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Electronic Supporting Information for

Stepwise and selective synthesis of chelating, multimetallic and mixed-metal π-diborene complexes

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Contents

Methods and materials

All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å molecular sieves. Liquid-phase NMR spectra were acquired on a Bruker Avance 500 (^{1}H: 500.1 MHz, ^{11}B: 160.5 MHz, ^{13}C: 125.8 MHz, ^{19}F: 470.6 MHz, ^{31}P: 202.5 MHz) or Bruker Avance 600 (^{1}H: 600.2 MHz, ^{11}B: 192.7 MHz, ^{13}C: 150.9 MHz) spectrometer. Chemical shifts (δ)are reported in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) (C_6D_6: 128.1, C_6D_5Br: 122.6) or residual protons (^{1}H) (C_6D_6: 7.16, C_6D_5Br: 7.30) of the solvent. Heteronuclei NMR spectra are referenced to external standards (^{11}B: $BF_3{\cdot}OEt_2$, ^{19}F: $CFCl_3$, ^{31}P: 85% aq. H_3PO_4). Resonances are given as singlet (s), doublet (d), triplet (t), septet (sept), multiplet (m) or broad (br). High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer. UV-vis spectra were acquired on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer.

Solvents and reagents were purchased from Sigma-Aldrich, ABCR or Alfa Aesar. $B_2(SIDep)_2$,[1] [(SIDep)HB=B(2-C_5H_4N)(SIDep)] (**1**),[2] $[Cu(C_6F_5)]_4$,[3] $[AgCl(PPh_3)]$[4] and $[AuCl(PPh_3)]$[5] were prepared according to literature procedures.

Synthetic procedures

Synthesis of [(SIDep)HB=B(2-C_5H_4N)(SIDep)][CuCl] (2-CuCl)

1 (20.0 mg, 26 µmol, 1.00 equiv.) and [CuCl(SMe_2)] (2.6 mg, 26 µmol, 1.00 equiv.) were combined in benzene (0.6 mL) and stirred at room temperature for 30 minutes. The volatiles were removed *in vacuo* and the residue was washed with *n*-hexane (1 mL). After drying under reduced pressure, the residue was extracted with benzene and by slow diffusion of *n*-pentane into the solution the product crystallized as orange blocks (10.6 mg, 12 µmol, 46%), which were also suitable for X-ray diffractometry.

^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 8.36 – 8.34 (m, 1H, H^{Pyr}), 7.28 – 7.22 (m, 4H, H^{Ar}), 7.08 – 7.05 (m, 2H, H^{Ar}), 7.01 – 7.00 (m, 2H, H^{Ar}), 6.88 – 6.84 (m, 4H, H^{Ar}), 6.31 – 6.25 (m, 2H, H^{Pyr}), 4.90 – 4.88 (m, 1H, H^{Pyr}), 3.33 – 3.19 (m, 4H, CH_2^{Et} + NCH_2), 3.15 – 3.11 (m, 2H, NCH_2), 3.05 – 3.00 (m, 2H, NCH_2), 2.98 – 2.84 (m, 6H, CH_2^{Et} + NCH_2), 2.70 – 2.53 (m, 7H, CH_2^{Et} + NCH_2 + B*H*), 2.19 (dq, $^2J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 7.8 Hz, 2H, CH_2^{Et}), 1.75 (dq, $^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2^{Et}), 1.34 – 1.32 (two overlapping t, $^3J_{HH}$ = 7.7, 7.5 Hz, 12H, CH_3^{Et}), 1.26 (t, $^3J_{HH}$ = 7.6 Hz, 6H, CH_3^{Et}), 0.99 (t, $^3J_{HH}$ = 7.8 Hz, 6H, CH_3^{Et}) ppm.

^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6): δ = **^{13}C{^{1}H} NMR** (125.8 MHz, C_6D_6): δ = 191.8 ($C^{Carbene}$), 185.7 ($C^{Carbene}$), 176.1 ($C^{2\text{-}Pyr}$), 145.5 (C^{Pyr}), 142.2 (C^q), 141.7 (C^q), 141.5 (C^q), 140.8 (C^q), 138.7 (C^q), 137.2 (C^q), 131.5 (C^{Pyr}), 128.3 (C^{Pyr}), 126.9 (C^{Ar}), 125.9 (C^{Ar}), 125.7 (C^{Ar}), 125.4 (C^{Ar}), 116.0 (C^{Pyr}), 50.8 (NCH_2), 50.6 (NCH_2), 24.5 (CH_2^{Et}), 24.3 (CH_2^{Et}), 23.9 (CH_2^{Et}), 23.2 (CH_2^{Et}), 14.1 (CH_3^{Et}), 13.7 (CH_3^{Et}), 13.5 (CH_3^{Et}) ppm.

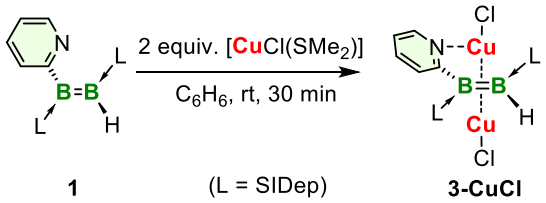
^{11}B{^{1}H} NMR (160.5 MHz, C_6D_6): δ = 23.9 (NC*B*), 5.1 (*B*H) ppm.

HRMS(LIFDI): m/z ($C_{51}H_{65}B_2N_5CuCl$) = calc.: 867.4405, found: 867.4389.

UV-vis (C_6H_6): λ_{max} = 437 nm.

Synthesis of [(SIDep)HB=B(2-C_5H_4N)(SIDep)][CuCl]$_2$ (3-CuCl)

Route a: **2-Cu** (20.0 mg, 23 µmol, 1.00 equiv.) and [CuCl(SMe_2)] (3.7 mg, 23 µmol, 1.00 equiv.) were combined in benzene (0.6 mL) and stirred at room temperature for 30 minutes. The volatiles were removed *in vacuo* and the residue was washed with *n*-hexane (1 mL). After drying under reduced pressure, the residue was extracted with benzene and by slow diffusion of *n*-pentane into the solution the product crystallized as red blocks (11.7 mg, 12 µmol, 46%).



Scheme S1 Alternative synthetic route for **3-CuCl**.

Route b: **1** (20.0 mg, 26 µmol, 1.00 equiv) and [CuCl(SMe$_2$)] (5.2 mg, 52 µmol, 2.00 equiv) were combined in benzene (0.6 mL) and stirred at room temperature for 30 minutes. The volatiles were removed *in vacuo* and the residue was washed with *n*-hexane (1 mL). After drying under reduced pressure, the residue was extracted with benzene and by slow diffusion of *n*-pentane into the solution the product crystallized as red blocks (11.3 mg, 12 µmol, 46%), which were also suitable for X-ray diffractometry.

^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 8.01 (m, 1H, H^{Pyr}), 6.96 – 6.90 (m, 4H, H^{Ar}), 6.83 (d, $^{3}J_{HH}$ = 7.5 Hz, 4H, H^{Ar}), 6.73 (d, $^{3}J_{HH}$ = 7.5 Hz, 4H, H^{Ar}), 6.00 – 5.98 (m, 1H, H^{Pyr}), 5.96 – 5.92 (m, 1H, H^{Pyr}), 5.50 – 5.49 (m, 1H, H^{Pyr}), 3.22 (dq, $^{2}J_{HH}$ = 15.4 Hz, $^{3}J_{HH}$ = 7.7 Hz, 4H, CH_2^{Et}), 3.12 – 3.06 (m, 4H, CH_2^{Et}), 2.99 (s, 4H, NCH_2), 2.92 (s, 4H, NCH_2), 2.69 – 2.59 (m, 8H, CH_2^{Et}), 1.34 (t, $^{3}J_{HH}$ = 7.5 Hz, 12H, CH_3^{Et}), 1.24 (t, $^{3}J_{HH}$ = 7.7 Hz, 12H, CH_3^{Et}) ppm. (*Note: The BH resonance could not be detected due to broadening.)*

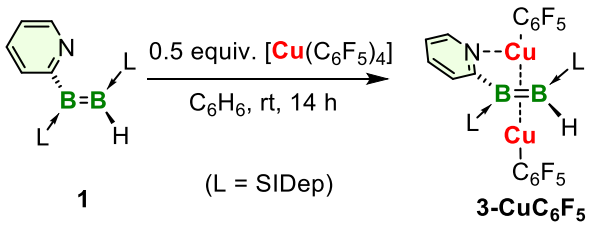
^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6): δ = 185.0 ($C^{Carbene}$, *identified by HMBC*), 184.8 ($C^{Carbene}$, *identified by HMBC*), 173.4 ($C^{2\text{-}Pyr}$, *identified by HMBC*), 144.3 (CH^{Pyr}), 141.1 (C^{q}), 140.4 (C^{q}), 137.9 (C^{q}), 137.6 (C^{q}), 132.6 (C^{Ar}), 128.2 (C^{Ar}), 128.2 (C^{Ar}), 126.4 (C^{Ar}), 126.0 (C^{Ar}), 117.0 (C^{Pyr}), 51.9 (NCH_2), 51.1 (NCH_2), 25.1 (CH_2^{Et}), 24.8 (CH_2^{Et}), 14.0 (CH_3^{Et}), 13.6 (CH_3^{Et}) ppm.

^{11}B{^{1}H} NMR (192.7 MHz, C_6D_6): δ = 10.2 (NC*B*), 0.0 (*B*H) ppm.

HRMS(LIFDI): m/z: calc.: 965.3359 ($C_{51}H_{65}B_2N_5Cu_2Cl_2$), 932.3683 ($C_{51}H_{65}B_2N_5Cu_2Cl$), found: 932.3661.

UV-vis (C_6H_6): λ_{max} = 355 nm (shoulder), 476 nm.

Synthesis of [(SIDep)HB=B(2-C_5H_4N)(SIDep)][(CuC_6F_5)]$_2$ (3-CuC_6F_5)



Scheme S2 Synthesis of **3-CuCl**.

1 (20.0 mg, 26 µmol, 1.00 equiv) and [Cu(C_6F_5)]$_4$ (12.0 mg. 13 µmol, 0.50 equiv) were dissolved in benzene (0.6 mL) and stirred at room temperature for 14 hours. The volatiles were removed *in vacuo* and the residue was washed with *n*-hexane (3 x 0.5 mL). The solid was dried *in vacuo* and after crystallization from toluene the product was obtained as red crystals (11.0 mg, 9 µmol, 35%). Crystals suitable for x-ray diffractometry were obtained by slow evaporation of a saturated *n*-hexane solution.

^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 7.55 (m, 1H, CH^{Pyr}), 6.93 (t, 2H, $^3J_{HH}$ = 7.6 Hz, C$H^{4\text{-}Ar}$), 6.88 (t, 2H, $^3J_{HH}$ = 7.6 Hz, C$H^{4\text{-}Ar}$), 6.73 (d, 4H, $^3J_{HH}$ = 7.6 Hz, C$H^{3\text{-}Ar}$), 6.64 (d, 4H, $^3J_{HH}$ = 7.6 Hz, C$H^{3\text{-}Ar}$), 6.48 – 6.46 (m, 1H, CH^{Pyr}), 6.19 – 6.16 (m, 1H, CH^{Pyr}), 5.92 – 5.90 (m, 1H, CH^{Pyr}), 2.94 (s, 4H, NCH_2), 2.93 (s, 4H, NCH_2), 2.66 – 2.38 (m, 16H, CH_2^{Et}), 1.04 – 1.00 (m, 24H, CH_3^{Et}) ppm. (*Note: The BH resonance could not be detected due to broadening.)*

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 204.1 (*C*^{Carbene}, *identified by HMBC*), 185.8 (*C*^{Carbene}, *identified by HMBC*), 173.9 (*C*$^{q\text{-}Pyr}$, *identified by HMBC*), 150.0 (br, C_6F_5), 149.7 (br, C_6F_5), 148.2 (br, C_6F_5), 144.7 (*C*^{Pyr}), 141.8 (*C*$^{2\text{-}Pyr}$), 140.5 (*C*$^{Ortho\text{-}Ar}$), 140.0 (*C*$^{Ortho\text{-}Ar}$), 138.7 (*C*-N), 137.7 (*C*-N), 132.9 (*C*^{Pyr}), 128.2 (*C*$^{Para\text{-}Ar}$), 127.9 (*C*$^{Para\text{-}Ar}$), 126.1 (*C*$^{Meta\text{-}Ar}$), 125.9 (*C*$^{Meta\text{-}Ar}$), 52.2 (NCH$_2$), 51.2 (NCH$_2$), 24.6 (*C*H$_2^{Et}$), 24.5 (*C*H$_2^{Et}$), 13.1 (*C*H$_3^{Et}$) ppm. (*Note: Some signals are overlapped by the C_6D_6 signal.)*

^{11}B{^{1}H} NMR (160.5 MHz, C_6D_6): δ = 13.9 (NC*B*), 6.5 (*B*H) ppm.

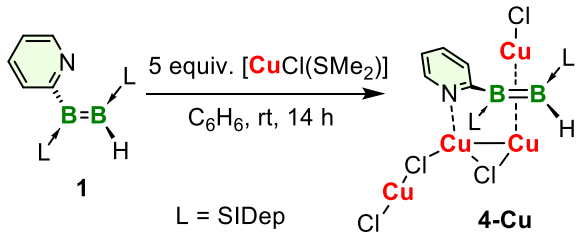
^{19}F NMR (470.6 MHz, C_6D_6): δ = −110.3 (m, 4F, CF^{Ar}), −161.3 (m, 2F, C$F^{Ar\text{-}Para}$), −162.7 (m, 4F, CF^{Ar}) ppm.

HRMS(LIFDI): m/z ($C_{63}H_{65}B_2N_5Cu_2F_{10}$) = calc.: 1229.3853, found: 1229.3845.

UV/Vis (C_6H_6): λ_{max} = 379, 400 – 600 (br) nm.

Synthesis of [(SIDep)HB=B(2-C_5H_4N)(SIDep)][CuCl]$_4$ (4-Cu)

Route a: **3-CuCl** (15.0 mg, 15.5 µmol, 1.00 equiv) and [CuCl(SMe_2)] (7.5 mg, 46.5 µmol, 3.00 equiv) were combined in benzene (0.6 mL) and stirred at room temperature for 14 h. The excess [CuCl(SMe_2)] was removed by filtration of the suspension and after drying *in vacuo* the product was obtained as a yellow solid (10.2 mg, 8.7 µmol, 56%).



Scheme S3 Alternative synthetic route for **4-Cu**.

Route b: **1** (10.0 mg, 13.0 µmol, 1.00 equiv) and [CuCl(SMe$_2$)] (10.5 mg. 65.0 µmol, 5.00 equiv) were dissolved in benzene (0.6 mL) and stirred at room temperature for 14 h. The excess [CuCl(SMe$_2$)] was removed by filtration of the suspension and after drying *in vacuo* the product was obtained as a yellow solid (8.5 mg, 7.3 µmol, 56%).

^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 8.62 – 8.61 (m, 1H, C*H*$^{Ar,2\text{-}pyr}$), 6.98 – 6.91 (m, 2H, C*H*^{Ar}), 6.87 – 6.85 (m, 2H, C*H*^{Ar}), 6.79 – 6.77 (m, 4H, C*H*^{Ar}), 6.64 (br. s, 4H, C*H*^{Ar}), 6.21 – 6.20 (m, 1H, C*H*$^{Ar,4\text{-}pyr}$), 6.13 – 6.10 (m, 1H, C*H*$^{Ar,3\text{-}pyr}$), 5.90 – 5.88 (m 1H, C*H*$^{Ar,5\text{-}pyr}$), 3.20 (br. s, 1H, B*H*), 3.08 (br. s, 4H, NC*H*$_2$), 2.94 (br. s, 4H, C*H*$_2^{Et}$), 2.90 (br. s, 4H, NC*H*$_2$), 2.82 (br. s, 4H, C*H*$_2^{Et}$), 2.63 (br. s, 4H, C*H*$_2^{Et}$), 2.46 – 2.38 (m, 4H, C*H*$_2^{Et}$), 1.28 – 1.26 (m, 24H, C*H*$_3^{Et}$) ppm.

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 203.7 (*C*^{Carbene}), 182.9 (*C*^{Carbene}), 170.8 (B*C*=N), 148.7 (*C*H$^{Ar,2\text{-}pyr}$), 141.6 (*C*^{q}), 140.2 (*C*^{q}), 137.0 (*C*^{q}), 136.6 (*C*^{q}), 132.6 (*C*H$^{Ar,4\text{-}pyr}$), 132.4 (*C*H$^{Ar,3\text{-}pyr}$), 129.2 (*C*^{Ar}), 129.2 (*C*^{Ar}), 128.8 (*C*^{Ar}), 126.4 (*C*^{Ar}), 120.3 (*C*H$^{Ar,5\text{-}pyr}$), 52.2 (NCH$_2$), 51.4 (NCH$_2$), 24.6 (*C*H$_2^{Et}$), 24.3 (*C*H$_2^{Et}$), 14.4 (*C*H$_3^{Et}$), 13.5 (*C*H$_3^{Et}$) ppm. (*Note: Some signals are overlapped by the C_6D_6 signal.*)

^{11}B{^{1}H} NMR (160.5 MHz, C_6D_6): δ = 16.5 (NC*B*), 0.3 (*B*H) ppm.

HRMS(LIFDI): m/z: calc.: 1165.1317 ($C_{51}H_{65}B_2N_5Cu_4Cl_4$), 1130.1623 ($C_{51}H_{65}B_2N_5Cu_4Cl_3$), 1030.2668 ($C_{51}H_{65}B_2N_5Cu_3Cl_2$), 932.3683 ($C_{51}H_{65}B_2N_5Cu_2Cl$), found: 1130.1592, 1030.2629, 932.3644.

UV/Vis (C_6H_6): λ_{max} = 367, 400 – 600 (br) nm.

Synthesis of [(SIDep)HB=B(2-C$_5$H$_4$N)(SIDep)][AgCl] (2-AgCl)

1 (15.0 mg, 22 µmol, 1.00 equiv) and [AgCl(PPh$_3$)] (8.1 mg. 22 µmol, 1.00 equiv) were dissolved in C_6D_6 (0.6 mL) and stirred at room temperature overnight. The volatiles were removed *in vacuo* and the residue was washed with *n*-hexane (3 x 0.5 mL). The solid was dried *in vacuo* and after crystallization from toluene the product was obtained as yellow crystals (10.7 mg, 12 µmol, 54%), which were also suitable for X-ray diffractometry.

^{1}H{^{11}B} NMR (500.1 MHz, C_6D_6): δ = 8.34 – 8.33 (m, 1H, *H*^{Pyr}), 7.27 – 7.21 (m, 4H, *H*^{Ar}), 7.08 (t, $^3J_{HH}$ = 7.6 Hz, *H*^{Ar}), 7.00 – 6.99 (m, 2H, *H*^{Ar}), 6.91 – 6.89 (m, 2H, *H*^{Ar}), 6.83 – 6.81 (m, 2H, *H*^{Ar}), 6.31

– 6.28 (m, 1H, H^{Pyr}), 6.24 – 6.21 (m, 1H, H^{Pyr}), 5.02 – 5.00 (m, 1H, H^{Pyr}), 3.26 (dq, $^{2}J_{HH}$ = 15.0 Hz, $^{3}J_{HH}$ = 7.5 Hz, 2H, CH_2^{Et}), 3.19 – 3.01 (m, 6H, NCH_2), 2.92 – 2.84 (m, 4H, CH_2^{Et} + NCH_2), 2.77 (dq, $^{2}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2H, CH_2^{Et}), 2.63 (dq, $^{2}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2H, CH_2^{Et}), 2.55 – 2.44 (m, 4H, CH_2^{Et}), 2.18 (dq, $^{2}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2H, CH_2^{Et}), 1.80 – 1.73 (m, 2H, CH_2^{Et}), 1.36 – 1.31 (m, 12H, CH_3^{Et}), 1.26 (t, $^{3}J_{HH}$ = 7.6 Hz, 6H, CH_3^{Et}), 0.99 (t, $^{3}J_{HH}$ = 7.6 Hz, 6H, CH_3^{Et}) ppm. (*Note: The BH resonance could not be detected due to broadening.)*

$^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6): δ = 191.2 ($C^{Carbene}$), 185.8 ($C^{Carbene}$, *identified by HMBC),* 174.4 ($C^{q\text{-}Pyr}$, *identified by HMBC*), 146.2 (C^{Pyr}), 142.1 (C^{q}), 141.7 (C^{q}), 141.2 (C^{q}), 140.7 (C^{q}), 138.3 (C^{q}), 137.0 (C^{q}), 131.3 (C^{Pyr}), 128.5 (C^{Pyr}), 126.9 (C^{Ar}), 126.0 (C^{Ar}), 125.9 (C^{Ar}), 125.6 (C^{Ar}), 116.2 (C^{Pyr}), 50.7 (NCH_2), 50.5 (NCH_2), 24.4 (CH_2^{Et}), 24.2 (CH_2^{Et}), 23.9 (CH_2^{Et}), 23.2 (CH_2^{Et}), 22.4 (CH_2^{Et}), 14.1 (CH_3^{Et}), 13.9 (CH_3^{Et}), 13.7 (CH_3^{Et}), 13.6 (CH_3^{Et}) ppm. (*Note: Some signals are overlapped by the C_6D_6 signal.*)

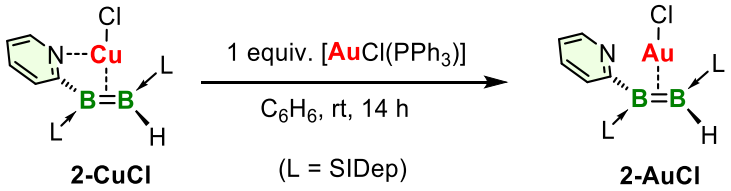
$^{11}B\{^{1}H\}$ NMR (160.5 MHz, C_6D_6): δ [ppm] = 27.0 (NC*B*), 4.1 (*B*H).

HRMS(LIFDI): m/z ($C_{51}H_{65}B_2N_5AgCl$) = calc.: 913.4157, found: 913.4145.

UV/Vis (C_6H_6): λ_{max} = 427 nm.

Synthesis of [(SIDep)HB=B(2-C_5H_4N)(SIDep)][AuCl] (2-AuCl)

Route a: **1** (20.0 mg, 26 µmol, 1.00 equiv) and [AuCl(PPh_3)] (12.9 mg, 26 µmol, 1.00 equiv) were dissolved in C_6D_6 (0.6 mL) and stirred at room temperature overnight. The volatiles were removed *in vacuo* and the residue was washed with *n*-hexane (3 x 0.5 mL). The solid was dried *in vacuo* and after crystallization from toluene the product was obtained as yellow crystals (13 mg, 13 µmol, 50%), which were also suitable for X-ray diffractometry.



Scheme S4 Alternative synthetic route for **2-AuCl**.

Route b: **2-CuCl** (20.0 mg, 23 µmol, 1.00 equiv) and [AuCl(PPh_3)] (11.4 mg, 23 µmol, 1.00 equiv) were combined in benzene (0.6 mL) and stirred at room temperature for 30 minutes. The suspension was filtered, and all volatiles were removed *in vacuo*. The residue was washed with n-hexane (3 x 0.5 mL) and extracted with benzene. By slow diffusion of *n*-pentane into the solution the product crystallized as yellow crystals (10.0 mg, 10 µmol, 43%).

$^{1}H\{^{11}B\}$ NMR (500.1 MHz, C_6D_6): δ = 8.25 – 8.23 (m, 1H, H^{Pyr}), 7.23 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, H^{Ar}), 7.18 – 7.16 (m (*obstructed by solvent signal*), 1H, H^{Ar}), 7.04 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, H^{Ar}), 6.94 (d,

$^{3}J_{HH}$ = 7.4 Hz, 2H, H^{Ar}), 6.89 (d, $^{3}J_{HH}$ = 7.2 Hz, 2H, H^{Ar}), 6.79 (d, $^{3}J_{HH}$ = 7.2 Hz, 2H, H^{Ar}), 6.62 – 6.61 (m, 2H, H^{Pyr}), 6.39 – 6.35 (m, 1H, H^{Pyr}), 3.21 – 3.16 (m, 2H, NCH_2), 3.14 – 3.06 (m, 2H, CH_2^{Et}), 3.04 – 2.90 (m, 8H, CH_2^{Et} + NCH_2), 2.77 (dq, $^{2}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2H, CH_2^{Et}), 2.64 (dq, $^{2}J_{HH}$ = 15.0 Hz, $^{3}J_{HH}$ = 7.0 Hz, 2H, CH_2^{Et}), 2.51 – 2.31 (m, 6H, CH_2^{Et}), 2.16 (dq, $^{2}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2H, CH_2^{Et}), 1.31 (t, $^{3}J_{HH}$ = 7.5 Hz, 6H, CH_3^{Et}), 1.27 (t, $^{3}J_{HH}$ = 7.6 Hz, 6H, CH_3^{Et}), 1.22 (t, $^{3}J_{HH}$ = 7.6 Hz, 6H, CH_3^{Et}), 1.14 (t, $^{3}J_{HH}$ = 7.5 Hz, 6H, CH_3^{Et}) ppm. (*Note: The BH resonance could not be detected due to broadening.)*

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 190.8 ($C^{Carbene}$), 187.8 ($C^{Carbene}$), 176.1 ($C^{q\text{-}Pyr}$, *identified by HMBC*), 146.3 (C^{Pyr}), 141.2 (C^{q}), 141.2 (C^{q}), 141.1 (C^{q}), 140.5 (C^{q}), 138.0 (C^{q}), 137.2 (C^{q}), 130.8 (C^{Pyr}), 128.4 (C^{Pyr}), 126.5 (C^{Ar}), 126.1 (C^{Ar}), 125.8 (C^{Ar}), 125.5 (C^{Ar}), 116.7 (C^{Pyr}), 51.3 (NCH$_2$), 50.9 (NCH$_2$), 24.3 (CH$_2^{Et}$), 23.9 (CH$_2^{Et}$), 23.8 (CH$_2^{Et}$), 23.6 (CH$_2^{Et}$), 14.1 (CH$_3^{Et}$), 14.0 (CH$_3^{Et}$), 13.9 (CH$_3^{Et}$), 13.5 (CH$_3^{Et}$) ppm. (*Note: Some signals are overlapped by the C_6D_6 signal.*)

^{11}B{^{1}H} NMR (160.5 MHz, C_6D_6): δ = 15.0 (NC*B*), 6.3 (*B*H) ppm.

HRMS(LIFDI): m/z ($C_{51}H_{65}B_2N_5AuCl$) = calc.: 1001.4775, found: 1001.4749.

UV/Vis (C_6H_6): λ_{max} = 400 nm.

Synthesis of [(SIDep)HB=B(2-C_5H_4N)(SIDep)][AuBr] (2-AuBr)

1 (20.0 mg, 26 µmol, 1.00 equiv) and [AuBr(PCy$_3$)] (14.5 mg. 26 µmol, 1.00 equiv) were dissolved in C_6D_6 (0.6 mL) and stirred at room temperature for three days. The volatiles were removed *in vacuo* and the residue was washed with *n*-hexane until the green color of the washing phases faded. The solid was dried *in vacuo* and after crystallization from a toluene/*n*-hexane mixture (1/4 v/v) at −30 °C the product was obtained as yellow crystals (10 mg, 10 µmol, 38%). Crystals suitable for X-ray diffractometry were obtained by slow evaporation of a saturated toluene solution.

^{1}H {^{11}B} NMR (500.1 MHz, C_6D_6): δ = 8.24 – 8.22 (m, 1H, H^{Pyr}), 7.22 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, H^{Ar}), 7.17 – 7.16 (m (overlapped by C_6D_6 signal), H^{Ar}), 7.04 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H, H^{Ar}), 6.93 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, H^{Ar}), 6.90 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, H^{Ar}),), 6.80 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, H^{Ar}), 6.62 – 6.60 (m, 2H, H^{Pyr}), 6.39 – 6.35 (m, 1H, H^{Pyr}), 3.19 – 3.12 (m, 4H, NCH_2 + CH_2^{Et}), 3.06 – 2.89 (m, 8H, NCH_2 + CH_2^{Et}), 2.77 (dq, $^{2}J_{HH}$ = 15.0 Hz, $^{3}J_{HH}$ = 7.5 Hz, 2H, CH_2^{Et}), 2.64 (dq, $^{2}J_{HH}$ = 15.0 Hz, $^{3}J_{HH}$ = 7.5 Hz, 2H, CH_2^{Et}), 2.49 – 2.40 (m, 4H, CH_2^{Et}), 2.34 (dq, $^{2}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2H, CH_2^{Et}), 2.16 (dq, $^{2}J_{HH}$ = 15.2 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2H, CH_2^{Et}), 1.31 (t, $^{3}J_{HH}$ = 7.5 Hz, 6H, CH_3^{Et}), 1.27 (t, $^{3}J_{HH}$ = 7.5 Hz, 6H, CH_3^{Et}), 1.23 (t, $^{3}J_{HH}$ = 7.6 Hz, 6H, CH_3^{Et}), 1.15 (t, $^{3}J_{HH}$ = 7.6 Hz, 6H, CH_3^{Et}) ppm. (*Note: The BH resonance could not be detected due to broadening.)*

^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 190.5 ($C^{Carbene}$, *identified by HMBC*), 187.5 ($C^{Carbene}$, *identified by HMBC*), 175.9 ($C^{q\text{-}Pyr}$, *identified by HMBC*), 146.3 (C^{Pyr}), 141.2 (C^{q}), 141.1 (C^{q}), 141.0 (C^{q}), 140.5

(C^{q}), 138.0 (C^{q}), 137.3 (C^{q}), 131.0 (C^{Pyr}), 130.6 (C^{Pyr}), 128.4 (C^{Ar}), 128.2 (C^{Ar}), 126.5 (C^{Ar}), 126.1 (C^{Ar}),125.8 (C^{Ar}), 125.5 (C^{Ar}), 116.7 (C^{Pyr}), 51.2 (NCH_2), 50.9 (NCH_2), 24.4 (CH_2^{Et}), 23.9 (CH_2^{Et}), 23.8 (CH_2^{Et}), 23.7 (CH_2^{Et}), 14.0 (CH_3^{Et}), 13.9 (CH_3^{Et}), 13.9 (CH_3^{Et}), 13.4 (CH_3^{Et}) ppm. (*Note: Some signals are overlapped by the C_6D_6 signal.)*

$^{11}B\{^1H\}$ NMR (160.5 MHz, C_6D_6): δ = 15.5 (NC*B*), 6.6 (*B*H) ppm.

HRMS(LIFDI): m/z ($C_{51}H_{65}B_2N_5AuBr$) = calc.: 1046.4303, found: 1046.4269.

UV/Vis (C_6H_6): λ_{max} = 401 nm.

Synthesis of [(SIDep)HB=B(2-C_5H_4N)(SIDep)][AuCl][CuCl] (3-CuAu)

Route a: **2-AuCl** (39.0 mg, 39 µmol, 1.00 equiv) and [Cu(SMe_2)Cl] (6.3 mg, 20 µmol, 1.00 equiv) were combined in benzene (0.6 mL) and stirred at room temperature for 30 minutes. The volatiles were removed *in vacuo* and the residue was washed with *n*-hexane (1 mL). After drying under reduced pressure, the residue was extracted with benzene and by slow diffusion of *n*-pentane into the solution the product crystallized as red needles (28.3 mg, 25 µmol, 64%), which were also suitable for X-ray diffractometry.

Route b: **3-CuCl** (20 mg, 21 µmol, 1.00 equiv) and [AuCl(PPh_3)] (10.4 mg, 21 µmol, 1.00 equiv) were combined in benzene (0.6 mL) and stirred at room temperature for 30 minutes. The suspension was filtered, and all volatiles were removed *in vacuo*. The residue was washed with n-hexane (3 x 0.5 mL) and extracted with benzene. By slow diffusion of *n*-pentane into the solution the product crystallized as red needles (12.1 mg, 11 µmol, 52%).

$^1H\{^{11}B\}$ NMR (600.2 MHz, C_6D_6): δ = 8.03 – 8.02 (m, 1H, H^{Pyr}), 7.04 – 7.03 (m, 2H, H^{Ar}), 6.96 – 6.92 (m, 6H, H^{Ar}), 6.70 – 6.69 (m, 2H, H^{Ar}), 6.44 – 6.43 (m, 2H, H^{Ar}), 6.12 – 6.07 (m, 2H, H^{Pyr}), 5.74 – 5.73 (m, 1H, H^{Pyr}), 3.83 (dq, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2^{Et}), 3.42 (dq, $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2^{Et}), 3.12 – 3.95 (m, 10H, CH_2^{Et} + NCH_2), 2.84 (br s, B*H*), 2.81 – 2.64 (m, 6H, CH_2^{Et}), 2.41 – 2.27 (m, 4H, CH_2^{Et}), 1.38 – 1.33 (two overlapping t, $^3J_{HH}$ = 7.6 Hz, 7.6 Hz, 12H, CH_3^{Et}), 1.27 (t, $^3J_{HH}$ = 7.6 Hz, 6H, CH_3^{Et}), 1.05 (t, $^3J_{HH}$ = 7.5 Hz, 6H, CH_3^{Et}) ppm.

$^{13}C\{^1H,^{11}B\}$ NMR (150.9 MHz, C_6D_6): δ = 185.5 ($C^{Carbene}$), 184.0 ($C^{Carbene}$), 173.1 ($C^{2\text{-}Pyr}$), 145.5 (C^{Pyr}), 142.1 (C^{q}), 141.3 (C^{q}), 141.1 (C^{q}), 141.0 (C^{q}), 137.0 (C^{q}), 137.3 (C^{q}), 133.7 (C^{Pyr}), 128.8 (C^{Ar}), 128.5 (C^{Ar}), 128.4 (C^{Ar}), 127.3 (C^{Ar}), 126.6 (C^{Ar}), 126.5 (C^{Ar}), 126.4 (C^{Ar}), 117.7 (CH^{Pyr}), 52.2 (NCH_2), 51.6 (NCH_2), 26.3 (CH_2^{Et}), 25.4 (CH_2^{Et}), 25.2 (CH_2^{Et}), 24.1 (CH_2^{Et}), 14.9 (CH_3^{Et}), 14.5 (CH_3^{Et}), 14.3 (CH_3^{Et}), 14.1 (CH_3^{Et}) ppm.

$^{11}B\{^1H\}$ NMR (192.7 MHz, C_6D_6): δ = 4.7 (NC*B*), −3.4 (*B*H) ppm.

UV-vis (C_6H_6): λ_{max} = 446 nm.

NMR spectra of isolated compounds

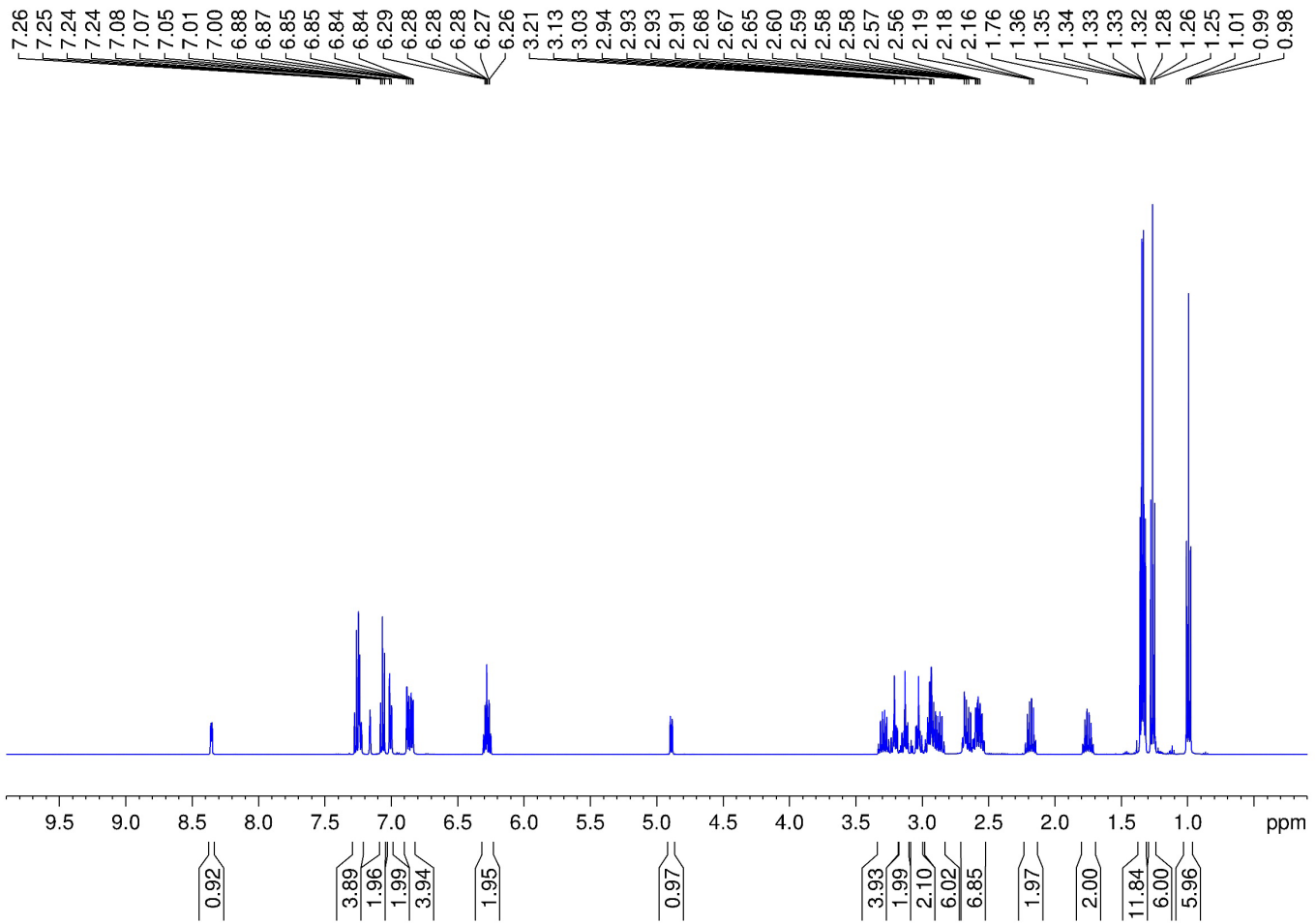


Fig. S1 $^{1}H\{^{11}B\}$ NMR spectrum of **2-CuCl** in C_6D_6.

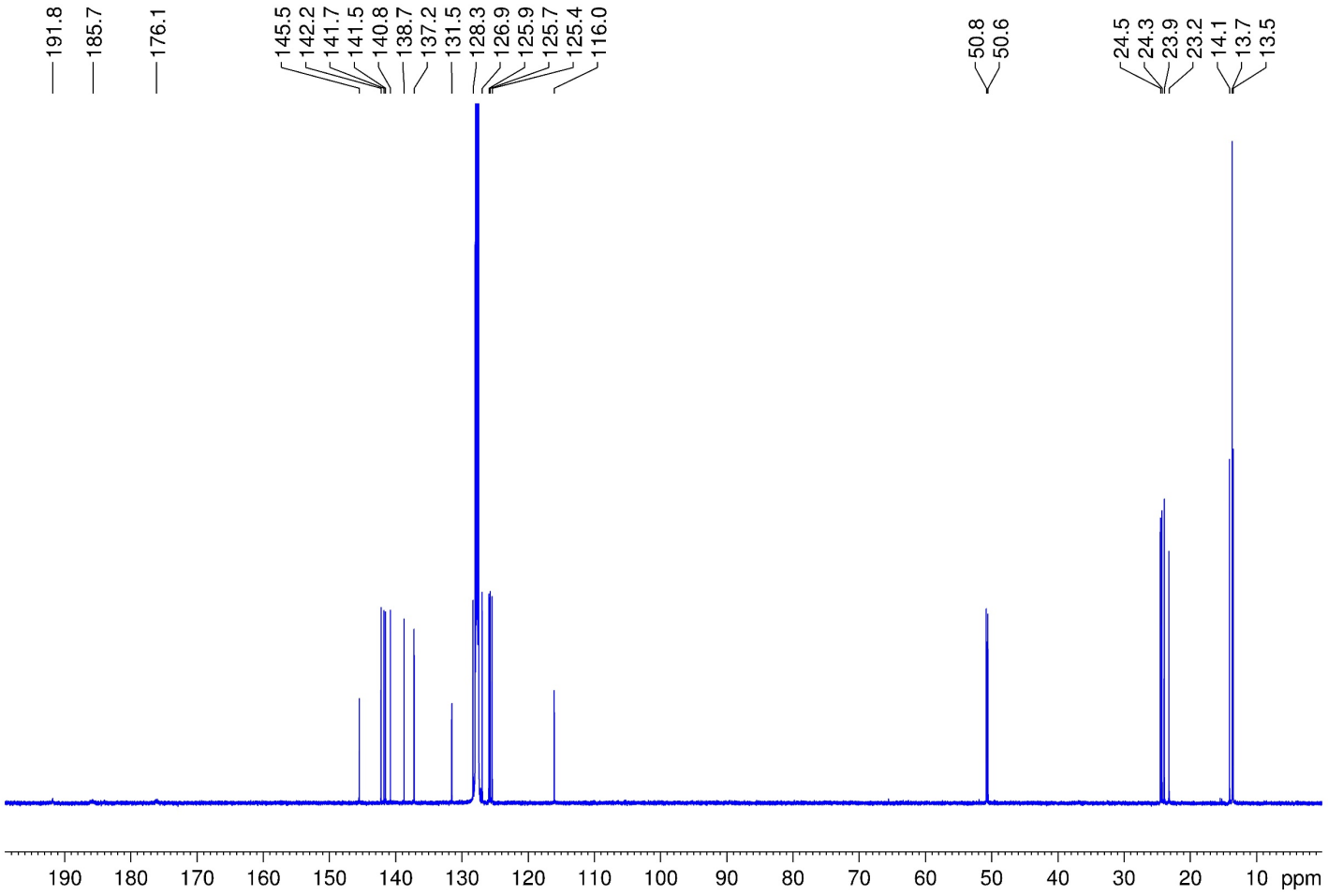


Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of **2-CuCl** in C_6D_6.

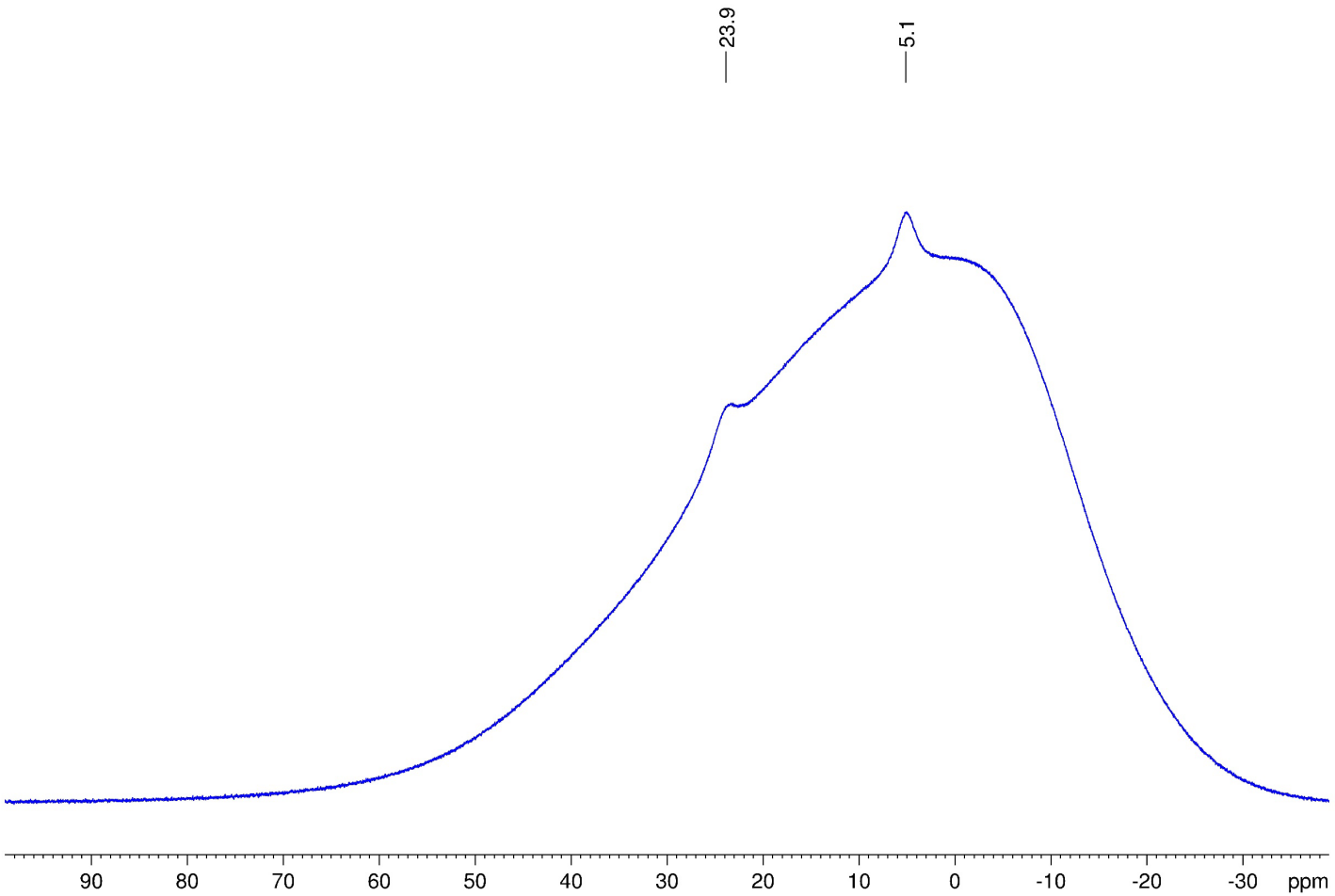


Fig. S3 $^{11}B\{^{1}H\}$ NMR spectrum of **2-CuCl** in C_6D_6.

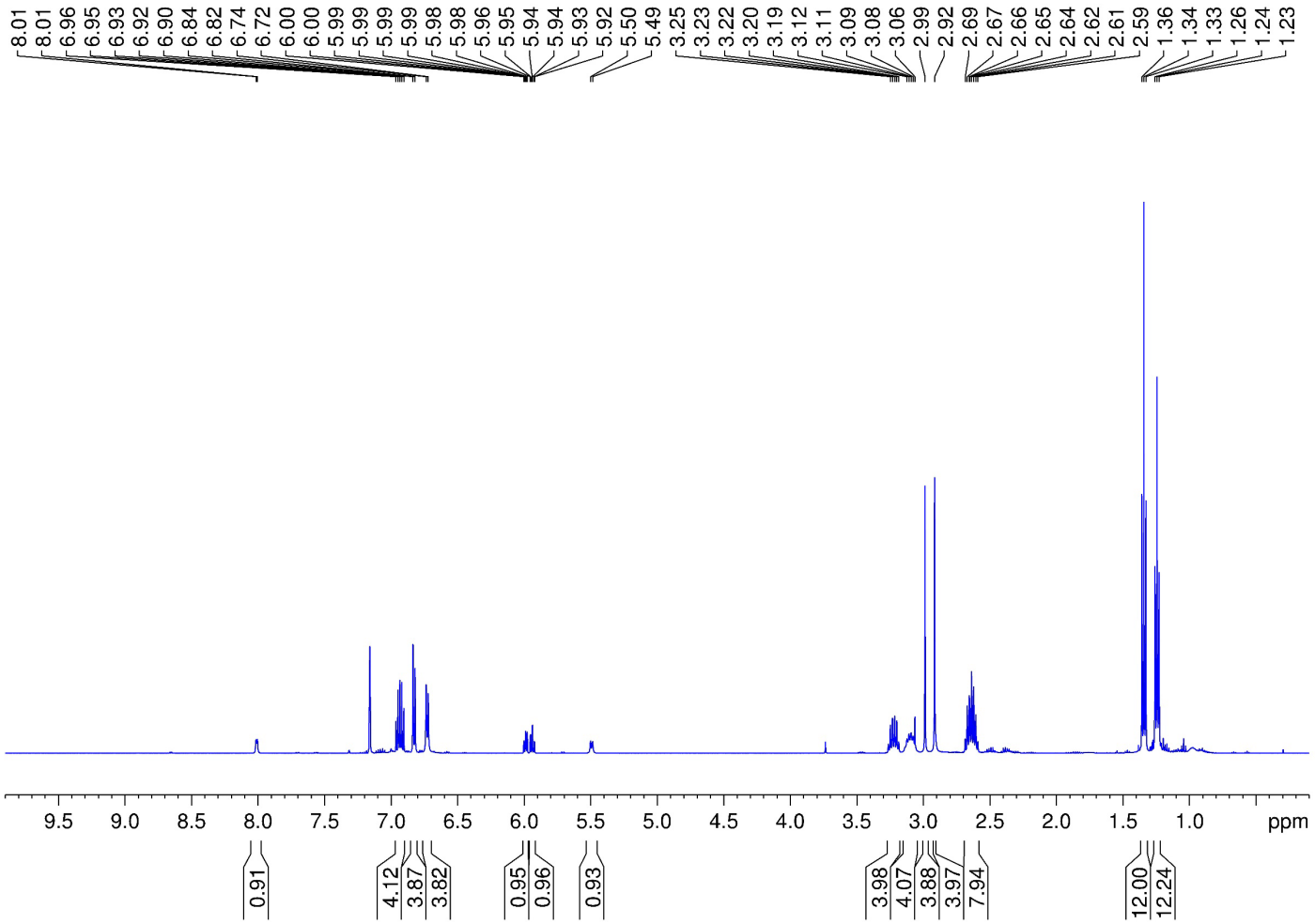


Fig. S4 $^{1}H\{^{11}B\}$ NMR spectrum of **3-CuCl** in C_6D_6.

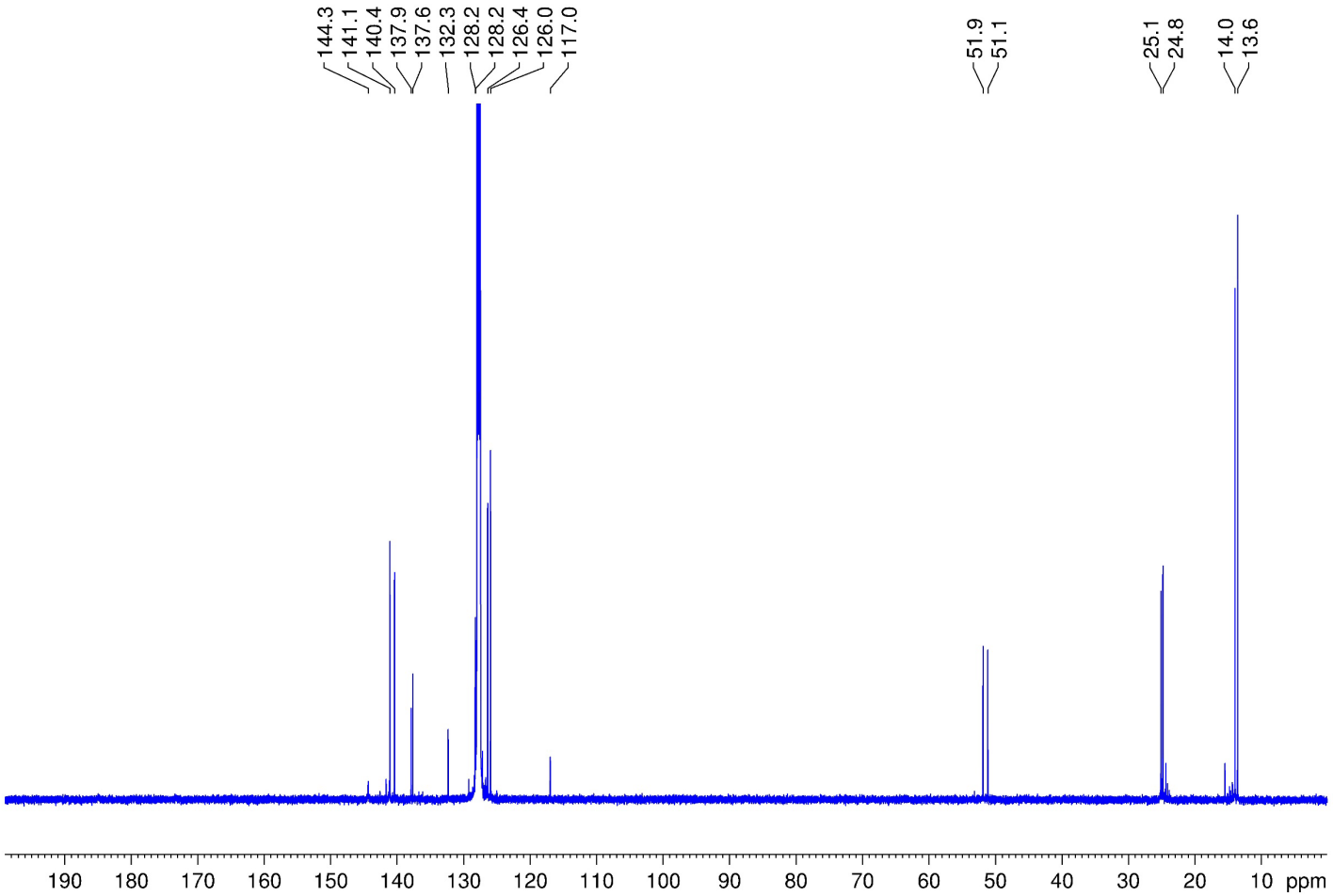


Fig. S5 $^{13}C\{^{1}H\}$ NMR spectrum of **3-CuCl** in C_6D_6.

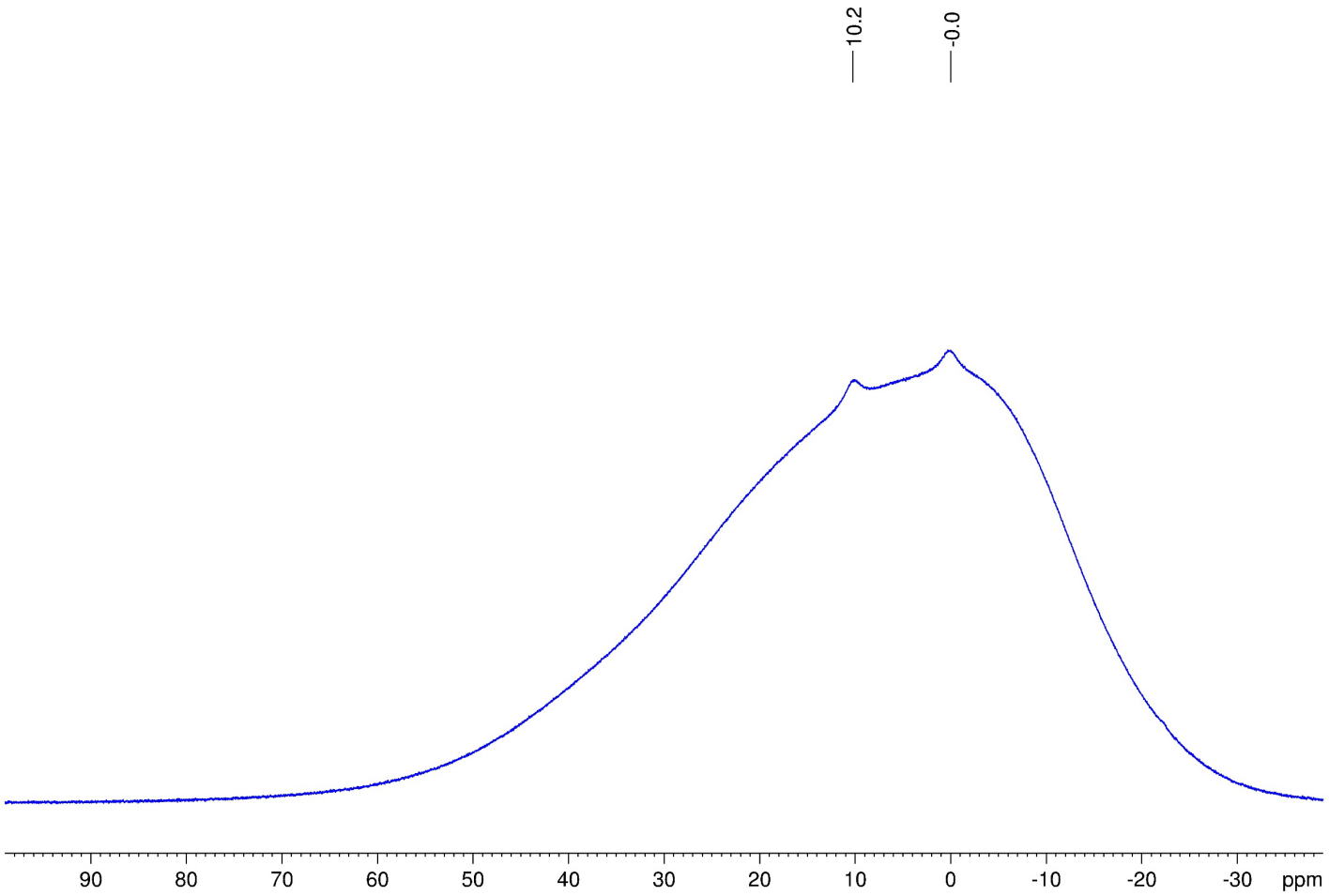


Fig. S6 $^{11}B\{^{1}H\}$ NMR spectrum of **3-CuCl** in C_6D_6.

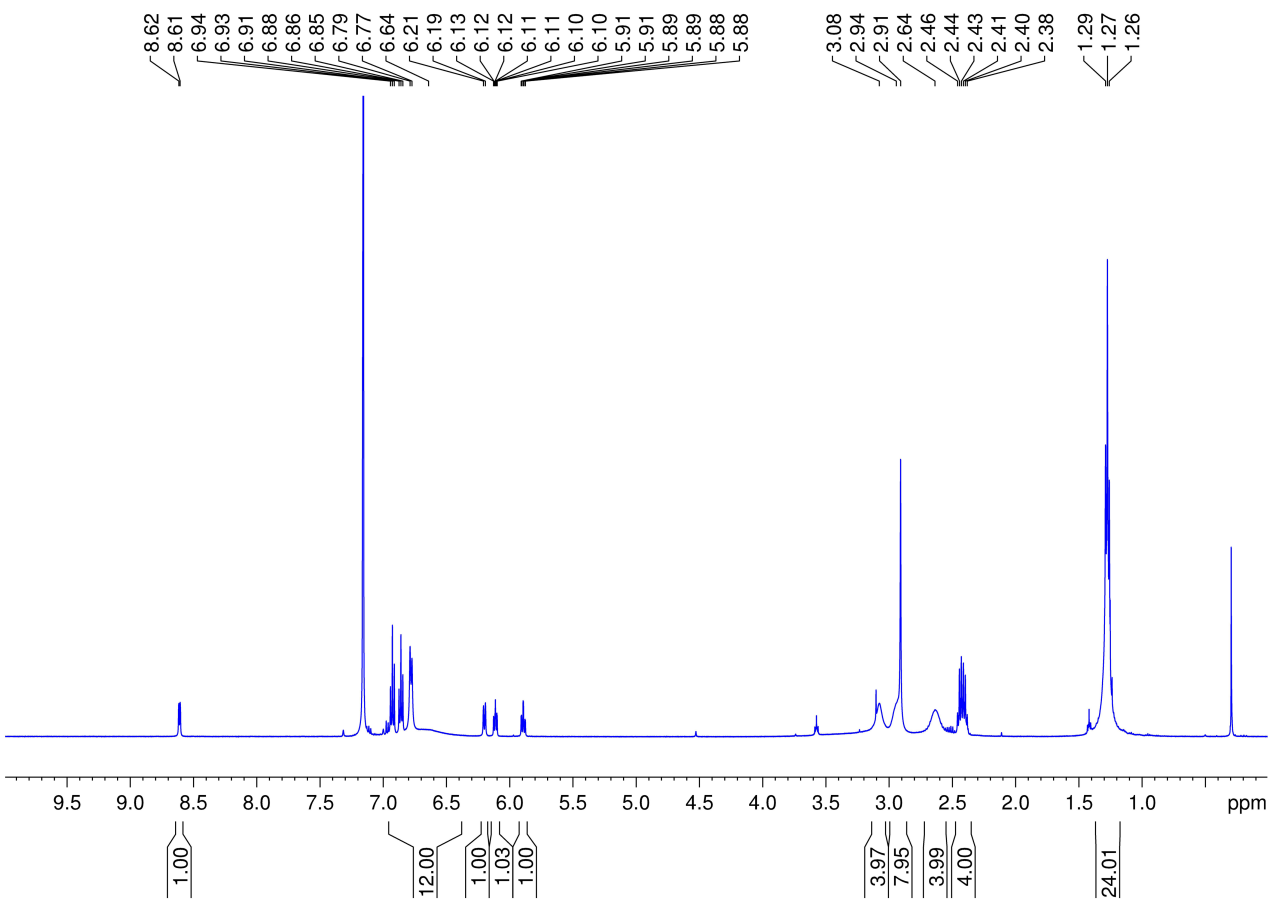


Fig. S7 $^{1}H\{^{11}B\}$ NMR spectrum of **4-Cu** in C_6D_6.

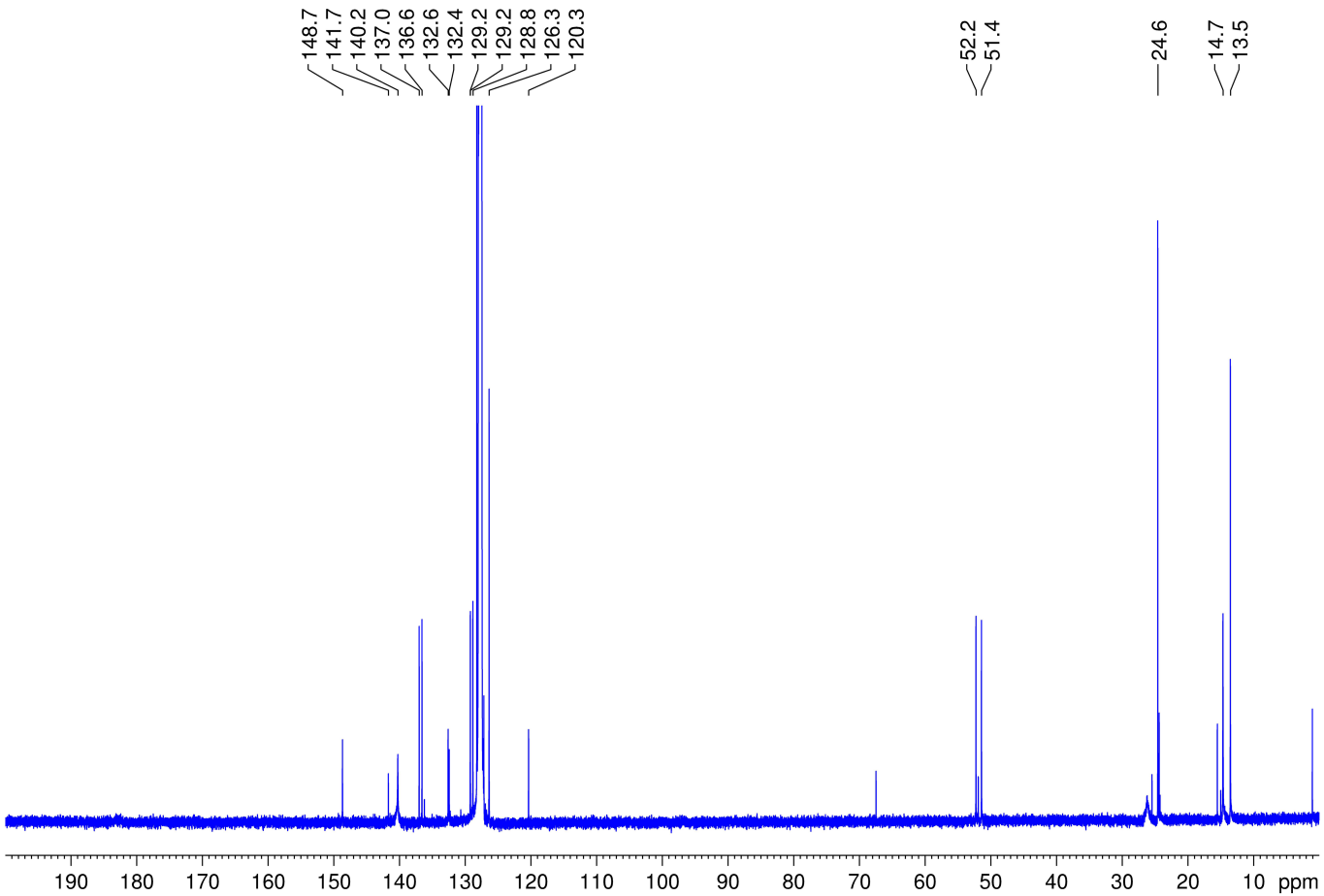


Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of **4-Cu** in C_6D_6.

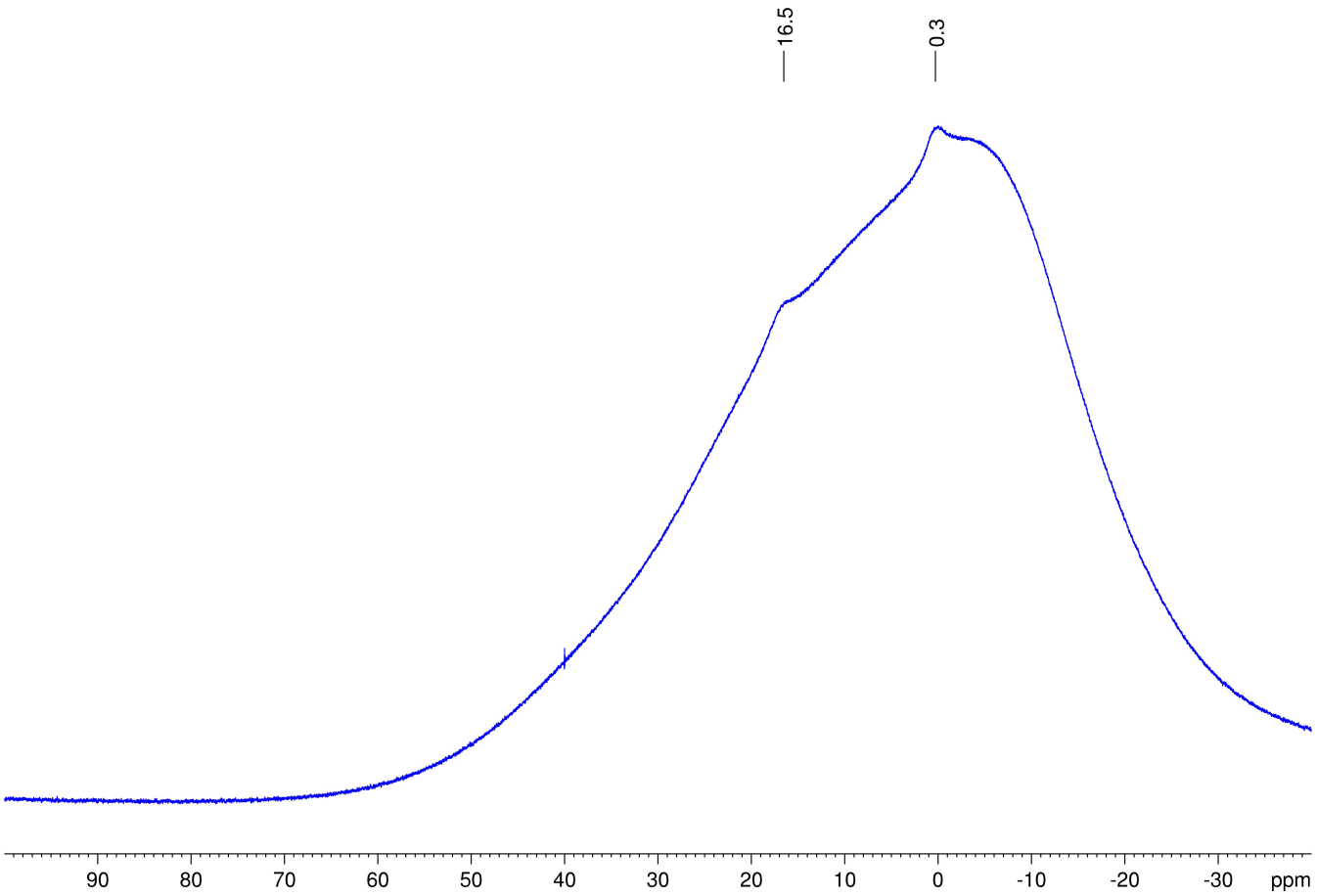


Fig. S9 $^{11}B\{^{1}H\}$ NMR spectrum of **4-Cu** in C_6D_6.

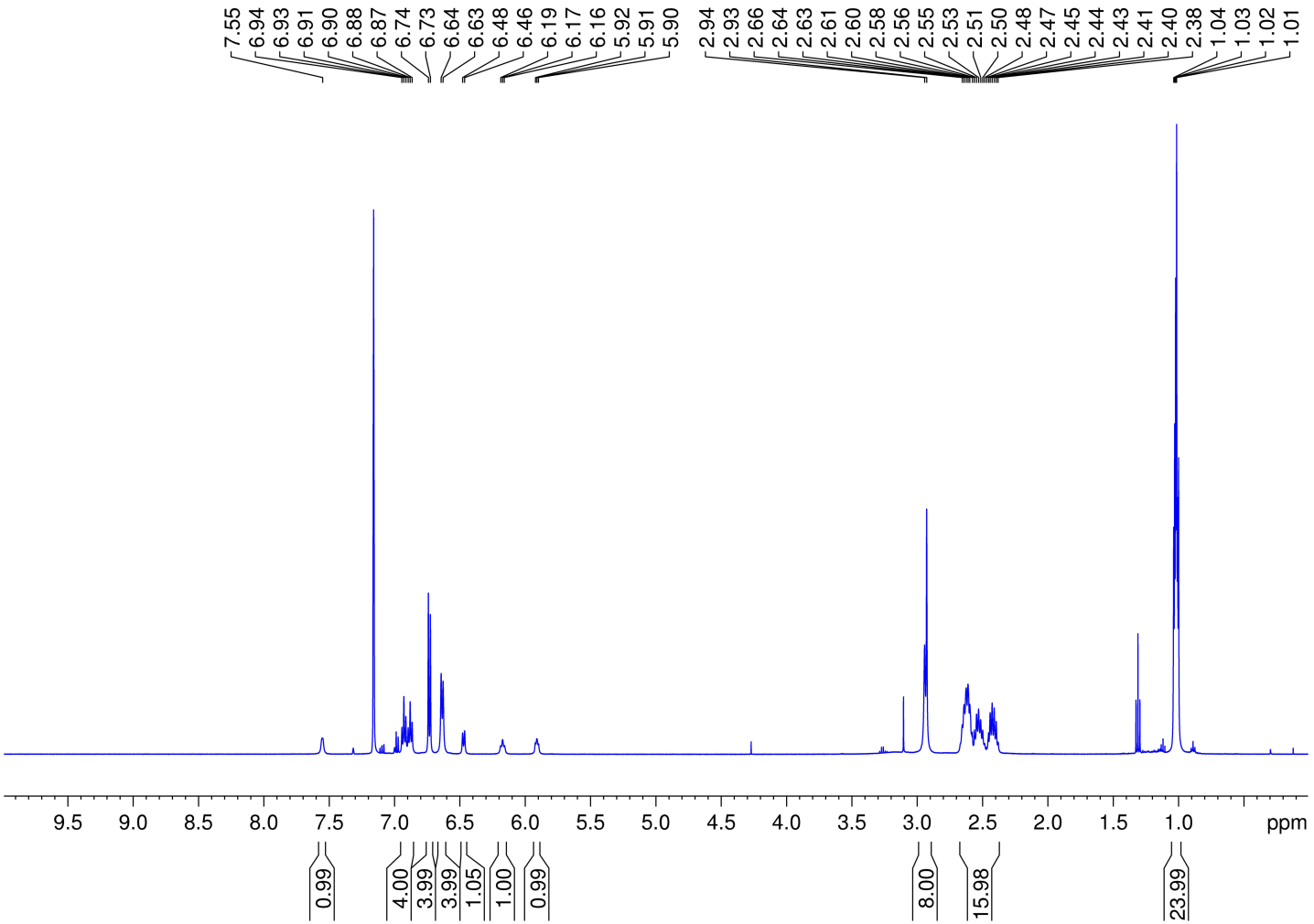


Fig. S10 $^{1}H\{^{11}B\}$ NMR spectrum of **3-CuC$_6$F$_5$** in C_6D_6.

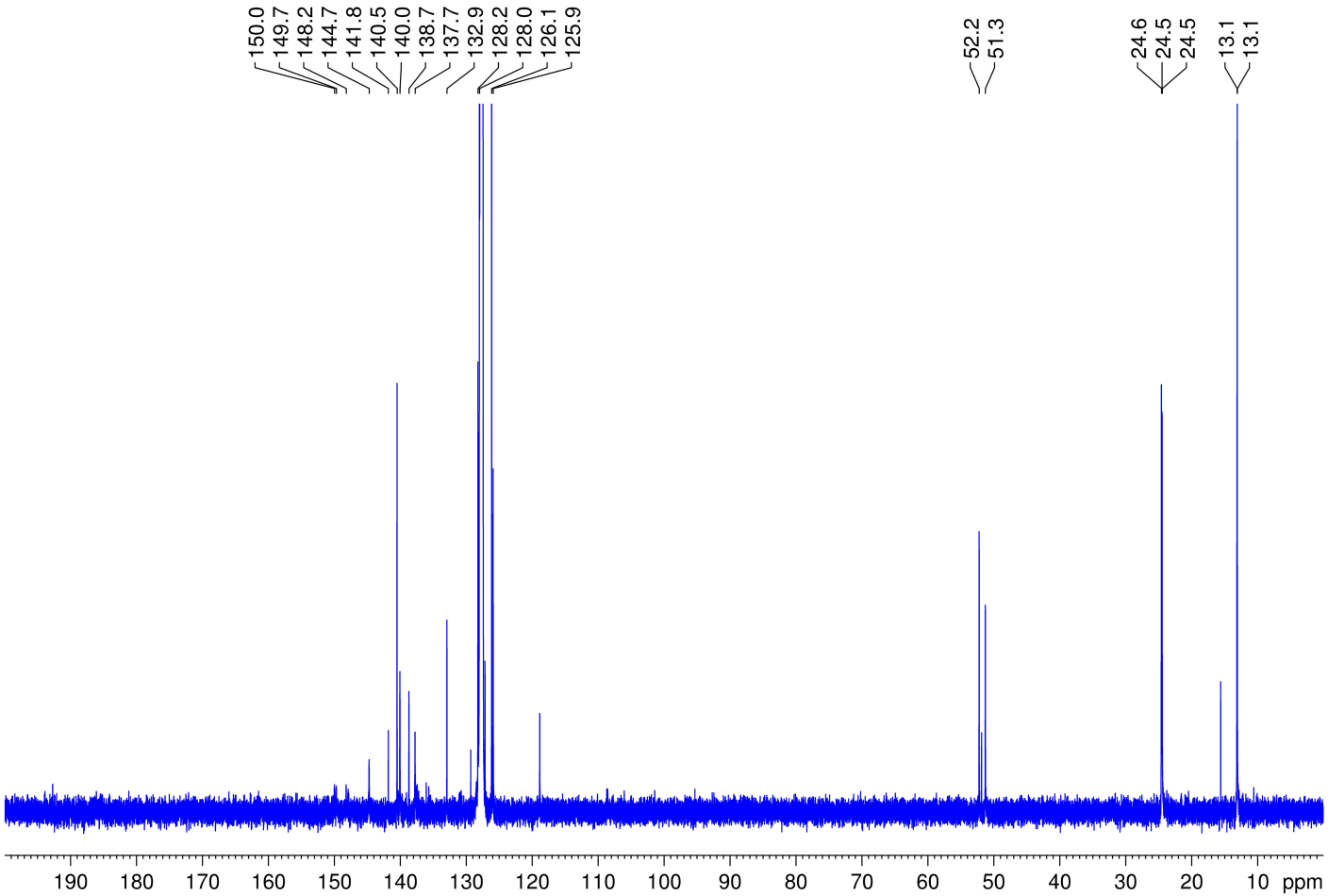


Fig. S11 $^{13}C\{^{1}H\}$ NMR spectrum of **3-CuC$_6$F$_5$** in C_6D_6.

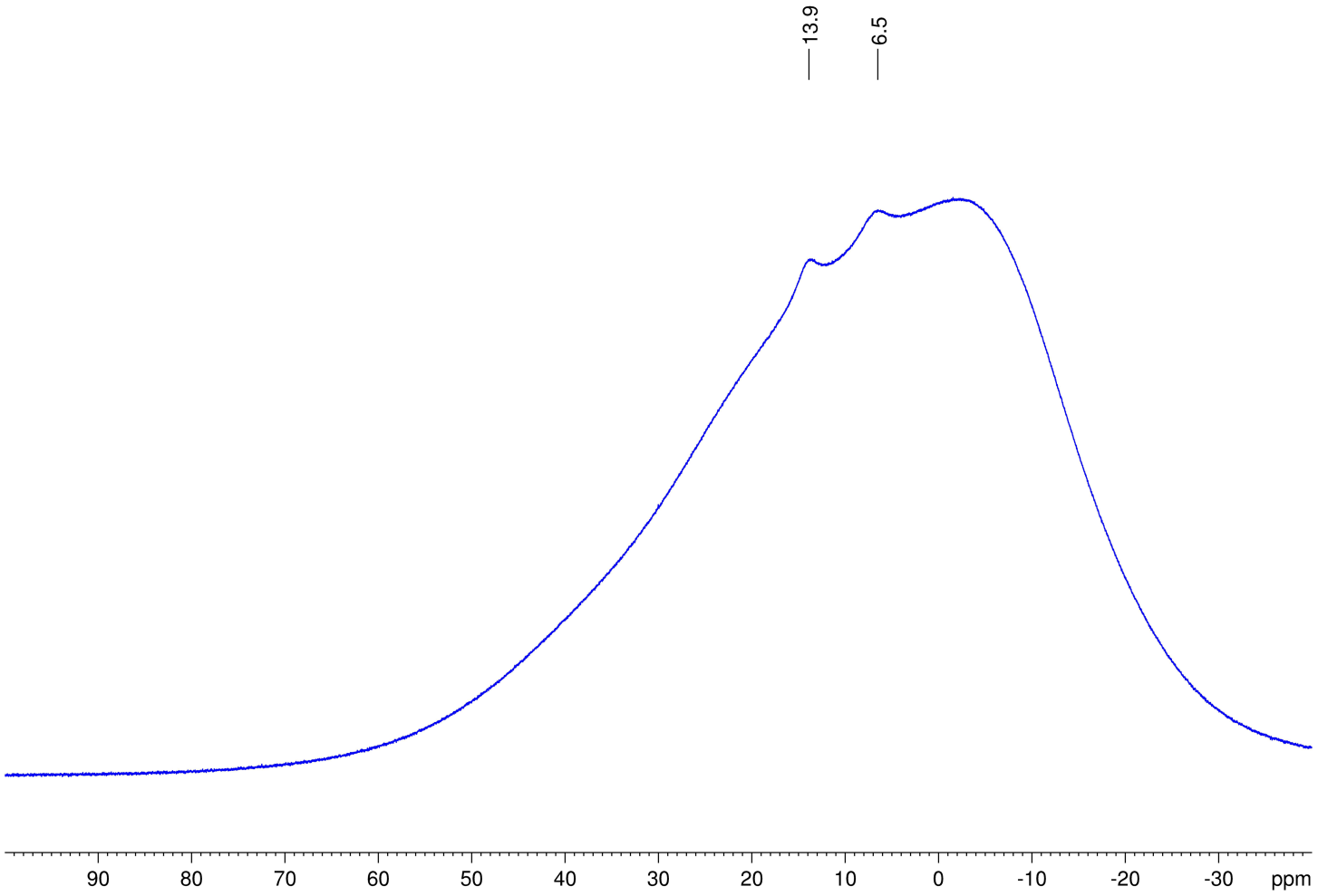


Fig. S12 $^{11}B\{^{1}H\}$ NMR spectrum of **3-CuC$_6$F$_5$** in C_6D_6.

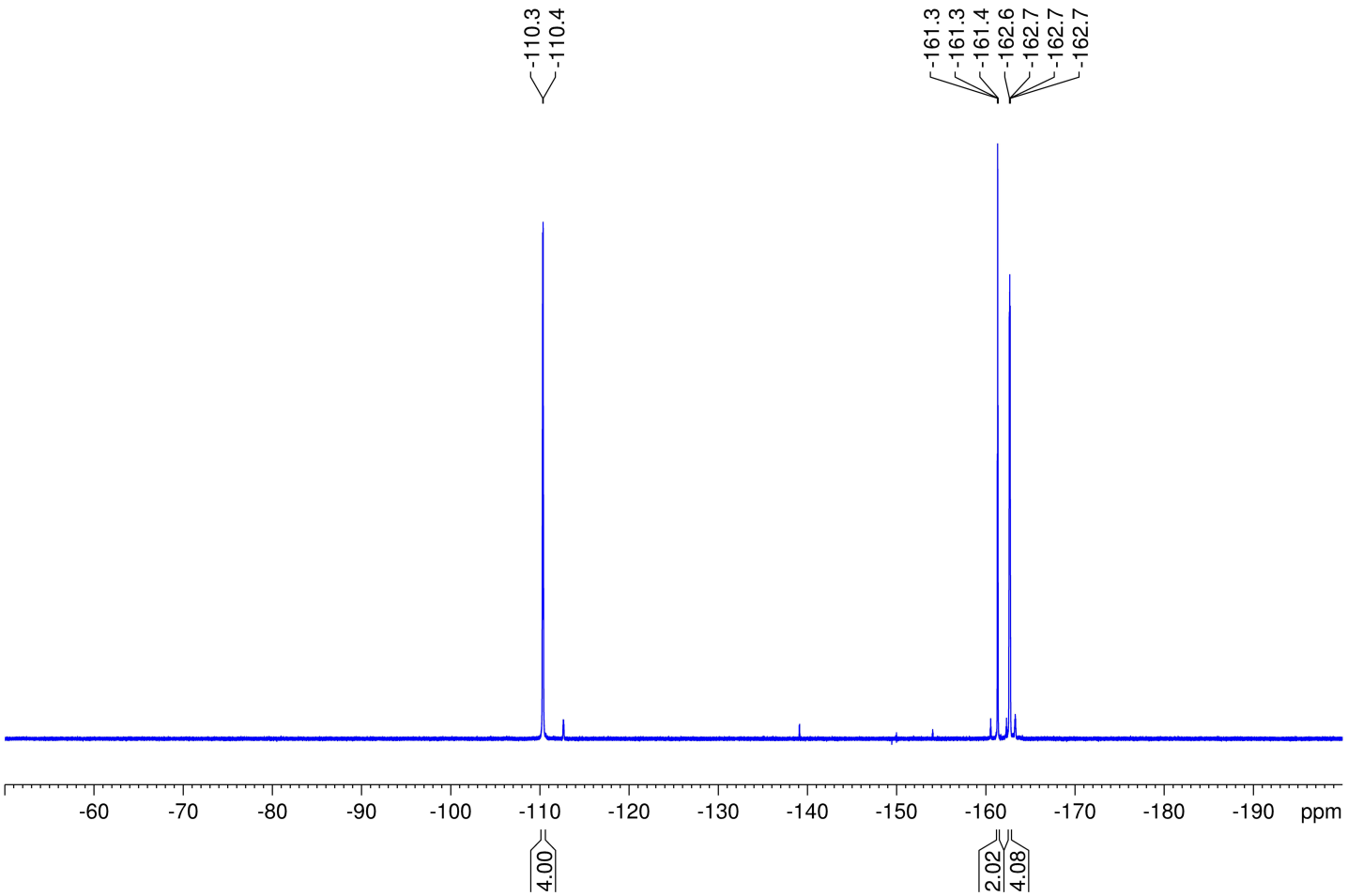


Fig. S13 ^{19}F NMR spectrum of **3-CuC$_6$F$_5$** in C_6D_6.

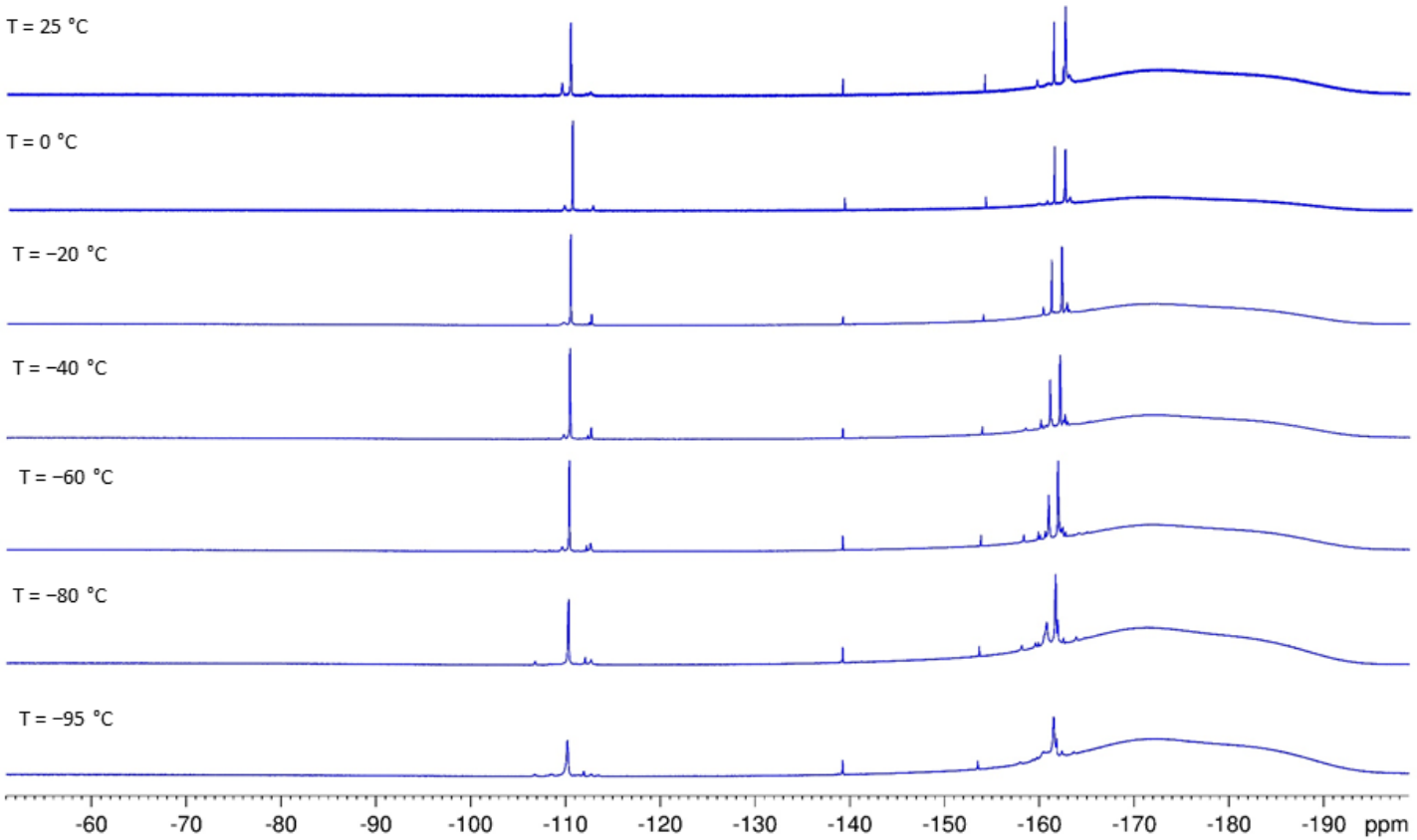


Fig. S14 ^{19}F VT NMR spectrum of **3-CuC$_6$F$_5$** in Toluene-*d*$_8$.

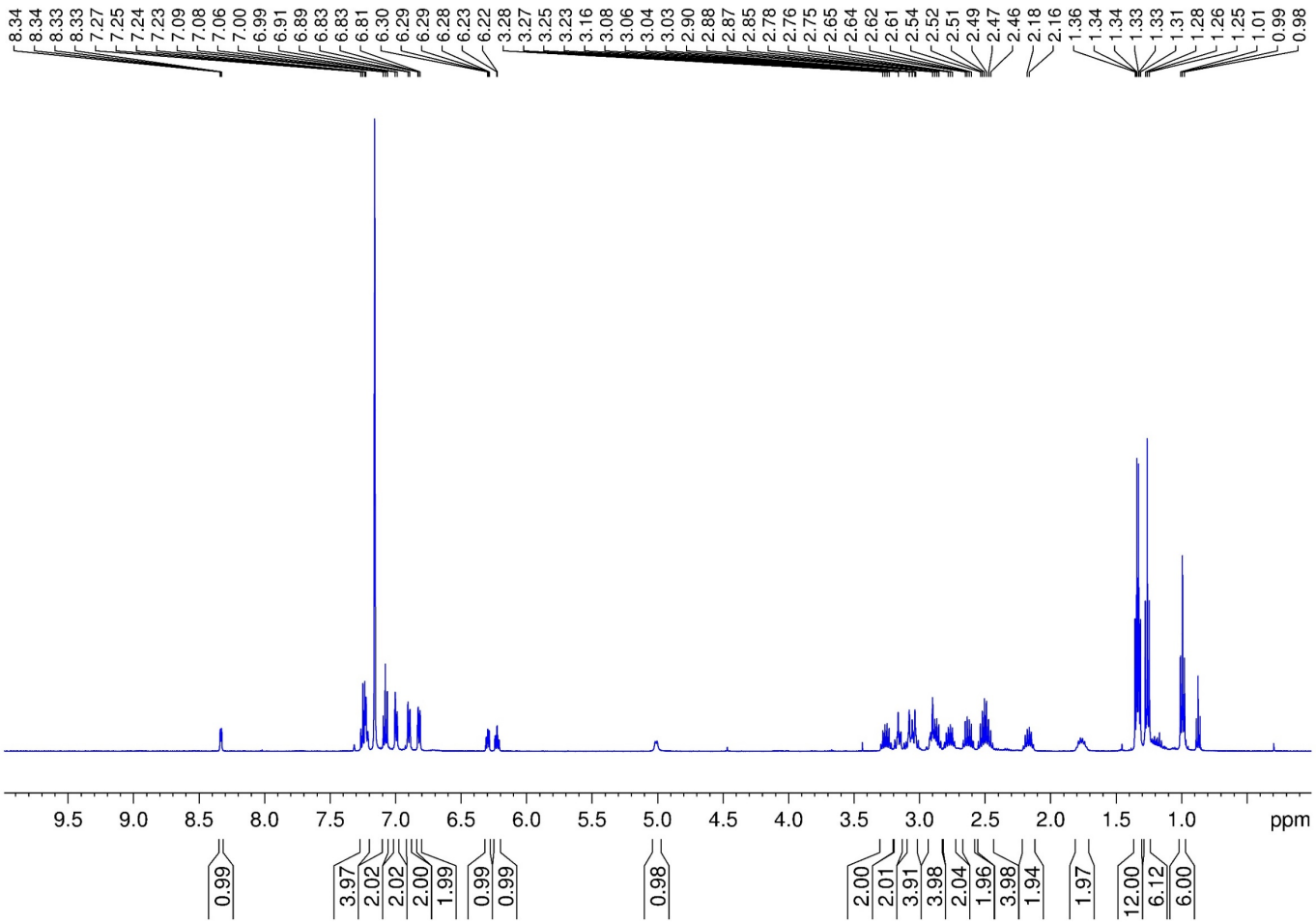


Fig. S15 $^{1}H\{^{11}B\}$ NMR spectrum of **2-AgCl** in C_6D_6.

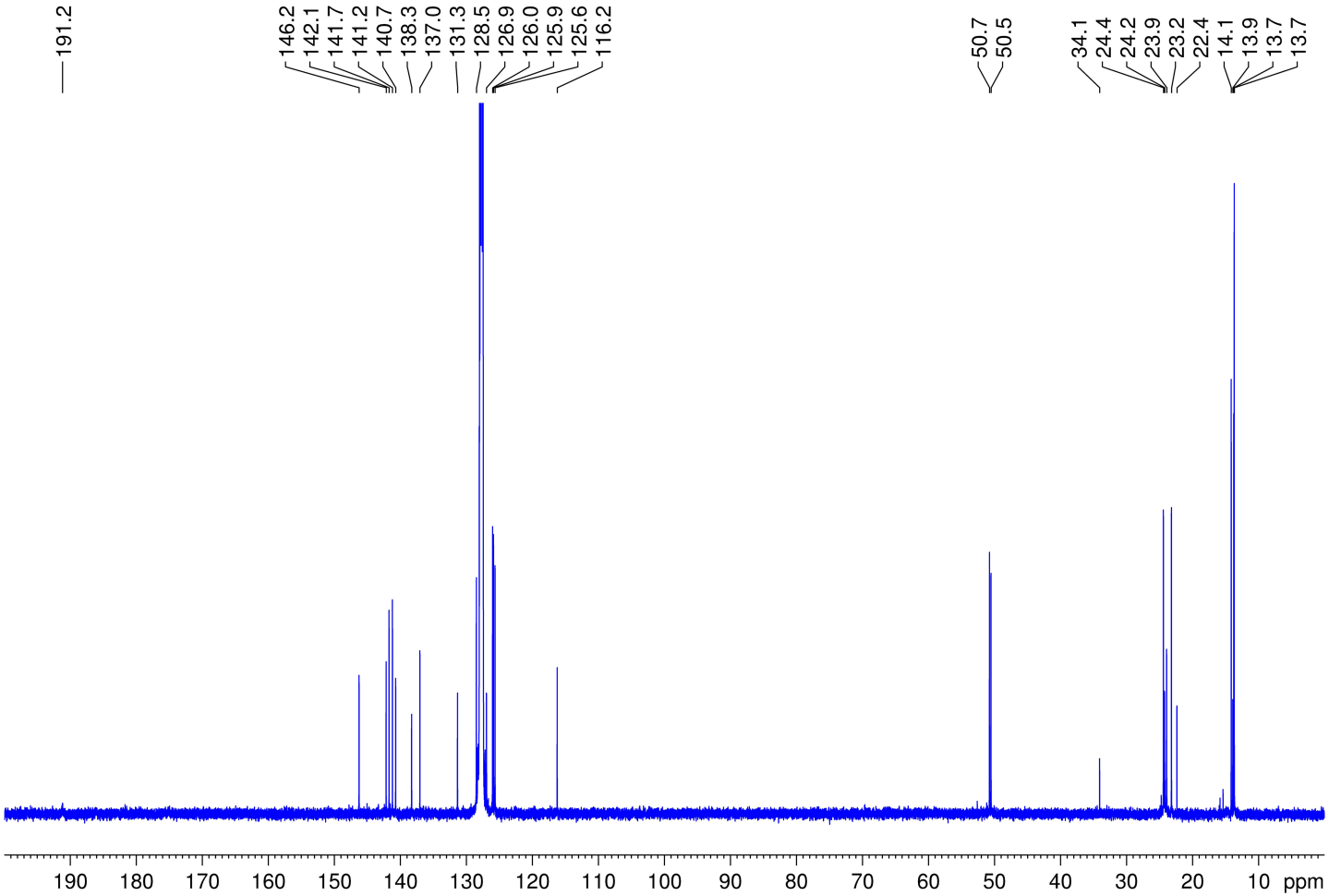


Fig. S16 $^{13}C\{^{1}H\}$ NMR spectrum of **2-AgCl** in C_6D_6.

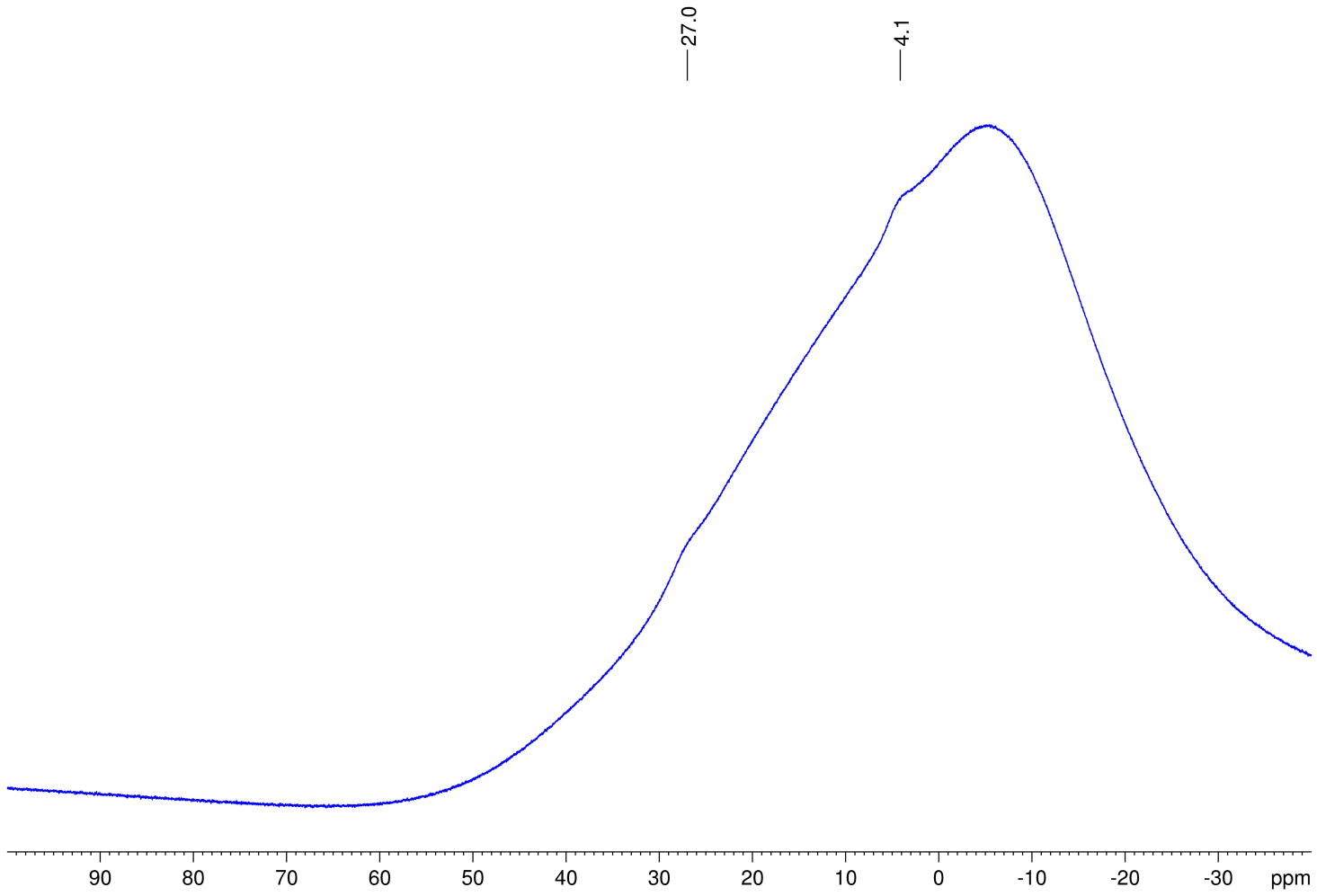


Fig. S17 $^{11}B\{^{1}H\}$ NMR spectrum of **2-AgCl** in C_6D_6.

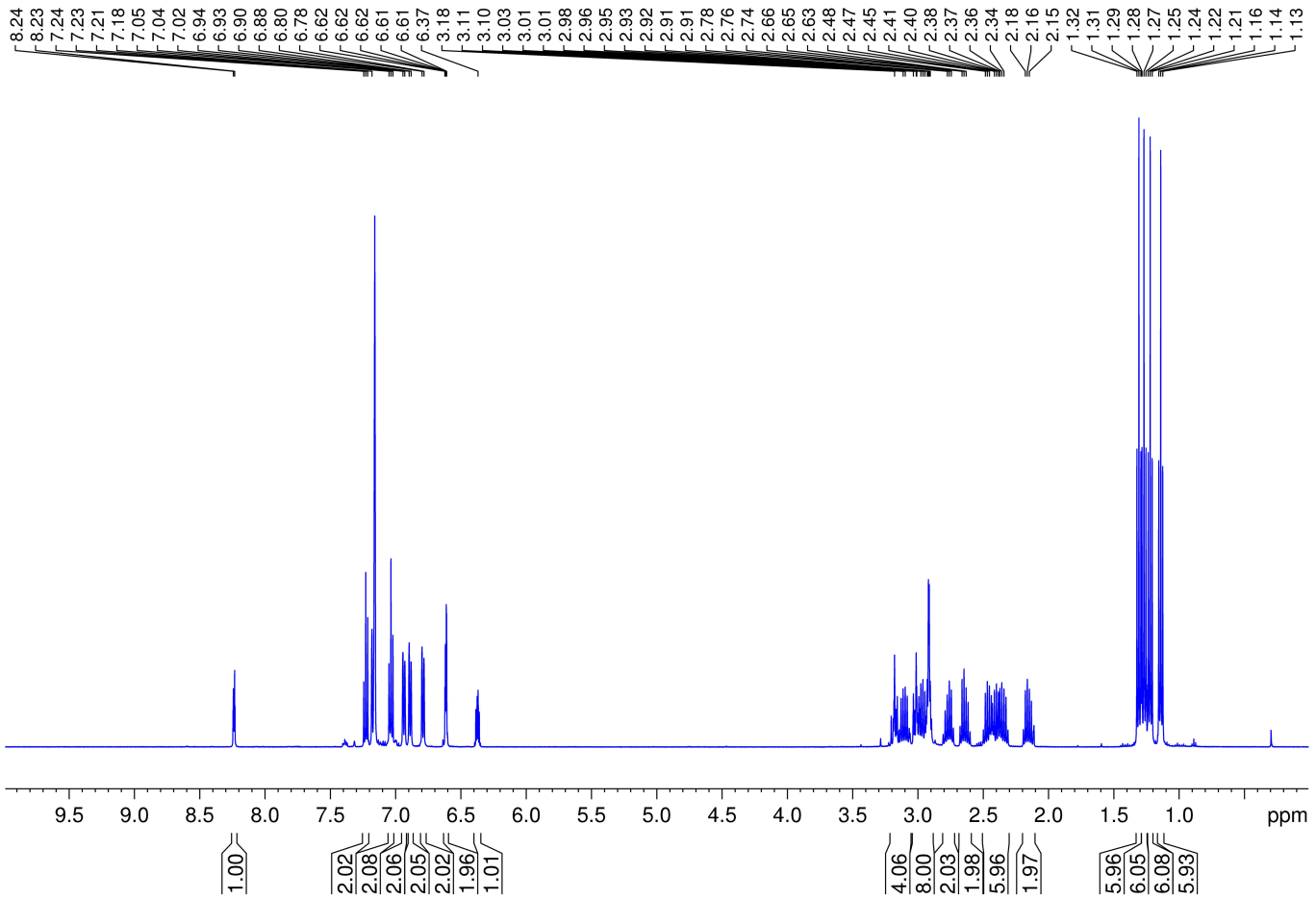


Fig. S18 $^{1}H\{^{11}B\}$ NMR spectrum of **2-AuCl** in C_6D_6.

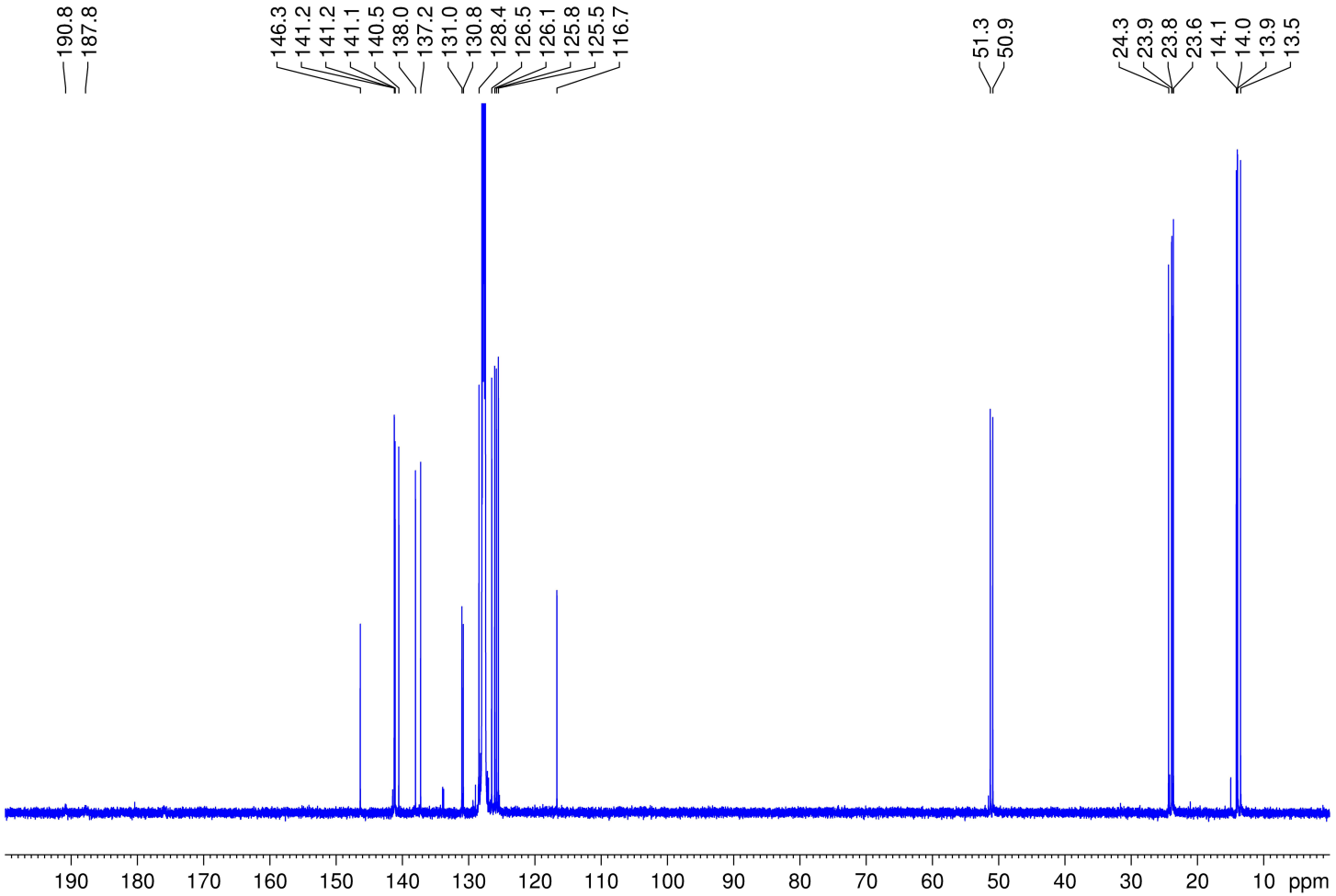


Fig. S19 $^{13}C\{^{1}H\}$ NMR spectrum of **2-AuCl** in C_6D_6.

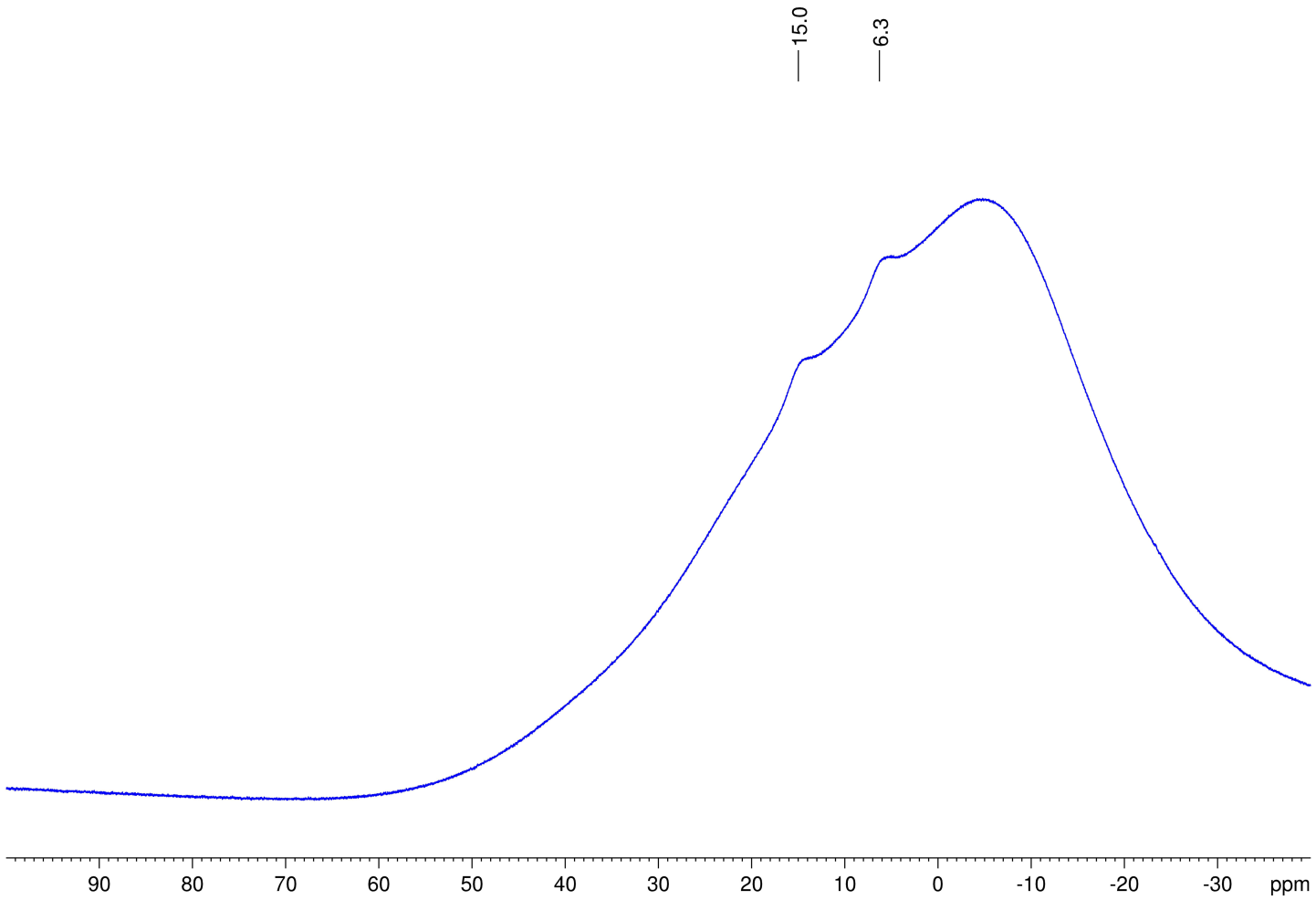


Fig. S20 $^{11}B\{^{1}H\}$ NMR spectrum of **2-AuCl** in C_6D_6.

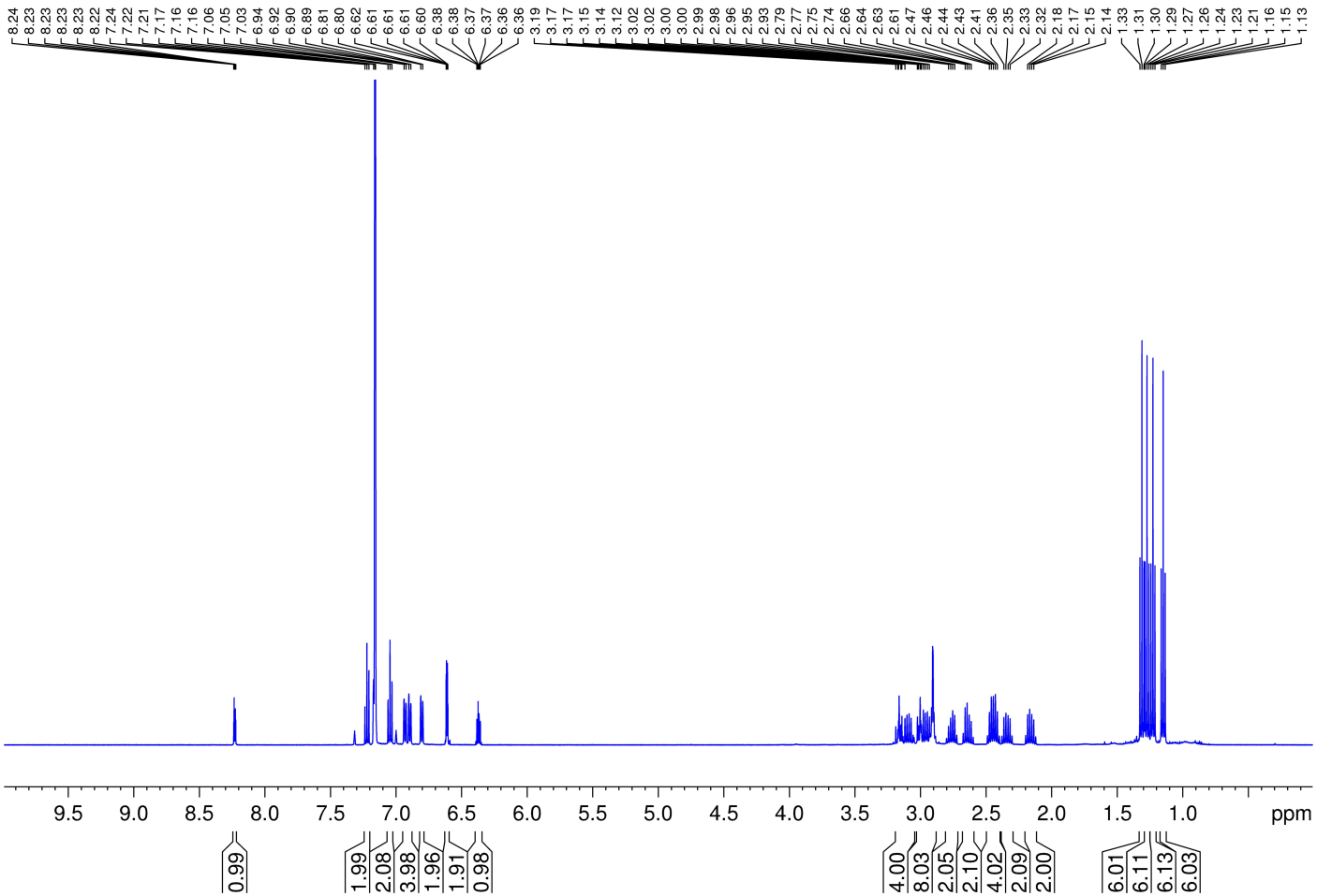


Fig. S21 $^{1}H\{^{11}B\}$ NMR spectrum of **2-AuBr** in C_6D_6.

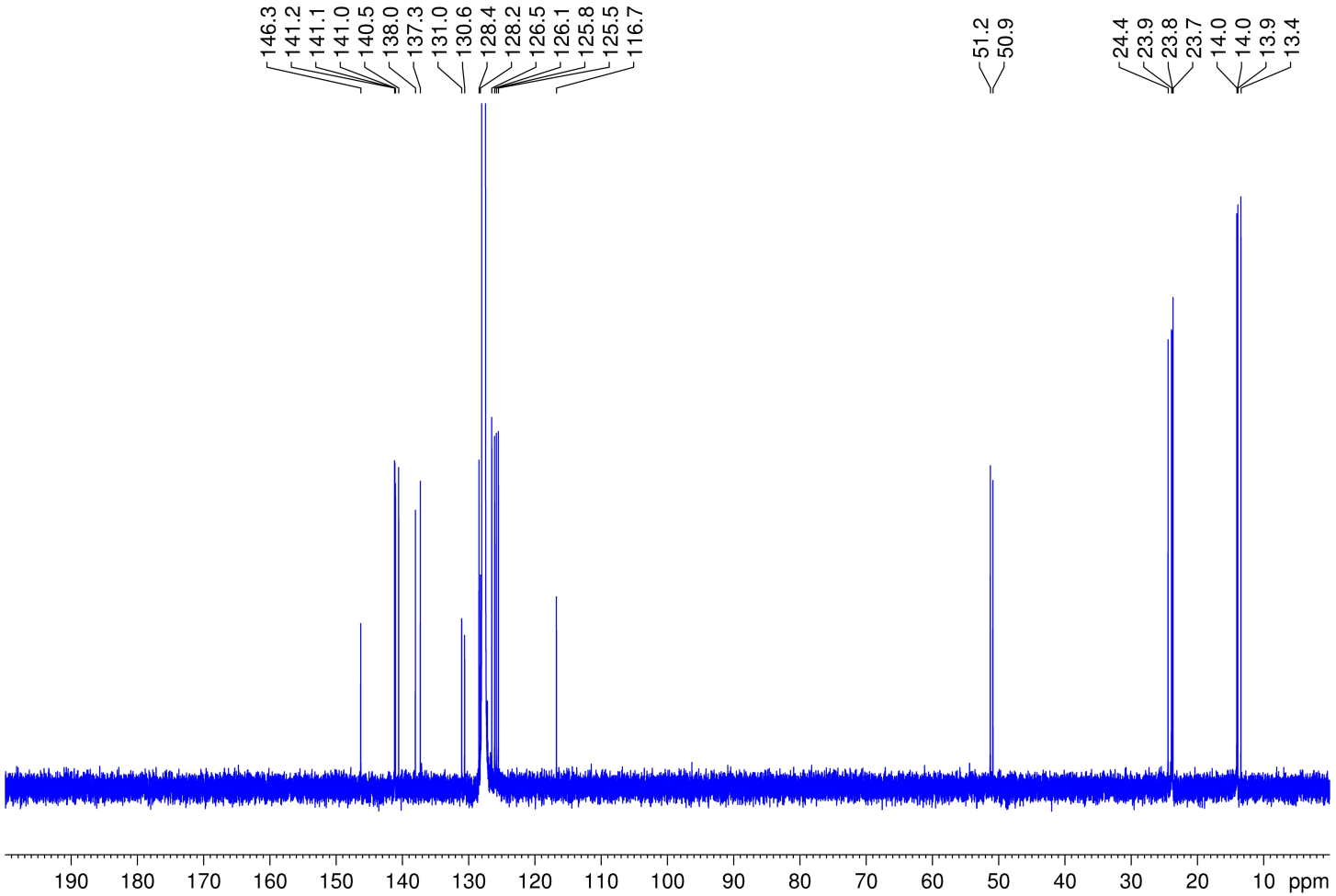


Fig. S22 $^{13}C\{^{1}H\}$ NMR spectrum of **2-AuBr** in C_6D_6.

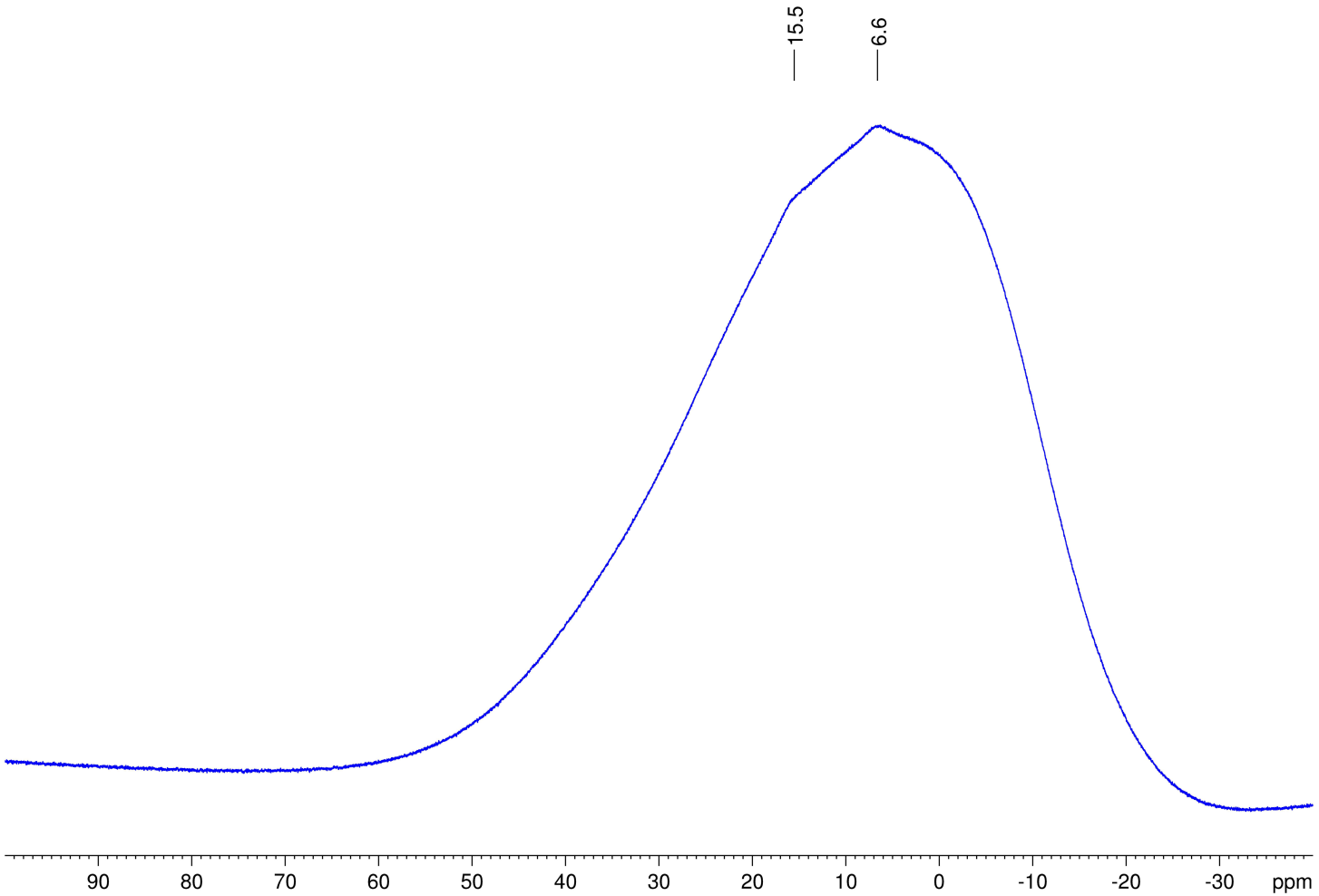


Fig. S23 $^{11}B\{^{1}H\}$ NMR spectrum of **2-AuBr** in C_6D_6.

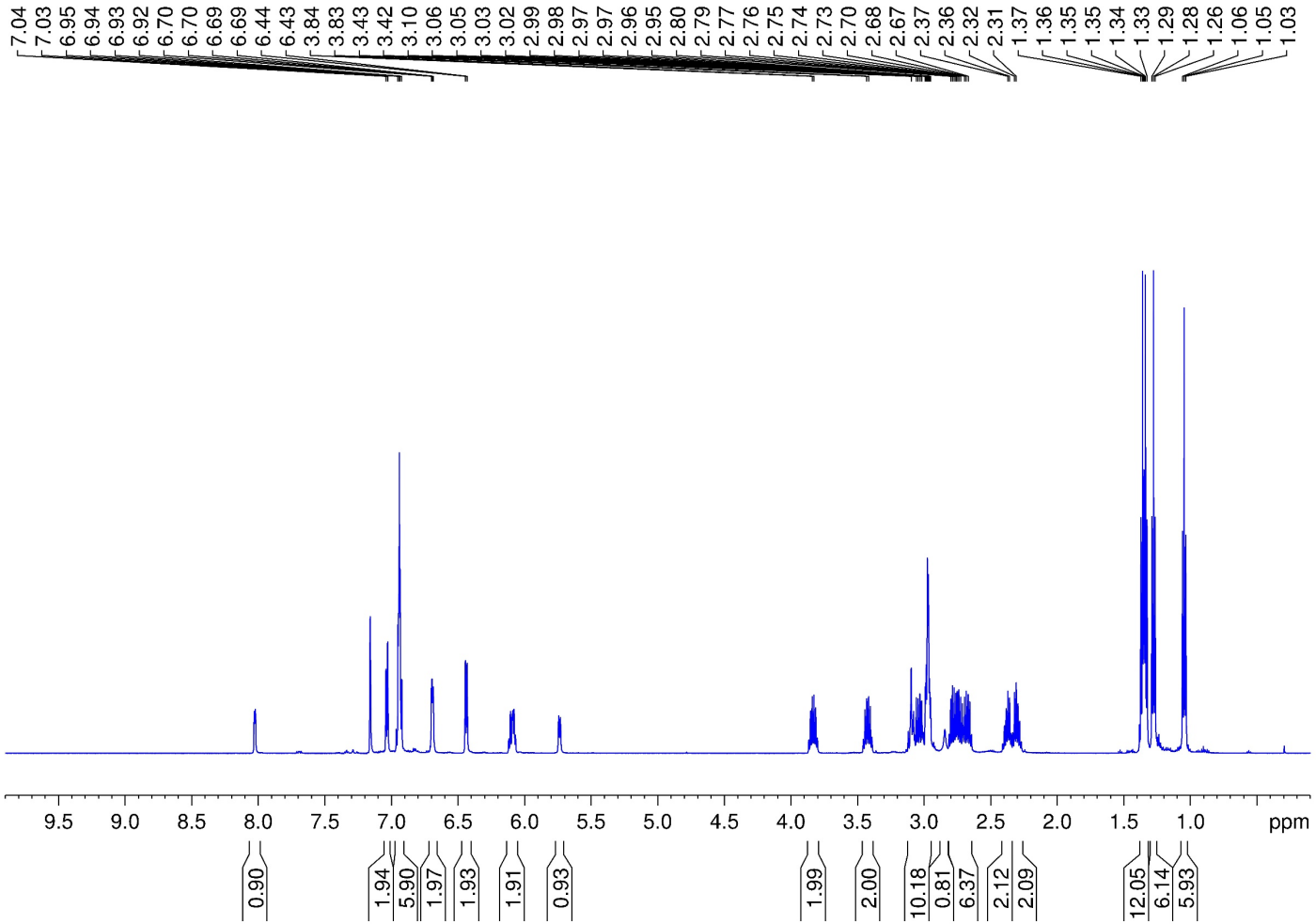


Fig. S24 $^{1}H\{^{11}B\}$ NMR spectrum of **3-CuAu** in C_6D_6.

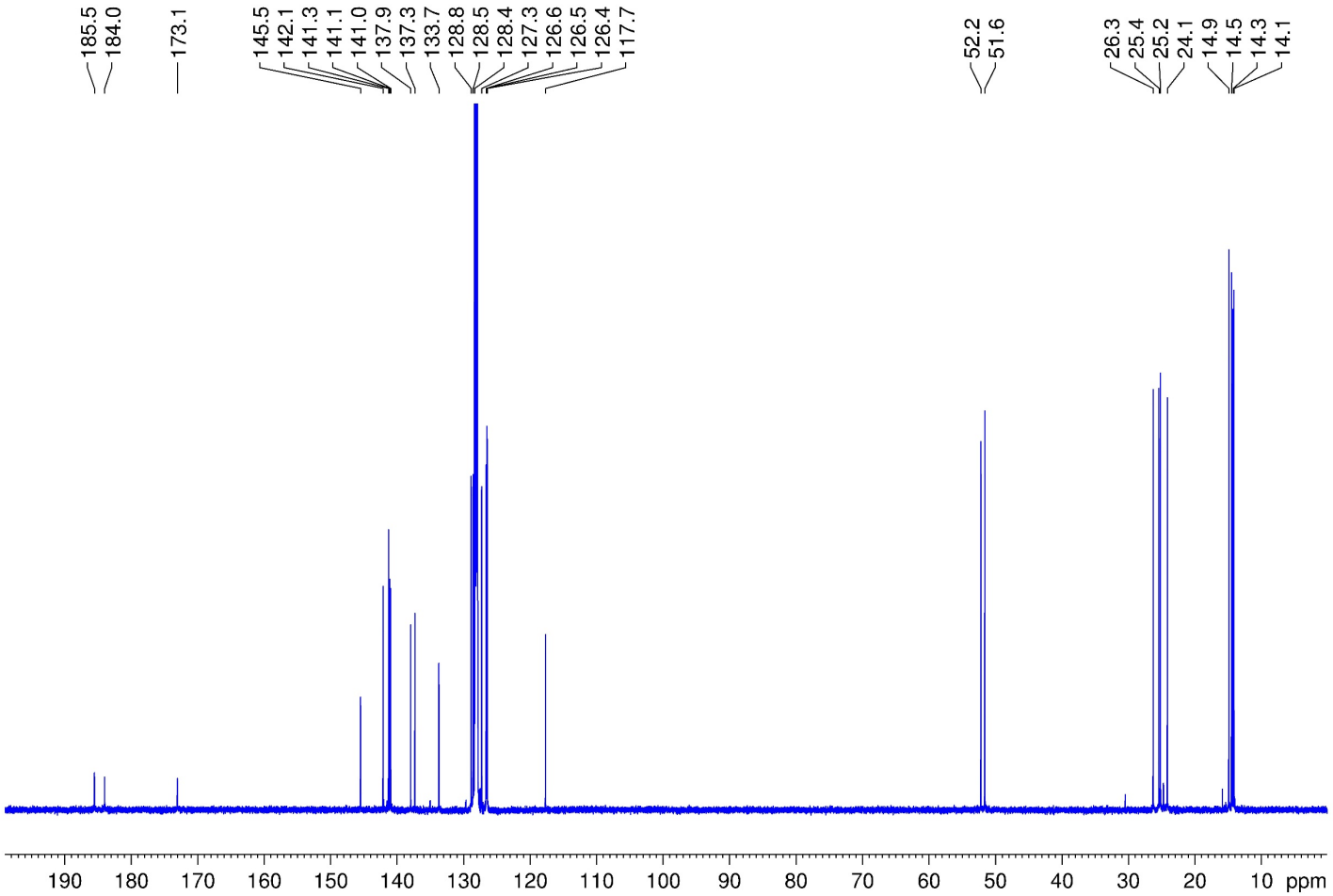


Fig. S25 $^{13}C\{^{1}H, ^{11}B\}$ NMR spectrum of **3-CuAu** in C_6D_6.

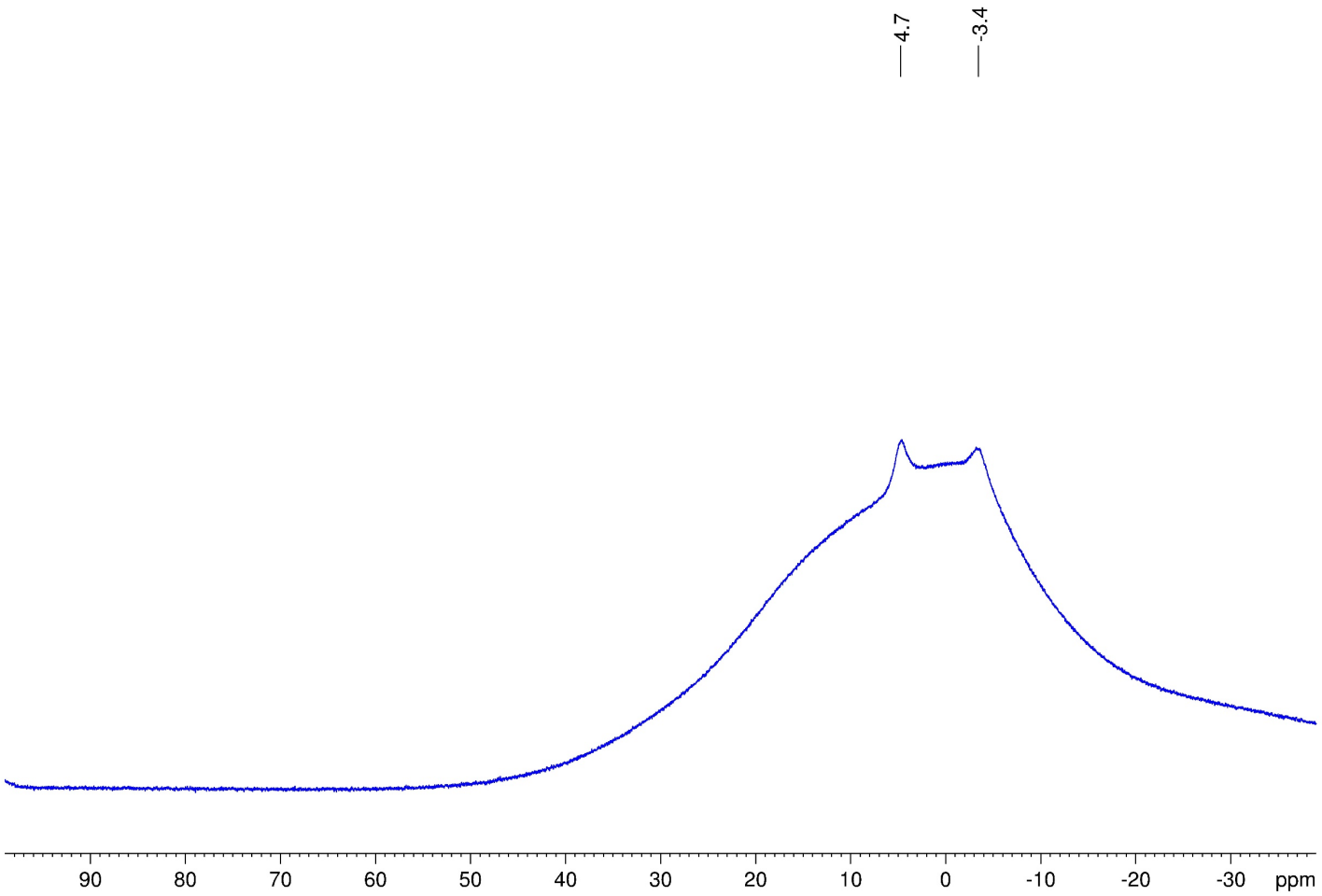


Fig. S26 $^{11}B\{^{1}H\}$ NMR spectrum of **3-CuAu** in C_6D_6.

UV-vis spectra

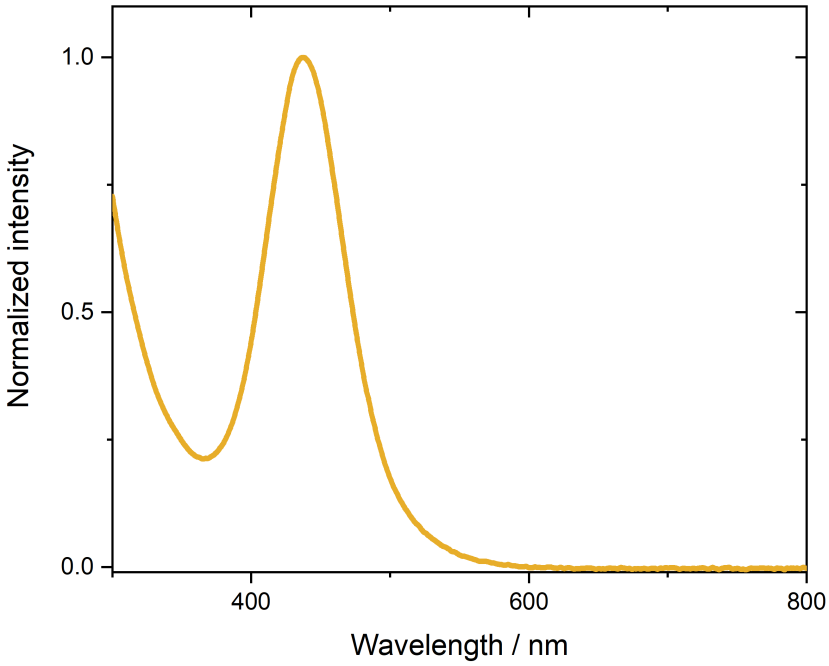


Fig. S27 UV-vis spectrum of **2-CuCl** in C_6H_6.

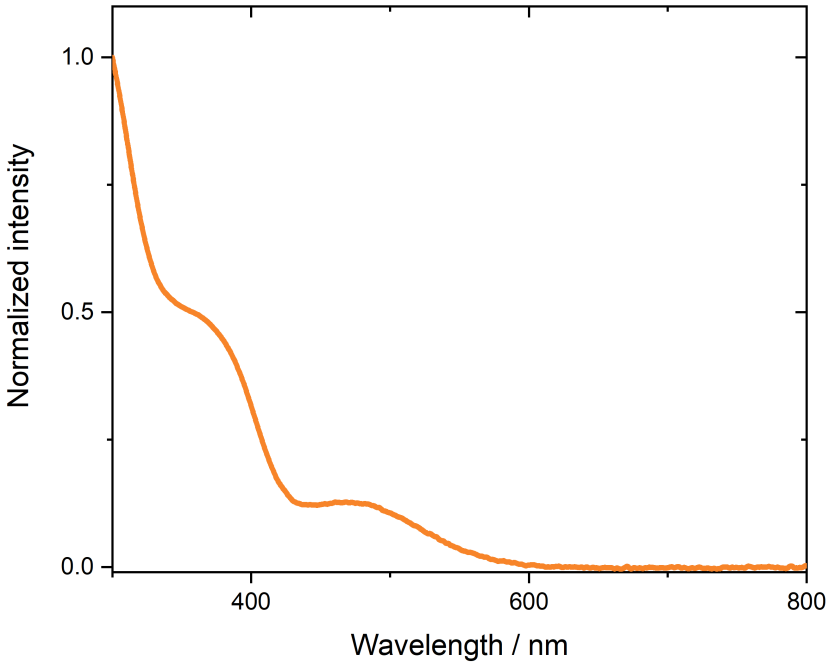


Fig. S28 UV-vis spectrum of **3-CuCl** in C_6H_6.

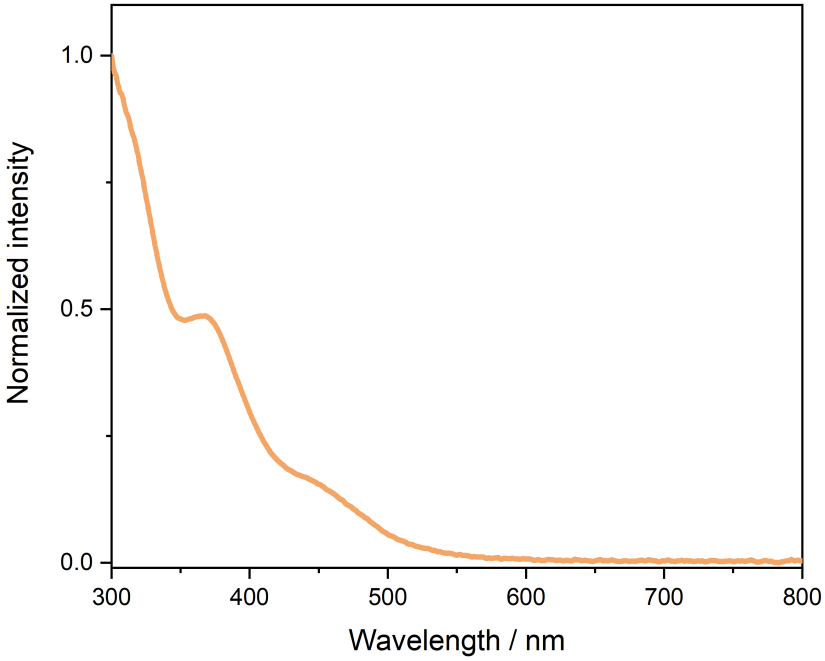


Fig. S29 UV-vis spectrum of **4-Cu** in C_6H_6.

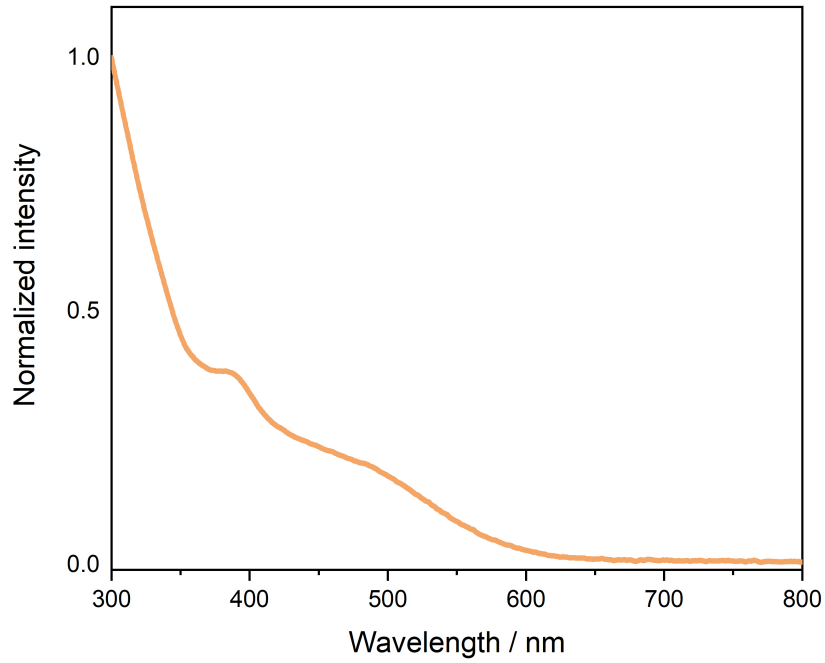


Fig. S30 UV-vis spectrum of **3-CuC$_6$F$_5$** in C_6H_6.

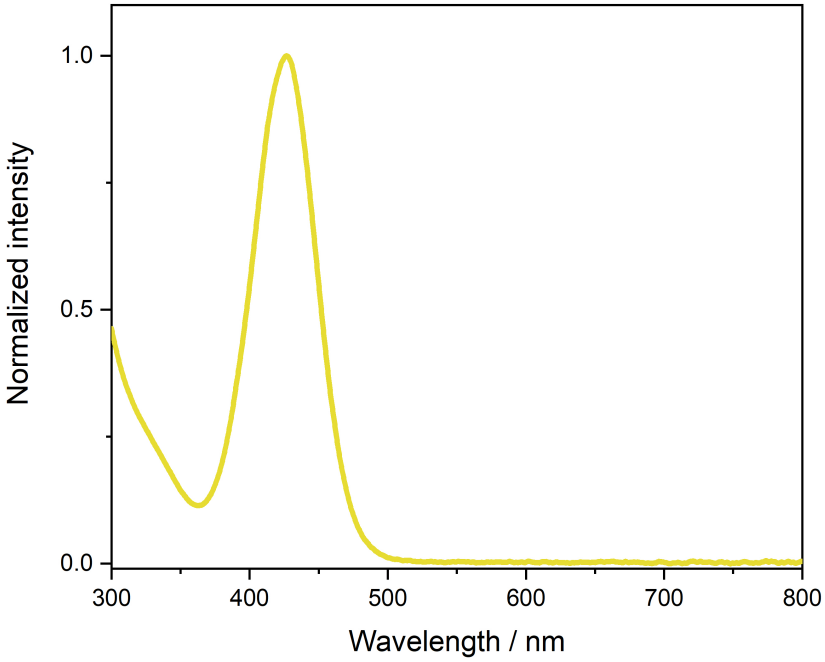


Fig. S31 UV-vis spectrum of **2-AgCl** in C_6H_6.

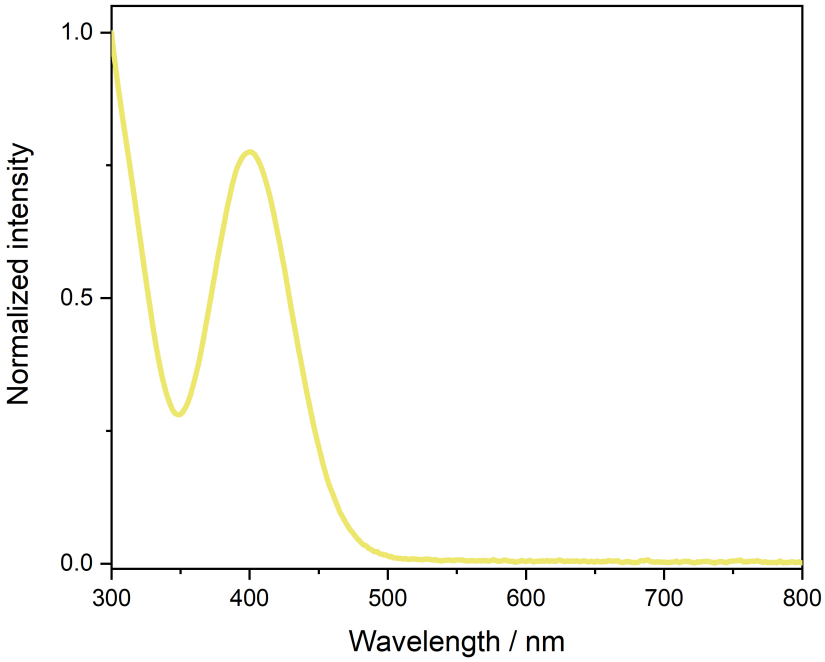


Fig. S32 UV-vis spectrum of **2-AuCl** in C_6H_6.

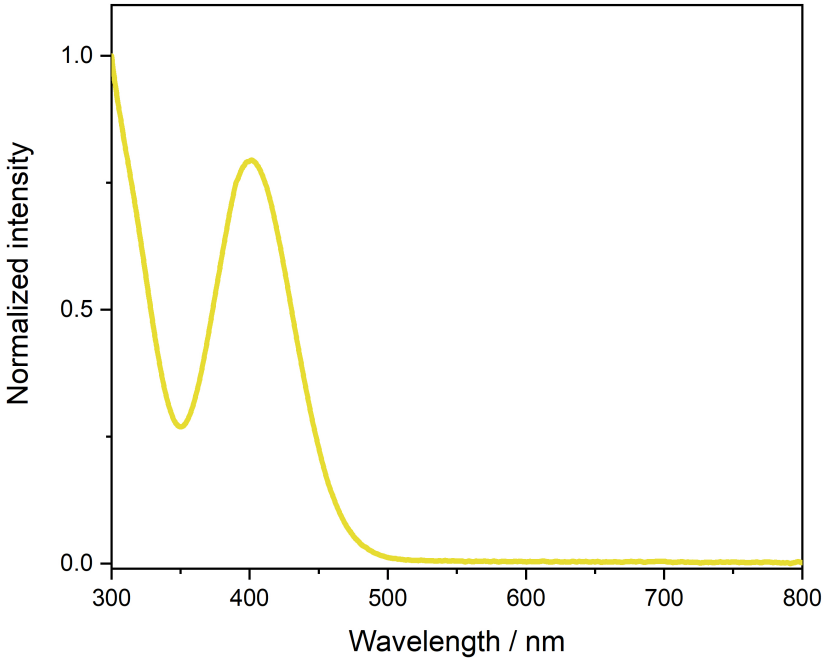


Fig. S33 UV-vis spectrum of **2-AuBr** in C_6H_6.

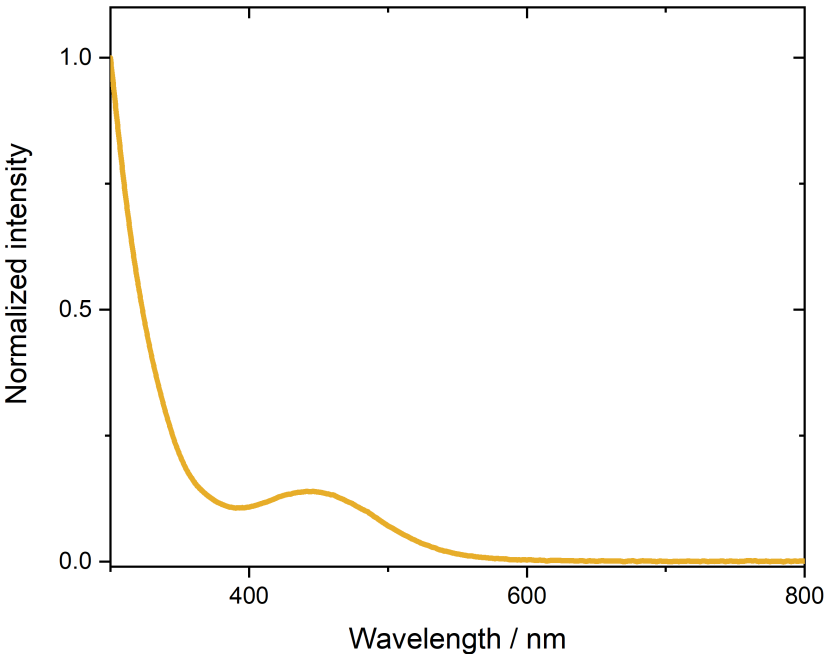


Fig. S34 UV-vis spectrum of **3-CuAu** in C_6H_6.

X-ray crystallographic data

The crystal data of **4-Cu**, **2-AuCl**, **2-AuBr** and **3-CuAu** were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **3-CuC$_6$F$_5$** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **2-AuCl**, **2-CuCl** and **3-CuCl** was collected on a *XtaLAB Synergy Dualflex HyPix* diffractometer with a Hybrid Pixel array detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,[6] refined with the ShelXL program[7] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC numbers: 2290304 (**2-CuCl**), 2290303 (**3-CuCl**), 2290301 (**3-CuC$_6$F$_5$**), 2290307 (**4-Cu**), 2290309 (**2-AgCl**), 2290306 (**2-AuCl**), 2290302 (**2-AuBr**), 2290308 (**3-CuAu**)). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

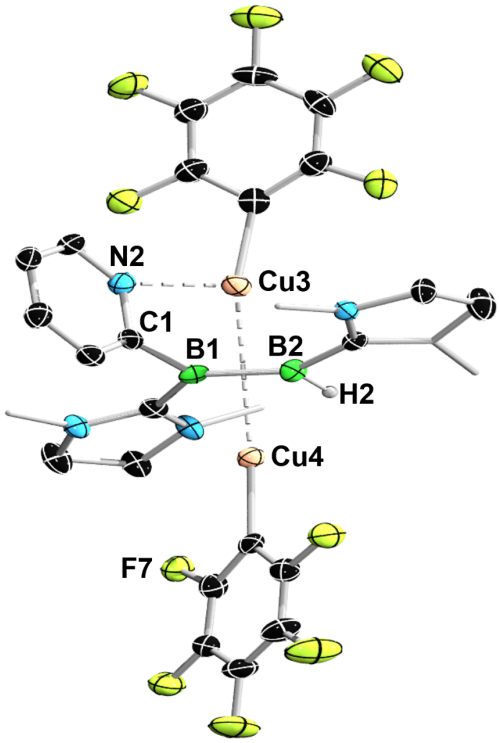


Fig. S35 Crystallographically-derived structure of **3-CuC$_6$F$_5$**. Ellipsoids are shown at the 50% probability level. Aryl groups of the NHC units and all hydrogen atoms except that bound to the boron are omitted for clarity.

Special refinement details for 2-CuCl: All hydrogen atoms except H2_1 were assigned to idealized positions. The coordinates of H2_1 were refined freely. **Crystal data for 2-CuCl:** $C_{51}H_{65}B_2ClCuN_5$, M_r = 868.69, red block, 0.250×0.130×0.090 mm^3, monoclinic space group $P2_1/c$, a = 13.70400(10) Å,

b = 13.75780(10) Å, c = 24.4253(2) Å, α = 90°, β = 101.3180(10)°, γ = 90°, V = 4515.51(6) Å^3, Z = 4, ρ_{calcd} = 1.278 g·cm^{-3}, μ = 1.531 mm^{-1}, F(000) = 1848, T = 100(2) K, R_1 = 0.0383, wR_2 = 0.0910, 9291 independent reflections [2θ ≤ 150.656°] and 553 parameters.

Special refinement details for 3-CuCl: All hydrogen atoms except H2_1 were assigned to idealized positions. The coordinates of H2_1 were refined freely. The displacement parameters of atoms of the residues PYR were restrained to the same value with similarity restraint SIMU. The 1–2 and 1–3 distances in PYR residues were restrained to the same values with SAME. **Crystal data for 3-CuCl:** $C_{51}H_{63}B_2Cl_2Cu_2N_5$, M_r = 965.66, red block, 0.310×0.130×0.070 mm^3, monoclinic space group $P2_1/c$, a = 18.1438(2) Å, b = 11.81800(10) Å, c = 23.6127(2) Å, α = 90°, β = 112.1500(10)°, γ = 90°, V = 4689.46(8) Å^3, Z = 4, ρ_{calcd} = 1.368 g·cm^{-3}, μ = 2.473 mm^{-1}, F(000) = 2024, T = 100(2) K, R_1 = 0.0581, wR_2 = 0.1333, 8530 independent reflections [2θ ≤136.48°] and 625 parameters.

Special refinement details for 4-Cu: All hydrogen atoms except H1 and H2 were assigned to idealized positions. The coordinates of H1 and H2 were refined freely. The unit cell contains 2.2381 benzene molecules, which were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[8] The displacement parameters of atoms of the disordered [$CuCl_2$] moieties were restrained to the same value with similarity restraint SIMU and RIGU. The distances between atoms of the disordered [$CuCl_2$] moieties were restrained during refinement to the same value with the SADI restraint. **Crystal data for 4-Cu:** $C_{63}H_{64}B_2Cl_4Cu_4N_5$[+2.2381($C_6H_6$)], M_r = 1408.2, orange block, 0.156×0.089×0.078 mm^3, triclinic space group $P\bar{1}$, a = 15.0923(11) Å, b = 17.1901(14) Å, c = 25.434(2) Å, α = 102.384(3)°, β = 91.280(2)°, γ = 90.589(3)°, V = 6442.7(9) Å^3, Z = 4, ρ_{calcd} = 1.452 g·cm^{-3}, μ = 1.515 mm^{-1}, F(000) = 2920, T = 293(2) K, R_1 = 0.1387, wR_2 = 0.2759, 25361 independent reflections [2θ≤52.044°] and 1293 parameters.

Special refinement details for 3-CuC$_6$F$_5$: All hydrogen atoms except H2_1 were assigned to idealized positions. The coordinates of H2_1 were refined freely. One diethylphenyl moiety showed disorder. The atomic displacement parameters (ADPs) of overlapping atoms from different PARTs (C1, C2, C3, C4, C5, C6, C7, C8, C9, C10 of RESIs 11/111) were restrained using similarity restraint SIMU and rigid body restraint RIGU. The N5_7-C1_11 and The N5_7-C1_111 distances between the imidazole and the diethylphenyl moieties were restrained using same distance restraint SADI. **Crystal data for 3-CuC$_6$F$_5$:** $C_{63}H_{65}B_2Cu_2F_{10}N_5$, M_r = 1230.90, red plate, 0.418×0.248×0.15 mm^3, triclinic space group $P\bar{1}$, a = 11.432(4) Å, b = 14.578(7) Å, c = 17.780(5) Å, α = 93.226(16)°, β = 107.118(10)°, γ = 94.524(14)°, V = 2813.3(18) Å^3, Z = 2, ρ_{calcd} = 1.453 g·cm^{-3}, μ = 0.835 mm^{-1}, F(000) = 1272, T = 100(2) K, R_1 = 0.1118, wR^2 = 0.1480, 11078 independent reflections [2θ ≤ 52.042°] and 819 parameters.

Special refinement details for 2-AgCl: All hydrogen atoms except H1_1 were assigned to idealized positions. The coordinates of H1_1 were refined freely. The displacement parameters of atoms C1_8 and C1_18 were constrained to the same value with EADP keyword. The coordinates of atoms C1_8 and C1_18 were constrained to the same value. The displacement parameters of atoms C1_10 to C6_10, C1_8 to N6_18, C1_7 to C10_17, C1_6 to C10_16, C1_5 to C10_15 and C1_4 to C10_14 were restrained to the same value with similarity restraint SIMU. The 1–2 and 1–3 distances in the pyridyl group were restrained to the same values with SAME. Reflections [-4 0 4] and [0 0 6] were omitted. **Crystal data for 2-AgCl:** $C_{60}H_{74}AgB_2ClN_5$, M_r = 1030.18, yellow block, 0.094×0.076×0.060 mm^3, monoclinic space group *I*2/*a*, a = 23.88640(10) Å, b = 12.68250(10) Å, c = 36.1057(2) Å, α = 90°, β = 95.5220(10)°, γ = 90°, V = 10887.08(12) Å^3, Z = 8, ρ_{calcd} = 1.257 g·cm^{-3}, μ = 3.735 mm^{-1}, F(000) = 4344, T = 99.99(11) K, R_1 = 0.0396, wR_2 = 0.0988, 11200 independent reflections [2θ ≤150.992°] and 1066 parameters.

Special refinement details for 2-AuCl: All hydrogen atoms except H1_1 were assigned to idealized positions. The coordinates of H1_1 were refined freely. The displacement parameters of atoms C1_7 to C7_7 and C1_17 to C7_17 were restrained to the same value with similarity restraint SIMU. The displacement parameters of atoms C1_8 to C2_18 were restrained to the same value with similarity restraint SIMU. The distances between atoms C1_8, C2_8, C1_18, C2_18, C6_4 were restrained during refinement to the same value with the SADI restraint. The Uii displacement parameters of atoms C2_8 and C2_18 were restrained with ISOR keyword to approximate isotropic behavior. The displacement parameters of atoms C1_5 and C1_15 were constrained to the same value with keyword EADP. The coordinates of atoms C1_5 and C1_15 were constrained to the same position. The displacement parameters of atoms C1_5 to C6_15 were restrained to the same value with similarity restraint SIMU. The atomic displacement parameters of atoms C1_5 to C6_15 were restrained with RIGU keyword in ShelXL input. The 1-2 and 1-3 distances of residues 8 and 18 were restrained to the same values with SAME. The following reflections were omitted as they were covered by the beamstop: [1 0 0], [0 1 1], [0 2 1], [1 1 1], [−1 1 1]. **Crystal data for 2-AuCl:** $C_{123}H_{154}Au_2B_4Cl_2N_{10}$, M_r = 2280.63, yellow block, 0.245×0.204×0.174 mm^3, monoclinic space group $P2_1/c$, a = 13.643(3) Å, b = 21.105(5) Å, c = 19.074(5) Å, β = 91.484(7)°, V = 5490(2) Å^3, Z = 2, ρ_{calcd} = 1.380 g·cm^{-3}, μ = 2.772 mm^{-1}, F(000) = 2348, T = 100(2) K, R_1 = 0.0424, wR^2 = 0.0788, 15405 independent reflections [2θ ≤59.24°] and 689 parameters.

Special refinement details for 2-AuBr: All hydrogen atoms except H1_1 were assigned to idealized positions. The coordinates of H1_1 were refined freely. The displacement parameters of atoms C1_2 and C1_12 were constrained to the same value with the keyword EADP. The coordinates of atoms C1_2 and C1_12 were constrained to the same value. The displacement parameters of atoms C1_2 to C6_12, C1_9 to C2_19, C1_10 to C2_110, BR4_11 to BR4_111 and C1_13 to C7_13 were restrained to the

same value with similarity restraint SIMU. The U_{ii} displacement parameters of atoms BR4_11 and BR4_111 were restrained with keyword ISOR to approximate isotropic behavior. The distances between atoms C1_9 and C38_1, C1_19 and C38_1, C1_9 and C2_9, C1_19 and C2_19 were restrained during refinement to the same value. The 1–2 and 1–3 distances in the pyridyl group were restrained to the same values with SAME. **Crystal data for 2-AuBr:** $C_{109}H_{138}Au_2B_4Br_2N_{10}$, M_r = 2185.28, yellow block, 0.362×0.359×0.228 mm^3, monoclinic space group $P2_1/n$, a = 12.547(6) Å, b = 18.489(8) Å, c = 21.362(8) Å, α = 90°, β = 93.295(13)°, γ = 90°, V = 4947(4) Å^3, Z = 2, ρ_{calcd} = 1.467 g·cm^{-3}, μ = mm^{-1}, F(000) = 2220, T = 100(2) K, R_1 = 0.0516, wR_2 = 0.0753, 9121 independent reflections [2θ ≤50.902°] and 662 parameters.

Special refinement details for 3-CuAu: Refined as a two-component inversion twin. The BASF parameter was refined to 24.9%. The displacement parameters of atoms of the residues ET and disordered DEP and BENZ residues were restrained to the same value with similarity restraint SIMU. The 1–2 and 1–3 distances in disordered DEP residue were restrained to the same values with SAME. The 1–2 distances in disordered ET residues were restrained to the same values with SADI. The atom distances in disordered benzene fragments were fitted with the AFIX 66 keyword. **Crystal data for 3-CuAu:** $C_{120}H_{148}Au_2B_4Cl_4Cu_2N_{10}$, M_r = 2436.53, red block, 0.290×0.242×0.121 mm^3, monoclinic space group Cc, a = 35.642(9) Å, b = 11.768(3) Å, c = 26.907(7) Å, α = 90°, β = 101.525(12)°, γ = 90°, V = 11058(5) Å^3, Z = 4, ρ_{calcd} = 1.463 g·cm^{-3}, μ = 3.175 mm^{-1}, F(000) = 4968, T = 100(2) K, R_1 = 0.0326, wR_2 = 0.0744, Flack parameter = 0.249(6), 19946 independent reflections [2θ ≤50.698°] and 1411 parameters.

Computational details

All calculations were carried out using the Gaussian 16, Revision C.01,[9] the ADF 2019.304,[10, 11] and the ORCA 5.0.3[12] quantum chemistry program packages. Geometry optimizations for **2-AuCl**, **3-AuCl**, **3-AuCu**, **3-CuAu**, and **3-CuCl** were performed at the ωB97X-D[13]/Def2-SVP[14] level of theory. The optimized geometries were determined as minima on their respective potential energy surfaces through vibrational frequency calculations, which confirmed the presence of only positive eigenvalues in the Hessian matrices.

To analyze the bonding situations in the various systems Mayer Bond Orders (MBOs)[15] were obtained at the ωB97X-D/Def2-TZVP[14] level of theory. For these calculations, the Multiwfn 3.8[16] tool was used. A further evaluation of the bonding situation took place through the calculations based on the intrinsic bond orbital (IBO)[17] method at the ωB97X-D/Def2-TZVP level of theory. For the calculations and graphical representations of the IBO method, the IBOView software, version v20211019-RevA,[17, 18] was used. Further bonding investigations of **2-AuCl** were performed by the energy decomposition analysis with the natural orbitals for chemical valence (EDA-NOCV)[19-21] method at the PBE0-D3[22, 23]/TZ2P[24] level of theory. The main results are displayed in Table S1. To take the relativistic effect into account the EDA-NOCV calculations of **2-AuCl** were performed with the zeroth-order regular approximation (ZORA).[25, 26]

Table S1. Orbital interactions of the EDA-NOCV analysis of **2-AuCl** calculated at the PBE0-D3/TZ2P level of theory. The chosen fragments are (SIDep)HB=B(2-C_5H_4N)(SIDep) and AuCl (electron-sharing (B=B)–Au bond) and (SIDep)HB=B(2-C_5H_4N)(SIDep)$^-$ and $AuCl^+$ (dative $(B=B)^-$–Au^+ bond). Energy terms are given in kcal mol^{-1}. For ΔV_{elstat}, ΔE_{disp}, and ΔE_{orb}, the percentage weighting of the total attractive interaction is given. For $\Delta E_{orb\text{-}n}$ the given percentage weighting is with respect to the total orbital interaction ΔE_{oi}.

	2-AuCl	
	Electron-sharing (B=B)–Au bond	Dative $(B=B)^-$–Au^+ bond
ΔE_{int}	–102.74	–379.42
ΔE_{Pauli}	209.79	206.99
ΔV_{elstat}	–211.47 (67.7%)	–290.46 (49.5%)l
ΔE_{disp}	–14.71 (4.7%)	–14.71 (2.5%)
ΔE_{orb}	–86.34 (27.6%)	–281.23 (48.0%)
$\Delta E_{orb\text{-}1}$	–45.51 (52.7%)	–163.80 (58.2%)
$\Delta E_{orb\text{-}2}$	–17.16 (19.9%)	–62.82 (22.3%)
$\Delta E_{orb\text{-}3}$	–5.71 (6.6%)	–14.21 (5.1%)
$\Delta E_{orb\text{-}rest}$	–17.96 (20.8%)	–40.40 (14.4%)

Table S2. Mayer bond orders (MBOs) for **2-AuCl**, **3-AuCl**, **3-AuCu**, **3-CuAu**, and **3-CuCl** at the ωB97X-D/Def2-TZVP level of theory.

	2-AuCl	**3-AuCl**	**3-AuCu**	**3-CuAu**	**3-CuCl**
B1–Au	0.46	0.30 / 0.12	0.25	0.33	–
B2–Au	0.20	0.14 / 0.51	0.23	0.32	–
B1–Cu	–	–	0.37	0.32	0.29 / 0.40
B2–Cu	–	–	0.34	0.30	0.41 / 0.31

Cartesian Coordinates

Complex 2-AuCl, ωB97X-D/Def2-SVP

Geometry of the ground state

Energy = –2899.74855620 E_h

B	-0.926569000	0.252041000	0.128785000
Au	0.646101000	1.138122000	-1.244705000
Cl	1.429283000	2.469775000	-3.072112000
B	0.490592000	-0.563908000	0.206339000
H	-1.836428000	-0.079123000	-0.599321000
C	-1.552140000	1.186436000	1.243457000
N	-1.160370000	2.374717000	1.737110000
C	-2.176405000	2.976684000	2.601867000
H	-2.678294000	3.799020000	2.064826000
H	-1.726289000	3.395255000	3.511663000
N	-2.718296000	0.857248000	1.834609000
C	-3.107513000	1.803324000	2.876545000
H	-2.942001000	1.358626000	3.872438000
H	-4.173354000	2.059782000	2.791163000
C	-0.093261000	3.204253000	1.266170000
C	-0.269052000	3.919956000	0.068413000
C	0.784268000	4.731954000	-0.355665000
H	0.714398000	5.259189000	-1.305971000
C	1.944287000	4.840280000	0.402366000
H	2.764949000	5.464615000	0.043282000
C	2.070262000	4.164464000	1.611595000
H	2.983435000	4.280712000	2.196212000
C	1.045913000	3.336989000	2.074816000
C	-1.554315000	3.782440000	-0.724960000
H	-2.395590000	4.138880000	-0.103550000
H	-1.745217000	2.709539000	-0.889860000
C	-1.581528000	4.484511000	-2.074841000
H	-2.539658000	4.290481000	-2.579289000
H	-1.472755000	5.575562000	-1.974950000
H	-0.772970000	4.106307000	-2.718946000
C	1.125207000	2.606202000	3.398275000

H	1.122311000	1.523379000	3.202591000
H	0.198231000	2.794818000	3.964043000
C	2.305437000	2.967892000	4.288999000
H	2.264731000	2.388608000	5.222879000
H	3.266070000	2.737194000	3.807511000
H	2.303939000	4.037718000	4.550917000
C	-3.569596000	-0.258414000	1.576189000
C	-4.589936000	-0.094332000	0.617724000
C	-5.560222000	-1.089651000	0.522767000
H	-6.369976000	-0.991638000	-0.201050000
C	-5.504099000	-2.221619000	1.334823000
H	-6.275947000	-2.989772000	1.247370000
C	-4.456698000	-2.390411000	2.229156000
H	-4.400410000	-3.294659000	2.841522000
C	-3.469643000	-1.406969000	2.369969000
C	-4.578145000	1.126996000	-0.273927000
H	-3.595641000	1.152500000	-0.773189000
H	-4.608642000	2.034334000	0.354279000
C	-5.671727000	1.197950000	-1.328828000
H	-5.550653000	2.105902000	-1.936760000
H	-5.620373000	0.334716000	-2.009531000
H	-6.678547000	1.225649000	-0.883894000
C	-2.358483000	-1.590268000	3.374750000
H	-1.580784000	-0.832575000	3.208322000
H	-1.878095000	-2.563396000	3.178747000
C	-2.829593000	-1.545839000	4.829372000
H	-1.983031000	-1.680351000	5.518912000
H	-3.309151000	-0.583633000	5.066031000
H	-3.565376000	-2.336786000	5.039585000
C	0.821217000	-1.684796000	-0.898778000
N	-0.030890000	-2.203722000	-1.811691000
C	0.652505000	-2.972182000	-2.851685000
H	0.623034000	-2.428266000	-3.809281000
H	0.152007000	-3.940476000	-2.996685000
N	2.042340000	-2.207979000	-1.146251000
C	2.068393000	-3.098992000	-2.301354000
H	2.323153000	-4.125242000	-1.987030000

H	2.835798000	-2.766768000	-3.015793000
C	-1.457284000	-2.190908000	-1.864331000
C	-2.095172000	-1.473667000	-2.887737000
C	-3.474157000	-1.650034000	-3.049364000
H	-3.990485000	-1.107753000	-3.845095000
C	-4.189448000	-2.503164000	-2.219970000
H	-5.263091000	-2.639579000	-2.368209000
C	-3.541174000	-3.167949000	-1.182733000
H	-4.109552000	-3.811421000	-0.508706000
C	-2.171647000	-3.016615000	-0.976869000
C	-1.348264000	-0.494925000	-3.765749000
H	-1.287955000	-0.892413000	-4.794173000
H	-0.315707000	-0.392194000	-3.405068000
C	-1.971698000	0.901473000	-3.791941000
H	-1.291001000	1.605340000	-4.290681000
H	-2.943774000	0.918315000	-4.308115000
H	-2.118173000	1.267287000	-2.764624000
C	-1.501851000	-3.715511000	0.183540000
H	-0.845569000	-2.995920000	0.699057000
H	-2.285213000	-3.981679000	0.909992000
C	-0.716886000	-4.973612000	-0.187855000
H	-0.308037000	-5.458550000	0.711625000
H	-1.357334000	-5.702226000	-0.707715000
H	0.132972000	-4.742180000	-0.845203000
C	3.270851000	-2.019287000	-0.440434000
C	3.547625000	-2.876582000	0.642005000
C	4.774424000	-2.735331000	1.288260000
H	5.016580000	-3.366285000	2.144208000
C	5.702455000	-1.790404000	0.852056000
H	6.659234000	-1.693024000	1.370226000
C	5.411847000	-0.968146000	-0.226541000
H	6.137505000	-0.218554000	-0.551494000
C	4.185508000	-1.061821000	-0.894367000
C	2.521200000	-3.906094000	1.062927000
H	2.412315000	-4.648329000	0.252582000
H	1.541083000	-3.410947000	1.132835000
C	2.799870000	-4.633757000	2.369574000

H	1.974875000	-5.322289000	2.604592000
H	3.723607000	-5.230293000	2.323024000
H	2.895432000	-3.923264000	3.204732000
H	2.847958000	-0.295735000	-2.390197000
H	5.869917000	0.018954000	-2.925397000
H	4.839506000	-1.226316000	-3.658211000
C	3.872032000	-0.127110000	-2.034060000
H	3.860317000	0.900847000	-1.638974000
C	4.834687000	-0.216836000	-3.216109000
H	4.531852000	0.498134000	-3.994461000
N	2.605361000	0.330429000	1.343146000
C	3.467212000	0.385048000	2.350020000
C	2.184129000	-1.115153000	3.684375000
H	2.005782000	-1.678282000	4.604685000
C	1.283808000	-1.182407000	2.624432000
H	0.391613000	-1.806577000	2.699530000
C	1.516419000	-0.460731000	1.439516000
C	3.315983000	-0.319143000	3.545081000
H	4.060786000	-0.234399000	4.338522000
H	4.341147000	1.030783000	2.201371000

Complex 3-AuCl, ωB97X-D/Def2-SVP

Geometry of the ground state

Energy = –3494.48788129 E_h

B	-0.800696000	-0.254475000	-0.050726000
B	0.777256000	0.178163000	0.234087000
Cu	-0.160308000	-0.445492000	2.017783000
Cl	0.000403000	-1.502858000	3.927587000
Cu	0.237376000	0.433800000	-1.833368000
Cl	1.302756000	1.214737000	-3.599658000
C	-1.130523000	-1.839894000	-0.059467000
N	-2.326671000	-2.391221000	0.248472000
C	-2.288212000	-3.851488000	0.282945000
H	-2.910181000	-4.266847000	-0.527359000
H	-2.688602000	-4.217223000	1.239151000
C	-0.803418000	-4.146202000	0.112134000
H	-0.341618000	-4.479643000	1.053966000

H	-0.586992000	-4.895237000	-0.661777000
N	-0.257591000	-2.844803000	-0.275532000
C	1.534666000	1.563461000	0.281962000
N	2.882884000	1.614311000	0.284844000
C	3.377087000	2.968213000	0.041745000
H	3.684240000	3.070590000	-1.010958000
H	4.240672000	3.188335000	0.683752000
C	2.151601000	3.813460000	0.352340000
H	2.174948000	4.255375000	1.364822000
H	1.995728000	4.623059000	-0.371504000
N	1.070680000	2.830744000	0.274032000
C	-2.021397000	0.683470000	-0.519628000
C	-3.050247000	1.273810000	0.222942000
C	-3.991149000	2.129435000	-1.815054000
H	-4.756226000	2.682889000	-2.362158000
C	-2.914078000	1.564790000	-2.486954000
H	-2.793181000	1.673971000	-3.569559000
N	-1.970148000	0.864532000	-1.857729000
C	-3.616385000	-1.775174000	0.318536000
C	-4.187162000	-1.501249000	1.567982000
C	-5.484644000	-0.973589000	1.588802000
H	-5.952008000	-0.748441000	2.550418000
C	-6.183502000	-0.744315000	0.412952000
H	-7.194532000	-0.332443000	0.450494000
C	-5.607263000	-1.052984000	-0.818055000
H	-6.173219000	-0.874016000	-1.732582000
C	-4.322129000	-1.585157000	-0.890046000
C	1.040075000	-2.817729000	-0.880349000
C	1.142310000	-2.587503000	-2.264306000
C	2.410377000	-2.647493000	-2.845858000
H	2.510754000	-2.433865000	-3.912247000
C	3.531524000	-2.965926000	-2.087796000
H	4.515326000	-3.013873000	-2.560141000
C	3.402977000	-3.199521000	-0.724607000
H	4.287792000	-3.415266000	-0.122375000
C	2.162171000	-3.111919000	-0.091206000
C	4.617105000	0.135889000	-0.606593000

C	3.825883000	0.553247000	0.474230000
C	5.661631000	-0.759992000	-0.350241000
H	6.288146000	-1.088990000	-1.183623000
C	5.889598000	-1.254831000	0.925934000
H	6.705141000	-1.959153000	1.105283000
C	5.058383000	-0.868702000	1.974663000
H	5.216586000	-1.275561000	2.976673000
C	4.022094000	0.044778000	1.774362000
C	-0.251675000	3.310116000	0.506472000
C	-0.775486000	3.258379000	1.815080000
C	-1.989347000	3.907213000	2.066882000
H	-2.396979000	3.905683000	3.079549000
C	-2.653375000	4.586944000	1.053119000
H	-3.592342000	5.101653000	1.268460000
C	-2.127121000	4.610695000	-0.233560000
H	-2.664235000	5.129400000	-1.031481000
C	-0.919724000	3.974087000	-0.534911000
C	-3.460596000	-1.749090000	2.868983000
H	-2.459085000	-2.162240000	2.686654000
H	-4.017123000	-2.513883000	3.437332000
C	-3.303764000	-0.497475000	3.730717000
H	-2.735978000	-0.734697000	4.639959000
H	-4.274057000	-0.060481000	4.012994000
H	-2.723889000	0.266481000	3.191809000
C	-3.676382000	-1.944706000	-2.209566000
H	-3.427411000	-3.019022000	-2.203541000
H	-2.712959000	-1.420318000	-2.274156000
C	-4.479795000	-1.628871000	-3.462023000
H	-3.905701000	-1.910077000	-4.356549000
H	-4.699043000	-0.552873000	-3.534915000
H	-5.434441000	-2.176241000	-3.493104000
C	-0.055591000	-2.320678000	-3.145502000
H	-0.749840000	-1.621681000	-2.655571000
H	0.292942000	-1.789435000	-4.042585000
C	-0.810614000	-3.586959000	-3.548236000
H	-1.648187000	-3.345378000	-4.219798000
H	-1.227754000	-4.106247000	-2.671987000

H	-0.147465000	-4.293915000	-4.069273000
C	2.082744000	-3.272905000	1.407717000
H	1.102044000	-2.954086000	1.784508000
H	2.794892000	-2.561935000	1.855051000
C	2.402669000	-4.682113000	1.905012000
H	2.314124000	-4.728987000	3.000161000
H	3.425154000	-4.985570000	1.632107000
H	1.717120000	-5.430284000	1.476080000
C	4.365705000	0.596379000	-2.019473000
H	4.274104000	-0.301156000	-2.650781000
H	3.383420000	1.078400000	-2.107333000
C	5.459243000	1.499572000	-2.589939000
H	5.196309000	1.811388000	-3.611172000
H	6.433714000	0.987949000	-2.629233000
H	5.596545000	2.408745000	-1.983270000
C	3.169774000	0.468211000	2.945443000
H	2.110784000	0.485102000	2.652226000
H	3.224618000	-0.308879000	3.721442000
C	3.567760000	1.815691000	3.546996000
H	2.929148000	2.060991000	4.408678000
H	3.467901000	2.632719000	2.816221000
H	4.613695000	1.805239000	3.889012000
C	-0.039476000	2.561064000	2.886790000
H	1.036711000	2.449493000	2.735788000
C	-0.570646000	2.039202000	3.996789000
H	-1.643185000	2.076701000	4.204220000
H	0.049556000	1.505729000	4.719007000
C	-0.369052000	4.028098000	-1.939452000
H	0.469613000	3.328670000	-2.056572000
H	-1.144222000	3.648519000	-2.623074000
C	0.044863000	5.430023000	-2.388631000
H	0.444811000	5.397627000	-3.412311000
H	0.823498000	5.856479000	-1.736644000
H	-0.804477000	6.130577000	-2.377971000
H	1.608236000	-0.685450000	0.380326000
H	-3.070034000	1.156564000	1.305510000
C	-4.046618000	1.986269000	-0.427886000

H	-4.864059000	2.432649000	0.142545000

Complex 3-AuCu, ωB97X-D/Def2-SVP

Geometry of the ground state

Energy = –4999.04528793 E_h

B	-0.815465000	-0.279037000	0.006711000
B	0.746027000	0.352573000	0.280238000
Cu	-0.390673000	0.477685000	2.015997000
Cl	-0.495396000	0.932093000	4.124435000
Au	0.615138000	-0.556862000	-1.709955000
Cl	1.442356000	-1.156016000	-3.837814000
C	-1.172540000	-1.716059000	0.716168000
N	-2.389673000	-2.060450000	1.196229000
C	-2.354789000	-3.280034000	2.003950000
H	-3.152782000	-3.965868000	1.685791000
H	-2.519920000	-3.028437000	3.063660000
C	-0.957037000	-3.815023000	1.738593000
H	-0.401410000	-4.047126000	2.657479000
H	-0.950012000	-4.712872000	1.100538000
N	-0.316838000	-2.709581000	1.028932000
C	1.455808000	1.750183000	-0.025787000
N	2.785962000	1.875604000	0.118929000
C	3.291074000	3.138125000	-0.418888000
H	3.826802000	2.951217000	-1.363865000
H	3.992921000	3.603306000	0.286502000
C	2.010354000	3.937206000	-0.621587000
H	1.856792000	4.712386000	0.148113000
H	1.947562000	4.414031000	-1.609177000
N	0.973066000	2.910754000	-0.489382000
C	-2.090906000	0.443947000	-0.674622000
C	-2.963187000	1.294260000	0.021092000
C	-4.334364000	1.457843000	-1.932377000
H	-5.213519000	1.823098000	-2.466459000
C	-3.399682000	0.651834000	-2.573170000
H	-3.526821000	0.384783000	-3.628926000
N	-2.323025000	0.155593000	-1.968262000
C	-3.691439000	-1.541802000	0.902816000

C	-4.389033000	-0.830554000	1.889351000
C	-5.704371000	-0.451977000	1.603590000
H	-6.273667000	0.112952000	2.343843000
C	-6.293246000	-0.778225000	0.388779000
H	-7.319997000	-0.468277000	0.181779000
C	-5.585514000	-1.502200000	-0.567256000
H	-6.065852000	-1.753157000	-1.513530000
C	-4.275583000	-1.914479000	-0.323436000
C	1.041486000	-2.922267000	0.631847000
C	1.303137000	-3.490600000	-0.626512000
C	2.639058000	-3.699039000	-0.981985000
H	2.863468000	-4.086801000	-1.978237000
C	3.667618000	-3.396771000	-0.098892000
H	4.707003000	-3.552764000	-0.396135000
C	3.376919000	-2.894902000	1.165247000
H	4.187168000	-2.657566000	1.856966000
C	2.061795000	-2.644636000	1.554545000
C	4.533973000	0.222700000	-0.288977000
C	3.745602000	0.941081000	0.622263000
C	5.618604000	-0.502834000	0.217039000
H	6.249429000	-1.065953000	-0.475139000
C	5.889626000	-0.530280000	1.578227000
H	6.743239000	-1.098442000	1.954877000
C	5.050970000	0.137080000	2.468667000
H	5.240054000	0.080049000	3.543647000
C	3.964354000	0.885843000	2.012246000
C	-0.370961000	3.344553000	-0.694252000
C	-1.020238000	3.991314000	0.374457000
C	-2.229775000	4.642132000	0.114526000
H	-2.761961000	5.125197000	0.936510000
C	-2.763022000	4.651548000	-1.169842000
H	-3.710469000	5.160215000	-1.360810000
C	-2.116148000	3.984386000	-2.203359000
H	-2.560478000	3.968204000	-3.201327000
C	-0.903734000	3.320558000	-1.990846000
C	-3.742170000	-0.475675000	3.208465000
H	-2.649012000	-0.532030000	3.110348000

H	-4.013313000	-1.243574000	3.955549000
C	-4.095254000	0.902103000	3.761415000
H	-3.458088000	1.123787000	4.627868000
H	-5.147422000	0.973630000	4.075750000
H	-3.909461000	1.687714000	3.013182000
C	-3.481386000	-2.735274000	-1.315745000
H	-3.122739000	-3.648461000	-0.807961000
H	-2.579915000	-2.164862000	-1.591981000
C	-4.204160000	-3.121099000	-2.596953000
H	-3.538624000	-3.716858000	-3.237490000
H	-4.498013000	-2.229356000	-3.170927000
H	-5.109024000	-3.717566000	-2.402161000
C	0.217347000	-3.909423000	-1.590636000
H	-0.731166000	-3.417652000	-1.338398000
H	0.488834000	-3.538593000	-2.591054000
C	0.016461000	-5.425649000	-1.643169000
H	-0.775509000	-5.687364000	-2.360852000
H	-0.265677000	-5.838519000	-0.661713000
H	0.938418000	-5.937423000	-1.957868000
C	1.786214000	-2.081210000	2.928550000
H	0.747204000	-1.732273000	3.008071000
H	2.402307000	-1.178799000	3.058357000
C	2.087503000	-3.058204000	4.065036000
H	1.865036000	-2.595036000	5.037435000
H	3.145842000	-3.360552000	4.065297000
H	1.487132000	-3.977926000	3.981065000
C	4.225182000	0.183557000	-1.765900000
H	3.977874000	-0.856488000	-2.033741000
H	3.301812000	0.738896000	-1.976209000
C	5.345715000	0.692608000	-2.670391000
H	5.038258000	0.620653000	-3.723421000
H	6.269448000	0.106487000	-2.550115000
H	5.595676000	1.744084000	-2.455672000
C	3.044278000	1.562372000	3.002035000
H	2.002060000	1.283410000	2.785266000
H	3.245952000	1.135125000	3.995808000
C	3.143211000	3.084475000	3.099414000

H	2.518383000	3.441792000	3.930587000
H	2.777038000	3.583267000	2.191200000
H	4.178297000	3.413097000	3.279892000
C	-0.434398000	3.975086000	1.731314000
H	0.069640000	3.053772000	2.041871000
C	-0.505355000	4.977389000	2.611103000
H	-0.981876000	5.931825000	2.367188000
H	-0.088388000	4.862725000	3.613931000
C	-0.197790000	2.643708000	-3.139619000
H	0.652590000	2.058434000	-2.766337000
H	-0.883365000	1.899136000	-3.573234000
C	0.281776000	3.606546000	-4.225331000
H	0.785421000	3.051071000	-5.029438000
H	0.994419000	4.345232000	-3.825106000
H	-0.553214000	4.167066000	-4.672806000
H	1.559465000	-0.303206000	0.890577000
H	-2.749658000	1.544930000	1.062914000
C	-4.100868000	1.788677000	-0.599567000
H	-4.794828000	2.429673000	-0.051438000

Complex 3-CuAu, ωB97X-D/Def2-SVP

Geometry of the ground state

Energy = –4999.03621526 E_h

B	0.778221000	-0.272664000	0.209205000
B	-0.845864000	0.161600000	-0.009365000
Au	0.171759000	-0.223257000	-1.958038000
Cl	0.091081000	-0.676876000	-4.284897000
Cu	-0.239670000	0.263416000	2.057862000
Cl	-1.349091000	0.746360000	3.900928000
C	1.174872000	-1.856133000	0.182050000
N	2.393753000	-2.341029000	-0.135911000
C	2.407544000	-3.795568000	-0.279766000
H	3.065297000	-4.246290000	0.481169000
H	2.798127000	-4.071151000	-1.269981000
C	0.938539000	-4.163388000	-0.098962000
H	0.475425000	-4.499622000	-1.039293000
H	0.767350000	-4.939606000	0.659498000

N	0.338754000	-2.898859000	0.326044000
C	-1.617342000	1.558105000	0.010406000
N	-2.964885000	1.579151000	0.010626000
C	-3.493268000	2.907238000	0.317651000
H	-3.816038000	2.944605000	1.370231000
H	-4.355468000	3.140039000	-0.321203000
C	-2.284937000	3.794036000	0.064171000
H	-2.314061000	4.300137000	-0.917186000
H	-2.141757000	4.557894000	0.838737000
N	-1.182420000	2.830582000	0.084307000
C	1.977172000	0.671303000	0.720469000
C	2.955512000	1.354868000	-0.010685000
C	3.945243000	2.074156000	2.056270000
H	4.713519000	2.607133000	2.618922000
C	2.910631000	1.426246000	2.717940000
H	2.827332000	1.448460000	3.809376000
N	1.964254000	0.746338000	2.068472000
C	3.659375000	-1.673009000	-0.156891000
C	4.228069000	-1.295843000	-1.381560000
C	5.501761000	-0.715896000	-1.351202000
H	5.969053000	-0.401686000	-2.286352000
C	6.180037000	-0.539222000	-0.153366000
H	7.172895000	-0.083732000	-0.152443000
C	5.607497000	-0.950593000	1.048042000
H	6.157858000	-0.809963000	1.978659000
C	4.342903000	-1.535518000	1.069848000
C	-0.978404000	-2.934359000	0.881725000
C	-1.126398000	-2.806647000	2.273828000
C	-2.413050000	-2.915898000	2.805160000
H	-2.552346000	-2.780198000	3.879762000
C	-3.504799000	-3.177225000	1.984933000
H	-4.504388000	-3.261938000	2.417196000
C	-3.330943000	-3.300999000	0.611936000
H	-4.196199000	-3.462608000	-0.034106000
C	-2.069520000	-3.164365000	0.031037000
C	-4.656760000	-0.007987000	0.784559000
C	-3.886033000	0.517349000	-0.262699000

C	-5.679064000	-0.907190000	0.460060000
H	-6.291233000	-1.321142000	1.265796000
C	-5.903228000	-1.299037000	-0.852467000
H	-6.700596000	-2.008543000	-1.085353000
C	-5.094353000	-0.800621000	-1.871168000
H	-5.253504000	-1.122477000	-2.903506000
C	-4.082705000	0.122827000	-1.601253000
C	0.133256000	3.374960000	-0.022630000
C	0.687666000	3.569457000	-1.304909000
C	1.882294000	4.293235000	-1.400771000
H	2.315446000	4.483032000	-2.384275000
C	2.496653000	4.806460000	-0.266408000
H	3.422100000	5.378799000	-0.361531000
C	1.935151000	4.597126000	0.988086000
H	2.428060000	4.994453000	1.878654000
C	0.742243000	3.885410000	1.136304000
C	3.515411000	-1.509907000	-2.697375000
H	2.460646000	-1.755151000	-2.510712000
H	3.950483000	-2.398347000	-3.188797000
C	3.575182000	-0.326113000	-3.660296000
H	2.934592000	-0.522180000	-4.529972000
H	4.597674000	-0.122616000	-4.012060000
H	3.185780000	0.586052000	-3.182773000
C	3.695114000	-2.005773000	2.353720000
H	3.461347000	-3.080005000	2.264455000
H	2.723893000	-1.499810000	2.450415000
C	4.487737000	-1.774864000	3.631226000
H	3.917380000	-2.138540000	4.497893000
H	4.684807000	-0.704027000	3.791479000
H	5.453943000	-2.302491000	3.621893000
C	0.040499000	-2.581446000	3.207467000
H	0.738536000	-1.844837000	2.781416000
H	-0.344664000	-2.105260000	4.119987000
C	0.806401000	-3.855019000	3.563179000
H	1.607289000	-3.637094000	4.285676000
H	1.276217000	-4.310490000	2.678344000
H	0.139024000	-4.607393000	4.010055000

C	-1.936730000	-3.198866000	-1.473290000
H	-0.930685000	-2.877087000	-1.775507000
H	-2.611809000	-2.430159000	-1.882407000
C	-2.267089000	-4.552371000	-2.100734000
H	-2.154896000	-4.507698000	-3.193807000
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H	-1.605057000	-5.347243000	-1.721757000
C	-4.404771000	0.345698000	2.227696000
H	-4.284768000	-0.594569000	2.787611000
H	-3.433683000	0.843674000	2.345579000
C	-5.514921000	1.174958000	2.873288000
H	-5.253672000	1.409259000	3.915460000
H	-6.477121000	0.639223000	2.874854000
H	-5.676419000	2.126481000	2.342220000
C	-3.257053000	0.678123000	-2.735757000
H	-2.200253000	0.727513000	-2.439829000
H	-3.278314000	-0.035880000	-3.571742000
C	-3.710605000	2.050051000	-3.233519000
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H	-4.760397000	2.030687000	-3.563622000
C	0.007713000	3.054369000	-2.508804000
H	-1.050594000	2.803318000	-2.398436000
C	0.579003000	2.832581000	-3.695848000
H	1.644196000	3.002471000	-3.873881000
H	0.007603000	2.402552000	-4.519466000
C	0.134194000	3.720640000	2.507490000
H	-0.698149000	3.006025000	2.484985000
H	0.882517000	3.250588000	3.163739000
C	-0.328361000	5.033664000	3.139975000
H	-0.770425000	4.840749000	4.128041000
H	-1.088388000	5.539366000	2.523423000
H	0.504501000	5.741395000	3.272217000
H	-1.698826000	-0.685825000	-0.076746000
H	2.930146000	1.318418000	-1.099921000
C	3.954087000	2.044045000	0.660168000
H	4.736813000	2.560876000	0.100819000

Complex 3-CuCl, ωB97X-D/Def2-SVP

Geometry of the ground state

Energy = –6503.59332055 E_h

B	-0.798479000	-0.335076000	-0.033085000
B	0.823489000	0.334943000	0.112243000
Au	-0.461322000	1.069987000	1.743273000
Cl	-0.734652000	2.265018000	3.751093000
Au	0.667956000	-1.002493000	-1.623054000
Cl	1.548074000	-2.059845000	-3.539716000
C	-1.183292000	-1.630497000	0.918074000
N	-2.419046000	-1.887917000	1.396508000
C	-2.420587000	-2.923254000	2.430134000
H	-3.195002000	-3.672960000	2.213732000
H	-2.647091000	-2.469459000	3.407944000
C	-1.005703000	-3.474685000	2.350762000
H	-0.493810000	-3.497135000	3.322938000
H	-0.957894000	-4.486028000	1.917622000
N	-0.339875000	-2.530318000	1.455394000
C	1.575090000	1.585627000	-0.555321000
N	2.907519000	1.707491000	-0.434300000
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C	-2.971973000	1.148876000	-0.561769000
C	-4.198539000	0.757902000	-2.580925000
H	-5.038530000	0.947877000	-3.251662000
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C	-4.426049000	-0.523370000	1.730074000

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C	-6.274526000	-0.794598000	0.183932000
H	-7.288050000	-0.530560000	-0.126191000
C	-5.546791000	-1.722666000	-0.556159000
H	-5.998526000	-2.177562000	-1.438211000
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C	1.032093000	-2.810787000	1.158896000
C	1.333917000	-3.644747000	0.068707000
C	2.680485000	-3.918624000	-0.188199000
H	2.937223000	-4.519628000	-1.063481000
C	3.679878000	-3.417868000	0.636023000
H	4.728268000	-3.629470000	0.414508000
C	3.349133000	-2.645376000	1.744244000
H	4.137212000	-2.251184000	2.388316000
C	2.022100000	-2.325508000	2.026786000
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H	6.329034000	-1.325496000	-0.136320000
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C	5.063888000	0.601132000	2.361036000
H	5.217789000	0.818067000	3.421142000
C	4.009261000	1.222693000	1.689846000
C	-0.205205000	2.975814000	-1.656573000
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C	-2.101913000	4.399418000	-1.257870000
H	-2.663310000	5.079643000	-0.615258000
C	-2.612352000	4.046243000	-2.499755000
H	-3.568149000	4.458328000	-2.830510000
C	-1.927685000	3.149738000	-3.312529000
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H	-4.094310000	-0.510142000	3.844045000

C	-4.226317000	1.551941000	3.226946000
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C	-3.435897000	-3.106809000	-0.927847000
H	-3.117776000	-3.889954000	-0.216543000
H	-2.511721000	-2.621596000	-1.280525000
C	-4.113782000	-3.758178000	-2.123253000
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H	-0.680843000	-3.756681000	-0.691447000
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C	0.097317000	-5.771583000	-0.551472000
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C	5.507740000	-0.206521000	-2.742521000
H	5.219899000	-0.547509000	-3.747232000
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H	3.198130000	1.964542000	3.511641000
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H	-0.375644000	2.688940000	-5.726455000
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C	-4.065085000	1.429874000	-1.368719000
H	-4.802533000	2.172665000	-1.056693000

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