Supporting Information

for

Carbazole Substituted Amidinato Silylene: Synthesis, Bond-ing, and Coordination Behavior with Coinage Metals

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Contents

S1. Crystallographic Details of 1-8.

Crystal data for **1**-**8** were collected on a Bruker Smart Apex Duo diffractometer at 100 K using Mo Kα radiation (λ = 0.71073 Å). The absorption correction was done using multi-scan method (SADABS). The structures were solved by direct methods and refined by full-matrix least-squares methods against F2 (SHELXL-2014/6) and Olex1 with the ShelXT2 structure solution program.[41] Attempts to refine peaks of residual electron density as disordered or partial occupancy solvent toluene carbon atoms were unsuccessful. The data were corrected for disordered electron density using the SQUEEZE procedure, as implemented in PLATON.[42] Crystallographic data file for the **1-8** have been deposited with the Cambridge Crystallographic Data Centre. CCDC No.: 2092910 (**1**), 2092912 (**2**), 2092913 (**3**), 2092914 (**4**), 2092915 (**5**), 2092916 (**6**), 2092917 (**7**), 2092918 (**8**).

Table S1. Crystal data and structure refinement data for **1-8**.

	1	**2**	**3**	**4**
Chemical formula	$C_{27}H_{31}N_3Si$	$C_{33}H_{36}CoN_3OSi$	$C_{27}H_{31}N_3SiAuCl$	$C_{54}H_{62}N_6Si_2Cu_2Br_2$
Formula weight	425.64 g/mol	577.67 g/mol	658.06 g/mol	1322.4 g/mol
Temperature	100 K	100 K	100 K	100 K
Wavelength	0.71703 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P* -1	*P2₁/n*	*C2/c*	*P* -1
Unit cell dimensions	*a* = 9.7178(17) Å	*a* = 9.9383(4) Å	*a* = 18.969(9) Å	*a* = 10.7857(19) Å
	b = 11.2040 (17) Å	*b* = 13.7155(5) Å	*b* = 18.011(9) Å	*b* = 17.269(3) Å
	c = 12.647 (2) Å	*c* = 20.9815(9) Å	47(11) Å	85(3) Å
	α = 107.961(5)°	*α* = 90°	*α* = 90°	*α* = 99.213(5)°
	β = 107.208 (6)°	*β* = 94.859(2)°	*β* = 121.69(2)°	*β* = 98.840(5)°
	γ = 103.138(5)°	*γ* = 90°	*γ* = 90°	*γ* = 106.744(5)°
Volume	1171.8 (3) $Å^3$	2849.7(2) $Å^3$	5246(5) $Å^3$	3129.2(10) $Å^3$
Z	2	4	8	2
Density (calculated)	1.206 g/cm^3	1.074 g/cm^3	1.666 g/cm^3	1.403 g/cm^3
Absorption coefficient	0.119 mm^{-1}	0.676 mm^{-1}	5.775 mm^{-1}	2.041 mm^{-1}
F(000)	456.00	1216.00	2592.00	1368.0
Theta range for data collection	2.34 to 28.10°	2.45 to 28.333°	2.52 to 26.547°	2.017 to 28.357°
Index ranges	-12<=h<=12, -13<=k<=14, -16<=l<=16	-13<=h<=13, -18<=k<=18, -28<=l<=28	-23<=h<=23, -22<=k<=22, -22<=l<=22	-14<=h<=14, -23<=k<=23, -24<=l<=24
Reflections collected	28909	100069	94570	83965
Independent reflections	5731 [R(int) = 0.0968]	7076 [R(int) = 0.1131]	5469 [R(int) = 0.2074]	15564 [R(int) = 0.1690]
Coverage of independent reflections	97.9%	99.6%	99.7%	99.3%
Function minimized	Σ w(Fo^2 - Fc^2)^2	Σ w(Fo^2 - Fc^2)^2	Σ w(Fo^2 - Fc^2)^2	Σ w(Fo^2 - Fc^2)^2
Data / restraints / parameters	5731/0/286	7076/ 0 / 358	5469 / 0 / 299	15564/ 0 / 735
Goodness-of-fit on F^2	1.050	1.067	1.021	1.052
Δ/σ max	0.000	0.000	0.002	0.001
Final R indices	3786 data[I>2σ(I)], R1 = 0.0612, wR2 = 0.1111	5000 data[I>2σ(I)], R1 = 0.0523, wR2 = 0.0937	3961 data[I>2σ(I)], R1 = 0.0557, wR2 = 0.0808	7712 data[I>2σ(I)], R1 = 0.0867, wR2 = 0.1300
	all data , R1 = 0.1155, wR2 = 0.1272	all data , R1 = 0.0937, wR2 = 0.1064	all data, R1 = 0.0661, wR2 = 0.0877	all data, R1 = 0.2099, wR2 = 0.1628
Largest diff. peak and hole	0.551 and -0.318 $eÅ^{-3}$	0.94 and -0.57 $eÅ^{-3}$	1.921 and -0.985 $eÅ^{-3}$	0.94 to -0.84 $eÅ^{-3}$
R.M.S. deviation from mean	0.063 $eÅ^{-3}$	0.079 $eÅ^{-3}$	0.170 $eÅ^{-3}$	0.126 $eÅ^{-3}$

	5	**6**	**7**	**8**
Chemical formula	C_{54} $H_{61}N_6Si_2CuI$	$C_{56}H_{62}N_6O_2S_2Si_2F_6Cu_2$	$C_{54}H_{62}N_6Si_2Br_2Ag_2$	$C_{57}H_{62}N_6Si_2Ag_2I_2$
Formula weight	1040.70 g/mol	1276.49 g/mol	1226.83 g/mol	1575.59 g/mol
Temperature	100 K	100 K	100 K	100 K
Wavelength	0.71703 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P* 2_1/c	*P* 2_1/n	*P* 2_1/*n*	*P*-1
Unit cell dimensions	*a* = 15.0498(9) Å	*a* = 11.561(3) Å	*a* = 10.699(4) Å	*a* = 14.8886(17)Å
	b = 44.112(3) Å	*b* = 18.692(4) Å	*b* = 15.525(4) Å	*b* = 15.2459(19)Å
	c = 9.1050(5) Å	*c* = 14.271(4) Å	*c* = 17.296(5) Å	*c* = 16.403(2)Å
	α = 90°	α = 90°	α = 90°	α = 67.202(4)°
	β = 103.835(2)°	β = 113.576(12)°	β = 107.452(10)°	β = 89.316(4)°
	γ = 90°	γ = 90°	γ = 90°	γ = 67.948(4)°
Volume	5869.2(6) $Å^3$	2826.5(13) $Å^3$	2740.7(14) $Å^3$	3142.3(7) $Å^3$
Z	4	4	2	2
Density (calculated)	1.178 g/cm^3	1.500 g/cm^3	1.487 g/cm^3	1.940 g/cm^3
Absorption coefficient	0.975 mm^{-1}	0.945 mm^{-1}	2.256 mm^{-1}	1.665 mm^{-1}
F(000)	2148.00	1320.00	1240.00	1564.0
Theta range for data collection	2.31 to 26.407°	2.68 to 28.425°	2.40 to 34.315°	1.859 to 25.250°
Index ranges	-18<=h<=18, -55<=k<=55, -11<=l<=11	-15<=h<=15, -25<=k<=25, -19<=l<=19	-16<=h<=16, -24<=k<=24, -27<=l<=27	-17<=h<=17, -18<=k<=18, -19<=l<=19
Reflections collected	151515	77987	131405	160529
Independent reflections	12038 [R(int) = 0.1161]	7065 [R(int) = 0.1945]	11343 [R(int) = 0.0545]	11375 [R(int) = 0.0541]
Coverage of independent reflections	99.8%	100%	99.1%	100%
Function minimized	Σ w(Fo^2 - Fc^2)^2	Σ w(Fo^2 - Fc^2)^2	Σ w(Fo^2 - Fc^2)^2	Σ w(Fo^2 - Fc^2)^2
Data / restraints / parameters	12038/0/589	7065/ 0 / 367	11343 / 0 / 304	11375/ 0 / 689
Goodness-of-fit on F^2	1.099	1.091	1.058	1.104
Δ/σ max	0.001	0.000	0.002	0.001
Final R indices	9145 data[I>2σ(I)], R1 = 0.0715, wR2 = 0.1686	4249 data[I>2σ(I)], R1 = 0.0660, wR2 = 0.1143	7614 data[I>2σ(I)], R1 = 0.0463, wR2 = 0.0705	9826 data[I>2σ(I)], R1 = 0.0347, wR2 = 0.0963
	all data , R1 = 0.1006, wR2 = 0.1809	all data , R1 = 0.1486, wR2 = 0.1474	all data, R1 = 0.0964, wR2 = 0.0843	all data, R1 = 0.0439, wR2 = 0.1094
Largest diff. peak and hole	2.152 and -0.929 e$Å^{-3}$	0.60 and -0.99 e$Å^{-3}$	0.743 and -1.002 e$Å^{-3}$	1.513 to -1.384 e$Å^{-3}$

S2. NMR Spectroscopic Data for Complexes 1-8.

* corresponds to Benzene-d_6, # corresponds to Chloroform-*d*

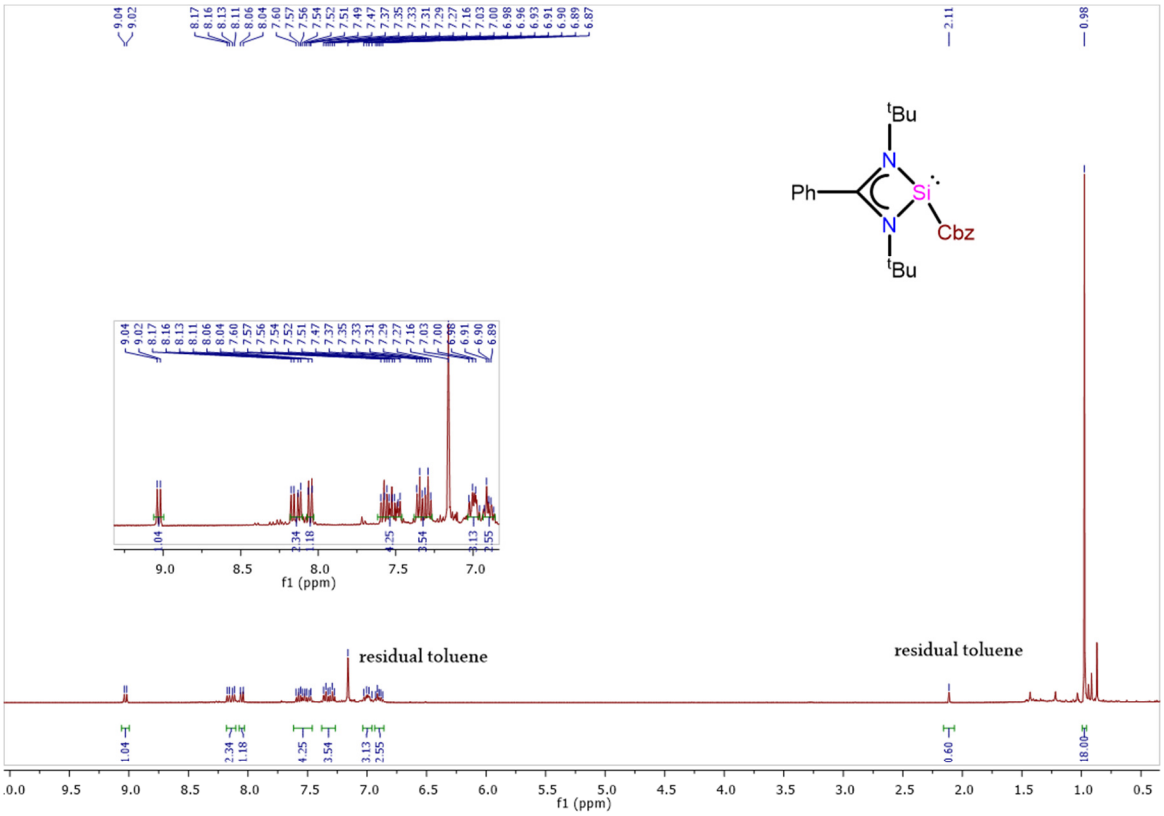


Figure S1. ^{1}H NMR of **1**

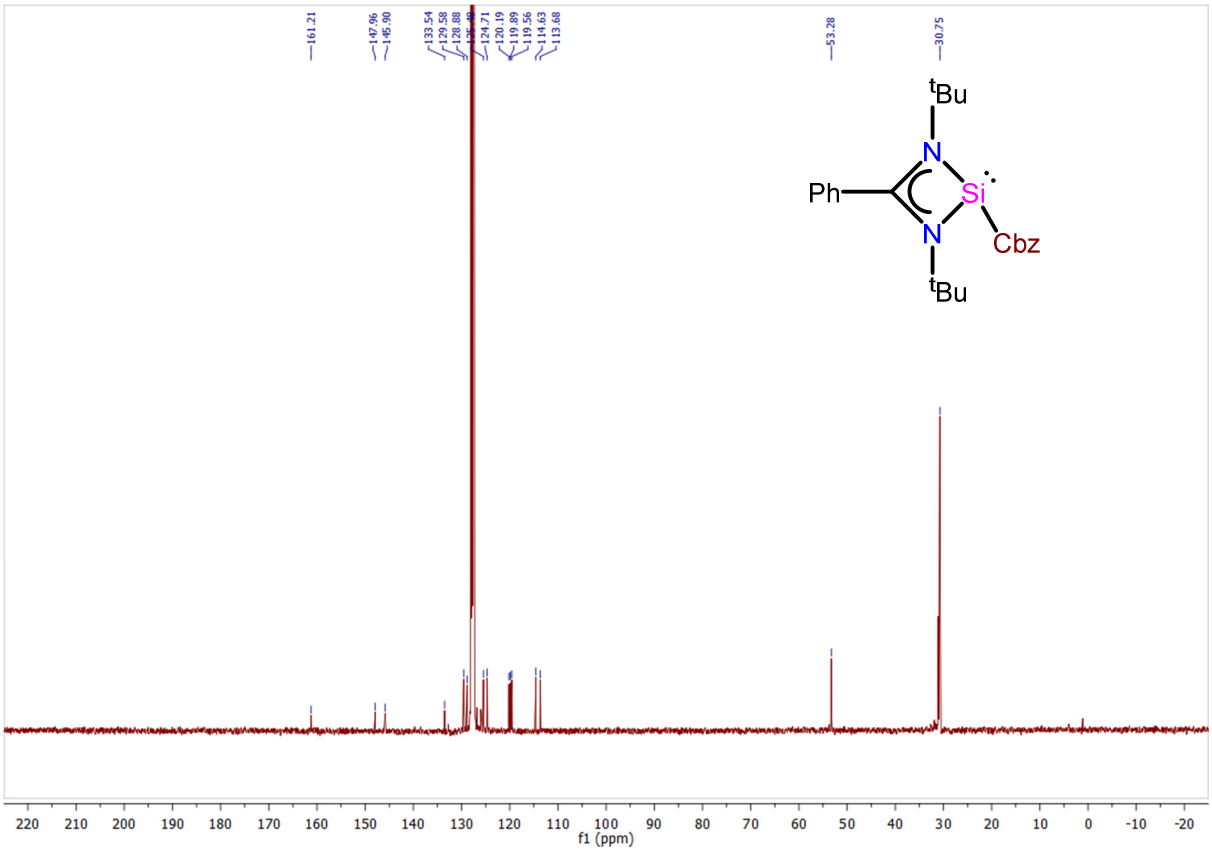


Figure S2. ^{13}C NMR of **1**

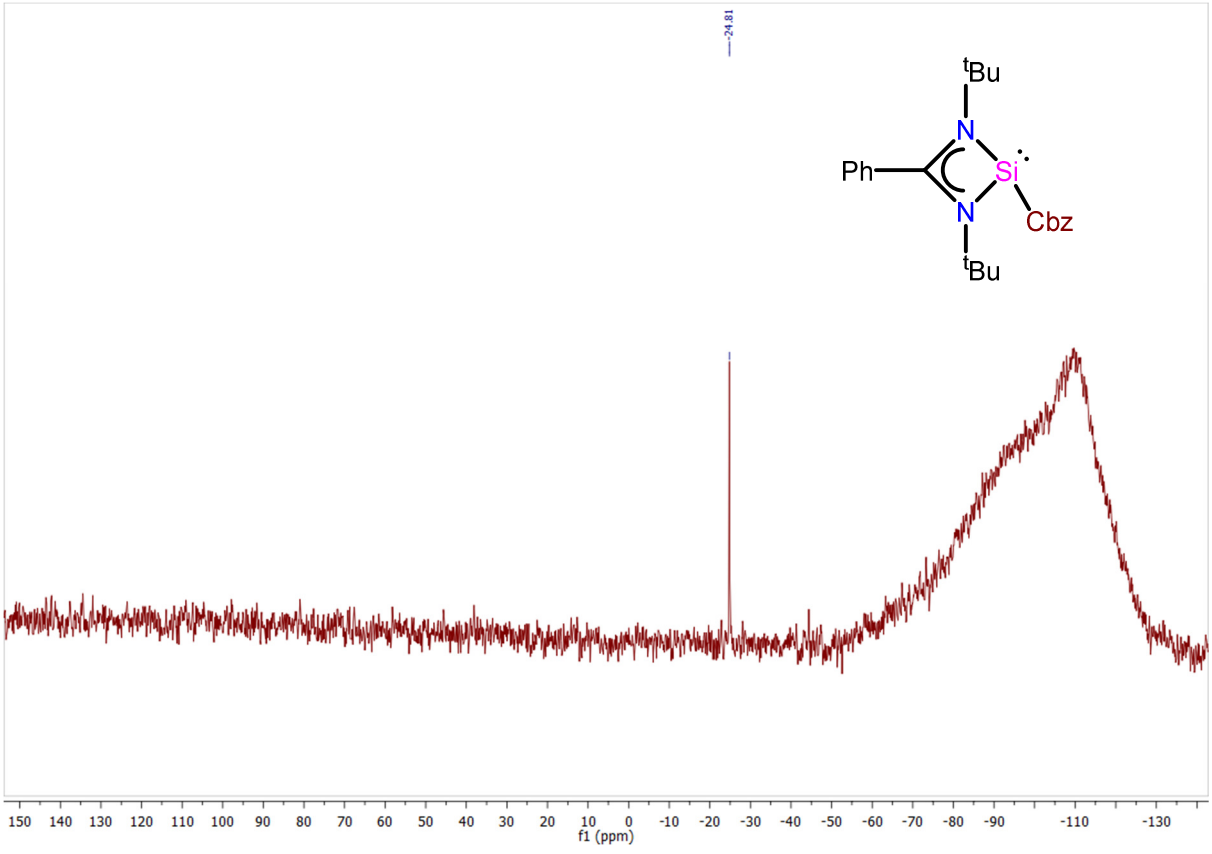


Figure S3. ^{29}Si NMR of **1**

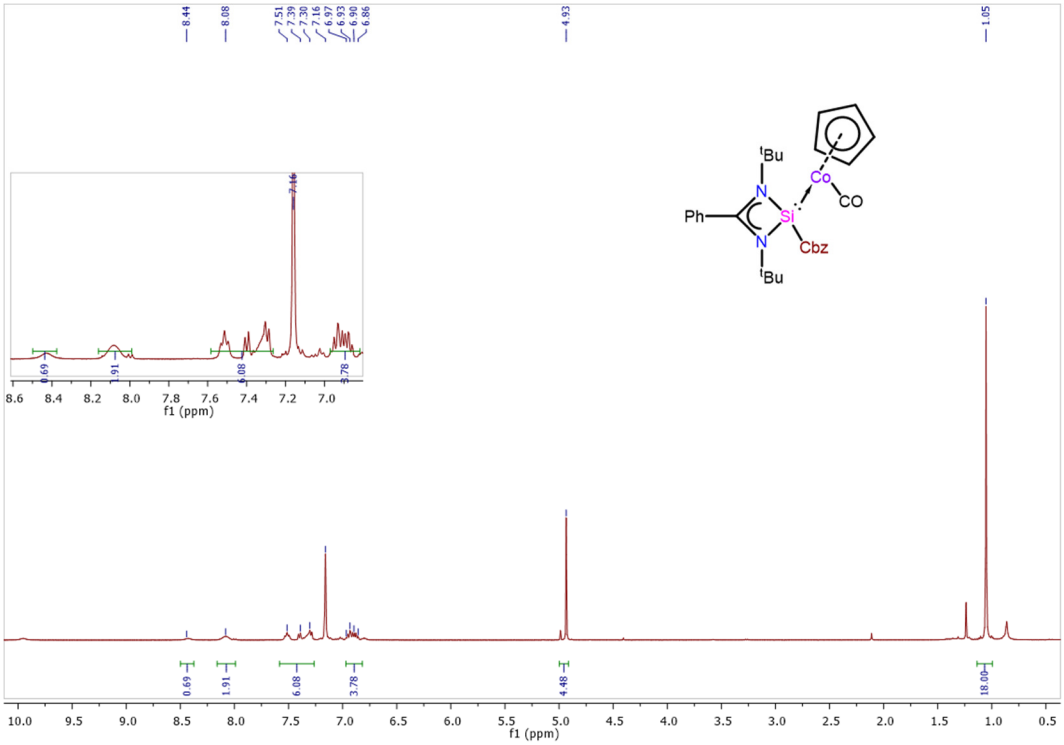


Figure S4. ^{1}H NMR of complex **2**

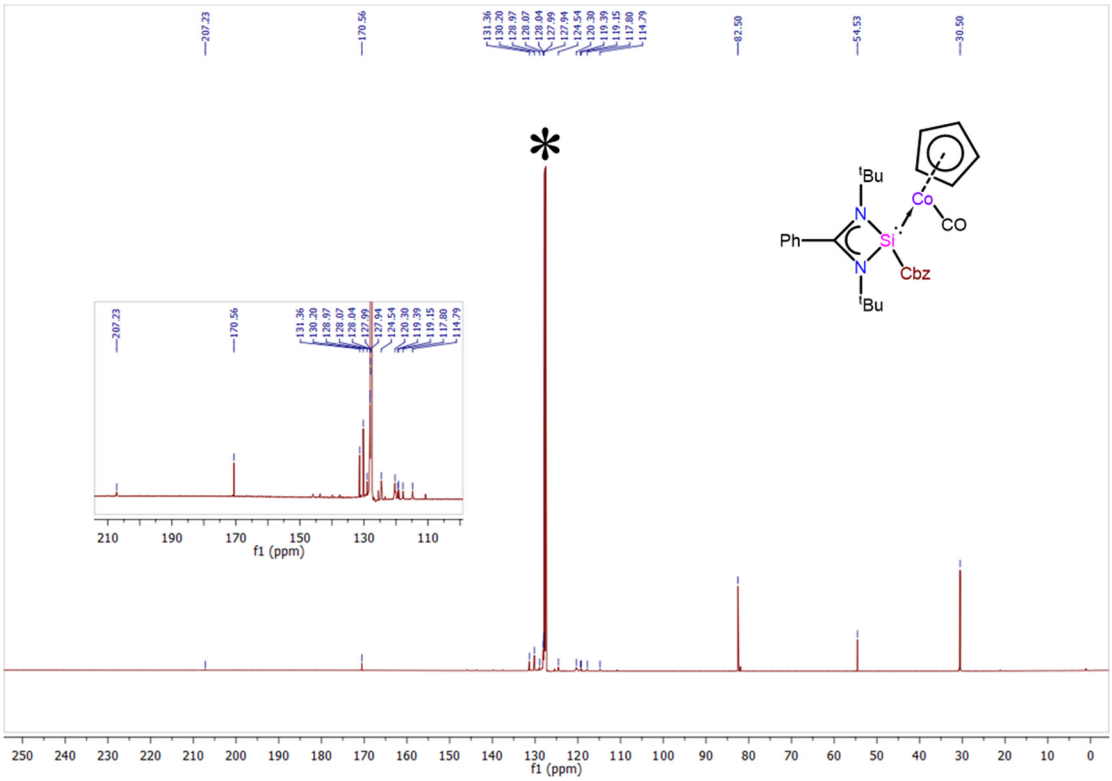


Figure S5. ^{13}C NMR of complex **2**

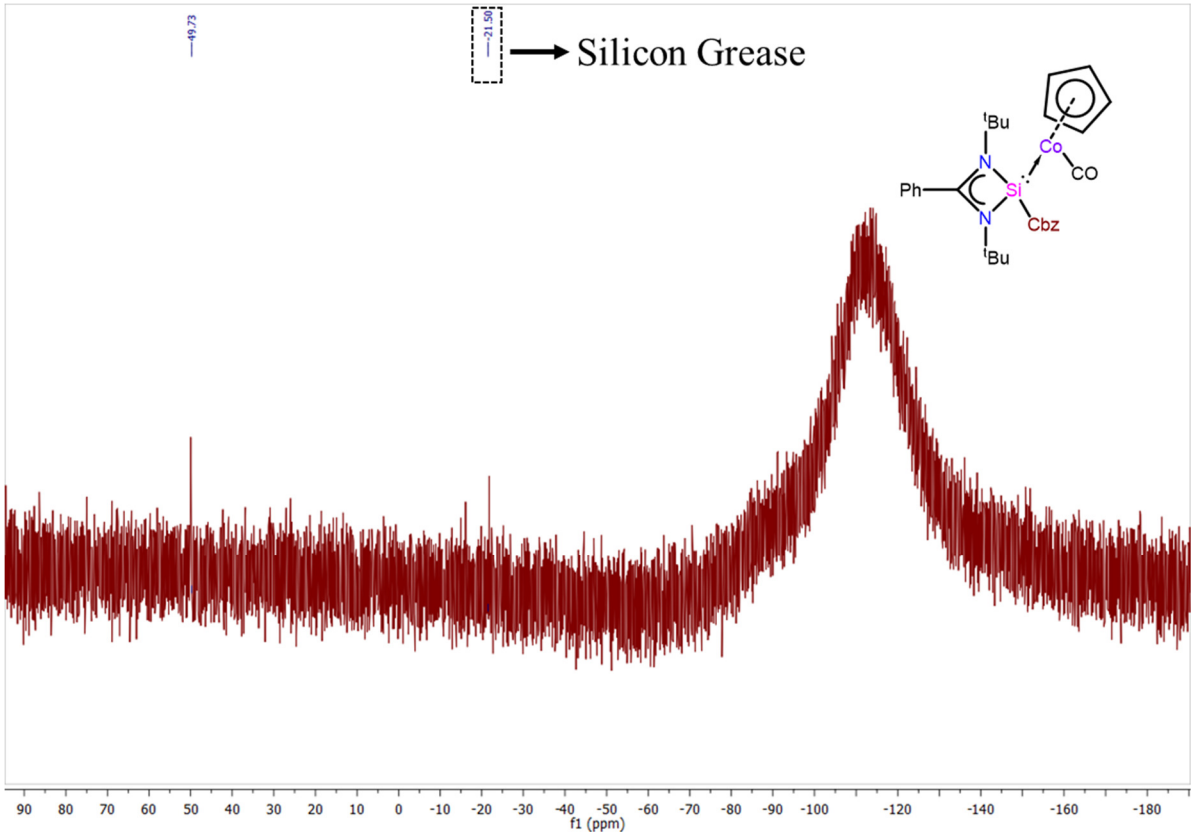


Figure S6. ^{29}Si NMR of **2**

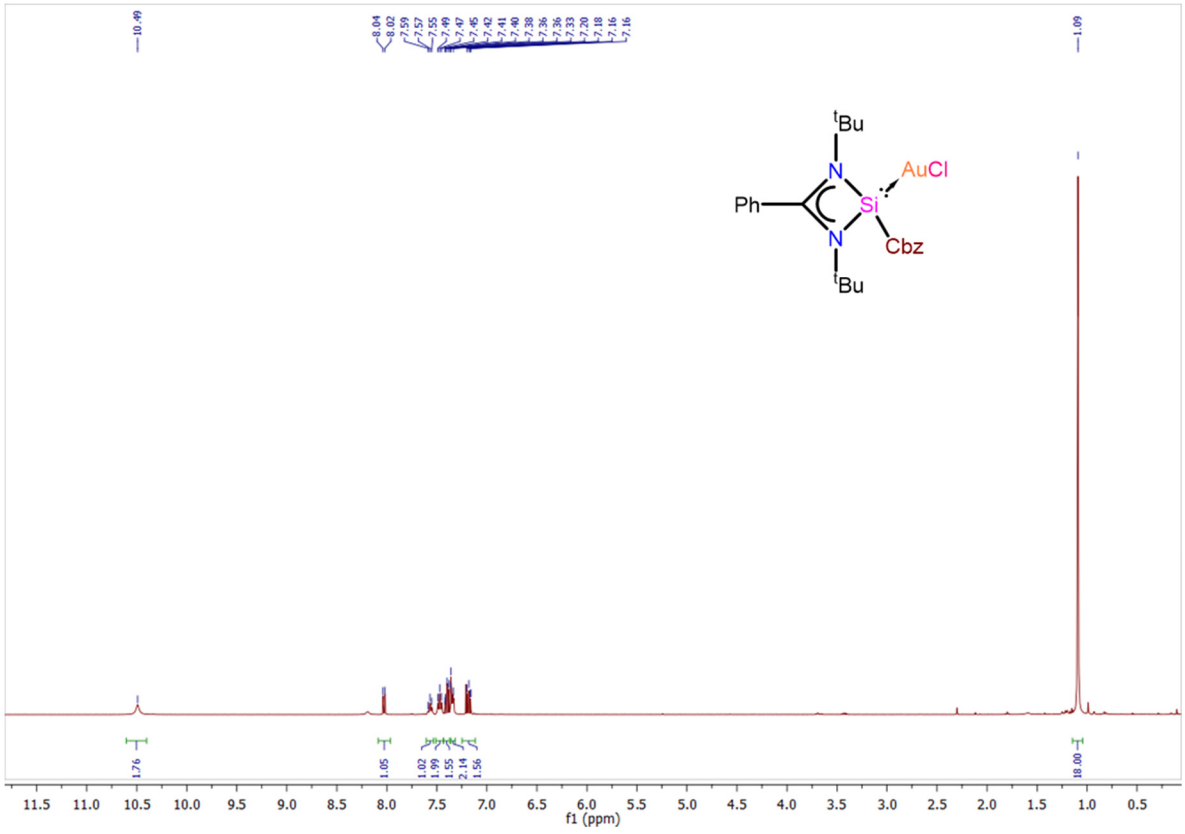


Figure S7. ^{1}H NMR of **3**

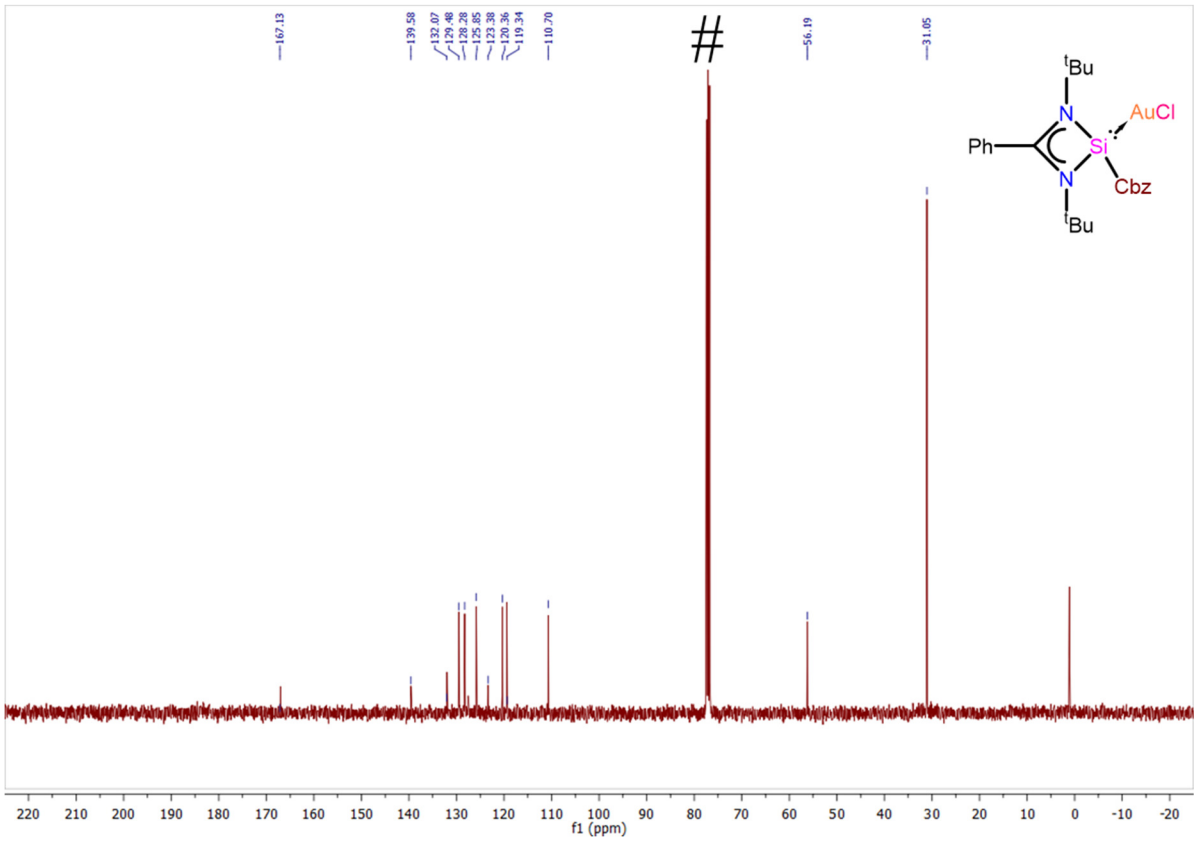


Figure S8. ^{13}C NMR of **3**

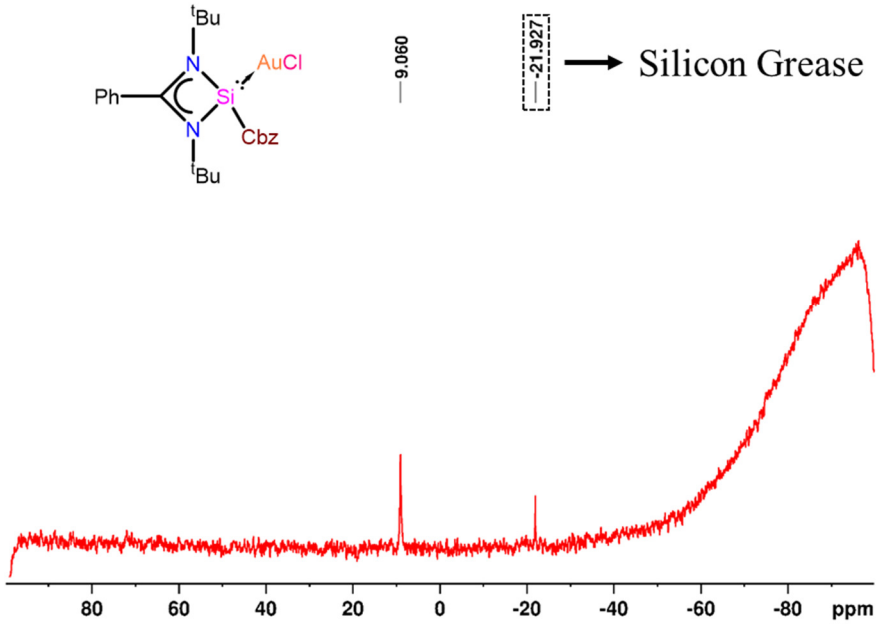


Figure S9. ^{29}Si NMR of **3**

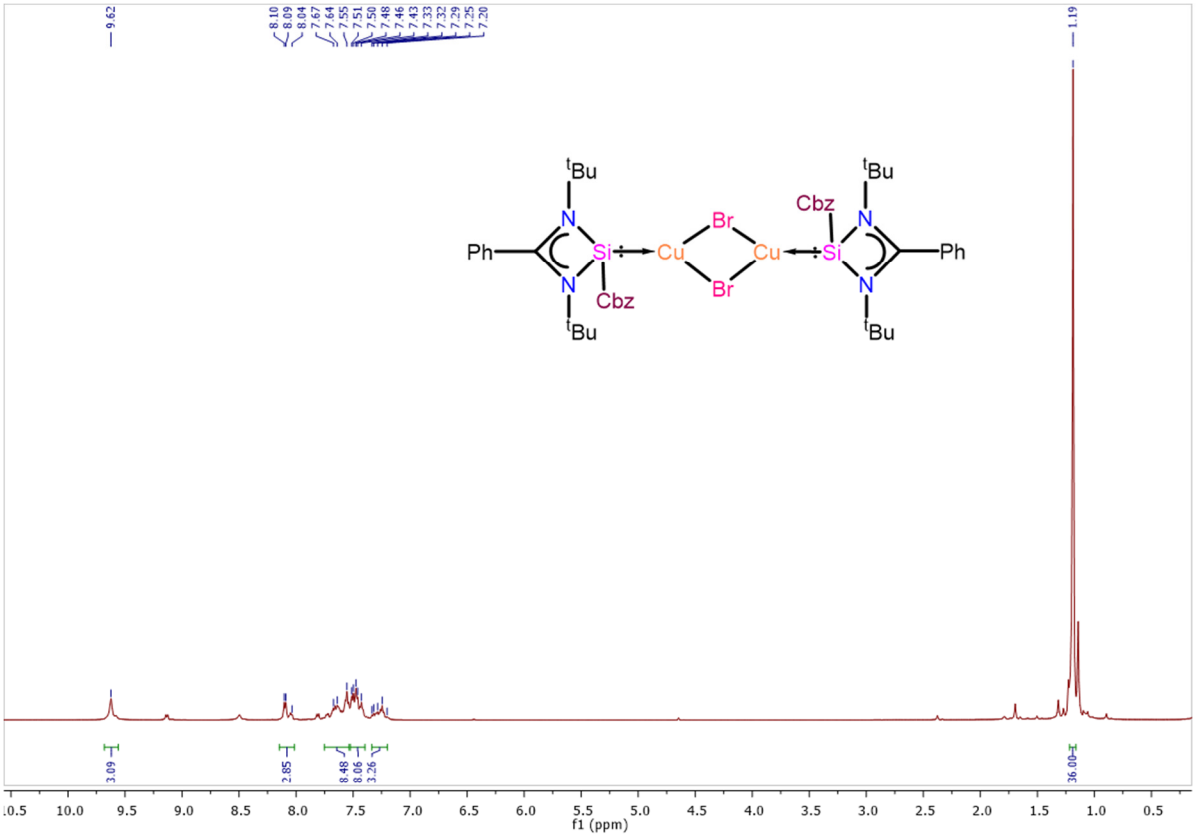


Figure S10. ^{1}H NMR of **4**

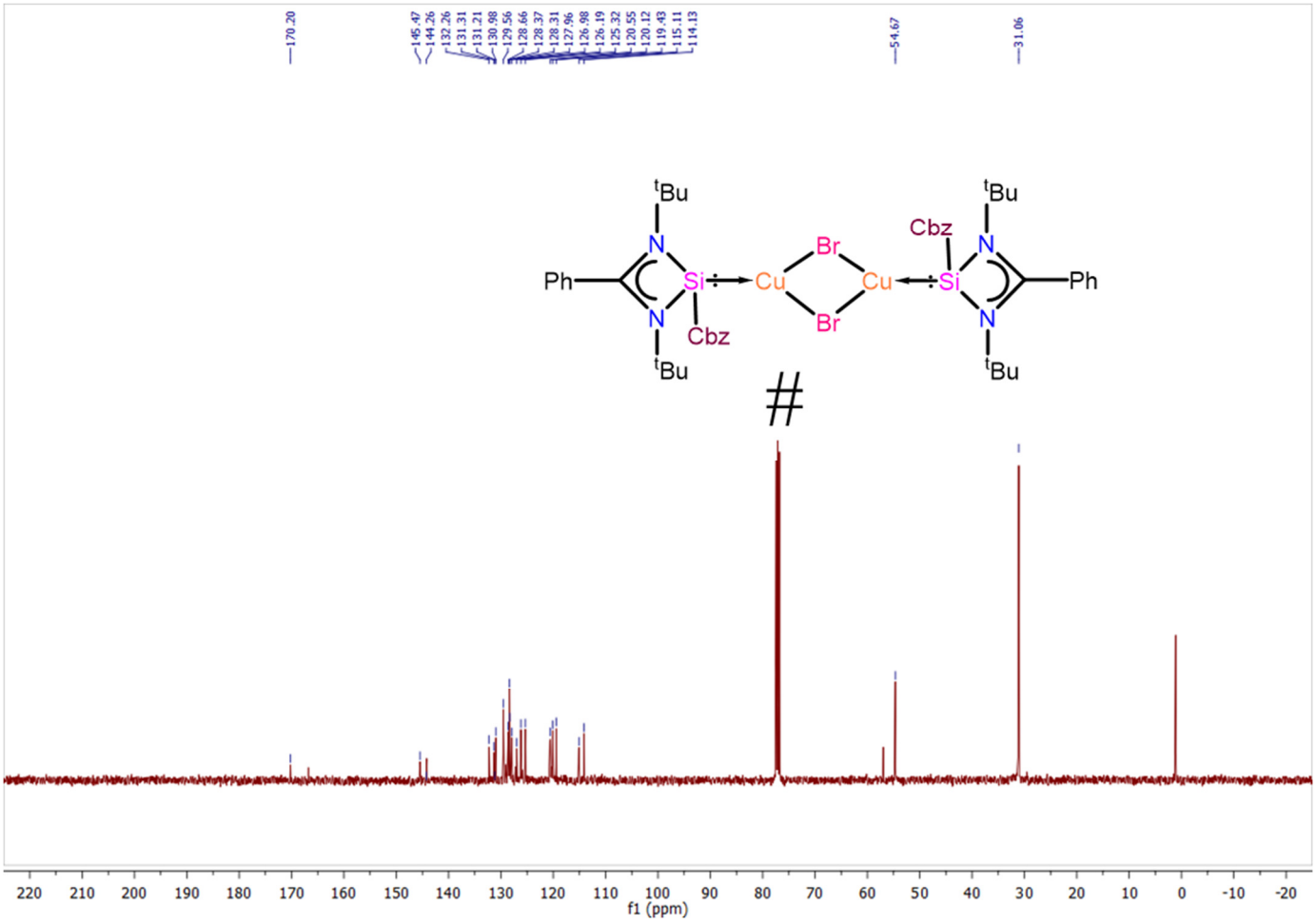


Figure S11. ^{13}C NMR of **4**

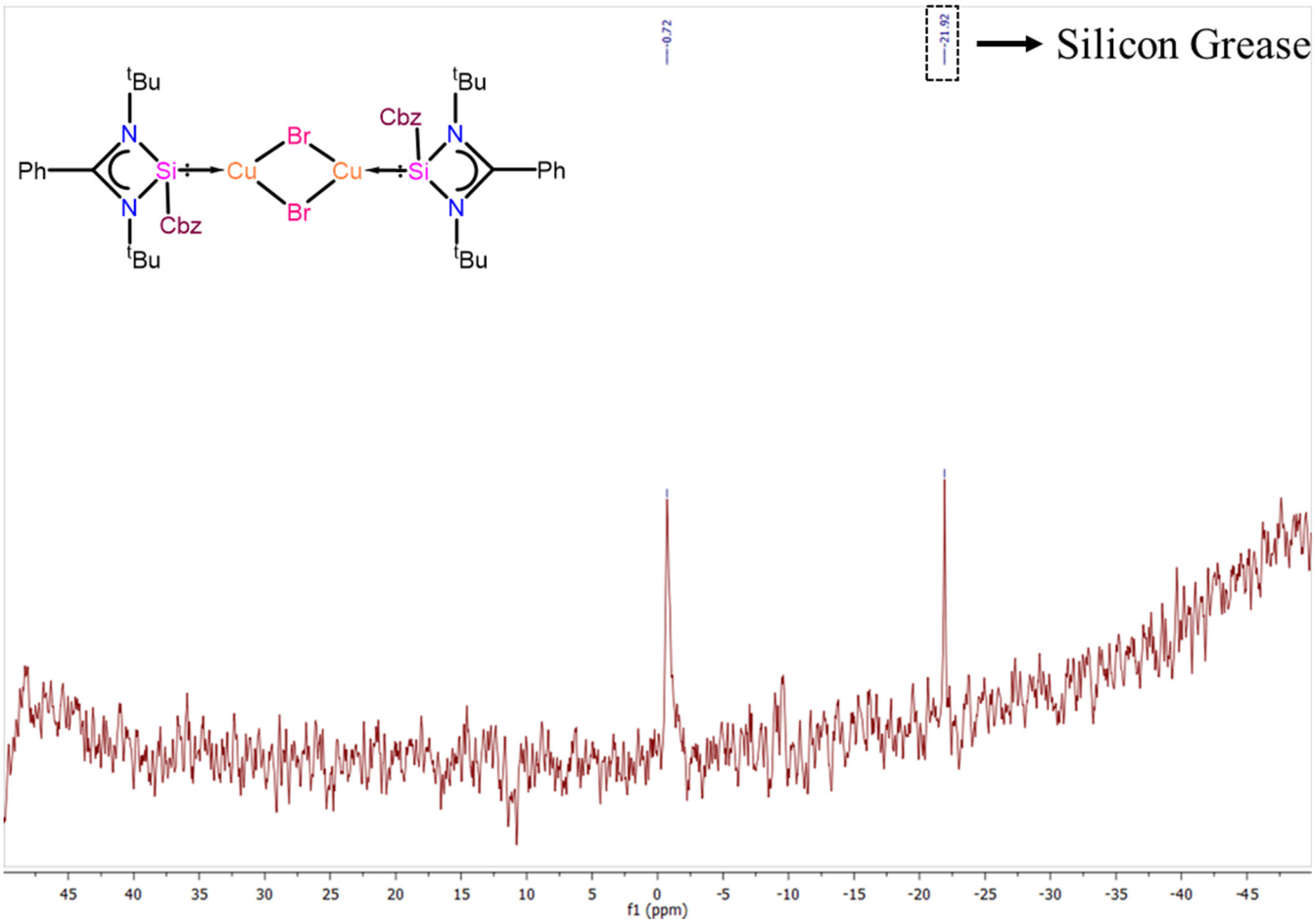


Figure S12. ^{29}Si NMR of **4**

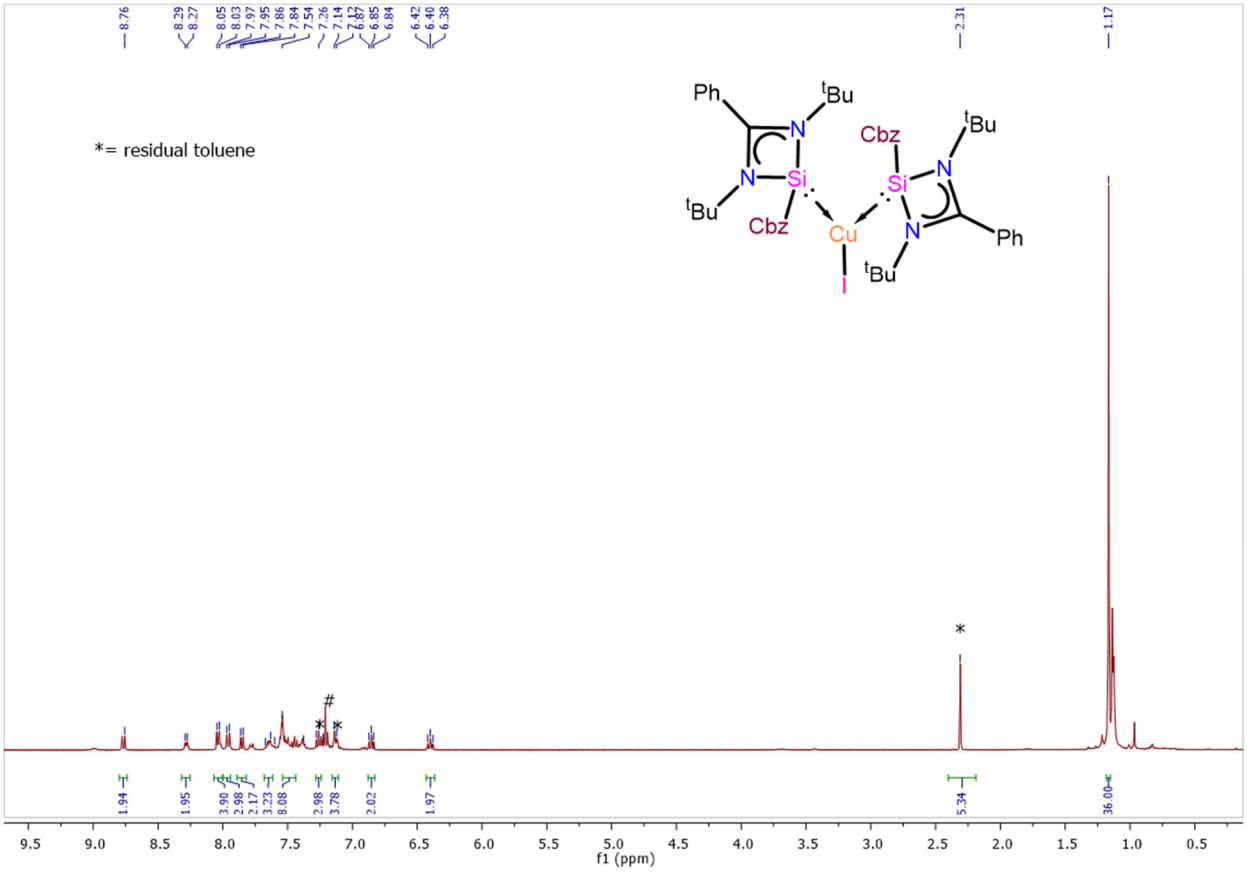


Figure S13. ^{1}H NMR of **5**

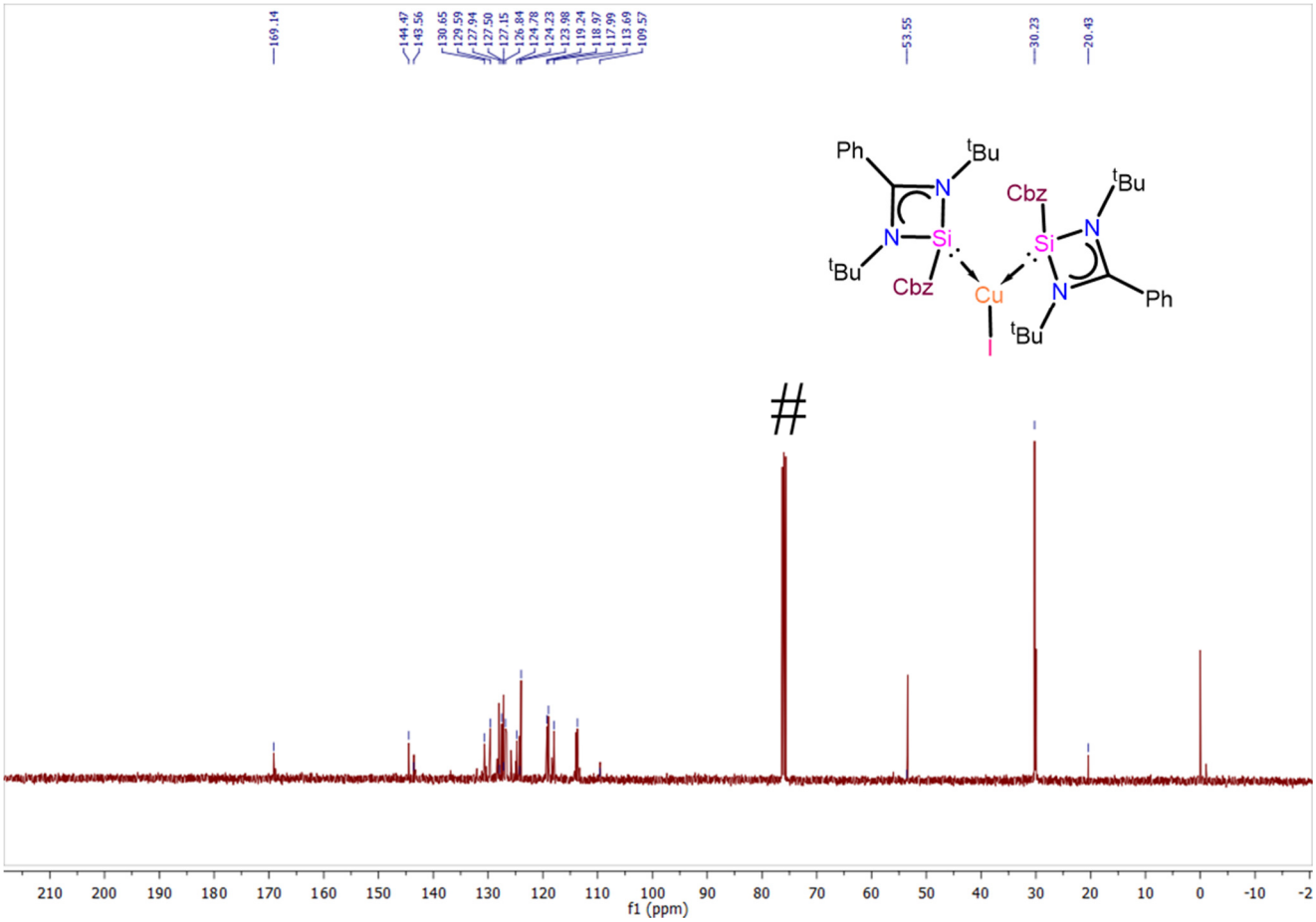


Figure S14. ^{13}C NMR of **5**

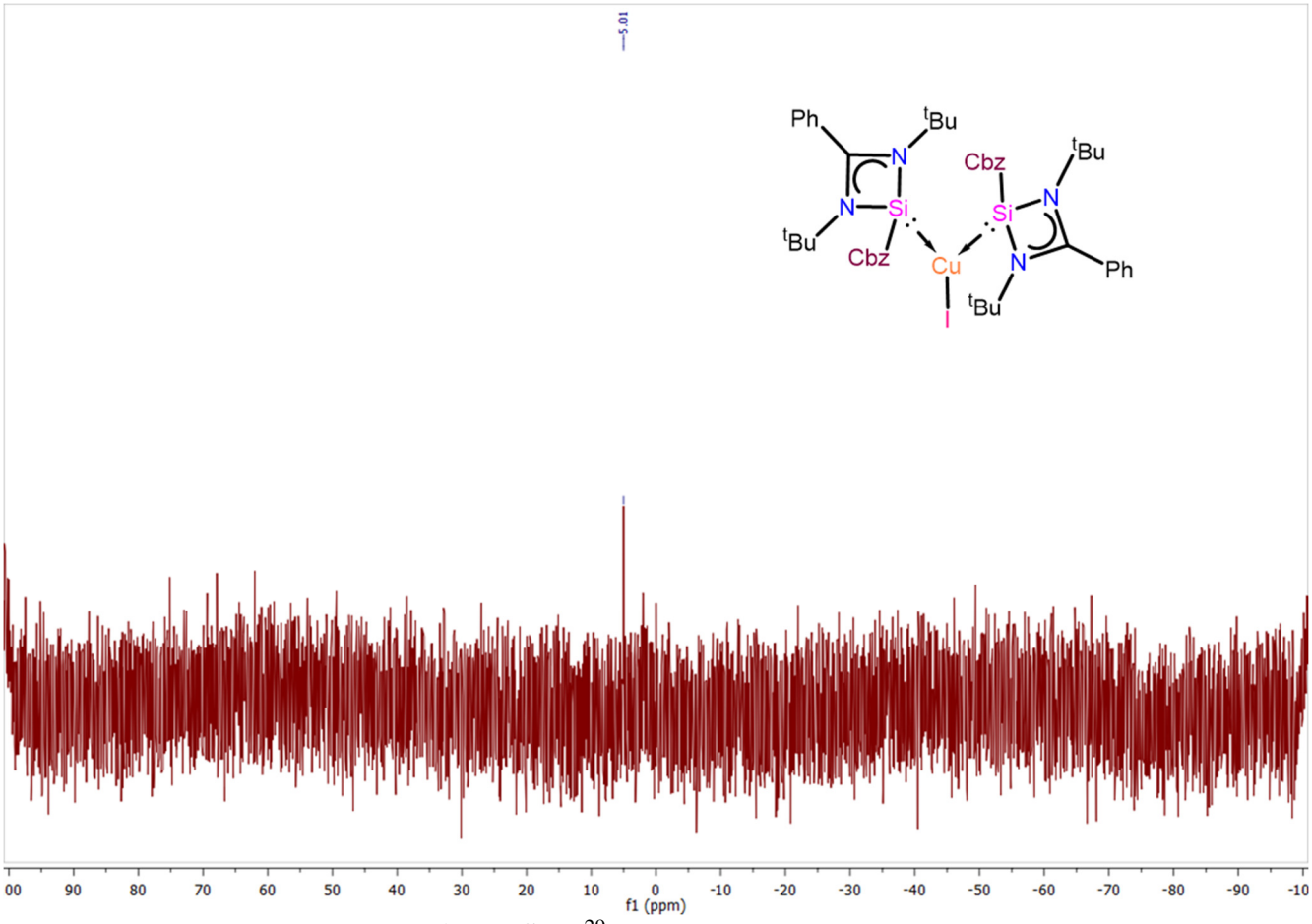


Figure S15. ^{29}Si NMR of **5**

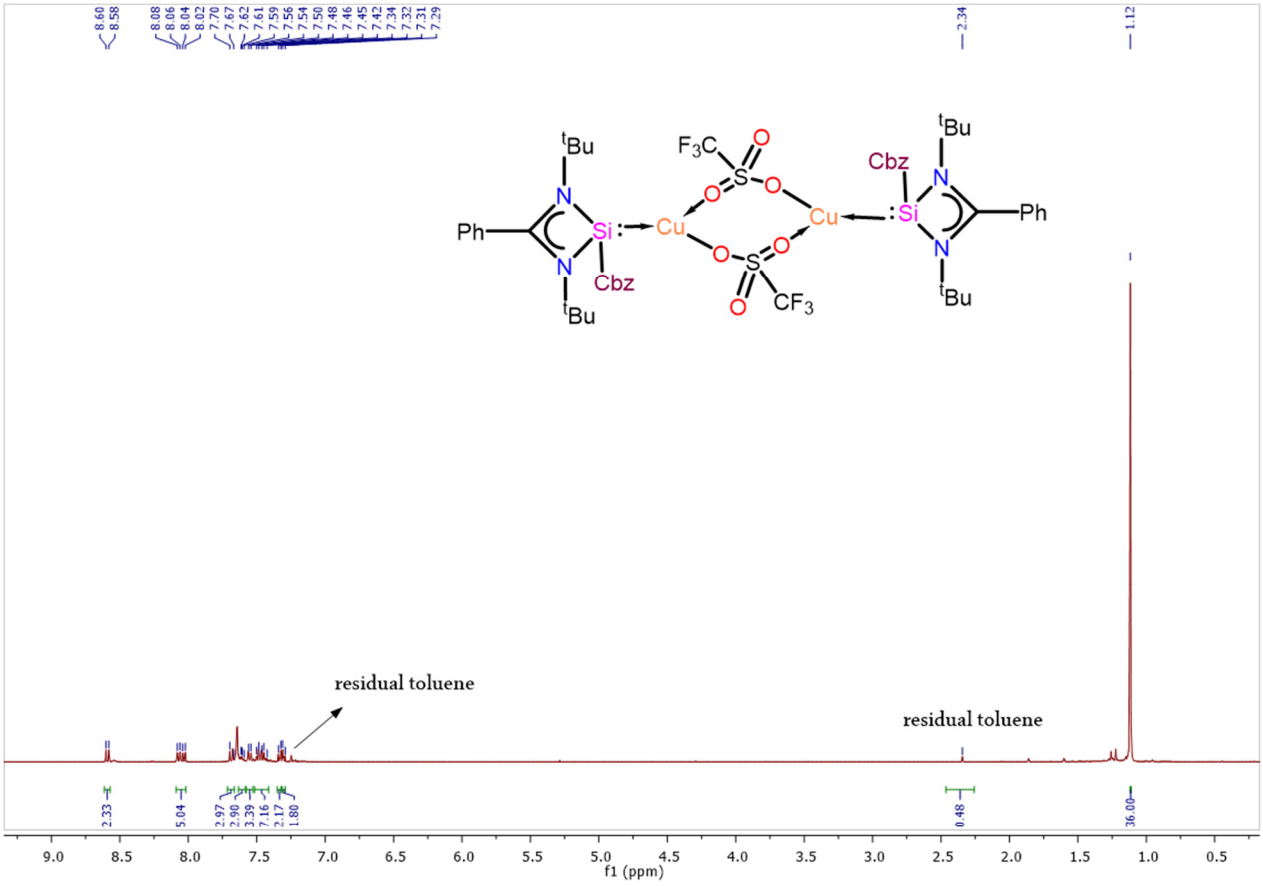


Figure S16. ^{1}H NMR of **6**

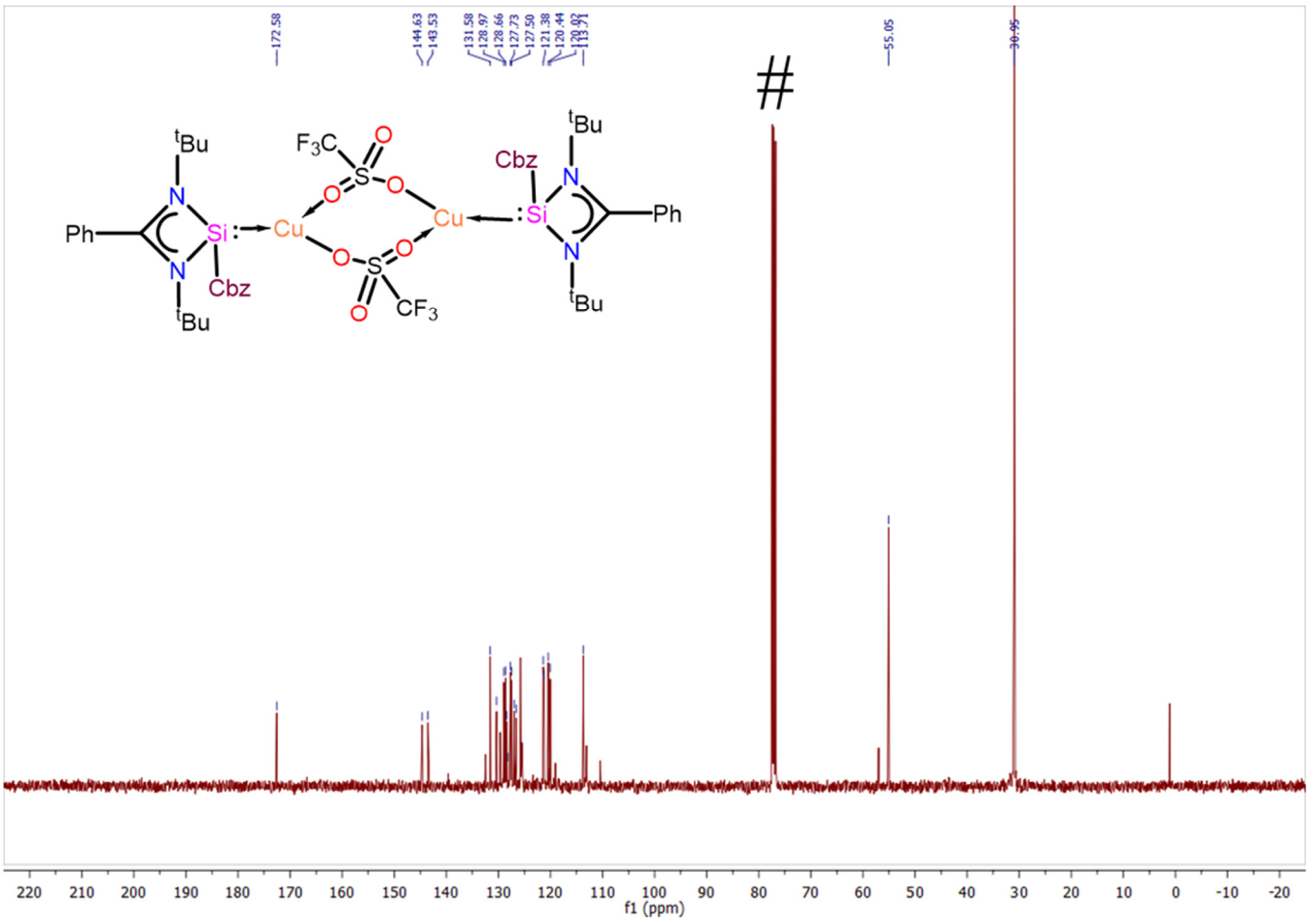


Figure S17. ^{13}C NMR of **6**.

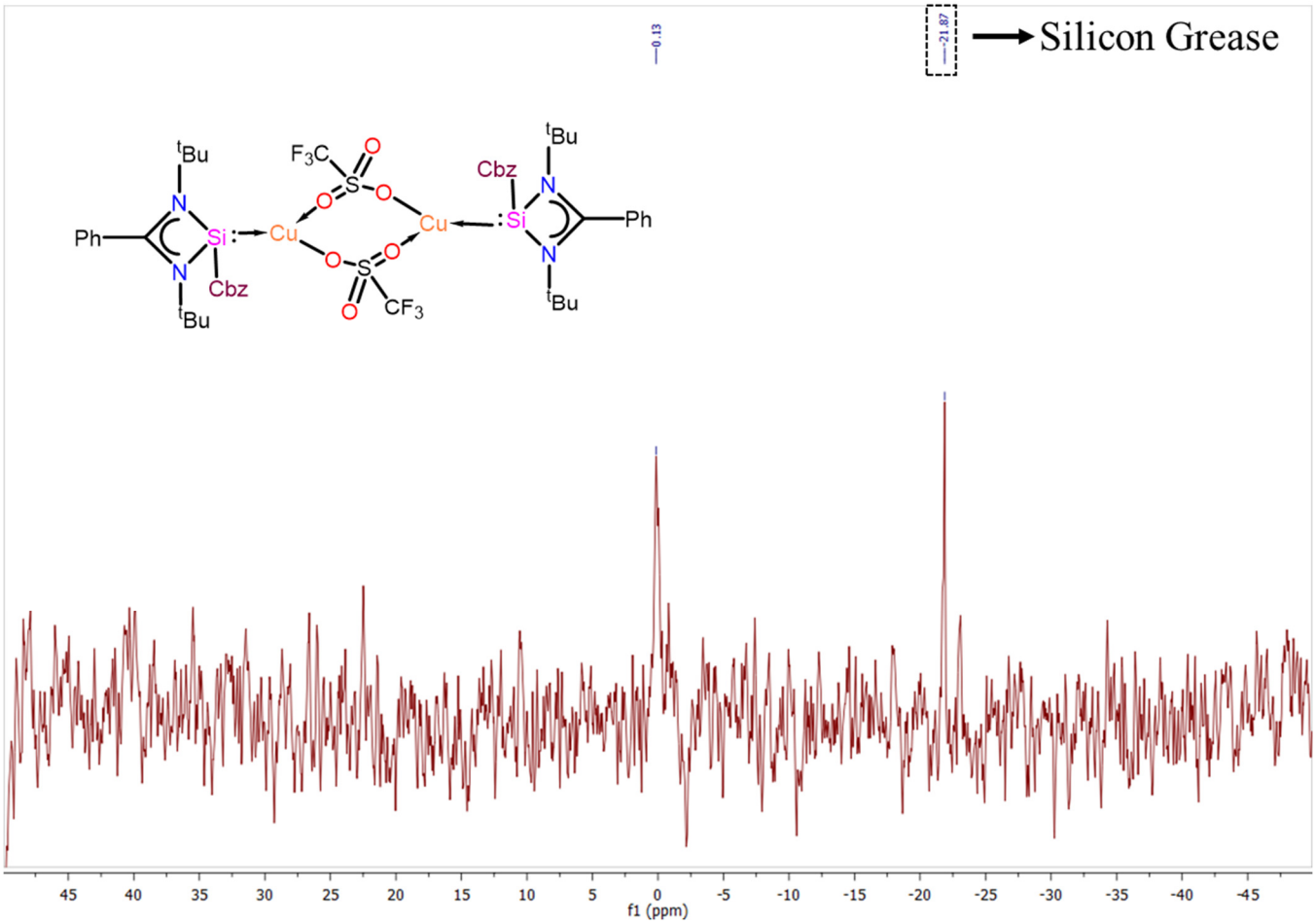


Figure S18. ^{29}Si NMR of **6**

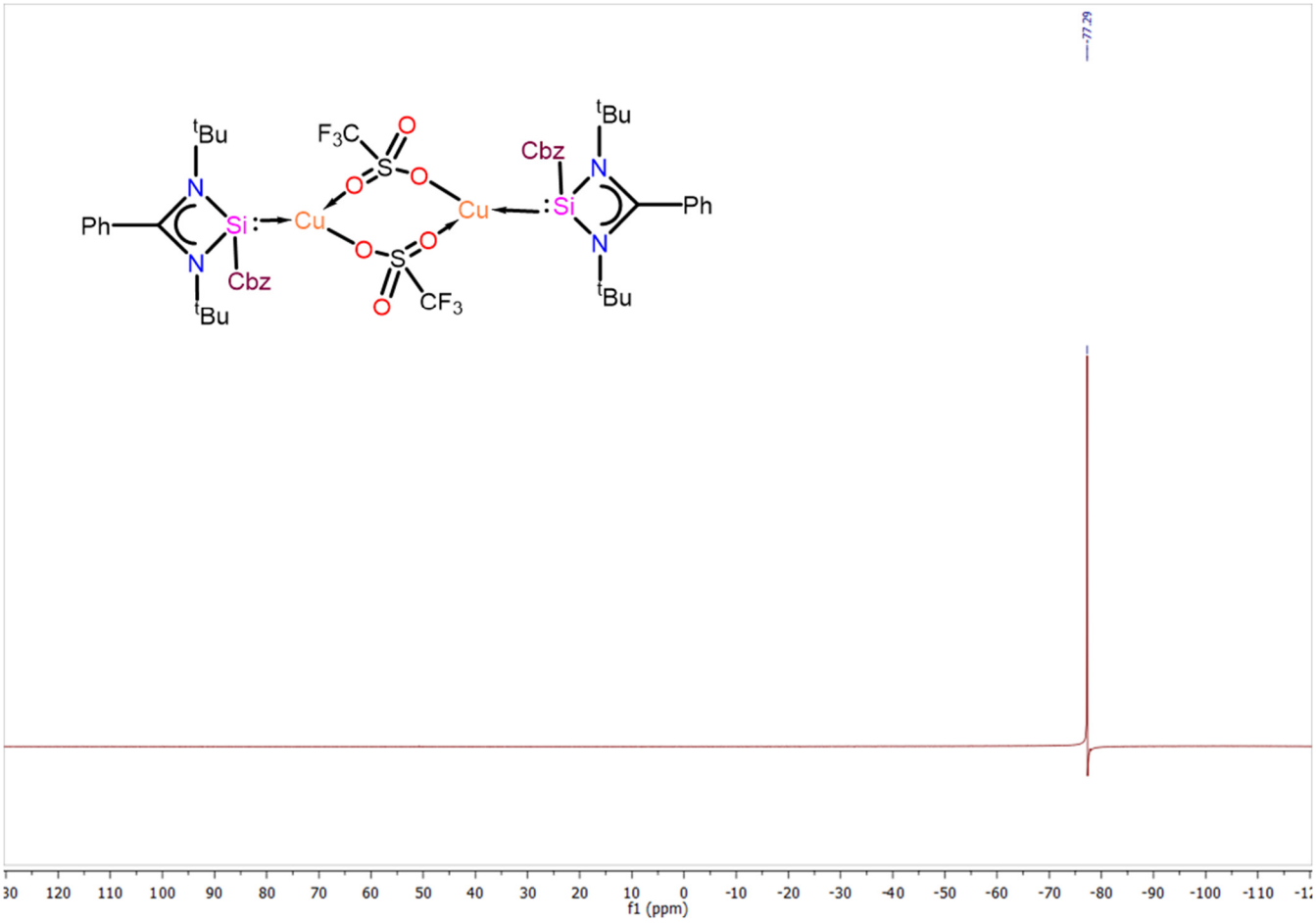


Figure S19. ^{19}F NMR of **6**

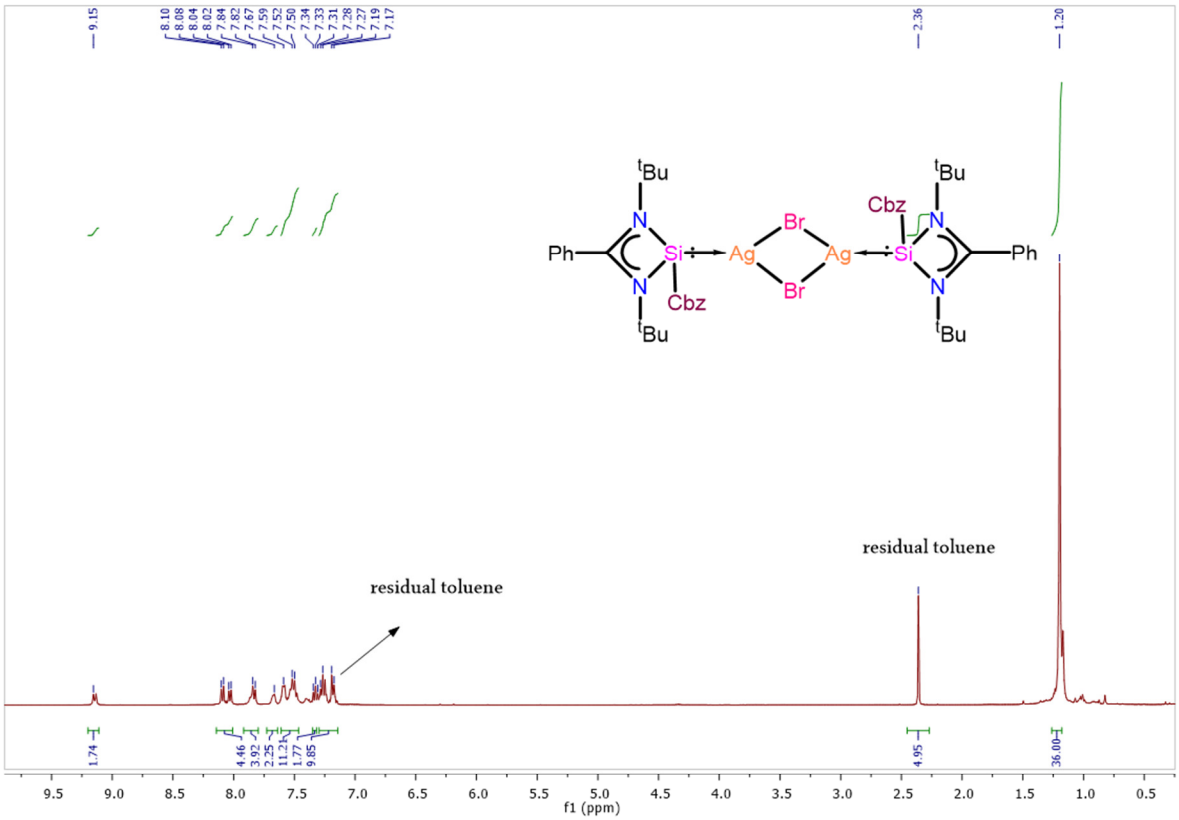


Figure S20. ^{1}H NMR of **7**

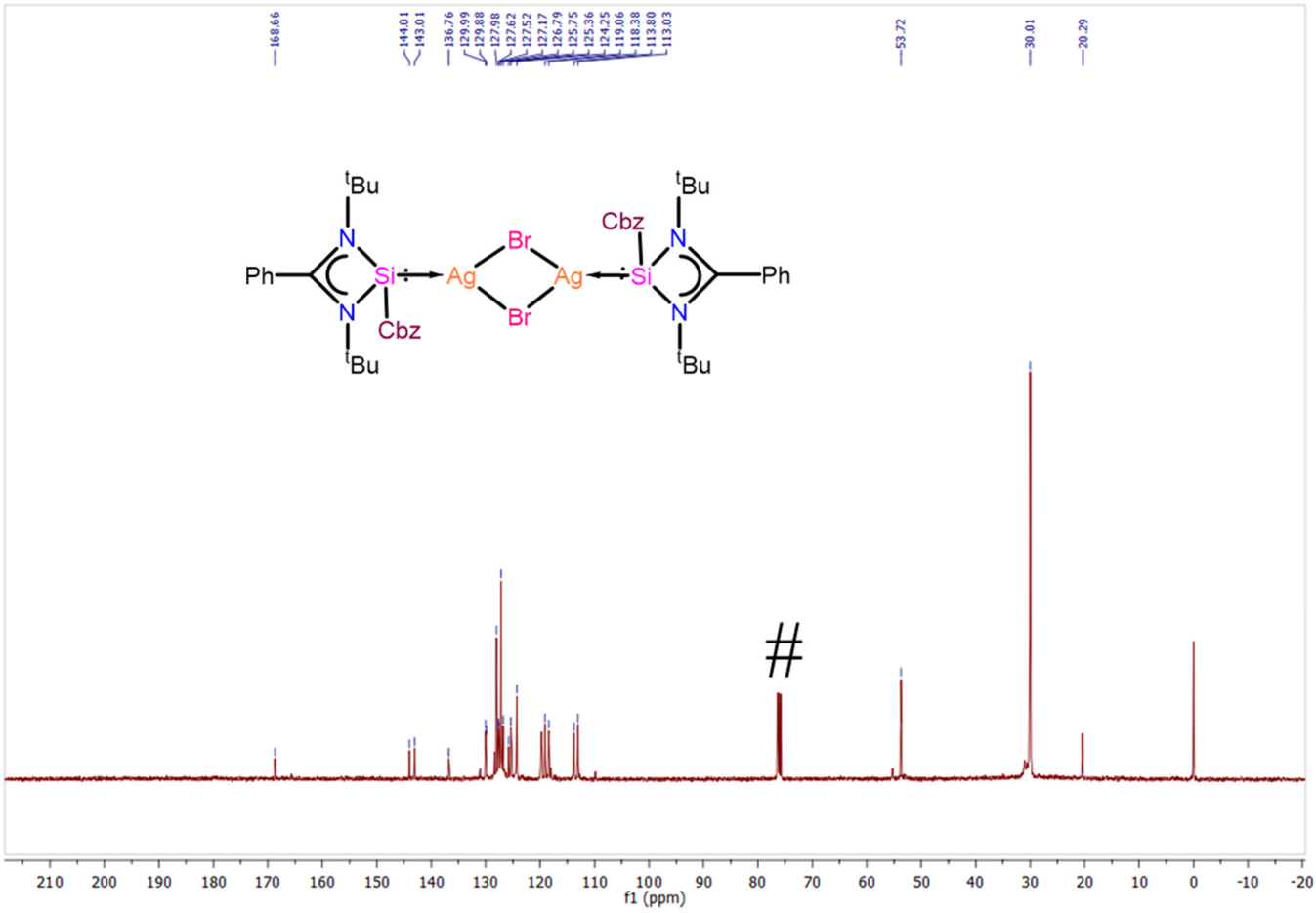


Figure S21. ^{1}H NMR of **7**

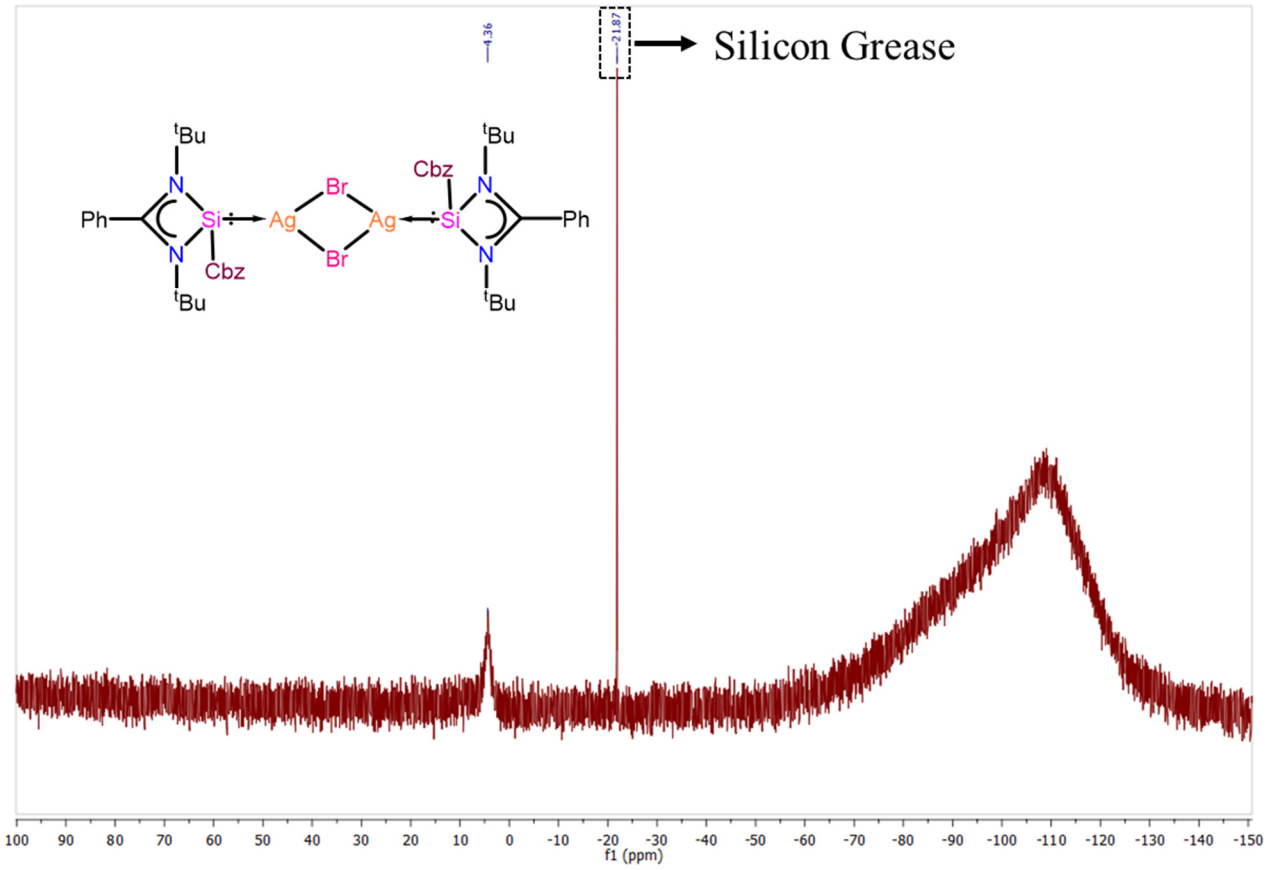


Figure S22. ^{29}Si NMR of **7**

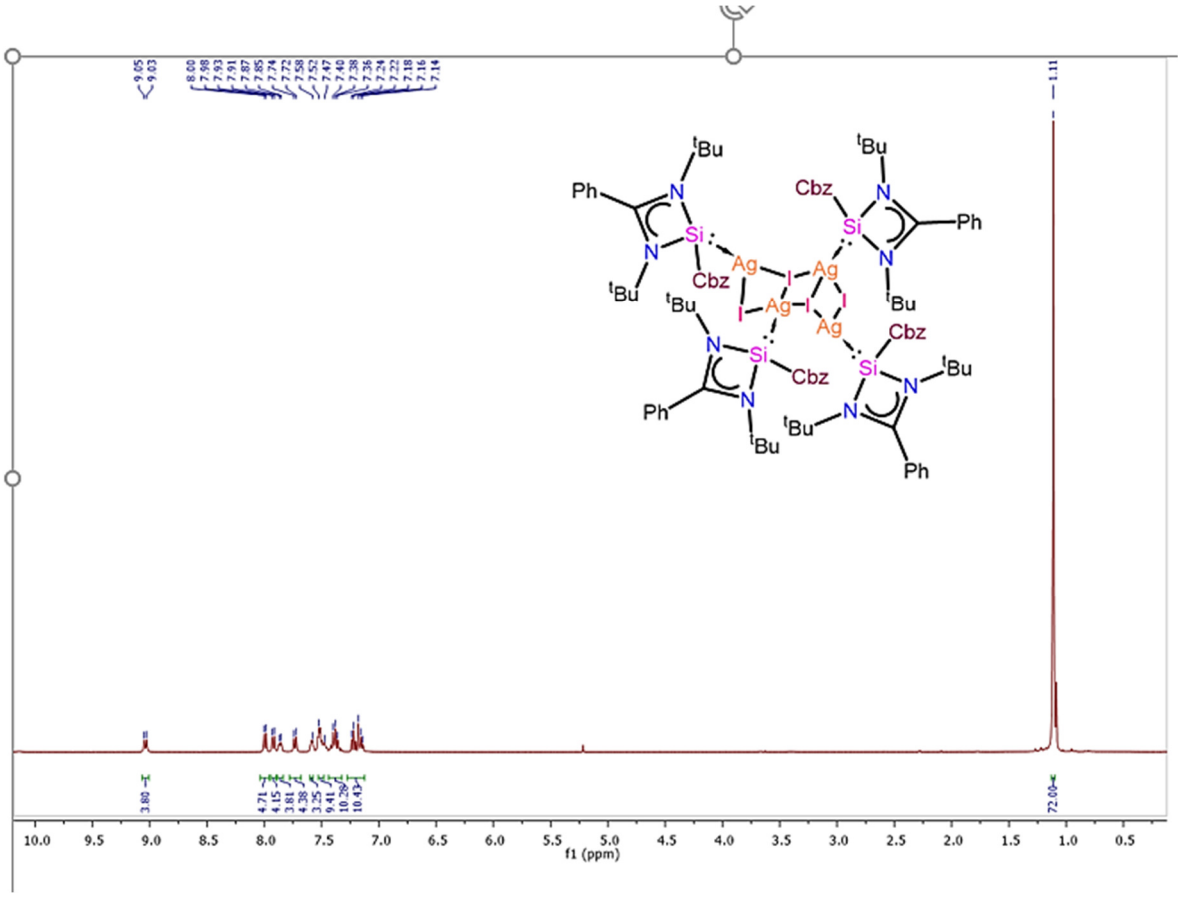


Figure S23. ^{1}H NMR of **8**

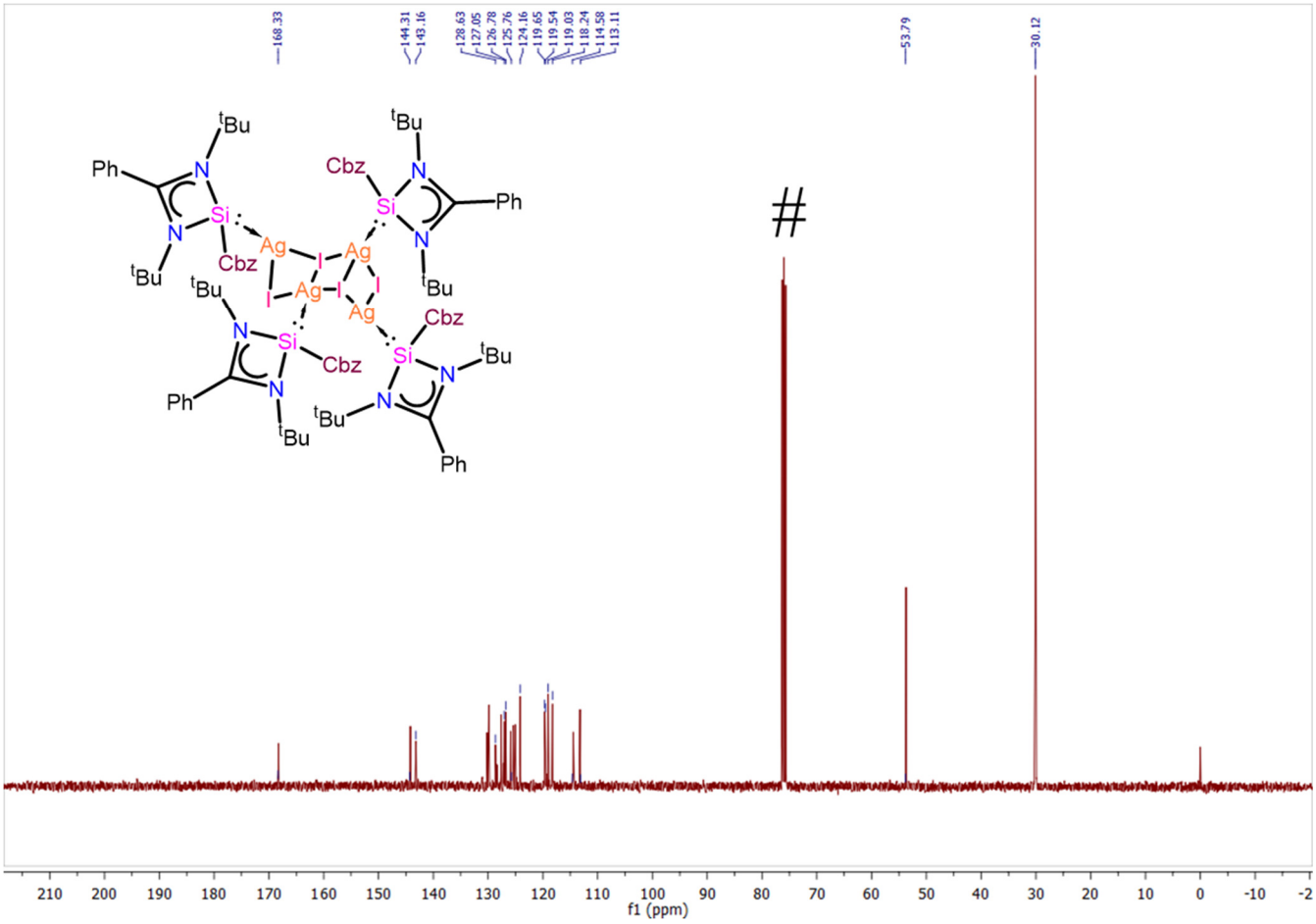


Figure S24. ^{13}C NMR of **8**

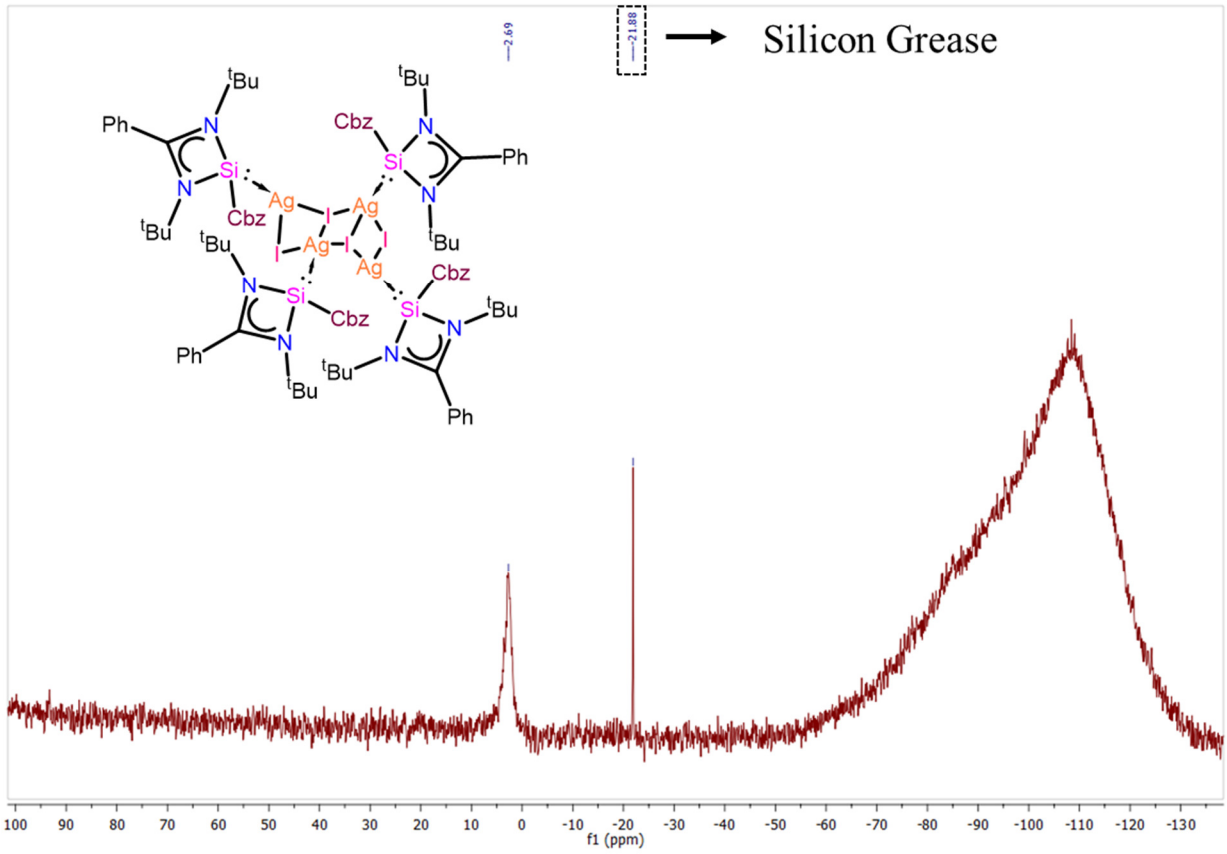
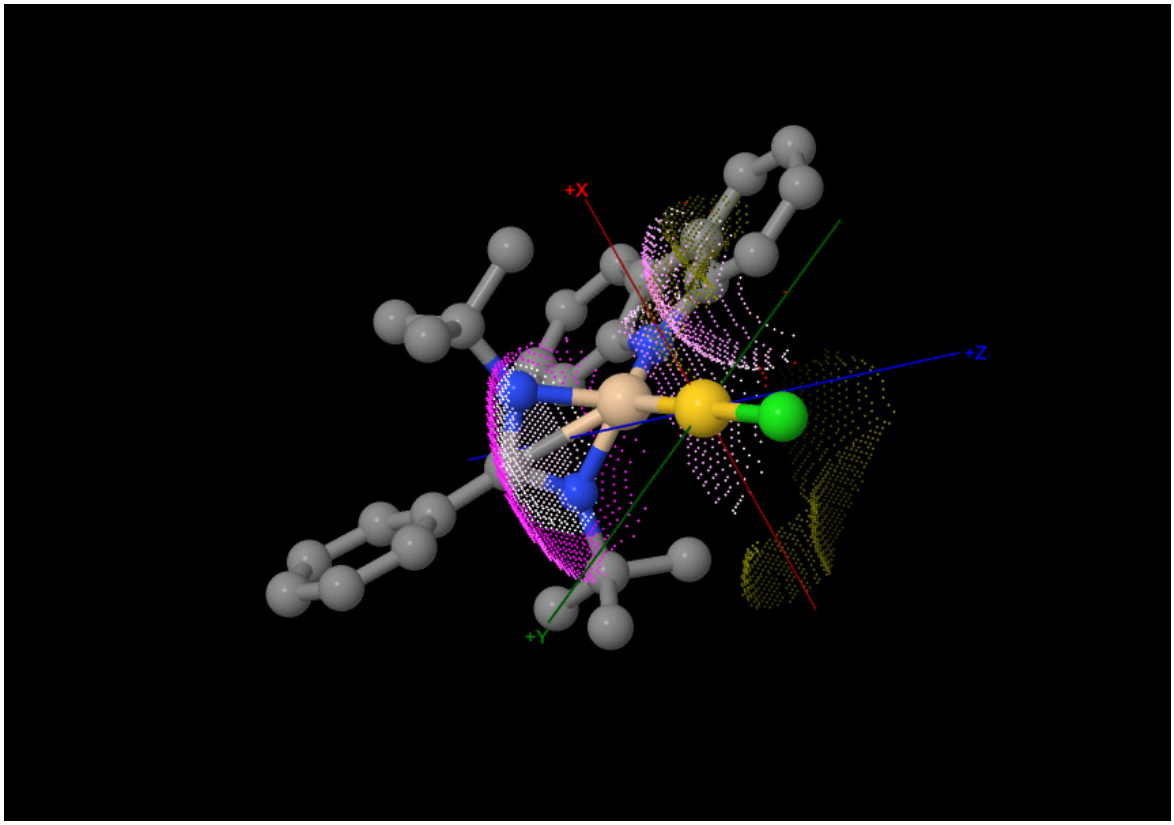


Figure S25. ^{29}Si NMR of **8**

S3. Buried Volume (%V_{bur}), Steric map of 1 and IR Stretching Frequency of 2.



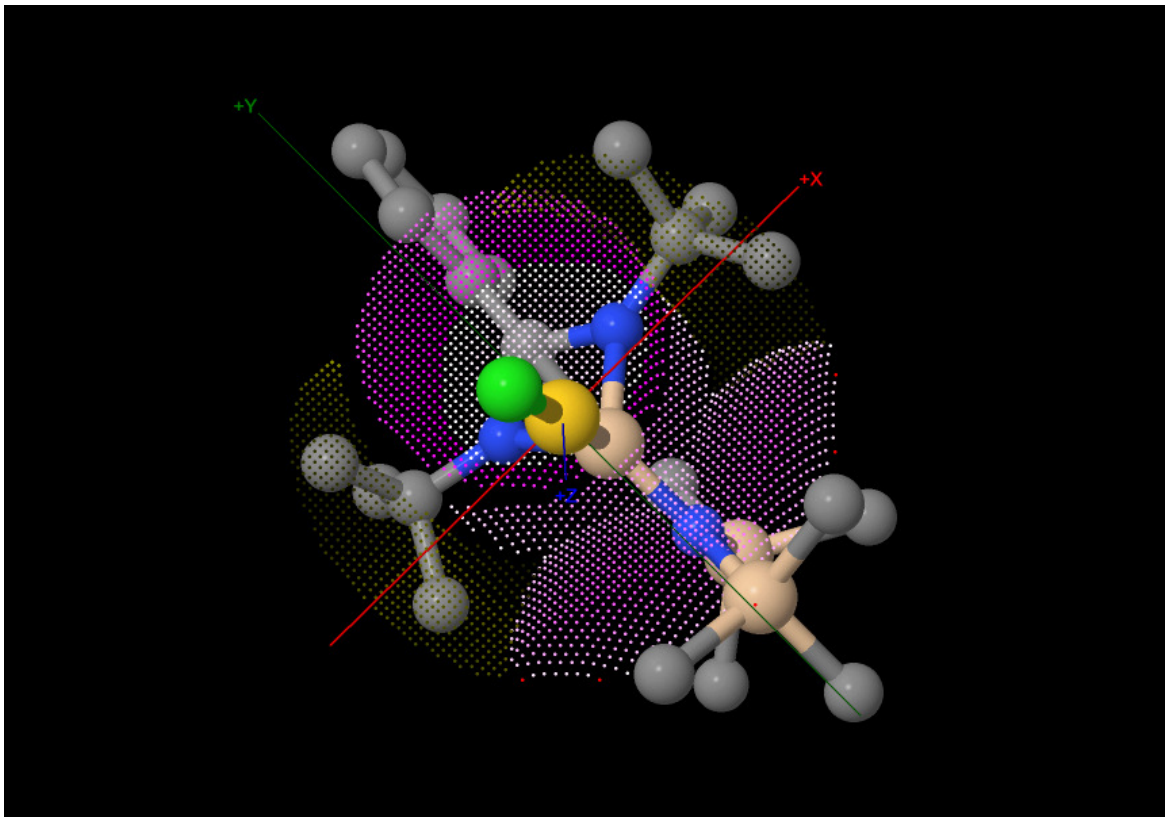


Figure S26. Visualization of percentage buried volume of complex **3** (top) and [PhC(N^{t}Bu)$_2$Si{N(TMS)$_2$}AuCl] (63.5 %) (bottom). Percent buried volumes were calculated with the SambVca 2.0 web tool (https://www.molnac.unisa.it/OMtools/sambvca2.0/).

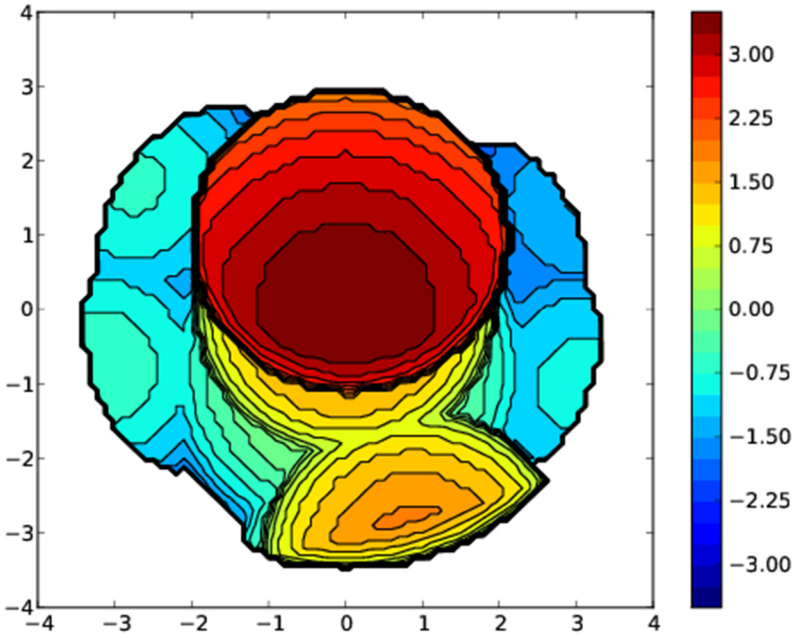


Figure S27 Steric map of complex **3**.

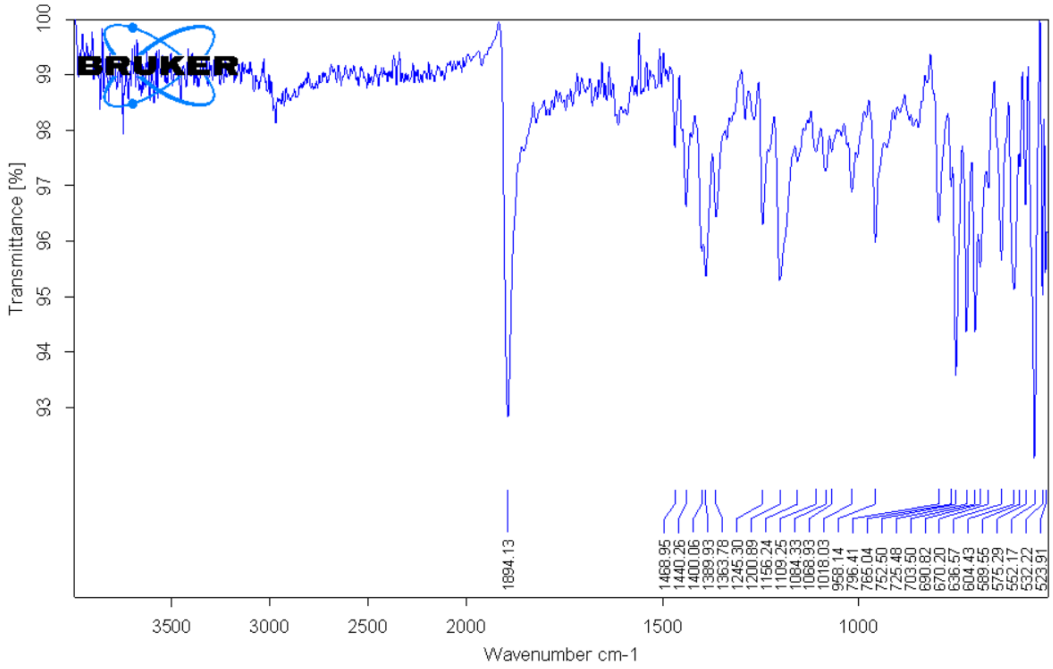


Figure S28. IR spectra of complex **2**.

S4. UV-Visible Spectra of Complexes 1, 3-7.

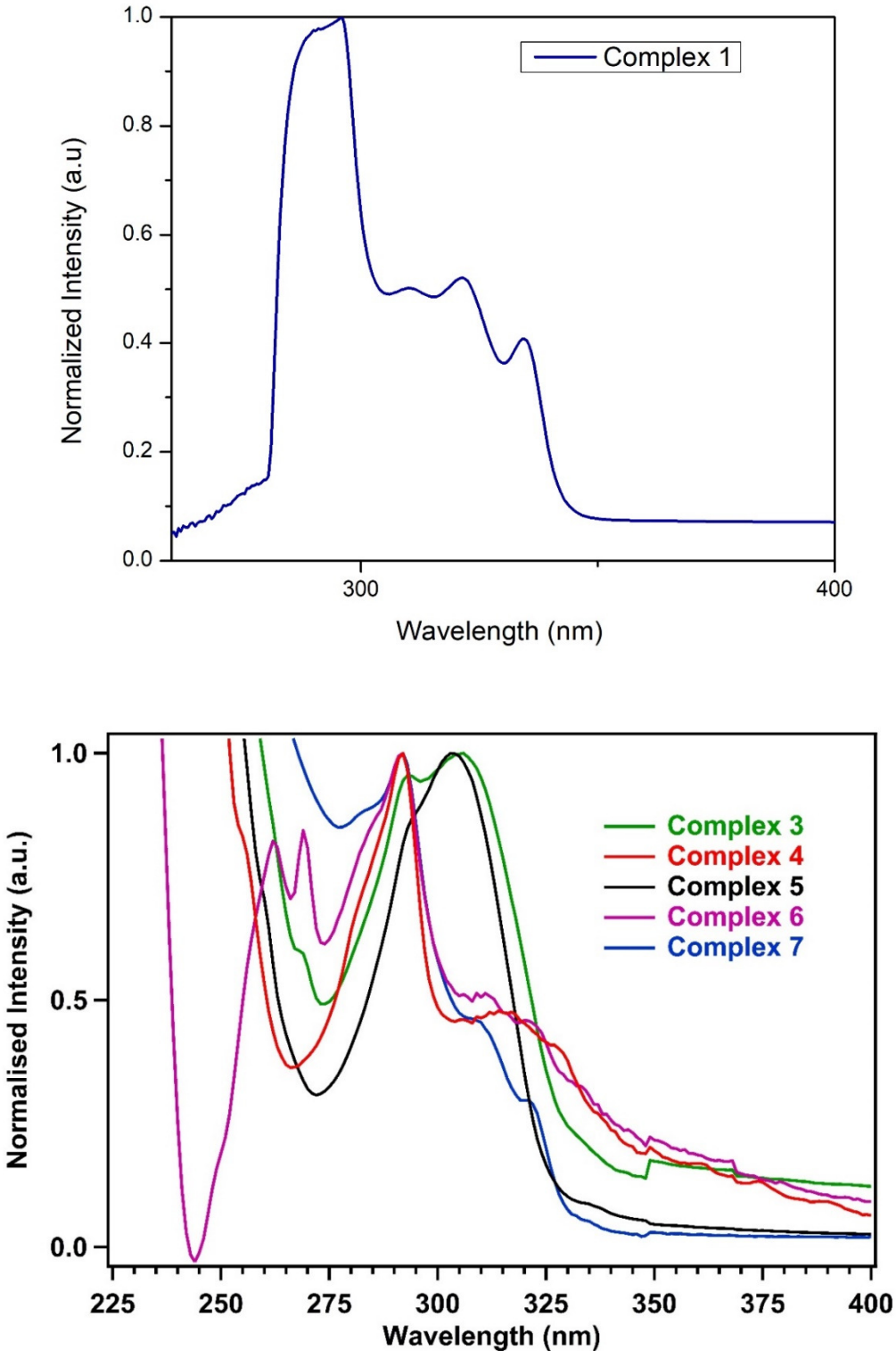


Figure S29. Absorption spectra of **1** (top) (in toluene) and **3-7** (in DCM) with 3µM compound concentration.

The absorption spectrums show only $\pi \rightarrow \pi^*$ transitions (ranging from 290 to 330 nm) for carbazolide moiety and are in accordance to the previously reported carbazolide based systems.[S1] The spectrums showed vibrational features. We observed some scattering effect in the absorption spectra of **3**, **6** and **7** due to insoluble metal particle suspension. The HOMO-LUMO gaps have been calculated taking the right most transition into account.[S2]

Table S2. The observed UV-Visible peaks for **1, 3-7.**

Complexes	Peak wavelength (nm)
1	334, 321, 310, 294
3	306, 293
4	327, 314, 292
5	303, 294
6	321, 311, 292, 269, 262
7	322, 310, 292, 282

Table S3. DFT Calculated and Observed HOMO-LUMO Energy levels and gaps for **1, 3-7.**

Complex	HOMO	LUMO	E (eV) (Calc.)	λ (nm) (Calc.)	λ (nm) (Obs.)	E (eV) (Obs.)
1	-5.46	-1.23	4.28	290	334	3.71
3	-6.06	-1.63	4.42	280	306	4.06
4	-5.16	-1.58	3.58	346	327	3.79
5	-5.15	-1.18	3.96	313	303	4.10
6	-5.78	-1.19	4.59	269	321	3.87
7	-5.78	-1.38	4.40	282	322	3.85

S.5 Computational Details

DFT calculations were performed at the Grimme's dispersion corrected B3LYP functional and Def2-TZVPP basis set with ultrafine numerical integration grid and tight convergence criteria using Gaussian 09 program[S3] package to visualize the bonding pictures of the various molecular complexes discussed in this work. Harmonic frequencies were calculated for all the molecular complexes to confirm that geometries correspond to their local minima.

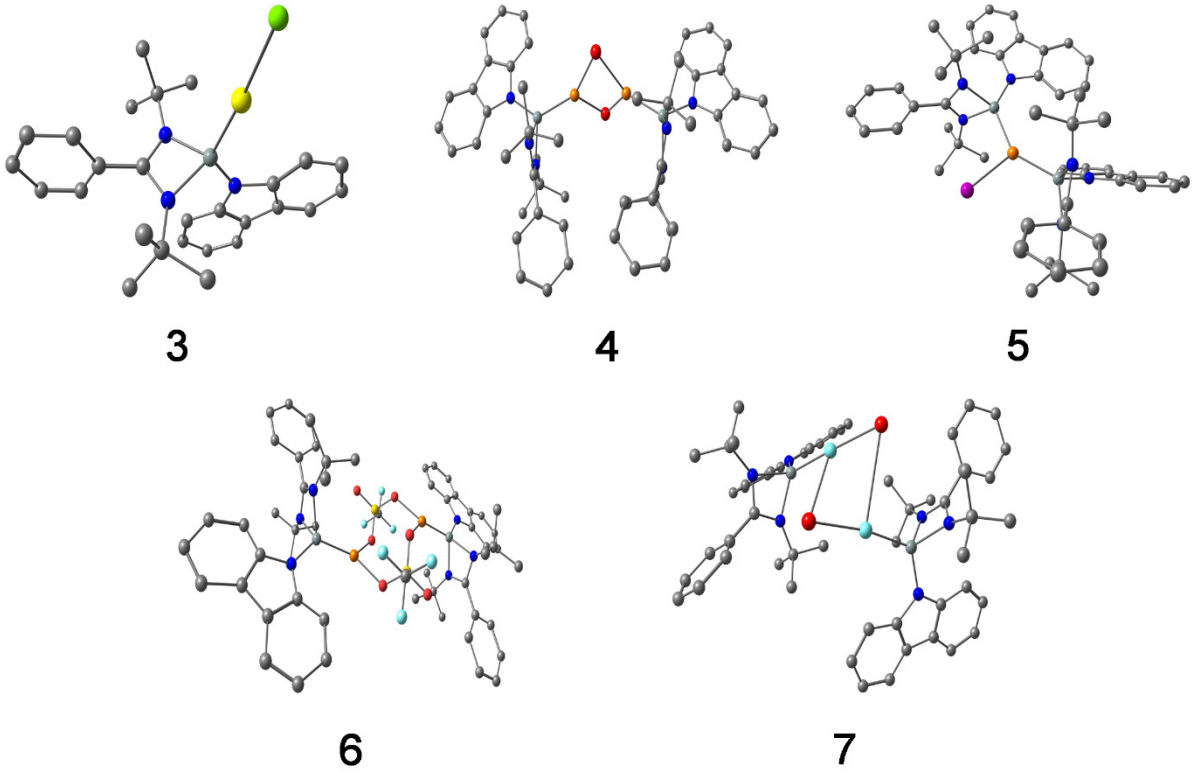


Figure S30. Optimized geometries of **3-7** calculated at the B3LYP-D3/Def2-TZVPP level of theory.

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