Supplementary Information for

A Remarkably Stable Ring-Expanded NHC-Supported Copper Boryl and its Reactivity towards Heterocumulenes

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Experimental

General considerations and starting materials

All reactions dealing with air- and moisture-sensitive compounds were carried out under argon atmosphere using standard Schlenk line and glovebox techniques. NMR experiments using air-sensitive compounds were conducted in J. Young's tap NMR tubes prepared and sealed in a glovebox under argon. Toluene and hexane were purified using an MBraun Solvent Purification System and stored over 4Å molecular sieves. C_6D_6 was dried over a potassium mirror prior to vacuum transfer into a sealed ampoule and storage in the glove box under argon. All NMR data were acquired at 298 K on an Agilent ProPulse instrument for ^{1}H (500 MHz), $^{13}C\{^{1}H\}$ (126 MHz) and ^{11}B (160 MHz), a Bruker Avance 400 instrument for ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz) and ^{11}B (128 MHz) or a Bruker AV300 spectrometer for ^{1}H (300 MHz). ^{1}H and ^{13}C NMR spectra were referenced using residual solvent resonances. Elemental analyses were performed by Elemental Microanalysis Ltd., Okehampton, Devon, U.K. Bis(pinacolato)diboron was purchased from Fluorochem and used as received. Isocyanates, *tert*-butyl isothiocyanate and diisopropyl carbodiimide were purchased from Sigma-Aldrich and distilled before use. (6-Dipp)CuO^{t}Bu was prepared according to literature procedure.[1]

Synthesis of compound 1, (6-Dipp)CuBpin

In a glove box, toluene (4 mL) was added to a mixture of (6-Dipp)CuO^{t}Bu (100 mg, 0.19 mmol) and Pin_2B_2 (48 mg, 0.19 mmol) with a stirrer bar in a vial shielded from light by foil. Upon dissolution, the reaction was sealed and left stirring in the glovebox overnight. The reaction mixture was filtered and volatiles were removed *in vacuo* yielding a white powder. The powder was washed with hexane and dried *in vacuo* to give **1** (83 mg, 0.14 mmol, 76%). Colourless crystals suitable for X-ray diffraction were grown from a vapour diffusion of hexane into a concentrated toluene solution. (As similarly noted in the reported synthesis for IPrCuBpin,[2] samples typically contained ca. 5% **2**).

^{1}H NMR (500 MHz, C_6D_6) δ 7.20 – 7.14 (m, 2H, Ar-*H*), 7.10 – 7.07 (m, 4H, Ar-*H*), 3.08 (hept, J = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 2.69 (t, J = 5.9 Hz, 4H, NC*H*$_2$), 1.59 (d, J = 6.8 Hz, 12H, CH(C*H*$_3)_2$), 1.48 (p, 5.9 Hz, 2H, NCH_2CH_2), 1.21 (d, J = 7.0 Hz, 12H, CH(C*H*$_3)_2$), 1.01 (s, 12H, OC(C*H*$_3)_2$). ^{13}C NMR (126 MHz, C_6D_6) δ 205.5 (Cu*C*), 145.8 (Ar-*C*), 141.5 (Ar-*C*), 129.0 (Ar-*C*), 124.5 (Ar-*C*), 78.7 (O*C*$(CH_3)_2$), 46.1 (N*C*H_2), 29.0 (*C*H$(CH_3)_2$), 26.1 (OC(*C*H$_3)_2$), 25.3 (CH(*C*H$_3)_2$), 24.7 (CH(*C*H$_3)_2$), 20.5 (NCH_2CH_2). ^{11}B NMR (160 MHz, C_6D_6) δ 41.2 (FWHM = 700 Hz). Analysis calculated for $C_{34}H_{52}CuO_2N_2B$ (MW = 595.16 g/mol): Expected: C, 68.60; H, 8.82; N, 4.71. Found: C, 68.43; H, 8.89; N, 4.33.

Synthesis of compound 2, (6-Dipp)CuOBpin

In a glove box, toluene (0.5 mL) was added to a mixture of (6-Dipp)CuO^{t}Bu (40 mg, 0.08 mmol) and Pin_2B_2 (19 mg, 0.08 mmol) in a vial and left standing overnight. The reaction mixture was filtered and isopropyl isocyanate (8 µL, 0.08 mmol) was added. Left to stand overnight, colourless crystals suitable for X-ray diffraction grew from the reaction mixture. The supernatant solution was decanted, the crystals were washed with hexane and dried *in vacuo* to give **2** (8 mg, 0.01 mmol, 20 %).

^{1}H NMR (500 MHz, C_6D_6) δ 7.22 – 7.14 (m, 2H, Ar-*H*), 7.09 – 7.04 (m, 4H, Ar-*H*), 2.99 (hept, J = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 2.67 (t, J = 5.9 Hz, 4H, NC*H*$_2$), 1.50 (d, J = 6.8 Hz, 12H, CH(C*H*$_3)_2$), 1.43 (p, J = 5.8 Hz, 2H, NCH_2CH_2), 1.19 (d, J = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 1.08 (s, 12H, OC(C*H*$_3)_2$). ^{13}C NMR (126 MHz, C_6D_6) δ 203.0 (Cu*C*), 145.6 (Ar-*C*), 142.3 (Ar-*C*), 129.4 (Ar-*C*), 124.8 (Ar-*C*), 78.5 (O*C*$(CH_3)_2$), 46.1 (N*C*H_2), 29.0 (*C*H$(CH_3)_2$), 25.3 (OC(*C*H$_3)_2$), 25.1 (CH(*C*H$_3)_2$), 24.7 (CH(*C*H$_3)_2$), 20.3 (NCH_2CH_2). ^{11}B NMR (160 MHz, C_6D_6) δ 21.2 (FWHM = 650 Hz). Analysis calculated for $C_{34}H_{52}CuO_3N_2B$ (MW = 611.16 g/mol): Expected: C, 66.81; H, 8.59; N, 4.58. Found: C, 66.44; H, 8.58; N, 4.40.

Synthesis of compound 3, (6-Dipp)CuSBpin

In a vial in the glovebox, *tert*-butyl isothiocyanate (5.3 µL, 0.04 mmol) was added to a solution of **1** (50 mg, 0.08 mmol) in toluene (0.5 mL), resulting in a brown solution. Left to stand overnight, precipitate formed from the reaction mixture. The supernatant solution was decanted and the solid was washed with hexane (2 × 0.5 mL) to give **3** (18 mg, 0.03 mmol, 68 %). Colourless crystals suitable for X-ray diffraction were grown from benzene. The supernatant toluene solution was combined with the hexane washes. Overnight, yellow crystals of **6** (10 mg, 0.02 mmol, 35 %) crystallised from the solution.

^{1}H NMR (400 MHz, C_6D_6) δ 7.21 – 7.16 (m, 2H, Ar-*H*), 7.10 – 7.07 (m, 4H, Ar-*H*), 3.05 (hept, J = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 2.74 (t, J = 5.9 Hz, 4H, NC*H*$_2$), 1.56 – 1.47 (m, 14H, CH(C*H*$_3)_2$), NCH_2CH_2), 1.21 (d, J = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 0.99 (s, 12H, OC(C*H*$_3)_2$). ^{13}C NMR (101 MHz, C_6D_6) δ 202.0 (Cu*C*), 145.7 (Ar-*C*), 141.9 (Ar-*C*), 129.5 (Ar-*C*), 124.8 (Ar-*C*), 81.6 (O*C*$(CH_3)_2$), 46.2 (N*C*H_2), 29.0 (*C*H$(CH_3)_2$), 25.3 (OC(*C*$H_3)_2$), 24.9 (CH(*C*$H_3)_2$), 24.8 (CH(*C*$H_3)_2$), 20.3 (NCH_2*C*H_2). ^{11}B NMR (128 MHz, C_6D_6) δ 34.3 (FWHM = 220 Hz). Analysis calculated for $C_{34}H_{52}CuSO_2N_2B$ (MW = 627.22 g/mol): Expected: C, 65.10; H, 8.37; N, 4.47. Found: C, 64.83; H, 8.41; N, 4.47.

Synthesis of compound 4, (6-Dipp)Cu[CN(Ph)C(=O)N(Ph)Bpin]

In a vial in the glovebox, phenyl isocyanate (18 µL, 0.16 mmol) was added to a solution of **1** (50 mg, 0.08 mmol) in toluene (0.4 mL). Left to stand overnight, material crystallised from the reaction mixture. The supernatant solution was decanted and the solid washed with benzene (0.5 mL) yielding **4** (13 mg, 0.02 mmol, 19%) as a pale yellow crystalline solid. The isolated crystals were of sufficient quality for analysis by X-ray diffraction.

^{1}H NMR (500 MHz, C_6D_6) δ 7.74 – 7.71 (m, 2H, Ar-*H*), 7.15 – 7.12 (m, 2H, Ar-*H*), 7.01 – 6.90 (m, 10H, Ar-*H*) , 6.75 – 6.72 (m, 2H, Ar-*H*), 2.87 (hept, *J* = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 2.66 (t, *J* = 6.0 Hz, 4H, NC*H*$_2$), 1.37 (p, *J* = 6.0 Hz, 2H, NCH_2CH_2), 1.18 (d, *J* = 6.9 Hz, 12H CH(C*H*$_3)_2$), 1.10 (s, 6H, OC(C*H*$_3)_2$), 1.07 – 104 (m, 18 H, OC(C*H*$_3)_2$, CH(C*H*$_3)_2$). ^{13}C NMR (126 MHz, C_6D_6) δ 205.5 (Cu*C*), 145.6 (Ar-*C*), 144.8 (Ar-*C*), 143.5 (Ar-*C*), 141.8 (Ar-*C*), 129.3 (Ar-*C*), 129.1 (Ar-*C*), 128.6 (Ar-*C*), 127.9 (Ar-*C*), 127.5 (Ar-*C*), 125.6 (Ar-*C*), 125.3 (Ar-*C*), 125.0 (Ar-*C*), 79.1 (O*C*$(CH_3)_2$), 47.2 (N*C*H_2), 28.9 (*C*H$(CH_3)_2$), 28.7 (OC(*C*$H_3)_2$), 27.0 (OC(*C*$H_3)_2$), 24.9 (CH(*C*$H_3)_2$), 24.5 (CH(*C*$H_3)_2$), 21.1 (NCH_2*C*H_2). ^{11}B NMR (160 MHz, C_6D_6) δ 7.8 (FWHM = 320 Hz). Analysis calculated for $C_{48}H_{63}CuO_3N_4B$ (MW = 818.33 g/mol): Expected: C, 70.44; H, 7.76; N, 6.85. Found: C, 70.54; H, 7.40; N, 6.28.

Synthesis of compound 5, (6-Dipp)Cu[CN(^{t}Bu)C(=O)N(Ph)Bpin]

In a vial in the glovebox, phenyl isocyanate (5 µL, 0.05 mmol) was added to a solution of **6** (23 mg, 0.03 mmol) in toluene (0.5 mL) resulting in a colourless solution. Left to stand overnight material crystallised from the reaction mixture. The supernatant solution was decanted and the solid washed with toluene (0.5 mL) yielding **5** (17 mg, 0.02 mmol, 63%) as a pale yellow crystalline solid. Colourless crystals suitable for X-ray diffraction were grown from a vapour diffusion of hexane into a concentrated toluene solution.

^{1}H NMR (500 MHz, C_6D_6) δ 7.68 – 7.65 (m, 2H, Ar-*H*), 7.18 – 7.10 (m, 4H, Ar-*H*), 7.04 – 7.01 (m, 4H, Ar-*H*), 6.97 – 6.93 (m, 1H, Ar-*H*), 3.14 (hept, *J* = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 2.90 (t, *J* = 6.1 Hz, 4H, NC*H*$_2$), 1.57 (p, *J* = 5.7 Hz, 2H, NCH_2CH_2), 1.49 (s, 9H, C(C*H*$_3)_3$), 1.42 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3)_2$), 1.08 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3)_2$), 1.00 (s, 6H, OC(C*H*$_3)_2$), 0.99 (s, 6H, OC(C*H*$_3)_2$). ^{13}C NMR (126 MHz, C_6D_6) δ 207.4 (Cu*C*), 188.5 (*C*O), 145.2 (Ar-*C*), 143.8 (Ar-*C*), 142.0 (Ar-*C*), 129.6 (Ar-*C*), 129.4 (Ar-*C*), 125.7 (Ar-*C*), 124.7 (Ar-*C*), 78.8 (O*C*$(CH_3)_2$), 60.4 (N*C*$(CH_3)_3$), 48.2 (N*C*H_2), 31.6 (NC(*C*$H_3)_3$), 28.8 (*C*H$(CH_3)_2$), 28.7 (OC(*C*$H_3)_2$), 27.0 (OC(*C*$H_3)_2$), 26.0 (CH(*C*$H_3)_2$), 24.6 (CH(*C*$H_3)_2$), 21.5 (NCH_2*C*H_2). ^{11}B NMR (160 MHz, C_6D_6) δ 7.2 (FWHM =

160 Hz). Analysis calculated for $C_{46}H_{66}CuO_3N_4B$ (MW = 797.52 g/mol): Expected: C, 69.62; H, 8.40; N, 7.06. Found: C, 69.60; H, 8.42; N, 7.01.

Synthesis of compound 6, (6-Dipp)CuC(=N^{t}Bu)Bpin

In a vial in the glovebox, *tert*-butyl isocyanide (8.0 µL, 0.07 mmol) was added to a solution of **1** (30 mg, 0.05 mmol) in toluene (0.4 mL) resulting in a yellow solution. Hexane vapour was allowed to diffuse into this solution overnight, resulting in the formation of yellow precpitate. The supernatant solution was decanted. The solid was washed with hexane (0.5 mL) and dried *in vacuo*, yielding **6** (23 mg, 0.03 mmol, 67 %).

^{1}H NMR (500 MHz, C_6D_6) δ 7.20 – 7.17 (m, 2H, Ar-*H*), 7.10 – 7.07 (m, 4H, Ar-*H*), 3.09 (hept, *J* = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 2.78 (t, *J* = 5.9 Hz, 4H, NCH_2), 1.53 (p, *J* = 5.9 Hz, 2H, NCH_2CH_2), 1.49 (d, *J* = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.19 (d, *J* = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.09 (s, 12H, OC(CH_3)$_2$), 1.03 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (126 MHz, C_6D_6) δ 205.8 (Cu*C*), 145.5 (Ar-*C*), 142.2 (Ar-*C*), 129.4 (Ar-*C*), 125.1 (Ar-*C*), 81.2 (O*C*$(CH_3)_2$), 57.8 (N*C*$(CH_3)_3$), 47.1 (N*C*H_2), 31.6 (NC(*C*H_3)$_3$), 29.0 (*C*H$(CH_3)_2$), 25.7 (OC(*C*H_3)$_2$), 25.1 (CH(*C*H_3)$_2$), 25.0 (CH(*C*H_3)$_2$), 20.6 (NCH_2CH_2). ^{11}B NMR (160 MHz, C_6D_6) δ 28.3 (FWHM = 610 Hz). Analysis calculated for $C_{39}H_{61}CuO_2N_3B$ (MW = 678.39 g/mol): Expected: C, 69.04; H, 9.08; N, 6.20. Found: C, 68.99; H, 9.06; N, 6.24.

Synthesis of compound 7, (6-Dipp)Cu[C(Bpin)N(^{t}Bu)C(=NPh)S]

In a vial in the glovebox, to a solution of **1** (40 mg, 67 µmol) in toluene (0.3 mL) was added *tert*-butyl isocyanide (8.3 µL, 0.07 mmol) to give a yellow solution, followed by phenyl isothiocyanate (8.8 µL, 0.07 mmol) to give a pale brown solution. Material began to crystalise from the solution within a few minutes and the reaction was left to stand overnight. The supernatant solution was decanted and the colourless crystals were washed with hexane (0.5 mL) yielding **7** (17 mg, 0.02 mmol, 31%). The isolated crystals were of sufficient quality for analysis by XRD.

^{1}H NMR (500 MHz, C_6D_6) δ 7.42 – 7.39 (m, 2H, Ar-*H*), 7.38 – 7.33 (m, 2H, Ar-*H*), 7.21 (t, J = 7.7 Hz, 2H, Ar-*H*), 7.11 – 7.07 (m, 4H, Ar-*H*), 6.96 – 6.91 (m, 1H, Ar-*H*), 3.06 – 2.93 (m, 4H, C*H*$(CH_3)_2$), 2.79 – 2.67 (m, 4H, NCH_2), 1.52 – 1.49 (m, 12H, CH(CH_3)$_2$), 1.48 – 1.43 (m, 11H, C(CH_3)$_3$, NCH_2CH_2), 1.19 (d, J = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.15 (d, J = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.02 (s, 6H, OC(CH_3)$_2$), 1.00 (s, 6H, OC(CH_3)$_2$). ^{13}C NMR (126 MHz, C_6D_6) δ 203.6 (Cu*C*), 152.6 (S*C*N), 151.9 (Ar-*C*), 145.7 (Ar-*C*), 145.4 (Ar-*C*), 142.3 (Ar-*C*), 129.5 (Ar-*C*), 128.7 (Ar-*C*), 125.3 (Ar-*C*), 125.0 (Ar-*C*), 122.0 (Ar-*C*), 119.2 (Ar-*C*), 81.9 (O*C*$(CH_3)_2$), 56.2 *C*$(CH_3)_3$, 46.5 (N*C*H_2), 29.0 (*C*H$(CH_3)_2$), 29.0 (*C*H$(CH_3)_2$), 27.8 C(*C*H_3)$_3$, 25.7 (OC(*C*H_3)$_2$), 25.3 (CH(*C*H_3)$_2$), 25.2 (CH(*C*H_3)$_2$), 25.2 (CH(*C*H_3)$_2$), 25.0 (CH(*C*H_3)$_2$), 23.8 (O*C*$(CH_3)_2$), 20.2 (NCH_2CH_2). ^{11}B NMR (160 MHz, C_6D_6) δ 21.6 (FWHM ≈ 630 Hz). Analysis calculated for $C_{46}H_{66}CuSO_2N_4B$ (MW = 813.58 g/mol): Expected: C, 67.91; H, 8.19; N, 6.89. Found: C, 67.71; H, 8.16; N, 6.76.

Synthesis of compound 8, (6-Dipp)Cu[CN(^{i}Pr)C(=N^{i}Pr)N(^{i}Pr)Bpin]

In a vial in the glovebox, diisopropyl carbodiimide (8 µL, 0.05 mmol) was added to a solution of **1** (30 mg, 0.05 mmol) in C_6D_6 (0.5 mL). The reaction was transferred to a J. Young's NMR tube. After 9 days the solution had turned pale yellow and ^{11}B NMR spectroscopy confirmed the quantitative consumption of **1**. The reaction was filtered. Hexane vapour was allowed to diffuse into the filtrate overnight, resulting in the formation of yellow crystals of **8** (7 mg, 0.01 mmol, 40%). The isolated crystals were of sufficient quality for analysis by X-ray diffraction.

^{1}H NMR (500 MHz, C_6D_6) δ 7.16 – 7.13 (m, 2H, Ar-*H*), 7.02 – 6.99 (m, 4H, Ar-*H*), 4.37 – 4.25 (m, 2H, NC*H*$(CH_3)_2$), 3.76 (hept, J = 6.8 Hz, 1H, NC*H*$(CH_3)_2$), 3.00 (hept, J = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 2.70 (t, J = 5.9

Hz, 4H, NCH_2), 1.60 (d, J = 6.8 Hz, 6H, NCH(CH_3)$_2$), 1.50 – 1.47 (m, 12H, NCH(CH_3)$_2$, OC(CH_3)$_2$), 1.37 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.33 (d, J = 6.0 Hz, 6H, NCH(CH_3)$_2$), 1.09 (d, J = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.07 (s, 6H, OC(CH_3)$_2$). ^{13}C NMR (126 MHz, C_6D_6) δ 205.3 (Cu*C*), 145.0 (Ar-*C*), 141.8 (Ar-*C*), 129.7 (Ar-*C*), 125.6 (Ar-*C*), 78.0 (O*C*(CH$_3$)$_2$), 47.7 (N*C*H$_2$), 47.2 (N*C*H(CH$_3$)$_2$), 46.6 (N*C*H(CH$_3$)$_2$), 43.1 (N*C*H(CH$_3$)$_2$), 30.0 (OC(*C*H$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 28.3 (OC(*C*H$_3$)$_2$), 25.7 (NCH(*C*H$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 23.9 (NCH(*C*H$_3$)$_2$), 23.1 (NCH(*C*H$_3$)$_2$), 21.1 (NCH$_2$*C*H$_2$). ^{11}B NMR (160 MHz, C_6D_6) δ 8.0 (FWHM = 100 Hz). MS (ESI) Expected: 789.5268, found: 789.5256 $[M]^+$ (err [ppm] = -1.51).

X-ray Crystallography

Data for compounds **1**-**5**, **7**, **8** were collected on a either a RIGAKU SuperNova or XCALIBUR diffractometer. The crystals were kept at 150.00(10) K during data collection. **1**-**4**, **7** were collected with Cu source (λ = 1.54184); **5**, **8** were collected with Mo source (λ = 0.71073). Using Olex2,[3] the structures were solved with the SHELXT[4] and refined with the ShelXL[4] refinement package using Least Squares minimisation.

The asymmetric unit in **1** was seen to contain one molecule of the copper complex, and some disordered solvent. It is not unsurprising that the solvent is not ordered in this structure as it is located in lattice channels that are most visible when viewed down the *a* axis. An allowance for 2 molecules of hexane per unit cell has been made, in the formula as presented, based on the computations from the solvent mask algorithm available in Olex-2 which was employed in this instance.

Some disorder modelling was needed for **2**. In particular, the Bpin oxygens and methyl groups plus all atoms in the isopropyl group based on C23 were each refined as 2 components, in a 75:25 ratio. Distance and ADP restraints were employed in disordered regions, to assist convergence.

The asymmetric unit in **3** contains 1 molecule of the copper complex and a total of 2 molecules of benzene. The latter present as 2 crystallographically independent molecule halves (each close to an inversion centre) plus one full benzene moiety disorder in a 50:50 ratio over 2 positions. The rings in the disordered solvent were refined as rigid hexagons.

One molecule of benzene is present as a guest, in the asymmetric unit of **4**.

The dipp group based on C5 was treated for 63:37 disorder in **5**. Distance and ADP restraints were employed for partial occupancy atoms, in the latter refinement stages, to assist convergence.

In the asymmetric unit in **7** there exists a potential C-H···S interaction involving H40, for which U_{iso} was freely refined.

While the crystal structure determination of **8** is unambiguous, the esd associated with the *c* axis, the residuals and the ADPs are indicative of the fact that the sample itself was not of optimal quality. A beta angle of 90.118(4)^{o} led to considerable scrutiny of the raw data frames, but this did not afford compelling evidence for twinning at a credible level. In particular, a parallel integration as a twin followed by a subsequent solution and refinement with said data did not yield any improvement in the model and suggested that <5% of the diffraction arose from a putative second component. The isopropyl group based on C34 was treated for disorder in a 60:40 ratio, with the inclusion of distance and ADP restraints to assist convergence to a chemically sensible model.

Table S1 Crystal data and structure refinement details

Identification code	**1**	**2**	**3**	**4**	**5**	**7**	**8**
Empirical formula	$C_{37}H_{59}BCuN_2O_2$	$C_{34}H_{52}BCuN_2O_3$	$C_{46}H_{64}BCuN_2O_2S$	$C_{54}H_{68}BCuN_4O_3$	$C_{46}H_{66}BCuN_4O_3$	$C_{46}H_{66}BCuN_4O_2S$	$C_{45}H_{73}BCuN_5O_2$
Formula weight	638.21	611.12	783.40	895.47	797.37	813.43	790.43
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	P-1	$P2_1/c$	$Pbca$	P-1	$P2_1/n$
a/ Å	12.5417(1)	13.13010(10)	10.4440(5)	13.1041(1)	16.4325(2)	10.9964(2)	11.4621(5)
b/ Å	15.3496(1)	17.33930(10)	12.3254(5)	20.9155(2)	21.3202(4)	11.2752(2)	17.3090(7)
c/ Å	19.7734(2)	15.07540(10)	19.4836(8)	19.0050(2)	25.9216(5)	19.2382(3)	22.5662(11)
α/ °	90	90	76.032(4)	90	90	93.552(1)	90
β/ °	100.749(1)	99.7840(10)	88.810(3)	107.294(1)	90	103.108(2)	90.118(4)
γ/ °	90	90	67.215(4)	90	90	90.514(1)	90
U/ Å^3	3739.79(6)	3382.25(4)	2236.54(18)	4973.38(8)	9081.5(3)	2318.02(7)	4477.1(3)
Z	4	4	2	4	8	2	4
ρ_{calc}/ g cm^{-3}	1.134	1.200	1.163	1.196	1.166	1.165	1.173
μ/ mm^{-1}	1.051	1.166	1.396	0.966	0.523	1.377	0.528
F(000)	1380.0	1312.0	840.0	1912.0	3424.0	872.0	1712.0
Crystal size/ mm^3	0.313 × 0.175 × 0.13	0.348 × 0.253 × 0.209	0.317 × 0.091 × 0.049	0.299 × 0.096 × 0.048	0.401 × 0.282 × 0.162	0.188 × 0.155 × 0.084	0.523 × 0.395 × 0.209
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2θ range for data collection/ °	7.174 to 146.582	7.836 to 146.076	8.042 to 146.088	6.448 to 146.324	5.87 to 58.26	7.858 to 146.254	5.898 to 58.316
Index ranges	−13 ≤ h ≤ 15, −13 ≤ k ≤ 19, −22 ≤ l ≤ 24	−15 ≤ h ≤ 16, −21 ≤ k ≤ 15, −18 ≤ l ≤ 18	−12 ≤ h ≤ 7, −15 ≤ k ≤ 15, −24 ≤ l ≤ 23	−16 ≤ h ≤ 11, −25 ≤ k ≤ 25, −15 ≤ l ≤ 23	−22 ≤ h ≤ 22, −29 ≤ k ≤ 29, −35 ≤ l ≤ 33	−13 ≤ h ≤ 13, −10 ≤ k ≤ 13, −23 ≤ l ≤ 23	−15 ≤ h ≤ 11, −23 ≤ k ≤ 23, −30 ≤ l ≤ 29
Reflections collected	25521	25199	15667	34742	78752	27517	42619
Independent reflections, R_{int}	7337, 0.0203	6726, 0.0172	8732, 0.0249	9839, 0.0230	11957, 0.0621	9228, 0.0195	11558, 0.0468
Data/restraints/parameters	7337/0/373	6726/155/463	8732/15/520	9839/0/580	11957/293/623	9228/0/512	11558/79/534
Goodness−of−fit on F2	1.039	1.032	1.038	1.032	1.052	1.028	1.034
Final R1, wR2 [I>=2σ (I)]	0.0313, 0.0878	0.0372, 0.0983	0.0420, 0.1046	0.0330, 0.0859	0.0512, 0.1032	0.0316, 0.0842	0.0829, 0.2219
Final R1, wR2 [all data]	0.0332, 0.0894	0.0384, 0.0993	0.0489, 0.1102	0.0368, 0.0888	0.0996, 0.1241	0.0331, 0.0855	0.1344, 0.2552
Largest diff. peak/hole / e Å^{-3}	0.34/−0.39	0.35/−0.53	0.47/−0.48	0.39/−0.36	0.72/−0.39	0.48/−0.27	1.64/−0.38

In situ reaction monitoring by NMR spectroscopy

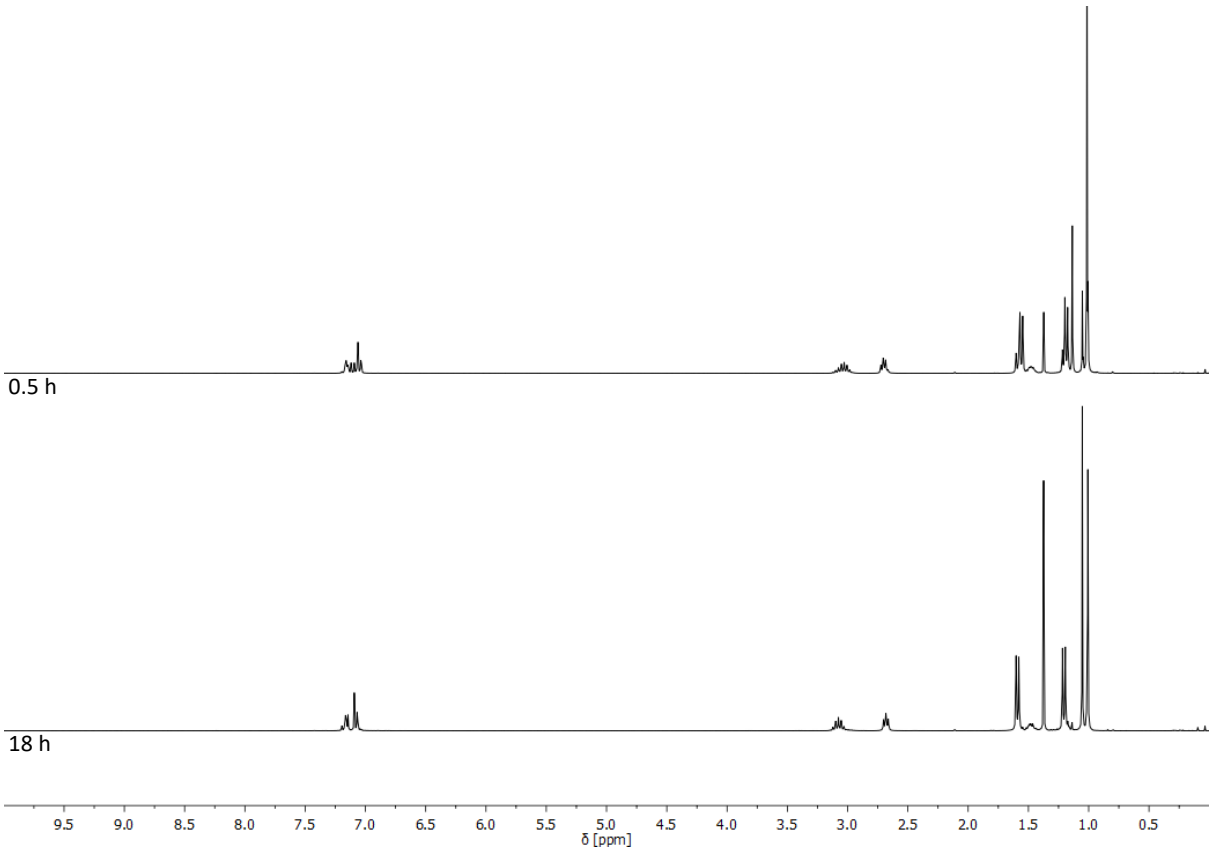

Figure S1: The reaction between (6-Dipp)CuO^{t}Bu and pin_2B_2 in C_6D_6, monitored by ^{1}H NMR spectroscopy

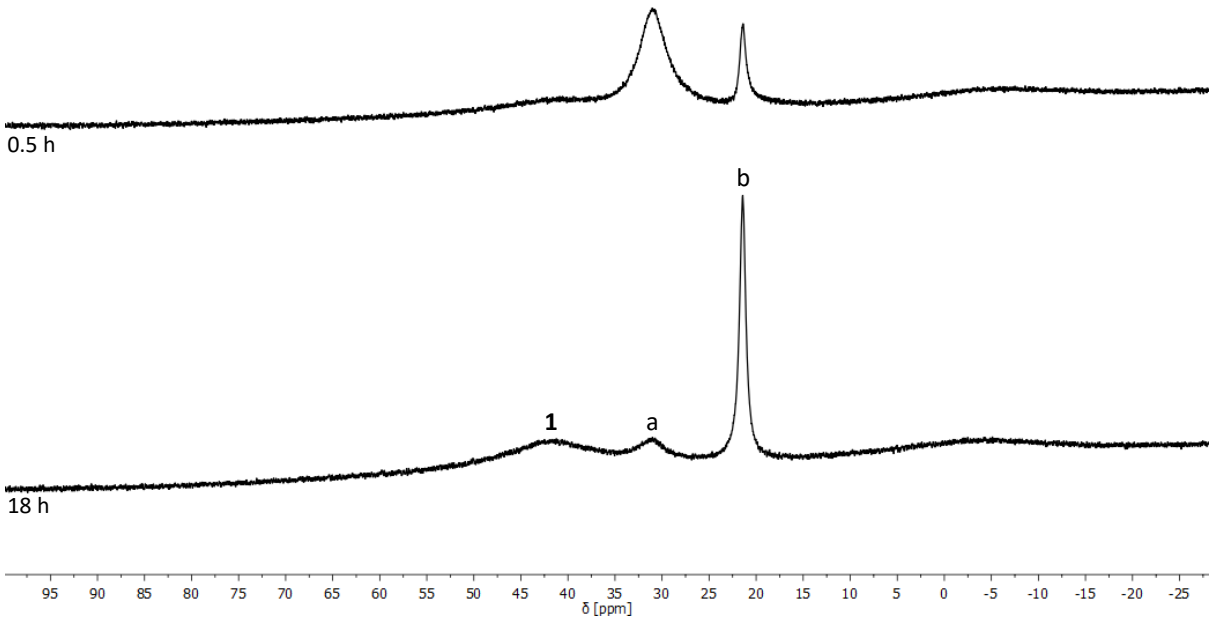

Figure S2: The reaction between (6-Dipp)CuO^{t}Bu and pin_2B_2 in C_6D_6, monitored by ^{11}B NMR spectroscopy, showing the formation of compound **1**, where a = pin_2B_2; b = pinBO^{t}Bu.

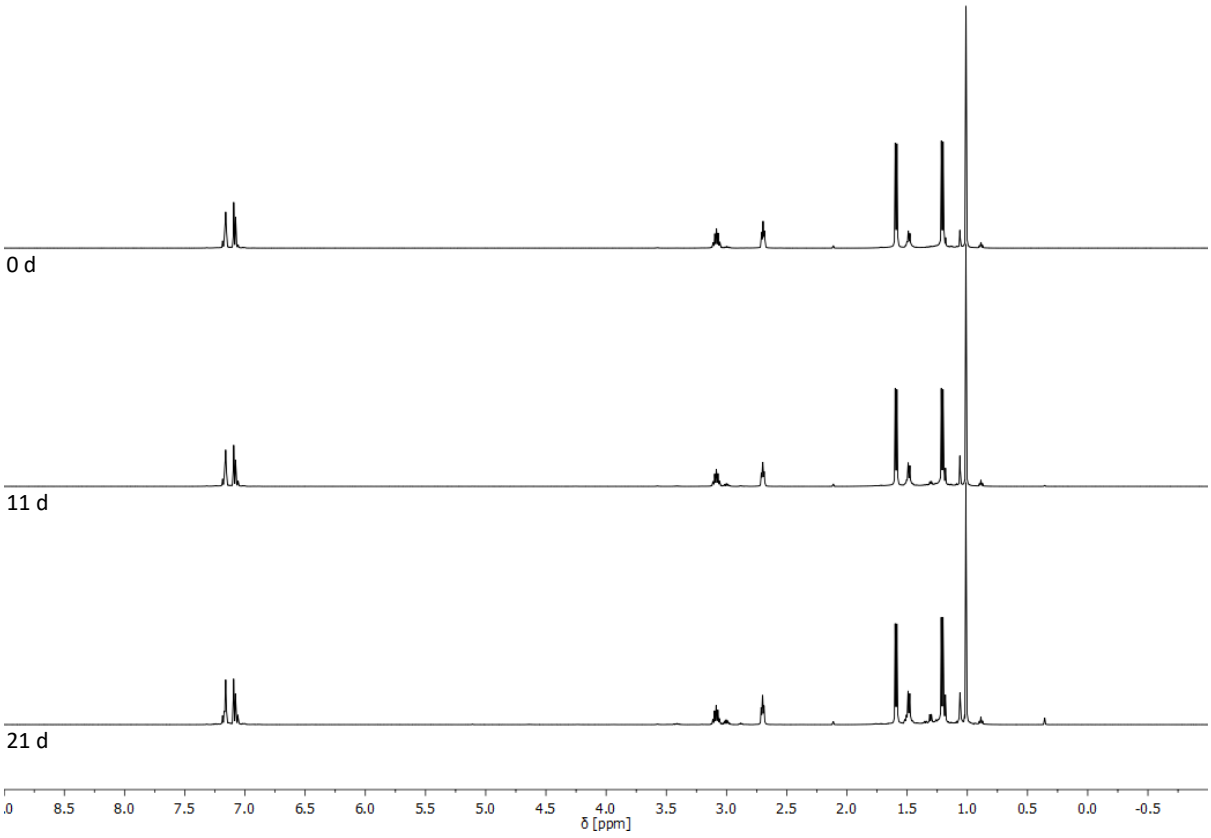

Figure S3: Stability of **1** in C_6D_6 at room temperature, monitored by ^{1}H NMR spectroscopy.

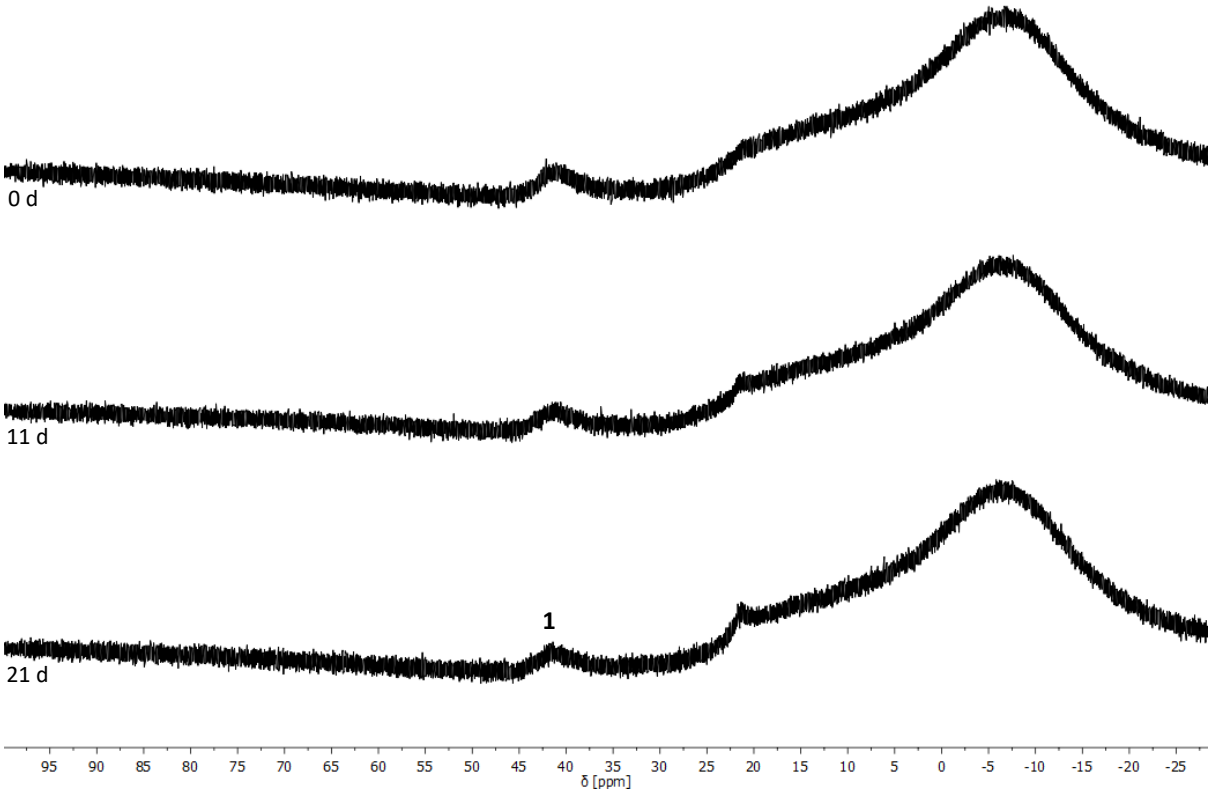

Figure S4: Stability of **1** in C_6D_6 at room temperature, monitored by ^{11}B NMR spectroscopy.

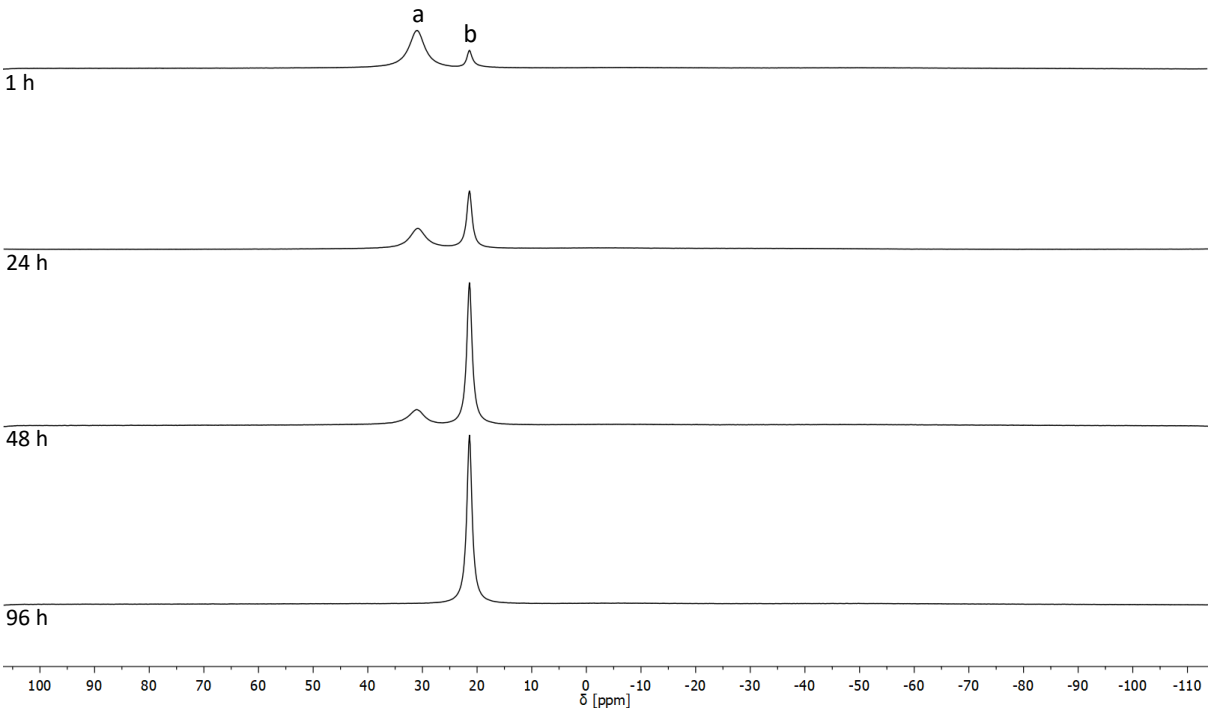

Figure S5: The reaction of pin_2B_2 under an atmosphere of $^{13}CO_2$ with 10 mol% of (6-Dipp)CuO^{t}Bu in C_6D_6, monitored by ^{11}B NMR spectroscopy, where a = pin_2B_2; b = pinBOBpin.

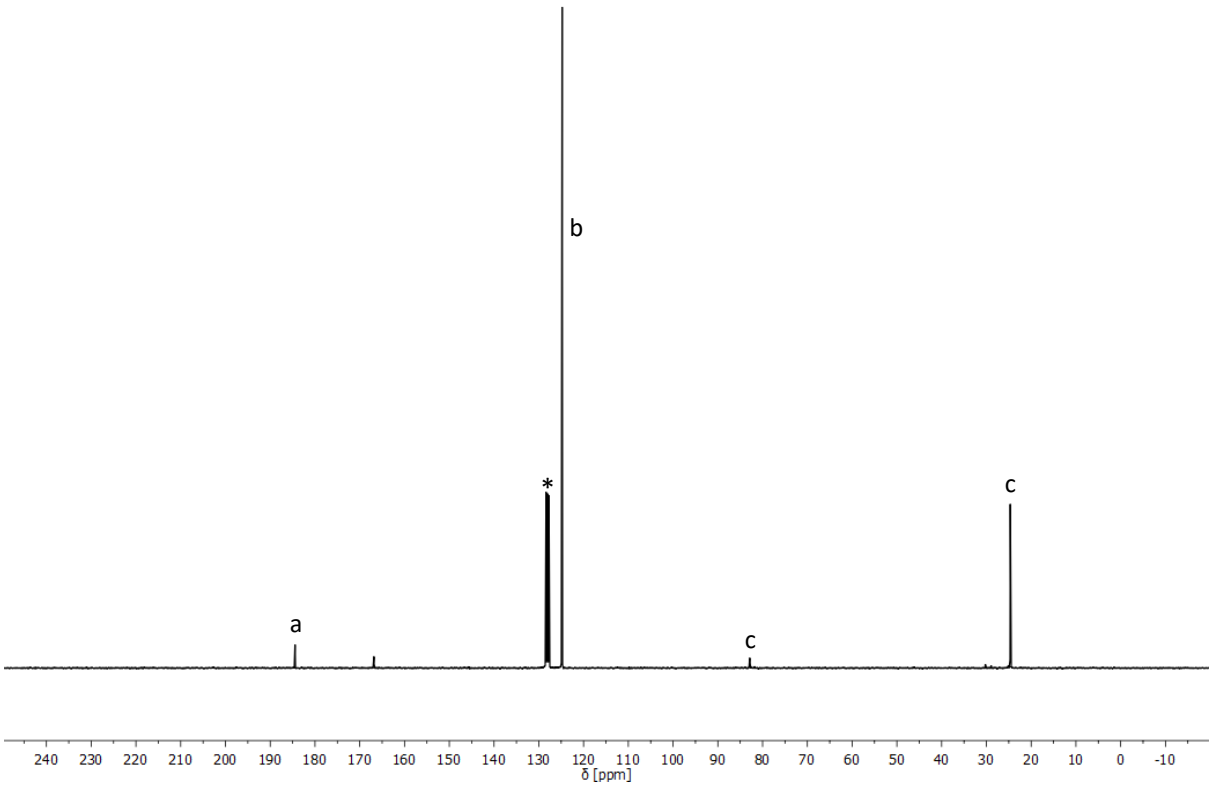

Figure S6: The $^{13}C\{^1H\}$ NMR spectrum of the reaction of pin_2B_2 under an atmosphere of $^{13}CO_2$ with 10 mol% of (6-Dipp)CuO^{t}Bu in C_6D_6 after 96 hours, where a = ^{13}CO; b = $^{13}CO_2$; c = pinBOBpin; * = solvent signal.

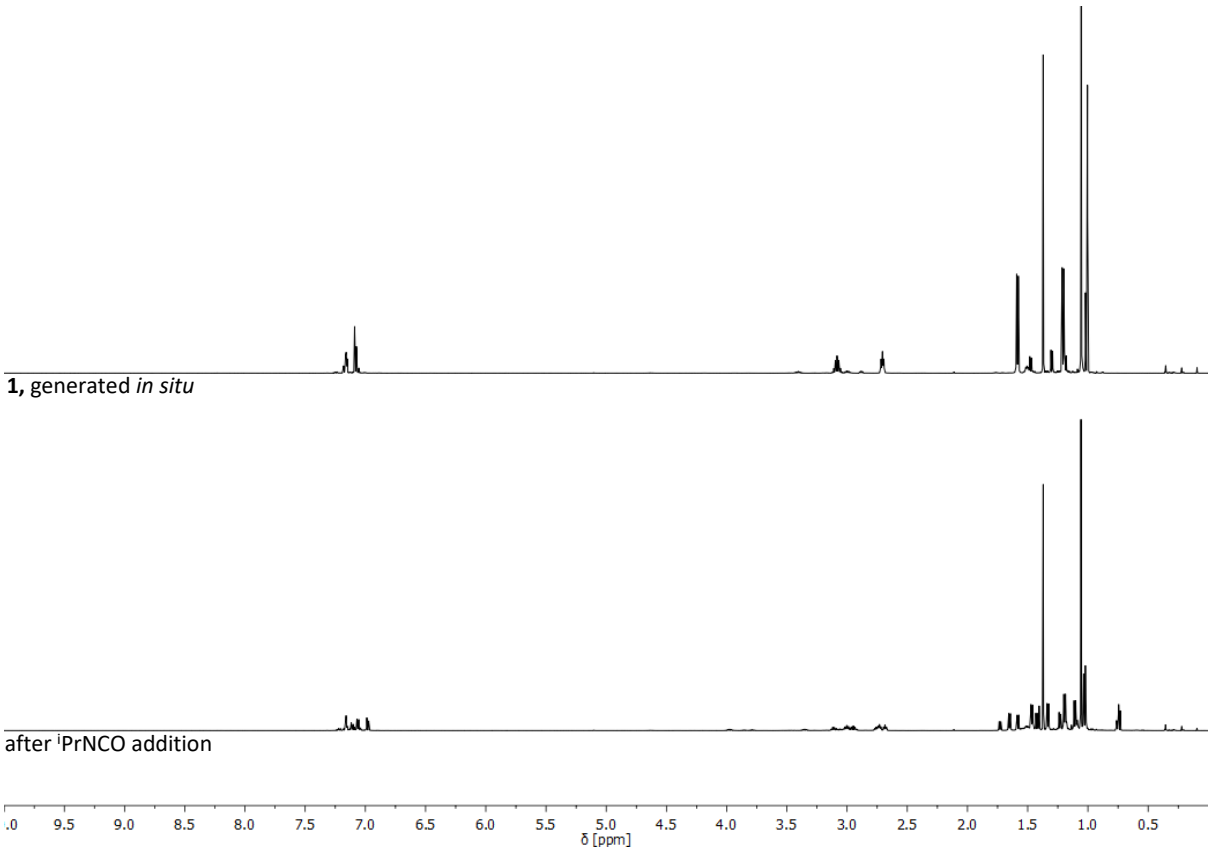

Figure S7: The reaction between isopropyl isocyanate and **1**, generated *in situ* from (6-Dipp)CuO^{t}Bu and pin_2B_2 in C_6D_6, monitored by ^{1}H NMR spectroscopy.

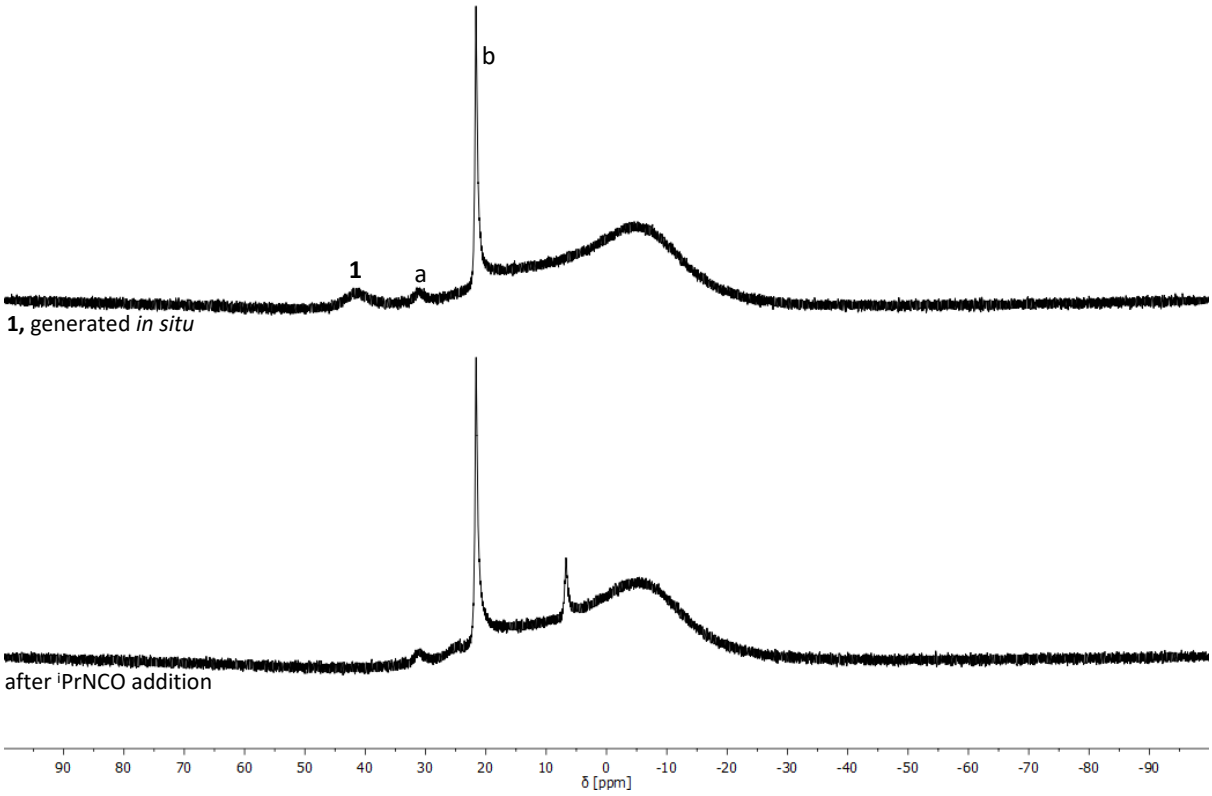

Figure S8: The reaction between isopropyl isocyanate and **1**, generated *in situ* from (6-Dipp)CuO^{t}Bu and pin_2B_2 in C_6D_6, monitored by ^{11}B NMR spectroscopy, where a = pin_2B_2; b = pinBO^{t}Bu.

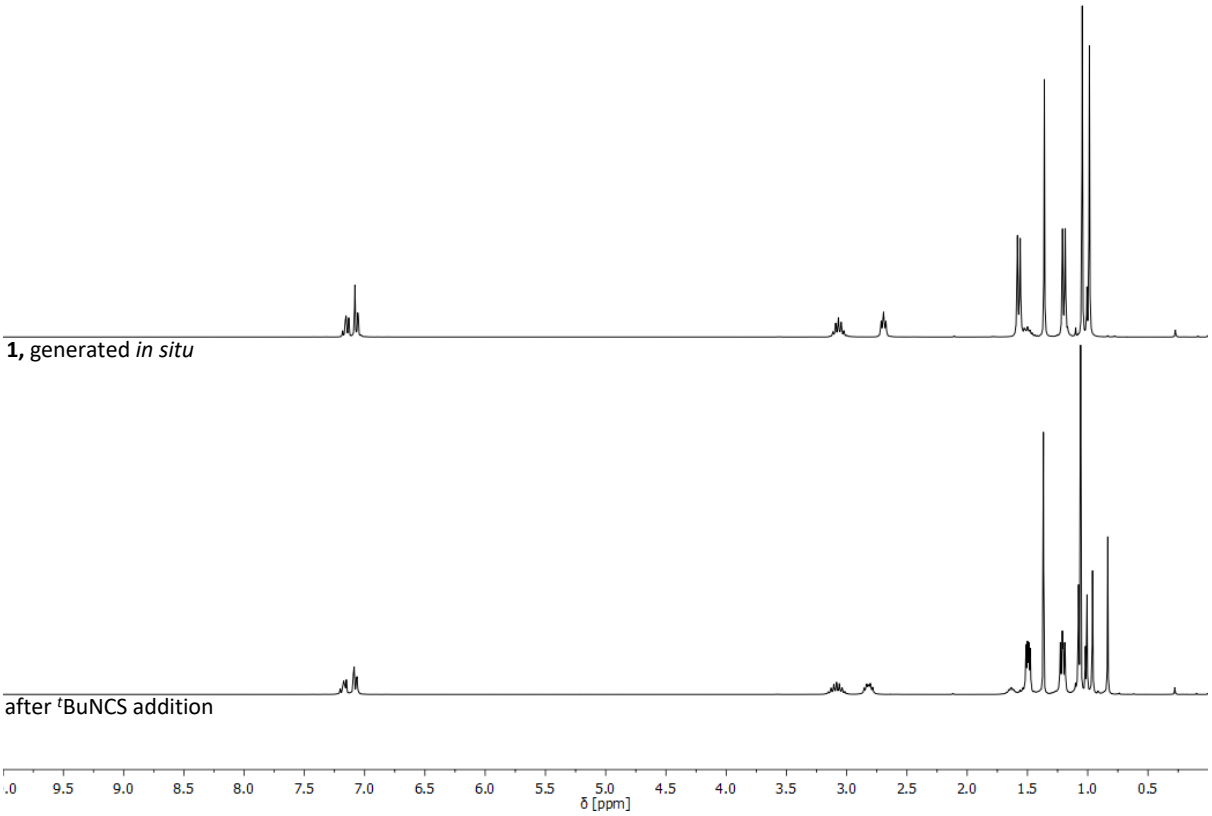

Figure S9: The reaction between *tert*-butyl isothiocyanate and **1**, generated *in situ* from (6-Dipp)CuO^{t}Bu and pin_2B_2 in C_6D_6, monitored by ^{1}H NMR spectroscopy.

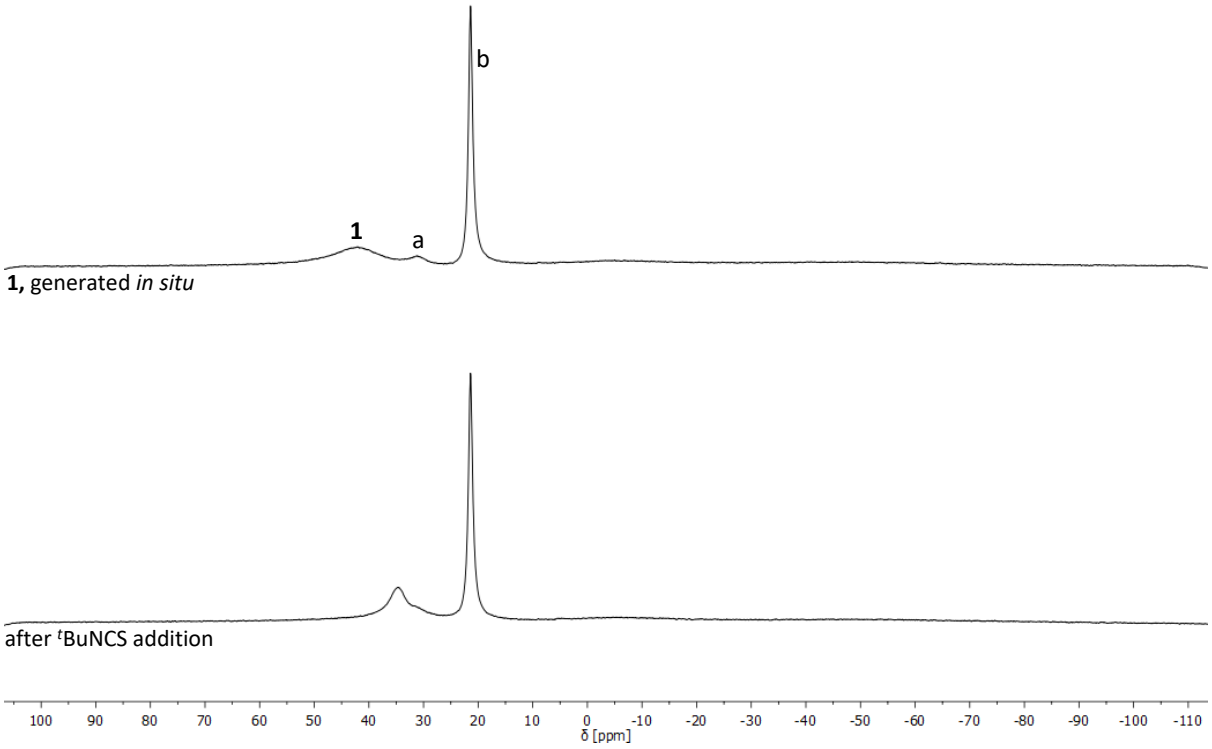

Figure S10: The reaction between *tert*-butyl isothiocyanate and **1**, generated *in situ* from (6-Dipp)CuO^{t}Bu and pin_2B_2 in C_6D_6, monitored by ^{11}B NMR spectroscopy, where a = pin_2B_2; b = pinBO^{t}Bu.

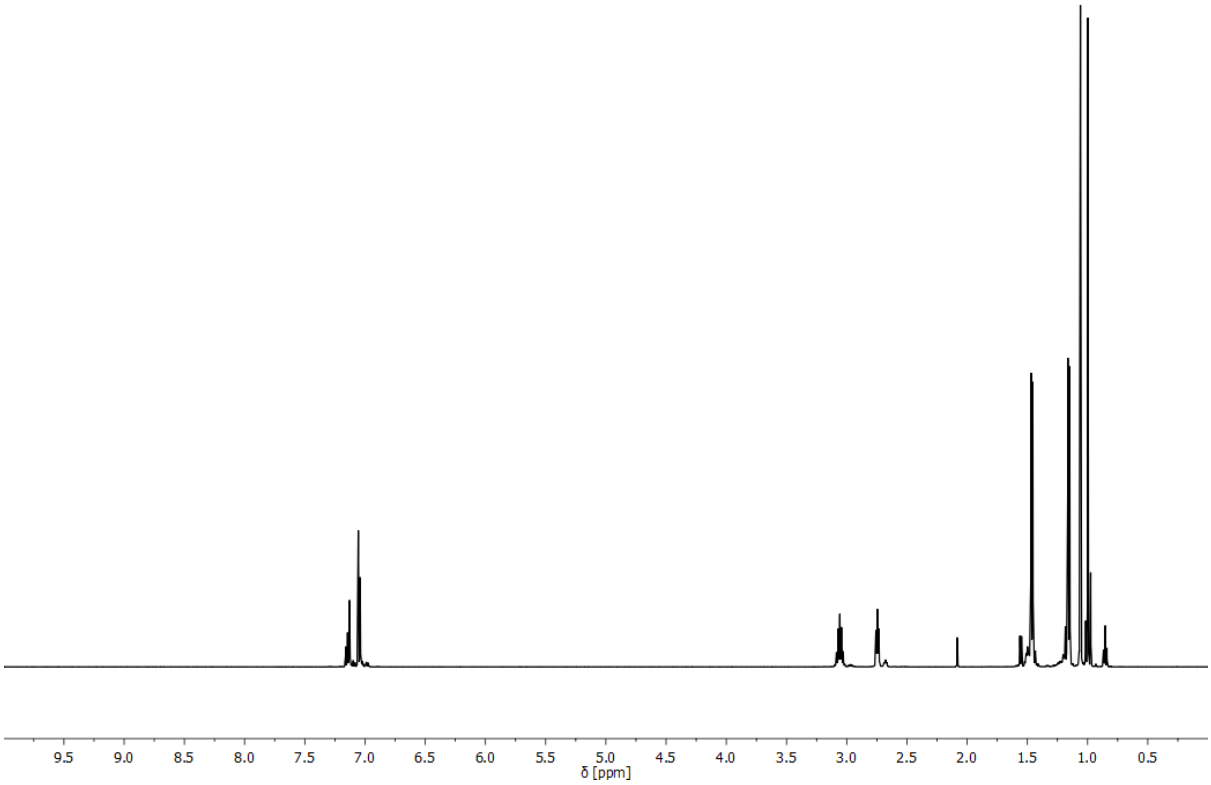

Figure S11: The ^{1}H NMR spectrum of the reaction between *tert*-butyl isocyanide and **1**.

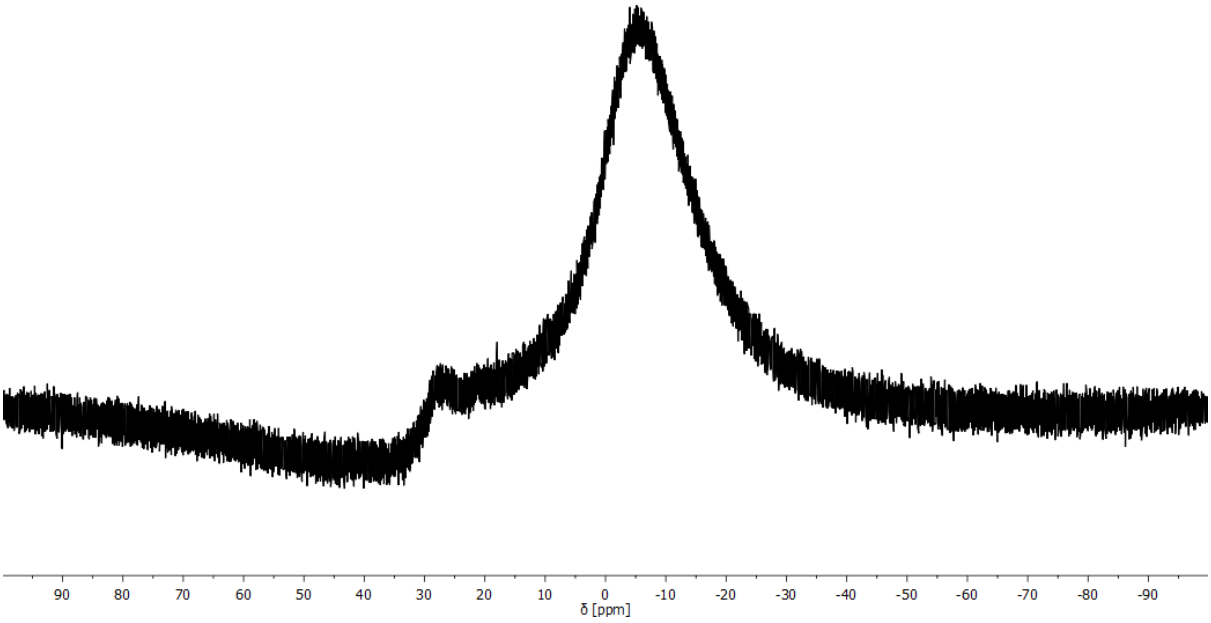

Figure S12: The ^{11}B NMR spectrum of the reaction between *tert*-butyl isocyanide and **1**.

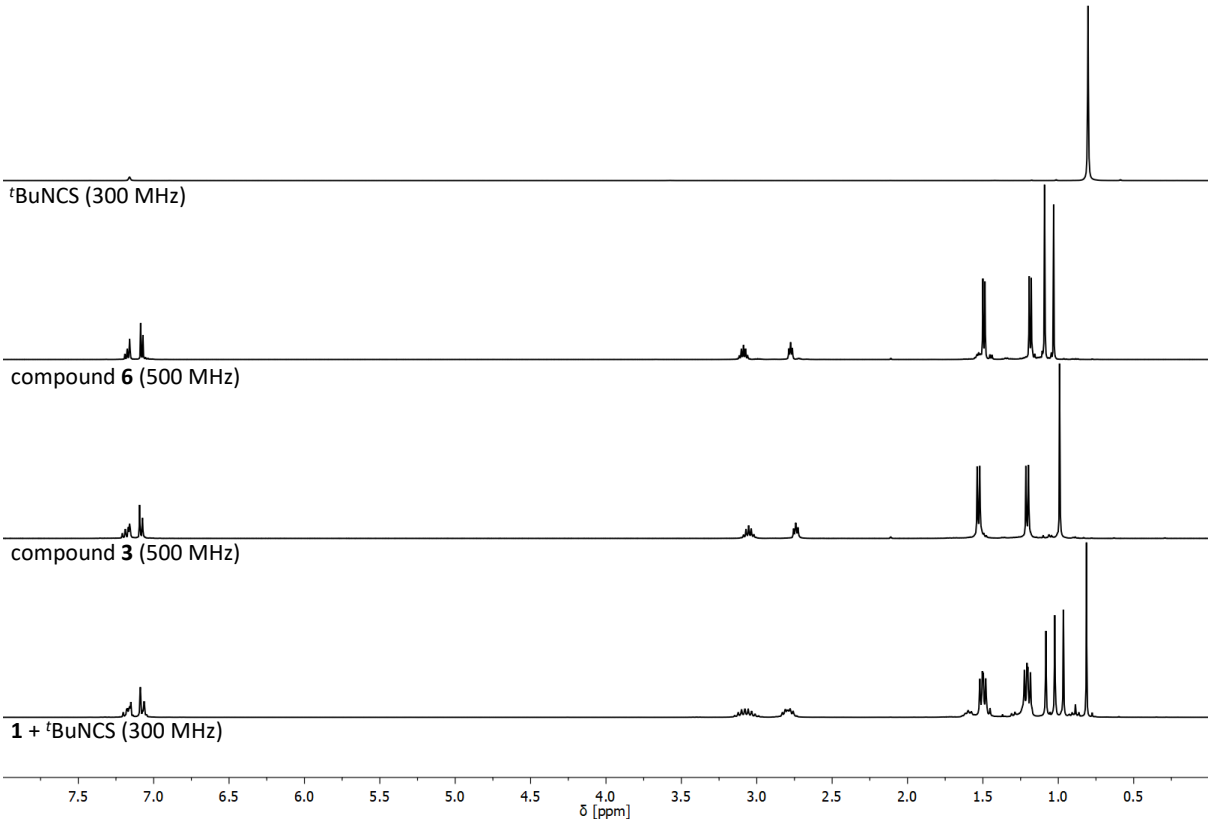

Figure S13: The ^{1}H NMR spectrum of the reaction between *tert*-butyl isothiocyanate and isolated **1**, compared with isolated reagents and products.

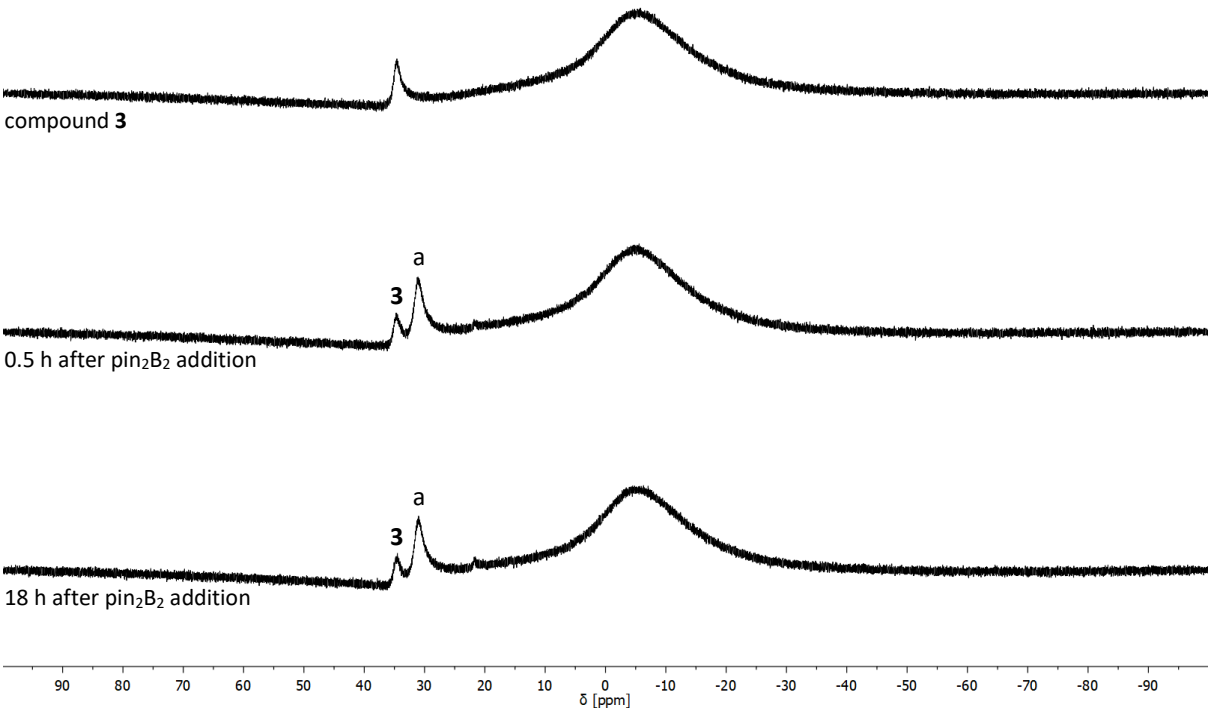

Figure S14: The reaction between pin_2B_2 and **3** in C_6D_6, monitored by ^{11}B NMR spectroscopy, where a = pin_2B_2.

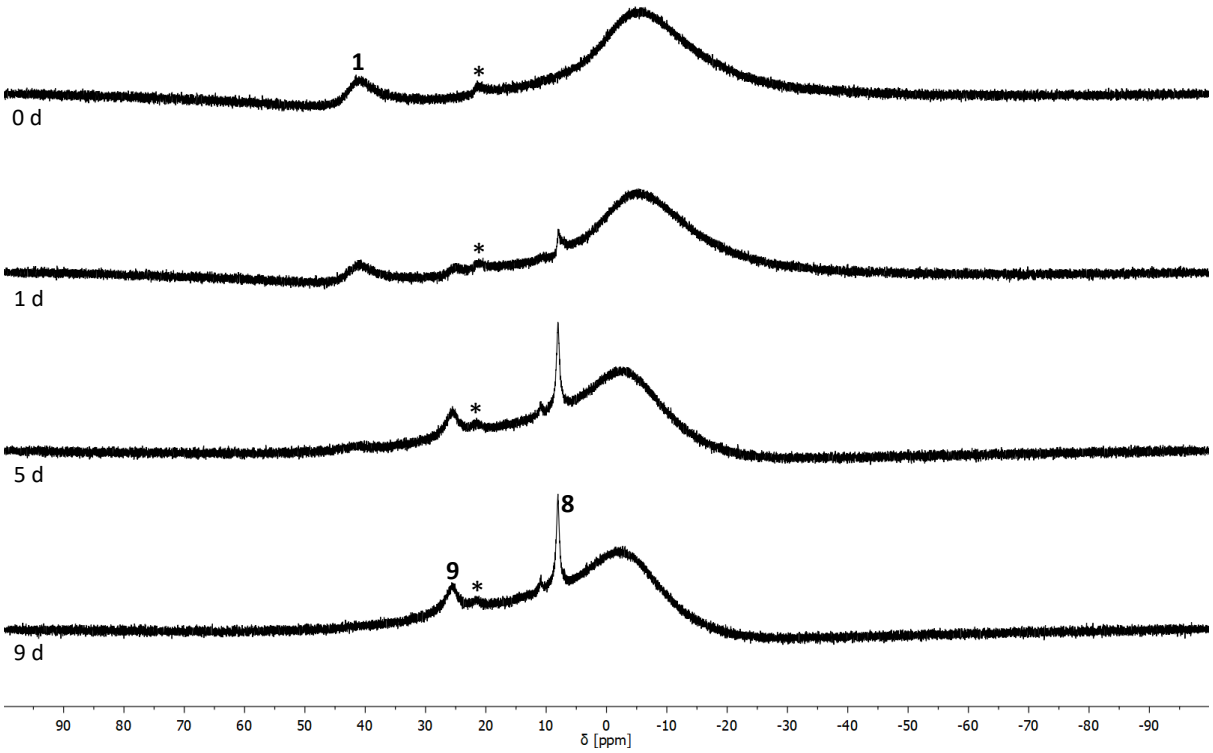

Figure S15: The reaction between diisopropyl carbodiimide and **1** in C_6D_6, monitored by ^{11}B NMR spectroscopy (*: residual **2** from starting material).

NMR spectra of compounds 1-8

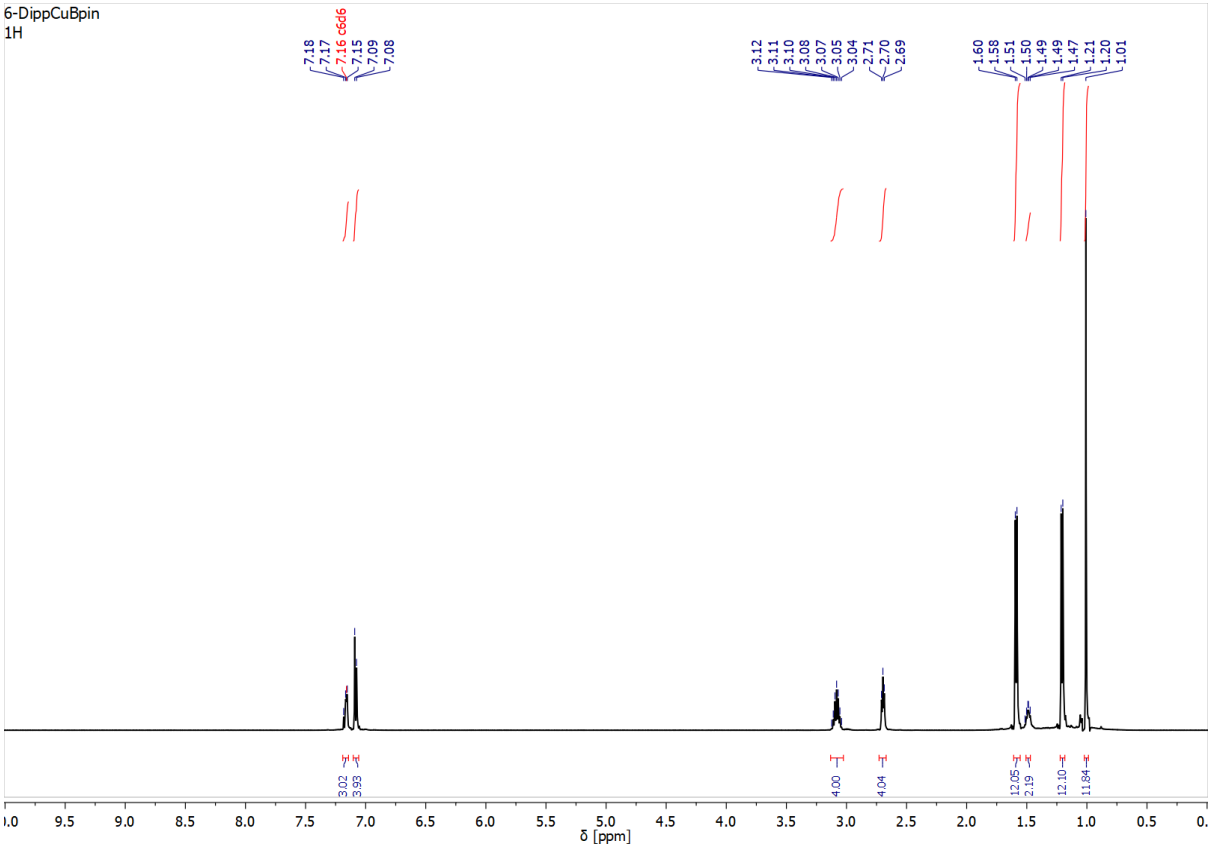

Figure S16: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **1**.

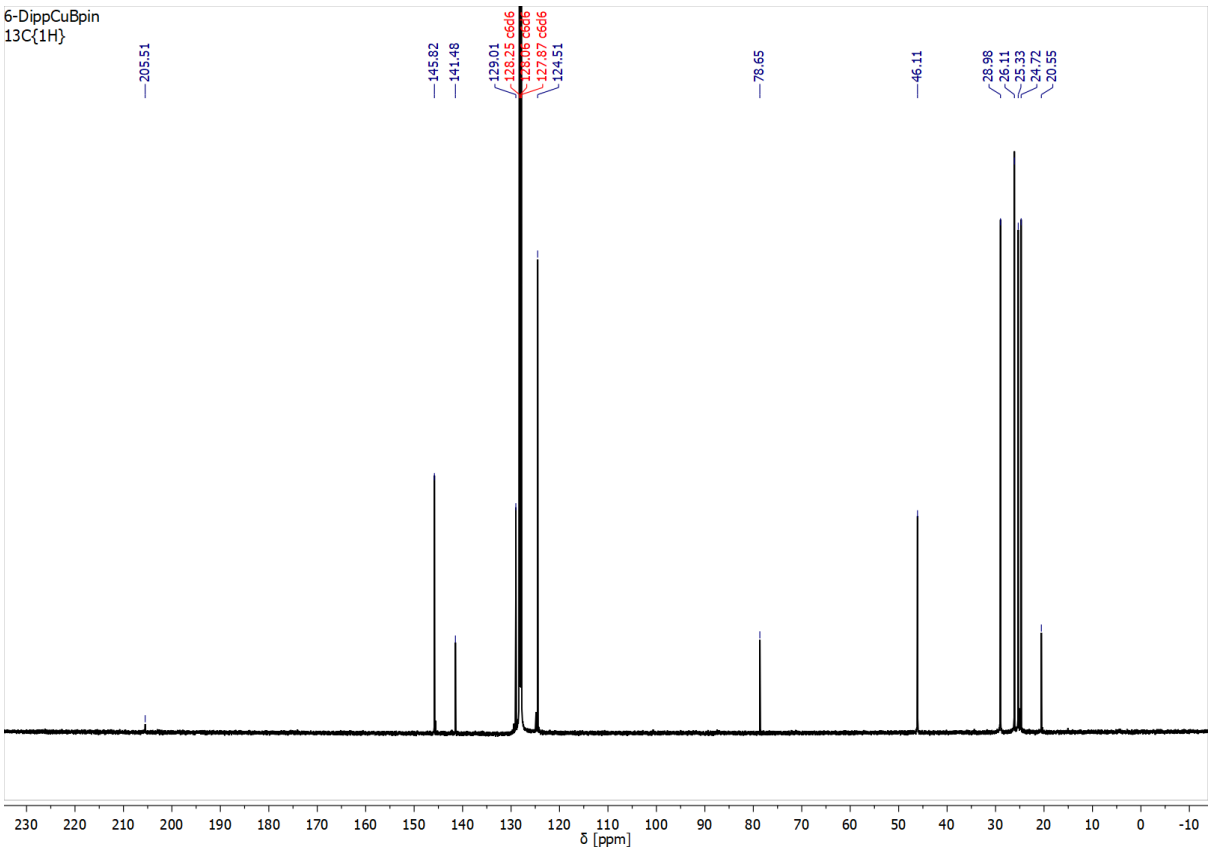

Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **1**.

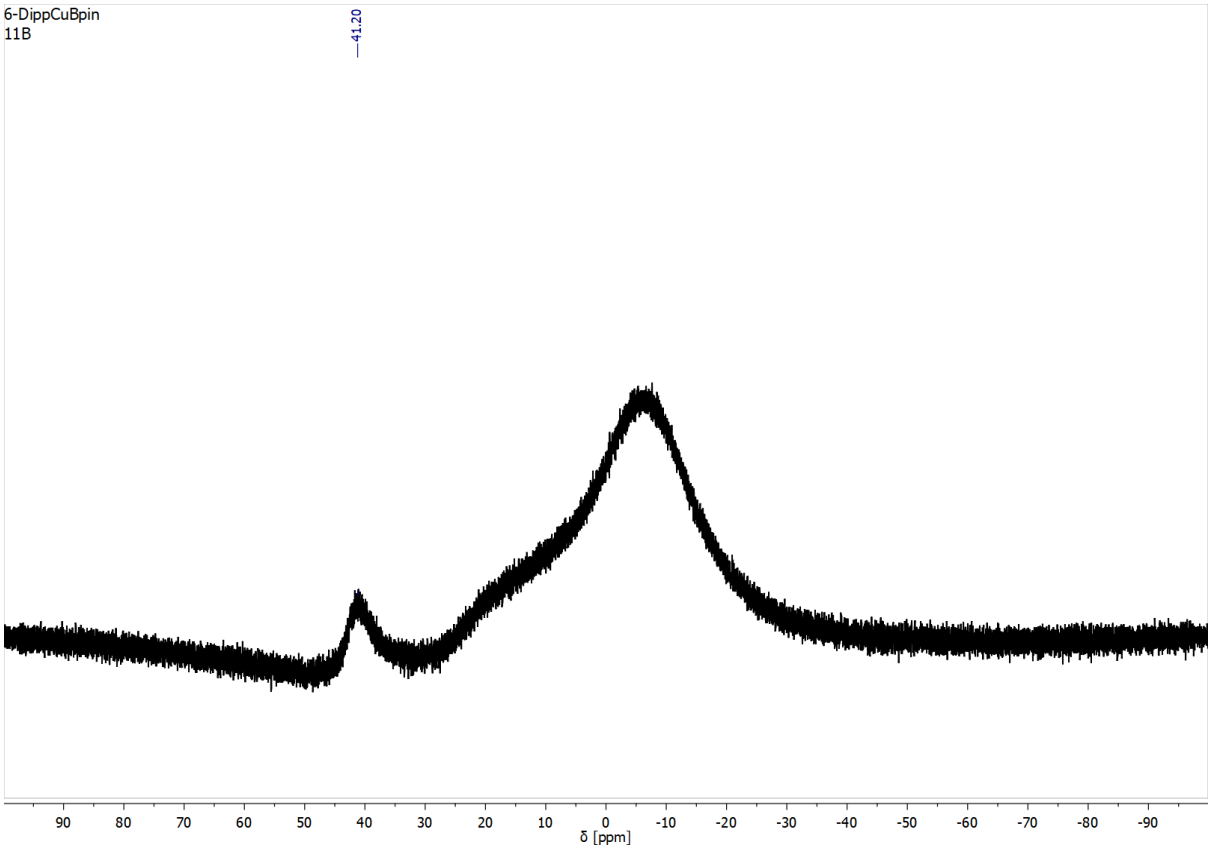

Figure S18: ^{11}B NMR spectrum (160 MHz, C_6D_6) of compound **1**.

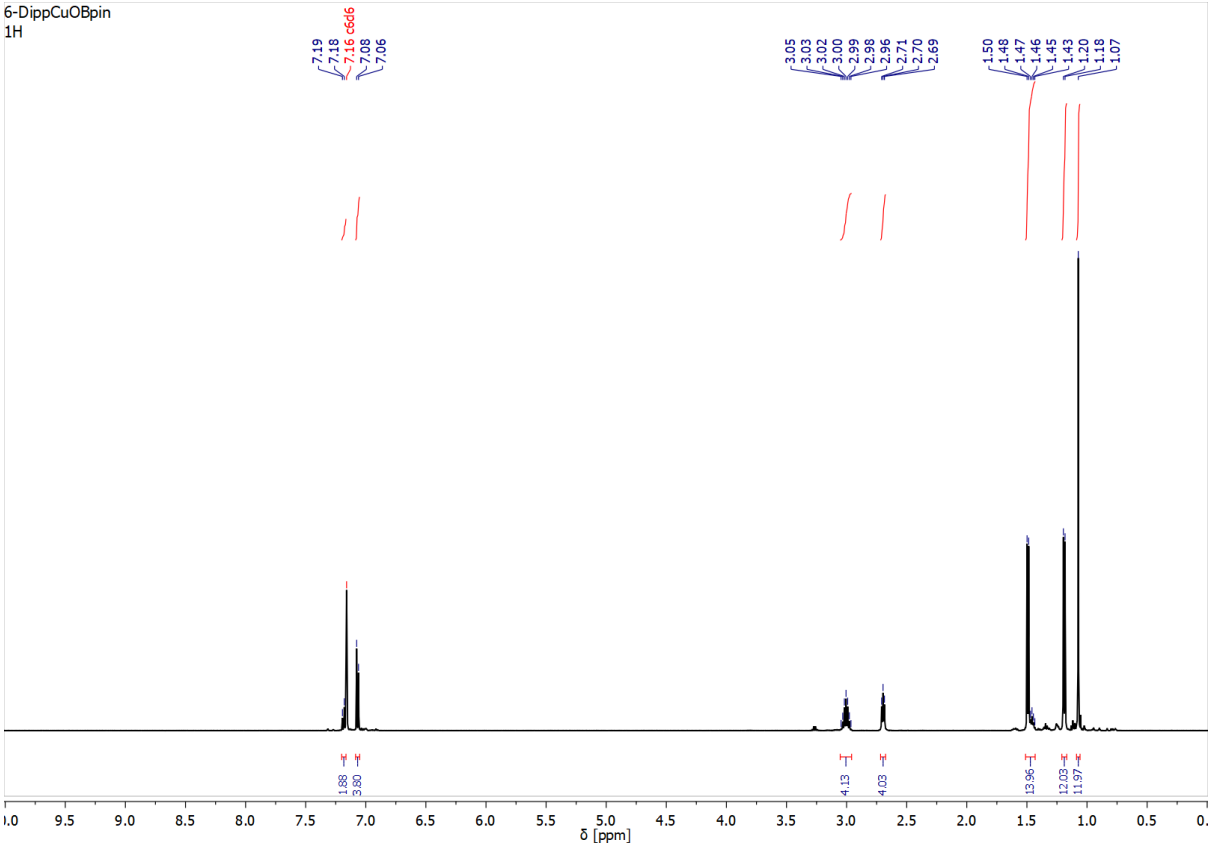

Figure S19: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **2**.

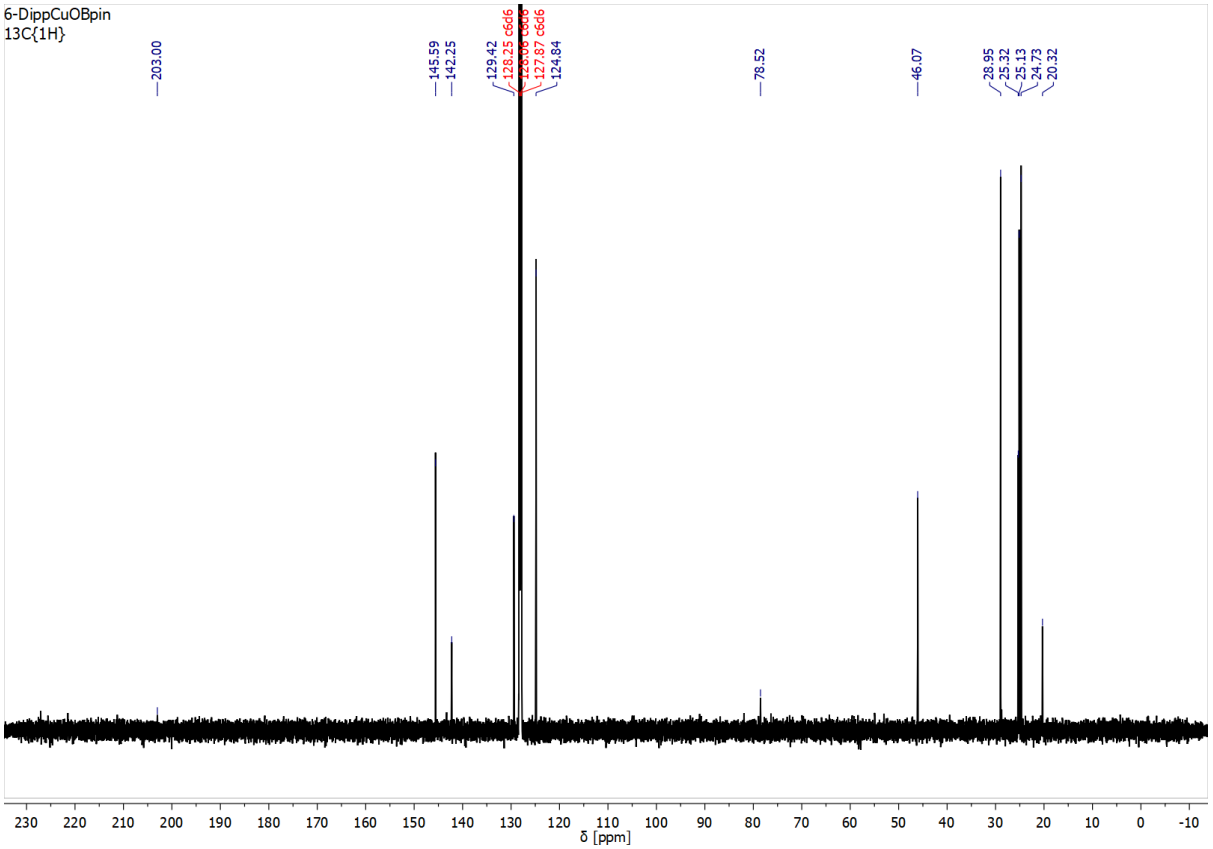

Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **2**.

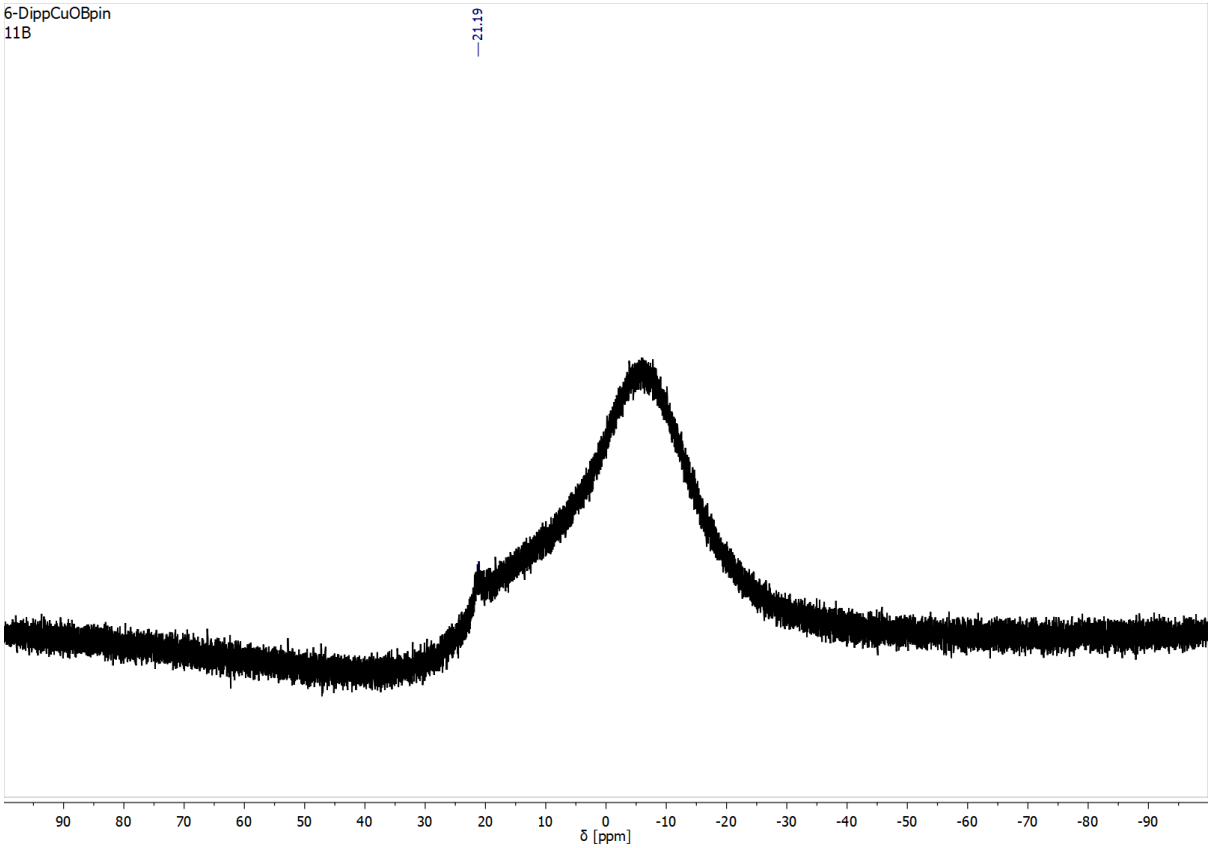

Figure S21: ^{11}B NMR spectrum (160 MHz, C_6D_6) of compound **2**.

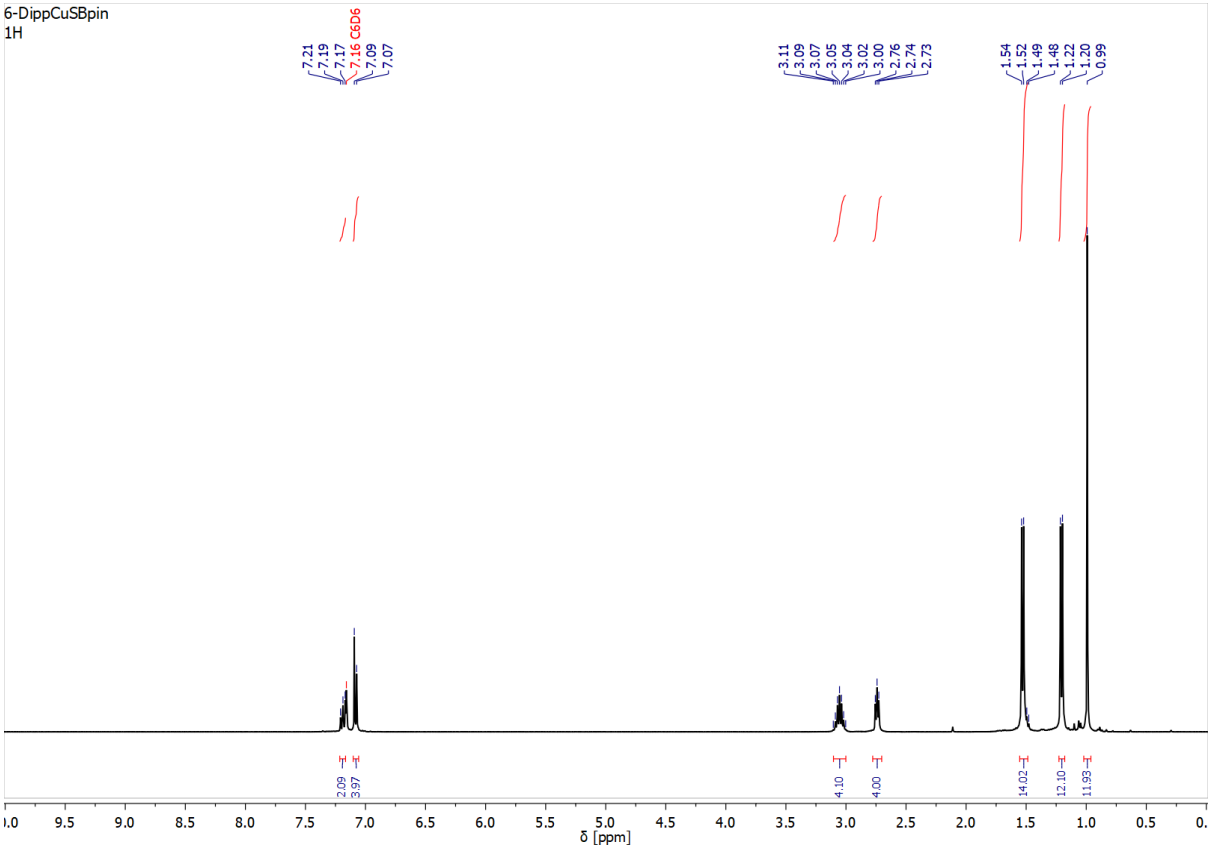

Figure S22: ^{1}H NMR spectrum (400 MHz, C_6D_6) of compound **3**.

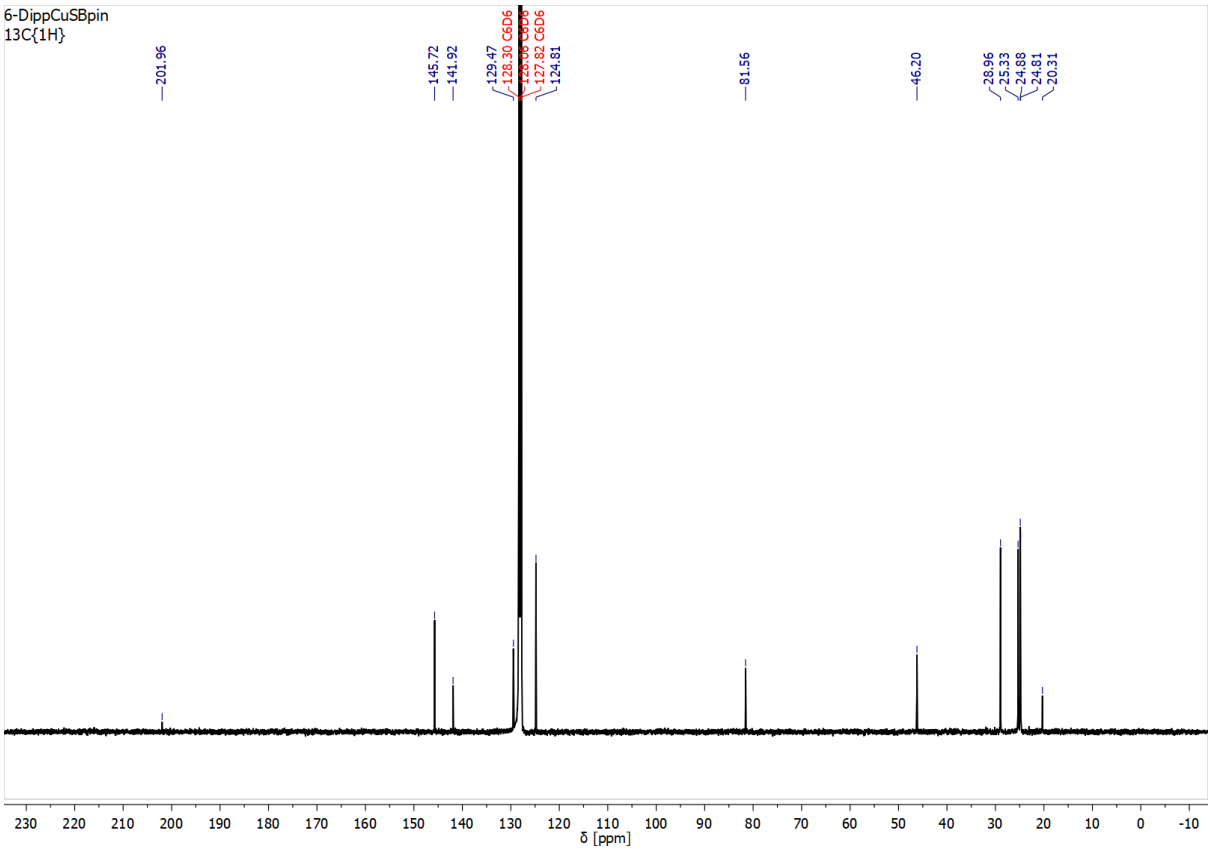

Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, C_6D_6) of compound **3**.

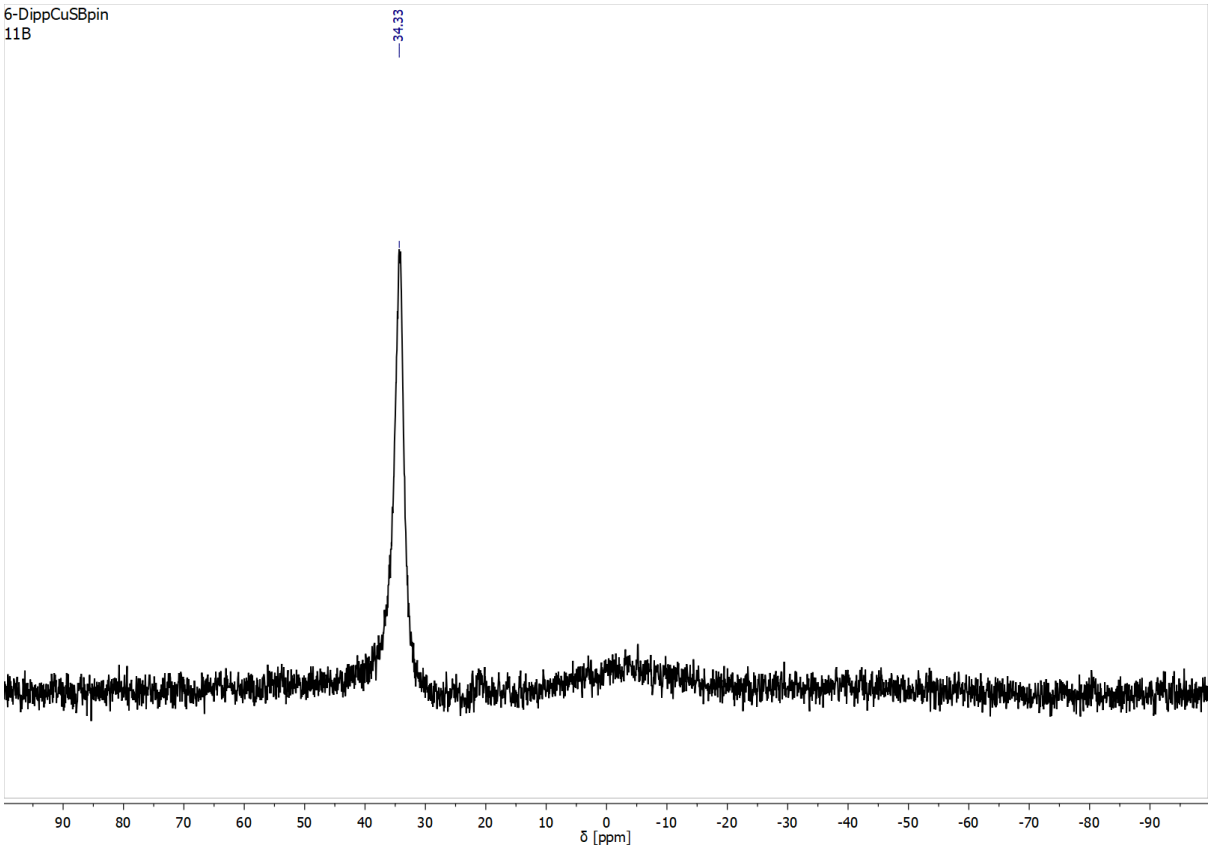

Figure S24: ^{11}B NMR spectrum (128 MHz, C_6D_6) of compound **3**.

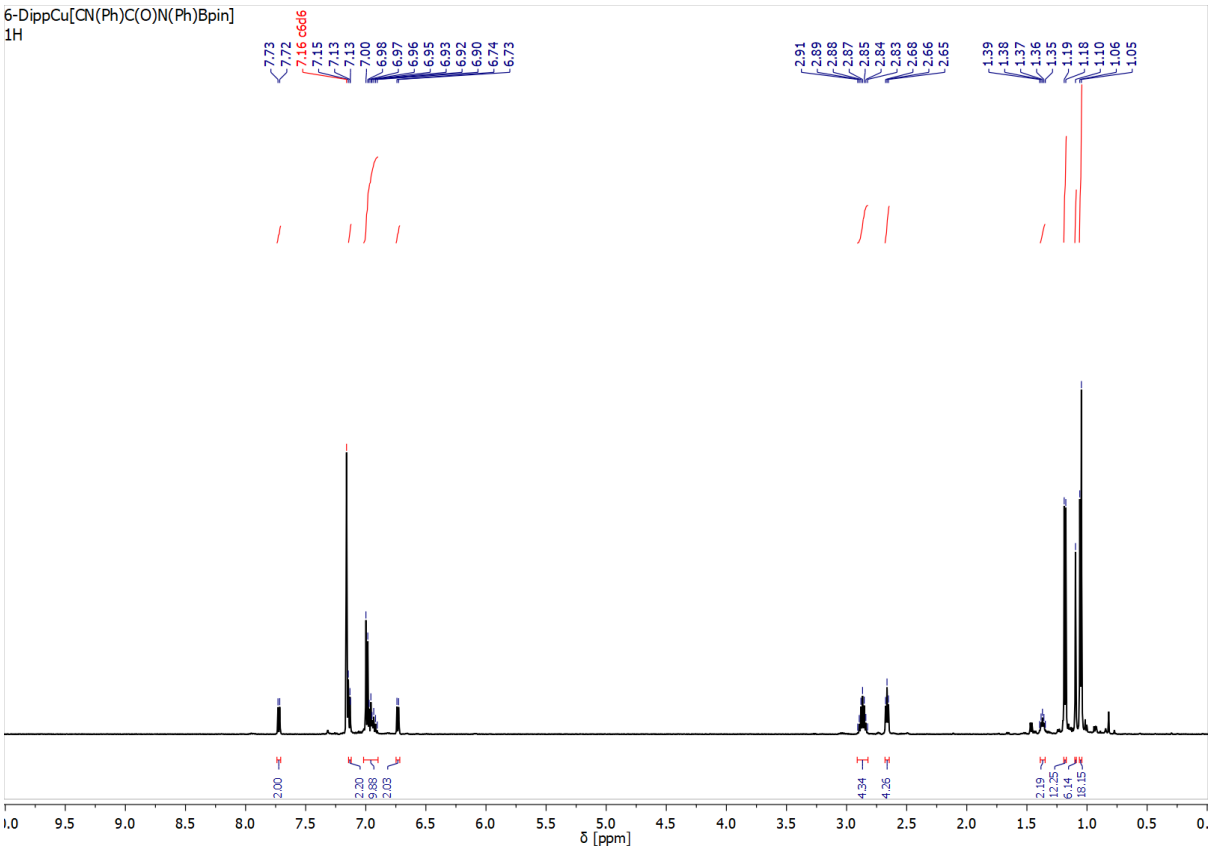

Figure S25: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **4**.

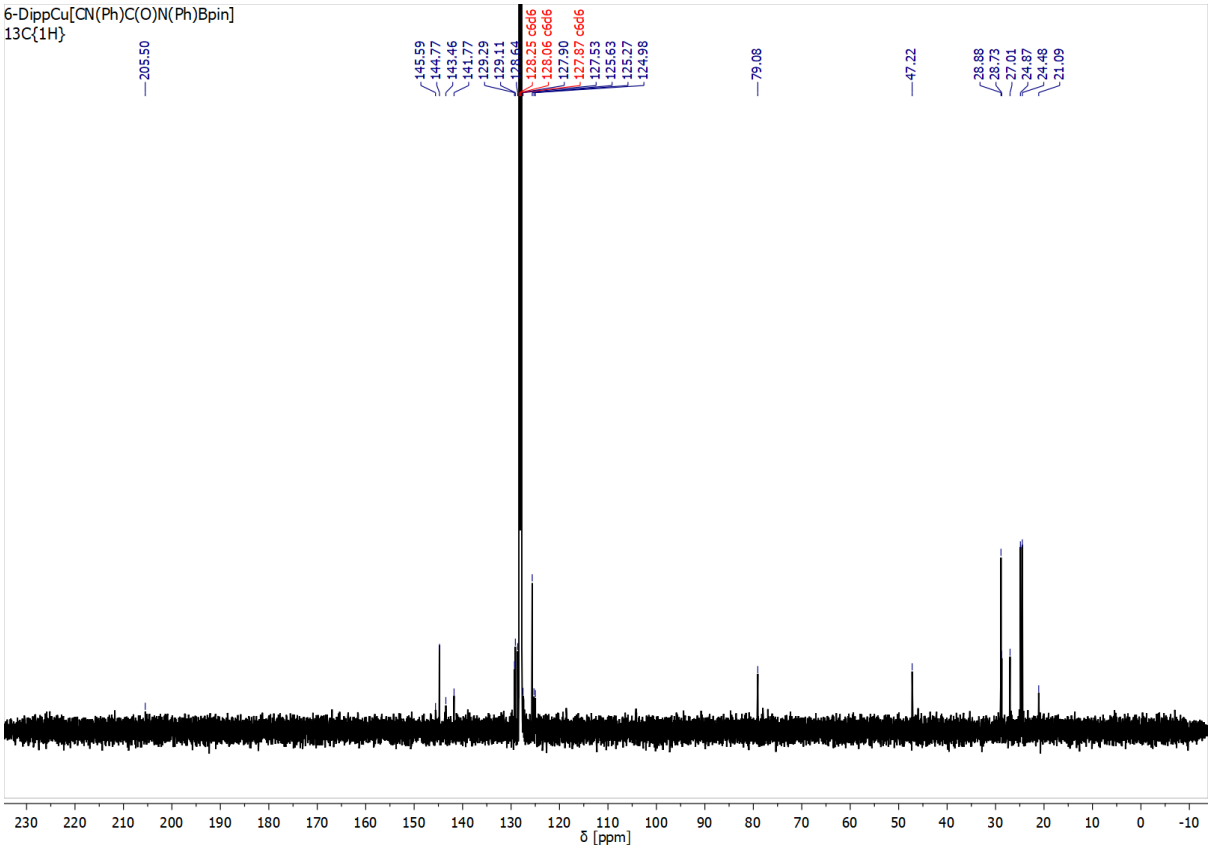

Figure S26: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **4**.

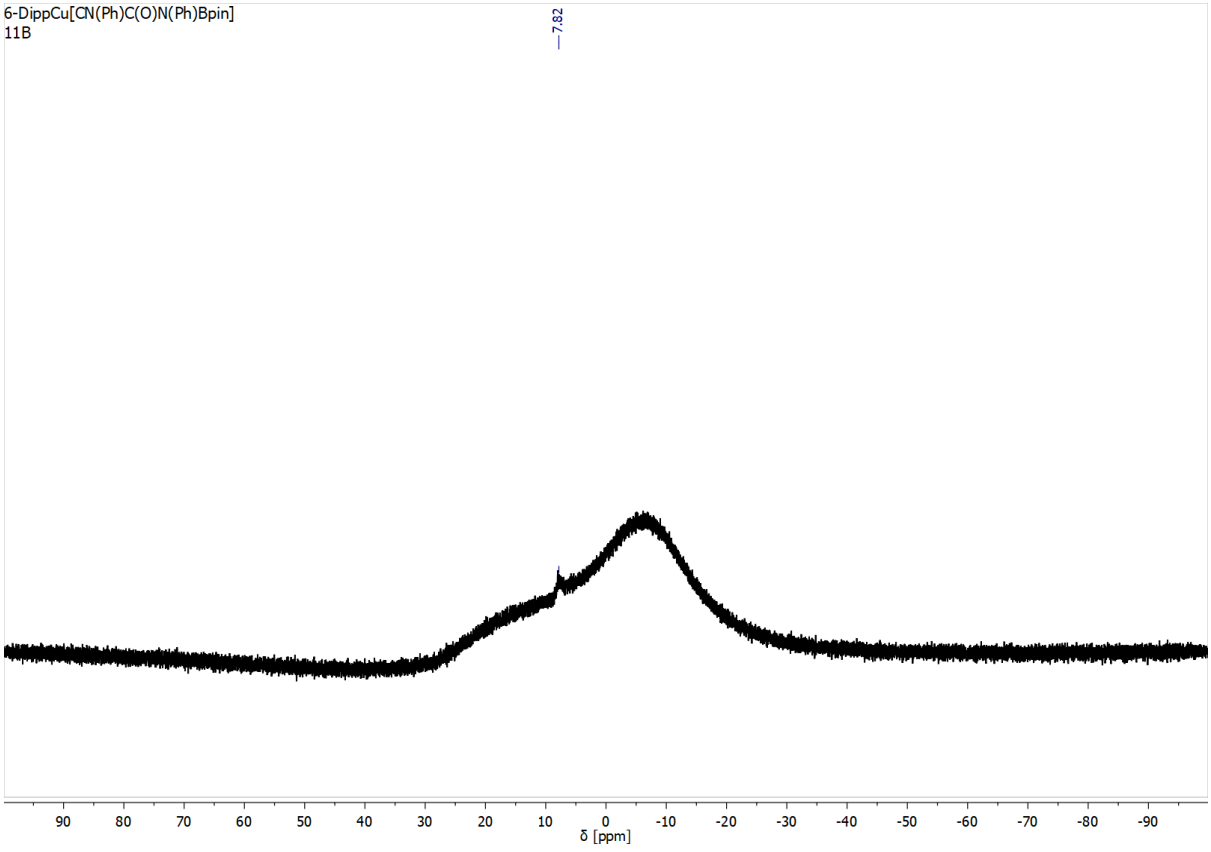

Figure S27: ^{11}B NMR spectrum (160 MHz, C_6D_6) of compound **4**.

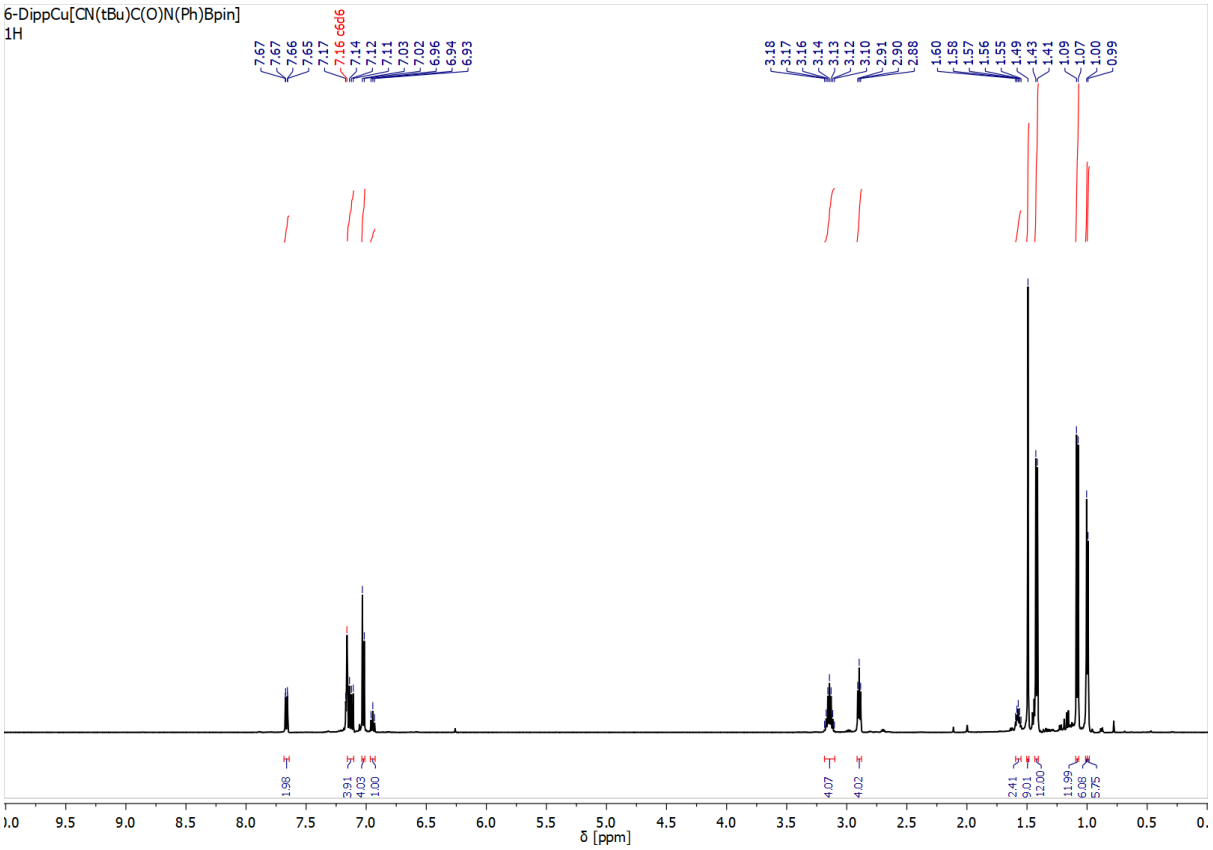

Figure S28: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **5**.

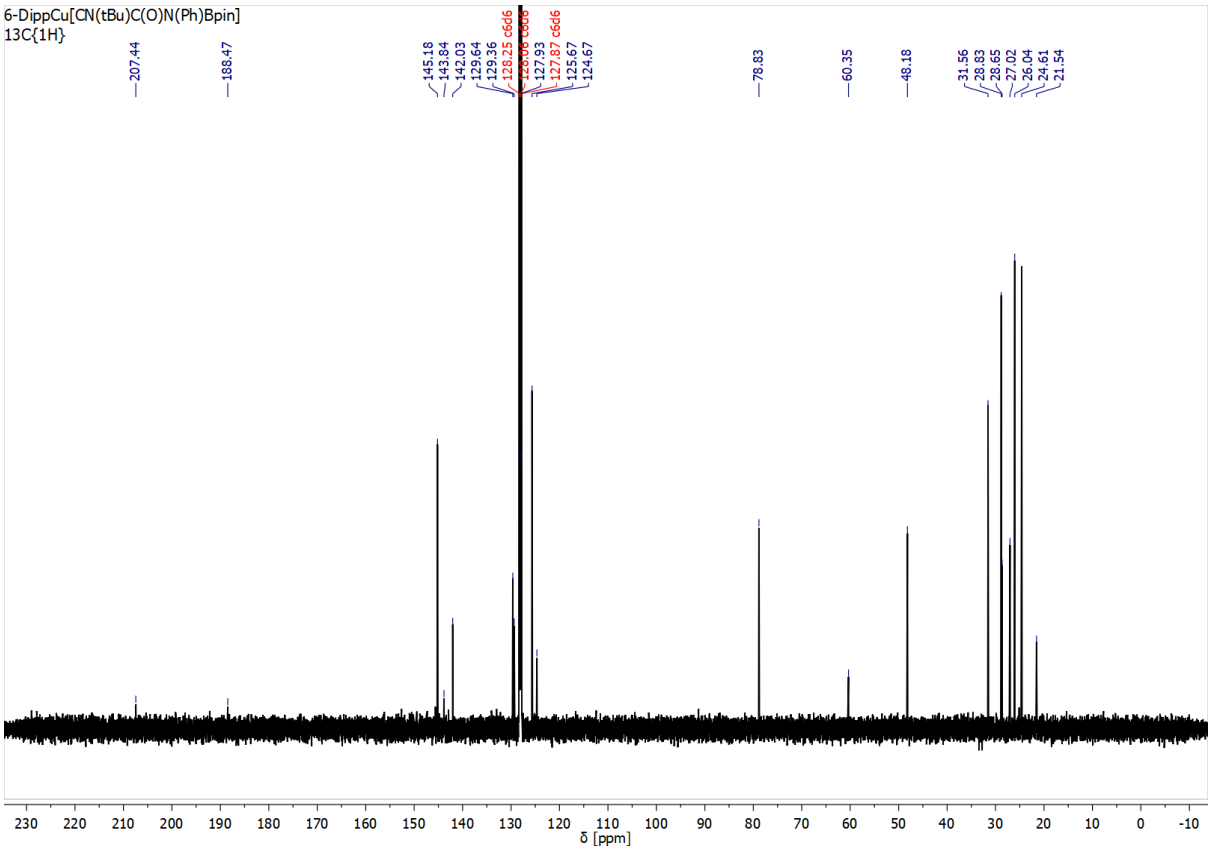

Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **5**.

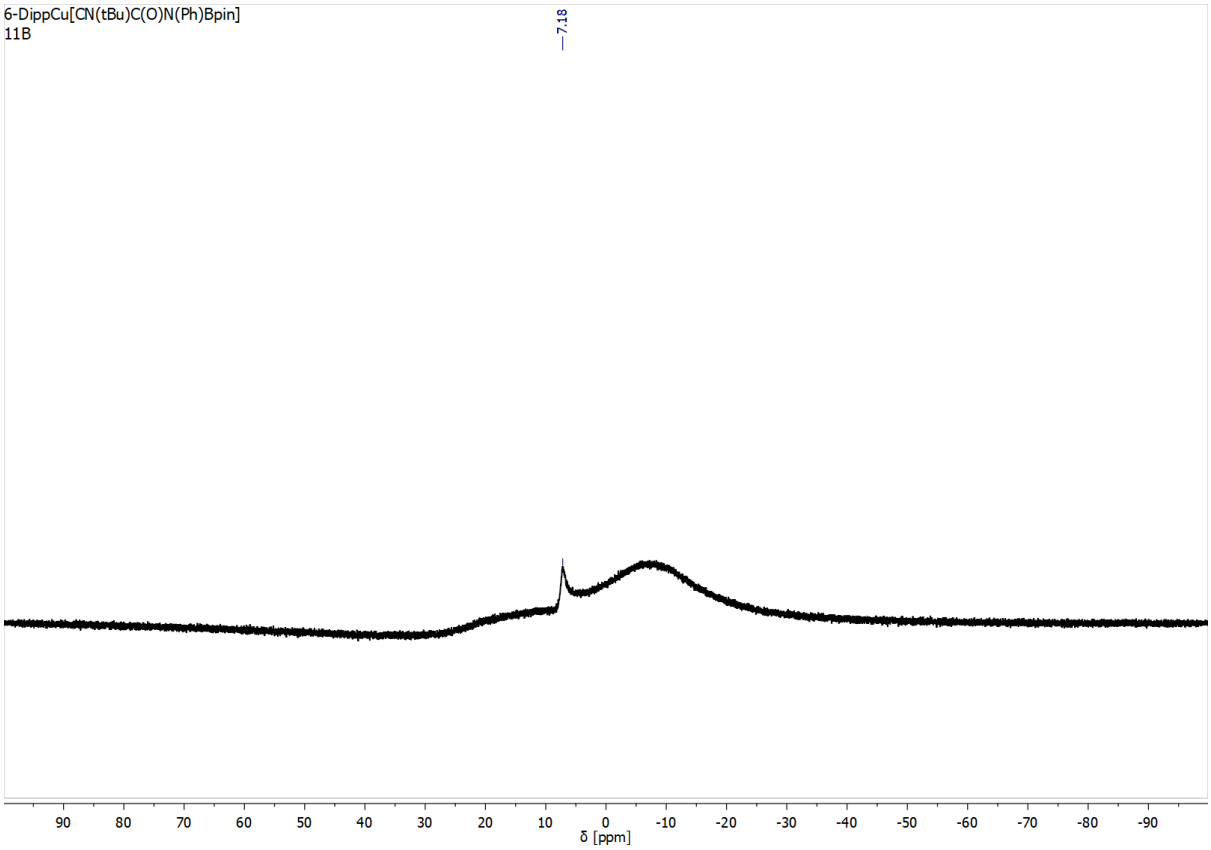

Figure S30: ^{11}B NMR spectrum (160 MHz, C_6D_6) of compound **5**.

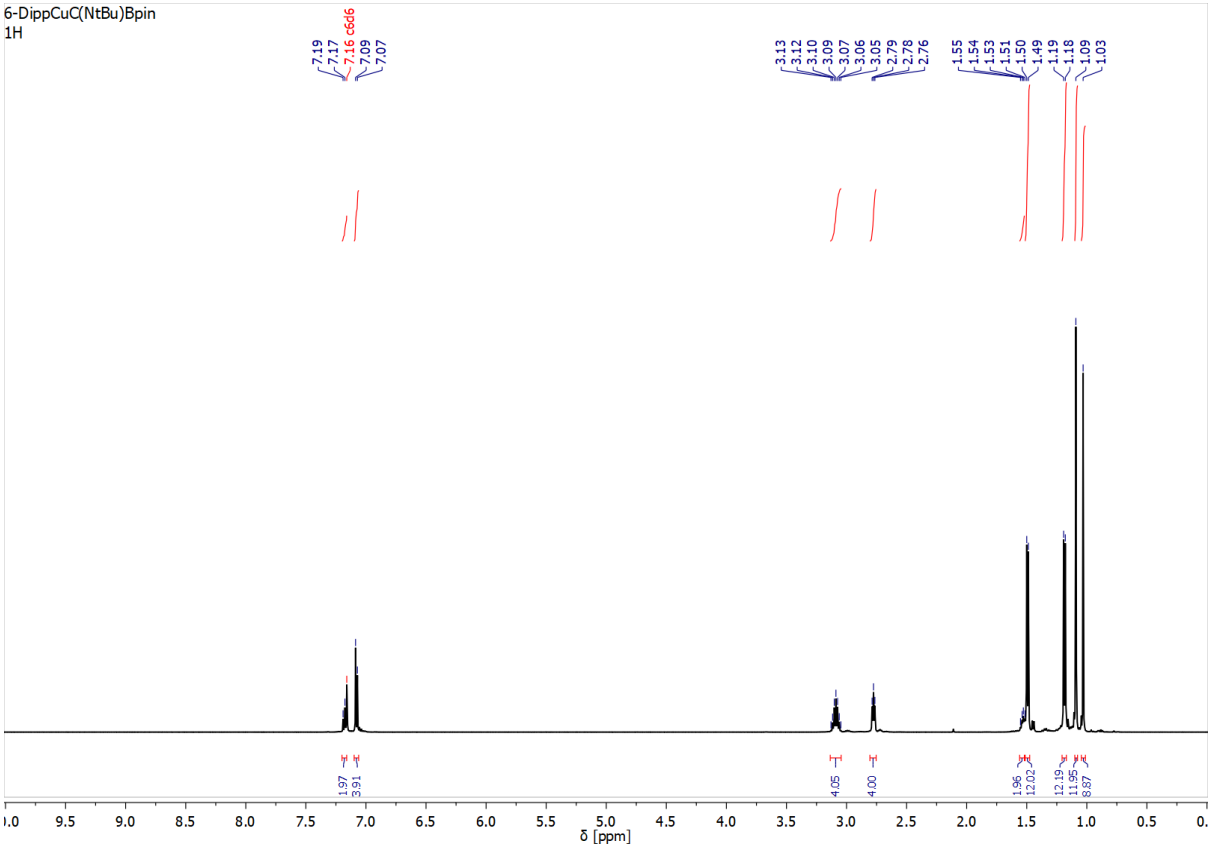

Figure S31: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **6**.

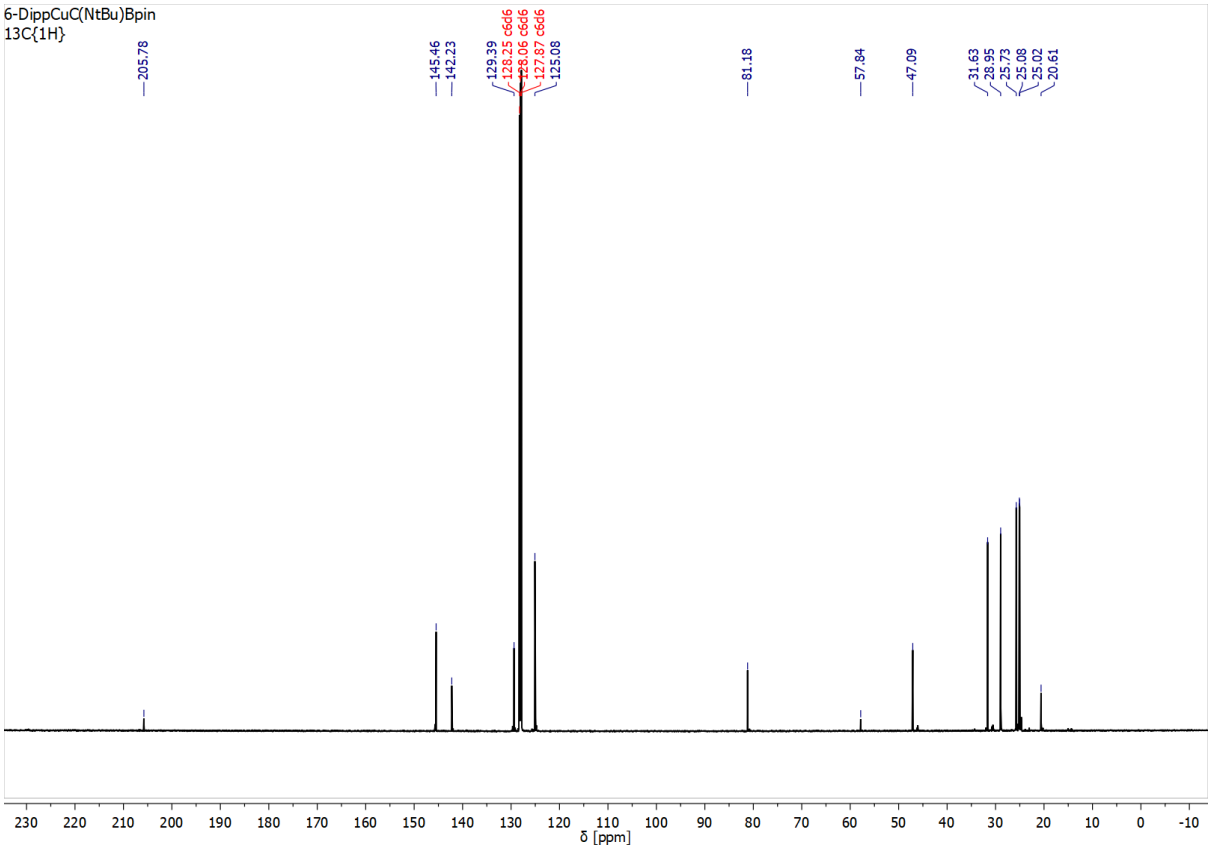

Figure S32: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **6**.

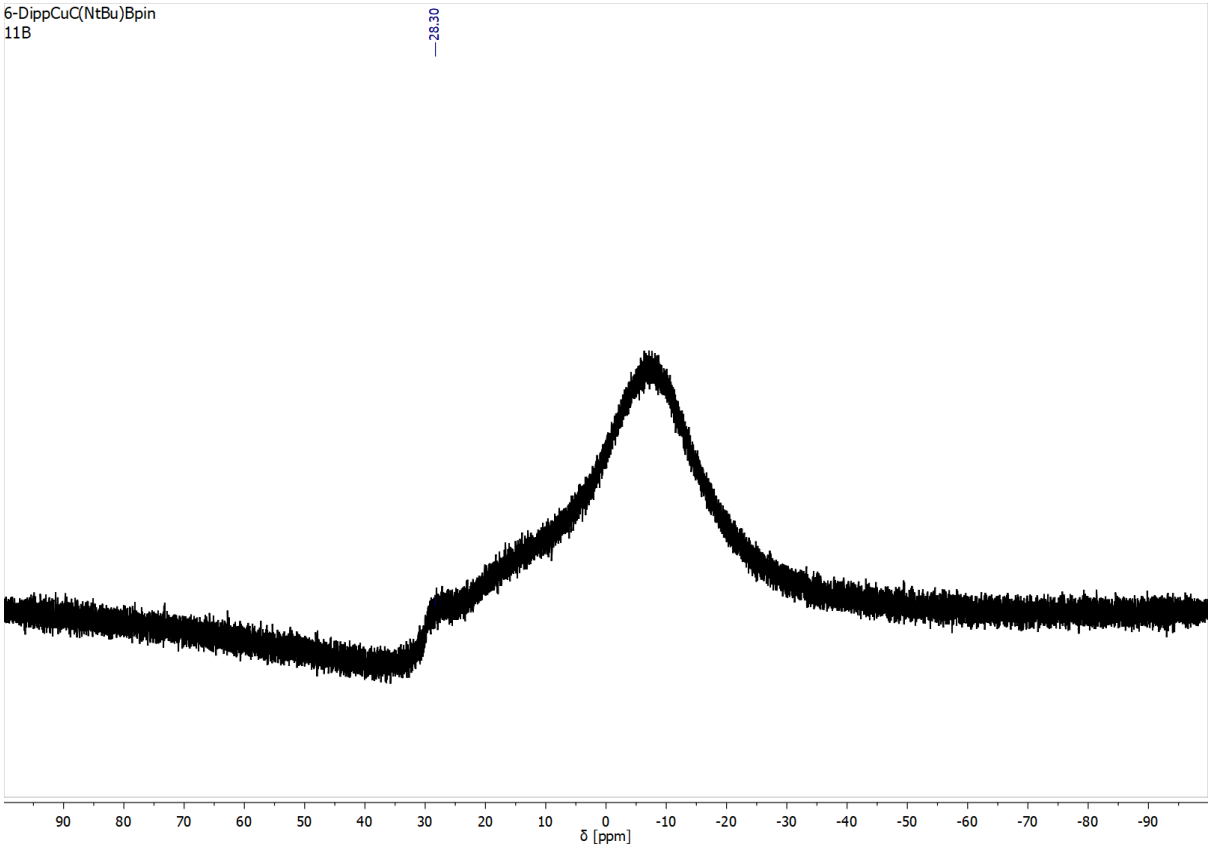

Figure S33: ^{11}B NMR spectrum (160 MHz, C_6D_6) of compound **6**.

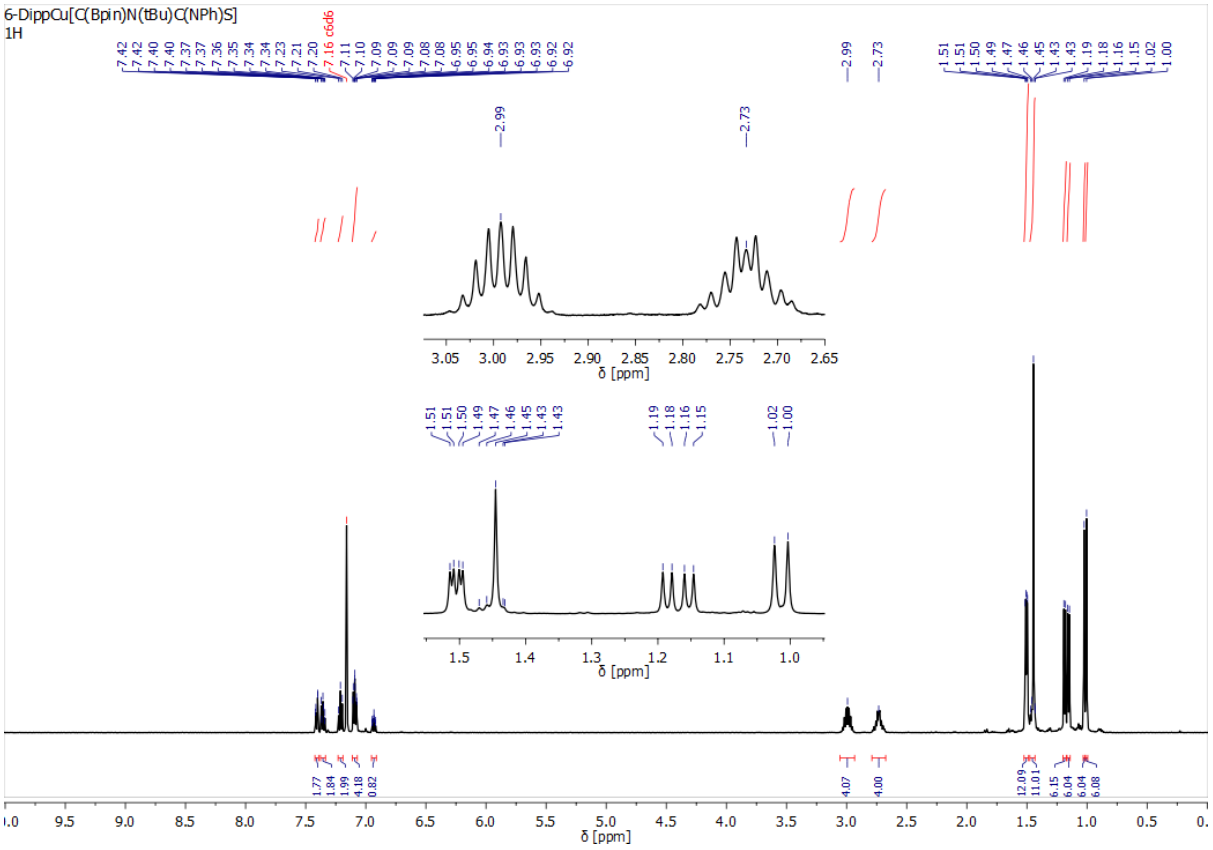

Figure S34: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **7**.

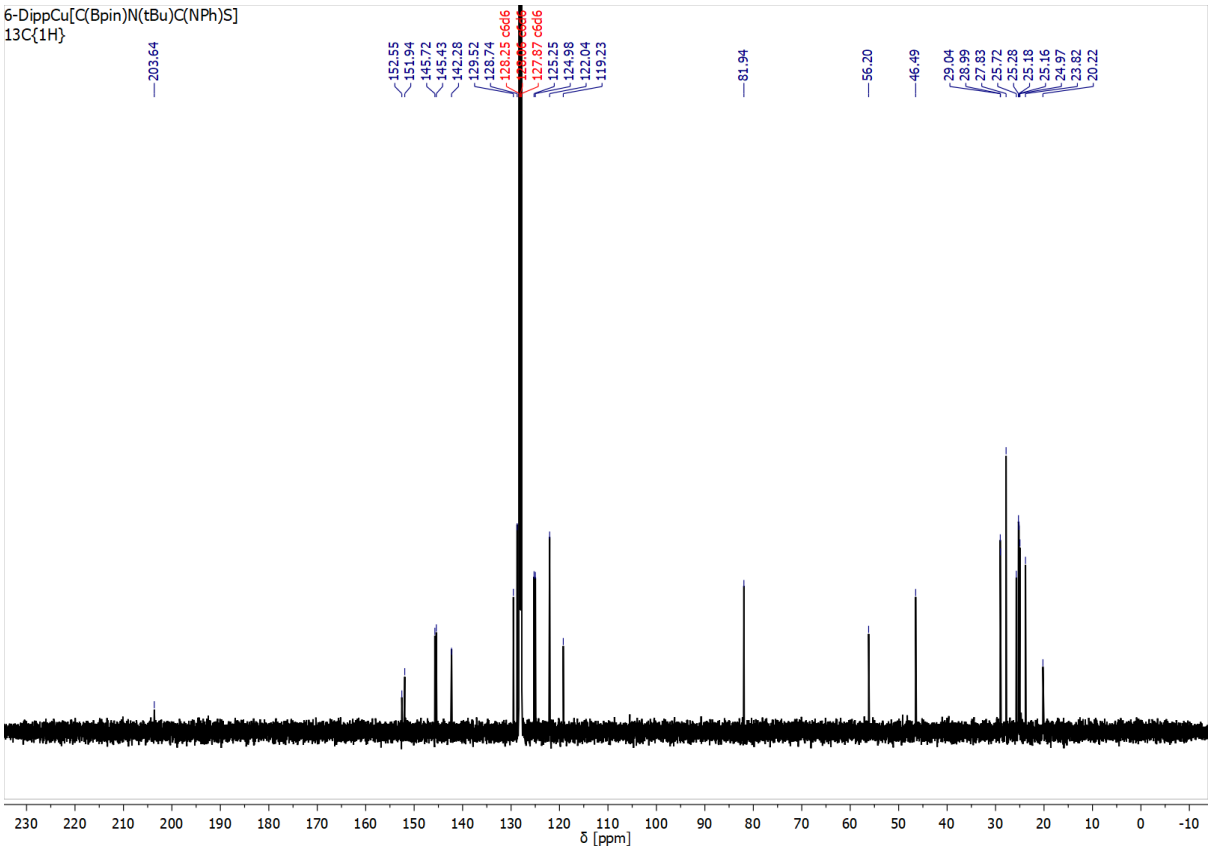

Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **7**.

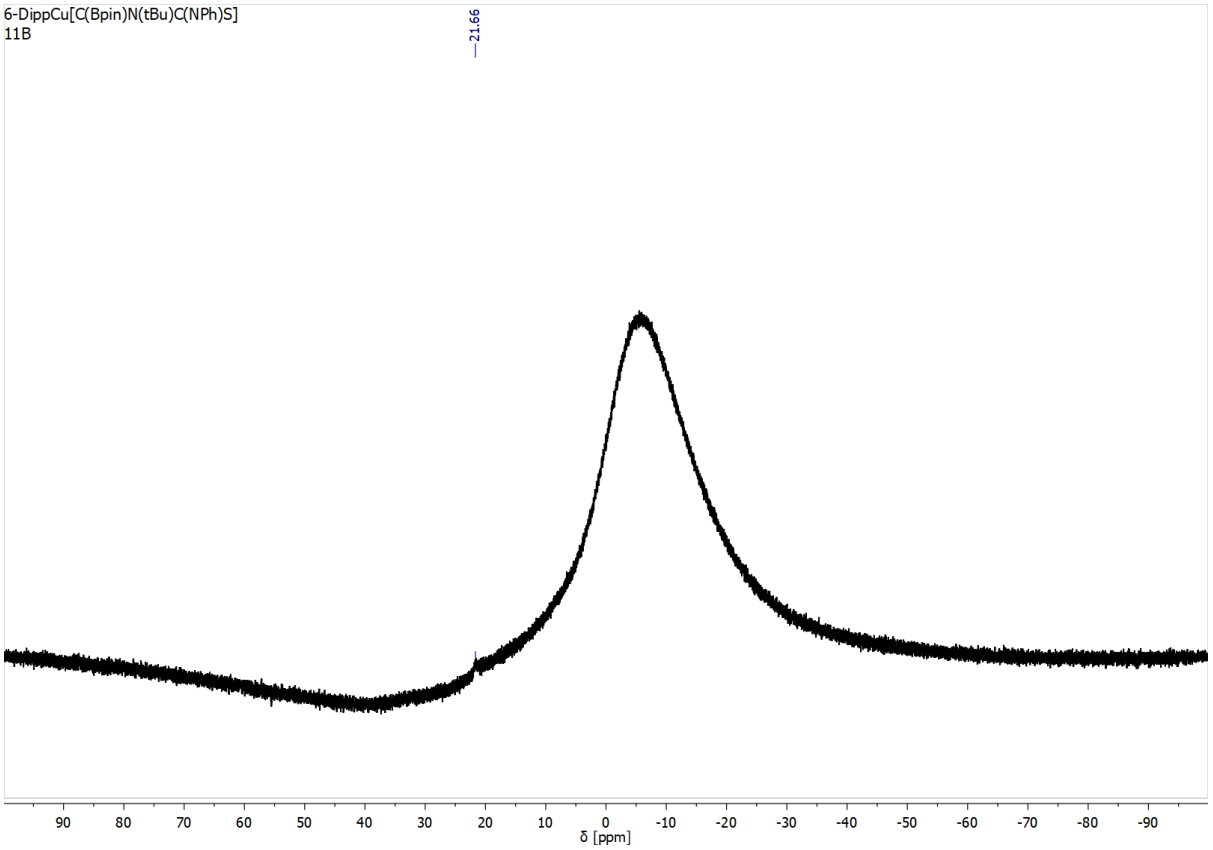

Figure S36: ^{11}B NMR spectrum (160 MHz, C_6D_6) of compound **7**.

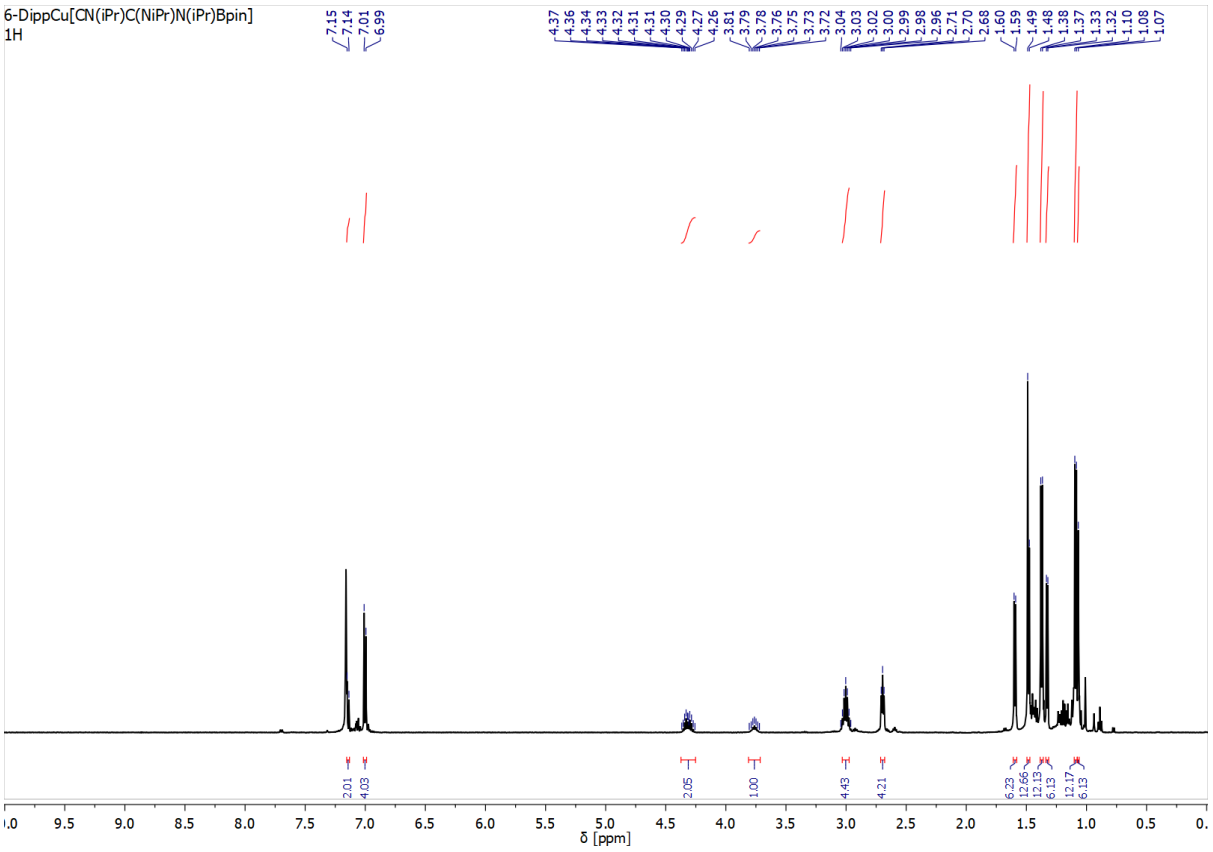

Figure S37: ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **8**.

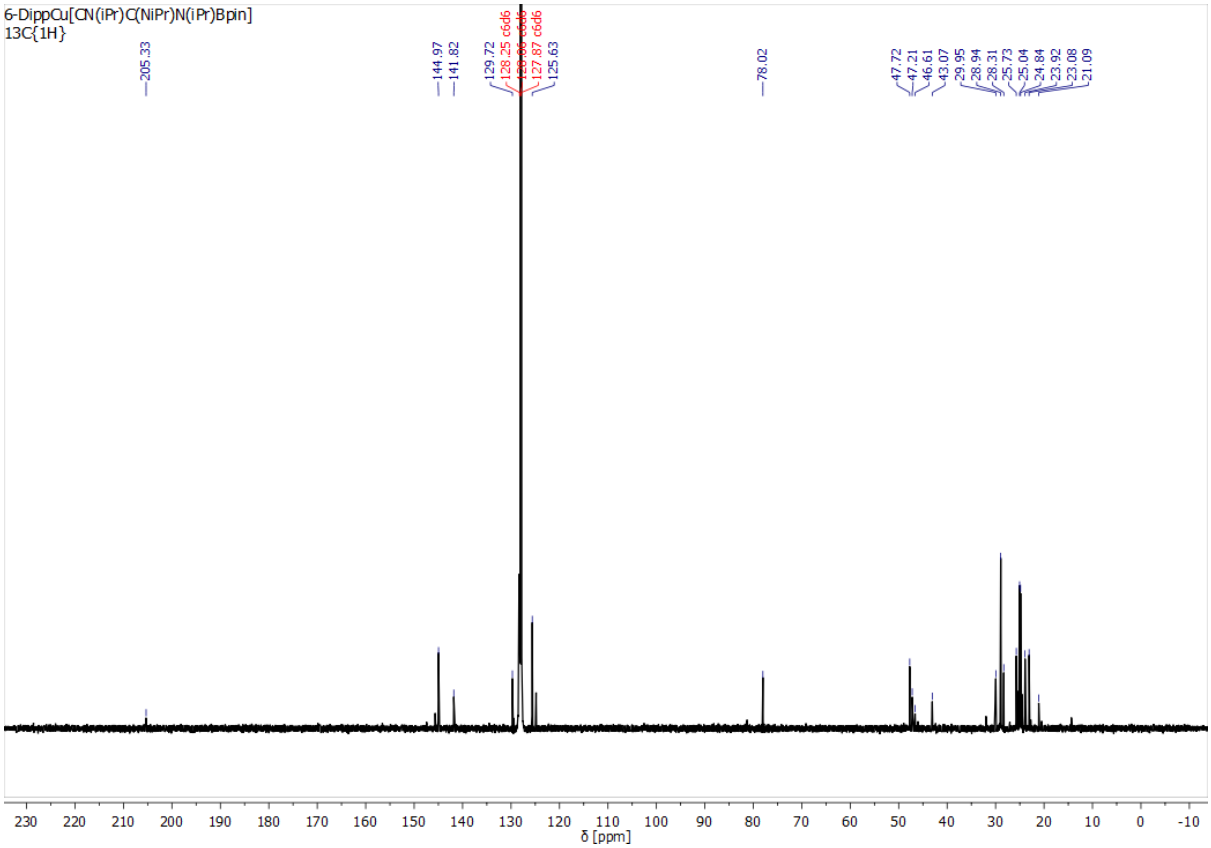

Figure S38: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, C_6D_6) of compound **8**.

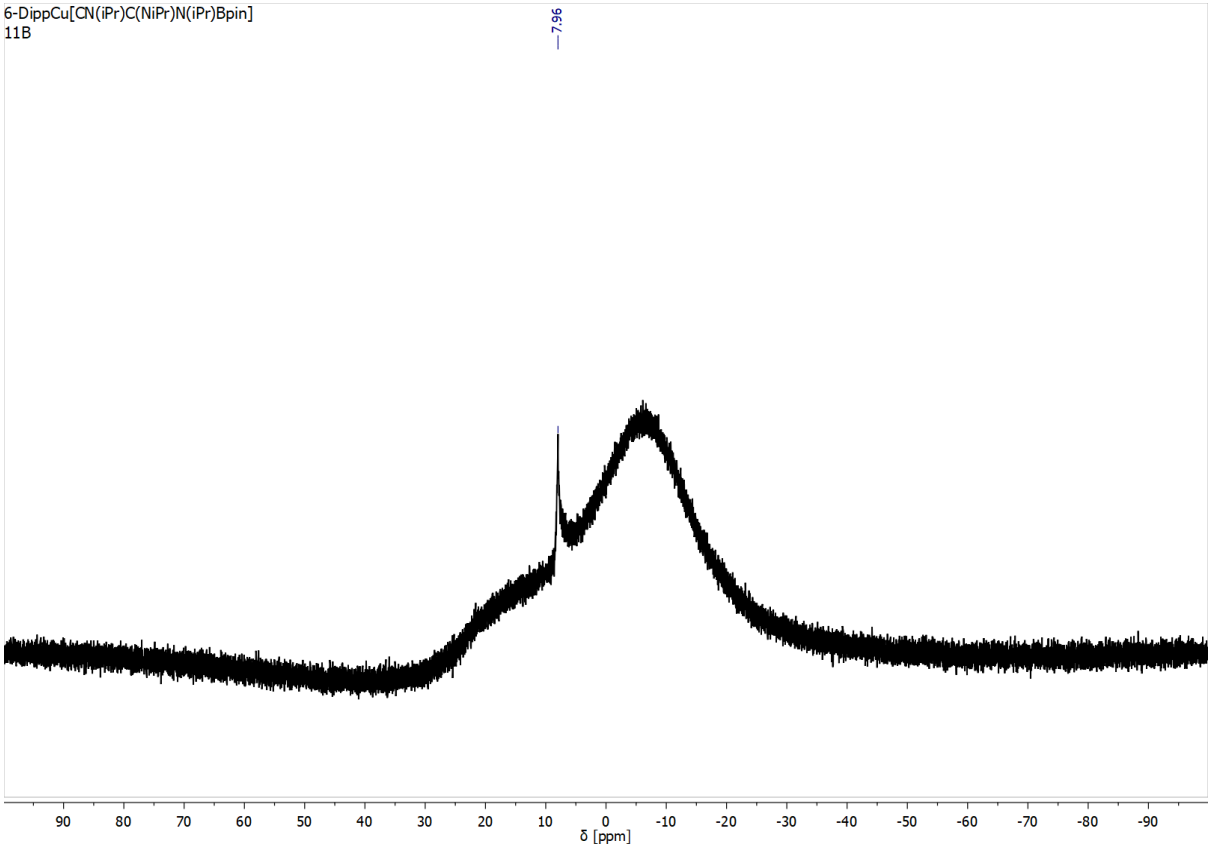

Figure S ^{11}B NMR spectrum (160 MHz, C_6D_6) of compound **8**.

Mass Spectrometry Data for Compound 8

References

1. A. J. Jordan, C. M. Wyss, J. Nasca and J. P. Sadighi, *Organometallics*, 2016, **35**, 613-616.
2. D. S. Laitar, P. Müller and J. P. Sadighi, *J. Am. Chem. Soc.*, 2005, **127**, 17196-17197.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.
4. G. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3-8.