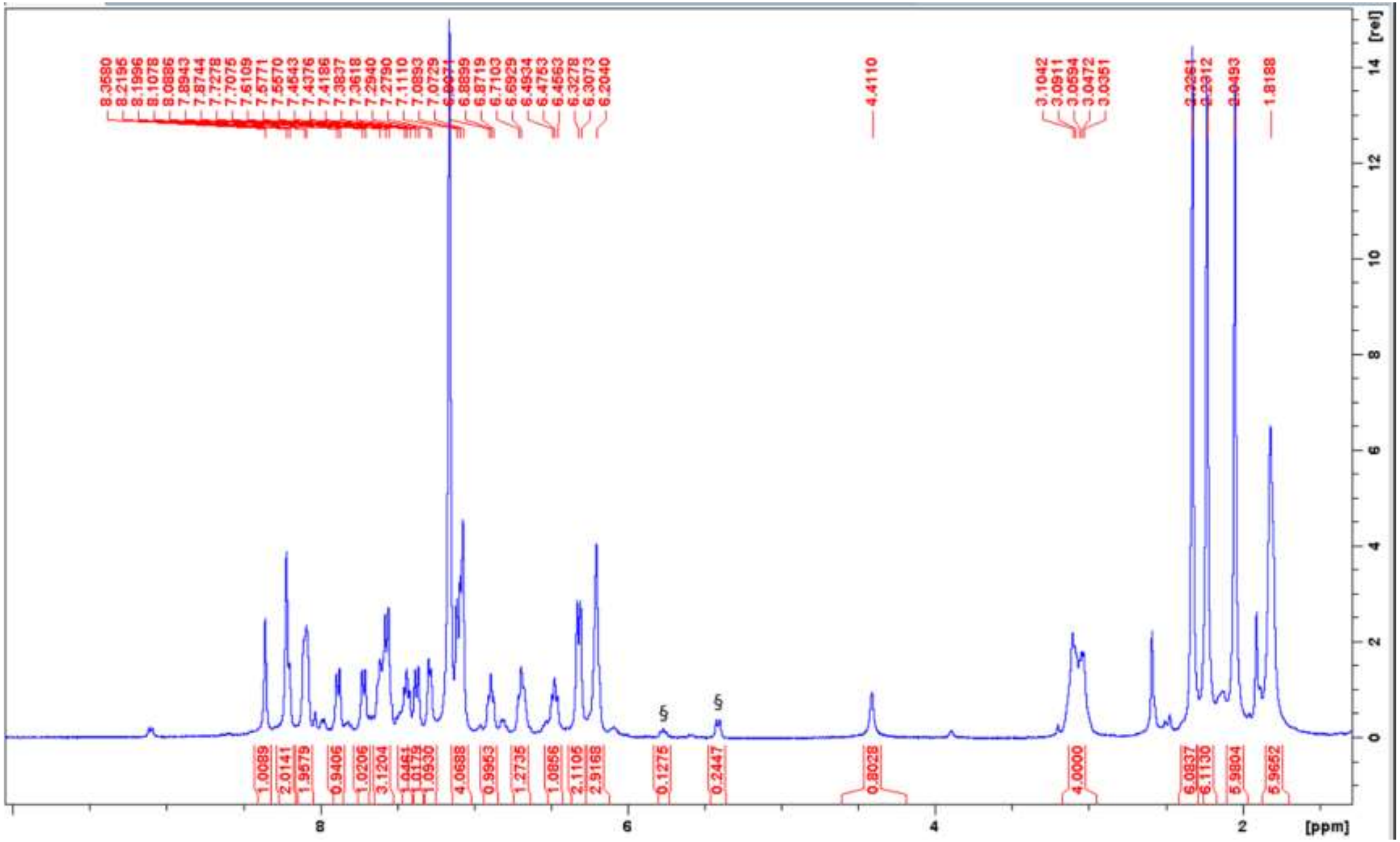


Figure S4. $^{1}H\{11B\}$ NMR spectrum of **$2b^{NMe2}$** in C_6D_6 shortly after isolation. The resonances marked with § correspond to the diborylaniline decomposition product **$5b^{NMe2}$** (ca. 10%).

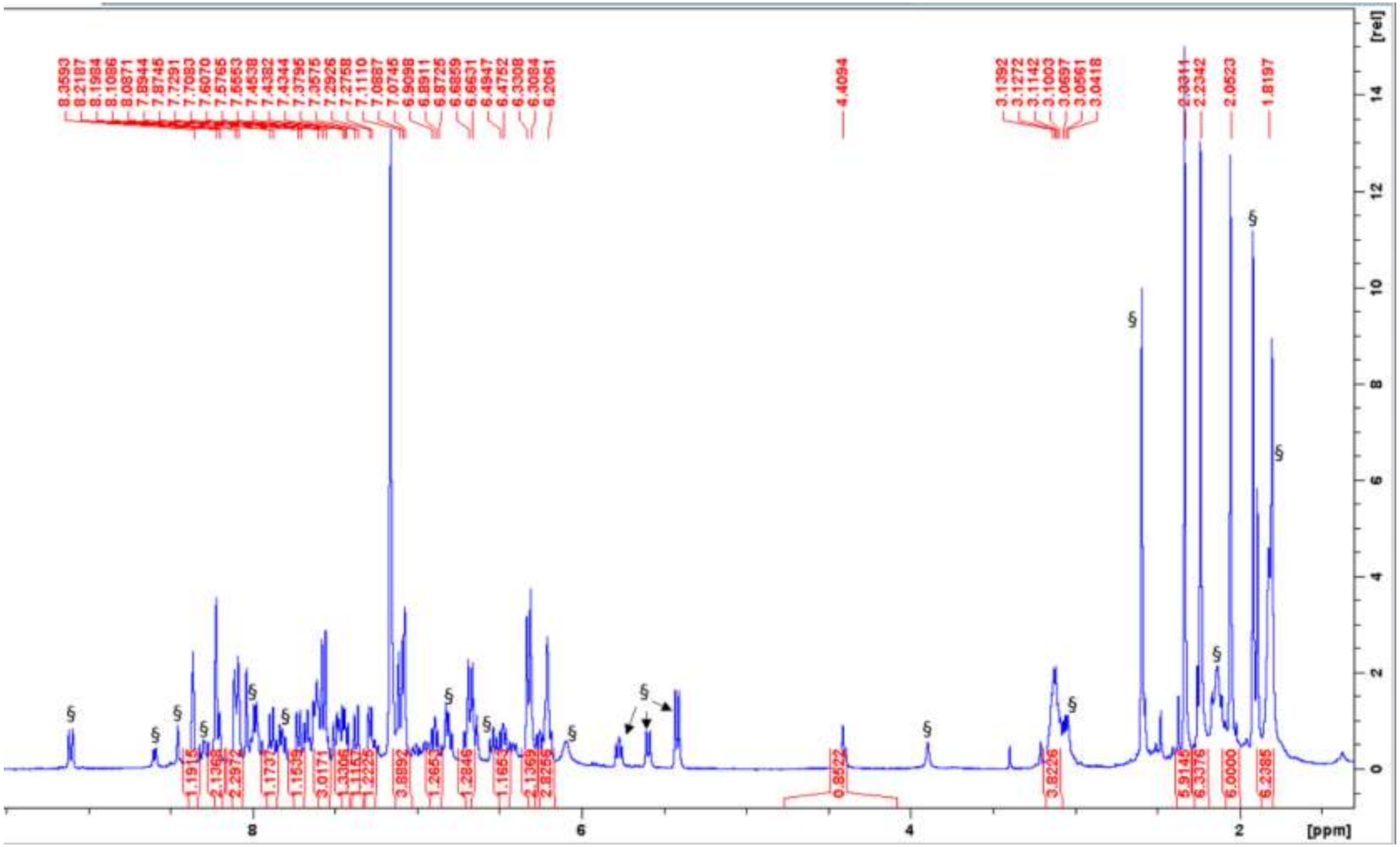


Figure S5. ^{1}H{^{11}B} NMR spectrum of **2b^{NMe2}** in C_6D_6 after two weeks at room temperature. The resonances picked and integrated correspond to **2b^{NMe2}**. Resonances marked with § correspond to **5b^{NMe2}** (ca. 40%).

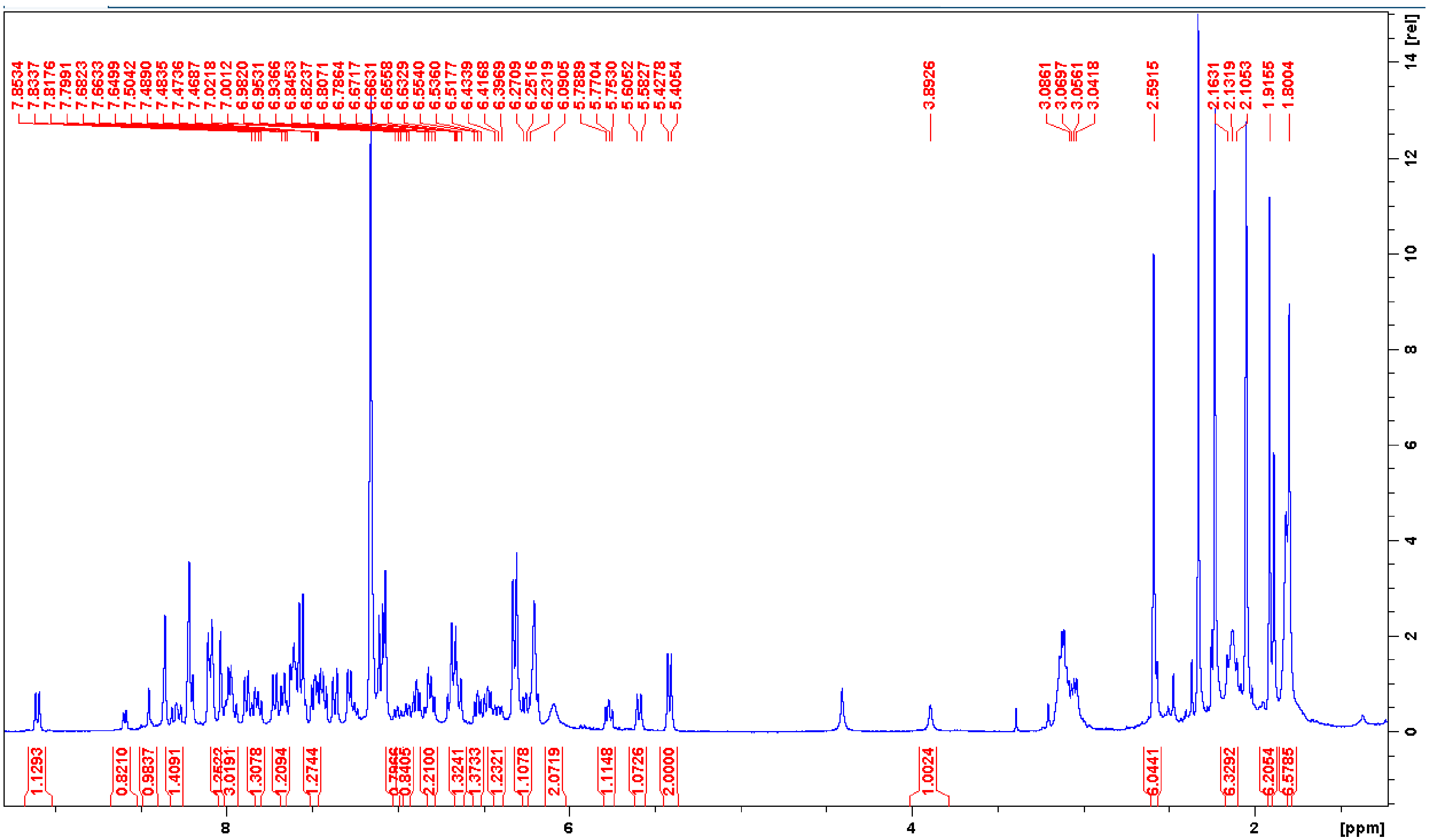


Figure S6. $^{1}H\{^{11}B\}$ NMR spectrum of of **2b**$^{\mathbf{NMe2}}$ in C_6D_6 after two weeks at room temperature. The resonances picked and integrated correspond to **5b**$^{\mathbf{NMe2}}$ (ca. 40%).

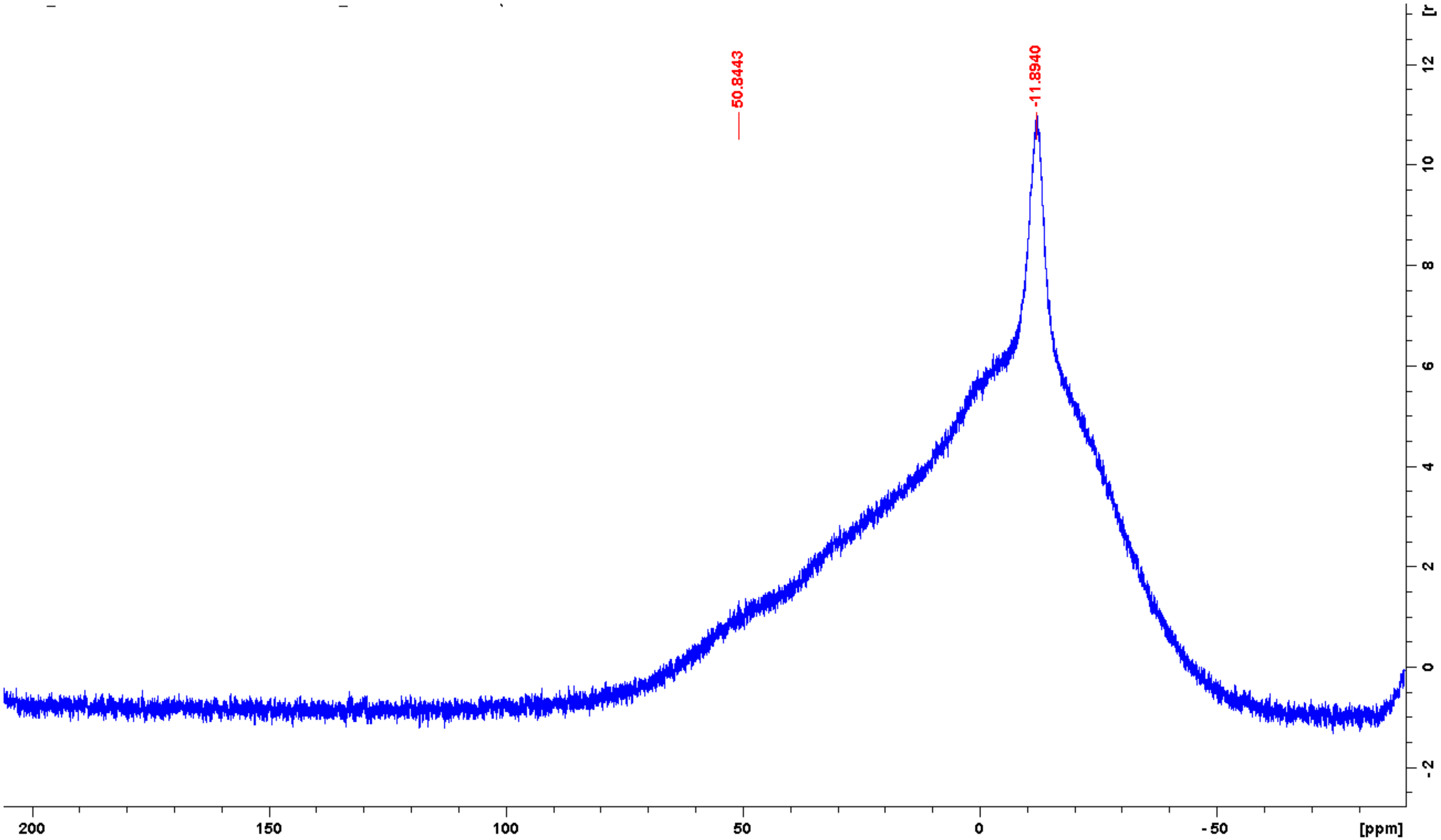


Figure S7. ^{11}B NMR spectrum of **2b**$^{\mathbf{NMe2}}$ in C_6D_6.

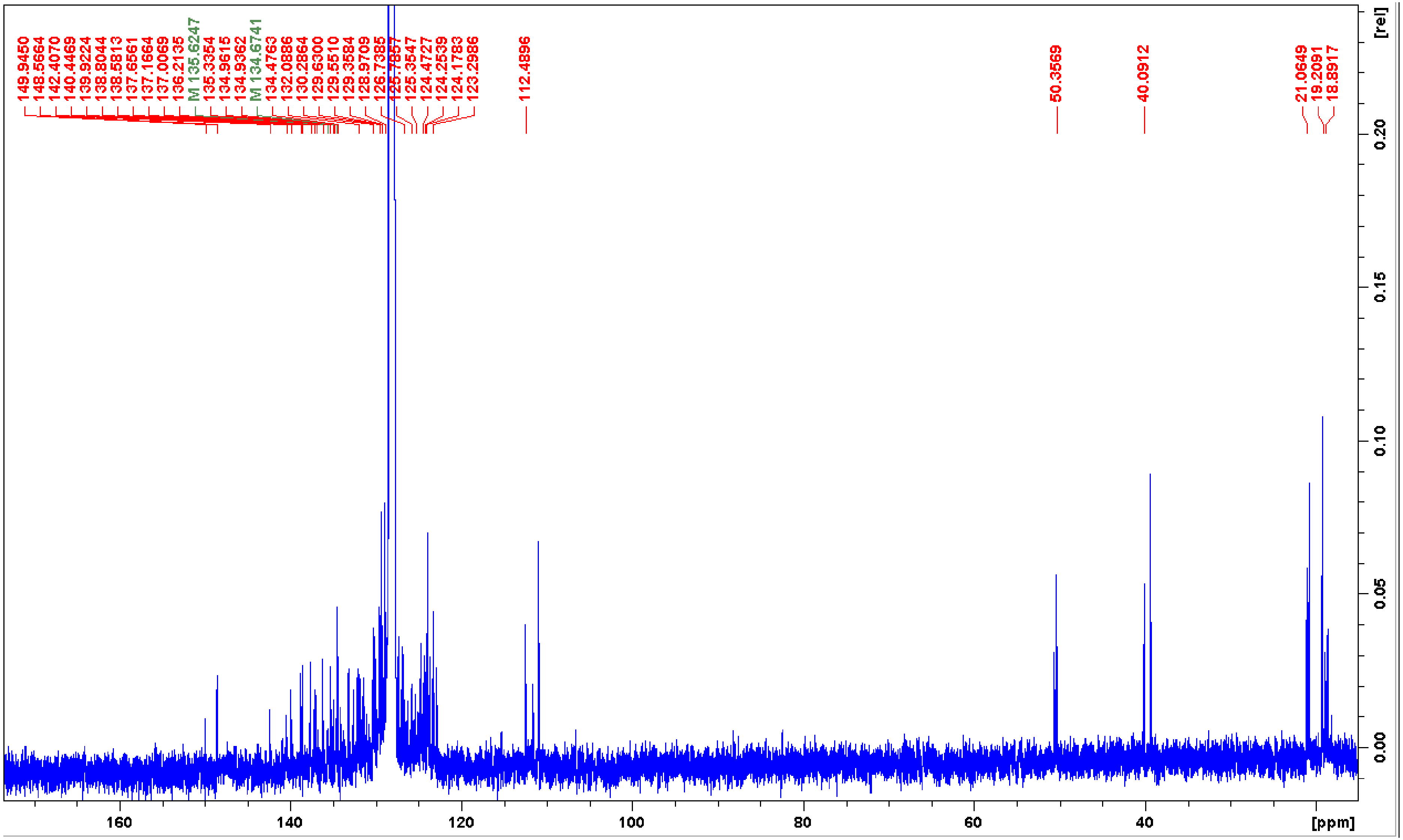


Figure S8. $^{13}C\{^1H\}$ NMR spectrum of **2b**$^{\mathbf{NMe2}}$ in C_6D_6. The resonances picked correspond to **2b**$^{\mathbf{NMe2}}$, the others to **5b**$^{\mathbf{NMe2}}$.

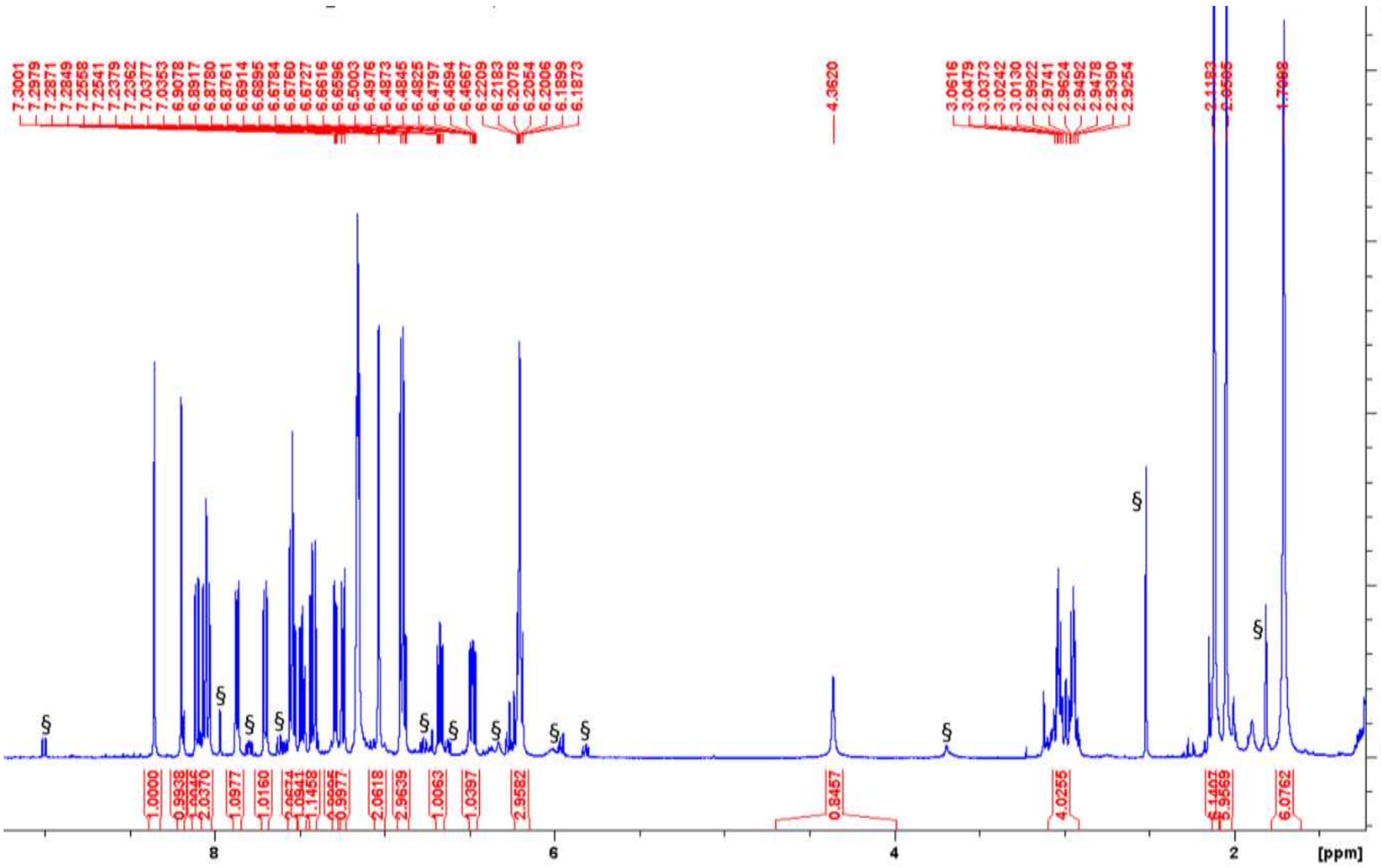


Figure S9. $^{1}H\{^{11}B\}$ NMR spectrum of **2b^{CF3}** in C_6D_6. Resonances marked with § correspond to the diborylaniline decomposition product **5b^{CF3}**.

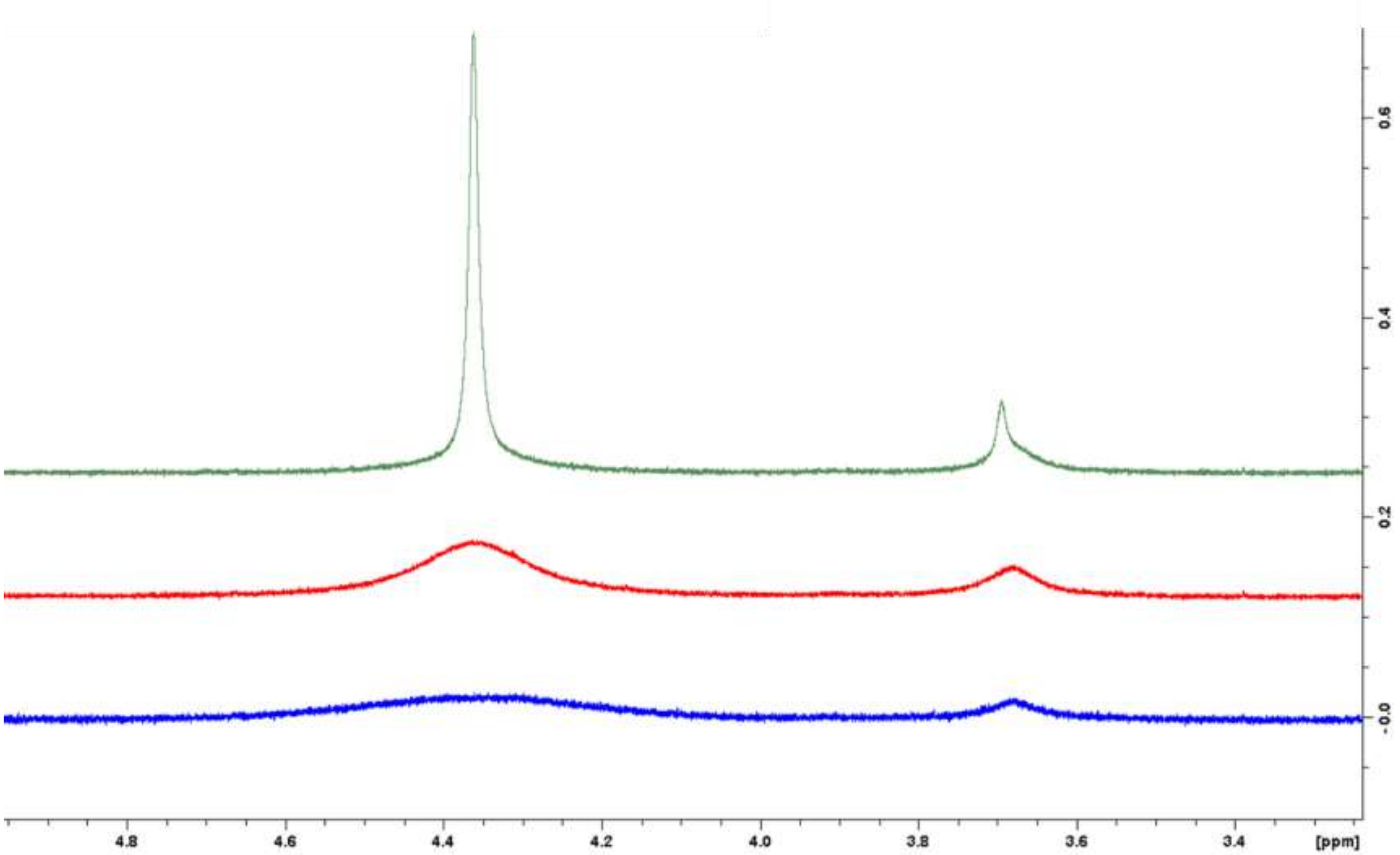


Figure S10. Width changes of the B*H* resonance (δ = 4.36 ppm) in the $^{1}H\{^{11}B\}$ NMR spectrum of **2b**$^{\mathbf{CF3}}$ in C_6D_6 with decoupler offset of −12.0 ppm (top, green) and 50.0 ppm (middle, red). The non-decoupled spectrum is provided at the bottom (blue).

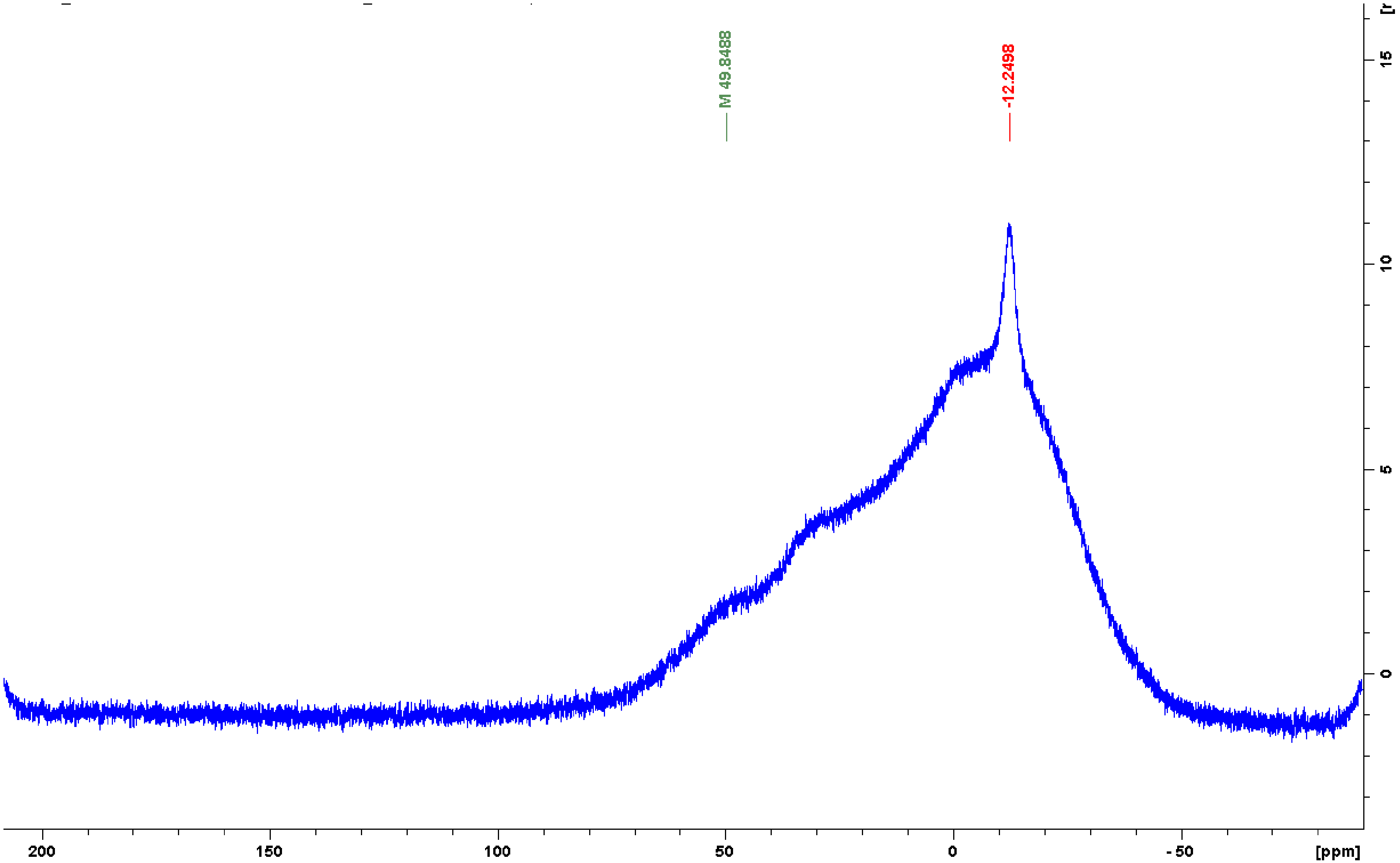


Figure S11. ^{11}B NMR spectrum of **2b^{CF3}** in C_6D_6.

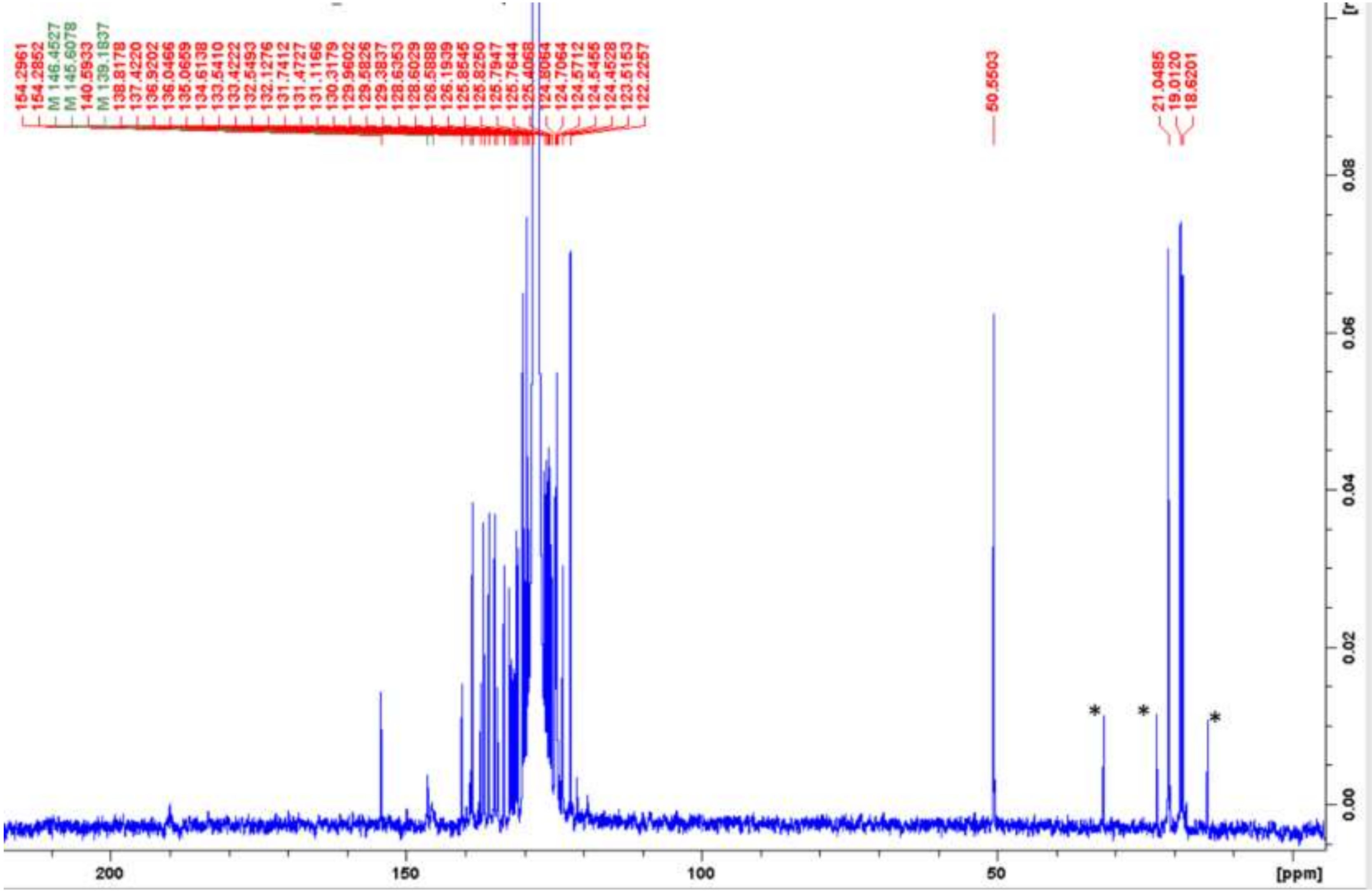


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **2b^{CF3}** in C_6D_6. Resonances marked with * correspond to residual hexane.

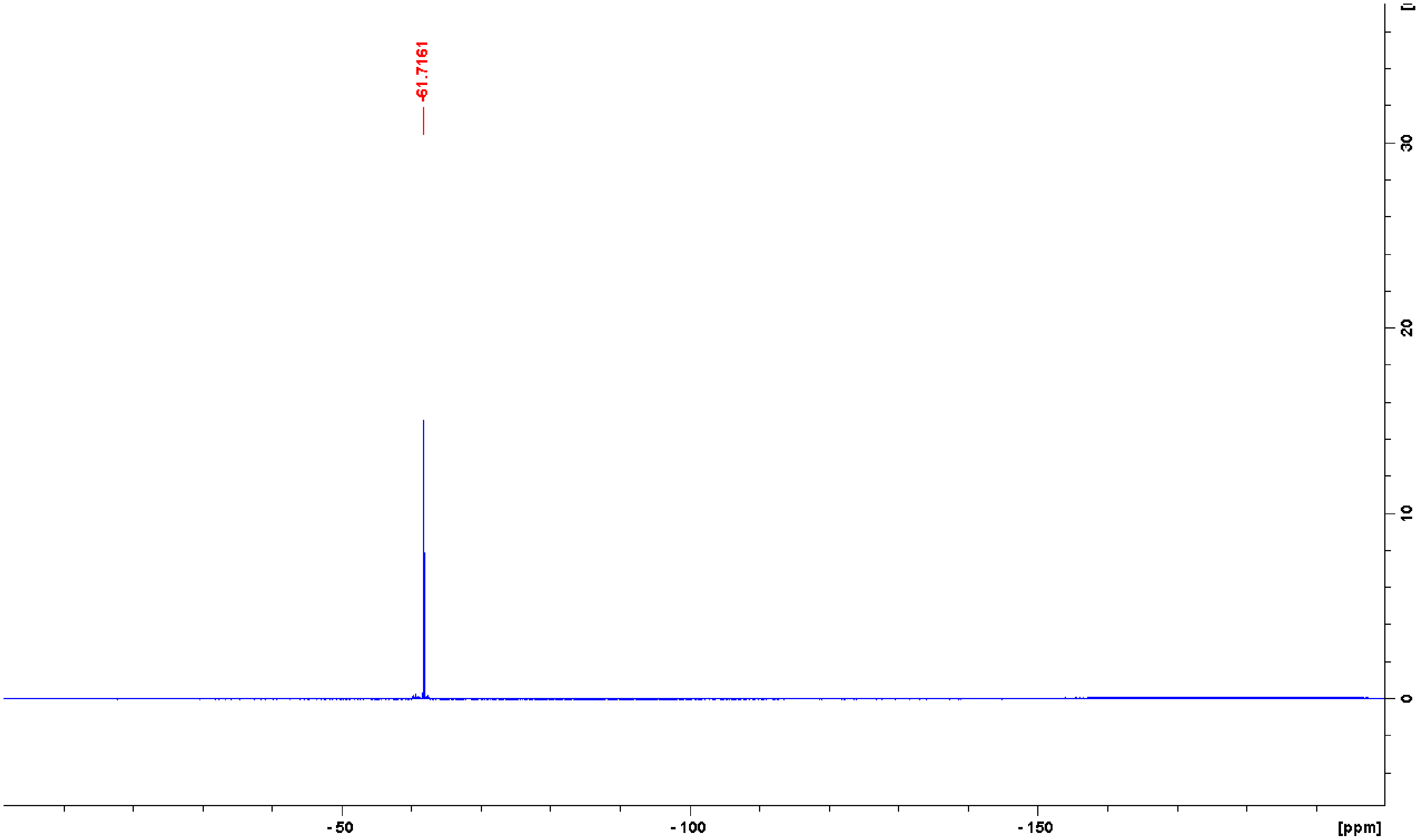


Figure S13. $^{19}F\{^{1}H\}$ NMR spectrum of **2b^{CF3}** in C_6D_6.

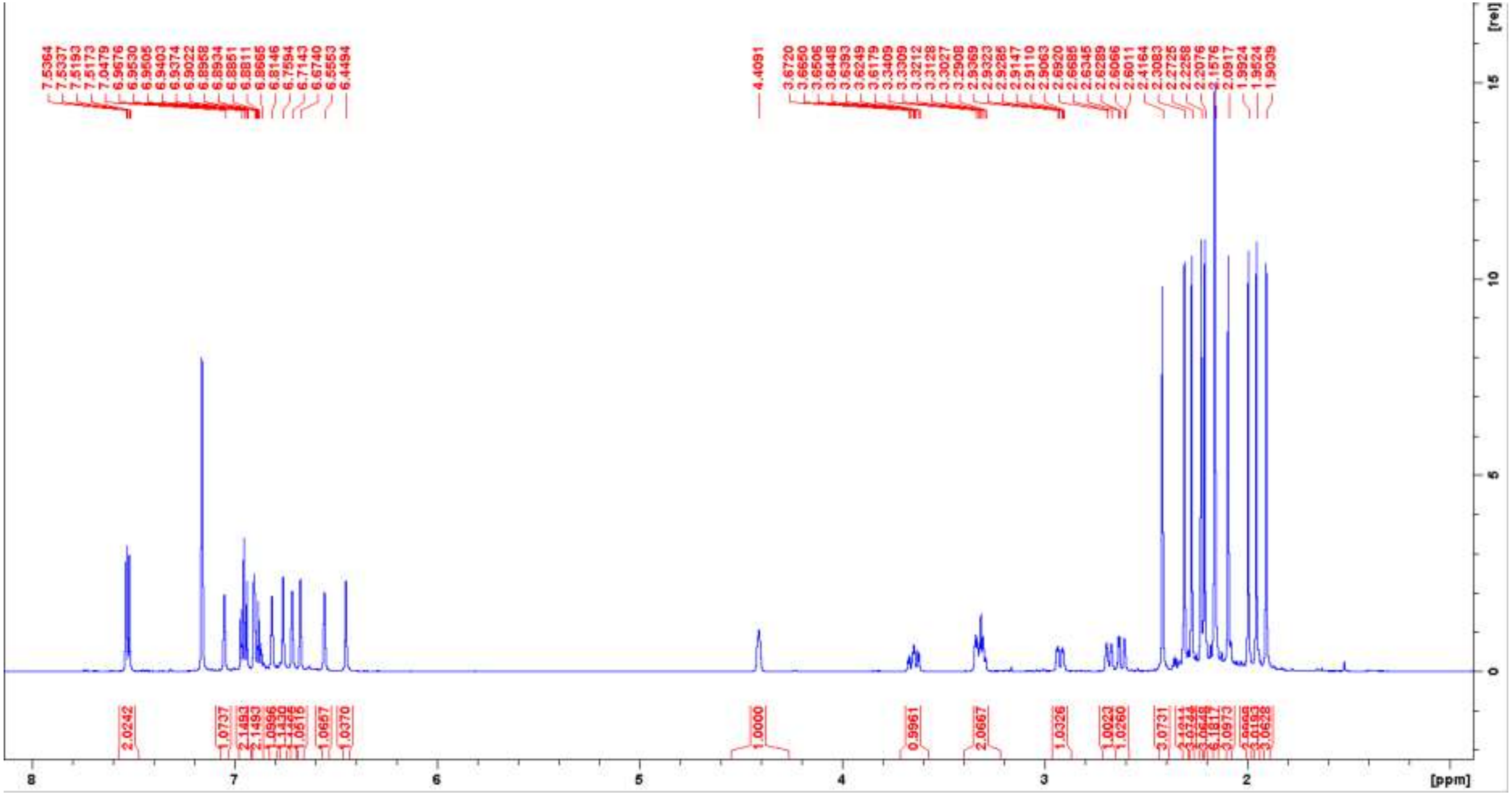


Figure S14. ^{1}H NMR spectrum of $\mathbf{3a^H}$ in C_6D_6.

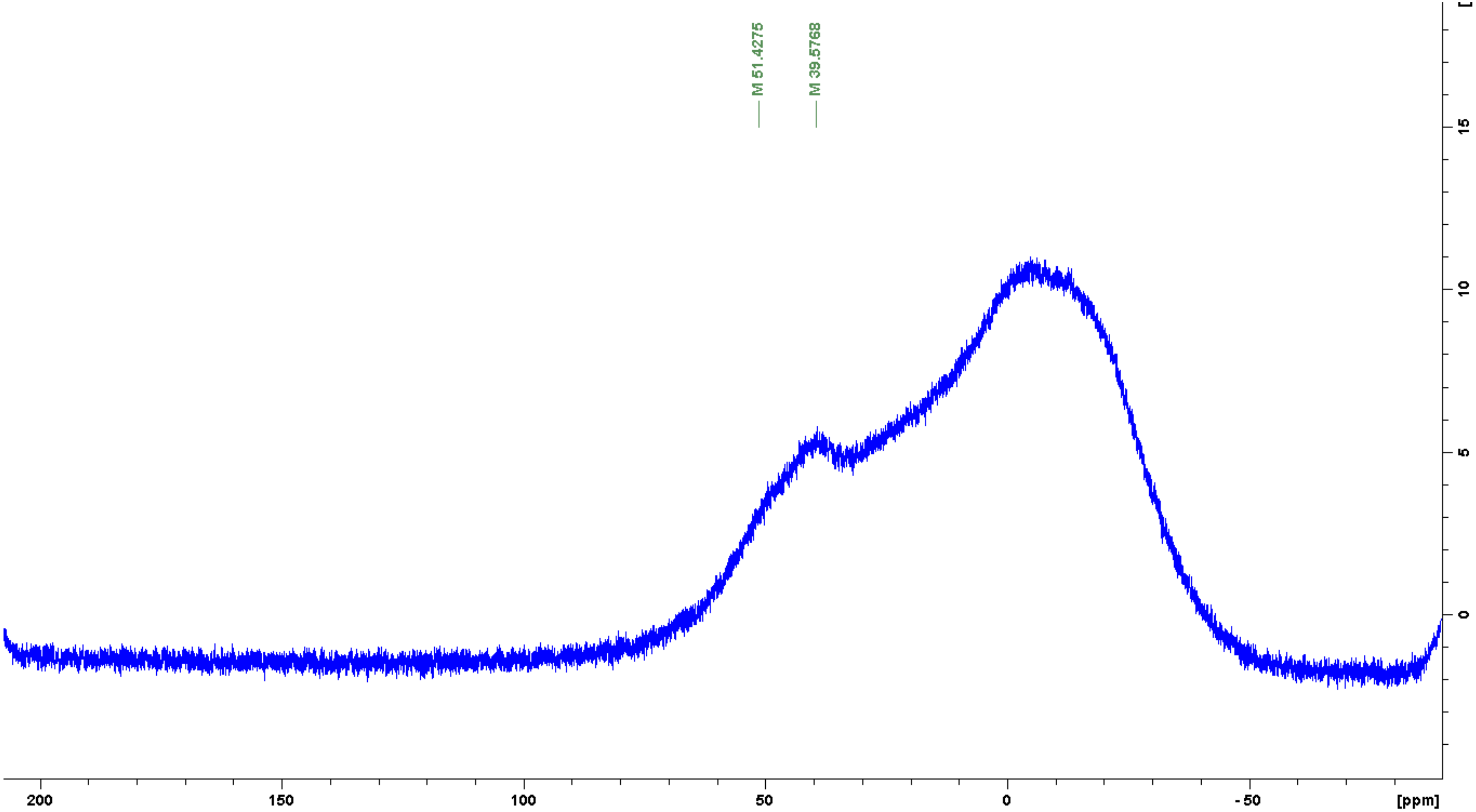


Figure S15. ^{11}B NMR spectrum of **3a^{H}** in C_6D_6.

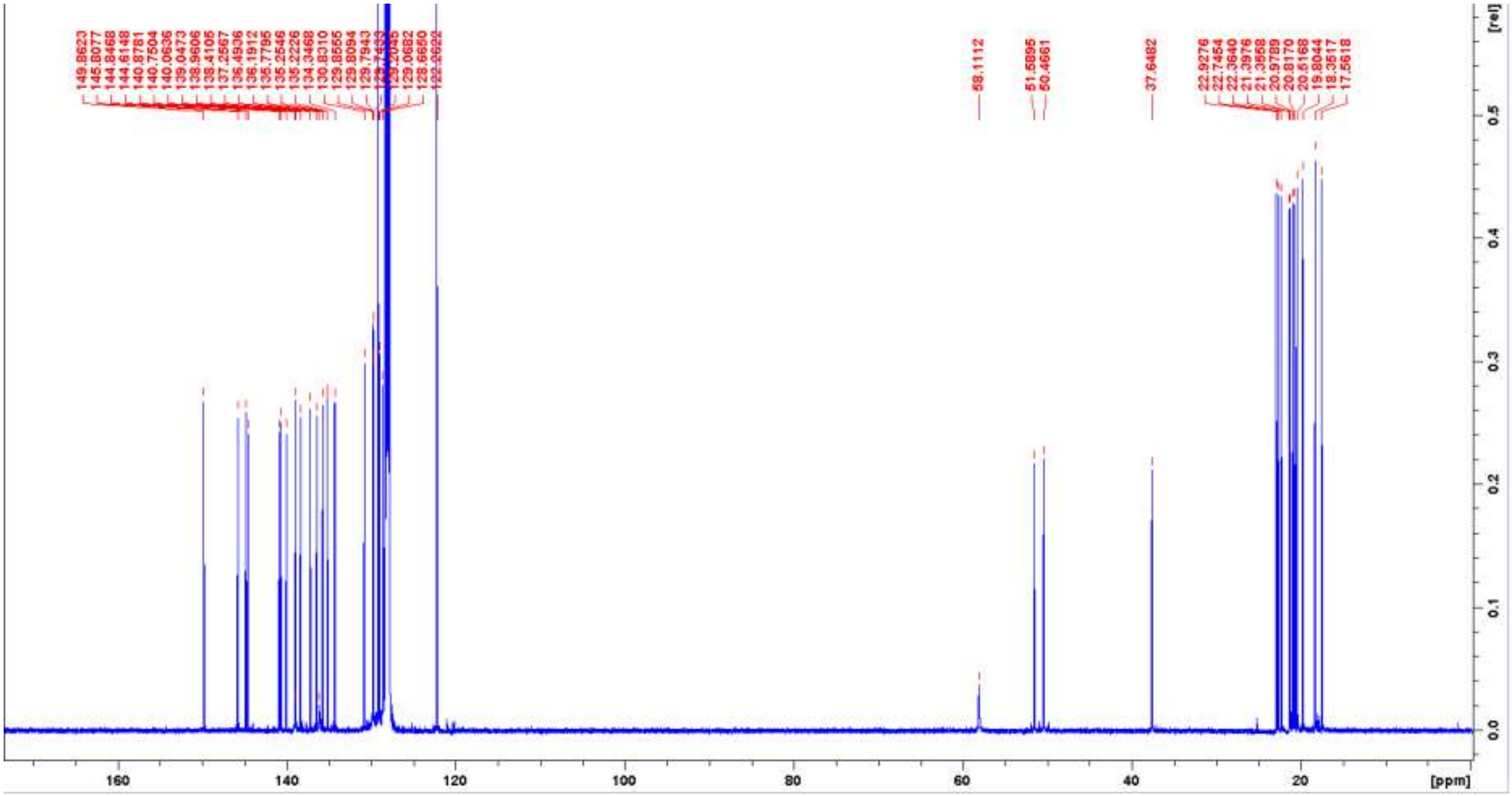


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{3a^{H}}$ in C_6D_6.

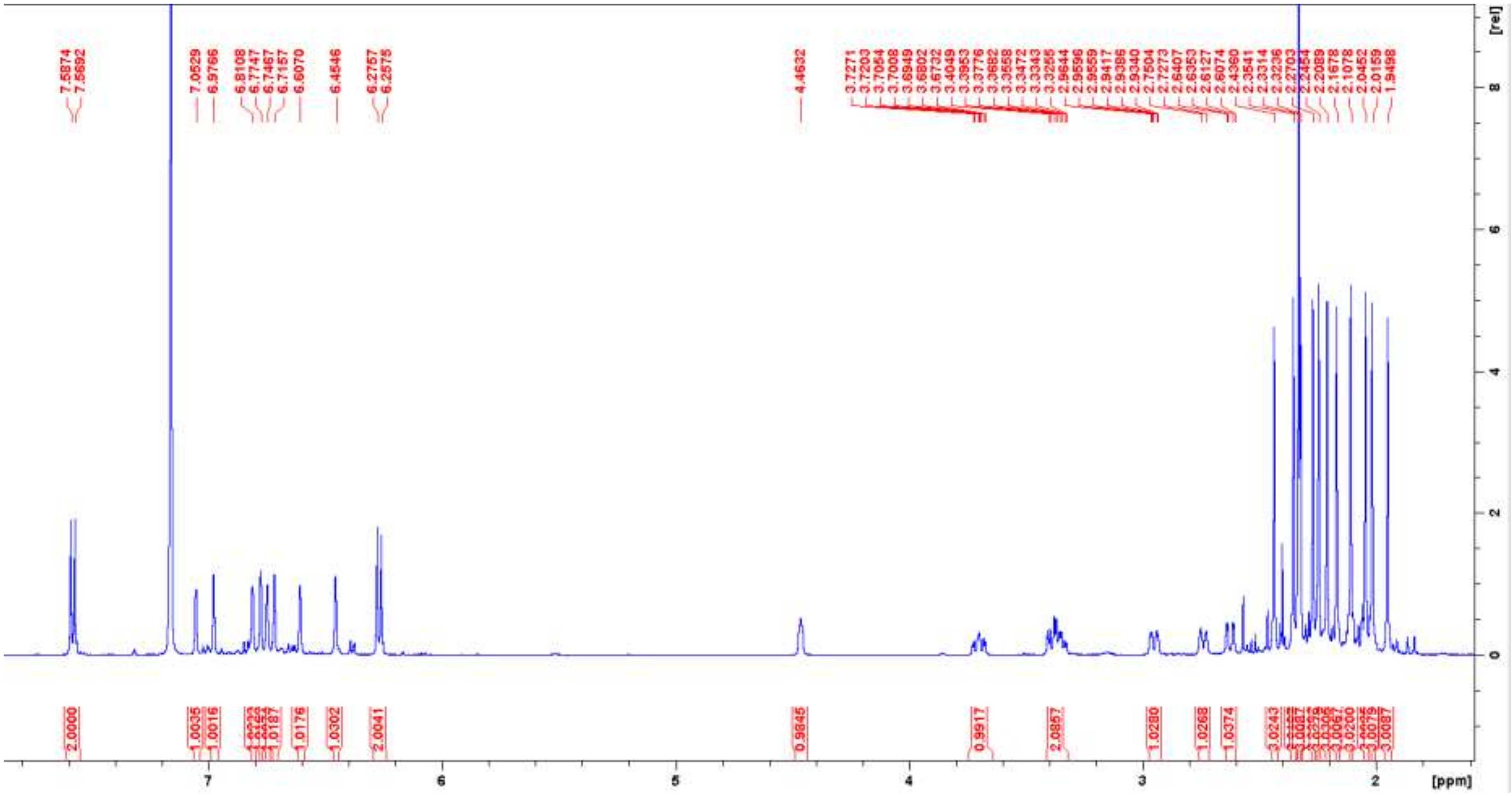


Figure S17. ^{1}H NMR spectrum of **3a**$^{\mathbf{NMe2}}$ in C_6D_6.

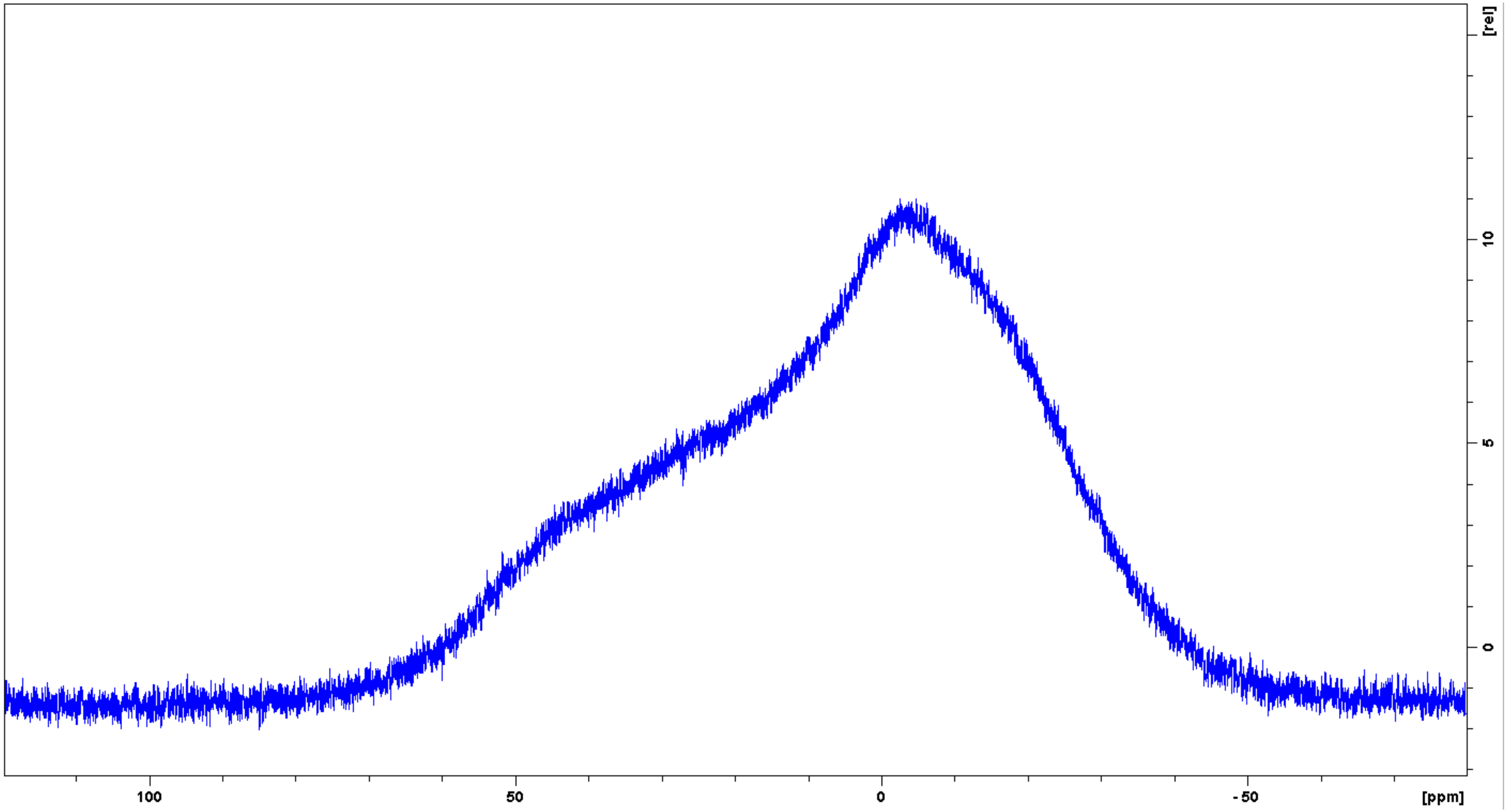


Figure S18. ^{11}B NMR spectrum of **3a$^{\mathbf{NMe2}}$** in C_6D_6.

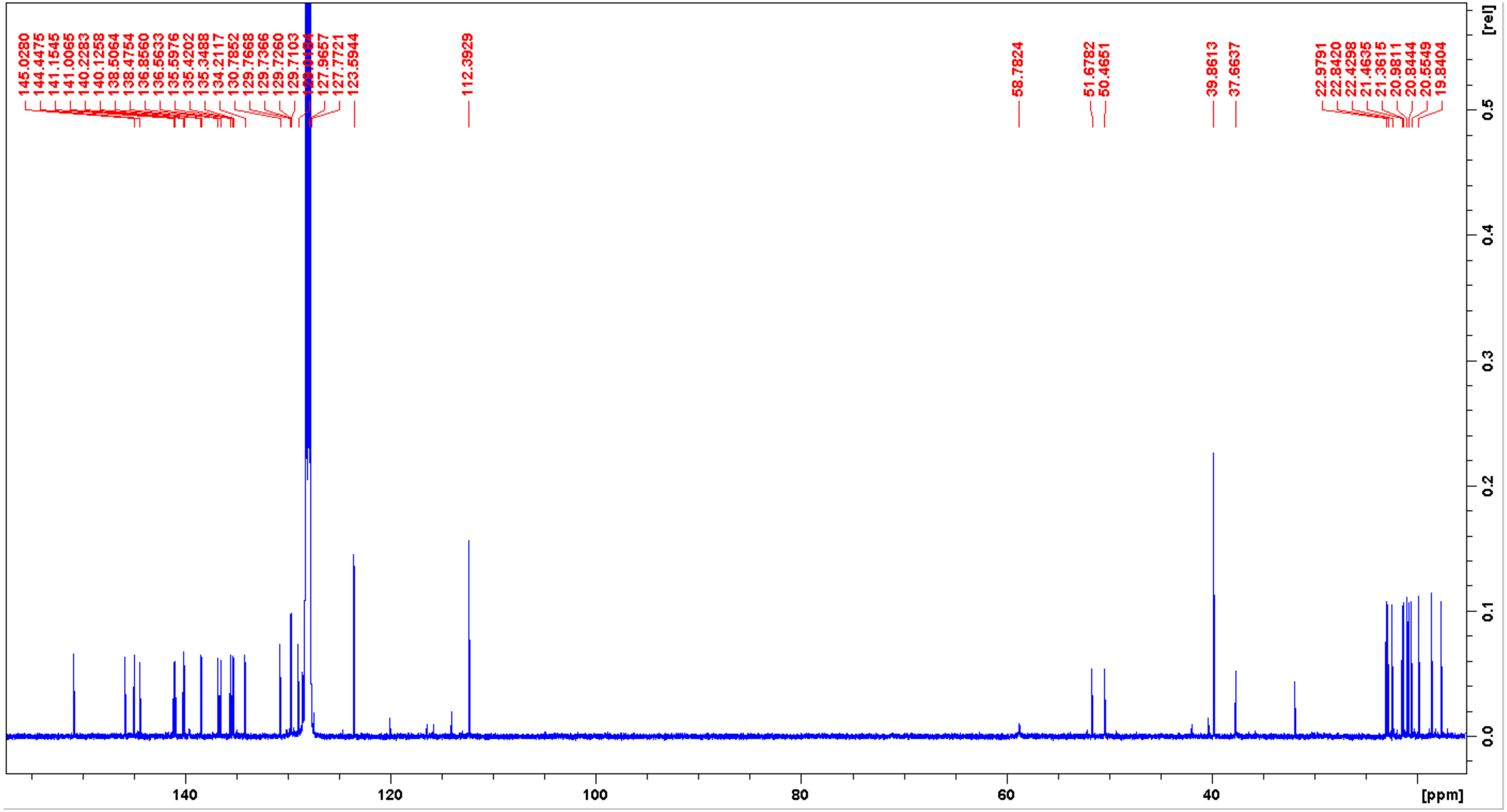


Figure S19. $^{13}C\{^1H\}$ NMR spectrum of **3a**$^{\mathbf{NMe2}}$ in C_6D_6.

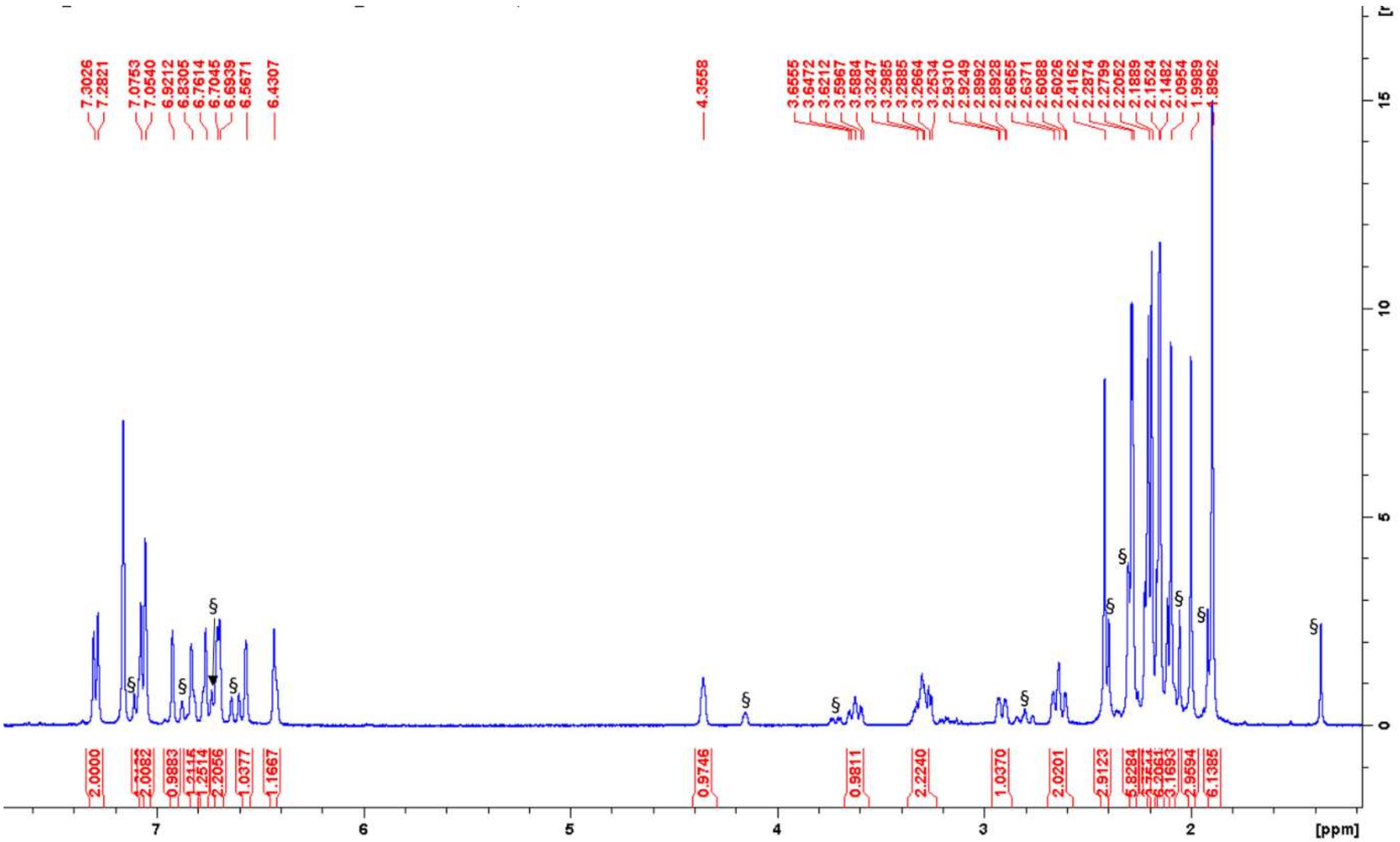


Figure S20. ^{1}H NMR spectrum of **3a**$^{\mathbf{CF3}}$ in C_6D_6. Resonances marked with § correspond to the diborylaniline decomposition product **4a**$^{\mathbf{CF3}}$.

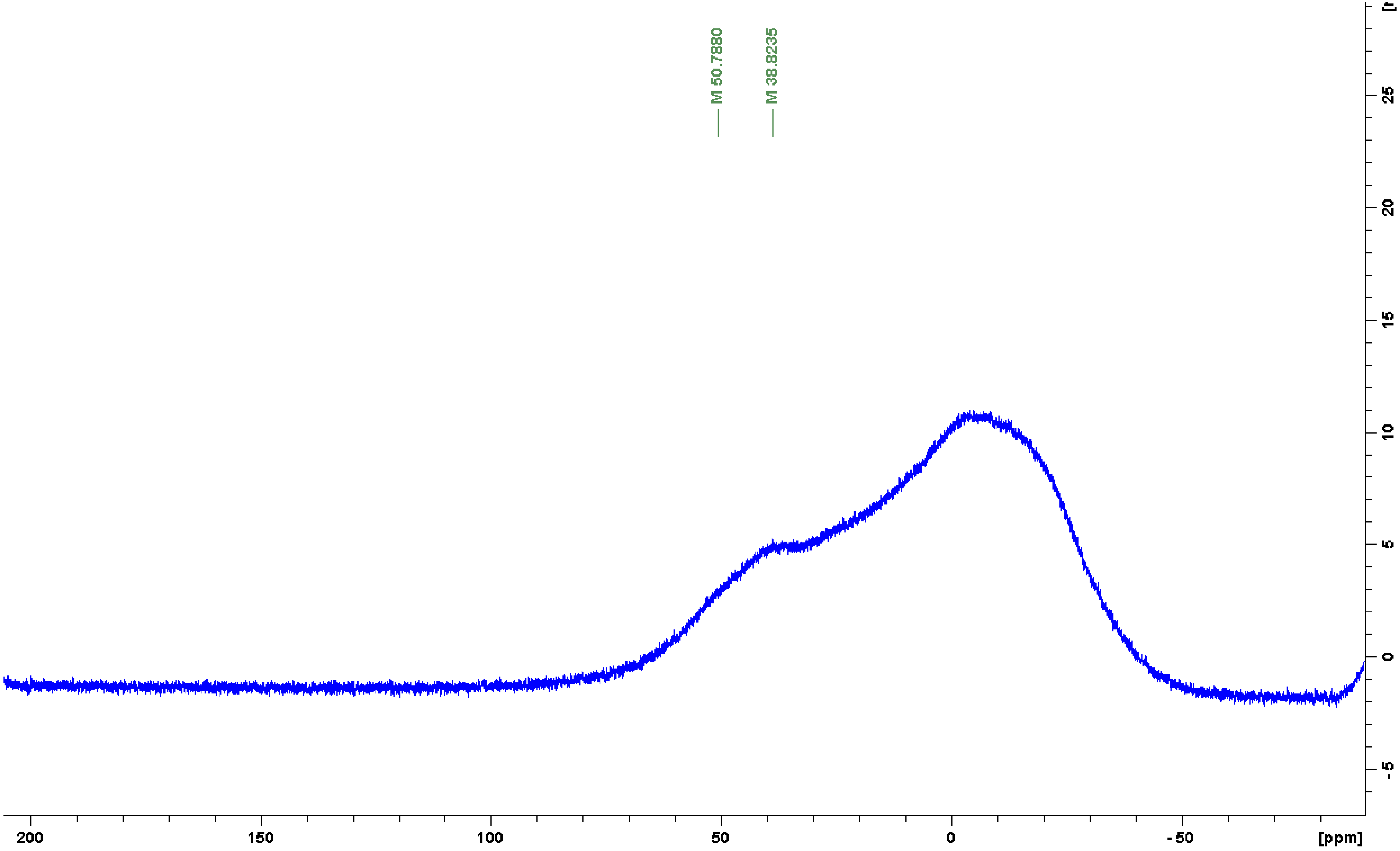


Figure S21. ^{11}B NMR spectrum of **3a$^{\mathbf{CF3}}$** in C_6D_6.

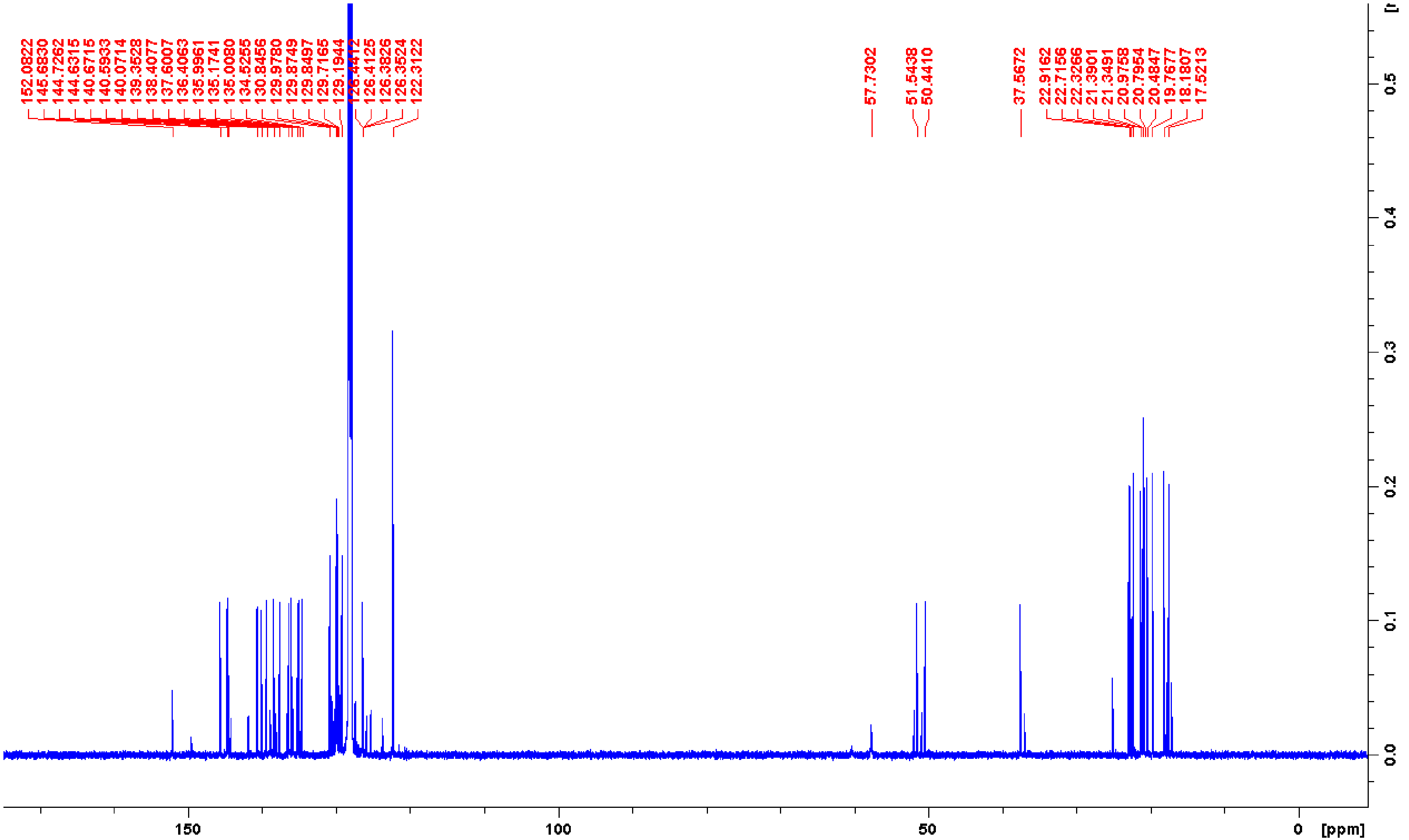


Figure S22. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{3a}^{\mathbf{CF3}}$ in C_6D_6.

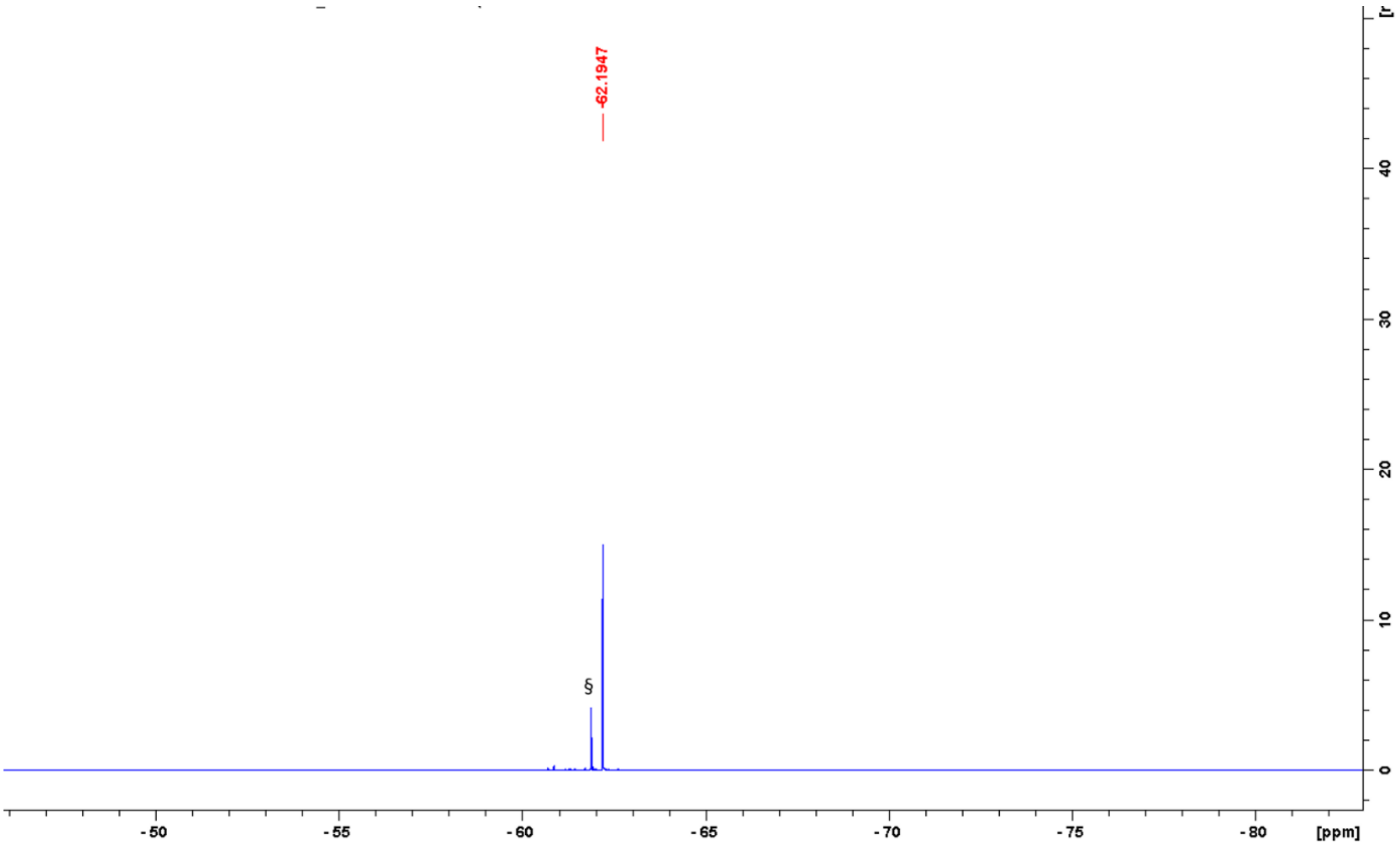


Figure S23. $^{19}F\{^{1}H\}$ NMR spectrum of **3a**$^{\mathbf{CF3}}$ in C_6D_6. The resonance marked with § corresponds to the diborylaniline decomposition product **4a**$^{\mathbf{CF3}}$.

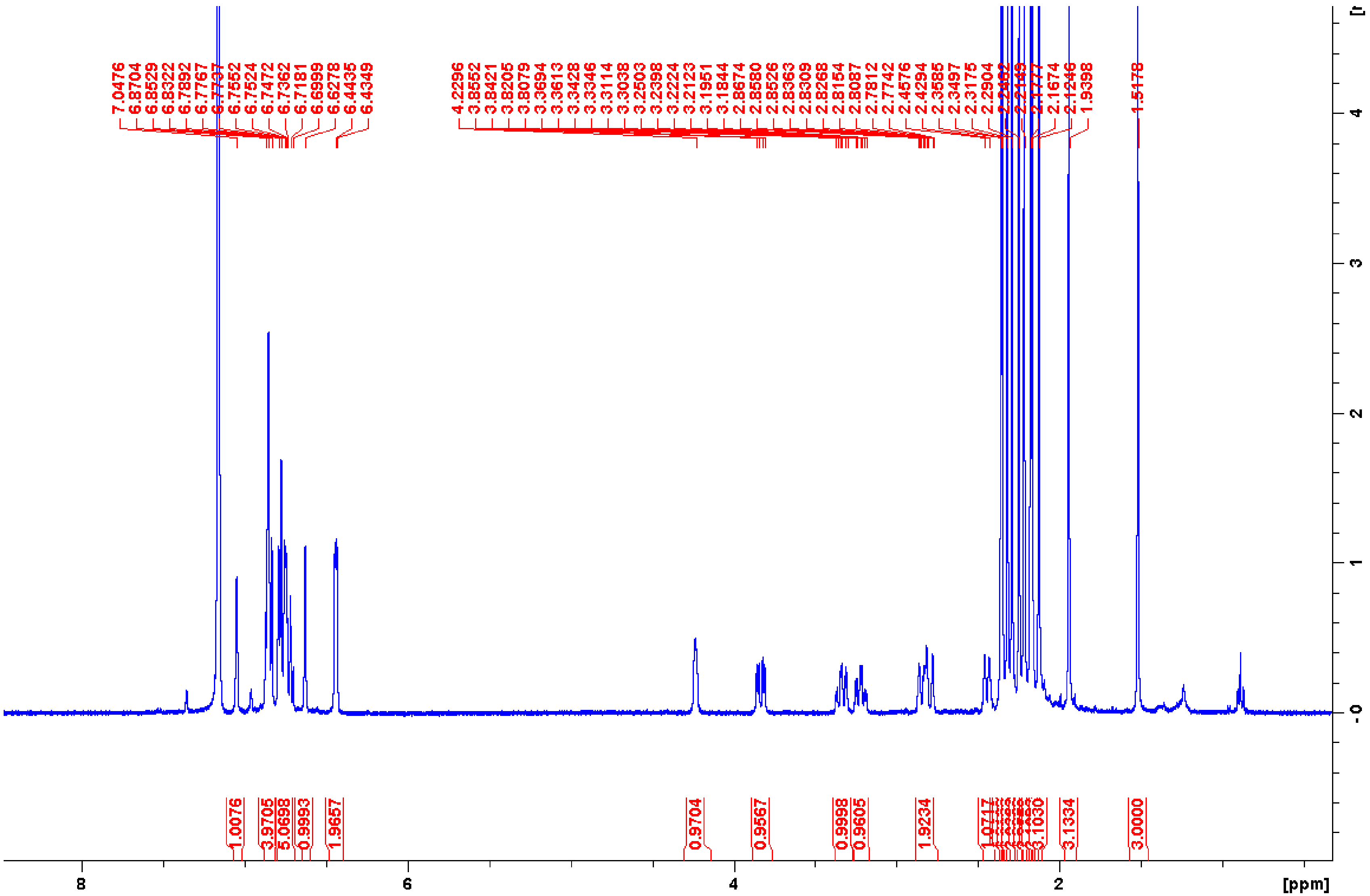


Figure S24. ^{1}H NMR spectrum of **4a$^{\mathbf{H}}$** in C_6D_6.

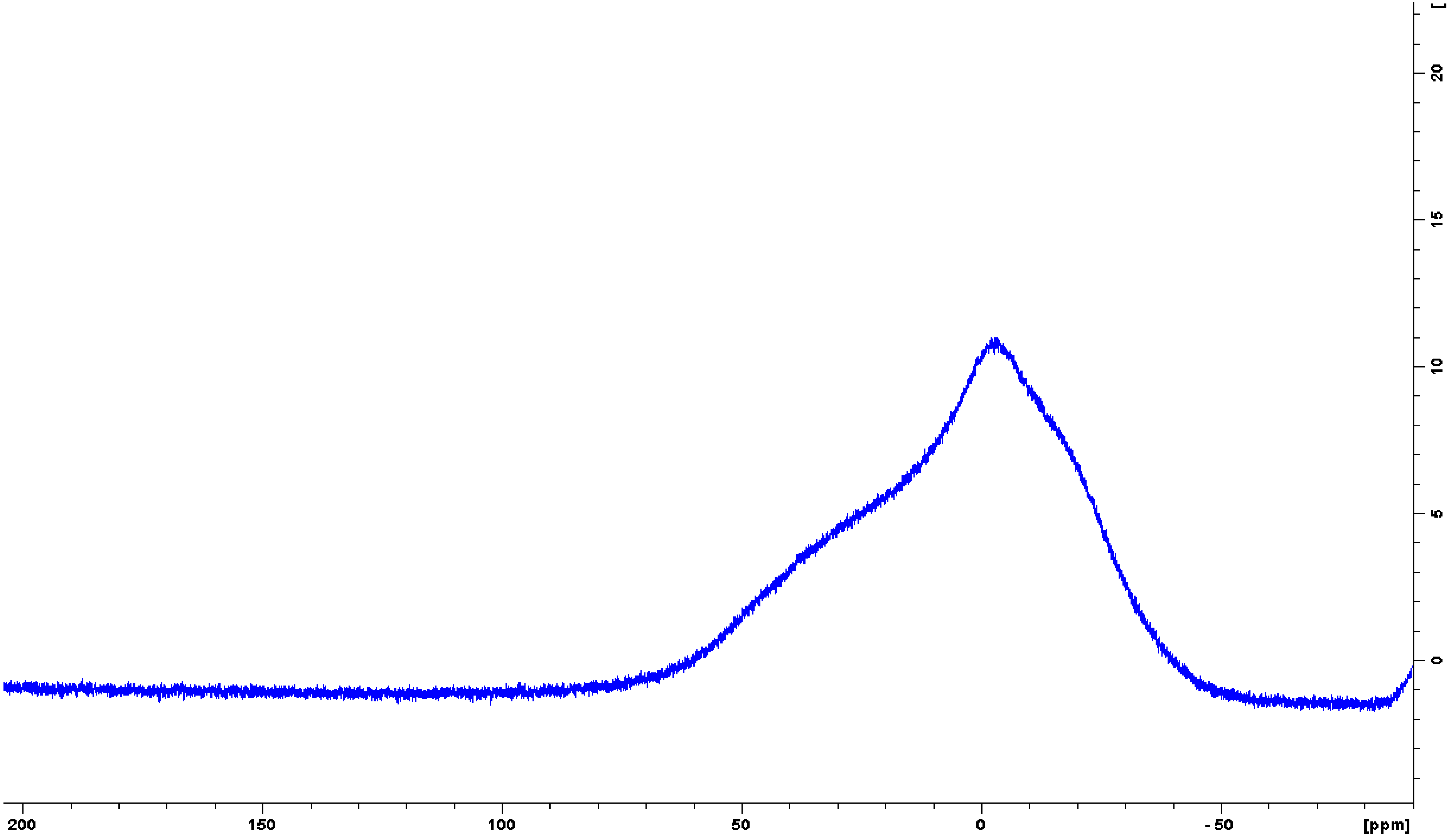


Figure S25. ^{11}B NMR spectrum of **4a$^{\mathbf{H}}$** in C_6D_6.

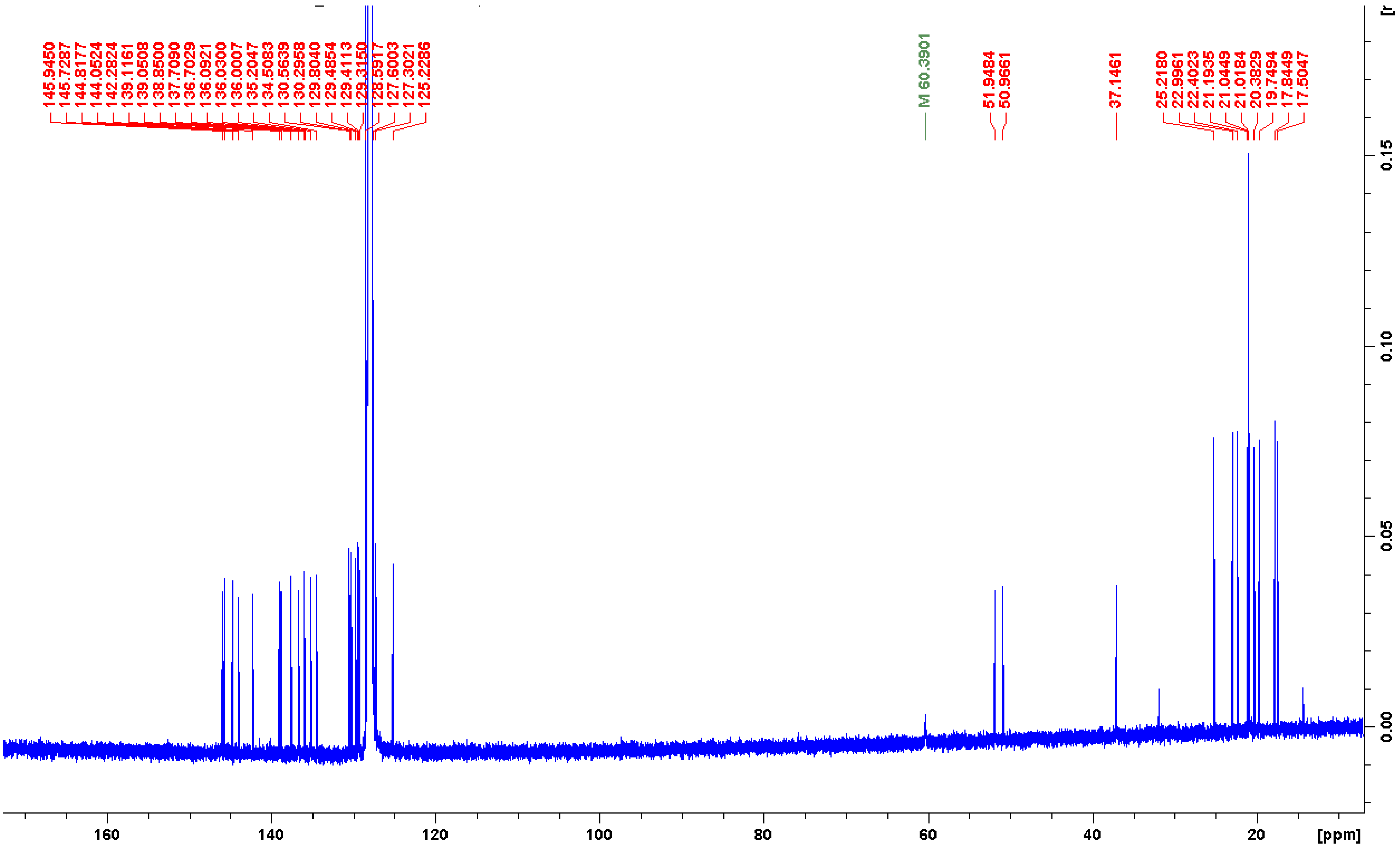


Figure S26. $^{13}C\{^1H\}$ NMR spectrum of $\mathbf{4a^H}$ in C_6D_6.

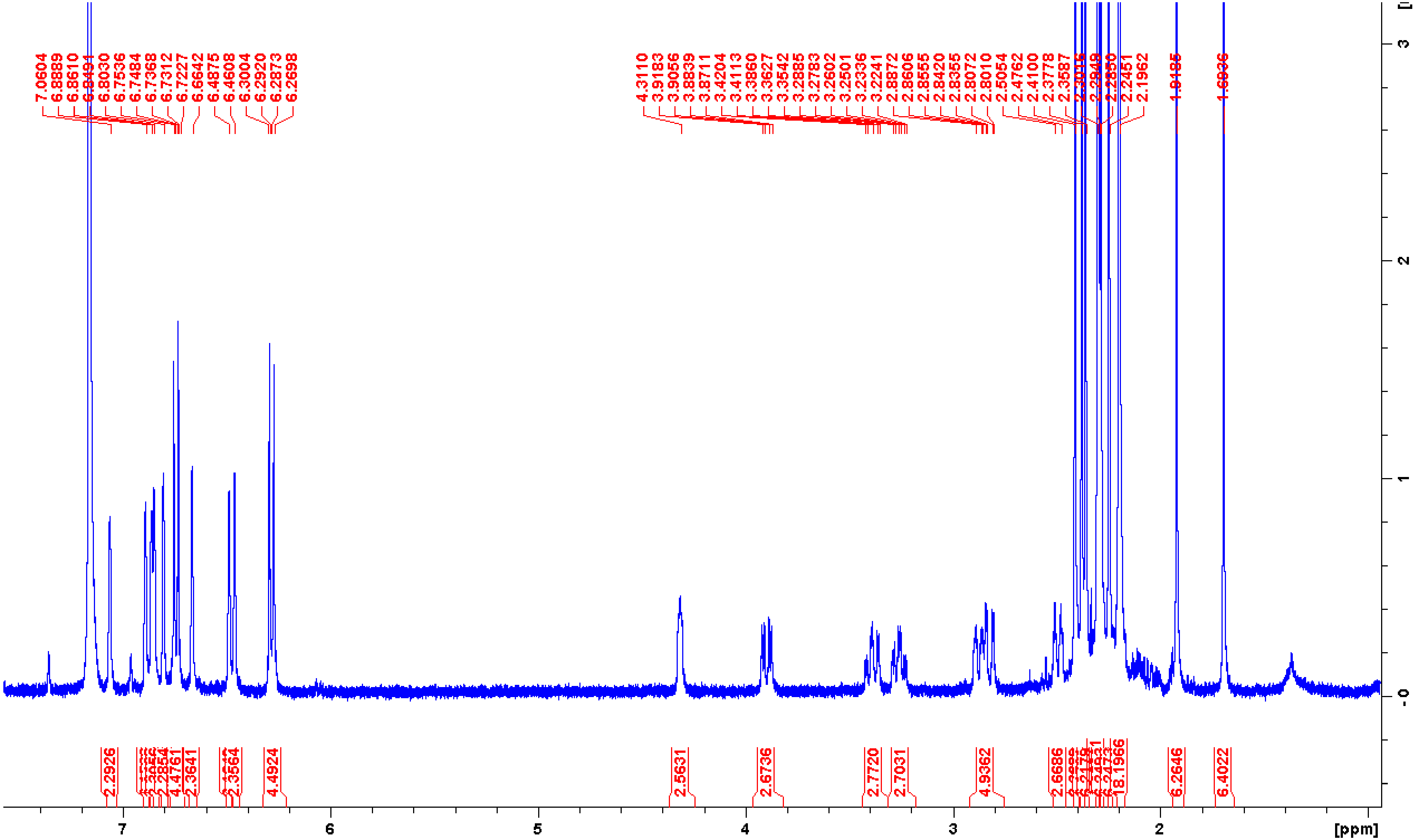


Figure S27. ^{1}H NMR spectrum of **4a$^{\mathbf{NMe2}}$** in C_6D_6.

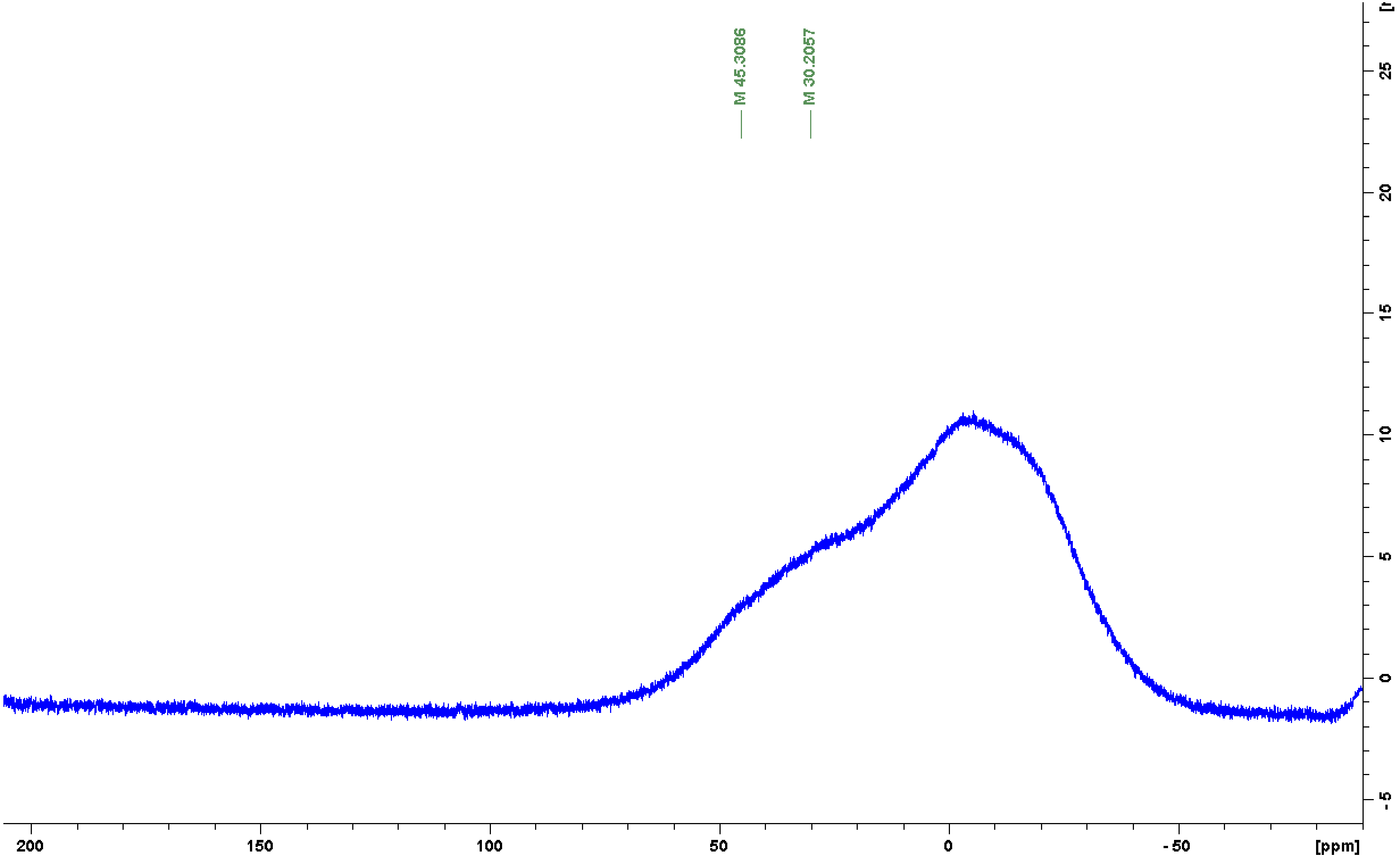


Figure S28. ^{11}B NMR spectrum of **4a**$^{\mathbf{NMe2}}$ in C_6D_6.

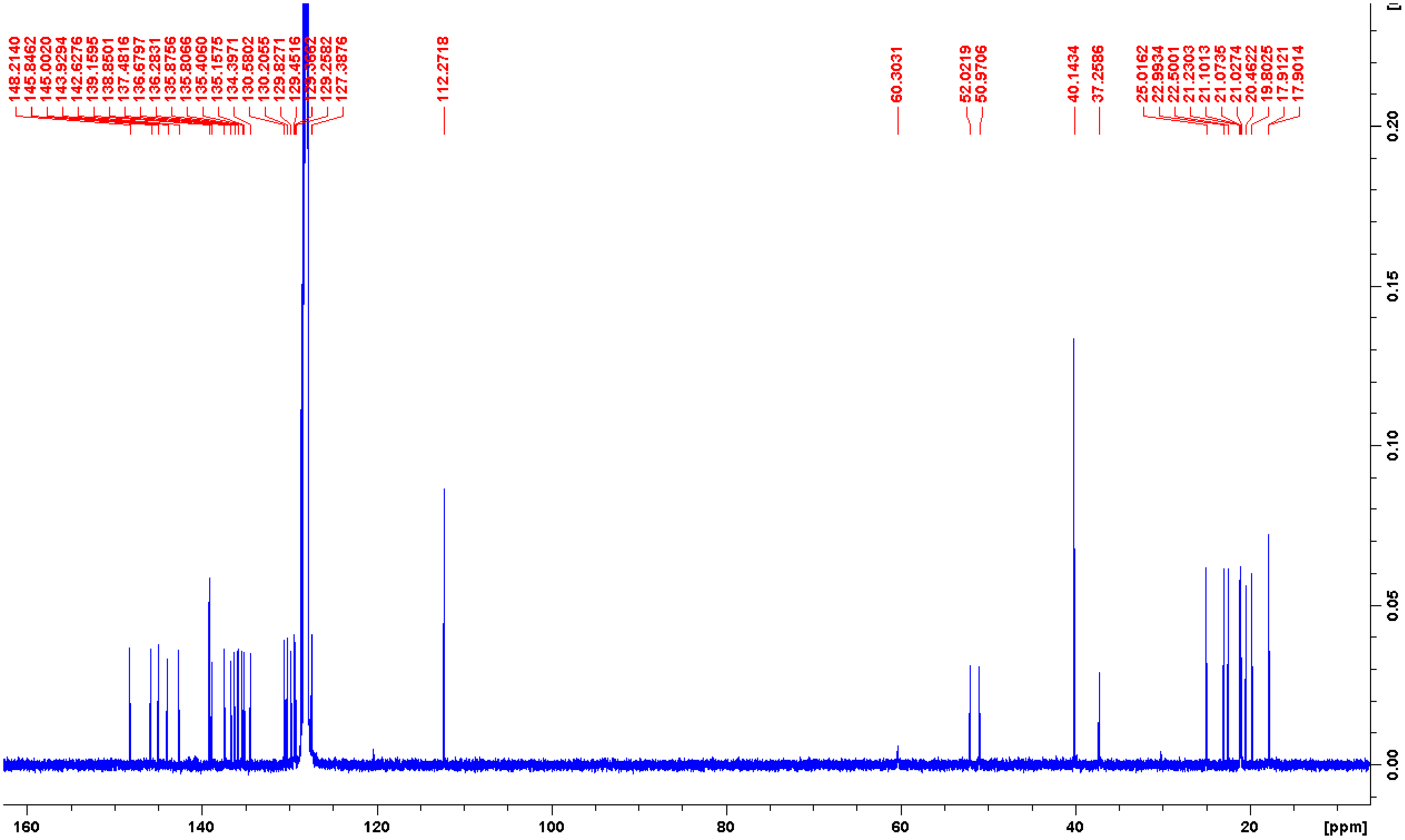


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **4a**$^{\mathbf{NMe2}}$ in C_6D_6.

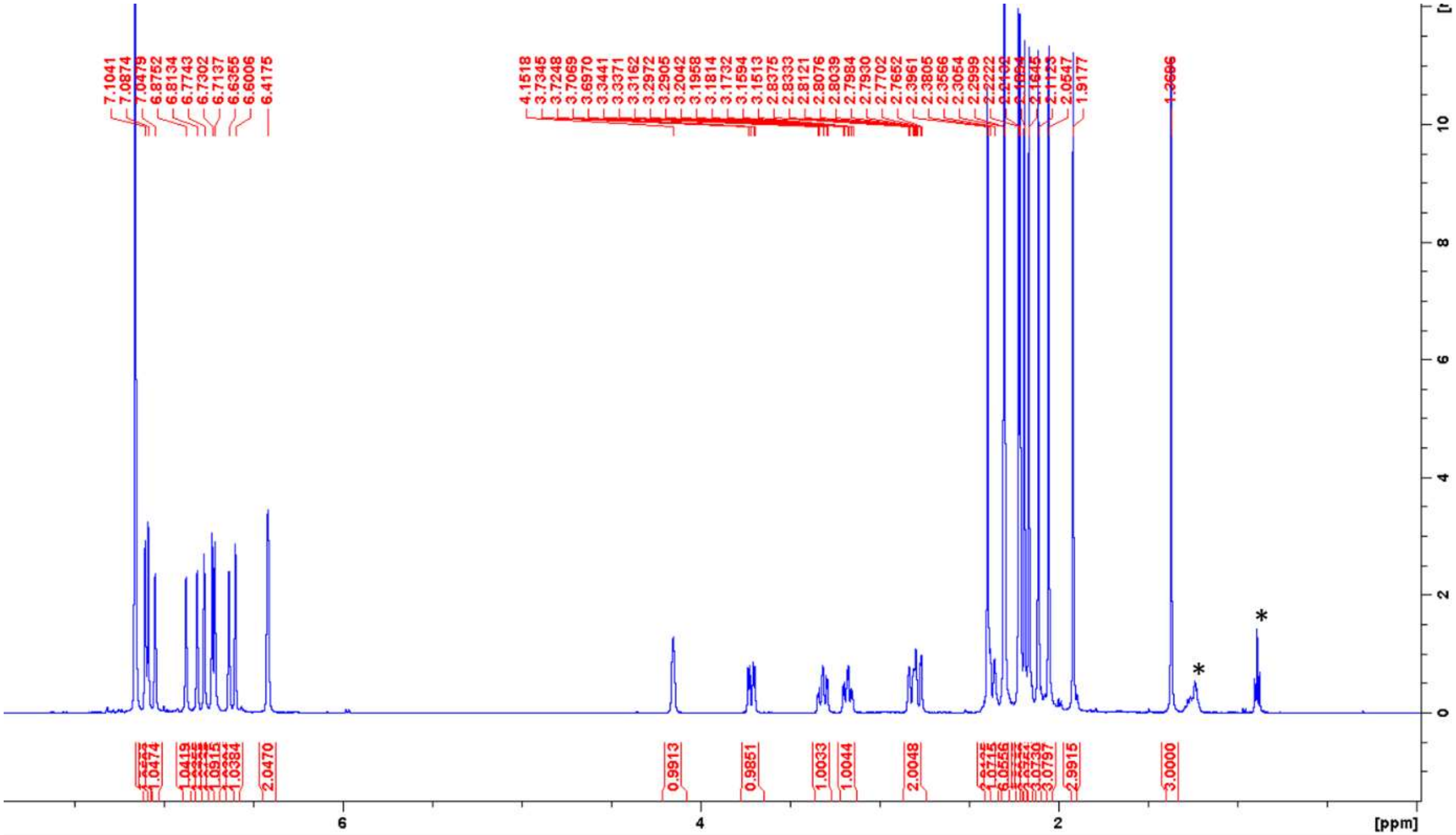


Figure S30. ^{1}H NMR spectrum of **4a**$^{\mathbf{CF3}}$ in C_6D_6. The resonances marked with * correspond to residual hexane.

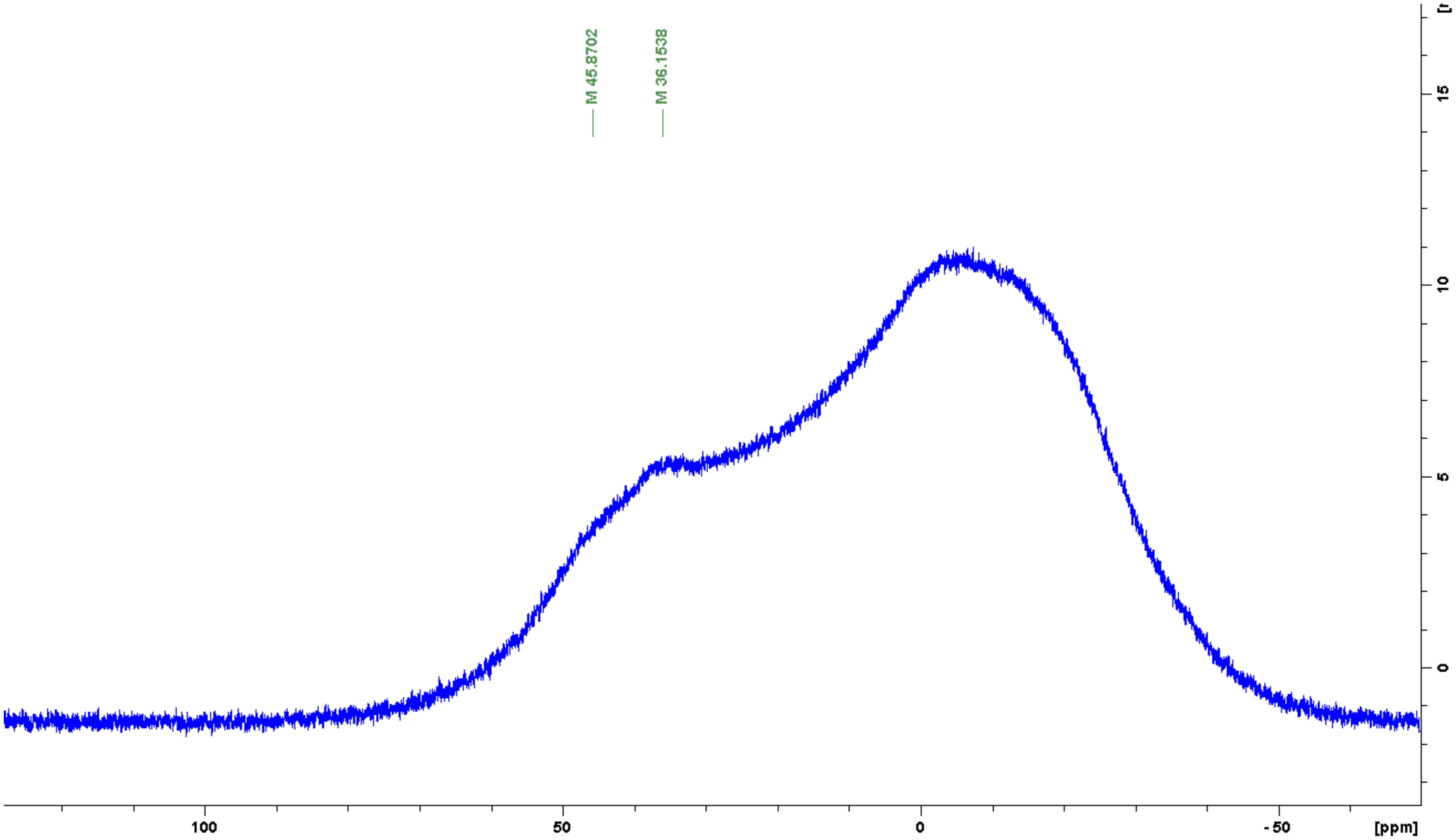


Figure S31. ^{11}B NMR spectrum of **4a**$^{\mathbf{CF3}}$ in C6D6.

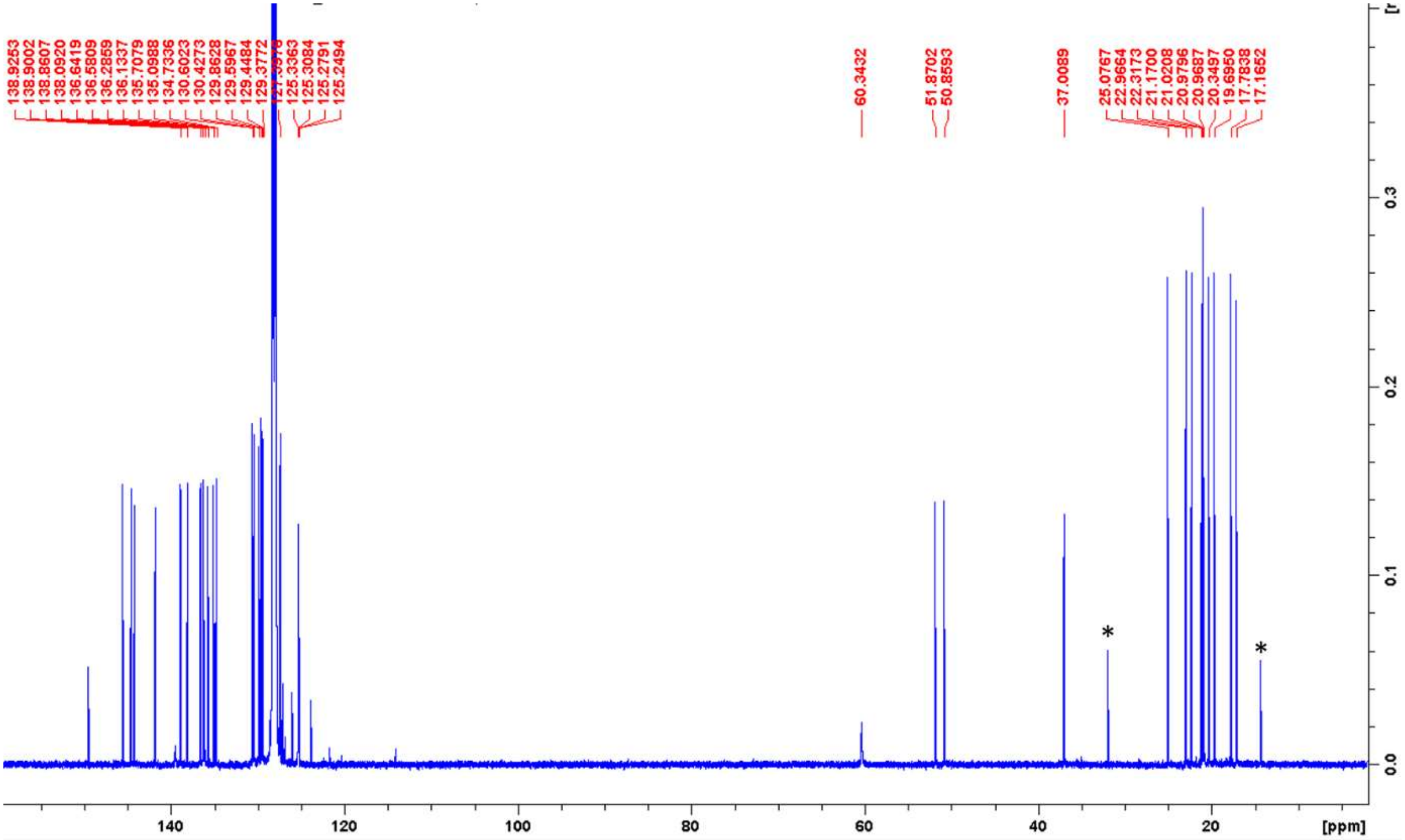


Figure S32. $^{13}C\{^1H\}$ NMR spectrum of **4a^{CF3}** in C_6D_6. The resonances marked with * correspond to residual hexane.

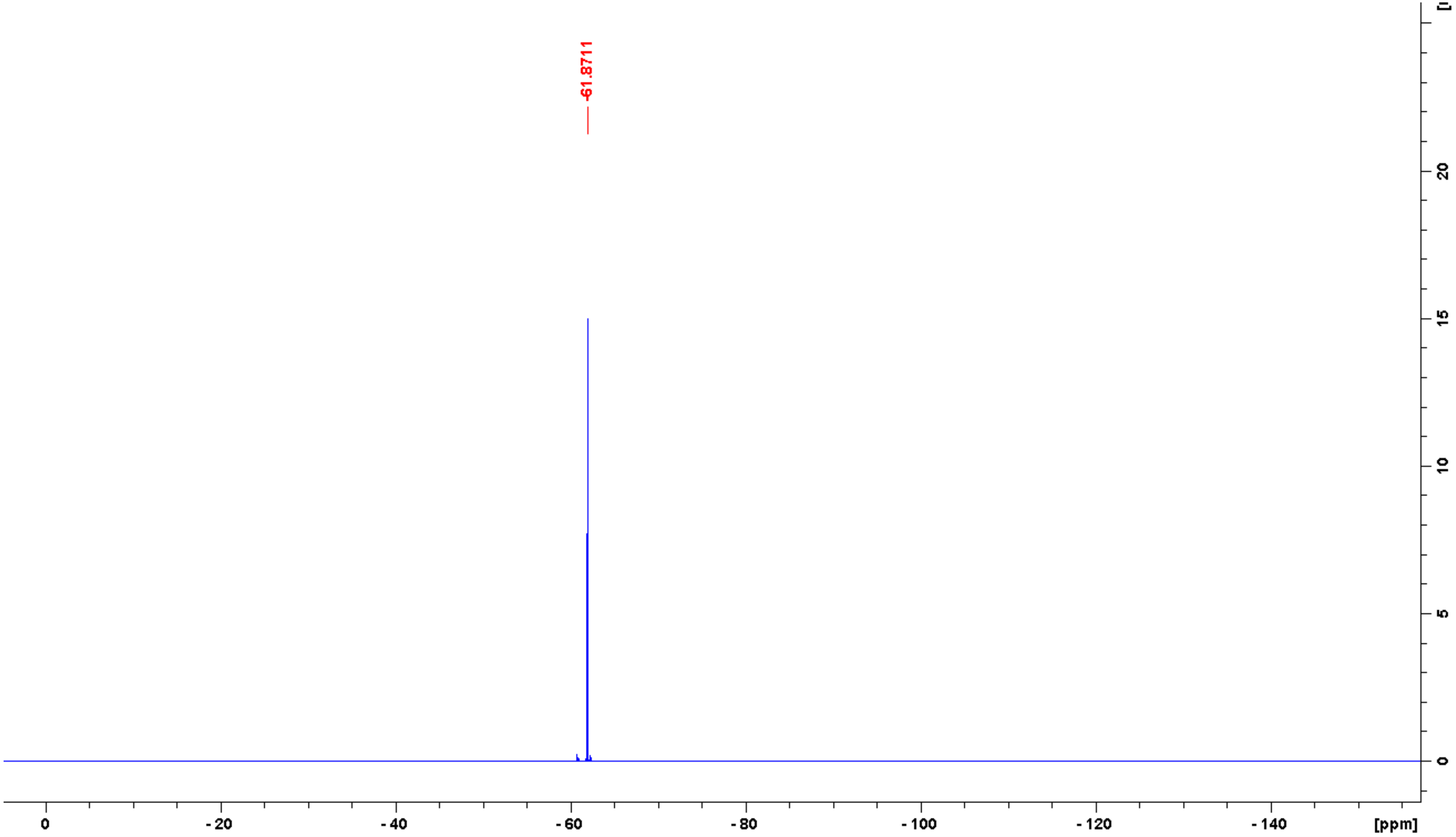


Figure S33. ^{19}F NMR spectrum of **4a$^{\mathbf{CF3}}$** in C_6D_6.

Rearrangement and decomposition series of 2a^{R} and 2b^{R}

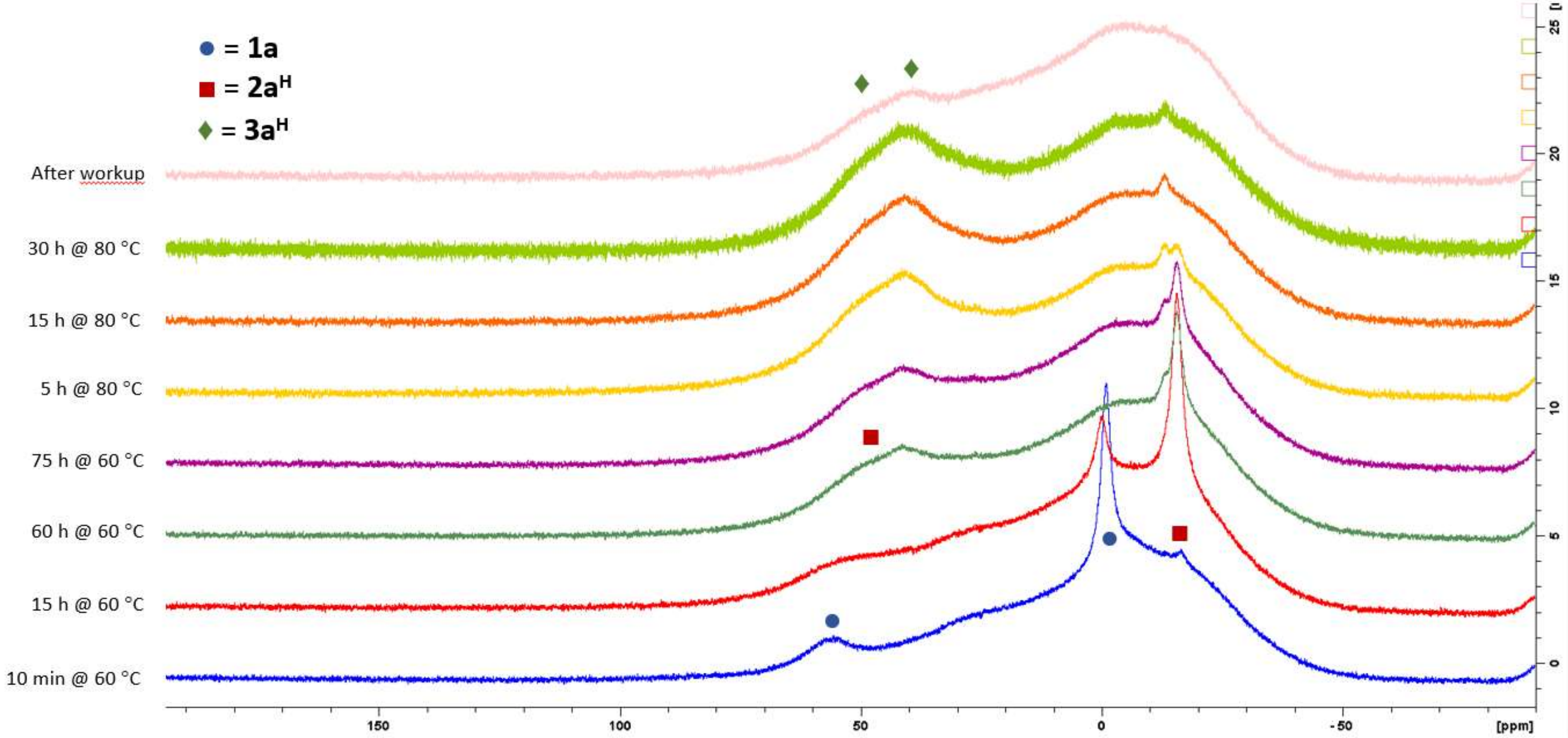


Figure S34. Stack-plot of ^{11}B NMR spectra of the reaction of **1a** (●) with phenylazide, showing the intermediate formation of **2a^{H}** (■) and its rearrangement to **3a^{H}** (♦).

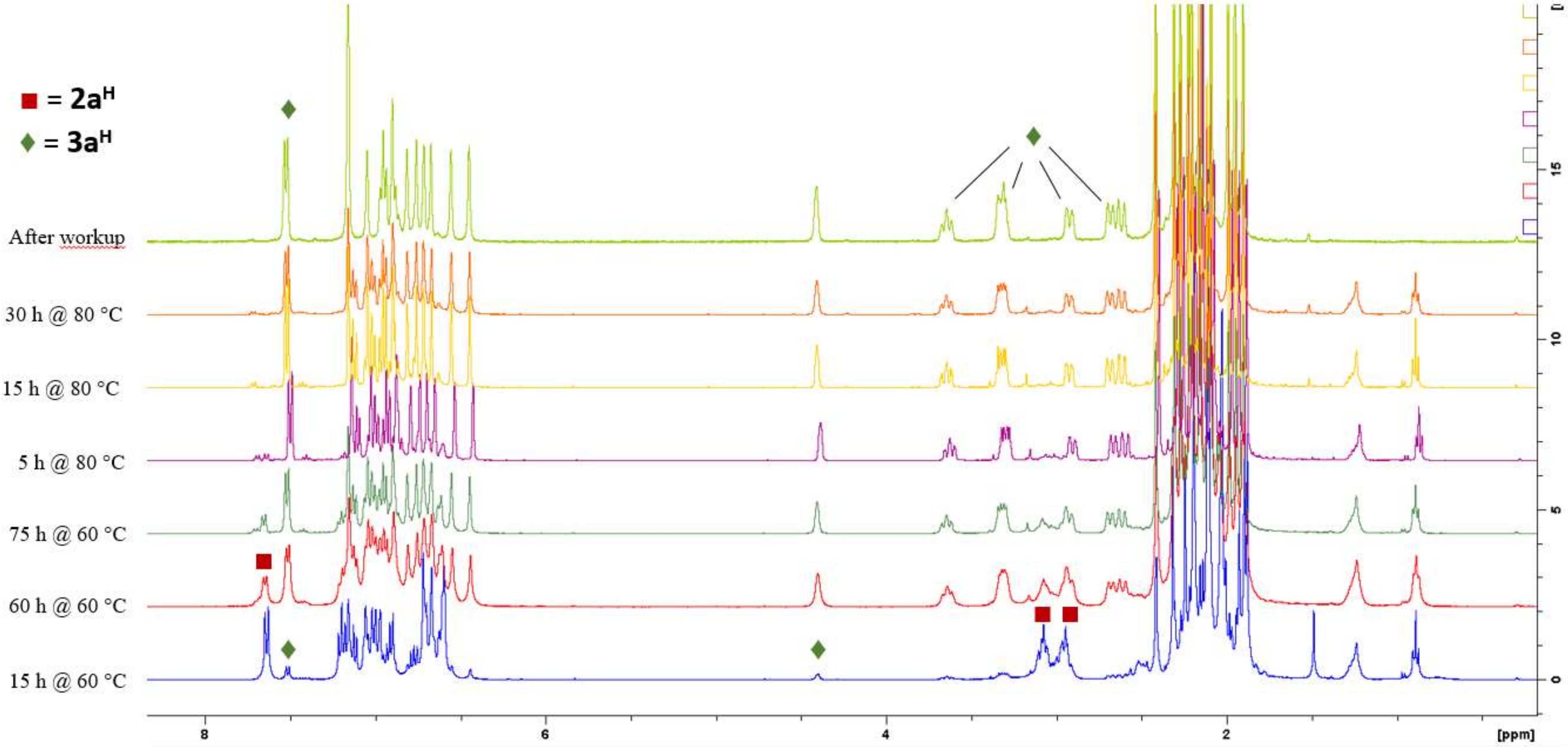


Figure S35. Stack-plot of ^{1}H NMR spectra of the reaction of **1a** with phenylazide, showing the intermediate formation of **2a$^{\mathbf{H}}$** (■) and its rearrangement to **3a$^{\mathbf{H}}$** (♦).

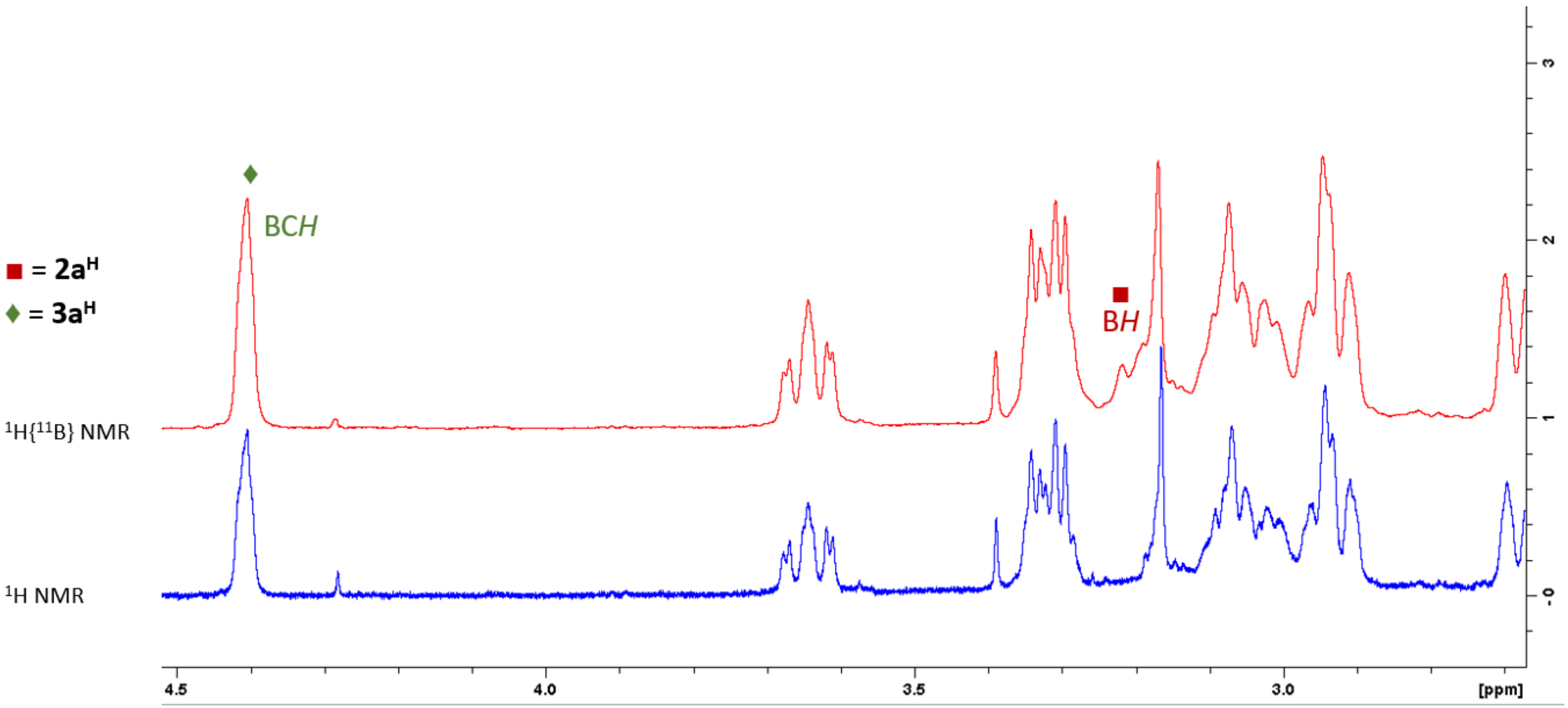


Figure S36. Stack-plot of the ^{1}H and ^{1}H{^{11}B} NMR spectra of the reaction of **1a** with phenylazide after 60 h at 60 °C, revealing the position of the B*H* resonance of the intermediate **2a$^{\mathbf{H}}$** (■).

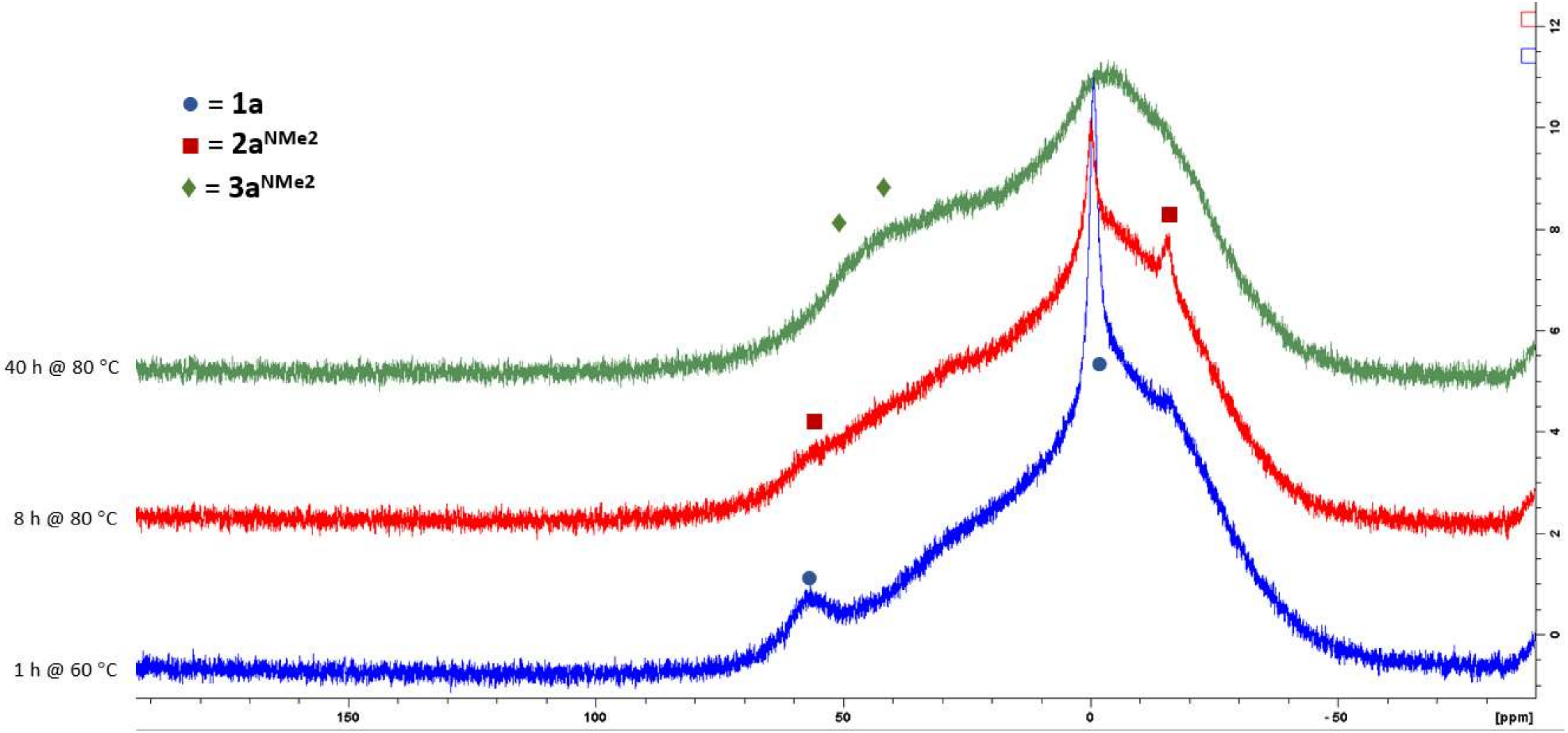


Figure S37. Stack-plot of ^{11}B NMR spectra of the reaction of **1a** (●) with *p*-dimethylaminophenylazide, showing the intermediate formation of **2a**$^{\mathbf{NMe2}}$ (■) and its rearrangement to **3a**$^{\mathbf{NMe2}}$ (♦).

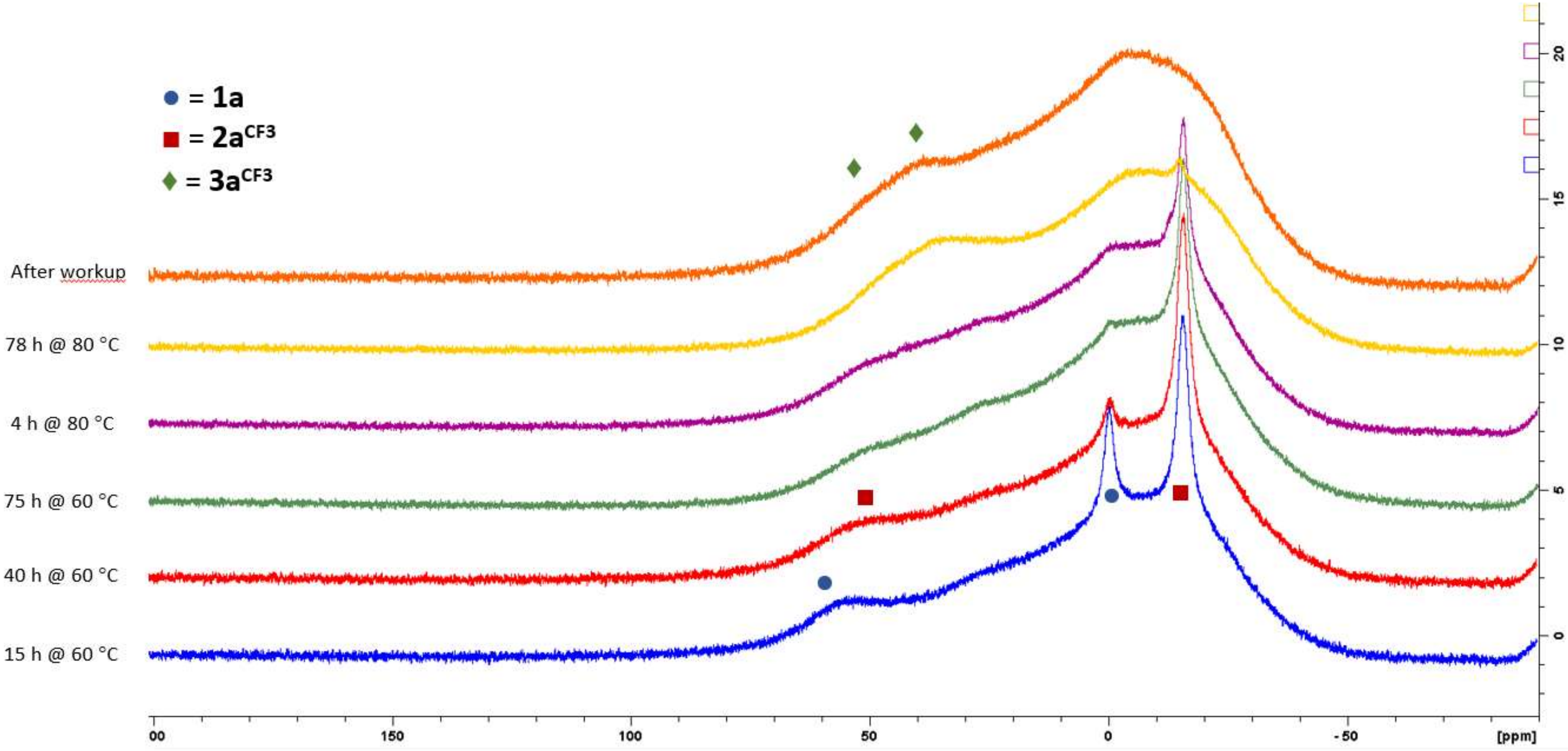


Figure S38. Stack-plot of ^{11}B NMR spectra of the reaction of **1a** (●) with *p*-trifluoromethylphenylazide, showing the intermediate formation of **2a**$^{\mathbf{CF3}}$ (■) and its rearrangement to **3a**$^{\mathbf{CF3}}$ (♦).

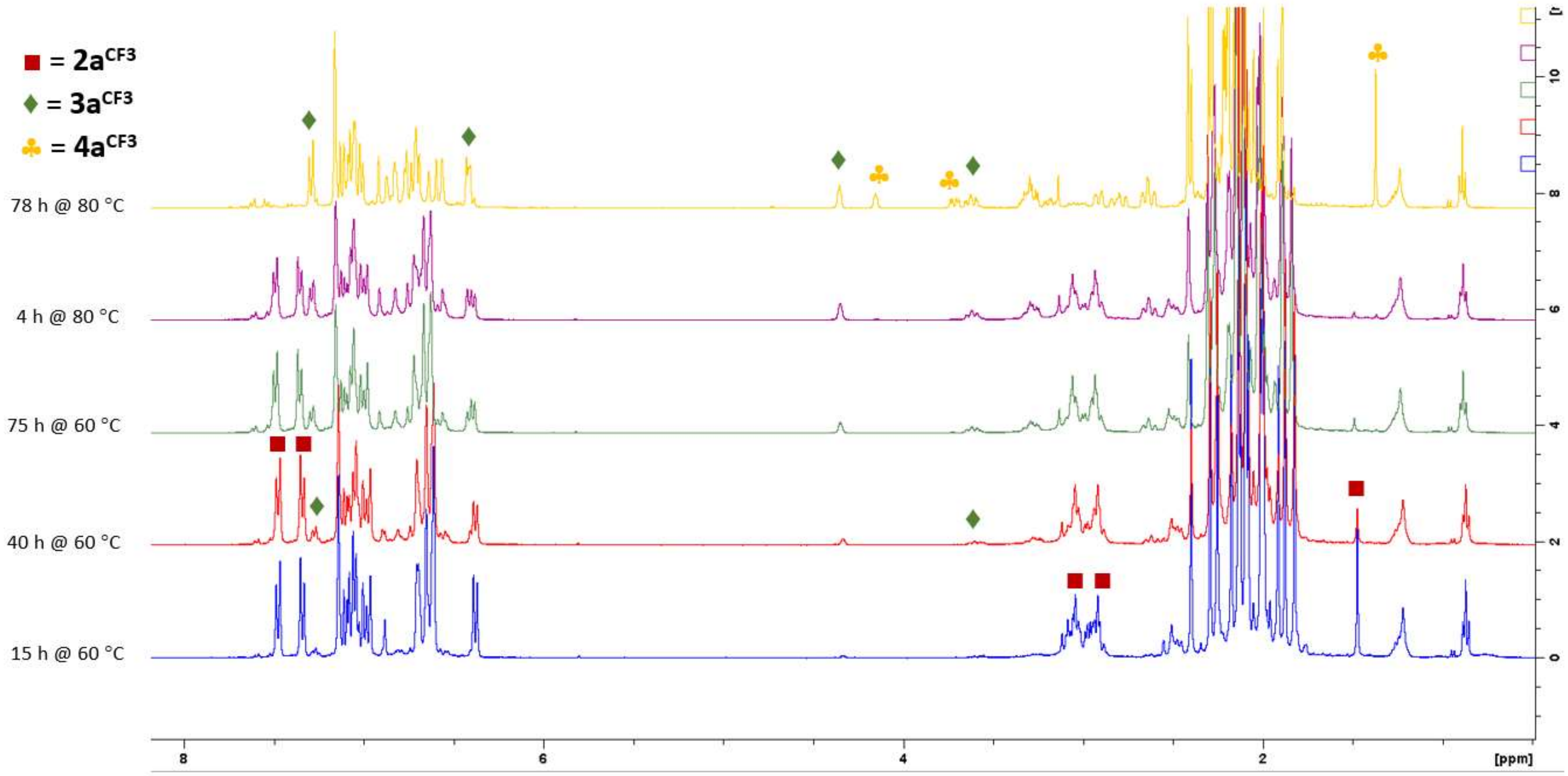


Figure S39. Stack-plot of ^{1}H NMR spectra of the reaction of **1a** with *p*-trifluoromethylphenylazide, showing the intermediate formation of **2a**$^{\mathbf{CF3}}$ (■) and its rearrangement to **3a**$^{\mathbf{CF3}}$ (♦) and ultimately its decomposition to **4a**$^{\mathbf{CF3}}$ (♣).

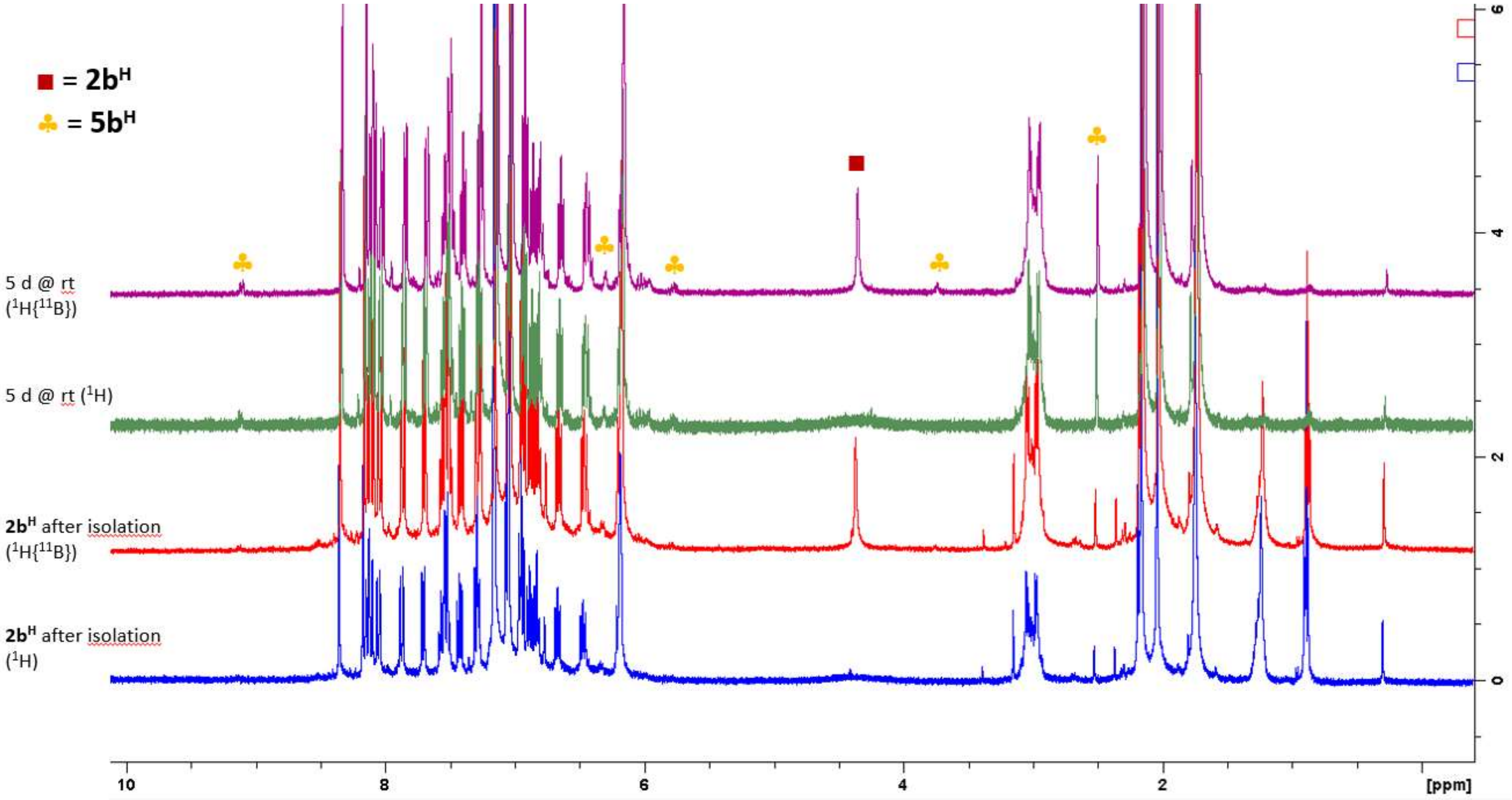


Figure S40. Stack-plot of ^{1}H and ^{1}H{^{11}B} NMR spectra of the very slow rt decomposition of **2b$^{\mathbf{H}}$** (■) into **5b$^{\mathbf{H}}$** (♣).

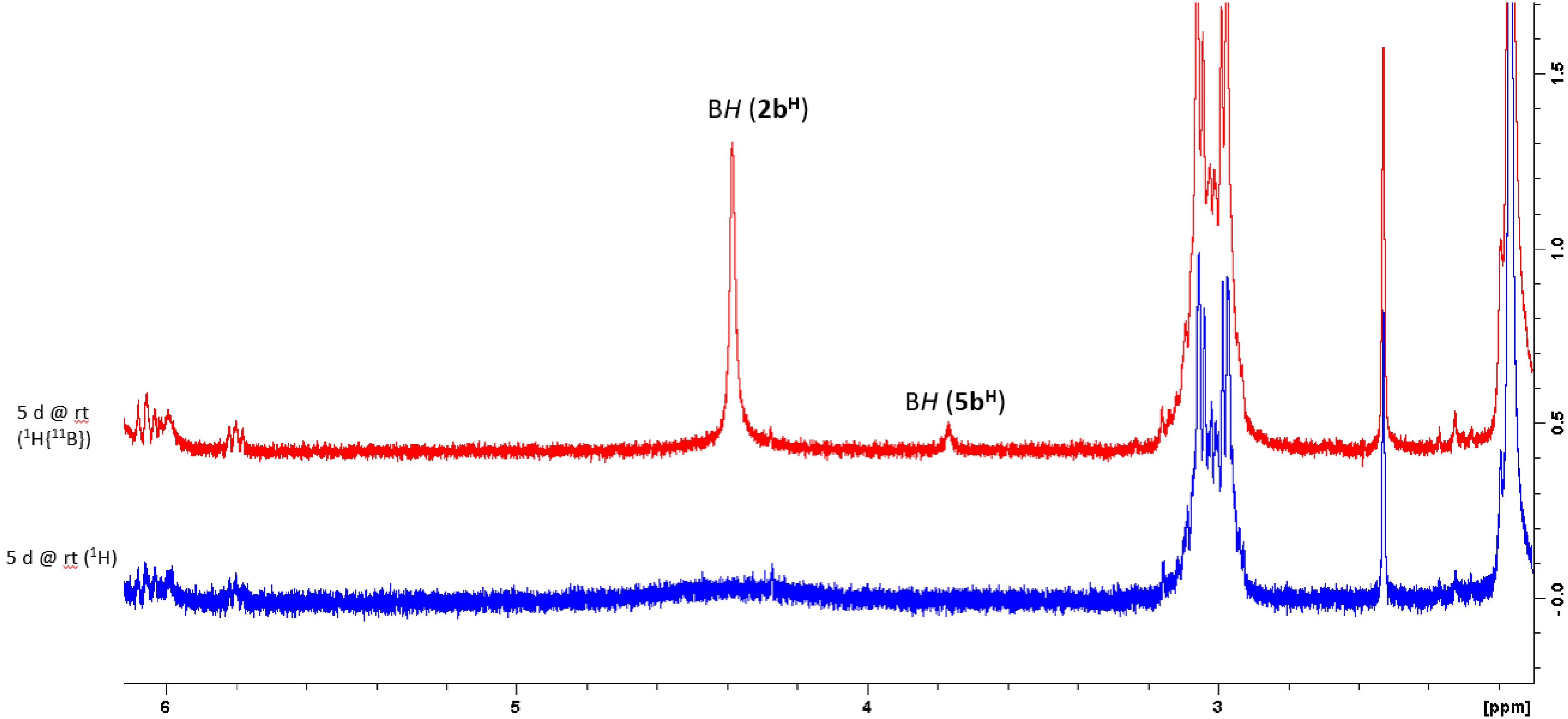


Figure S41. ^{1}H and ^{1}H{^{11}B} NMR spectrum between 2 and 6 ppm of the decomposition of **2b$^\mathbf{H}$** into **5b$^\mathbf{H}$** after 5 days at rt, showing the B*H* resonances.

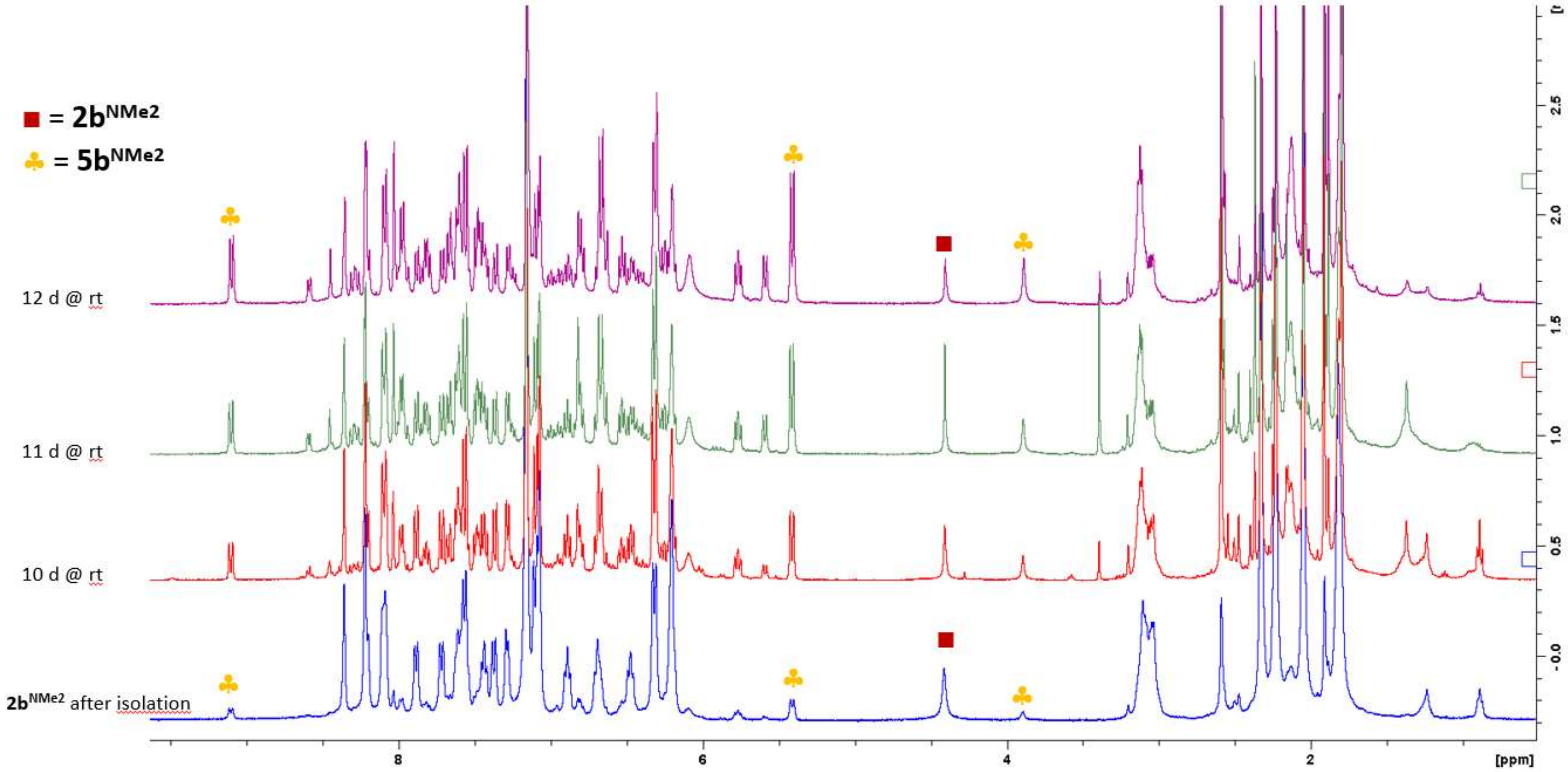


Figure S42. Stack-plot of $^{1}H\{^{11}B\}$ NMR spectra of the very slow rt decomposition of **2b**$^{\mathbf{NMe2}}$ (■) into **5b**$^{\mathbf{NMe2}}$ (♣).

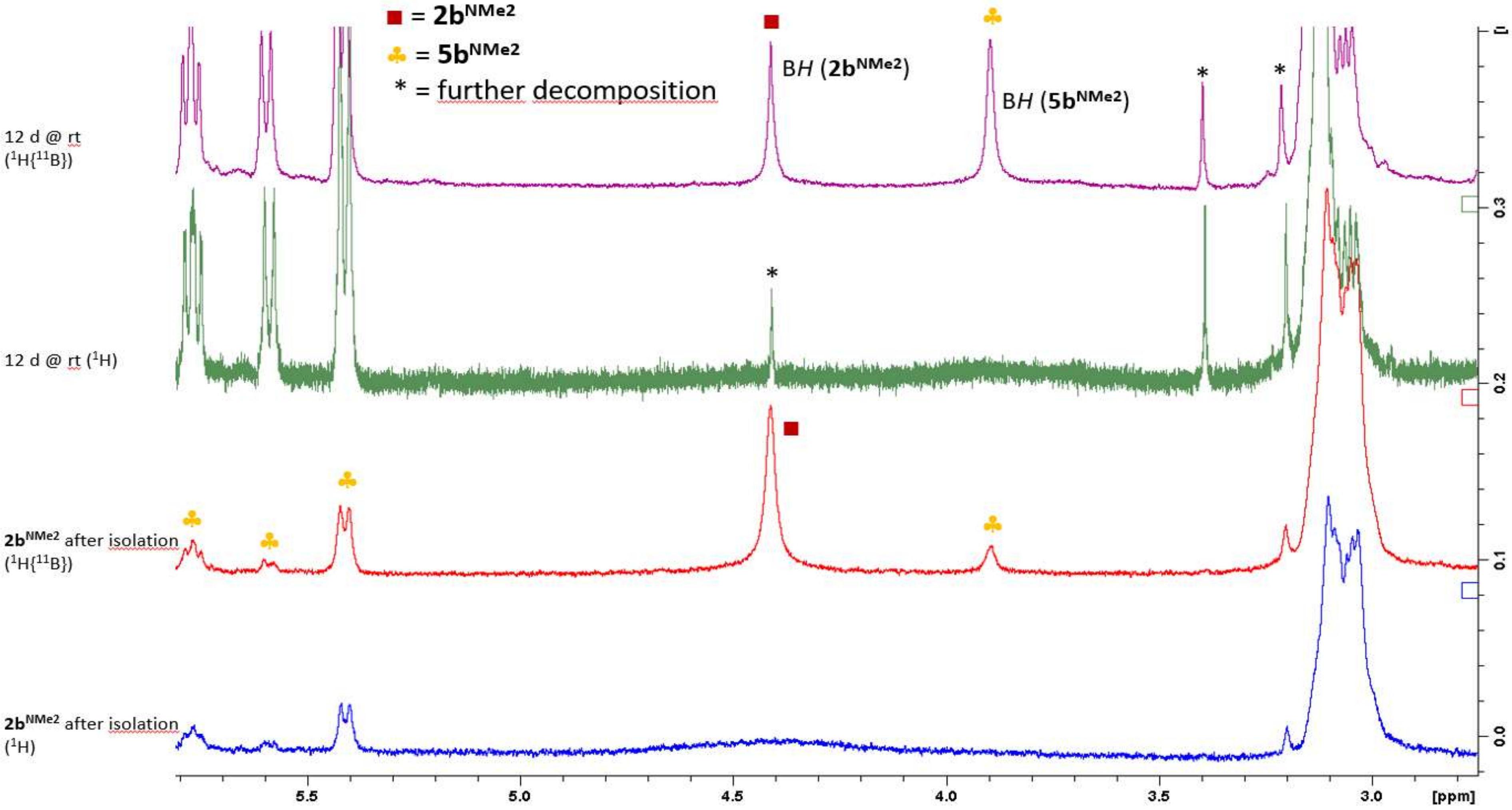


Figure S43. Stack-plot of ^{1}H and ^{1}H{^{11}B} NMR spectra between 3 and 6 ppm of the very slow rt decomposition of **2b^{NMe2}** (■) into **5b^{NMe2}** (♣), showing the B*H* resonances and indications of further decomposition.

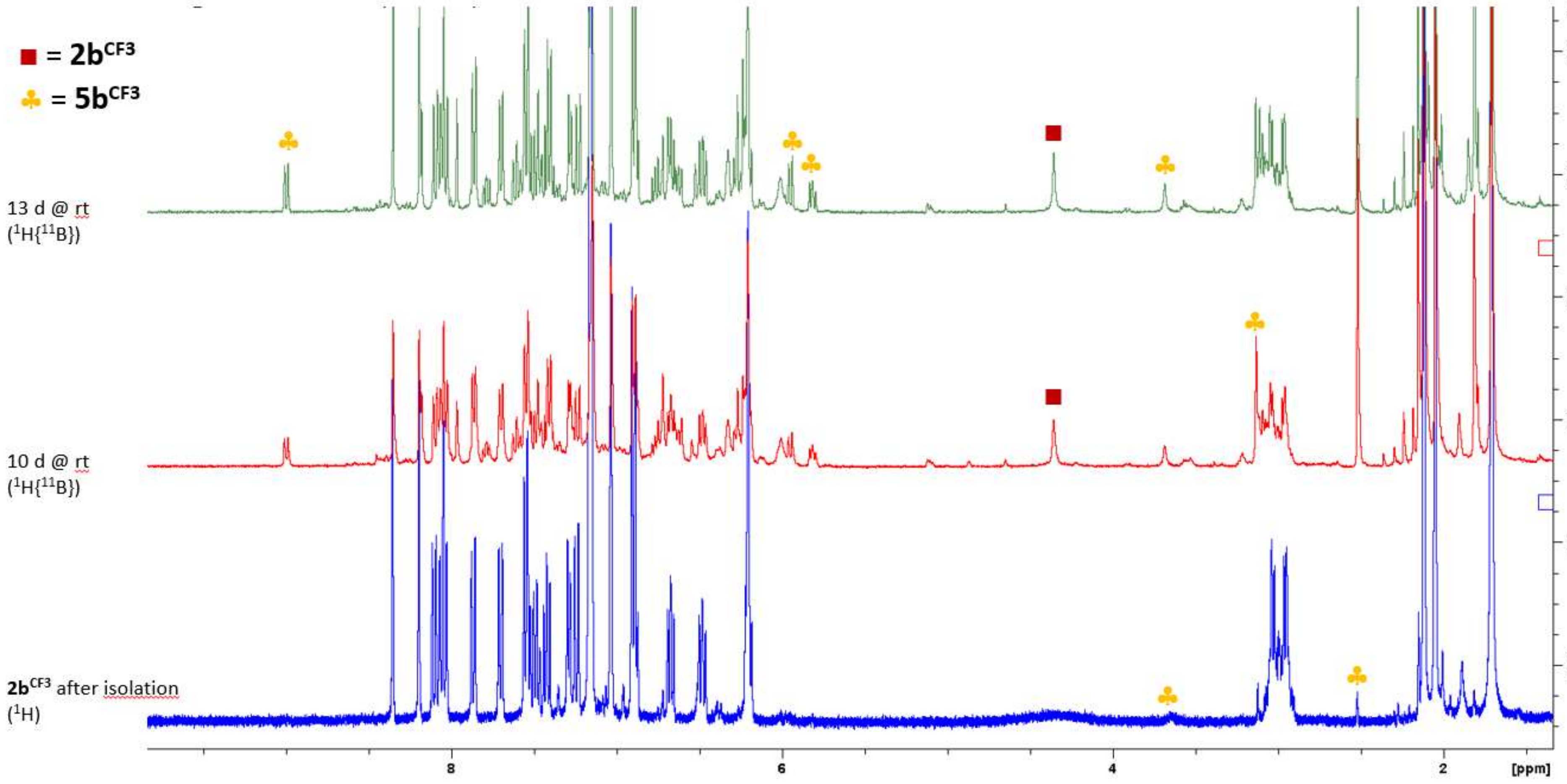


Figure S44. Stack-plot of ^{1}H{^{11}B} NMR spectra of the very slow rt decomposition of **2b^{CF3}** (■) into **5b^{CF3}** (♣).

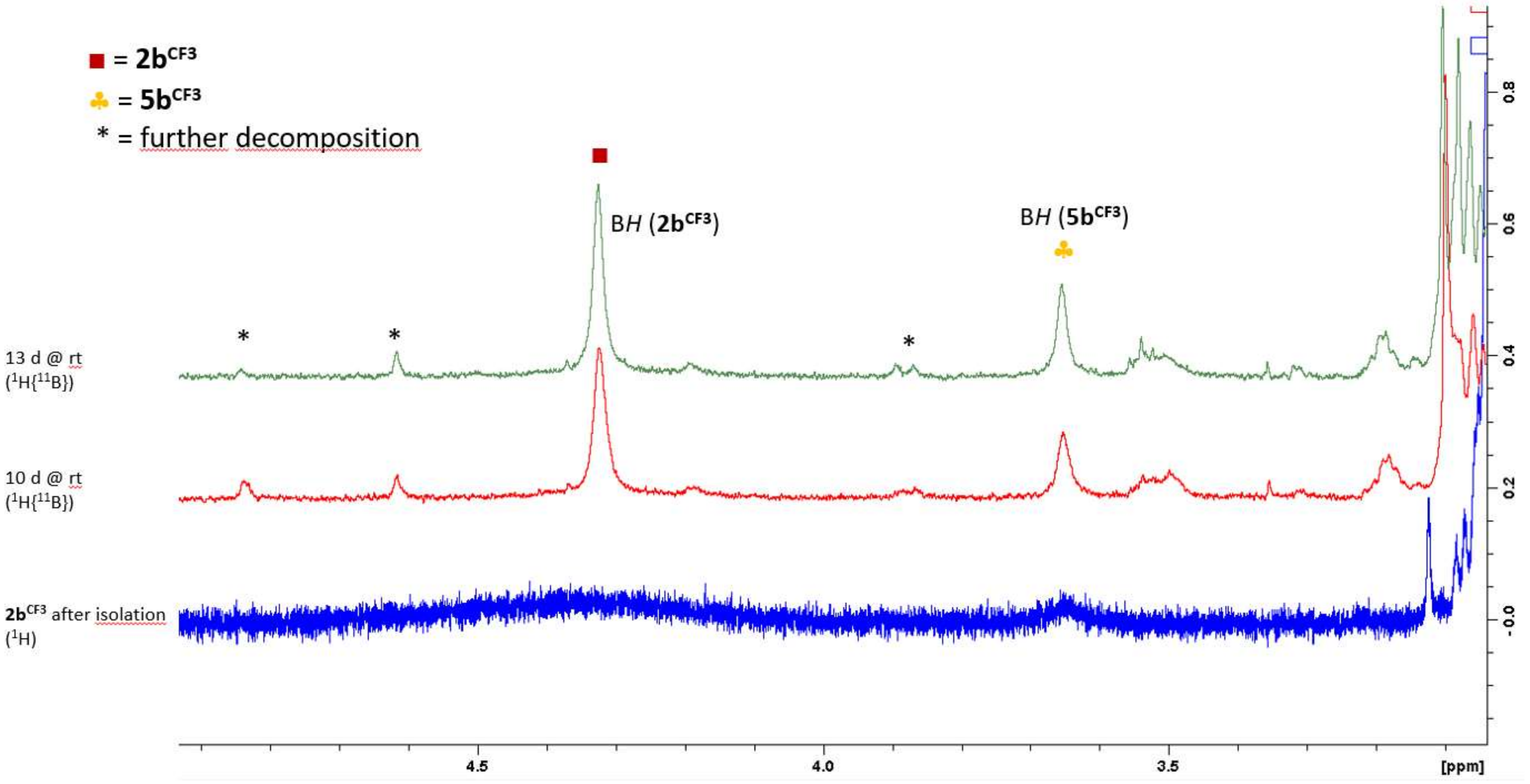


Figure S45. Stack-plot of ^{1}H and ^{1}H{^{11}B} NMR spectra between 3 and 5 ppm of the very slow rt decomposition of **2b**$^{\mathbf{CF3}}$ (■) into **5b**$^{\mathbf{CF3}}$ (♣), showing the B*H* resonances and indications of further decomposition.

UV/Vis spectroscopy

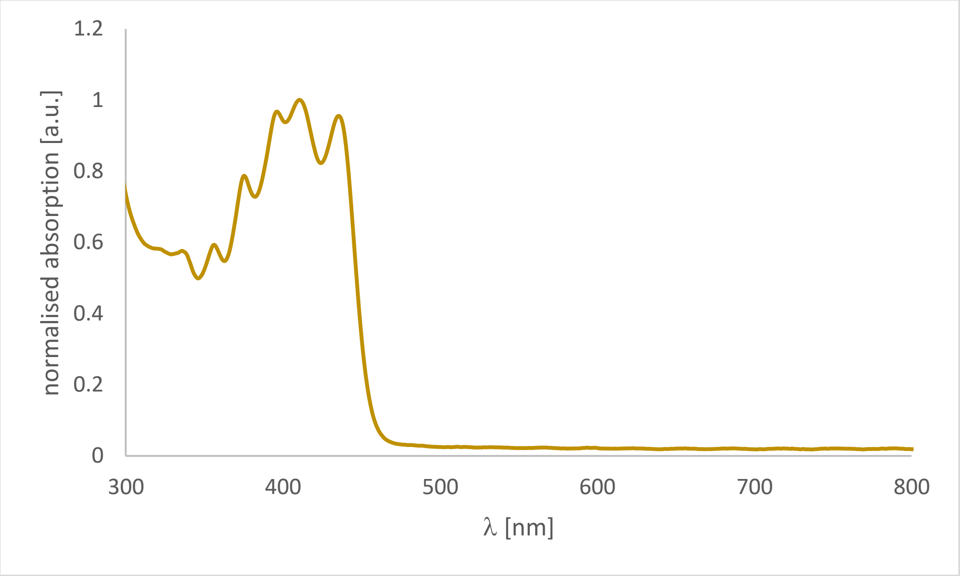


Figure S46. UV/Vis absorption spectrum of **2b**$^{\mathbf{H}}$ in benzene at rt. Wavelengths (nm) of absorption maxima: 336, 356, 375, 396, 411, 435.

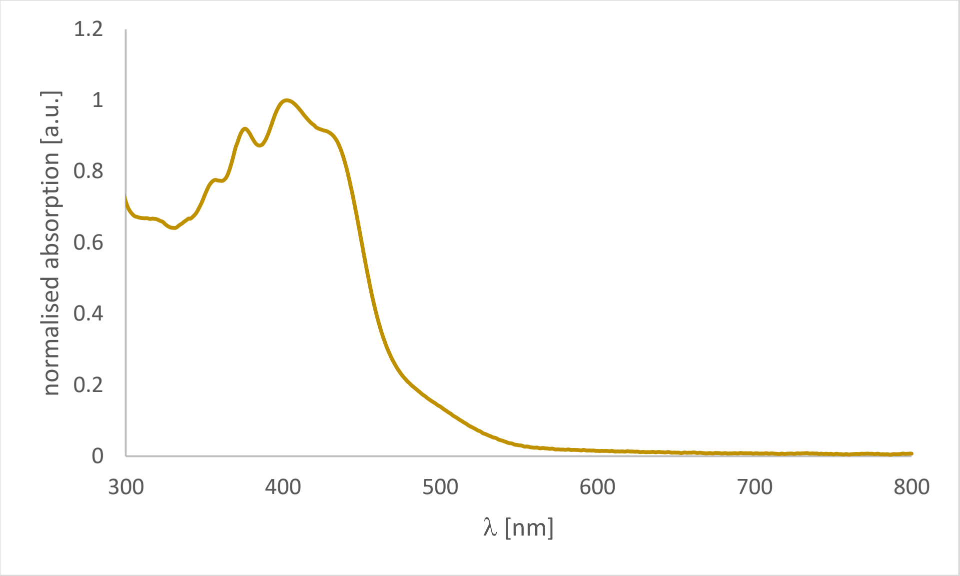


Figure S47. UV/Vis absorption spectrum of **2b**$^{\mathbf{NMe2}}$ in benzene at rt. Wavelengths (nm) of absorption maxima: 357, 376, 402, 431.

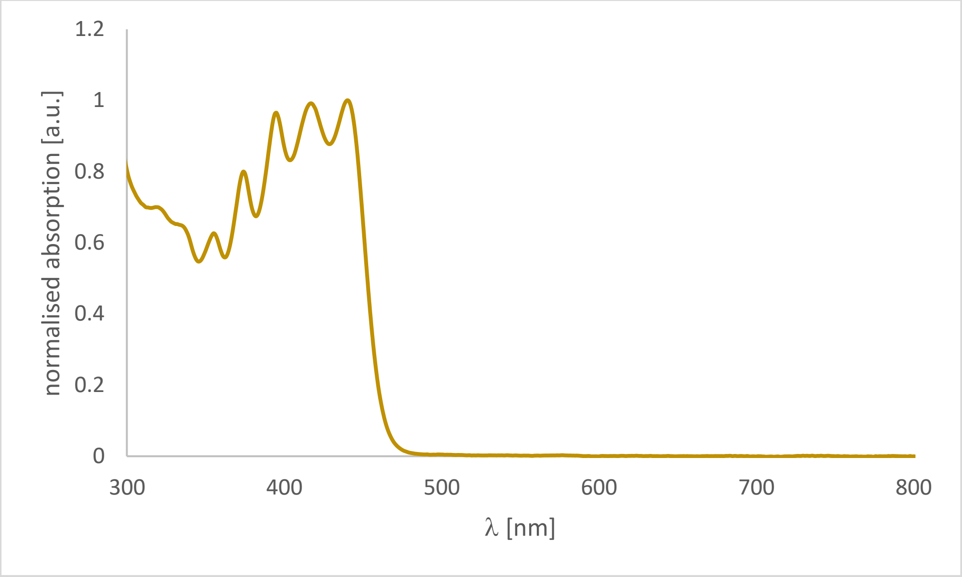


Figure S48. UV/Vis absorption spectrum of $\mathbf{2b}^{\mathbf{CF3}}$ in benzene at rt. Wavelengths (nm) of absorption maxima: 335, 355, 374, 395, 417, 440.

IR spectroscopy

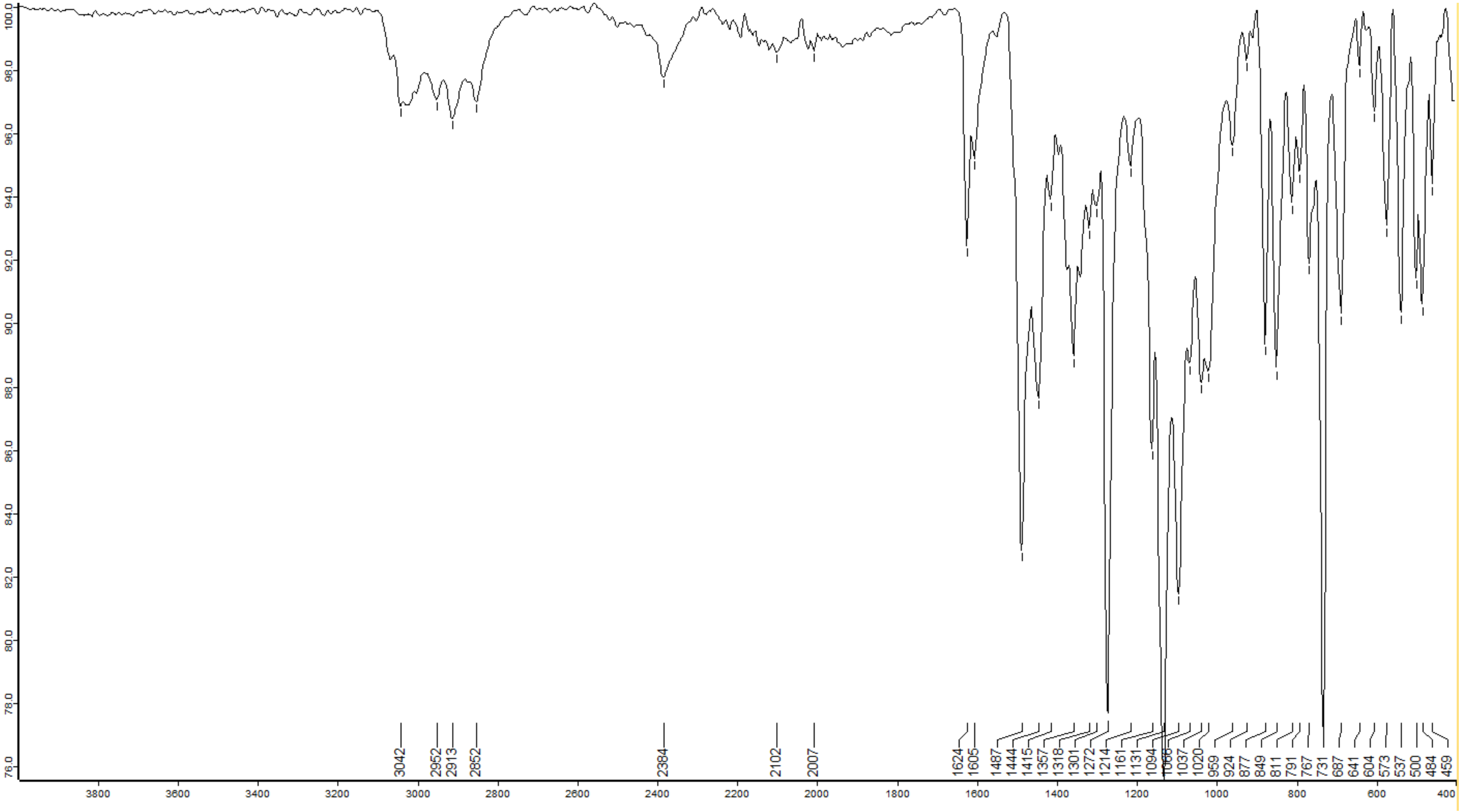


Figure S49. Solid-state IR spectrum of **2b$^{\mathbf{H}}$**.

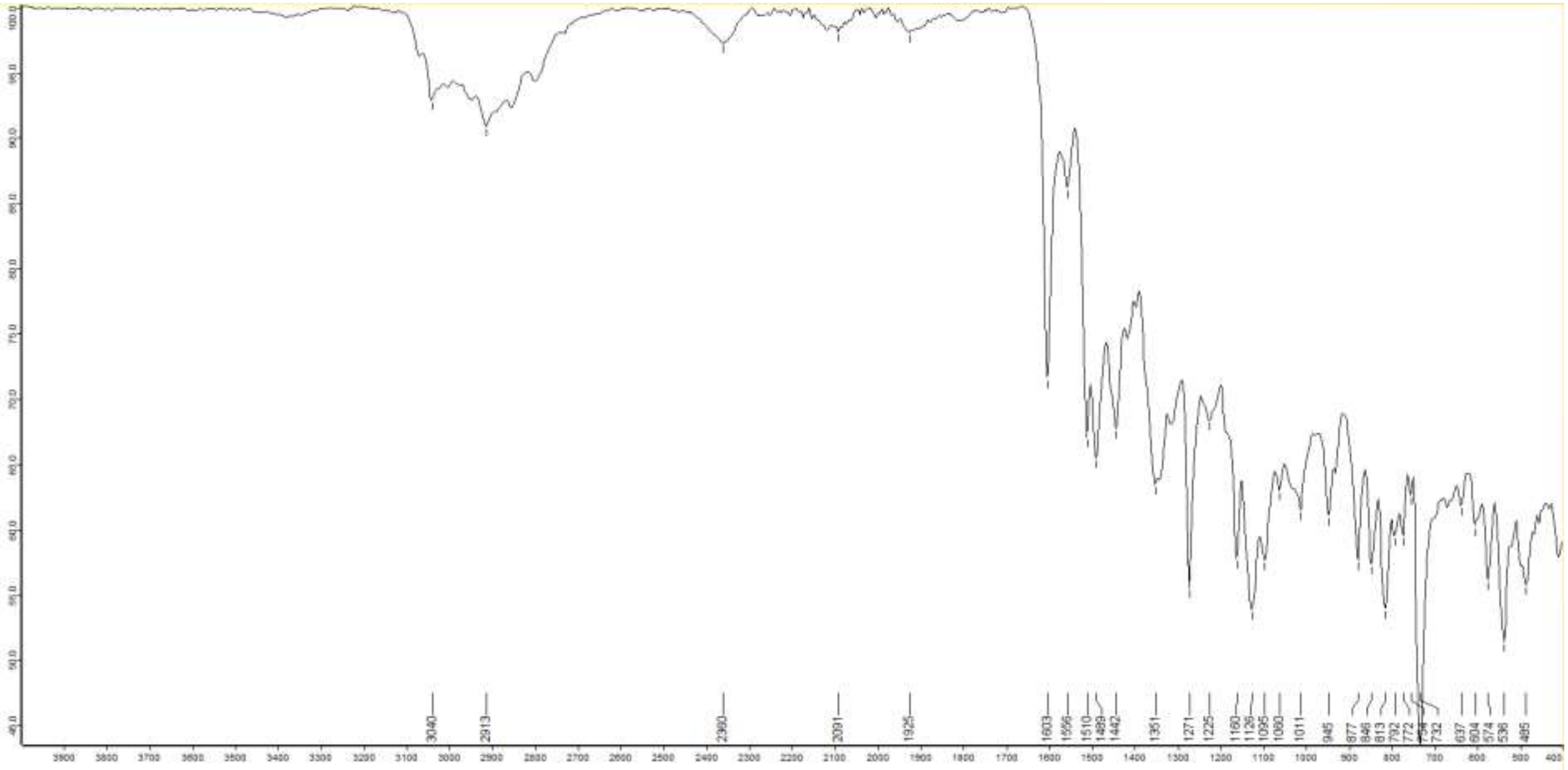


Figure S50. Solid-state IR spectrum of $\mathbf{2b}^{\mathbf{NMe2}}$.

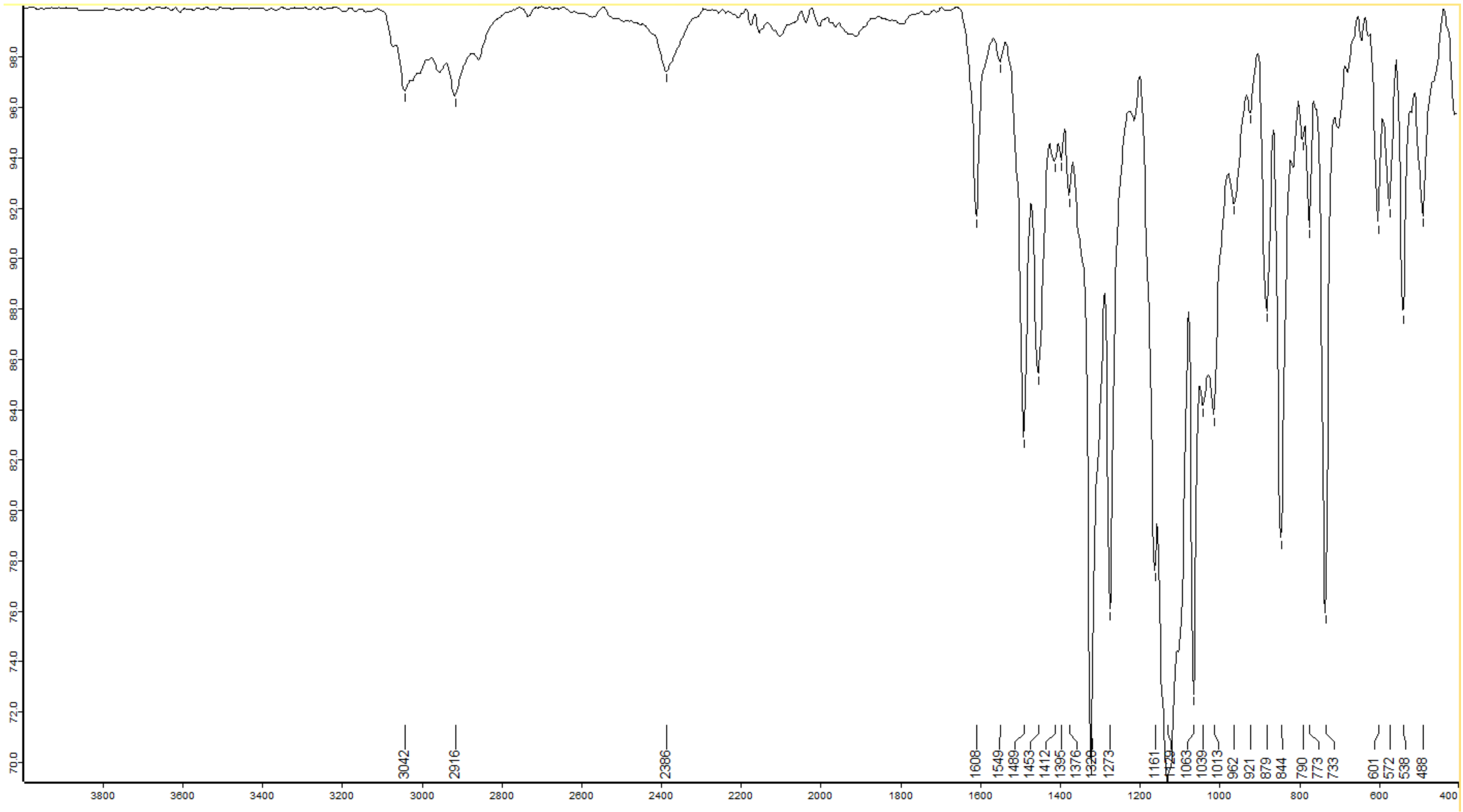


Figure S51. Solid-state IR spectrum of **2b$^{\mathbf{CF3}}$**.

X-ray crystallographic details

The crystal data of **3a**$^{\mathbf{H}}$ and **4a**$^{\mathbf{NMe2}}$ were collected on a BRUKER D8 QUEST diffractometer with a CCD-area or a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **2b**$^{\mathbf{H}}$ and **3a**$^{\mathbf{NMe2}}$ were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **3a**$^{\mathbf{CF3}}$, **2b**$^{\mathbf{CF3}}$, **4a**$^{\mathbf{H}}$ and **4a**$^{\mathbf{CF3}}$ were collected on a *XtaLAB Synergy* diffractometer with a Hybrid Pixel Array detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation.

The structures were solved using the intrinsic phasing method,[6] refined with the SHELXL program,[7] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All Hydrogen atoms except those attached to boron were assigned to idealised positions. The coordinates of the latter were refined freely.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1993145-1993152. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Refinement details for 2b$^{\mathbf{H}}$**:** The asymmetric unit contains two benzene molecules located close to each other, each with an occupation factor of 88% and modelled as twofold disordered in a 56:32 ratio, as well as a hexane molecules with an occupation factor of 12% spanning the two sites. The benzene rings were modelled with AFIX 66 and the 1,2- and 1,3-distances in the hexane molecule restrained to 1.53 and 2.55 Angstrom, respectively, with DFIX. All ADPs within these disordered solvents were restrained with SIMU 0.003. The asymmetric unit also contains two crystallographically distinct molecules of **2b**$^{\mathbf{H}}$, one of which displays a twofold disorder in one of the Mes groups (RESI 12 and 13 Mes, atoms C13 > C21) in a 55:45 ratio. 1,2- and 1,3-distances within the 2 parts of the disorder were restrained to similarity using SAME C13 > C21 and ADPs were restrained with SIMU 0.002.

Crystal data for 2b$^{\mathbf{H}}$: $C_{55}H_{49}B_2N_5$, 0.878 (C_6H_6), 0.061 (C_6H_{14}), $M_r = 879.72$, yellow block, 0.181×0.178×0.111 mm^3, Triclinic space group $P\,\bar{1}$, $a = 16.155(4)$ Å, $b = 17.629(3)$ Å,

c = 18.200(4) Å, α = 76.749(8)°, β = 76.424(9)°, γ = 74.29(2)°, V = 4773.7(18) Å^3, Z = 4, ρ_{calcd} = 1.224 g·cm^{-3}, μ = 0.071 mm^{-1}, F(000) = 1864, T = 100 K, R_1 = 0.0867, wR^2 = 0.1416, 18816 independent reflections [2θ≤52.044°] and 1386 parameters.

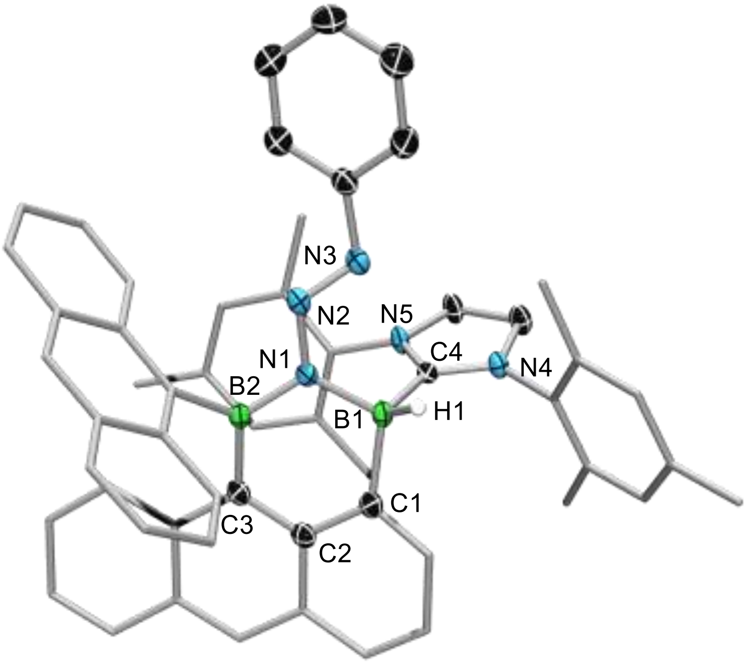


Figure S52. Crystallographically-derived molecular structures of **2b$^{\mathbf{H}}$** (only one of the two crystallographically distinct molecules of **2b$^{\mathbf{H}}$** present in the asymmetric unit shown). Thermal ellipsoids at 50% probability. Thermal ellipsoids of ligand periphery and hydrogen atoms omitted for clarity, except for H1. Selected bond lengths (Å) and angles (°): B1-H1 1.120(19), B1-N1 1.557(3), B2-N1 1.417(3), N1-N2 1.382(2), N2-N3 1.258(2), B1-C4 1.645(3), $\Sigma\angle_{B2}$ 359.31(17), torsion angles B1-N1-N2-N3 13.4(2), B2-N1-N2-N3 –177.94(15).

Refinement details for 2b$^{\mathbf{CF3}}$: The unit cell contains five benzene molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions using the Platon program SQUEEZE.[8]

Crystal data for 2b$^{\mathbf{CF3}}$: 2 ($C_{56}H_{51}B_2F_3N_5$), C_6H_6 [+ squeezed solvent], M_r = 1817.33, yellow plate, 0.138×0.101×0.068 mm^3, monoclinic space group P 2_1/n, a = 20.8855(2) Å, b = 17.84136(11) Å, c = 29.1284(3) Å, β = 109.8873(11)°, V = 10206.70(16) Å^3, Z = 4, ρ_{calcd} = 1.183 g·cm^{-3}, μ = 0.610 mm^{-1}, F(000) = 3816, T = 100(2) K, R_1 = 0.0769, wR^2 = 0.1569, 20046 independent reflections [2θ≤144.254°] and 1264 parameters.

Crystal data for 3a^{H}: $C_{45}H_{53}B_2N_5$, M_r = 685.54, yellow block, 0.373×0.195×0.15 mm^3, triclinic space group $P\bar{1}$, a = 10.776(4) Å, b = 12.867(4) Å, c = 15.077(4) Å, α = 99.007(10)°, β = 108.967(15)°, γ = 90.735(9)°, V = 1948.1(10) Å^3, Z = 2, ρ_{calcd} = 1.169 g·cm^{-3}, μ = 0.068 mm^{-1}, F(000) = 736, T = 100(2) K, R_1 = 0.0785, wR^2 = 0.1449, 7667 independent reflections [$2\theta \leq 52.042°$] and 480 parameters.

Refinement details for 3a^{NMe2}: The asymmetric unit contains a benzene molecule which was modelled as threefold disordered, using three FVAR summed up to 1.0 and refined to a 29:33:38 ratio. The rings were modelled with AFIX 66 and ADPs restrained with SIMU 0.003.

Crystal data for 3a^{NMe2}: $C_{47}H_{58}B_2N_6$, C_6H_6, M_r = 806.72, yellow block, 0.202×0.149×0.105 mm^3, Triclinic space group $P\bar{1}$, a = 13.097(5) Å, b = 14.799(7) Å, c = 14.975(5) Å, α = 63.842(16)°, β = 85.29(2)°, γ = 64.034(18)°, V = 2319.9(17) Å^3, Z = 2, ρ_{calcd} = 1.155 g·cm^{-3}, μ = 0.067 mm^{-1}, F(000) = 868, T = 100 K, R_1 = 0.0678, wR^2 = 0.1258, 9500 independent reflections [$2\theta \leq 52.744°$] and 638 parameters.

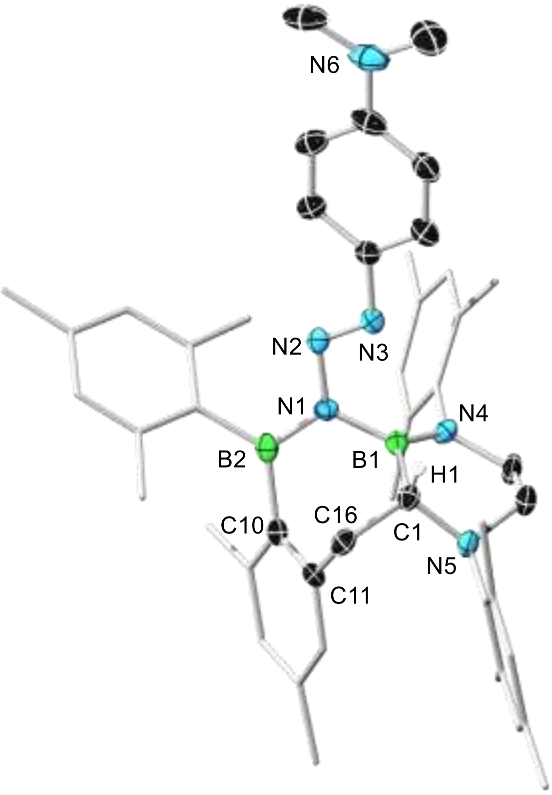


Figure S53. Crystallographically-derived molecular structures of **3a^{NMe2}**. Thermal ellipsoids at 50% probability. Thermal ellipsoids of ligand periphery and hydrogen atoms omitted for clarity, except for H1. Selected bond lengths (Å) and angles (°): B1-N1 1.506(2), B2-N1 1.416(2), N1-N2 1.3867(17), N2-N3 1.2548(18), B1-N4 1.387(2), B1-C1 1.569(2), C1-N5

1.4623(18), C1-C16 1.534(2), $\Sigma\angle_{B1}$ 359.75(13), $\Sigma\angle_{B2}$ 359.97(14), torsion angles B1-N1-N2-N3 3.70(16), B2-N1-N2-N3 –165.65(12).

Refinement details for 3a$^{\mathbf{CF3}}$: The asymmetric unit contains **3a$^{\mathbf{CF3}}$** and **4a$^{\mathbf{CF3}}$** overlapping, with all atoms in common except the N_2Ph^{CF3} (RESI AZI) / Ph^{CF3} (RESI ANIL) moieties. The two parts were refined to a 93:7 ratio. The phenyl rings in each were modelled with AFIX 66 and all ADPs within these two parts were restrained with SIMU 0.005.

Crystal data for 3a$^{\mathbf{CF3}}$: 0.93 ($C_{46}H_{52}B_2F_3N_5$), 0.7 ($C_{46}H_{52}B_2F_3N_3$), C_6H_6, $M_r = 829.78$, yellow block, 0.276×0.193×0.083 mm^3, triclinic space group $P\ \bar{1}$, $a = 10.5695(2)$ Å, $b = 15.3466(3)$ Å, $c = 16.2221(3)$ Å, $\alpha = 65.195(2)°$, $\beta = 87.805(2)°$, $\gamma = 72.0887(19)°$, $V = 2260.22(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.222$ g·cm^{-3}, $\mu = 0.633$ mm^{-1}, $F(000) = 884$, $T = 100(2)$ K, $R_1 = 0.0555$, $wR^2 = 0.1452$, 8844 independent reflections [$2\theta \leq 144.254°$] and 637 parameters.

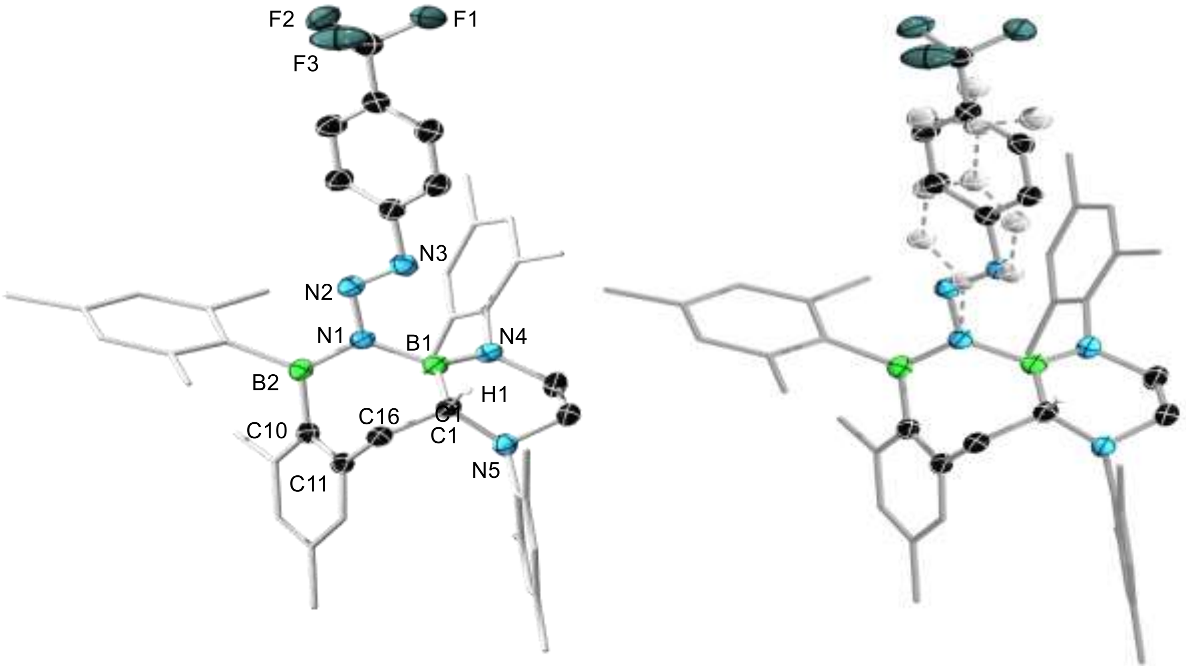


Figure S54. Crystallographically-derived molecular structures of **3a$^{\mathbf{CF3}}$** (left) and overlay of the two molecules of **3a$^{\mathbf{CF3}}$** and **4a$^{\mathbf{CF3}}$** (p-$CF_3C_6H_4$ group in light grey and dashed bonds) overlapping in a 93:7 ratio in the asymmetric unit. Thermal ellipsoids at 50% probability. Thermal ellipsoids of ligand periphery and hydrogen atoms omitted for clarity, except for H1. Selected bond lengths (Å) and angles (°): B1-N1 1.512(2), B2-N1 1.432(2), N1-N2 1.3736(19), N2-N3 1.2548(18), B1-N4 1.385(2), B1-C1 1.579(2), C1-N5 1.4717(18), C1-C16 1.530(2), $\Sigma\angle_{B1}$ 359.93(13), $\Sigma\angle_{B2}$ 359.90(13), torsion angles B1-N1-N2-N3 –9.8(2), B2-N1-N2-N3 –169.4(2).

Crystal data for 4a^H: $C_{45}H_{53}B_2N_3$, M_r = 657.52, colourless plate, 0.300×0.107×0.025 mm^3, triclinic space group $P\bar{1}$, a = 10.4340(3) Å, b = 12.8967(5) Å, c = 15.2156(5) Å, α = 71.824(3)°, β = 84.929(2)°, γ = 86.835(3)°, V = 1936.87(11) Å^3, Z = 2, ρ_{calcd} = 1.127 g·cm^{-3}, μ = 0.483 mm^{-1}, F(000) = 708.000, T = 100.01(10)K, R_1 = 0.0542, wR^2 = 0.1346, 8114 independent reflections [$2\theta \leq 155.716°$] and 462 parameters.

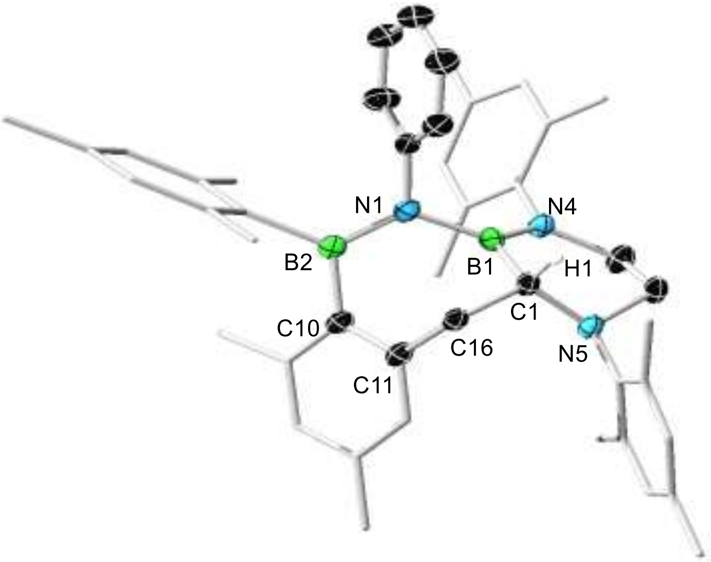


Figure S55. Crystallographically-derived molecular structures of **4a^H**. Thermal ellipsoids at 50% probability. Thermal ellipsoids of ligand periphery and hydrogen atoms omitted for clarity, except for H1. Selected bond lengths (Å) and angles (°): B1-N1 1.4949(17), B2-N1 1.4184(18), B1-N4 1.3949(18), B1-C1 1.5829(19), C1-N5 1.4694(16), C1-C16 1.5296(17), $\Sigma\angle_{B1}$ 359.97(11), $\Sigma\angle_{B2}$ 359.75(11).

Crystal data for 4a^{NMe2}: $C_{47}H_{58}B_2N_4$, M_r = 700.59, yellow block, 0.432×0.38×0.185 mm^3, Triclinic space group $P\bar{1}$, a = 8.538(2) Å, b = 11.120(3) Å, c = 21.468(6) Å, α = 98.920(10)°, β = 91.290(16)°, γ = 96.808(12)°, V = 1997.6(9) Å^3, Z = 2, ρ_{calcd} = 1.165 g·cm^{-3}, m = 0.067 mm^{-1}, F(000) = 756, T = 100(2) K, R_1 = 0.0641, wR^2 = 0.1349, 7886 independent reflections [$2\theta \leq 52.044°$] and 491 parameters.

Crystal data for 4a^{CF3}: $C_{46}H_{52}B_2F_3N_3$, M_r = 725.52, yellow block, 0.189×0.149×0.120 mm^3, triclinic space group $P\bar{1}$, a = 8.36154(12) Å, b = 13.32837(19) Å, c = 18.5663(2) Å, α = 74.6571(12)°, β = 78.6214(12)°, γ = 85.0559(11)°, V = 1954.91(5) Å^3, Z = 2, ρ_{calcd} = 1.233 g·cm^{-3}, μ = 0.641 mm^{-1}, F(000) = 772.000, T = 100.00(10) K, R_1 = 0.0400, wR^2 = 0.1017, 7701 independent reflections [$2\theta \leq 144.25°$] and 498 parameters.

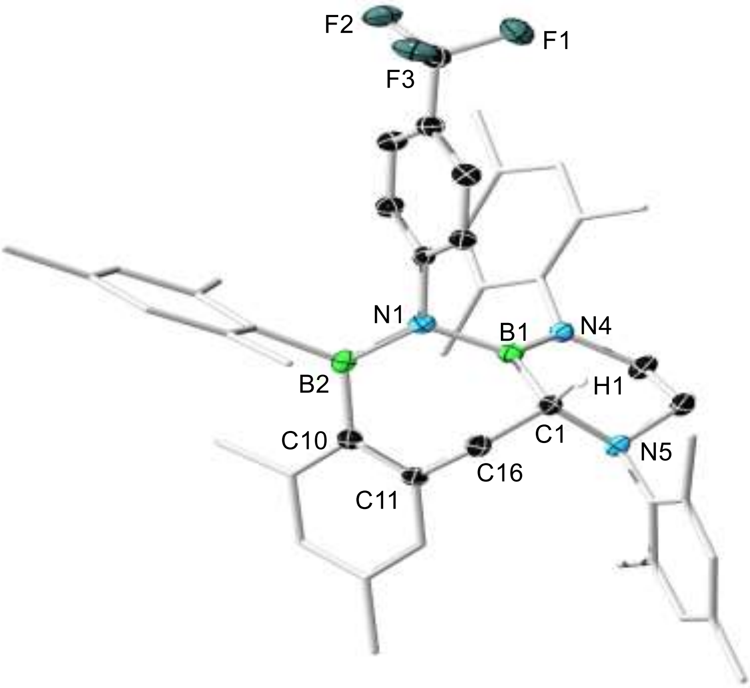


Figure S56. Crystallographically-derived molecular structures of **$4a^{CF3}$**. Thermal ellipsoids at 50% probability. Thermal ellipsoids of ligand periphery and hydrogen atoms omitted for clarity, except for H1. Selected bond lengths (Å) and angles (°): B1-N1 1.4999(15), B2-N1 1.4222(16), B1-N4 1.3953(16), B1-C1 1.5839(16), C1-N5 1.4684(14), C1-C16 1.5261(15), $\Sigma\angle_{B1}$ 359.77(10), $\Sigma\angle_{B2}$ 359.70(10).

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