Supporting information for:

Bis(σ-B–H) Complexes of Copper(I): Precursors to a Heterogeneous Amine-Borane Dehydrogenation Catalyst

Adi E. Nako, Andrew J. P. White and Mark R. Crimmin*

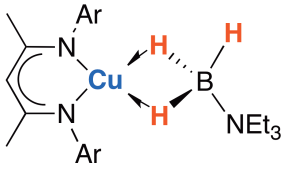
Department of Chemistry, Imperial College London, South Kensington, London, SW7 2AZ, U.K

1. General Experimental

All manipulations were carried out under standard Schlenk-line or glovebox techniques under an inert atmosphere of dinitrogen. An MBraun Labmaster glovebox operating at <0.1 ppm O_2 and <0.1 H_2O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 hours at 120 ^{o}C prior to use. d_6-Benzene and d_8-toluene were dried over molten K, distilled, and stored over molecular sieves prior to use.

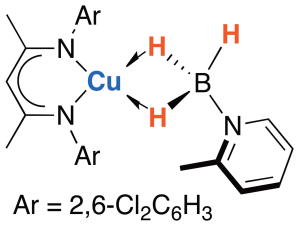
NMR spectra were obtained on Bruker 300, 400 or 500 MHz machines, all peaks are referenced against residual solvent and values are quoted in ppm. Data were processed in Topspin or MestReNova. Infrared spectra were obtained from solids on an ATR cell. **1_2•toluene** was prepared according to literature procedures.[1] Boranes were purchased from Sigma-Aldrich and used without further purification. The products of hydroboration were assigned based on the comparison of ^{11}B NMR chemical shifts and $^{1}J_{11B–1H}$ coupling constants to those reported in the liertature.

2.1 Preparation of bis(σ-B–H) complexes of Cu(I)



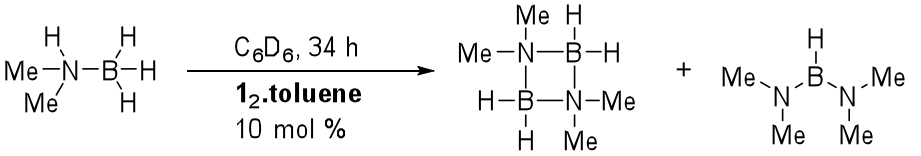
Ar = 2,6-$Cl_2C_6H_3$

*Synthesis of **2a**:* In a glovebox, **1_2•toluene** (0.200 g, 0.20 mmol) was weighed into a vial and dissolved in toluene (2.5 mL). Similarly trimethylamine borane (0.029 g, 0.40 mmol) was weighed and dissolved in toluene (1 mL). The solution containing the copper complex was cooled to -35 °C and after 1 h, the solution containing the borane was added drop-wise to the stirred reaction mixture. The reaction mixture was allowed to warm to 25 ^{o}C and stirred for 1 h at this temperature. The off-yellow solution was passed through a glass filter and reduced to half of its volume under vacuum. The solution was stored at -35 °C overnight. The resulting yellow crystals were isolated by filtration and dried under vacuum to give **2a** (0.132 g. 0.25 mmol, 63 % yield). Due to the fast-exchange equilibrium observed in solution the following data represents a time average of **2a**, trimethylamine borane and **1•arene**. ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 1.77 (br s, 15H), 2.25 (br m, 3H), 4.89 (s, 1H), 6.24 (t, 2H, $^{3}J_{^{1}H\text{-}^{1}H}$ 8.0 Hz), 7.01 (d, 4H, $^{3}J_{^{1}H\text{-}^{1}H}$ 8.0 Hz); ^{13}C NMR (C_6D_6, 298 K, 100 MHz) δ 23.1, 53.0, 94.2, 123.1, 130.4, 147.5, 162.7, 1 quartnary carbon not observed; ^{11}B (C_6D_6, 298 K, 128 MHz) δ -8.1 (br); ^{1}H NMR (C_7D_8, 193 K, 500 MHz) δ 1.10 (s, 9H), 1.66 (s, 2H), 1.85 (s, 6H), 2.45 (s, 1H), 4.93 (s, 1H), 6.45 (t, 2H, $^{3}J_{^{1}H\text{-}^{1}H}$ 8.0 Hz), 7.11 (d, 4H, $^{3}J_{^{1}H\text{-}^{1}H}$ 8.0 Hz); ^{13}C NMR (C_7D_8, 298 K, 100 MHz) δ 23.4, 52.3, 94.4, 122.6, 129.8, 148.4, 162.7, 1 quartnary carbon not observed; ^{11}B (C_7D_8, 298 K, 128 MHz) δ -7.2 (br); Elemental analysis calc. for $C_{20}H_{25}BCl_4CuN_3$: C, 45.88 %; H, 4.81 %; N, 8.03 %. Found C, 45.79 %; H, 4.74 %; N, 7.98 %.



*Synthesis of **2b**:* In a glovebox, **1_2•toluene** (0.141 g, 0.14 mmol) was weighed into a vial and dissolved in toluene (2 mL). Similarly 2-methylpyridine borane (0.030 g, 0.28 mmol) was weighed and dissolved in toluene (0.5 mL). The solution containing the copper complex was cooled to -35 °C and after 1 h, the solution containing the borane was added drop-wise to the stirred reaction mixture. The reaction mixture was allowed to warm to 25 ^{o}C and stirred for 1 h. The orange solution was passed through a glass filter and reduced to half of its volume under vacuum. The solution was stored at -35 °C overnight. The resulting yellow crystals were isolated by filtration and dried under vacuum to give **2b** (0.135 g, 0.24 mmol, 85 % yield). Due to the fast-exchange equilibrium observed in solution the following data represent a time average of **2b**, 2-methylpyridine borane and **1•arene**. ^{1}H NMR (C_6D_6, 298 K, 400 MHz) δ 1.77 (s, 6H), 2.26 (s, 3H), 2.77 – 3.78 (br m, 3H), 4.91 (s, 1H), 6.03 (t, 1H, $^{3}J_{^{1}H-^{1}H}$ 6.4 Hz), 6.09 (d, 1H, $^{3}J_{^{1}H-^{1}H}$ 7.6 Hz) 6.38 (t, 2H, $^{3}J_{^{1}H-^{1}H}$ 8.0 Hz), 6.52 (t, 1H, $^{3}J_{^{1}H-^{1}H}$ 7.6 Hz), 7.03 (m, 4H), 8.20 (s, 1H); ^{13}C NMR (C_6D_6, 298 K, 100 MHz) δ 22.3, 23.4, 94.7, 122.1, 123.4, 126.3, 130.7, 138.5 147.9, 148.4, 157.3 164.0, 1 quartnary carbon not observed; ^{11}B (C_6D_6, 298 K, 128 MHz) δ -15.5 (br); ^{1}H NMR (C_7D_8, 193 K, 500 MHz) δ 1.83 (s, 6H), 1.89 (s, 3H), 2.90 – 3.58 (br s, 3H), 4.91 (s, 1H), 5.60 (m, 2H), 6.04 (t, 2H, $^{3}J_{^{1}H-^{1}H}$ 8.0 Hz), 6.40 (m, 1H), 6.74 (d, 4H, $^{3}J_{^{1}H-^{1}H}$ 8.0 Hz), 7.48 (d, 1H, $^{3}J_{^{1}H-^{1}H}$ 6.5 Hz); ^{13}C NMR (C_7D_8, 193 K, 125 MHz) δ 22.0, 23.3, 94.6, 122.4, 123.4, 126.0, 130.3, 138.6, 146.9, 148.3, 155.8, 162.8, 1 quartnary carbon not observed; ^{11}B (C_7D_8, 193 K, 160 MHz) δ -12.1 (br); due to its air sensitive nature satisfactory elemental analysis for $C_{23}H_{23}BCl_4CuN_3$: C, 49.54 %; H, 4.16 %; N, 7.54 % have not been acquired despite repeated attempts.

2.2 Amine-Borane Dehydrogenation



Temp.	Additive	Conversion (%)	Conversion (%)
25 °C	n/a	9	0.5
50 °C	n/a	34	1
80 °C	n/a	81.5	14
80 °C	Hg	4	2.5

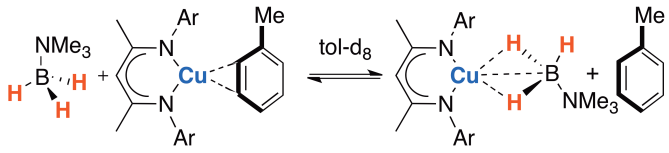
Rections conducted in 510 mM C_6D_6 solution. Conversions obtained by ^{11}B NMR as a percentage of total intensity.

NMR scale procedure

In a glovebox, dimethylamineborane (18 mg, 0.3 mmol) was dissolved in C_6D_6 (150 μL) and transferred to a Youngs tap NMR tube containing **1_2•toluene** (15 mg, 0.015 mmol, 10 mol% **1**) in C_6D_6 (450 μL). The tube was sealed, removed from the box and either stored at room temperature, or at 50 / 80 ^{o}C in an isothermal bath. The reaction was monitored by ^{1}H and ^{11}B NMR spectroscopy over the course of 34 hours, conversions obtained by ^{11}B NMR as a percentage of total intensity. Product assignments were based upon the literature data.[2] For the Hg test, four drops of Hg were added to the tube and the reaction performed as described.

2.3 VT NMR data on Compounds 2a-b

Figure S1 ^{1}H NMR stackplot for a 37 mM C_7D_8 solution of **2a** between 193 K and 353 K.



Ar = 2,6-$Cl_2C_6H_3$

1.toluene

Fast exchange regime > –20 °C: Time-averaged chemical shifts observed.
Slow exchange regime < –20 °C: Diagnostic resonances for the methine protons of the beta-dketiminate ligand of **1.toluene** (δ = 4.75 ppm) and **2a** (δ = 4.93 ppm) resolve.

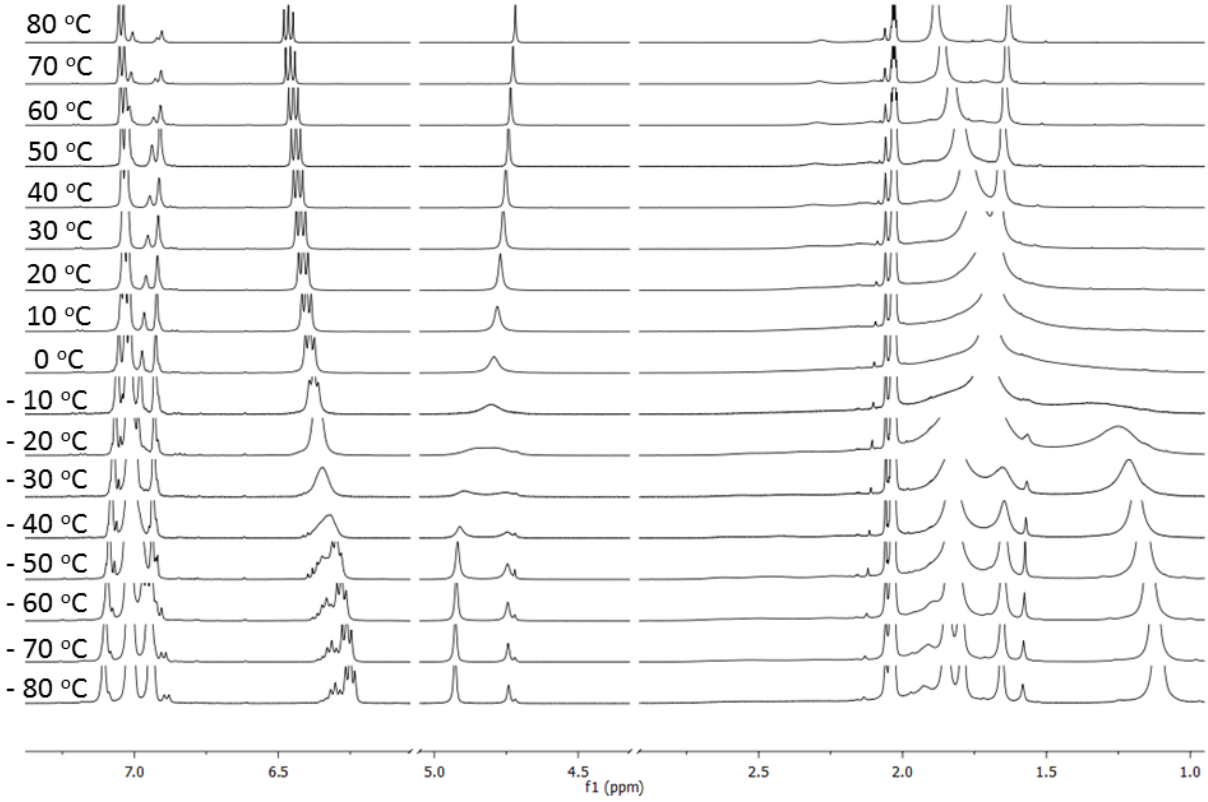
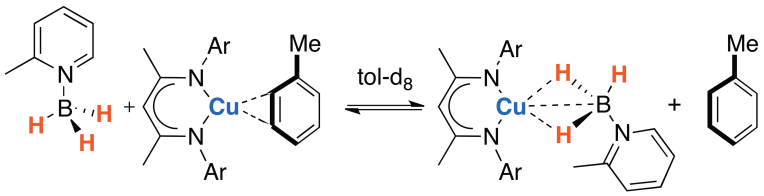


Figure S2 ^{1}H NMR stackplot for a 37 mM C_7D_8 solution of **2b** between 193 K and 353 K.



Ar = 2,6-$Cl_2C_6H_3$

1.toluene

Fast exchange regime > –30 °C: Time-averaged chemical shifts observed.
Slow exchange regime < –30 °C: Diagnostic resonances for the methine protons of the beta-dketiminate ligand of **1.toluene** (δ = 4.75 ppm) and **2a** (δ = 4.91 ppm) resolve. In this case decoalescence of the B–H resonance and environments of the lutidine fragment can also be observed.

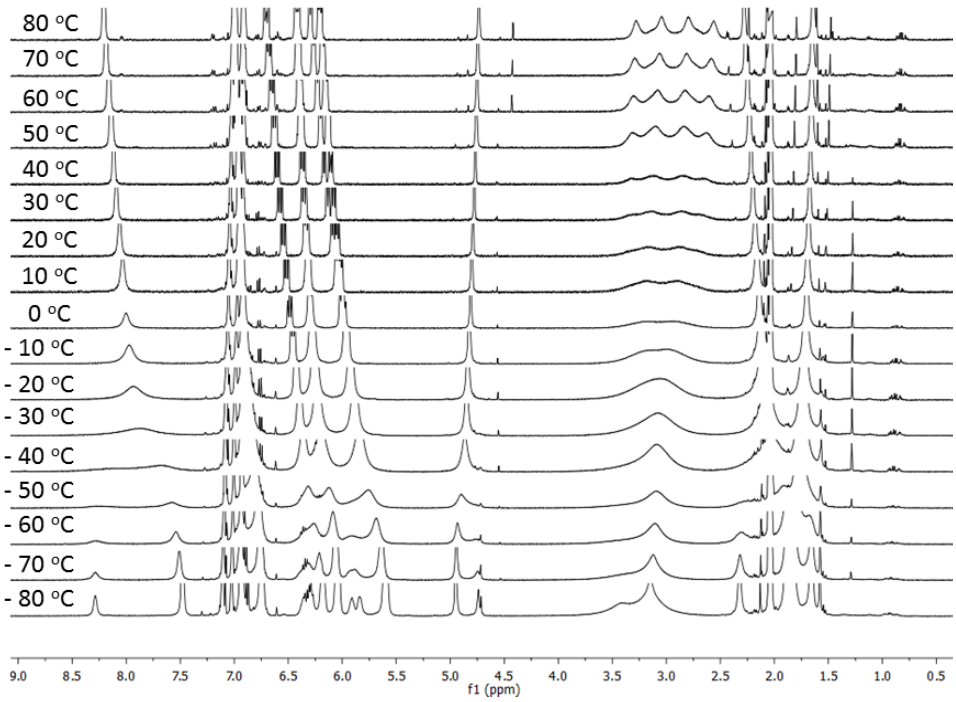
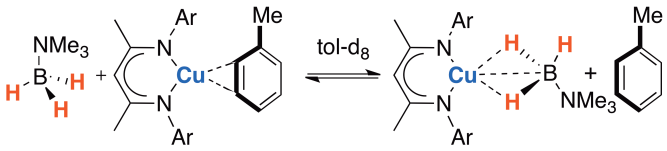
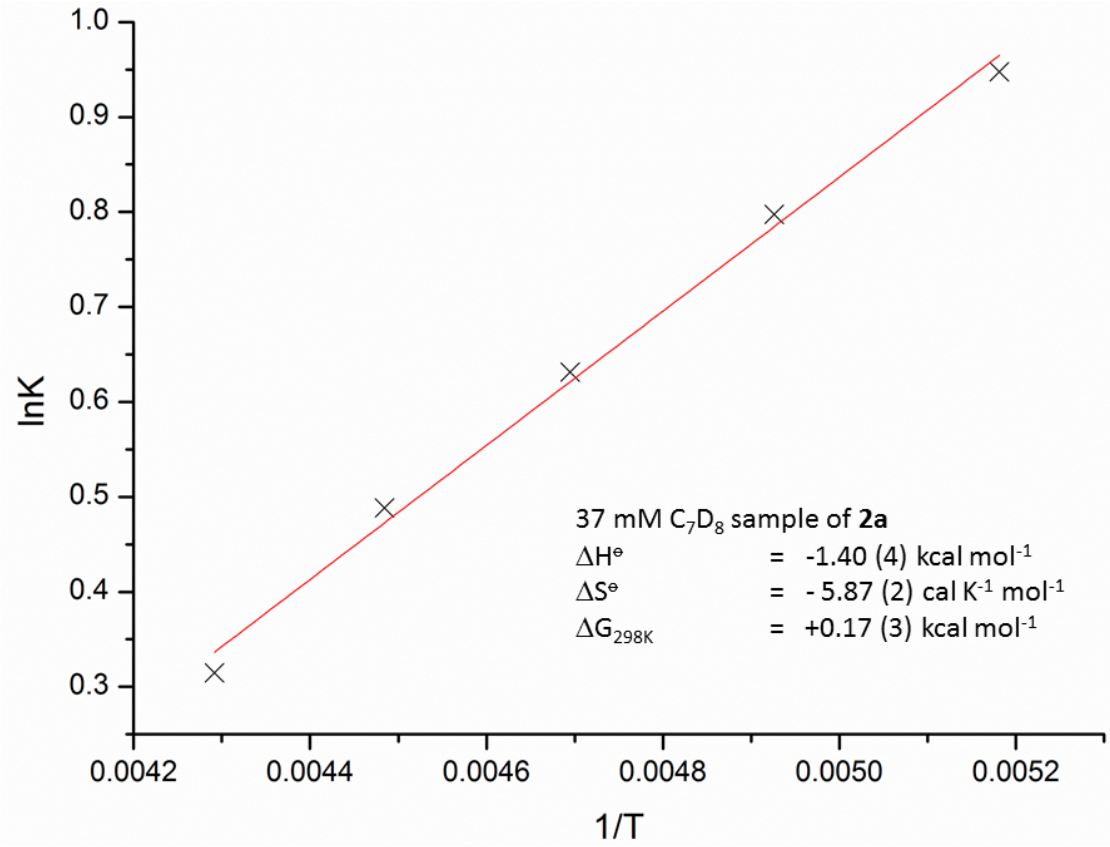


Figure S3 van't Hoff analysis on a 37 mM C_7D_8 solution of **2a** between 193K and 243 K



Ar = 2,6-$Cl_2C_6H_3$

1.toluene



2.4 X-ray Crystallographic Data

The X-ray crystal structure of 2a

Crystal data for **2a**: $C_{20}H_{25}BCl_4CuN_3$, M = 523.58, orthorhombic, *Pnma* (no. 62), a = 16.9427(9), b = 19.9103(10), c = 6.8692(4) Å, V = 2317.2(2) Å^3, Z = 4 [C_S symmetry], D_c = 1.501 g cm^{-3}, μ(Cu-Kα) = 5.663 mm^{-1}, T = 173 K, pale yellow needles, Agilent Xcalibur PX Ultra A diffractometer; 2289 independent measured reflections (R_{int} = 0.0342), F^2 refinement,[3] R_1(obs) = 0.0440, wR_2(all) = 0.1181, 1925 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 147°], 161 parameters. CCDC 1048449.

The structure of **2a** can be solved and refined to a similar quality in two related space groups, *Pnma* (as reported here) and its non-centrosymmetric counterpart *Pna*2$_1$, which differ only by the respective presence or absence of a mirror plane; if present, the mirror plane would pass though the metal and C2 and bisect the N–Cu–N angle. Both approaches were tried, and though the centrosymmetric version has been preferred, each has its distinct problems. For the *Pnma* case, the BH_3NMe_3 unit would be necessarily disordered across the mirror plane, making it impossible to reliably locate the BH_3 hydrogen atoms. The *Pna*2$_1$ approach sidesteps this disorder by not having the mirror plane, but results in a slightly distorted geometry at the NMe_3 nitrogen centre, has an unclear Flack parameter of 0.34(7), and still does not result in reliable location of the BH_3 hydrogen atoms. With the non-centrosymmetric version offering no tangible benefits, the centrosymmetric model was chosen.

As a result of the disorder across the mirror plane, the presumed BH_3 hydrogen atoms could not be located from ΔF maps, and so they were omitted. Consequently, the atom list for the asymmetric unit is low by 1.5H and that for the unit cell is low by 12H.

The X-ray crystal structure of 2b

Crystal data for **2b**: $C_{23}H_{23}BCl_4CuN_3$, M = 557.59, monoclinic, $P2_1/c$ (no. 14), a = 11.0385(2), b = 15.6053(3), c = 14.7655(3) Å, β = 97.005(2)°, V = 2524.50(9) Å^3, Z = 4, D_c = 1.467 g cm^{-3}, μ(Mo-Kα) = 1.305 mm^{-1}, T = 173 K, yellow blocks, Agilent Xcalibur 3E diffractometer; 5062 independent measured reflections (R_{int} = 0.0228), F^2 refinement,[2] R_1(obs) = 0.0327, wR_2(all) = 0.0731, 4141 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 56°], 305 parameters. CCDC 1048450.

The three B–H hydrogen atoms in the structure of **2b** were all located from ΔF maps and refined freely.

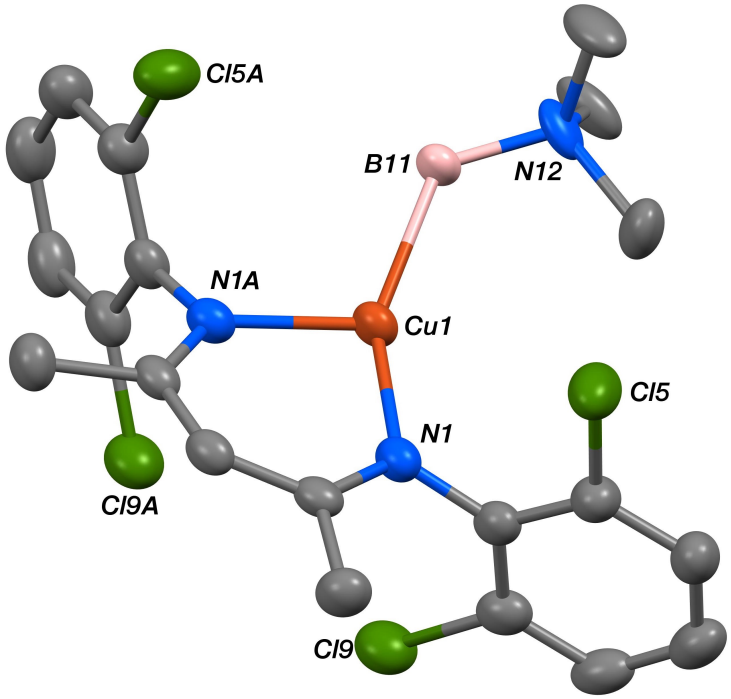


Figure. S4 The crystal structure of **2a** (50% probability ellipsoids).

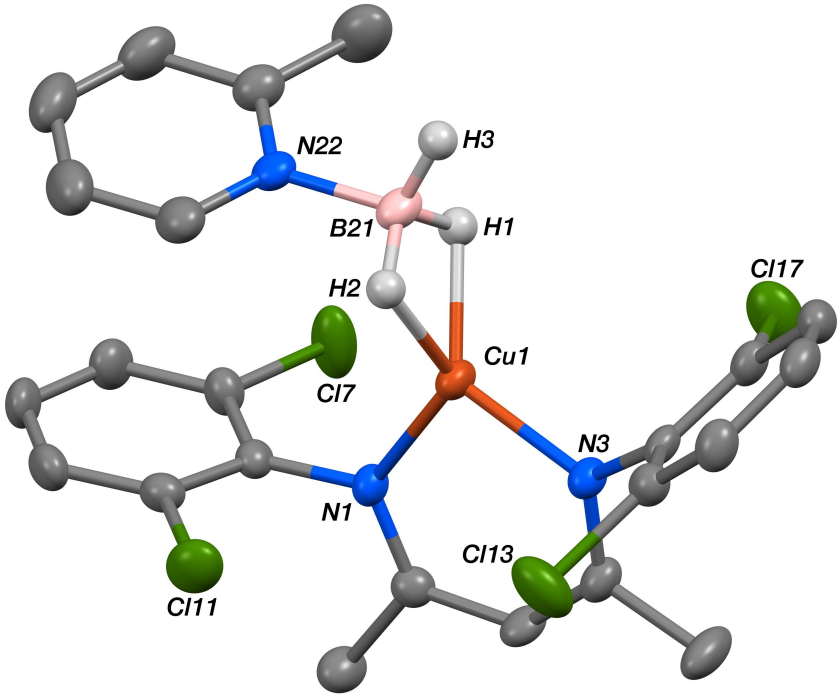


Figure. S5 The crystal structure of **2b** (50% probability ellipsoids).

2.5 DFT Studies

2.5.1 General

Calculations were conducted in Gaussian09.[4] All minima were confirmed by frequency calculations and solid-state data were used as an input for the atom coordinates. NBO calculations were run using NBO v5.9 within g09. In all cases the geometries were compared against the solid-state data, an series of functionals using the 6-31+G* basis set were investigated (Figure S2). Due to an accurate match of the pertinent metrics, the M06 functional was used for further calculations. Bader analysis was conducted on optimized geometries in the AIMALL package.[5]

Table S1: Comparison of Calculated and Solid-State Data for **2b**

	Exp.	Calc. (M062x)	Max. Error	Calc. (B3PW91)	Max. Error	Calc. (M06)	Max. Error
Cu–N	1.94,1.95	2.02, 2.05	5.7%	1.97,1.96	1.5%	1.97,1.97	1.5%
Cu–B	2.15	2.26	5.1%	2.17	0.9%	2.15	0.0%
Cu–H	1.79,1.81	1.91,1.93	7.3%	1.81,1.82	1.7%	1.80,1.83	2.2%
N–Cu–N	98.6	96.3	2.4%	99.1	0.5%	98.3	0.4%
B–H	1.04	1.20	**15.4%**	1.21	**16.3%**	1.21	**16.3%**
B–H	1.15,1.16	1.23,1.23	**7.0%**	1.24,1.24	**7.8%**	1.24,1.24	**7.8%**

2.5.2 NBO Analysis

Table S2: Wiberg Bond Indices

	2a	2b	2c
Cu–H	0.05	0.05	0.05
B–H_b	0.93,0.94	0.91,0.93	0.93,0.93
B–H_t	0.97	0.95	0.97
Cu–B	0.14	0.13	0.14

Table S3: Natural Population Analysis Charge

	Cu	B	B–H	Cu--**H**–B
2a	0.87	-0.32	0.00	-0.02
2b	0.87	-0.33	0.02	-0.02
2c	0.87	-0.32	0.00	-0.02

3. References

1. (a) Badiei, Y. M.; Dinescu, A.; Dai, X.; Palomino, R. M.; Heinemann, F. W.; Cundari, T. R.; Warren, T. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 9961. (b) Badiei, Y. M.; Warren, T. H.; Chiang, K. P.; Holland, P. L. *Inorg. Synth.* **2010**, *35*, 50-53.

2. M. S. Hill, G. Kociok-Koehn, T. P. Robinson, *Chem. Commun.* **2010**, *46*, 7587.

3. (a) SHELXTL, Bruker AXS, Madison, WI; (b) SHELX-97, G.M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112-122; (c) SHELX-2013, http://shelx.uni-ac.gwdg.de/SHELX/index.php

4. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

5. AIMAll (Version 13.10.19), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, 2013 (aim.tkgristmill.com)

4. Z-Matrices

2a – B3PW91/6-31+G*

Sum of electronic and zero-point Energies= -4446.501764
Sum of electronic and thermal Energies= -4446.469642
Sum of electronic and thermal Enthalpies= -4446.468698
Sum of electronic and thermal Free Energies= -4446.569248
Lowest frequency vibrations = 18.6, 24.2, 31.0 cm^{-1}

0 1

Cu	0.07731900	0.23676800	0.00015800
N	1.67814200	-0.92578900	0.00066600
C	1.56625300	-2.24831000	0.00213400
C	0.33233400	-2.93282300	0.00278100
H	0.41271200	-4.01343900	0.00392200
C	2.81751100	-3.09777400	0.00317100
H	3.42961900	-2.88443500	-0.87975000
H	2.57429200	-4.16155700	0.00465500
H	3.42984700	-2.88201600	0.88534700
C	2.93712300	-0.31789600	0.00017500
C	3.58914900	0.05389500	1.19423900
Cl	2.85350100	-0.36464200	2.71943300
C	4.80006700	0.73976400	1.20483600
H	5.25707800	0.99830600	2.15422400
C	5.40677000	1.08205900	-0.00097600
H	6.35106700	1.61788400	-0.00143100
C	4.80080200	0.73645800	-1.20621700
H	5.25839800	0.99242200	-2.15602200
C	3.58987200	0.05062900	-1.19450200
Cl	2.85509600	-0.37197100	-2.71899200
N	-1.30562300	-1.14512800	0.00085400
C	-0.98308100	-2.44121500	0.00216800
C	-2.09324400	-3.46895300	0.00326500
H	-2.73182900	-3.35348500	-0.87935800
H	-1.69074500	-4.48314300	0.00407700
H	-2.73138400	-3.35187700	0.88600400
C	-2.64514300	-0.75459700	0.00029500
C	-3.35539500	-0.49948400	1.19451100
Cl	-2.55689800	-0.77643800	2.71924500
C	-4.66629300	-0.02999500	1.20484700
H	-5.16249500	0.14159100	2.15447100
C	-5.32358300	0.20445000	-0.00097400
H	-6.34749900	0.56558700	-0.00146000
C	-4.66614400	-0.03279000	-1.20617000
H	-5.16222200	0.13662200	-2.15624900
C	-3.35525000	-0.50226300	-1.19460300
Cl	-2.55657000	-0.78274500	-2.71857900
C	-0.67012900	4.35855500	1.20795700
H	-0.77905900	3.73101500	2.09372900
H	0.32605600	4.80299100	1.20893400
H	-1.43279900	5.14467700	1.21179900

C	-2.16536600	2.88851300	-0.00208400
H	-2.27008800	2.26139600	-0.88777100
H	-2.26977800	2.26204600	0.88409800
H	-2.93522200	3.66751500	-0.00223700
N	-0.81646300	3.50919700	-0.00252900
B	0.35890900	2.38531600	-0.00209400
H	1.41120500	2.97289300	-0.00261400
H	0.21404400	1.72830600	1.04065300
H	0.21363600	1.72685900	-1.04378100
C	-0.67035000	4.35733800	-1.21389000
H	0.32566400	4.80215700	-1.21525800
H	-0.77897300	3.72882600	-2.09901000
H	-1.43330300	5.14318300	-1.21861700

2b – B3PW91/6-31+G*

Sum of electronic and zero-point Energies= -4559.593739
Sum of electronic and thermal Energies= -4559.560710
Sum of electronic and thermal Enthalpies= -4559.559766
Sum of electronic and thermal Free Energies= -4559.664018
Lowest frequency vibrations = 10.5, 17.5, 19.2 cm^{-1}

0 1

Cu	-0.31070000	0.03202000	-0.06335800
H	-0.03283500	1.64220600	0.71063900
H	-0.03270500	1.30146600	-1.33937200
H	-0.62419000	3.05372700	-0.56910800
N	0.71792900	-1.60592900	0.22893000
C	0.10695600	-2.77075100	0.45603500
C	-1.28733100	-2.94001900	0.49621800
H	-1.61627600	-3.95373200	0.69221300
N	-2.13104500	-0.71314700	0.08348500
C	-2.32878600	-2.00383000	0.32419000
C	0.95000800	-4.00468600	0.69183500
H	1.57918200	-4.21918300	-0.17901500
H	0.32487900	-4.87789000	0.88487500
H	1.61659900	-3.86234100	1.54951600
C	-3.74318900	-2.52951900	0.42638400
H	-4.29298800	-2.01111900	1.21928400
H	-3.75328800	-3.59908500	0.64274100
H	-4.28556700	-2.36194900	-0.51056700
C	2.11119400	-1.53480800	0.20022800
C	2.87014400	-1.19660000	1.34277700
Cl	2.04119000	-0.95054600	2.85571300
C	4.25475900	-1.05689300	1.31139000
H	4.78416000	-0.80371600	2.22402700
C	4.94089900	-1.25494900	0.11531600
H	6.02201000	-1.15831400	0.08565200
C	4.23714300	-1.58524700	-1.04049000
H	4.75253500	-1.75228500	-1.98084000
C	2.85187100	-1.71532900	-0.98874100
Cl	1.99786800	-2.11535200	-2.45683100
C	-3.21104000	0.15972400	-0.07596900
C	-3.76655900	0.44120100	-1.34152500

Cl	-3.16520800	-0.42049100	-2.73348900
C	-4.77572000	1.38188500	-1.52427700
H	-5.16497500	1.55793900	-2.52151600
C	-5.26979000	2.08235900	-0.42671600
H	-6.05603300	2.81887900	-0.56134500
C	-4.75431200	1.83708700	0.84356300
H	-5.12768800	2.37043800	1.71142000
C	-3.74534800	0.89222800	1.00436700
Cl	-3.11749100	0.60355400	2.60614700
B	0.12572700	2.12135200	-0.42589400
N	1.62431200	2.63988600	-0.52069400
C	2.06677300	3.64342800	0.28245000
C	3.37963700	4.10143500	0.15768100
H	3.71346700	4.90274300	0.80824900
C	4.23984700	3.54018100	-0.77736700
H	5.26047700	3.89899000	-0.87163300
C	3.76860400	2.50778100	-1.58434200
H	4.39619000	2.02603200	-2.32523900
C	2.46046000	2.08774900	-1.42481500
H	2.03564600	1.28622400	-2.01692100
C	1.12878100	4.22712700	1.28655100
H	0.25574400	4.66628400	0.79389100
H	1.63384700	4.99436300	1.87637800
H	0.74700300	3.45019700	1.95684800

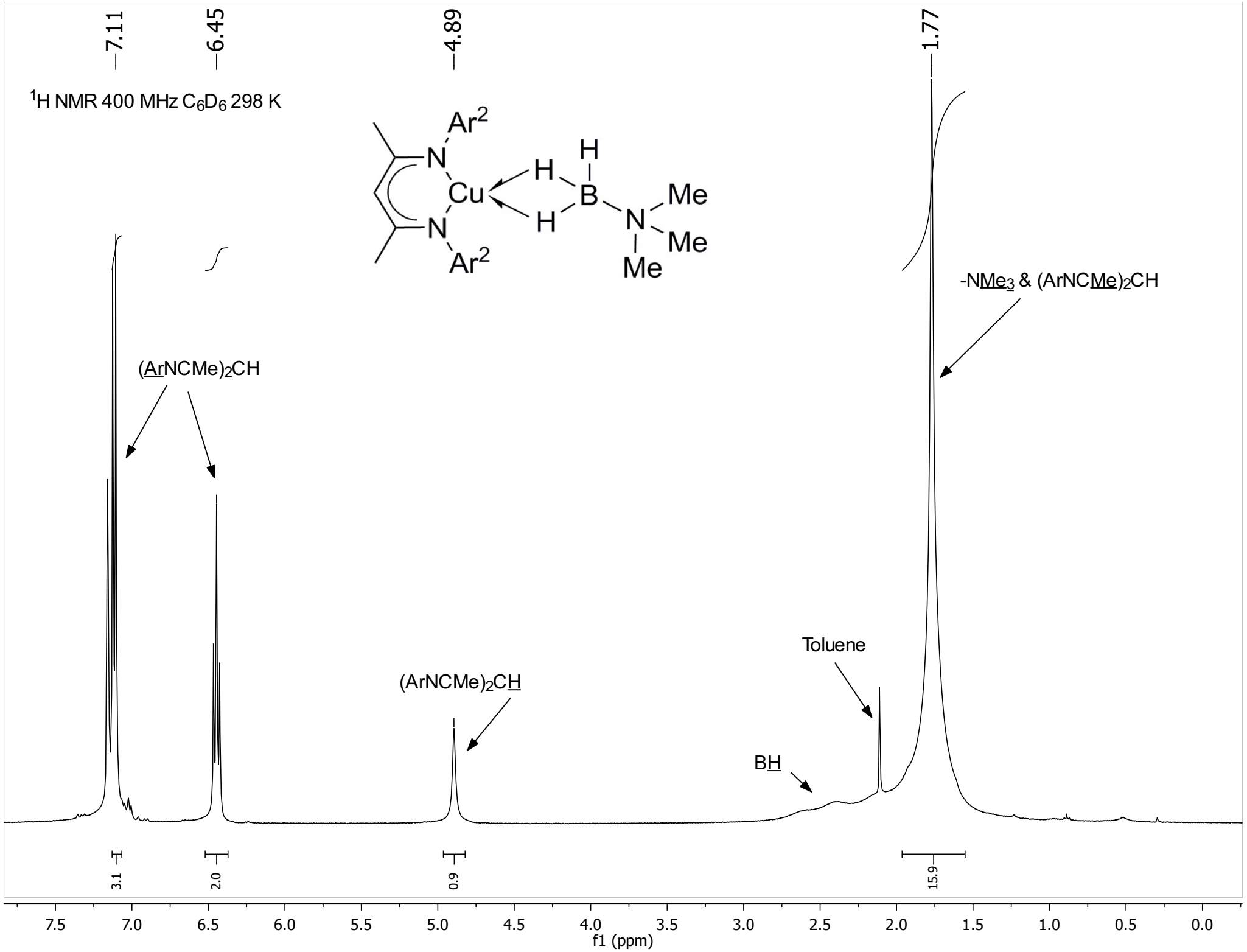
2c – B3PW91/6-31+G*

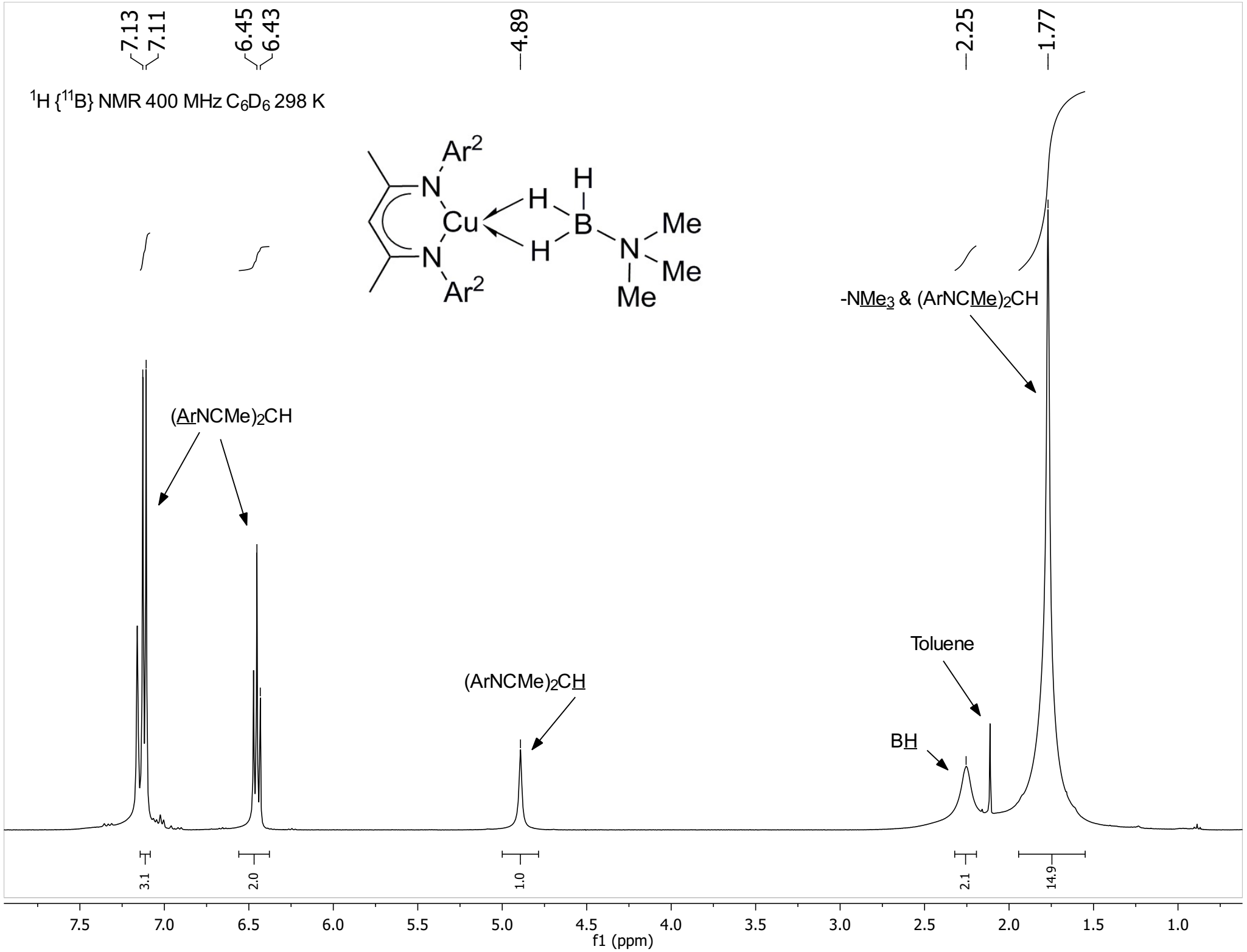
Sum of electronic and zero-point Energies= -4407.234827
Sum of electronic and thermal Energies= -4407.203732
Sum of electronic and thermal Enthalpies= -4407.202787
Sum of electronic and thermal Free Energies= -4407.301588
Lowest frequency vibrations = 18.6, 24.9, 30.9 cm^{-1}

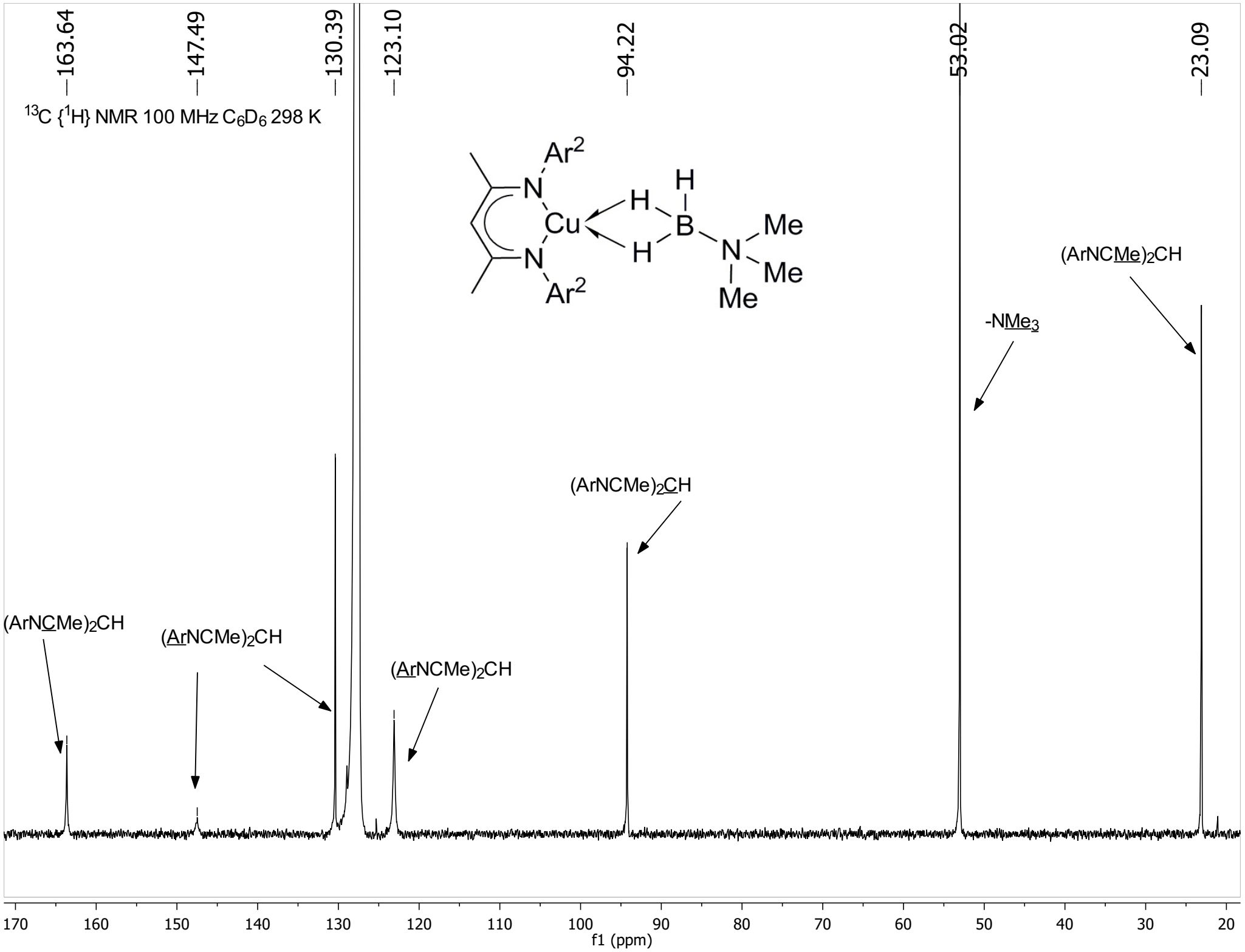
0 1

Cu	0.07186100	0.36536500	-0.09118600
N	1.66198600	-0.80336500	0.06478400
C	1.53929400	-2.11557000	0.22057800
C	0.29949900	-2.78639300	0.28726000
H	0.37060600	-3.86052900	0.41115500
C	2.78311500	-2.96774000	0.33912400
H	3.41233600	-2.86041000	-0.55088600
H	2.53059600	-4.02282700	0.45703600
H	3.38225100	-2.65783400	1.20228900
C	2.92473800	-0.20532400	0.01349700
C	3.55558300	0.30916100	1.16526100
Cl	2.78962600	0.08056500	2.71545500
C	4.76725800	0.99169600	1.11462200
H	5.20696400	1.36473300	2.03360200
C	5.39661300	1.18436600	-0.11263600
H	6.34137700	1.71713000	-0.16124400
C	4.81326900	0.69242200	-1.27751200
H	5.28922500	0.83012000	-2.24267000
C	3.60117200	0.01252500	-1.20470100

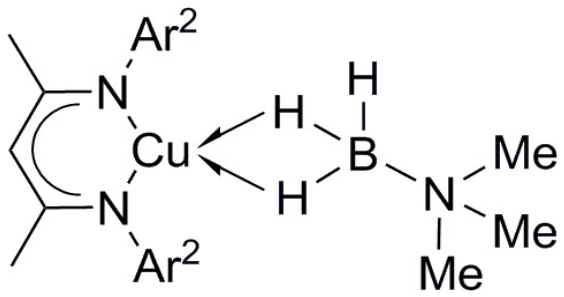
Cl	2.89415800	-0.59498500	-2.67907300
N	-1.32098900	-0.99615000	0.07378000
C	-1.01114600	-2.28603800	0.22949900
C	-2.13141100	-3.29478600	0.35571400
H	-2.78207800	-3.26756700	-0.52531200
H	-1.73918300	-4.30749800	0.46092600
H	-2.75461200	-3.07583000	1.22979000
C	-2.65585300	-0.59105800	0.05719300
C	-3.34069200	-0.20681300	1.23231100
Cl	-2.52058000	-0.34220000	2.76388500
C	-4.64510900	0.28045500	1.21686000
H	-5.12107300	0.55505600	2.15251000
C	-5.32263300	0.39988000	0.00521500
H	-6.34207900	0.77291700	-0.01375400
C	-4.69070400	0.03308300	-1.18097100
H	-5.20251500	0.11146400	-2.13458600
C	-3.38499600	-0.44959300	-1.14409800
Cl	-2.61487400	-0.88641500	-2.64640900
C	-0.88246800	4.57586600	0.47476100
H	-1.14177500	4.06547500	1.40415000
H	0.10721300	5.02132400	0.58157900
H	-1.62527700	5.34948500	0.25716200
C	-2.17188100	2.95830700	-0.83646000
H	-2.10711800	2.26460400	-1.67470400
H	-2.45371000	2.39844200	0.05662000
H	-2.91829100	3.73193100	-1.04082300
N	-0.84011500	3.56842000	-0.61187700
B	0.34818400	2.49345200	-0.37333900
H	1.38296200	3.11171500	-0.36256300
H	0.12556800	1.97367700	0.73359500
H	0.30316000	1.70743100	-1.32944500
H	-0.57909400	4.05671900	-1.46880200


7.11
6.45
4.89
1.77
^{1}H NMR 400 MHz C_6D_6 298 K
Ar^2
N
Cu
N
Ar^2
H
H
H
B
N
Me
Me
Me
-N<u>Me</u>$_3$ & (ArNC<u>Me</u>)$_2$CH
(<u>Ar</u>NCMe)$_2$CH
(ArNCMe)$_2$C<u>H</u>
Toluene
B<u>H</u>
3.1
2.0
0.9
15.9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

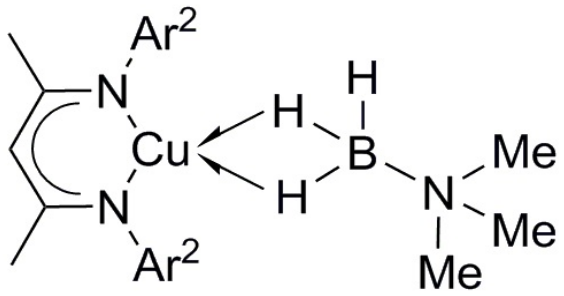

7.13
7.11
6.45
6.43
4.89
2.25
1.77
^{1}H {^{11}B} NMR 400 MHz C_6D_6 298 K
Ar2
N
Cu
N
Ar2
H
H
B
H
N
Me
Me
Me
-NMe3 & (ArNCMe)2CH
(ArNCMe)2CH
(ArNCMe)2CH
Toluene
BH
3.1
2.0
1.0
2.1
14.9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


163.64
147.49
130.39
123.10
94.22
53.02
23.09
^{13}C {^{1}H} NMR 100 MHz C_6D_6 298 K
Ar2
N
Cu
H
B
Me
(ArNCMe)2CH
-NMe3
(ArNCMe)2CH
(ArNCMe)2CH
(ArNCMe)2CH
(ArNCMe)2CH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

^{11}B NMR 128 MHz C_6D_6 298 K

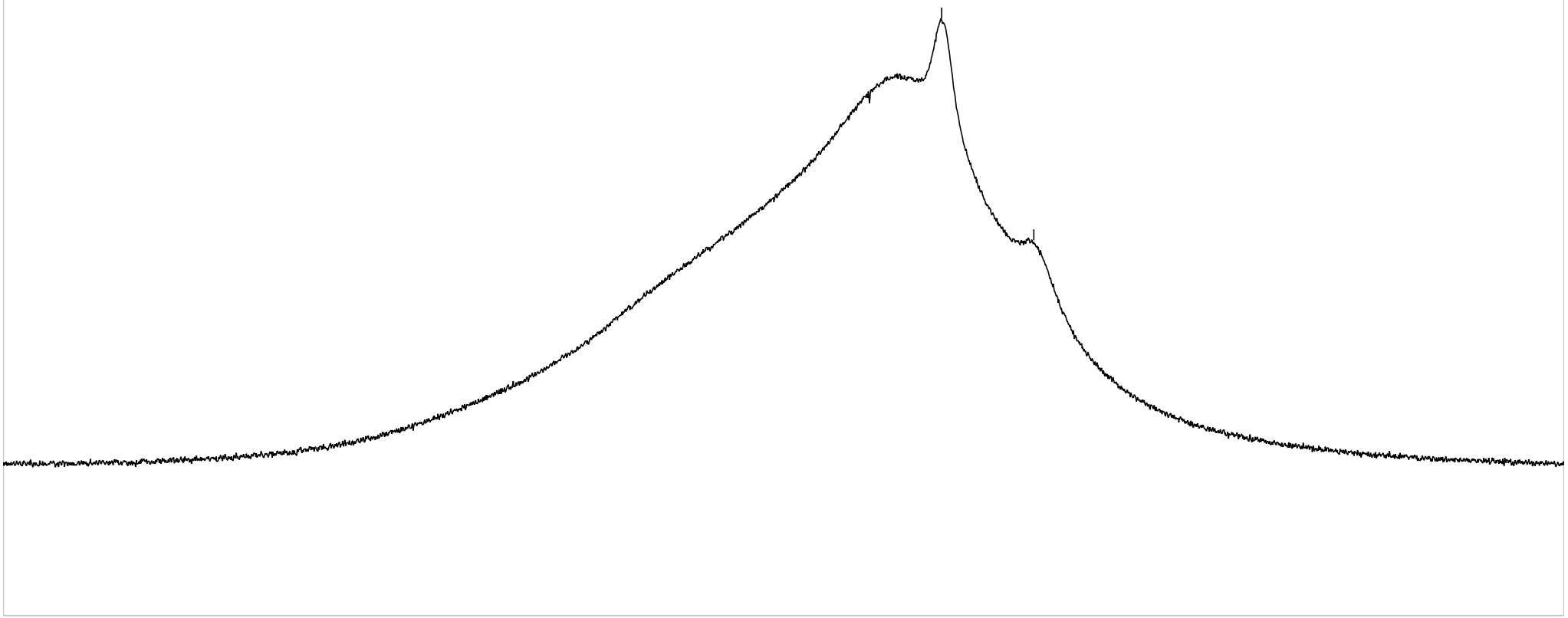


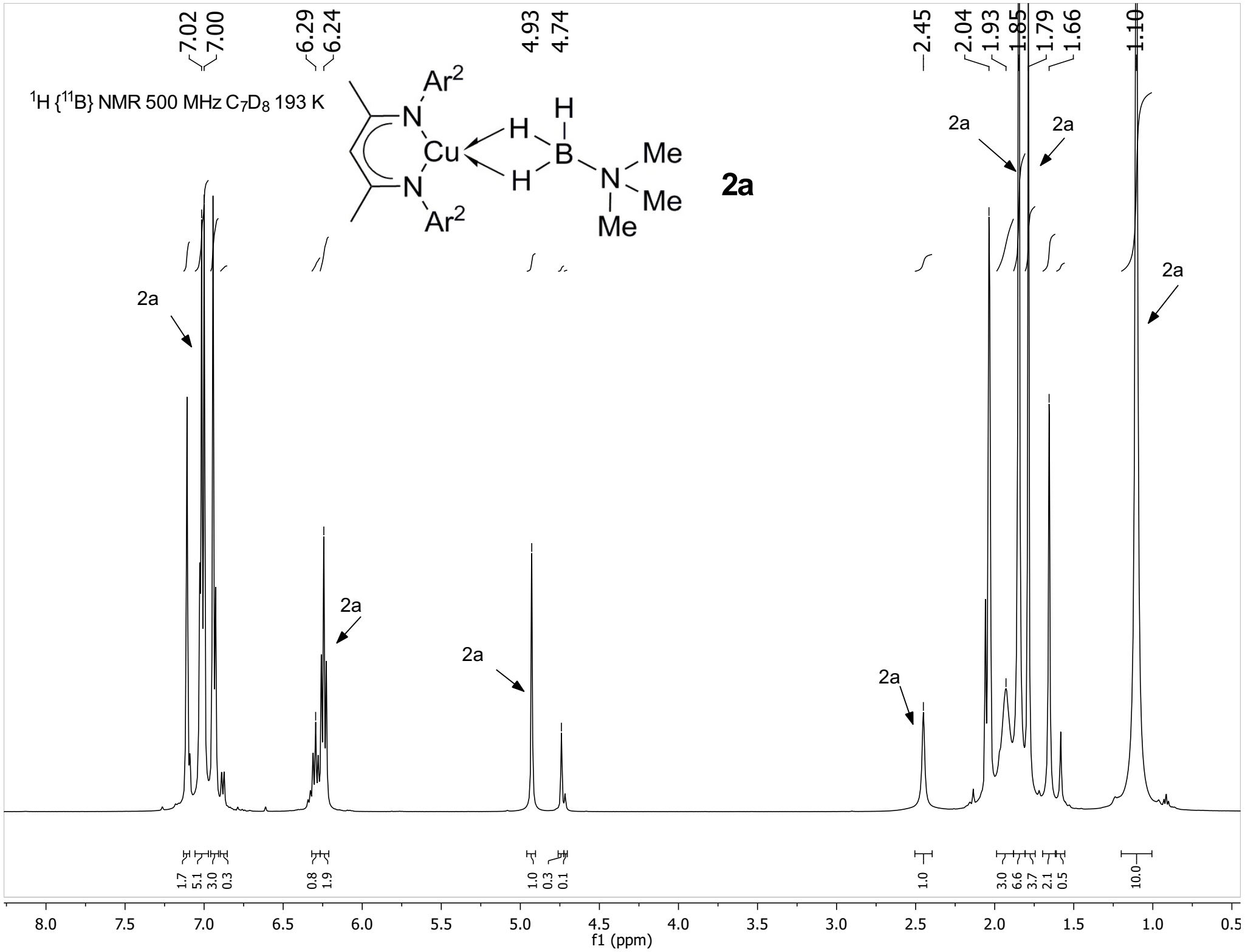
^{11}B NMR 160 MHz C_7D_8 193 K

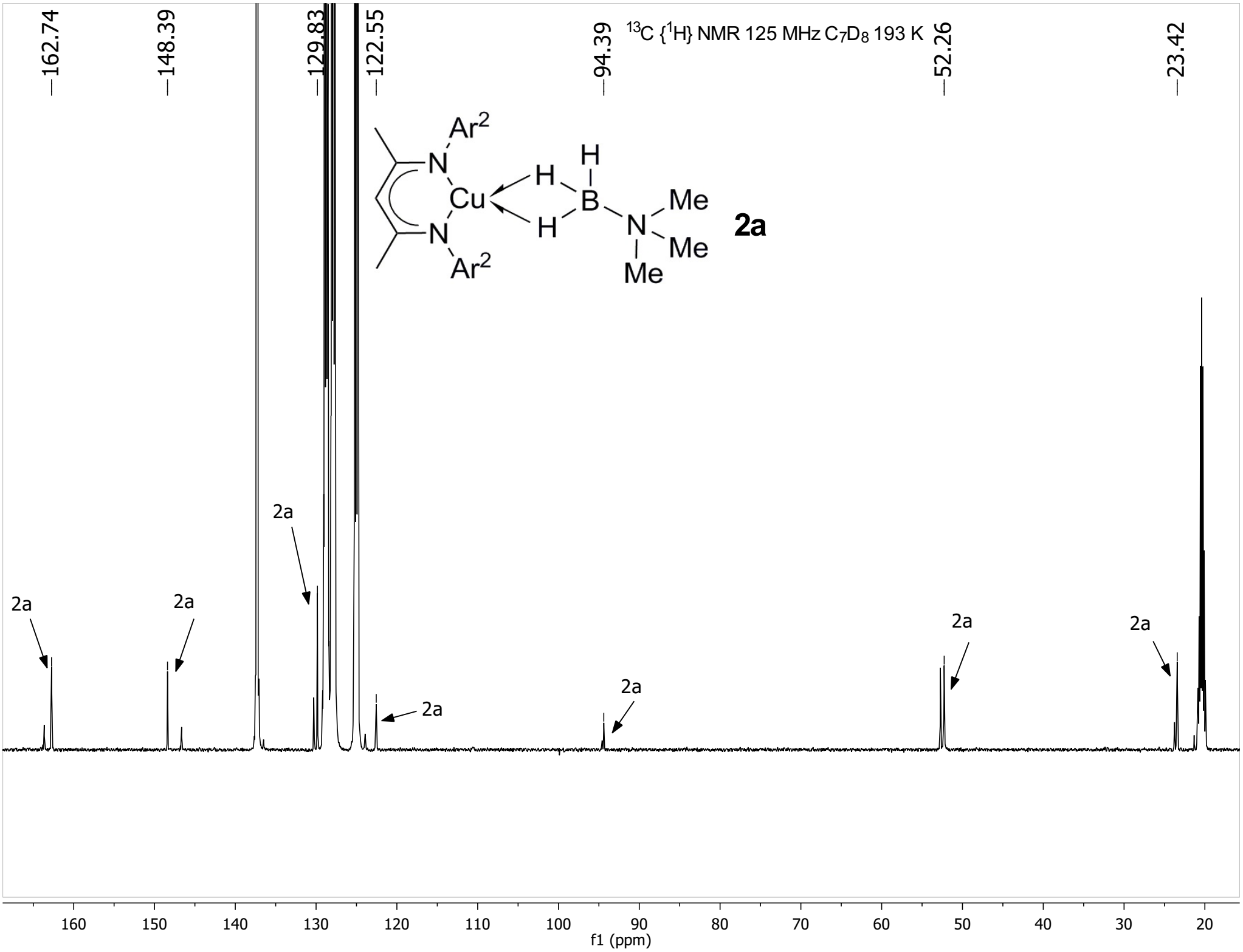


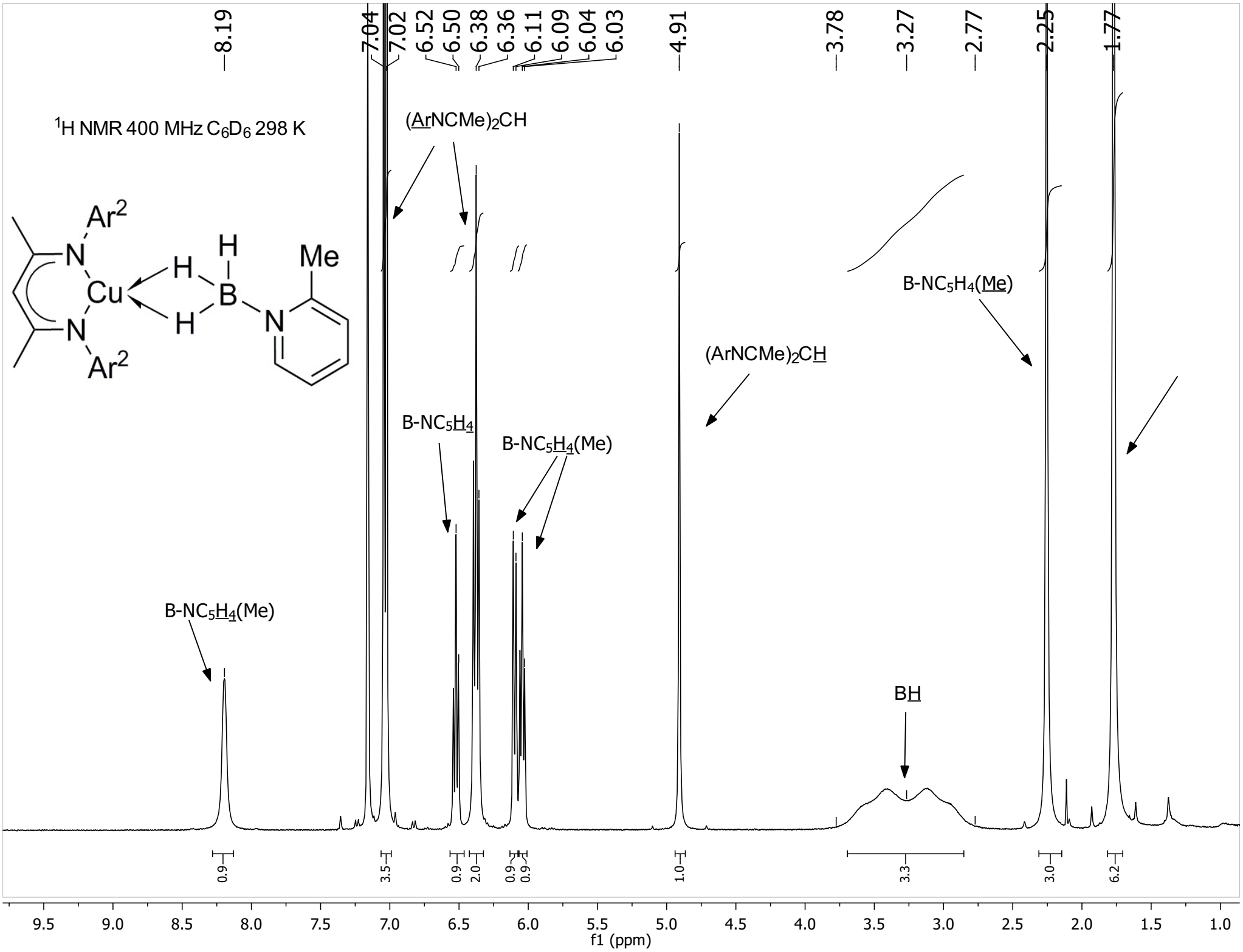
-7.18

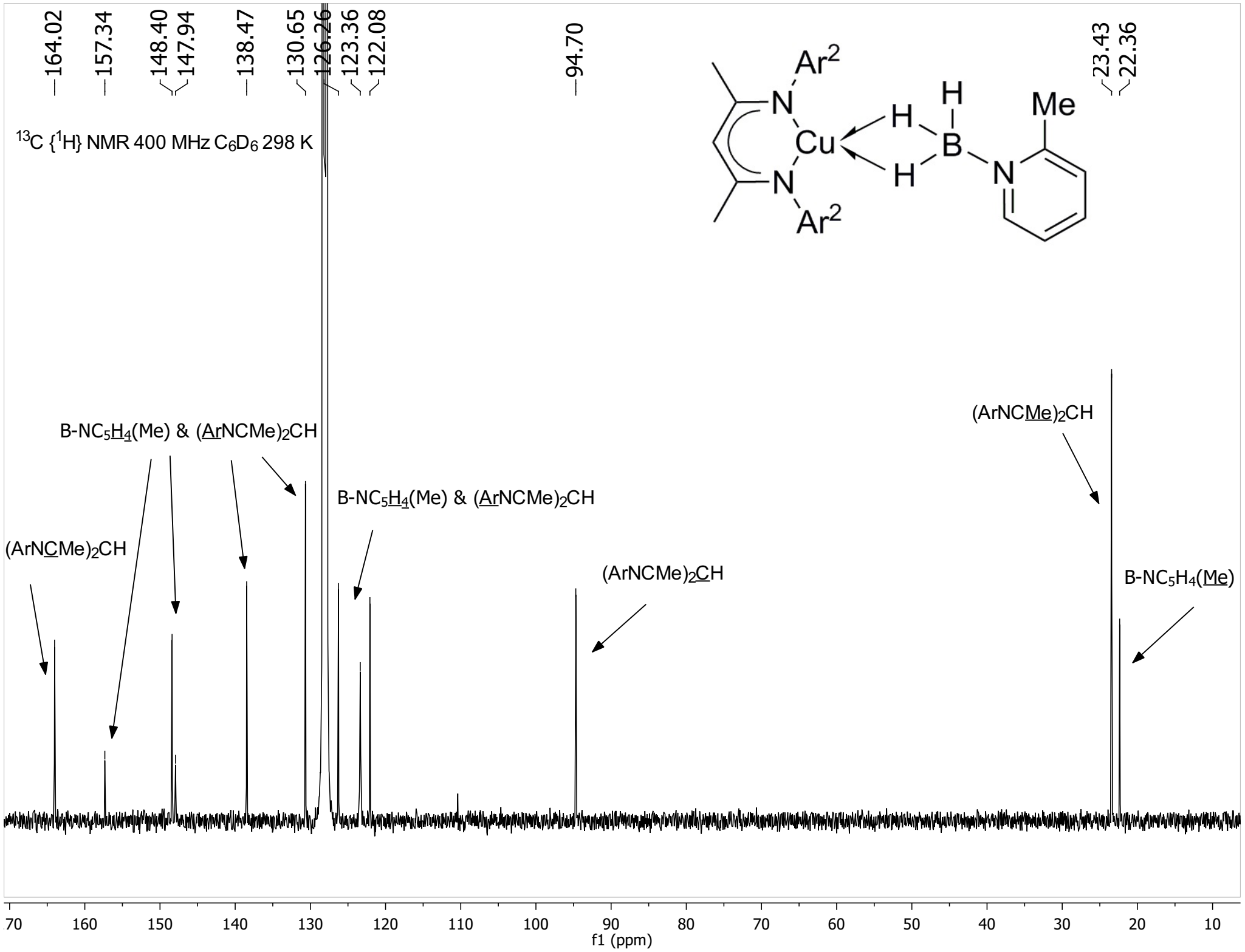
-16.37



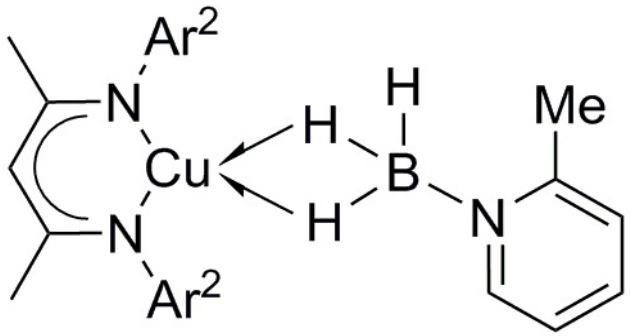

7.02
7.00
6.29
6.24
4.93
4.74
2.45
2.04
1.93
1.85
1.79
1.66
1.10
$^1H\{^{11}B\}$ NMR 500 MHz C_7D_8 193 K
Ar2
N
Cu
H
H
B
N
Me
Me
Me
2a
2a
2a
2a
2a
2a
2a
1.7
5.1
3.0
0.3
0.8
1.9
1.0
0.3
0.1
1.0
3.0
6.6
3.7
2.1
0.5
10.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


162.74
148.39
129.83
122.55
94.39
52.26
23.42
^{13}C {^{1}H} NMR 125 MHz C_7D_8 193 K
Ar2
N
Cu
N
Ar2
H
H
H
B
N
Me
Me
Me
2a
2a
2a
2a
2a
2a
2a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


8.19
7.04
7.02
6.52
6.50
6.38
6.36
6.11
6.09
6.04
6.03
4.91
3.78
3.27
2.77
2.25
1.77
1H NMR 400 MHz C6D6 298 K
(ArNCMe)2CH
B-NC5H4(Me)
(ArNCMe)2CH
B-NC5H4
B-NC5H4(Me)
B-NC5H4(Me)
BH
Ar2
N
Cu
H
B
Me
0.9
3.5
0.9
2.0
0.9
0.9
1.0
3.3
3.0
6.2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


164.02
157.34
148.40
147.94
138.47
130.65
126.26
123.36
122.08
94.70
23.43
22.36
13C {1H} NMR 400 MHz C6D6 298 K
Ar2
N
Cu
N
Ar2
H
H
B
H
Me
N
B-NC5H4(Me) & (ArNCMe)2CH
(ArNCMe)2CH
B-NC5H4(Me) & (ArNCMe)2CH
(ArNCMe)2CH
(ArNCMe)2CH
B-NC5H4(Me)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

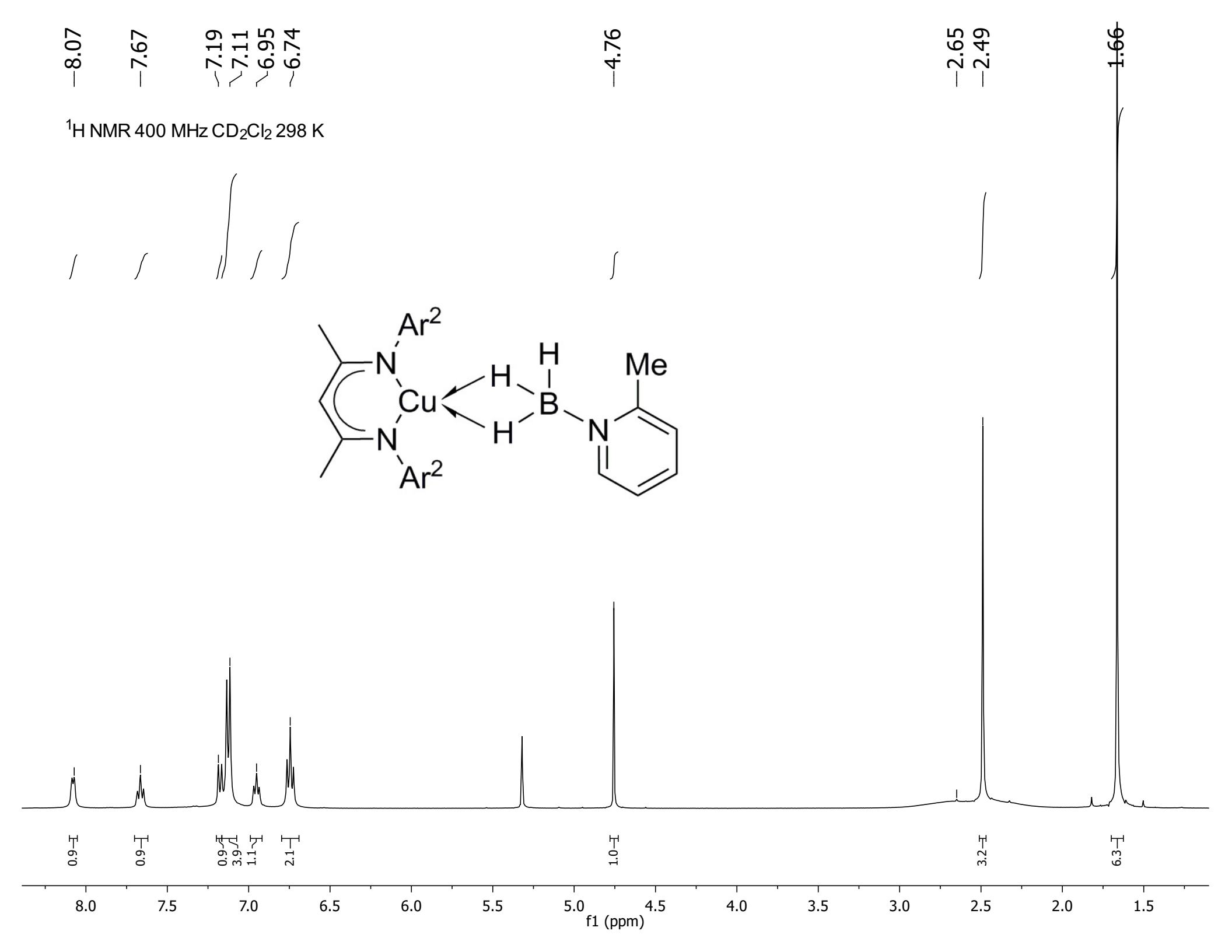
^{11}B NMR 128 MHz C_6D_6 298 K



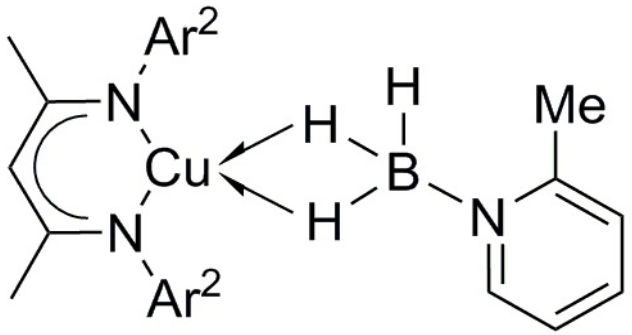
-15.52

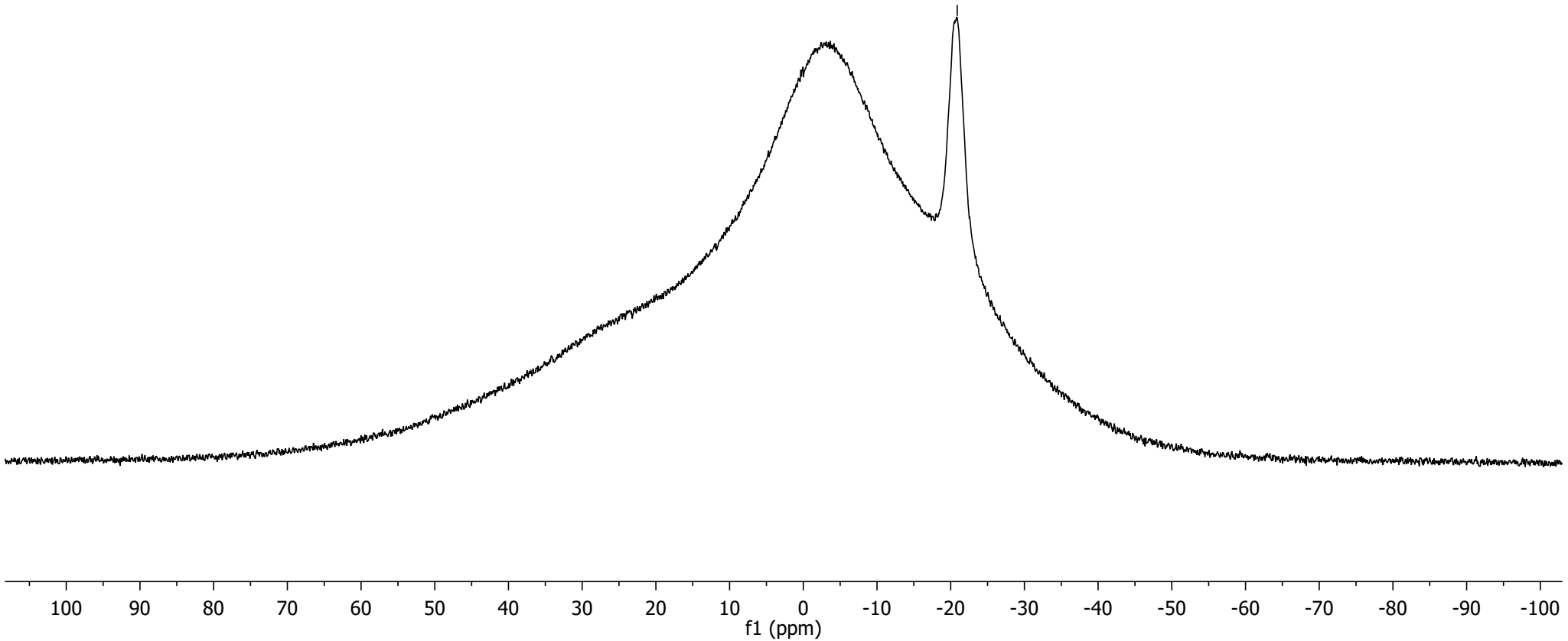
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50

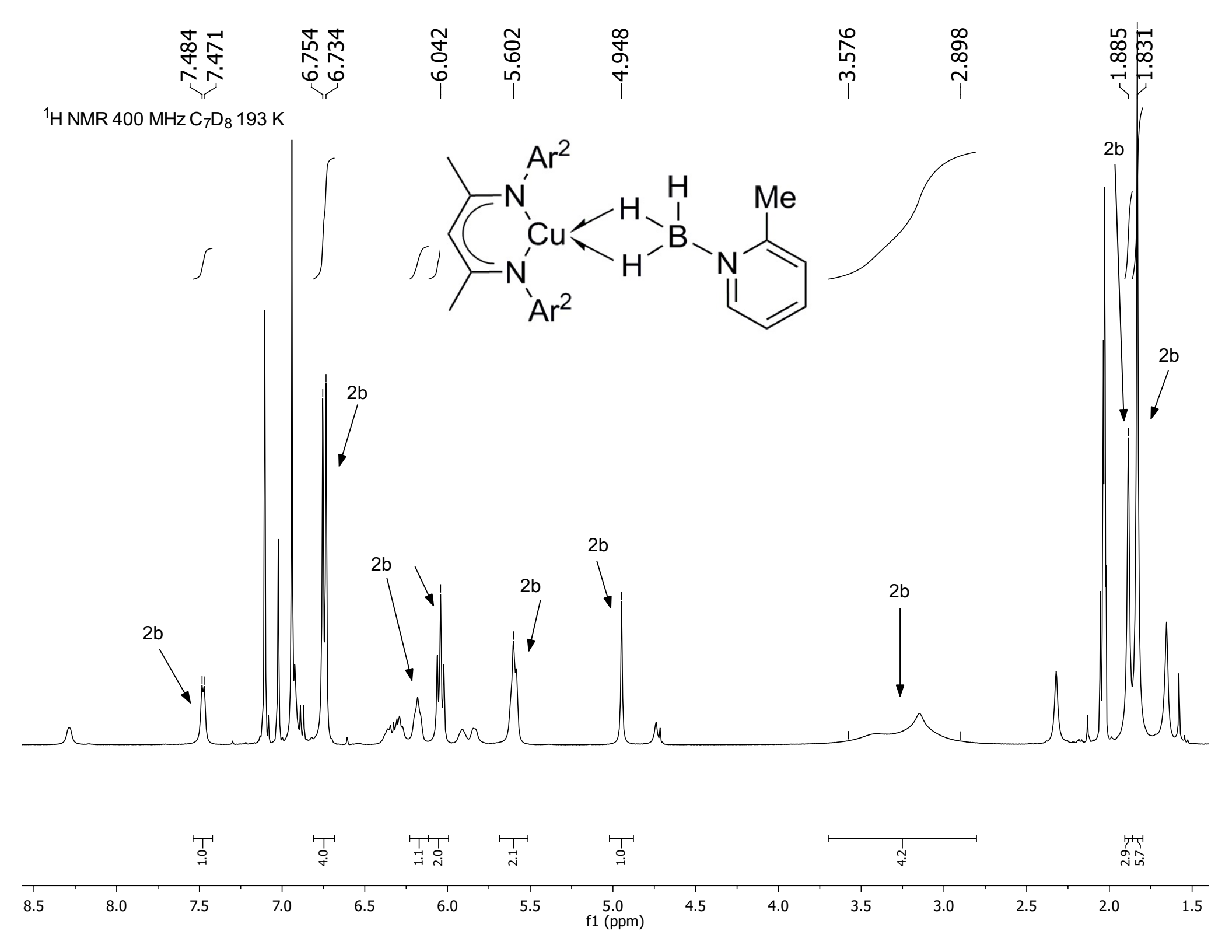
f1 (ppm)


8.07
7.67
7.19
7.11
6.95
6.74
4.76
2.65
2.49
1.66
^{1}H NMR 400 MHz CD_2Cl_2 298 K
Ar2
N
Cu
N
Ar2
H
H
B
H
N
Me
0.9
0.9
0.9
3.9
1.1
2.1
1.0
3.2
6.3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

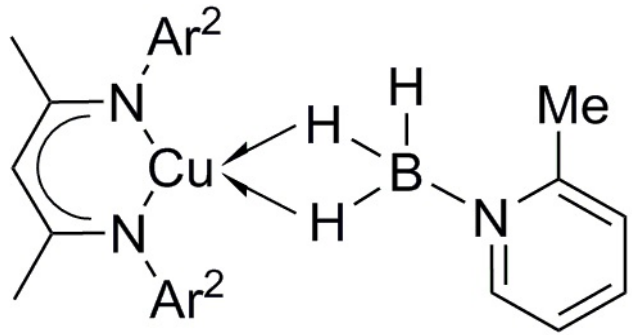
^{11}B NMR 128 MHz CD_2Cl_2 298 K






7.484
7.471
6.754
6.734
6.042
5.602
4.948
3.576
2.898
1.885
1.831
^{1}H NMR 400 MHz C_7D_8 193 K
Ar^2
N
Cu
N
Ar^2
H
H
B
H
Me
N
2b
2b
2b
2b
2b
2b
2b
1.0
4.0
1.1
2.0
2.1
1.0
4.2
2.9
5.7
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

$^{1}H\{^{11}B\}$ NMR 400 MHz C_7D_8 193 K



2b

2b

2b

2b

2b

2b

2b

1.0

0.3

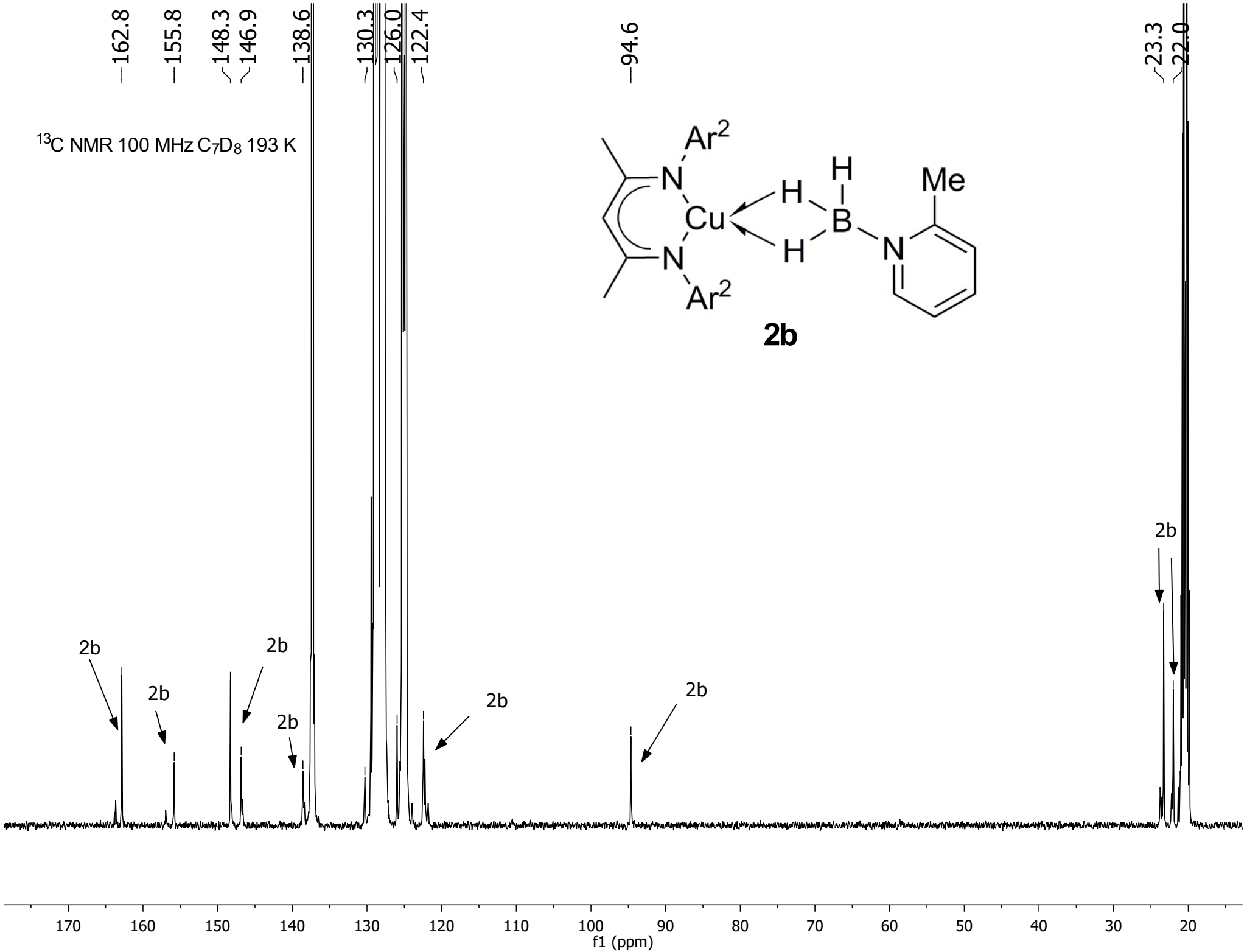
0.1

1.1

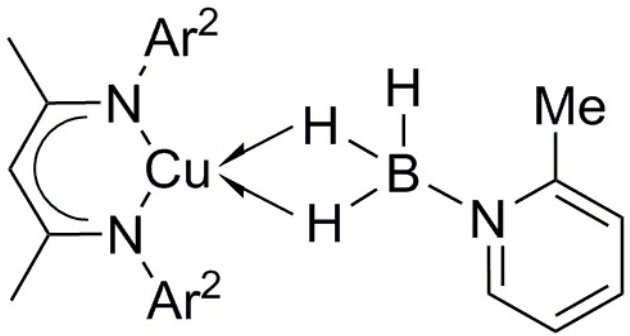
2.9

1.2

f1 (ppm)


162.8
155.8
148.3
146.9
138.6
130.3
126.0
122.4
94.6
23.3
22.0
^{13}C NMR 100 MHz C_7D_8 193 K
Ar2
N
Cu
N
Ar2
H
H
B
H
N
Me
2b
2b
2b
2b
2b
2b
2b
2b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

^{11}B NMR 128 MHz C_6D_6 193 K



-12.14