Supporting Information

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1. General methods

The experiments were performed following standard Schlenk line and glove box techniques using Argon as the inert gas. Solvents were dried using a MBraun SPS column. Deuterated solvents were degassed via Argon bubbling and stored under Ar over 4 Å molecular sieves. NMR spectra were collected on Bruker machine AV400. Chemical shifts for ^{1}H and ^{13}C analyses are relative to TMS. Chemical shifts for ^{11}B, ^{31}P and ^{19}F analyses are relative to $F_3B.Et_2O$, 85% H_3PO_4 and CCl_3F respectively. Chemical shifts are reported in ppm (δ) and coupling constants in Hertz (Hz). The following abbreviations were used, s – singlet, d – doublet, t – triplet, quart – quartet, br- broad and m – multiplet. Elemental analyses were performed in the facility available in Laboratoire de Chimie de Coordination du CNRS using PerkinElmer 2400 Series Analyzer. Infrared spectra were recorded in a nitrogen-filled glove box on an Agilent Cary 630 FT-IR spectrophotometer equipped with ATR module. Compounds **A** and $RuH_2(H_2)_2P(Cy_3)_2$ were synthesized following reported procedures.[1]

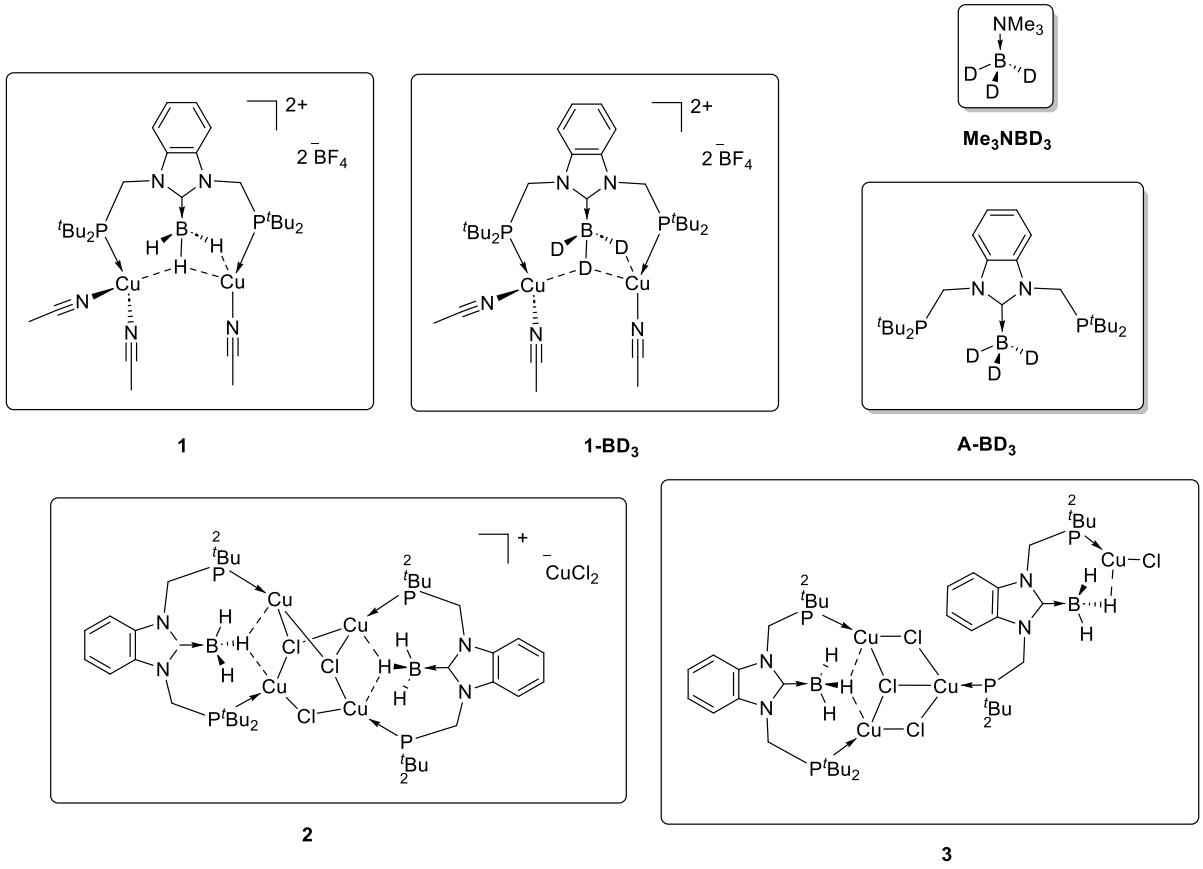
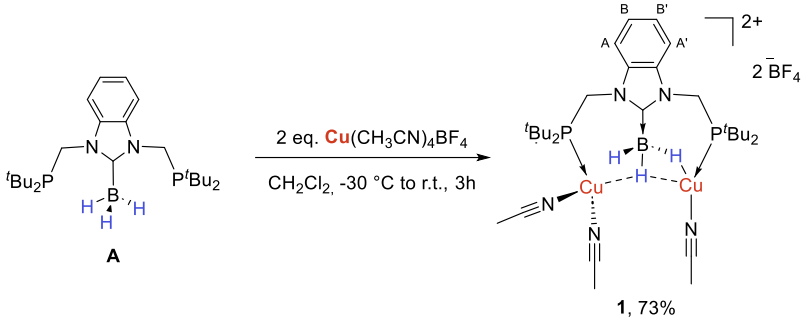


Figure S1 – Compounds synthesized in the present work

Synthesis and characterization of compound **1**



A mixture of **A** (100 mg, 0.223 mmol) and [$Cu(CH_3CN)_4BF_4$] (140 mg, 0.446 mmol) was dissolved at -30°C in dichloromethane (7 mL). The solution was then allowed to reach room temperature stirred during 45 minutes to reach completion, protected from light exposure. The crude mixture was filtrated over a filtrating cannula and the volatiles were evacuated under vacuum. The residue was washed with a mixture of dichloromethane/pentane (3 x 1/3 mL) then with pentane (2 x 2 mL) and dried under dynamic vacuum, affording **1** as white powder (153 mg, 0.169 mmol, 73%). Colorless crystals suitable for X-ray analysis were obtained from pentane diffusion into a concentrated dichloromethane solution at room temperature, after one day, protected from light exposure.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ 7.83 (AA'BB' system, $^{3}J_{AB}$ = 8.5 Hz, $^{3}J_{BB'}$ = 6.6 Hz, $^{4}J_{AB'}$ = 1.3 Hz, $^{5}J_{AA'}$ = 0.0 Hz, 2H, H_A and $H_{A'}$), 7.67 (AA'BB' system, $^{3}J_{AB}$ = 8.5 Hz, $^{3}J_{BB'}$ = 6.6 Hz, $^{4}J_{AB'}$ = 1.3 Hz, $^{5}J_{AA'}$ = 0.0 Hz, 2H, H_B and $H_{B'}$), 4.79 (d, $^{2}J_{P\text{-}H}$ = 2.2 Hz, 4H, NCH_2P), 2.80 (br. quart, 3H, BH_3), 2.37 (s, 9H, CH_3CN), 1.27 (d, $^{3}J_{P\text{-}H}$ = 14.2 Hz, 36H, $P(C(CH_3)_3)$). **^{1}H{^{11}B} NMR** (400 MHz, CD_2Cl_2, 298 K) δ 2.80 (t, $^{3}J_{P\text{-}H}$ = 11.4 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2, 298 K) δ 168.0 ($C_{quat.}$ *C*-B) 133.1 (s, $C_{quat.}$ Ar), 127.0 (s, $CHAr_{B/B'}$), 120.1 (s, $C_{quat.}$ CH_3CN), 112.6 (s, $CHAr_{A/A'}$), 39.6 (d, $^{1}J_{P\text{-}C}$ = 10.5 Hz, NCH_2P), 34.3 (d, $^{1}J_{P\text{-}C}$ = 10.3 Hz, $PC(CH_3)_3$), 29.5 (d, $^{2}J_{P\text{-}C}$ = 7.2 Hz, $PC(CH_3)_3$), 2.8 (s, CH_3CN). Carbenic carbon is detected through the coupling with methylene protons in HMBC $^{13}C\{^{1}H\}/^{1}H$ spectrum. **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 298 K) δ 30.7 (s, P^tBu_2). **^{11}B NMR** (128 MHz, CD_2Cl_2, 298 K) δ -1.1 (s, BF_4), -33.1 (quart, $^{1}J_{B\text{-}H}$ = 85 Hz, BH_3). **^{19}F NMR** (377 MHz, CD_2Cl_2, 298 K) δ -152.0 (BF_4) **Elemental analysis** calcd. for $C_{31}H_{56}B_3Cu_2F_8N_5P_2$ (871.28 g.mol^{-1}) C, 42.69; H, 6.47; N, 8.03; found: C, 41.51; H, 6.56; N, 7.73. Despite several attempts, better elemental analyses could not be obtained. We suspect that the amount of coordinated acetonitrile does not remain strictly to three. **ATR-FTIR** (cm^{-1}) 2943, 2901, 2873, 2423, 2317, 2277, 1470, 1446, 1399, 1372, 1283, 1270, 1180, 1049, 1021, 811, 781, 749.

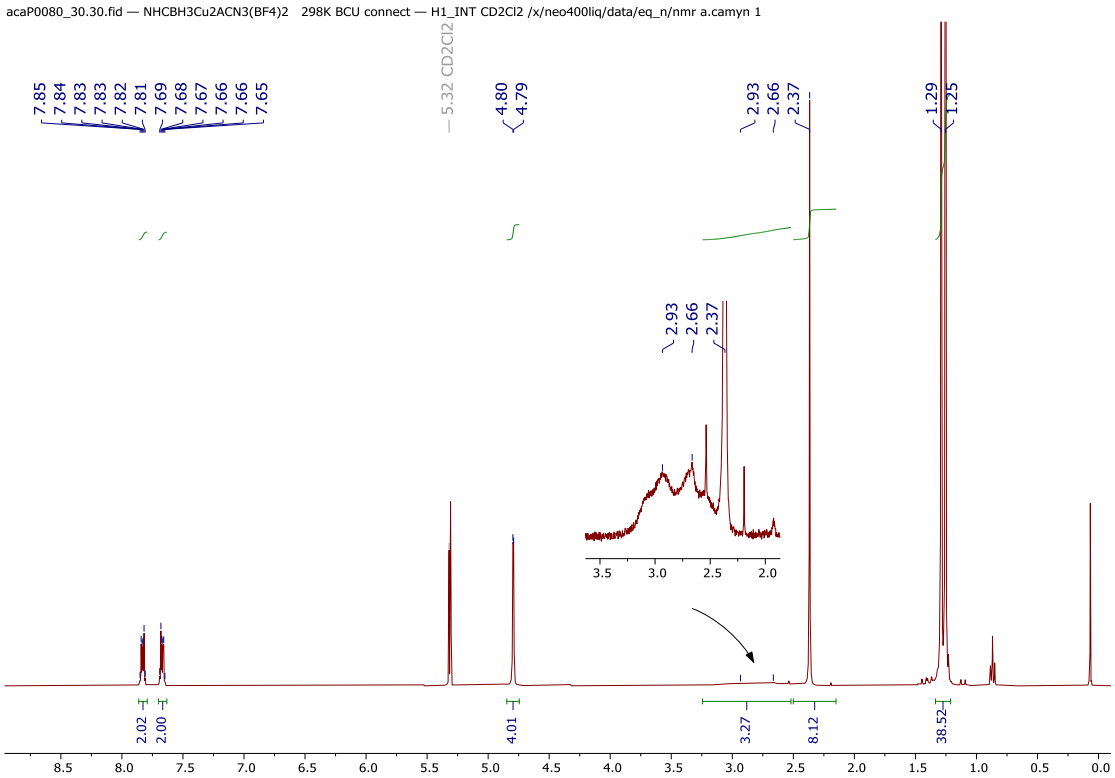


*Figure S2 – ^{1}H NMR spectrum of **1** at 298 K in CD_2Cl_2 (D1 = 30 sec)*

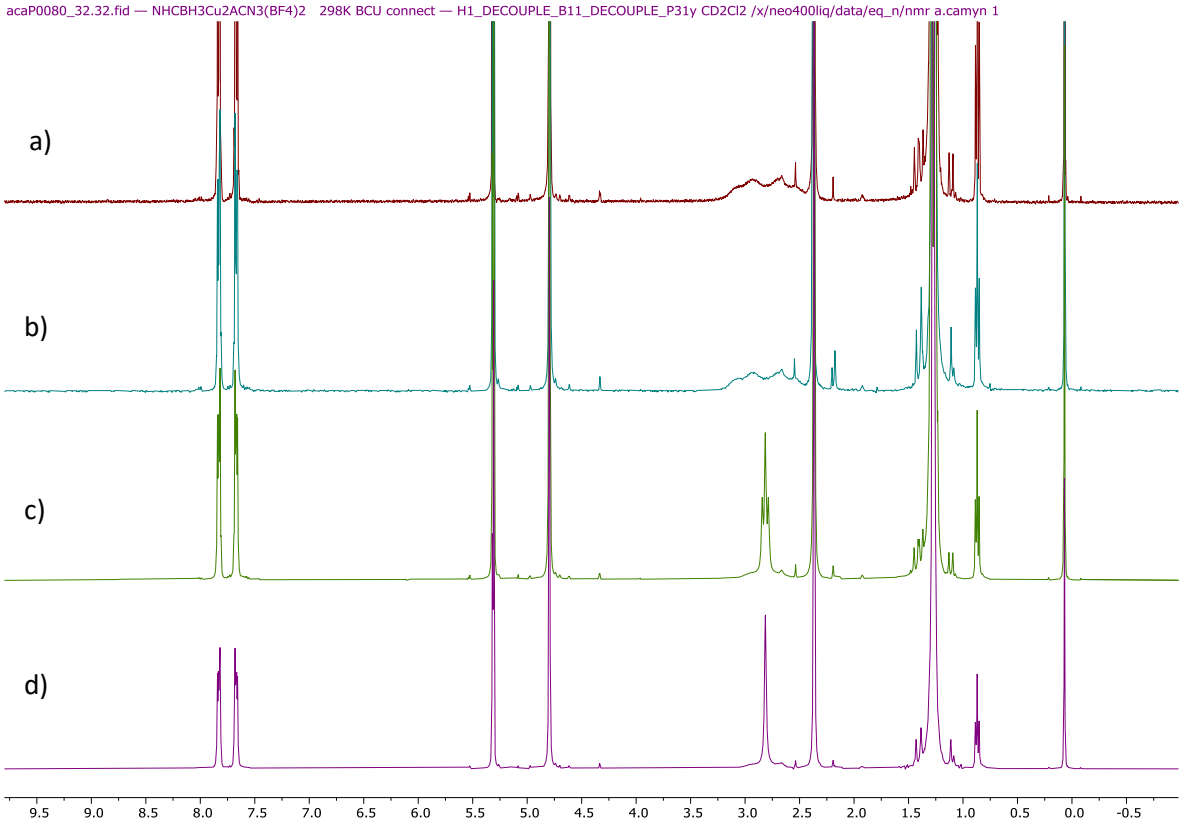


*Figure S3 – Stack of a) ^{1}H, b) $^{1}H\{^{31}P\}$, c) $^{1}H\{^{11}B\}$ and d) $^{1}H\{^{11}B\}\{^{31}P\}$ NMR spectra of **1** at 298 K in CD_2Cl_2 (D1 = 30 sec for each spectrum)*

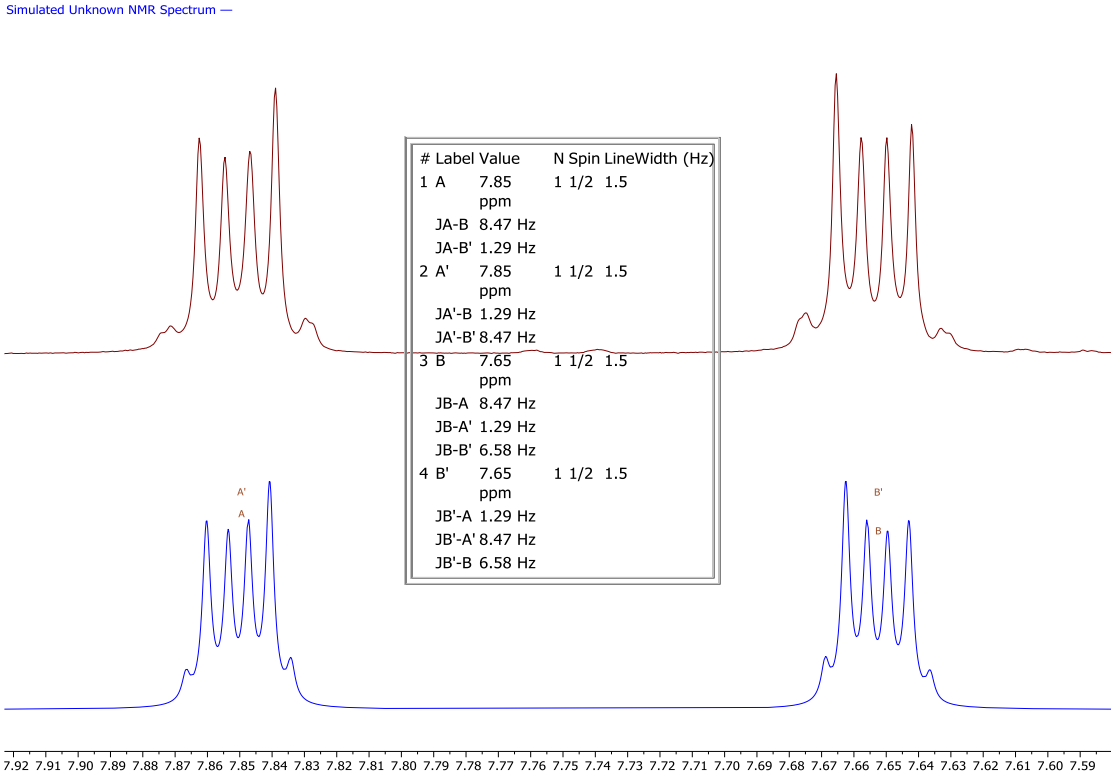


*Figure S4 – Stacked ^{1}H NMR spectrum of **1** at 298 K in CD_2Cl_2 (top) and simulation of AA'BB' system (bottom). Zoom of the aromatic region*

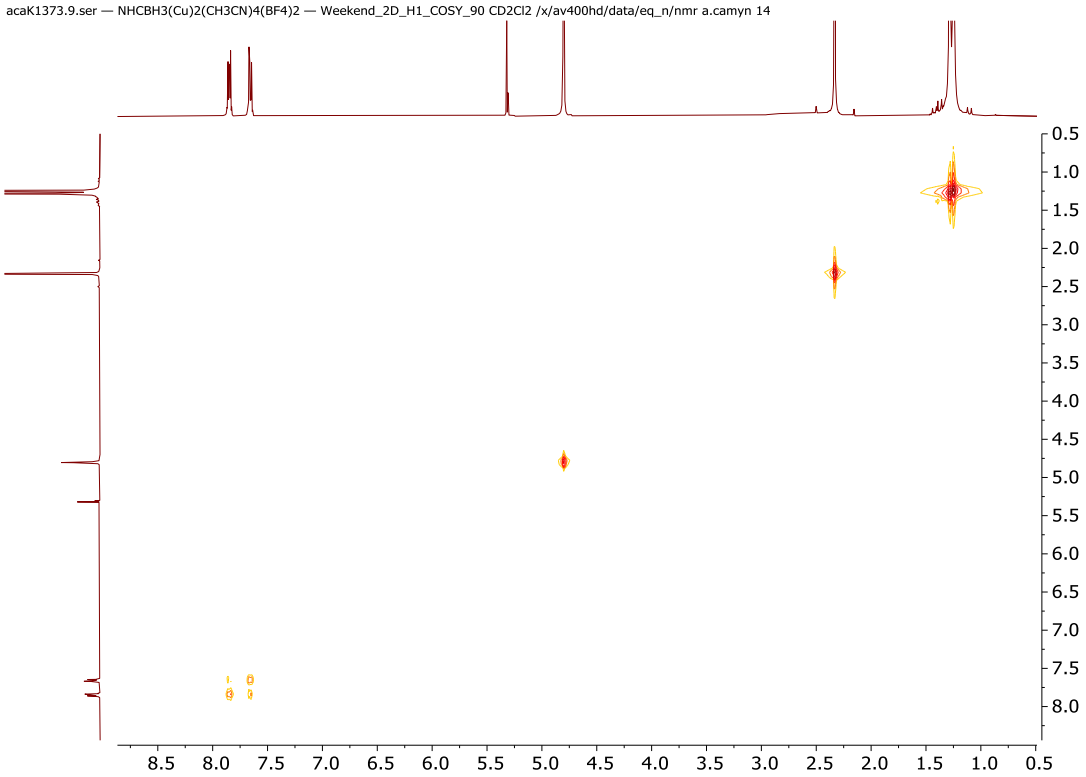


*Figure S5 – COSY $^{1}H/^{1}H$ NMR spectrum of **1** at 298 K in CD_2Cl_2*

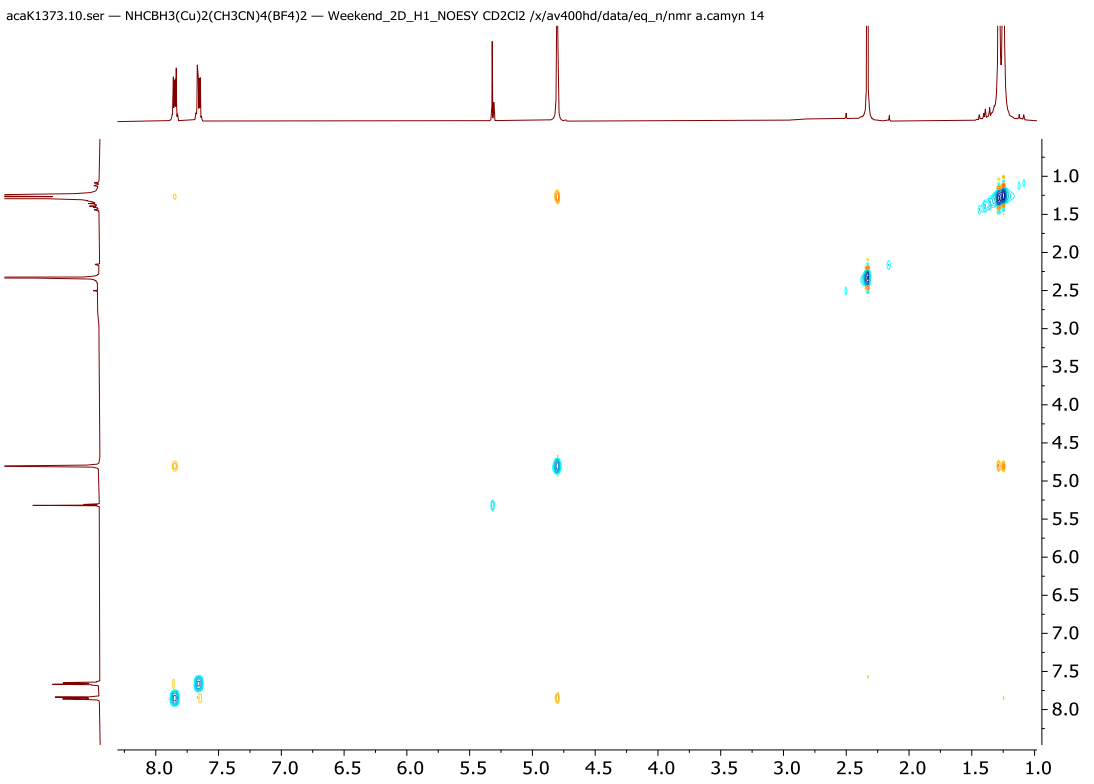


*Figure S6 – NOESY $^{1}H/^{1}H$ NMR spectrum of **1** at 298 K in CD_2Cl_2 (Mixing time = 0.5 s)*

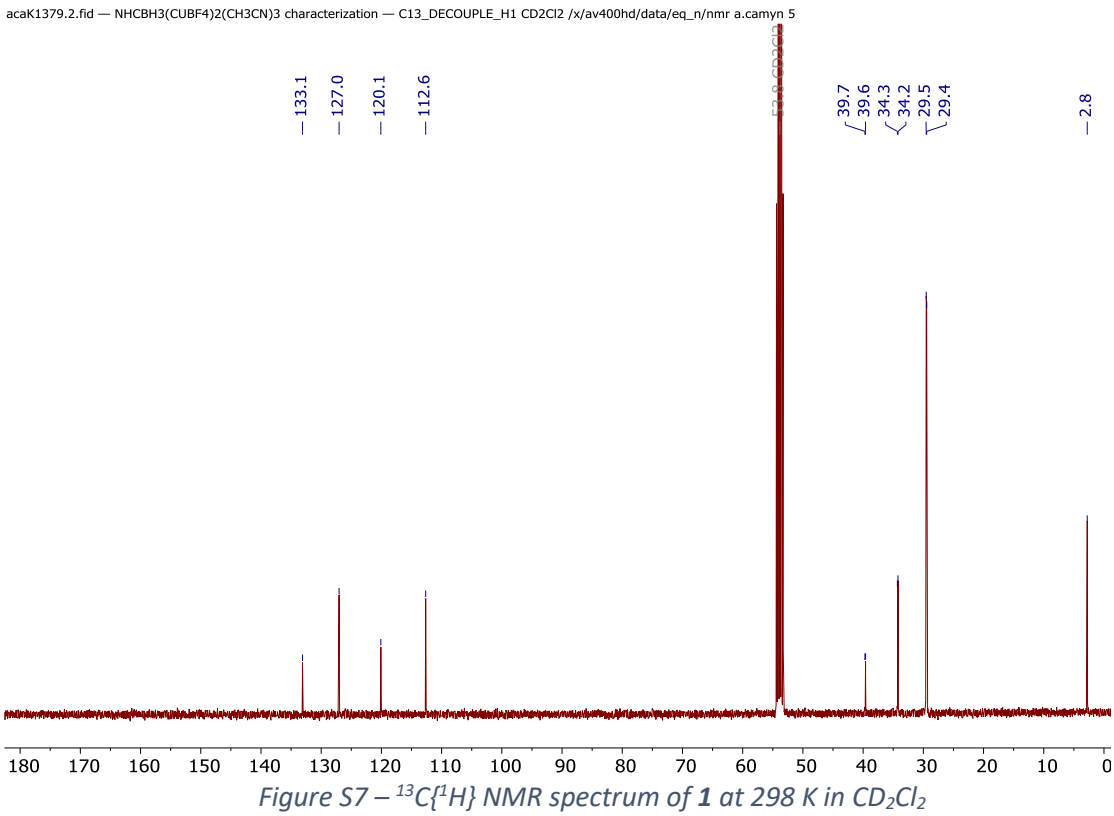


*Figure S7 – $^{13}C\{^{1}H\}$ NMR spectrum of **1** at 298 K in CD_2Cl_2*

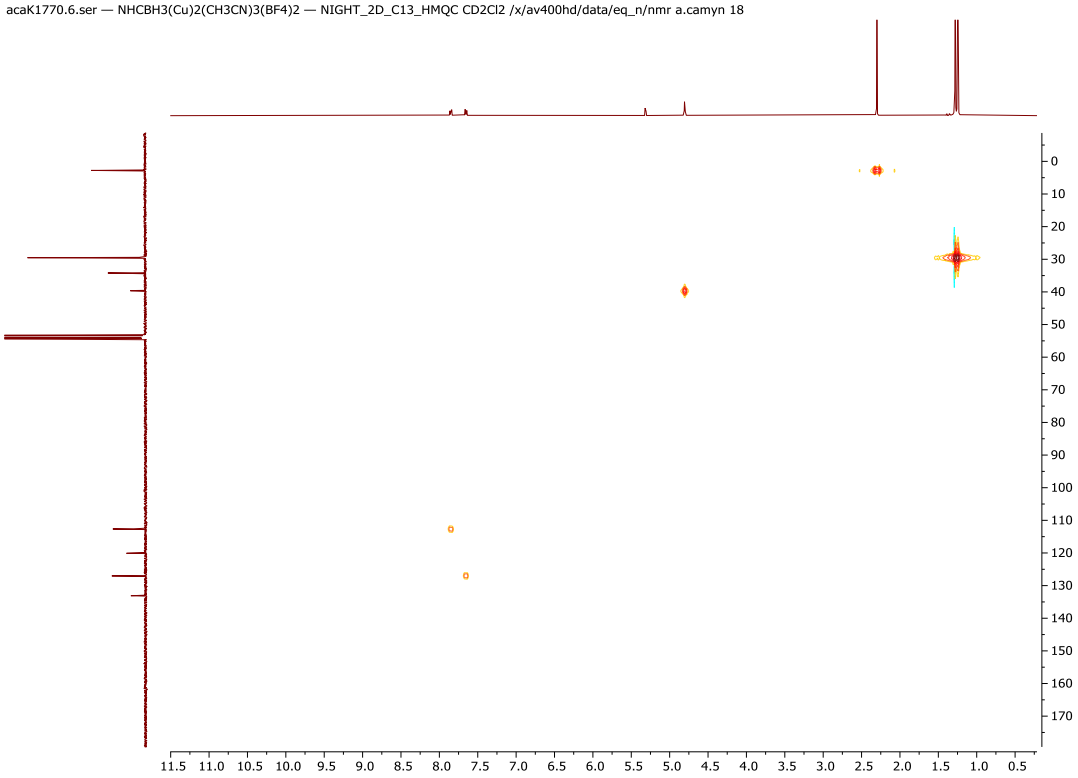


*Figure S8 – HMQC $^{13}C\{^{1}H\}/^{1}H$ NMR spectrum of **1** at 298 K in CD_2Cl_2*

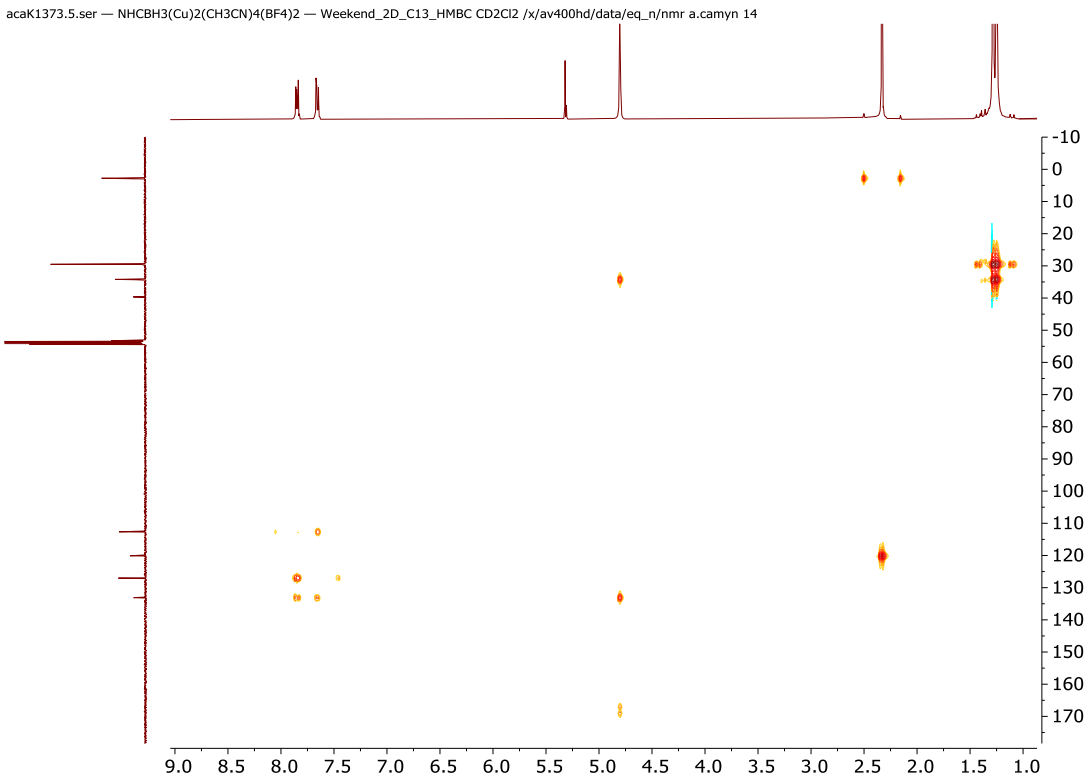


*Figure S9 – HMBC $^{13}C\{^{1}H\}/^{1}H$ NMR spectrum of **1** at 298 K in CD_2Cl_2*

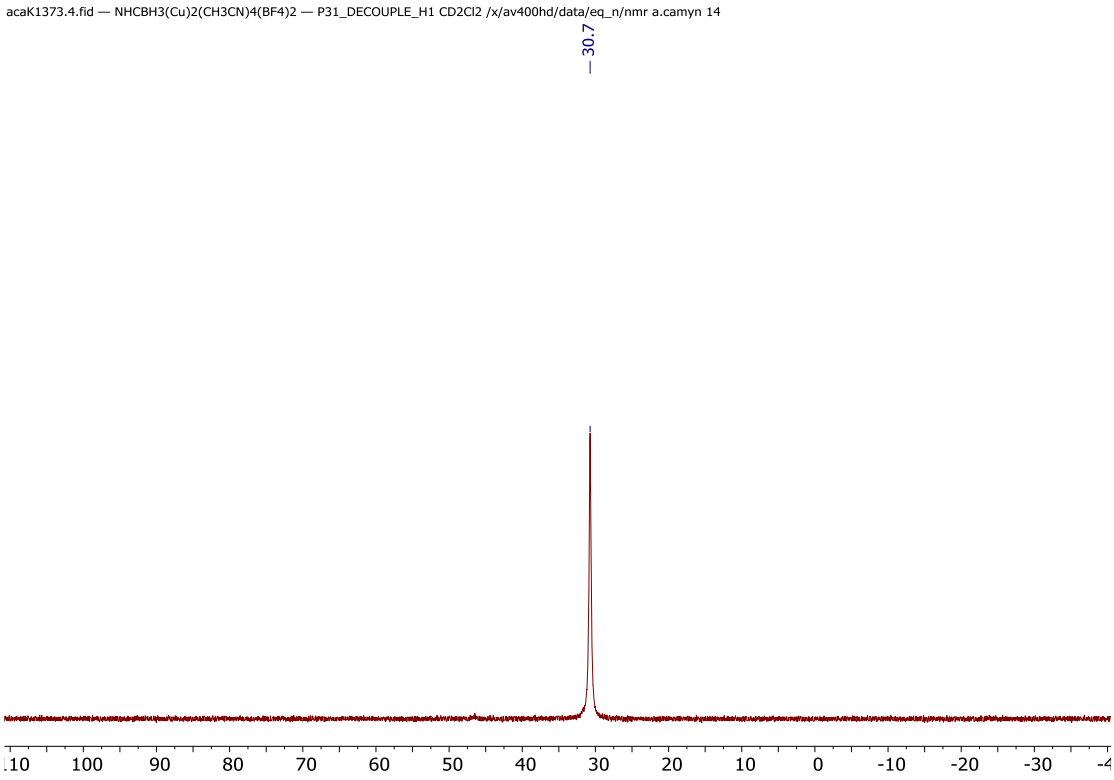


*Figure S10 – $^{31}P\{^{1}H\}$ NMR spectrum of **1** at 298 K in CD_2Cl_2*

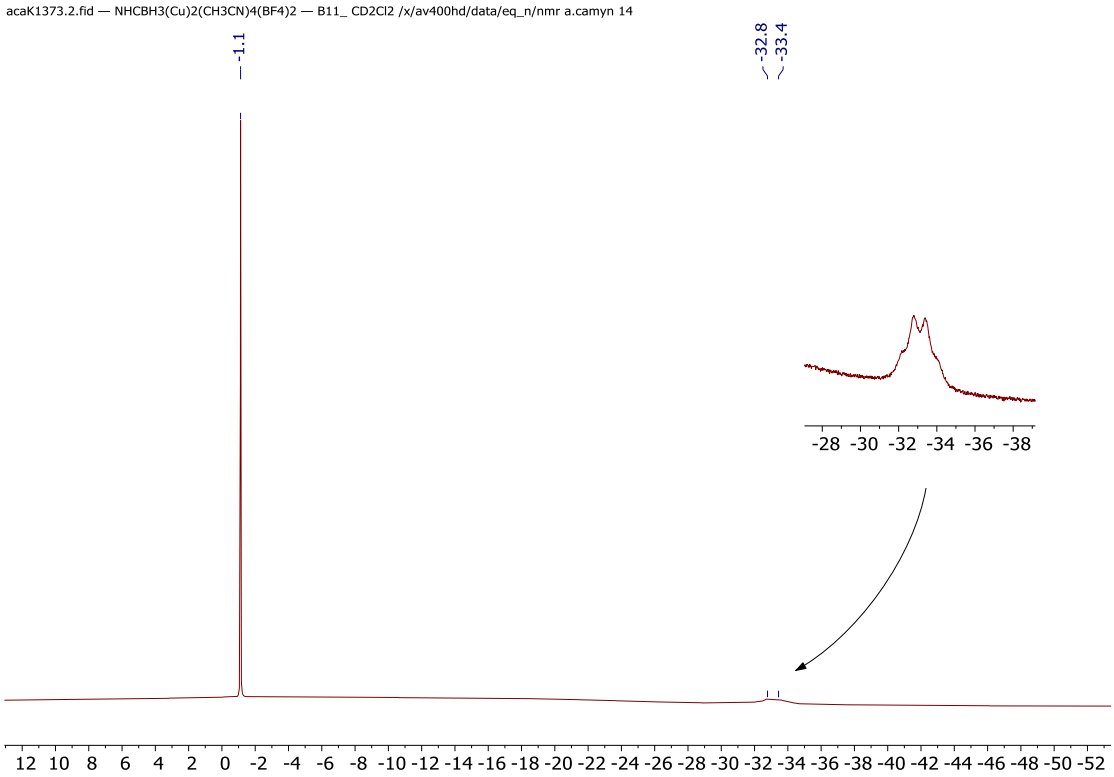


*Figure S11 – ^{11}B NMR spectrum of **1** at 298 K in CD_2Cl_2*

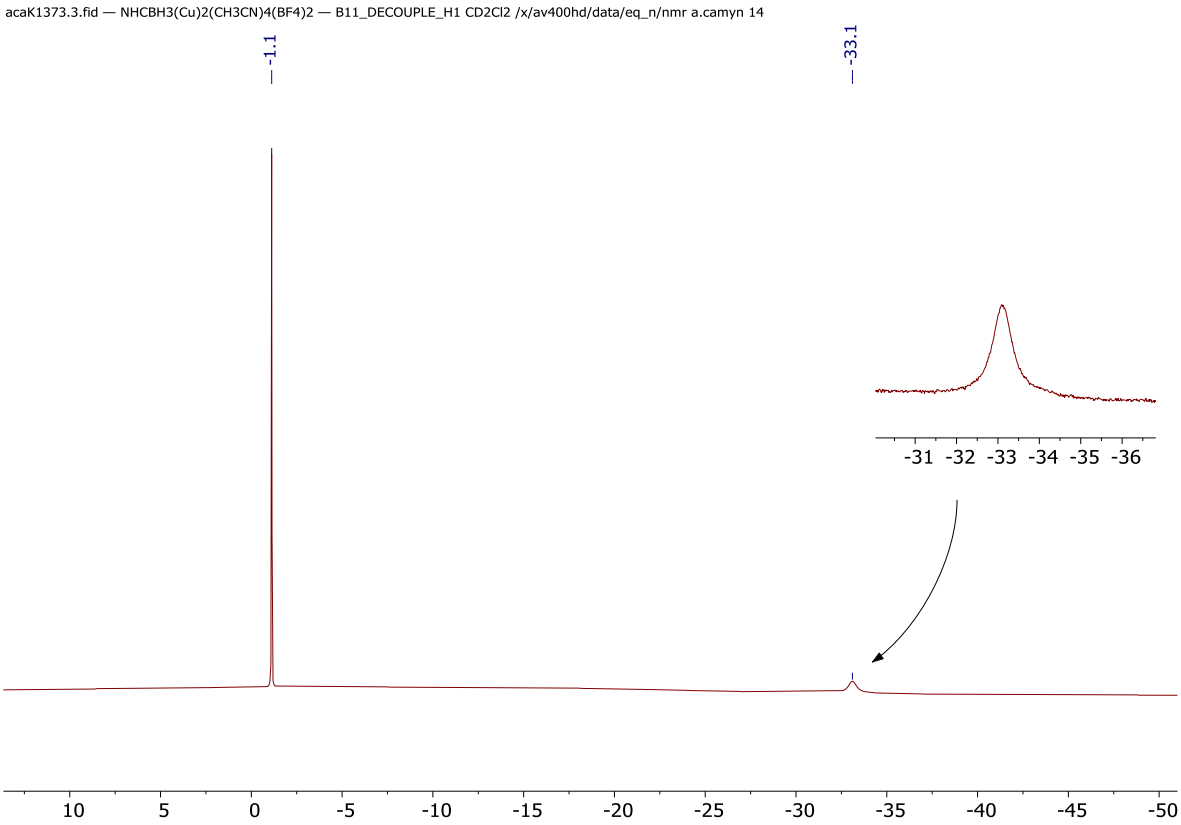


*Figure S12 – $^{11}B\{^{1}H\}$ NMR spectrum of **1** at 298 K in CD_2Cl_2*

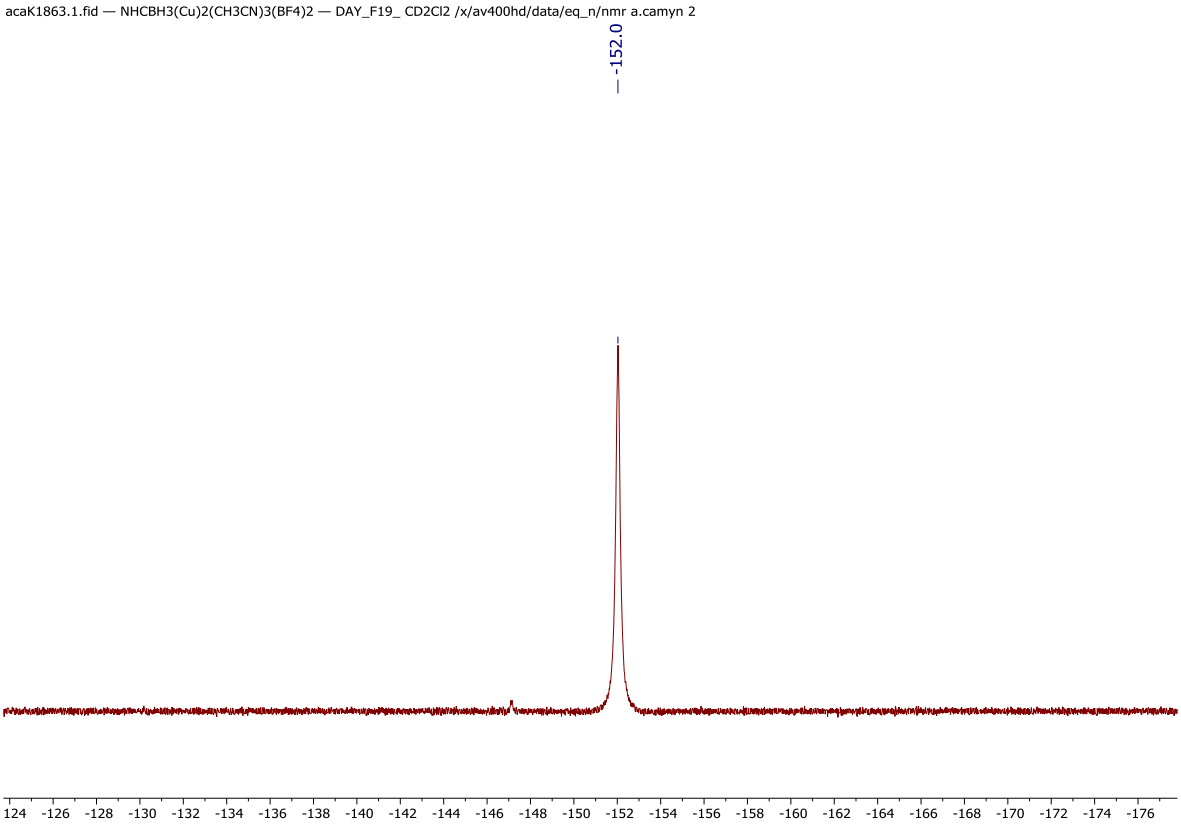


*Figure S13 – ^{19}F NMR spectrum of **1** at 298 K in CD_2Cl_2*

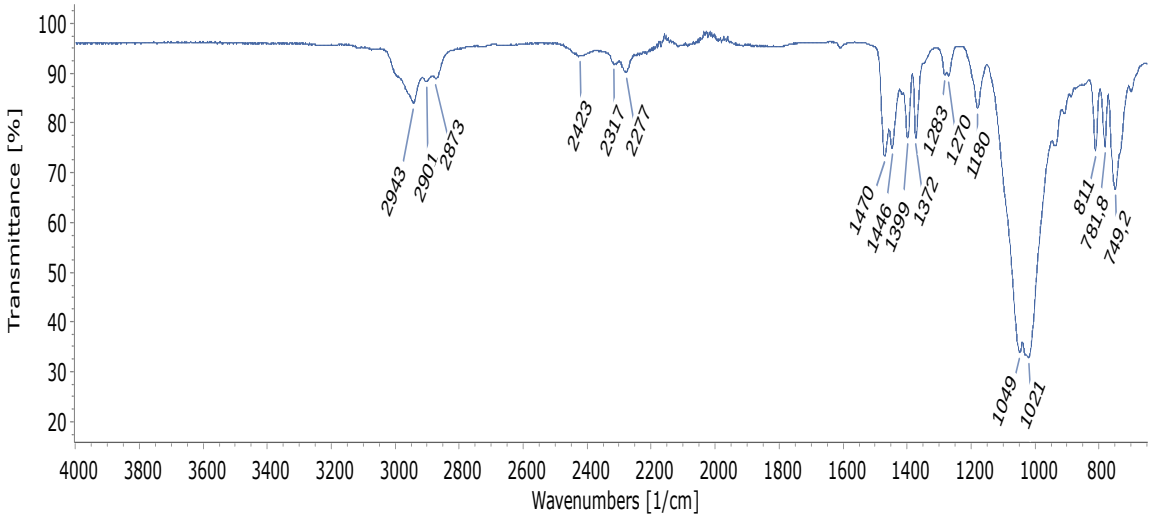


*Figure S14 – ATR-FTIR spectrum of complex **1***

Summary of variable temperature analyses conducted on complex 1 (Figure S15-S17).

A J. Young NMR tube containing a CD_2Cl_2 solution of complex **1** was placed in a 400 MHz NMR apparatus. The sample was stabilized for 10 minutes at a given temperature, the NMR spectra were recorded every 20 °C steps (from 183 K to 283 K, then at 298 K).

^{1}H NMR analysis

Lowering the temperature led to the coalescence of the BH_3 signal in ^{1}H NMR spectra, from a quartet to a singlet (Figure S15). This is assigned to a quadrupole-induced thermal decoupling between hydrogen and boron. Such behavior has been described in NHC-BH_3 tungsten or copper borate complexes at low temperatures.[6–8] [2]

^{1}H{^{11}B} NMR analysis

At 298 K, the ^{1}H{^{11}B} NMR shows a $^2J_{P\text{-}H}$ coupling constant of 11.3 Hz corresponding to the coupling of the hydrides with the two Cu-P fragments. Lowering the temperature led to a broadening of the triplet into a unique large singlet (Figure S16).

^{1}H{^{11}B}{^{31}P} NMR analysis

Starting at 183 K, the hydride signal appears as a broad singlet at 2.60 ppm in ^{1}H{^{11}B}{^{31}P} NMR spectrum (Figure S17). At this temperature, the fluxional behavior is not slow enough to observe distinct chemical shift for terminal and bridging BH. By increasing the temperature up to 298 K, the signal sharpens into a singlet.

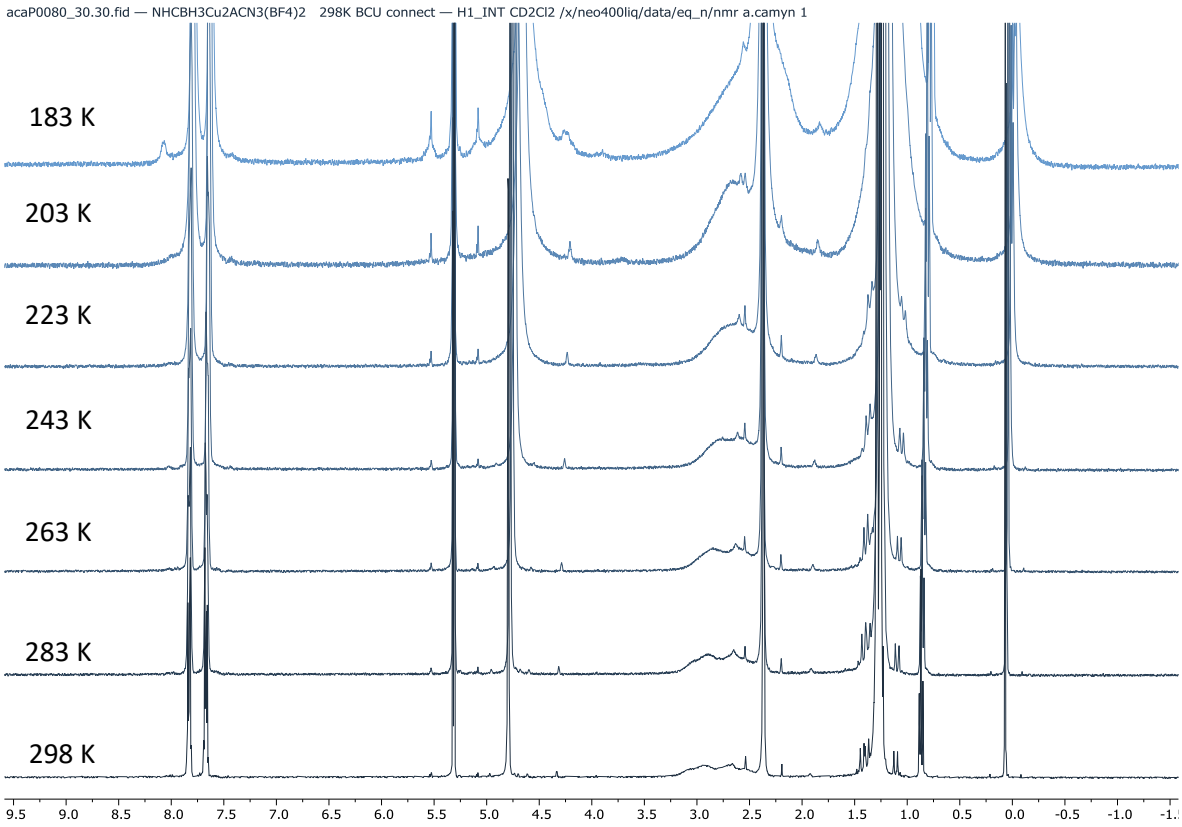


*Figure S15 – Stack of ^{1}H NMR spectra of **1** at different temperatures in CD_2Cl_2 (D1 = 30 sec)*

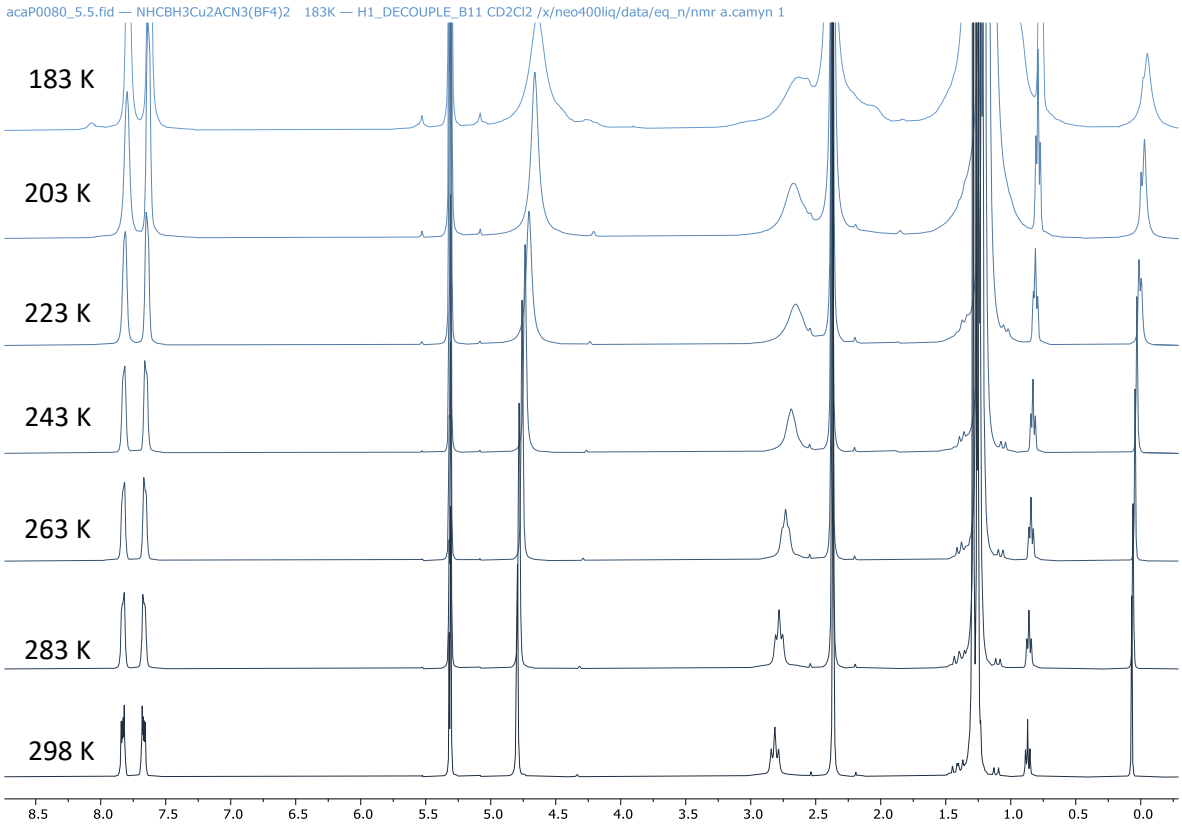


*Figure S16 – Stack of $^{1}H\{^{11}B\}$ NMR spectra of **1** at different temperatures in CD_2Cl_2 (D1 = 30 sec)*

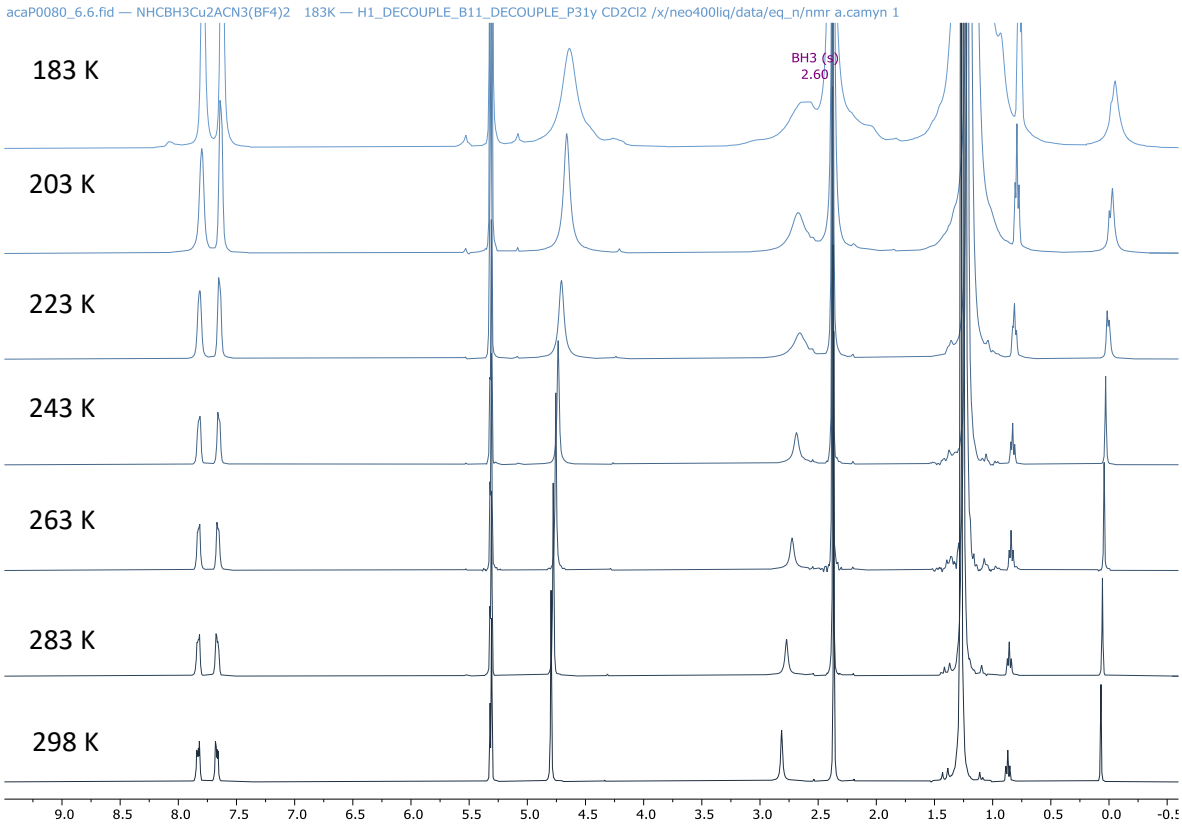
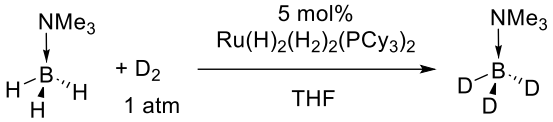


*Figure S17 – Stack of $^{1}H\{^{11}B\}\{^{31}P\}$ NMR spectra of **1** at different temperatures in CD_2Cl_2 (D1 = 30 sec)*

Synthesis and characterization of compound **$Me_3N\rightarrow BD_3$**



A mixture of $Me_3N\rightarrow BH_3$ (30 mg, 0.411 mmol) and $RuH_2(H_2)_2P(Cy_3)_2$ (13 mg, 0.019 mmol) was dissolved in THF (1 mL) in a J. Young tube. The head-space was purged at room temperature before adding 1 atm of D_2. The conversion into $Me_3N\rightarrow BD_3$ was monitored by $^{11}B\{^1H\}$ NMR spectroscopy. The head-space was renewed seven times by fresh D_2 over a period of nine days. The crude mixture was filtrated over a Celite pad and rinsed with 2 mL of THF. THF was removed using trap-to-trap technic and the residue dried under dynamic vacuum in an ice bath to prevent the loss of **$Me_3N\rightarrow BD_3$**. 25 mg of white-off powder were isolated (Y < 79%).

^1H NMR (400 MHz, Tol-d_8, 289 K) δ 2.00 (s, 9H, *Me_3*). **$^{11}B\{^1H\}$ NMR** (128 MHz, Tol-d_8, 289 K) δ -7.5 (m). The level of deuterium incorporation was estimated at 83% from ^1H NMR integration of one of the four signals of the BH_3 fragment versus NMe_3 signal. However, the relaxation time and some overlapping signals impact the accuracy of this calculation. A consistent estimation (82%, *vide infra*) was deduced in the next step for the formation of **A-BD_3**.
In addition to $Me_3N\rightarrow BD_3$ and $Me_3N\rightarrow BH_3$ signals, adduct of $Me_3N\rightarrow BD_3$ with Ru complexes are detected in ^1H NMR spectrum between 1.05 to 1.88 ppm and in $^{11}B\{^1H\}$ NMR spectrum at -43.0 ppm.

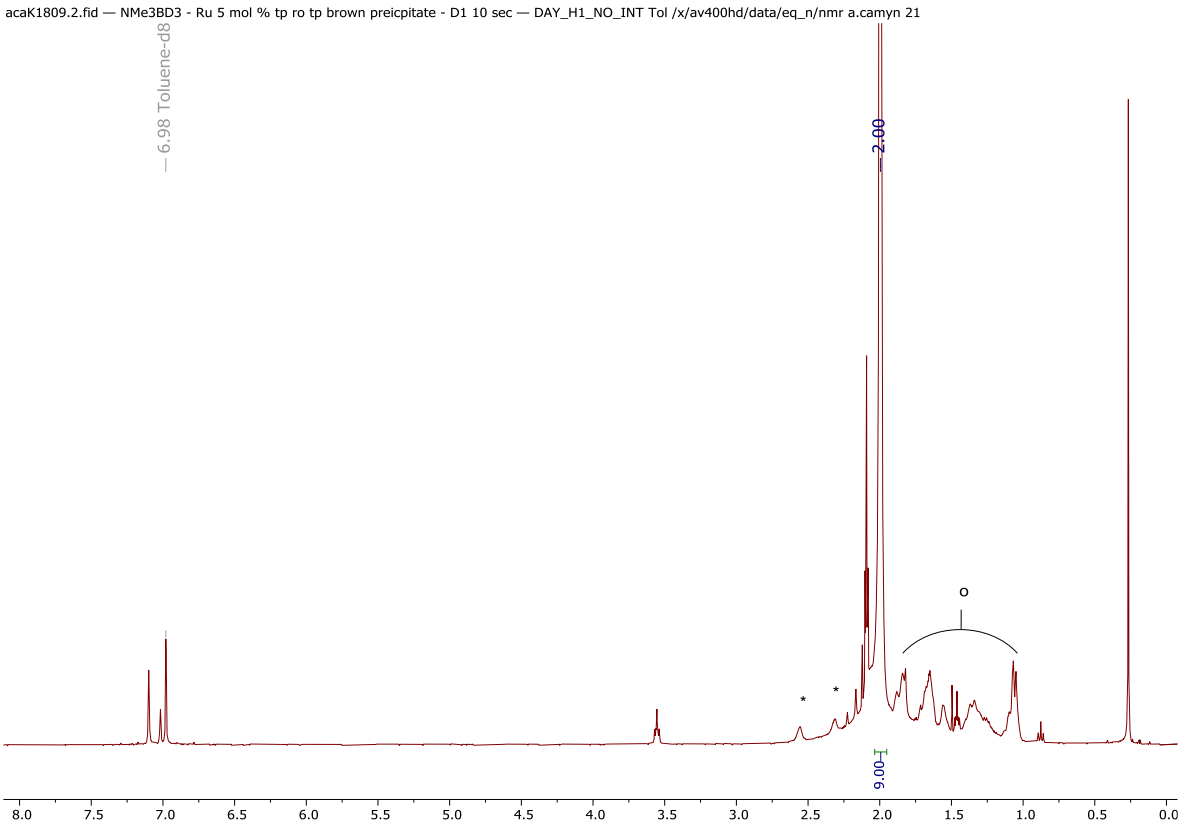


*Figure S18 – ^1H NMR spectrum of **$Me_3N\rightarrow BD_3$** at 298 K in Tol-d_8 (D1 = 10 sec) * corresponds to $Me_3N\rightarrow BH_3$, ° corresponds to **$Me_3N\rightarrow BH_3$** ruthenium adduct.*

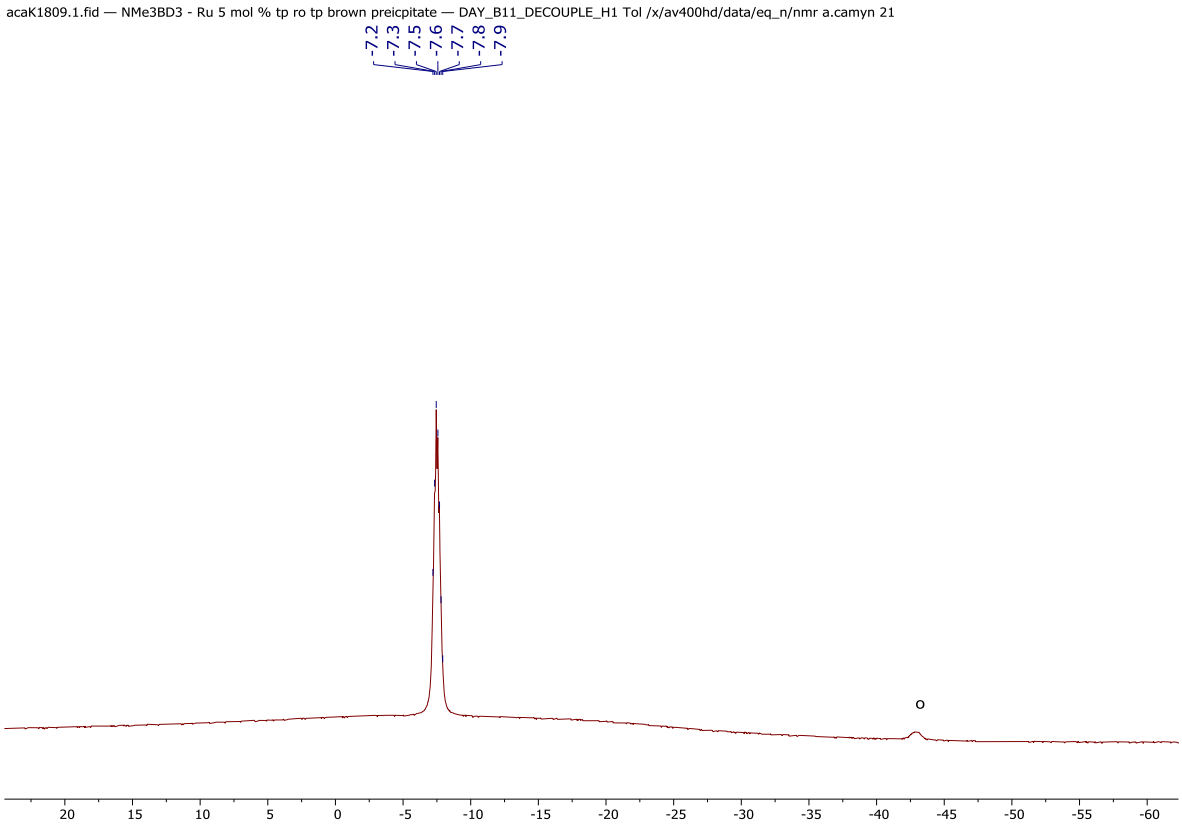
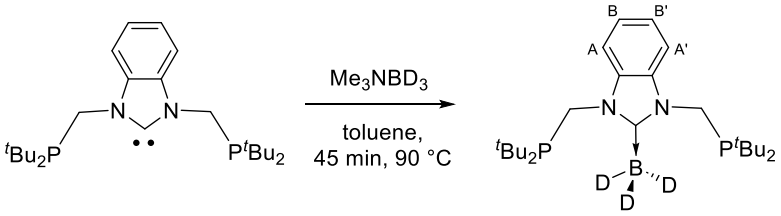


*Figure S19 – ^{11}B NMR spectrum of **$Me_3N{\rightarrow}BD_3$** at 298 K in Tol-d_8, ^{o} corresponds to a **$Me_3N{\rightarrow}BH_3$** ruthenium adduct*

Synthesis and characterization of compound **A-BD$_3$**



bis(phosphine)NHC **A-BD$_3$**

A mixture of the **bis(phosphine)NHC** (219 mg, 0.505 mmol) and **Me$_3$N⟶BD$_3$** (50 mg, 0.660 mmol) in toluene (6 mL) was stirred for 45 min at 90 °C. The solution was then cooled to room temperature and the crude concentrated to half of the initial volume. The crude mixture was filtrated over a pad of silica, washed with toluene (4x5 mL) and the volatiles removed under vacuum to give a brown oil. The toluene was co-evaporated with 3 x 3 mL of pentane. Two successive crystallizations in cold pentane afforded compound **A-BD$_3$** (50 mg, 0.119 mmol, < 23%). The ^{1}H NMR spectrum shows trace amount of **Me$_3$N⟶BH$_3$** ruthenium adduct. **A** is also observed as a singlet at 2.32 ppm in ^{1}H{^{11}B} NMR spectrum. The ratio between CH_2 and BH_3 signal in ^{1}H NMR analysis indicates a deuterium incorporation of 82%.

^{1}H{^{11}B} NMR (400 MHz, C_6D_6, 298 K) δ 8.09 (m, 2H, H_A), 7.07 (m, 2H, H_B), 4.87 (d, $^2J_{P\text{-}H}$ = 1.8 Hz, 4H, NCH_2P), 1.11 (d, $^3J_{P\text{-}H}$ = 11.1 Hz, 36H, P(C(CH_3)$_3$). **^{2}H NMR** (61 MHz, None, 298 K) δ 2.29 (br. s). **^{31}P{^{1}H} NMR** (162 MHz, C_6D_6, 298 K) δ 16.6 (s). **^{11}B NMR** (128 MHz, C_6D_6, 298 K) δ -34.3 (br.). **Elemental Analysis**. Calcd. For $C_{25}H_{45}D_3BN_2P_2$, (452.36 g.mol^{-1}) C, 66.37; H, 11.36; N, 6.19; found C, 66.35; H, 10.44; N, 5.70. **ATR-FTIR** (cm^{-1}) 2987, 2938, 2898, 2862, 2368, 2346, 2319, 2287, 1776, 1731, 1610, 1469, 1428, 1397, 1368, 1256, 1174, 1017, 932, 811, 786, 735.

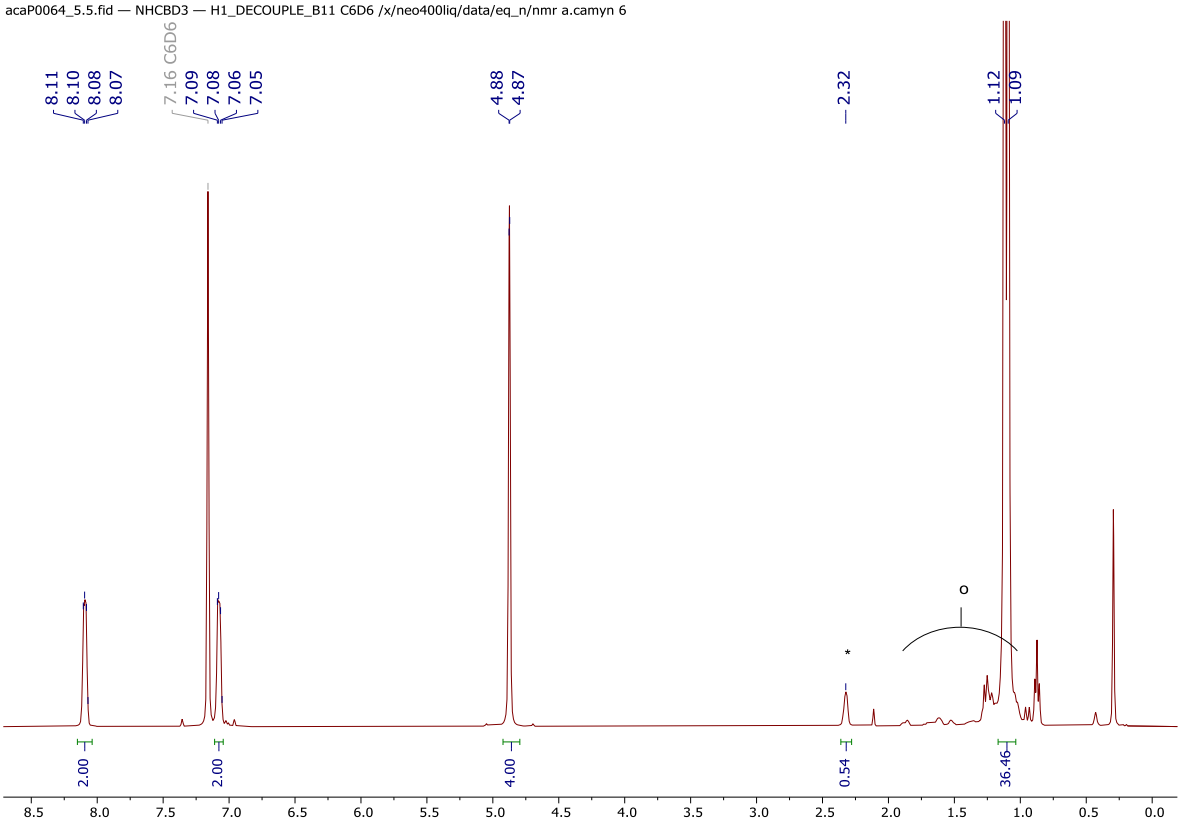


*Figure S20 – $^{1}H\{^{11}B\}$ NMR spectrum of **A-BD₃** at 298 K in C_6D_6 (D1 = 30 sec) * corresponds to **A-BH₃**, ^{o} corresponds to a **Me₃N⟶BH₃** ruthenium adduct*

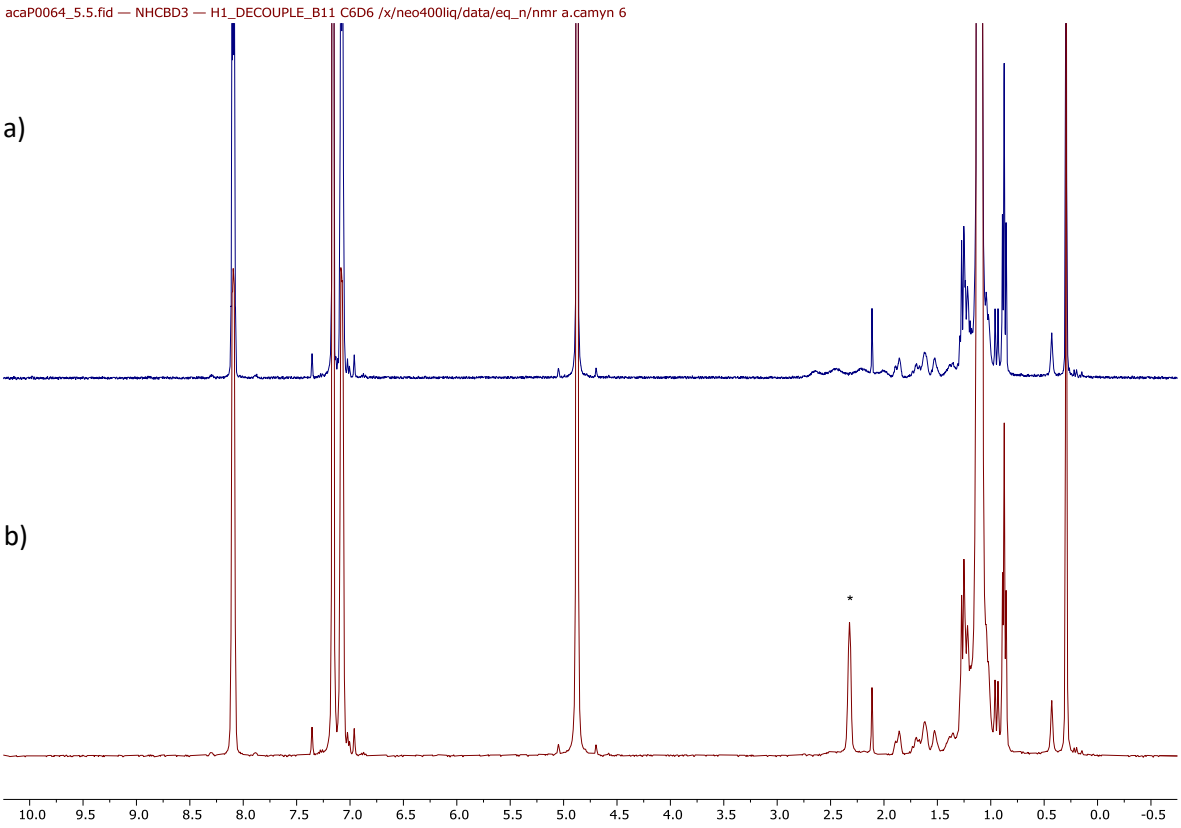


*Figure S21 – Stack of a) ^{1}H and b) $^{1}H\{^{11}B\}$ NMR spectra of **A-BD₃** at 298 K in C_6D_6 (D1 = 30 sec), * corresponds to **A-BH₃***

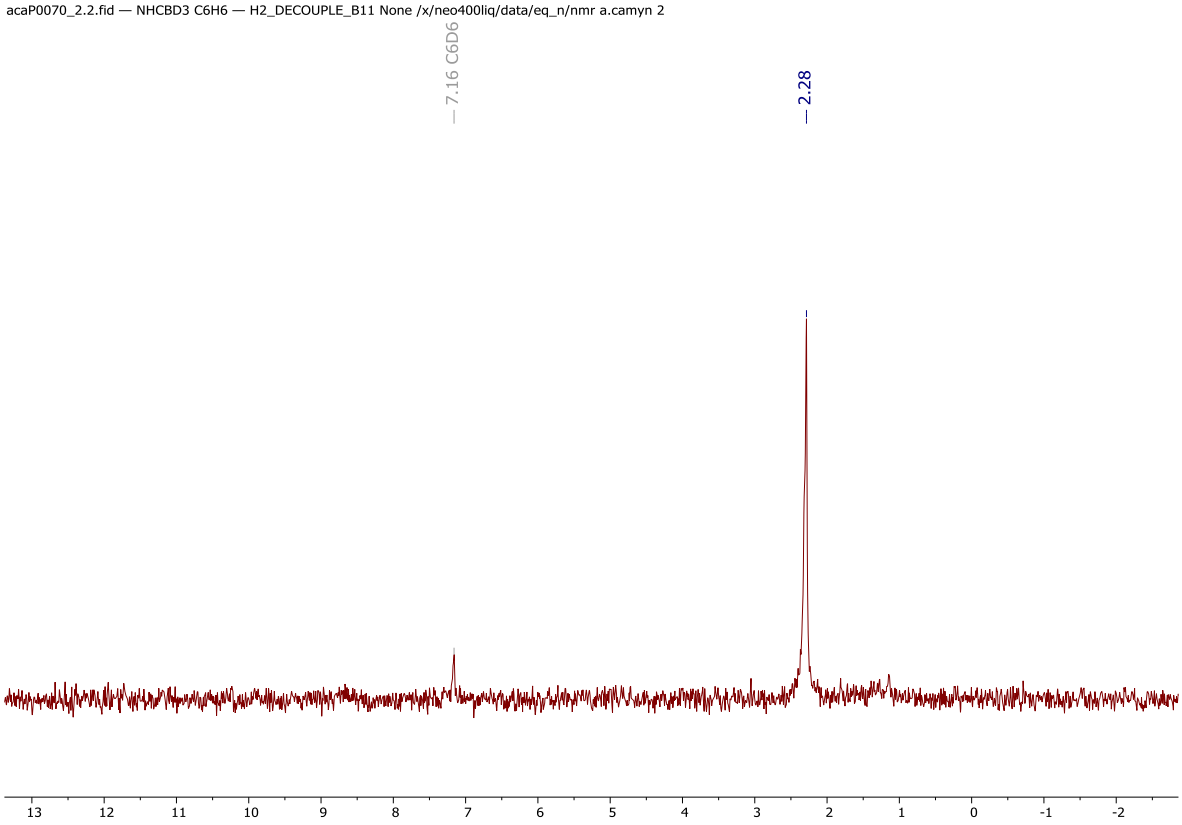


*Figure S22 – $^{2}H\{^{11}B\}$ NMR spectrum of **A-BD₃** at 298 K in C_6H_6 (D1 = 10 sec, Scan number = 20)*

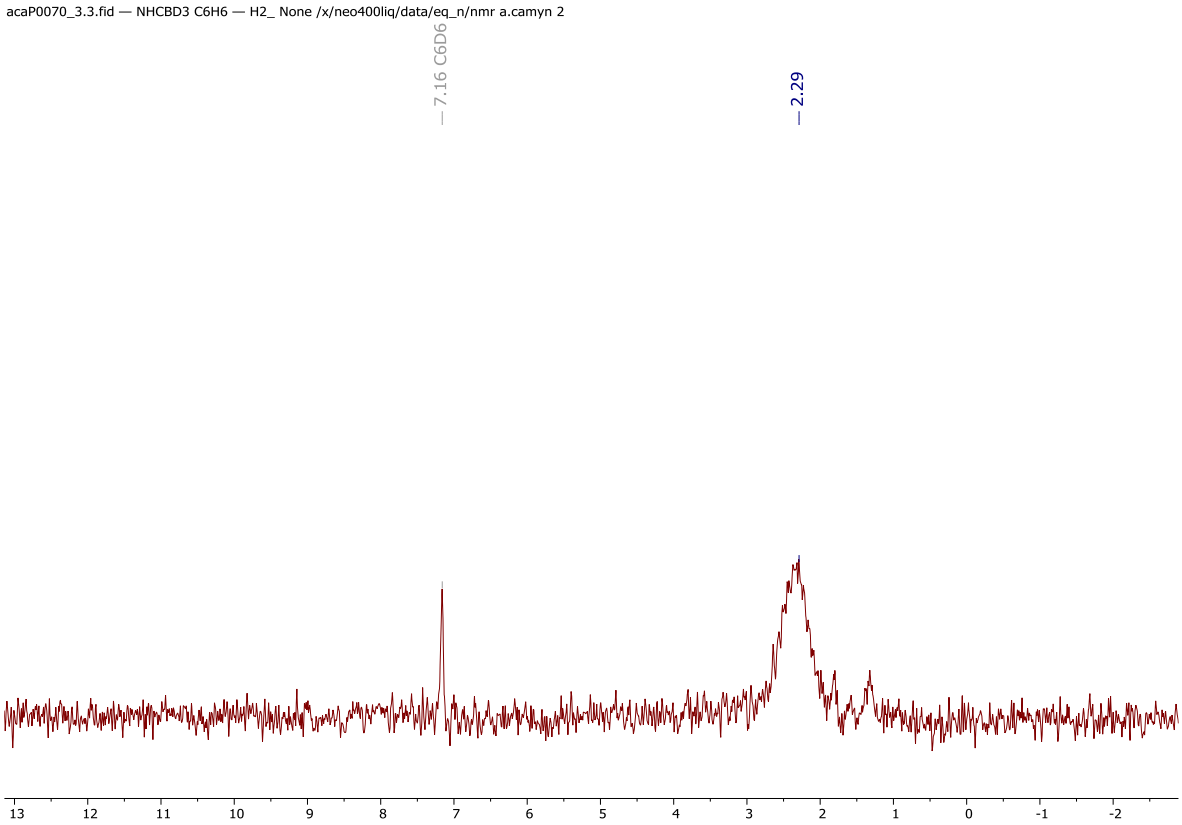


*Figure S23 – ^{2}H NMR spectrum of **A-BD₃** at 298 K in C_6H_6 (D1 = 10 sec, Scan number = 50)*

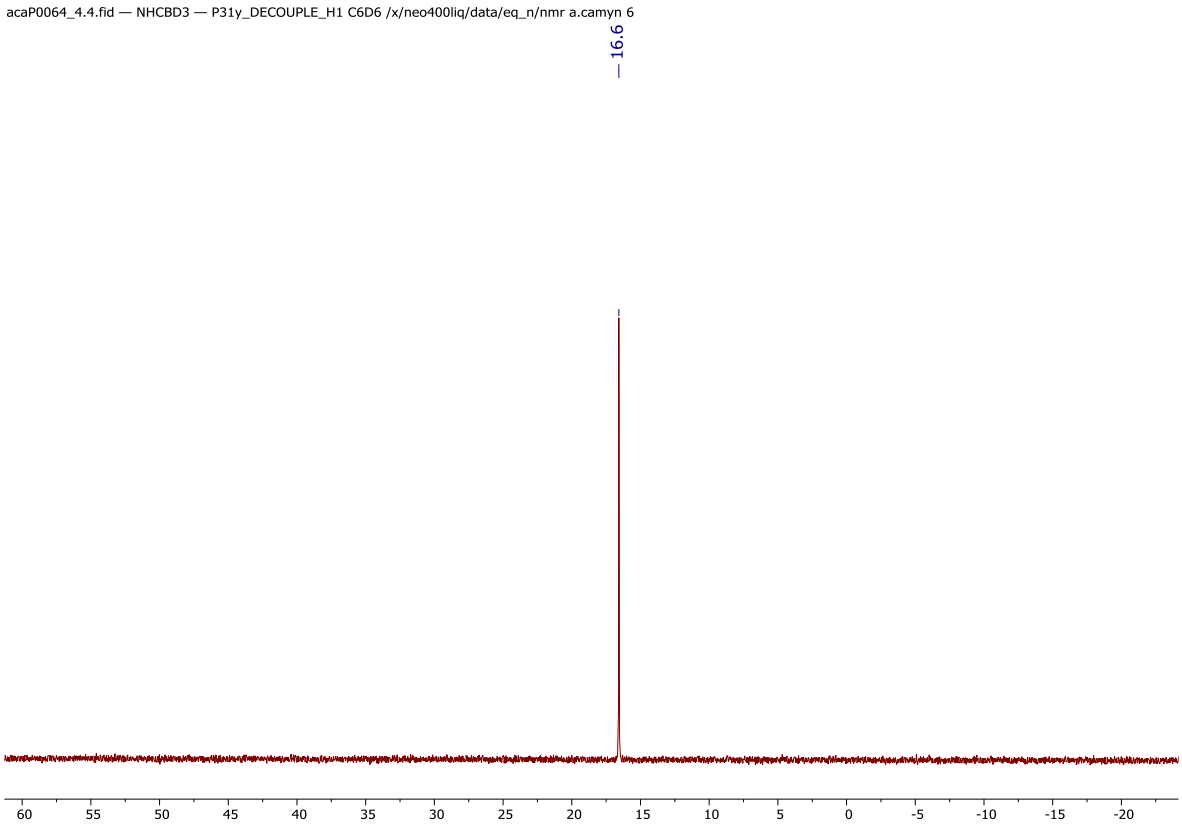


*Figure S24 – $^{31}P\{^{1}H\}$ NMR spectrum of **A-BD₃** at 298 K in C_6D_6*

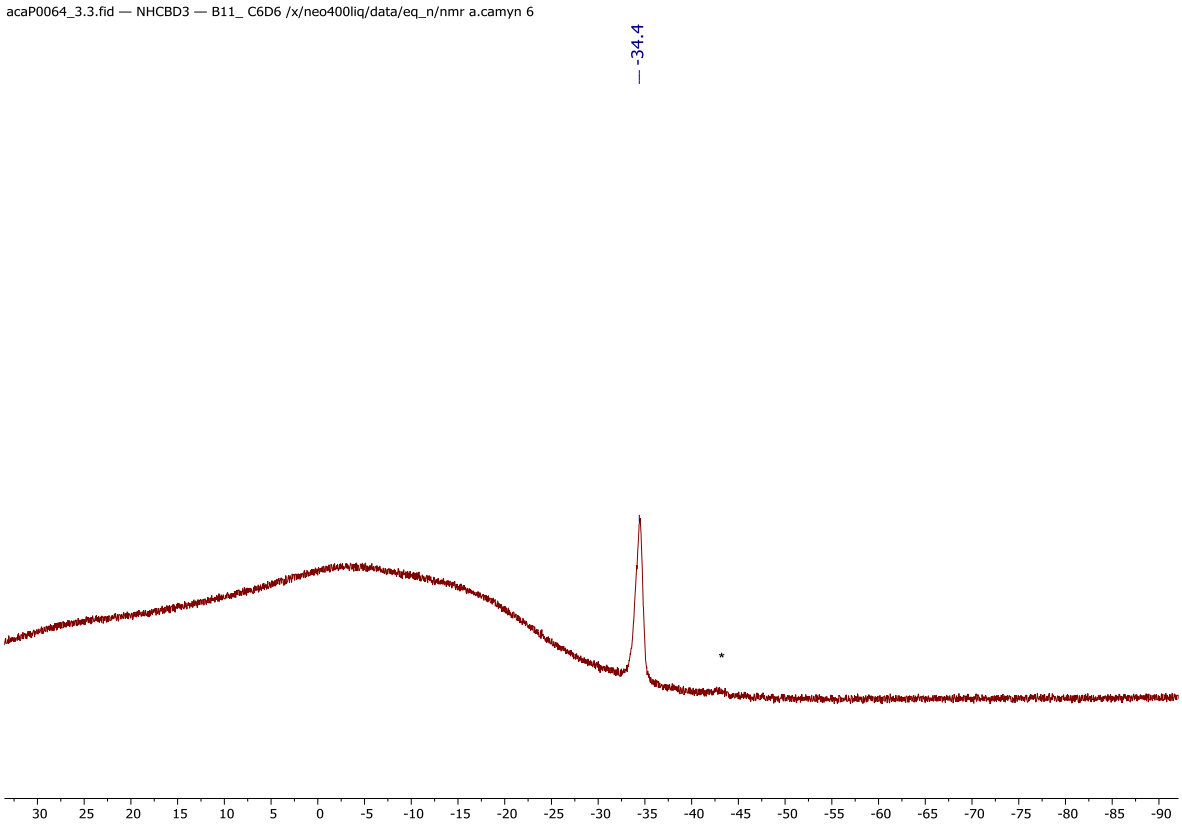


*Figure S25 – ^{11}B NMR spectrum of **A-BD₃** at 298 K in C_6D_6 (* corresponds possibly to a **Me₃N→BH₃** ruthenium adduct)*

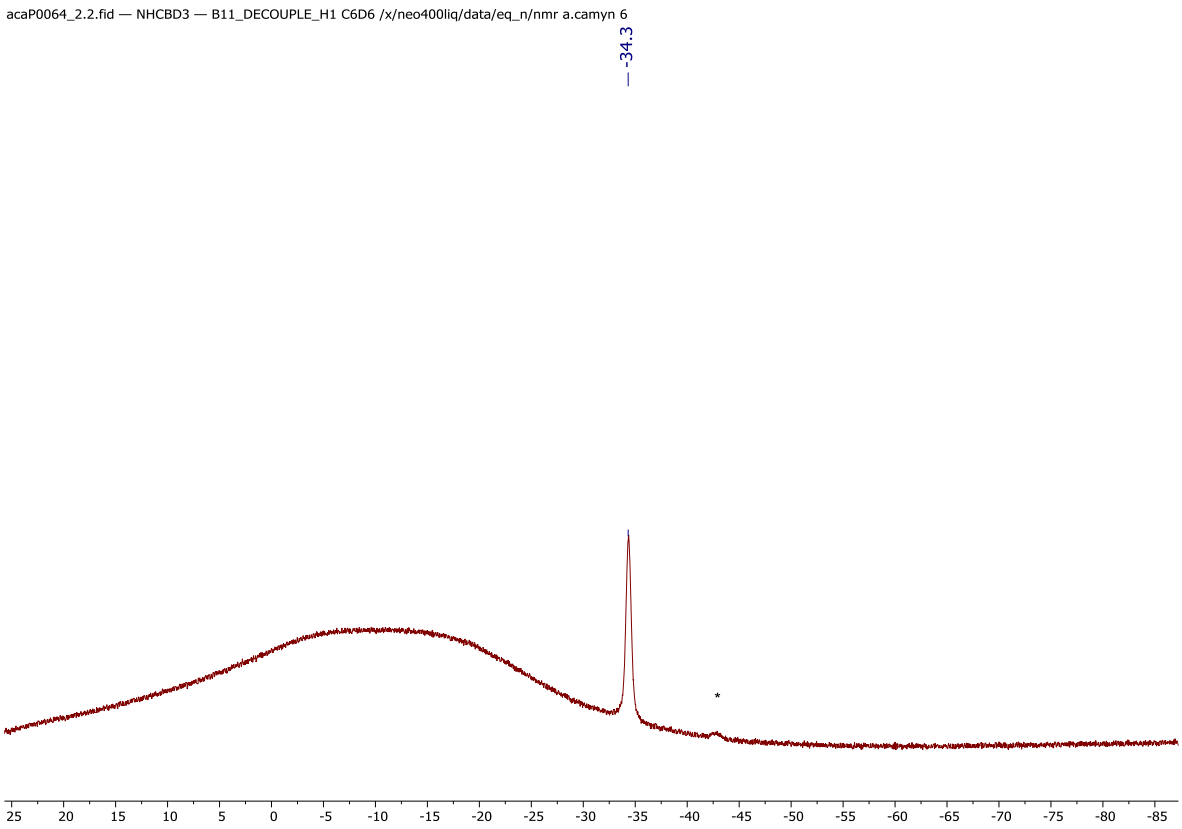


*Figure S26 – $^{11}B\{^{1}H\}$ NMR spectrum of **A-BD₃** at 298 K in C_6D_6 (* corresponds possibly to a **Me₃N⟶BH₃** ruthenium adduct)*

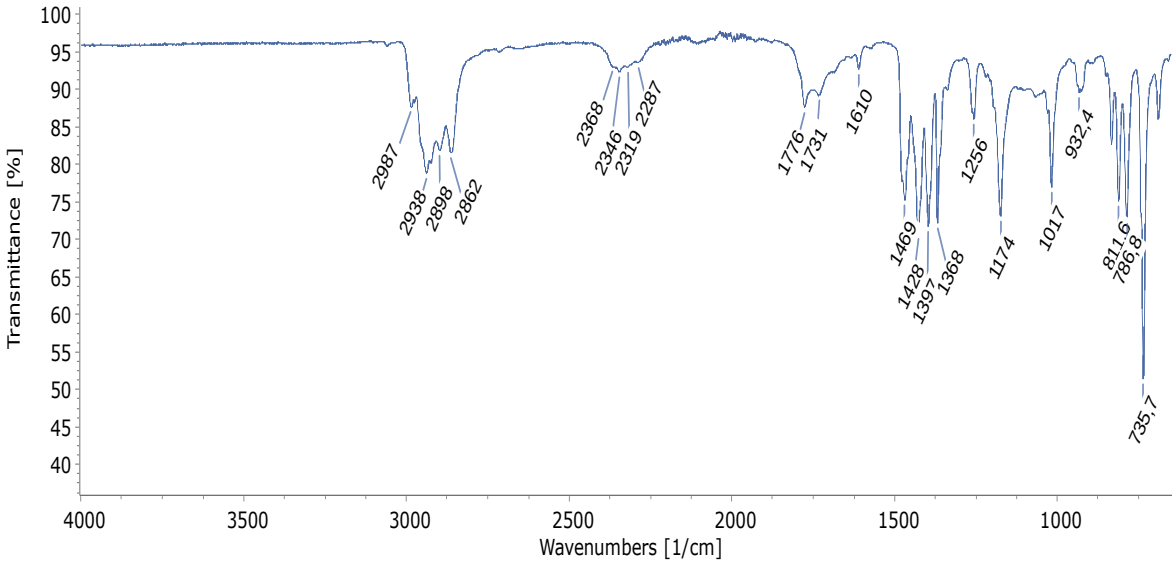
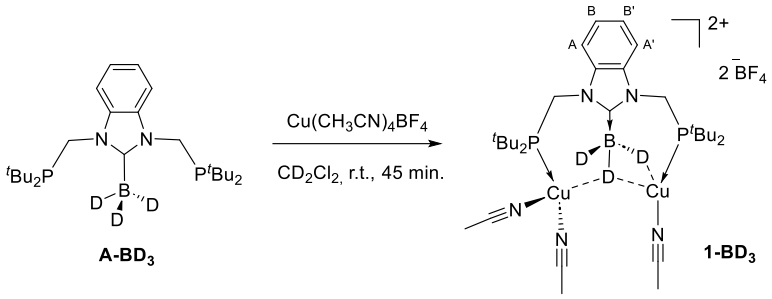


*Figure S27 – ATR-FTIR spectrum of **A-BD₃***

*Figure S28 – Superimposed ATR-FTIR spectra of **A** (blue curve), **A-BD$_3$** (orange curve).*

Synthesis and characterization of compound **1-BD$_3$**



A mixture of **A-BD$_3$** (25 mg, 0.055 mmol) and [Cu(CH$_3$CN)$_4$BF$_4$] (35 mg, 0.110 mmol) was dissolved at room temperature in CD_2Cl_2 (1 mL) in a J. Young NMR tube. The solution was shaken by hand and protected from light exposure. Completion of the reaction was reached after 45 minutes. Compound **1-BD$_3$** was characterized by NMR and IR spectroscopy without further purification.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ 7.87 (AA'BB' system, $^3J_{AB}$ = 8.20 Hz, $^3J_{BB'}$ = 7.03 Hz, $^4J_{AB'}$ = 1.08 Hz, $^5J_{AA'}$ = 0.00 Hz, 2H, H_A and $H_{A'}$), 7.65 (AA'BB' system, $^3J_{AB}$ = 8.20 Hz, $^3J_{BB'}$ = 7.03 Hz, $^4J_{AB'}$ = 1.08 Hz, $^5J_{AA'}$ = 0.00 Hz, 2H, H_B and $H_{B'}$), 4.82 (d, $^2J_{P\text{-}H}$ = 2.6 Hz, 4H, NCH_2P), 2.11 (s, 27H, CH_3CN and traces of [Cu(CH$_3$CN)$_4$BF$_4$]), 1.27 (d, $^3J_{P\text{-}H}$ = 13.9 Hz, 36H, P(C(CH_3)$_3$). **^{2}H{^{11}B} NMR** (61 MHz, CH_2Cl_2, 298 K) δ 2.60 (br. s). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 298 K) δ 31.5 (s). **^{11}B{^{1}H} NMR** (128 MHz, CD_2Cl_2, 298 K) δ -1.1 (BF_4), -34.0 (BD_3). **ATR-FTIR** (cm^{-1}) 2997, 2941, 2904, 2870, 2415, 2315, 2281, 1808, 1722, 1610, 1467, 1446, 1398, 1372, 1264, 1182, 1047, 1021, 935, 808, 760, 745.

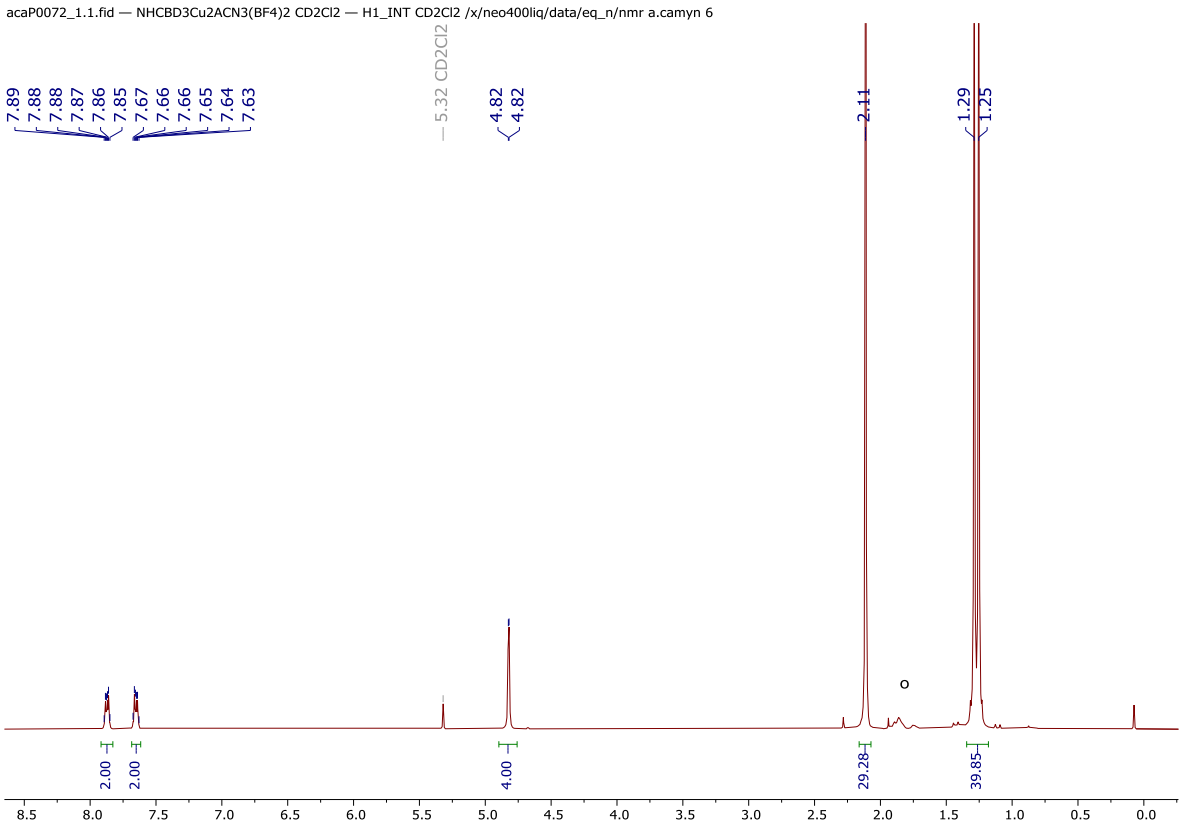


*Figure S29 – ^{1}H NMR spectrum of **1-BD$_3$** at 298 K in CD_2Cl_2 (D1 = 30 sec), ^{o} corresponds to traces of ruthenium adduct*

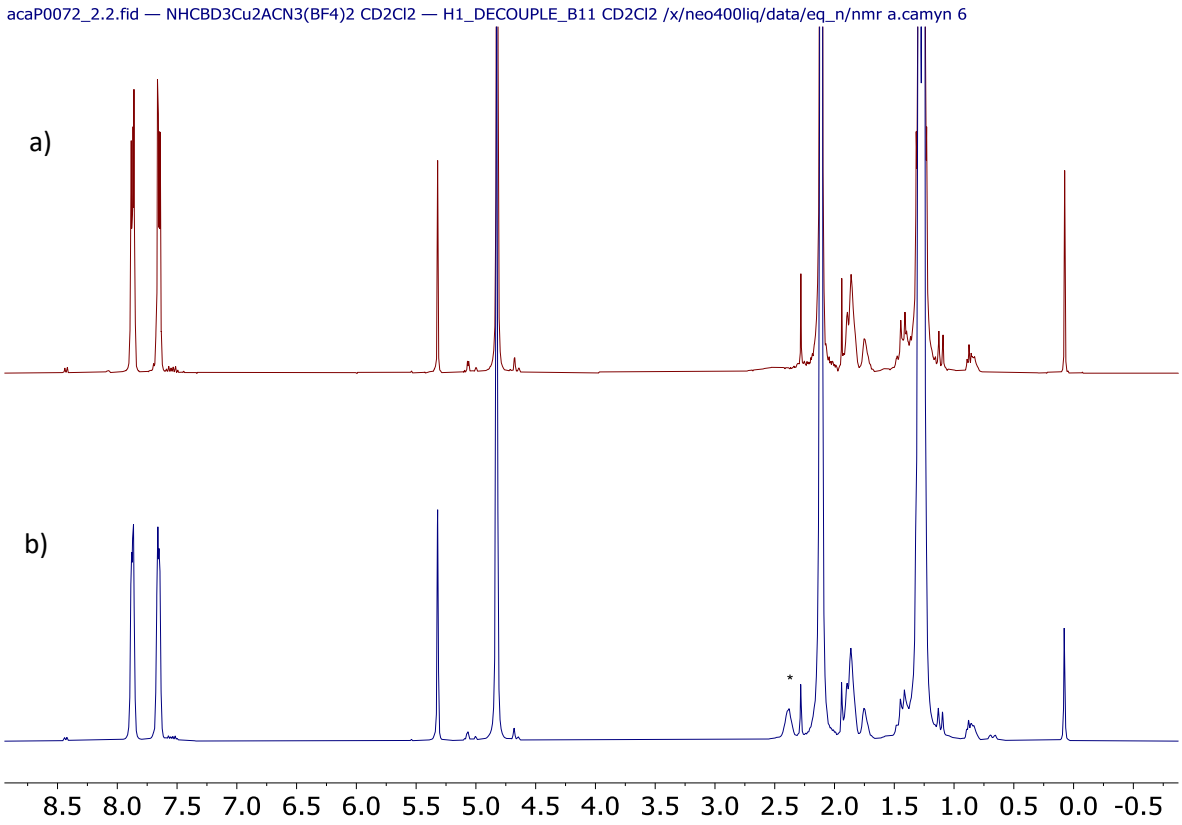


*Figure S30 – Stack of a) ^{1}H and b) $^{1}H\{^{11}B\}$ NMR spectra of **1-BD₃** at 298 K in CD_2Cl_2 (D1 = 30 sec) * corresponds to remaining **Me₃N⟶BH₃***

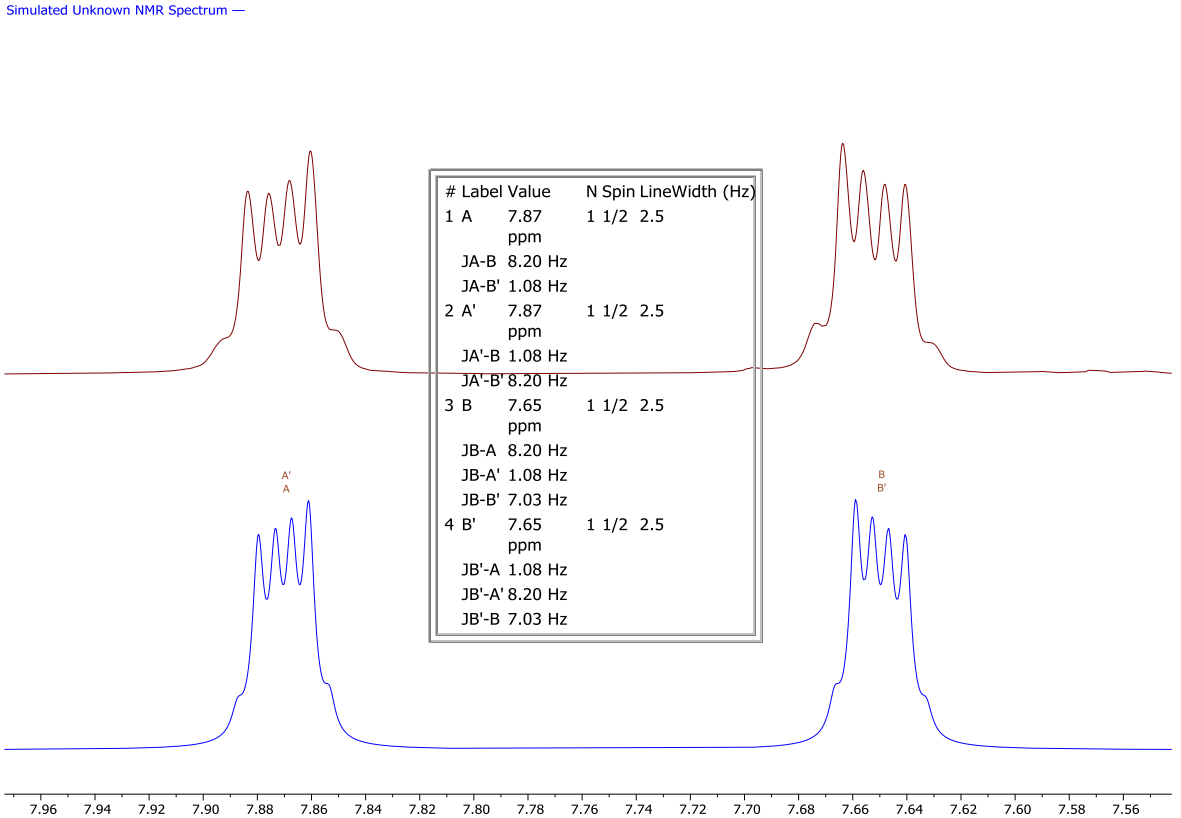


*Figure S31 – Stacked ^{1}H NMR spectrum of **1-BD₃** at 298 K in CD_2Cl_2 (top) and simulation of AA'BB' system (bottom). Zoom of the aromatic region*

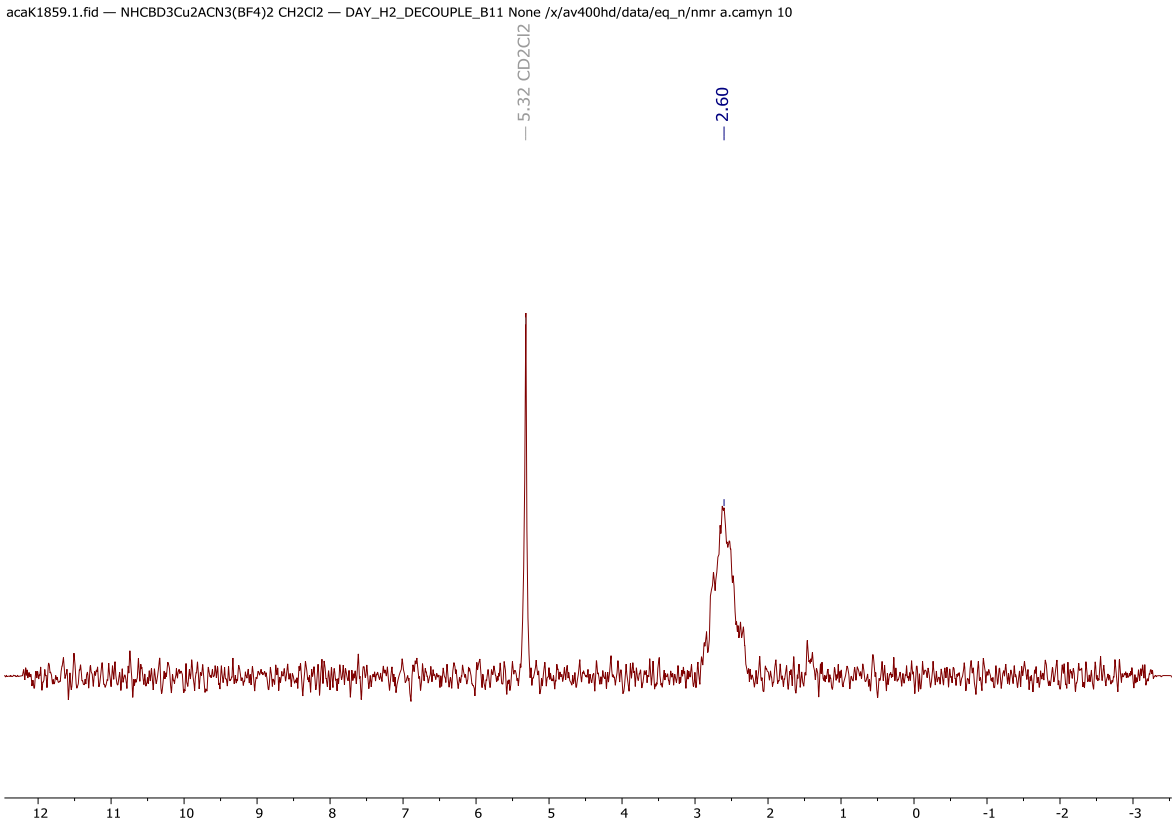


*Figure S32 – $^{2}H\{^{11}B\}$ NMR spectrum of **1-BD₃** at 298 K in CH_2Cl_2 (D1 = 10 sec, Scan number = 30)*

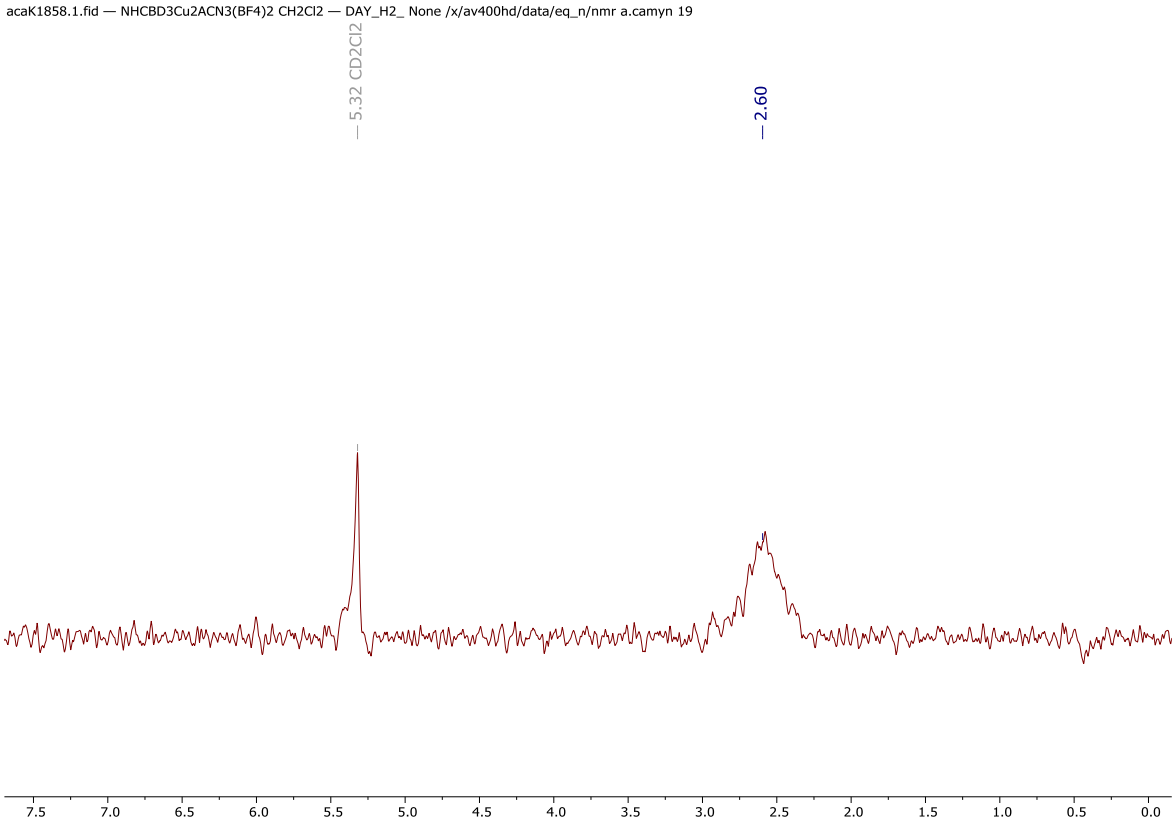


*Figure S33 – ^{2}H NMR spectrum of **1-BD₃** at 298 K in CH_2Cl_2 (D1 = 10 sec, Scan number = 18)*

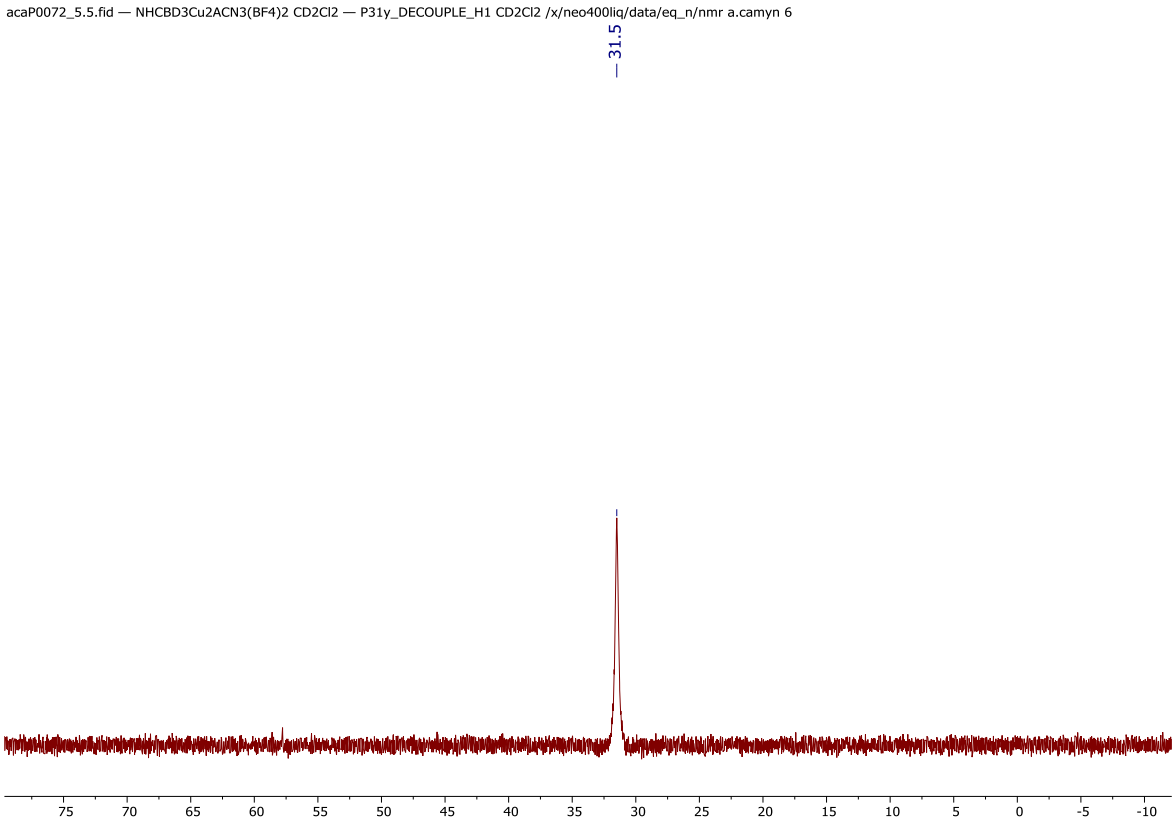


*Figure S34 – $^{31}P\{^{1}H\}$ NMR spectrum of **1-BD$_3$** at 298 K in CD_2Cl_2*

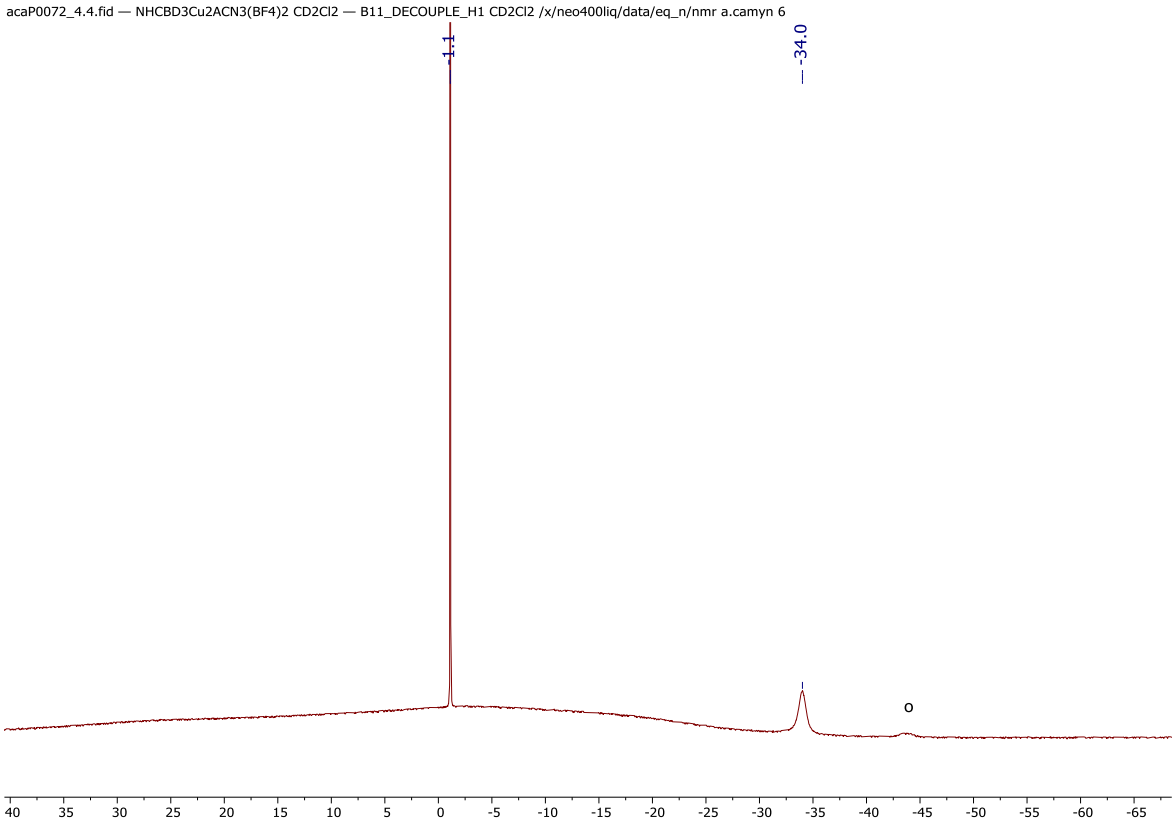


*Figure S35 – $^{11}B\{^{1}H\}$ NMR spectrum of **1-BD$_3$** at 298 K in CD_2Cl_2 (o corresponds to a ruthenium adduct)*

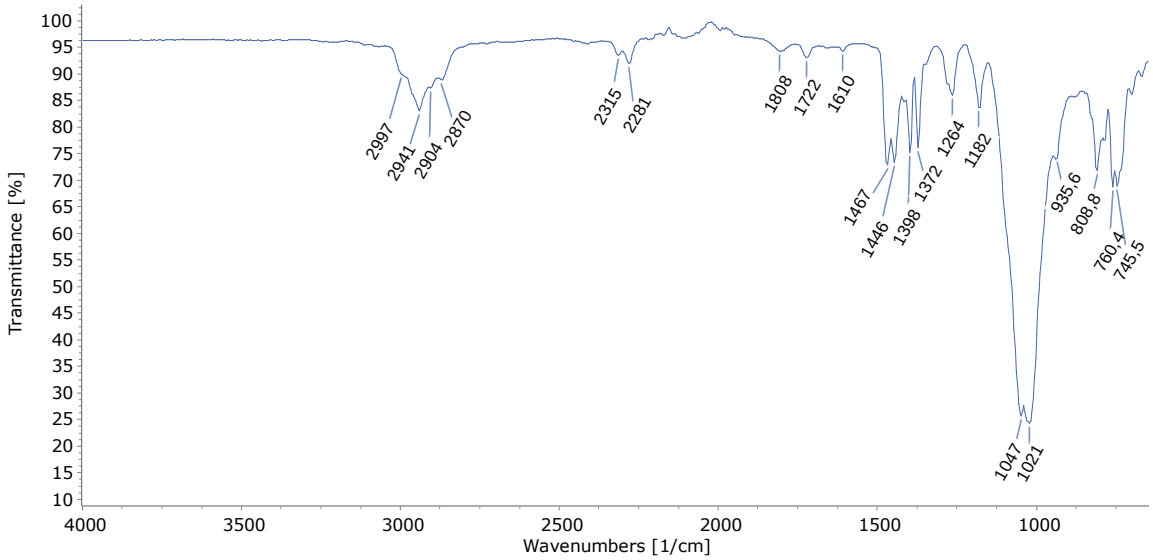


*Figure S36 – ATR-FTIR spectrum of complex **1-BD₃***

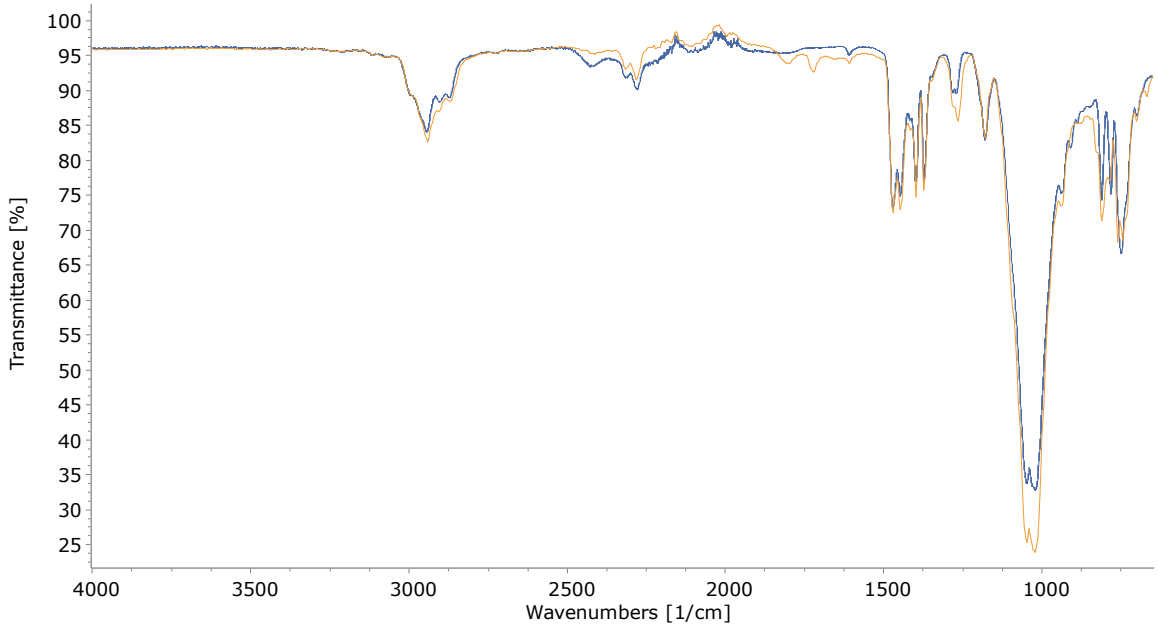
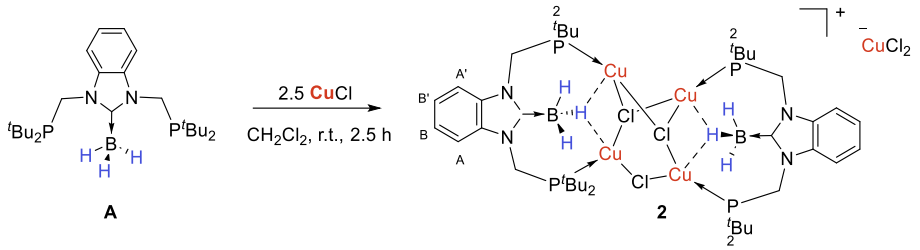


*Figure S37 – Superimposed ATR-FTIR spectra of complexes **1** (blue curve) and **1-BD₃** (orange curve)*

Synthesis and characterization of compound **2**



A mixture of **A** (200 mg, 0.446 mmol) and CuCl (133 mg, 1.339 mmol) in dichloromethane (10 mL) was stirred for 2.5 hours at room temperature, protected from light. At the initial stage, fine powder of CuCl is barely soluble in CH_2Cl_2. The suspension evolves to a clear solution within 1 h, leaving only small amount of insoluble residue. At the end of the reaction, the residue was cannulated off and the filtrate concentrated under vacuum. After one night at –25 °C, a white precipitate formed, which was washed with dichloromethane at – 35 °C (0.5 mL) then dried at room temperature. The residue was washed with a mixture of pentane/dichloromethane (3 x 2/1mL), then dried. Elemental analysis showed that the obtained white powder (247 mg, 0.178 mmol, < 40 %) is not pure complex **2** and presumably contain excess of CuCl. Adding one equivalent of CuCl to the elemental analysis calculation afford more accurate data. Colorless crystals suitable for X-Ray analysis were obtained from a concentrated dichloromethane solution layered by Et_2O, after one day at room temperature, protected from light exposure.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ 7.66 (AA'BB' system, $^3J_{AB}$ = 8.3 Hz, $^3J_{BB'}$ = 7.4 Hz, $^4J_{AB'}$ = 1.0 Hz, $^5J_{AA'}$ = 0.0 Hz, 4H, H_A and $H_{A'}$), 7.57 (AA'BB' system, $^3J_{AB}$ = 8.3 Hz, $^3J_{BB'}$ = 7.4 Hz, $^4J_{AB'}$ = 1.0 Hz, $^5J_{AA'}$ = 0.0 Hz, 4H, H_B and $H_{B'}$), 4.71 (br. s, 8H, NCH_2P), 2.59 (br., 6H, BH_3), 1.30 (br. s, 72H, P(C(CH_3)$_3$)$_3$). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2, 298 K) δ 173.8 (br., *C*-B), 133.2 (s, $C_{quat.}$Ar), 125.7 (s, *C*HAr$_{B/B'}$), 112.3 (s, *C*HAr$_{A/A'}$), 39.1 (d, $^1J_{P-C}$ = 7.6 Hz, NCH_2P), 34.6 (m, P*C*(CH$_3$)$_3$), 29.4 (d, $^2J_{P-C}$ = 7.3 Hz, PC(*C*H$_3$)$_3$). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 298 K) δ 30.1 (br., P^{t}Bu$_2$). **^{11}B NMR** (128 MHz, CD_2Cl_2, 298 K) δ -33.9 (br., *B*H$_3$). **Elemental Analysis**. Calcd. For $C_{50}H_{88}B_2Cl_5Cu_5N_4P_4$, (1386.15 g.mol^{-1}) C, 43.15; H, 6.81; N, 4.03 Exp. C, 40.62; H, 6.98 N, 3.50 Calcd. with 1 eq of CuCl: For $C_{50}H_{88}B_2Cl_6Cu_6N_4P_4$, C, 40.28; H, 6.36; N, 3.76. **ATR-FTIR** (cm^{-1}) 2960, 2945, 2900, 2866, 2397, 2318, 1470, 1442, 1394, 1369, 1260, 1177, 1085, 1018, 932, 798, 743.

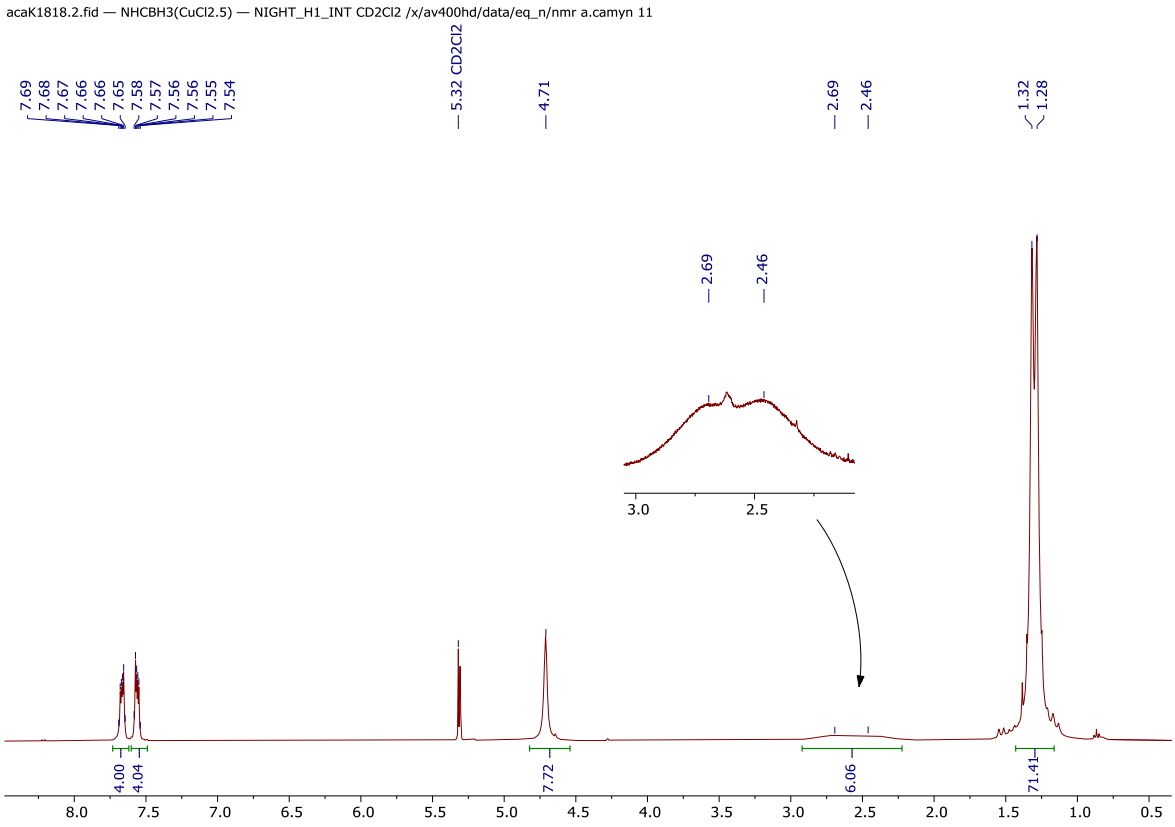


*Figure S38 – ^{1}H NMR spectrum of **2** at 298 K in CD_2Cl_2 (D1 = 30 sec)*

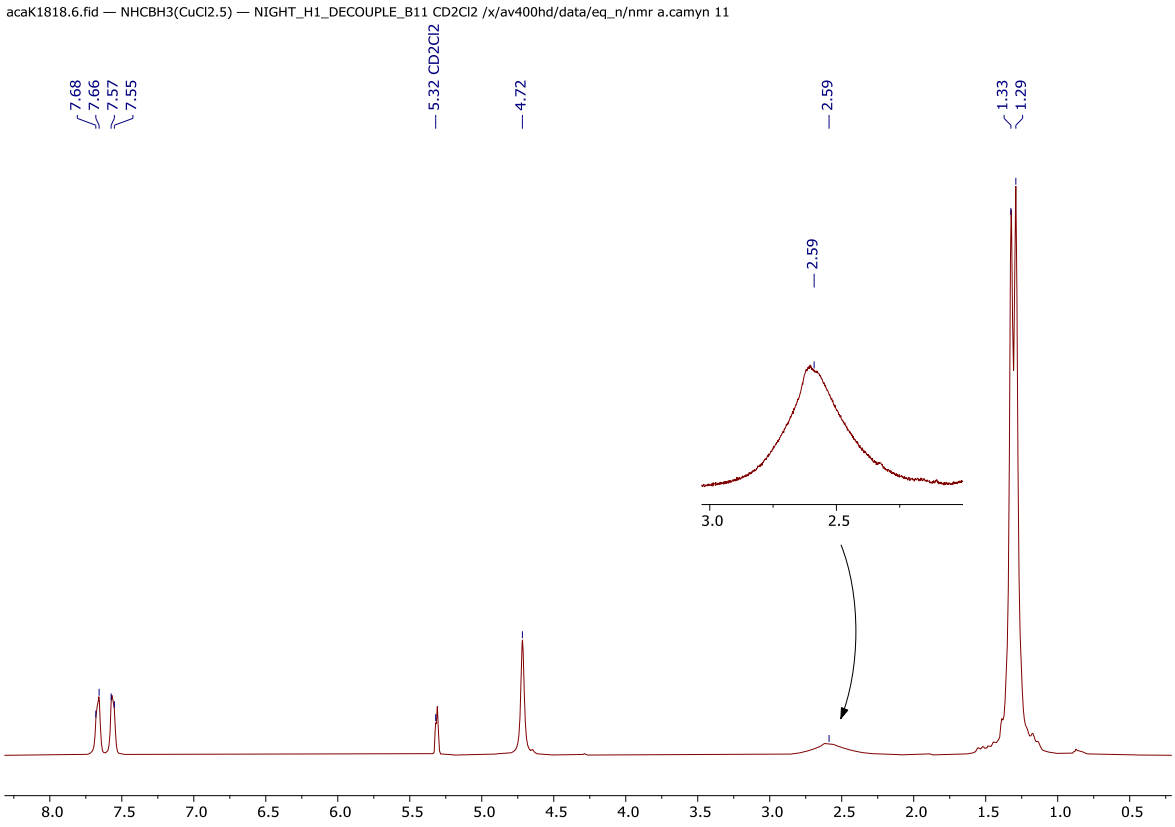


*Figure S39 – $^{1}H\{^{11}B\}$ NMR spectrum of **2** at 298 K in CD_2Cl_2 (D1 = 30 sec)*

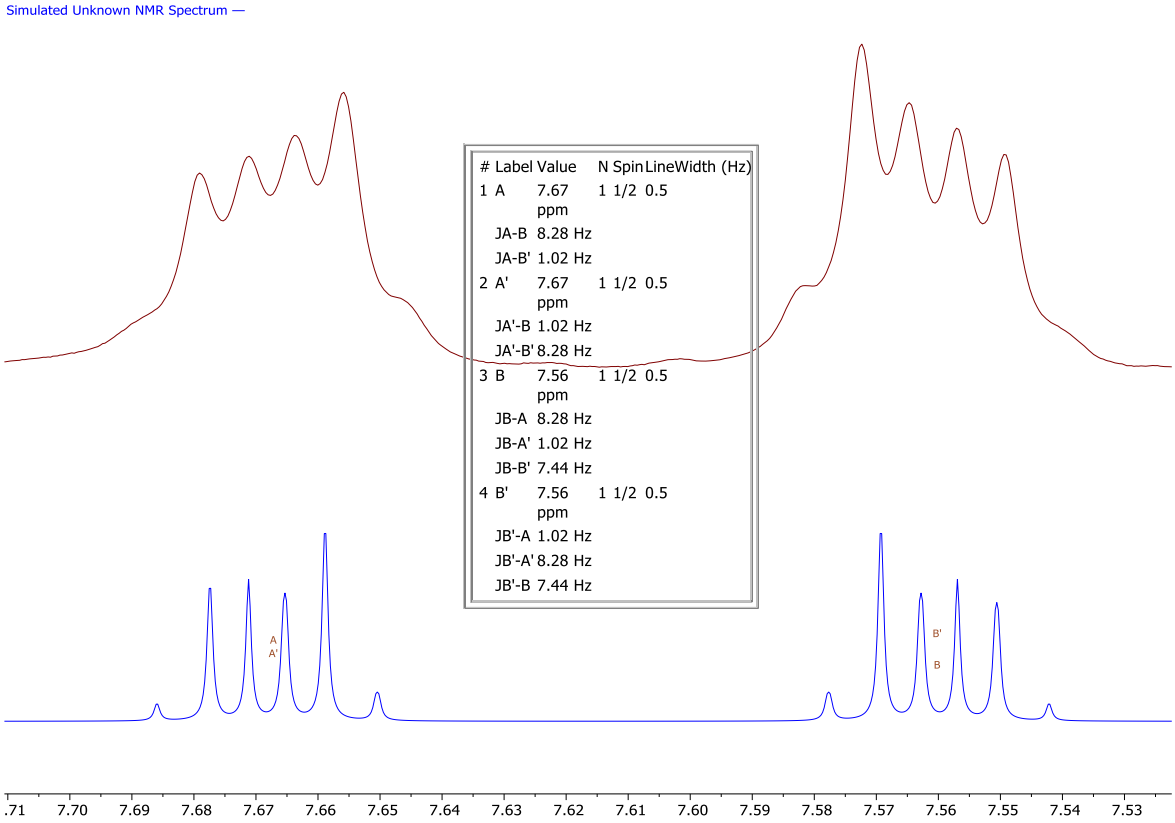


*Figure S40 – Stacked ^{1}H NMR spectrum of **2** at 298 K in CD_2Cl_2 (top) and simulation of AA'BB' system (bottom). Zoom of the aromatic region*

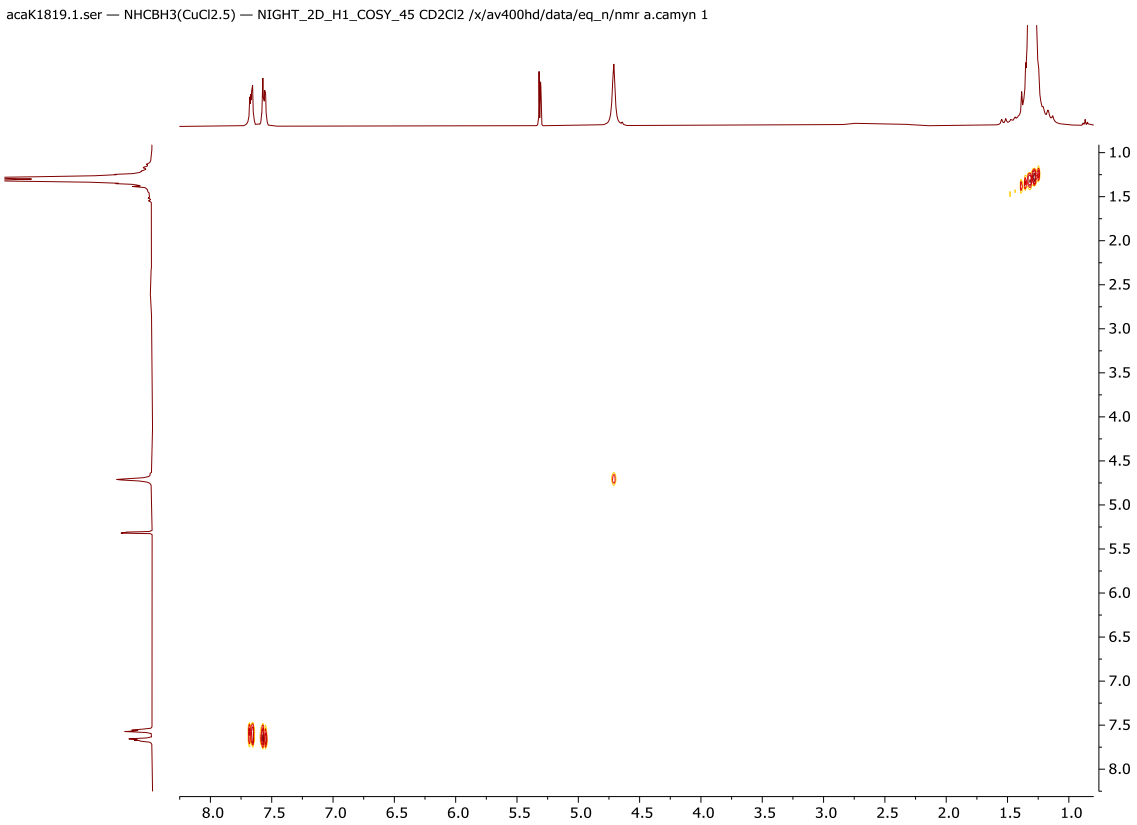


*Figure S41 – COSY $^{1}H/^{1}H$ NMR spectrum of **2** at 298 K in CD_2Cl_2*

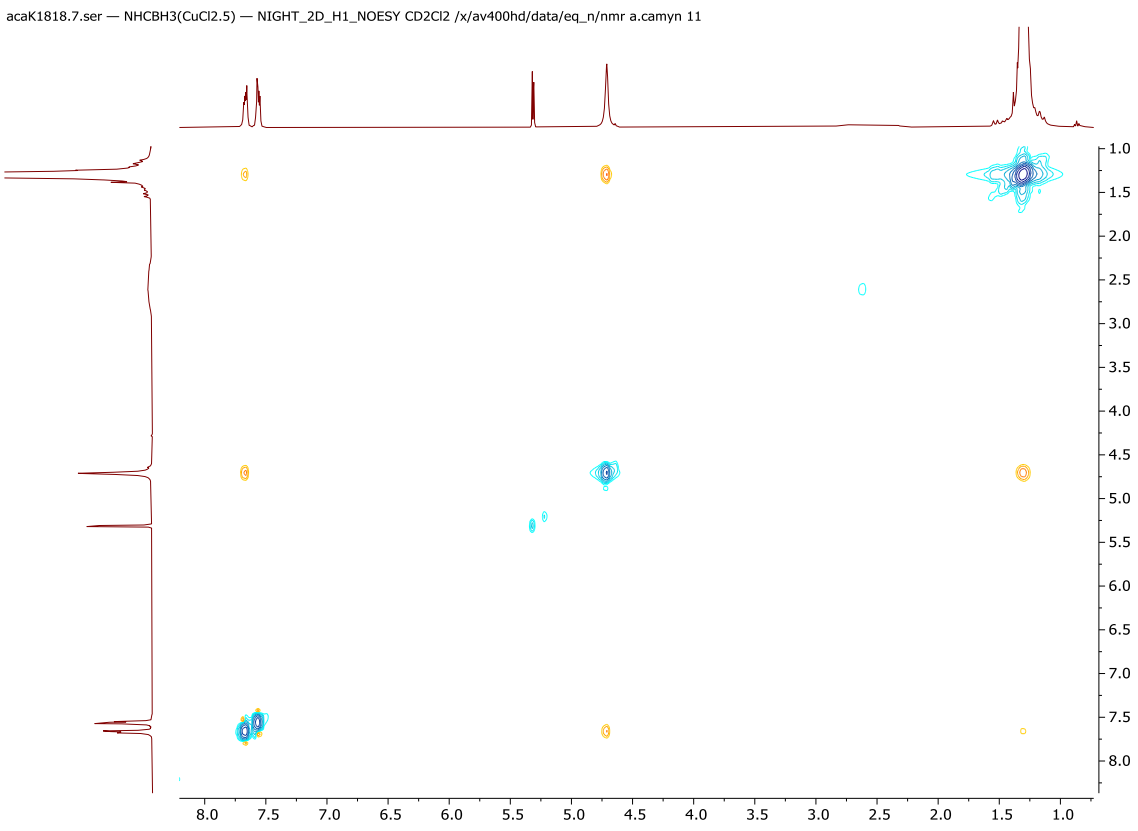


*Figure S42 – NOESY $^{1}H/^{1}H$ NMR spectrum of **2** at 298 K in CD_2Cl_2 (Mixing time = 0.5 s)*

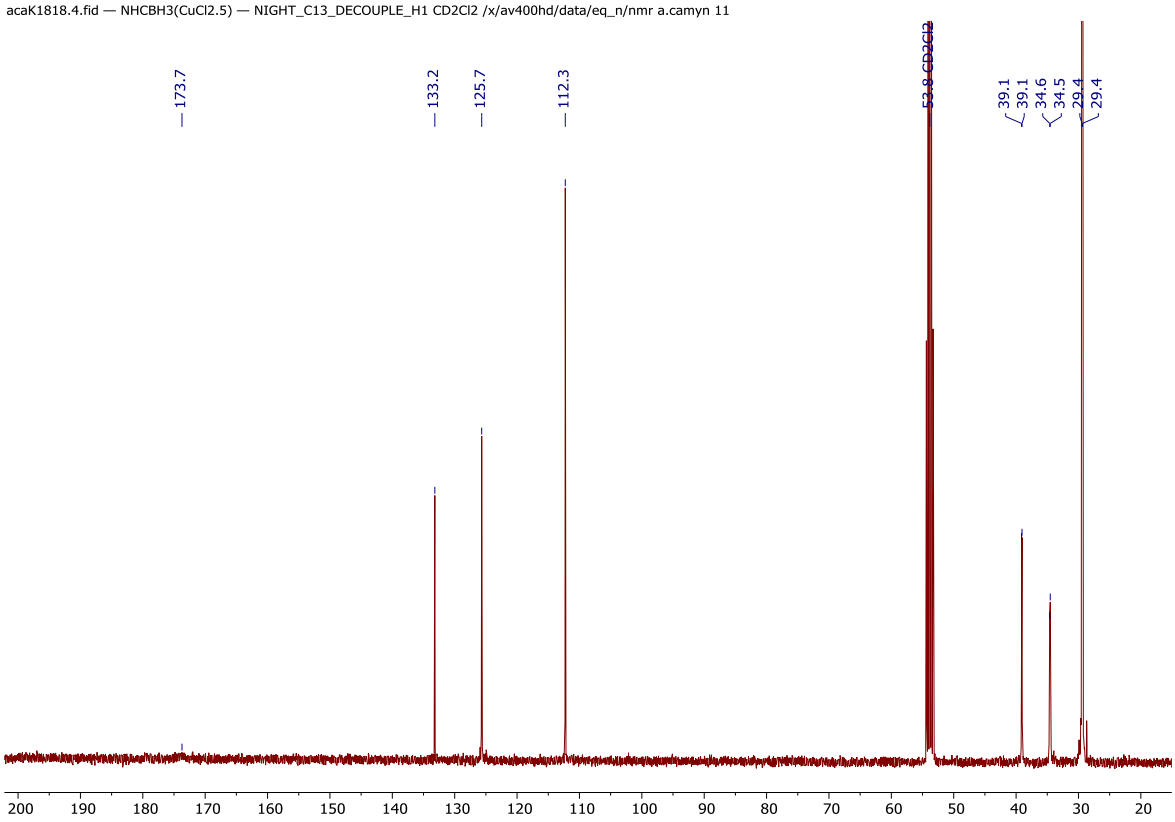


*Figure S43 – $^{13}C\{^{1}H\}$ NMR spectrum of **2** at 298 K in CD_2Cl_2*

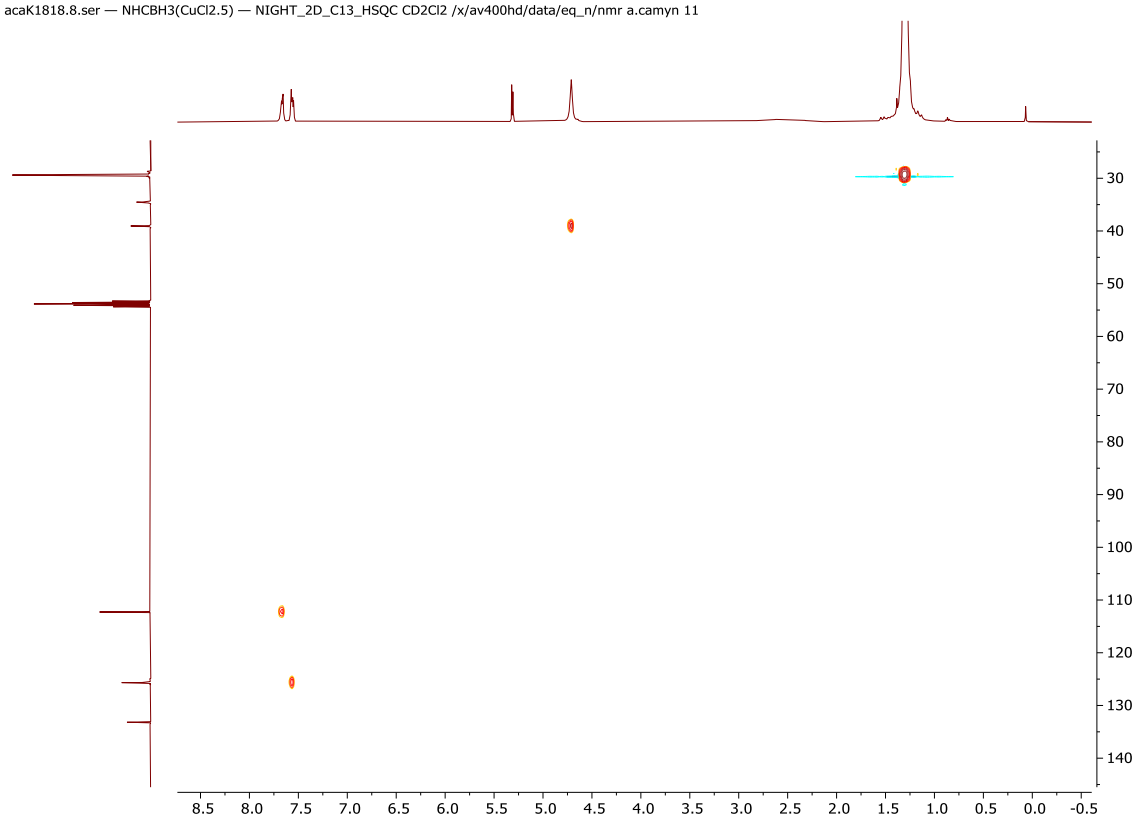


*Figure S44 – HSQC $^{13}C\{^1H\}/^1H$ NMR spectrum of **2** at 298 K in CD_2Cl_2*

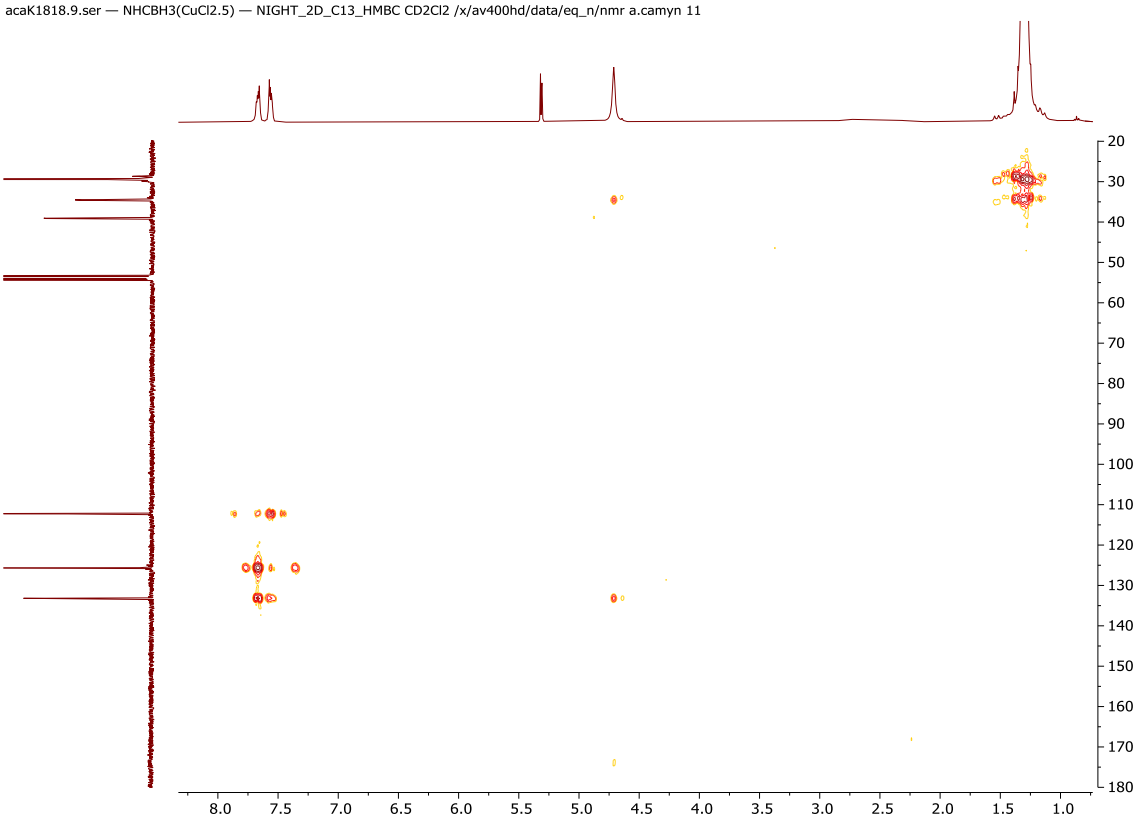


*Figure S45 – HMBC $^{13}C\{^1H\}/^1H$ NMR spectrum of **2** at 298 K in CD_2Cl_2*

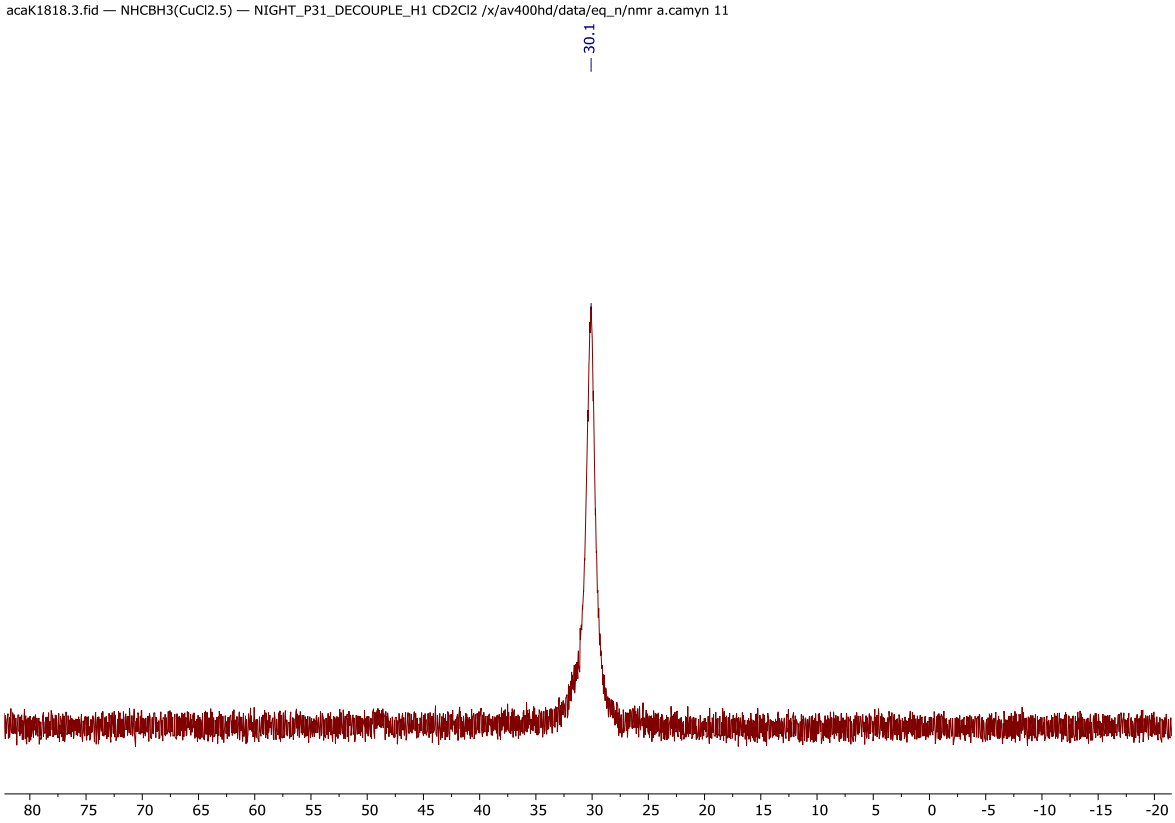


*Figure S46 – $^{31}P\{^{1}H\}$ NMR spectrum of **2** at 298 K in CD_2Cl_2*

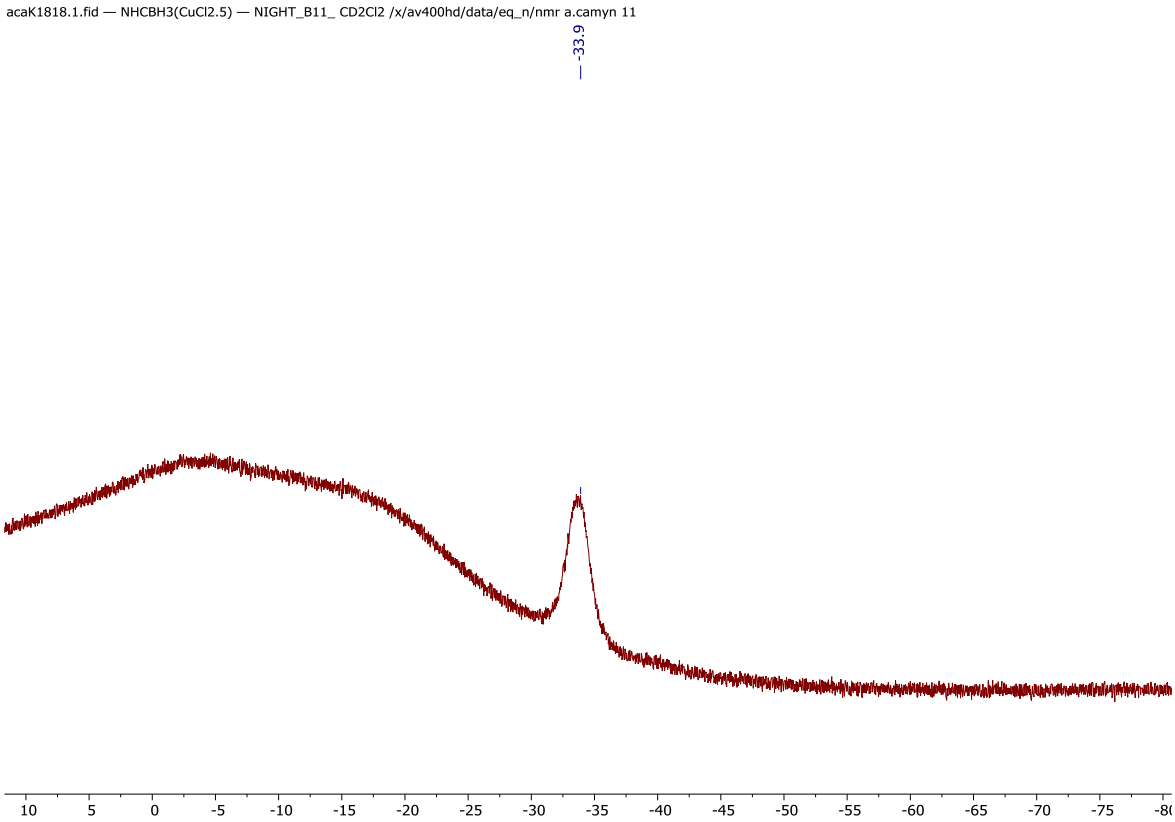


*Figure S47 – ^{11}B NMR spectrum of **2** at 298 K in CD_2Cl_2*

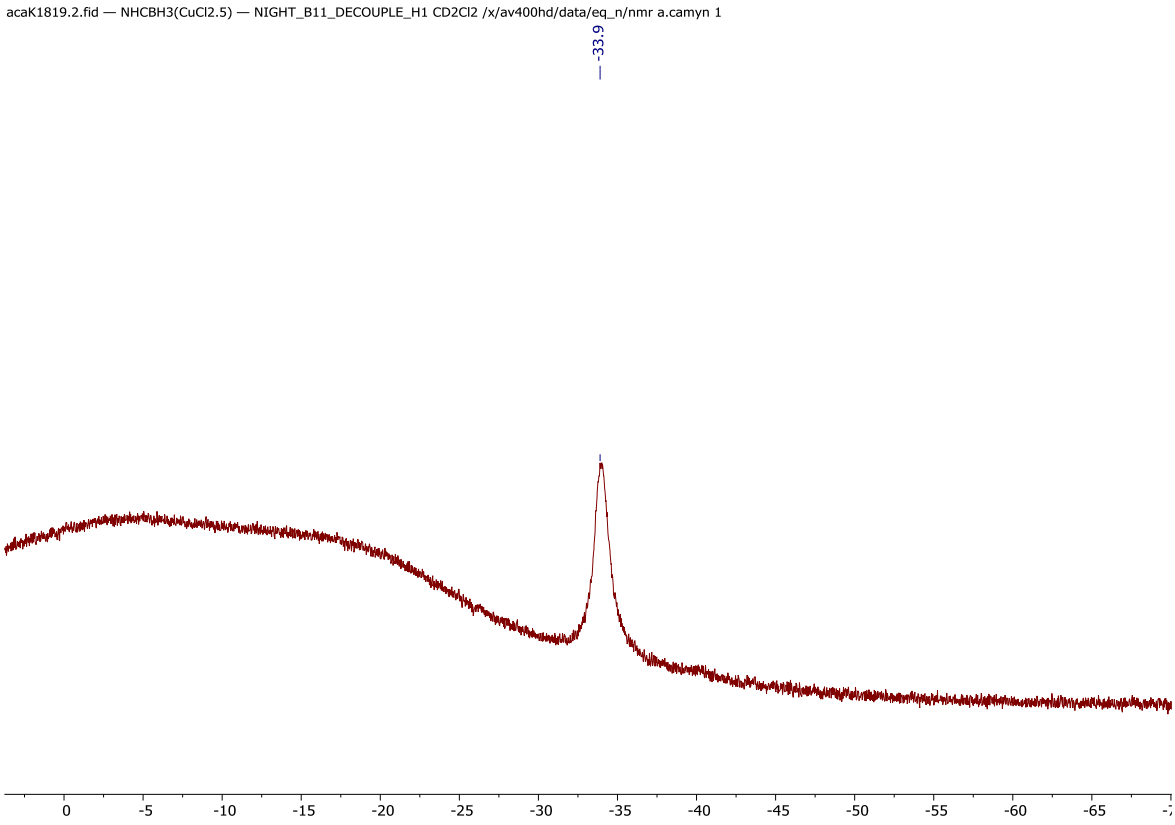


*Figure S48 – $^{11}B\{^{1}H\}$ NMR spectrum of **2** at 298 K in CD_2Cl_2*

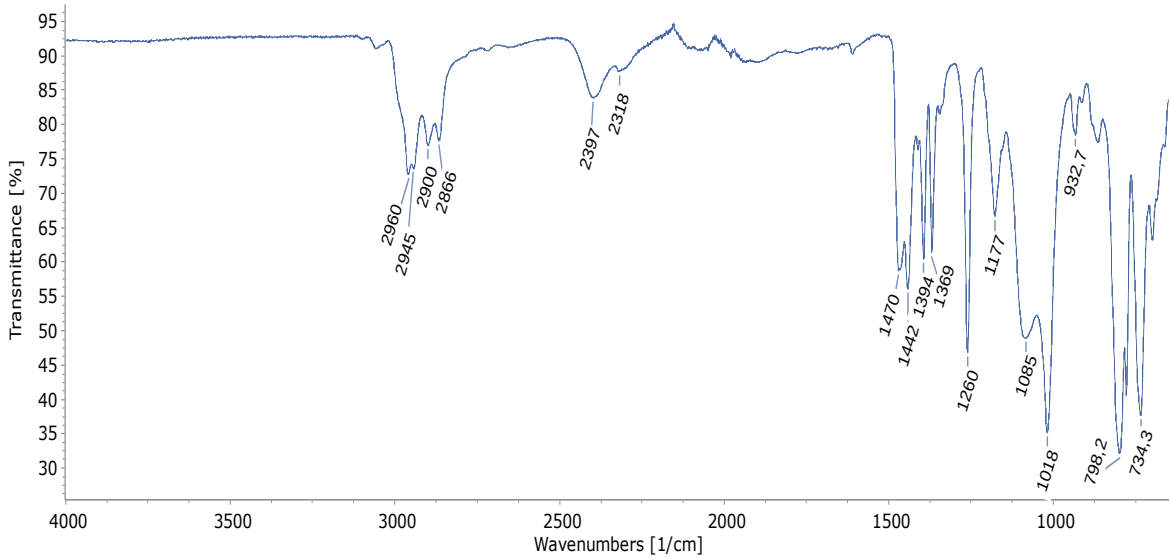
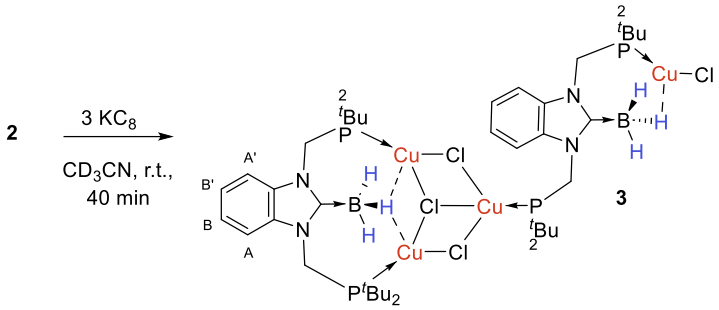


*Figure S49 – ATR-FTIR spectrum of complex **2***

Synthesis and characterization of compound **3**



To a solution of **2** (316 mg, 0.228 mmol) in acetonitrile (10 mL) was added potassium graphite (92 mg, 0.680 mmol) at room temperature. The reaction mixture was stirred for 40 min, protected from light. The suspension turned dark brown within one minute. The crude mixture was filtrated through a glass frit, rinsed with 3 x 5 mL of acetonitrile. The pale-yellow filtrate was dried under dynamic vacuum, yielding **3** as off-white powder (180 mg, 0.139 mmol, 61%). Pentane diffusion to a concentrated acetonitrile solution over two days yielded tiny pale-yellow crystals of **3** suitable for X-Ray analysis.

^{1}H NMR (400 MHz, CD_3CN, 298 K) δ 7.93 (AA'BB' system, $^{3}J_{AB}$ = 8.1 Hz, $^{3}J_{BB'}$ = 6.9 Hz, $^{4}J_{AB'}$ = 1.1 Hz, $^{5}J_{AA'}$ = 0.0 Hz, 4H, H_A and $H_{A'}$), 7.49 (AA'BB' system, $^{3}J_{AB}$ = 8.1 Hz, $^{3}J_{BB'}$ = 6.9 Hz, $^{4}J_{AB'}$ = 1.1 Hz, $^{5}J_{AA'}$ = 0.0 Hz, 4H, H_B and $H_{B'}$), 4.79 (br. d, 8H, NC*H*$_2$P), 2.16 (br. quart, 6H, B*H*$_3$), 1.25 (d, $^{2}J_{P\text{-}H}$ = 12.7 Hz, 72H, P(C(C*H*$_3$)$_3$). **^{13}C{^{1}H} NMR** (101 MHz, CD_3CN, 298 K) δ 133.9 (s, *C*$_{quat.}$Ar), 125.5 (s, *C*HAr$_{B/B'}$), 113.5 (s, *C*HAr$_{A/A'}$), 40.1 (d, $^{1}J_{P\text{-}C}$ = 5.6 Hz, N*C*H$_2$P), 34.6 (d, $^{1}J_{P\text{-}C}$ = 6.4 Hz, P*C*(CH$_3$)$_3$), 29.5 (d, $^{2}J_{P\text{-}C}$ = 7.8 Hz, PC(*C*H$_3$)$_3$). *Carbenic carbon is not observed.* **^{31}P{^{1}H} NMR** (162 MHz, CD_3CN, 298 K) δ 27.1 (br., P^{t}Bu$_2$). **^{11}B NMR** (128 MHz, CD_3CN, 298 K) δ -33.1 (quart, $^{1}J_{B\text{-}H}$ = 88 Hz, *B*H$_3$). **Elemental analysis** calcd. For $C_{50}H_{94}B_2Cl_4Cu_4N_4P_4$ (1288 g.mol^{-1}) C, 46.45; H, 7.33; N, 4.33; found C, 46.36; H, 7.41; N, 4.50. **ATR-FTIR** (cm^{-1}) 2942, 2899, 2866, 2379, 2321, 2291, 1470, 1438, 1393, 1370, 1264, 1177, 1084, 1020, 931, 810, 778, 739.

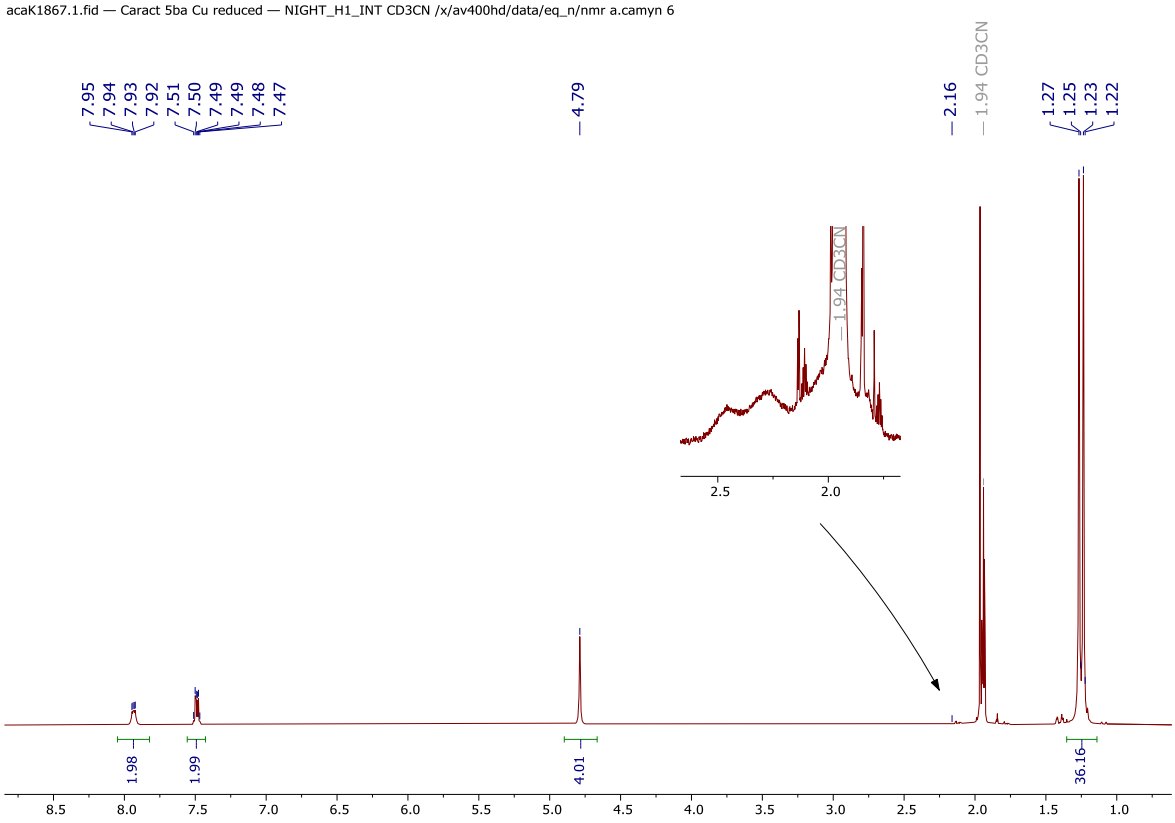


*Figure S50 – ^{1}H NMR spectrum of **3** at 298 K in CD_3CN (D1 = 30 sec)*

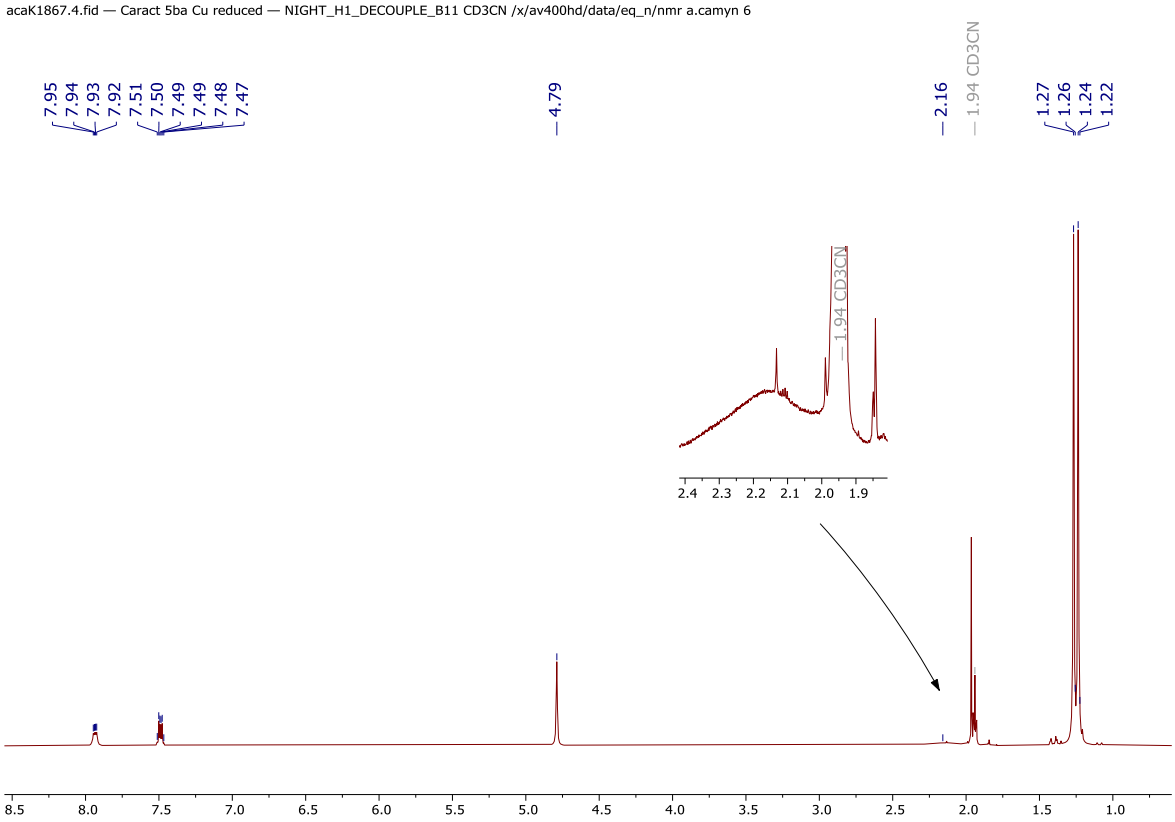


*Figure S51 – $^{1}H\{^{11}B\}$ NMR spectrum of **3** at 298 K in CD_3CN (D1 = 30 sec)*

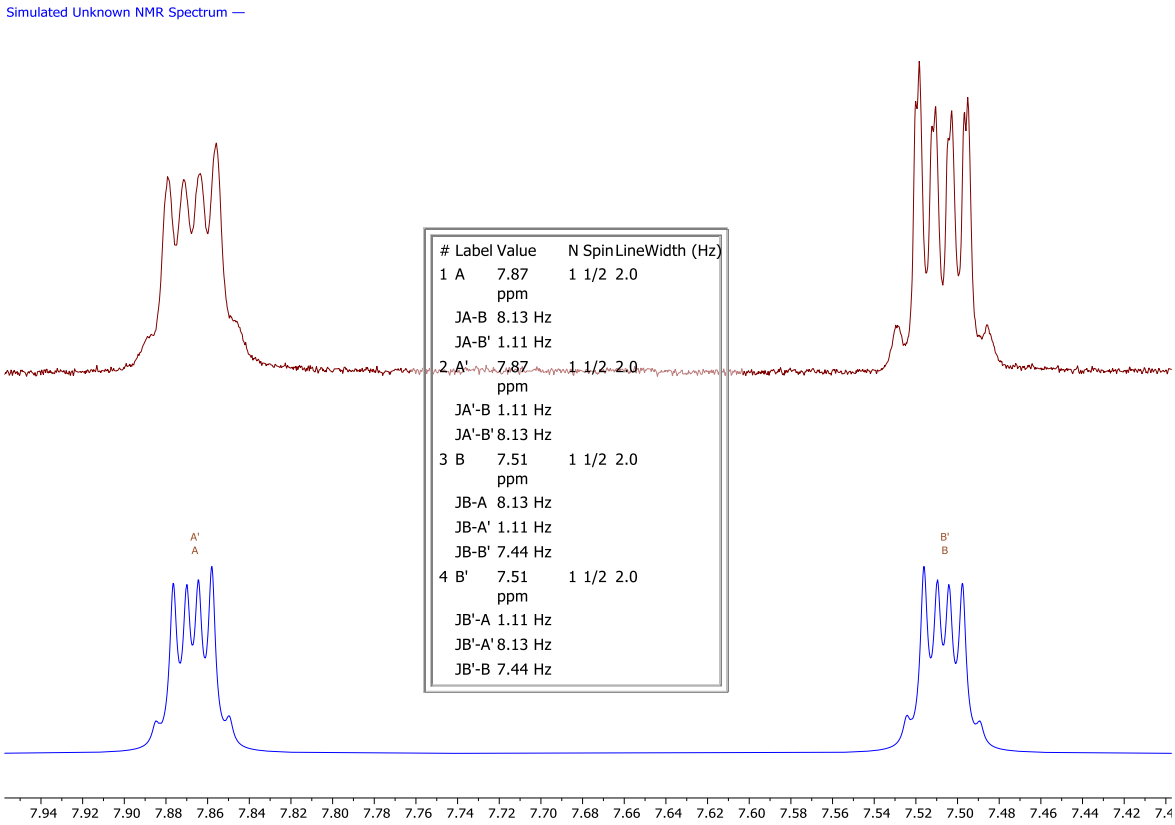


*Figure S52 – Stacked ^{1}H NMR spectrum of **3** at 298 K in CD_3CN (top) and simulation of AA'BB' system (bottom). Zoom of the aromatic region*

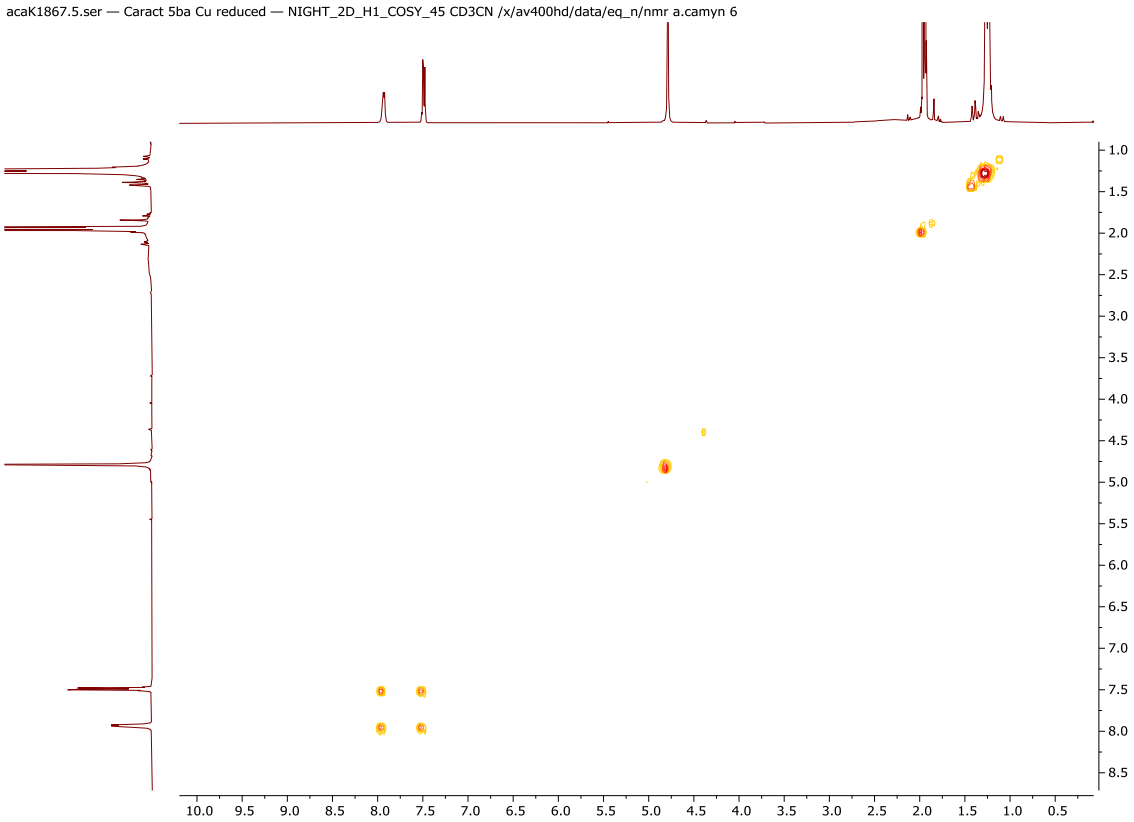


*Figure S53 – COSY $^{1}H/^{1}H$ NMR spectrum of **3** at 298 K in CD_3CN*

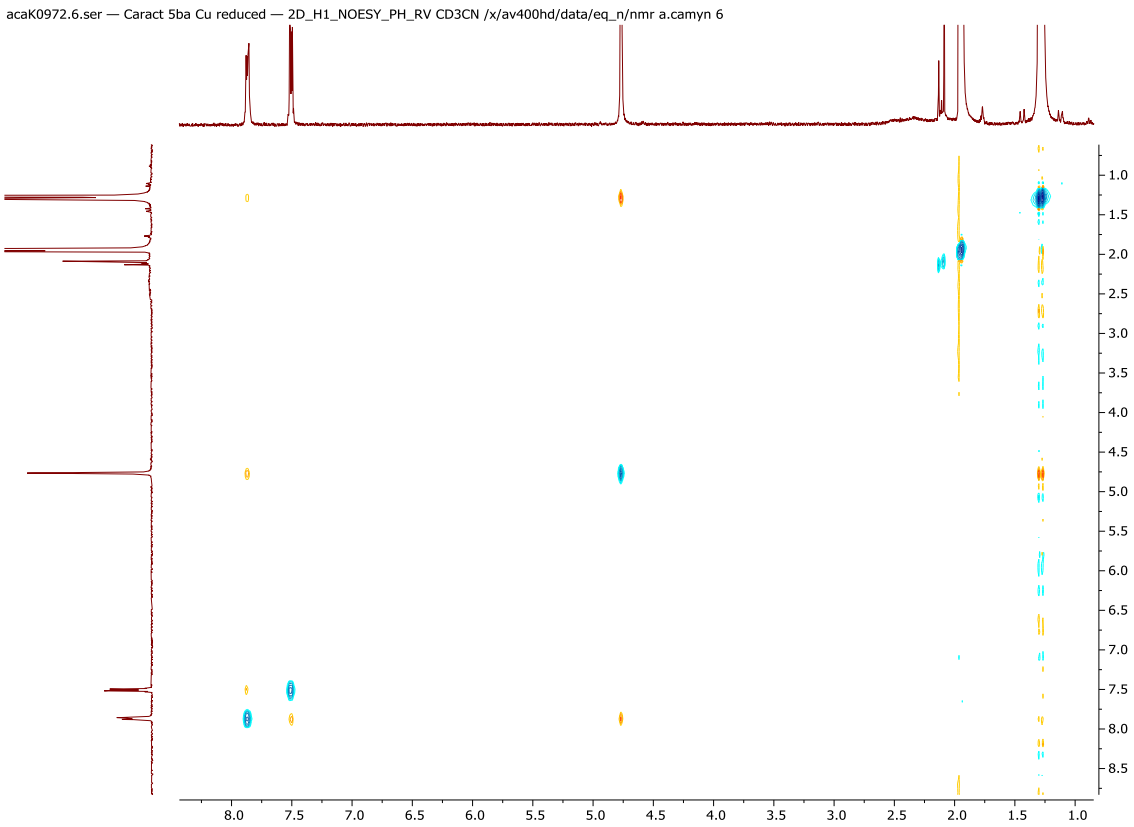


*Figure S54 – NOESY $^{1}H/^{1}H$ NMR spectrum of **3** at 298 K in CD_3CN (Mixing time = 1 s)*

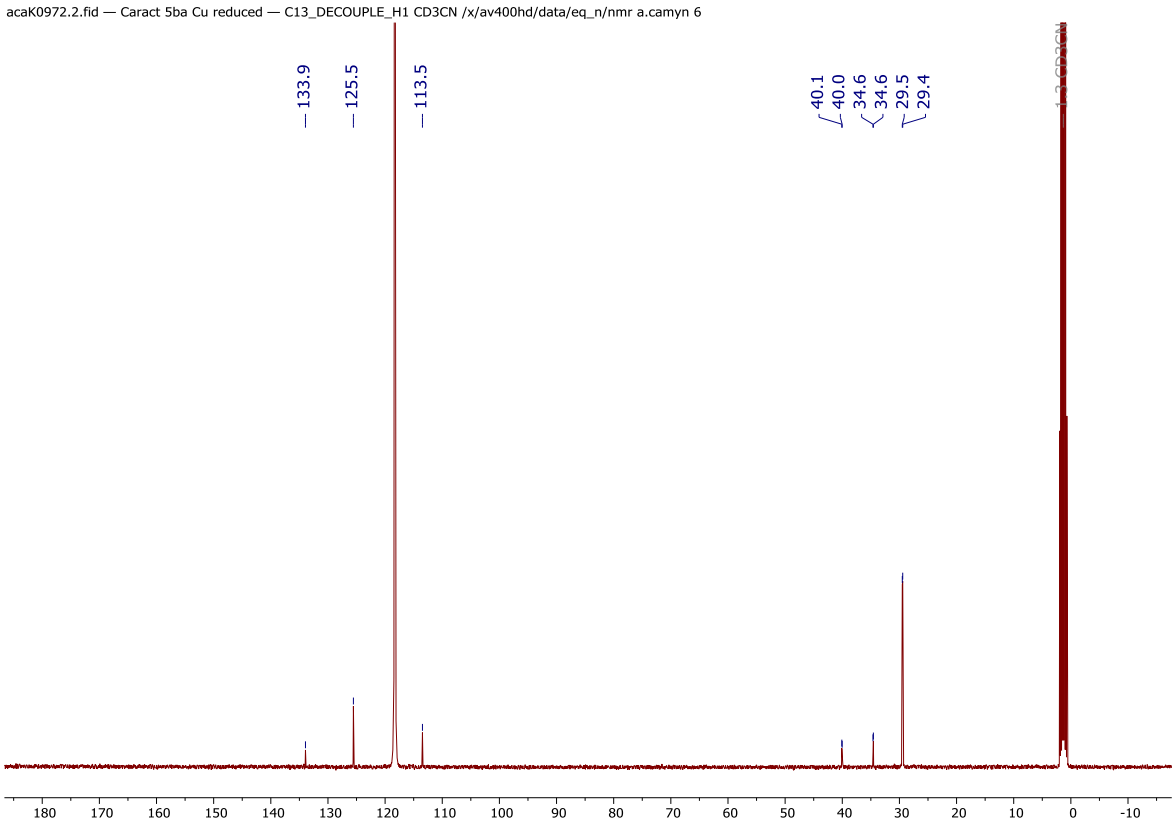


*Figure S55 – $^{13}C\{^{1}H\}$ NMR spectrum of **3** at 298 K in CD_3CN*

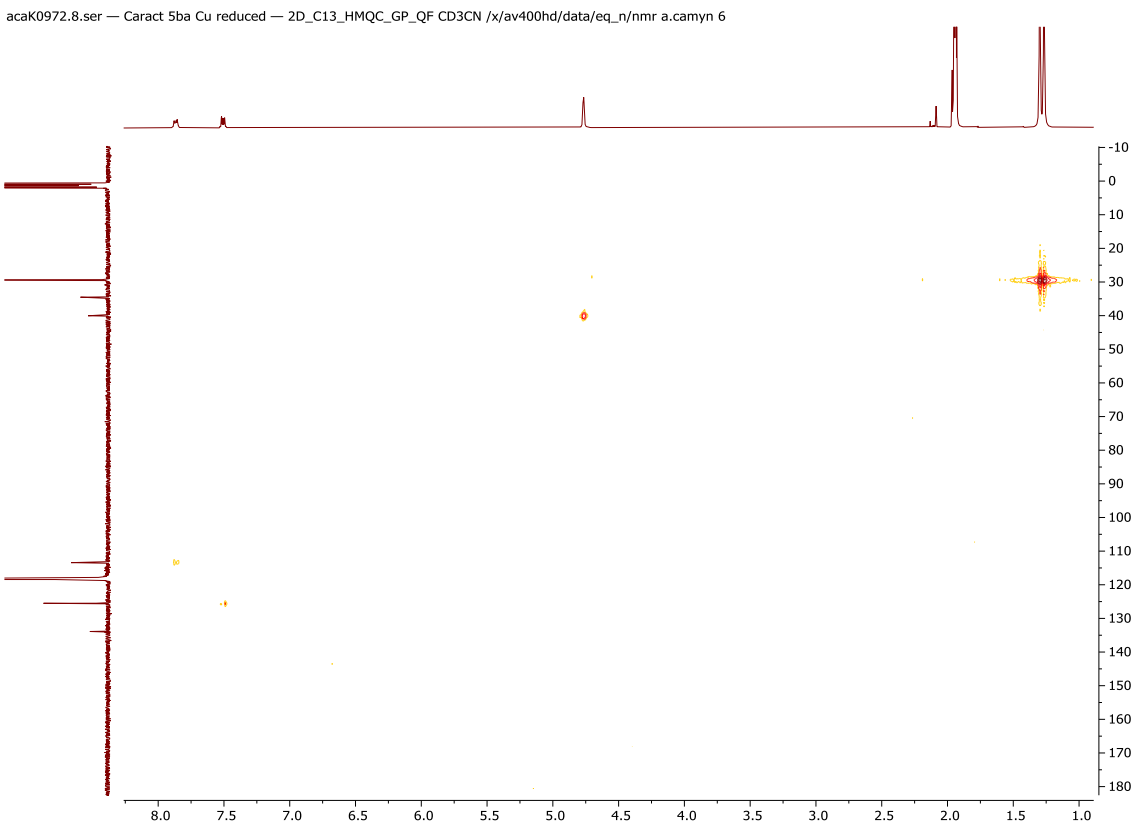


*Figure S56 – HMQC $^{13}C\{^{1}H\}/^{1}H$ NMR spectrum of **3** at 298 K in CD_3CN*

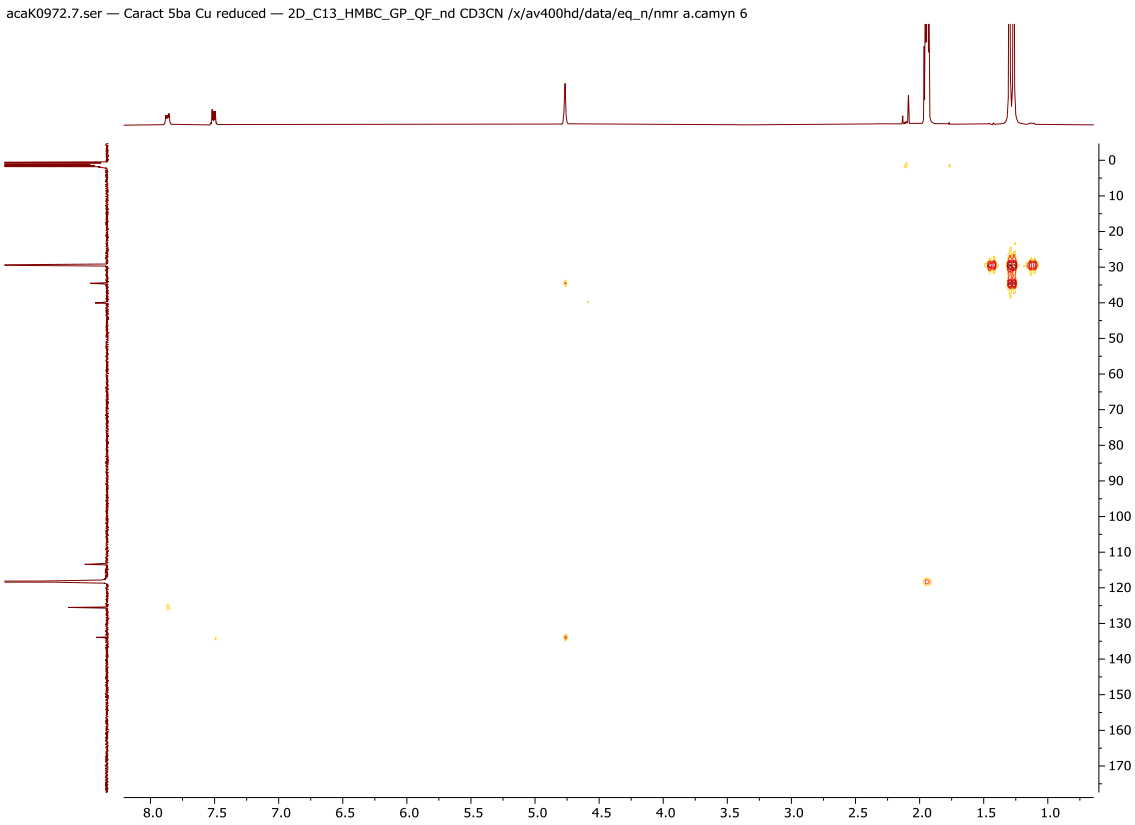


*Figure S57 – HMBC $^{13}C\{^{1}H\}/^{1}H$ NMR spectrum of **3** at 298 K in CD_3CN*

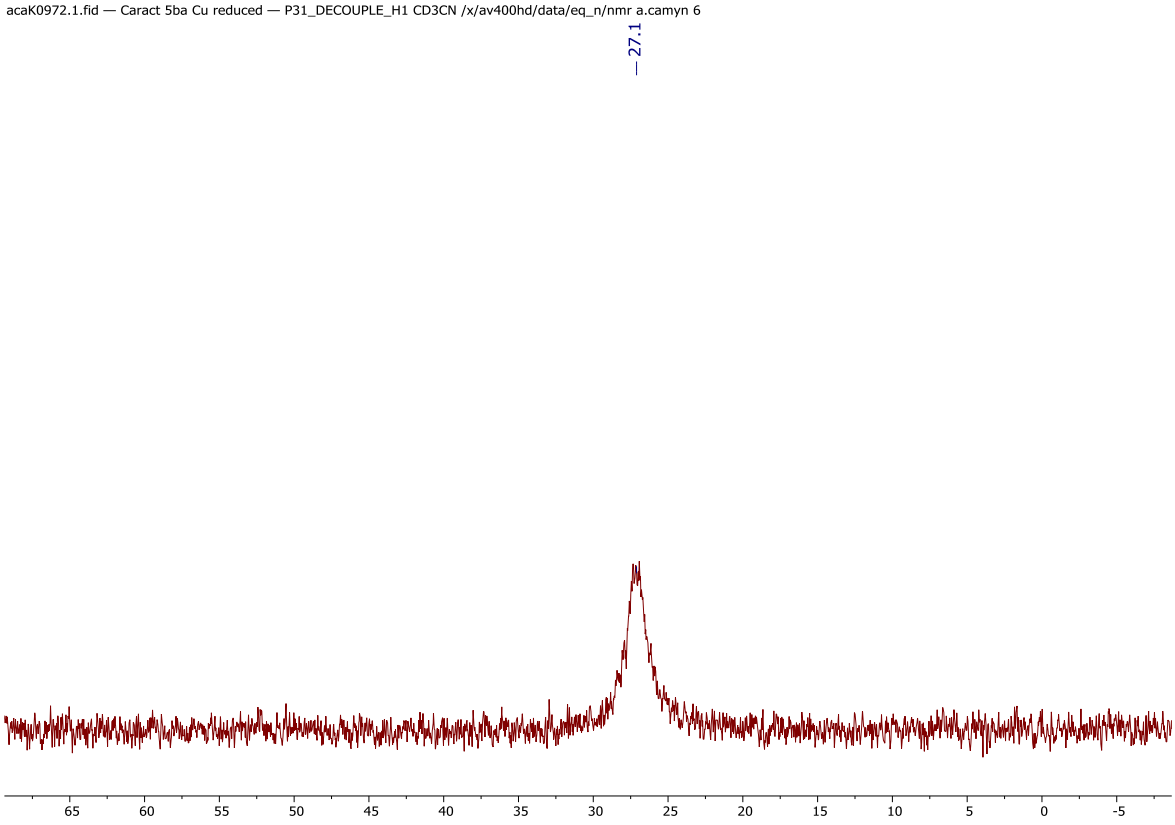


*Figure S58 – $^{31}P\{^{1}H\}$ NMR spectrum of **3** at 298 K in CD_3CN*

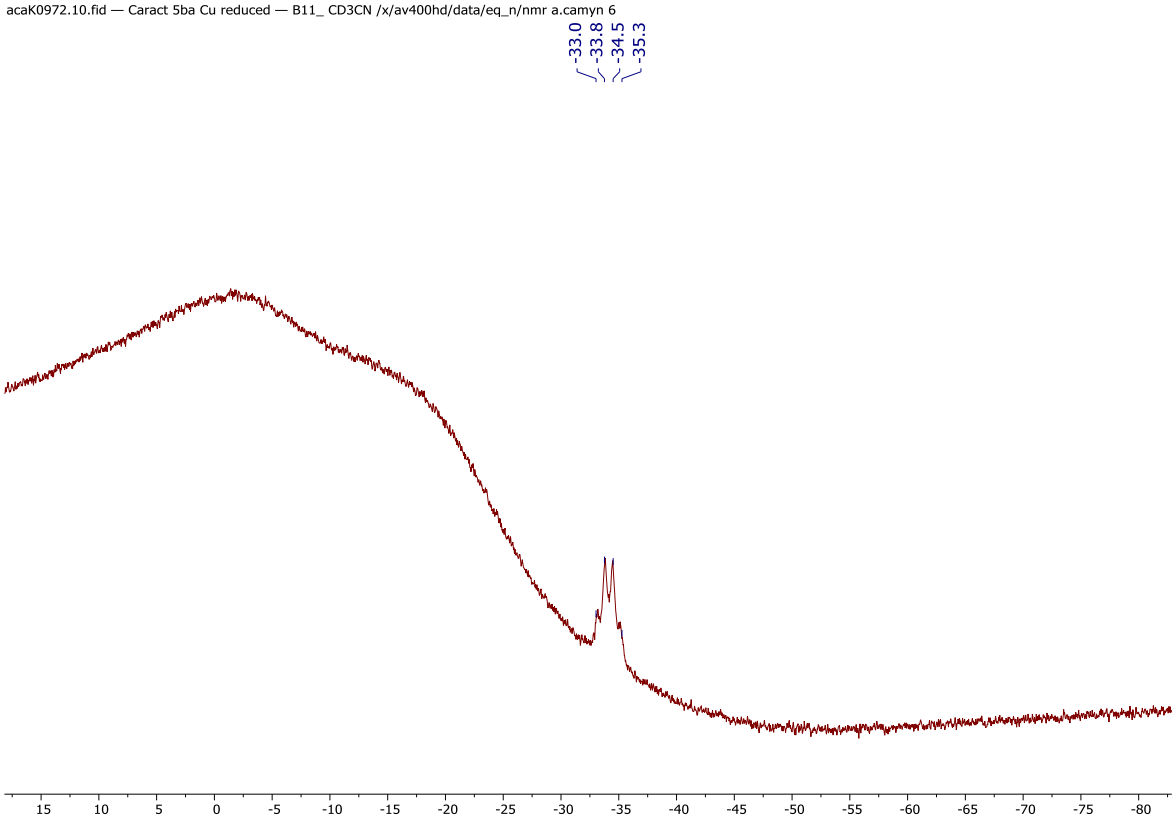


*Figure S59 – ^{11}B NMR spectrum of **3** at 298 K in CD_3CN*

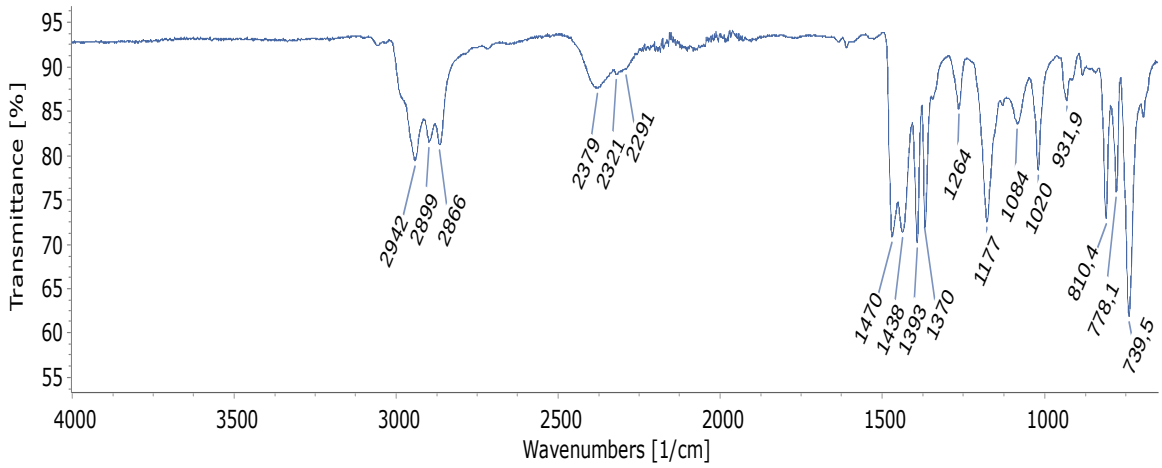


*Figure S60 – ATR-FTIR spectrum of complex **3***

DOSY experiments on compounds **A**, **2** and **3**

Diffusion NMR experiments were carried out on a Bruker Avance NEO 600 MHz instrument. The ^{1}H DOSY spectra were recorded at 300 K with bipolar gradient (STEBPGP) 1s pulse program from Bruker topspin software. All spectra were recorded with 16 K time domain data point in the t2 dimension and 16 t1 increments. The gradients strength was linearly incremented in 16 steps from 2% up to 95% of the maximum gradient strength. All measurements were performed with a compromise diffusion delay Δ of 100 ms and a gradient pulse length δ of 2.2 ms. The ligand **A**, complexes **2** and **3** samples were prepared in concentrations of 50 mM to reduce the effect of viscosity and intermolecular interactions. The diffusion coefficients were determined by regression analysis by fitting the peak areas to the Stejskal-Tanner equation from T1/T2 analysis in Topspin 4.4.1. The uncertainty of the diffusion constants obtained from T1/T2 analysis is D±0.1.

Compounds	**Diffusion coefficient (10^{-10} $m_2.s^{-1}$)**
A	9.3
2	6.3
3	6.0

*Table S1 – Diffusion coefficients of compounds **A**, **2** and **3***

2. X-ray analyses and structural figures of complexes **1**-**3**

Data were collected at low temperature (100 or 150 K) either on an Oxford Diffraction Gemini using a Cu-Kα radiation (λ = 1.54184 Å), or on a Bruker Kappa Apex II diffractometer using a Mo-Kα radiation (λ = 0.71073 Å) micro-source, both equipped with an Oxford Instrument or Oxford Cryosystems, Cooler Device.

The structures have been solved using the new dual-space algorithm program SHELXT,[3] or SUPERFLIP,[4] and refined by means of least-squares procedures using either SHELXL-2018[3] program included in the software package WinGX [5] version 1.639, or with the aid of the program CRYSTALS.[6] The Atomic Scattering Factors were taken from International Tables for X-Ray Crystallography.[7] Hydrogen atoms were placed geometrically and refined using a riding model. All non-hydrogen atoms were anisotropically refined, except for BH_3 fragments.

Moreover, it was not possible to resolve diffuse electron-density residuals (enclosed solvent molecule) for the structure ACN170122 (**2**, CCDC number 2429979). Treatment with the 'SQUEEZE facility from PLATON[8] resulted in a smooth refinement. Since a few low order reflections are missing from the data set, the electron count will be underestimated. Thus, the values given for D(calc), F(000) and the molecular weight are only valid for the ordered part of the structure.ms were anisotropically refined.

Ellipsoid plots in the figures of the crystallography section were generated using the software ORTEP-35.[9] The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 2429977-2429979 for ACN160421 (**3**), ACN250522 (**1**) and ACN170122 (**2**) respectively.

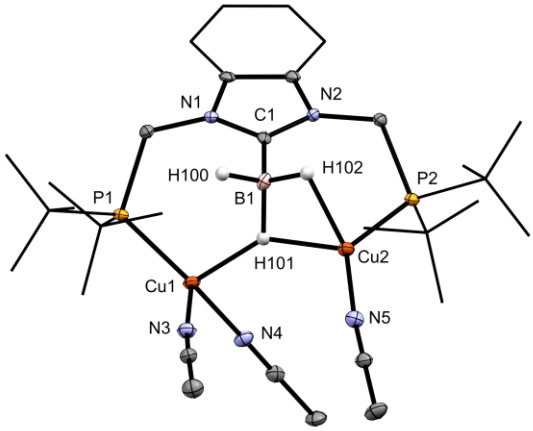


*Figure S61 - Structure of compound **1**. Thermal ellipsoids drawn at 30% probability (for clarity co-crystalized CD_2Cl_2, two BF_4 anions and hydrogens are omitted except BH_3). Hydrides were located in the difference Fourier map and refined freely without any constraint. Important elements are drawn with ellipsoid tool. Selected bond lengths [Å] and angles [°]: C1-B1 1.599(8), B1-H100 1.10(6), B1-H101 1.29(6), B1-H102 1.12(6), Cu1-H101 1.88(6), Cu2-H101 1.83(6), Cu2-H102 1.93(6), Cu1-Cu2 3.504(1), P1-Cu1 2.2081(15), P2-Cu2 2.2156(15), B1-H101-Cu1 125(4), B1-H101-Cu2 91(3), B1-H102-Cu2 92(4)*

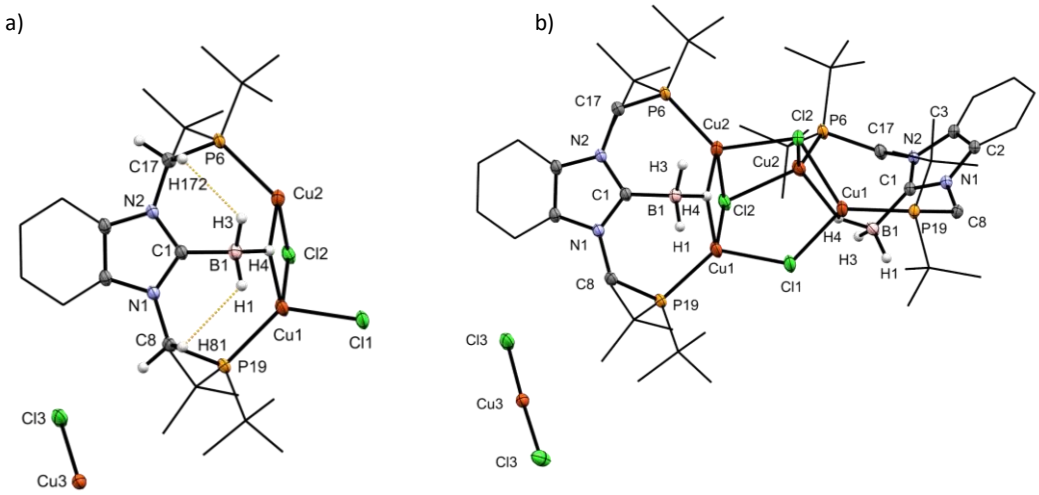


*Figure S62 - a) Fragment of **2** constituting the asymmetric unit, b) Structure of compound **2**. Thermal ellipsoids drawn at 30% probability (For clarity, hydrogens are omitted except hydrides on boron and methylenes). Hydrides were located in the difference Fourier map and refined freely without any constraint. Important elements are drawn with ellipsoid tool. Yellow dashed lines correspond to [C–H···H–B] interactions. Selected bond lengths [Å] and angles [°]: B1-C1 1.586(4), C1-N1 1.355(3), C1-N2 1.352(3), B1-H1 1.06(4), B1-H3 1.08(4), B1-H4 1.23(4), H3 ··H172 2.27, H1···H81 2.31, H4-Cu1 1.95(4), H4-Cu2 1.90(4), Cu1-P19 2.2085(7), Cu2-P6 2.2155(8), Cu1-Cu2 2.9174(6), Cu1-Cl1 2.2764(7), Cu1-Cl2 2.4259(8), Cu2-Cl2 2.4113(9), Cu3-Cl3 2.0846(8), N1-C1-N2 107.0(2), C17-H172-H3 112, B1-H3-H172 113, C8-H81-H1 111, B1-H1-H81 114, B1-H4-Cu1 121(3), B1-H4-Cu2 124(3)*

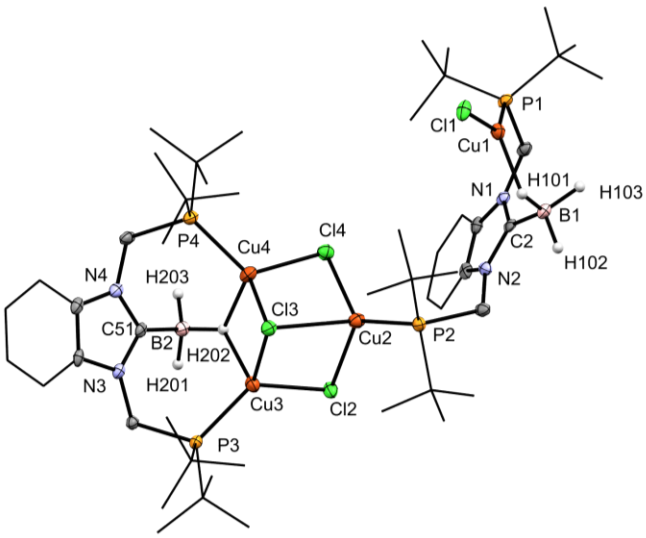


*Figure S63 - Structure of compound **3**. Thermal ellipsoids drawn at 30% probability (for clarity co-crystalized CD_3CN and hydrogens are omitted except BH_3). Hydrides were located in the difference Fourier map and refined freely without any constraint. Important elements are drawn with ellipsoid tool. Selected bond lengths [Å] and angles [°]: C2-B1 1.592(6), C51-B2 1.584(6), B1-H101 1.16(4), B1-H102 1.14(4), B1-H103 1.20(4), B2-H201 1.12(4), B2-H202 1.17(4), B2-H203 1.12(4), Cu1-H101 1.80(4), Cu3-H202 2.01(4), Cu4-H202 1.98(4), Cu3-Cu4 2.9617(7), P1-Cu1 2.1921(12), P2-Cu2 2.2036(12), P3-Cu3 2.1964(11), P4-Cu4 2.1967(11), B1-H101-Cu1 117(3), B2-H202-Cu3 125(3), B2-H202-Cu4 120(3)*

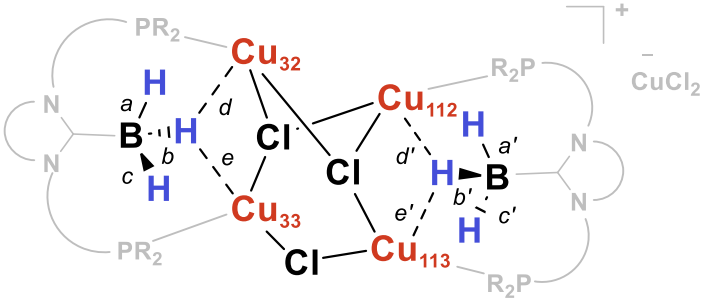
3. DFT investigations

Computational Details

Geometry optimizations of the complexes were performed without symmetry constraints using the Gaussian03[10] optimizer together with Turbomole 7.1[11] energies and gradients at the BP86[12]/def2-TZVP[13] level of theory using the D3 dispersion correction suggested by Grimme et al.[14] and the resolution-of-identity (RI) approximation.[11] This level is denoted RI-BP86D3/def2-TZVP. Vibrational analysis was performed to ensure that the optimized geometry corresponds to an energy minimum. With this analysis, IR spectra were simulated (*see IR_ESI.ppt*) by plotting the different vibrational modes in red and applying Lorentzian functions to plot the spectral line profile in blue. A scale factor of 0.9953 associated with the method used was also applied to all frequencies.[15] Wiberg Bond Indices were computed by means of the NBO6.0[16] method at the BP86-D3/def2-TZVP level.

All AIM results described in this work correspond to calculations performed at the BP86-D3/def2-TZVP&WTBS (for copper atoms) level on the optimized geometries obtained at the RI-BP86-D3/def2-TZVP level. The WTBS (well-tempered basis sets)[17] have been recommended for AIM calculations involving transition metals.[18] The topology of the electron density was conducted using the AIMAll program package.[19]

Natural Bond Orbital Analysis (NBO) for compound **2** and **3**



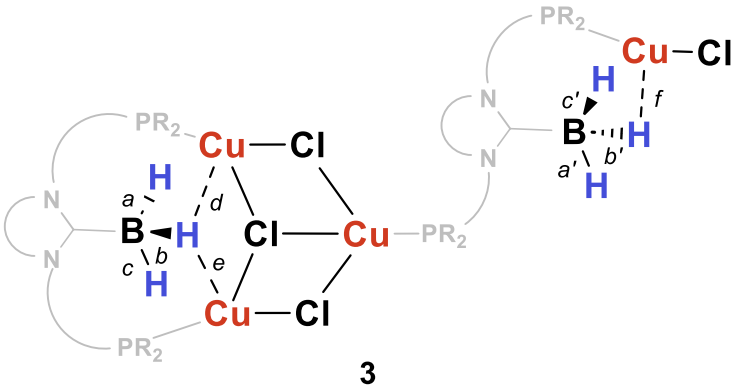
2

Interaction	WBI	Stabilization energy (kcal.mol^{-1})	
		Donation σ(B-H) → s(Cu)	Back-donation d(Cu) → σ*(B-H)
a / a’	0.9402		
b / b’	0.7887		
c / c’	0.9395		
d / d’	0.0550	-13.5	-2.7
e / e’	0.0584	-12.9	-2.6

*Table S2 – WBI and NBO data of **2** around σ-BH interactions*

Donor	Acceptor	Stabilization energy (kcal.mol^{-1})
3d(Cu 32 or Cu 112)	s(Cu 33 or Cu 113)	-0.44
3d(Cu 33 or Cu 113)	s(Cu 32 or Cu 112)	-0.49

*Table S3 – NBO data of **2** for the BH_3…Cu_2 moiety*



3

Interaction	WBI	Stabilization energy (kcal.mol^{-1}) Donation σ(B-H) → s(Cu)	Back-donation d(Cu) → σ*(B-H)
a	0.9413		
a’	0.9438		
b	0.8104		
b’	0.8417		
c	0.9355		
c’	0.9311		
d	0.0524	-11.9	-2.5
e	0.0445	-9.6	-2.1
f	0.0786	-20.5	-3.5

*Table S4 – NBO data of **3** for the BH_3…Cu_2 moiety*

Frontier Orbitals of compound **1**

The five higher occupied molecular orbitals (HOMO – 4 to HOMO) and lower unoccupied molecular orbitals (LUMO + 4 to LUMO) are represented in Figure S68. HOMOs were mostly located on both Cu(3d) and on the different B-H bonds (σ_{B-H}). The LUMO are located on the π* system involving the aromatic ring, both nitrogen atoms, the p vacant orbital of the carbene and σ^*_{B-H}. The rest of the selected LUMOs are mostly located on the acetonitrile ligands.

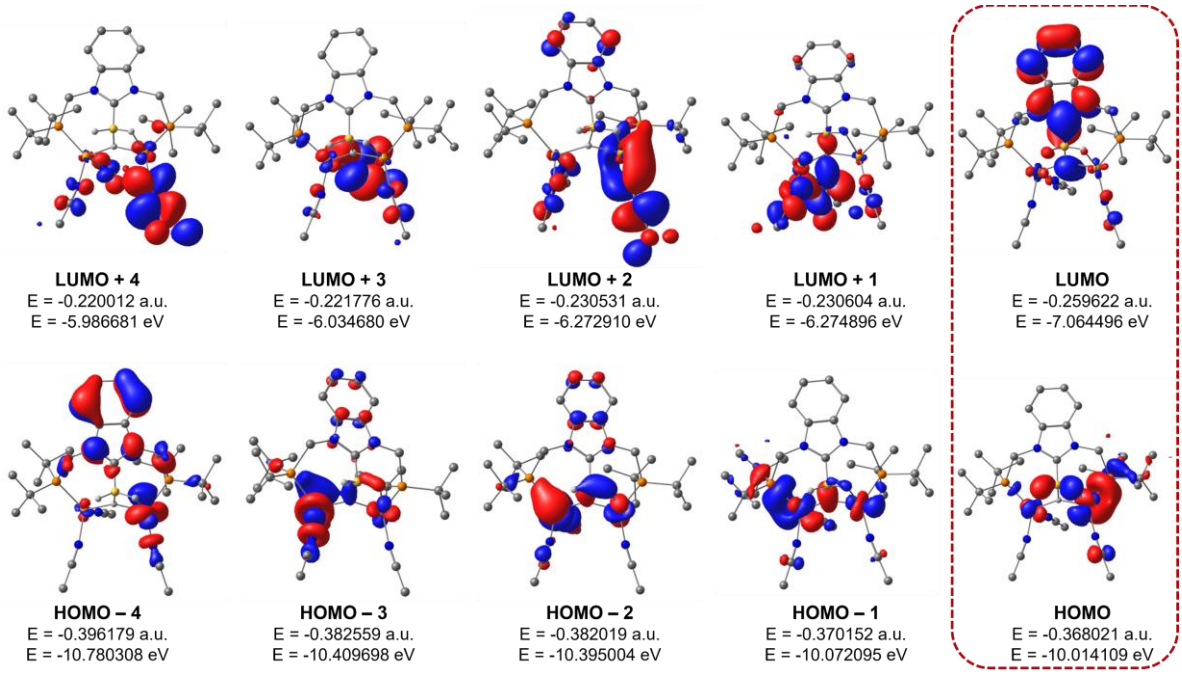


*Figure S64 – Frontier orbitals of compound **1** (HOMO - 4 to LUMO + 4)*

Cartesian coordinates

Cartesian coordinates (in Å) and Hartree-Fock energies (in a.u.) of all the stationary points described in the text (RI-BP86-D3/def2-TZVP).

Compound **1**

E = -5478.5234744

C	0.081424000	-1.222956000	-1.366515000
C	2.555072000	-1.724022000	-1.216589000
H	2.818746000	-1.415413000	-2.237284000
H	3.118462000	-2.635220000	-0.991011000
C	-2.410478000	-1.489708000	-1.410631000
H	-3.075478000	-2.359673000	-1.426726000
H	-2.476555000	-1.002695000	-2.390556000
C	-2.241514000	4.287284000	-0.383068000
C	-2.735681000	5.605867000	-0.723398000
H	-2.326992000	6.357443000	-0.033919000
H	-3.832603000	5.621749000	-0.653495000
H	-2.443722000	5.863237000	-1.751124000
C	-0.273536000	1.414154000	3.214511000
C	0.187438000	1.432294000	4.586795000
H	0.306753000	0.404110000	4.955758000
H	-0.542910000	1.954299000	5.221108000
H	1.153690000	1.950673000	4.655065000
C	2.481109000	4.373477000	-0.771605000
C	2.930077000	5.744673000	-0.894140000
H	2.574222000	6.175870000	-1.840476000
H	4.028634000	5.783171000	-0.878061000
H	2.543716000	6.345237000	-0.058758000
C	-3.551006000	-1.215192000	1.363631000
C	-3.969869000	-0.208271000	2.454124000
H	-4.099511000	-0.747786000	3.404554000
H	-4.918072000	0.291321000	2.229442000
H	-3.201699000	0.564167000	2.603439000
C	-4.662731000	-2.248911000	1.145322000
H	-4.771282000	-2.860220000	2.054059000
H	-4.446229000	-2.938401000	0.316796000
H	-5.633437000	-1.775239000	0.955641000
C	-2.264239000	-1.921677000	1.840154000
H	-1.416284000	-1.224380000	1.893368000
H	-1.982136000	-2.764957000	1.199279000
H	-2.434588000	-2.326574000	2.849124000
C	-4.518876000	0.444409000	-1.165872000
C	-5.337445000	1.356990000	-0.235604000
H	-6.053886000	1.935452000	-0.837774000
H	-4.694944000	2.067702000	0.305767000
H	-5.919029000	0.783558000	0.496583000

C	-3.918978000	1.306274000	-2.297815000
H	-4.742606000	1.799907000	-2.835352000
H	-3.363753000	0.716247000	-3.039370000
H	-3.245078000	2.079305000	-1.910297000
C	-5.427873000	-0.630801000	-1.786295000
H	-5.896387000	-1.277929000	-1.037714000
H	-4.900245000	-1.263548000	-2.512989000
H	-6.238367000	-0.129447000	-2.336930000
C	2.953885000	-0.942363000	1.670422000
C	1.496238000	-1.425308000	1.830504000
H	1.329629000	-2.412190000	1.382748000
H	0.780187000	-0.712886000	1.395519000
H	1.268322000	-1.518240000	2.903570000
C	3.148545000	0.283850000	2.585308000
H	2.927764000	-0.008620000	3.623670000
H	2.466540000	1.098291000	2.295943000
H	4.171770000	0.674478000	2.566071000
C	3.920705000	-2.068919000	2.053938000
H	4.966265000	-1.737039000	2.058300000
H	3.832234000	-2.936053000	1.384006000
H	3.685526000	-2.420484000	3.070382000
C	4.898956000	-0.118423000	-0.704603000
C	4.802116000	0.638963000	-2.047285000
H	5.818328000	0.815869000	-2.430537000
H	4.310237000	1.615158000	-1.926308000
H	4.259758000	0.076766000	-2.820216000
C	5.644837000	0.772970000	0.303670000
H	5.856903000	0.250200000	1.245033000
H	5.082808000	1.692048000	0.526709000
H	6.612173000	1.068679000	-0.128924000
C	5.660019000	-1.438743000	-0.914762000
H	6.693703000	-1.206522000	-1.212044000
H	5.231120000	-2.046540000	-1.723169000
H	5.712499000	-2.050292000	-0.006736000
C	-0.721581000	-3.307196000	-0.968182000
C	-1.506550000	-4.445403000	-0.769674000
H	-2.594303000	-4.414097000	-0.812140000
C	-0.835663000	-5.639196000	-0.511470000
H	-1.412035000	-6.550072000	-0.353553000
C	0.570103000	-5.695826000	-0.456618000
H	1.057234000	-6.649383000	-0.255897000
C	1.353742000	-4.562067000	-0.664366000
H	2.440676000	-4.623729000	-0.632789000
C	0.681345000	-3.365324000	-0.923744000
N	-1.048389000	-1.974771000	-1.230906000
N	1.136683000	-2.066560000	-1.172139000

N	-1.865609000	3.221548000	-0.117988000
N	-0.649918000	1.390670000	2.116414000
N	2.136118000	3.268585000	-0.678523000
P	-3.045979000	-0.228074000	-0.171554000
P	3.112608000	-0.322224000	-0.105476000
Cu	-1.539951000	1.340250000	0.359512000
Cu	1.809776000	1.398388000	-0.646348000
B	0.105754000	0.336044000	-1.672884000
H	1.146456000	0.685839000	-2.261185000
H	-0.843614000	0.706100000	-2.316348000
H	0.058529000	0.962809000	-0.537034000

Compound **1-BD_3**

E = -5478.5234747

C	0.081431000	-1.222959000	-1.366593000
C	2.555182000	-1.723744000	-1.216889000
H	2.818697000	-1.414977000	-2.237584000
H	3.118697000	-2.634911000	-0.991502000
C	-2.410491000	-1.489976000	-1.410302000
H	-3.075393000	-2.360020000	-1.426292000
H	-2.476708000	-1.003051000	-2.390271000
C	-2.241116000	4.287445000	-0.382256000
C	-2.735247000	5.606087000	-0.722383000
H	-2.330746000	6.356826000	-0.029537000
H	-3.832498000	5.620477000	-0.657663000
H	-2.438734000	5.865769000	-1.748211000
C	-0.273639000	1.414356000	3.214714000
C	0.187250000	1.433060000	4.587007000
H	0.309127000	0.405014000	4.955444000
H	-0.544428000	1.952913000	5.221533000
H	1.152200000	1.953815000	4.655524000
C	2.480585000	4.373608000	-0.772282000
C	2.929260000	5.744859000	-0.895292000
H	2.577733000	6.174033000	-1.844160000
H	4.027704000	5.784067000	-0.873975000
H	2.538515000	6.346738000	-0.062908000
C	-3.551264000	-1.215189000	1.363925000
C	-3.969956000	-0.208172000	2.454416000
H	-4.100198000	-0.747738000	3.404731000
H	-4.917822000	0.291949000	2.229497000
H	-3.201427000	0.563856000	2.604071000
C	-4.663195000	-2.248686000	1.145609000
H	-4.771585000	-2.860228000	2.054207000
H	-4.446984000	-2.937955000	0.316826000
H	-5.633887000	-1.774822000	0.956310000

C	-2.264679000	-1.921934000	1.840585000
H	-1.416536000	-1.224848000	1.893613000
H	-1.982807000	-2.765433000	1.199898000
H	-2.435089000	-2.326548000	2.849655000
C	-4.518837000	0.444121000	-1.165789000
C	-5.337644000	1.356663000	-0.235696000
H	-6.054399000	1.934636000	-0.837958000
H	-4.695370000	2.067813000	0.305374000
H	-5.918906000	0.783220000	0.496730000
C	-3.918771000	1.306007000	-2.297649000
H	-4.742286000	1.799771000	-2.835233000
H	-3.363515000	0.715946000	-3.039162000
H	-3.244834000	2.078972000	-1.910007000
C	-5.427715000	-0.631146000	-1.786305000
H	-5.896599000	-1.278008000	-1.037714000
H	-4.899913000	-1.264157000	-2.512646000
H	-6.237941000	-0.129786000	-2.337336000
C	2.953816000	-0.942391000	1.670090000
C	1.496160000	-1.425400000	1.829936000
H	1.329682000	-2.412347000	1.382271000
H	0.780165000	-0.713085000	1.394645000
H	1.268002000	-1.518158000	2.902960000
C	3.148446000	0.283755000	2.585067000
H	2.927285000	-0.008669000	3.623355000
H	2.466705000	1.098345000	2.295485000
H	4.171757000	0.674184000	2.566135000
C	3.920664000	-2.068990000	2.053473000
H	4.966216000	-1.737099000	2.057921000
H	3.832233000	-2.936005000	1.383384000
H	3.685419000	-2.420720000	3.069840000
C	4.899030000	-0.118239000	-0.704465000
C	4.802420000	0.639171000	-2.047180000
H	5.818683000	0.815924000	-2.430360000
H	4.310657000	1.615427000	-1.926227000
H	4.260019000	0.077060000	-2.820153000
C	5.644748000	0.773096000	0.303984000
H	5.856836000	0.250211000	1.245276000
H	5.082600000	1.692069000	0.527142000
H	6.612056000	1.068990000	-0.128543000
C	5.660060000	-1.438607000	-0.914456000
H	6.693740000	-1.206432000	-1.211781000
H	5.231115000	-2.046506000	-1.722766000
H	5.712522000	-2.050025000	-0.006339000
C	-0.721281000	-3.307305000	-0.968281000
C	-1.506080000	-4.445633000	-0.769809000
H	-2.593840000	-4.414433000	-0.812044000

C	-0.835022000	-5.639321000	-0.511597000
H	-1.411266000	-6.550264000	-0.353637000
C	0.570747000	-5.695793000	-0.456961000
H	1.058019000	-6.649287000	-0.256337000
C	1.354225000	-4.561974000	-0.664918000
H	2.441166000	-4.623531000	-0.633611000
C	0.681659000	-3.365291000	-0.924116000
N	-1.048295000	-1.974893000	-1.230804000
N	1.136824000	-2.066435000	-1.172338000
N	-1.865378000	3.221531000	-0.117641000
N	-0.649973000	1.390650000	2.116605000
N	2.135748000	3.268694000	-0.678818000
P	-3.046052000	-0.228256000	-0.171295000
P	3.112652000	-0.322031000	-0.105641000
Cu	-1.539982000	1.339982000	0.359552000
Cu	1.809700000	1.398436000	-0.646405000
B	0.105538000	0.336107000	-1.672765000
H	1.146133000	0.686188000	-2.261130000
H	-0.843977000	0.706251000	-2.315999000
H	0.058546000	0.962514000	-0.536686000

Compound **2**

E = -11541.7822291

C	4.310779000	0.477327000	1.397729000
C	6.336287000	0.167897000	0.420230000
C	6.062590000	-0.957993000	1.218241000
C	6.970094000	-2.013697000	1.323469000
C	8.157874000	-1.907653000	0.599642000
C	8.430650000	-0.783289000	-0.200470000
C	7.526180000	0.273847000	-0.302388000
C	5.109339000	2.304262000	-0.116349000
C	3.539805000	4.370176000	-1.362645000
C	4.867093000	5.077652000	-1.682680000
C	3.038981000	4.847284000	0.018263000
C	2.473633000	4.727947000	-2.413303000
C	4.175790000	1.668187000	-2.897731000
C	4.518460000	0.209959000	-2.527280000
C	5.370922000	2.315914000	-3.606545000
C	4.105994000	-1.677577000	2.641767000
C	2.973894000	-3.674403000	0.714375000
C	3.842944000	-2.977770000	-0.353272000
C	3.722798000	-4.869140000	1.313799000
C	1.684266000	-4.138194000	0.017114000
C	1.684323000	-2.967169000	3.530597000
C	2.618527000	-3.791656000	4.431665000

C	0.444531000	-3.793270000	3.150463000
C	1.205950000	-1.713326000	4.295240000
C	2.949507000	1.644851000	-3.832239000
N	5.236520000	1.015043000	0.546911000
N	4.807952000	-0.738352000	1.782908000
Cl	-0.000004000	2.868003000	0.000078000
Cl	1.015124000	-0.517984000	-1.410910000
P	2.481775000	-2.313571000	1.936659000
P	3.633381000	2.474330000	-1.271069000
Cu	1.814569000	1.555954000	-0.437862000
Cu	1.319352000	-0.713987000	0.981473000
B	3.005147000	1.173838000	1.957750000
H	6.766101000	-2.887901000	1.940369000
H	8.891102000	-2.711394000	0.659311000
H	9.370649000	-0.733752000	-0.749207000
H	7.746795000	1.141473000	-0.922661000
H	4.976000000	3.077394000	0.649854000
H	6.046931000	2.507276000	-0.645035000
H	5.258067000	4.823567000	-2.673734000
H	5.647418000	4.866578000	-0.937659000
H	4.699096000	6.166069000	-1.665862000
H	2.101446000	4.356939000	0.307552000
H	3.773059000	4.683143000	0.819035000
H	2.857803000	5.932075000	-0.035293000
H	1.542856000	4.166718000	-2.244465000
H	2.240208000	5.801163000	-2.337849000
H	2.825517000	4.540241000	-3.435947000
H	3.736684000	-0.234442000	-1.895320000
H	5.483223000	0.122263000	-2.013308000
H	4.583827000	-0.388314000	-3.448966000
H	5.114642000	3.294702000	-4.030714000
H	6.239356000	2.443057000	-2.943420000
H	5.690369000	1.671592000	-4.440962000
H	4.785498000	-2.504838000	2.873726000
H	3.849995000	-1.170423000	3.580122000
H	3.373766000	-2.045488000	-0.699471000
H	3.940068000	-3.645332000	-1.223064000
H	4.855923000	-2.757565000	0.000140000
H	3.080019000	-5.467658000	1.972172000
H	4.065784000	-5.529194000	0.501484000
H	4.614070000	-4.566242000	1.882329000
H	1.024202000	-4.705216000	0.681395000
H	1.944516000	-4.788462000	-0.832656000
H	1.126077000	-3.275126000	-0.373095000
H	3.473520000	-3.206606000	4.797732000
H	2.056651000	-4.120681000	5.319933000

H	3.002094000	-4.690483000	3.935300000
H	0.504651000	-1.118642000	3.694717000
H	0.689086000	-2.036144000	5.212532000
H	2.030576000	-1.054179000	4.598336000
H	2.671379000	2.643948000	-4.186112000
H	2.077754000	1.199394000	-3.333409000
H	3.187721000	1.032228000	-4.715900000
H	-0.142675000	-3.996814000	4.059224000
H	0.710344000	-4.761512000	2.706894000
H	-0.200191000	-3.243193000	2.450487000
H	3.105112000	2.379335000	1.923676000
H	2.730031000	0.750643000	3.059281000
H	1.934370000	0.926423000	1.248665000
C	-4.310780000	0.477286000	-1.397731000
C	-6.336318000	0.167524000	-0.420392000
C	-6.062512000	-0.958183000	-1.218631000
C	-6.969929000	-2.013938000	-1.324104000
C	-8.157738000	-1.908139000	-0.600284000
C	-8.430616000	-0.783966000	0.200069000
C	-7.526242000	0.273233000	0.302212000
C	-5.109583000	2.303920000	0.116582000
C	-3.540618000	4.369972000	1.362790000
C	-4.868777000	5.076878000	1.680517000
C	-3.037842000	4.847211000	-0.017344000
C	-2.476292000	4.728171000	2.415149000
C	-4.175501000	1.667906000	2.897910000
C	-4.518171000	0.209672000	2.527493000
C	-5.370506000	2.315481000	3.607062000
C	-4.105697000	-1.677464000	-2.642017000
C	-2.973764000	-3.674314000	-0.714346000
C	-3.842965000	-2.977716000	0.353197000
C	-3.722489000	-4.869151000	-1.313786000
C	-1.684177000	-4.137929000	-0.016917000
C	-1.684056000	-2.967053000	-3.530582000
C	-2.618323000	-3.791157000	-4.431941000
C	-0.444498000	-3.793501000	-3.150458000
C	-1.205293000	-1.713172000	-4.294926000
C	-2.949030000	1.644739000	3.832182000
N	-5.236616000	1.014784000	-0.546880000
N	-4.807837000	-0.738367000	-1.783150000
Cl	-1.014938000	-0.517794000	1.411072000
P	-2.481595000	-2.313506000	-1.936681000
P	-3.633492000	2.474113000	1.271103000
Cu	-1.814628000	1.555819000	0.437771000
Cu	-1.319258000	-0.713879000	-0.981470000
B	-3.005169000	1.173991000	-1.957584000

H	-6.765855000	-2.887992000	-1.941191000
H	-8.890889000	-2.711941000	-0.660110000
H	-9.370641000	-0.734612000	0.748782000
H	-7.746946000	1.140714000	0.922664000
H	-4.976523000	3.077190000	-0.649541000
H	-6.047113000	2.506736000	0.645459000
H	-5.264207000	4.818780000	2.668761000
H	-5.645986000	4.869353000	0.931244000
H	-4.700138000	6.165260000	1.668897000
H	-2.098023000	4.359550000	-0.303678000
H	-3.769255000	4.679770000	-0.819865000
H	-2.860313000	5.932651000	0.035512000
H	-1.545549000	4.166163000	2.248707000
H	-2.242007000	5.801151000	2.339006000
H	-2.830288000	4.541744000	3.437305000
H	-3.736440000	-0.234686000	1.895452000
H	-5.482980000	0.121954000	2.013593000
H	-4.583440000	-0.388621000	3.449172000
H	-5.114258000	3.294295000	4.031229000
H	-6.239118000	2.442480000	2.944141000
H	-5.689678000	1.671054000	4.441508000
H	-4.785141000	-2.504704000	-2.874225000
H	-3.849547000	-1.170161000	-3.580253000
H	-3.373693000	-2.045592000	0.699696000
H	-3.940427000	-3.645415000	1.222845000
H	-4.855810000	-2.757269000	-0.000433000
H	-3.079844000	-5.467118000	-1.972791000
H	-4.064713000	-5.529675000	-0.501539000
H	-4.614209000	-4.566400000	-1.881697000
H	-1.023869000	-4.704738000	-0.681139000
H	-1.944450000	-4.788345000	0.832732000
H	-1.126226000	-3.274792000	0.373487000
H	-3.473061000	-3.205800000	-4.798118000
H	-2.056361000	-4.120247000	-5.320129000
H	-3.002268000	-4.689931000	-3.935765000
H	-0.503613000	-1.118985000	-3.694353000
H	-0.688749000	-2.035923000	-5.212420000
H	-2.029692000	-1.053568000	-4.597650000
H	-2.671537000	2.643797000	4.186676000
H	-2.077060000	1.200181000	3.332938000
H	-3.186694000	1.031392000	4.715487000
H	0.142184000	-3.997965000	-4.059352000
H	-0.710586000	-4.761308000	-2.706113000
H	0.200810000	-3.243276000	-2.451138000
H	-3.105151000	2.379472000	-1.923283000
H	-2.730134000	0.751036000	-3.059235000

H	-1.934155000	0.926382000	-1.248863000

Compound **3**

E = -12002.2455437

C	4.726277000	-2.138248000	-0.175436000
C	2.970207000	-2.708443000	-1.496338000
C	3.812050000	-1.866386000	-2.241749000
C	3.500927000	-1.515163000	-3.555994000
H	4.142471000	-0.859518000	-4.143840000
C	2.317110000	-2.029555000	-4.090205000
H	2.031119000	-1.754986000	-5.105307000
C	1.490177000	-2.891821000	-3.353123000
H	0.565013000	-3.264520000	-3.789732000
C	1.806151000	-3.255436000	-2.042118000
H	1.183671000	-3.957935000	-1.491408000
C	7.990361000	1.249243000	-0.839543000
C	8.518103000	1.161332000	-2.281349000
H	9.591744000	1.410126000	-2.285076000
H	8.015878000	1.860697000	-2.959603000
H	8.424308000	0.149060000	-2.699375000
C	8.235122000	2.655487000	-0.265315000
H	7.790826000	2.759698000	0.735652000
H	7.832612000	3.444392000	-0.913956000
H	9.320204000	2.822783000	-0.175661000
C	8.748314000	0.236405000	0.043735000
H	9.826781000	0.457531000	-0.003615000
H	8.604067000	-0.803006000	-0.279533000
H	8.426031000	0.302111000	1.092998000
C	5.030173000	2.162110000	-1.393820000
C	5.465982000	2.690735000	-2.765528000
H	4.690366000	3.370905000	-3.153271000
H	5.587841000	1.884412000	-3.504518000
H	6.404031000	3.258945000	-2.714299000
C	3.641036000	1.512078000	-1.512983000
H	3.301952000	1.076648000	-0.564247000
H	3.590617000	0.731114000	-2.279395000
H	2.904730000	2.276257000	-1.799194000
C	4.925840000	3.313641000	-0.372807000
H	4.126963000	3.999346000	-0.694310000
H	5.850724000	3.896212000	-0.293596000
H	4.679755000	2.936227000	0.631526000
C	1.923410000	-1.296549000	2.673837000
C	2.350814000	-0.118467000	1.774609000
H	2.807783000	0.669132000	2.392315000
H	1.498719000	0.287964000	1.212205000

H	3.111010000	-0.422844000	1.038942000
C	3.096599000	-1.729767000	3.564350000
H	3.978487000	-2.032147000	2.990406000
H	2.823017000	-2.543129000	4.248669000
H	3.417458000	-0.863534000	4.163471000
C	0.761700000	-0.820739000	3.560584000
H	1.090264000	0.080958000	4.101066000
H	0.481629000	-1.570966000	4.312838000
H	-0.126876000	-0.560414000	2.971209000
C	0.357358000	-4.025768000	2.278663000
C	1.020118000	-4.561578000	3.554294000
H	1.037546000	-3.808000000	4.351886000
H	2.052734000	-4.896549000	3.377722000
H	0.449391000	-5.427027000	3.929207000
C	-1.064633000	-3.504799000	2.570134000
H	-1.671197000	-4.332668000	2.972228000
H	-1.540882000	-3.139604000	1.649236000
H	-1.081996000	-2.688973000	3.299674000
C	0.207936000	-5.158181000	1.241018000
H	1.145178000	-5.700005000	1.052780000
H	-0.191801000	-4.772692000	0.291251000
H	-0.513783000	-5.894838000	1.627609000
C	5.987175000	-0.665770000	-1.755891000
H	5.880317000	-0.385283000	-2.810010000
H	6.922820000	-1.228219000	-1.641905000
C	2.894221000	-3.491246000	0.886056000
H	3.624397000	-3.580069000	1.696696000
H	2.607283000	-4.498741000	0.563452000
C	-5.709562000	-2.824515000	-1.875177000
C	-7.206687000	-2.842015000	-2.226099000
H	-7.383298000	-3.612789000	-2.993758000
H	-7.548443000	-1.887555000	-2.651319000
H	-7.842576000	-3.083082000	-1.366831000
C	-4.891717000	-2.524461000	-3.149896000
H	-3.813194000	-2.516622000	-2.941758000
H	-5.153436000	-1.559726000	-3.606005000
H	-5.098500000	-3.309547000	-3.894975000
C	-5.269191000	-4.198273000	-1.339640000
H	-5.377657000	-4.947283000	-2.139966000
H	-5.885063000	-4.529850000	-0.492828000
H	-4.212869000	-4.182700000	-1.032349000
C	-5.904742000	-1.833432000	1.115351000
C	-7.361553000	-2.310152000	1.146434000
H	-7.709643000	-2.346254000	2.191540000
H	-7.476058000	-3.318749000	0.728250000
H	-8.035842000	-1.631581000	0.602256000

C	-4.985952000	-2.858778000	1.811855000
H	-3.949334000	-2.494924000	1.844550000
H	-4.990157000	-3.838525000	1.320619000
H	-5.331443000	-2.999444000	2.848692000
C	-5.779604000	-0.500675000	1.880823000
H	-5.939462000	-0.691077000	2.953794000
H	-6.532753000	0.231808000	1.567613000
H	-4.778253000	-0.061032000	1.766191000
C	-6.123294000	-0.026629000	-1.274030000
H	-6.058134000	-0.098726000	-2.367035000
H	-7.181309000	-0.067250000	-0.990425000
C	-6.304621000	2.221740000	-0.137915000
C	-5.446910000	3.328781000	0.008182000
C	-5.856229000	4.478544000	0.685808000
H	-5.200442000	5.340983000	0.798330000
C	-7.146579000	4.485166000	1.217405000
H	-7.496579000	5.366747000	1.753994000
C	-8.004117000	3.381203000	1.069012000
H	-9.007836000	3.422216000	1.491548000
C	-7.598557000	2.233586000	0.386110000
H	-8.271391000	1.384826000	0.269943000
C	-3.102552000	3.871059000	-0.757422000
H	-3.360023000	4.837305000	-0.309401000
H	-2.892154000	4.030924000	-1.822454000
C	-0.244352000	4.228336000	-0.967960000
C	-0.169881000	3.638903000	-2.392445000
H	0.615623000	4.171770000	-2.952632000
H	-1.109082000	3.757210000	-2.950599000
H	0.077478000	2.569541000	-2.375622000
C	1.119851000	4.017740000	-0.291464000
H	1.905316000	4.446266000	-0.933153000
H	1.338882000	2.948352000	-0.159012000
H	1.188198000	4.516403000	0.683714000
C	-0.566386000	5.729471000	-1.064068000
H	-0.617873000	6.219561000	-0.085855000
H	-1.508159000	5.921879000	-1.597570000
H	0.231395000	6.226657000	-1.639430000
C	-1.568948000	3.616345000	1.817207000
C	-2.918934000	3.080524000	2.336202000
H	-3.102792000	2.049386000	2.003730000
H	-3.760327000	3.714701000	2.030530000
H	-2.898745000	3.075844000	3.437226000
C	-1.454665000	5.107564000	2.156577000
H	-2.208030000	5.715547000	1.633063000
H	-0.460555000	5.511891000	1.926483000
H	-1.620119000	5.243794000	3.237579000

C	-0.438830000	2.821710000	2.504546000
H	-0.518827000	2.956381000	3.594906000
H	0.561394000	3.151766000	2.202145000
H	-0.525735000	1.749157000	2.287540000
C	-4.360596000	1.753783000	-1.215051000
N	4.874977000	-1.535879000	-1.398393000
N	3.544228000	-2.824597000	-0.232915000
N	-5.597513000	1.272264000	-0.871417000
N	-4.263720000	2.997028000	-0.646697000
P	6.147238000	0.839220000	-0.633282000
P	1.310389000	-2.611107000	1.439805000
P	-5.177019000	-1.512734000	-0.606995000
P	-1.512096000	3.172825000	-0.026098000
Cu	5.645312000	0.322332000	1.430870000
Cu	0.244955000	-1.823753000	-0.301256000
Cu	-3.009966000	-1.229603000	-0.513153000
Cu	-1.344111000	1.009309000	-0.391668000
Cl	5.329729000	1.498275000	3.238077000
Cl	-1.604884000	-2.890200000	-1.270200000
Cl	-2.134377000	-0.297494000	1.437153000
Cl	0.549957000	0.157204000	-1.399925000
B	5.784919000	-2.161776000	1.004135000
H	5.668450000	-3.200687000	1.631459000
H	6.905237000	-2.037755000	0.554157000
H	5.548681000	-1.317832000	1.919670000
B	-3.323444000	1.076601000	-2.193415000
H	-3.896650000	0.351666000	-2.978356000
H	-2.636616000	1.910566000	-2.741547000
H	-2.529605000	0.267605000	-1.569293000

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