

Supporting Information

for

Direct Coordination of Germanium(II) Dicationic Center to Transition Metals

Ravindra K. Raut and Moumita Majumdar*

Contents

1.	Experimental details	S2
2.	Plots of NMR spectra	S5
3.	UV-Vis spectra	S15
4.	DFT calculations	S19
5.	X-ray data	S24

Department of Chemistry,
Indian Institute of Science, Education and Research, Pune
Pune-411008, Maharashtra
India
E-mail: moumitam@iiserpune.ac.in

1. Experimental details

General Remarks. All manipulations were carried out under a protective atmosphere of argon applying standard Schlenk techniques or in a dry box. Tetrahydrofuran was refluxed over sodium/benzophenone. Dichloromethane and acetonitrile were stirred and refluxed over calcium hydride and kept over 3 Å molecular sieves. All solvents were distilled and stored under argon and degassed prior to use. CD₃CN ampoules were purchased from Sigma Aldrich and used as it is. All chemicals were used as purchased. The tetradentate ligand L was prepared according to literature procedure.^{S1} The chlorogermylum ylidenes [LGeCl]⁺ were also obtained either by using one equivalent of TMSOTf or by auto-ionization of GeCl₂^{S2} in presence of ligand L. ¹H and ¹³C{¹H} NMR spectra were referenced to external SiMe₄ using the residual signals of the deuterated solvent (¹H) or the solvent itself (¹³C). ¹⁹F and ³¹P{¹H} NMR were referenced to external C₆H₅CF₃ (TFT) and 85% H₃PO₄ respectively. Solution phase UV/Vis spectra were acquired using a Thermo-Scientific Evolution 300 spectrometer using quartz cells with a path length of 1 cm. Melting points were determined under argon in closed NMR tubes and are uncorrected. Elemental analyses were performed on Elementar vario EL analyzer. Single crystal data were collected on both Bruker SMART APEX four-circle diffractometer equipped with a CMOS photon 100 detector (Bruker Systems Inc.) with a Cu K α radiation (1.5418 Å), and Bruker SMART APEX Duo diffractometer using Mo K α radiation (0.71073 Å).

Synthesis of [LGeCl][OTf]

Ligand L (0.4 g, 1.50 mmol) was dissolved in THF and was added to GeCl₂.dioxane (0.35 g, 1.50 mmol) in THF, followed by drop-wise addition of trimethylsilyl trifluoromethanesulphonate (0.27 mL, 1.50 mmol) at 0°C. Reaction mixture was stirred overnight, during which complete precipitation of the orange coloured product occurred. The product was isolated via filtration and washed thrice with THF. Product was dried under vacuum yielding 0.72 g (92%) of [LGeCl][OTf] (decomp. 130-132°C) as an orange solid.

Crystals suitable for X-ray measurement were grown by layering acetonitrile solution of the compound with diethyl ether at room temperature.

¹H NMR (400 MHz, CD₃CN, TMS) δ 8.96 (ddd, $J = 4.9, 1.6, 1.0$, 2H, *o*-Pyr-*H*); 8.26 – 8.14 (m, 4H, *m* and *p*-Pyr-*H*); 7.76 (ddd, $J = 7.4, 4.9, 1.3$, 2H, *m*-Pyr-*H*); 4.25 (s, 4H, -CH₂-CH₂-); 2.74 (s, 6H, -CH₃) ppm.
¹³C{¹H} NMR (101 MHz, CD₃CN, TMS) δ 172.72 (C-CH₃); 149.64 (Pyr-C_o); 147.15 (Pyr-C_o); 139.43 (Pyr-C_p); 127.52 (Pyr-C_m); 125.64 (Pyr-C_m); 122.75, 119.56 (CF₃SO₃); 49.27 (-CH₂-CH₂-); 17.62 (C-CH₃) ppm.

¹⁹F{¹H} NMR (377 MHz, CD₃CN, TFT) δ -79.24 (TMSOTf-*F*) ppm.

UV/Vis (acetonitrile) λ_{\max} (ϵ) 359 nm (1656 M⁻¹cm⁻¹).

Elemental Analysis: Calcd. for C₁₇H₁₉ClF₃GeN₄O₃S: C, 39.00; H, 3.47; N, 10.70. Found: C, 39.23; H, 3.56; N, 10.55.

Synthesis of [LGeCl][GeCl₃]

Ligand L (0.70 g, 2.63 mmol) was dissolved in THF and was added to a THF solution of GeCl₂.dioxane (1.22 g, 5.26 mmol). Orange coloured precipitation occurred upon overnight stirring. The precipitate was isolated via filtration and washed thrice with THF. Product was dried under vacuum yielding 1.63 g (85%) of [LGeCl][GeCl₃] (decomp. 143-145°C) as an orange solid.

Crystals suitable for X-ray measurement were grown by layering acetonitrile solution of the compound with diethyl ether at room temperature.

¹H NMR (400 MHz, CD₃CN, TMS) δ 8.96 (ddd, $J = 4.8, 1.5, 1.0$, 2H, *o*-Pyr-*H*); 8.33 – 8.09 (m, 4H, *m* and *p*-Pyr-*H*); 7.76 (ddd, $J = 7.4, 4.9, 1.3$, 2H, *m*-Pyr-*H*); 4.26 (s, 4H, -CH₂-CH₂-); 2.75 (s, 6H, -CH₃) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN , TMS) δ 172.69 (C- CH_3); 149.65 (Pyr- C_o); 147.14 (Pyr- C_o); 139.35 (Pyr- C_p); 127.48 (Pyr- C_m); 125.61 (Pyr- C_m); 49.31(- $\text{CH}_2\text{-CH}_2$ -); 17.71 (C- CH_3) ppm.

UV/Vis (acetonitrile) λ_{max} (ϵ) 358 nm ($2376 \text{ M}^{-1}\text{cm}^{-1}$).

Elemental Analysis: Calcd. for $\text{C}_{16}\text{H}_{18}\text{Cl}_4\text{Ge}_2\text{N}_4$: C, 34.73; H, 3.28; N, 10.12. Found: C, 34.58; H, 3.16; N, 10.02.

Compound 1

Ligand **1** (1.0 g, 3.75 mmol) was dissolved in dichloromethane and was added to a suspension of GeCl_2 .dioxane (0.869 g, 3.75 mmol) in dichloromethane, followed by drop-wise addition of TMSOTf (1.40 mL, 7.70 mmol) at 0°C . The solution was stirred overnight when yellow precipitation occurred. The precipitate was isolated via filtration and washed thrice with THF. The product was dried under vacuum yielding 2.20g (92%) of **1** (decomp. $170\text{-}172^\circ\text{C}$) as yellow solid.

Crystals of **1** suitable for X-ray measurement were grown by layering acetonitrile solution of the compound with diethyl ether at room temperature.

^1H NMR (400 MHz, CD_3CN , TMS) δ 9.30 (d, $J=5.4$, 2H, *o*-Pyr-*H*); 8.52 (td, $J=7.8$, 1.4, 2H, *p*-Pyr-*H*); 8.45 (d, $J=7.6$, 2H, *m*-Pyr-*H*); 8.14 – 8.09 (m, 2H, *m*-Pyr-*H*); 4.52 (s, 4H, - $\text{CH}_2\text{-CH}_2$ -); 2.75 (s, 6H, - CH_3) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN , TMS) δ 172.34 (C- CH_3); 148.20 (Pyr- C_o); 146.95 (Pyr- C_o); 143.98 (Pyr- C_p); 129.95 (Pyr- C_m); 126.90 (Pyr- C_m); 122.51, 119.35 (CF_3SO_3); 46.95 (- $\text{CH}_2\text{-CH}_2$ -); 16.21 (C- CH_3) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CD_3CN , TMS) δ -79.29 (TMSOTf- *F*) ppm.

UV/Vis (acetonitrile) λ_{max} (ϵ) 341 nm ($2440 \text{ M}^{-1}\text{cm}^{-1}$).

Elemental Analysis: Calcd. for $\text{C}_{18}\text{H}_{18}\text{F}_6\text{GeN}_4\text{O}_6\text{S}_2$: C, 33.93; H, 2.85; N, 8.79. Found: C, 33.97; H, 2.95; N, 8.85.

Compound 2

Compound **1** (0.20 g, 0.314 mmol) was dissolved in acetonitrile and added to an acetonitrile solution of silver trifluoromethanesulphonate (0.403 g, 0.156 mmol) maintained at 0°C and stirred overnight at room temperature. The solvent was completely removed under vacuum giving **2** (m.p. $186^\circ\text{C}\text{-}188^\circ\text{C}$) as yellow solid.

Crystals of **2** suitable for X-ray measurement were grown by layering acetonitrile solution of the compound with diethyl ether at room temperature. Crystallization yield = 0.140 g (59%)

^1H NMR (400 MHz, CD_3CN , TMS) δ 9.30 (d, $J=5.3$, 2H, *o*-Pyr-*H*); 8.56 (t, $J=7.8$, 2H, *p*-Pyr-*H*); 8.48 (d, $J=7.9$, 2H, *m*-Pyr-*H*); 8.15 (t, $J=6.5$, 2H, *m*-Pyr-*H*); 4.52 (s, 4H, - $\text{CH}_2\text{-CH}_2$ -); 2.78 (s, 6H, - CH_3) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN , TMS) δ 172.47 (C- CH_3); 148.16 (Pyr- C_o); 146.31 (Pyr- C_o); 144.55 (Pyr- C_p); 130.27 (Pyr- C_m); 127.07 (Pyr- C_m); 122.54, 119.35 (CF_3SO_3); 46.57 (- $\text{CH}_2\text{-CH}_2$ -); 16.28 (C- CH_3) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CD_3CN , TMS) δ -79.30 (TMSOTf- *F*) ppm.

UV/Vis (acetonitrile) λ_{max} (ϵ) 337 nm ($8640 \text{ M}^{-1}\text{cm}^{-1}$).

Elemental Analysis: Calcd. for $\text{C}_{37}\text{H}_{36}\text{AgF}_{15}\text{Ge}_2\text{N}_8\text{O}_{15}\text{S}_5$: C, 29.02; H, 2.37; N, 7.32. Found: C, 29.23; H, 2.46; N, 7.39.

Compound 3

Trimethylsilyl trifluoromethanesulphonate (42.5 μL , 0.235 mmol) was added to an acetonitrile solution of $\text{AuCl}\cdot\text{SMe}_2$ (0.058 g, 0.235 mmol) at room temperature. In another Schlenk flask compound **1** (0.30 g, 0.47 mmol) was dissolved in acetonitrile and added to the above solution at 0°C . Reaction mixture was

stirred overnight at room temperature. The solvent was completely removed under vacuum giving **3** (m.p. 198°C-200°C) as a very pale yellow solid.

Crystals of **3** suitable for X-ray measurement were grown by layering acetonitrile solution of the compound with diethyl ether at room temperature. Crystallization yield = 0.24 g (64 %)

¹H NMR (400 MHz, CD₃CN, TMS) δ 9.35 (d, *J*=5.4, 2H, *o*-Pyr-*H*), 8.67 (t, *J*=8.5, 2H, *p*-Pyr-*H*), 8.56 (d, *J*=7.5, 2H, *m*-Pyr-*H*), 8.26 – 8.21 (m, 2H, *m*-Pyr-*H*), 4.53 (d, *J*=50.5, 4H, -CH₂-CH₂-), 2.84 (s, 6H, -CH₃) ppm.

¹³C{¹H} NMR (101 MHz, CD₃CN, TMS) δ 173.09 (C-CH₃); 148.74 (Pyr- C_o); 146.60 (Pyr-C_o); 144.44 (Pyr-C_p); 131.25 (Pyr-C_m); 127.61 (Pyr-C_m); 122.39, 119.21 (CF₃SO₃); 45.22 (-CH₂-CH₂-); 16.50 (C-CH₃) ppm.

¹⁹F{¹H} NMR (377 MHz, CD₃CN, TMS) δ -79.26 (TMSOTf- *F*) ppm.

Elemental Analysis: Calcd. for C₃₇H₃₆AuF₁₅Ge₂N₈O₁₅S₅: C, 27.43; H, 2.24; N, 6.92. Found: C, 27.32; H, 2.16; N, 6.83.

Reaction of **1** with ^tBuNC

In a NMR tube, ^tBuNC (8 μL, 0.072 mmol) was added to compound **1** (0.045 g, 0.072 mmol) dissolved in 0.6 mL of acetonitrile-*d*₃, and shaken well. The NMR spectra were monitored at room temperature at different time intervals.

Reaction of **1** with PMe₃

In a NMR tube, PMe₃ (9 μL, 0.084 mmol) was added to compound **1** (0.054 g, 0.084 mmol) dissolved in 0.6 mL of acetonitrile-*d*₃, and shaken well. The NMR spectra were monitored at room temperature at different time intervals.

2. Plots of NMR spectra

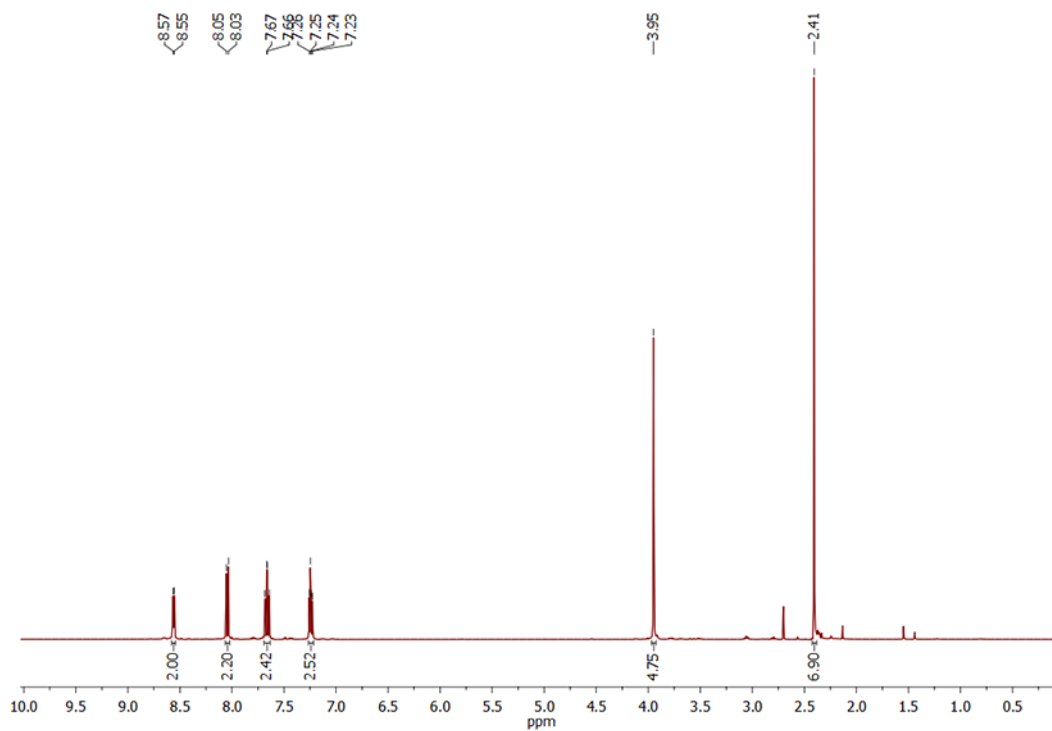


Figure S1. ^1H NMR of L

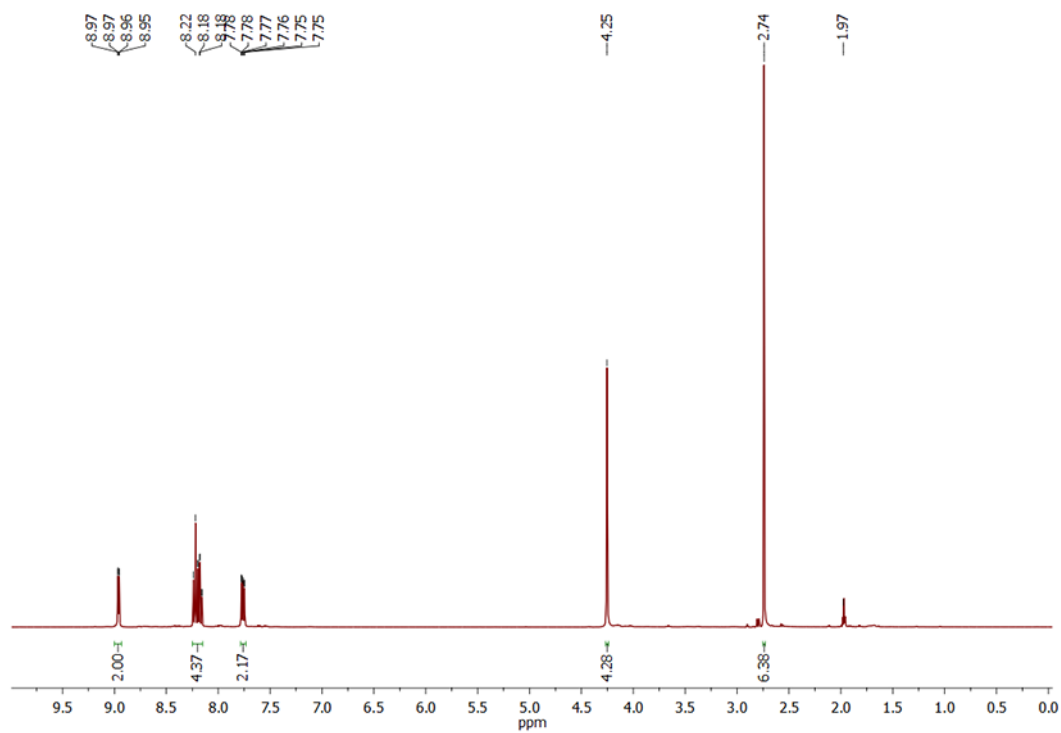


Figure S2. ^1H NMR of [LGeCl][OTf]

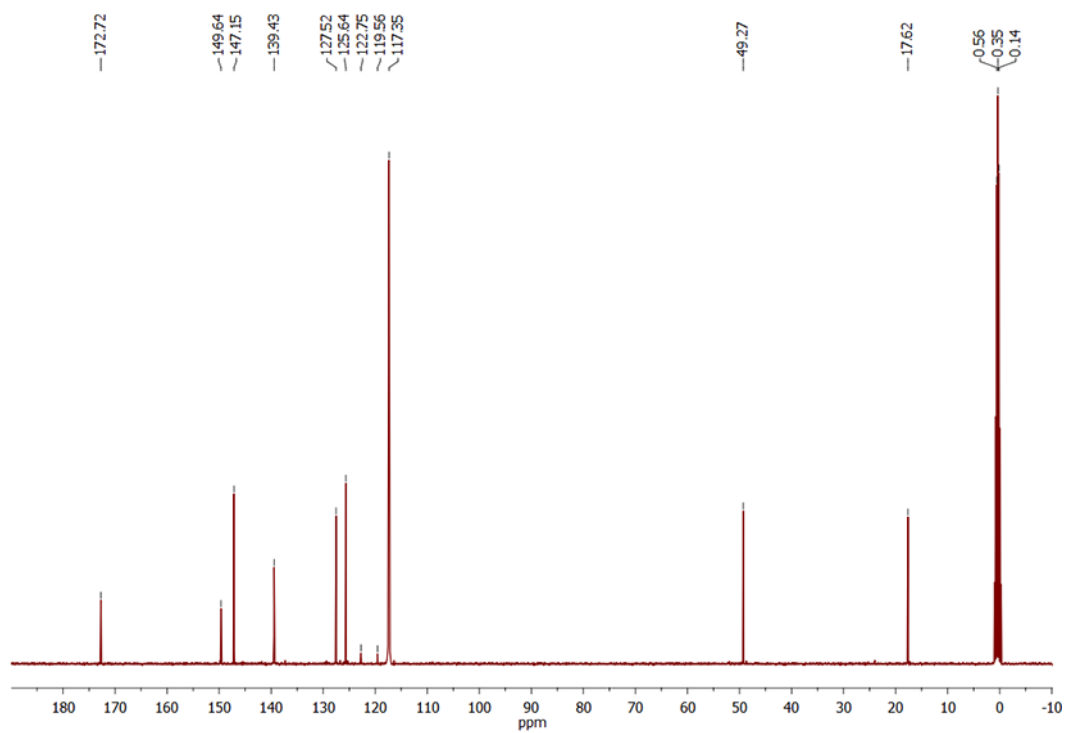


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR of $[\text{LGeCl}][\text{OTf}]$

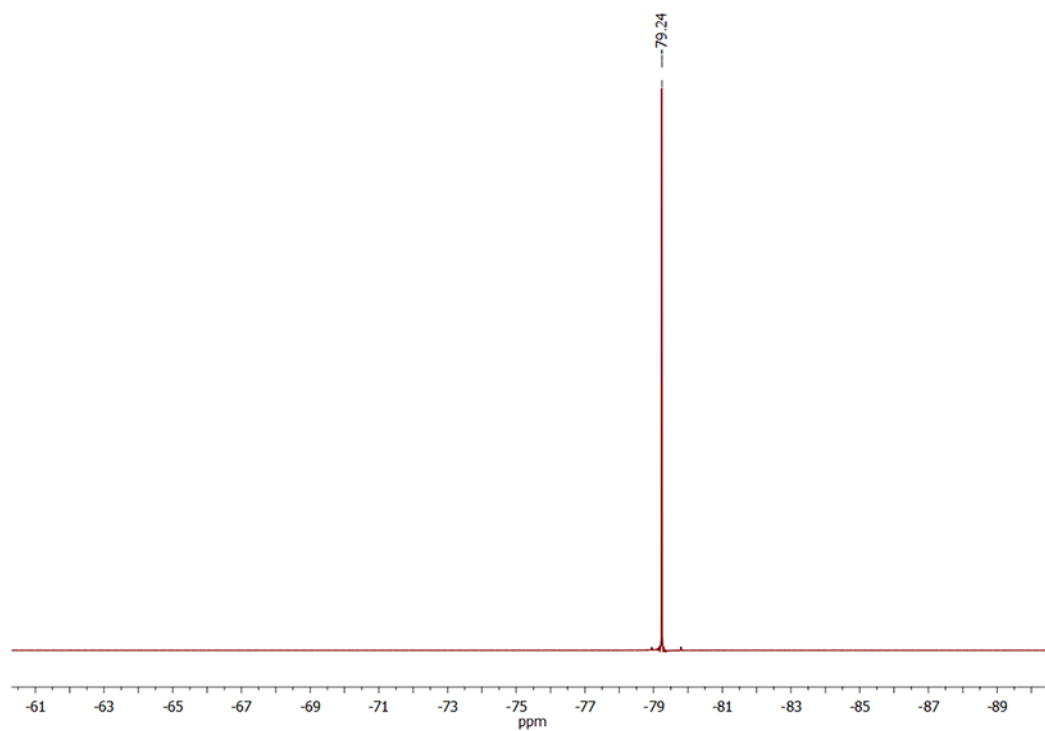


Figure S4. $^{19}\text{F}\{^1\text{H}\}$ NMR of $[\text{LGeCl}][\text{OTf}]$

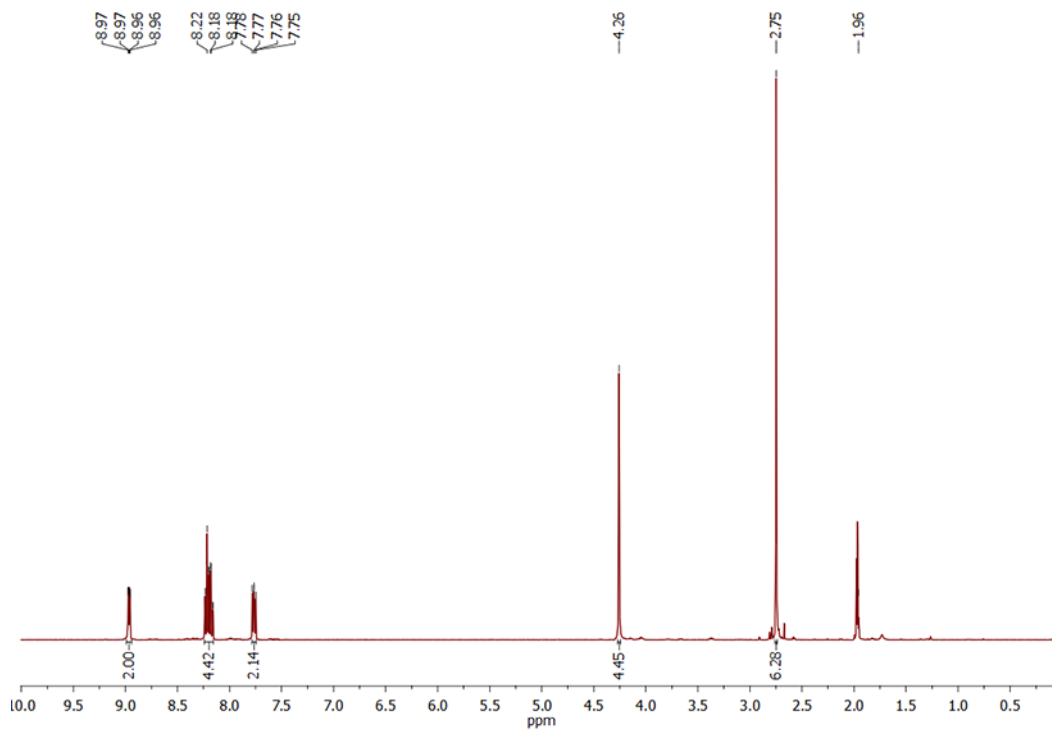


Figure S5. ^1H NMR of $[\text{LGeCl}][\text{GeCl}_3]$

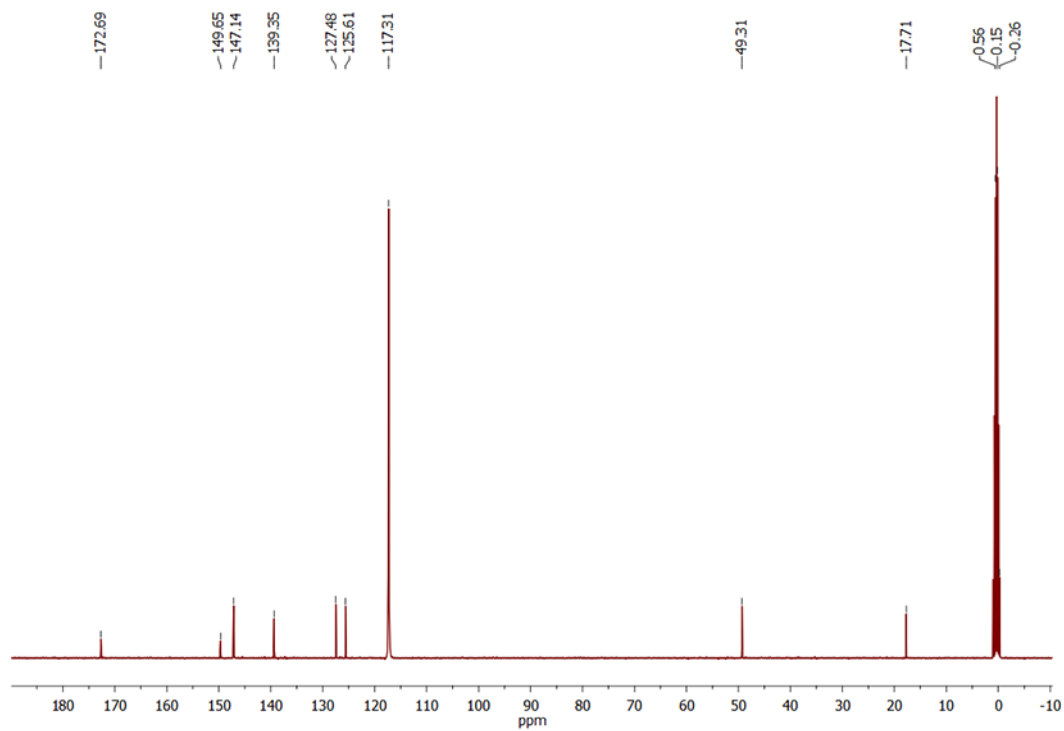


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR of $[\text{LGeCl}][\text{GeCl}_3]$

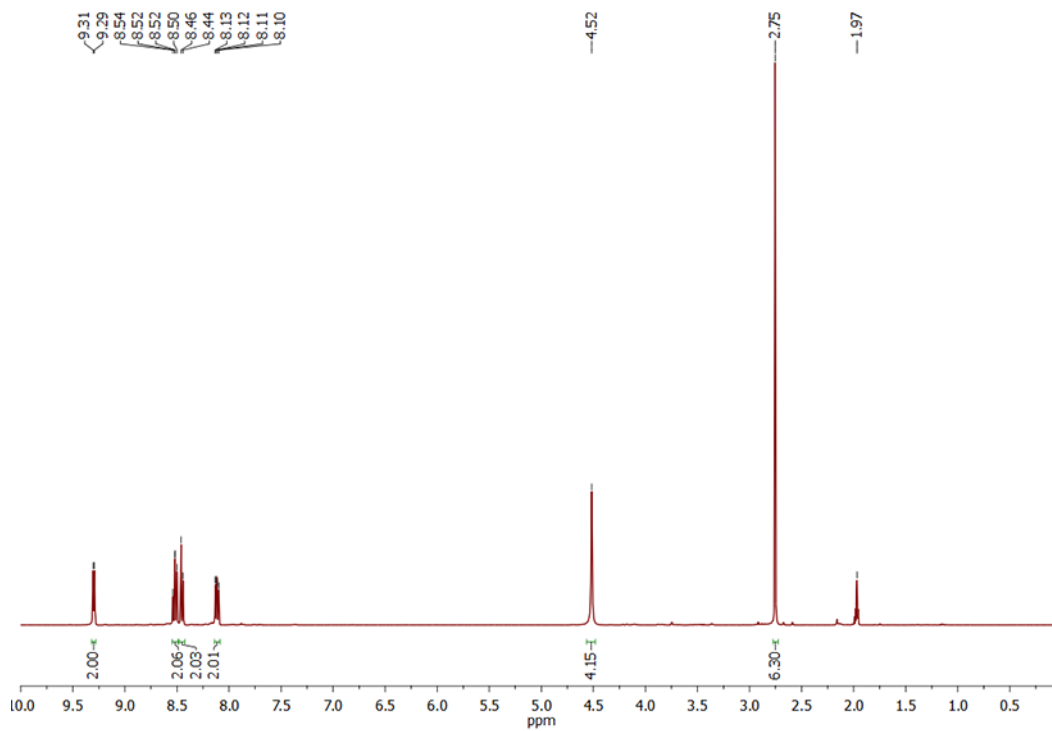


Figure S7. ^1H NMR of **1**

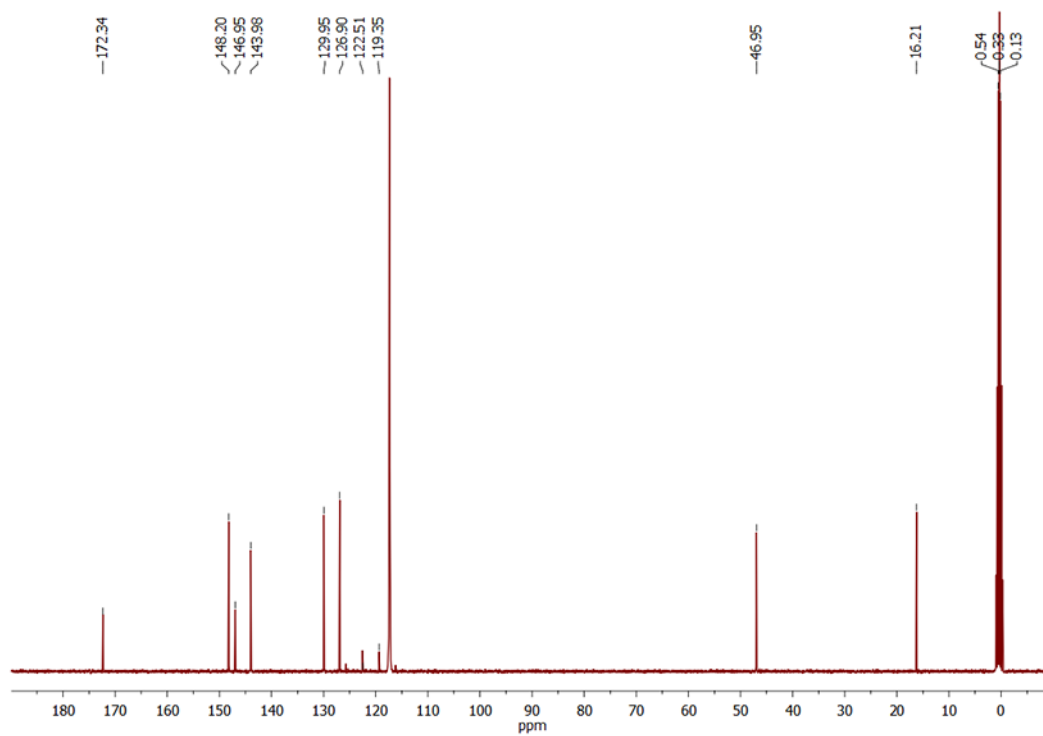


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR of **1**

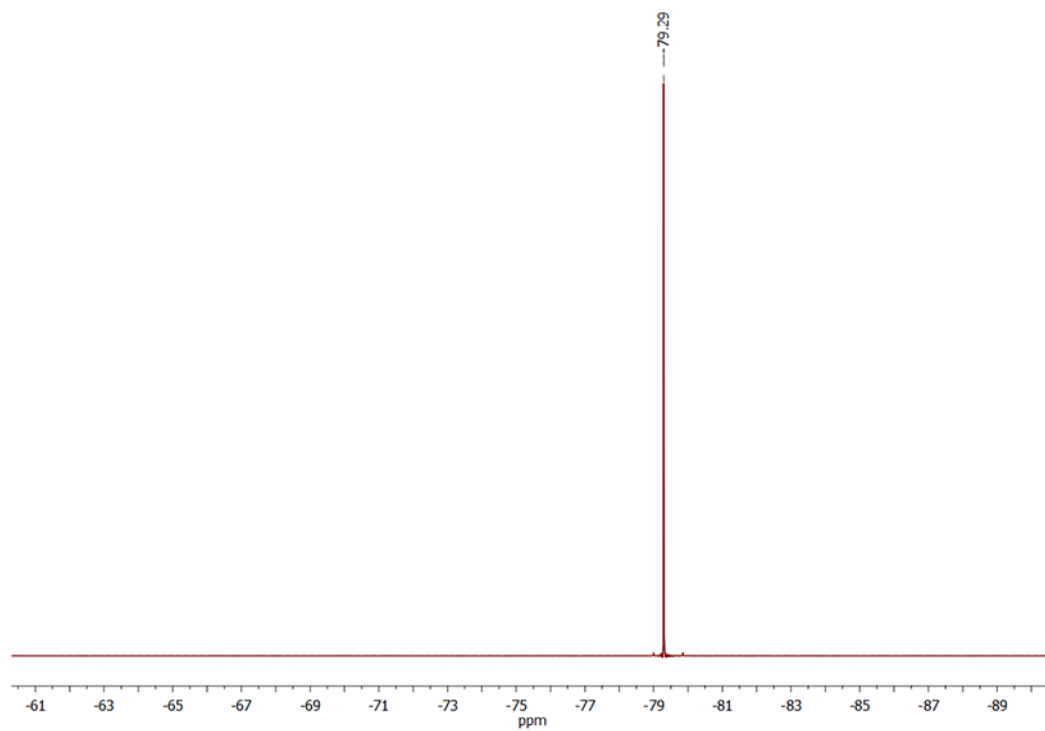


Figure S9. $^{19}\text{F}\{^1\text{H}\}$ NMR of 1

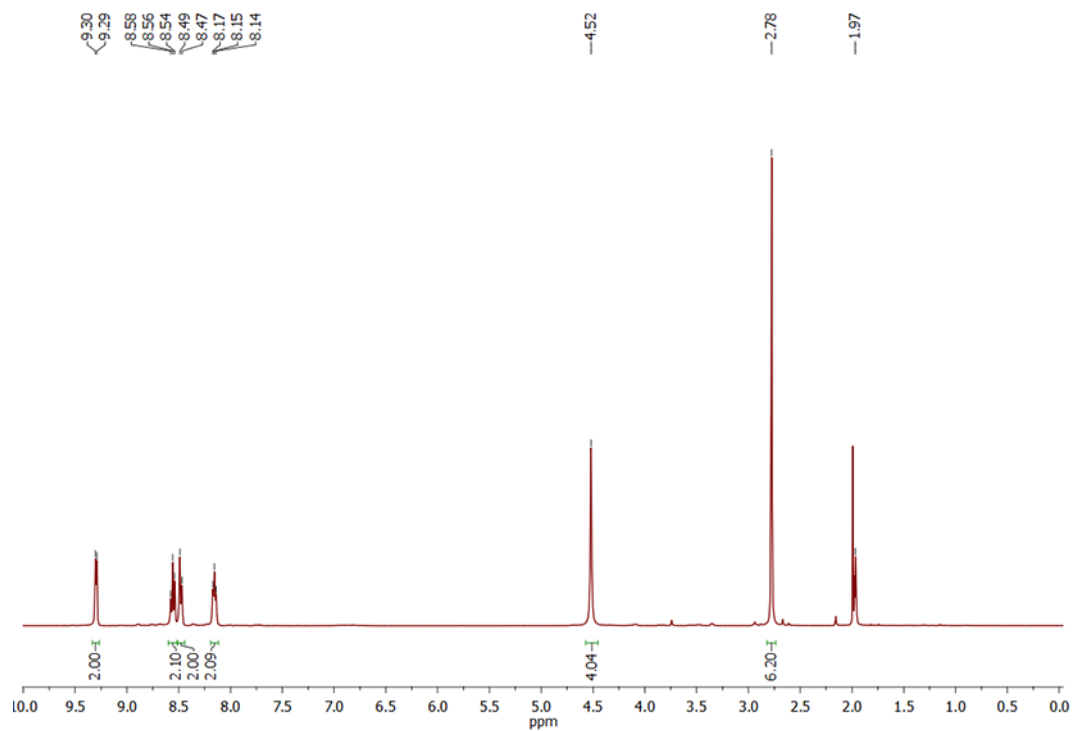


Figure S10. ^1H NMR of 2

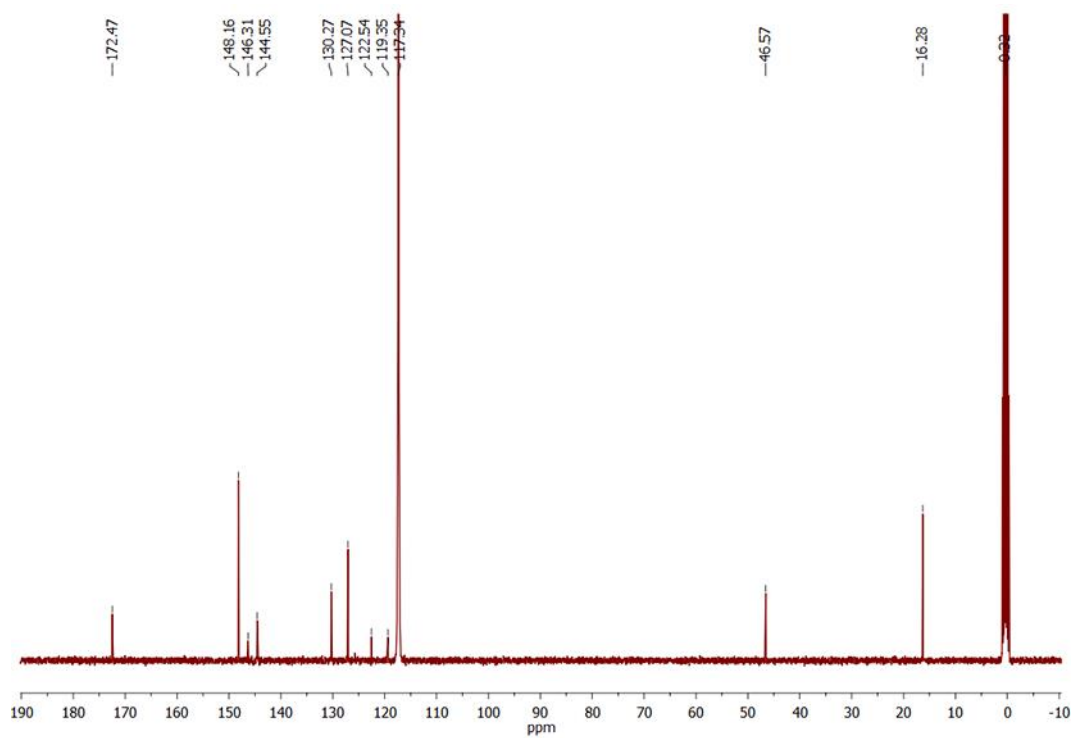


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR of **2**

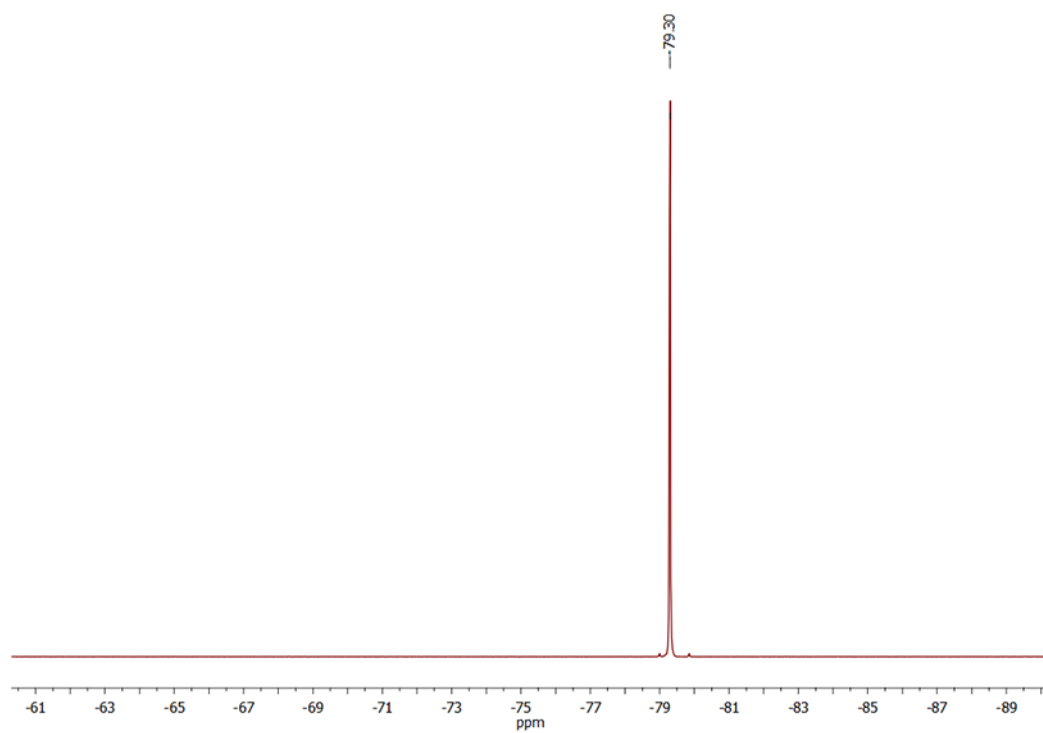


Figure S12. $^{19}\text{F}\{^1\text{H}\}$ NMR of **2**

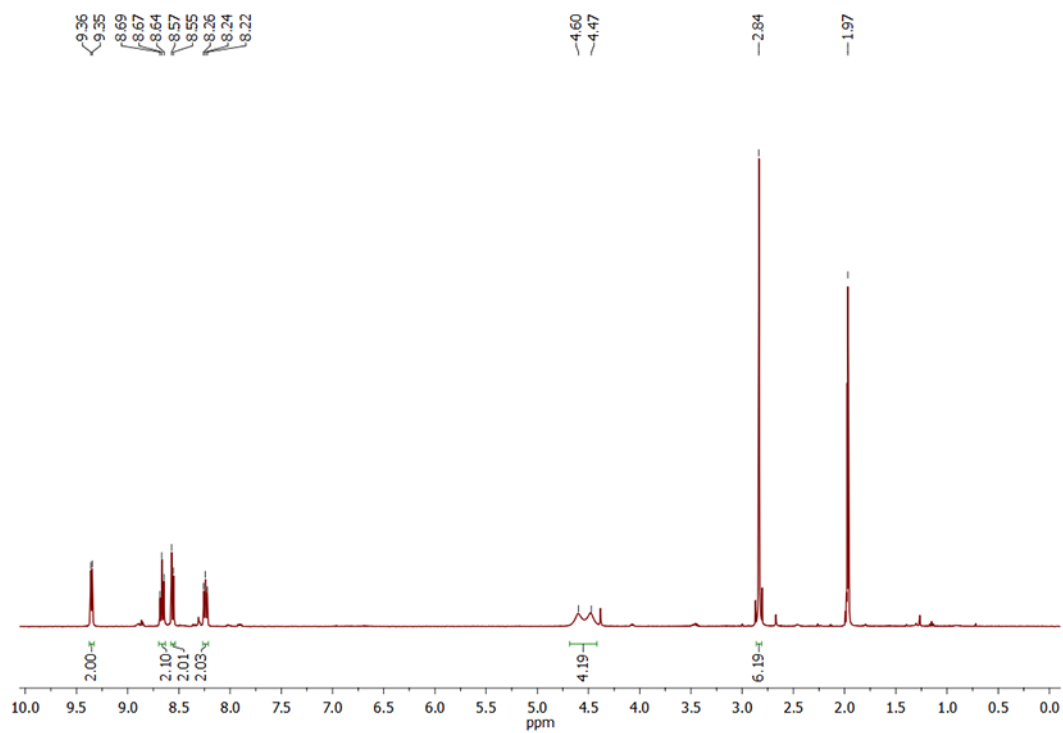


Figure S13. ^1H NMR of **3**

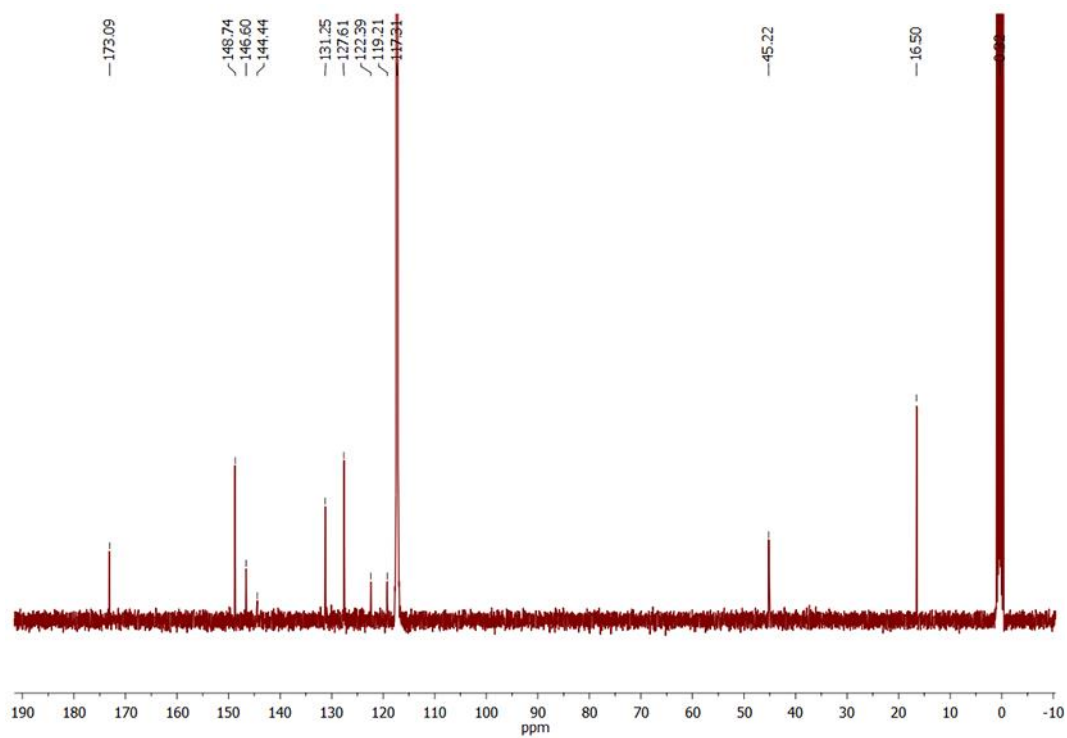


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR of **3**

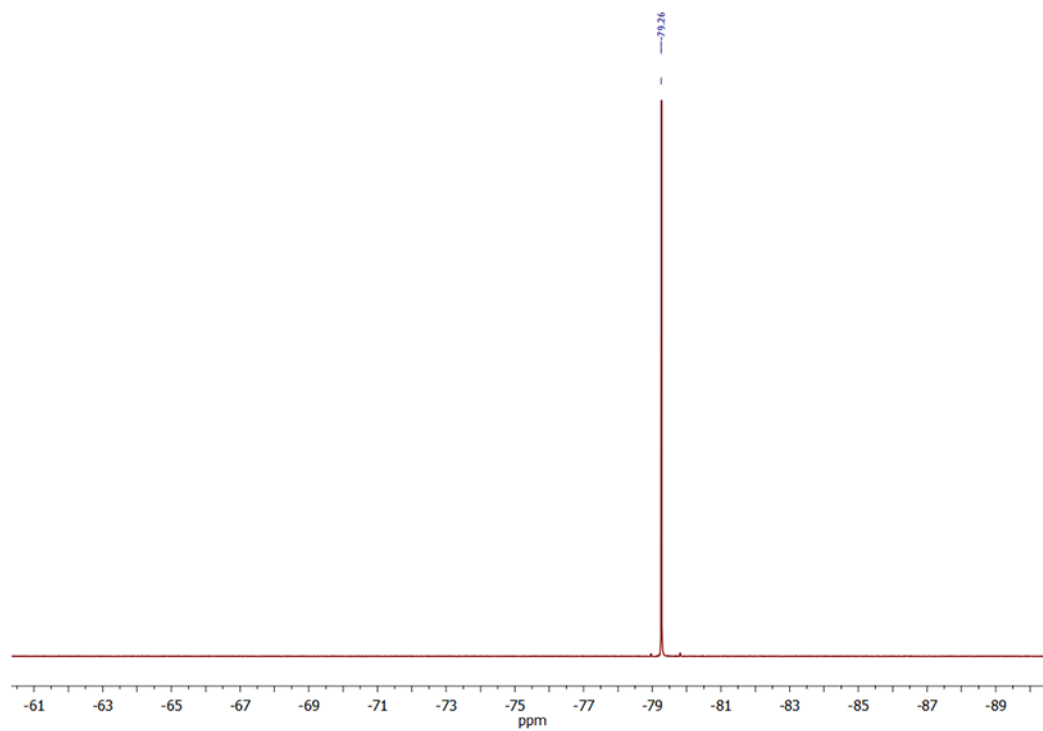


Figure S15. $^{19}\text{F}\{^1\text{H}\}$ NMR of **3**

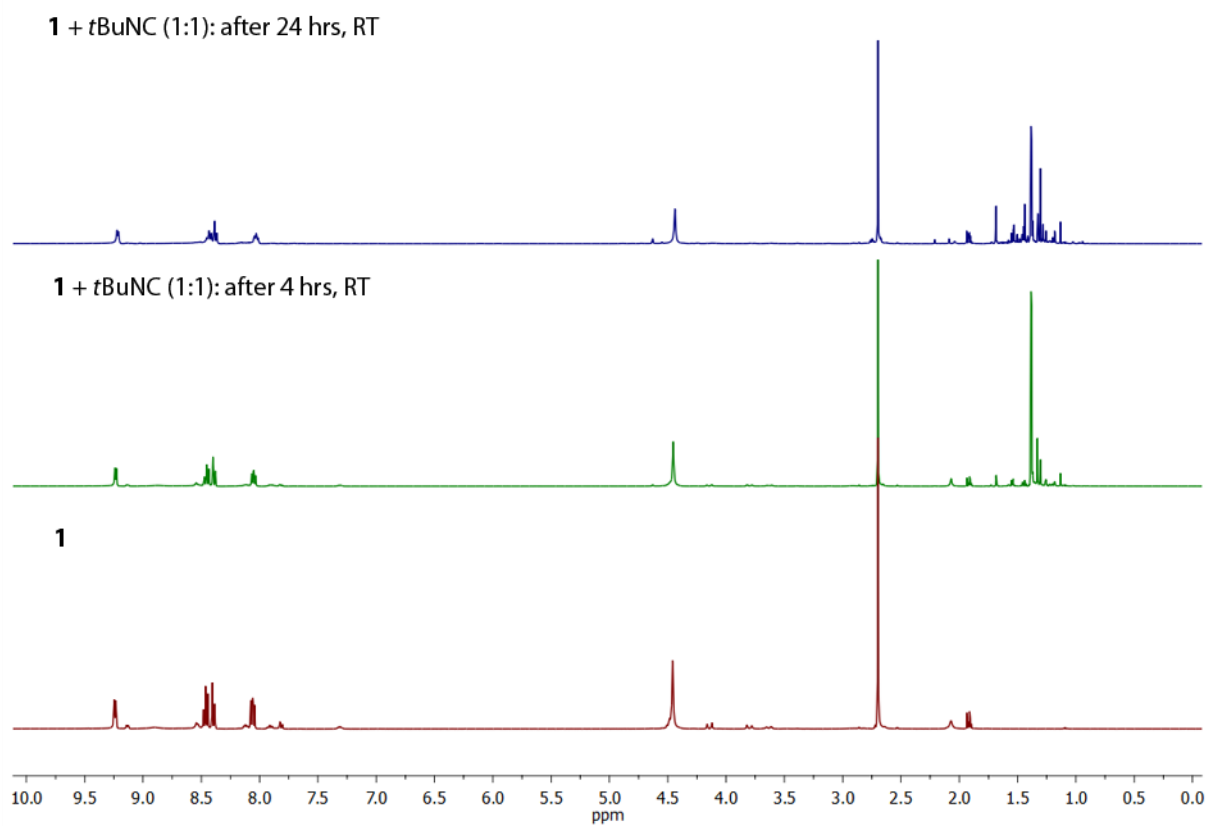


Figure S16. ^1H NMR of **1** + *t*BuNC (1:1 ratio)

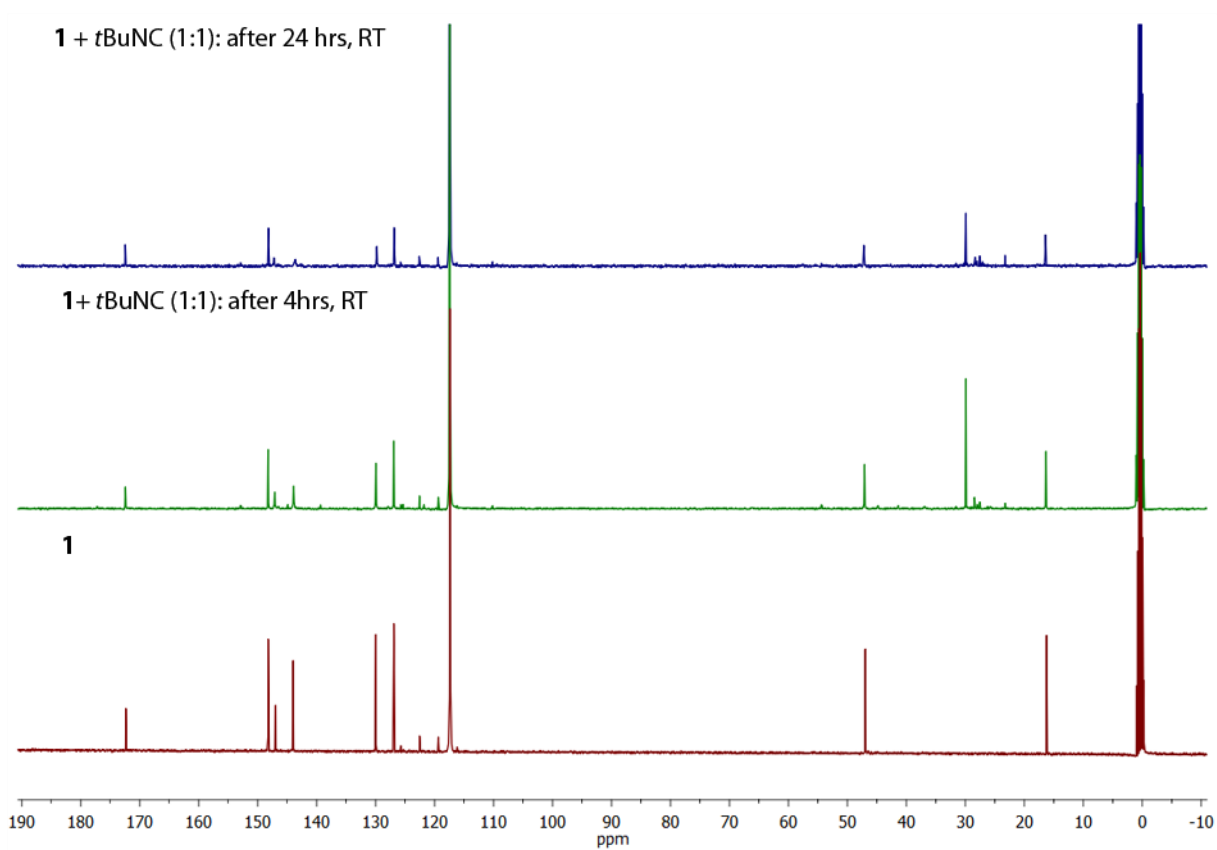


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR of **1** + $t\text{BuNC}$ (1:1 ratio)

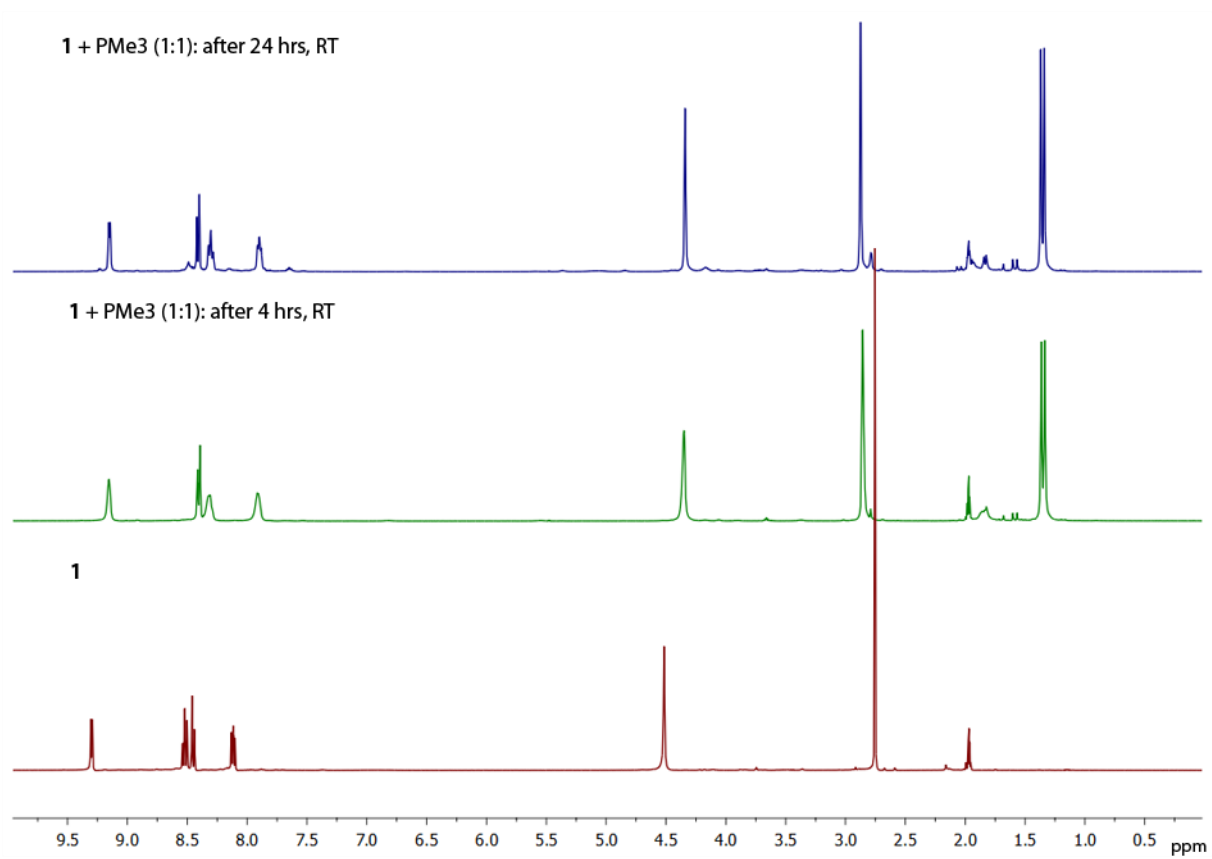


Figure S18. ^1H NMR of **1** + PMe_3 (1:1 ratio)

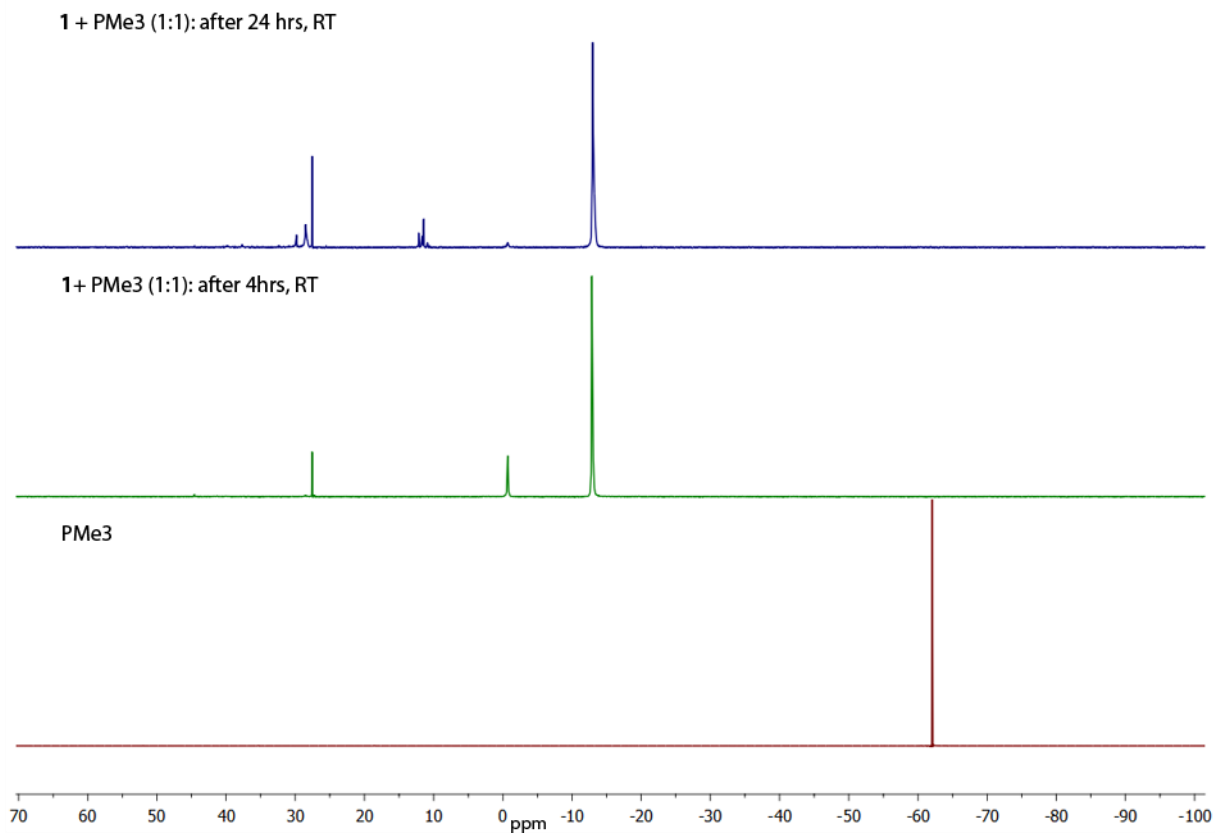


Figure S19. ^{31}P NMR of **1** + PMe₃ (1:1 ratio)

3. UV/Vis spectra

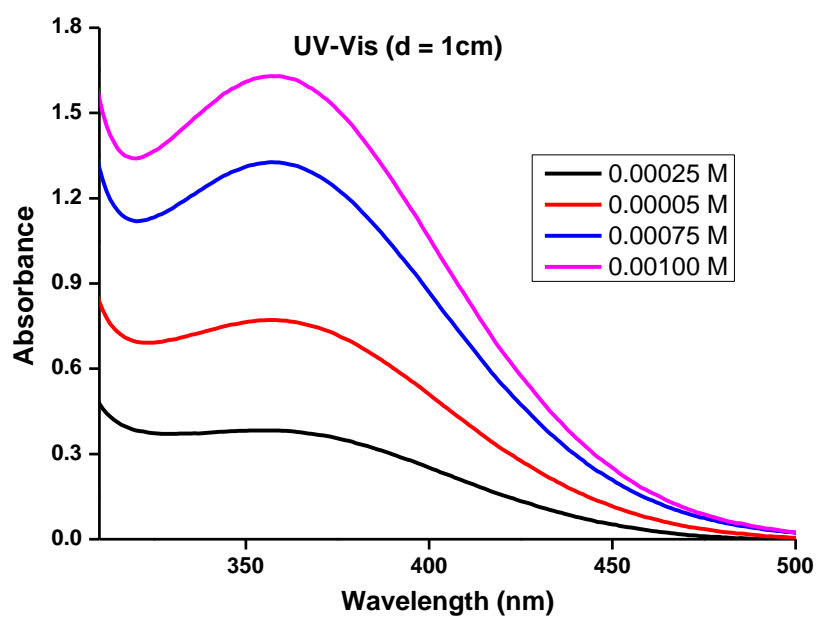


Figure S20. UV-Vis Spectra of [LGeCl][OTf] in acetonitrile.

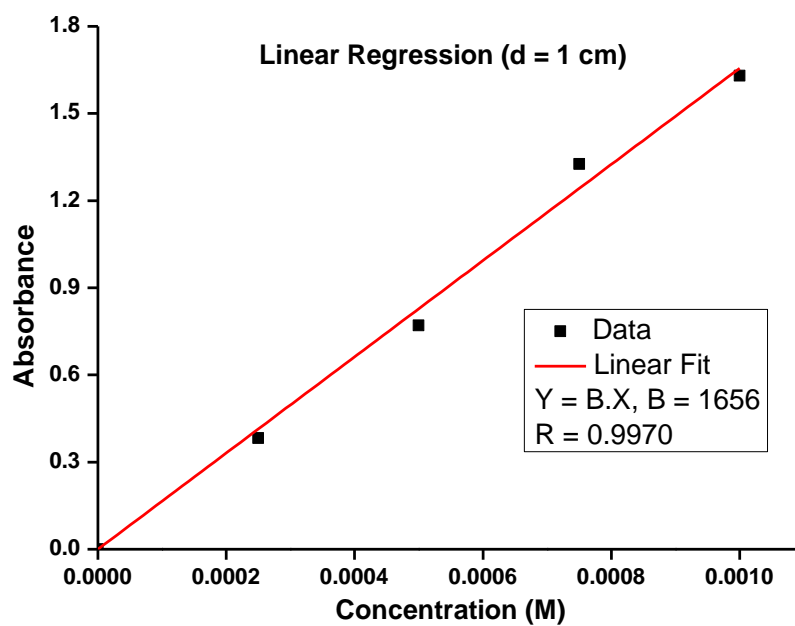


Figure S21. Linear Fit for UV-Vis data of [LGeCl][OTf]

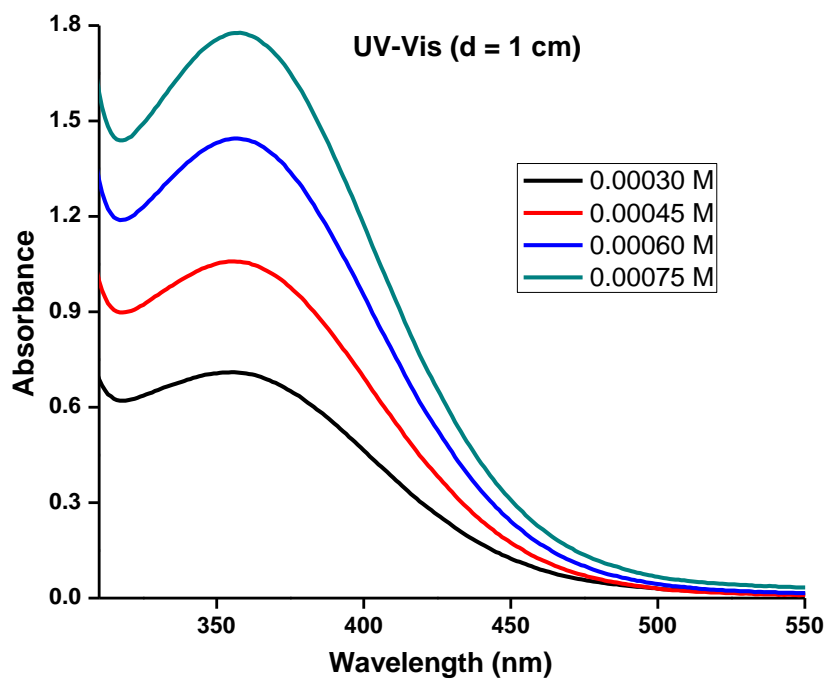


Figure S22. UV-Vis Spectra of [LGeCl][GeCl₃] in acetonitrile.

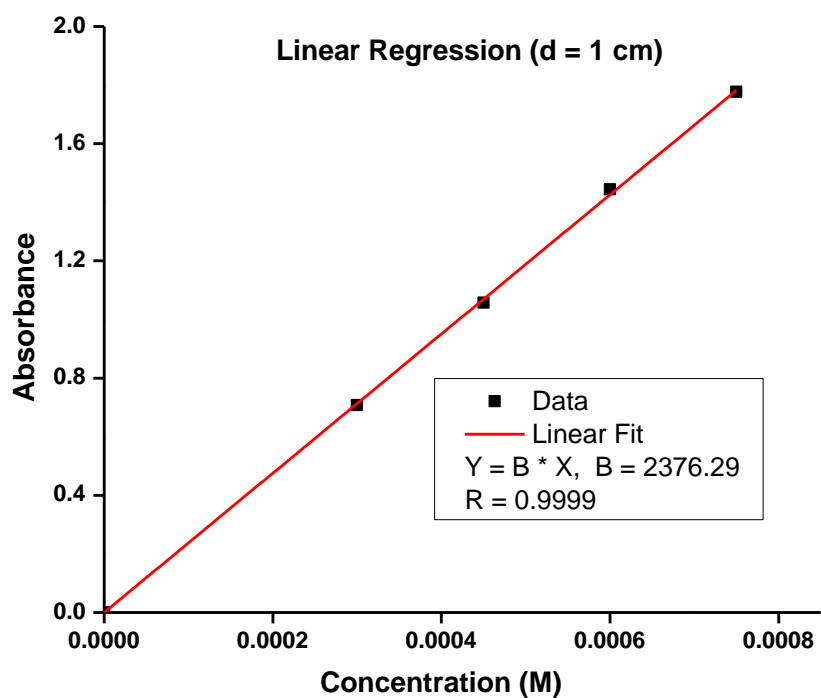


Figure S23. Linear Fit for UV-Vis data of [LGeCl][GeCl₃].

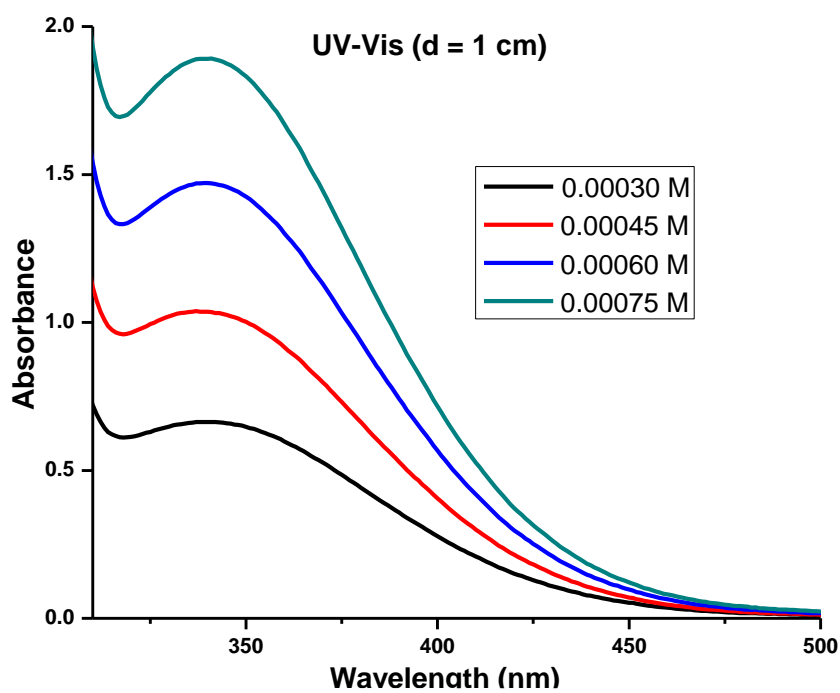


Figure S24 UV-Vis Spectra of **1** in acetonitrile.

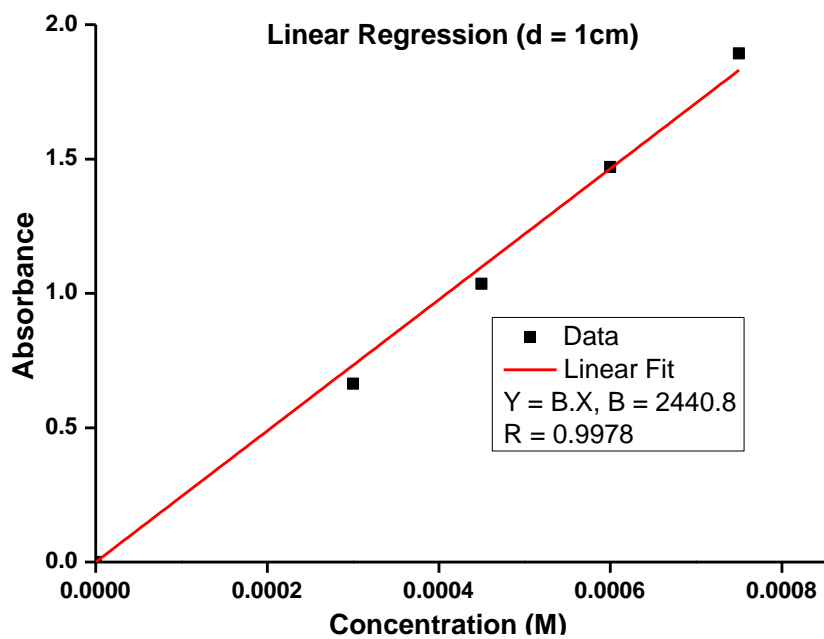


Figure S25. Linear Fit for UV-Vis data of **1**

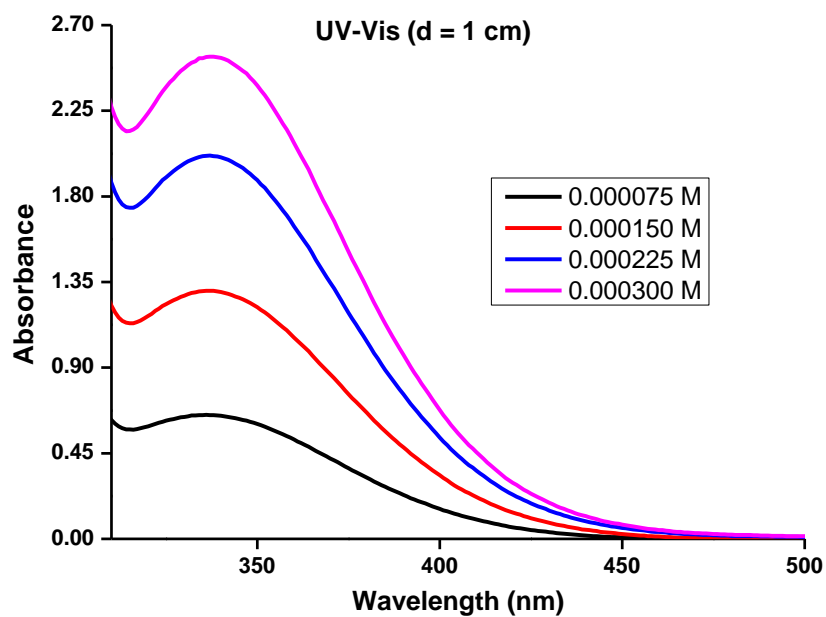


Figure S26 UV-Vis Spectra of **2** in acetonitrile.

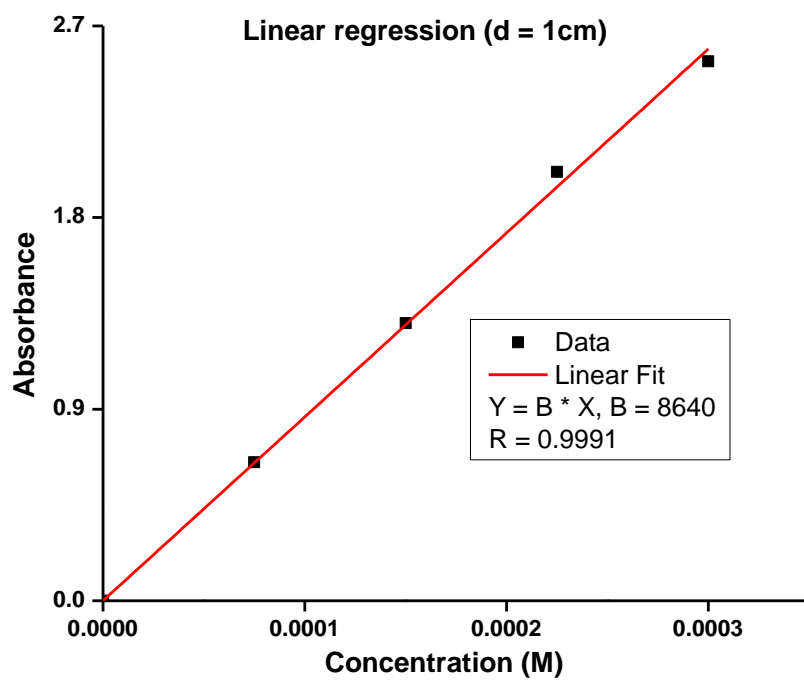


Figure S27. Linear Fit for UV-Vis data of **2**

4. DFT calculations

DFT calculations were performed on the cationic part of the experimental structures **1** and **3**, at the B3LYP level of theory (6-31G(d,p) basis set for Ge, C, N, H and LANL2DZ for Au) using *Gaussian 09* suite of programs.^{S3} Both compounds were optimized at the stationary point with number of imaginary frequency NIMAG = 0.

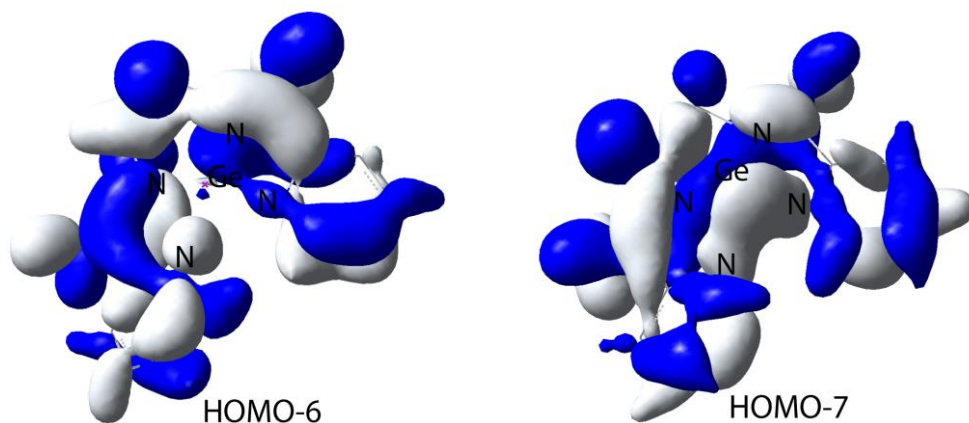
A. Compound 1'

Coordinates of Optimized structure 1'

Ge	0.04564500	-0.20866200	-1.09474600
N	1.59675300	-1.44606400	-0.43200400
N	-1.78116900	0.78078000	-0.28659000
N	-0.85735000	-1.62577200	0.13301300
N	1.34094400	1.04912200	0.05297000
C	2.69624200	-0.94120600	-0.00130000
C	-2.60064900	-0.07226400	0.37471500
C	1.16466500	-2.82717700	-0.54748300
H	1.89848600	-3.55591300	-0.19945400
H	0.94873500	-3.03227700	-1.60181700
C	2.59281400	0.52837100	0.21264200
C	-4.40333200	1.51727100	0.26651000
H	-5.42434700	1.80659100	0.49218900
C	-2.26365700	1.95043800	-0.72837000
H	-1.59228500	2.56481700	-1.32105800
C	-0.12923600	-2.90298500	0.29119400
H	-0.74510300	-3.74821900	-0.02767600
H	0.12394300	-3.03481800	1.34838600
C	-2.01639100	-1.40231700	0.66632500
C	-2.78288700	-2.39503300	1.48364700
H	-3.18727000	-1.92067200	2.38207600
H	-3.63312200	-2.77782100	0.90479900
H	-2.17541200	-3.24568000	1.78798900
C	-3.91756100	0.27311700	0.67729100
H	-4.56687900	-0.41896200	1.19947900
C	1.13841900	2.35130100	0.30433400
H	0.12753000	2.71848200	0.18208300
C	-3.56704100	2.36541800	-0.45515900

H	-3.91204900	3.32994400	-0.81033400
C	3.96326200	-1.67752200	0.29681100
H	4.27703700	-1.50548700	1.33143400
H	3.86368800	-2.74983100	0.13346800
H	4.76603700	-1.31269900	-0.35457700
C	3.65910200	1.32420400	0.61799900
H	4.64833600	0.89688600	0.73021400
C	3.44370500	2.68006400	0.87981900
H	4.26455800	3.31372200	1.19894600
C	2.15951900	3.19595100	0.73435200
H	1.94137700	4.23687400	0.94404500

Contour plots of $2'$ at 0.03 au isovalue



B. Compound 3'

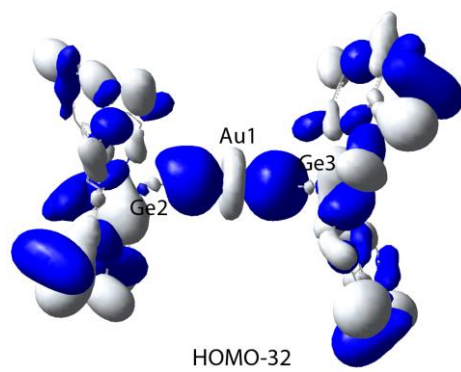
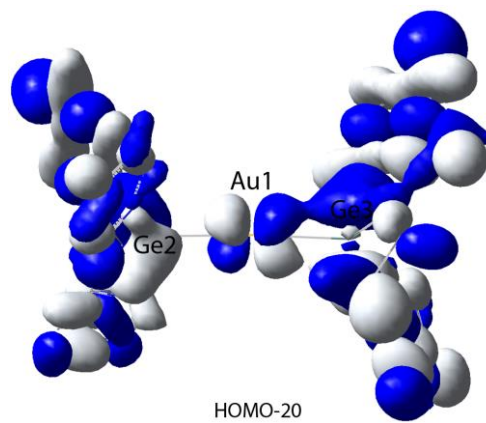
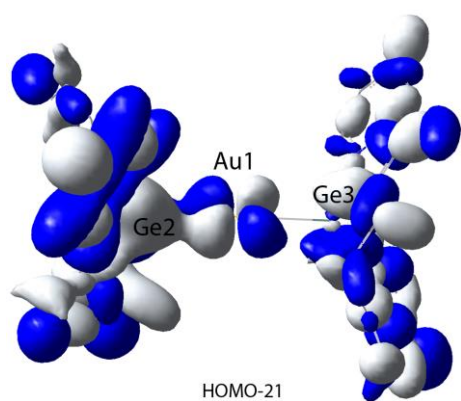
Coordinates of Optimized structure 3'

Au	0.00002800	0.04895300	0.00258900
Ge	-2.55172500	0.07549800	0.20843100
Ge	2.55346100	0.15753700	-0.14096200
N	3.70134600	0.09347400	1.58359500
N	3.55941600	0.61652200	-1.84372600
N	-2.99798200	-0.39275800	2.15271500
N	3.07765400	2.12187200	0.12305700
N	3.25409000	-1.74201200	-0.80743300
N	-3.58151500	1.69652300	0.86283200
N	-3.32759400	0.90450900	-1.59481100
N	-3.66558000	-1.66098700	0.01249300

C	4.04400700	1.32727100	2.07495700
C	2.92318500	-2.94264700	-0.29945300
H	2.25921300	-2.95001400	0.55953900
C	-4.02506400	-2.26183000	-1.13892700
H	-3.80764700	-1.73867200	-2.05960600
C	-4.27424000	2.40207600	0.01732100
C	-3.02179000	0.52559300	-2.84864700
H	-2.33905000	-0.31143700	-2.95929200
C	-4.40578100	2.25834000	-3.77813500
H	-4.84381000	2.77670300	-4.62661600
C	-4.67683800	-3.49546300	-1.16621500
H	-4.96302600	-3.92719600	-2.12005900
C	-4.58364300	-3.51754100	1.23678900
H	-4.80397500	-3.99394800	2.18560600
C	-3.94734800	-2.28232200	1.20244500
C	-3.60718400	-1.50098300	2.42111700
C	3.72752800	2.47466500	1.18351200
C	-3.63867700	1.89556400	2.33211200
H	-4.68117700	1.83360500	2.65845300
H	-3.25036900	2.88254700	2.59867500
C	4.71155800	1.46015900	3.28676100
H	4.97929400	2.44256000	3.65944500
C	-4.67743800	2.68797200	-2.47137300
H	-5.30817200	3.55409700	-2.30393100
C	4.53122500	-2.83136300	-2.52617500
H	5.14306000	-2.76972000	-3.41930300
C	4.02049100	-1.68057200	-1.93080300
C	2.88620200	2.86466900	-1.11960200
H	3.25903700	3.88828800	-1.07528400
H	1.81557700	2.89939300	-1.34523900
C	-4.11798900	1.99558800	-1.40020300
C	4.03013600	-1.00496300	2.29167300
H	3.76412100	-1.96412000	1.87003000
C	4.19480000	3.85260200	1.51671800
H	3.85706600	4.59918800	0.79953000

H	5.29065600	3.88464700	1.56574700
H	3.82434500	4.14587900	2.50624000
C	3.65741300	2.05654300	-2.18714600
H	3.24889700	2.23963300	-3.18489000
H	4.71110200	2.35107200	-2.18436600
C	4.20684100	-0.31578600	-2.47939600
C	-3.55231600	1.17243800	-3.96747800
H	-3.30099800	0.82090800	-4.96314100
C	3.40533200	-4.13548900	-0.84378000
H	3.13522700	-5.08338400	-0.38933600
C	4.23526200	-4.08046500	-1.96234800
H	4.63599900	-4.98880000	-2.40369500
C	5.05454400	0.31408200	4.01926300
H	5.58741600	0.40426000	4.96189000
C	-4.01186400	-1.98123500	3.77520500
H	-3.61544400	-2.98830900	3.95069300
H	-5.10468600	-2.05320600	3.84626500
H	-3.65308300	-1.33713800	4.57667600
C	4.71015900	-0.93434200	3.50819300
H	4.96881000	-1.85064000	4.02934300
C	-2.81194800	0.77743200	3.00658000
H	-1.74694000	1.02981100	3.02769500
H	-3.14696000	0.62334600	4.03271200
C	5.06969200	-0.09126200	-3.67530400
H	5.14251900	0.95542400	-3.96478800
H	4.67618000	-0.65274900	-4.53267900
H	6.08184700	-0.47145100	-3.48789900
C	-4.95816000	-4.13857700	0.03604400
H	-5.46743400	-5.09829600	0.05020200
C	-5.15824600	3.54618600	0.38386900
H	-6.17225700	3.37896100	-0.00011700
H	-4.79155500	4.46868100	-0.08550300
H	-5.21944900	3.71763300	1.45695800

Contour plots of $\mathbf{3}'$ at 0.02 au isovalue



6. X-ray data

Table S1. Crystal data and structure refinement for [LGeCl][OTf].

Empirical formula	C17 H18 Cl F3 Ge N4 O3 S	
Formula weight	523.45	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.5748(10) Å	$\alpha = 90^\circ$.
	b = 13.4785(7) Å	$\beta = 99.802(3)^\circ$.
	c = 14.7382(8) Å	$\gamma = 90^\circ$.
Volume	4027.5(4) Å ³	
Z	8	
Density (calculated)	1.727 Mg/m ³	
Absorption coefficient	4.775 mm ⁻¹	
F(000)	2112	
Crystal size	0.41 x 0.34 x 0.33 mm ³	
Theta range for data collection	3.938 to 72.714°.	
Index ranges	-25<=h<=25, -16<=k<=16, -18<=l<=17	
Reflections collected	36440	
Independent reflections	7885 [R(int) = 0.1057]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.207 and 0.178	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7885 / 0 / 545	
Goodness-of-fit on F ²	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0772, wR2 = 0.1397	
R indices (all data)	R1 = 0.1342, wR2 = 0.1635	
Largest diff. peak and hole	0.802 and -0.578 e.Å ⁻³	

Table S2. Crystal data and structure refinement for [LGeCl][GeCl₃].

Empirical formula	C16 H18 Cl Ge N4, Cl3 Ge	
Formula weight	553.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.872(3) Å	α = 90.296(7)°.
	b = 10.214(4) Å	β = 93.135(8)°.
	c = 12.585(5) Å	γ = 107.603(7)°.
Volume	1085.1(7) Å ³	
Z	2	
Density (calculated)	1.694 Mg/m ³	
Absorption coefficient	3.271 mm ⁻¹	
F(000)	548	
Crystal size	0.38 x 0.32 x 0.25 mm ³	
Theta range for data collection	1.621 to 29.140°.	
Index ranges	-12 ≤ h ≤ 11, -6 ≤ k ≤ 13, -17 ≤ l ≤ 17	
Reflections collected	21205	
Independent reflections	5806 [R(int) = 0.0577]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.340 and 0.300	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5806 / 0 / 237	
Goodness-of-fit on F ²	1.097	
Final R indices [I > 2σ(I)]	R1 = 0.0340, wR2 = 0.0884	
R indices (all data)	R1 = 0.0476, wR2 = 0.0949	
Largest diff. peak and hole	0.390 and -0.468 e.Å ⁻³	

Table S3. Crystal data and structure refinement for **1**.

Empirical formula	C16 H18 Ge N4, C F3 O3 S, C F3 O3 S, C H2 Cl2	
Formula weight	722.00	
Temperature	100 (2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.4372(5) Å	$\alpha = 69.771(3)^\circ$.
	b = 13.0507(8) Å	$\beta = 85.531(3)^\circ$.
	c = 13.3070(8) Å	$\gamma = 81.999(3)^\circ$.
Volume	1360.79(14) Å ³	
Z	2	
Density (calculated)	1.762 Mg/m ³	
Absorption coefficient	5.561 mm ⁻¹	
F(000)	724	
Crystal size	0.50 x 0.32 x 0.28 mm ³	
Theta range for data collection	3.541 to 72.741°.	
Index ranges	-10<=h<=10, -16<=k<=16, -16<=l<=16	
Reflections collected	14142	
Independent reflections	5317 [R(int) = 0.0497]	
Completeness to theta = 67.679°	99.3 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.211 and 0.177	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5317 / 0 / 363	
Goodness-of-fit on F ²	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1298	
R indices (all data)	R1 = 0.0832, wR2 = 0.1417	
Largest diff. peak and hole	0.877 and -0.511 e.Å ⁻³	

Table S4. Crystal data and structure refinement for **2**.

Empirical formula	C ₃₉ H ₃₉ Ag F ₁₅ Ge ₂ N ₉ O ₁₅ S ₅	
Formula weight	1572.14	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 14.699(2) Å	α = 112.989(6)°.
	b = 15.176(3) Å	β = 103.063(6)°.
	c = 15.433(3) Å	γ = 106.078(6)°.
Volume	2819.6(8) Å ³	
Z	2	
Density (calculated)	1.852 Mg/m ³	
Absorption coefficient	6.848 mm ⁻¹	
F(000)	1564	
Crystal size	0.32 x 0.24 x 0.22 mm ³	
Theta range for data collection	3.360 to 73.391°.	
Index ranges	-17 ≤ h ≤ 18, -18 ≤ k ≤ 18, -19 ≤ l ≤ 14	
Reflections collected	24387	
Independent reflections	10814 [R(int) = 0.0506]	
Completeness to theta = 67.679°	97.6 %	
Absorption correction	multi-scan	
Max. and min. transmission	0.222 and 0.174	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10814 / 0 / 780	
Goodness-of-fit on F ²	1.031	
Final R indices [I > 2σ(I)]	R1 = 0.0571, wR2 = 0.1360	
R indices (all data)	R1 = 0.0660, wR2 = 0.1417	
Largest diff. peak and hole	3.065 and -1.348 e.Å ⁻³	

Table S5. Crystal data and structure refinement for **3**.

Empirical formula	C ₃₇ H ₃₆ Au F ₁₅ Ge ₂ N ₈ O ₁₅ S ₅	
Formula weight	1620.18	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.421(3) Å	α = 85.383(5)°.
	b = 12.980(3) Å	β = 72.526(5)°.
	c = 17.648(4) Å	γ = 75.017(5)°.
Volume	2621.8(11) Å ³	
Z	2	
Density (calculated)	2.052 Mg/m ³	
Absorption coefficient	9.527 mm ⁻¹	
F(000)	1584	
Crystal size	0.52 x 0.43 x 0.37 mm ³	
Theta range for data collection	2.625 to 73.011°.	
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 16, -19 ≤ l ≤ 21	
Reflections collected	29573	
Independent reflections	10213 [R(int) = 0.0485]	
Completeness to theta = 67.679°	98.9 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.029 and 0.018	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10213 / 0 / 752	
Goodness-of-fit on F ²	1.095	
Final R indices [I > 2σ(I)]	R1 = 0.0364 wR2 = 0.0965	
R indices (all data)	R1 = 0.0369, wR2 = 0.0970	
Largest diff. peak and hole	1.402 and -1.968 e.Å ⁻³	

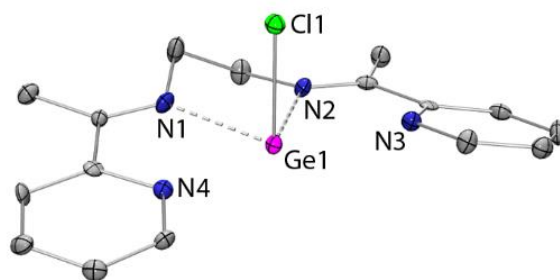


Figure S28. Structure of [LGeCl][OTf] in the solid state (thermal ellipsoids at 30%, H atoms, triflate anion omitted for clarity). Selected bond lengths [Å]: Ge1-Cl1 = 2.2807 (18) Å, Ge1-N1 = 2.220(5) Å, Ge1-N2 = 2.180 (6) Å.

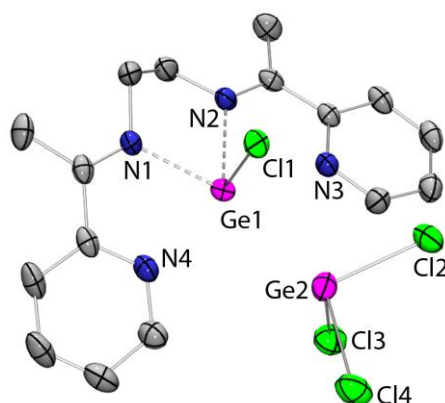


Figure S29. Structure of [LGeCl][GeCl₃] in the solid state (thermal ellipsoids at 30%, H atoms omitted for clarity). Selected bond lengths [Å]: Ge1-Cl1 = 2.2754(9), Ge1-N1 = 2.2327(19), Ge1-N2 = 2.1764(16).

⁵¹ S. Banerjee, J. Gangopadhyay, C. -Z. Lu, J. -T. Chen and A. Ghosh, *Eur. J. Inorg. Chem.*, 2004, 2533.

⁵² F. Cheng, J. M. Dyke, F. Ferrante, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Dalton Trans.*, 2010, **39**, 847; A. P. Singh, H. W. Roesky, E. Carl, D. Stalke, J. -P. Demers and A. Lange, *J. Am. Chem. Soc.*, 2012, **134**, 4998; M. Bouška, L. Dostál, A. Růžička and R. Jambor, *Organometallics*, 2013, **32**, 1995; Y. Xiong, S. Yao, S. Inoue, A. Berkefeld and M. Driess, *Chem. Comm.*, 2012, **48**, 12198; Y. Xiong, S. Yao, G. Tan, S. Inoue and M. Driess, *J. Am. Chem. Soc.*, 2013, **135**, 5004.

⁵³ Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.