Synthesis, Structural Characterization and Thermal Properties of Copper and Silver Silyl Complexes

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-Supporting Information-

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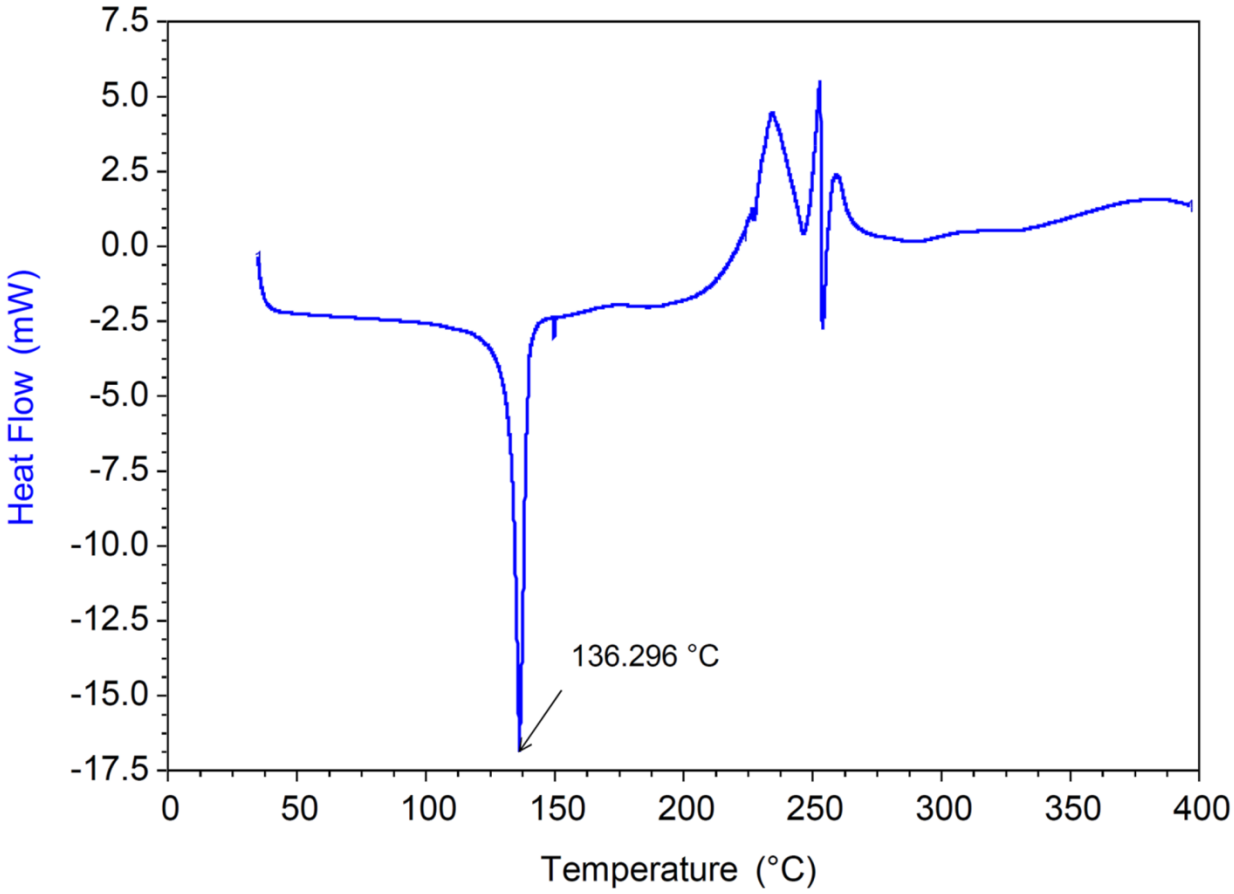

Figure S1. DSC trace of (IMe)CuSi($SiMe_3$)$_3$ **(1)**.

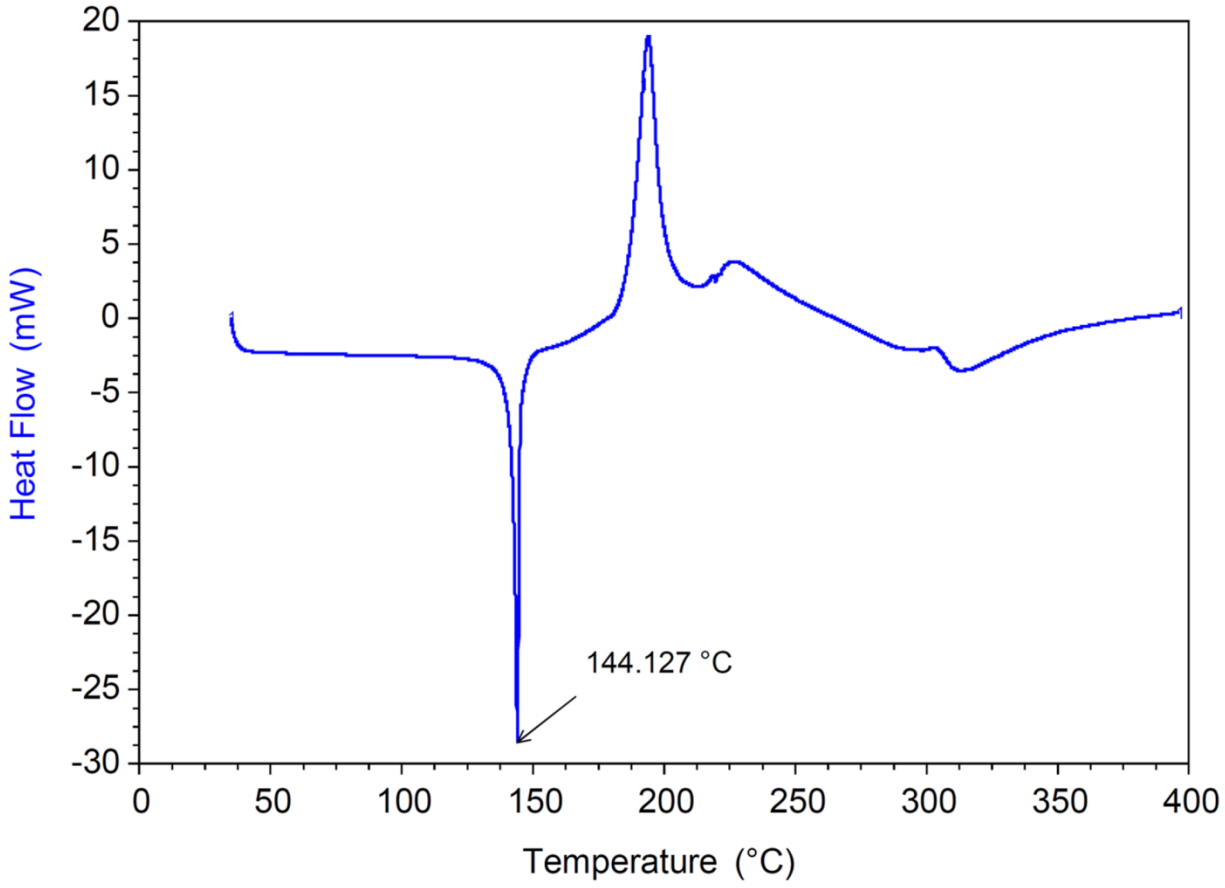

Figure S2. DSC trace of (IMe)AgSi(SiMe$_3$)$_3$ **(2)**.

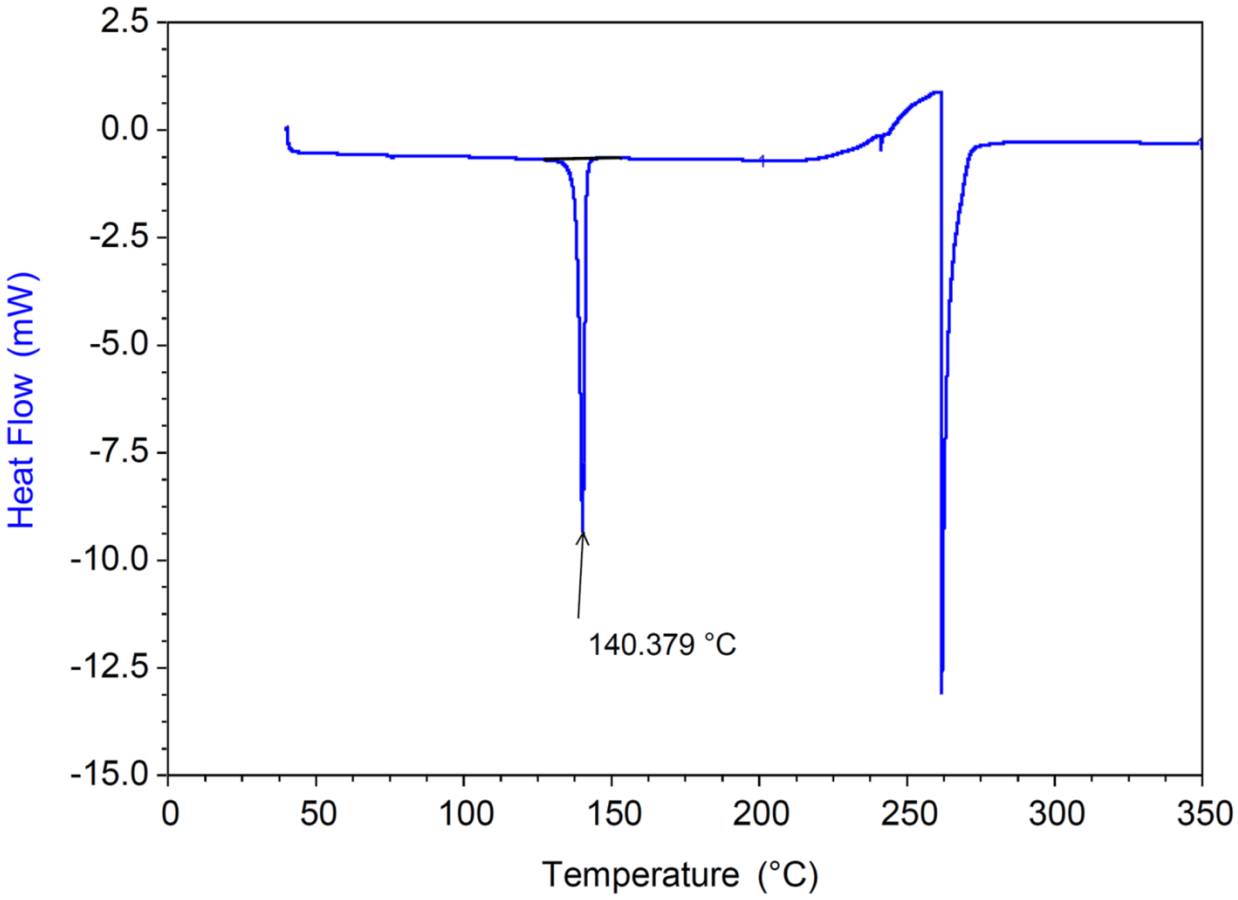

Figure S3. DSC trace of (ItBu)CuSi(SiMe$_3$)$_3$ **(3)**.

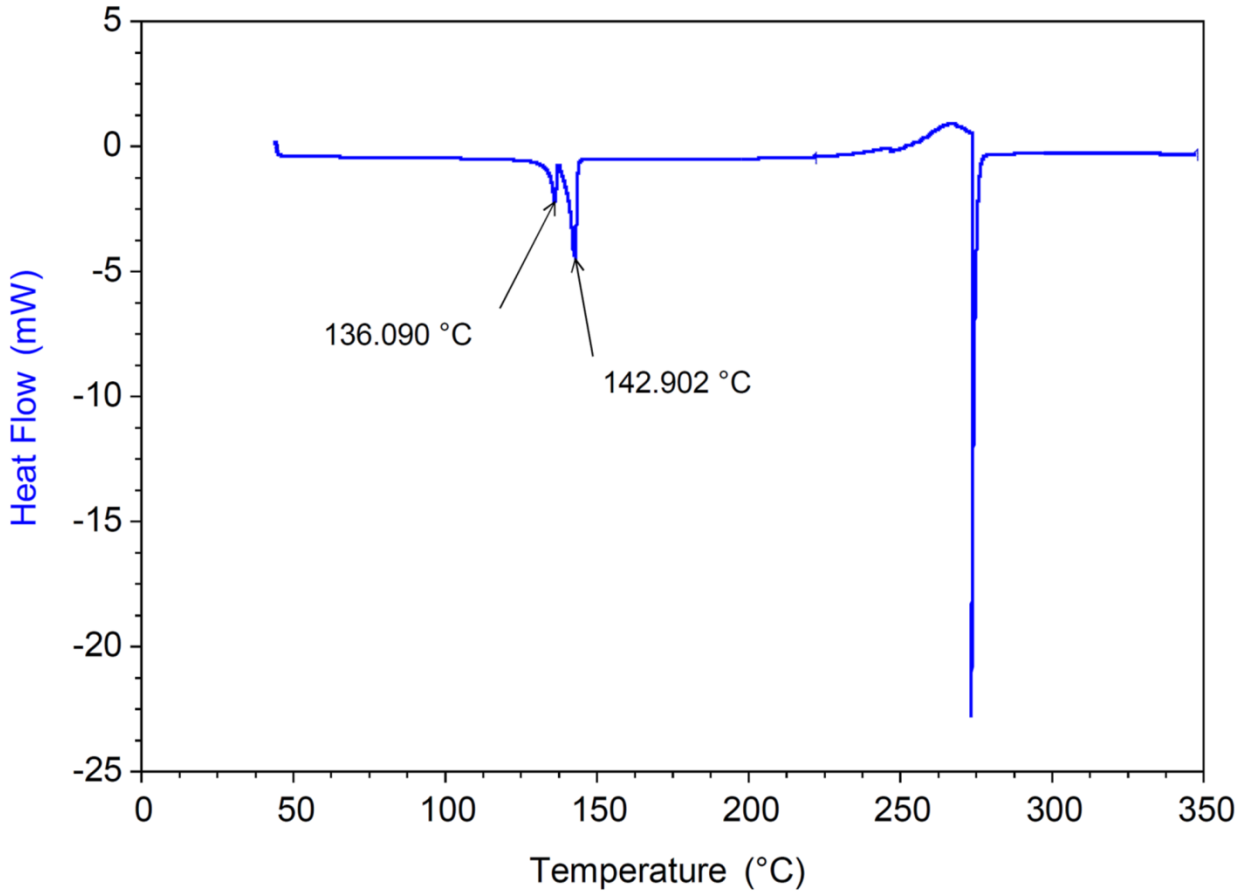

Figure S4. DSC trace of (ItBu)AgSi(SiMe$_3$)$_3$ **(4)**.

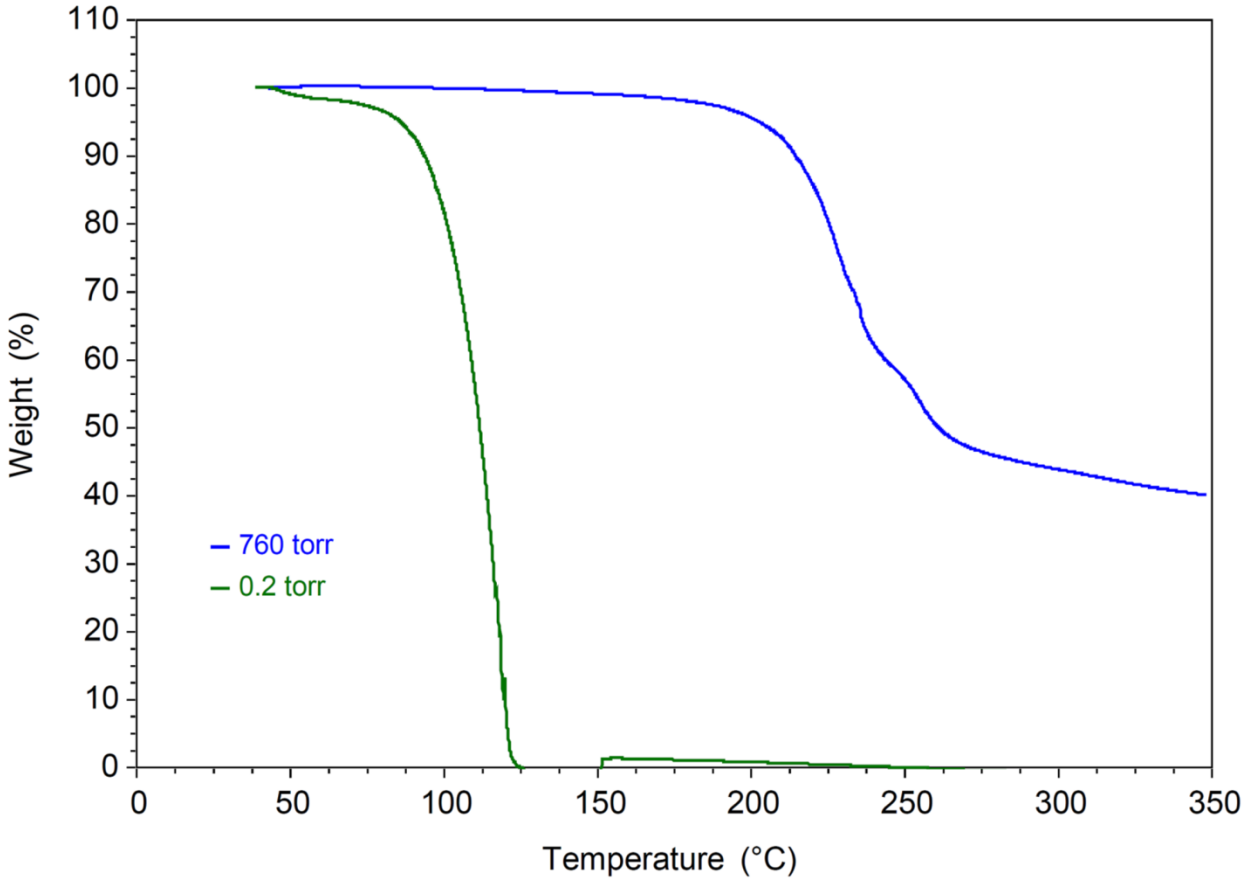

Figure S5. TGA plots of (IMe)CuSi($SiMe_3$)$_3$ **(1)** at 760 torr and 0.2 torr.

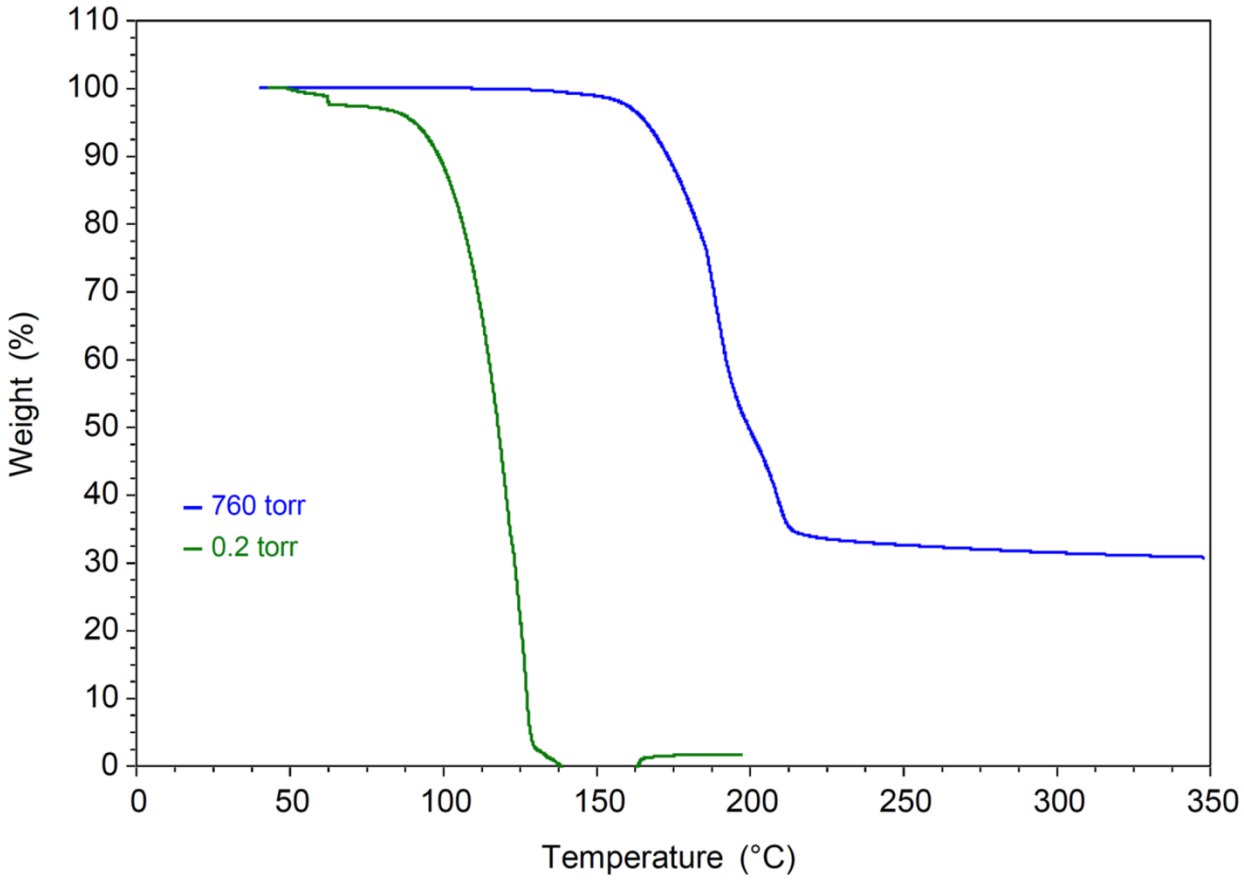

Figure S6. TGA plots of (IMe)AgSi($SiMe_3$)$_3$ **(2)** at 760 torr and 0.2 torr.

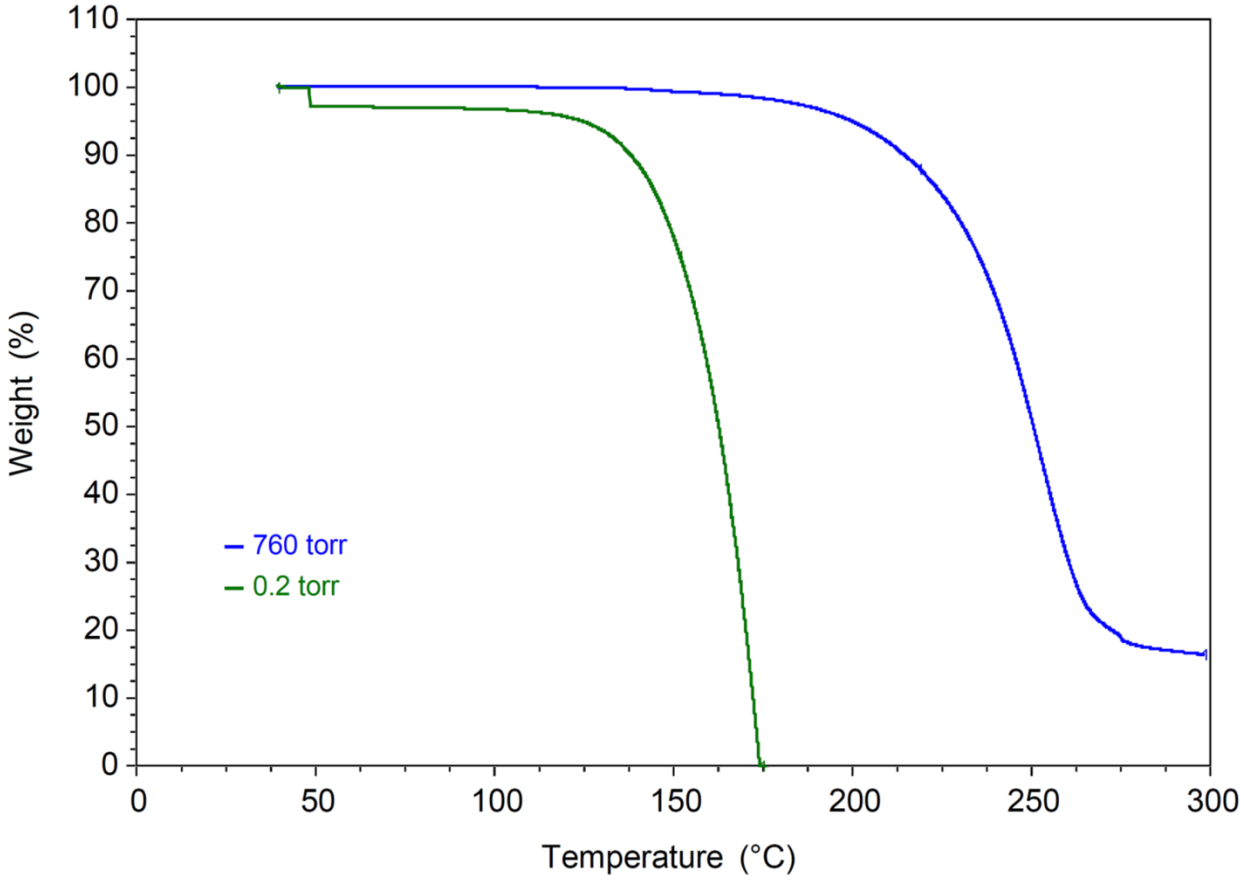

Figure S7. TGA plots of (ItBu)CuSi(SiMe$_3$)$_3$ **(3)** at 760 torr and 0.2 torr.

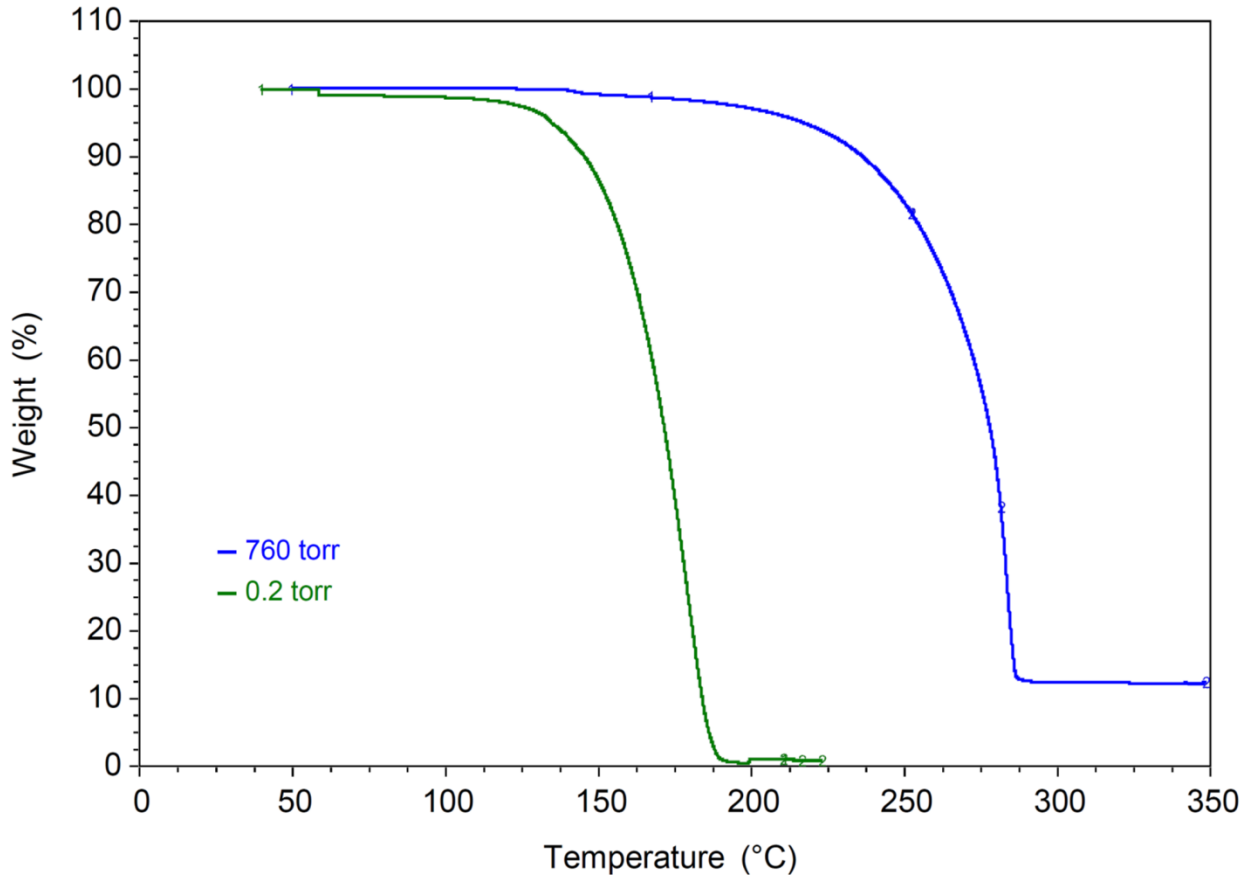

Figure S8. TGA plots of (ItBu)AgSi($SiMe_3$)$_3$ **(4)** at 760 torr and 0.2 torr.

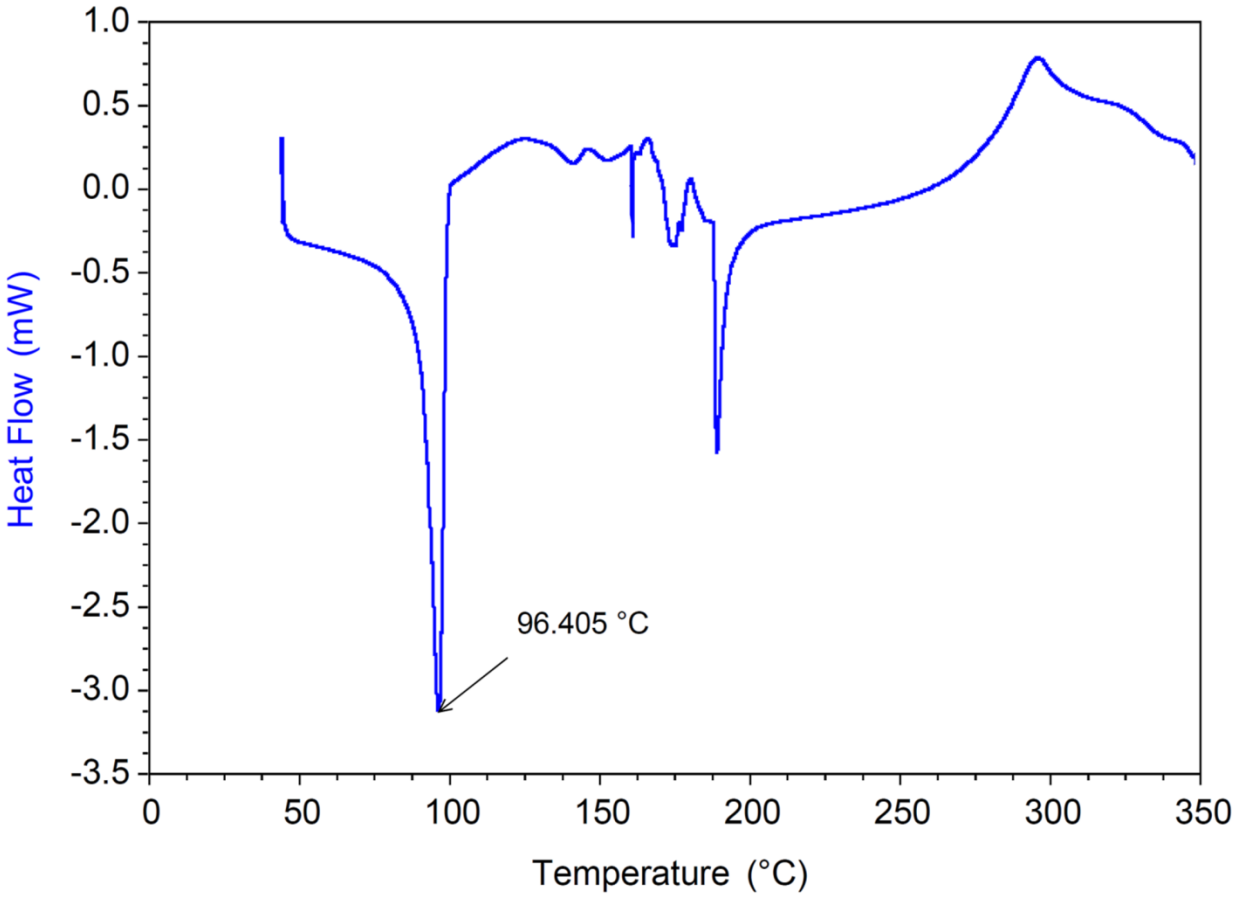

Figure S9. DSC trace of (IMe)CuSiEt($SiMe_3$)$_2$ **(5)**.

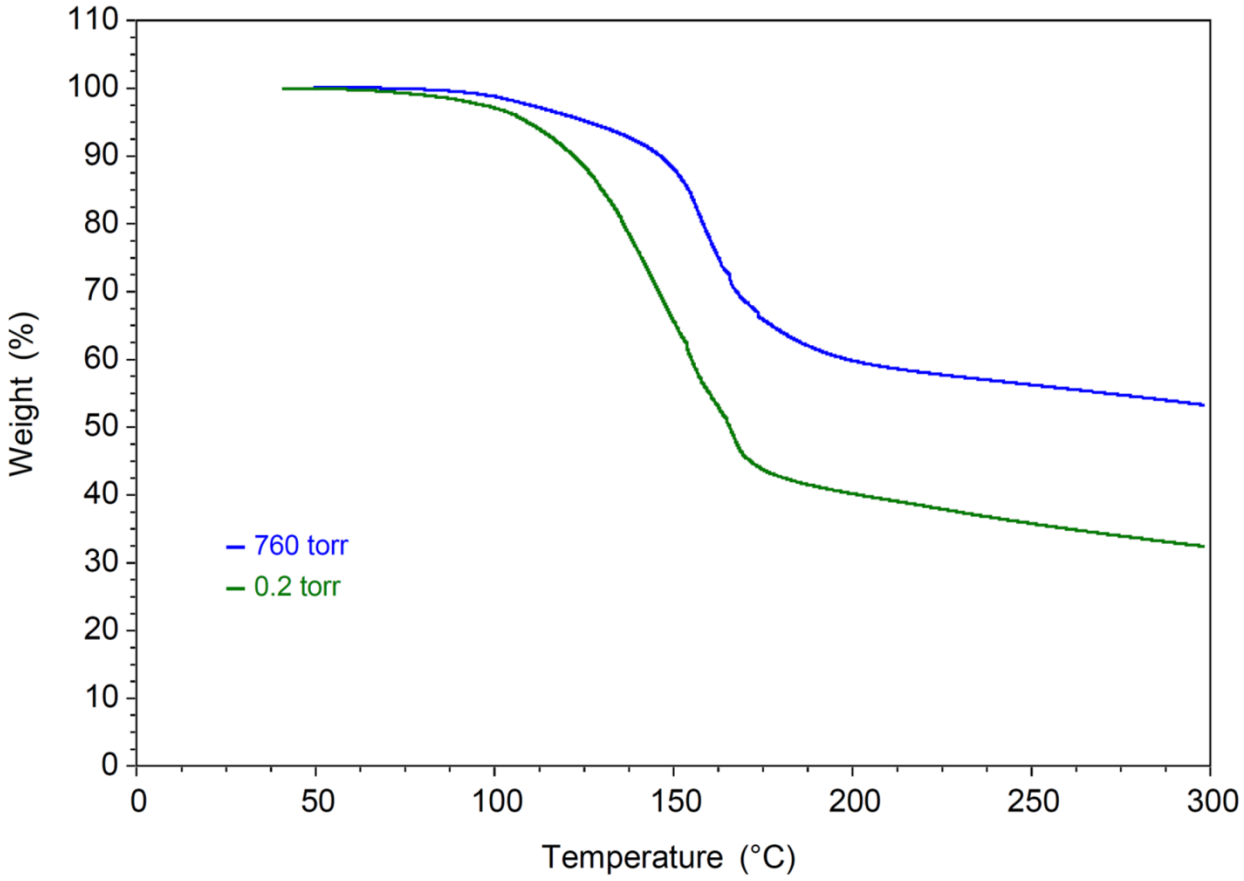

Figure S10. TGA plots of (IMe)CuSiEt($SiMe_3$)$_2$ **(5)** at 760 torr and 0.2 torr.

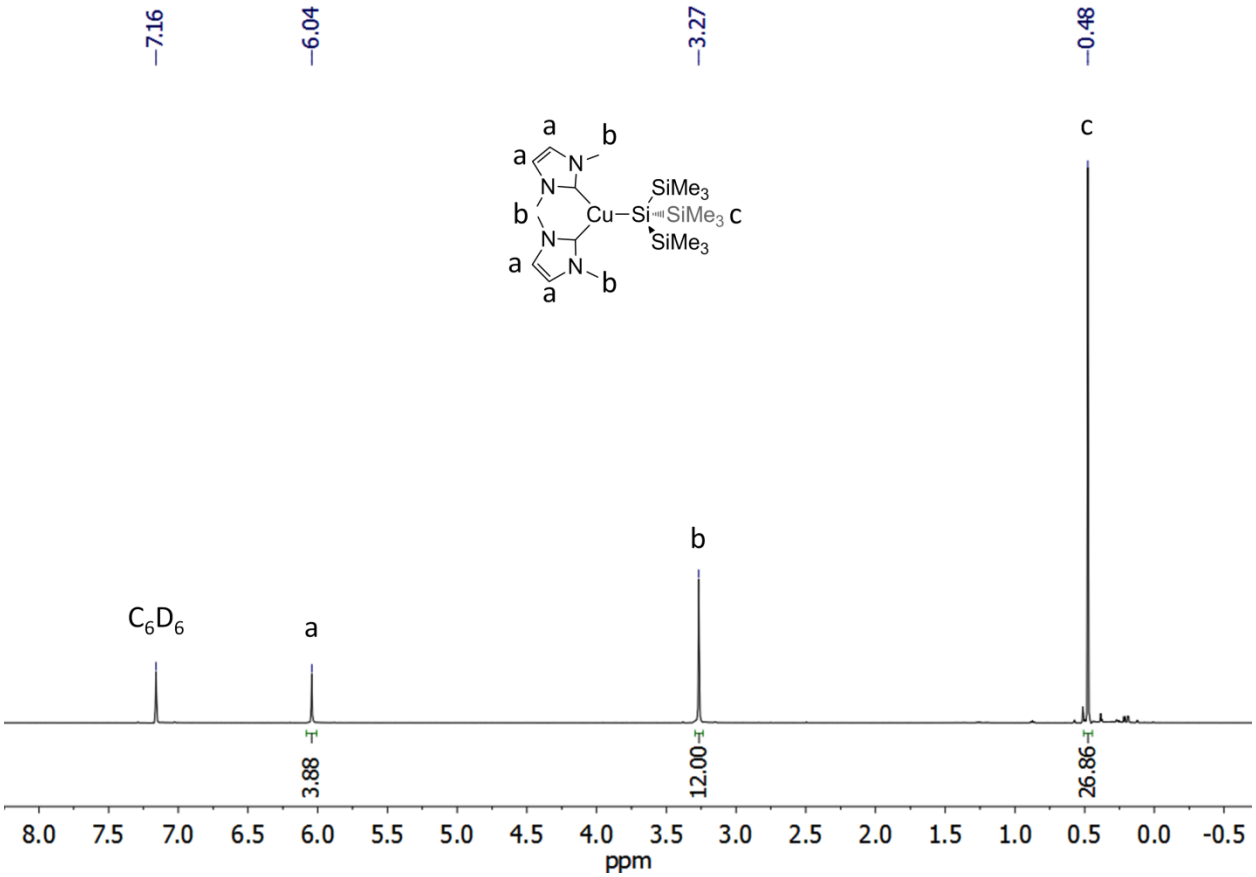

Figure S11. ^{1}H NMR spectrum of $(IMe)_2CuSi(SiMe_3)_3$ **(7)** in C_6D_6.

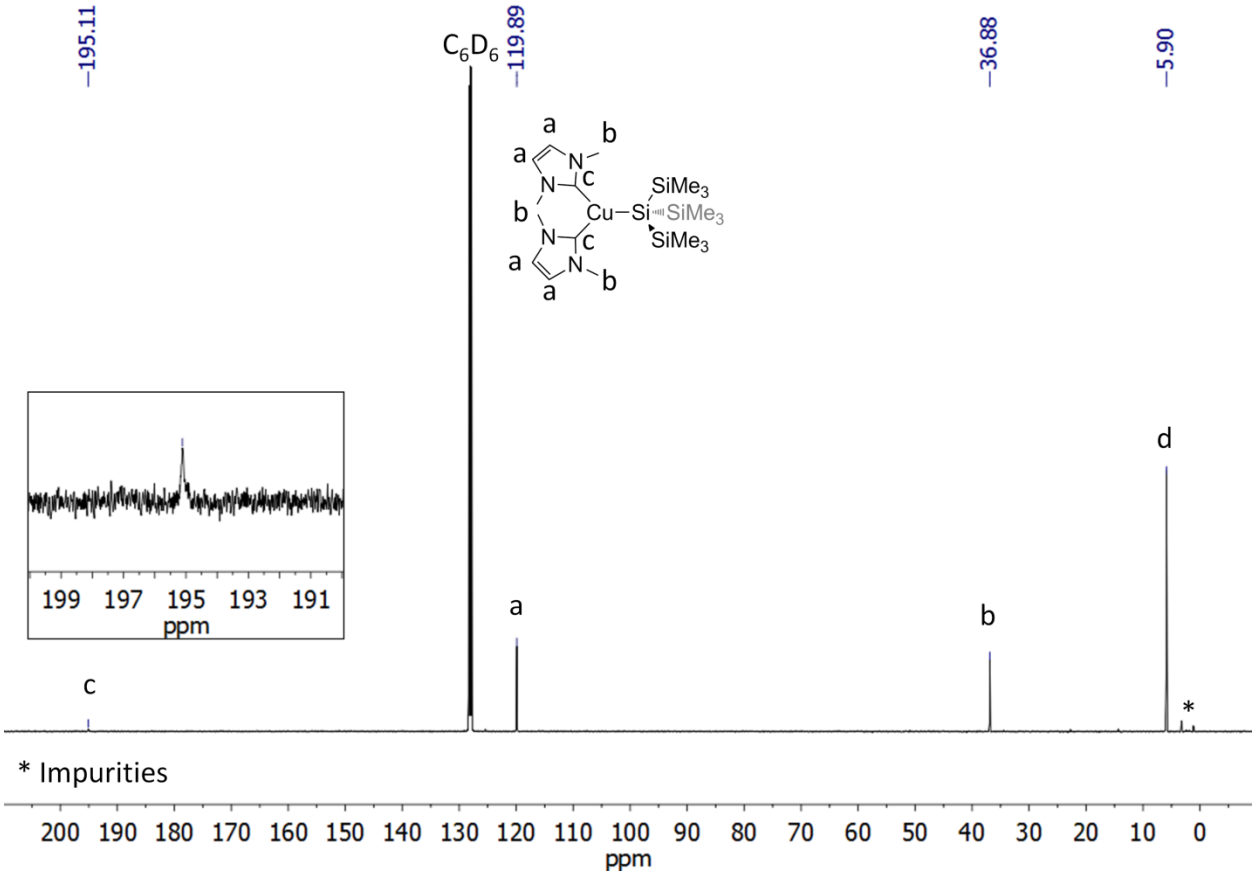

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of $(IMe)_2CuSi(SiMe_3)_3$ **(7)** in C_6D_6.

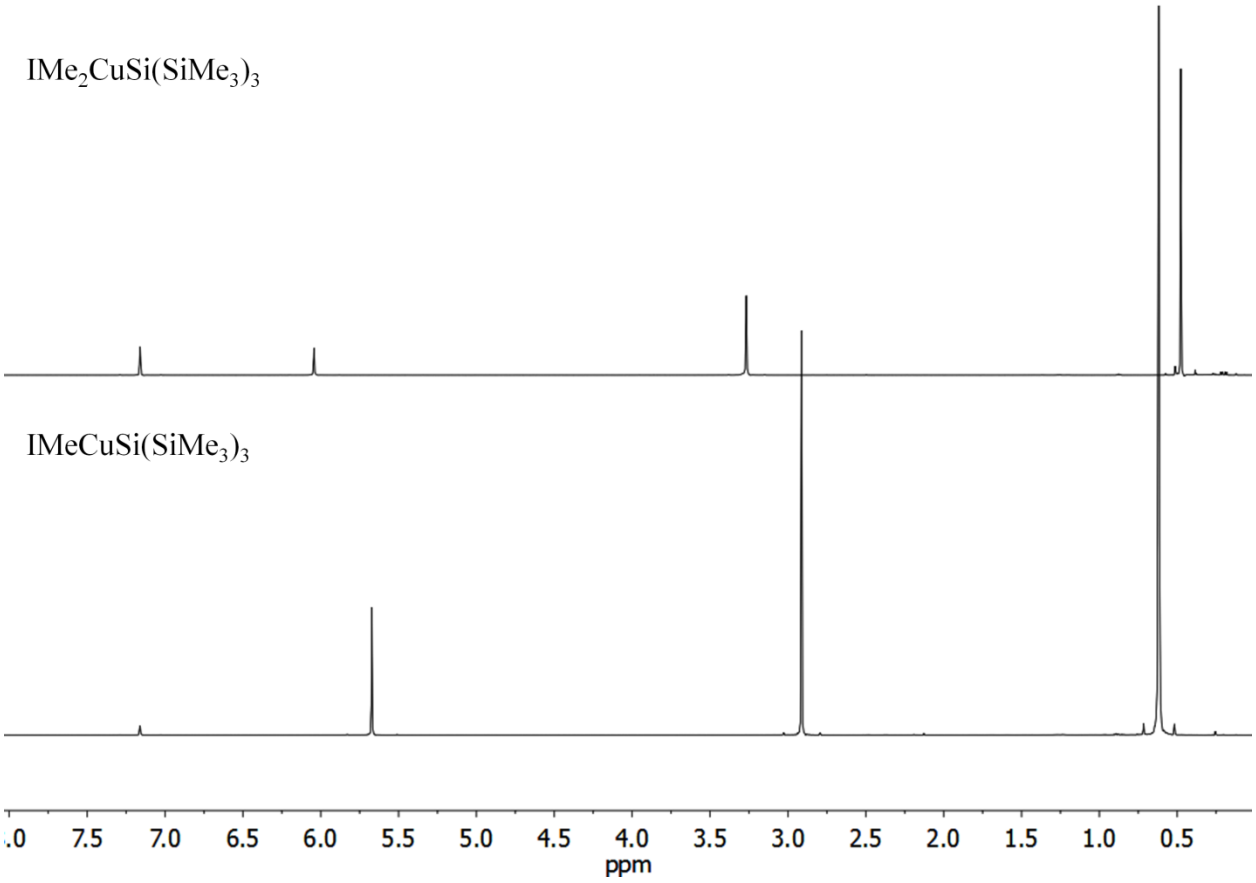

Figure S13. Stack of the ^{1}H NMR spectra of $(IMe)_2CuSi(SiMe_3)_3$ **(7)** and $(IMe)CuSi(SiMe_3)_3$ **(1)** in C_6D_6.

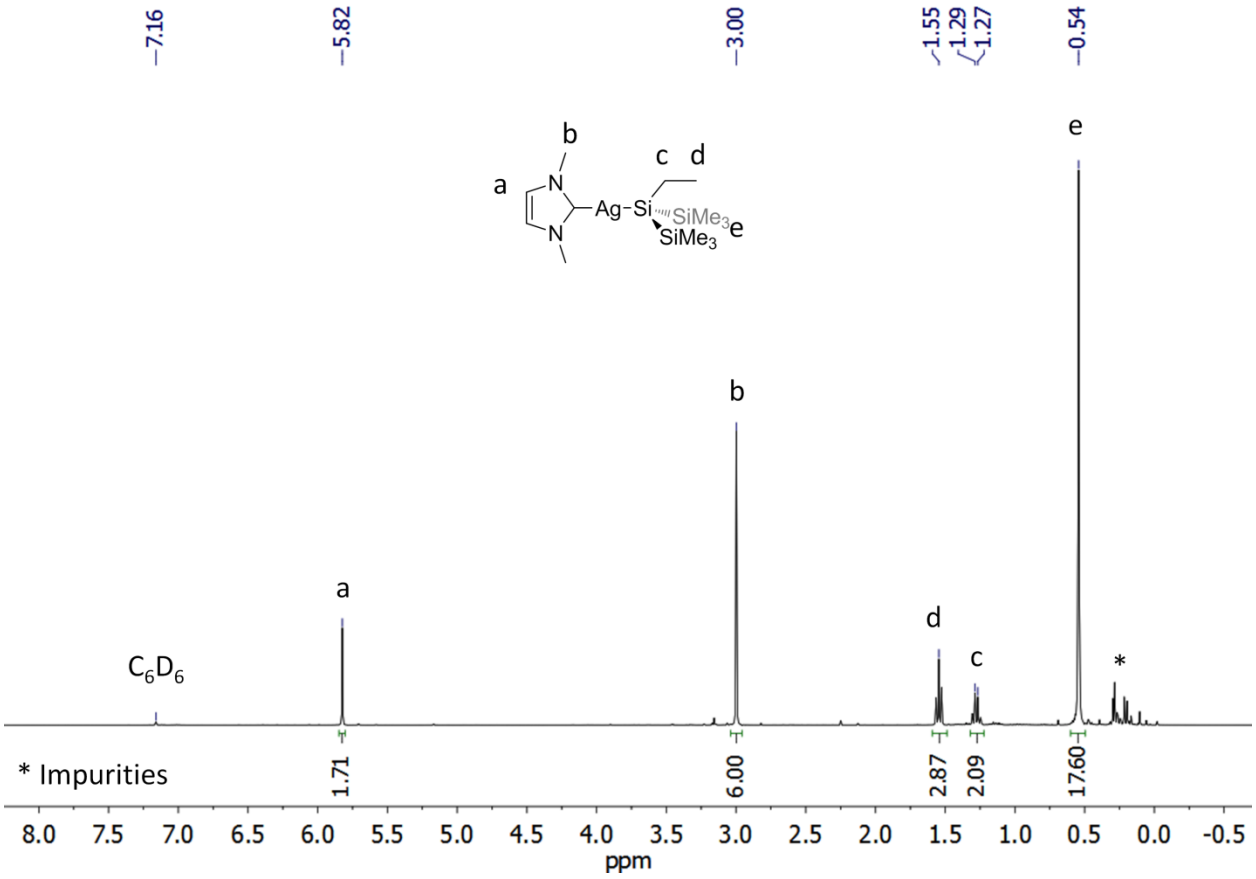

Figure S14. ^{1}H NMR spectrum of (IMe)AgSiEt(SiMe$_3$)$_2$ **(8)** in C_6D_6.

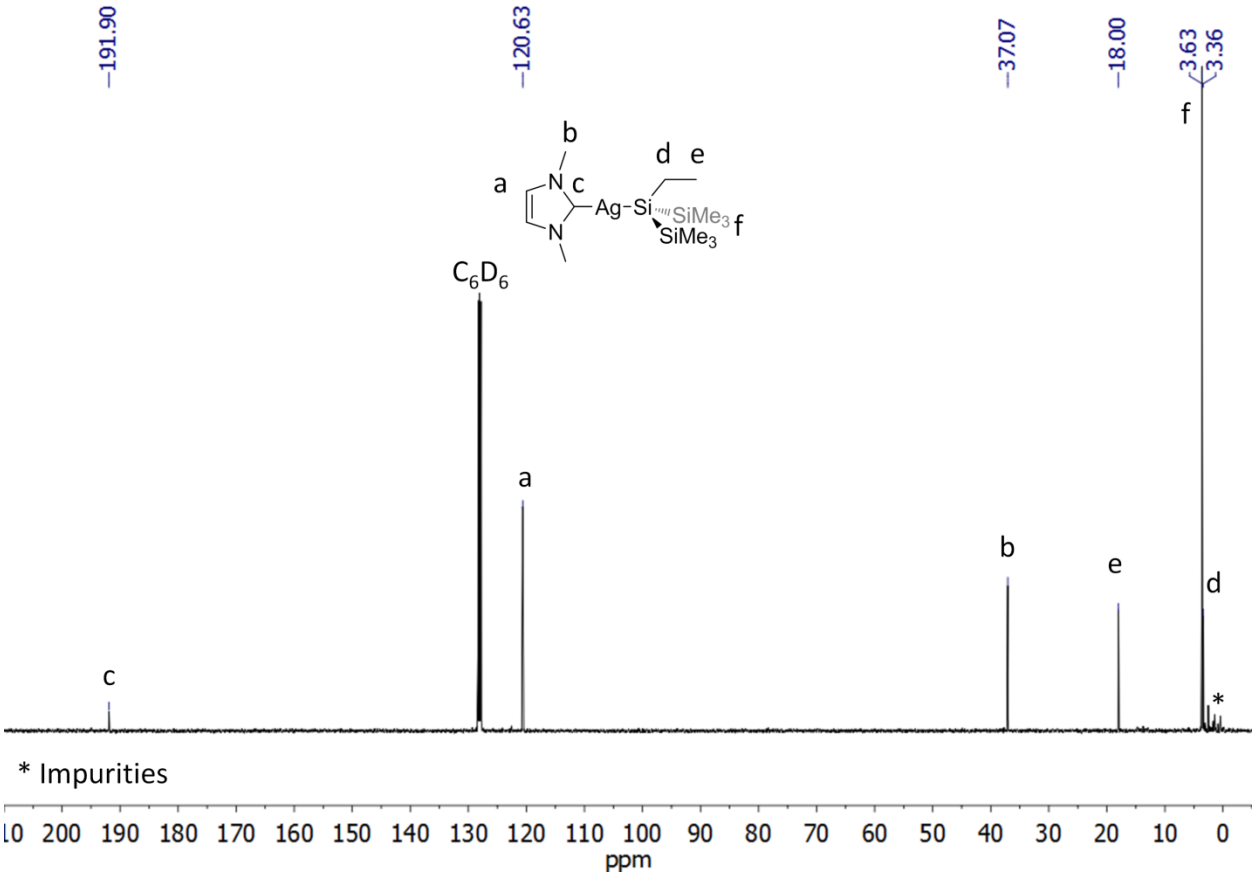

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of (IMe)AgSiEt($SiMe_3$)$_2$ **(8)** in C_6D_6.

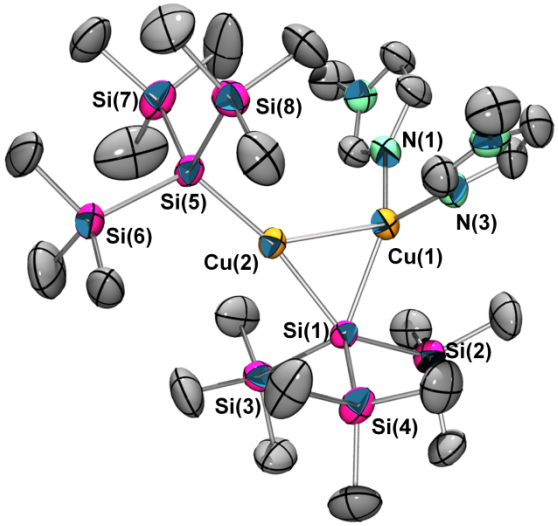

Figure S16. POV-Ray depiction of the molecular structure of **11** (50-% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Cu: copper. H-atoms omitted for clarity. Selected bond distances (Å) and angles (°): Cu(1)-N(1) 2.0185(17), Cu(1)-N(3) 2.0382(17), Cu(1)-Si(1) 2.3369(5), Cu(1)-Cu(2) 2.4328(4), Cu(2)-Si(5) 2.2907(5), Cu(2)-Si(1) 2.4003(5), N(1)-Cu(1)-N(3) 102.64(7), N(1)-Cu(1)-Si(1) 132.11(5), N(3)-Cu(1)-Si(1) 123.91(5), N(1)-Cu(1)-Cu(2) 106.30(5), N(3)-Cu(1)-Cu(2) 121.60(5), Si(1)-Cu(1)-Cu(2) 60.389(14), Si(5)-Cu(2)-Si(1) 168.514(19), Si(5)-Cu(2)-Cu(1) 132.853(17), Si(1)-Cu(2)-Cu(1) 57.827(13), Cu(1)-Si(1)-Cu(2) 61.784(14).

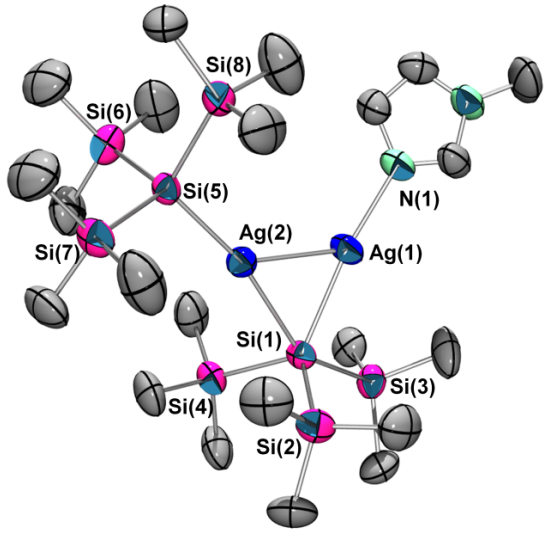

Figure S17. POV-Ray depiction of the molecular structure of **12** (50% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Ag: slate blue. H-atoms omitted for clarity. Selected bond distances (Å) and angles (°): Ag(1)-Si(1) 2.438(2), Ag(2)-Si(1) 2.6413(19), Ag(2)-Si(5) 2.412(2), Ag(1)-N(1) 2.154(6), Ag(1)-Ag(2) 2.6815(8), N(1)-Ag(1)-Si(1) 168.49(19), N(1)-Ag(1)-Ag(2) 129.28(19), Si(1)-Ag(1)-Ag(2) 61.91(5), Si(5)-Ag(2)-Si(1) 168.12(7), Si(5)-Ag(2)-Ag(1) 136.90(5), Si(1)-Ag(2)-Ag(1) 54.51(5), Ag(1)-Si(1)-Ag(2) 63.59(5).

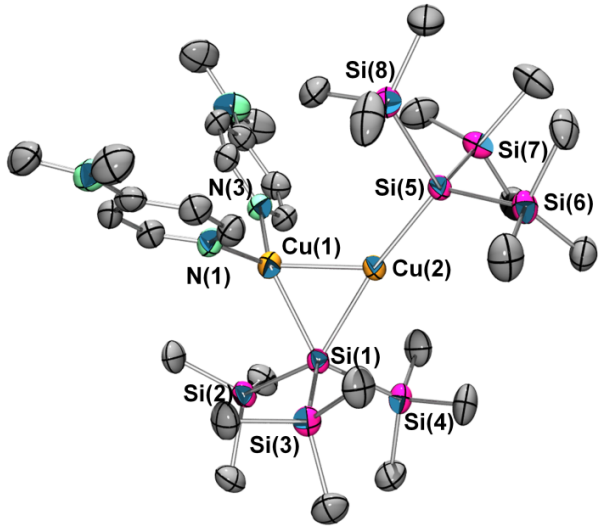

Figure S18. POV-Ray depiction of the molecular structure of $(DMAP)_2[CuSi(SiMe_3)_3]_2$ (50% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Cu: copper. Selected bond distances (Å) and angles (°): Cu(1)-N(1) 2.032(3), Cu(1)-N(3) 2.013(3), Cu(1)-Si(1) 2.3363(10), Cu(1)-Cu(2) 2.4276(6), Cu(2)-Si(5) 2.2910(10), Cu(2)-Si(1) 2.4034(10), N(1)-Cu(1)-N(3) 109.09(12), N(1)-Cu(1)-Si(1) 118.88(9), N(3)-Cu(1)-Si(1) 130.34(9), N(1)-Cu(1)-Cu(2) 118.74(9), N(3)-Cu(1)-Cu(2) 107.13(8), Si(1)-Cu(1)-Cu(2) 60.56(3), Si(5)-Cu(2)-Si(1) 170.96(4), Si(5)-Cu(2)-Cu(1) 130.56(3), Si(1)-Cu(2)-Cu(1) 57.84(3), Cu(1)-Si(1)-Cu(2) 61.60(3).

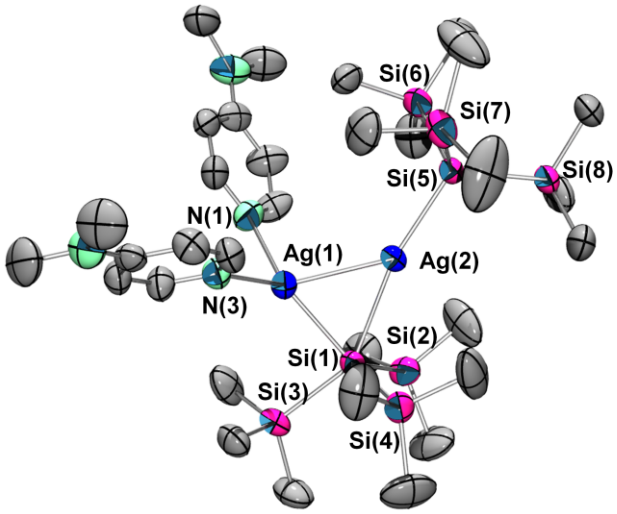

Figure S19. POV-Ray depiction of the molecular structure of **13** (50% thermal ellipsoids). C; gray, N; aquamarine, Si: deep pink, Ag: slate blue. H-atoms omitted for clarity. Selected bond distances (Å) and angles (°): Ag(1)-N(1) 2.295(5), Ag(1)-N(3) 2.297(5), Ag(1)-Si(1) 2.4577(15), Ag(1)-Ag(2) 2.6913(6), Ag(2)-Si(5) 2.4195(14), Ag(2)-Si(1) 2.5949(14), N(1)-Ag(1)-N(3) 95.78(18), N(1)-Ag(1)-Si(1) 132.81(14), N(3)-Ag(1)-Si(1) 129.79(12), N(1)-Ag(1)-Ag(2) 103.47(13), N(3)-Ag(1)-Ag(2) 128.70(12), Si(1)-Ag(1)-Ag(2) 60.32(3), Si(5)-Ag(2)-Si(1) 167.45(5), Si(5)-Ag(2)-Ag(1) 137.12(4), Si(1)-Ag(2)-Ag(1) 55.37(3), Ag(1)-Si(1)-Ag(2) 64.30(4).

Table S1. Crystallographic parameters for **1-3**.

	(IMe)CuSiTMS$_3$ (**1**)	(IMe)AgSiTMS$_3$ (**2**)	(ItBu)CuSiTMS$_3$ (**3**)
formula	$C_{14}H_{35}CuN_2Si_4$	$C_{14}H_{35}AgN_2Si_4$	$C_{20}H_{47}CuN_2Si_4$
fw	407.34	451.67	491.50
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	C2/c	C2/c	P2(1)/c
a, Å	32.0070(9)	32.4050(8)	9.7847(4)
b, Å	8.8040(2)	8.7450(2)	16.8005(7)
c, Å	22.5600(7)	23.0820(6)	20.3185(8)
α, deg	90	90	90
β, deg	132.0781(10)	132.996(1)	118.196(1)
γ, deg	90	90	90
V, Å^3	4718.5(2)	4784.1(2)	2943.8(2)
Z	8	8	4
T, K	173(2)	150(2)	173(2)
λ, Å	0.71073	0.71073	1.54178
ρ_{calc}, g/cm$_3$	1.147	1.254	1.109
F(000)	1744.0	1888.0	1064.0
μ, mm^{-1}	1.126	1.040	2.653
crystal size, mm^{-3}	0.20 x 0.12 x 0.08	0.16 x 0.08 x 0.08	0.16 x 0.13 x 0.10
transmission factor	0.9153-0.8061	0.9214-0.8512	0.7773-0.6762
θ range, deg	2.48-27.54	1.72-25.00	3.61-67.83
Data/restraints/param	5417/0/201	4191/0/201	5299/0/259
GoF	1.089	1.193	1.036
R_1 ($I > 2\sigma(I)$)	0.0535	0.0604	0.0301
wR_2 (all data)	0.1172	0.1446	0.0839
residual density, e/Å^3	0.542 and -0.293	1.077 and -0.515	0.436 and -0.147

Table S2. Crystallographic parameters for **4-6**.

	(ItBu)AgSiTMS$_3$ (**4**)	(IMe)CuSiEtTMS$_2$ (**5**)	(IMe)$_2$CuSiEtTMS$_2$ (**6**)
formula	$C_{20}H_{47}AgN_2Si_4$	$C_{26}H_{62}Cu_2N_4Si_6$	$C_{18}H_{39}CuN_2Si_3$
fw	535.83	726.42	459.34
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	P2(1)/c	C2/c	P2(1)/c
a, Å	9.7854(4)	20.7709(10)	12.9210(5)
b, Å	16.9170(7)	9.2426(4)	14.1060(5)
c, Å	20.6366(7)	21.9292(10)	14.5670(4)
α, deg	90	90	90
β, deg	118.306(1)	103.296(2)	92.340(2)
γ, deg	90	90	90
V, Å^3	3007.7(2)	4097.1(3)	2652.82(16)
Z	4	4	4
T, K	173(2)	173(2)	173(2)
λ, Å	1.54178	1.54178	0.71073
ρ_{calc}, g/cm$_3$	1.183	1.178	1.150
F(000)	1136.0	1552.0	984.0
μ, mm^{-1}	6.949	3.108	0.968
crystal size, mm^{-3}	0.28 x 0.22 x 0.22	0.23 x 0.18 x 0.18	0.16 x 0.16 x 0.12
transmission factor	0.3101-0.2164	0.6047-0.5351	0.8927-0.8605
θ range, deg	3.57-68.35	4.14-68.41	2.14-27.18
Data/restraints/param	5437/0/259	3736/0/186	5860/0/246
GoF	1.055	1.042	1.086
R_1 ($I > 2\sigma(I)$)	0.0251	0.0478	0.0648
wR_2 (all data)	0.0663	0.1391	0.1504
residual density, e/Å^3	0.546 and -0.283	0.902 and -0.658	0.455 and -0.221

Table S3. Crystallographic parameters for **9-10**.

	(ItBu)CuSiEtTMS$_2$ (**9**)	(ItBu)AgSiEtTMS$_2$ (**10**)
formula	$C_{19}H_{43}CuN_2Si_3$	$C_{19}H_{43}AgN_2Si_3$
fw	447.36	491.69
crystal system	Triclinic	Triclinic
space group	P-1	P-1
a, Å	10.7614(5)	10.8059(4)
b, Å	11.7907(5)	11.9323(4)
c, Å	11.9641(5)	11.9508(4)
α, deg	73.042(2)	72.469(2)
β, deg	75.264(2)	75.151(2)
γ, deg	69.343(2)	70.359(2)
V, Å^3	1339.10(10)	1363.09(8)
Z	2	2
T, K	173(2)	173(2)
λ, Å	1.54178	1.54178
ρ_{calc}, g/cm$_3$	1.110	1.198
F(000)	484.0	520.0
μ, mm^{-1}	2.459	7.218
crystal size, mm^{-3}	0.27 x 0.18 x 0.18	0.29 x 0.19 x 0.15
transmission factor	0.6659-0.5565	0.7530-0.5153
θ range, deg	3.92-67.98	3.94-67.93
Data/restraints/param	4747/0/239	4817/0/228
GoF	1.062	1.084
R_1 ($I > 2\sigma(I)$)	0.0334	0.0273
wR_2 (all data)	0.0922	0.0742
residual density, e/Å^3	0.393 and -0.410	0.745 and -0.570

Table S4. Crystallographic parameters for **11**, **12** and $(DMAP)_2[CuSi(SiMe_3)_3]_2$.

	(Me-imid)$_2$ [CuSiTMS$_3$]$_2$ (**11**)	(Me-imid) [AgSiTMS$_3$]$_2$ (**12**)	(DMAP)$_2$ [CuSiTMS$_3$]$_2$
formula	$C_{26}H_{66}Cu_2N_4Si_8$	$C_{22}H_{60}Ag_2N_2Si_8$	$C_{32}H_{74}Cu_2N_4Si_8$
fw	786.63	793.18	866.75
crystal system	Monoclinic	Orthorhombic	Orthorhombic
space group	P2(1)/c	Pc2(1)n	Pbca
a, Å	19.9568(13)	13.1230(3)	18.3990(7)
b, Å	12.5634(8)	13.7360(7)	19.4950(8)
c, Å	18.0525(12)	22.3580(4)	27.347(1)
α, deg	90	90	90
β, deg	97.617(3)	90	90
γ, deg	90	90	90
V, Å^3	4486.3(5)	4030.2(2)	9809.1(7)
Z	4	4	8
T, K	173(2)	173(2)	173(2)
λ, Å	1.54178	0.71073	0.71073
ρ_{calc}, g/cm$_3$	1.165	1.307	1.174
F(000)	1680.0	1648.0	3712.0
μ, mm^{-1}	3.368	1.224	1.087
crystal size, mm^{-3}	0.32 x 0.24 x 0.09	0.18 x 0.08 x 0.08	0.20 x 0.20 x 0.20
transmission factor	0.7514-0.4121	0.9084-0.8098	0.8119-0.8119
θ range, deg	2.23-68.18	2.82-27.51	2.48-27.66
Data/restraints/param	8160/0/381	8872/1/314	10989/0/437
GoF	1.030	1.160	1.188
R_1 ($I > 2\sigma(I)$)	0.0321	0.0556	0.0592
wR_2 (all data)	0.0911	0.1175	0.1034
residual density, e/Å^3	0.584 and -0.334	0.710 and -0.445	0.618 and -0.411

Table S5. Crystallographic parameters for **13**-**15**.

	$(DMAP)_2[AgSiTMS_3]_2$ (**13**)	$Bipy[CuSiTMS_3]_2$ (**14**)	$Bipy[AgSiTMS_3]_2$ (**15**)
formula	$C_{32}H_{74}Ag_2N_4Si_8$	$C_{28}H_{62}Cu_2N_2Si_8$	$C_{28}H_{62}Ag_2N_2Si_8$
fw	955.41	778.60	867.26
crystal system	Monoclinic	Orthorhombic	Orthorhombic
space group	P2(1)/c	Pbca	Pbca
a, Å	14.0170(4)	19.6672(8)	19.7039(9)
b, Å	21.7790(5)	18.8226(6)	18.9384(9)
c, Å	19.3560(6)	23.8417(9)	24.2994(10)
α, deg	90	90	90
β, deg	121.6380(14)	90	90
γ, deg	90	90	90
V, Å ^{3}	5030.7(2)	8825.9(6)	9067.6(7)
Z	4	8	8
T, K	173(2)	173(2)	173(2)
λ, Å	0.71073	1.54178	1.54178
ρ_{calc}, g/cm$_3$	1.261	1.172	1.271
F(000)	2000.0	3312.0	3600.0
μ, mm^{-1}	0.993	3.408	9.093
crystal size, mm^{-3}	0.12 x 0.12 x 0.08	0.33 x 0.19 x 0.17	0.23 x 0.17 x 0.13
transmission factor	0.9248-0.8901	0.7531-0.5790	0.7531-0.5425
θ range, deg	1.55-27.68	3.71-68.50	3.64-68.63
Data/restraints/param	11588/0/437	7908/0/361	8349/0/361
GoF	1.195	1.021	1.038
R_1 ($I > 2\sigma(I)$)	0.0683	0.0346	0.0278
wR_2 (all data)	0.1159	0.0978	0.0757
residual density, e/Å^3	0.658 and -0.407	0.377 and -0.285	0.520 and -0.284