Electronic Supporting Information

Copper-Induced Ammonia N-H Functionalization

María Álvarez,[§] Eleuterio Álvarez,[≠] Manuel R. Fructos,[§] Juan Urbano[§] and Pedro J. Pérez*

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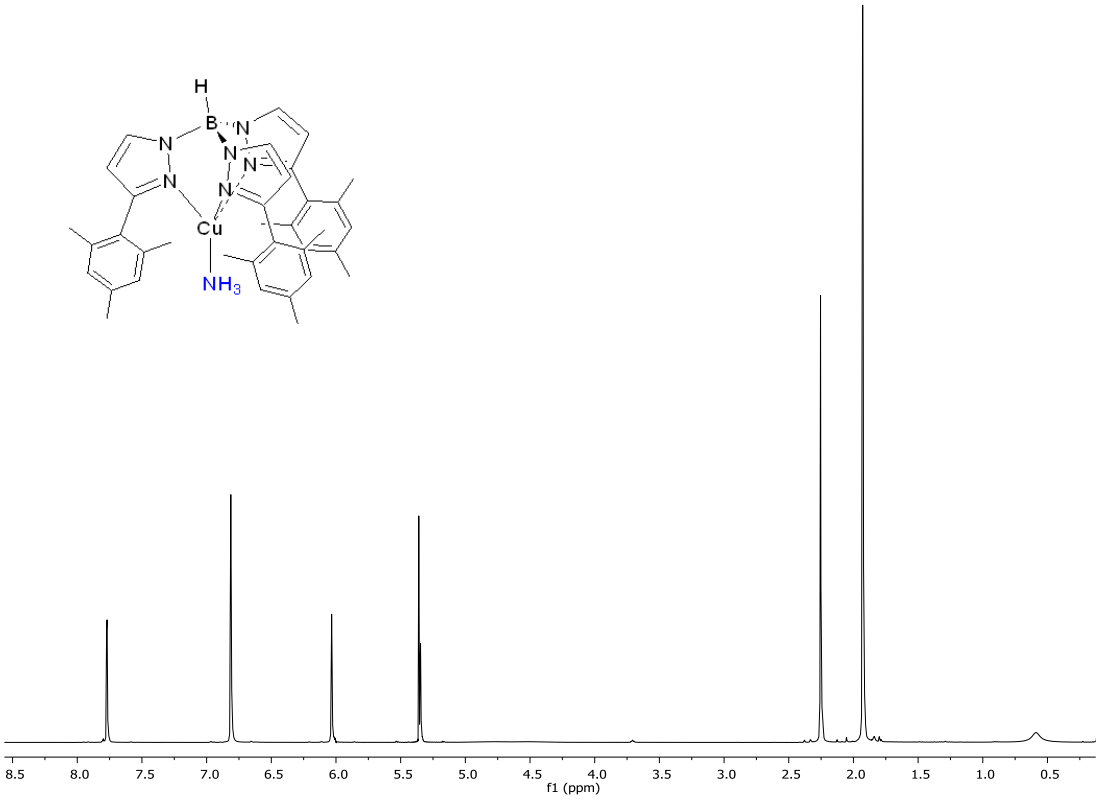
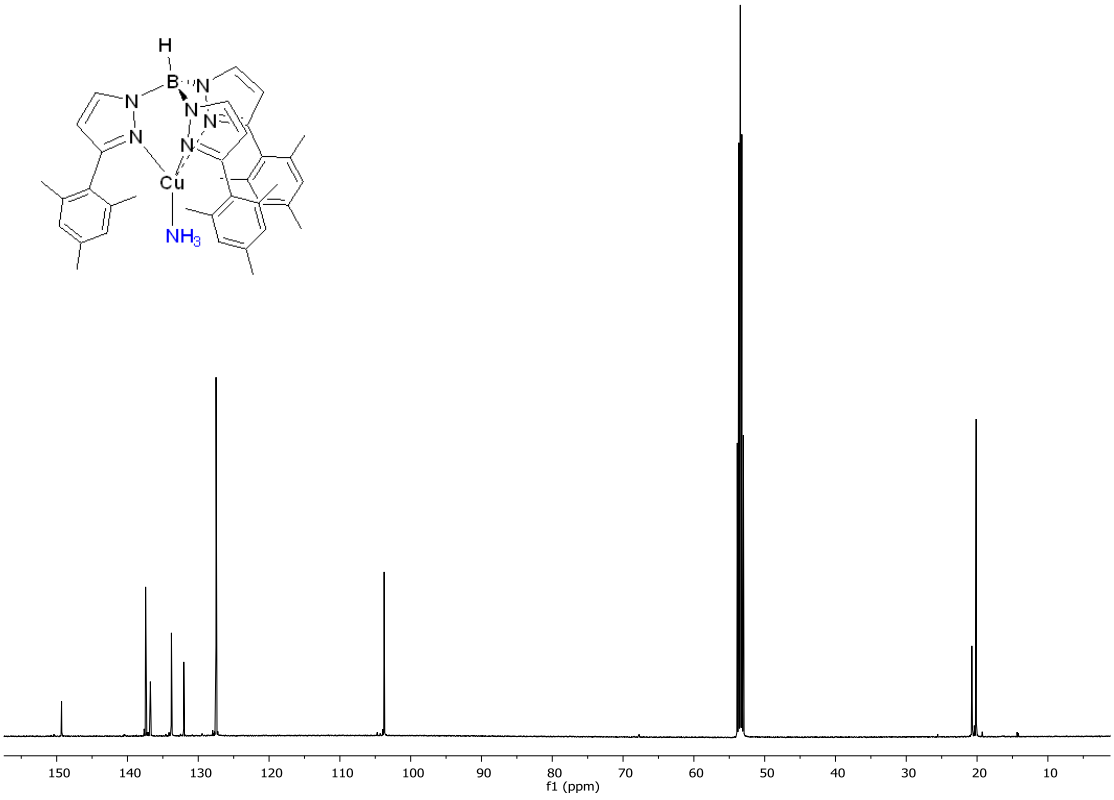
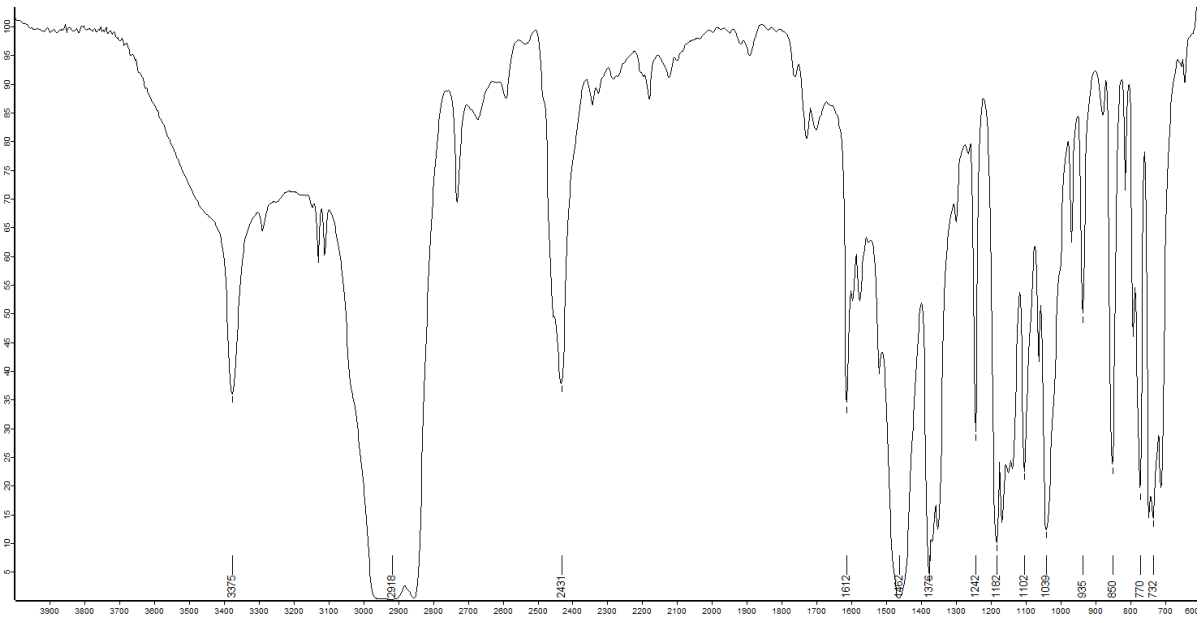
NMR spectra of compounds.



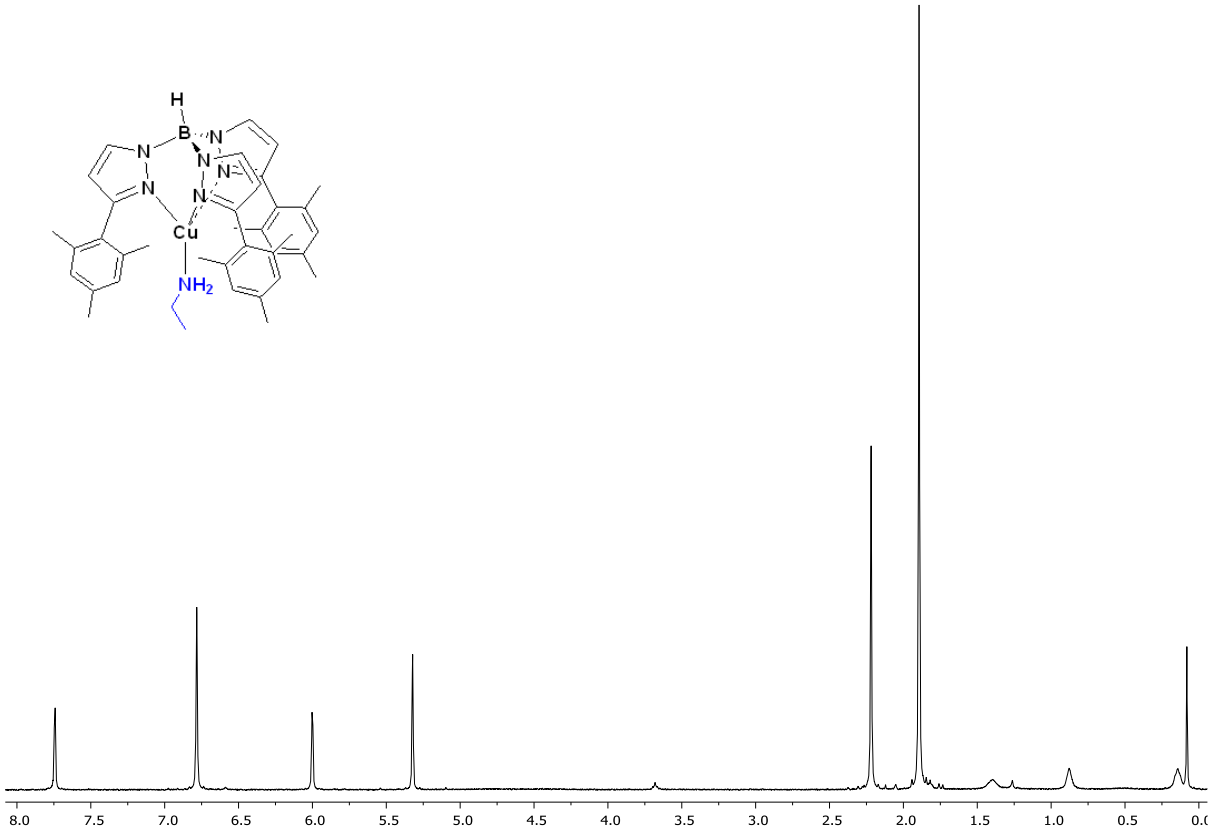
^{1}H NMR spectrum of Tp^{Ms}Cu(NH$_3$) (**1**) (CD_2Cl_2, 500 MHz)



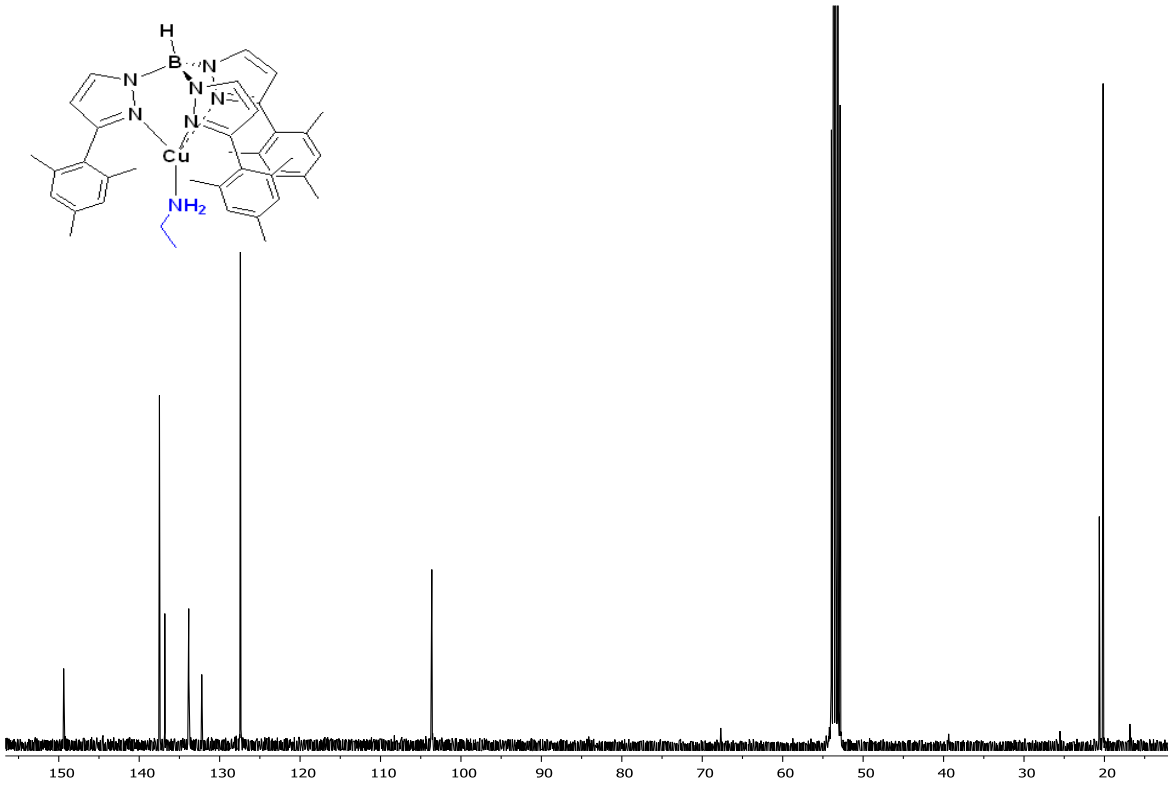
^{13}C{^{1}H} NMR spectrum of Tp^{Ms}Cu(NH$_3$) (**1**) (CD_2Cl_2, 500 MHz)



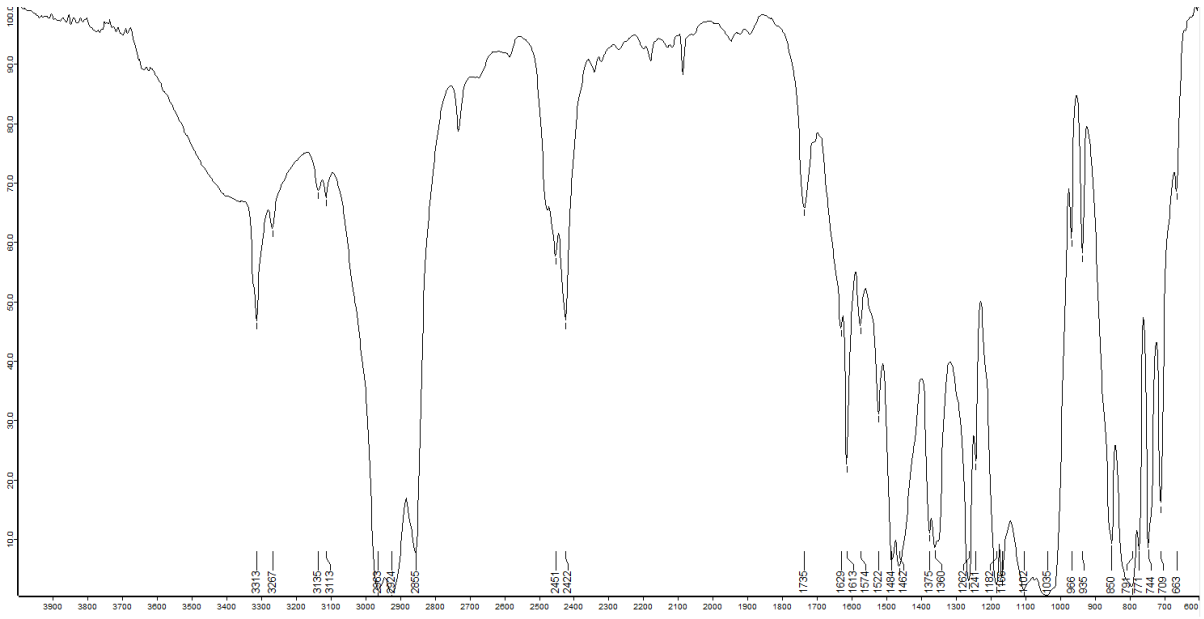
IR spectrum of $Tp^{Ms}Cu(NH_3)$ (**1**)



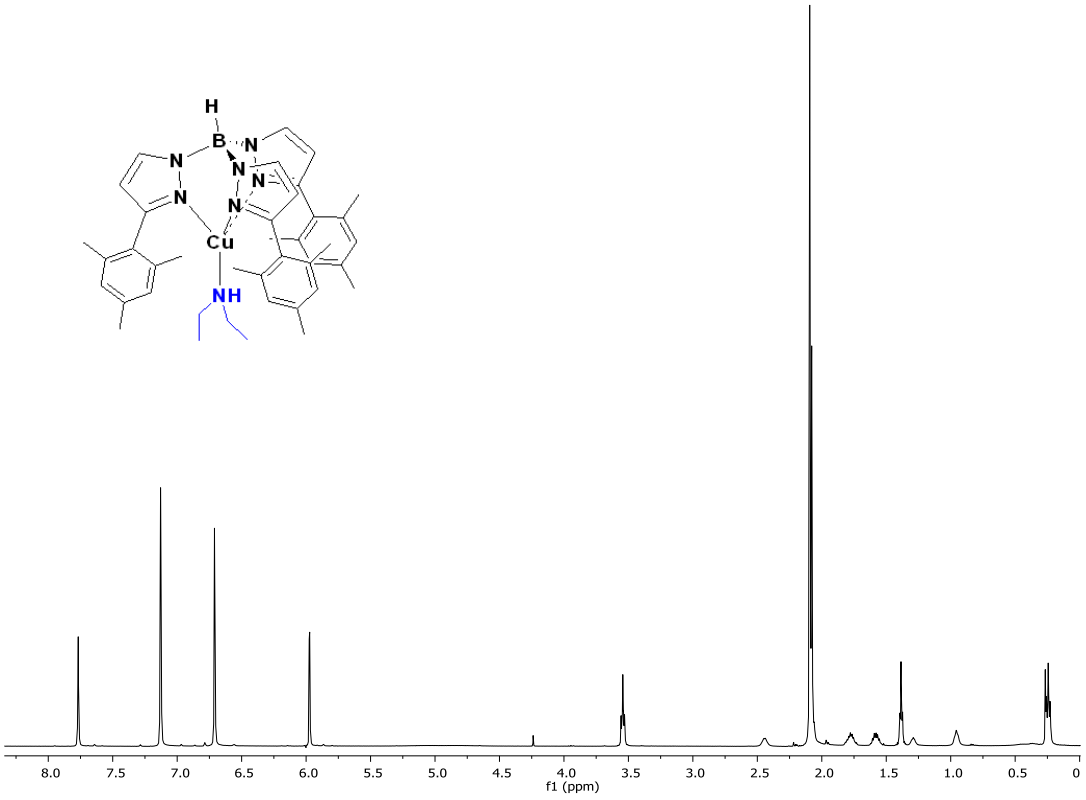
^{1}H NMR spectrum of Tp^{Ms}Cu(ethylamine) (**2**) (CD_2Cl_2, 500 MHz)



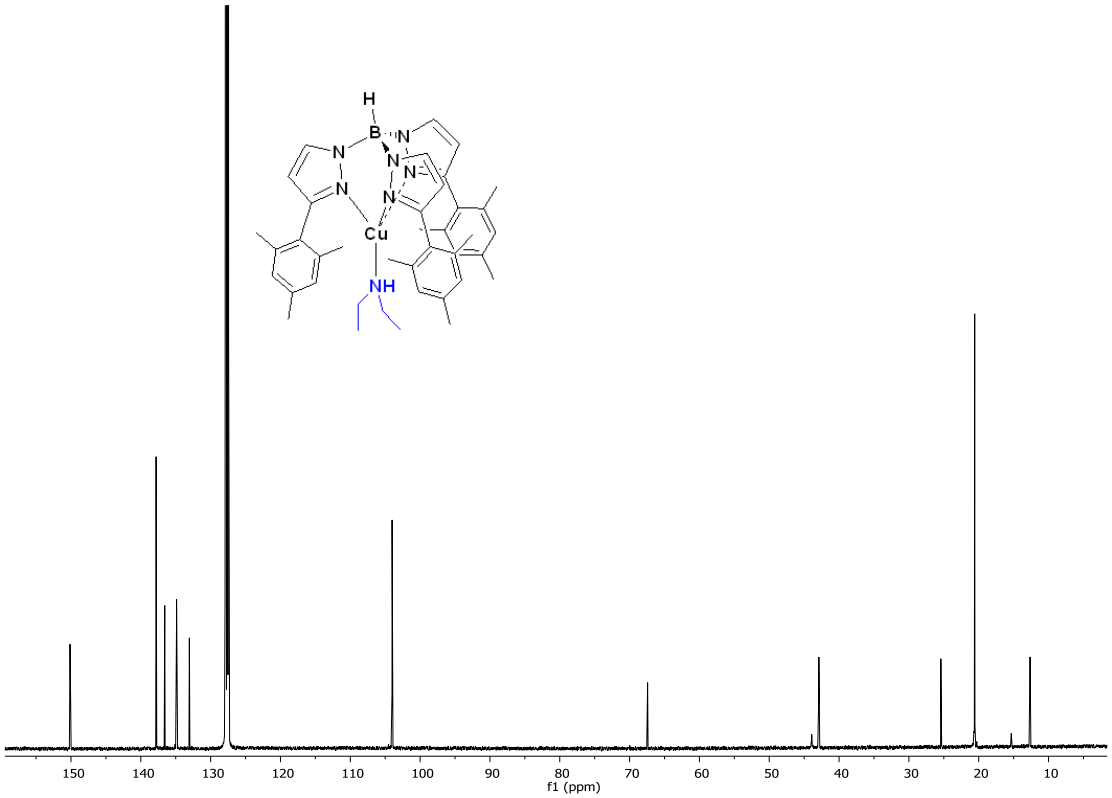
^{13}C{^{1}H} NMR spectrum of Tp^{Ms}Cu(ethylamine) (**2**) (CD_2Cl_2, 500 MHz)



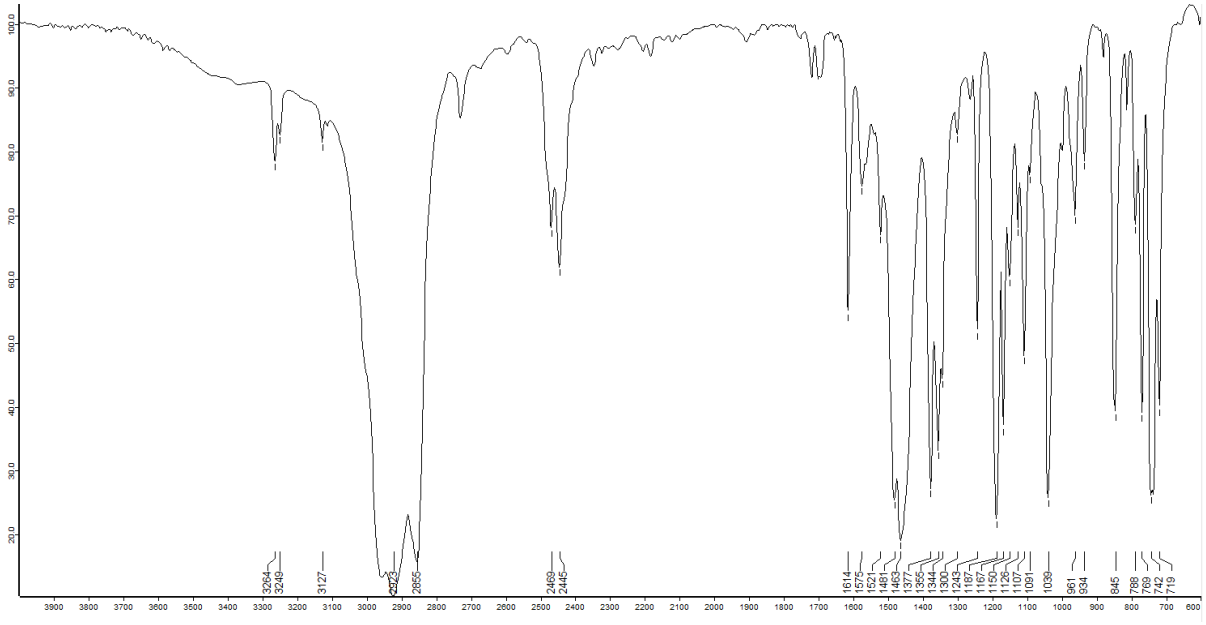
IR spectrum of $Tp^{Ms}Cu$(ethylamine) (**2**)



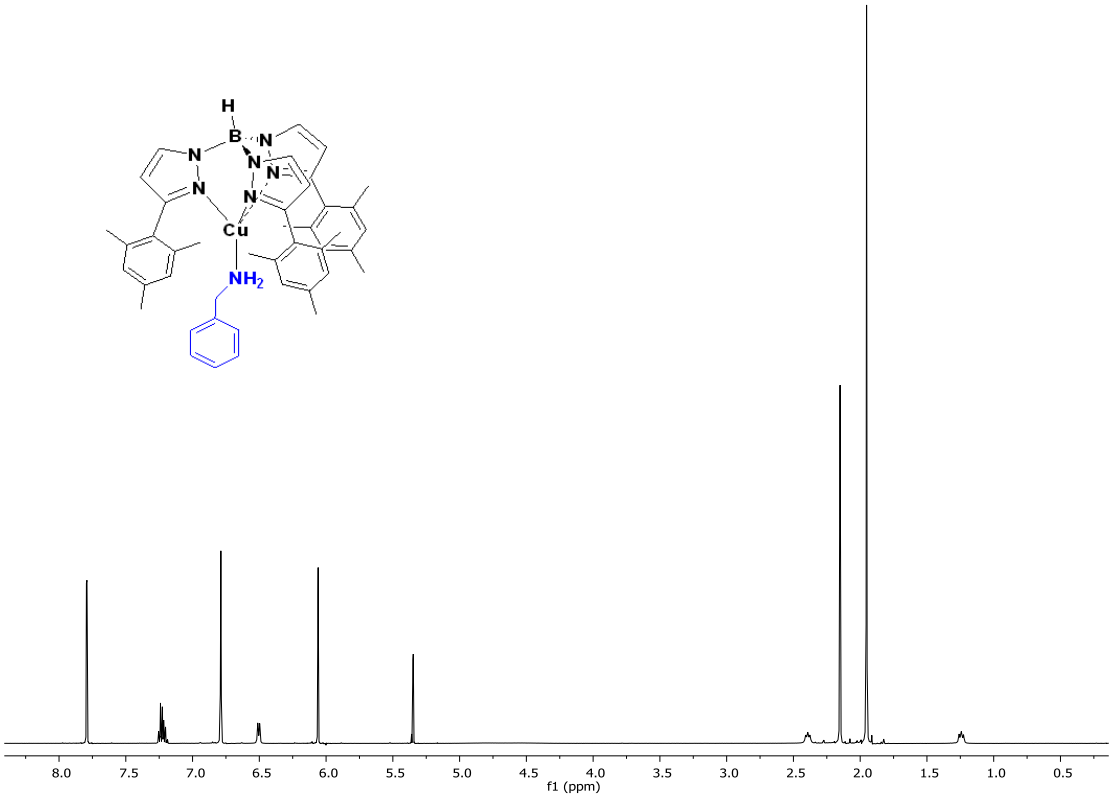
^{1}H NMR spectrum of Tp^{Ms}Cu(diethylamine) (**3**) (C_6D_6, 500 MHz)



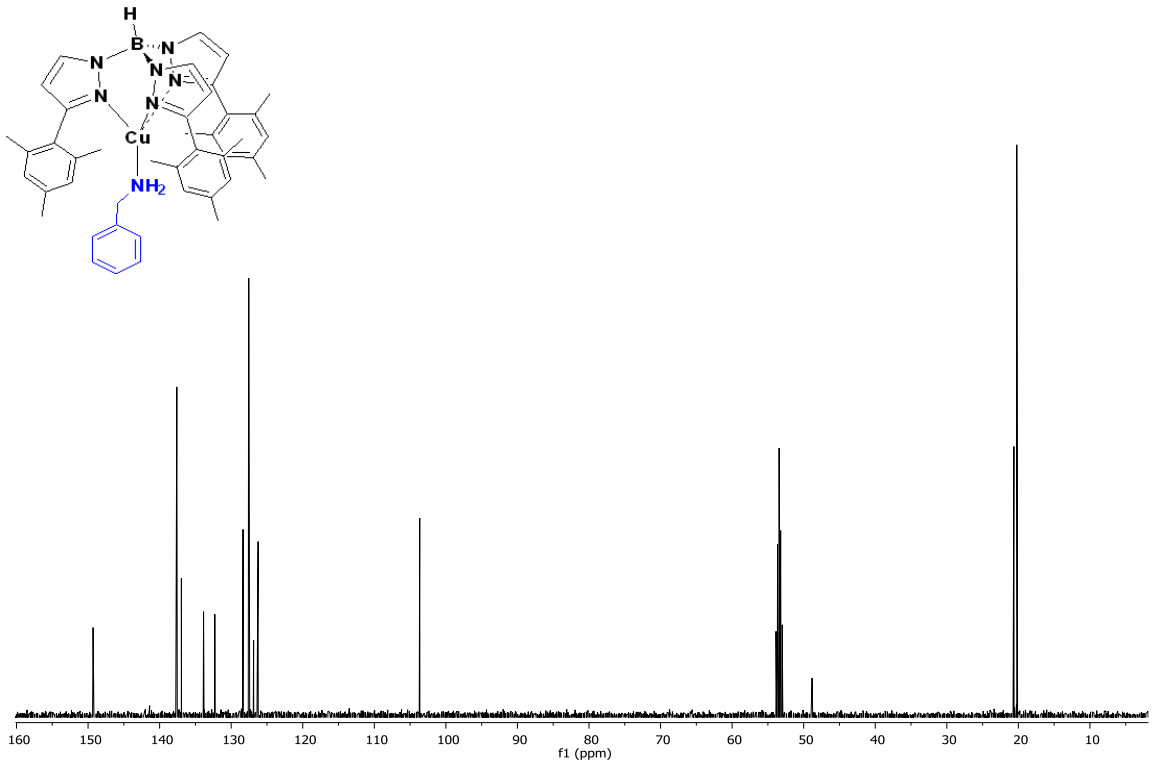
^{13}C{^{1}H} NMR spectrum of Tp^{Ms}Cu(diethylamine) (**3**) (C_6D_6, 500 MHz)



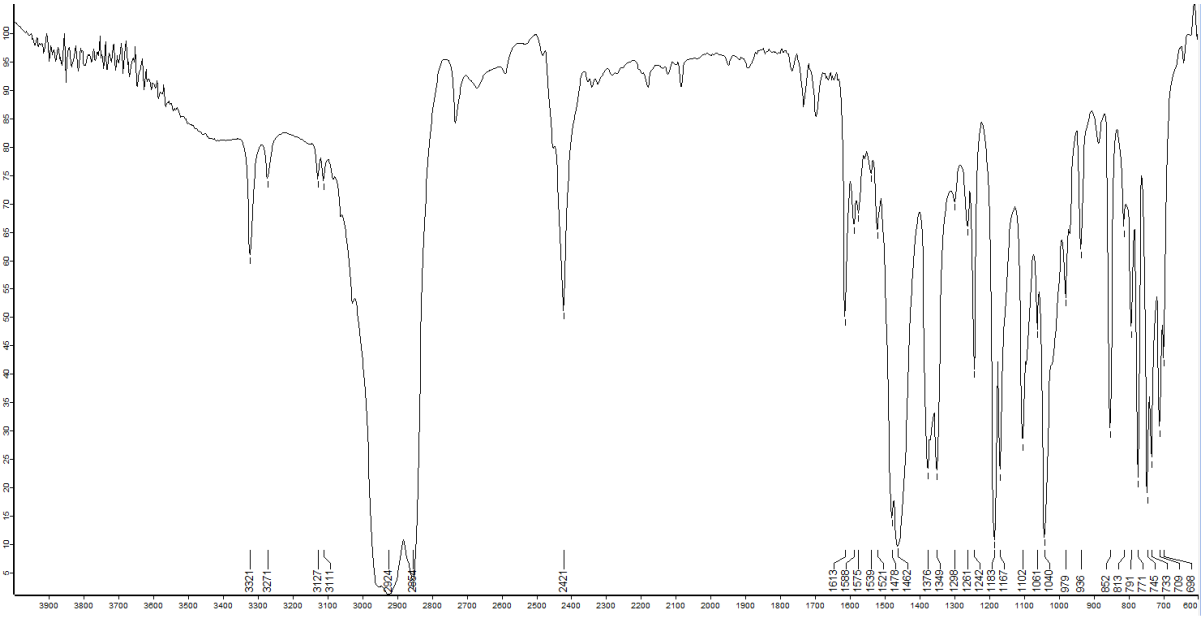
IR spectrum of $Tp^{Ms}Cu$(diethylamine) (**3**)



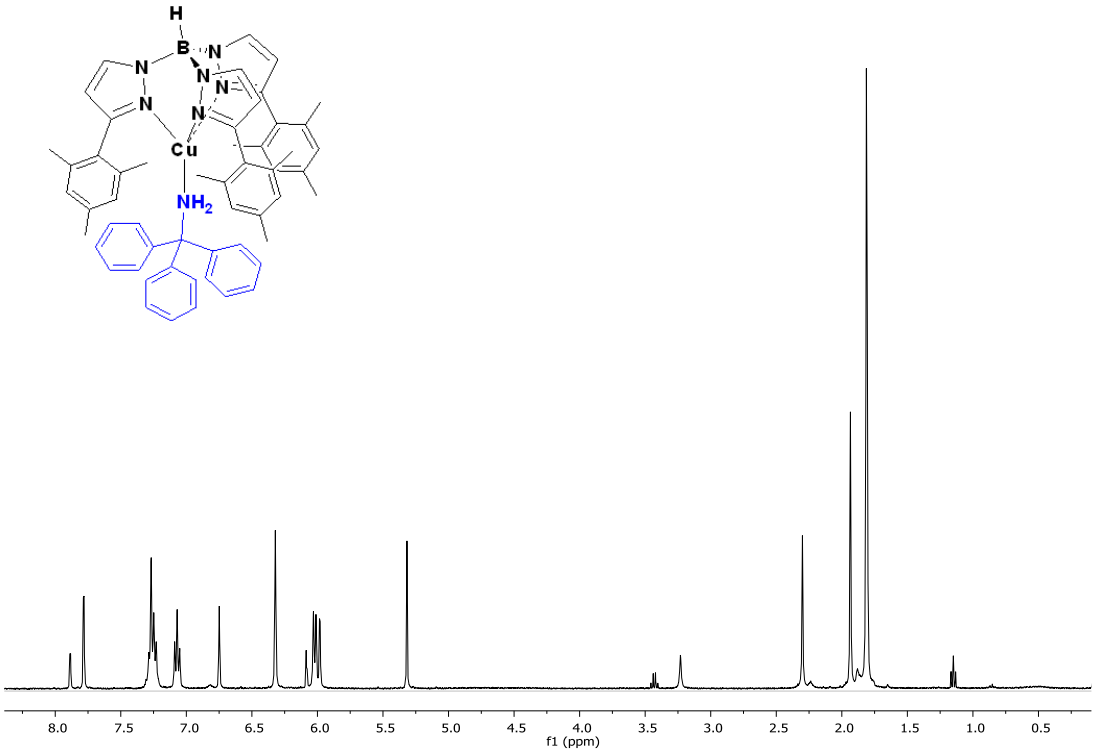
^{1}H NMR spectrum of Tp^{Ms}Cu(bencylamine) (**4**) (CD_2Cl_2, 500 MHz)



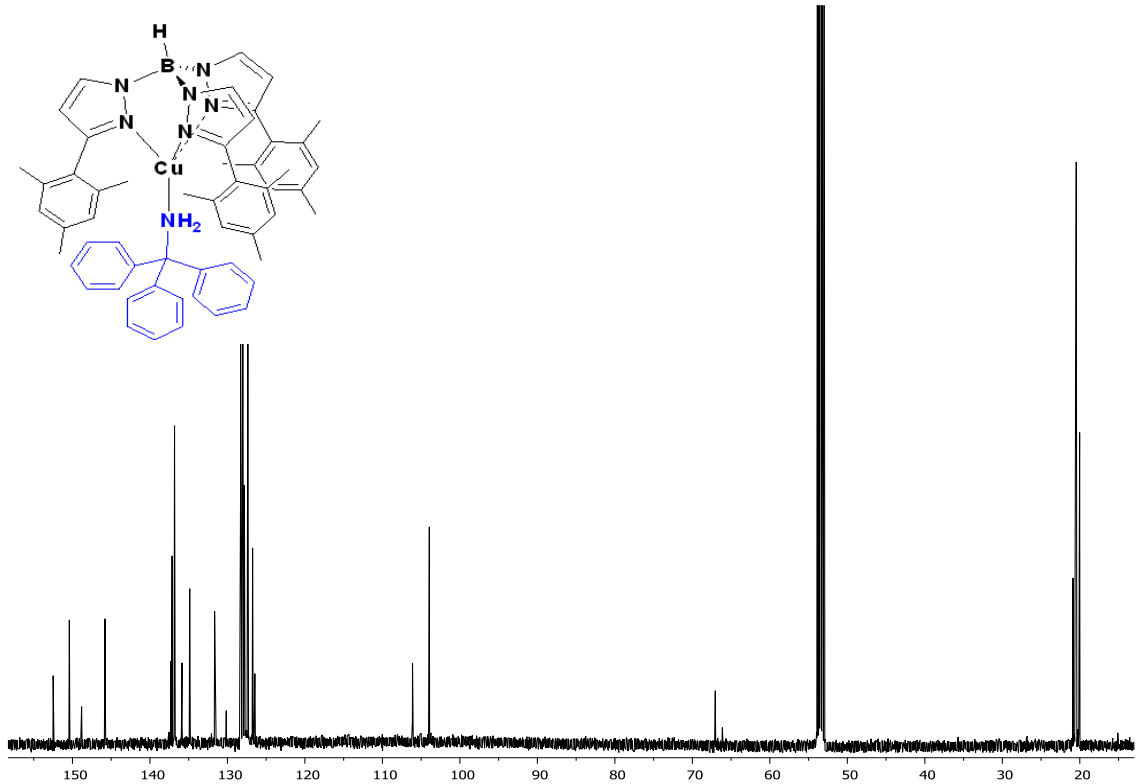
^{13}C{^{1}H} NMR spectrum of Tp^{Ms}Cu(bencylamine) (**4**) (CD_2Cl_2, 500 MHz)



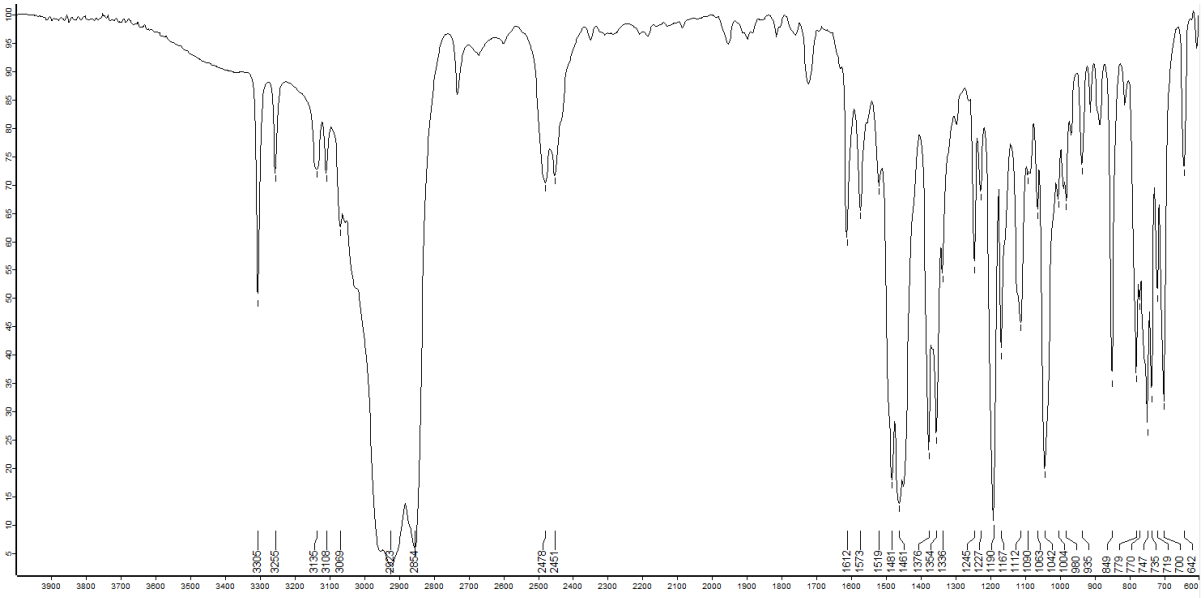
IR spectrum of $Tp^{Ms}Cu$(bencylamine) (**4**)



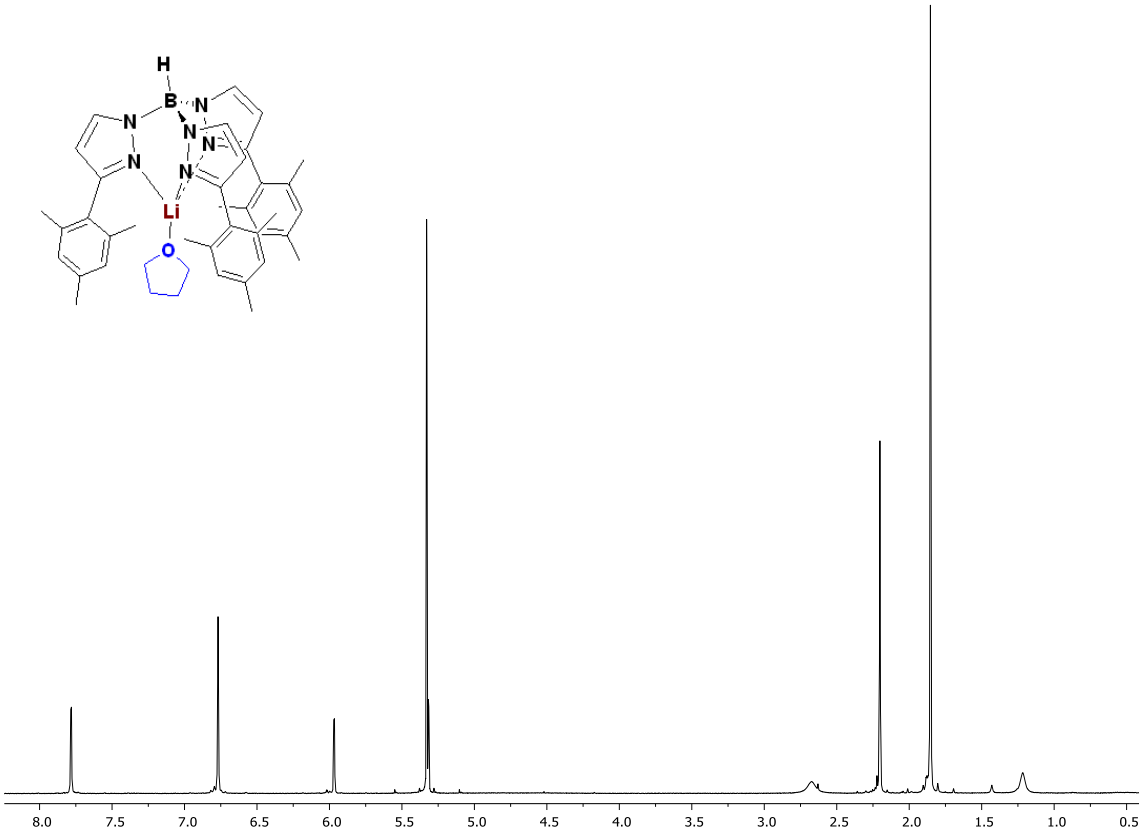
^{1}H NMR spectrum of Tp^{Ms}Cu(Triphenylmethylamine) (**5**) (CD_2Cl_2, 500 MHz)



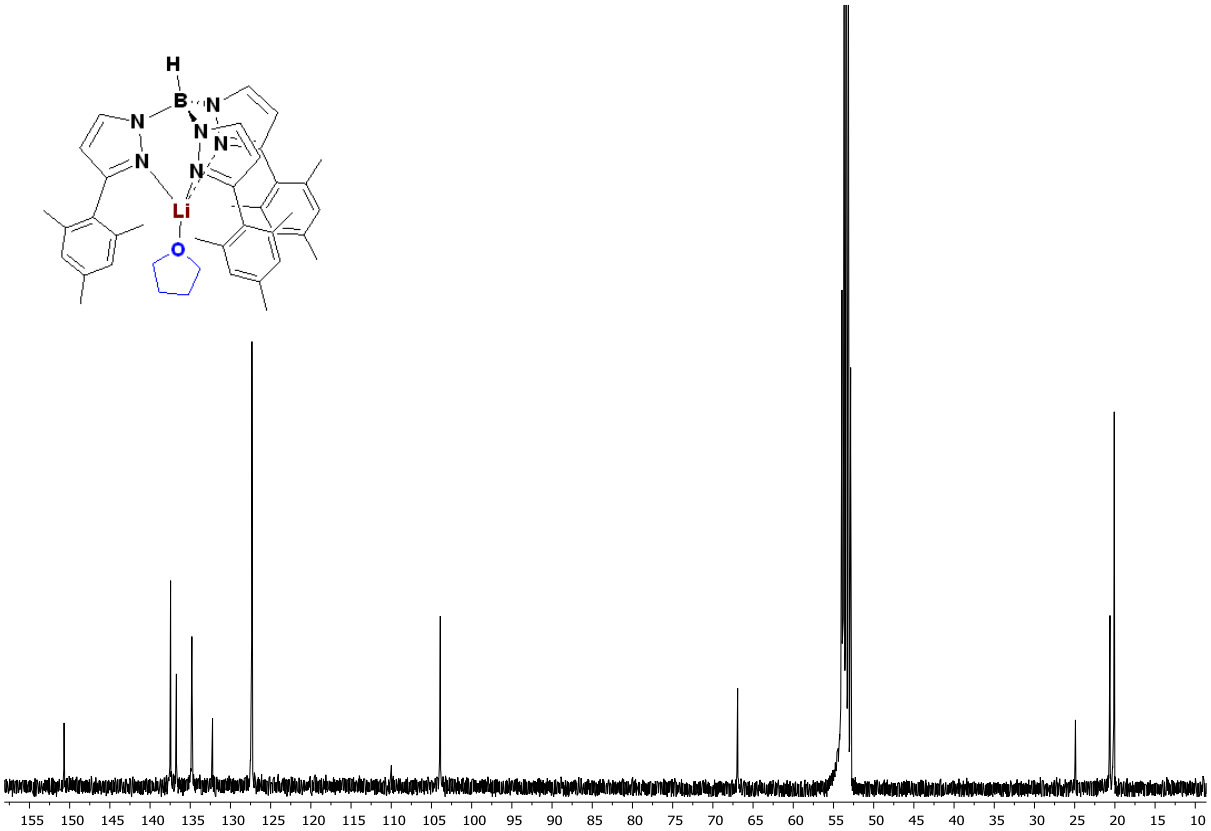
^{13}C{^{1}H} NMR spectrum of Tp^{Ms}Cu(Triphenylmethylamine) (**5**) (CD_2Cl_2, 500 MHz)



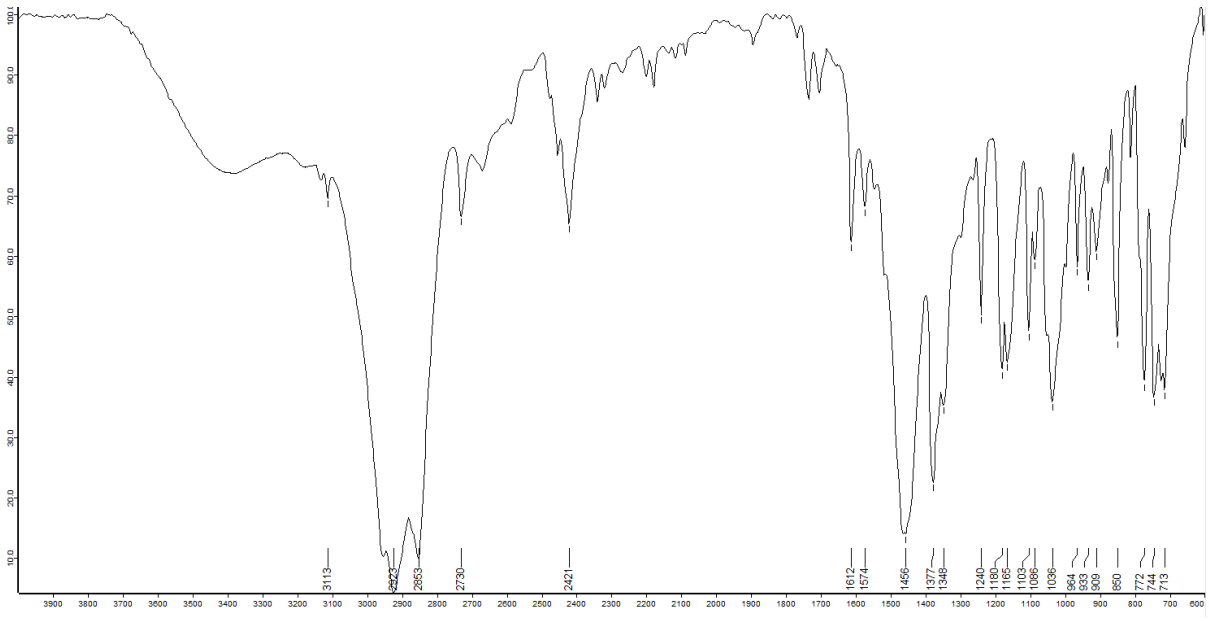
IR spectrum of $Tp^{Ms}Cu$(Triphenylmethylamine) (**5**)



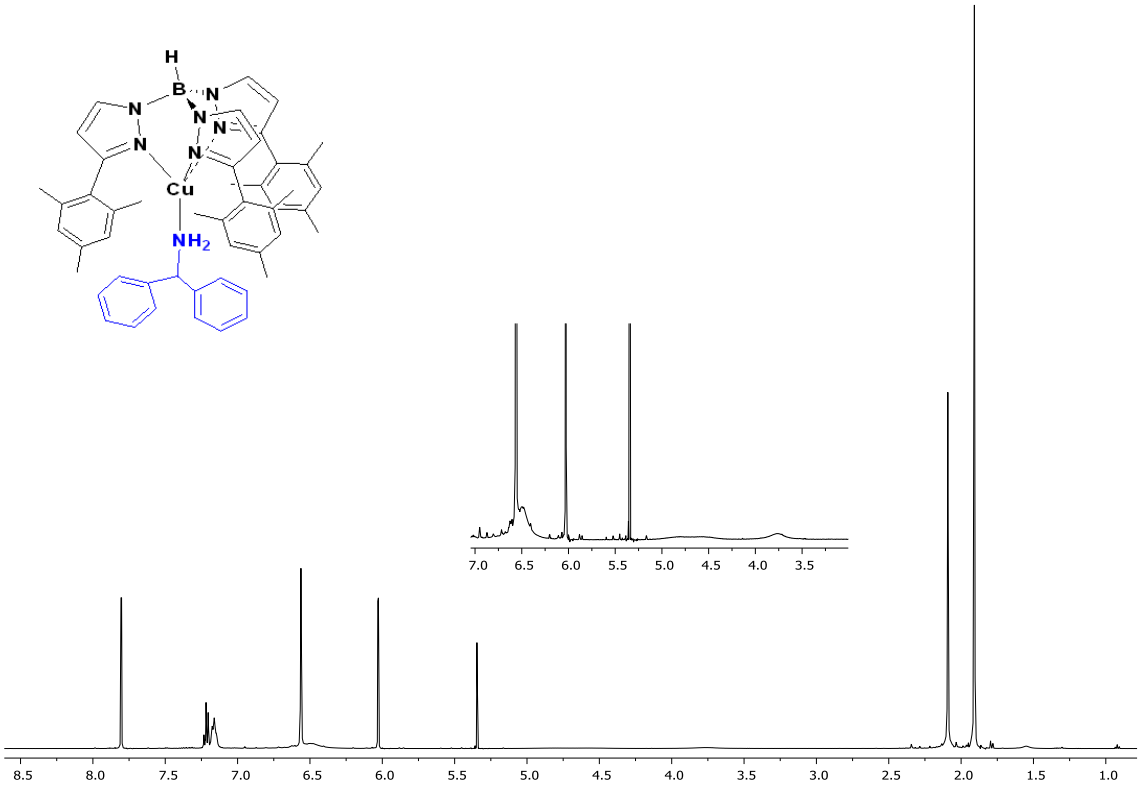
^{1}H NMR spectrum of Tp^{Ms}Li(thf) (**6**) (CD_2Cl_2, 500 MHz)



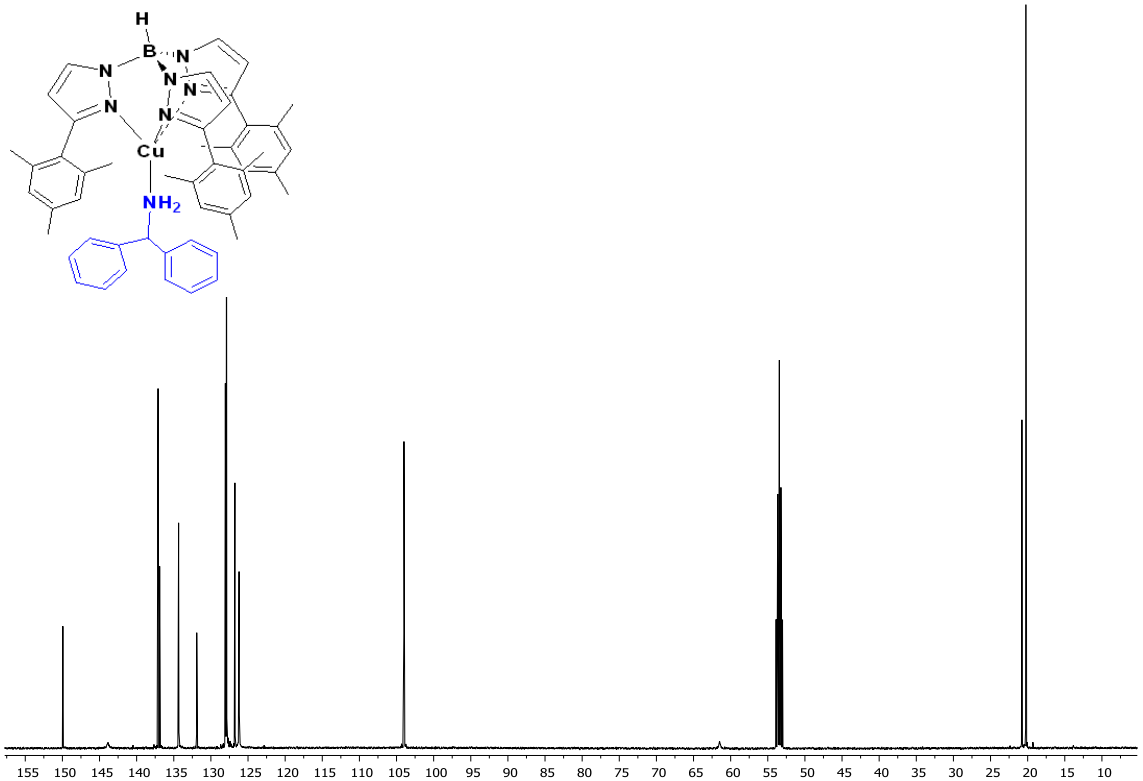
^{13}C{^{1}H} NMR spectrum of Tp^{Ms}Li(thf) (**6**) (CD_2Cl_2, 500 MHz)



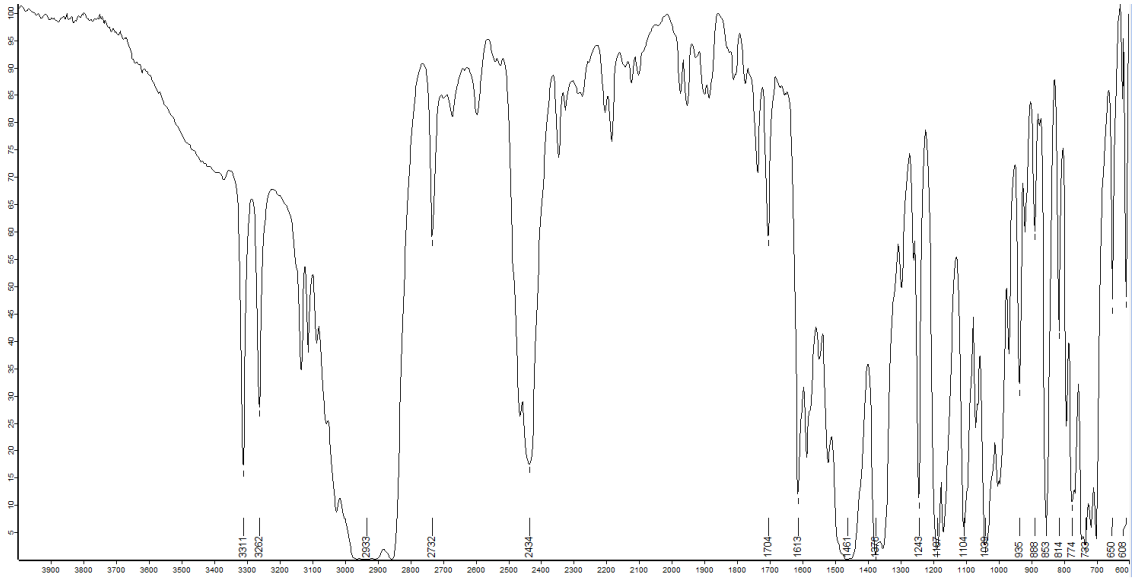
IR spectrum of $Tp^{Ms}Li(thf)$ (**6**)



^{1}H NMR spectrum of Tp^{Ms}Cu(Diphenylmethylamine) (**7**) (CD_2Cl_2, 500 MHz)



^{13}C{^{1}H} NMR spectrum of Tp^{Ms}Cu(Diphenylmethylamine) (**7**) (CD_2Cl_2, 500 MHz)



IR spectrum of $Tp^{Ms}Cu$(Diphenylmethylamine) (**7**)

Crystal X-Ray structure analysis for 1-7.

Crystals of suitable size for X-ray diffraction analysis were coated with dry perfluoropolyether and mounted on glass fibers and fixed in a cold nitrogen stream (T = 100 K) to the goniometer head. Data collection was performed on a Bruker-Nonius X8Apex-II CCD diffractometer, using monochromatic radiation λ(Mo K_α) = 0.71073 Å, by means of ω and ϕ scans with a width of 0.50 degree. The data were reduced (SAINT) [1] and corrected for absorption effects by the multi-scan method (SADABS) [2]. The structures were solved by direct methods (SIR-2002) [3] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12) [4] minimizing $w[F_o^2\text{-}F_c^2]^2$. All the non-hydrogen atoms were refined anisotropically, while C-H hydrogen atoms were placed in geometrically calculated positions using a riding model. The structures **3** and **4** appear with a positional disorder in the group amine and were refined in two positions with identical factors of occupation. While the structures **2**, **5** and **6** appear with a positional disorder in the group amine around a crystallographic 3-fold axis and they were refined in three positions imposed by the symmetry with identical factors of occupation of 0.3333. In addition for the structure **5** also the Cu atom appears off the crystallographic 3-fold axis and it was refined jointly with the trityl amine group. Some geometric restraints (DFIX command), the ADP restraint SIMU and the rigid bond restraint DELU were used to make the geometric and ADP values of the disordered atoms more reasonable. A search for solvent accessible voids in the crystal structure **7** using PLATON [5], showed a potential solvent volume, impossible to model even with the most severe restraints. The corresponding CIF data represent SQUEEZE [6] treated structure, with the undefined solvent excluded from the structural model. The SQUEEZE result was appended to the CIF.

X-Ray Crystallographic data of 1.

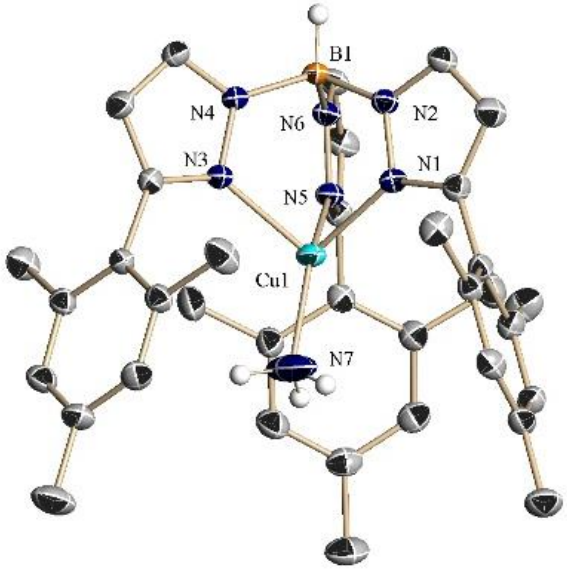


Fig. S1: ORTEP drawing of **1**, hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for **1**

Empirical formula	$C_{37}H_{45}BCl_2CuN_7$	
Formula weight	733.05	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 2_1	
Unit cell dimensions	a = 16.3142(6) Å	α= 90°.
	b = 11.7106(4) Å	β= 90°.
	c = 19.3881(6) Å	γ = 90°.
Volume	3704.1(2) $Å^3$	
Z	4	
Density (calculated)	1.315 Mg/m^3	
Absorption coefficient	0.770 mm^{-1}	
F(000)	1536	
Crystal size	0.50 x 0.40 x 0.30 mm^3	
Theta range for data collection	2.03 to 30.51°.	
Index ranges	-23<=h<=14, -14<=k<=16, -27<=l<=15	
Reflections collected	45530	

Independent reflections	8145 [R(int) = 0.0191]
Completeness to theta = 30.51°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8018 and 0.6993
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8145 / 7 / 443
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0765
R indices (all data)	R1 = 0.0350, wR2 = 0.0808
Absolute structure parameter	-0.006(8)
Largest diff. peak and hole	0.534 and -0.343 e.$Å^{-3}$

X-Ray Crystallographic data of 2.

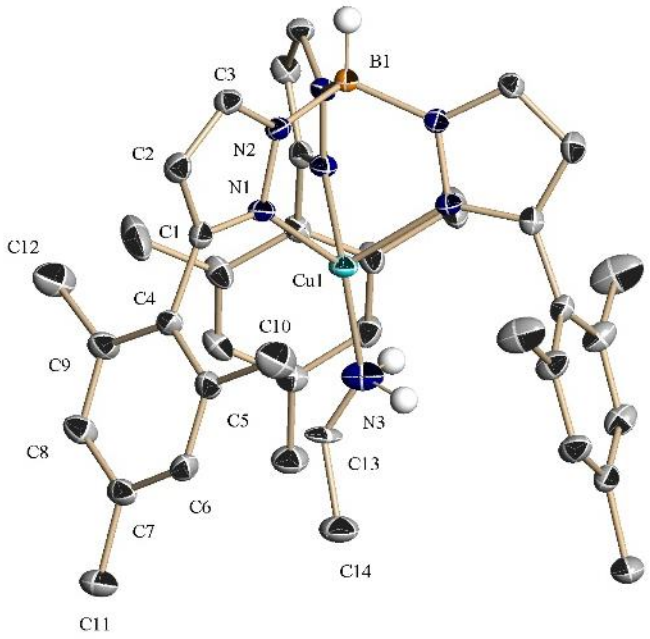


Fig. S2*:* ORTEP drawing of **2**, hydrogen atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for **2**

Empirical formula	$C_{38}H_{47}BCuN_7$	
Formula weight	676.18	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R 3 c	
Unit cell dimensions	a = 11.6413(4) Å	α= 90°.
	b = 11.6413(4) Å	β= 90°.
	c = 45.352(3) Å	γ = 120°.
Volume	5322.7(4) $Å^3$	
Z	6	
Density (calculated)	1.266 Mg/m^3	
Absorption coefficient	0.653 mm^{-1}	
F(000)	2147.9	

Crystal size	0.50 x 0.10 x 0.10 mm^3
Theta range for data collection	2.21 to 25.22°.
Index ranges	-8<=h<=13, -13<=k<=11, -53<=l<=50
Reflections collected	16469
Independent reflections	2119 [R(int) = 0.0480]
Completeness to theta = 25.22°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9376 and 0.9361
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2119 / 13 / 154
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.0972
R indices (all data)	R1 = 0.0409, wR2 = 0.1006
Absolute structure parameter	0.00(2)
Largest diff. peak and hole	0.809 and -0.229 e.$Å^{-3}$

X-Ray Crystallographic data of 3.

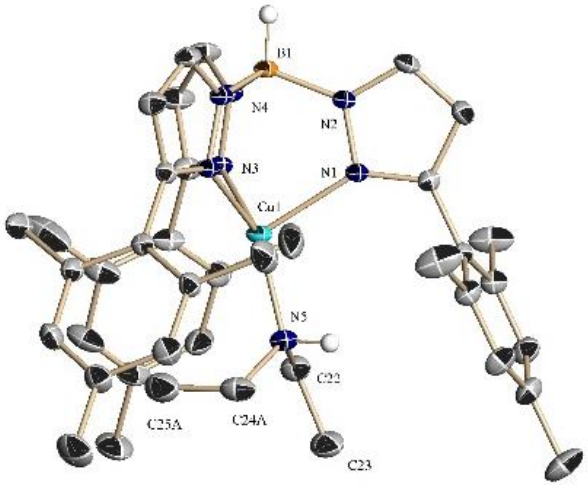


Fig. S3: ORTEP drawing of **3**, hydrogen atoms are omitted for clarity.

Table S3. Crystal data and structure refinement for **3**

Empirical formula	$C_{40}H_{51}BCuN_7$	
Formula weight	704.23	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	C m c 2_1	
Unit cell dimensions	a = 17.1818(9) Å	α= 90°.
	b = 13.6111(6) Å	β= 90°.
	c = 16.4367(9) Å	γ = 90°.
Volume	3843.9(3) $Å^3$	
Z	4	
Density (calculated)	1.217 Mg/m^3	
Absorption coefficient	0.605 mm^{-1}	
F(000)	1496	
Crystal size	0.25 x 0.20 x 0.20 mm^3	
Theta range for data collection	1.91 to 25.25°.	
Index ranges	-19<=h<=20, -16<=k<=16, -17<=l<=19	
Reflections collected	17014	
Independent reflections	3354 [R(int) = 0.0268]	
Completeness to theta = 25.25°	100.0 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.8885 and 0.8634
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3354 / 77 / 266
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0791
R indices (all data)	R1 = 0.0340, wR2 = 0.0810
Absolute structure parameter	-0.003(14)
Largest diff. peak and hole	0.265 and -0.241 e.$Å^{-3}$

X-Ray Crystallographic data of 4

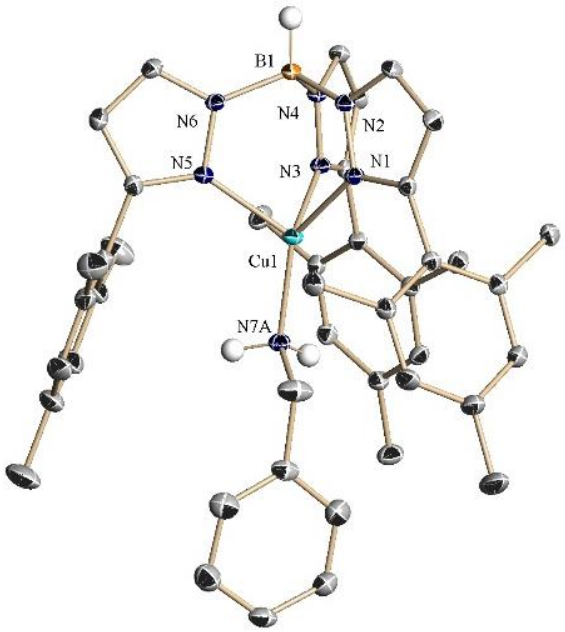


Fig. S4: ORTEP drawing of **4**, hydrogen atoms are omitted for clarity.

Table S4. Crystal data and structure refinement for **4**

Empirical formula	$C_{43}H_{49}BCuN_7$	
Formula weight	738.24	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 19.5923(5) Å	α= 90°.
	b = 11.7255(3) Å	β= 90.8290(10)°.
	c = 16.7466(4) Å	γ = 90°.
Volume	3846.79(17) $Å^3$	
Z	4	
Density (calculated)	1.275 Mg/m^3	
Absorption coefficient	0.608 mm^{-1}	
F(000)	1560	
Crystal size	0.50 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.12 to 25.25°.	
Index ranges	-23<=h<=23, -14<=k<=14, -20<=l<=20	
Reflections collected	75457	

Independent reflections	6963 [R(int) = 0.0323]
Completeness to theta = 25.25°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9417 and 0.8508
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6963 / 396 / 550
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0840
R indices (all data)	R1 = 0.0396, wR2 = 0.0886
Largest diff. peak and hole	0.268 and -0.409 e.$Å^{-3}$

X-Ray Crystallographic data of 5.

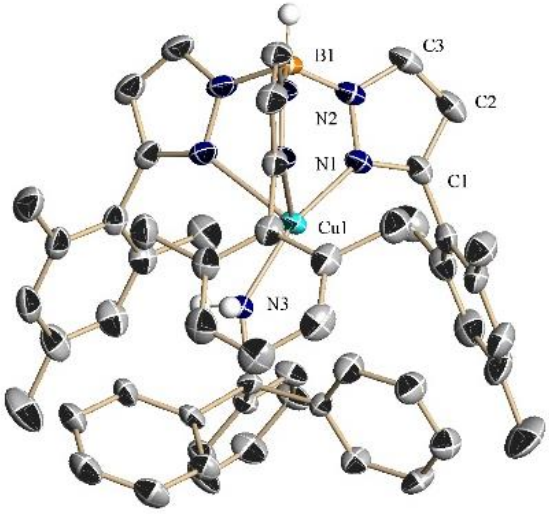


Fig. S5: ORTEP drawing of **5**, hydrogen atoms are omitted for clarity.

Table S5. Crystal data and structure refinement for **5**

Empirical formula	$C_{58}H_{63}BCl_6CuN_7$	
	$[C_{55}H_{57}BCuN_7, 3(CH_2Cl_2)]$	
Formula weight	1145.20	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R -3	
Unit cell dimensions	a = 20.1415(4) Å	α= 90°.
	b = 20.1415(4) Å	β= 90°.
	c = 24.6108(12) Å	γ = 120°.
Volume	8646.5(5) $Å^3$	
Z	6	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	0.701 mm^{-1}	
F(000)	3576	
Crystal size	0.50 x 0.40 x 0.25 mm^3	
Theta range for data collection	1.43 to 25.24°.	
Index ranges	-24<=h<=24, -24<=k<=24, -29<=l<=29	
Reflections collected	74684	

Independent reflections	3478 [R(int) = 0.0316]
Completeness to theta = 25.24°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8443 and 0.7208
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3478 / 337 / 328
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1131
R indices (all data)	R1 = 0.0507, wR2 = 0.1218
Largest diff. peak and hole	0.255 and -0.193 e.$Å^{-3}$

X-Ray Crystallographic data of 6.

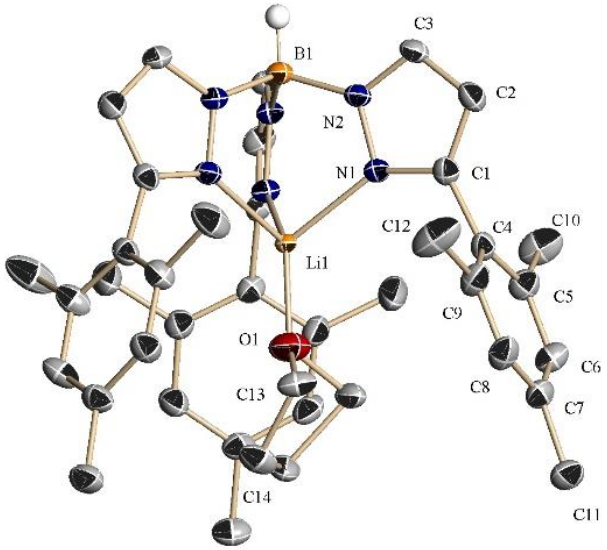


Fig. S6: ORTEP drawing of **6**, hydrogen atoms are omitted for clarity.

Table S6. Crystal data and structure refinement for **6**

Empirical formula	$C_{40}H_{48}BLiN_6O$	
Formula weight	646.59	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R 3 c	
Unit cell dimensions	a = 11.90130(10) Å	□= 90°.
	b = 11.90130(10) Å	□= 90°.
	c = 45.2468(10) Å	□ = 120°.
Volume	5550.18(14) $Å^3$	
Z	6	
Density (calculated)	1.161 Mg/m^3	
Absorption coefficient	0.070 mm^{-1}	
F(000)	2076	
Crystal size	0.50 x 0.50 x 0.45 mm^3	
Theta range for data collection	2.67 to 25.23°.	
Index ranges	-14<=h<=14, -14<=k<=14, -54<=l<=54	
Reflections collected	37671	
Independent reflections	1124 [R(int) = 0.0258]	

Completeness to theta = 25.23°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9703 and 0.9671
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1124 / 51 / 158
Goodness-of-fit on F^2	1.393
Final R indices [I>2sigma(I)]	R1 = 0.0660, wR2 = 0.1856
R indices (all data)	R1 = 0.0667, wR2 = 0.1864
Largest diff. peak and hole	0.570 and -0.575 e.$Å^{-3}$

X-Ray Crystallographic data of 7.

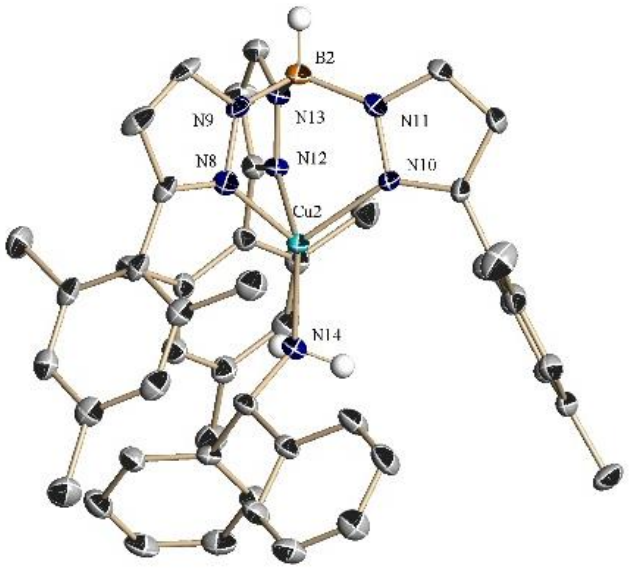


Fig. S7: ORTEP drawing of **7**, hydrogen atoms are omitted for clarity.

Table S7. Crystal data and structure refinement for **7**

Empirical formula	$C_{50}H_{55}BCl_2CuN_7$	
	$[C_{49}H_{53}BCuN_7, CH_2Cl_2]$	
Formula weight	899.26	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Unit cell dimensions	a = 18.5242(10) Å	α= 90°.
	b = 14.3774(9) Å	β= 97.093(3)°.
	c = 36.400(2) Å	γ = 90°.
Volume	9620.3(10) $Å^3$	
Z	8	
Density (calculated)	1.242 Mg/m^3	
Absorption coefficient	0.606 mm^{-1}	
F(000)	3776	
Crystal size	0.20 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.13 to 25.25°.	
Index ranges	-22<=h<=22, -17<=k<=17, -43<=l<=43	
Reflections collected	199250	

Independent reflections	17359 [R(int) = 0.0947]
Completeness to theta = 25.25°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9703 and 0.8884
Refinement method	Full-matrix-block least-squares on F^2
Data / restraints / parameters	17359 / 28 / 1117
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.10, wR2 = 0.27
R indices (all data)	R1 = 0.13, wR2 = 0.25
Largest diff. peak and hole	1.173 and -1.067 e.$Å^{-3}$

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