Electronic Supplementary Material (ESI) for ChemComm.

$B(C_6F_5)_3$- and $HB(C_6F_5)_2$-Mediated Transformations of Isothiocyanates

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General Considerations

All reactions were carried out under an inert atmosphere of argon or nitrogen with rigorous exclusion of oxygen and moisture using standard glovebox and Schlenk techniques unless stated otherwise. The glass equipment was stored in an oven at 120 °C and evacuated prior to use. Solvents were distilled over Na/K alloy and benzophenone or CaH_2 under nitrogen atmosphere. Solid materials were stored and weighted in a glove box or dried under high vacuum prior to use. The isothiocyanates **1a**-**c** were commercially available and were stored under inert atmosphere. In this context, solid **1b** has been used as received and liquid **1a,c** have been freeze-pump-thaw degassed three times prior to use. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1a-c** were recorded in C_6D_6 for reasons of comparison (Figures S4-S9). Piers' borane ($HB(C_6F_5)_2$) was synthesized according to literature procedures.[S1-S3] $B(C_6F_5)_3$ was synthesized by a modified literature procedure.[S4]

NMR spectra were recorded on a Bruker Avance 300, Bruker Avance 500, and Bruker Avance III 500 spectrometer. ^{1}H NMR spectra were referenced to the residual solvent resonance as internal standard (benzene-d_6 (C_6D_6): $\delta^{1}H(C_6D_5H)$ = 7.16 ppm; toluene-d_8 (C_7D_8): $\delta^{1}H(C_7D_7H)$ = 2.08 ppm), and $^{13}C\{^{1}H\}$ spectra by using the central line of the solvent signal (benzene-d_6 (C_6D_6): $\delta^{13}C\{^{1}H\}(C_6D_6)$ = 128.06 ppm; toluene-d_8: $\delta^{13}C\{^{1}H\}(C_7D_8)$ = 20.4 ppm). $^{11}B\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra were referenced against external standards [BF_3•OEt_2 ($\delta^{11}B\{^{1}H\}(BF_3$•$OEt_2)$ = 0.0 ppm; $CFCl_3$ ($\delta^{19}F\{^{1}H\}(CFCl_3)$ = 0.0 ppm)]. The given chemical shifts of the ^{15}N NMR spectra result out of $^{15}N/^{1}H$ HMQC/HMBC NMR experiments with nitromethane as externals standard (δ = 378.9 ppm vs. NH_3).

Infrared spectra were measured on a Bruker Tensor 27 spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system.

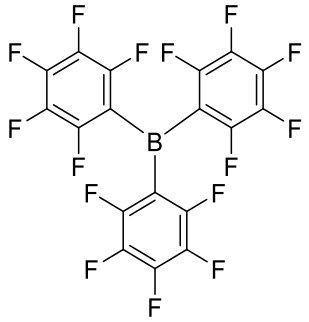
Melting points were determined using a "Mel-Temp" by Laboratory Devices, Cambridge, U.K..

Elemental analyses (C, H, N, S) were carried out on an EuroEA 3000 Elemental Analyzer.

Synthesis and Characterization of Compounds

Starting Materials

$B(C_6F_5)_3$



An ampoule of condensed boron trichloride (4.416 g, 37.69 mmol) was broken up in air and quickly added to a precooled solution of *n*-hexane (approximately 30 mL). **Caution:** Due to breaking up the ampoule in air, wearing appropriate safety clothing and working in a fume hood is mandatory. **Note:** The amount of boron trichloride used is determined by previously weighing the Schlenk flask with the *n*-hexane. After transferring the boron trichloride, the flask is weighed again and the amount is determined by forming the difference. To a stirring solution of bromopentafluorobenzene (27.925 g, 113.08 mmol) in *n*-hexane (approximately 300 mL), *n*-butyllithium (45.2 mL, 113.08 mmol, 2.5 M in *n*-hexane) was added dropwise via a dropping funnel at -80 °C so that a temperature of -75 °C was not exceeded. **Caution:** *Maintaining the temperature is extremely important to prevent aryne formation by elimination of LiF!* After the addition, the reaction solution was stirred for an additional hour at -80 °C. The prepared boron trichloride / *n*-hexane solution was added rapidly via cannula and the resulting colourless suspension was stirred for an additional hour at -80 °C, and subsequently slowly warmed to room temperature followed by additional 16 h of stirring at room temperature. All volatile components were removed under vacuum and the colourless solid was transferred to a glove box and grounded in a mortar. The solid was transferred to a round bottom flask equipped with a sublimation apparatus. Sublimation at 80 °C and $1 \cdot 10^{-3}$ bar for some hours affords a sticky slightly brown product, being contaminated $B(C_6F_5)_3$. Subsequent sublimation at 100 °C and $1 \cdot 10^{-3}$ bar yields analytically pure $B(C_6F_5)_3$ as a colourless crystalline solid (the sublimation was carried out over the course of several days and the product was collected in fractions).

Yield: 16.124 g (31.49 mmol, 84%).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 305 K): δ = 121.7 (br, $C_{q,Ar}B$), 137.4 (dm, $^1J_{C,F}$ = 253.4 Hz, $B(C_q\underline{C}_5F_5)_3$), 144.9 (dm, $^1J_{C,F}$ = 263.0 Hz, $B(C_q\underline{C}_5F_5)_3$), 148.0 (dm, $^1J_{C,F}$ = 251.5 Hz, $B(C_q\underline{C}_5F_5)_3$) ppm.

$^{11}B\{^1H\}$ NMR (160 MHz, C_6D_6, 305 K): δ = 59.7 ppm

$^{19}F\{^1H\}$ NMR (470 MHz, C_6D_6, 305 K): δ = -160.1 (m, 6F, *m*-$F_{Ar}B$), -141.9 (m, 6F, *p*-$F_{Ar}B$), -128.8 (m, 6F, *o*-$F_{Ar}B$) ($\Delta\delta^{19}F_{m,p}$ = 18.2 ppm) ppm.

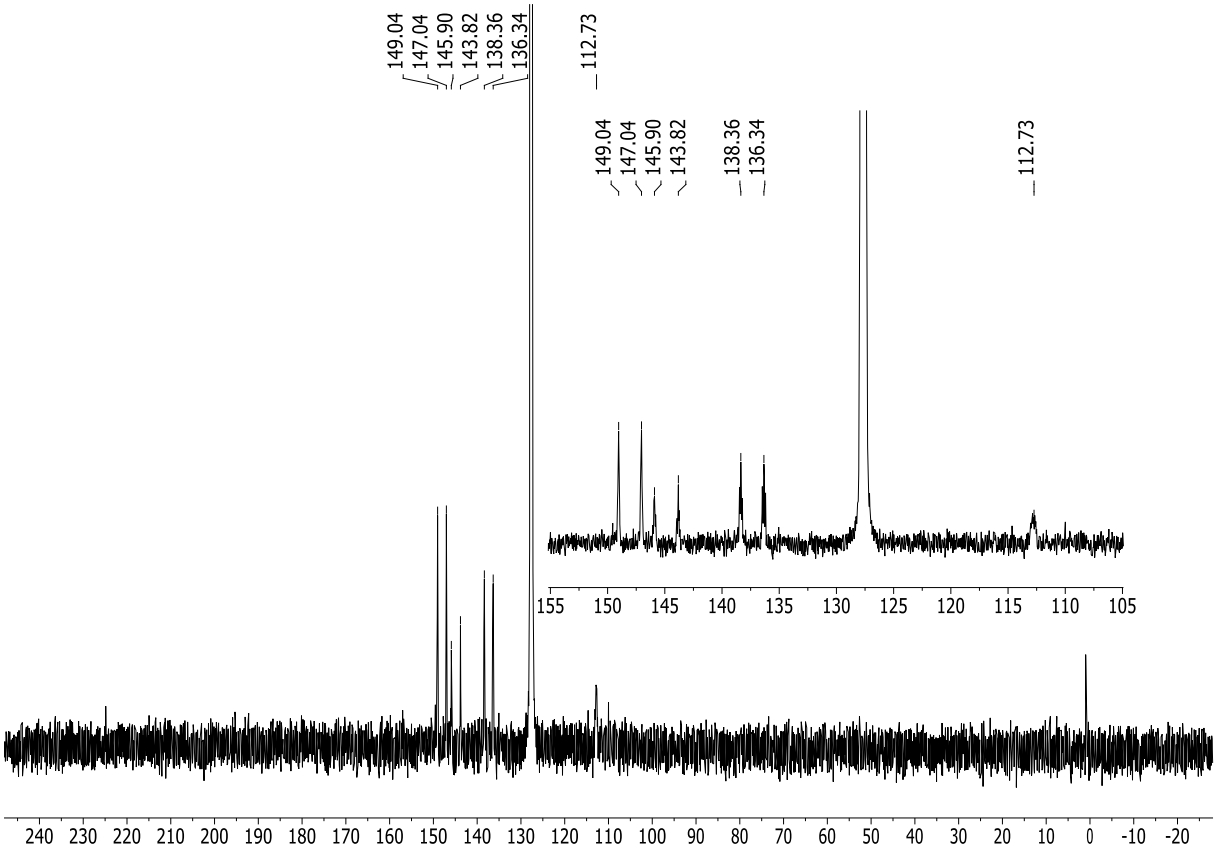


Figure S1: $^{13}C\{^1H\}$ NMR spectrum of $B(C_6F_5)_3$ (126 MHz, C_6D_6, rt); 1.4 ppm: silicon grease.

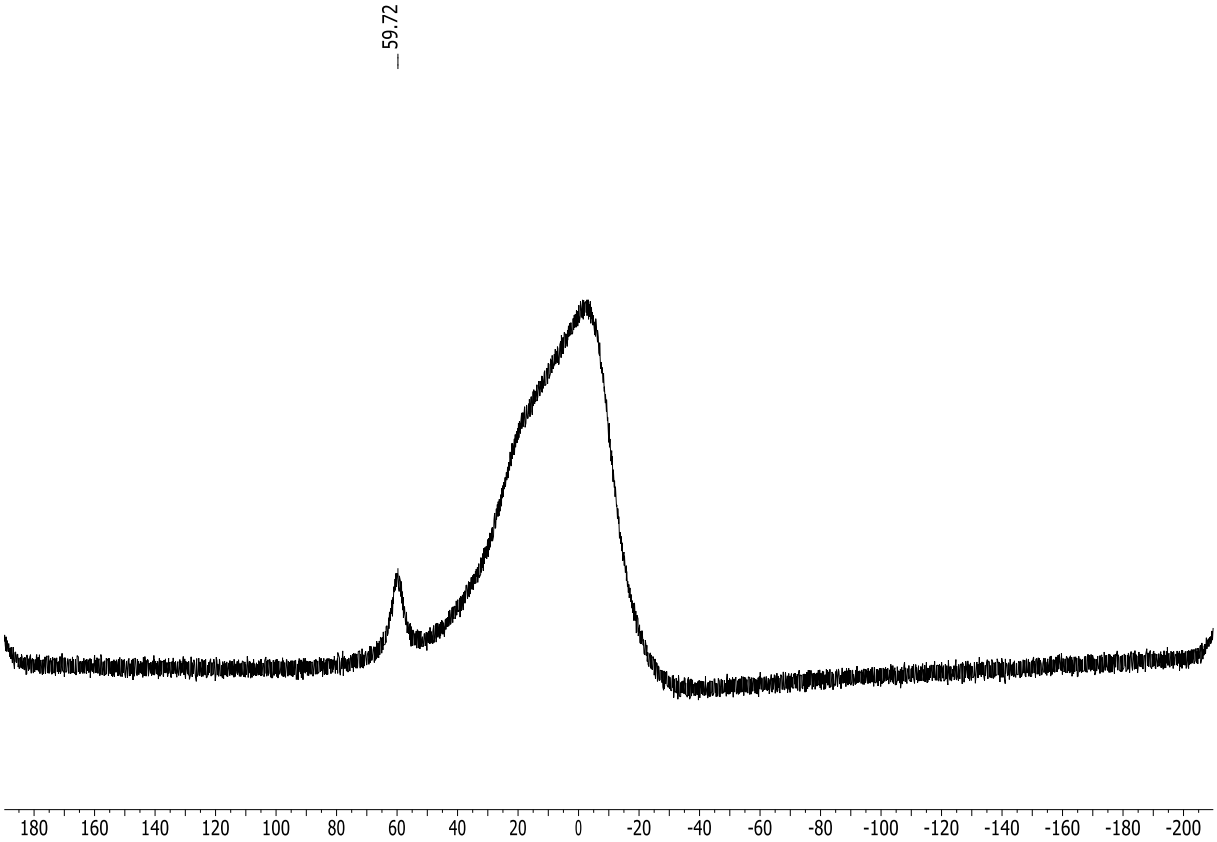


Figure S2: $^{11}B\{^{1}H\}$ NMR spectrum of $B(C_6F_5)_3$ (160 MHz, C_6D_6, rt).

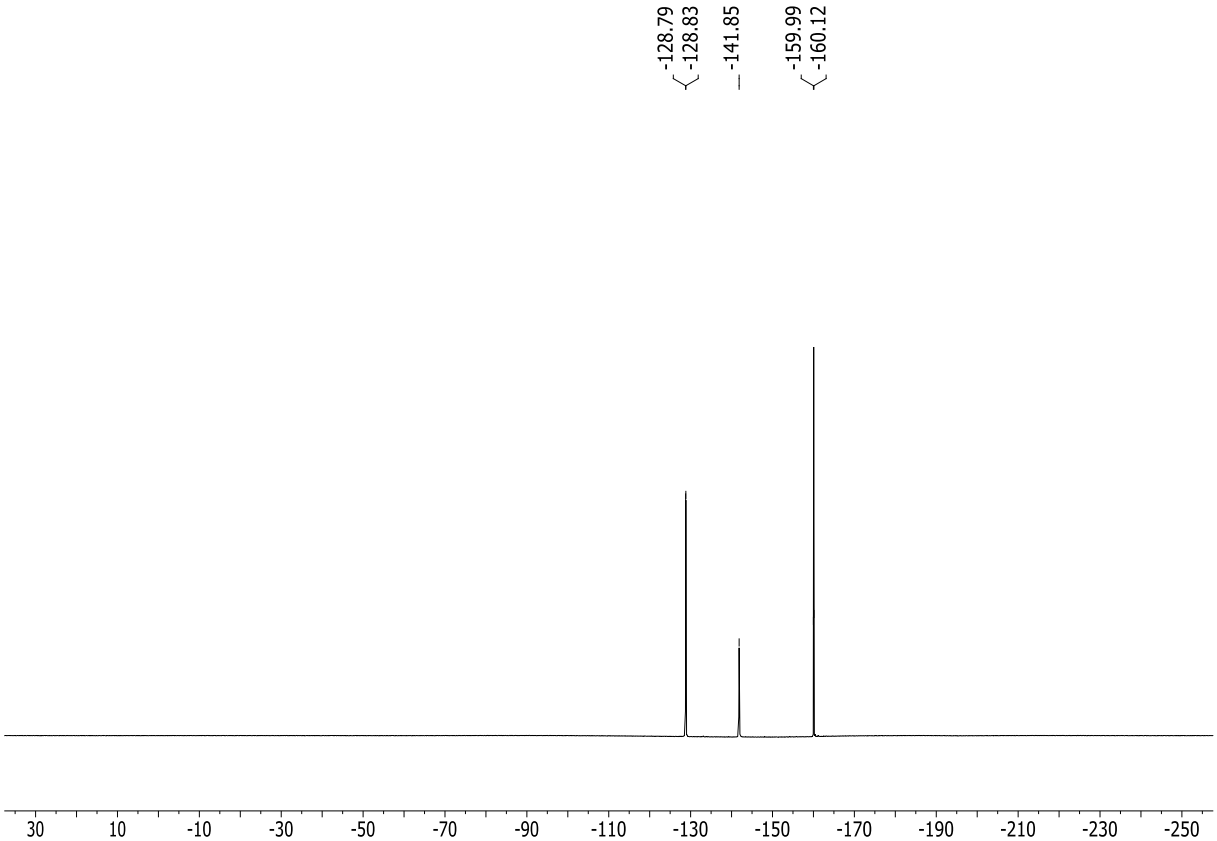
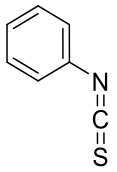


Figure S3: $^{19}F\{^{1}H\}$ NMR spectrum of $B(C_6F_5)_3$ (470 MHz, C_6D_6, rt).

1a



^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 6.57-6.60 (m, 2H, CH_{Ph}), 6.70-6.72 (m,3 H, CH_{Ph}) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 125.7 (CH_{Ph}), 127.0 (CH_{Ph}), 127.5-128.5 (N=C=S, $C_{q,Ph}$)*, 149.5 (CH_{Ph}) ppm. * = overlap with C_6D_6 signal

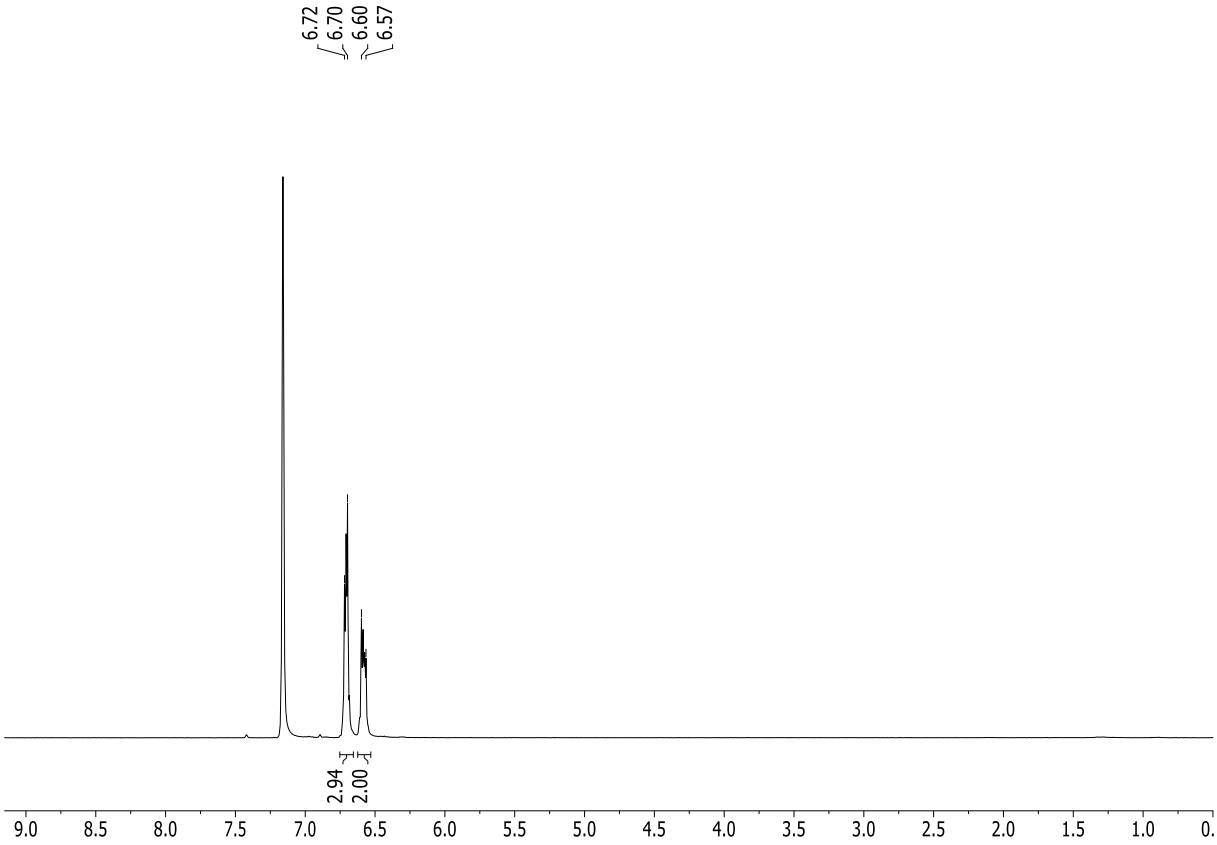


Figure S4: ^{1}H NMR spectrum of **1a** (500 MHz, C_6D_6, rt).

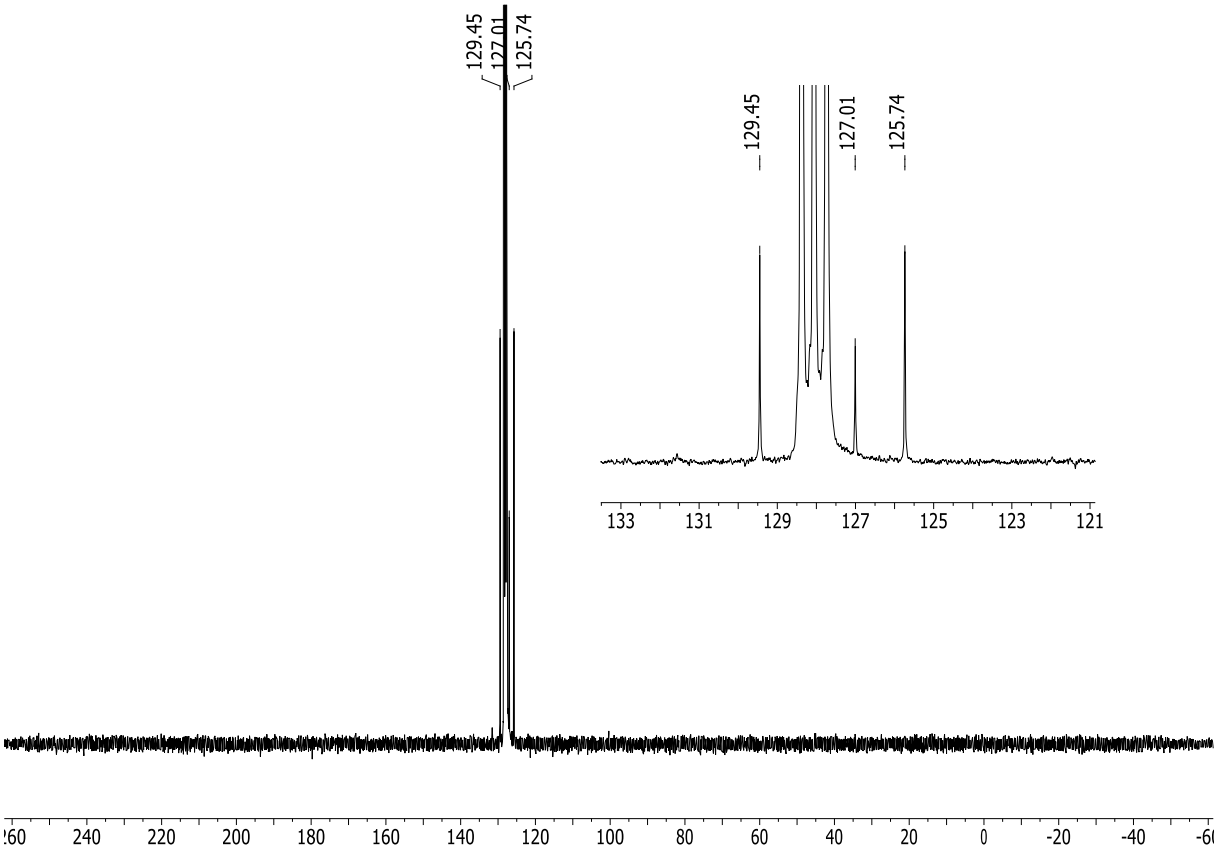
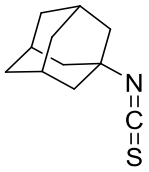


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of **1a** (126 MHz, C_6D_6, rt).

1b



^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 1.15-1.25 (m, 6H, $CH_{2,Ad}$), 1.52-1.53 (m, 6H, $CH_{2,Ad}$) 1.59-1.60 (m, 3H, CH_{Ad}) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 29.4 (CH_{Ad}), 35.5 ($CH_{2,Ad}$), 43.6 ($CH_{2,Ad}$), 58.4 ($C_{q,Ad}$), 128.4 (S=C=N)* ppm. * = overlap with C_6D_6 signal

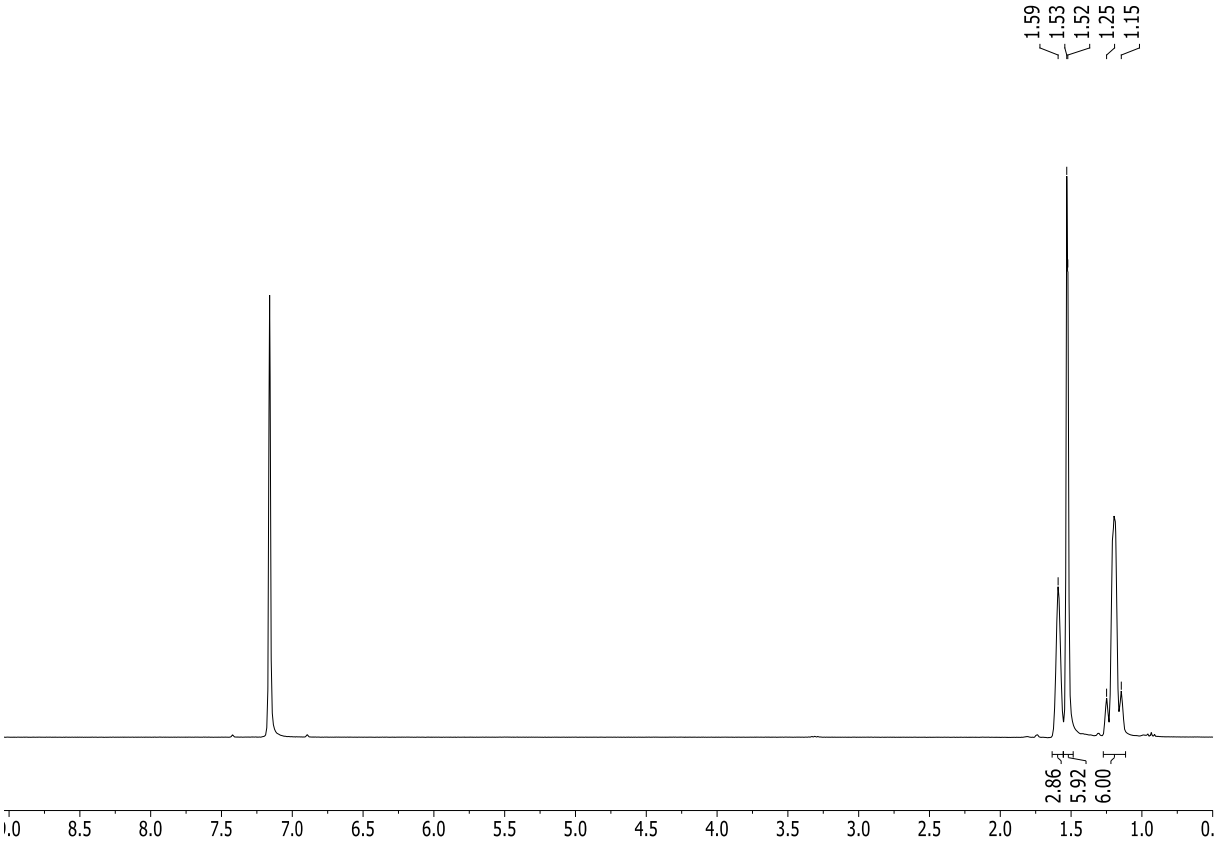


Figure S6: ^{1}H NMR spectrum of **1b** (500 MHz, C_6D_6, rt).

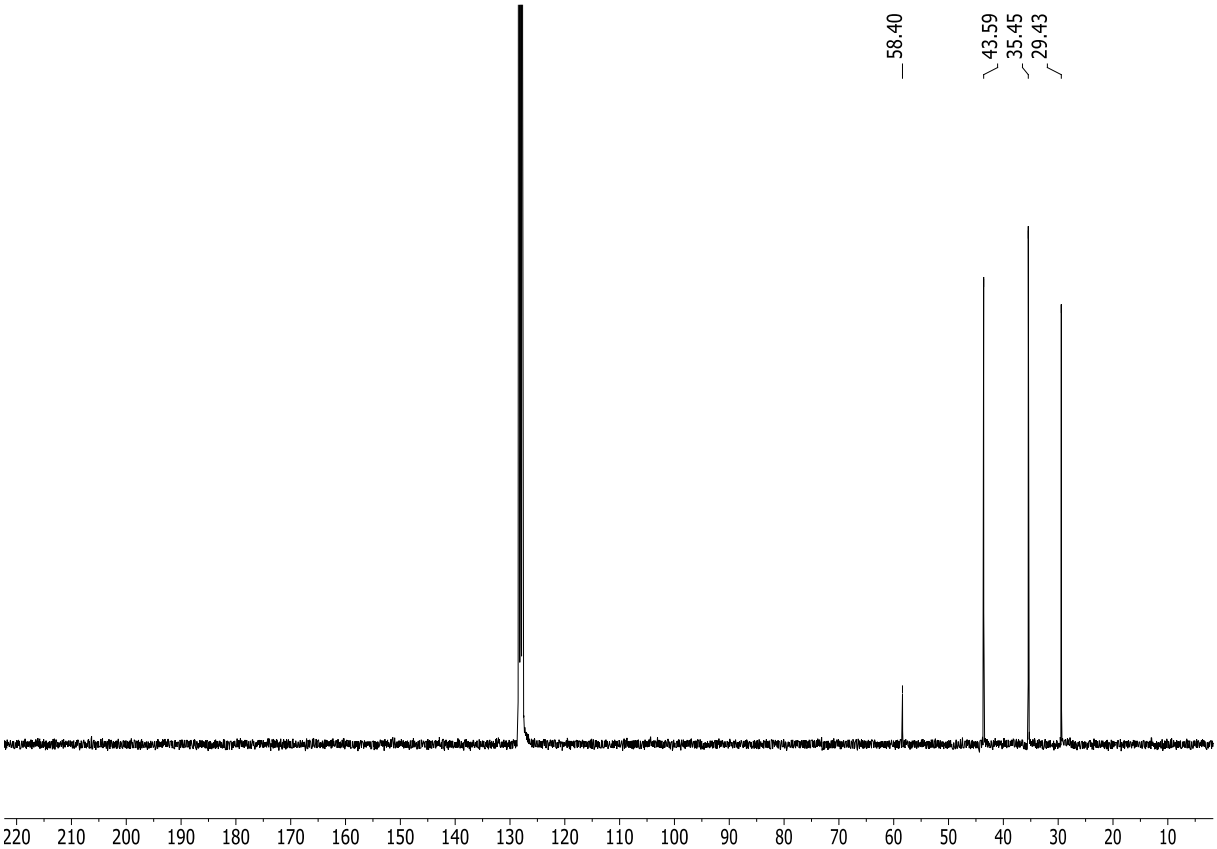
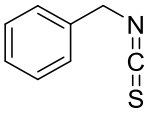


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum of **1b** (126 MHz, C_6D_6, rt).

1c



^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 3.63 (s, 2H, CH_2), 6.75-6.77 (m, 2H, CH_{Ph}), 6.95-6.97 (m, 3H, CH_{Ph}) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 48.8 (CH_2), 127.5 (CH_{Ph}), 128.9 (CH_{Ph})*, 129.6 (CH_{Ph}), 135.4 ($C_{q,Ph}$) ppm. * = overlap with C_6D_6 signal

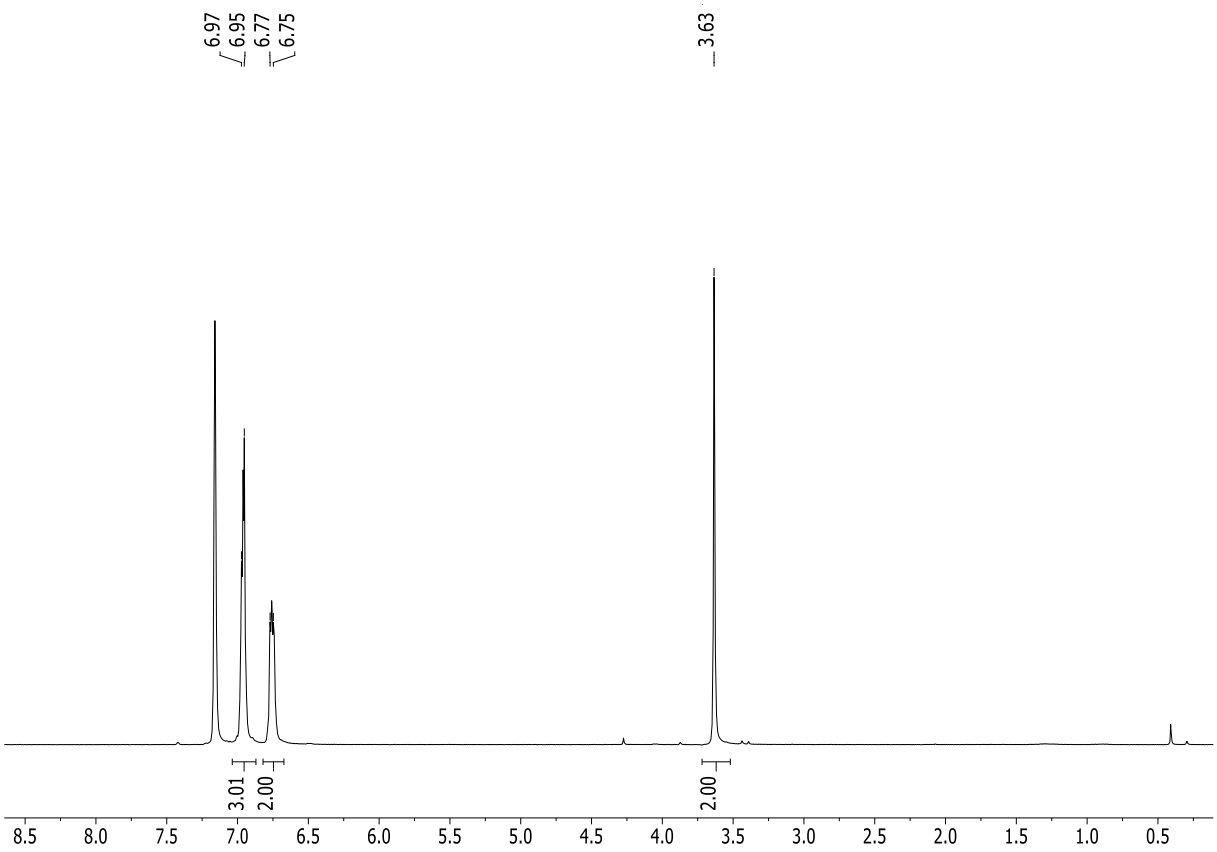


Figure S8: ^{1}H NMR spectrum of **1c** (500 MHz, C_6D_6, rt).

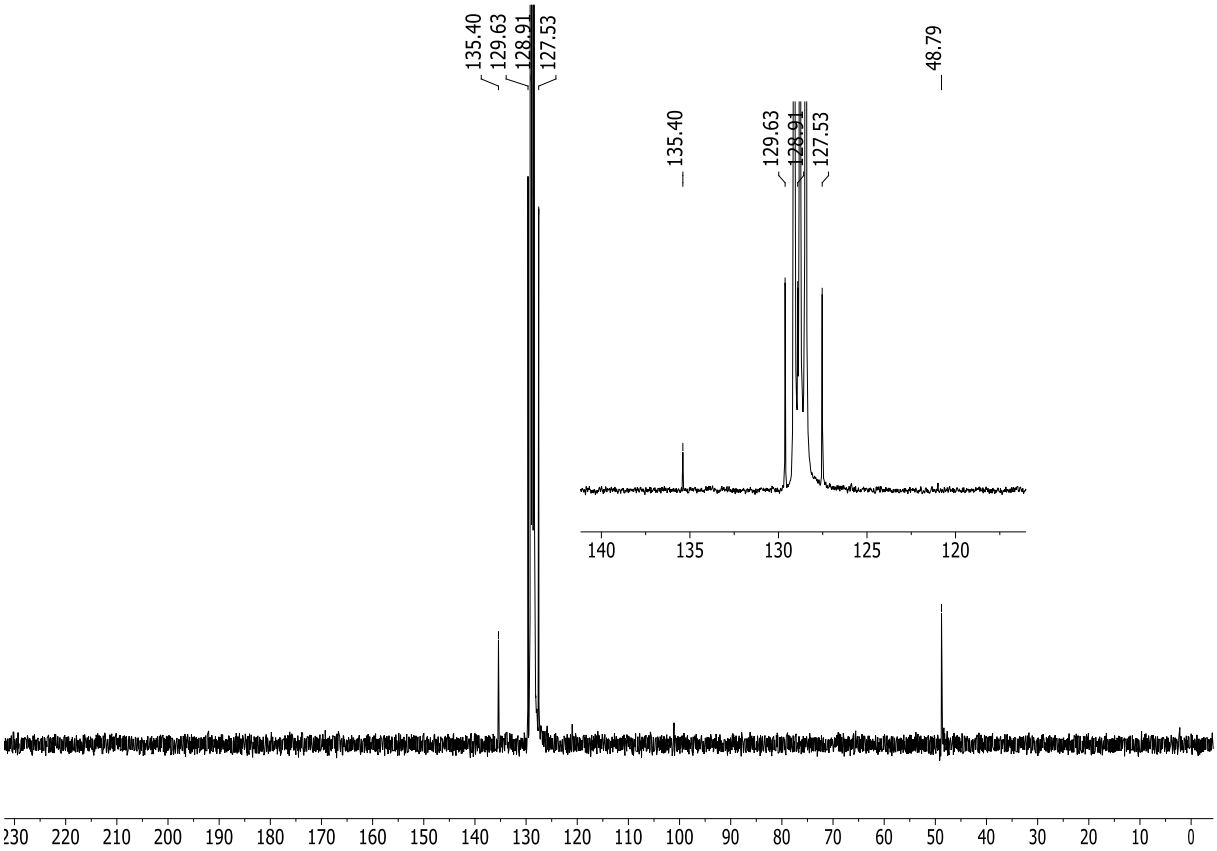
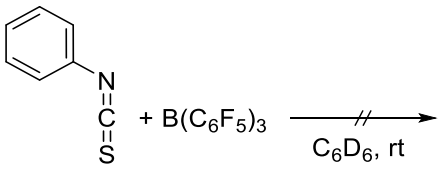


Figure S9: $^{13}C\{^{1}H\}$ NMR spectrum of **1c** (126 MHz, C_6D_6, rt).

New Compounds

Attempted reaction of 1a with $B(_6F_5)_3$



In a Young NMR-tube, phenyl isothiocyanate **1a** (0.010 g, 0.074 mmol) was dissolved in 0.6 mL of C_6D_6. $B(C_6F_5)_3$ (0.038 g, 0.074 mmol) was added to the solution and the sample was subsequently analyzed by multinuclear NMR spectroscopy, which revealed no conversion of both starting materials. Heating of the solution for several days at 80 °C also led to no reaction.

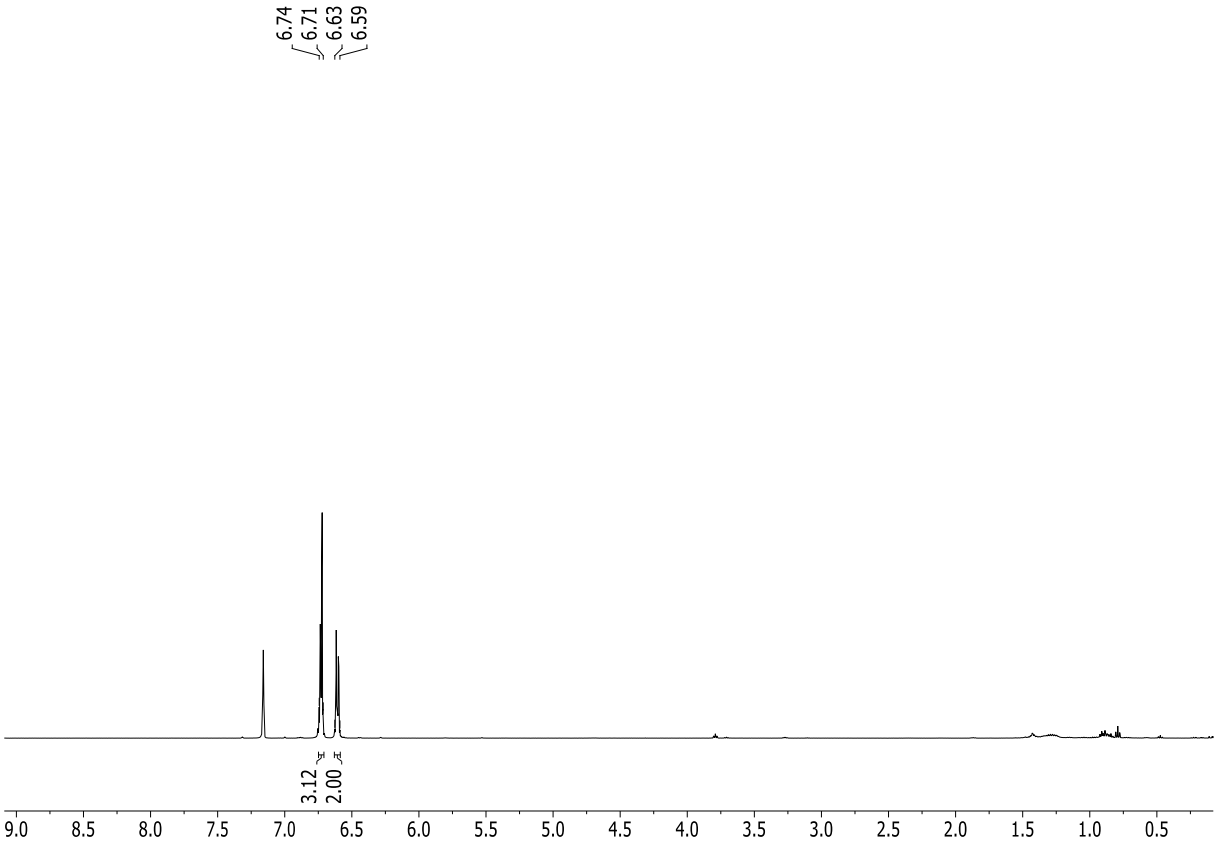


Figure S10: ^{1}H NMR spectrum of phenyl isothiocyanate **1a** and $B(C_6F_5)_3$ (500 MHz, C_6D_6, rt).

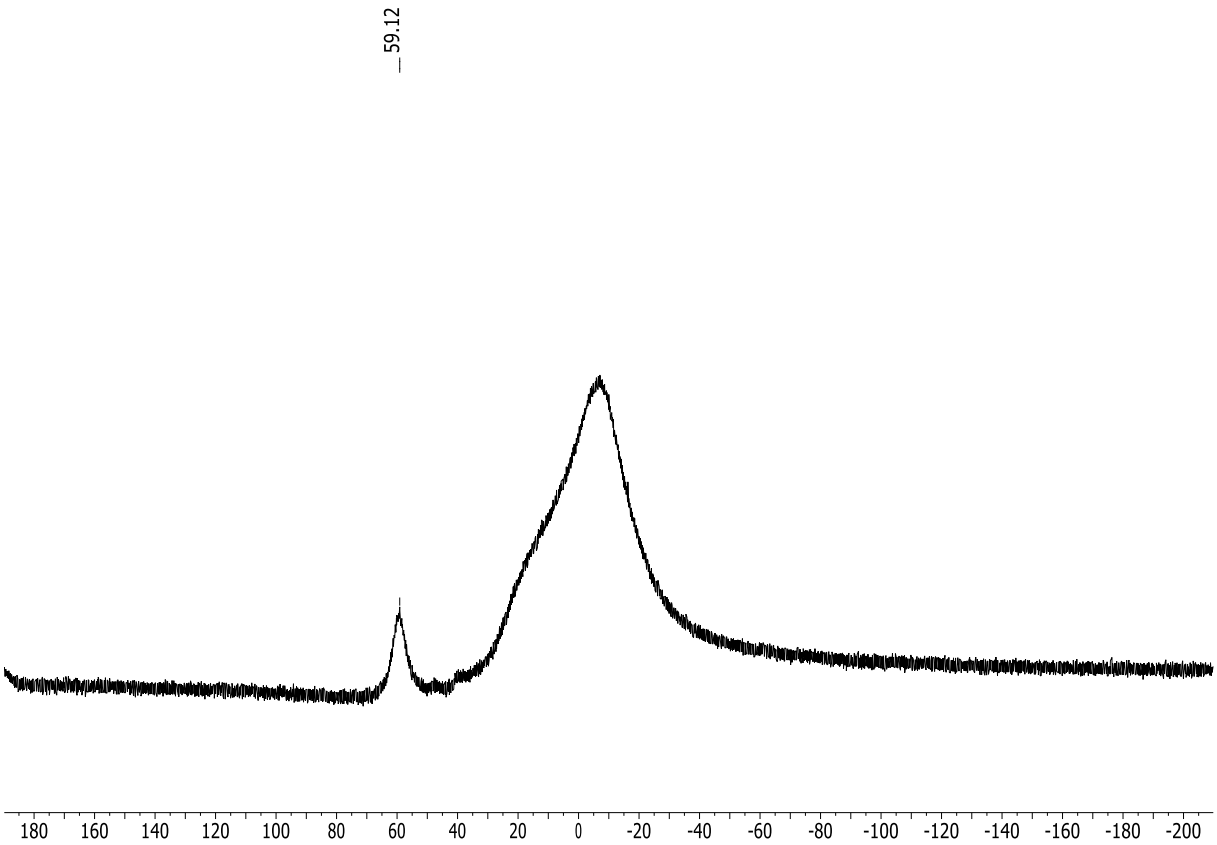


Figure S11: $^{11}B\{^{1}H\}$ NMR spectrum of phenyl isothiocyanate **1a** and $B(C_6F_5)_3$ (160 MHz, C_6D_6, rt).

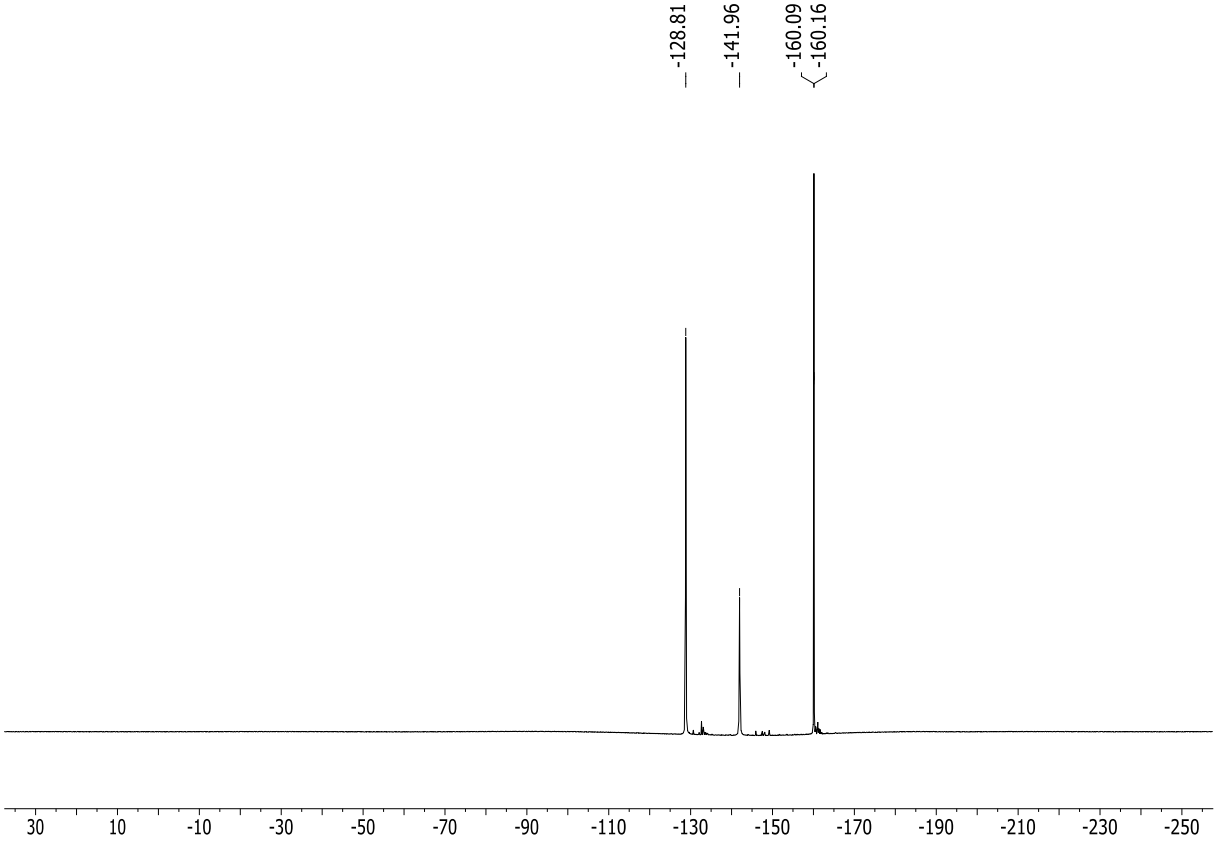


Figure S12: $^{19}F\{^{1}H\}$ NMR spectrum of phenyl isothiocyanate **1a** and $B(C_6F_5)_3$ (470 MHz, C_6D_6, rt).

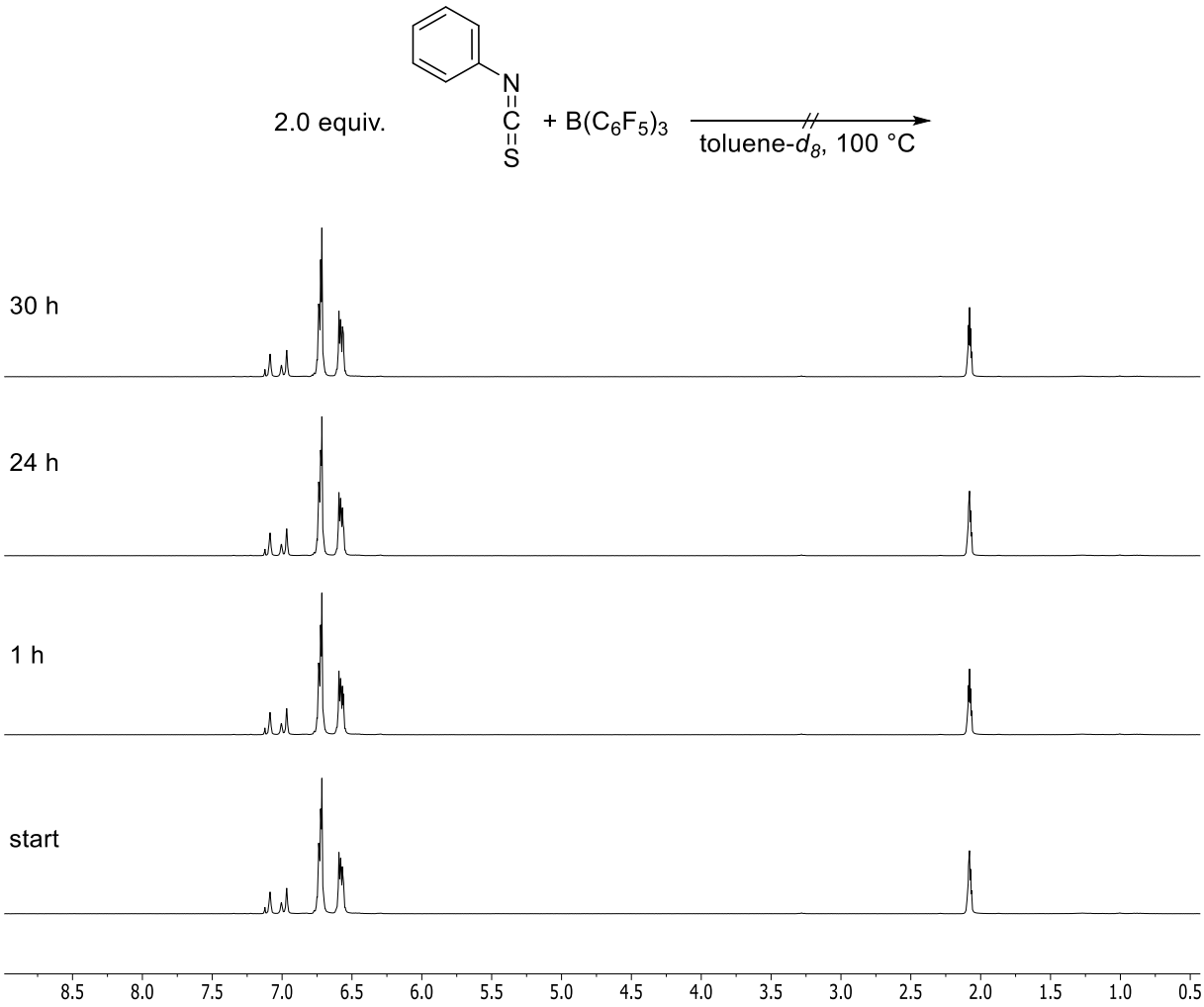
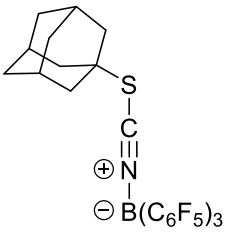


Figure S13: Time resolved ^{1}H NMR spectrum of phenyl isothiocyanate **1a** and $B(C_6F_5)_3$ (500 MHz, toluene-d_8, 373 K).

Synthesis of 2b



A) In a Young NMR-tube, 1-adamantyl isothiocyanate **1b** (0.015 g, 0.078 mmol) was dissolved in 0.6 mL of C_6D_6. $B(C_6F_5)_3$ (0.040 g, 0.078 mmol) was added to the solution and the sample was subsequently analyzed by multinuclear NMR spectroscopy, which revealed complete conversion of both starting materials after some minutes to yield compound **2b**.

B) 1-Adamantyl isothiocyanate **1b** (0.100 g, 0.517 mmol) was dissolved in 10 mL of toluene. $B(C_6F_5)_3$ (0.265 g, 0.517 mmol) was added and the reaction mixture was stirred for one hour at room temperature. All volatile components were removed under vacuum. The residue was washed with small amounts of *n*-hexane and dried subsequently under vacuum to yield **2b** as a slightly yellow solid.

Crystals suitable for single-crystal X-ray diffraction were obtained by layering the C_6D_6 solution of attempt **A** with *n*-hexane for several days.

Yield: 0.315 g (0.447 mmol, 86%).

Melting point: 182-184 °C.

IR (ATR): $\tilde{\nu}$ = 2934, 2915, 2863, 2231 (C≡N), 1648, 1519, 1457, 1383, 1345, 1287, 1101, 1084, 1026, 971, 951, 877, 821, 798, 773, 745, 728, 686, 678, 627, 610 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 1.15-1.16 (m, 6H, $CH_{2,Ad}$), 1.53-1.59 (m, 9H, $CH_{2,Ad}$, CH_{Ad}) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 31.5 (CH_{Ad}), 34.6 ($CH_{2,Ad}$), 44.4 ($CH_{2,Ad}$), 65.6 ($C_{q,Ad}$), 114.7 (N≡CS), 116.0 (br, $B(\underline{C}_qC_5F_5)_3$), 137.9 (dm, $^1J_{C,F}$ = 246.5 Hz, $B(C_q\underline{C}_5F_5)_3$), 141.0 (dm, $^1J_{C,F}$ = 251.4 Hz, $B(C_q\underline{C}_5F_5)_3$), 148.6 (dm, $^1J_{C,F}$ = 242.5 Hz, $B(C_q\underline{C}_5F_5)_3$) ppm.

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 305 K): δ = -9.7 ppm

^{19}F{^{1}H} NMR (470 MHz, C_6D_6, 305 K): δ = -163.3 (m, 6F, *m*-F_{Ar}B), -155.7 (t, $^3J_{F,F}$ = 20.1 Hz, 6F, *p*-F_{Ar}B), -134.0 (m, 6F, *o*-F_{Ar}B) ($\Delta\delta^{19}F_{m,p}$ = 7.6 ppm) ppm.

EA: Anal. calcd. for $C_{29}H_{15}BF_{15}NS$: C, 49.39; H, 2.14; N, 1.99; S, 4.55; Found: C, 49.57; H, 2.36; N, 1.80; S, 4.03.

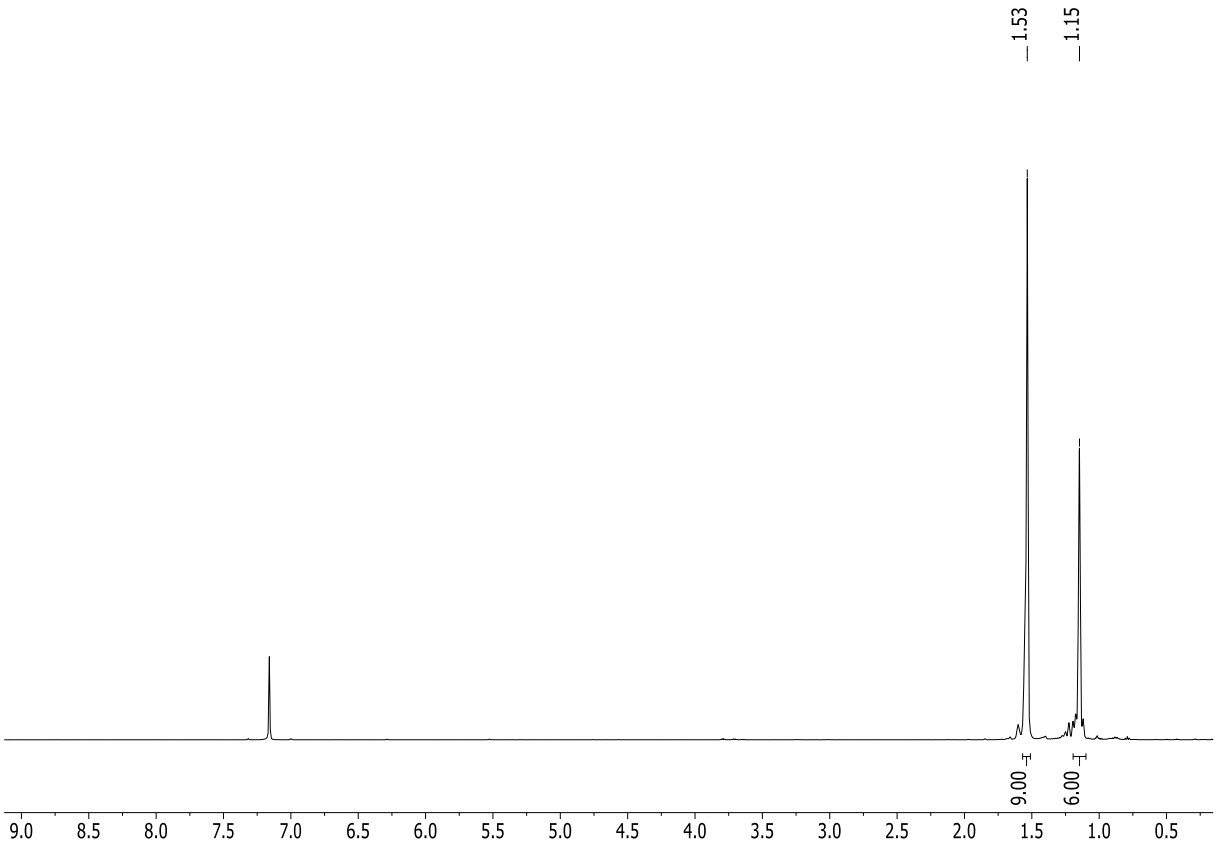


Figure S14: ^{1}H NMR spectrum of **2b** (500 MHz, C_6D_6, rt).

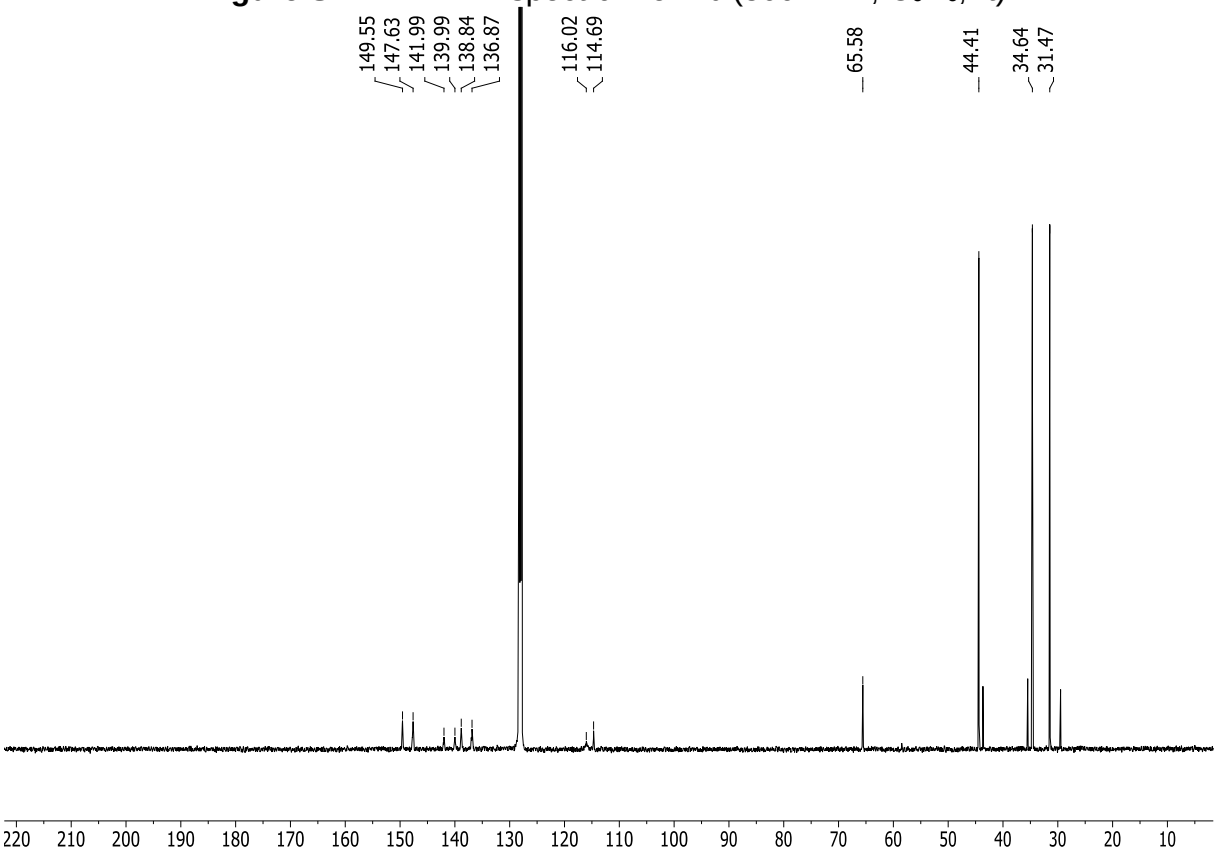


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of **2b** (126 MHz, C_6D_6, rt).

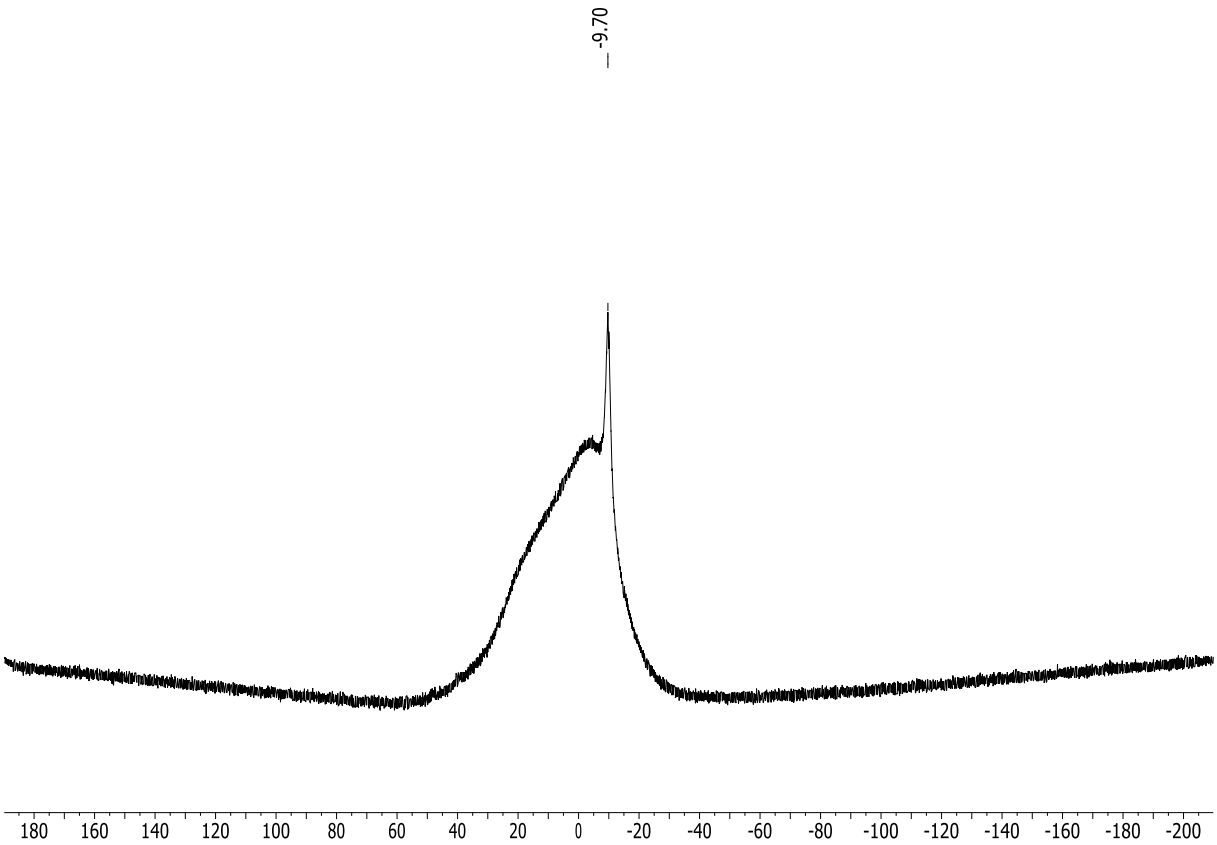


Figure S16: $^{11}B\{^{1}H\}$ NMR spectrum of **2b** (160 MHz, C_6D_6, rt).

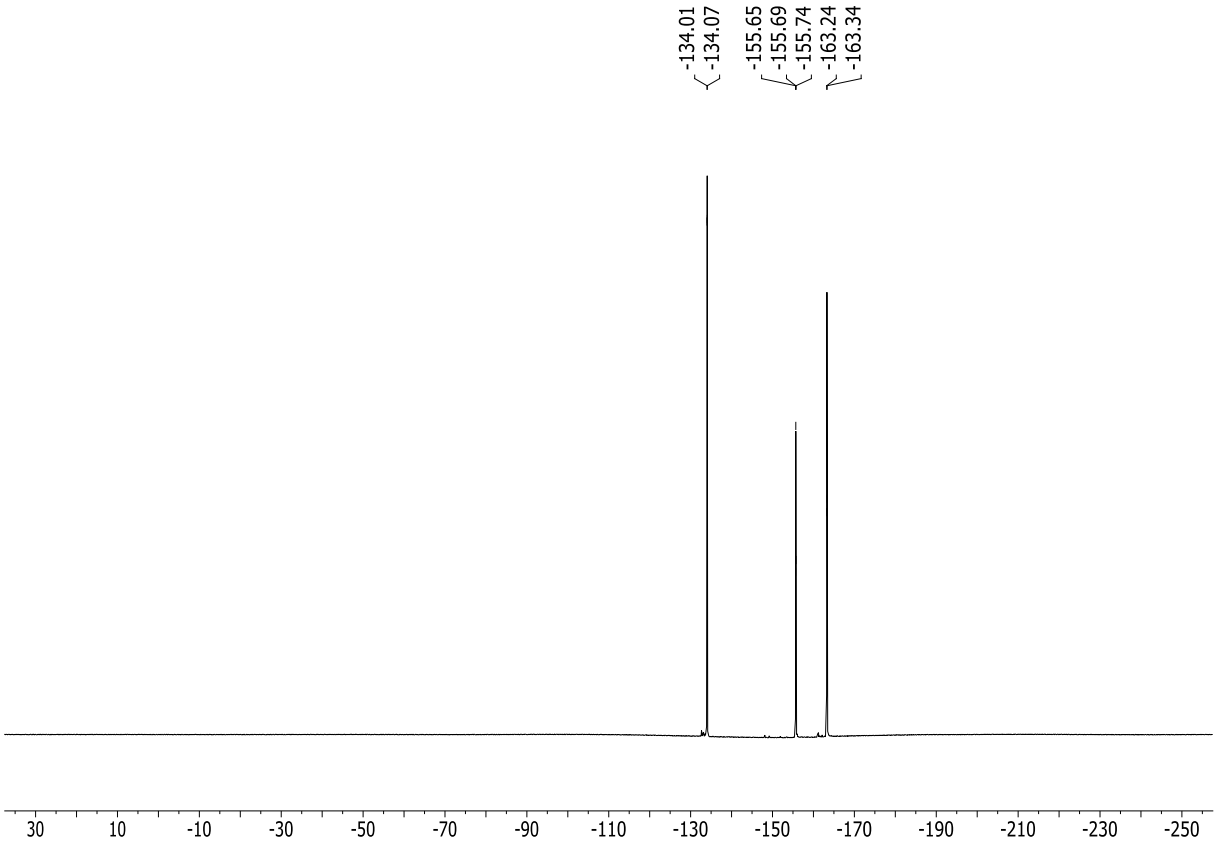
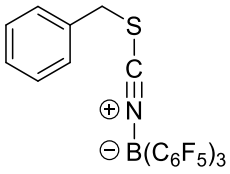


Figure S17: $^{19}F\{^{1}H\}$ NMR spectrum of **2b** (470 MHz, C_6D_6, rt).

Synthesis of 2c



A) In a Young NMR-tube, benzyl isothiocyanate **1c** (0.010 g, 0.067 mmol) was dissolved in 0.6 mL of C_6D_6. $B(C_6F_5)_3$ (0.034 g, 0.067 mmol) was added to the solution and the sample was subsequently analyzed by multinuclear NMR spectroscopy, which revealed complete conversion of both starting materials after several hours to yield compound **2b**.

B) Benzyl isothiocyanate **1c** (0.073 g, 0.488 mmol) was dissolved in 10 mL of toluene. $B(C_6F_5)_3$ (0.250 g, 0.488 mmol) was added and the reaction mixture was stirred for one hour at room temperature. All volatile components were removed under vacuum. The residue was washed with small amounts of *n*-hexane and dried subsequently under vacuum to yield **2b** as a slightly yellow solid.

Crystals suitable for single-crystal X-ray diffraction were obtained by layering the C_6D_6 solution of attempt **A** with *n*-hexane and subsequent slow evaporation of the solvents at room temperature.

Yield: 0.272 g (0.411 mmol, 84%).

Melting point: 118-120 °C.

IR (ATR): $\tilde{\nu}$ = 2247 (C≡N), 1649, 1518, 1461, 1383, 1287, 1243, 1100, 970, 864, 820, 773, 739, 696, 682, 661, 630, 618 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 2.91 (s, 2H, CH_2), 6.56-6.57 (m, 2H, *m*-C*H*$_{Ph}$$CH_2$), 6.80-6.86 (m, 3H, *o*-C*H*$_{Ph}$$CH_2$, *p*-C*H*$_{Ph}$$CH_2$) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 39.3 (CH_2), 114.5 (NCS), 115.6 (br, B($\underline{C}_qC_5F_5)_3$), 128.7 (*m*-$\underline{C}$H$_{Ph}$$CH_2$), 129.2 (*o*-$\underline{C}H_{Ph}$$CH_2$), 129.9 (*p*-$\underline{C}H_{Ph}$$CH_2$), 132.0 ($C_{q,Ph}$), 137.7 (dm, $^1J_{C,F}$ = 247.5 Hz, B($C_q\underline{C}_5F_5)_3$), 141.0 (dm, $^1J_{C,F}$ = 256.2 Hz, B($C_q\underline{C}_5F_5)_3$), 148.5 (dm, $^1J_{C,F}$ = 243.8 Hz, B($C_q\underline{C}_5F_5)_3$) ppm.

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 305 K): δ = -9.9 ppm

^{19}F{^{1}H} NMR (470 MHz, C_6D_6, 305 K): δ = -163.2 (m, 6F, *m*-F$_{Ar}$B), -155.8 (t, $^3J_{F,F}$ = 20.1 Hz, 6F, *p*-F$_{Ar}$B), -134.3 (m, 6F, *o*-F$_{Ar}$B) ($\Delta\delta^{19}F_{m,p}$ = 7.4 ppm) ppm.

EA: Anal. calcd. for $C_{26}H_7BF_{15}NS$: C, 47.23; H, 1.07; N, 2.12; S, 4.85; Found: C, 47.98; H, 1.01; N, 1.90; S, 3.64.

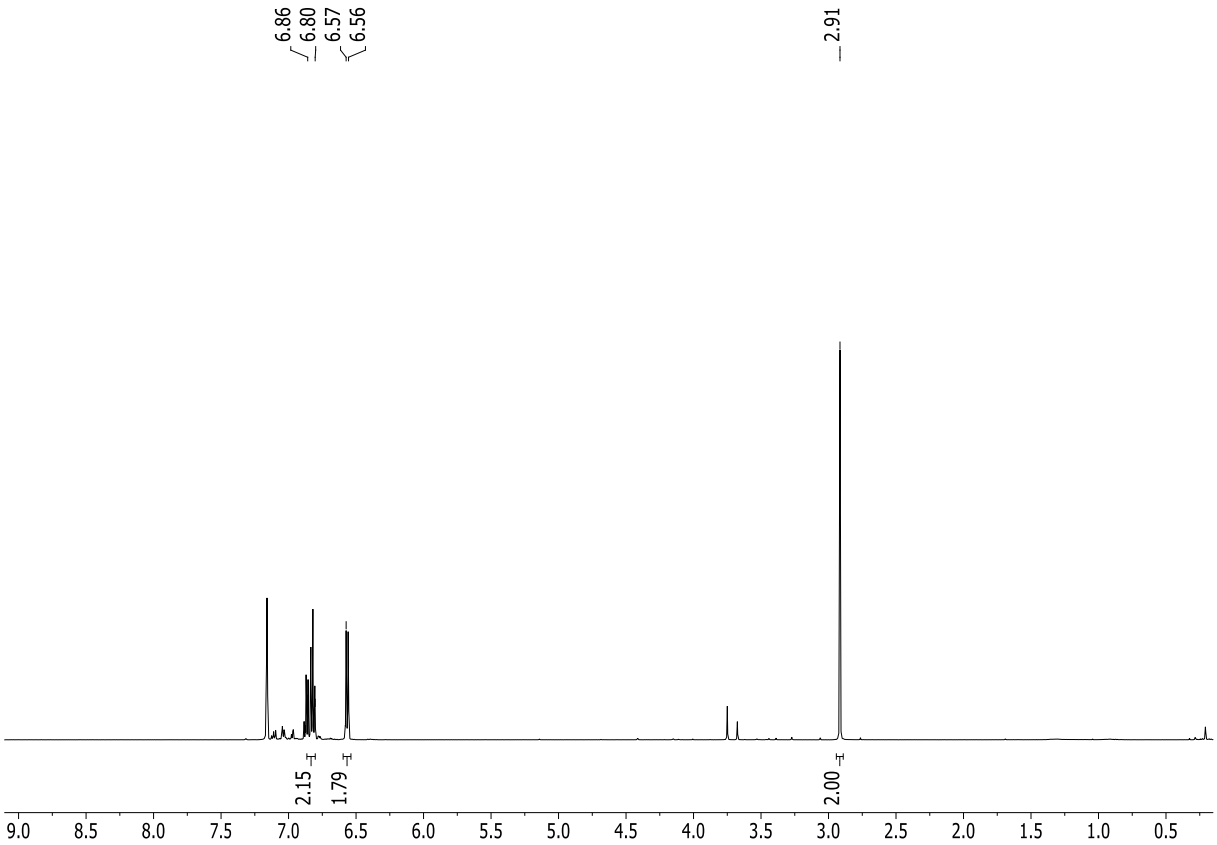


Figure S18: ^{1}H NMR spectrum of **2c** (500 MHz, C_6D_6, rt).

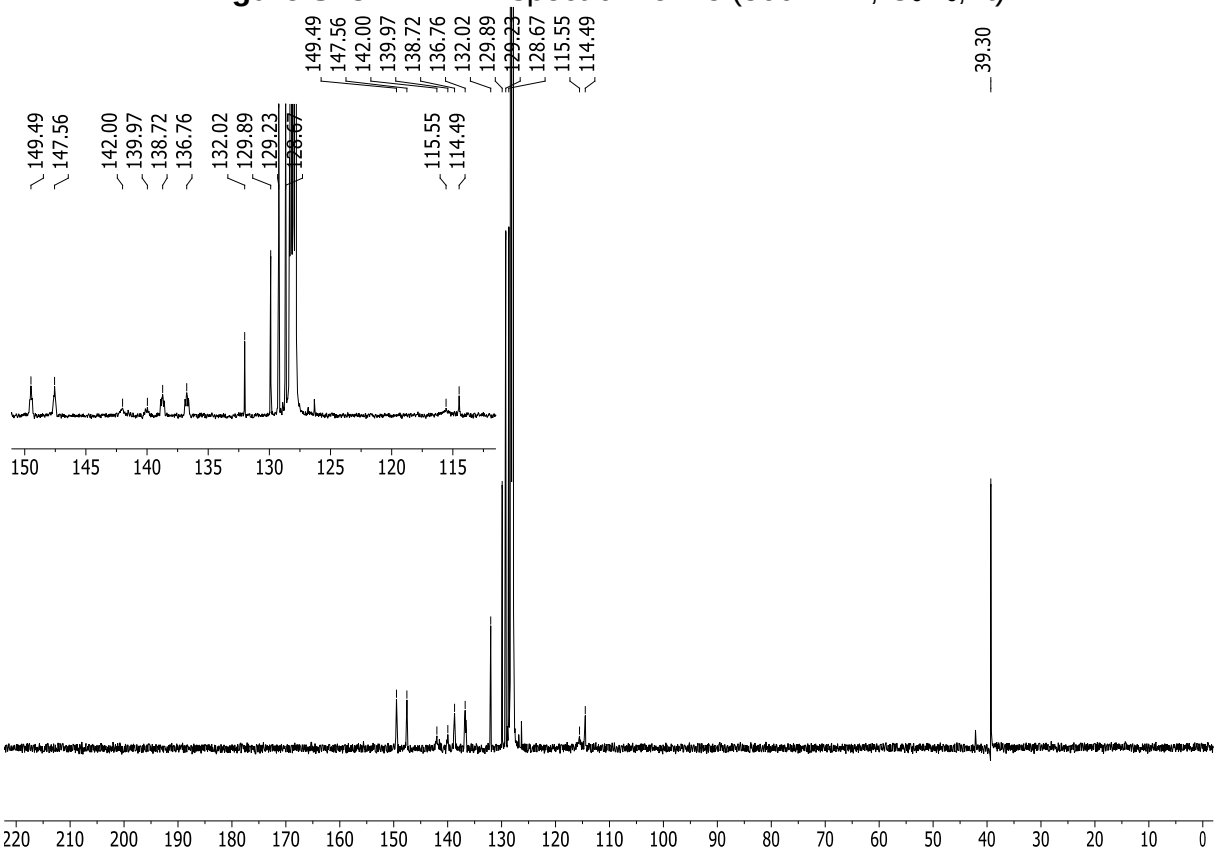


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of **2c** (126 MHz, C_6D_6, rt).

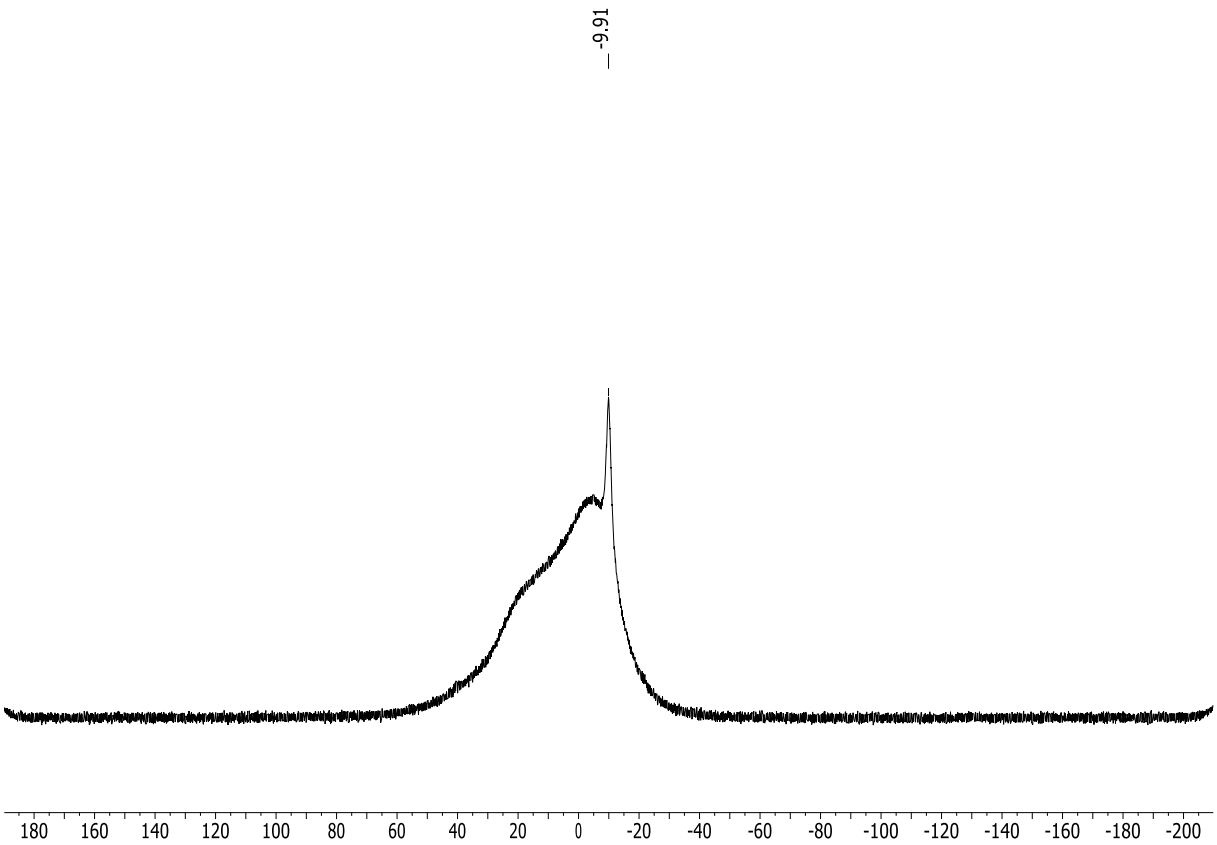


Figure S20: $^{11}B\{^{1}H\}$ NMR spectrum of **2c** (160 MHz, C_6D_6, rt).

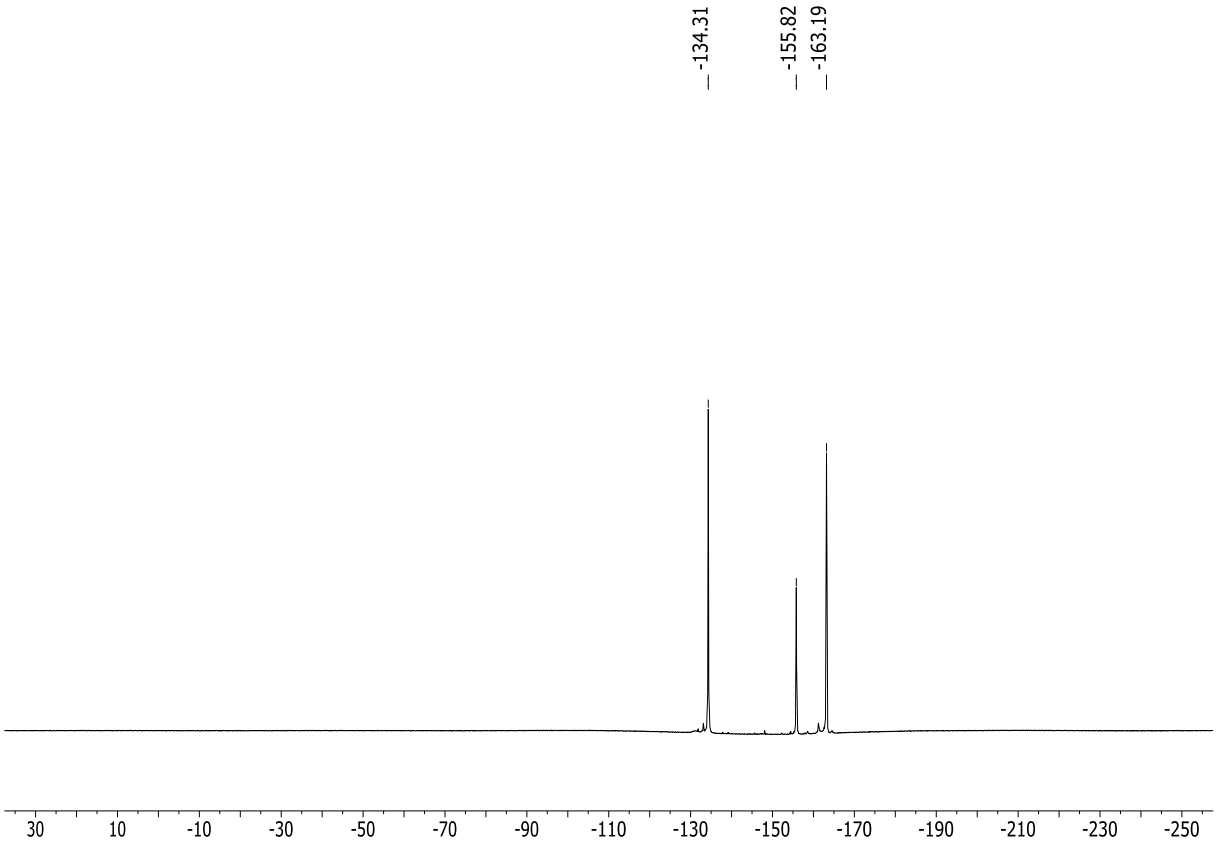
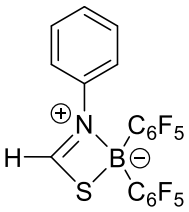


Figure S21: $^{19}F\{^{1}H\}$ NMR spectrum of **2c** (470 MHz, C_6D_6, rt).

Synthesis of 3a



A) In a Young NMR-tube, phenyl isothiocyanate **1a** (0.010 g, 0.074 mmol) was dissolved in 0.6 mL of C_6D_6. $HB(C_6F_5)_2$ (0.026 g, 0.074 mmol) was added to the solution and the sample was subsequently analyzed by multinuclear NMR spectroscopy, which revealed complete conversion of both starting materials after some minutes to yield compound **3a**.

B) Phenyl isothiocyanate **1a** (0.100 g, 0.740 mmol) was dissolved in 10 mL of toluene. $HB(C_6F_5)_2$ (0.256 g, 0.740 mmol) was added and the reaction mixture was stirred for one hour at room temperature. All volatile components have been removed under vacuum. The residue was washed with small amounts of *n*-hexane and dried subsequently under vacuum to yield **3a** as a yellow solid.

Yield: 0.298 g (0.619 mmol, 83%).

Melting point: 104-106 °C.

IR (ATR): $\tilde{\nu}$ = 1645, 1596, 1520, 1489, 1453, 1376, 1319, 1294, 1261, 1170, 1095, 1029, 1005, 972, 867, 784, 744, 690, 651, 620 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 6.64-6.66 (m, 2H, CH_{Ph}), 6.85-6.90 (m, 3H, CH_{Ph}), 7.87 (s, 1H, SC(H)=N) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 112.3 (br, $B(\underline{C}_qC_5F_5)_2$), 118.3 (2×$CH_{Ph}$), 128.2 ($CH_{Ph}$)*, 129.6 (2×$CH_{Ph}$), 137.7 (dm, $^1J_{C,F}$ = 250.1 Hz, $B(C_q\underline{C}_5F_5)_2$), 140.2 ($C_{q,Ph}$), 141.5 (dm, $^1J_{C,F}$ = 253.4 Hz, $B(C_q\underline{C}_5F_5)_2$), 148.5 (dm, $^1J_{C,F}$ = 244.7 Hz, $B(C_q\underline{C}_5F_5)_2$), 183.1 (SC(H)=N) ppm.

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 305 K): δ = 3.7 ppm

^{19}F{^{1}H} NMR (470 MHz, C_6D_6, 305 K): δ = -162.6 (m, 4F, *m*-$F_{Ar}B$), -153.7 (t, $^3J_{F,F}$ = 20.1 Hz, 2F, *p*-$F_{Ar}B$), -132.3 (m, 4F, *o*-$F_{Ar}B$) ($\Delta\delta^{19}F_{m,p}$ = 8.9 ppm) ppm.

EA: Anal. calcd. for $C_{19}H_6BF_{10}NS$: C, 47.43; H, 1.26; N, 2.91; S, 6.66; Found: C, 47.53; H, 0.77; N, 2.53; S, 4.55.

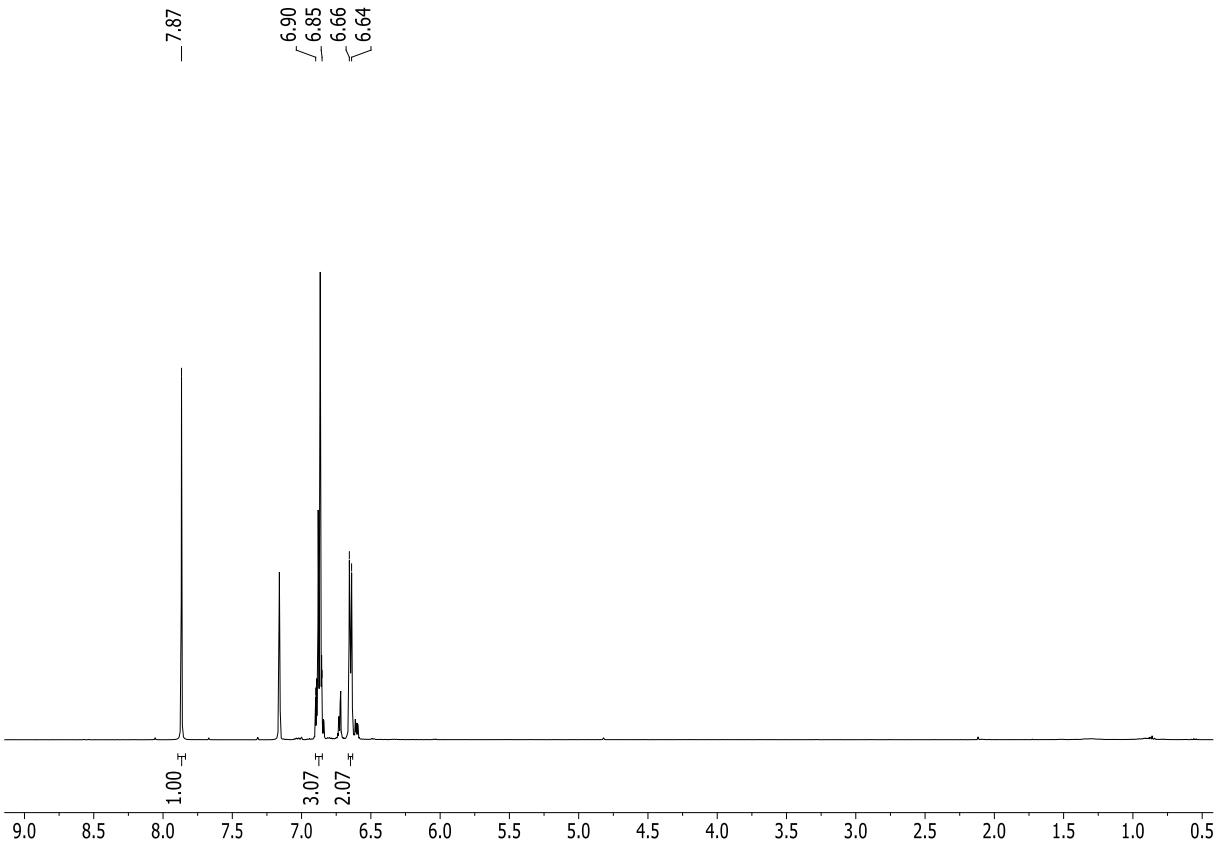


Figure S22: ^{1}H NMR spectrum of **3a** (500 MHz, C_6D_6, rt).

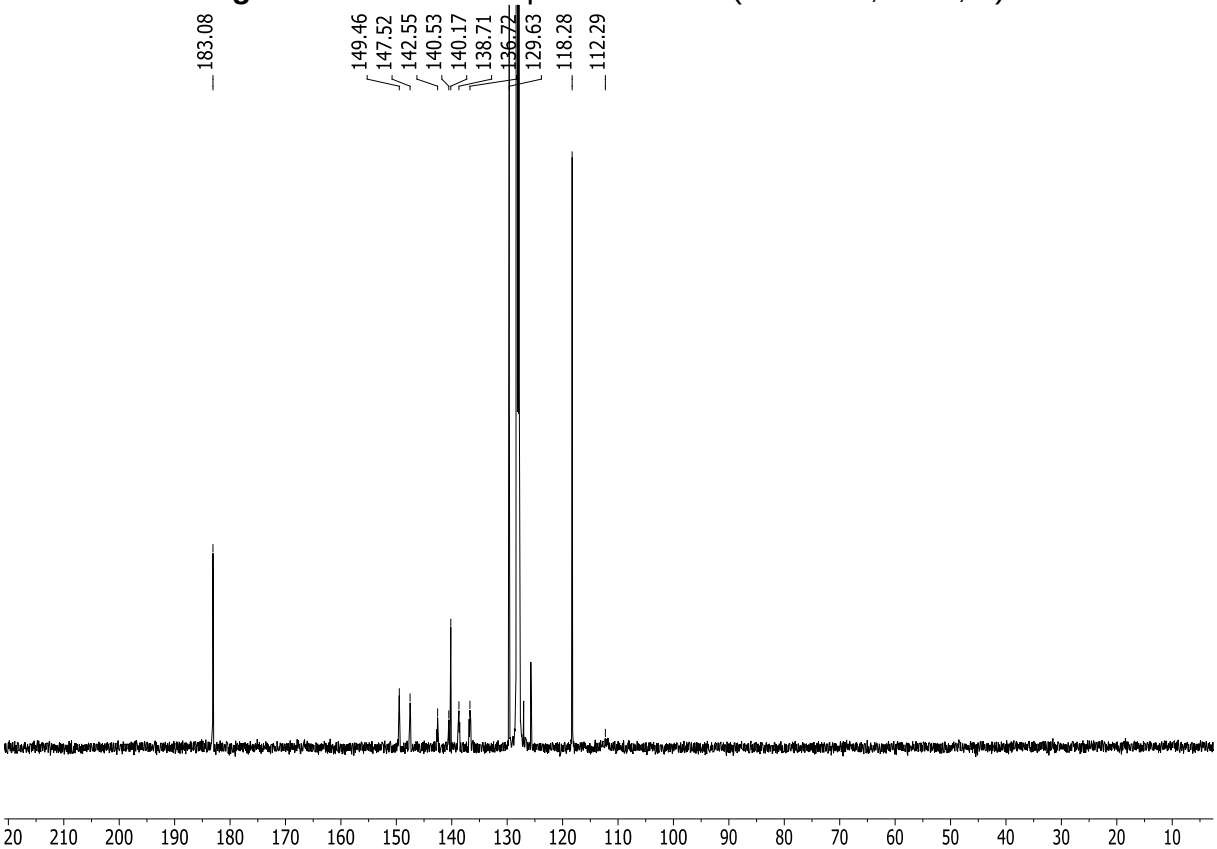


Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum of **3a** (126 MHz, C_6D_6, rt).

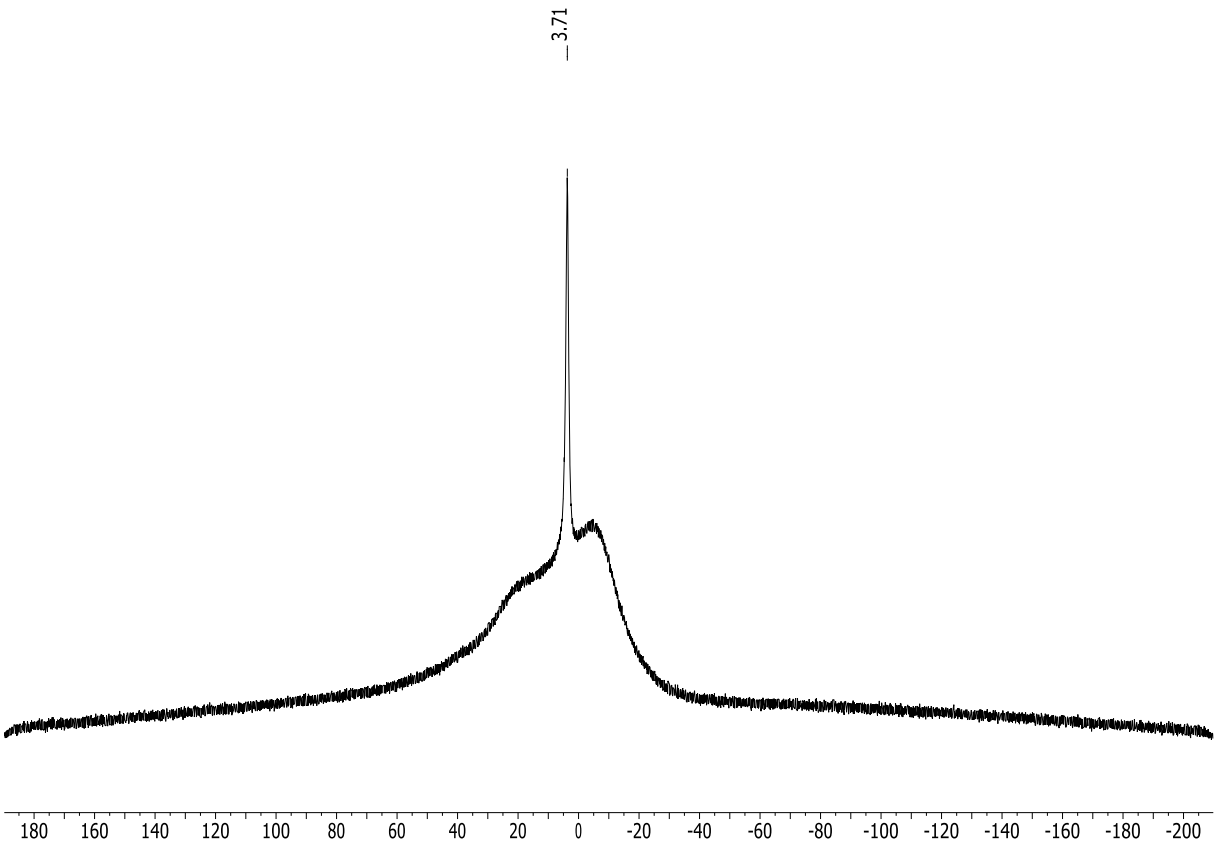


Figure S24: $^{11}B\{^{1}H\}$ NMR spectrum of **3a** (160 MHz, C_6D_6, rt).

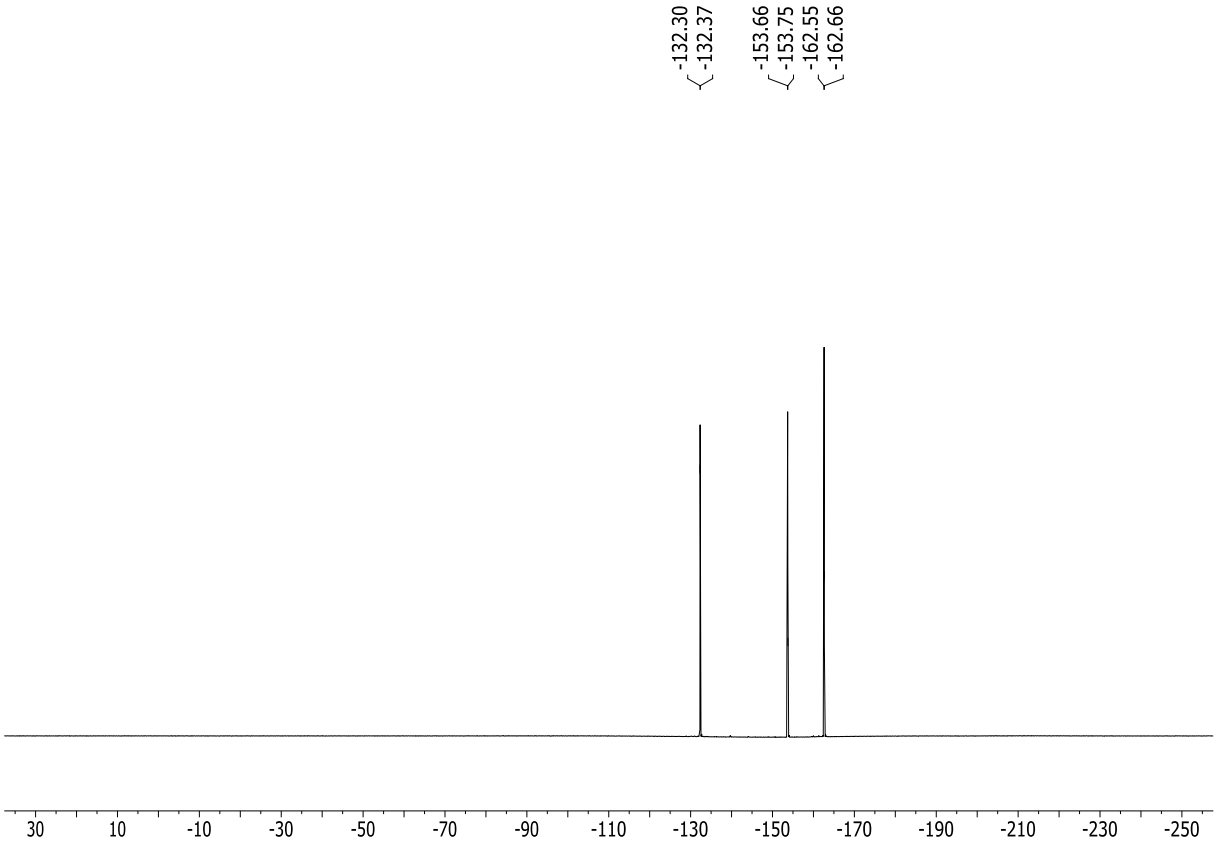
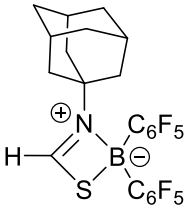


Figure S25: $^{19}F\{^{1}H\}$ NMR spectrum of **3a** (470 MHz, C_6D_6, rt).

Synthesis of 3b



A) In a Young NMR-tube, 1-adamantyl isothiocyanate **1b** (0.015 g, 0.078 mmol) was dissolved in 0.6 mL of C_6D_6. $HB(C_6F_5)_2$ (0.027 g, 0.078 mmol) was added to the solution and the sample was subsequently analyzed by multinuclear NMR spectroscopy, which revealed complete conversion of both starting materials after some minutes to yield compound **3b**.

B) 1-Adamantyl isothiocyanate (0.250 g, 1.293 mmol) was dissolved in 10 mL of toluene. $HB(C_6F_5)_2$ (0.447 g, 1.293 mmol) was added and the reaction mixture was stirred for one hour at room temperature. The solution was placed at -26 °C which results in the precipitation of colorless crystals after several days. The supernatant was removed and the crystalline material was washed with small amounts of *n*-hexane to yield **3b** as colorless crystals. These crystals were suitable for single-crystal X-ray diffraction.

Yield: 0.380 g (0.705 mmol, 55%).

Melting point: 168-170 °C.

IR (ATR): $\tilde{\nu}$ = 2920, 2857, 1648, 1538, 1520, 1462, 1385, 1359, 1305, 1291, 1259, 1229, 1116, 1100, 1045, 1025, 985, 961, 935, 924, 881, 817, 806, 783, 769, 739, 721, 681, 663, 643, 628 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 1.18-1.29 (m, 6H, $CH_{2,Ad}$), 1.51-1.52 (m, 6H, $CH_{2,Ad}$), 1.65-1.66 (m, 3H, CH_{Ad}), 7.91 (s, 1H, SC(H)=N) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 29.4 (CH_{Ad}), 35.6 ($CH_{2,Ad}$), 41.0 ($CH_{2,Ad}$), 61.6 ($C_{q,Ad}$), 114.0 (br, $B(\underline{C}_qC_5F_5)_2$), 137.8 (dm, $^1J_{C,F}$ = 248.7 Hz, $B(C_q\underline{C}_5F_5)_2$), 141.1 (dm, $^1J_{C,F}$ = 247.3 Hz, $B(C_q\underline{C}_5F_5)_2$), 148.3 (dm, $^1J_{C,F}$ = 243.0 Hz, $B(C_q\underline{C}_5F_5)_2$), 183.6 (SC(H)=N) ppm.

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 305 K): δ = 2.3 ppm

^{19}F{^{1}H} NMR (470 MHz, C_6D_6, 305 K): δ = -162.9 (m, 4F, *m*-F_{Ar}B), -155.1 (t, $^3J_{F,F}$ = 20.1 Hz, 2F, *p*-F_{Ar}B), -131.2 (m, 4F, *o*-F_{Ar}B) ($\Delta\delta^{19}F_{m,p}$ = 7.8 ppm) ppm.

EA: Anal. calcd. for $C_{23}H_{16}BF_{10}NS$: C, 51.23; H, 2.99; N, 2.60; S, 5.95; Found: C, 50.59; H, 1.96; N, 2.34; S, 4.30.

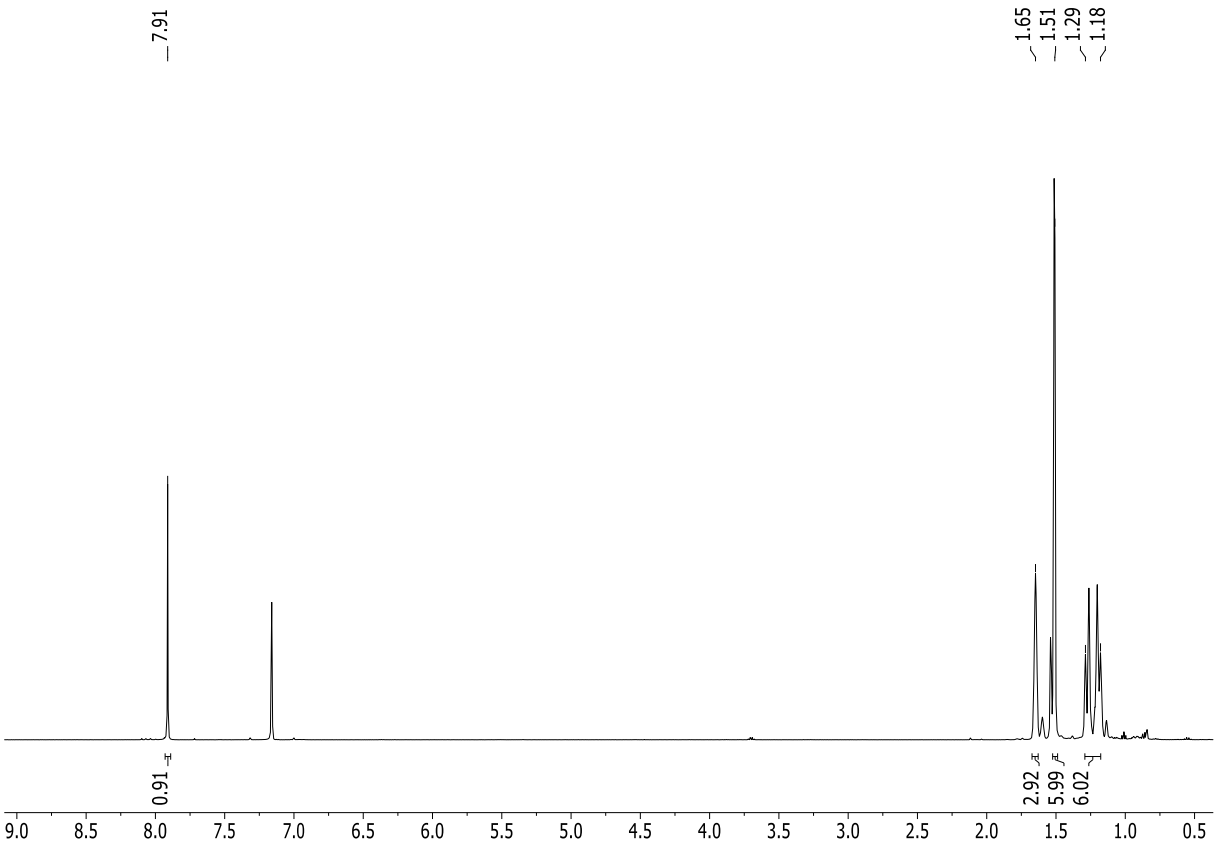


Figure S26: ^{1}H NMR spectrum of **3b** (500 MHz, C_6D_6, rt).

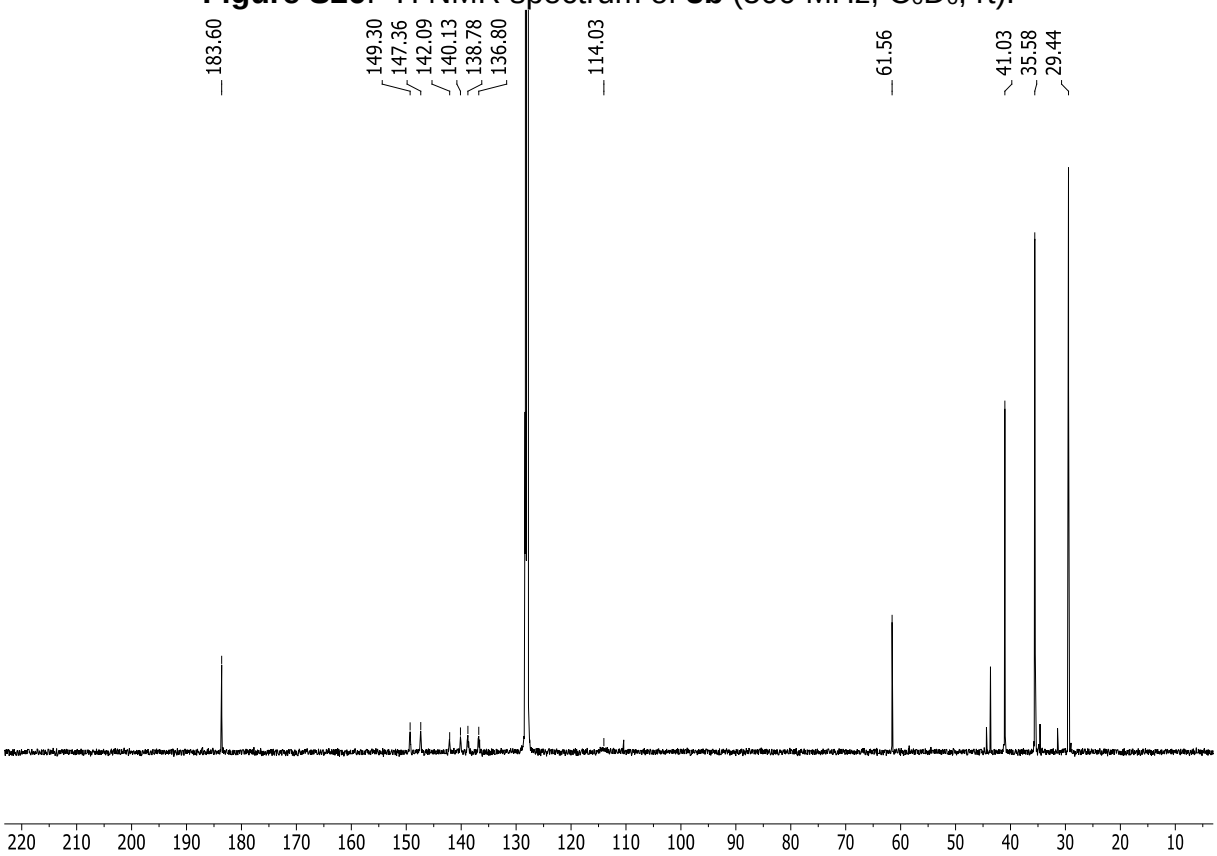


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum of **3b** (126 MHz, C_6D_6, rt).

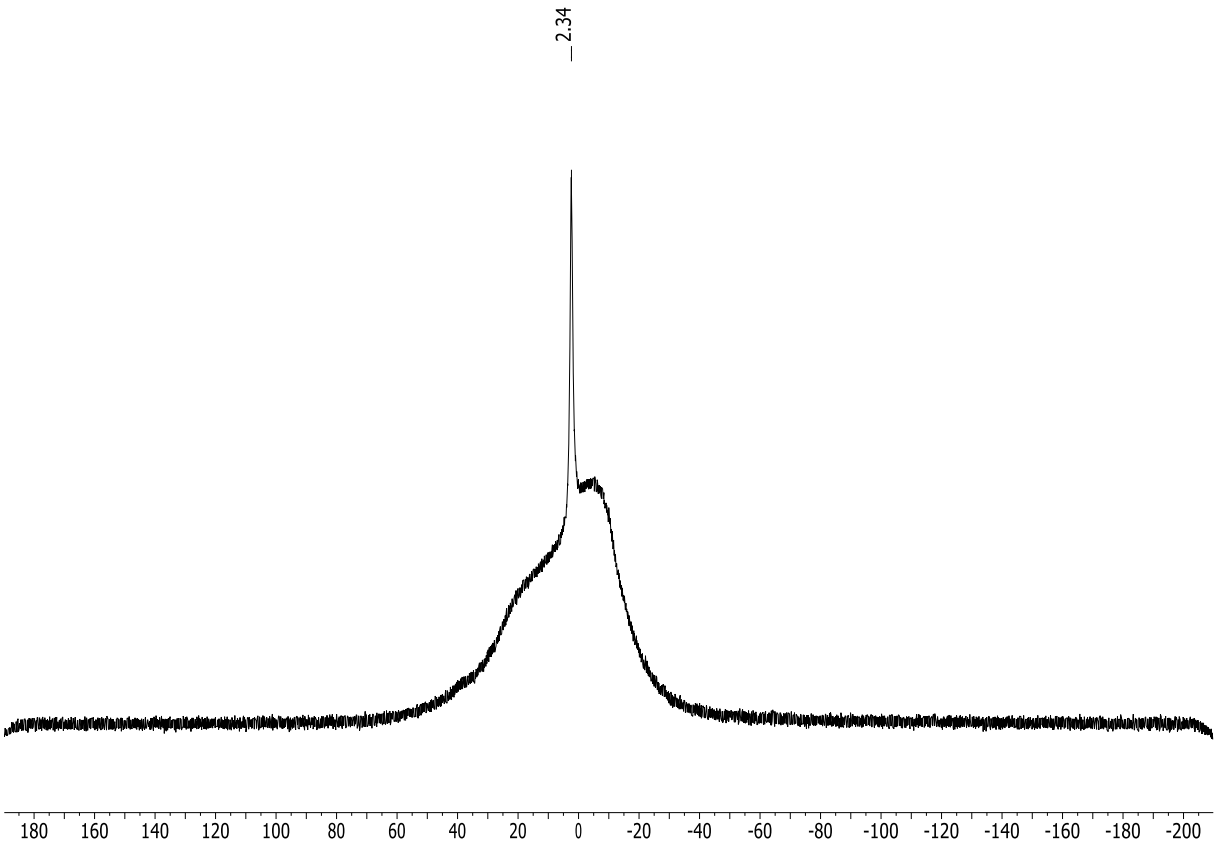


Figure S28: $^{11}B\{^{1}H\}$ NMR spectrum of **3b** (160 MHz, C_6D_6, rt).

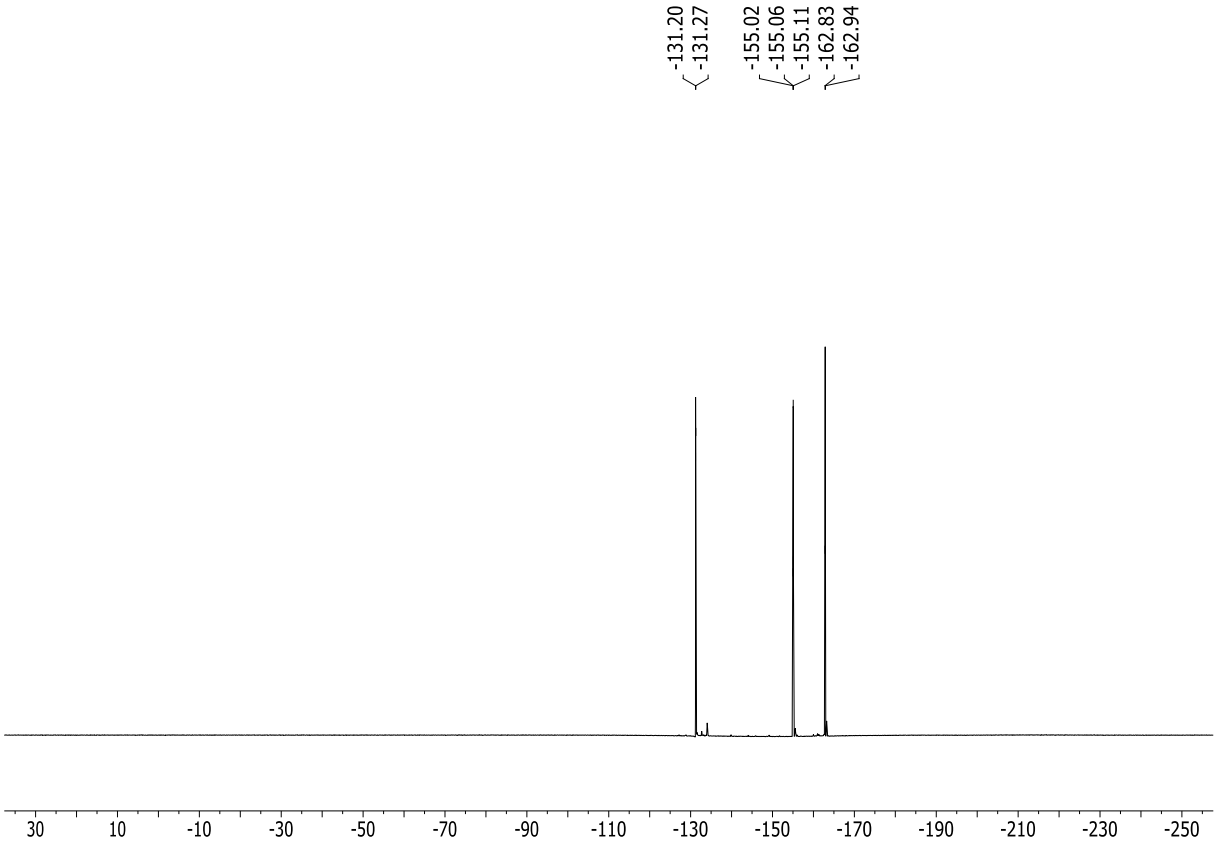
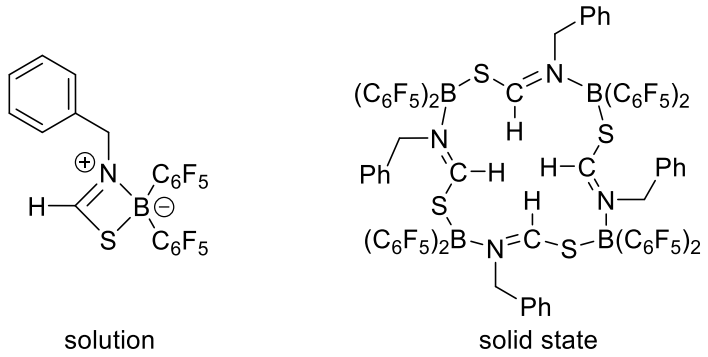


Figure S29: $^{19}F\{^{1}H\}$ NMR spectrum of **3b** (470 MHz, C_6D_6, rt).

Synthesis of 3c (4)



A) In a Young NMR-tube, benzyl isothiocyanate **1c** (0.010 g, 0.067 mmol) was dissolved in 0.6 mL of C_6D_6. $HB(C_6F_5)_2$ (0.023 g, 0.074 mmol) was added to the solution and the sample was subsequently analyzed by multinuclear NMR spectroscopy, which revealed complete conversion of both starting materials after some minutes to yield **3c**.

B) Benzyl isothiocyanate (0.065 g, 0.434 mmol) was dissolved in 10 mL of toluene. $HB(C_6F_5)_2$ (0.150 g, 1.293 mmol) was added and the reaction mixture was stirred for one hour at room temperature. All volatile components were removed under vacuum and the residue was washed several times with *n*-hexane followed by drying of the residue under vacuum to yield **4** as a colorless solid.

Crystals suitable for single crystal X-ray diffraction were obtained by layering the C_6D_6 solution of attempt **A** with *n*-hexane. Two types of differently shaped crystals were obtained (**4** and the other **4**•C_6D_6).

Yield: 0.148 g (0.299 mmol, 69%).

Melting point: 185-187 °C.

IR (ATR): $\tilde{\nu}$ = 2963, 1646, 1561, 1520, 1460, 1383, 1355, 1293, 1260, 1094, 1038, 1028, 980, 931, 866, 799, 779, 762, 744, 722, 692, 675, 647, 633, 613 cm^{-1}.

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 4.12 (s, 2H, CH_2), 6.68-6.70 (m, 2H, CH_{Ph}), 6.90-6.95 (m, 3H, CH_{Ph}), 7.25 (s, 1H, SC(H)=N) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 57.1 (CH_2), 129.2 (CH_{Ph}), 129.4 (CH_{Ph}), 129.7 (CH_{Ph}), 132.4 ($C_{q,Ph}$), 113.1 ($B(\underline{C}_qC_5F_5)_2$), 137.7 (dm, $^1J_{C,F}$ = 249.9 Hz, $B(C_q\underline{C}_5F_5)_2$), 141.1 (dm, $^1J_{C,F}$ = 251.5 Hz, $B(C_q\underline{C}_5F_5)_2$), 147.8 (dm, $^1J_{C,F}$ = 240.0 Hz, $B(C_q\underline{C}_5F_5)_2$), 186.2 (SC(H)=N) ppm.

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 305 K): δ = 3.1 ppm

$^{19}F\{^{1}H\}$ NMR (470 MHz, C_6D_6, 305 K): δ = -162.8 (m, 4F, *m*-$F_{Ar}B$), -155.0 (t, $^{3}J_{F,F}$ = 20.8 Hz, 2F, *p*-$F_{Ar}B$), -132.0 (m, 4F, *o*-$F_{Ar}B$) ($\Delta\delta^{19}F_{m,p}$ = 7.8 ppm) ppm.

EA: Anal. calcd. for $C_{20}H_8BF_{10}NS$: C, 48.52; H, 1.63; N, 2.83; S, 6.47; Found: C, 47.86; H, 1.02; N, 2.38; S, 4.75.

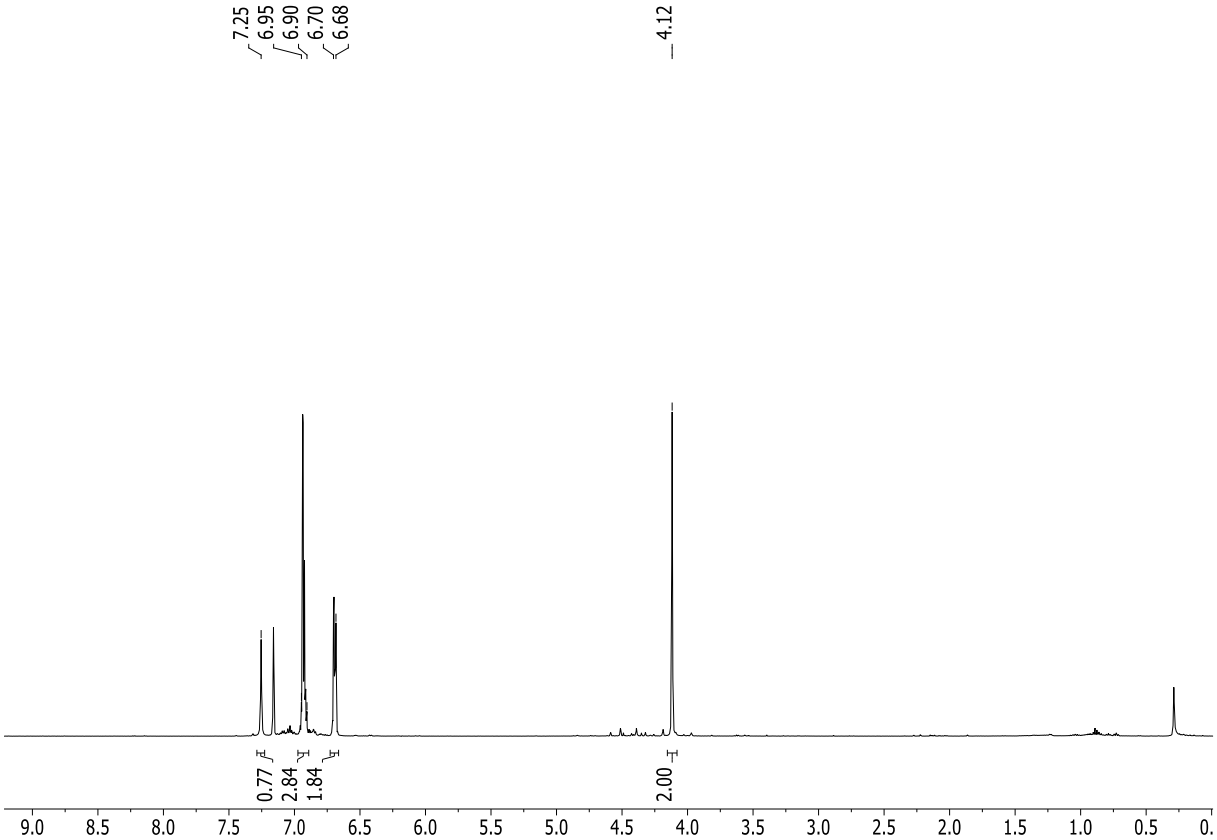


Figure S30: ^{1}H NMR spectrum of **3c** (500 MHz, C_6D_6, rt); 0.29 ppm: silicon grease.

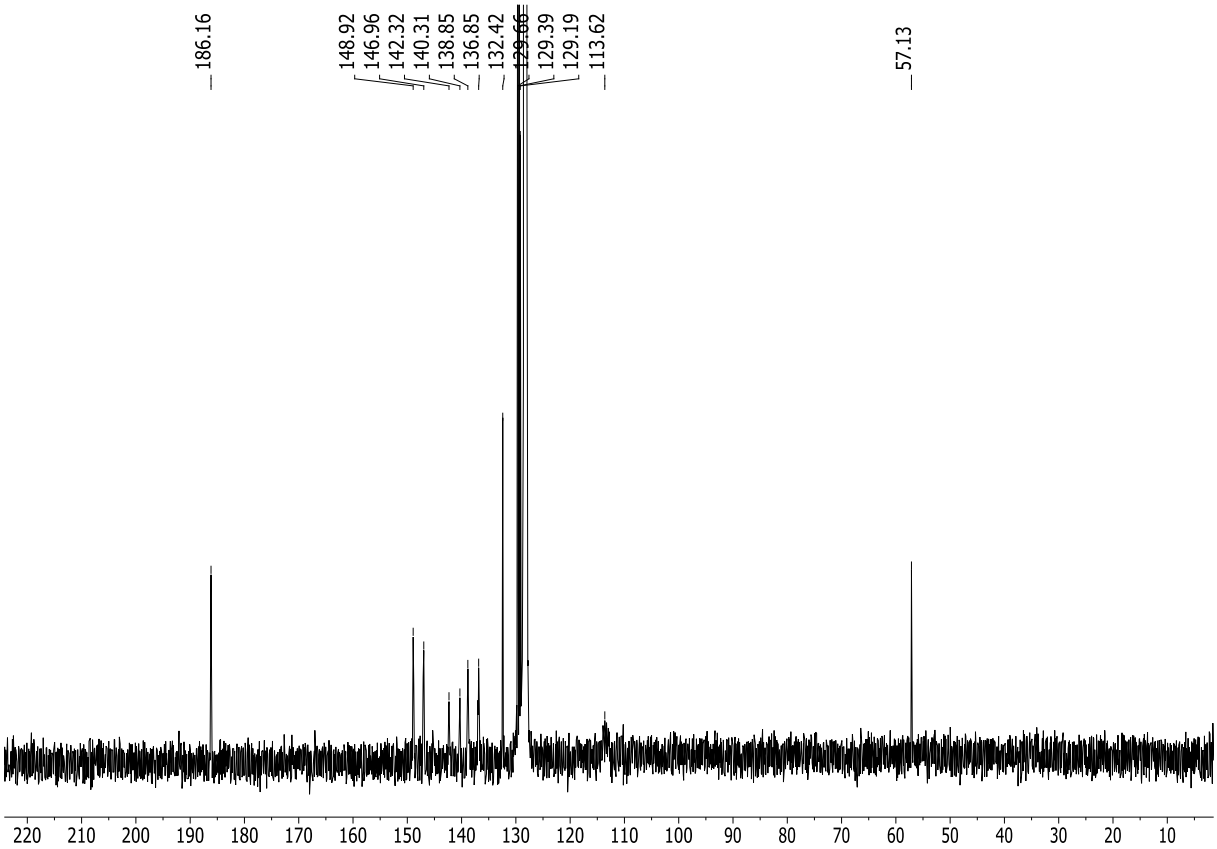


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum of **3c** (126 MHz, C_6D_6, rt).

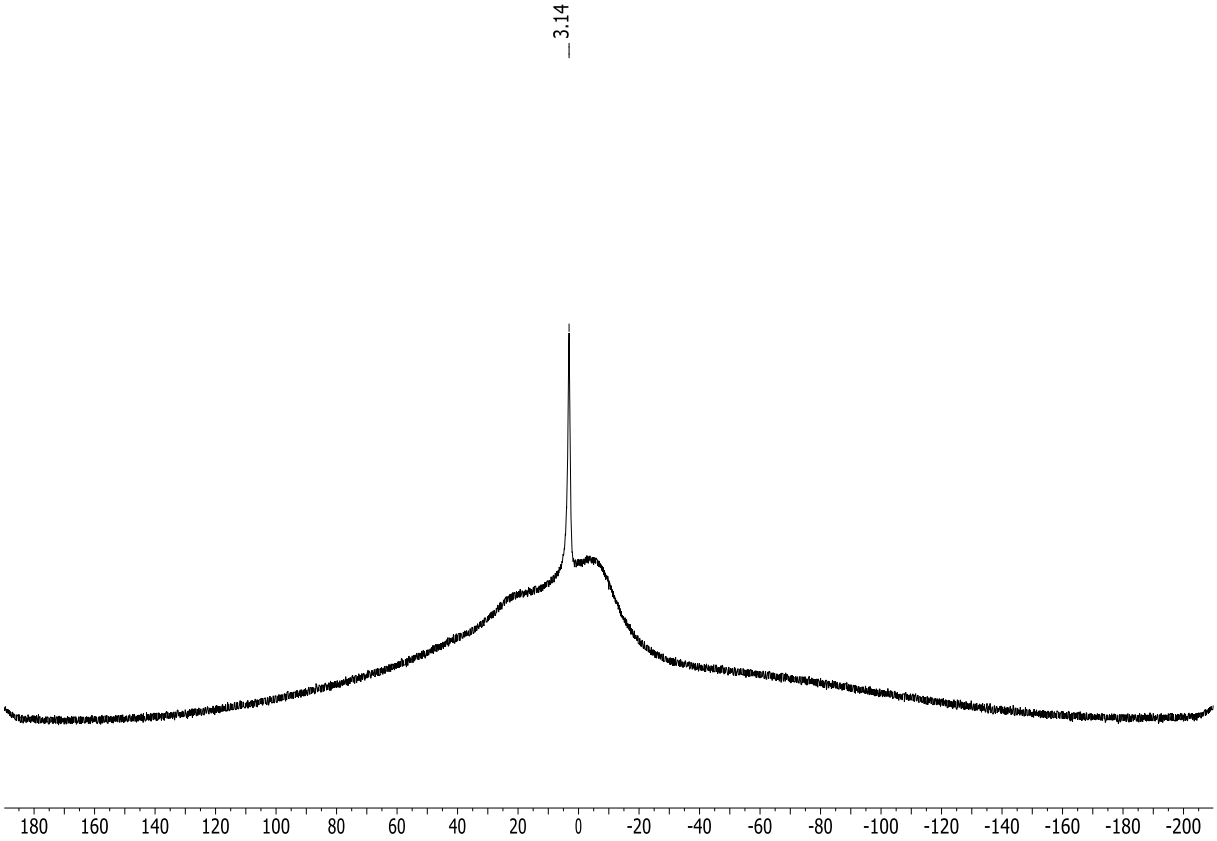


Figure S32: $^{11}B\{^{1}H\}$ NMR spectrum of **3c** (160 MHz, C_6D_6, rt).

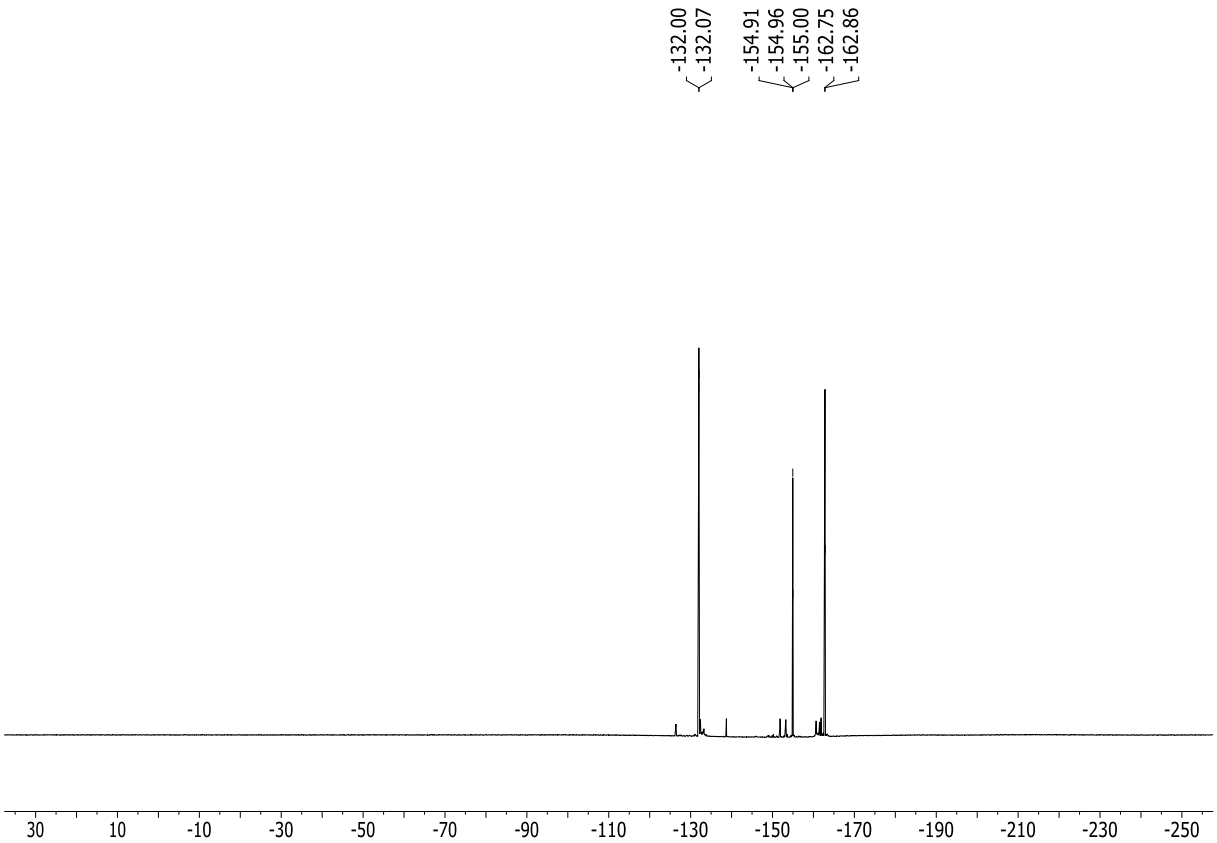


Figure S33: $^{19}F\{^{1}H\}$ NMR spectrum of **3c** (470 MHz, C_6D_6, rt).

Table S1: Selected NMR data of compounds 3a-c and HC(O)(NPh)Bpin[S14].[a]

	δ^{1}H/δ^{13}C N=C(H)–S	δ^{11}B	δ^{19}F ($\Delta\delta^{19}F_{m,p}$[b])
3a	7.87 / 183.1	3.7	-162.6, -153.7, -132.3 (8.9)
3b	7.91 / 183.6	2.3	-162.9, -155.1, -131.2 (7.8)
3c	7.25 / 186.2	3.1	-162.8, -155.0, -132.0 (7.8)
HC(O)(NPh)Bpin	8.10 / 168.7	5.1	-

[a]: Measurements were carried out in C_6D_6 at room temperature and values are given in ppm.

[b]: The planar structure of three-coordinate boron atoms effect the resonance between the empty 2p orbital localized at the boron atom and the neighboring perfluorinated aryl π system, leading to distinct deshielding of the *para*-fluorine atoms, which is hampered by coordination of a fourth substituent. As a consequence, the corresponding signal in the ^{19}F NMR spectrum is shifted to higher field, whereas the *meta*-fluorine atoms remain unaffected by the pyramidalization of the boron atom. Accordingly, the difference in the ^{19}F NMR chemical shifts $\Delta\delta^{19}F_{m,p}$ becomes smaller. For a more detailed description see S15.

DOSY Experiments

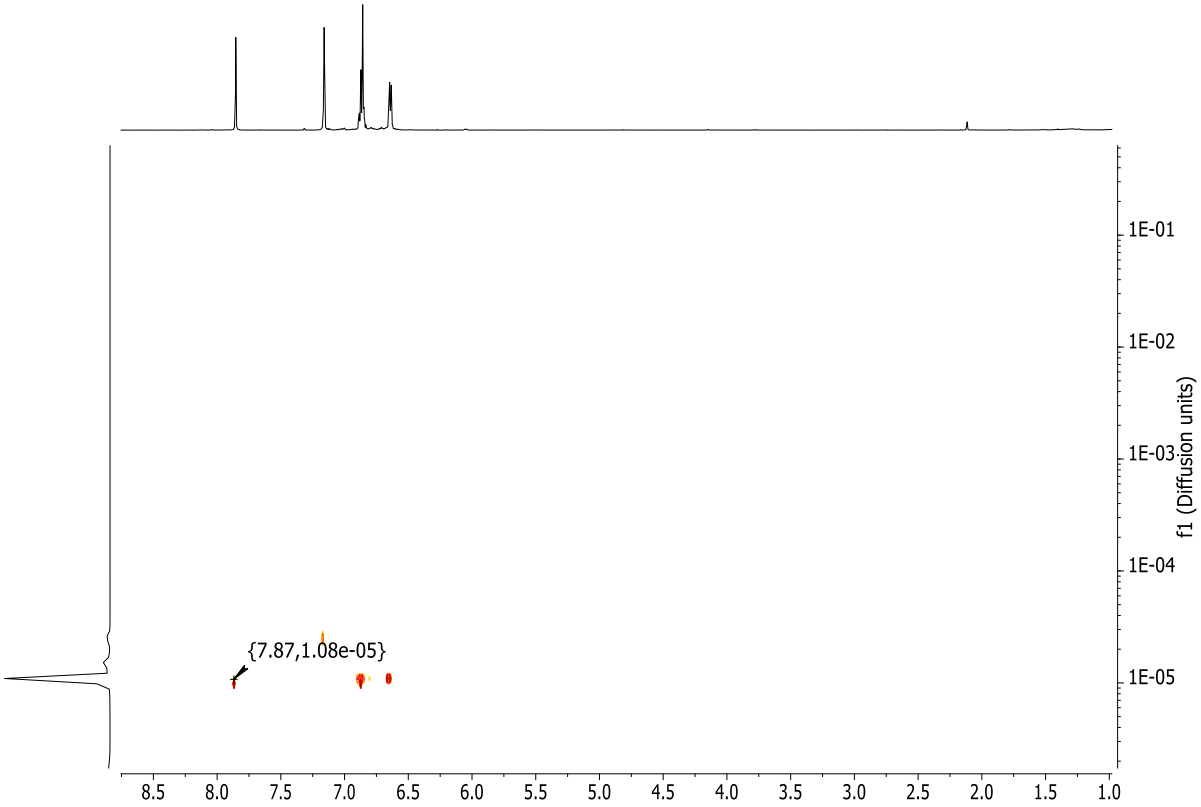


Figure S34: ^{1}H DOSY NMR of **3a**.

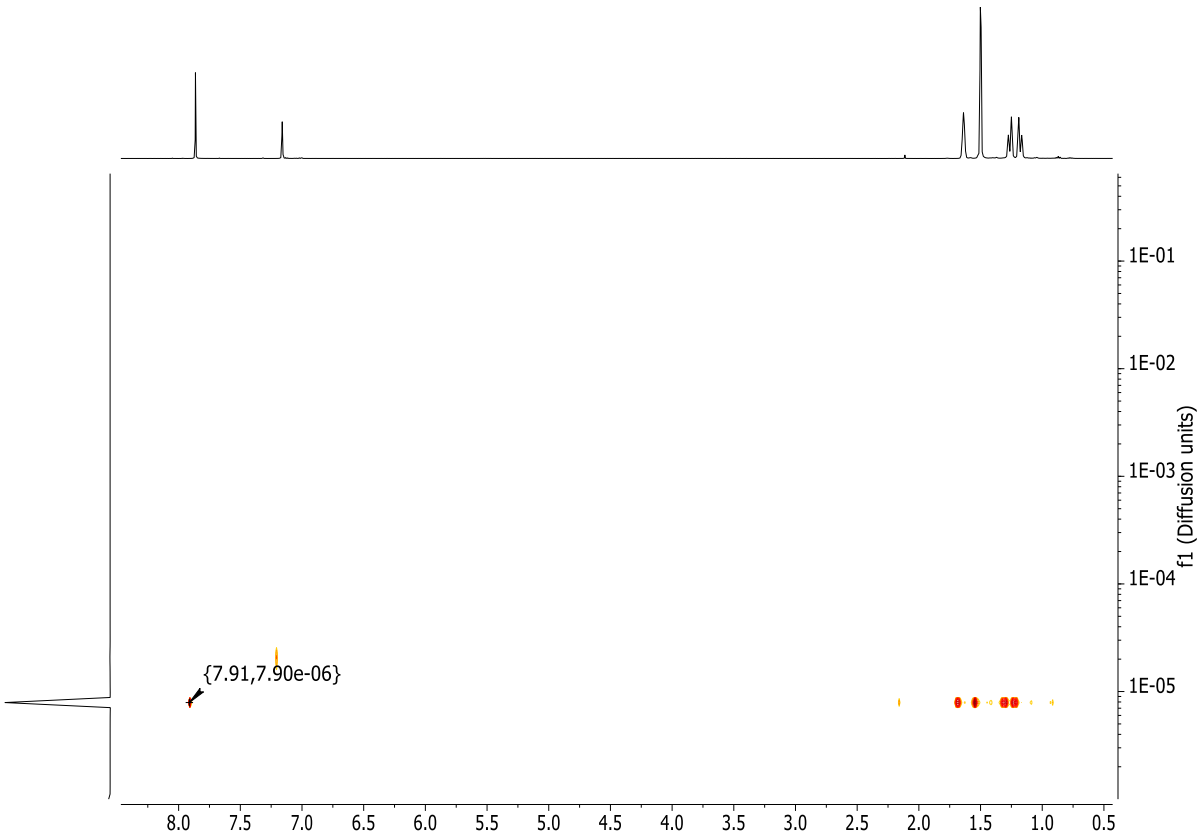


Figure S35: ^{1}H DOSY NMR of **3b**.

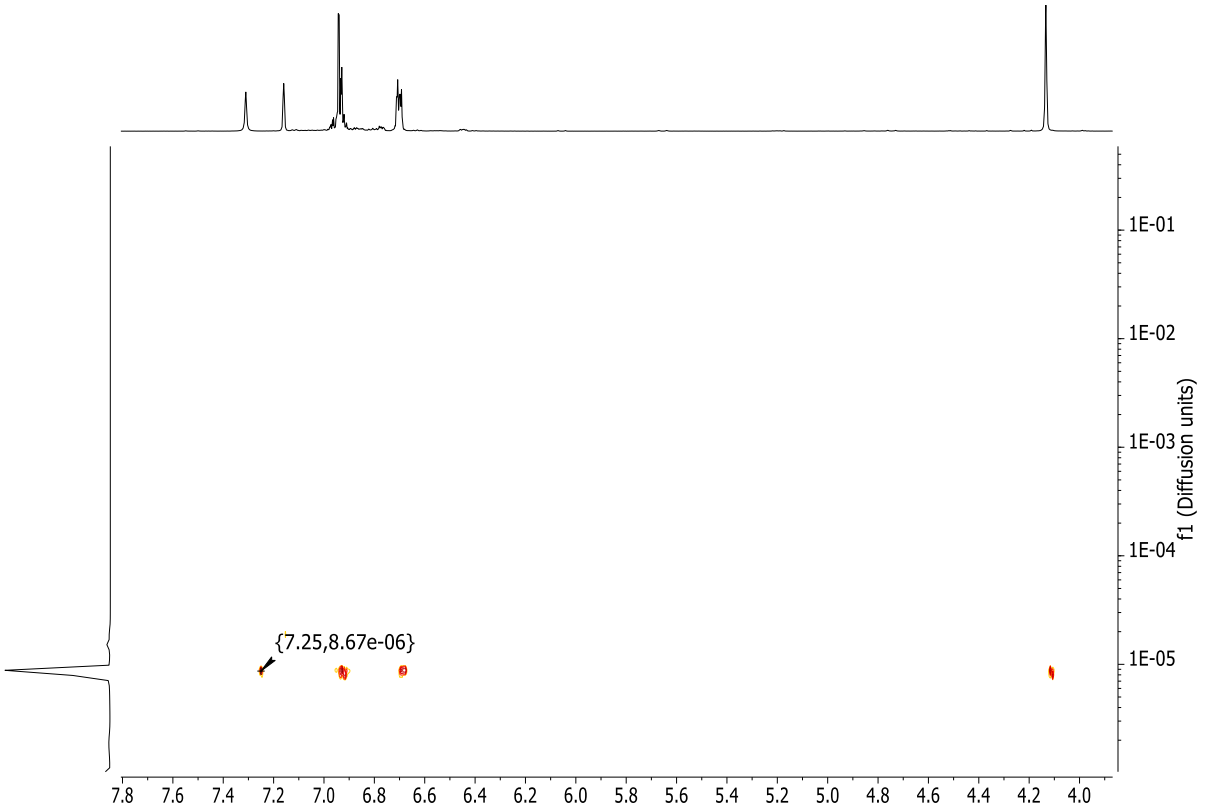
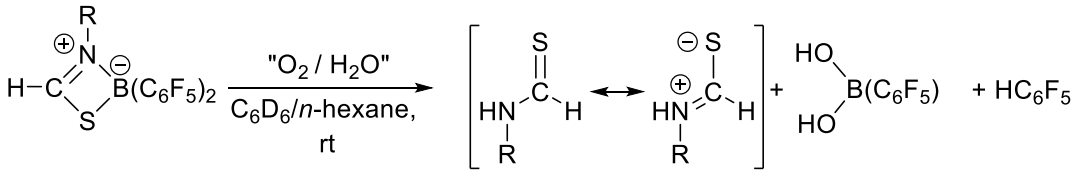


Figure S36: ^{1}H DOSY NMR of **3c**.

Table S2: Parameters derived from the ^{1}H DOSY NMR experiments of **3a**-**c**.

	D (cm^2/s)	D (m^2/s)	log D
3a	$1.08 \cdot 10^{-5}$	$1.08 \cdot 10^{-8}$	
3b	$7.90 \cdot 10^{-6}$	$7.90 \cdot 10^{-9}$	-8.10
3c	$8.67 \cdot 10^{-6}$	$8.67 \cdot 10^{-9}$	-8.06

Exposure of 3a and 3b to air and moisture:



3a: R = Ph
3b: R = Ad

5a: R = Ph
5b: R = Ad

6

7

The above mentioned NMR samples of **3a** and **3b** were slowly evaporated without protection from atmospheric moisture (the sample of **3a** was layered with *n*-hexane in advance), which resulted in the formation of two differently types of crystals in the case of **3b**. Single crystal X-ray diffraction and subsequent comparison of the unit cell parameters are in accordance to the formation of the previously reported boron containing compound $B(OH)_2(C_6F_5)_2$ (**6**) and *N*-(1-adamantyl)methanethioamide (**5b**). The product mixture was subsequently solved in C_6D_6 and NMR analyses verified, that also the 1,2,3,4,5-pentafluorobenzene (**7**) was formed during the hydrolysis of **3b**.

In the case of the sample of **3a**, colorless needles were formed which were also suitable for single crystal X-ray diffraction analysis. It was shown that the corresponding *N*-phenylmethanethioamide (**5a**) was formed during this reaction.

Literature data[S5-S8]

Table S3: Unit cell parameters of **6**.

Unit cell parameters of **6** (measured):	Unit cell parameters of **6** (ref. S5):
T = 100(2) K	T = 240 K
a = 7.33 Å; α = 90°	a = 7.45 Å; α = 90°
b = 4.98 Å; β = 96.08°	b = 5.01 Å; β = 96.78°
c = 9.86 Å; γ = 90° V = 358 Å^3	c = 10.06 Å; γ = 90° V = 372 Å^3
	CCDC: 940263

NMR data of the product mixture

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 1.18-1.30 (m, 12H, $CH_{2,Ad}$), 1.64-1.65 (m, 3H, CH_{Ad}), 5.04 (m(br), $B(OH)_2$), 5.84-5.86 (m, 1H, HC_6F_5), 8.12 (s(br), 1H, NH), 9.17 (d, $^3J_{H,H}$ = 15.5 Hz, HC=S) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 29.4 (CH_{Ad}), 35.7 ($CH_{2,Ad}$), 42.5 ($CH_{2,Ad}$), 55.5 ($C_{q,Ad}$), 187.1 (HC=S) ppm.

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 305 K): δ = 26.8 ppm

^{19}F{^{1}H} NMR (470 MHz, C_6D_6, 305 K): δ = -162.1 (m, 2F, *m*-F_{Ar}B), -151.2 (t, $^3J_{F,F}$ = 20.3 Hz, 1F, *p*-F_{Ar}B), -132.7 (m, 2F, *o*-F_{Ar}B) ($\Delta\delta^{19}F_{m,p}$ = 10.3 ppm); -162.4 (m,

2F, *m*-$F_{Ph}C_{q,ipso}$), -154.1 (t, $^{3}J_{F,F}$ = 20.7 Hz, 1F, *p*-$F_{Ph}C_{q,ipso}$), -139.1 (m, 2F, *o*- $F_{Ph}C_{q,ipso}$) ($\Delta\delta^{19}F_{m,p}$ = 8.3 ppm) ppm.

^{15}N NMR (202 MHz, C_6D_6, 305 K): δ = 185.9 ppm.

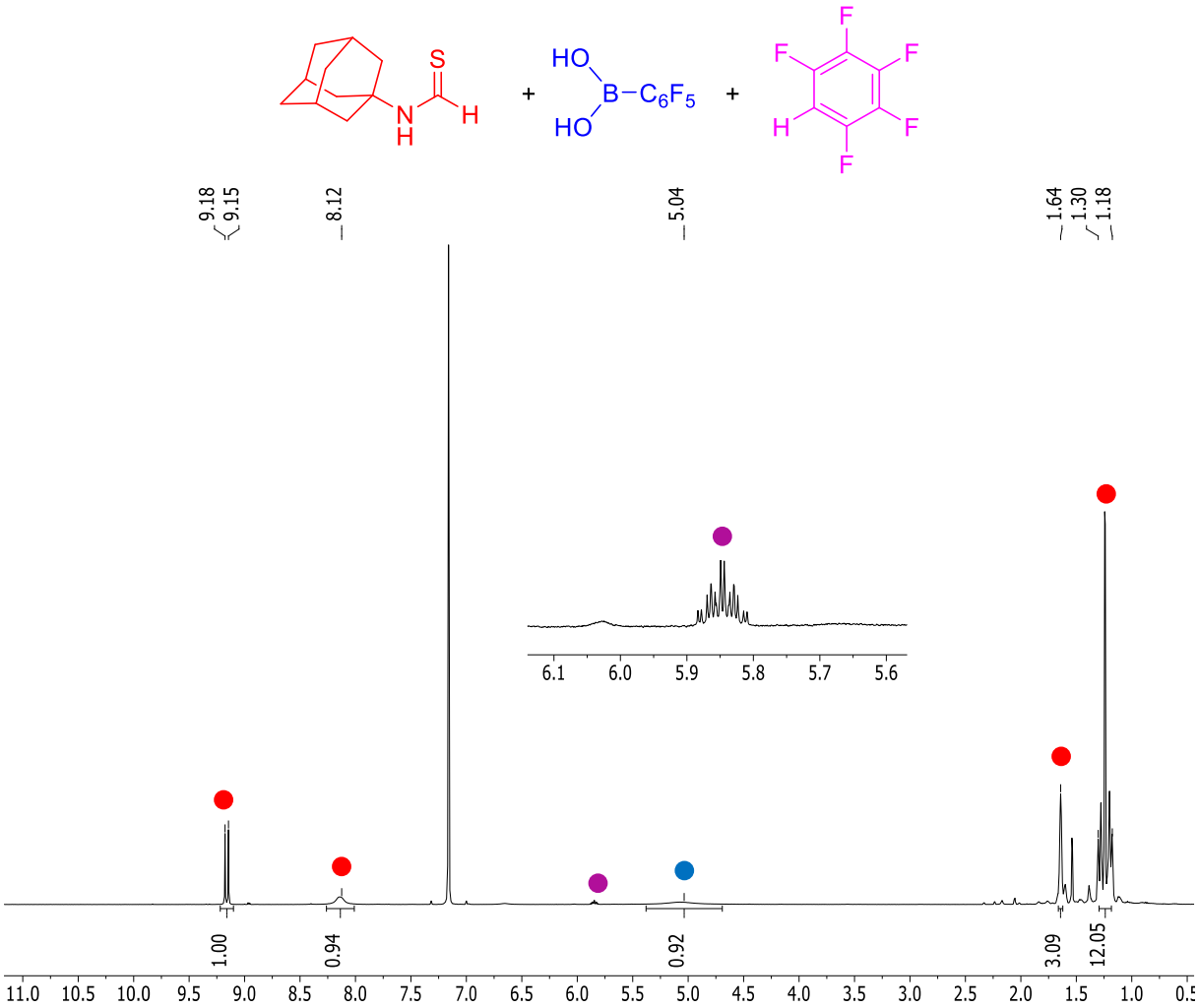


Figure S37: ^{1}H NMR spectrum of the product mixture of the hydrolysis of **3b** (500 MHz, C_6D_6, rt).

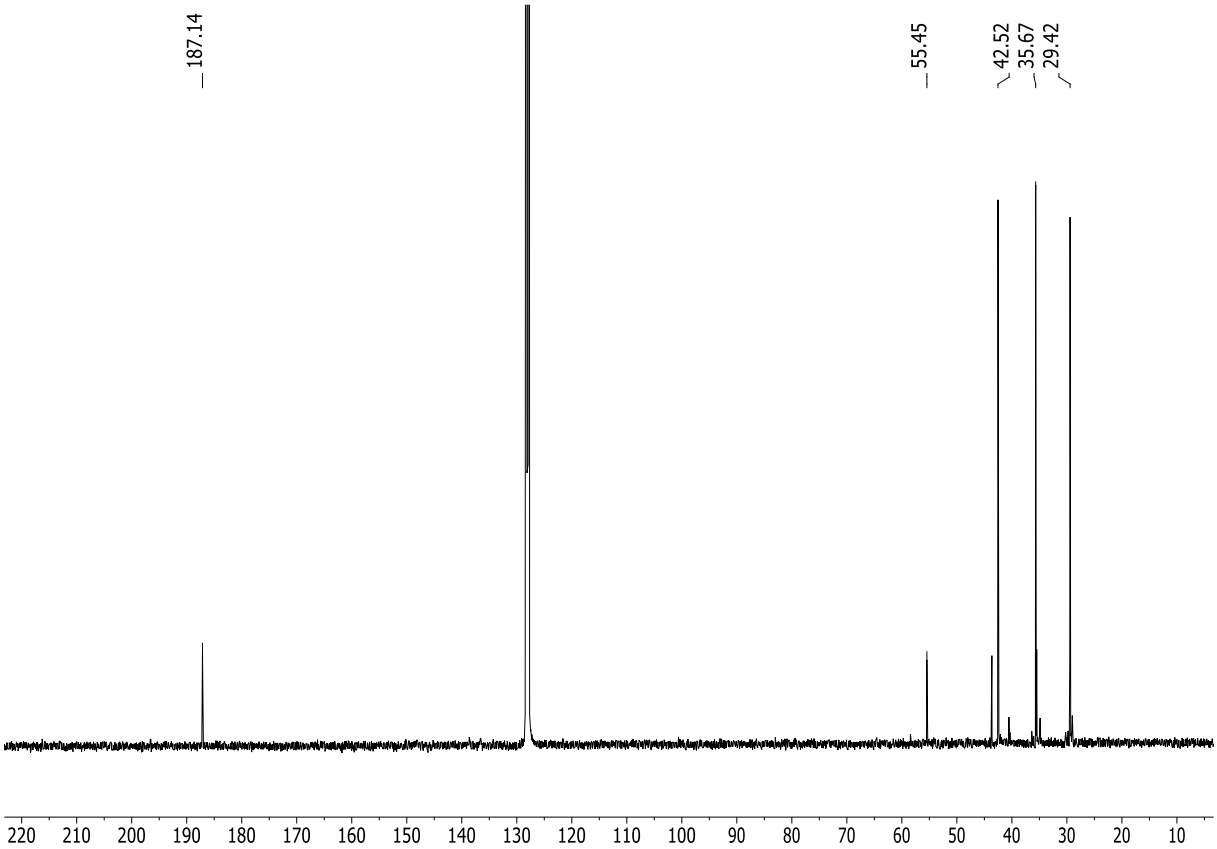


Figure S38: $^{13}C\{^{1}H\}$ NMR spectrum of the product mixture of the hydrolysis of **3b** (126 MHz, C_6D_6, rt).

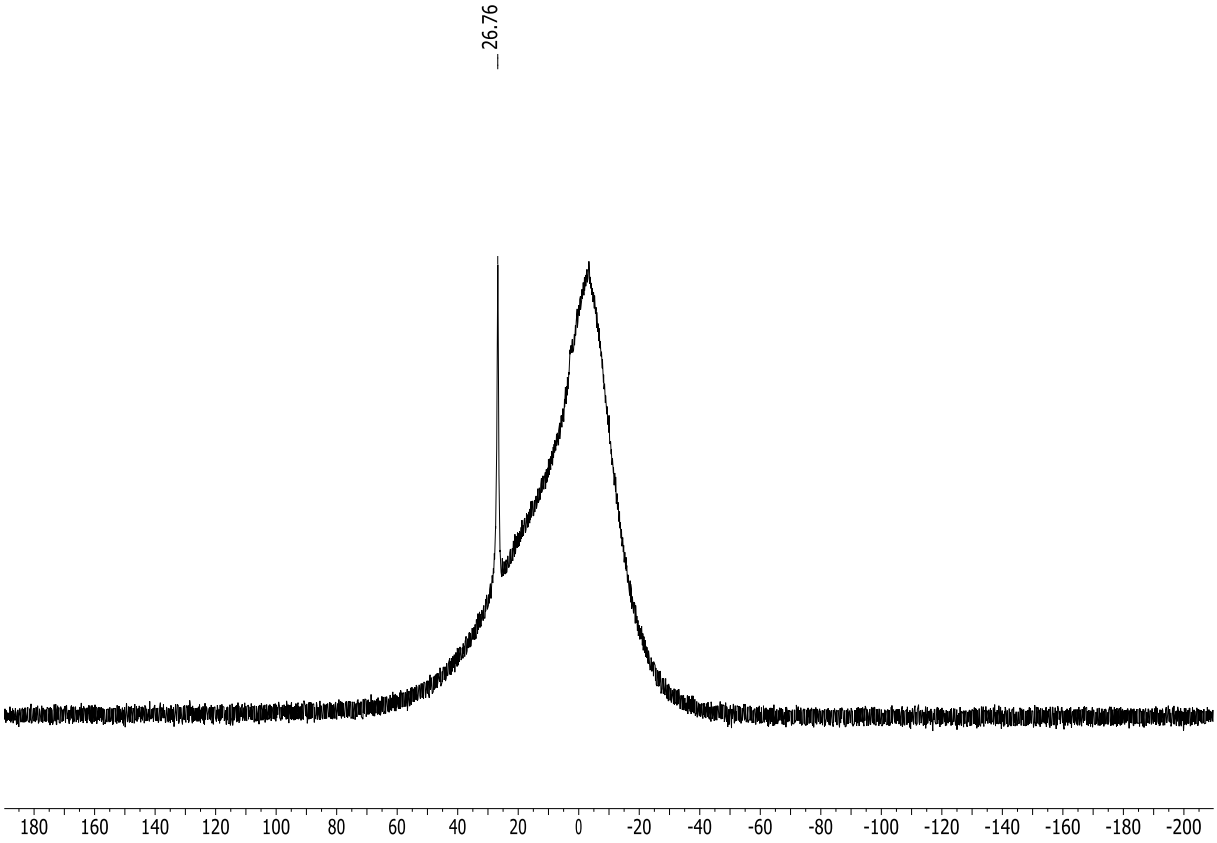


Figure S39: $^{11}B\{^{1}H\}$ NMR spectrum of the product mixture of the hydrolysis of **3b** (160 MHz, C_6D_6, rt).

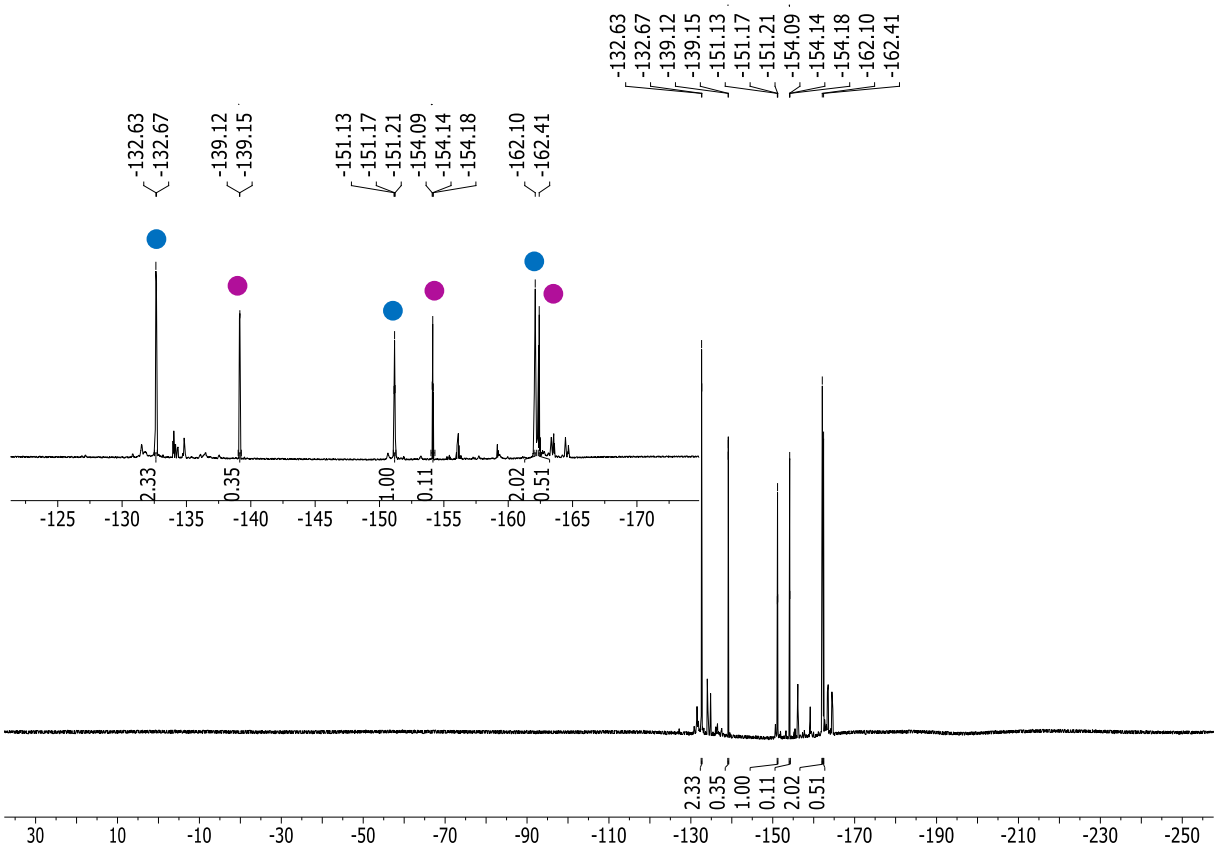


Figure S40: $^{19}F\{^{1}H\}$ NMR spectrum of the product mixture of the hydrolysis of **3b** (470 MHz, C_6D_6, rt).

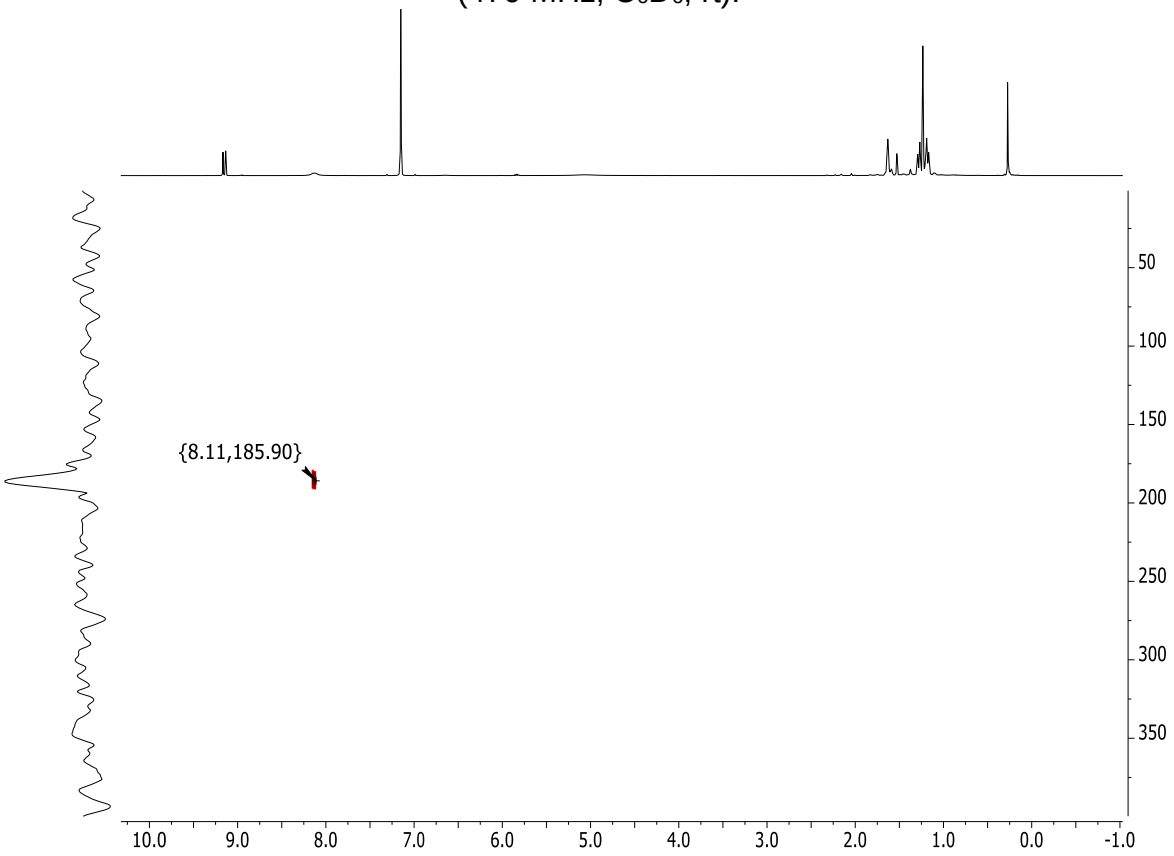


Figure S41: $^{15}N/^{1}H$ HMQC NMR spectrum of the product mixture of the hydrolysis of **3b** (51 MHz, C_6D_6, rt).

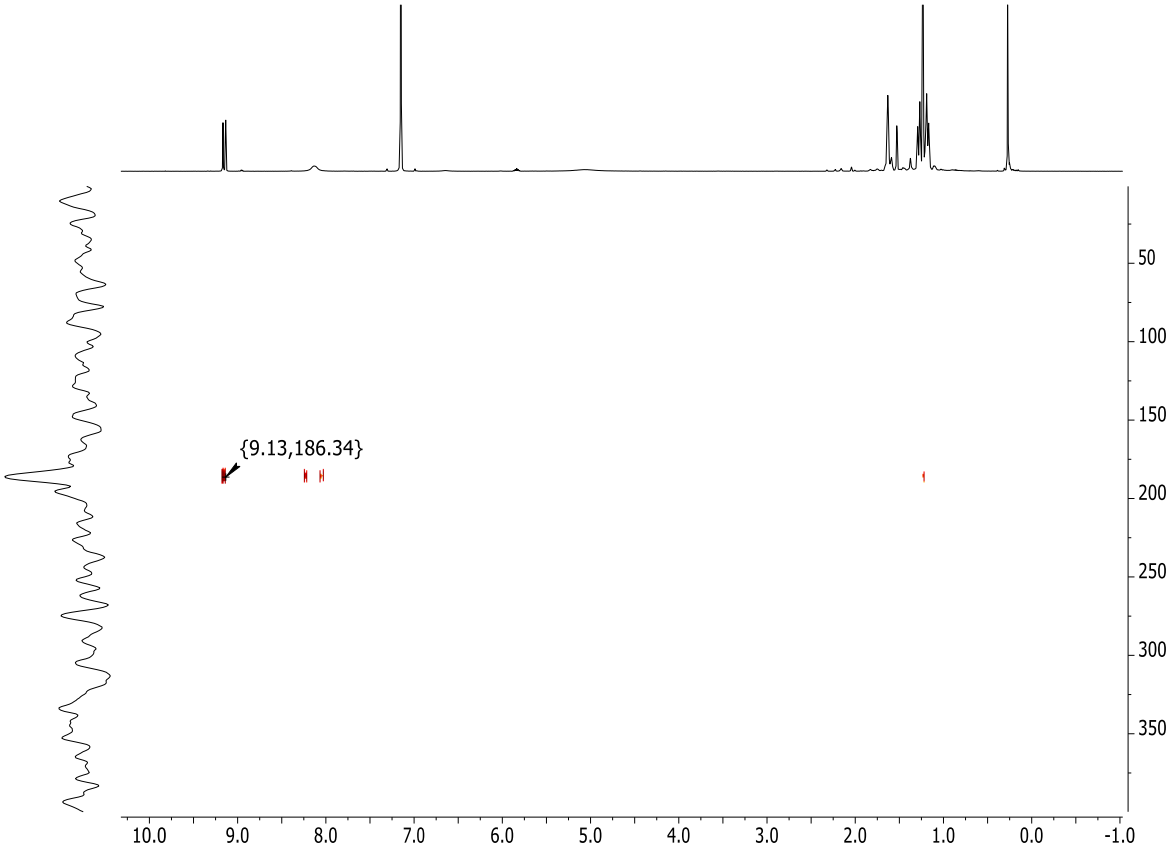
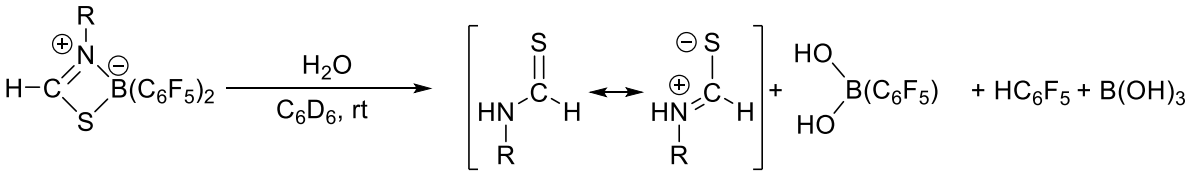


Figure S42: $^{15}N/^{1}H$ HMBC NMR spectrum of the product mixture of the hydrolysis of **3b** (51 MHz, C_6D_6, rt).

Reaction of 3b with H_2O:



3b: R = Ad **5b**: R = Ad **6** **7** **8**

3b (0.032 g, 0.059 mmol) was dissolved in 0.6 mL of C_6D_6. One drop of water (approx. 5 mg) were added and the sample was subsequently analyzed over time by ^{1}H NMR analysis. The evaluation of the NMR data and comparison with the literature verified that the compounds **5b** and **6**-**8** are obtained.[S5-S8, S13]

NMR data of the product mixture

^{1}H NMR (500 MHz, C_6D_6, 305 K): δ = 1.19-1.31 (m, 12H, $CH_{2,Ad}$), 1.64-1.65 (m, 3H, CH_{Ad}), 5.04 (m(br), $B(OH)_2$), 5.84-5.86 (m, 1H, HC_6F_5), 8.12 (s(br), 1H, NH), 9.12 (d, $^3J_{H,H}$ = 15.0 Hz, HC=S) ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 305 K): δ = 29.4 (CH_{Ad}), 35.6 ($CH_{2,Ad}$), 42.4 ($CH_{2,Ad}$), 55.7 ($C_{q,Ad}$), 186.9 (HC=S) ppm.

^{11}B{^{1}H} NMR (160 MHz, C_6D_6, 305 K): δ = 26.8 ($(HO)_2B(C_6F_5)$), 21.3 ($(HO)B(C_6F_5)_2$) ppm

^{19}F{^{1}H} NMR (470 MHz, C_6D_6, 305 K): δ = -162.2 (m, 2F, *m*-F_{Ar}B), -151.4 (t, $^3J_{F,F}$ = 20.3 Hz, 1F, *p*-F_{Ar}B), -132.7 (m, 2F, *o*-F_{Ar}B) ($\Delta\delta^{19}F_{m,p}$ = 10.8 ppm); -162.5 (m, 2F, *m*-$F_{Ph}C_{q,ipso}$), -154.2 (t, $^3J_{F,F}$ = 20.7 Hz, 1F, *p*-$F_{Ph}C_{q,ipso}$), -139.2 (m, 2F, *o*- $F_{Ph}C_{q,ipso}$) ($\Delta\delta^{19}F_{m,p}$ = 8.3 ppm) ppm.

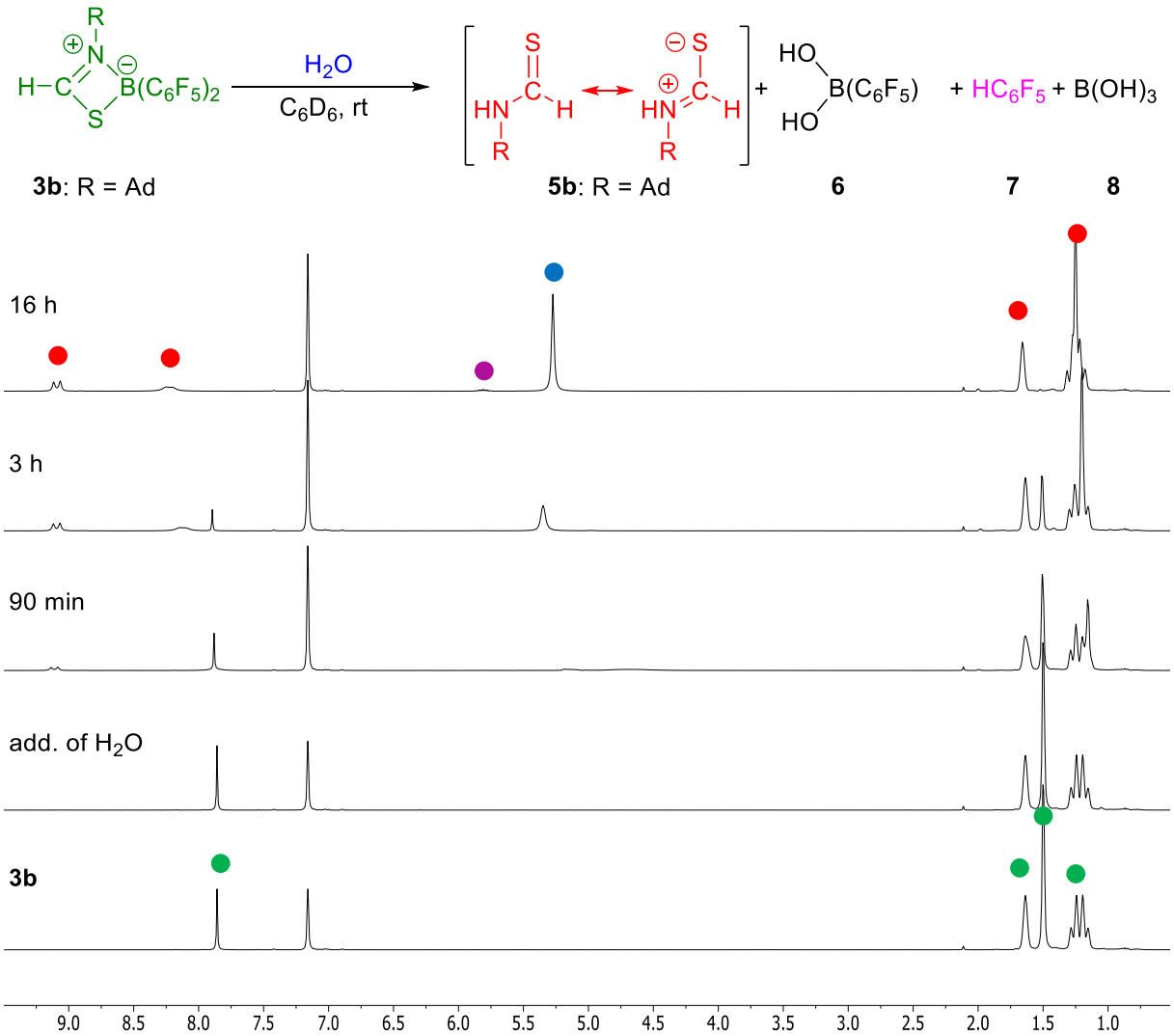


Figure S43: Time resolved ^{1}H NMR spectrum of the reaction of **3b** with water (500 MHz, C_6D_6, rt).

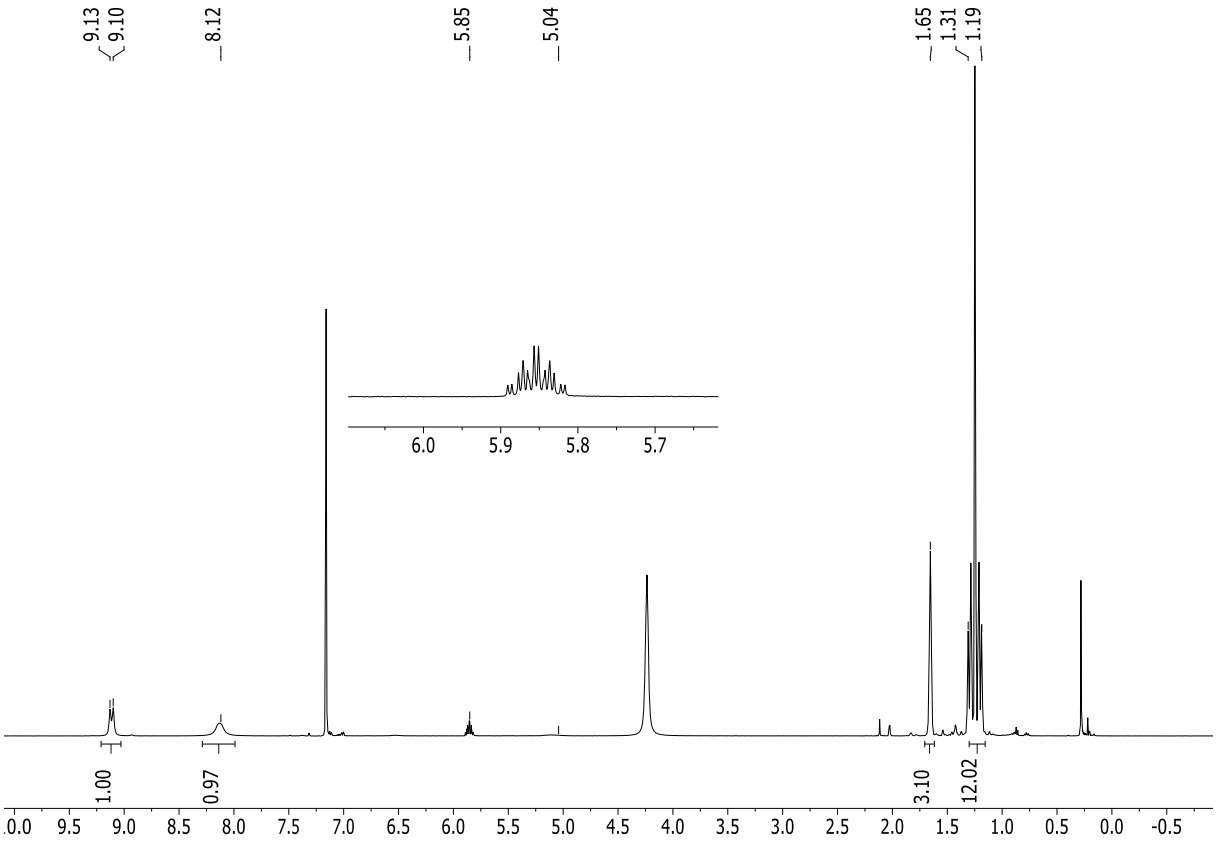


Figure S44: ^{1}H NMR spectrum of the reaction of **3b** with water (500 MHz, C_6D_6, rt).

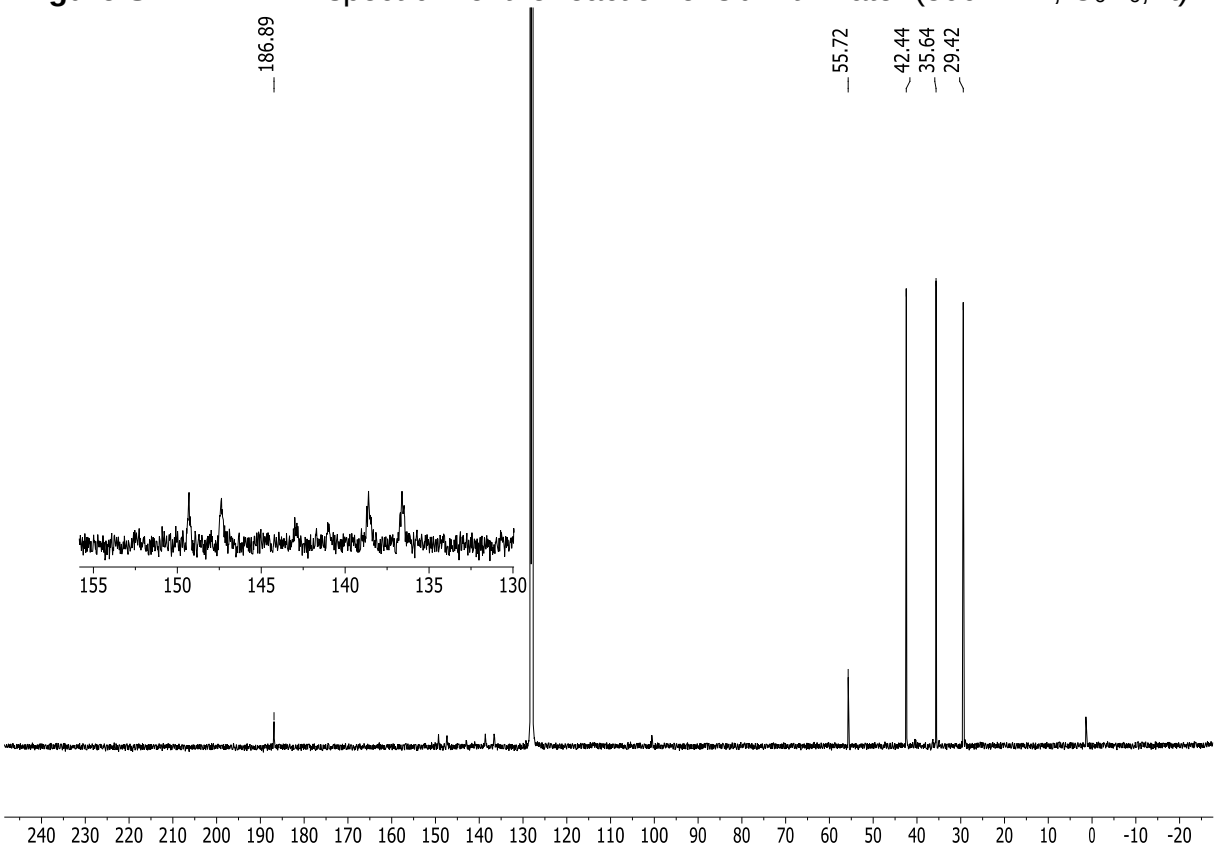


Figure S45: $^{13}C\{^{1}H\}$ NMR spectrum of the reaction of **3b** with water (126 MHz, C_6D_6, rt).

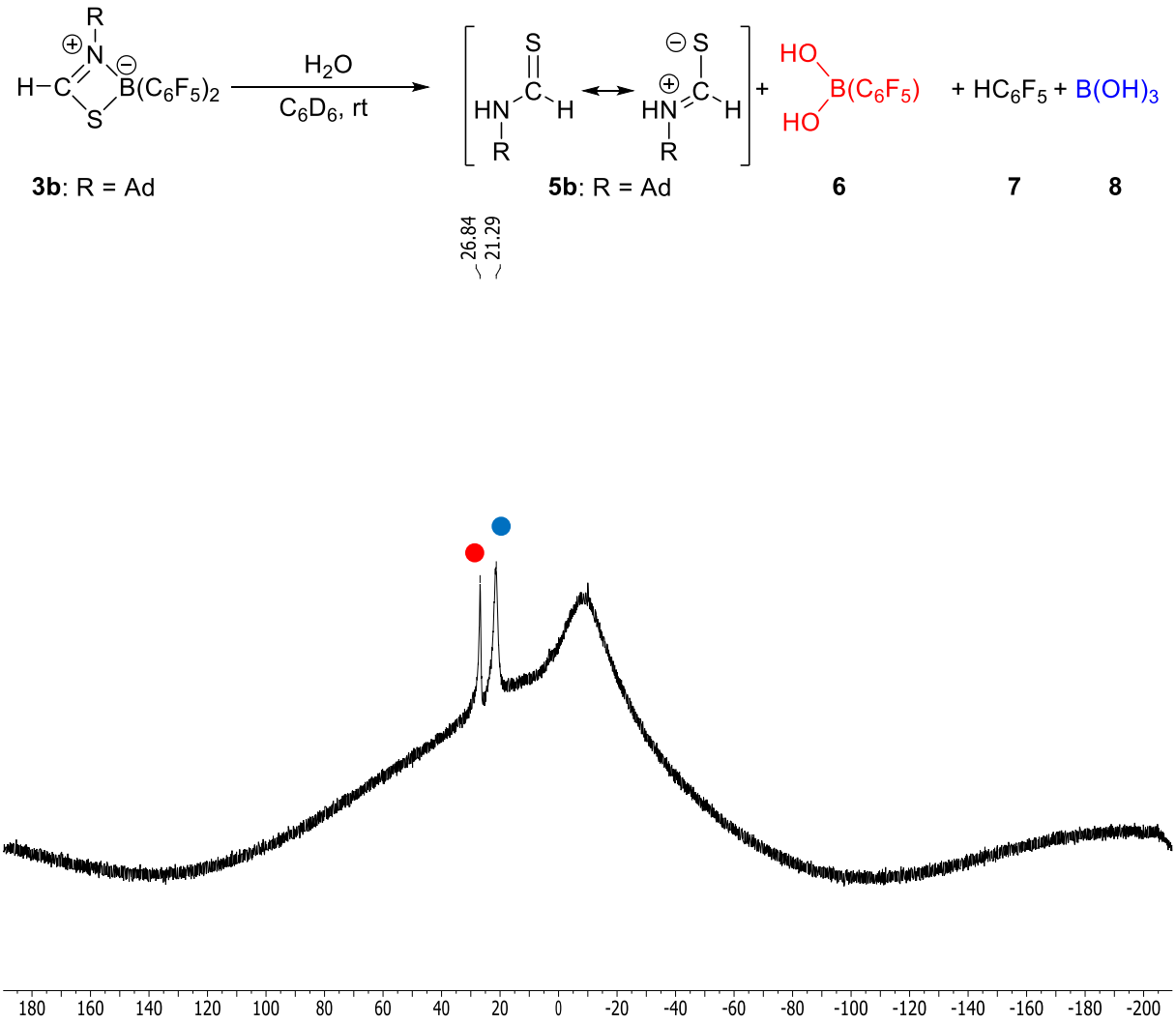


Figure S46: $^{11}B\{^{1}H\}$ NMR spectrum of the reaction of **3b** with water (160 MHz, C_6D_6, rt).

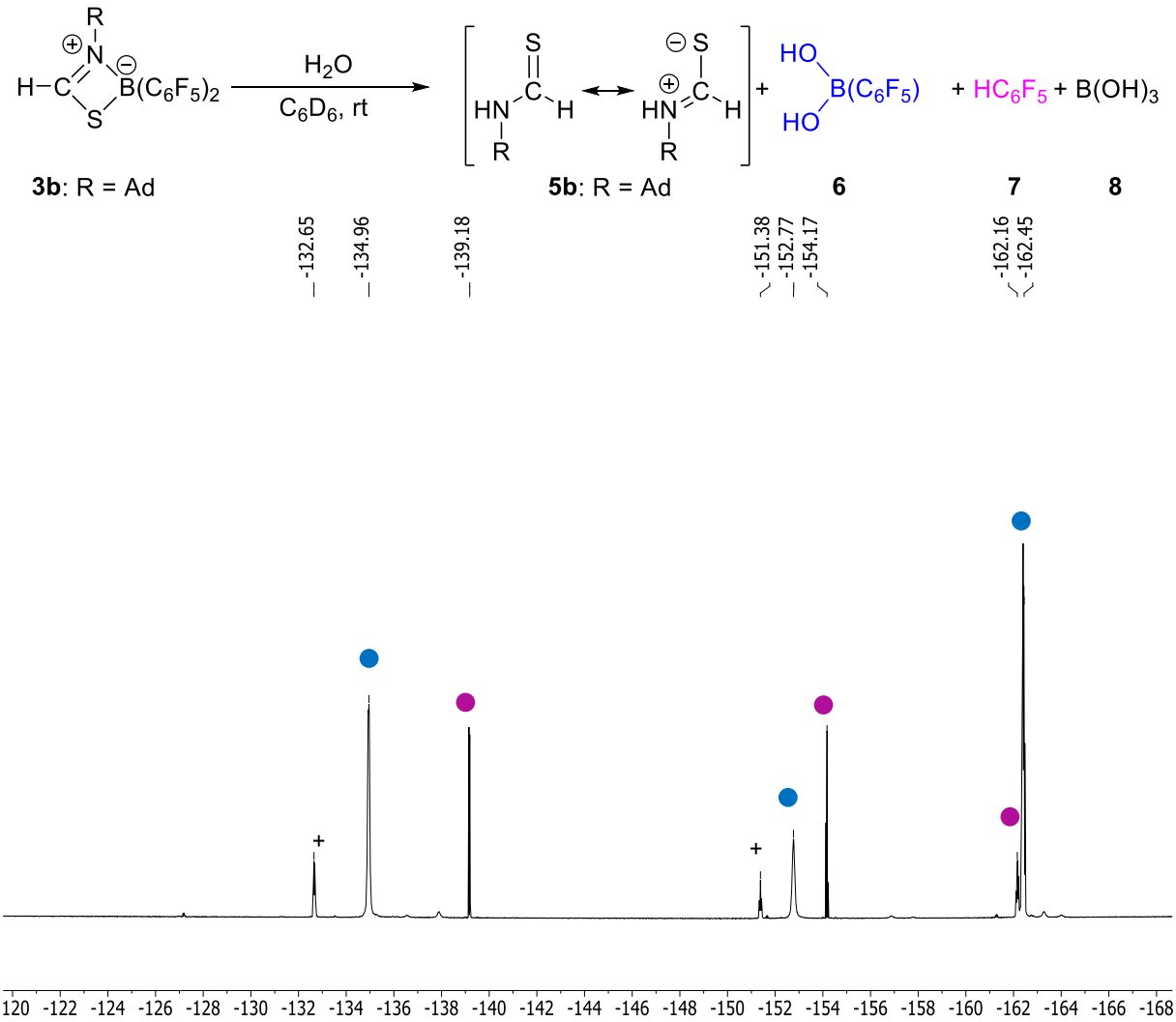


Figure S47: $^{19}F\{^{1}H\}$ NMR spectrum of the reaction of **3b** with water (470 MHz, C_6D_6, rt); $^{+}$: unidentified byproduct.

Crystallographic Data:

Single crystal X-ray data were measured at 100 K on a Bruker AXS D8 Venture diffractometer (multilayer optics, monochromated Mo-Kα radiation with λ = 0.71073 Å, Kappa 4-circle goniometer, Photon III C14 CPAD detector). Empirical absorption corrections using equivalent reflections were performed with the programs SADABS[S9] and, for **5b**, TWINABS; the structures were solved with the program SHELXS[S10] and refined with SHELXL[S11] using the OLEX2[S12] GUI. The crystallographic data can be obtained free of charge from https://www.ccdc.cam.ac.uk/structures/ quoting the CCDC numbers 1985529-1985534, and 1988662.

Table S4: Crystal Structure Data for Compounds **2b**, **2c**, **3b,** and **4a**.

	2b	**2c**	**3b**	**4**
CCDC	1985534	1985531	1985530	1985532
empirical formula	$C_{29}H_{15}BF_{15}NS$	$C_{29}H_7BD_3F_{15}NS$	$C_{23}H_{16}NF_{10}NS$	$C_{80}H_{32}B_4F_{40}N_4S_4$
fw	705.29	703.27	539.24	1980.57
colour	colorless	colorless	colorless	colorless
Habit	plate	block	block	tetragonal prism
cryst dimens, mm	0.20 x 0.13 x 0.04	0.14 x 0.06 x 0.05	0.12 x 0.08 x 0.05	0.15 x 0.10 x 0.10
cryst syst	triclinic	triclinic	monoclinic	tetragonal
space group	*P*-1	*P*-1	$P2_1$	$I4_1/a$
a, Å	10.6377(4)	11.0472(6)	10.5637(3)	25.7921(6)
b, Å	11.0835(4)	13.8833(7)	7.3903(2)	25.7921(6)
c, Å	12.3782(4)	18.2965(8)	13.8954(4)	11.5395(4)
α, deg	86.9491(13)	78.3352(18)	90	90
β, deg	70.7503(12)	79.4105(18)	98.8924(11)	90
γ, deg	73.9923(14)	86.855(2)	90	90
V, Å^3	1323.26(8)	2700.9(2)	1071.76(5)	7676.4(5)
Z	2	4	2	4
D_{caclcd}, g cm^{-3}	1.770	1.729	1.671	1.714
μ, mm^{-1}	0.253	0.247	0.251	0.273
T, K	100(2)	100(2)	100(2)	100(2)
θ range, deg	2.108 – 36.319	1.498 – 33.728	2.261 – 34.968	1.579 – 36.315
no. of rflns collected	145517	221213	67044	283547
no. of indep rflns (R(int))	12838 (0.0364)	21581 0.0494	9414 (0.0448)	9285 0.0433
no. of rflns with I>2σ(I)	10845	17092	8986	8138
abs cor	semi-empirical	semi-empirical	semi-empirical	semi-empirical
max, min transmission	1.0000 and 0.9499	1.0000 and 0.9437	1.0000 and 0.9404	1.0000 and 0.9417
final R indices [I>2σ(I)]	R1 = 0.0333 wR2 = 0.0911	R1 = 0.0426 wR2 = 0.1051	R1 = 0.0375 wR2 = 0.0983	R1 = 0.0321 wR2 = 0.0872
R indices (all data)	R1 = 0.0430 wR2 = 0.1013	R1 = 0.0591 wR2 = 0.1144	R1 = 0.0399 wR2 = 0.1000	R1 = 0.0391 wR2 = 0.0924
GOF on F^2	1.016	1.065	1.091	1.102
largest diff peak / hole (e.Å^{-3})	0.623 and -0.688	0.527 and -0.508	0.825 and -0.299	0.605 and -0.307

Table S5: Crystal Structure Data for Compounds **4•C_6D_6**, **5a**, and **5b**.

	4•C_6D_6	**5a**	**5b**	
CCDC	1985533	1988662	1985529	
empirical formula	$C_{92}H_{32}B_4D_{12}F_{40}N_4S_4$	C_7H_7NS	$C_{11}H_{17}NS$	
fw	2148.86	137.20	195.31	
colour	colorless	colorless	colorless	
Habit	oblique block	needles	plate	
cryst dimens, mm	0.13 x 0.09 x 0.04	0.08 x 0.02 x 0.02	0.08 x 0.05 x 0.015	
cryst syst	monoclinic	orthorhombic	monoclinic	
space group	*P*2_1/*c*	*Pnma*	*P*2_1/*n*	
a, Å	27.803(2)	17.6153(12)	7.4323(8)	
b, Å	16.1663(10)	7.9189(6)	6.7992(8)	
c, Å	19.7323(13)	4.8341(3)	19.910(2)	
α, deg	90	90	90	
β, deg	94.517(3)	90	93.113(4)	
γ, deg	90	90	90	
V, Å^3	8841.5(10)	674.33(8)	1004.65(19)	
Z	4	4	4	
D_{caclcd}, g cm^{-3}	1.614	1.351	1.291	
μ, mm^{-1}	0.243	3.427	0.274	
T, K	100(2)	100(2)	100(2)	
θ range, deg	1.458 – 28.699	5.021 – 74.312	2.877 – 30.027	
no. of rflns collected	319725	7400	4178	
no. of indep rflns (R(int))	22874 0.0576	729 0.0469	4178	
no. of rflns with I>2σ(I)	19354	644	3295	
abs cor	semi-empirical	semi-empirical	semi-empirical	
max, min transmission	1.0000 and 0.9525	1.0000 and 0.8792	1.000000 and 0.848914	
final R indices [I>2σ(I)]	R1 = 0.0407 wR2 = 0.0843	R1 = 0.0244 wR2 = 0.0626	R1 = 0.0899 wR2 = 0.1324	
R indices (all data)	R1 = 0.0520 wR2 = 0.0888	R1 = 0.0301 wR2 = 0.0660	R1 = 0.1188 wR2 = 0.1406	
GOF on F^2	1.092	1.037	1.194	
largest diff peak / hole (e.Å^{-3})	0.435 and -0.366	0.188 and -0.213	0.394 and -0.592	

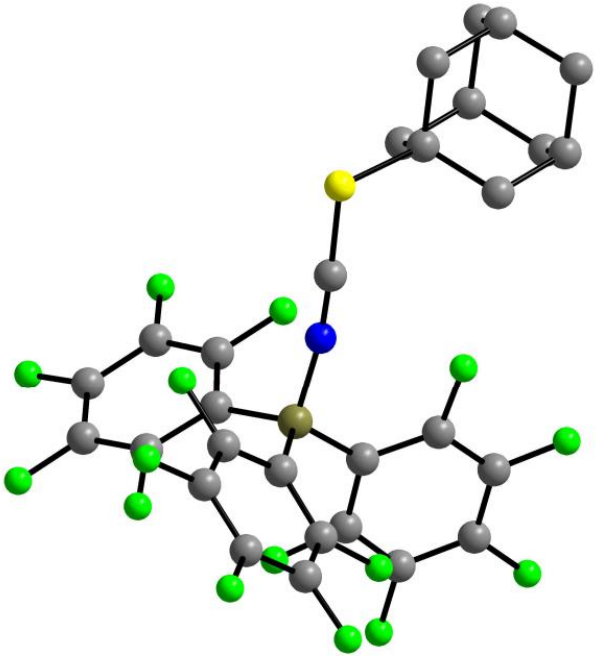


Figure S48: Molecular structure of **2b**.

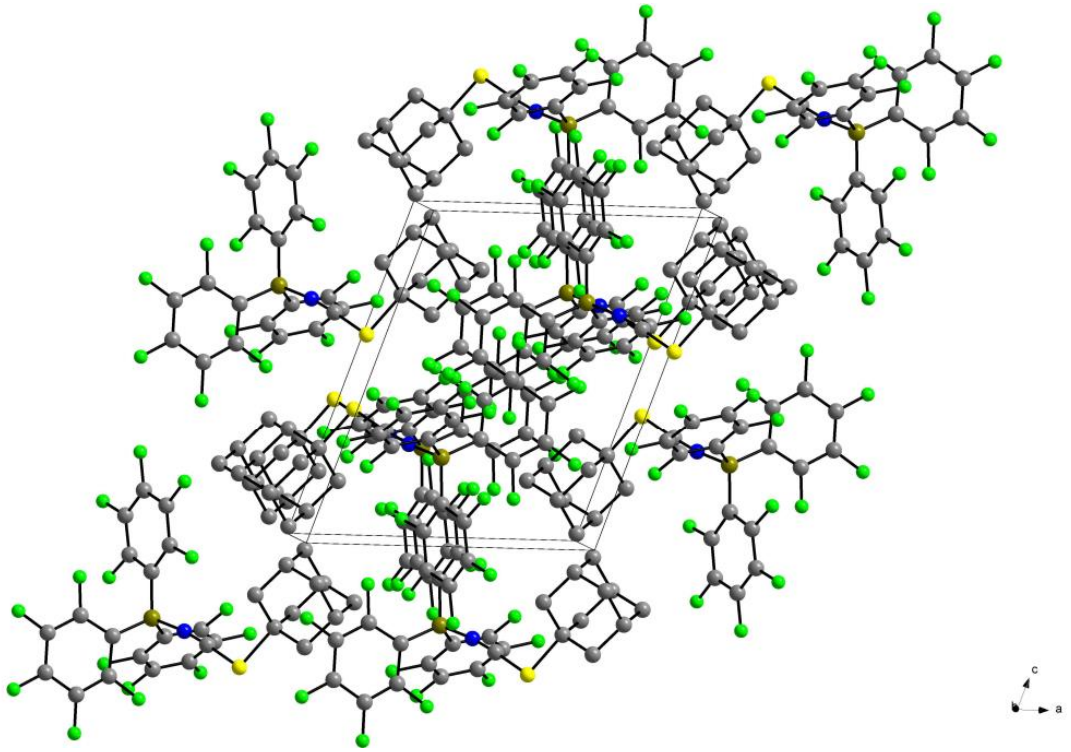


Figure S49: View along the *b* axis showing the packing of molecules in the crystal structure of complex **2b**. Hydrogen atoms have been omitted for clarity.

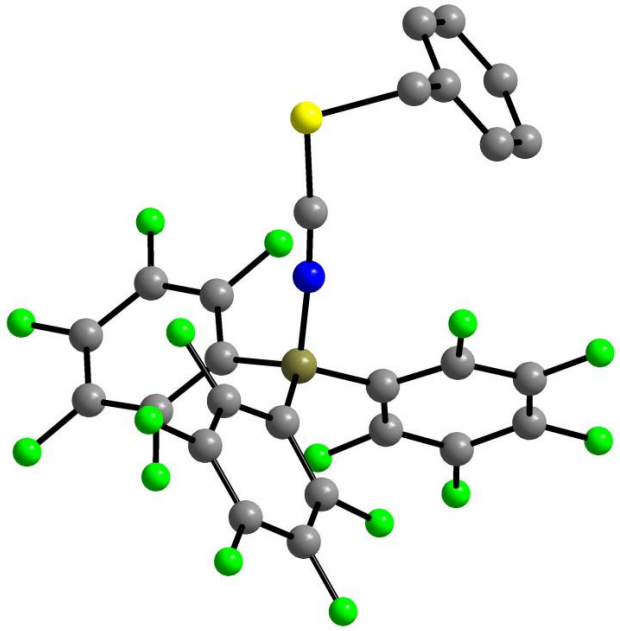


Figure S50: Molecular structure of **2c**.

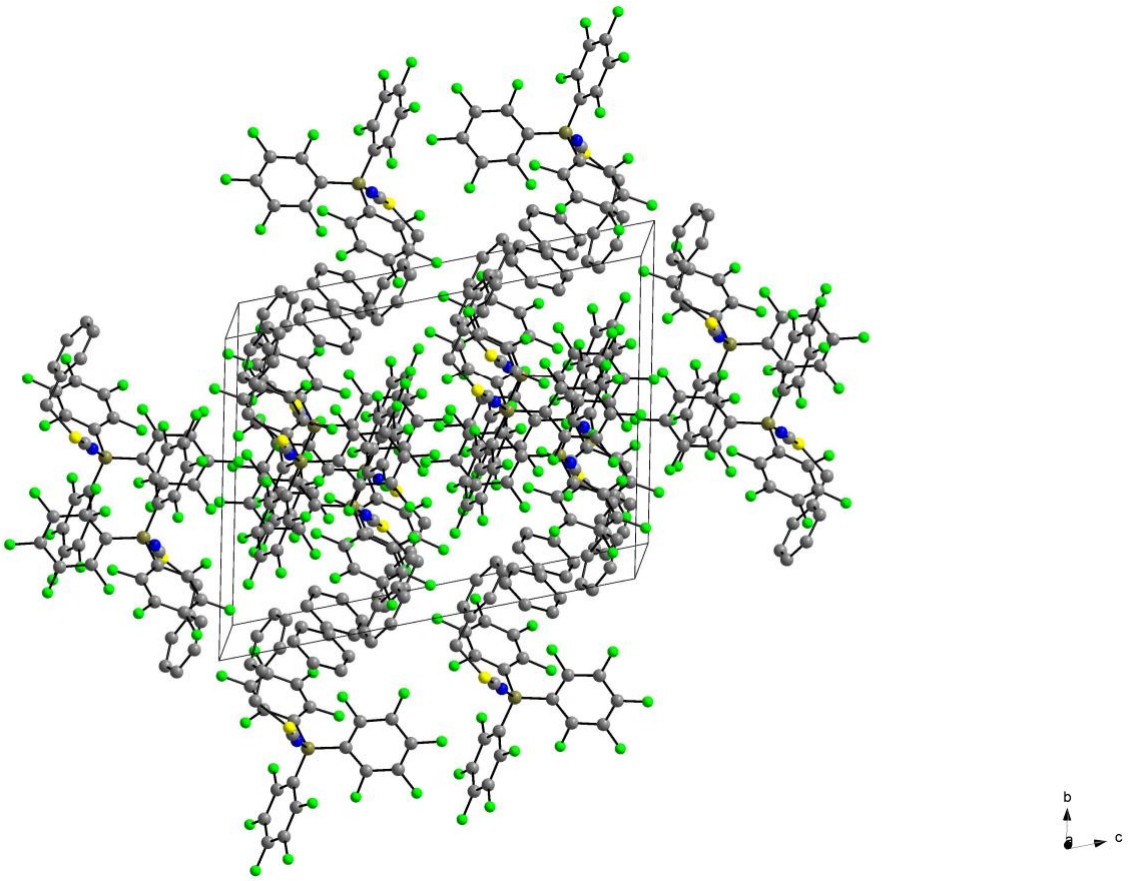


Figure S51: View along the *a* axis showing the packing of molecules in the crystal structure of complex **2c**. Hydrogen atoms have been omitted for clarity.

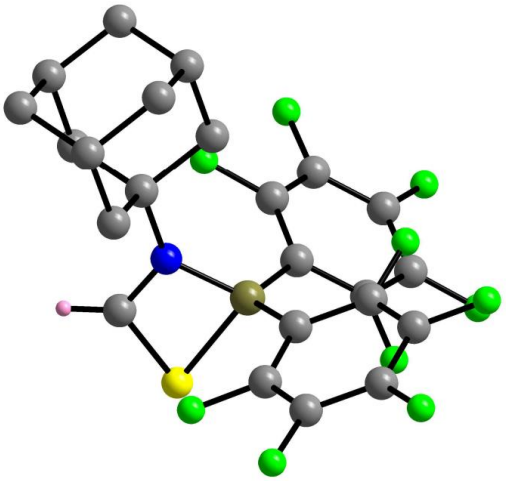


Figure S52: Molecular structure of **3b**.

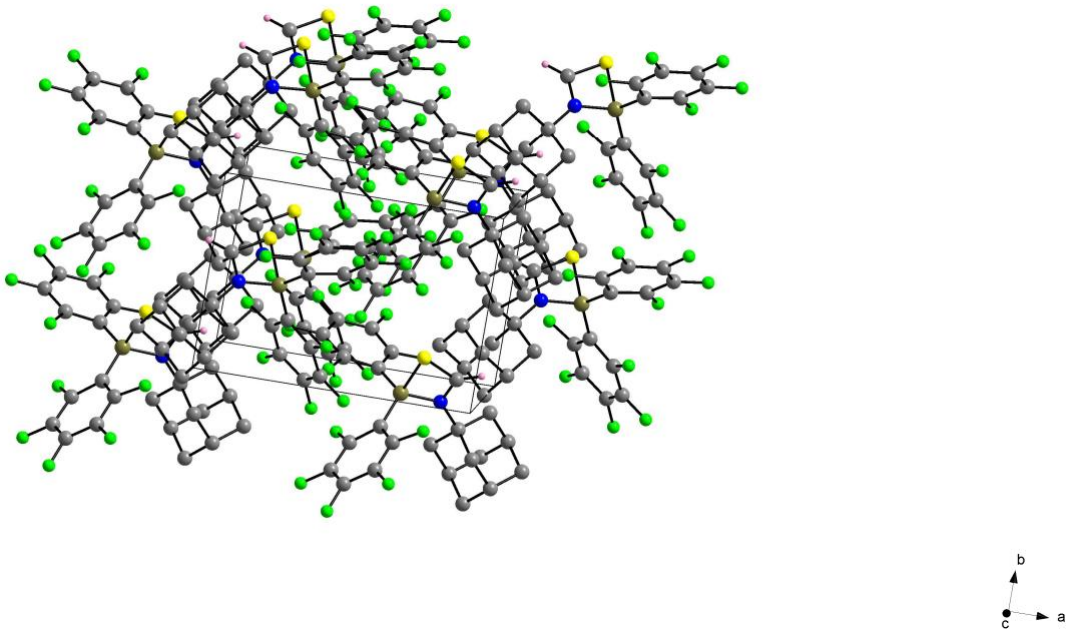


Figure S53: View along the *c* axis showing the packing of molecules in the crystal structure of complex **3b**. Hydrogen atoms have been omitted for clarity.

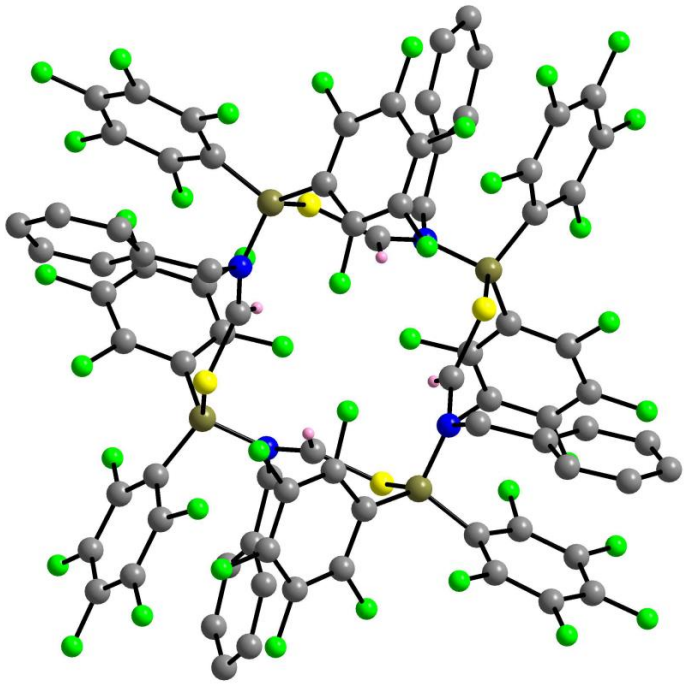


Figure S54: Molecular structure of **4**.

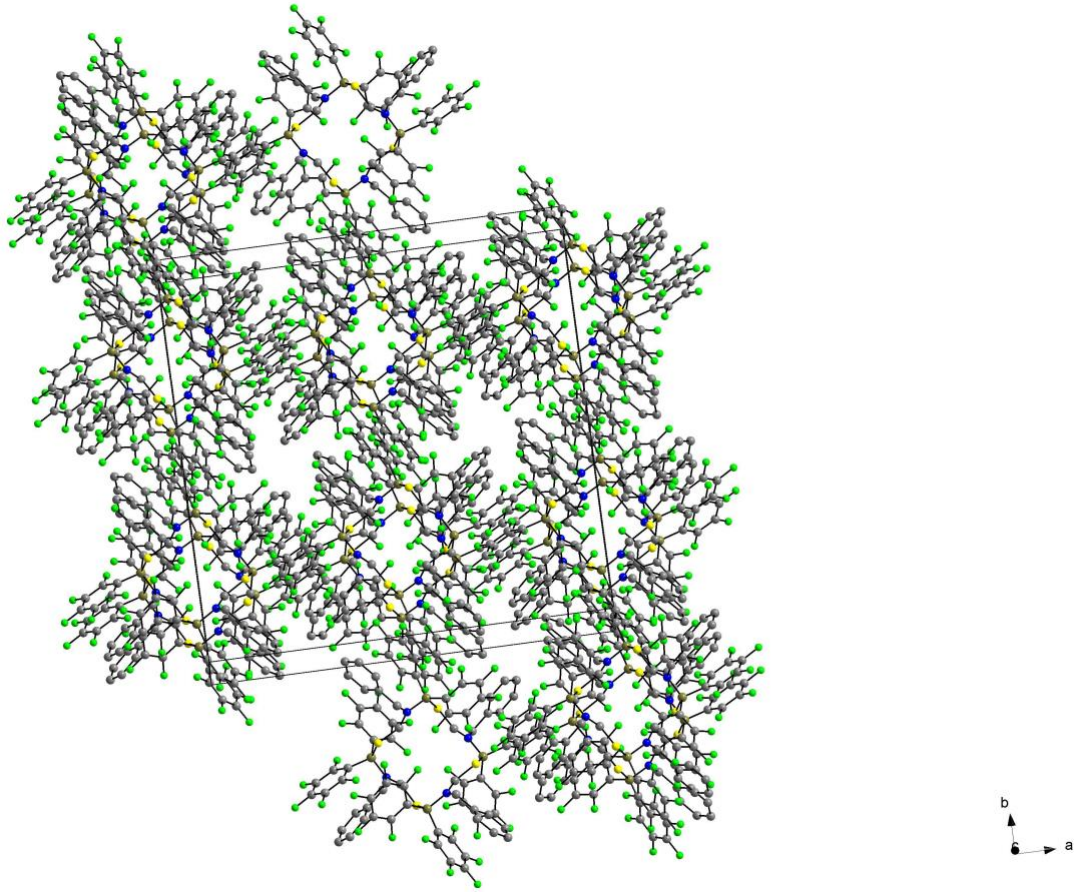


Figure S55: View along the *c* axis showing the packing of molecules in the crystal structure of complex **4**. Hydrogen atoms have been omitted for clarity.

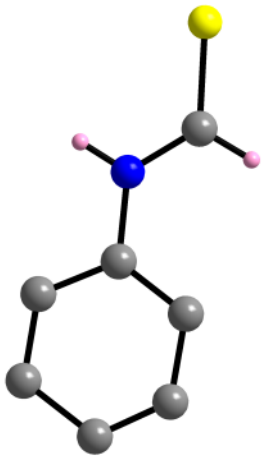


Figure S56: Molecular structure of **5a**.

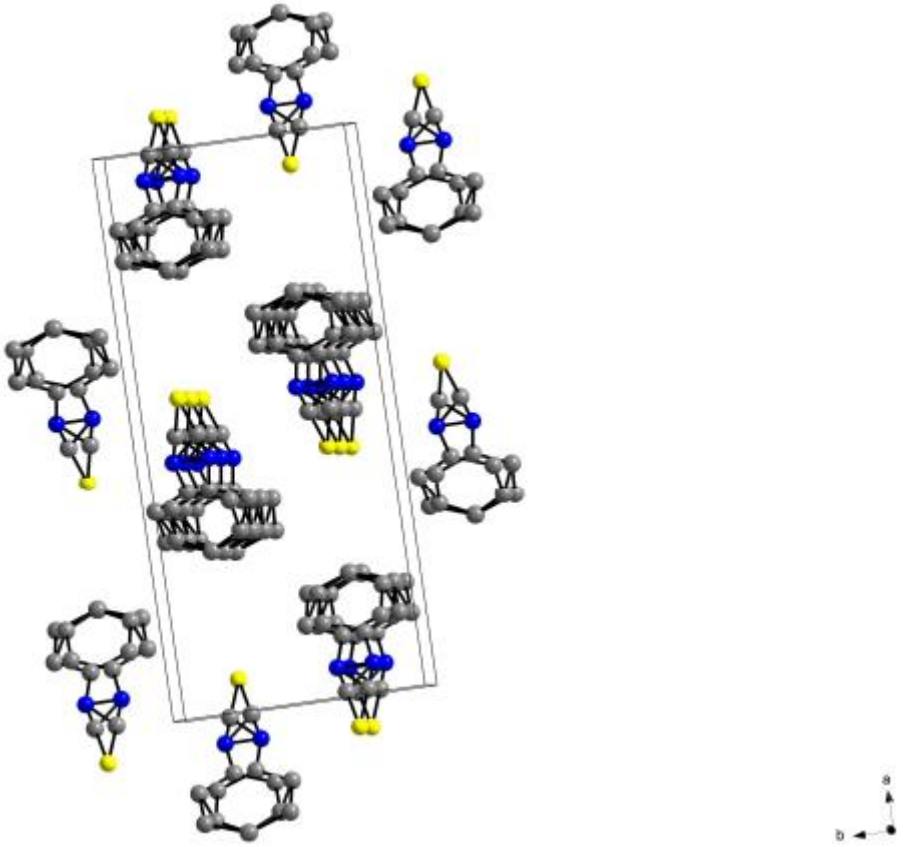


Figure S57: View along the *c* axis showing the packing of molecules in the crystal structure of complex **5a**. Hydrogen atoms have been omitted for clarity.

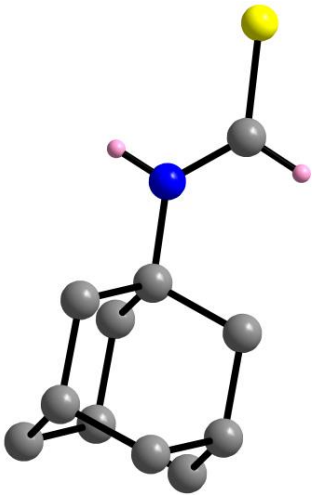


Figure S58: Molecular structure of **5b**.

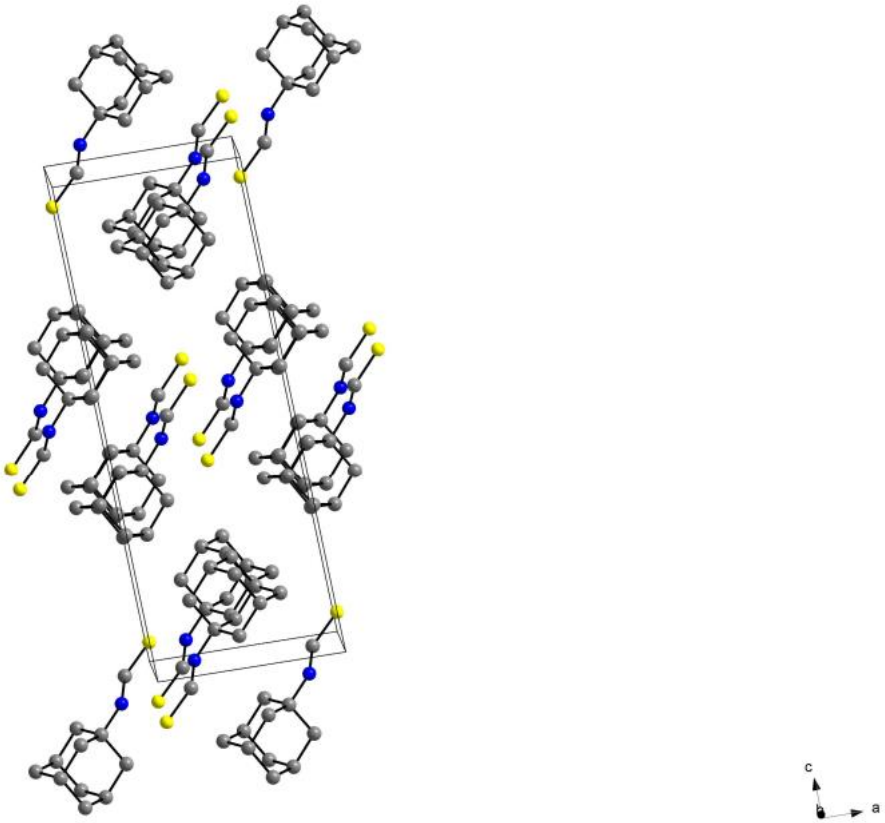


Figure S59: View along the *b* axis showing the packing of molecules in the crystal structure of complex **5b**. Hydrogen atoms have been omitted for clarity.

Author Contributions

Marc Schmidtmann: measurement of the single crystals via X-ray diffraction

Malte Fischer: project administration, investigation, data curation, writing of the publication

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