***Supporting Information***

# Air and Water Stable Germacarbonyl Compounds

Pritam Mahawar,[a] Pratima Shukla,[a] Prakash Chandra Joshi,[a] Dharmendra Singh,[a]

Hemant Kumar,[a] Goutam Mukherjee,[a,b] and Selvarajan Nagendran*

[a]*Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India*

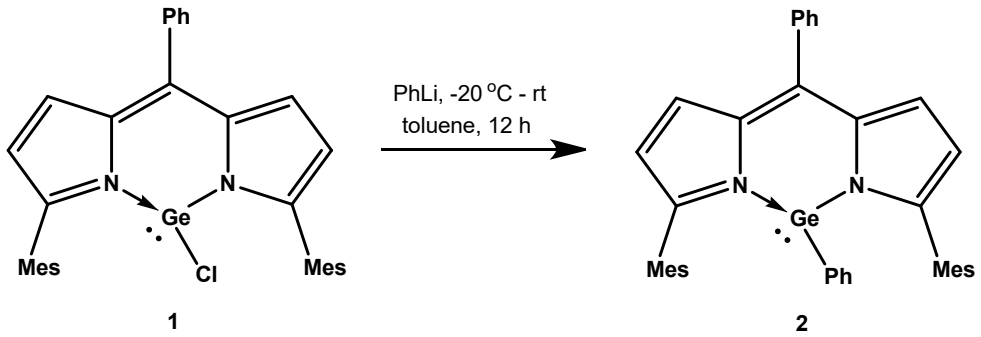
[b]*Present address: PharmCADD, 12F, 331, Jungang-daero, Dong-gu, Busan, Republic of Korea*

# Contents

## Experimental procedures

All the reactions and manipulations were performed under atmospheric conditions except for the synthesis of compounds **2** and **11**. As the synthesis of compounds **2** and **11** requires PhLi and $LiN(TMS)_2$, Schlenk/glovebox techniques were used; dry toluene and hexane used in synthesizing these compounds were dried according to the conventional procedure. $^{1}H$, $^{13}C$, $^{29}Si$, and $^{77}Se$ NMR spectra were recorded on a 300/400/500 MHz Bruker Topspin NMR spectrometer using non-dried $CDCl_3$. The chemical shifts $\delta$ are reported in ppm and referenced internally to the residual solvent and solvent resonances during the $^{1}H$ and $^{13}C$ NMR spectroscopic studies. The IR spectra of compounds **6** and **7** were recorded using an Agilent Resolutions Pro IR spectrophotometer. Mass Spectra were recorded on a Bruker Micro-TOF QII quadrupole time-of-flight (Q-TOF) mass spectrometer. Melting points were measured using the Unitech sales digital melting point apparatus; instead of melting, they became black solids at a particular temperature above 170 °C (Table S1).

**Synthesis of DPMGePh (2):**




**Scheme S1. Synthesis of phenylgermylene DPMGePh (2)**

To a solution of compound **1** (0.500 g, 0.88 mmol) in toluene (20 mL), PhLi (1.9 M solution in hexane) (0.513 mL) was added at **-**20 ºC. The reaction mixture was slowly brought to room temperature and stirred overnight. Then, the reaction mixture was filtered through a G4 frit with celite. The filtrate was dried under reduced pressure to yield compound **2** as a red solid. It

was washed with hexane and dried to obtain an analytically pure sample of compound **2**. Single crystals of compound **2** suitable for X-ray diffraction studies were grown from its tetrahydrofuran solution containing a few drops of toluene at room temperature.

Yield: 510 mg (95%); $^{1}$H NMR (500 MHz, $CDCl_3$): δ 1.19 (s, 6H, $CH_3$), 2.24 (s, 6H, $CH_3$), 2.26 (s, 6H, $CH_3$), 6.27 (d, *J* = 5 Hz, 2H, Ph), 6.63 (s, 2H, Py), 6.87 (s, 2H, Py), 6.93 (s, 4H, Mes), 7.02-7.06 (m, 3H, Ph), 7.56 (bs, 3H, Ph), 7.72-7.75 ppm (m, 2H, Ph); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): δ 19.4, 20.6, 21.3, 118.9, 127.3, 127.4, 127.7, 128.1, 128.3, 129.2, 130.0, 130.7, 131.1, 132.0, 133.4, 134.9, 136.2, 137.4, 138.6, 138.7, 146.0, 158.3, 159.1 ppm. HRMS (ESI-QTOF, $[M - Ph]^+$) m/z calcd for $[C_{33}H_{31}GeN_2]$ 529.1693, found 529.1682 (Δ 3.4 ppm).

**Synthesis of DPMGe(S)Ph (3):** To a solution of compound **2** (0.200 g, 0.33 mmol) in toluene (10 mL) elemental sulfur (0.012 g, 0.36 mmol) was added at room temperature. The reaction mixture was stirred for 1 h, and the solvent was removed under reduced pressure to get an orange-red solid. It was washed with hexane (3 x 5 mL) and dried *in vacuo* to afford compound **3** as an orange-red solid. Single crystals of compound **3** suitable for X-ray diffraction studies were grown from its tetrahydrofuran solution containing a few drops of toluene at room temperature.

Yield: 0.200 g (95%); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.14 (s, 6H, $CH_3$), 2.15 (s, 6H, $CH_3$), 2.33 (s, 6H, $CH_3$), 6.32 (s, 2H, Ph), 6.36 (d, *J* = 4 Hz, 2H, Py), 6.78 (s, 2H, Ph), 6.98 (d, *J* = 4 Hz, 2H, Py), 7.15 (bs, 4H, Mes), 7.57-7.59 (m, 3H, Ph), 7.69-7.71 (m, 2H, Ph); $^{13}$C{$^{1}$H} NMR (75 MHz, $CDCl_3$): δ 19.6, 21.2, 22.6, 121.0, 127.0, 127.6, 127.9, 128.0, 128.1, 129.9, 130.0, 130.7, 131.0, 133.4, 134.7, 135.9, 136.6, 138.3, 139.2, 139.6, 145.5, 162.5 ppm. HRMS (ESI-QTOF, $[M + H]^+$) *m/z* calcd for $[C_{39}H_{37}GeN_2S]$ 639.1883, found 639.1899 (Δ 1.1 ppm).

**Synthesis of DPMGe(Se)Ph (4):** To a solution of compound **2** (0.200 g, 0.33 mmol) in toluene (10 mL) elemental selenium (0.028 g, 0.36 mmol) was added at room temperature. The reaction mixture was stirred for 1 h, and the solvent was removed under reduced pressure to get a dark

orange-red solid. It was washed with hexane (3 x 5 mL) and dried *in vacuo* to obtain compound **4** as a dark orange-red solid. Single crystals of compound **4** suitable for X-ray diffraction studies were grown from its tetrahydrofuran solution containing a few drops of toluene at room temperature.

Yield: 0.210 g (93%); $^{1}$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.11 (s, 6H, $CH_3$), 2.15 (s, 6H, $CH_3$), 2.31 (s, 6H, $CH_3$), 6.34 (s, 4H, Mes), 6.76 (s, 2H, Py), 6.98 (d, $J$ = 5 Hz, 2H, Py), 7.14 (d, $J$ = 8 Hz, 2H, Ph), 7.16-7.19 (m, 2H, Ph), 7.28 (bs, 1H, Ph), 7.57-7.61 ppm (m, 3H, Ph), 7.69 (bs, 2H, Ph); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): $\delta$ 18.5, 20.2, 21.9, 120.3, 126.1, 126.6, 126.8, 127.0, 127.1, 128.9, 129.0, 129.7, 129.9, 132.5, 133.7, 134.9, 135.3, 135.6, 138.2, 144.4, 161.6 ppm. $^{77}$Se{$^{1}$H} (95.60 MHz, $CDCl_3$): $\delta$ -386 ppm. HRMS (ESI-QTOF, $[M + H]^+$) *m*/*z* calcd for $[C_{39}H_{37}GeN_2Se]$ 687.1334, found 687.1338 ($\Delta$ 0.6 ppm).

**Synthesis of DPMGe(S)OH (6):** To a solution of compound **5** (0.200 g, 0.36 mmol) in toluene (10 mL), elemental sulphur (0.012 g, 0.39 mmol) was added at room temperature. The reaction mixture was stirred for 20 min, and the solvent was removed under reduced pressure to get an orange-red solid. It was washed with hexane (3 x 5 mL) and dried *in vacuo* to obtain compound **6** as an orange-red solid.

Yield: 0.202 g (95%); $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.77 (s, 1H, OH), 2.15 (s, 6H, $CH_3$), 2.25 (s, 6H, $CH_3$), 2.30 (s, 6H, $CH_3$), 6.42 (d, $J$ = 3 Hz, 2H, Py), 6.81 (s, 2H, Mes), 6.87 (s, 2H, Mes), 6.97 (d, $J$ = 6 Hz, 2H, Py), 7.55 (bs, 2H, Ph), 7.58-7.63 (m, 3H, Ph); $^{13}$C{$^{1}$H} NMR (75 MHz, $CDCl_3$): $\delta$ 20.7, 21.4, 21.8, 120.8, 127.5, 128.1, 128.3, 130.2, 130.7, 130.9, 135.2, 136.4, 136.8, 138.2, 139.3, 139.7, 145.4, 162.4 ppm; ATR: $\nu$ = 3612 cm$^{-1}$ (OH). HRMS (ESI-QTOF, $[M + H]^+$) *m*/*z* calcd for $[C_{33}H_{33}GeN_2OS]$ 579.1516, found 579.1519 ($\Delta$ 1.7 ppm).

**Synthesis of DPMGe(Se)OH (7):** To a solution of compound **5** (0.200 g, 0.36 mmol) in toluene (10 mL), elemental selenium (0.030 g, 0.40 mmol) was added at room temperature. The reaction mixture was stirred for 20 min, and the solvent was removed under reduced

pressure to get an orange-red solid. It was washed with hexane (5 mL) and dried *in vacuo* to obtain compound **7** as an orange-red solid.

Yield: 0.220 g (96%); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 1.79 (s, 1H, OH), 2.15 (s, 6H, $CH_3$), 2.26 (s, 6H, $CH_3$), 2.31 (s, 6H, $CH_3$), 6.41 (d, *J* = 4 Hz, 2H, Py), 6.82 (s, 2H, Mes), 6.88 (s, 2H, Mes), 6.96 (d, *J* = 4 Hz, 2H, Py), 7.52-7.64 (m, 5H, Ph); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ 20.7, 21.3, 22.1, 120.8, 127.5, 128.1, 128.3, 130.1, 135.1, 135.3, 136.4, 138.3, 138.9, 139.6, 145.3, 162.3 ppm; $^{77}$Se{$^{1}$H} (95.60 MHz, $CDCl_3$): δ -340 ppm; ATR: ν = 3612 cm$^{-1}$ (OH). HRMS (ESI-QTOF, $[M + H]^+$) *m*/*z* calcd for $[C_{33}H_{33}GeN_2OSe]$ 649.0791, found 649.0783 (Δ 1.2 ppm).

**Synthesis of DPMGe(S)OEt (9):** To a solution of compound **8** (0.200 g, 0.34 mmol) in toluene (10 mL), elemental sulphur (0.012 g, 0.37 mmol) was added at room temperature. The reaction mixture was stirred for 20 min, and the solvent was removed under reduced pressure to get an orange-red solid. It was washed with hexane (3 x 5 mL) and dried *in vacuo* to provide compound **9** as an orange-red solid. Single crystals of compound **9** suitable for X-ray diffraction studies were grown from its tetrahydrofuran solution containing a few drops of toluene at room temperature.

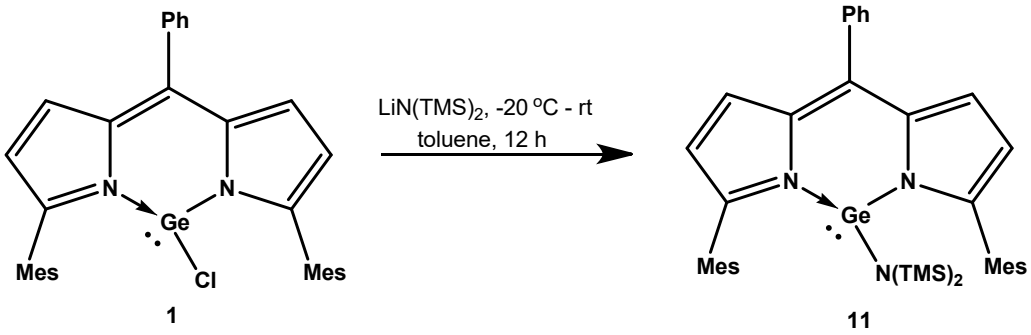
Yield: 0.205 g (97%); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 0.76 (t, *J* = 8 Hz, 3H, $CH_3$), 2.15 (s, 6H, $CH_3$), 2.26 (s, 6H, $CH_3$), 2.32 (s, 6H, $CH_3$), 2.56-2.62 (q, *J* = 8 Hz, 2H, $CH_2$), 6.39 (d, *J* = 4 Hz, 2H, Py), 6.84 (s, 2H, Mes), 6.88 (s, 2H, Mes), 6.94 (d, *J* = 4 Hz, 2H, Py), 7.54-7.57 (m, 3H, Ph), 7.59 (bs, 1H, Ph), 7.64 (bs, 1H, Ph); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): δ 17.0 (OEt), 20.8, 21.3, 21.9 ($CH_3$), 60.1 (OEt), 120.6, 127.4, 127.9, 128.1, 128.2, 128.6, 130.0, 130.7, 131.0, 135.2, 135.4, 136.9, 138.1, 139.1, 139.4, 145.3, 162.2 ppm. HRMS (ESI-QTOF, $[M + Na]^+$) *m*/*z* calcd for $[C_{35}H_{36}GeN_2NaOS]$ 629.1652, found 629.1645 (Δ 2.1 ppm).

**Synthesis of DPMGe(Se)OEt (10):** To a solution of compound **8** (0.200 g, 0.34 mmol) in toluene (10 mL), elemental selenium (0.029 g, 0.37 mmol) was added at room temperature.

The reaction mixture was stirred for 20 min, and the solvent was removed under reduced pressure to get an orange-red solid. It was washed with hexane (3 x 5 mL) and dried *in vacuo* to provide compound **10** as an orange-red solid.

Yield: 0.218 g (96%); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 0.74 (t, $J$ = 8 Hz, 3H, $CH_3$), 2.15 (s, 6H, $CH_3$), 2.26 (s, 6H, $CH_3$), 2.33 (s, 6H, $CH_3$), 2.55-2.57 (q, $J$ = 8 Hz, 2H, $CH_2$), 6.38 (d, $J$ = 4 Hz, 2H, Py), 6.85 (s, 2H, Mes), 6.88 (s, 2H, Mes), 6.94 (d, $J$ = 4 Hz, 2H, Py), 7.54-7.58 (m, 4H, Ph), 7.66 (bs, 1H, Ph); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): δ 16.7 (OEt), 20.9, 21.3, 22.3 ($CH_3$), 60.6 (OEt), 120.7, 127.6, 127.9, 128.1, 128.2, 128.6, 130.0, 130.7, 131.0, 135.2, 136.6, 138.2, 138.7, 139.4, 144.8, 162.2 ppm; $^{77}$Se{$^{1}$H} (95.60 MHz, $CDCl_3$): δ -379 ppm. HRMS (ESI-QTOF, $[M + Na]^+$) *m/z* calcd for $[C_{35}H_{36}GeN_2NaOSe]$ 677.1145, found 677.1095 (Δ 5.5 ppm).

**Synthesis of DPMGeN(TMS)$_2$ (11):**




**Scheme S2. Synthesis of aminogermylene DPMGeN(TMS)$_2$ (11)**

To a solution of compound **1** (0.500 g, 0.88 mmol) in toluene (15 mL), $LiN(TMS)_2$ (163.2 mg, 0.97 mmol) was added at -20 ºC. The reaction mixture was slowly brought to room temperature and stirred overnight, and the solvent was removed under reduced pressure to yield a brown-red solid. The solid was extracted using toluene (30 mL) and filtered through a G4 frit with celite. The filtrate was dried under reduced pressure to yield compound **11** as a brown-red solid. It was washed with hexane and dried to obtain an analytically pure sample of compound **11**. Single crystals of compound **11** suitable for X-ray diffraction studies were grown from its tetrahydrofuran solution containing a few drops of toluene at room temperature.

Yield: 590 mg (97%); $^{1}$H NMR (500 MHz, $CDCl_3$): δ -0.46 (s, 9H, $N(TMS)_2$), -0.25 (s, 9H, $N(TMS)_2$), 2.12 (s, 6H, $CH_3$), 2.27 (s, 12H, $CH_3$), 6.32 (bs, 2H, Py), 6.86 (s, 4H, Mes), 6.89 (d, $J$ = 10 Hz, 2H, Py), 7.49-7.51 (m, 3H, Ph), 7.60 (s, 2H, Ph); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$): δ 5.26 ($N(TMS)_2$), 21.1, 21.2, 21.8 ($CH_3$), 119.4, 128.4, 128.5, 129.1, 129.2, 130.6, 132.7, 136.5, 137.2, 137.7, 138.6, 160.3 ppm; $^{29}$Si{$^{1}$H} NMR (99.3 MHz, $CDCl_3$): δ -3, 2 ppm ($Si(CH_3)_3$). HRMS (ESI-QTOF, $[M - N(TMS)_2]^+$) *m/z* calcd for $[C_{33}H_{31}GeN_2]$ 529.1693, found 529.1719 (Δ 3.7 ppm).

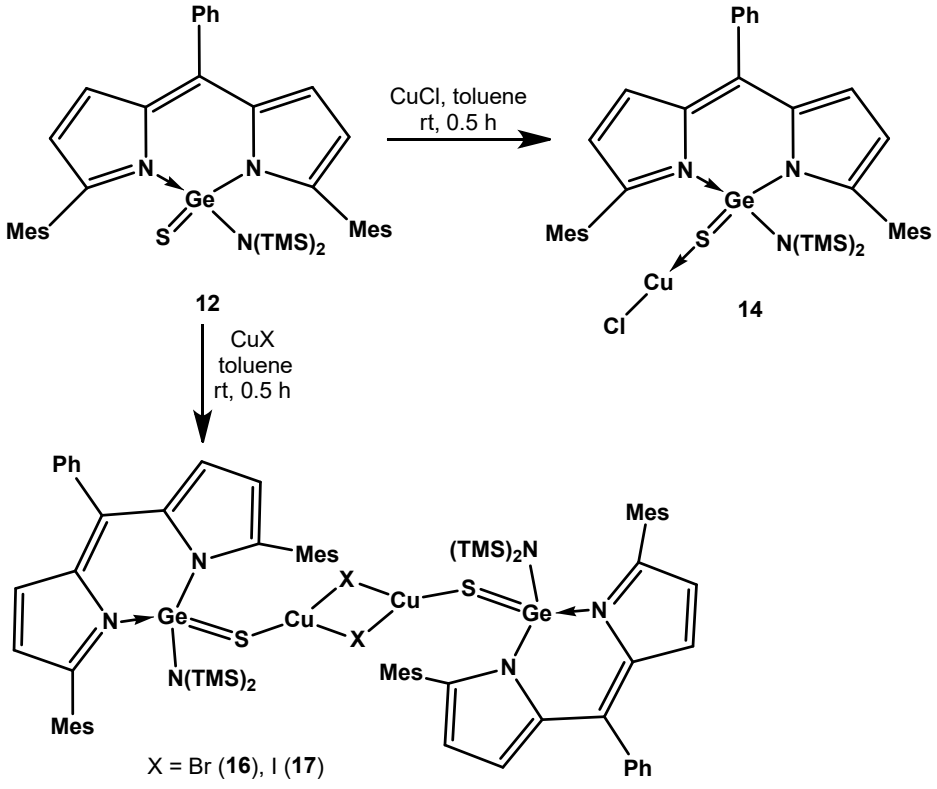
**Synthesis of DPMGe(S)N(TMS)$_2$ (12):** To a solution of compound **11** (0.200 g, 0.29 mmol) in toluene (10 mL), elemental sulphur (0.010 g, 0.31 mmol) was added, and the reaction was stirred for 12 h at 60 $^{o}$C. The solvent was removed under reduced pressure to get a red solid. It was washed with hexane (3 x 5 mL) and dried *in vacuo* to afford compound **12** as an orange-red solid. Single crystals of compound **12** suitable for X-ray diffraction studies were grown from its tetrahydrofuran solution containing a few drops of toluene at room temperature.

Yield: 198 mg (94%); $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ -0.05 (bs, 18H, $N(TMS)_2$), 2.23 (s, 6H, $CH_3$), 2.26 (s, 6H, $CH_3$), 2.33 (s, 6H, $CH_3$), 6.33 (d, $J$ = 3 Hz, 2H, Py), 6.83 (d, $J$ = 6 Hz, 4H, Mes), 6.88 (d, $J$ = 3 Hz, 2H, Py), 7.52-7.56 (m, 5H, Ph); $^{13}$C{$^{1}$H} NMR (75 MHz, $CDCl_3$): $\delta$ 6.4 ($N(TMS)_2$), 21.3, 22.8, 23.0 ($CH_3$), 122.1, 127.7, 127.8, 127.9, 128.4, 129.7, 130.2, 130.4, 131.3, 134.5, 136.2, 136.4, 137.7, 139.3, 140.5, 145.2, 163.5 ppm; $^{29}$Si{$^{1}$H} NMR (99.3 MHz, $CDCl_3$): δ -21.88 ppm ($Si(CH_3)_3$). HRMS (ESI-QTOF, $[M + Na]^+$) *m/z* calcd for $[C_{39}H_{49}GeN_3NaSSi_2]$ 744.2295, found 744.2321 (Δ 3.5 ppm).

**Synthesis of DPMGe(Se)N(TMS)$_2$ (13):** To a solution of compound **11** (0.200 g, 0.29 mmol) in toluene (10 mL), elemental selenium (0.024 g, 0.31 mmol) was added, and the reaction was stirred for 12 h at 60 $^{o}$C. The solvent was removed under reduced pressure to get a brown-red solid. It was washed with hexane (3 x 5 mL) and dried *in vacuo* to afford compound **13** as an

orange-red solid. Single crystals of compound **13** suitable for X-ray diffraction studies were grown from its tetrahydrofuran solution containing a few drops of toluene at room temperature. Yield: 0.210 g (94%); $^{1}$H NMR (400 MHz, $CDCl_3$): δ 0.02 (bs, 18H, $N(TMS)_2$), 2.25 (s, 6H, $CH_3$), 2.28 (s, 6H, $CH_3$), 2.29 (s, 6H, $CH_3$), 6.31 (d, $J$ = 4 Hz, 2H, Py), 6.83 (s, 4H, Mes), 6.87 (d, $J$ = 4 Hz, 2H, Py), 7.50-7.59 (m, 5H, Ph); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ 6.9 ($N(TMS)_2$), 21.3, 23.0, 23.3 ($CH_3$), 122.2, 127.8, 127.9, 128.0, 128.4, 129.8, 129.9, 130.4, 131.4, 134.4, 136.2, 137.4, 139.3, 140.1, 145.8, 163.5 ppm; $^{77}$Se{$^{1}$H} (95.60 MHz, $CDCl_3$): δ -178.0 ppm; $^{29}$Si{$^{1}$H} NMR (99.3 MHz, $CDCl_3$): δ -21.90 ppm ($Si(CH_3)_3$). HRMS (ESI-QTOF, $[M + Na]^+$) $m/z$ calcd for $[C_{39}H_{49}GeN_3NaSeSi_2]$ 792.1734, found 792.1732 (Δ 1.9 ppm).

**General procedure for the synthesis of thiogermaamide stabilized copper(I) halide complexes**




**Scheme S3. Synthesis of thiogermaamide 12 stabilized copper(I) halide complexes**

To a solution of $DPMGe(S)N(TMS)_2$ (**12**) in toluene (10 mL), corresponding CuX (X = Cl, Br, and I for complexes **14**, **16**, and **17**, respectively) was added under ambient conditions. The

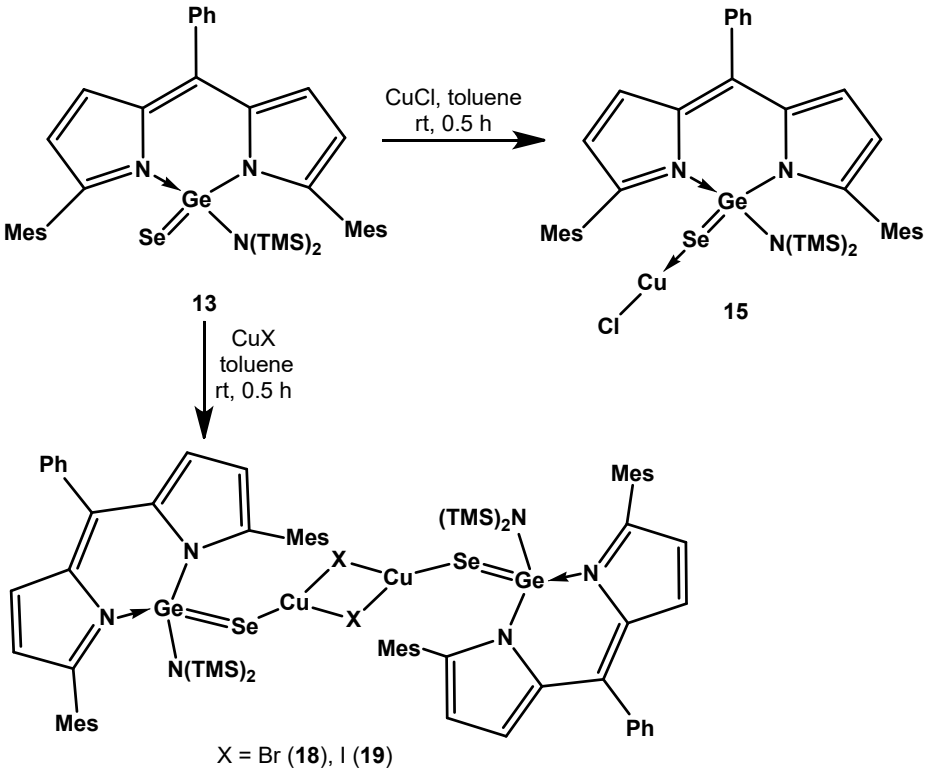
reaction mixture was stirred for 30 min, and the solvent was removed under reduced pressure to get a brown-red solid. It was washed with hexane (10 mL) and dried in vacuo to obtain the desired thiogermaamide stabilized copper(I) halide complex as a brown-red solid.

**Synthesis of [(DPMGe(S)N(TMS)$_2$)→CuCl] (14)**: Compound **12** (0.200 g, 0.27 mmol), Cu(I)Cl (.030 g, 0.30 mmol), toluene (10 mL), color and state: orange-red and solid. Single crystals of compound **14** suitable for X-ray diffraction studies were grown from its tetrahydrofuran solution containing a few drops of toluene at room temperature. Yield: 0.196 g (89%); $^{1}$H NMR (500 MHz, $CDCl_3$): δ -0.05 (bs, 18H, $N(TMS)_2$), 2.17 (s, 6H, $CH_3$), 2.29 (s, 6H, $CH_3$), 2.45 (s, 6H, $CH_3$), 6.42 (d, *J* = 4.3 Hz, 2H, Py), 6.85 (s, 2H, Mes), 6.91 (s, 2H, Mes), 6.99 (d, *J* = 4.8 Hz, 2H, Py), 7.49 (bs, 2H, Ph), 7.55 (bs, 2H, Ph), 7.93 ppm (d, *J* = 7.0 Hz, 1H, Ph); $^{13}$C{$^{1}$H} NMR (100 MHz): δ 5.7 ($N(TMS)_2$), 21.2, 23.4, 24.5 ($CH_3$), 123.3, 127.5, 128.0, 128.4, 128.9, 129.1, 129.6, 129.9, 132.0, 135.7, 136.6, 136.7, 137.6, 139.5, 140.3, 146.4, 163.3 ppm; $^{29}$Si{$^{1}$H} NMR (99.3 MHz, $CDCl_3$): δ -21.80 ppm ($Si(CH_3)_3$). HRMS (ESI-QTOF, [M - Cl]$^{+}$) *m*/*z* calcd for [$C_{39}H_{49}CuGeN_3SSi_2$] 784.1694, found 784.1672 (Δ 2.8 ppm).

**Synthesis of [(DPMGe(S)N(TMS)$_2$)→CuBr]$_2$ (16)**: Compound **12** (0.200 g, 0.27 mmol), Cu(I)Br (0.043 g, 0.30 mmol), toluene (10 mL), color and state: orange-red and solid. Single crystals of compound **16** suitable for X-ray diffraction studies were grown by slowly cooling its hot toluene solution to room temperature. Yield: 0.224 g (94%); $^{1}$H NMR (500 MHz, $CDCl_3$): δ -0.06 (bs, 36H, $N(TMS)_2$), 2.17 (s, 12H, $CH_3$), 2.28 (s, 12H, $CH_3$), 2.49 (s, 12H, $CH_3$), 6.41 (d, *J* = 5 Hz, 4H, Py), 6.84 (s, 4H, Mes), 6.90 (s, 4H, Mes), 6.97 (d, *J* = 5 Hz, 4H, Py), 7.47 (bs, 4H, Ph), 7.55 (bs, 4H, Ph), 8.02 ppm (bs, 2H, Ph); $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$): δ 5.7 ($N(TMS)_2$), 21.2, 23.5, 24.7 ($CH_3$), 123.2, 127.4, 128.0, 128.3, 128.9, 129.0, 129.6, 129.9, 132.0, 135.7, 136.5, 136.7, 137.6, 139.5, 140.2, 146.4, 163.2 ppm; $^{29}$Si{$^{1}$H} NMR (99.3 MHz, $CDCl_3$): δ -21.80 ppm ($Si(CH_3)_3$). HRMS (ESI-QTOF, [0.5 M - Br]$^{+}$) *m*/*z* calcd for [$C_{39}H_{49}CuGeN_3SSi_2$] 784.1694, found 784.1678 (Δ 2.0 ppm).

**Synthesis of [(DPMGe(S)N(TMS)$_2$)→CuI]$_2$ (17)**: Compound **12** (0.200 g, 0.27 mmol), Cu(I)I (0.057 g, 0.30 mmol), toluene (10 mL), color and state: orange-red and solid. Single crystals of compound **17** suitable for X-ray diffraction studies were grown by slowly cooling its hot toluene solution to room temperature. Yield: 0.226 g (90%); $^1$H NMR (500 MHz, $CDCl_3$): δ -0.06 (bs, 36H, N(TMS)$_2$), 2.17 (s, 12H, $CH_3$), 2.28 (s, 12H, $CH_3$), 2.50 (s, 12H, $CH_3$), 6.41 (d, *J* = 5 Hz, 4H, Py), 6.84 (s, 4H, Mes), 6.90 (s, 4H, Mes), 6.98 (d, *J* = 5 Hz, 4H, Py), 7.47 (bs, 4H, Ph), 7.54 (bs, 4H, Ph), 8.02 ppm (bs, 2H, Ph); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 5.8 (N(TMS)$_2$), 21.2, 23.5, 25.3 ($CH_3$), 123.1, 127.4, 127.9, 128.2, 128.9, 129.0, 129.9, 132.0, 135.9, 136.3, 136.6, 138.0, 139.6, 140.0, 146.4, 163.1 ppm; $^{29}$Si{$^1$H} NMR (99.3 MHz, $CDCl_3$): δ -21.90 ppm (Si(CH$_3$)$_3$). HRMS (ESI-QTOF, [0.5 M - I]$^+$) *m*/*z* calcd for [$C_{39}H_{49}CuGeN_3SSi_2$] 784.1694, found 784.1661 (Δ 4.2 ppm).

**General procedure for the synthesis of selenogermaamide stabilized copper(I) halide complexes**




**Scheme S4. Synthesis of selenogermaamide 13 stabilized copper(I) halide complexes**

To a solution of DPMGe(Se)N(TMS)$_2$ (**13**) in toluene (10 mL), CuX (X = Cl, Br, and I for complexes **15**, **18**, and 1**9**, respectively) were added under ambient conditions. The reaction mixture was allowed to stir for 30 min, and the solvent was removed under reduced pressure to get a brown-red solid. It was washed with hexane (10 mL) and dried *in vacuo* to afford selenogermaamide stabilized copper(I) halide complex as a brown-red solid.

**Synthesis of [(DPMGe(Se)N(TMS)$_2$)→CuCl] (15)**: Compound **13** (0.200 g, 0.26 mmol), Cu(I)Cl (0.028 g, 0.28 mmol), toluene (10 mL), color and state: red-orange and solid. Yield: 0.213 g (95%); $^1$H NMR (500 MHz, $CDCl_3$): δ 0.01 (bs, 18H, N(TMS)$_2$), 2.21 (s, 6H, $CH_3$), 2.30 (s, 6H, $CH_3$), 2.44 (s, 6H, $CH_3$), 6.40 (d, $J$ = 4.1 Hz, 2H, Py), 6.84 (s, 2H, Mes), 6.90 (s, 2H, Mes), 6.96 (d, $J$ = 4.5 Hz, 2H, Py), 7.49 (bs, 2H, Ph), 7.54 (bs, 2H, Ph), 7.91 ppm (s, 1H, Ph); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 6.2 (N(TMS)$_2$), 21.2, 21.5, 23.5, ($CH_3$), 123.2, 125.4,

127.4, 128.0, 128.3, 128.8, 128.8, 129.1, 129.4, 129.8, 132.1, 135.7, 136.3, 136.5, 137.3, 137.9, 139.4, 140.1, 145.1, 146.5, 163.5 ppm; $^{77}Se\{^{1}H\}$ (95.60 MHz, $CDCl_3$): δ -237 ppm; $^{29}Si\{^{1}H\}$ NMR (99.3 MHz, $CDCl_3$): δ -21.9 ppm ($Si(CH_3)_3$). HRMS (ESI-QTOF, $[M - Cl]^+$) *m*/*z* calcd for $[C_{39}H_{49}CuGeN_3SeSi_2]$ 832.1138, found 832.1101 (Δ 4.4 ppm).

**Synthesis of $[(DPMGe(Se)N(TMS)_2)\rightarrow CuBr]_2$ (18)**: Compound **13** (0.200 g, 0.26 mmol), Cu(I)Br (0.040 g, 0.28 mmol), toluene (10 mL), color and state: red-orange and solid. Yield: 0.217 g (92%); $^{1}H$ NMR (500 MHz, $CDCl_3$): δ 0.01 (bs, 36H, $N(TMS)_2$), 2.21 (s, 12H, $CH_3$), 2.30 (s, 12H, $CH_3$), 2.44 (s, 12H, $CH_3$), 6.39 (d, *J* = 5 Hz, 4H, Py), 6.84 (s, 4H, Mes), 6.89 (s, 4H, Mes), 6.97 (d, *J* = 5 Hz, 4H, Py), 7.49 (s, 4H, Ph), 7.55 (s, 4H, Ph), 7.96 ppm (d, *J* = 5 Hz, 2H, Ph); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 6.32 ($N(TMS)_2$), 21.2, 23.5, 25.1 ($CH_3$), 123.2, 127.4, 128.0, 128.3, 128.9, 129.0, 129.5, 129.9, 132.2, 136.3, 136.6, 137.5, 139.4, 140.1, 163.3 ppm; $^{29}Si\{^{1}H\}$ NMR (99.3 MHz, $CDCl_3$): δ -21.9 ppm ($Si(CH_3)_3$); $^{77}Se\{^{1}H\}$ (95.60 MHz, $CDCl_3$): δ -228 ppm. HRMS (ESI-QTOF, $[0.5\ M - Br]^+$) *m*/*z* calcd for $[C_{39}H_{49}CuGeN_3SeSi_2]$ 832.1138, found 832.1107 (Δ 3.7 ppm).

**Synthesis of $[(DPMGe(Se)N(TMS)_2)\rightarrow CuI]_2$ (19)**: Compound **13** (0.200 g, 0.26 mmol), Cu(I)I (0.053 g, 0.28 mmol), toluene (10 mL), color and state: red-orange and solid. Single crystals of compound **19** suitable for X-ray diffraction studies were grown by slowly cooling its hot toluene solution to room temperature. Yield: 0.234 g (94%); $^{1}H$ NMR (500 MHz, $CDCl_3$): δ 0.01 (bs, 36H, $N(TMS)_2$), 2.22 (s, 12H, $CH_3$), 2.28 (s, 12H, $CH_3$), 2.45 (s, 12H, $CH_3$), 6.37 (s, 4H, Py), 6.82 (s, 4H, Mes), 6.87 (s, 4H, Mes), 6.94 (d, *J* = 4.8 Hz, 4H, Py), 7.51 (bs, 8H, Ph), 7.93 ppm (bs, 2H, Ph); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 6.6 ($N(TMS)_2$), 21.3, 23.5, 25.2 ($CH_3$), 122.8, 127.5, 127.9, 128.2, 128.7, 129.3, 129.8, 129.9, 132.1, 135.8, 136.0, 136.4, 137.8, 139.6, 139.7, 163.3 ppm; $^{29}Si\{^{1}H\}$ NMR (99.3 MHz, $CDCl_3$): δ -21.9 ppm ($Si(CH_3)_3$); $^{77}Se\{^{1}H\}$ (95.60 MHz, $CDCl_3$): δ -235 ppm. HRMS (ESI-QTOF, $[0.5\ M - I]^+$) *m*/*z* calcd for $[C_{39}H_{49}CuGeN_3SeSi_2]$ 832.1138, found 832.1110 (Δ 3.4 ppm).

**Table S1. The temperature at which compounds 3-4, 6-7, and 9-19 started to become black solids**

| Compound | Temperature (˚C) |
|---|---|
| DPMGePh (**2**) | 175 |
| DPMGe(S)Ph (**3**) | 214 |
| DPMGe(Se)Ph (**4**) | 252 |
| DPMGe(S)OH (**6**) | 208 |
| DPMGe(Se)OH (**7**) | 241 |
| DPMGe(S)OEt (**9**) | 191 |
| DPMGe(Se)OEt (**10**) | 225 |
| $DPMGeN(TMS)_2$ (**11**) | 188 |
| $DPMGe(S)N(TMS)_2$ (**12**) | 212 |
| $DPMGe(Se)N(TMS)_2$ (**13**) | 240 |
| $[(DPMGe(S)(N(TMS)_2)\rightarrow CuCl]$ (**14**) | 178 |
| $[(DPMGe(S)(N(TMS)_2)\rightarrow CuBr]$ (**16**) | 179 |
| $[(DPMGe(S)(N(TMS)_2)\rightarrow CuI]$ (**17**) | 172 |
| $[(DPMGe(Se)(N(TMS)_2)\rightarrow CuCl]$ (**15**) | 186 |
| $[(DPMGe(Se)(N(TMS)_2)\rightarrow CuBr]$ (**18**) | 192 |
| $[(DPMGe(Se)(N(TMS)_2)\rightarrow CuI]$ (**19**) | 185 |

**NMR spectra**

**Figure S1. $^{1}$H NMR spectrum of compound 2**

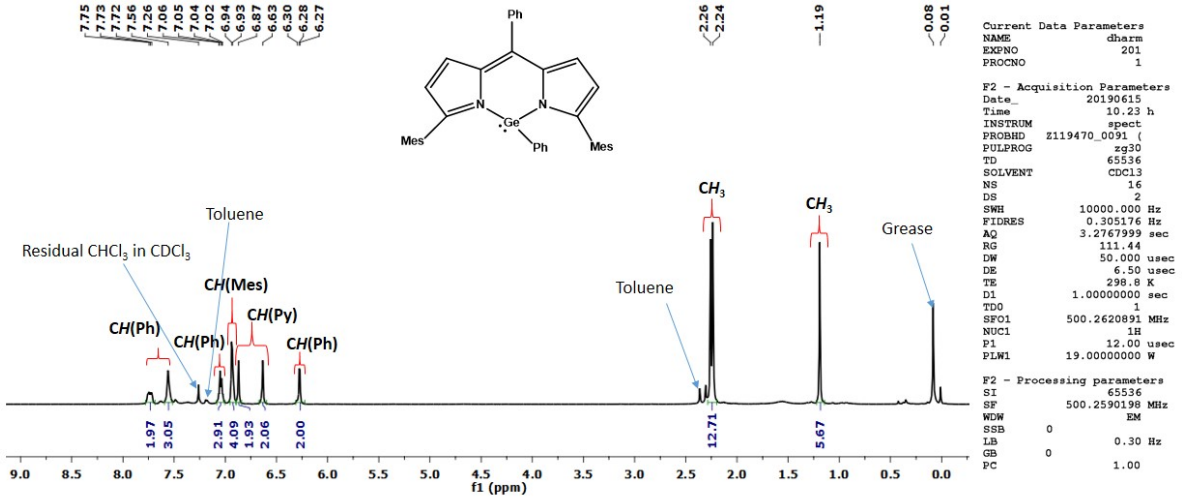



**Figure S2. $^{13}$C NMR spectrum of compound 2**

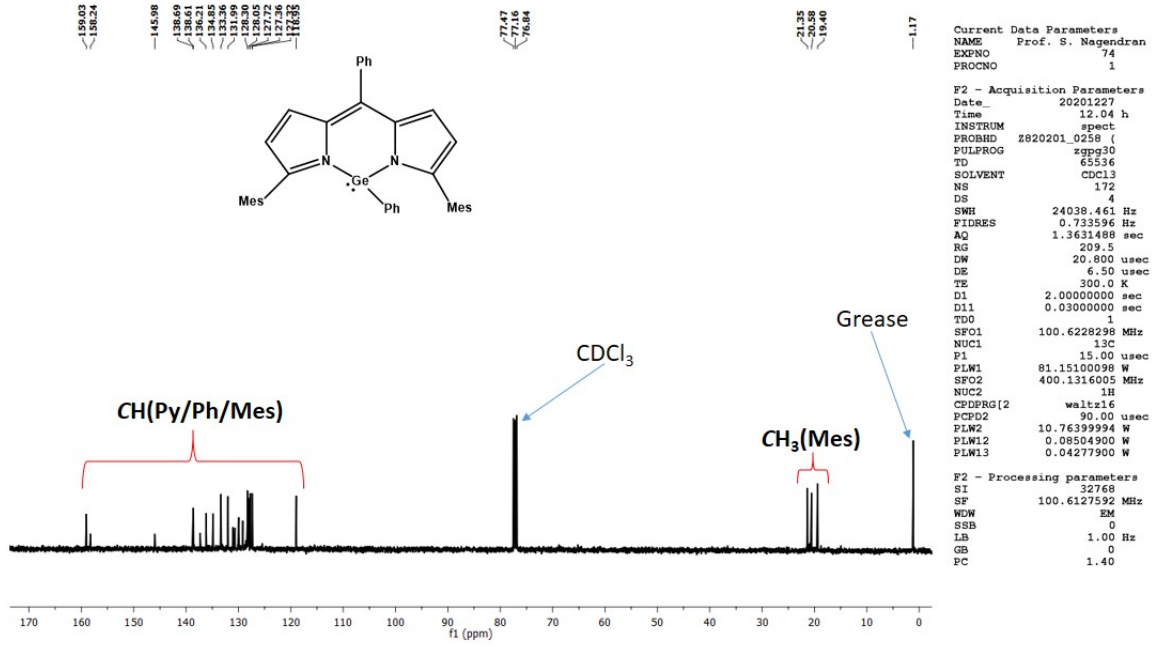


**Figure S3. Air stability of compound 2**

In an open vial, ~250 mg of a freshly prepared sample of compound **2** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S3 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S3 (**b**)] exactly matches that of the freshly prepared sample [Figure S3 (**a**)].

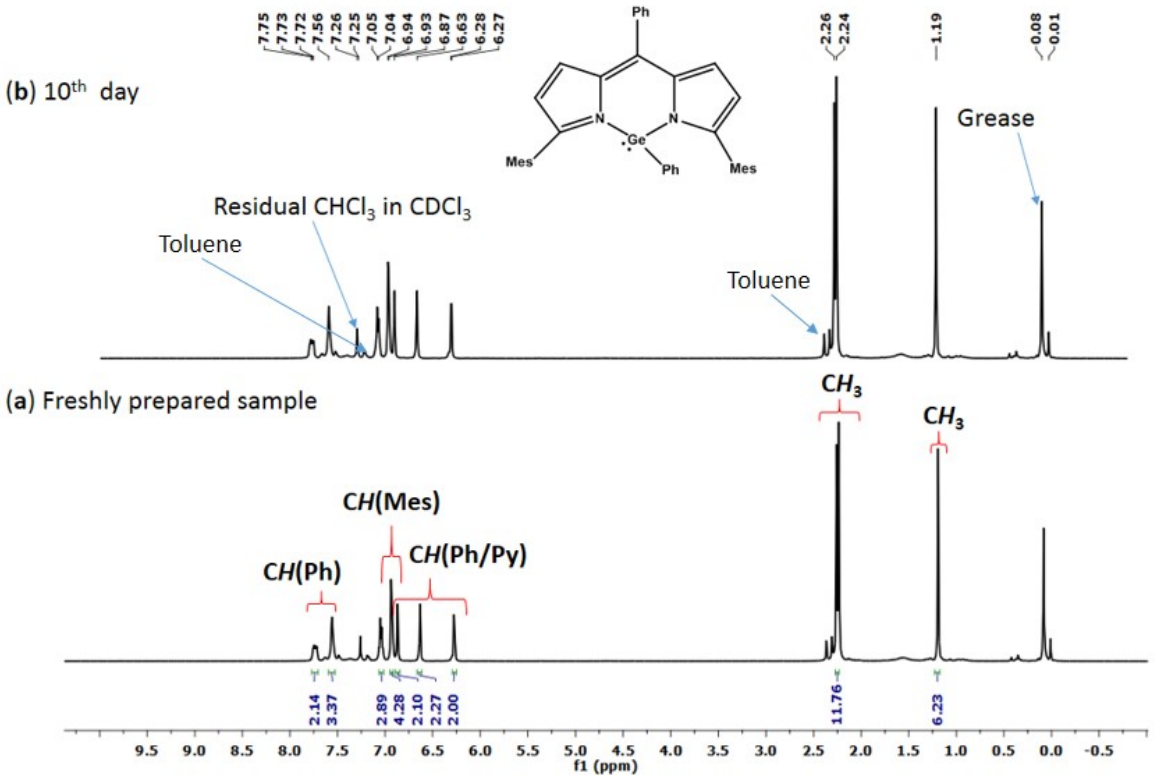


**Figure S4. Stability of compound 2 in water**

Around 10 mg of a freshly prepared sample of compound **2** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S4 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded daily. Up to 2 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 2nd day [Figure S4 (**b**)] exactly matches that of the freshly prepared sample [Figure S4 (**a**)].

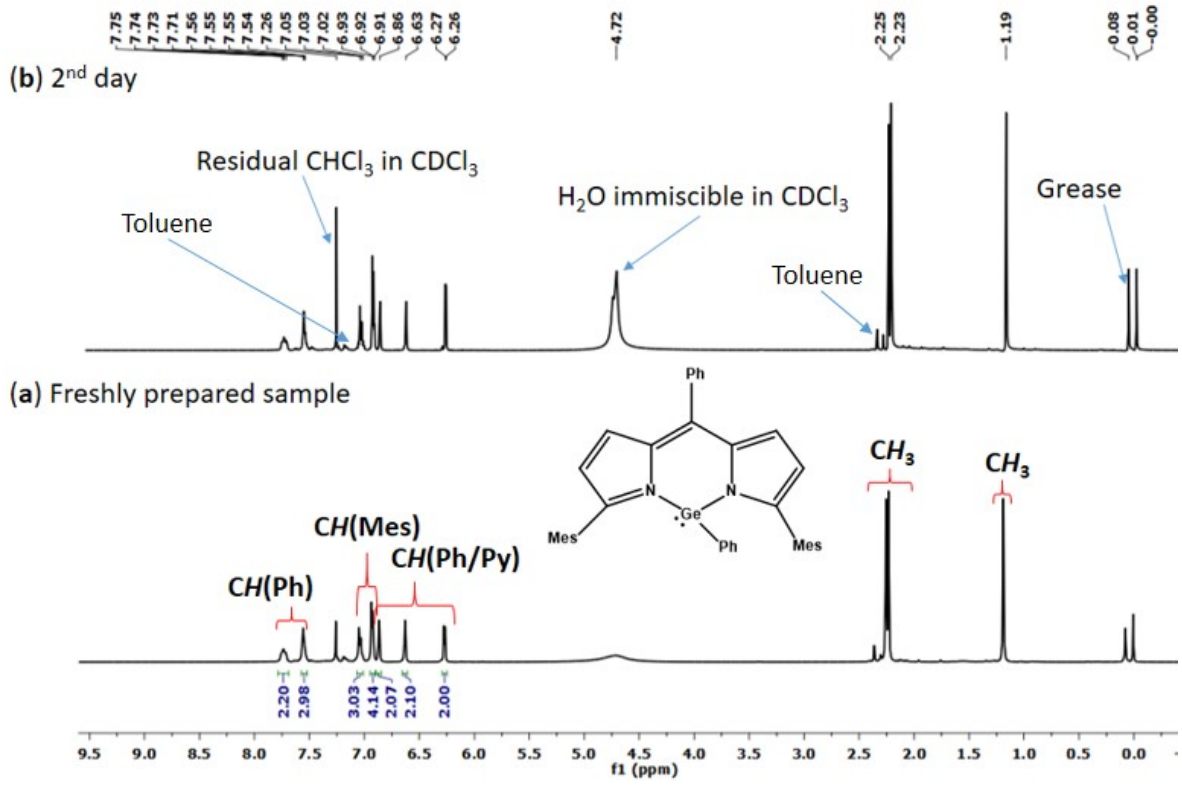


**Figure S5. $^{1}$H NMR spectrum of compound 3**

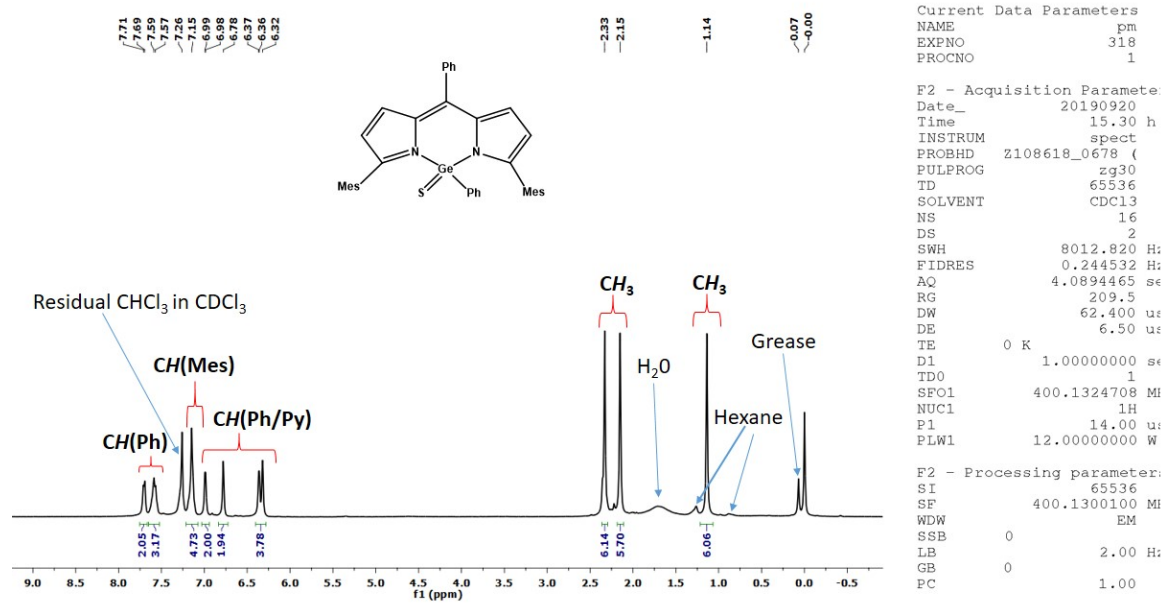



**Figure S6. $^{13}$C NMR spectrum of compound 3**

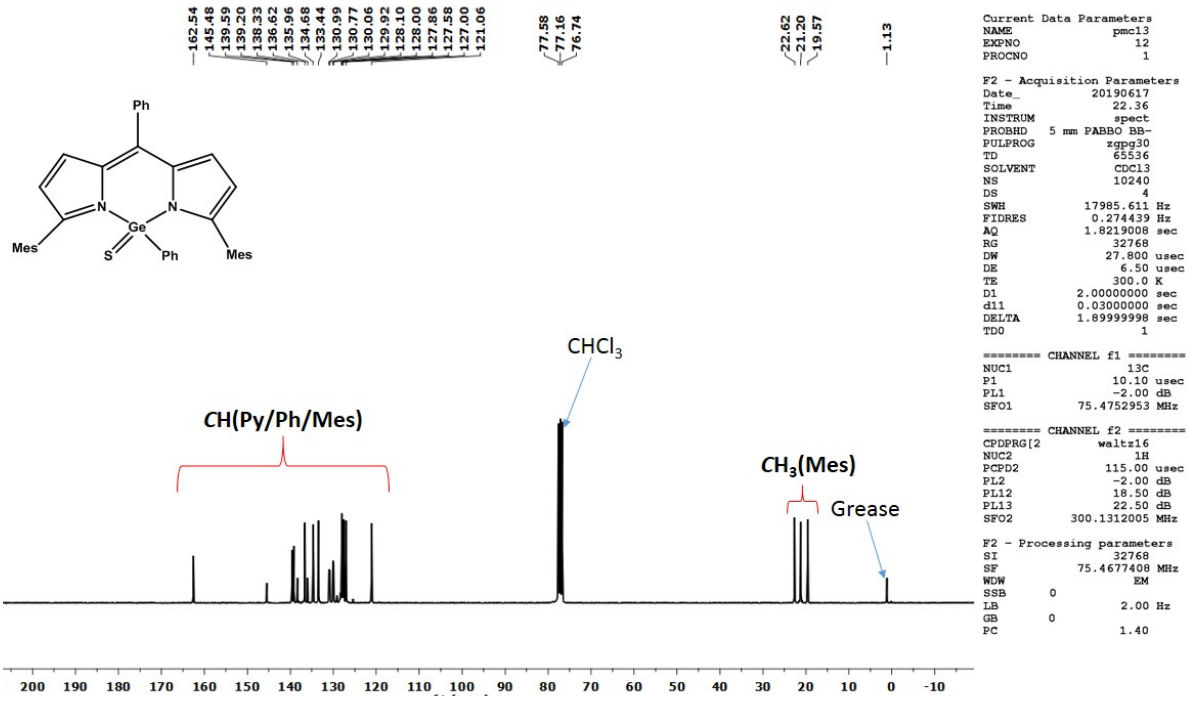


**Figure S7. Air stability of compound 3**

In an open vial, ~250 mg of a freshly prepared sample of compound **3** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S7 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S7 (**b**)] exactly matches that of the freshly prepared sample [Figure S7 (**a**)].

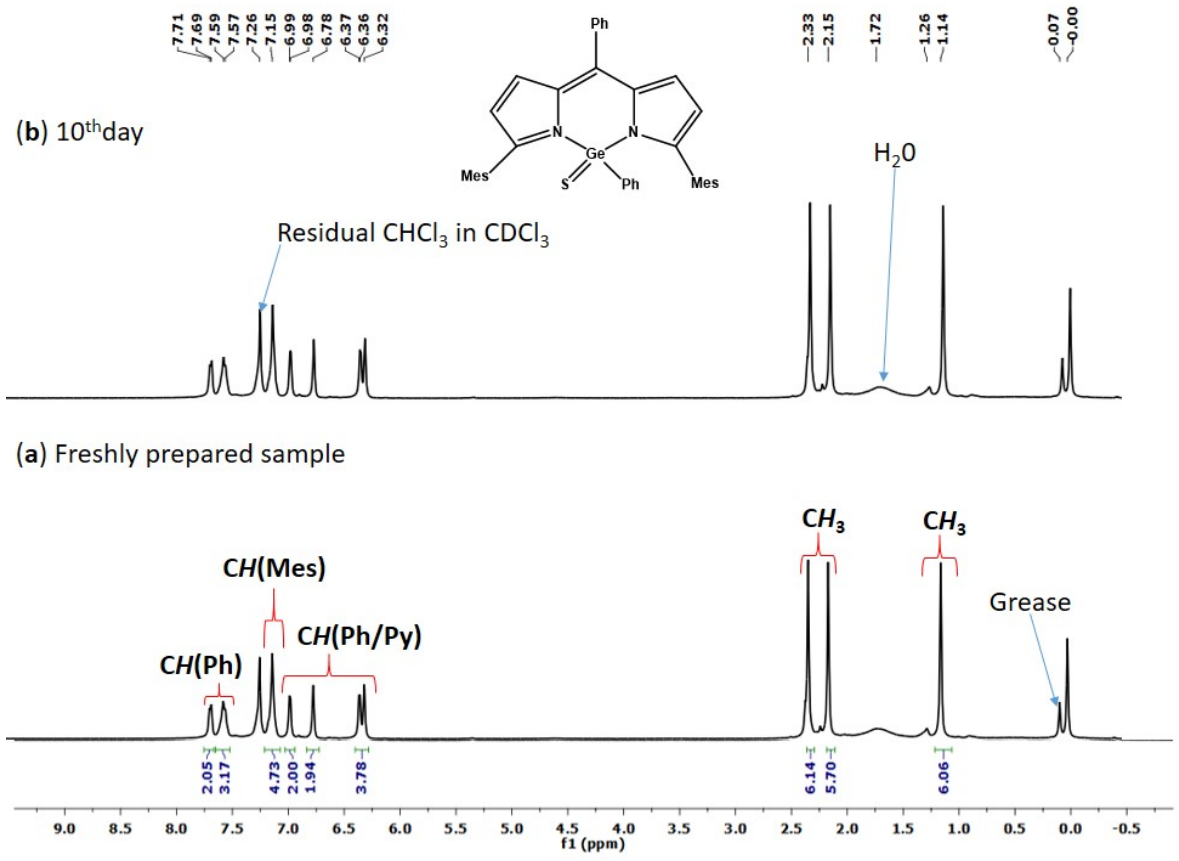


**Figure S8. Stability of compound 3 in water**

Around 10 mg of a freshly prepared sample of compound **3** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S8 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded daily. Up to 2 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 2nd day [Figure S8 (**b**)] exactly matches that of the freshly prepared sample [Figure S8 (**a**)].

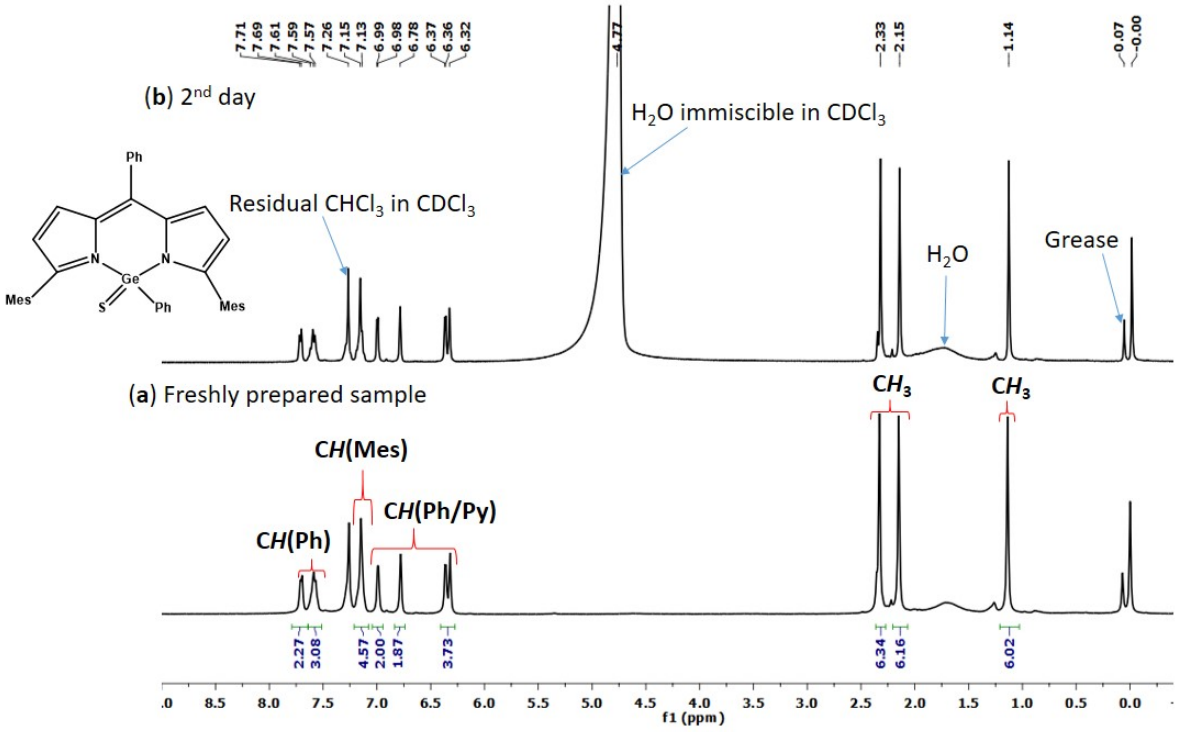


**Figure S9. $^{1}$H NMR spectrum of compound 4**

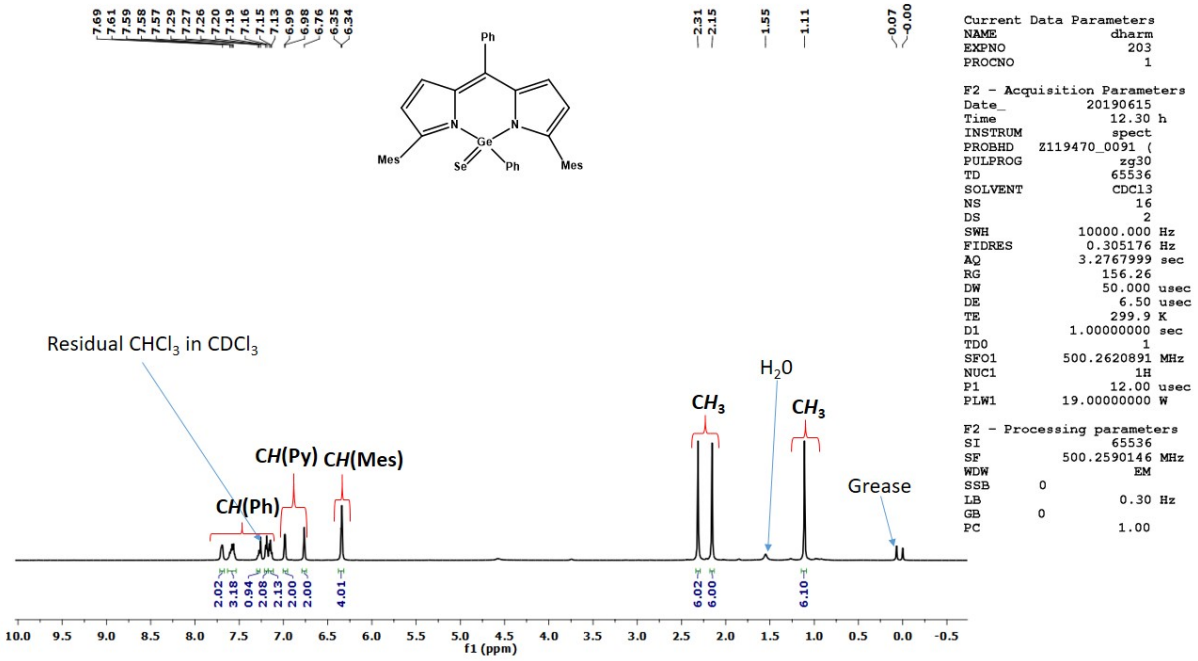



**Figure S10. $^{13}$C NMR spectrum of compound 4**

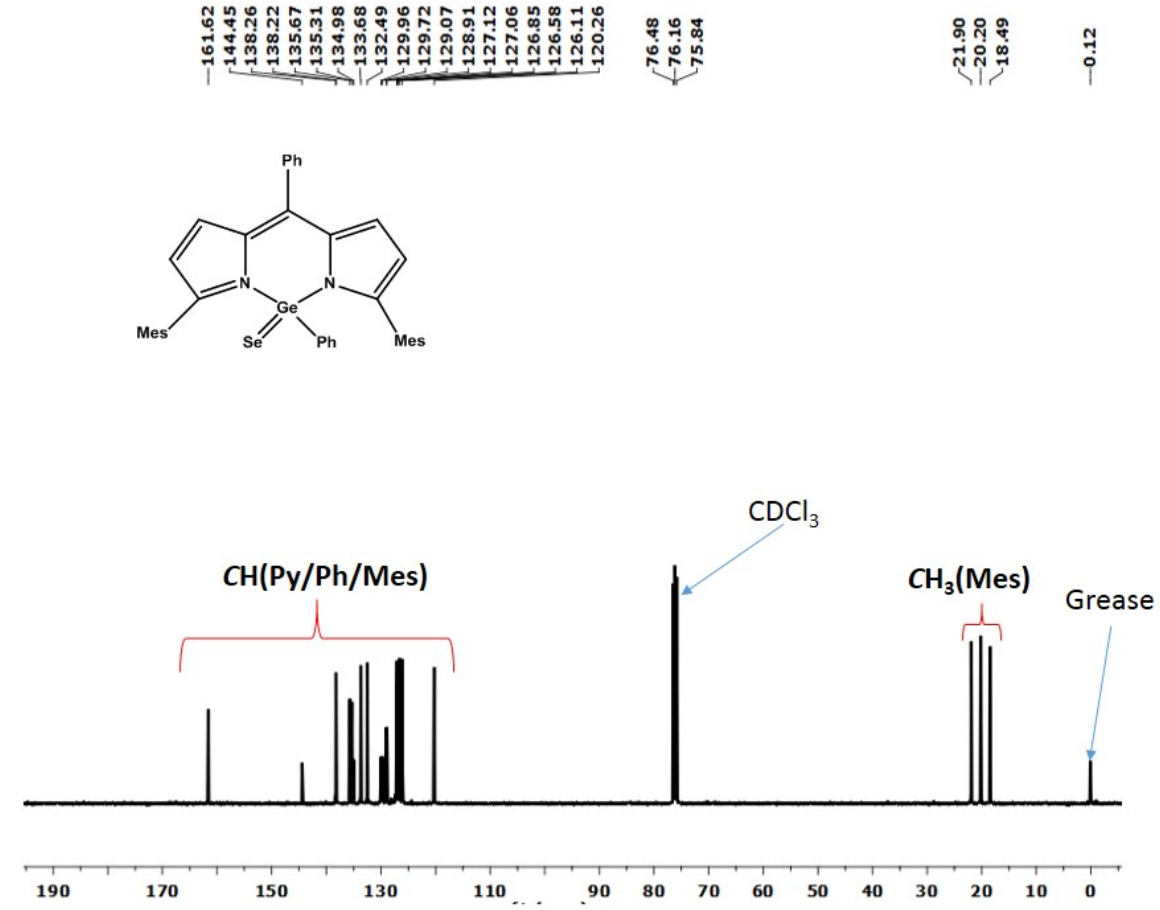


**Figure S11. Air stability of compound 4**

In an open vial, ~250 mg of a freshly prepared sample of compound **4** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S11 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S11 (**b**)] exactly matches that of the freshly prepared sample [Figure S11 (**a**)].

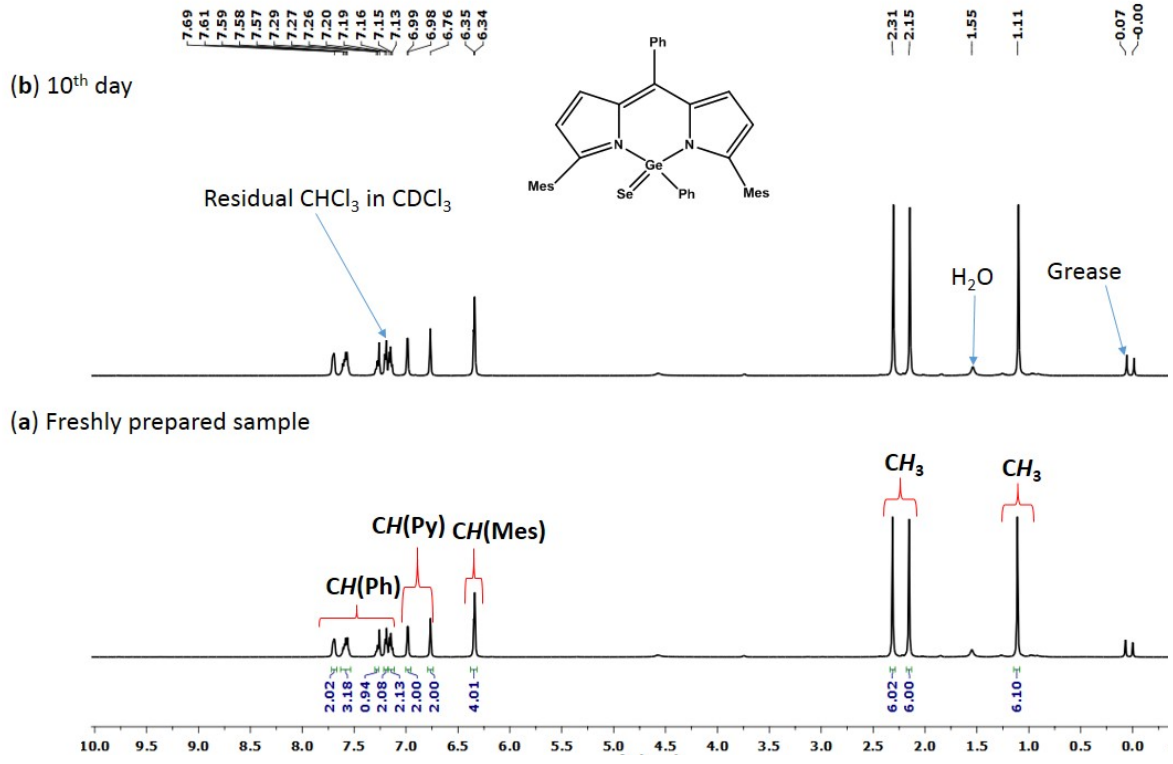


**Figure S12. Stability of compound 4 in water**

Around 10 mg of a freshly prepared sample of compound **4** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S12 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded daily. Up to 4 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 4$^{th}$ day [Figure S12 (**b**)] exactly matches that of the freshly prepared sample [Figure S12 (**a**)].

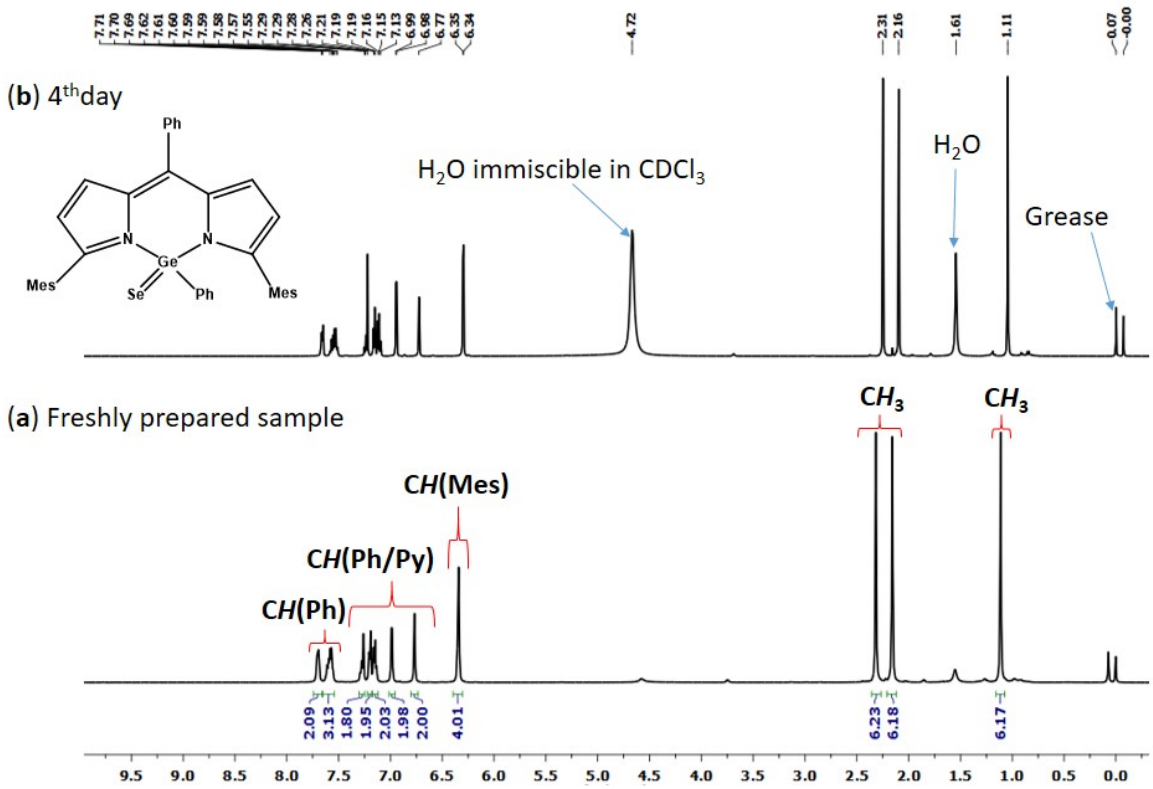


**Figure S13. $^{77}$Se NMR spectrum of compound 4**

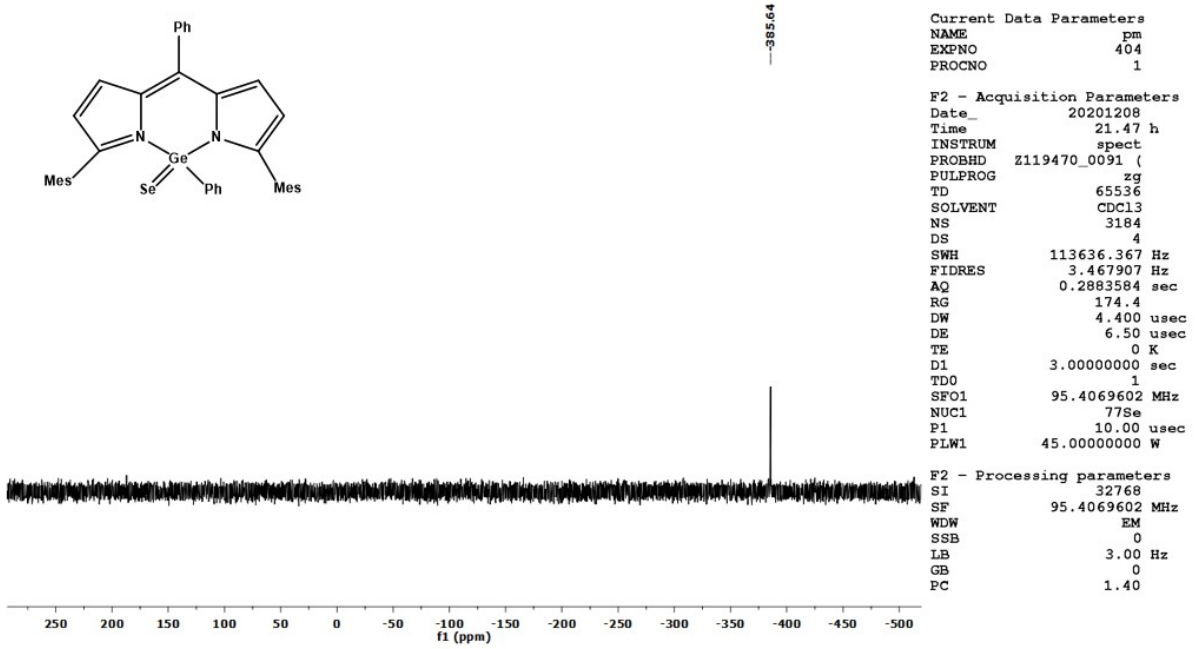


**Figure S14. $^{1}$H NMR spectrum of compound 6**

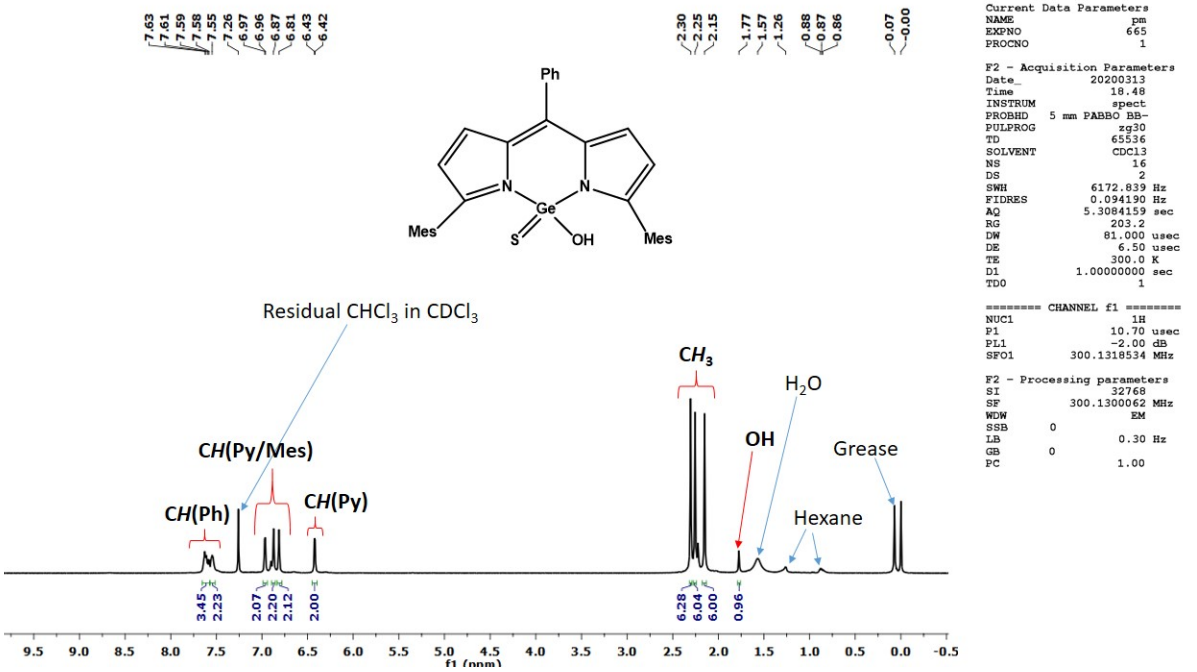



**Figure S15. $^{13}$C NMR spectrum of compound 6**

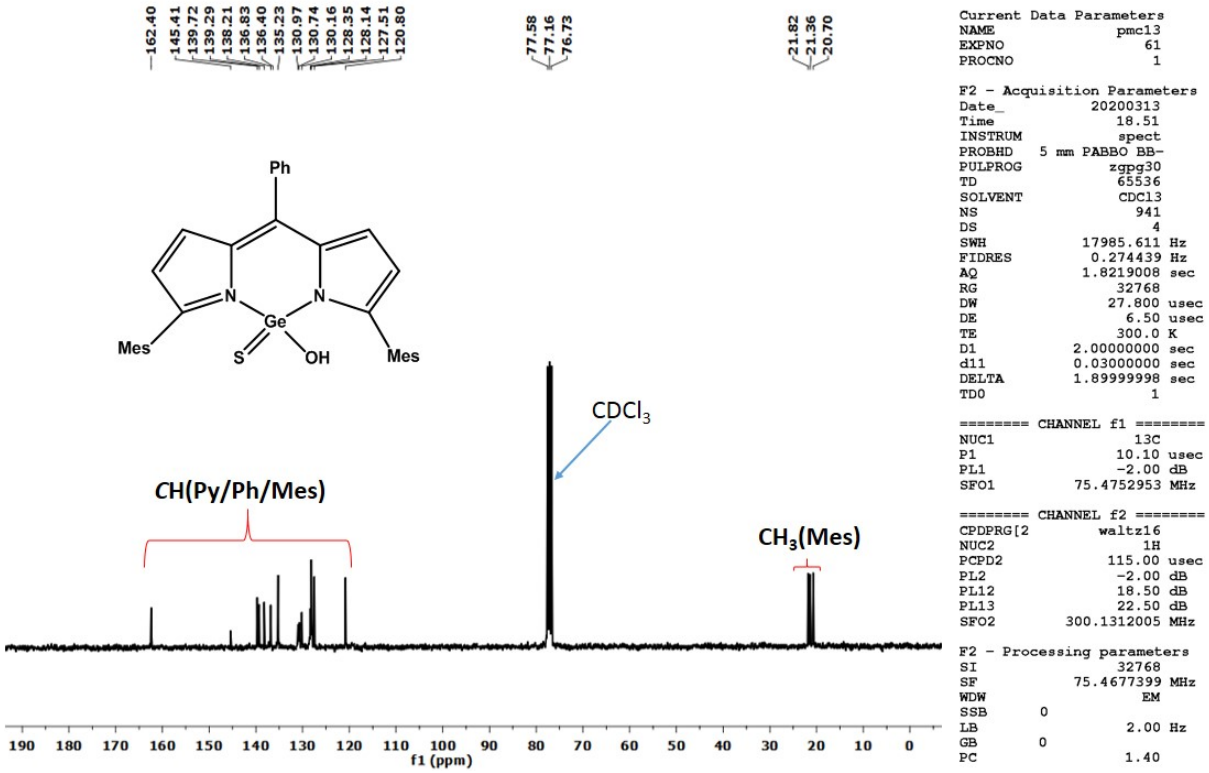


**Figure S16. Air stability of compound 6**

In an open vial, ~250 mg of a freshly prepared sample of compound **6** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S16 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S16 (**b**)] exactly matches that of the freshly prepared sample [Figure S16 (**a**)].

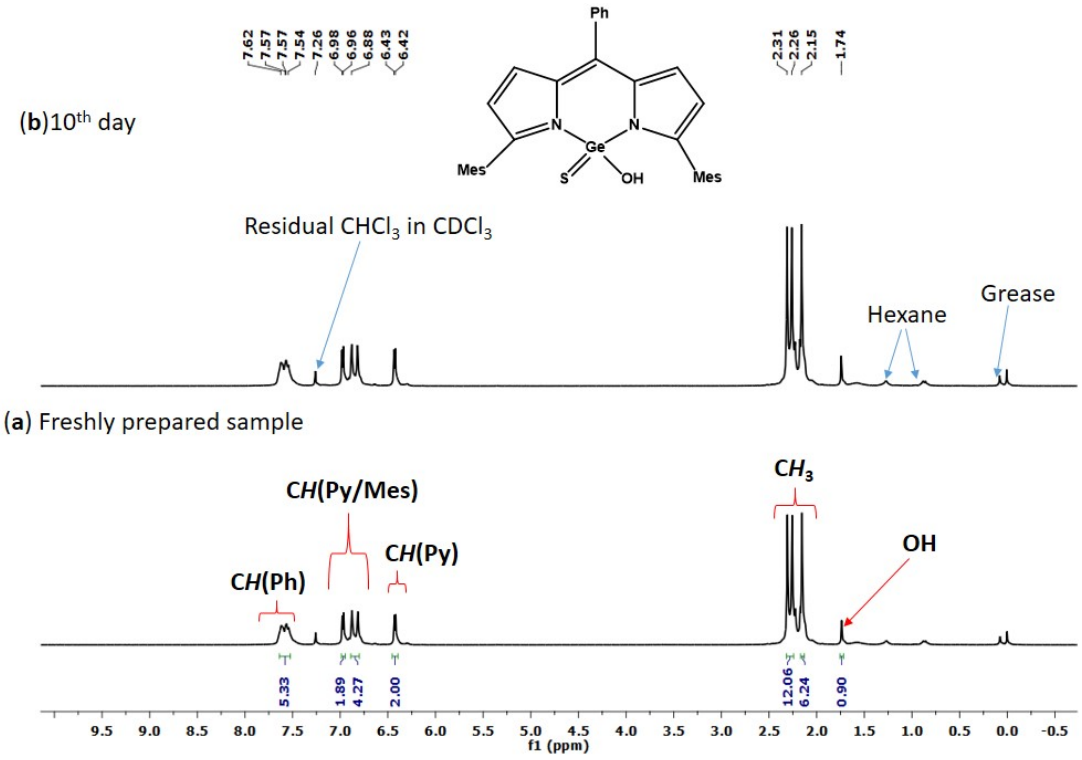


**Figure S17. $^{1}$H NMR spectrum of compound 7**

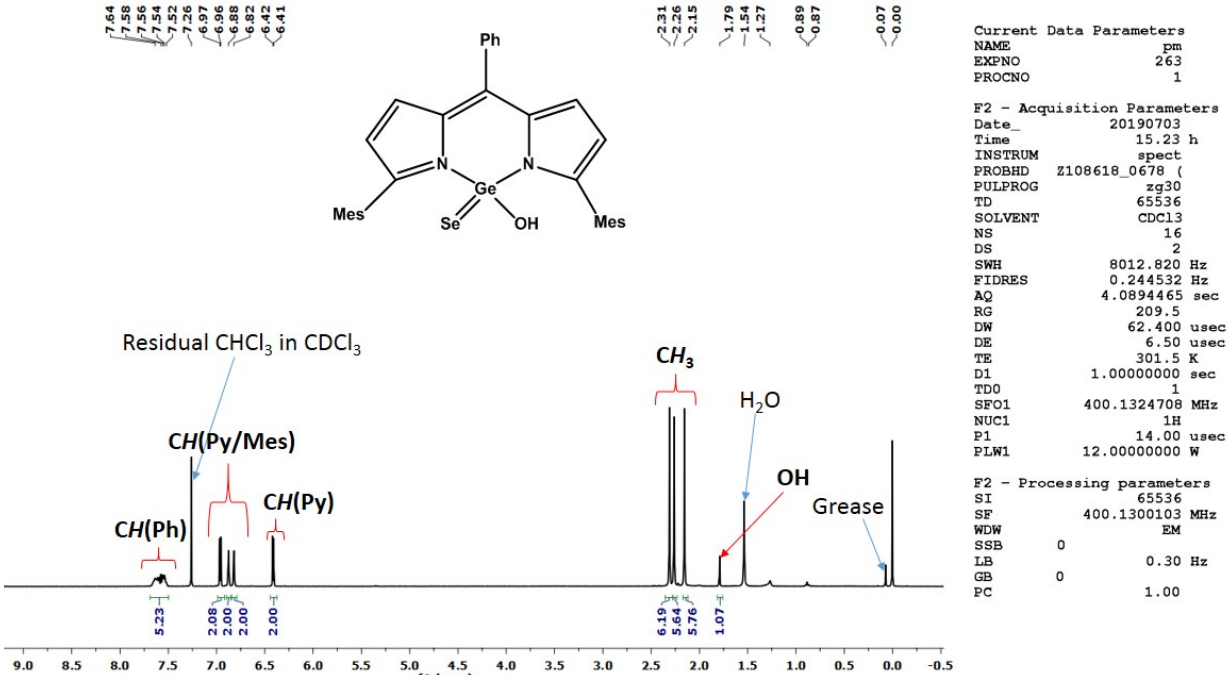



**Figure S18. $^{13}$C NMR spectrum of compound 7**

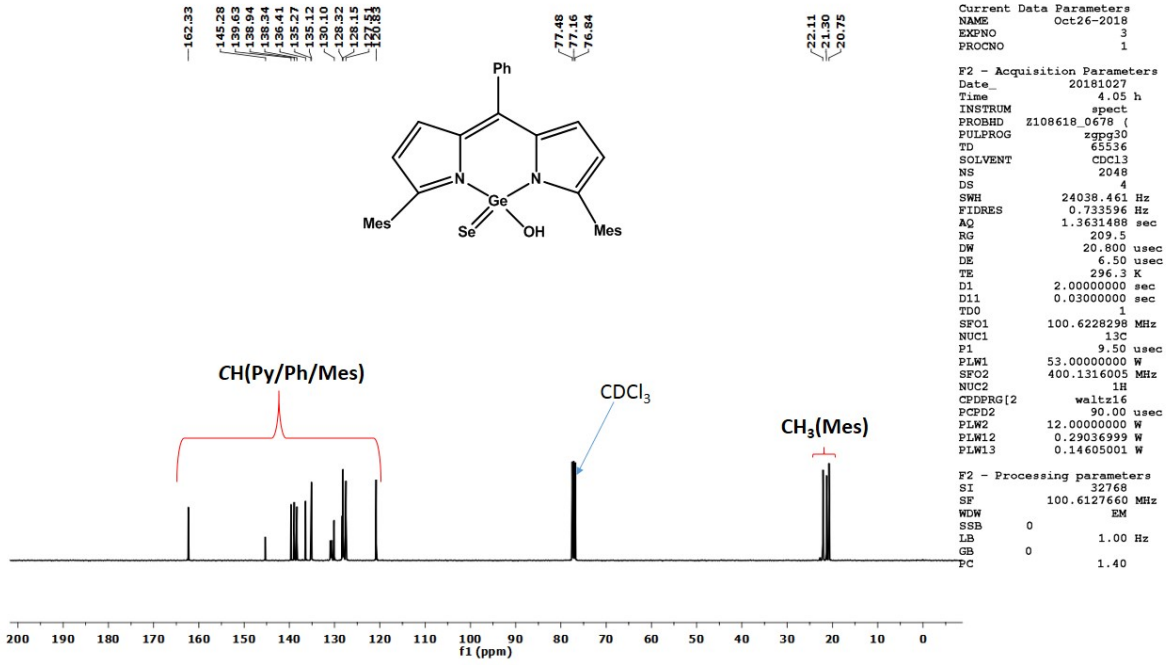


**Figure S19. Air stability of compound 7**

In an open vial, ~250 mg of a freshly prepared sample of compound **7** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S19 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S19 (**b**)] exactly matches that of the freshly prepared sample [Figure S19 (**a**)].

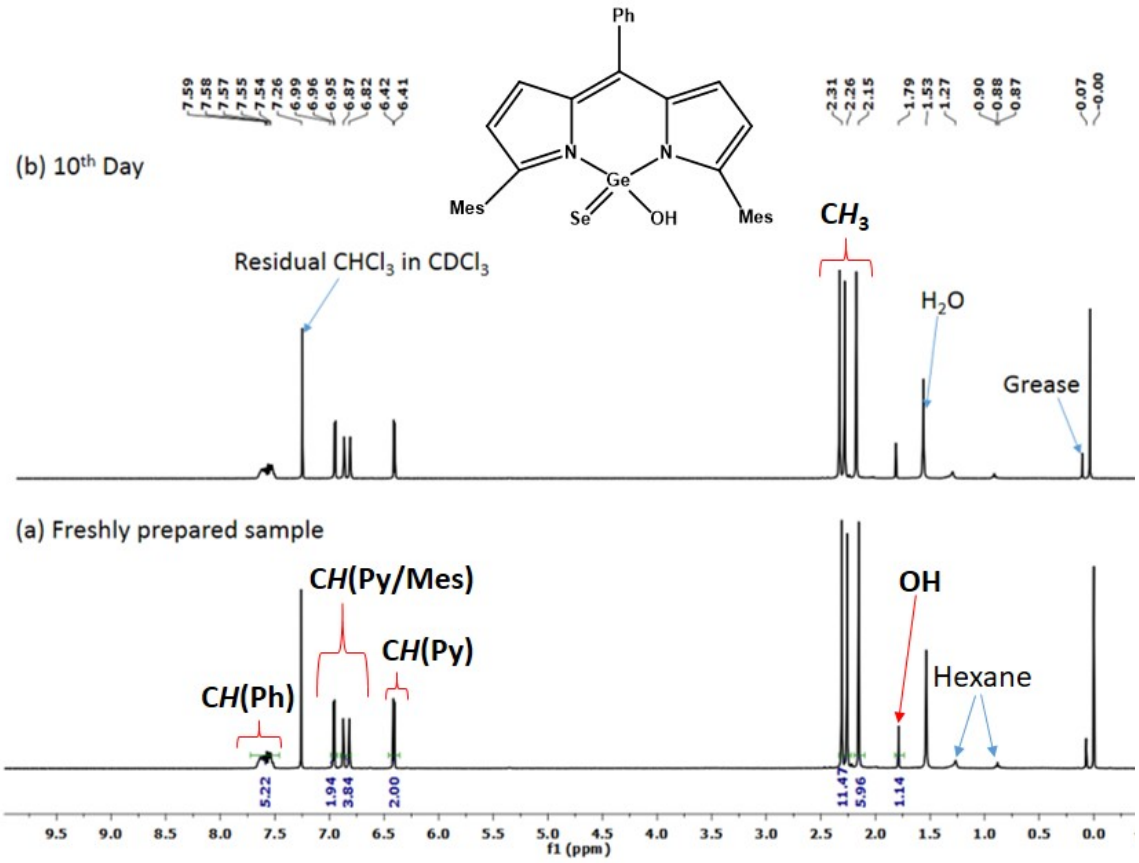


**Figure S20. Stability of compound 7 in water**

Around 10 mg of a freshly prepared sample of compound **7** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S20 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded every hour. Up to 6 h, we did not see any decomposition; the $^1H$ NMR spectrum recorded after 6 h [Figure S20 (**b**)] from the addition of water exactly matches that of the freshly prepared sample [Figure S20 (**a**)].

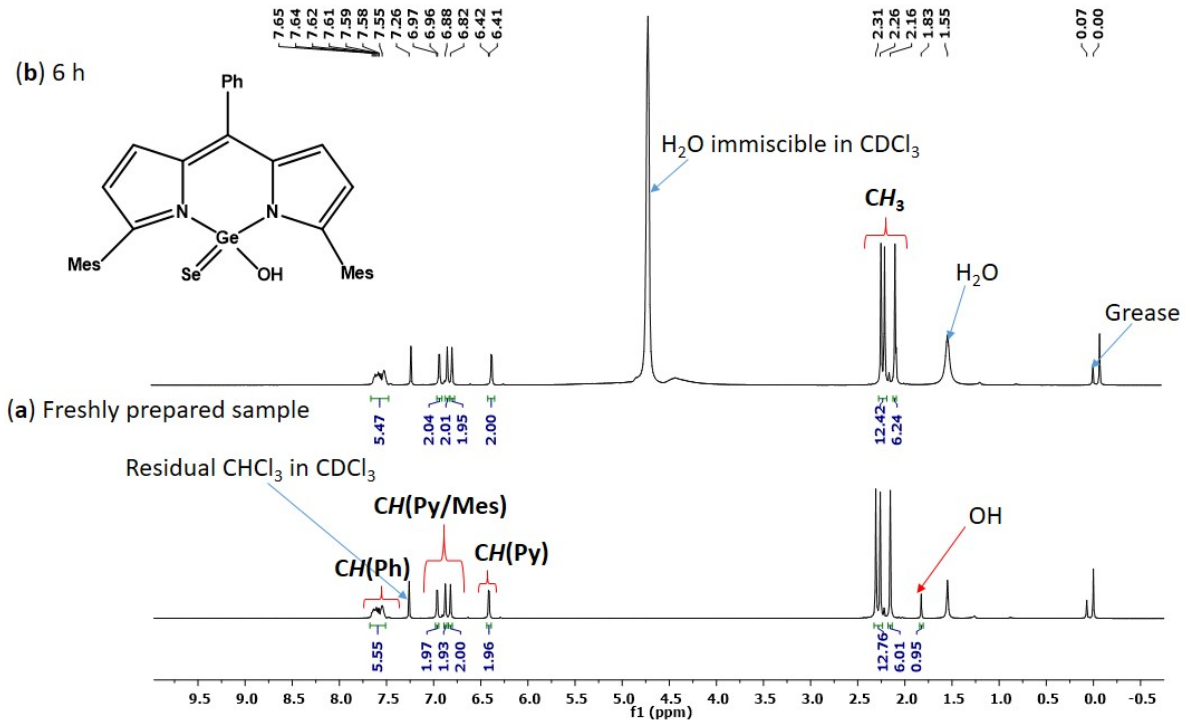
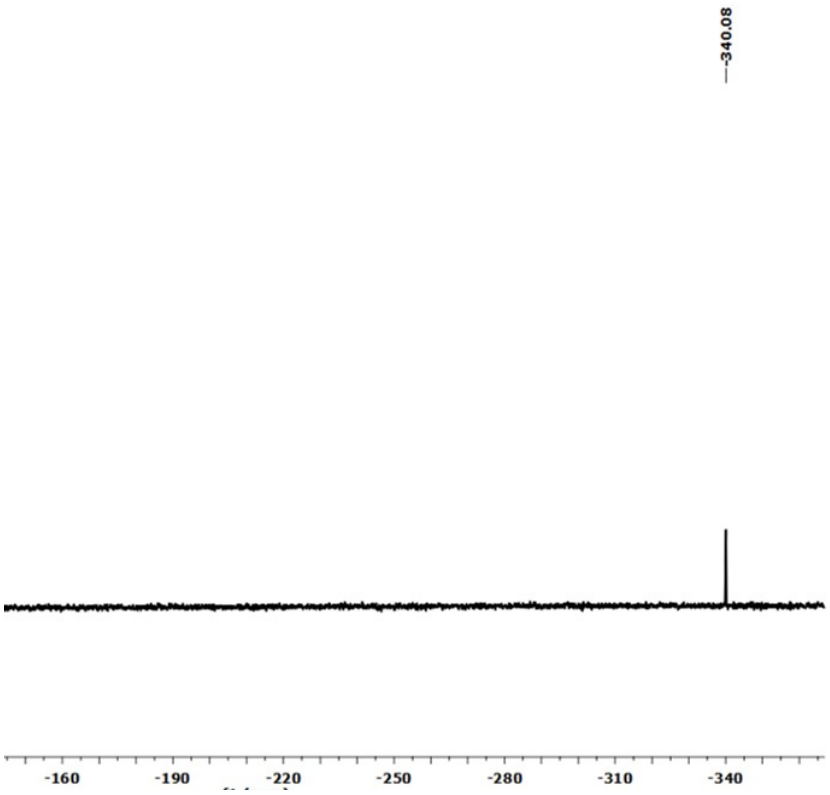


**Figure S21. $^{77}$Se NMR spectrum of compound 7**

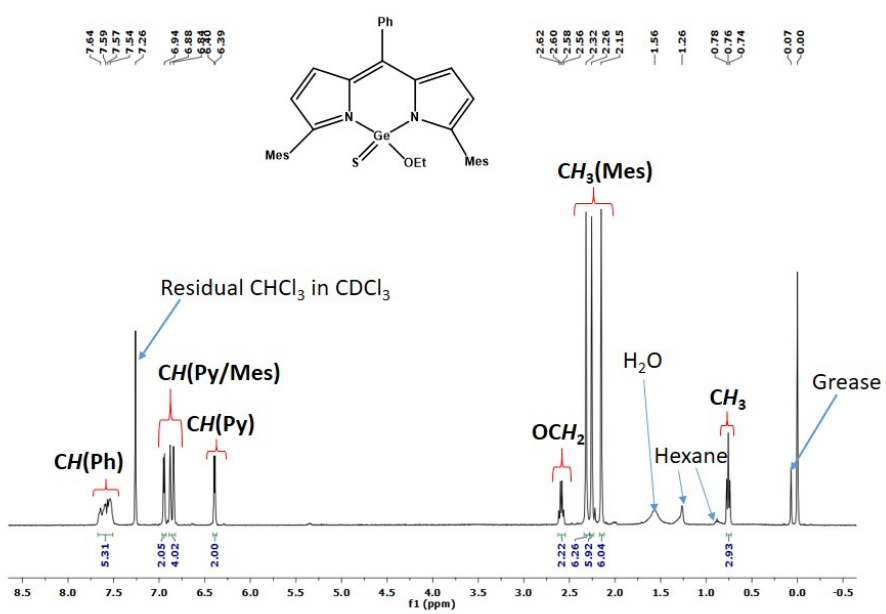



```
Current Data Parameters
NAME                   pm
EXPNO                 378
PROCNO                  1

F2 - Acquisition Parameters
Date_           20201129
Time               22.14 h
INSTRUM             spect
PROBHD   Z119470_0091 (
PULPROG                zg
TD                  65536
SOLVENT             CDCl3
NS                    156
DS                      4
SWH             75757.578 Hz
FIDRES           2.311938 Hz
AQ              0.4325376 sec
RG                 195.57
DW                  6.600 usec
DE                  6.50 usec
TE        0 K
D1             2.00000000 sec
TD0                     1
SFO1           95.4088684 MHz
NUC1                 77Se
P1                  10.00 usec
PLW1         45.00000000 W

F2 - Processing parameters
SI                  32768
SF             95.4069602 MHz
WDW                    EM
SSB       0
LB                  3.00 Hz
GB        0
PC                  1.40
```

**Figure S22. $^{1}$H NMR spectrum of compound 9**

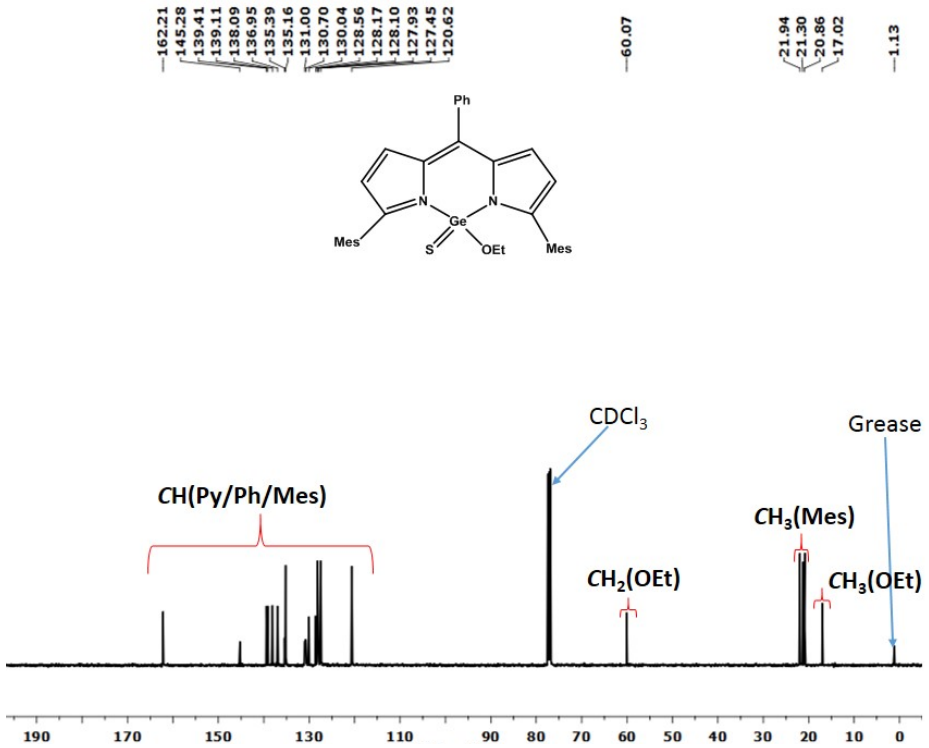



```
Current Data Parameters
NAME                  pm
EXPNO                205
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190418
Time              14.48 h
INSTRUM            spect
PROBHD    Z108618_0678 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ              4.0894465 sec
RG                 209.5
DW                62.400 usec
DE                 6.50 usec
TE                299.8 K
D1             1.00000000 sec
TD0                    1
SFO1          400.1324708 MHz
NUC1                  1H
P1                14.00 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                 65536
SF            400.1300094 MHz
WDW                   EM
SSB        0
LB                 0.30 Hz
GB         0
PC                 1.00
```

**Figure S23. $^{13}$C NMR spectrum of compound 9**




```
Current Data Parameters
NAME                 dharm
EXPNO                   83
PROCNO                   1

F2 - Acquisition Parameters
Date_           20190418
Time              15.30 h
INSTRUM            spect
PROBHD    Z119470_0091 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   718
DS                     4
SWH            29761.904 Hz
FIDRES          0.908261 Hz
AQ              1.1010048 sec
RG                 195.57
DW                16.800 usec
DE                 6.50 usec
TE                297.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          125.8028046 MHz
NUC1                  13C
P1                10.00 usec
PLW1          80.79399872 W
SFO2          500.2610010 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             80.00 usec
PLW2          19.00000000 W
PLW12          0.42750001 W
PLW13          0.21503000 W

F2 - Processing parameters
SI                 32768
SF            125.7902193 MHz
WDW                   EM
SSB        0
LB                 1.00 Hz
GB         0
PC                 1.40
```

**Figure S24. Air stability of compound 9**

In an open vial, ~250 mg of a freshly prepared sample of compound **9** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S24 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S24 (**b**)] exactly matches that of the freshly prepared sample [Figure S24 (**a**)].

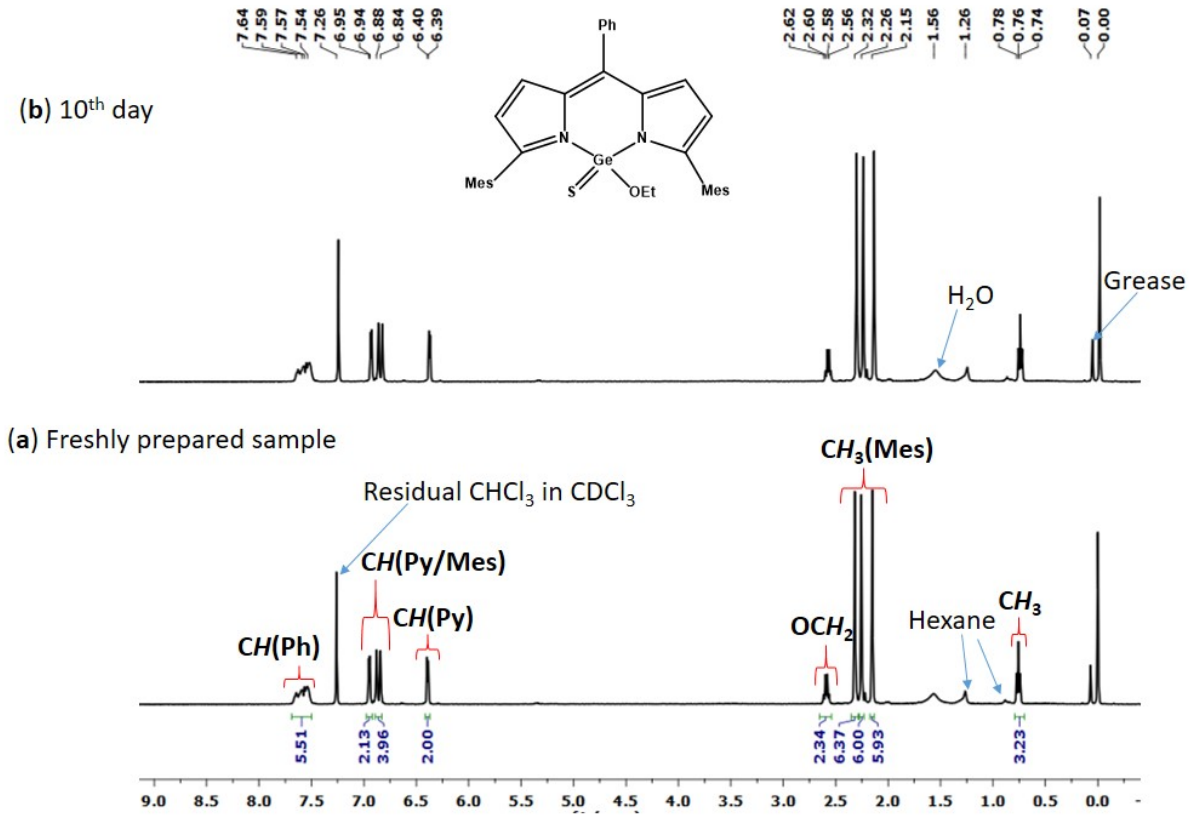


**Figure S25. Stability of compound 9 in water**

Around 10 mg of a freshly prepared sample of compound **9** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S25 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded daily. Up to 3 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 3rd day [Figure S25 (**b**)] exactly matches that of the freshly prepared sample [Figure S25 (**a**)].

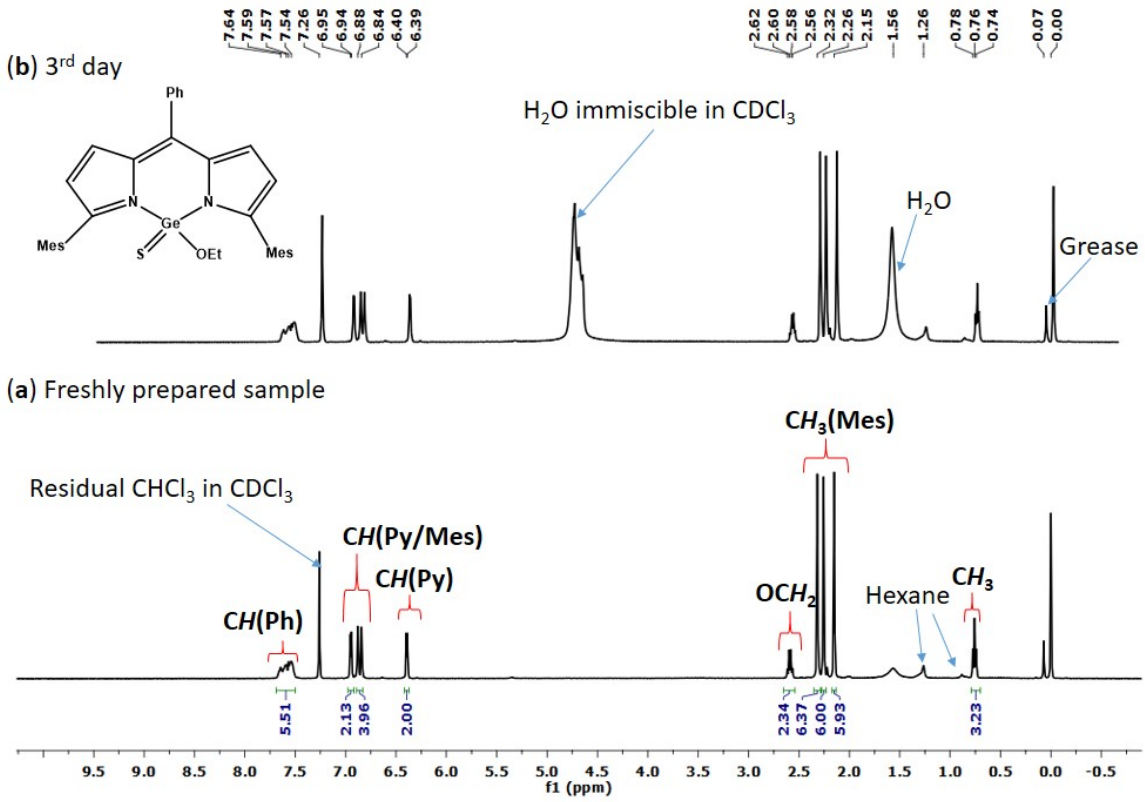


**Figure S26. $^{1}$H NMR spectrum of compound 10**

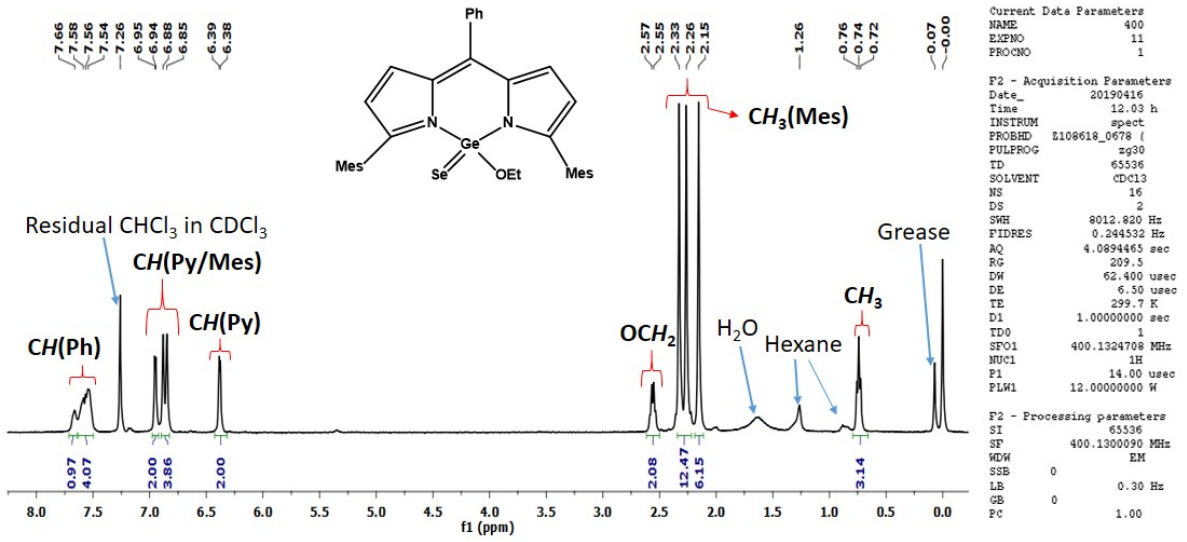



**Figure S27. $^{13}$C NMR spectrum of compound 10**

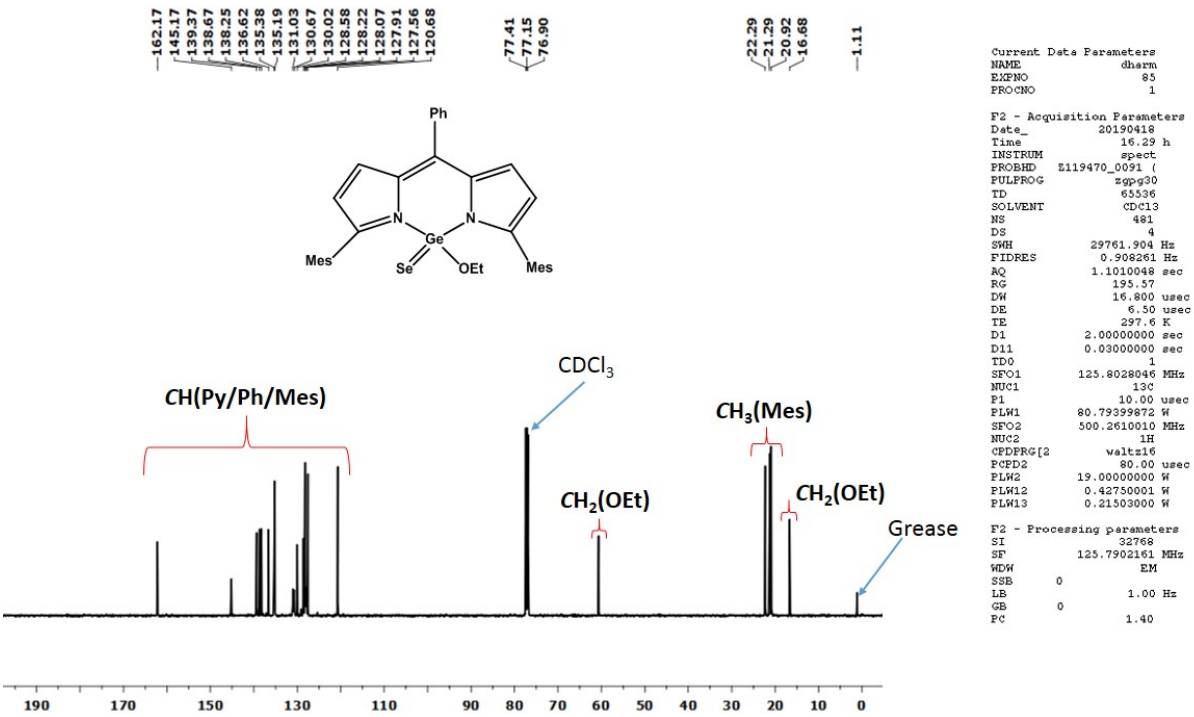


**Figure S28. Air stability of compound 10**

In an open vial, ~250 mg of a freshly prepared sample of compound **10** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S28 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S28 (**b**)] exactly matches that of the freshly prepared sample [Figure S28 (**a**)].

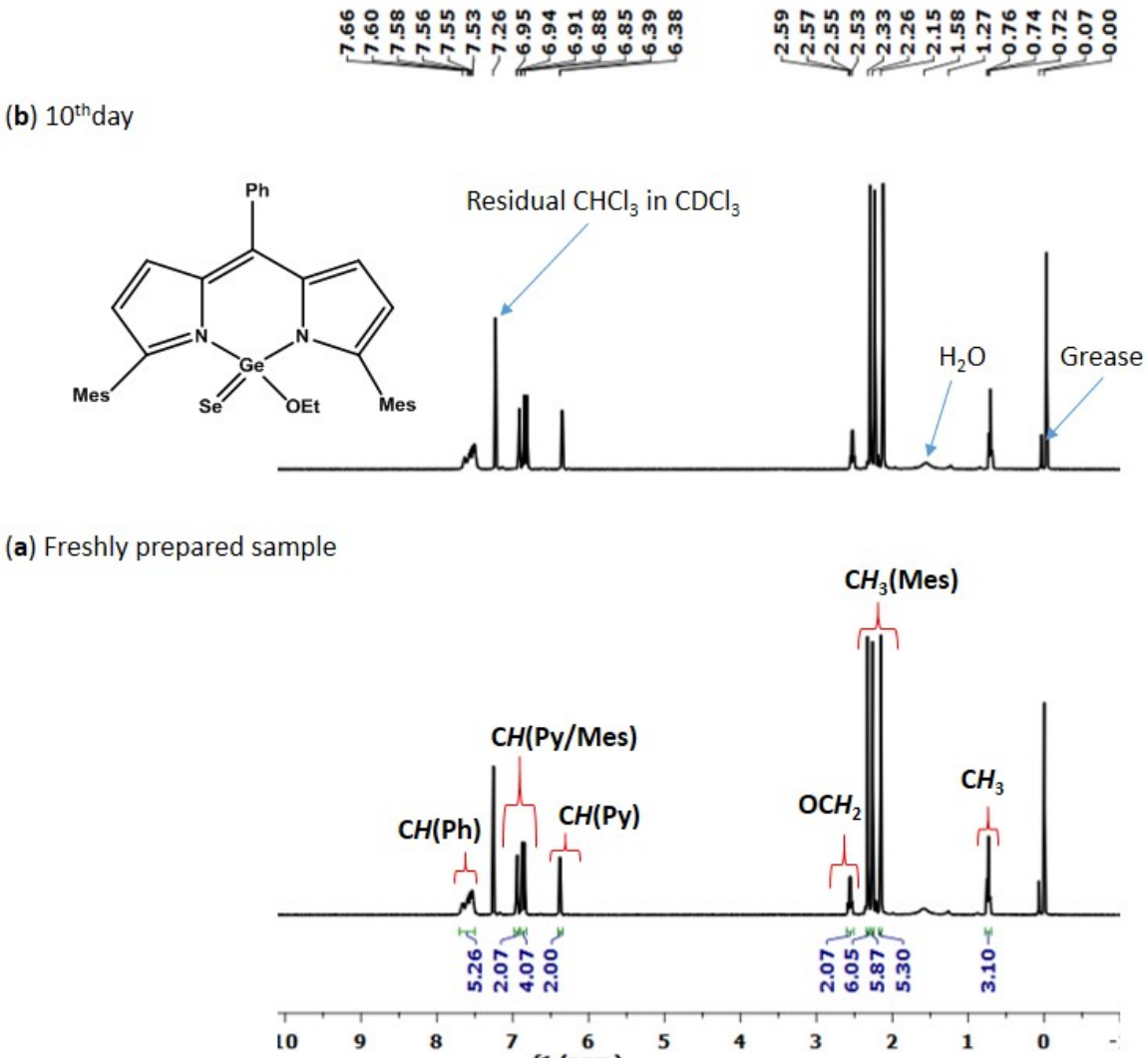


**Figure S29. Stability of compound 10 in water**

Around 10 mg of a freshly prepared sample of compound **10** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S29 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded daily. Up to 5 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 5$^{th}$ day [Figure S29 (**b**)] exactly matches that of the freshly prepared sample [Figure S29 (**a**)].

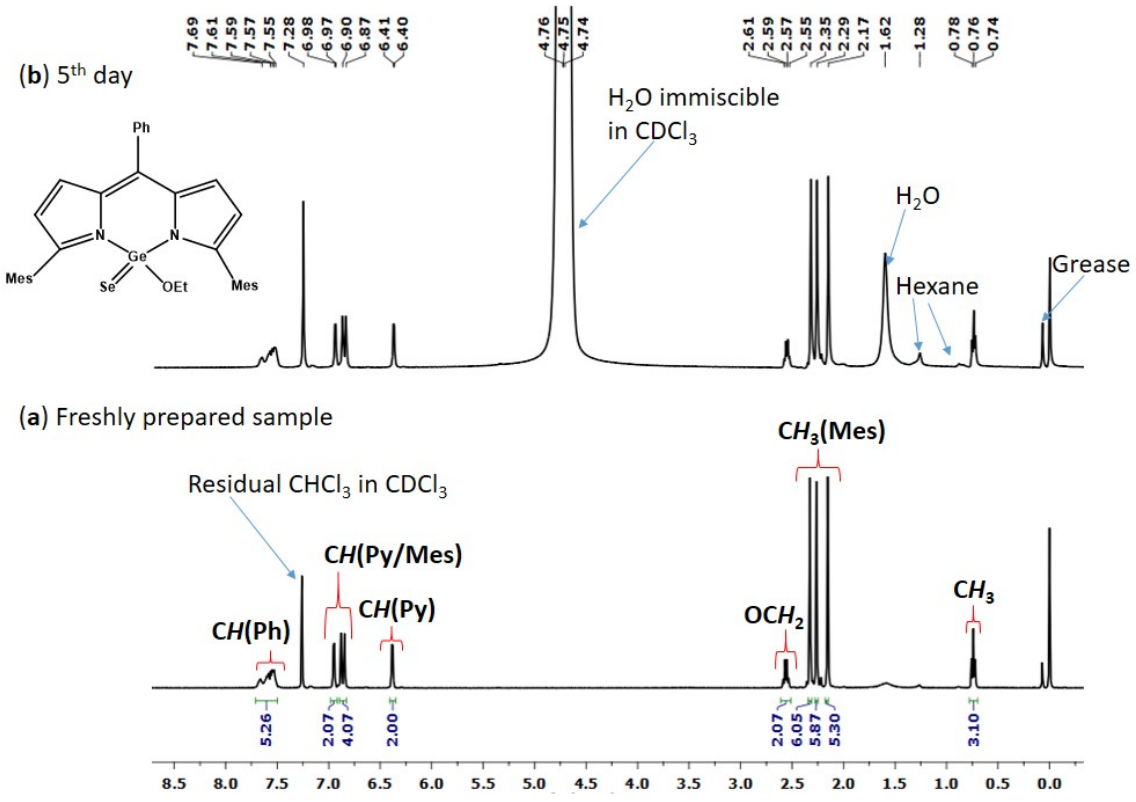


**Figure S30. $^{77}$Se NMR spectrum of compound 10**

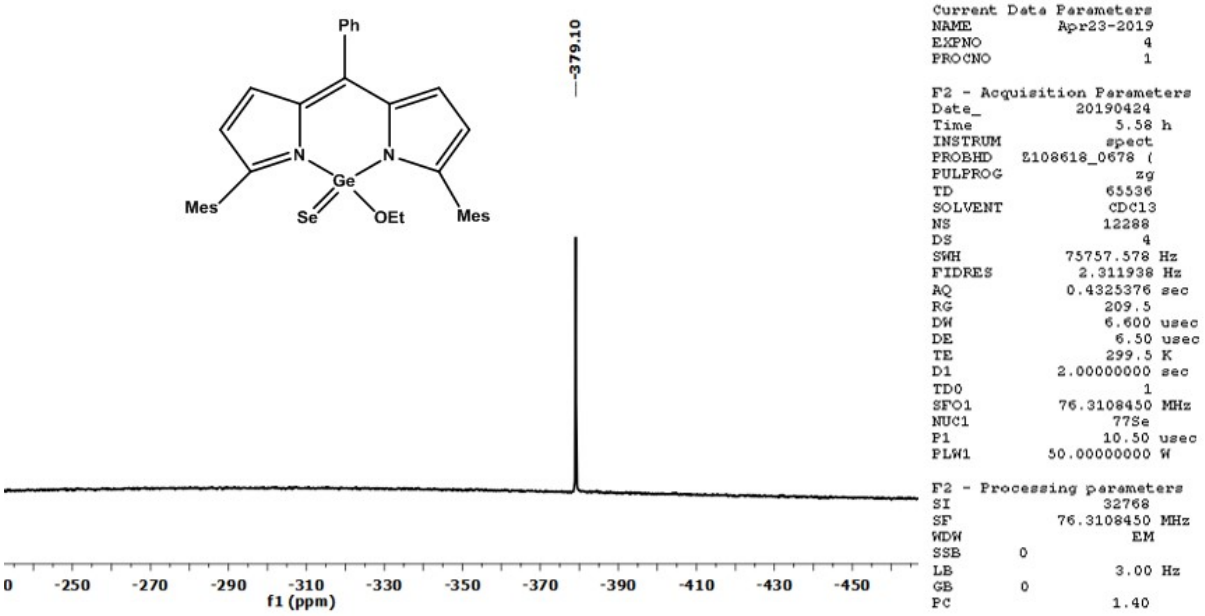


**Figure S31. $^{1}$H NMR spectrum of compound 11**

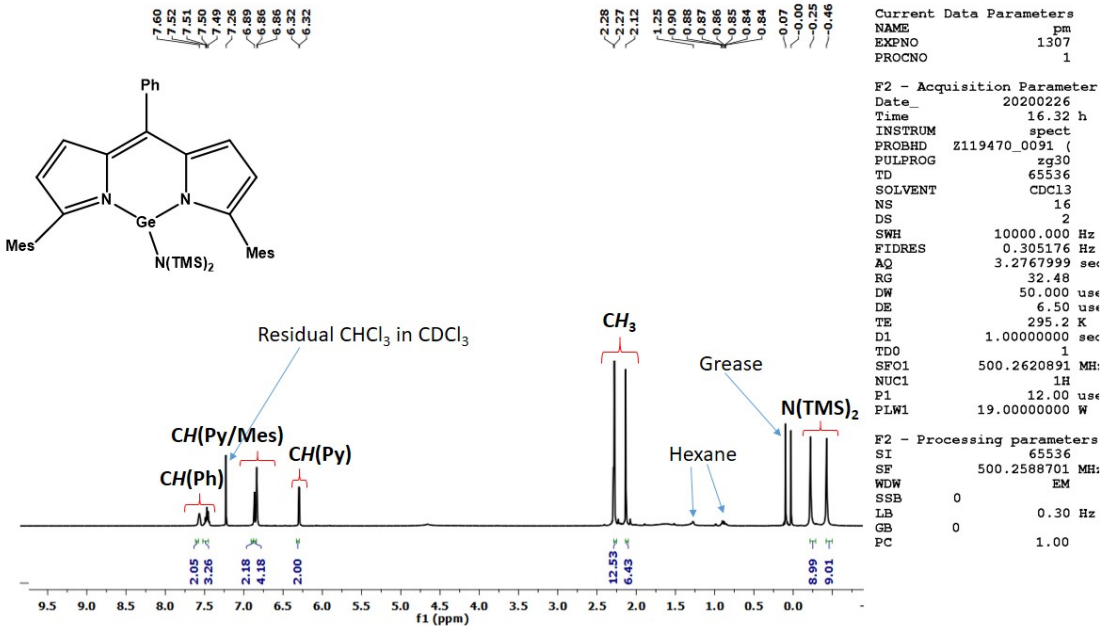



**Figure S32. $^{13}$C NMR spectrum of compound 11**

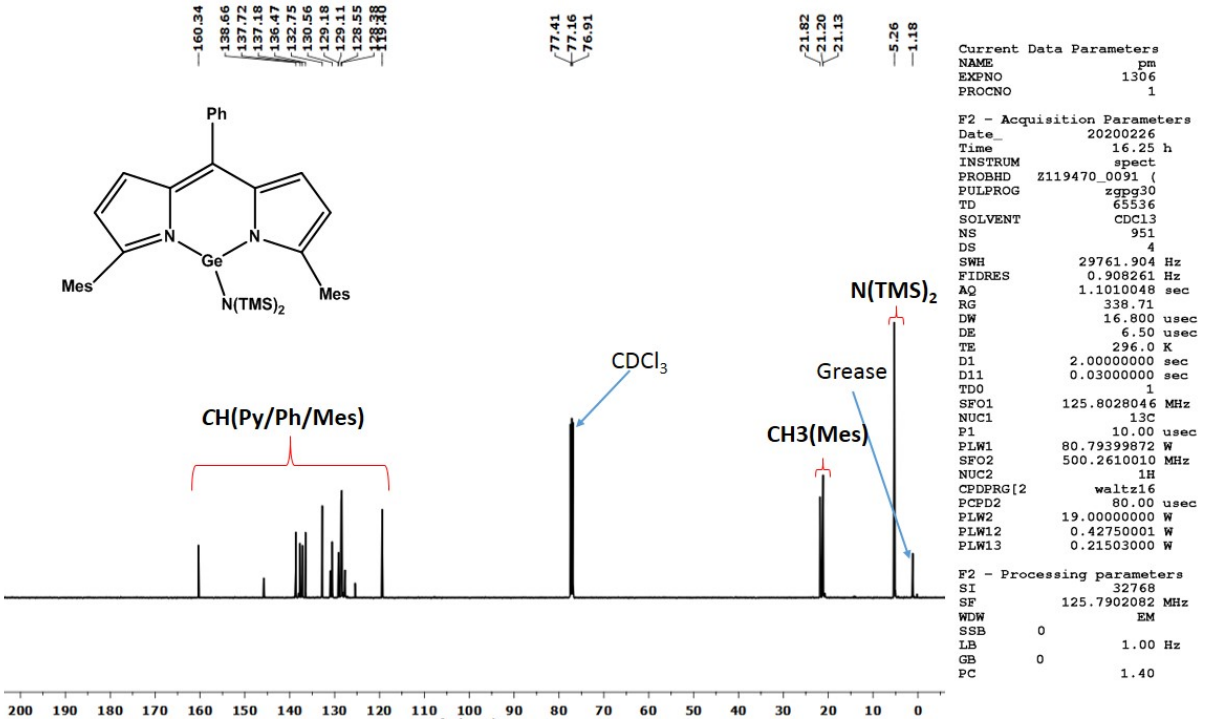


**Figure S33. Air stability of compound 11**

In an open vial, ~250 mg of a freshly prepared sample of compound **11** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S33 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S33 (**b**)] exactly matches that of the freshly prepared sample [Figure S33 (**a**)].

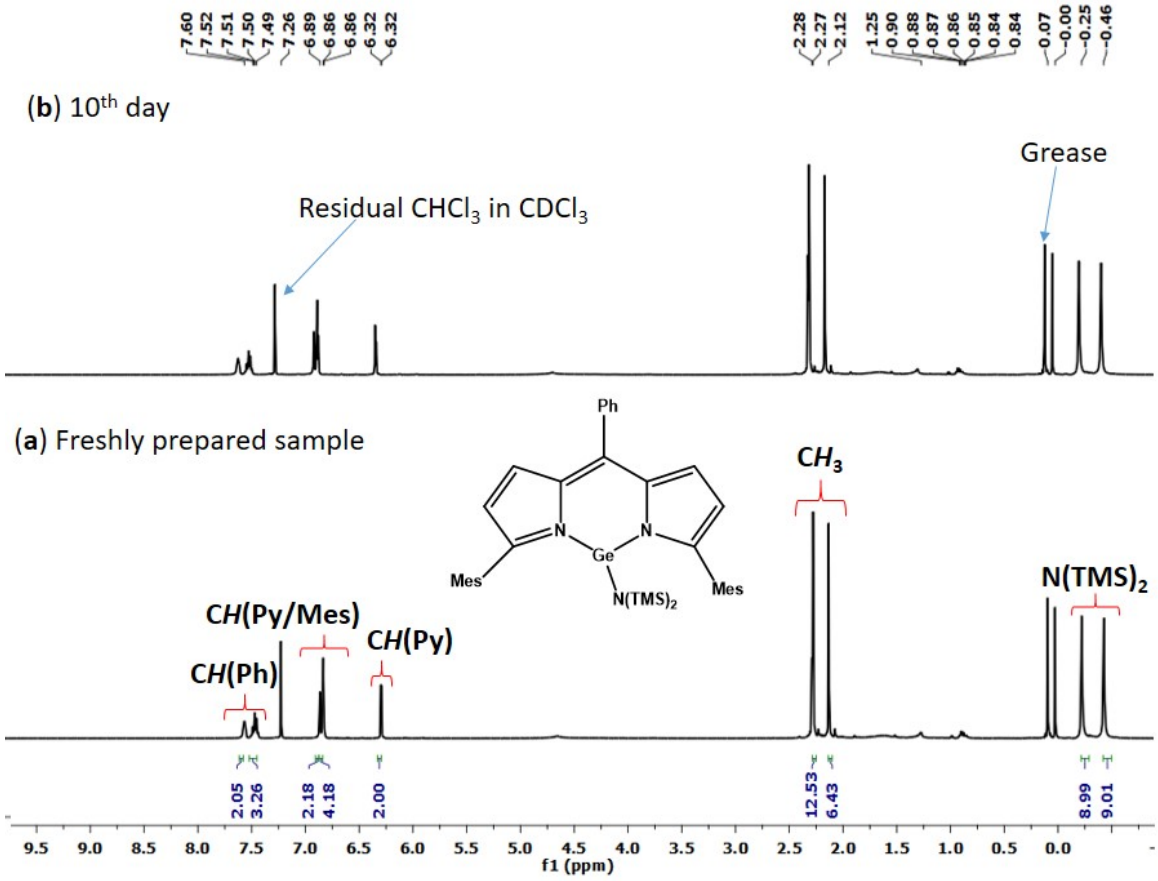


**Figure S34. Stability of compound 11 in water**

Around 10 mg of a freshly prepared sample of compound **11** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S34 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded daily. Up to 4 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 4$^{th}$ day [Figure S34 (**b**)] exactly matches that of the freshly prepared sample [Figure S34 (**a**)].

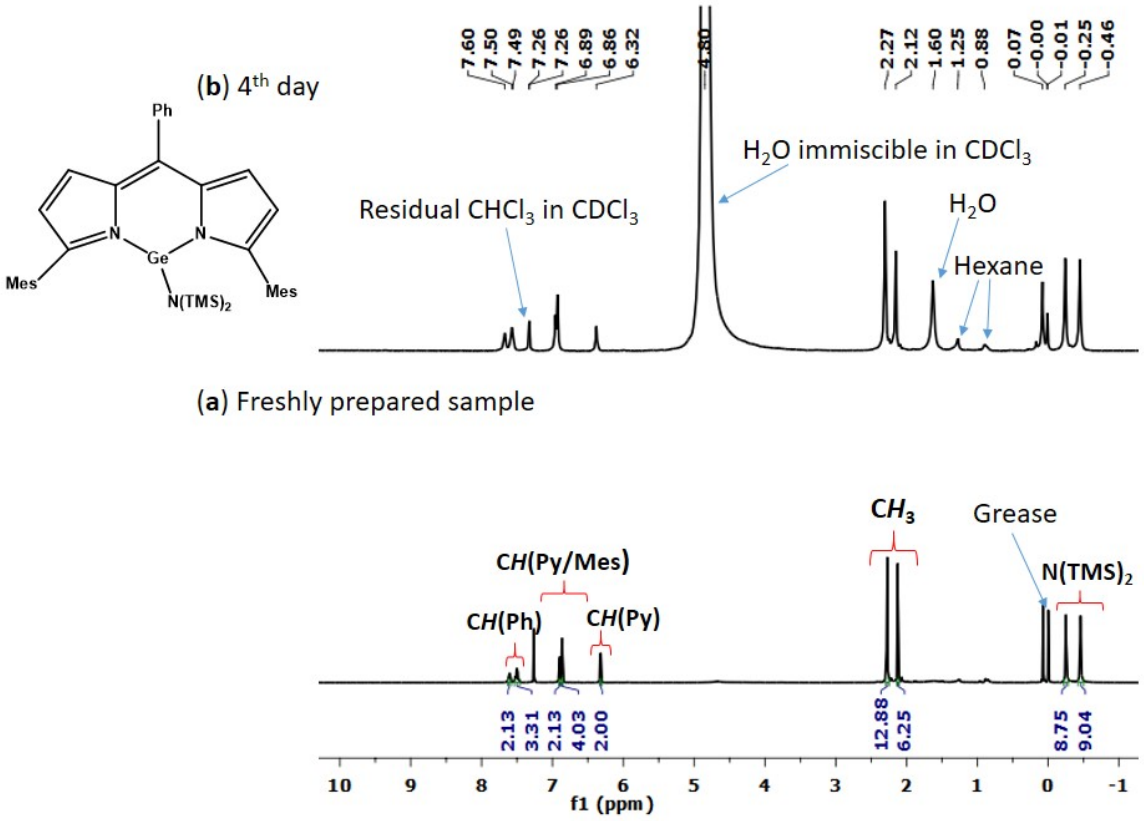
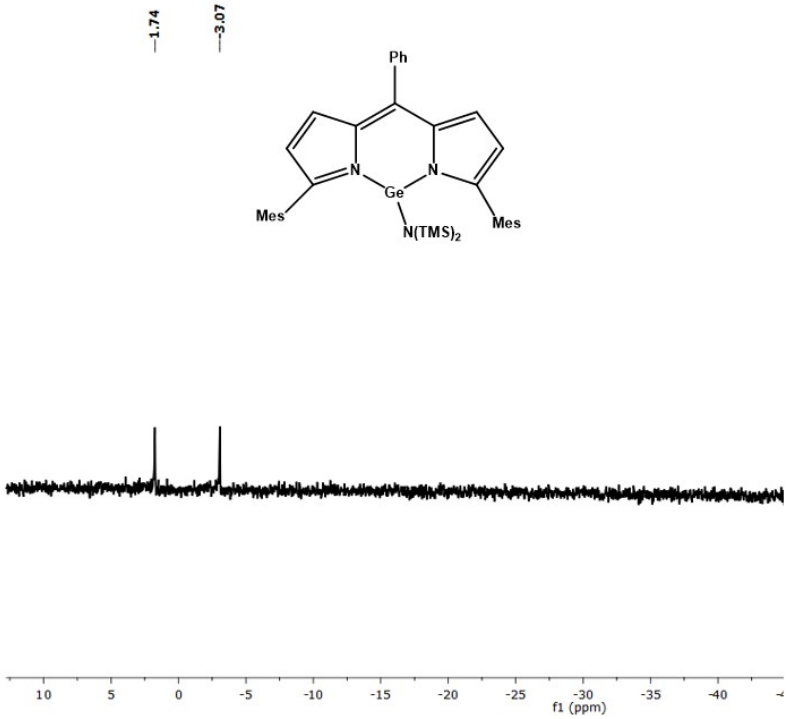


**Figure S35. $^{29}$Si NMR spectrum of compound 11**




```
Current Data Parameters
NAME                  pm
EXPNO                383
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201129
Time              23.45 h
INSTRUM             spect
PROBHD   Z119470_0091 (
PULPROG             zgig
TD                 65536
SOLVENT            CDCl3
NS                   697
DS                     4
SWH            39682.539 Hz
FIDRES          1.211015 Hz
AQ             0.8257536 sec
RG                195.57
DW                12.600 usec
DE                 6.50 usec
TE                    0 K
D1           5.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1          99.3774523 MHz
NUC1                29Si
P1                 10.00 usec
PLW1         45.00000000 W
SFO2         500.2610010 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2         19.00000000 W
PLW12         0.42750001 W

F2 - Processing parameters
SI                 32768
SF           99.3873910 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```

**Figure S36. $^{1}$H NMR spectrum of compound 12**

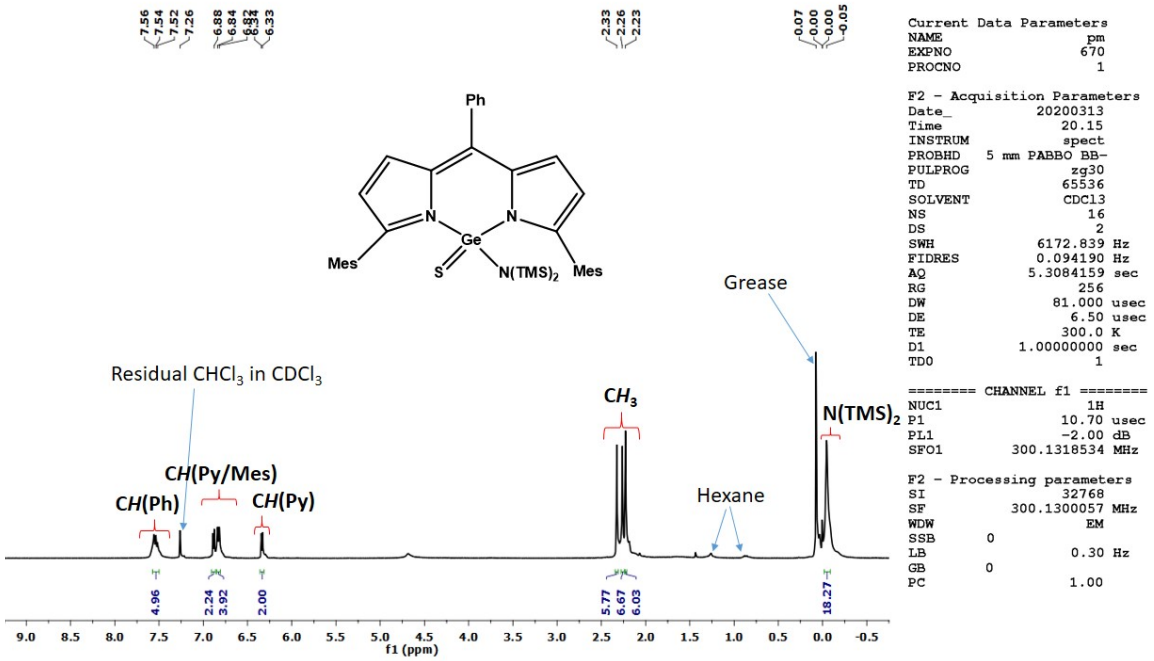



**Figure S37. $^{13}$C NMR spectrum of compound 12**

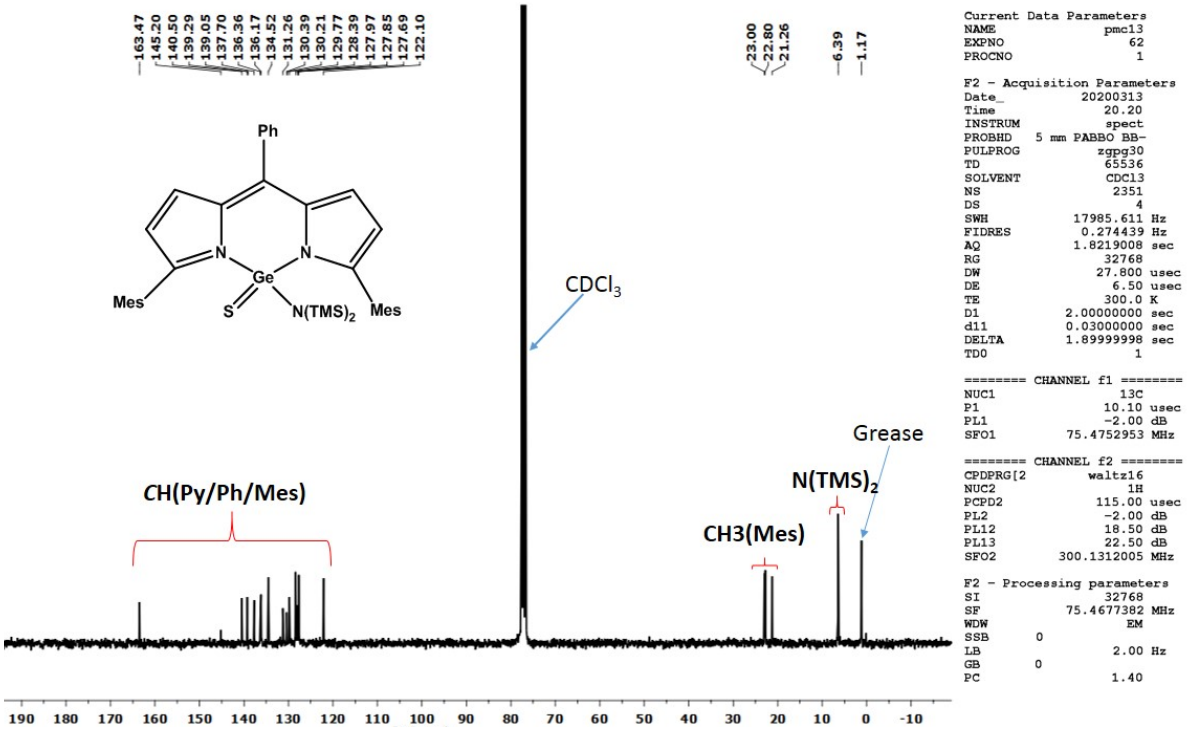


**Figure S38. Air stability of compound 12**

In an open vial, ~250 mg of a freshly prepared sample of compound **12** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S38 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S38 (**b**)] exactly matches that of the freshly prepared sample [Figure S38 (**a**)].

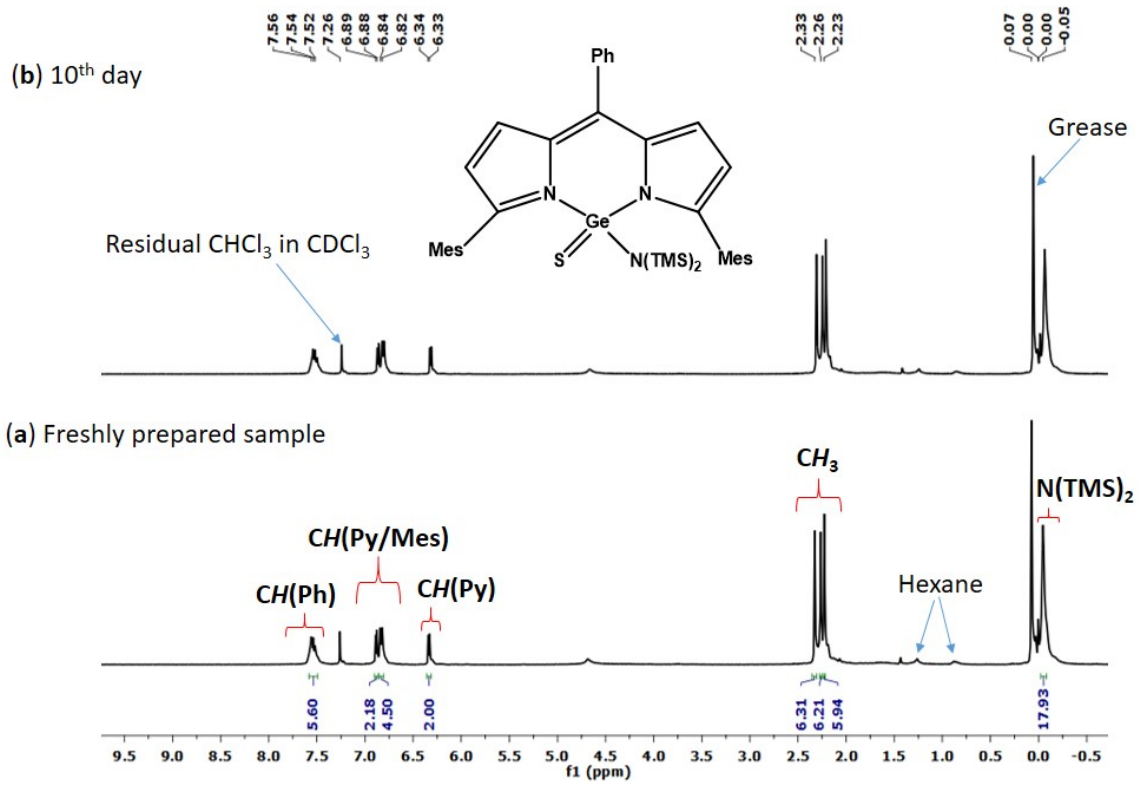


**Figure S39. Stability of compound 12 in water**

Around 10 mg of a freshly prepared sample of compound **12** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S39 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded daily. Up to 2 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 2nd day [Figure S39 (**b**)] exactly matches that of the freshly prepared sample [Figure S39 (**a**)].

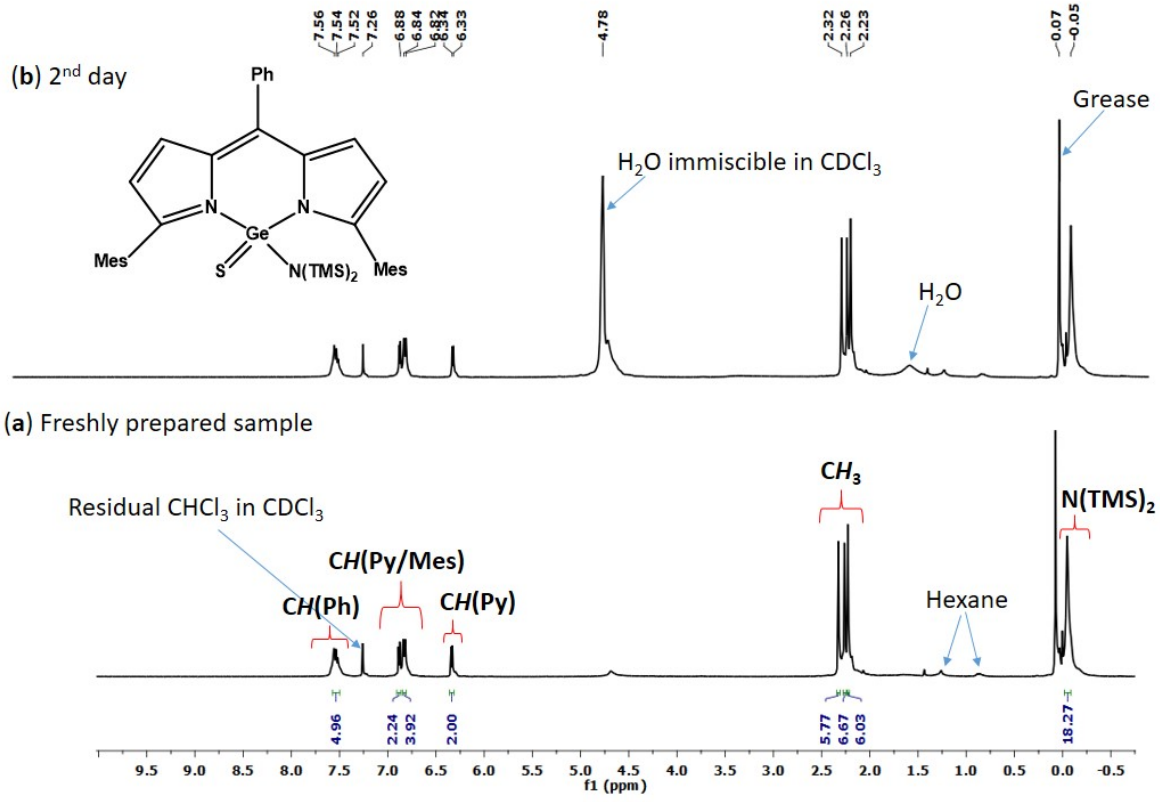
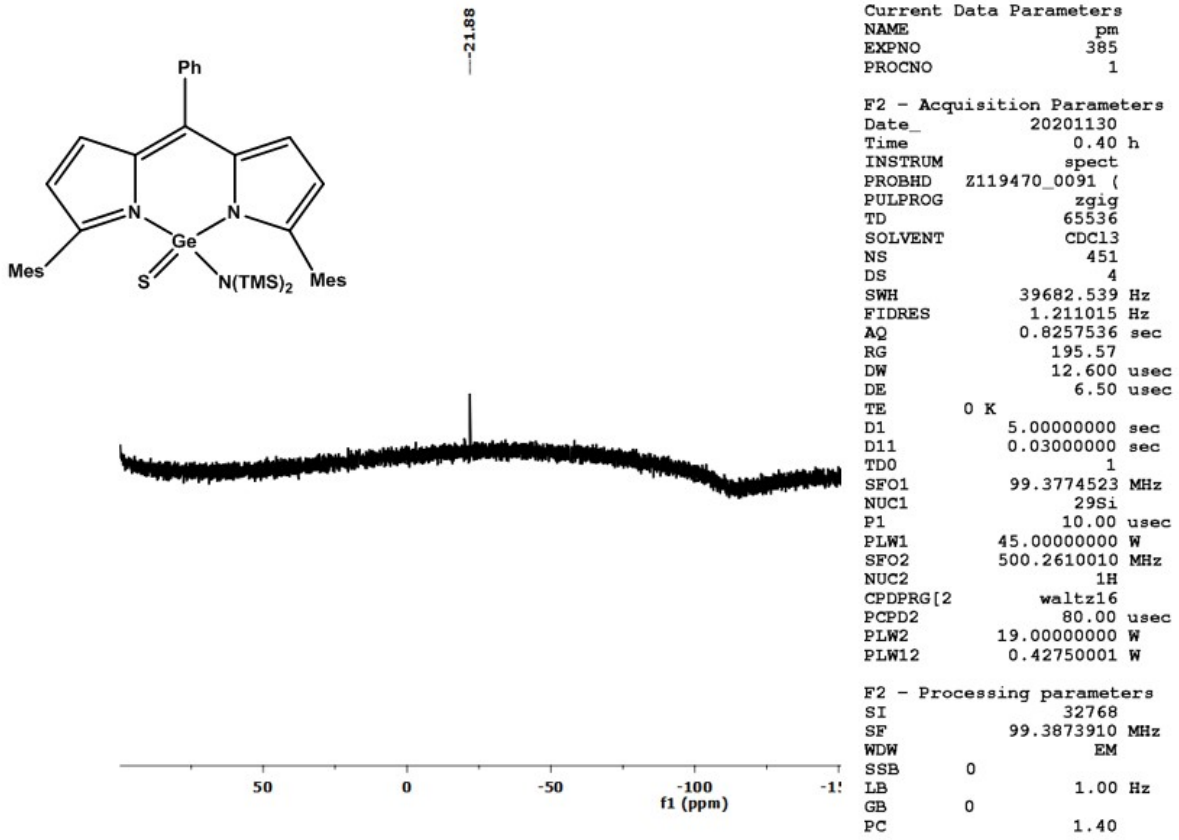


**Figure S40. $^{29}$Si NMR spectrum of compound 12**




```
Current Data Parameters
NAME                  pm
EXPNO                385
PROCNO                 1

F2 - Acquisition Parameters
Date_           20201130
Time                0.40 h
INSTRUM            spect
PROBHD   Z119470_0091 (
PULPROG             zgig
TD                 65536
SOLVENT            CDCl3
NS                   451
DS                     4
SWH            39682.539 Hz
FIDRES          1.211015 Hz
AQ              0.8257536 sec
RG                 195.57
DW                 12.600 usec
DE                  6.50 usec
TE        0 K
D1             5.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1           99.3774523 MHz
NUC1                29Si
P1                 10.00 usec
PLW1          45.00000000 W
SFO2          500.2610010 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2          19.00000000 W
PLW12          0.42750001 W

F2 - Processing parameters
SI                 32768
SF             99.3873910 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

**Figure S41. $^{1}$H NMR spectrum of compound 13**

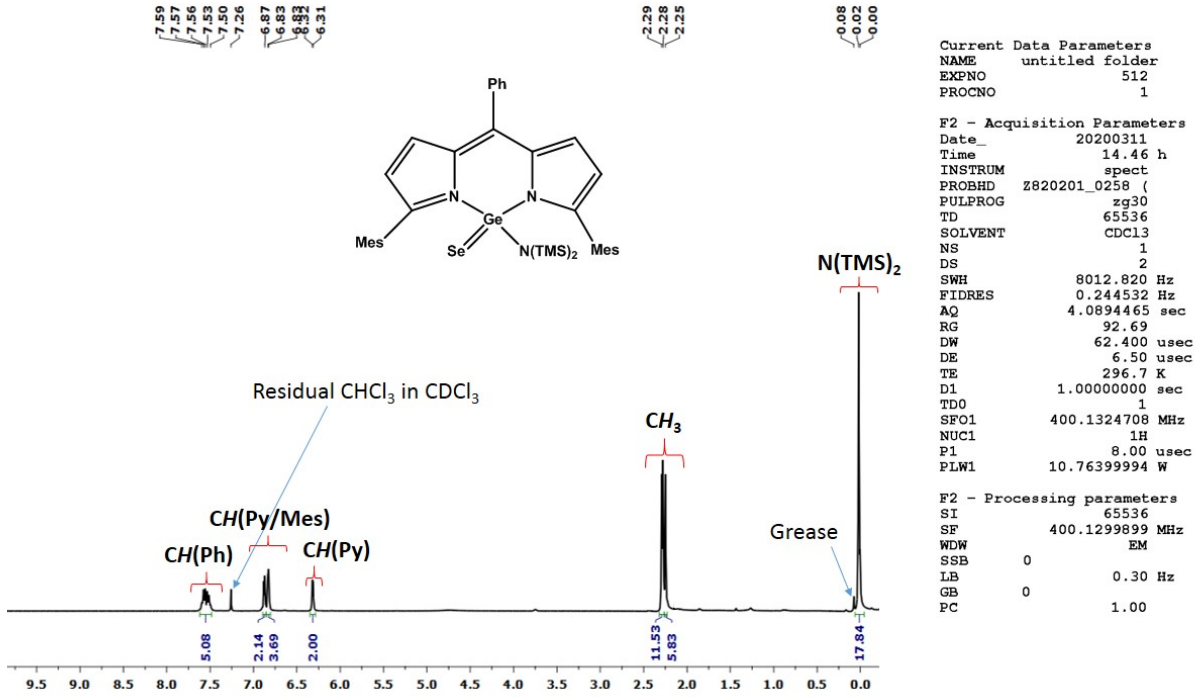



**Figure S42. $^{13}$C NMR spectrum of compound 13**

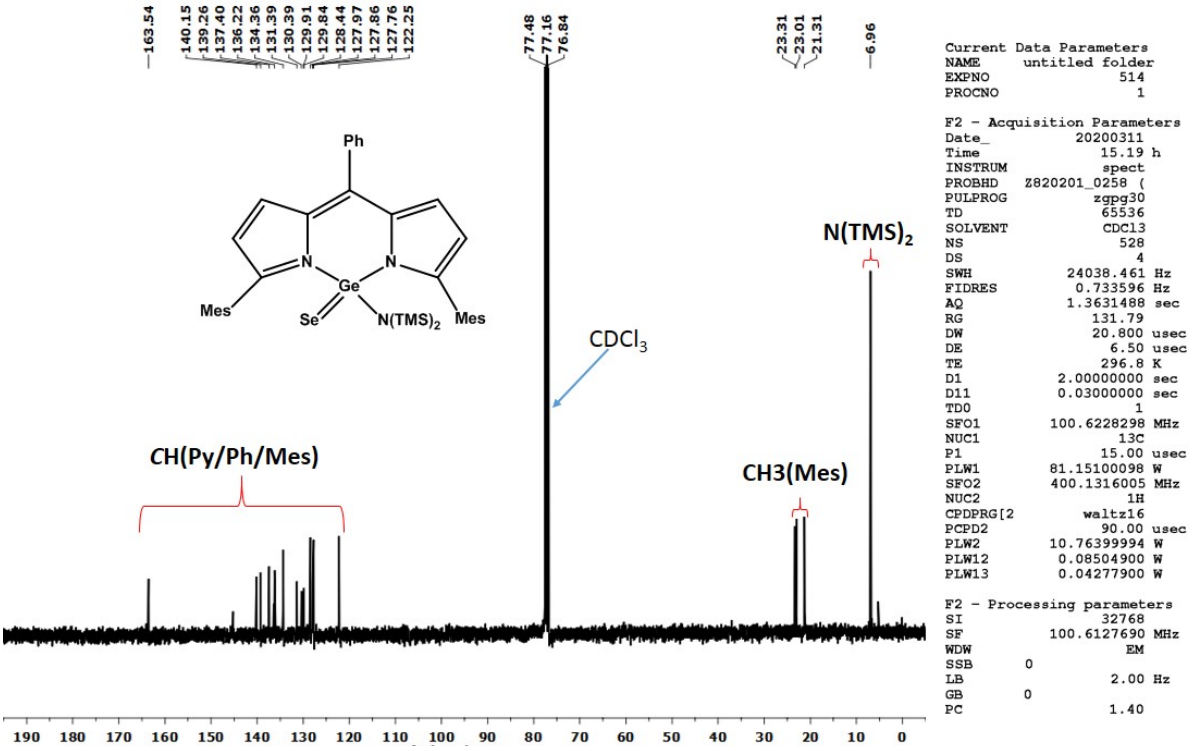


**Figure S43. Air stability of compound 13**

In an open vial, ~250 mg of a freshly prepared sample of compound **13** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S43 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S43 (**b**)] exactly matches that of the freshly prepared sample [Figure S43 (**a**)].

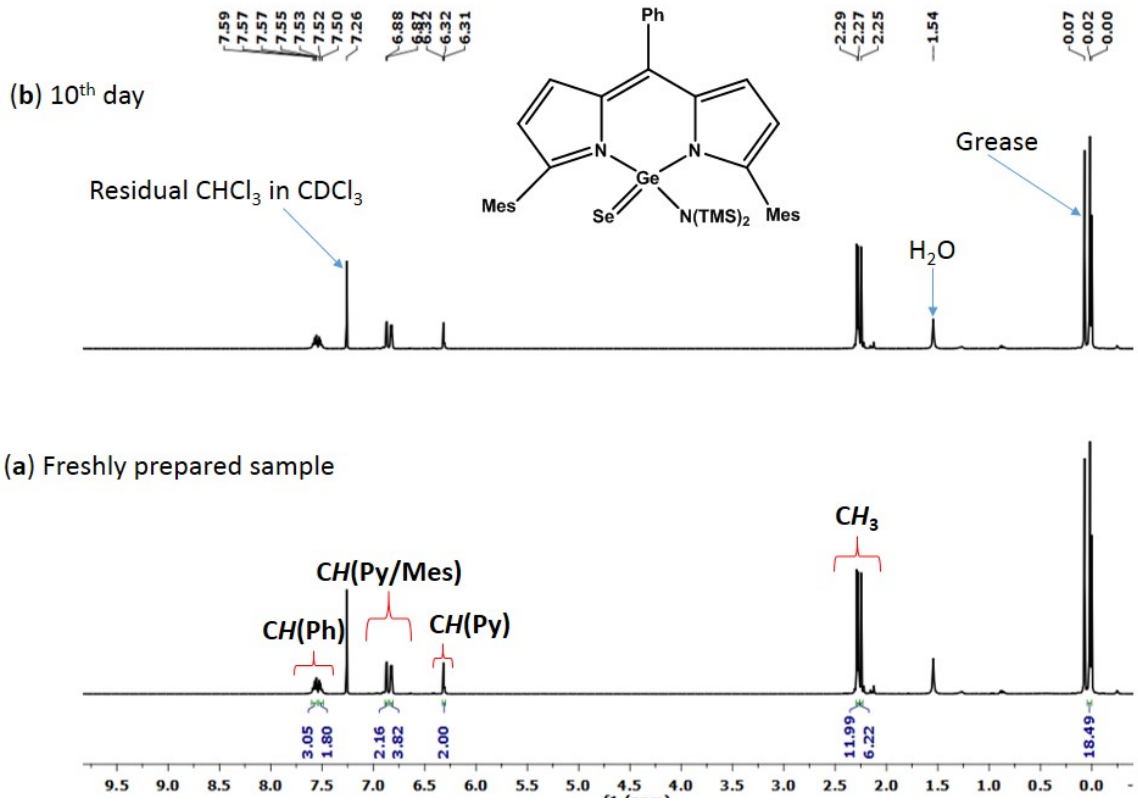


**Figure S44. Stability of compound 13 in water**

Around 10 mg of a freshly prepared sample of compound **13** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S44 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded daily. Up to 5 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 5$^{th}$ day [Figure S44 (**b**)] exactly matches that of the freshly prepared sample [Figure S44 (**a**)].

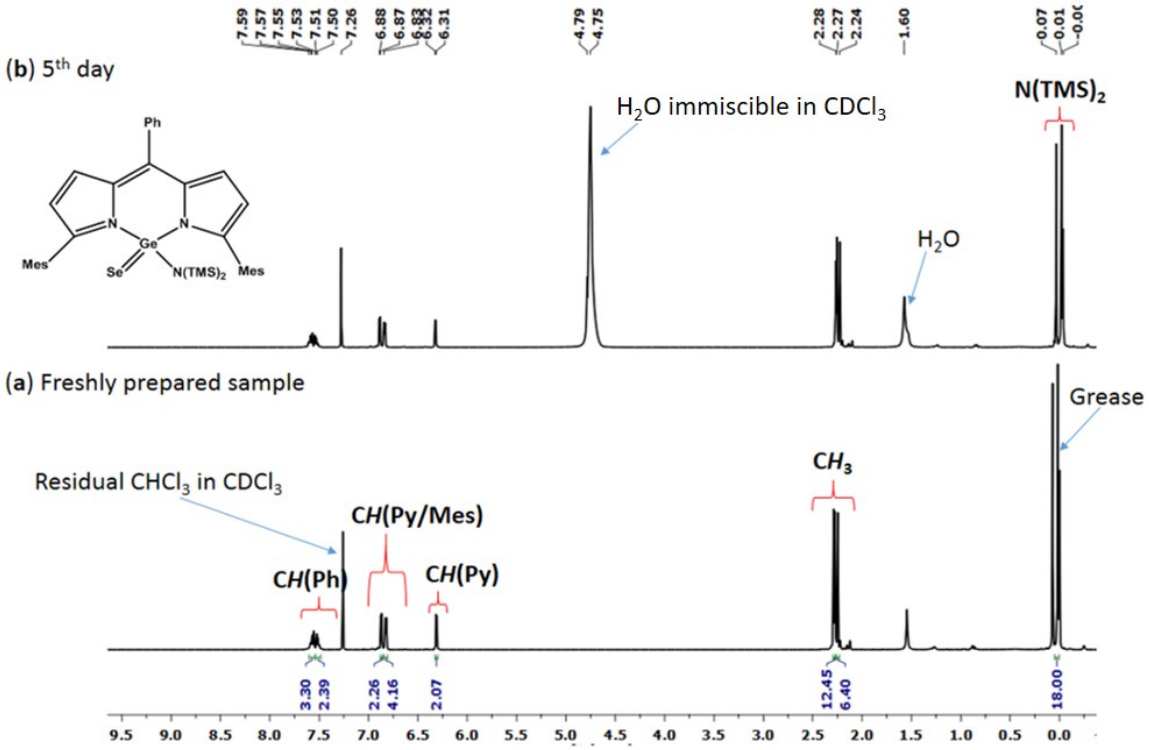


**Figure S45. $^{77}$Se NMR spectrum of compound 13**

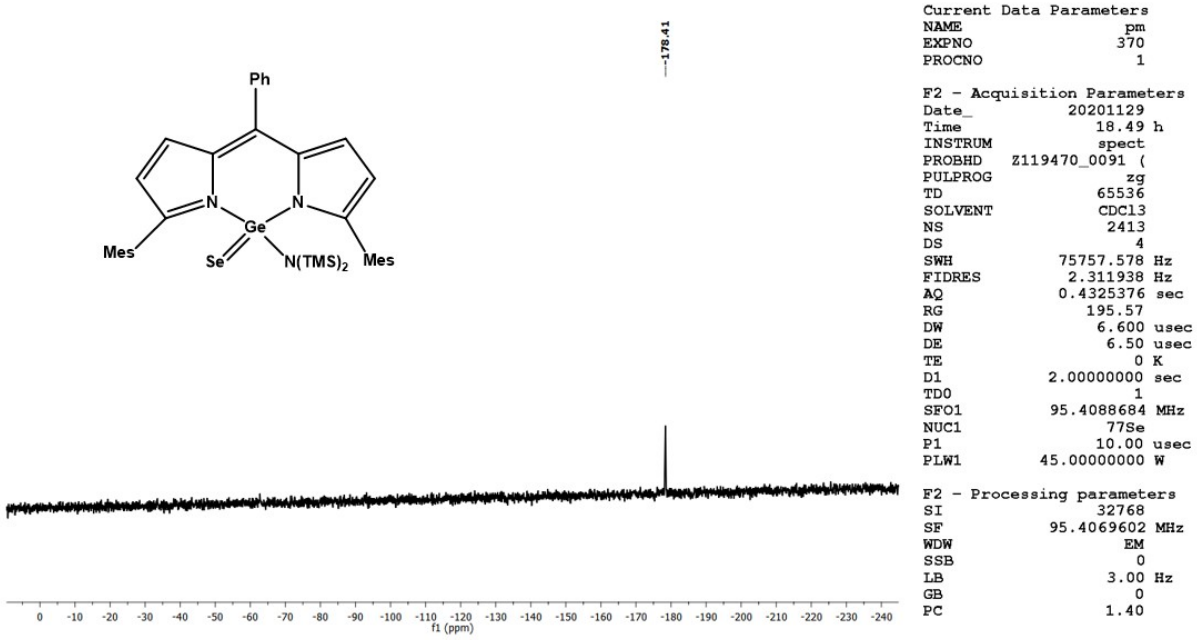



**Figure S46. $^{29}$Si NMR spectrum of compound 13**

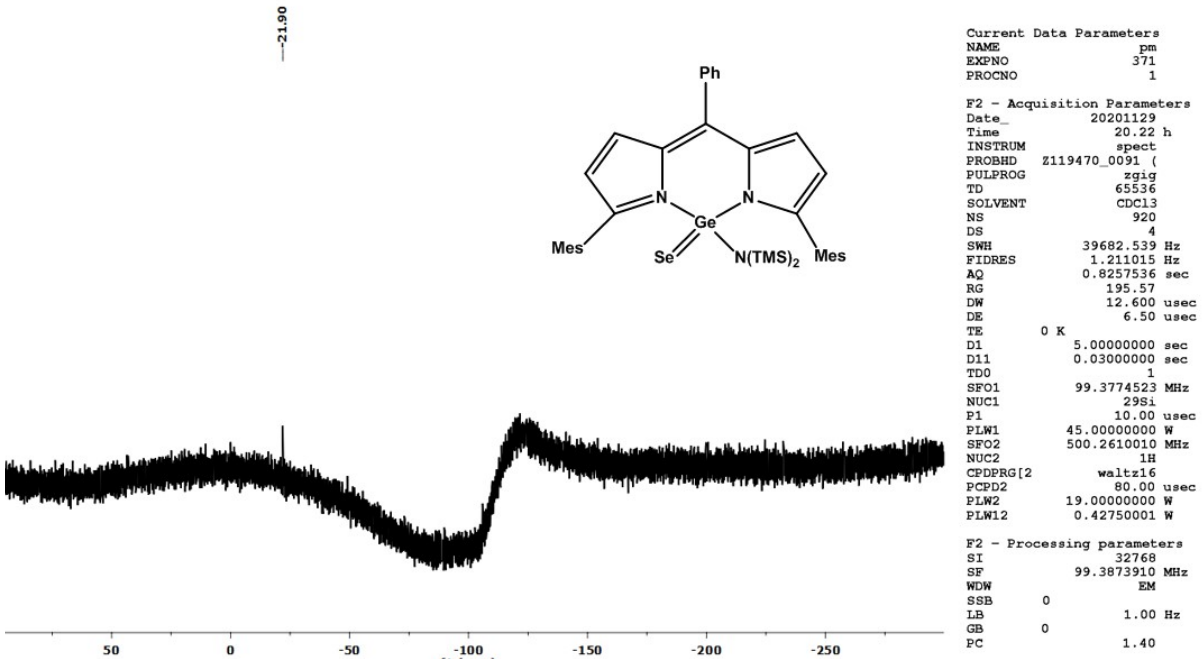


**Figure S47. $^{1}$H NMR spectrum of compound 14**

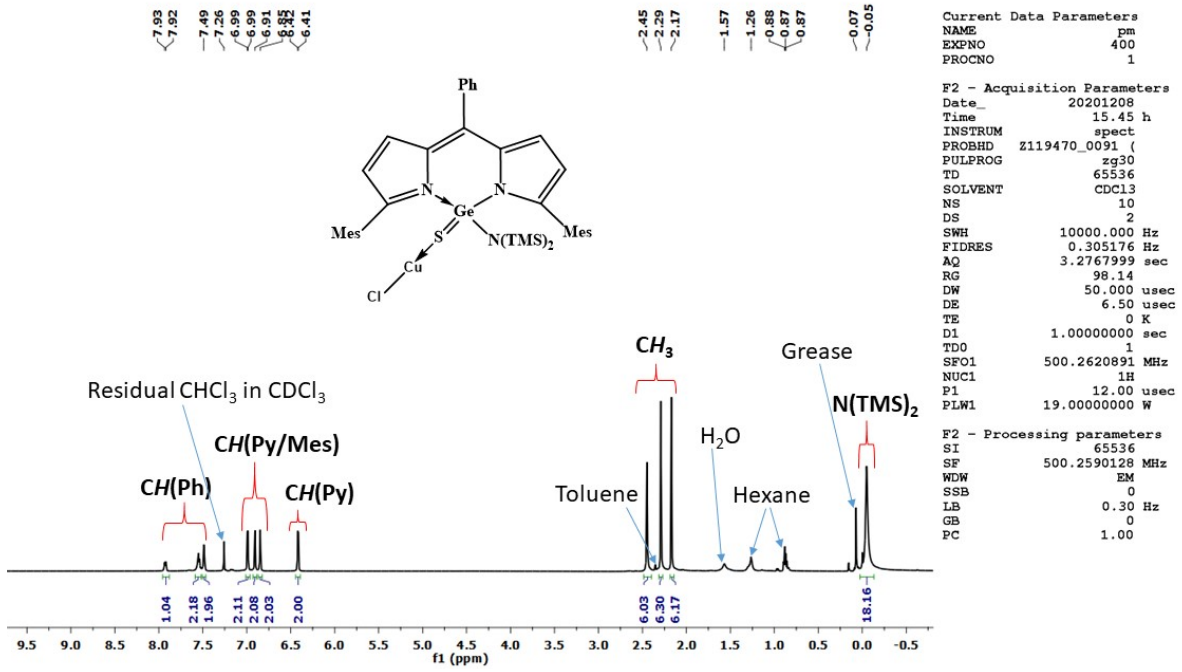



**Figure S48. $^{13}$C NMR spectrum of compound 14**

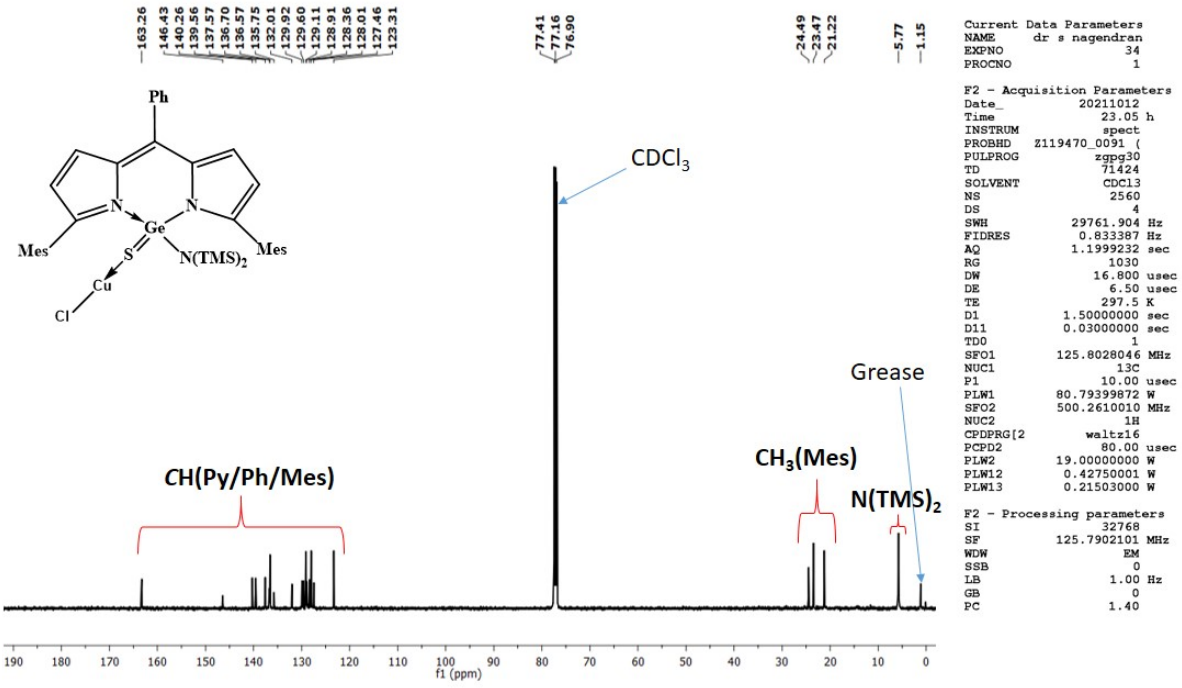


**Figure S49. Air stability of compound 14**

In an open vial, ~250 mg of a freshly prepared sample of compound **14** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S49 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S49 (**b**)] exactly matches that of the freshly prepared sample [Figure S49 (**a**)].

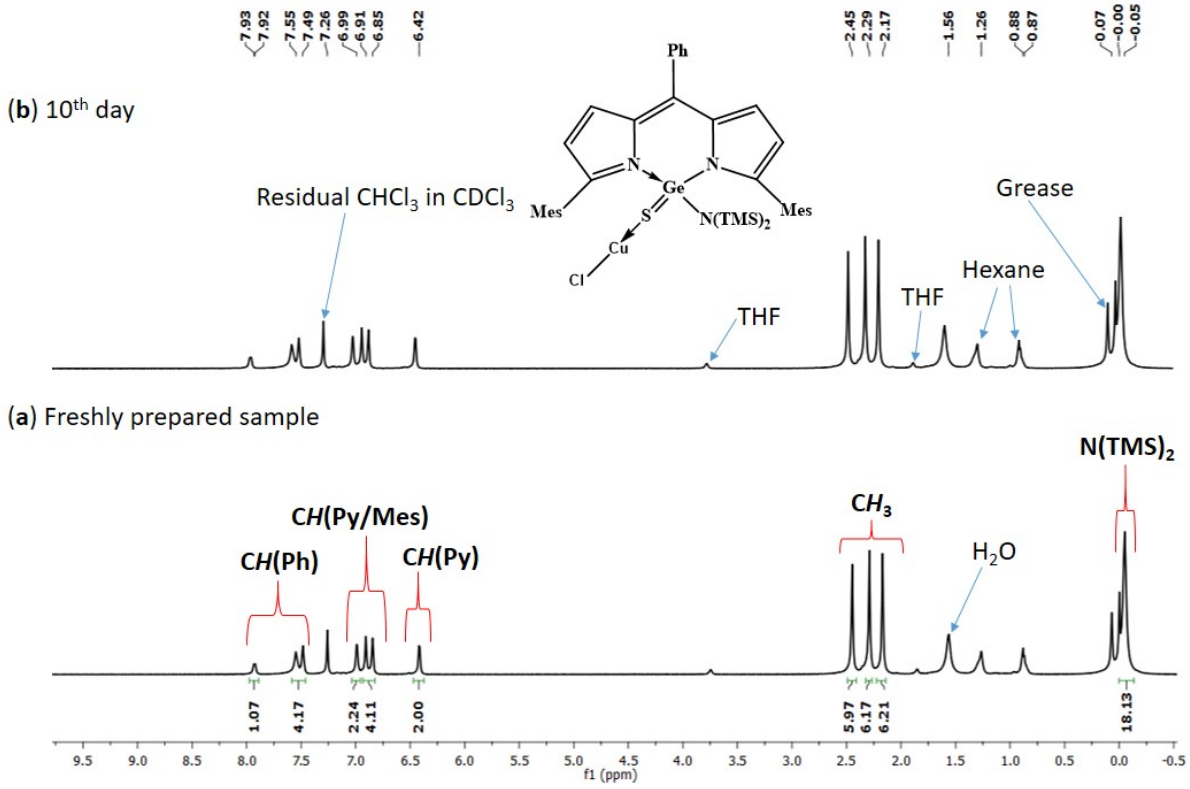


**Figure S50. Stability of compound 14 in water**

Around 10 mg of a freshly prepared sample of compound **14** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S50 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded every hour. Up to 3 h, we did not see any decomposition; the $^1H$ NMR spectrum recorded after 3 h [Figure S50 (**b**)] from the addition of water exactly matches that of the freshly prepared sample [Figure S50 (**a**)].

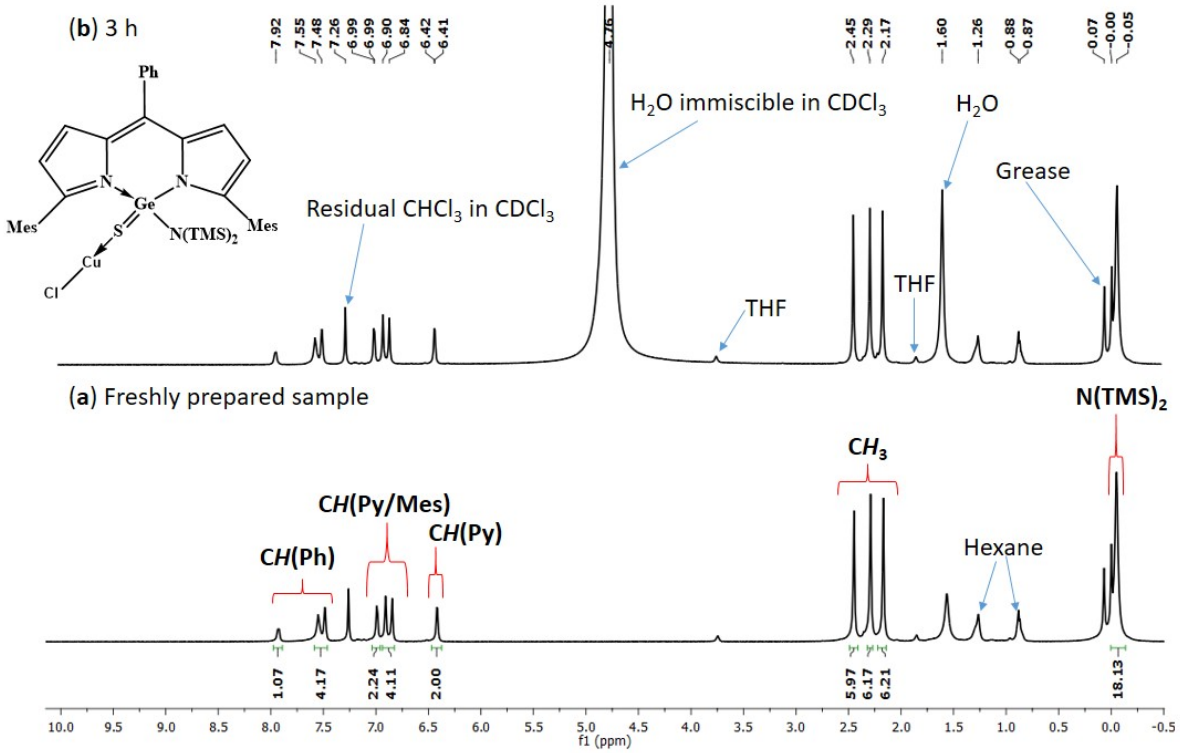
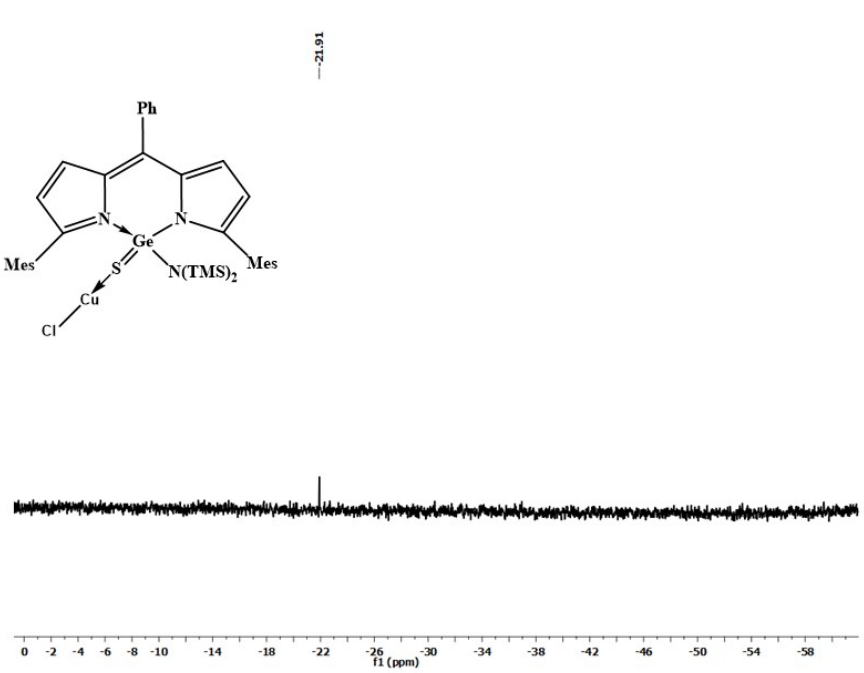


**Figure S51. $^{29}$Si NMR spectrum of compound 14**




```
Current Data Parameters
NAME                   pm
EXPNO                 438
PROCNO                  1

F2 - Acquisition Parameters
Date_            20201214
Time                9.51 h
INSTRUM            spect
PROBHD    Z119470_0091 (
PULPROG             zgig
TD                 65536
SOLVENT            CDCl3
NS                  5985
DS                     4
SWH            39682.539 Hz
FIDRES          1.211015 Hz
AQ             0.8257536 sec
RG                195.57
DW                12.600 usec
DE                 6.50 usec
TE                    0 K
D1             5.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1           99.3774523 MHz
NUC1                29Si
P1                 10.00 usec
PLW1          45.00000000 W
SFO2          500.2610010 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2          19.00000000 W
PLW12          0.42750001 W

F2 - Processing parameters
SI                 32768
SF            99.3873910 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                  1.40
```

**Figure S52. $^{1}$H NMR spectrum of compound 15**

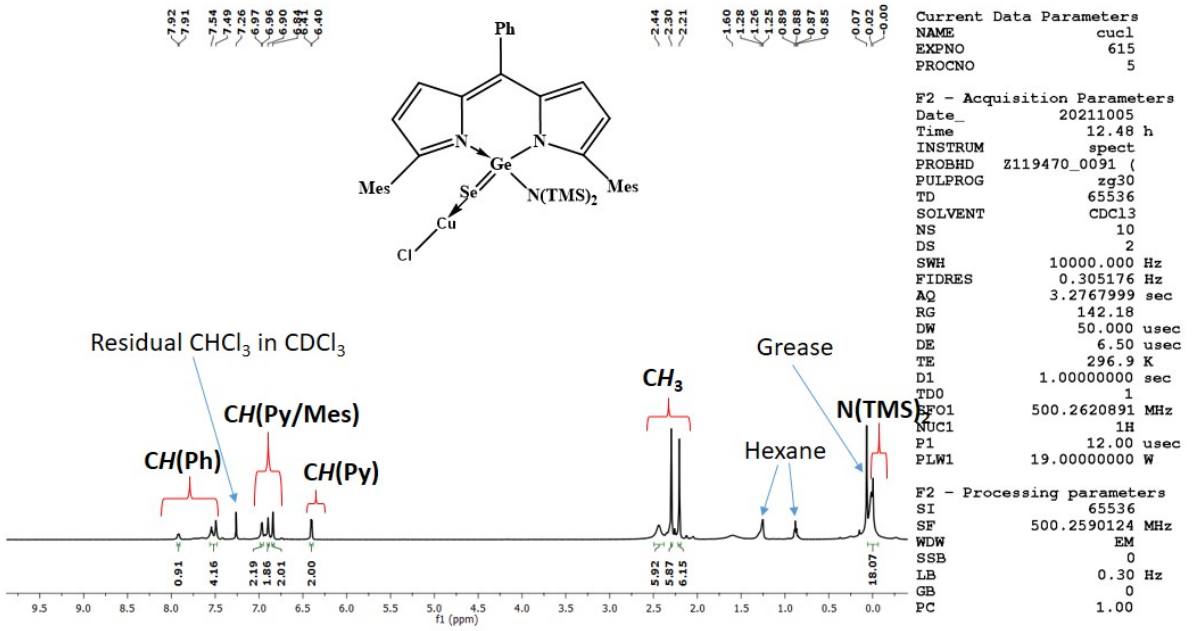



**Figure S53. $^{13}$C NMR spectrum of compound 15**

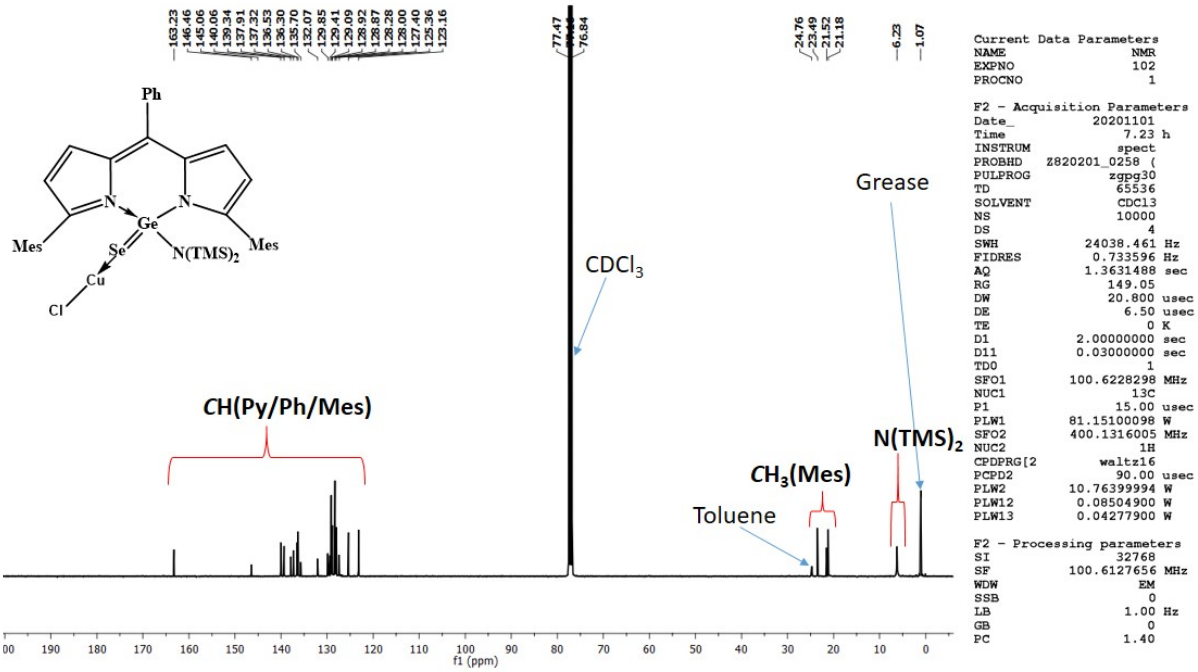


**Figure S54. Air stability of compound 15**

In an open vial, ~250 mg of a freshly prepared sample of compound **15** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S54 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S54 (**b**)] exactly matches that of the freshly prepared sample [Figure S54 (**a**)].

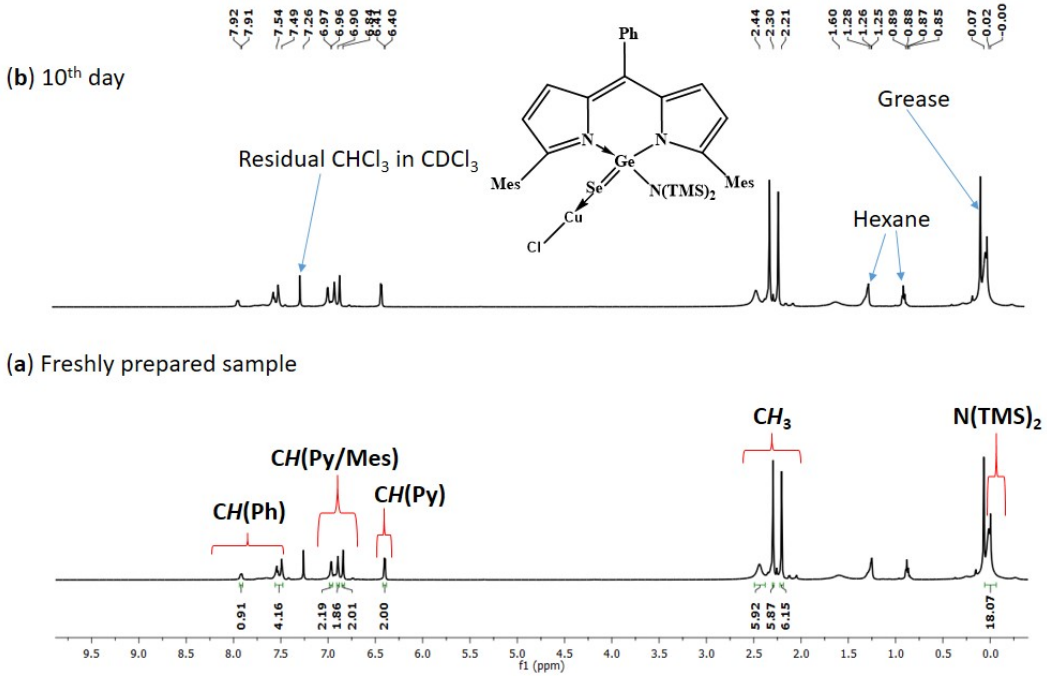


**Figure S55. Stability of compound 15 in water**

Around 10 mg of a freshly prepared sample of compound **15** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S55 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded every hour. Up to 3 h, we did not see any decomposition; the $^1H$ NMR spectrum recorded after 3 h [Figure S55 (**b**)] from the addition of water exactly matches that of the freshly prepared sample [Figure S55 (**a**)].

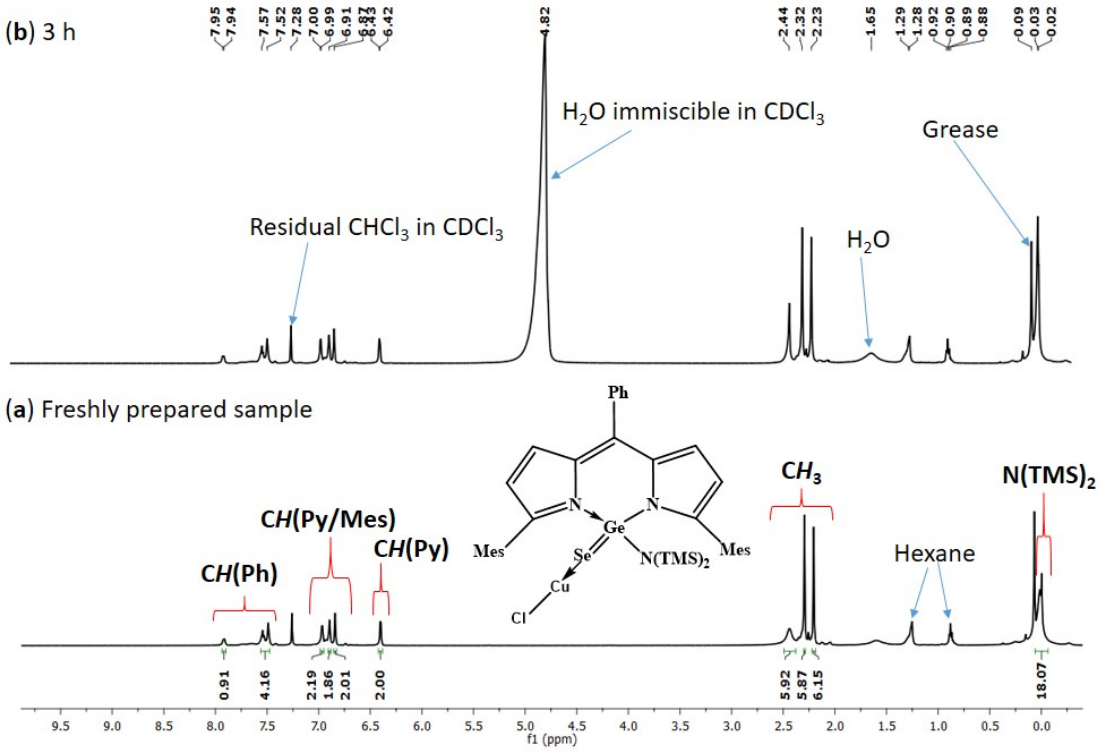


**Figure S56. $^{29}$Si NMR spectrum of compound 15**

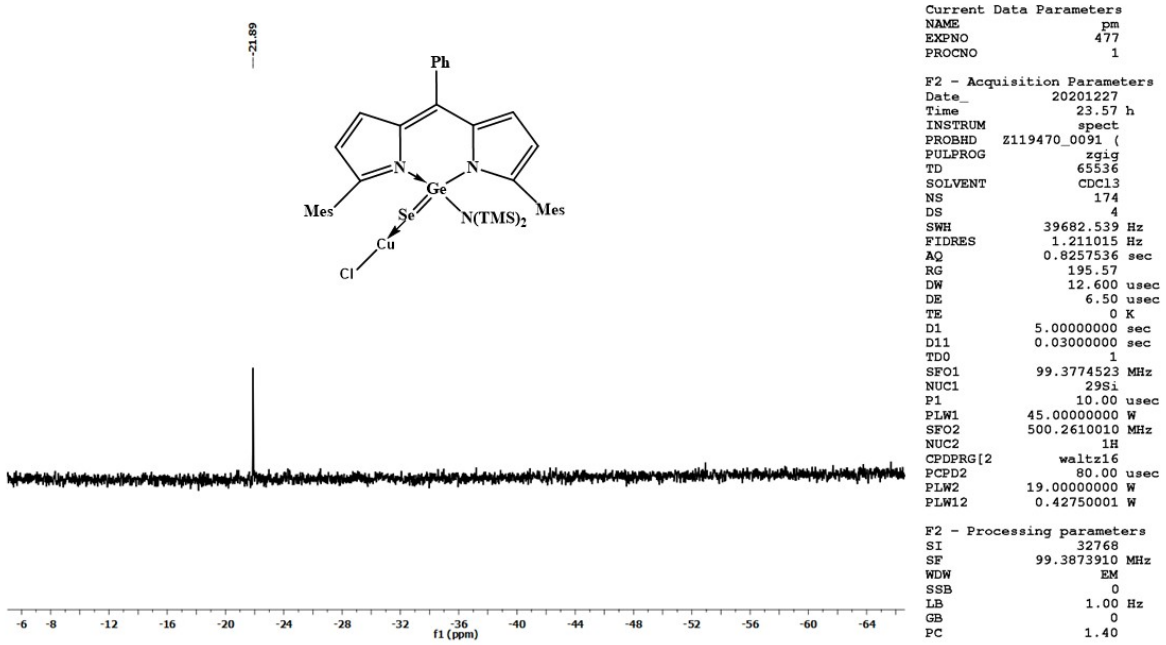



**Figure S57. $^{77}$Se NMR spectrum of compound 15**

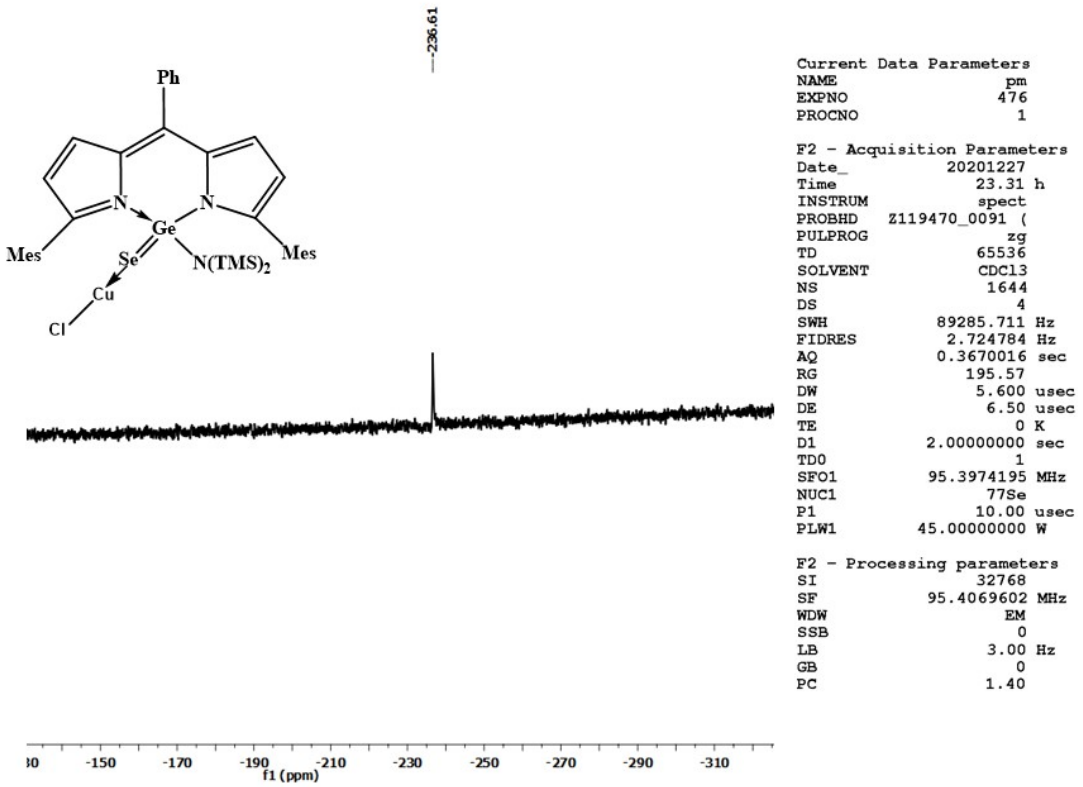


**Figure S58. $^{1}$H NMR spectrum of compound 16**

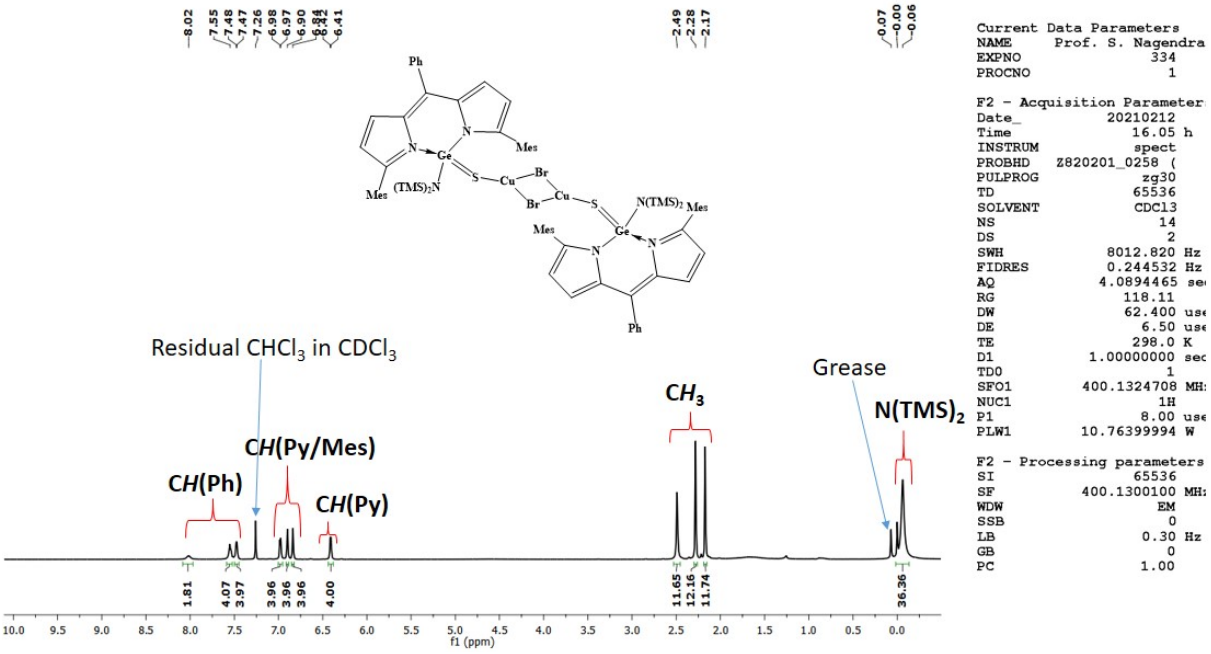



**Figure S59. $^{13}$C NMR spectrum of compound 16**

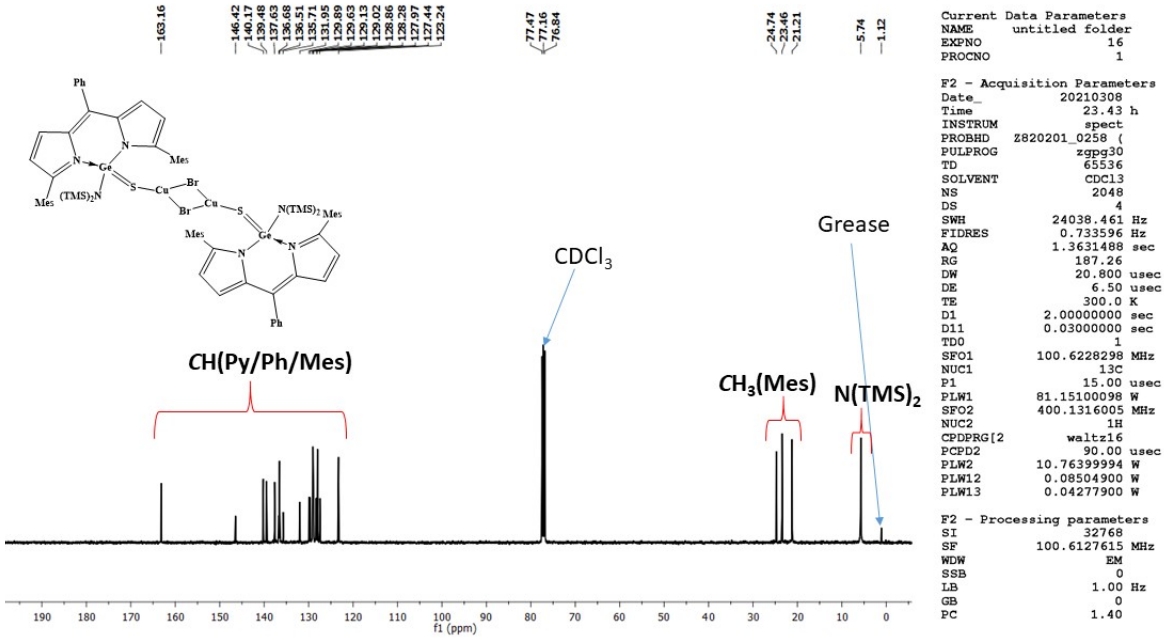


**Figure S60. Air stability of compound 16**

In an open vial, ~250 mg of a freshly prepared sample of compound **16** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S60 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S60 (**b**)] exactly matches that of the freshly prepared sample [Figure S60 (**a**)].

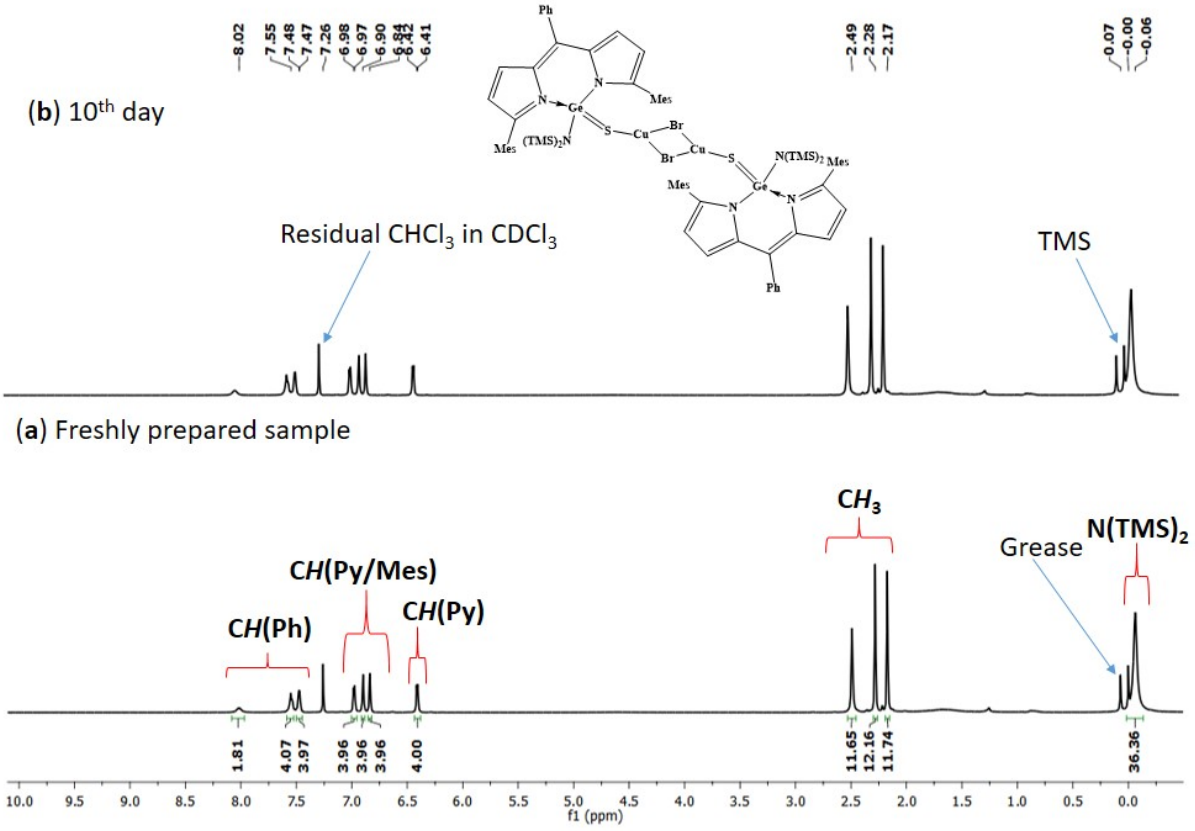


**Figure S61. Stability of compound 16 in water**

Around 10 mg of a freshly prepared sample of compound **16** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S61 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded every 6 h. Up to 24 h, we did not see any decomposition; the $^1H$ NMR spectrum recorded after 24 h [Figure S61 (**b**)] from the addition of water exactly matches that of the freshly prepared sample [Figure S61 (**a**)].

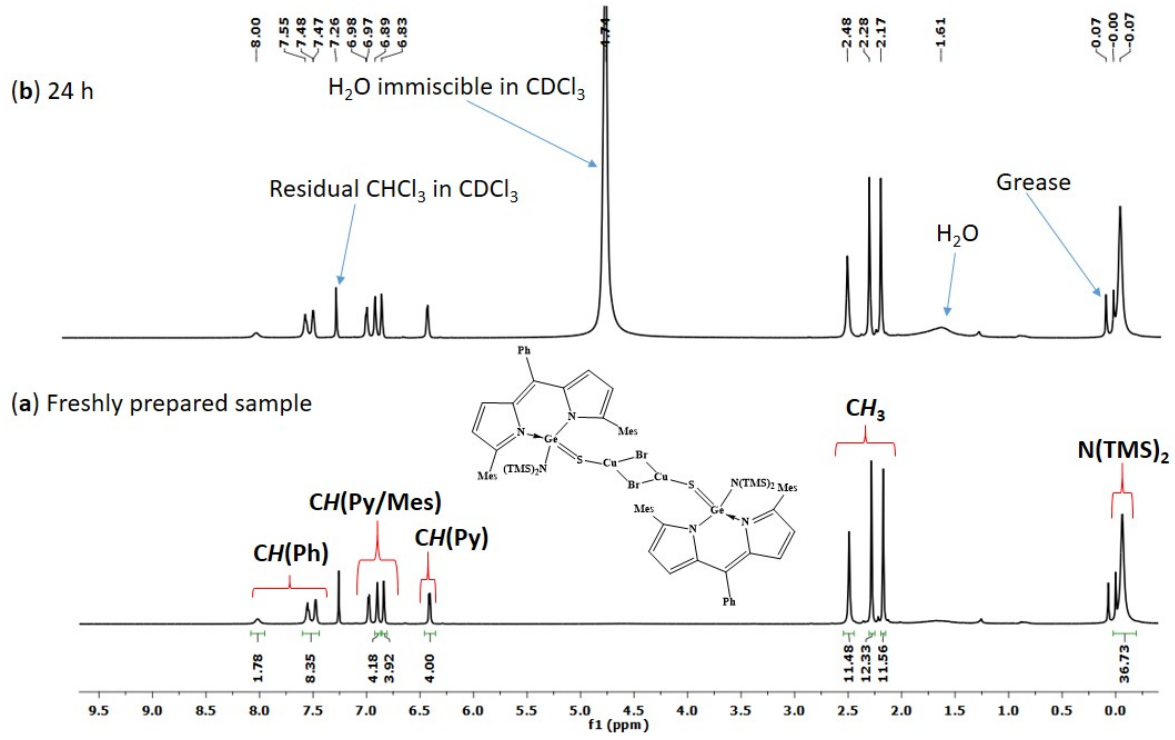
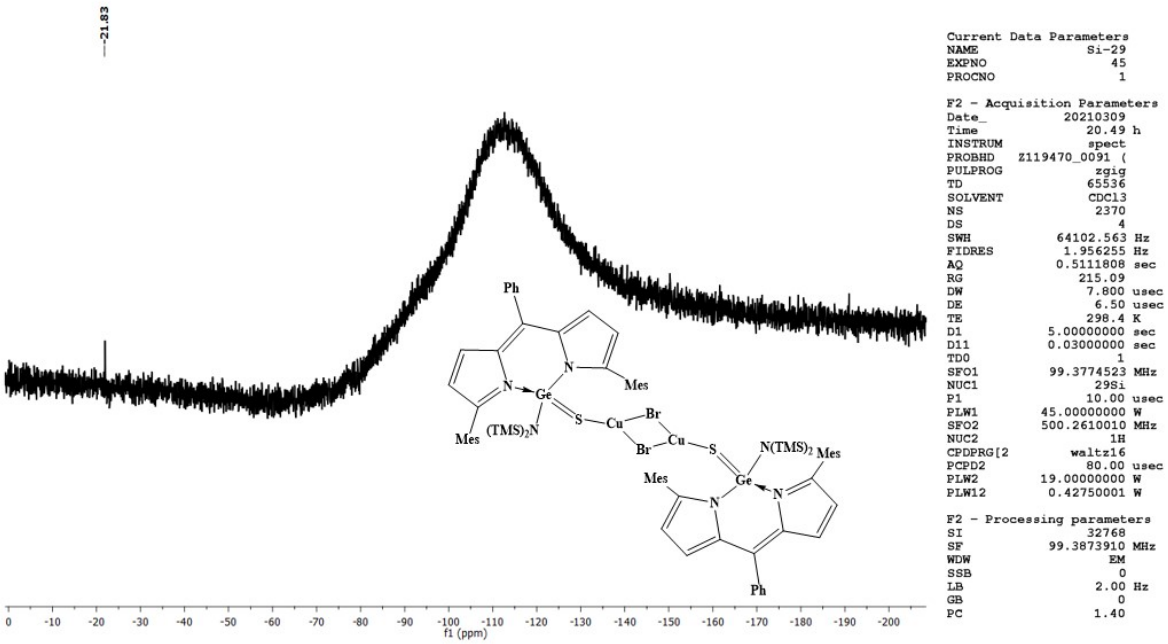


**Figure S62. $^{29}$Si NMR spectrum of compound 16**




```
Current Data Parameters
NAME                  Si-29
EXPNO                    45
PROCNO                    1

F2 - Acquisition Parameters
Date_              20210309
Time                 20.49 h
INSTRUM               spect
PROBHD    Z119470_0091 (
PULPROG               zgig
TD                   65536
SOLVENT              CDCl3
NS                    2370
DS                       4
SWH             64102.563 Hz
FIDRES           1.956255 Hz
AQ               0.5111808 sec
RG                  215.09
DW                   7.800 usec
DE                   6.50 usec
TE                  298.4 K
D1               5.00000000 sec
D11              0.03000000 sec
TD0                      1
SFO1            99.3774523 MHz
NUC1                  29Si
P1                   10.00 usec
PLW1            45.00000000 W
SFO2           500.2610010 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2                80.00 usec
PLW2            19.00000000 W
PLW12            0.42750001 W

F2 - Processing parameters
SI                   32768
SF             99.3873910 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    1.40
```

**Figure S63. $^{1}$H NMR spectrum of compound 17**

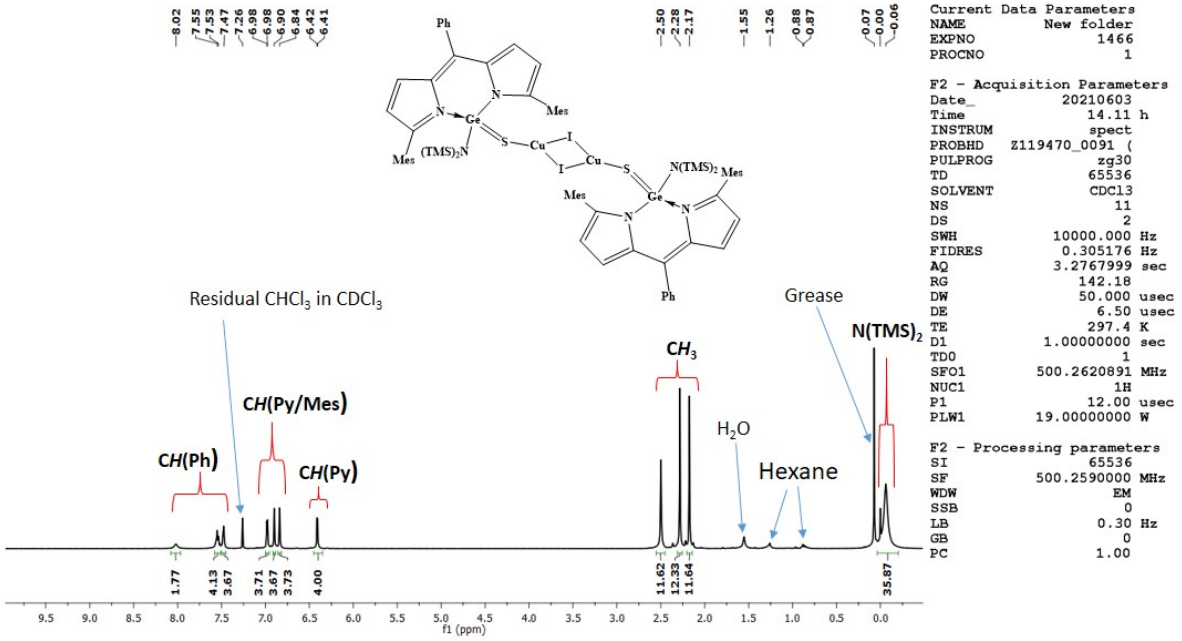



**Figure S64. $^{13}$C NMR spectrum of compound 17**

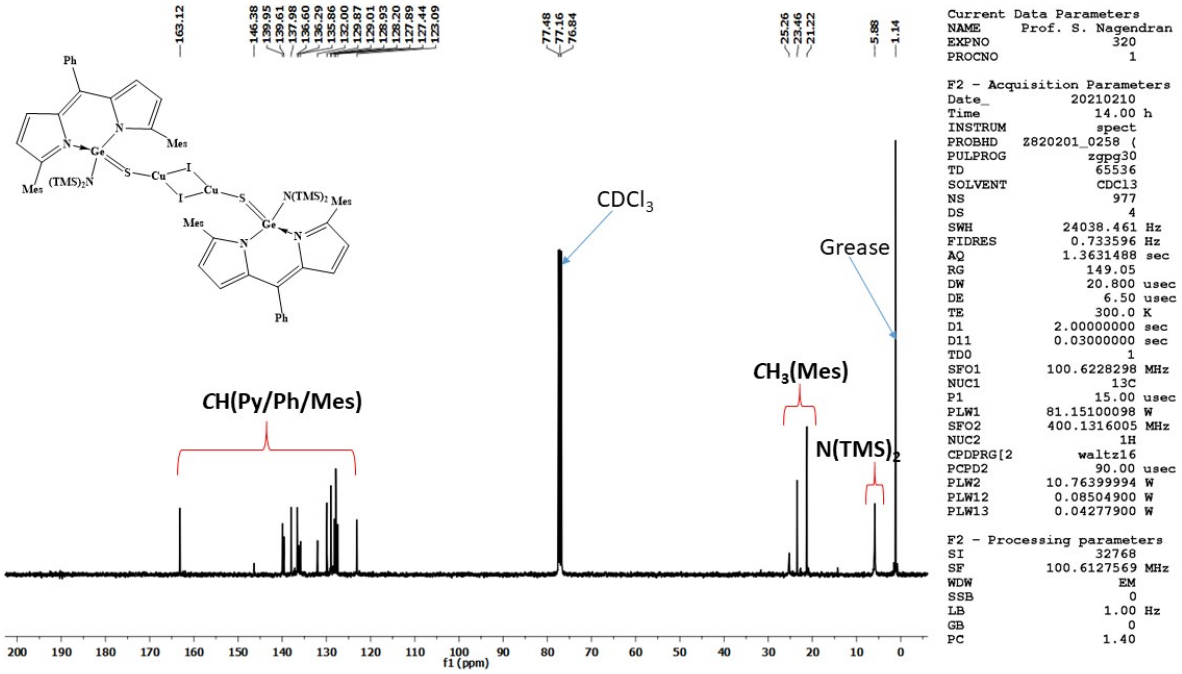


**Figure S65. Air stability of compound 17**

In an open vial, ~250 mg of a freshly prepared sample of compound **17** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S65 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S65 (**b**)] exactly matches that of the freshly prepared sample [Figure S65 (**a**)].

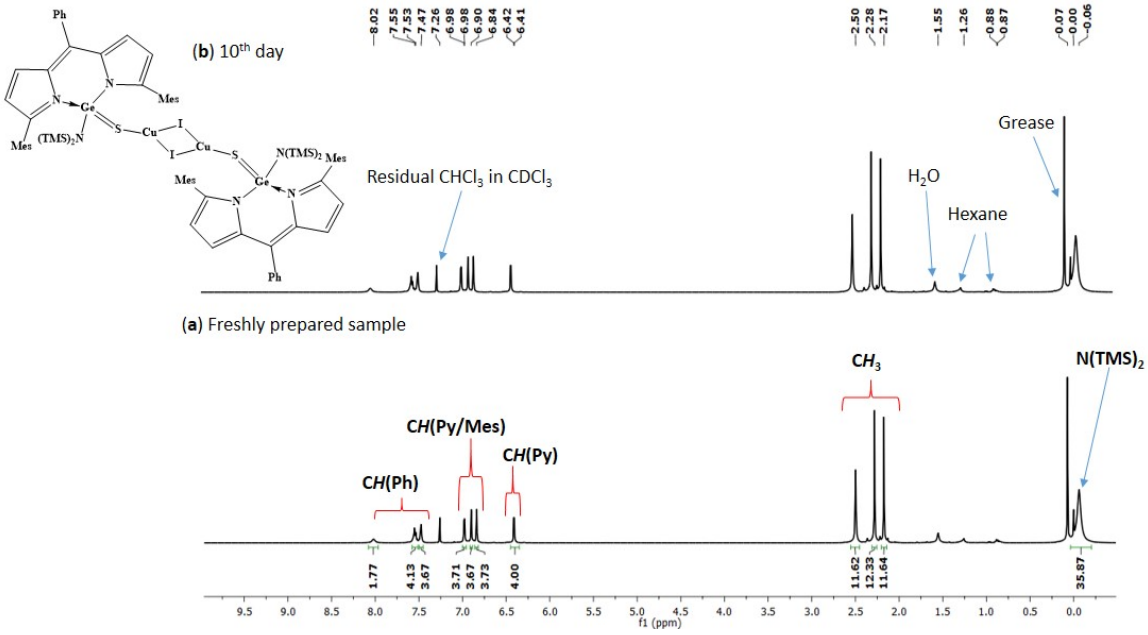


**Figure S66. Stability of compound 17 in water**

Around 10 mg of a freshly prepared sample of compound **17** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S66 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded daily. Up to 3 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 3rd day [Figure S66 (**b**)] exactly matches that of the freshly prepared sample [Figure S66 (**a**)].

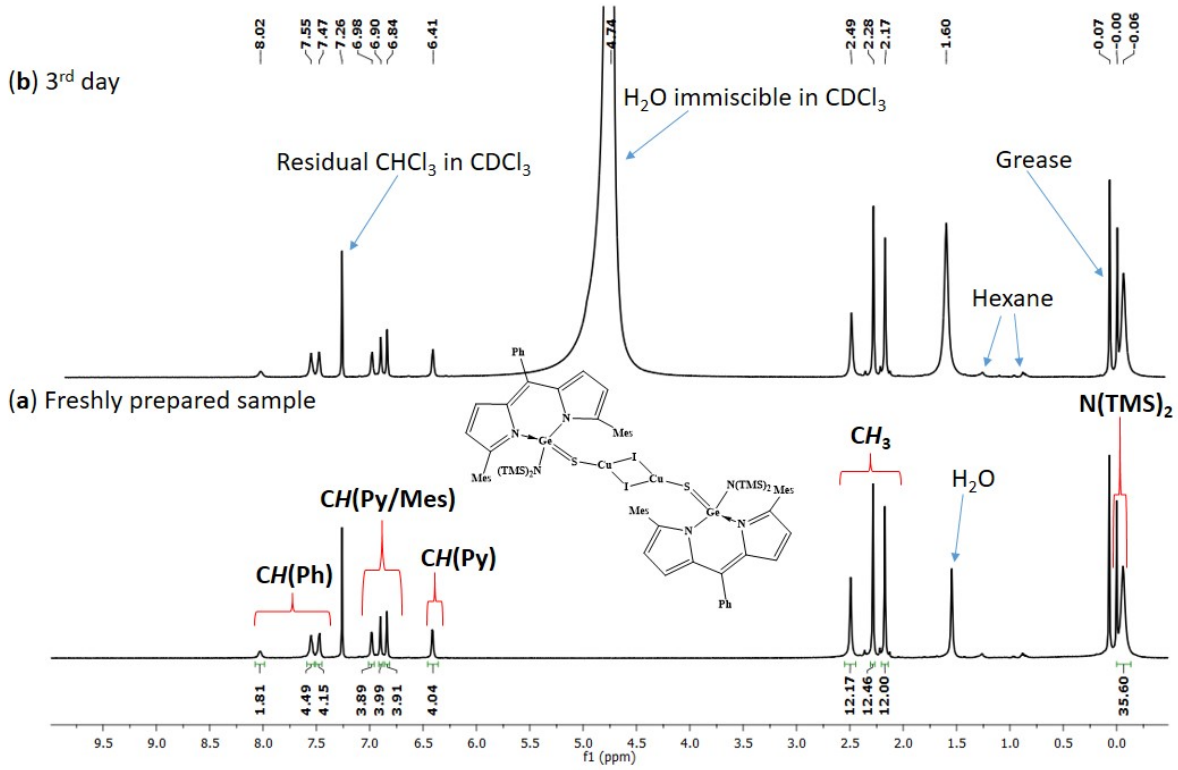


**Figure S67. $^{29}$Si NMR spectrum of compound 17**

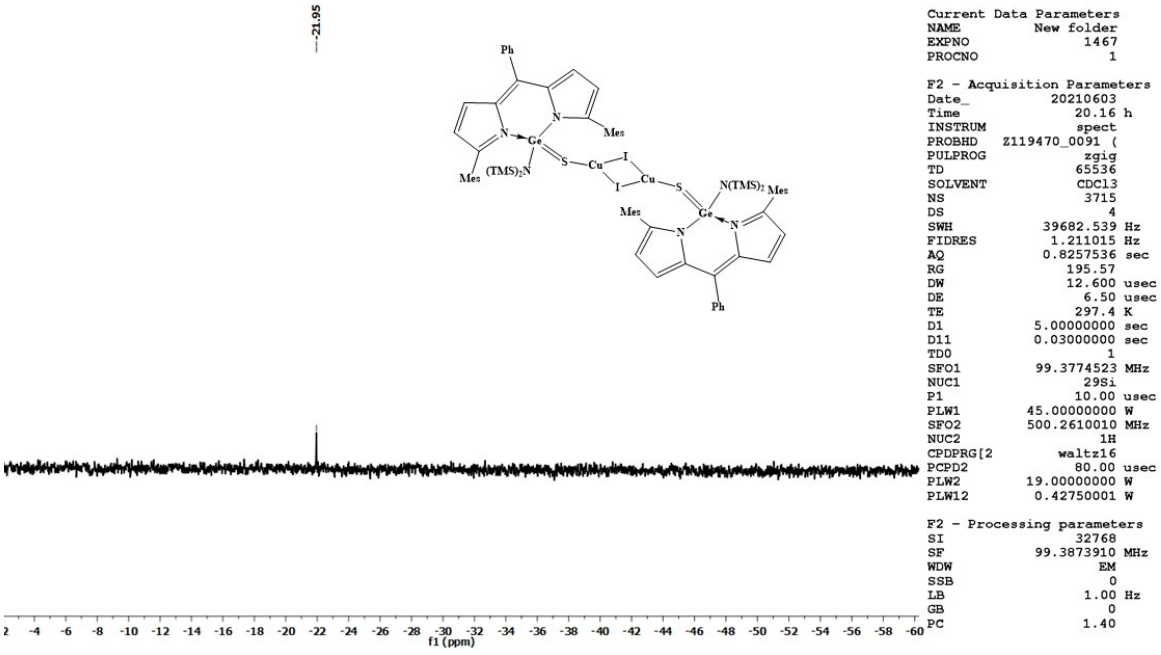


**Figure S68. $^{1}$H NMR spectrum of compound 18**

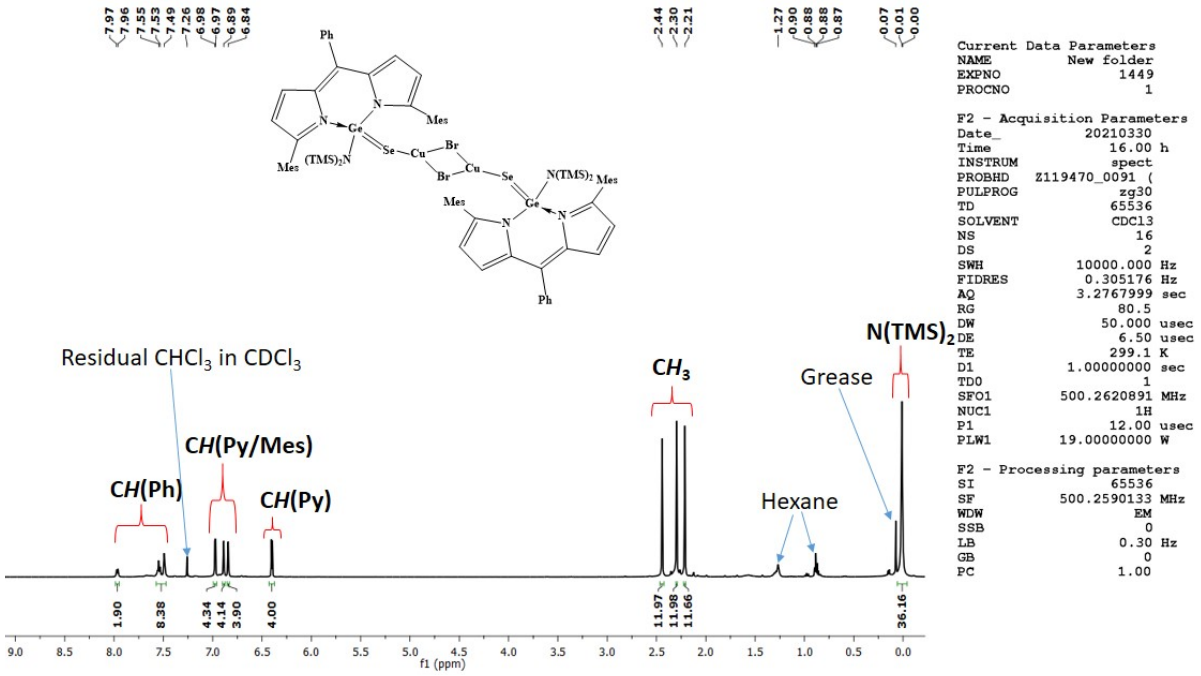



**Figure S69. $^{13}$C NMR spectrum of compound 18**

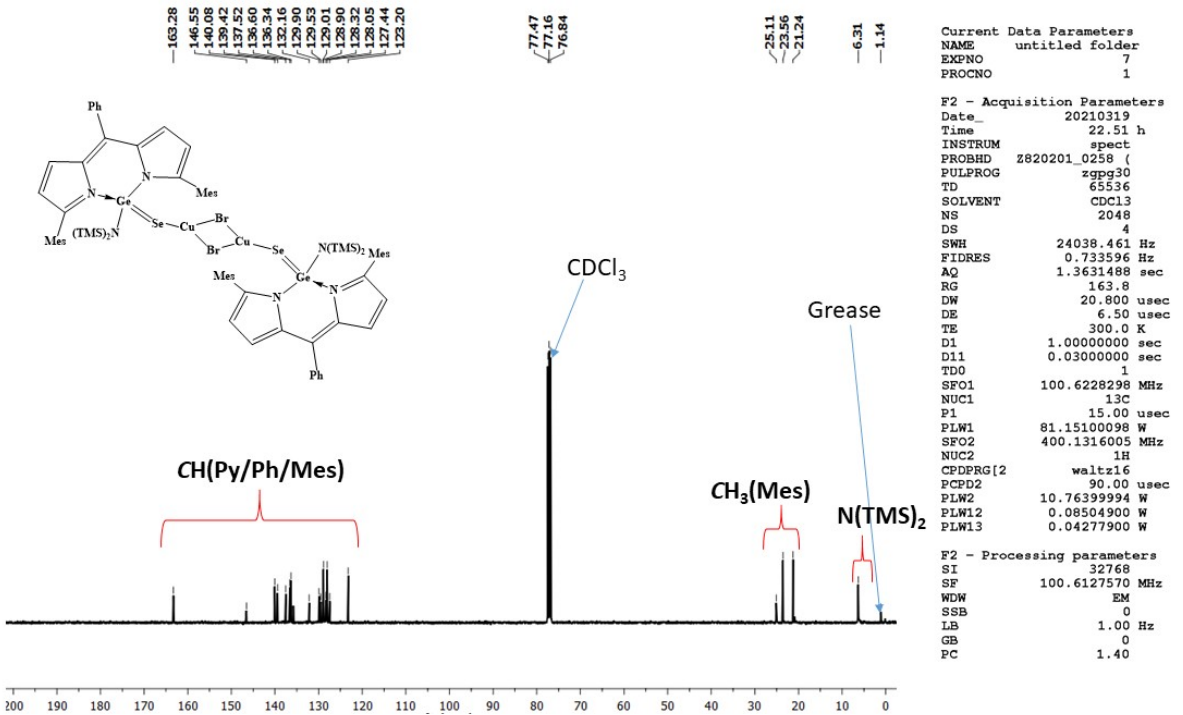


**Figure S70. Air stability of compound 18**

In an open vial, ~250 mg of a freshly prepared sample of compound **18** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S70 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S70 (**b**)] exactly matches that of the freshly prepared sample [Figure S70 (**a**)].

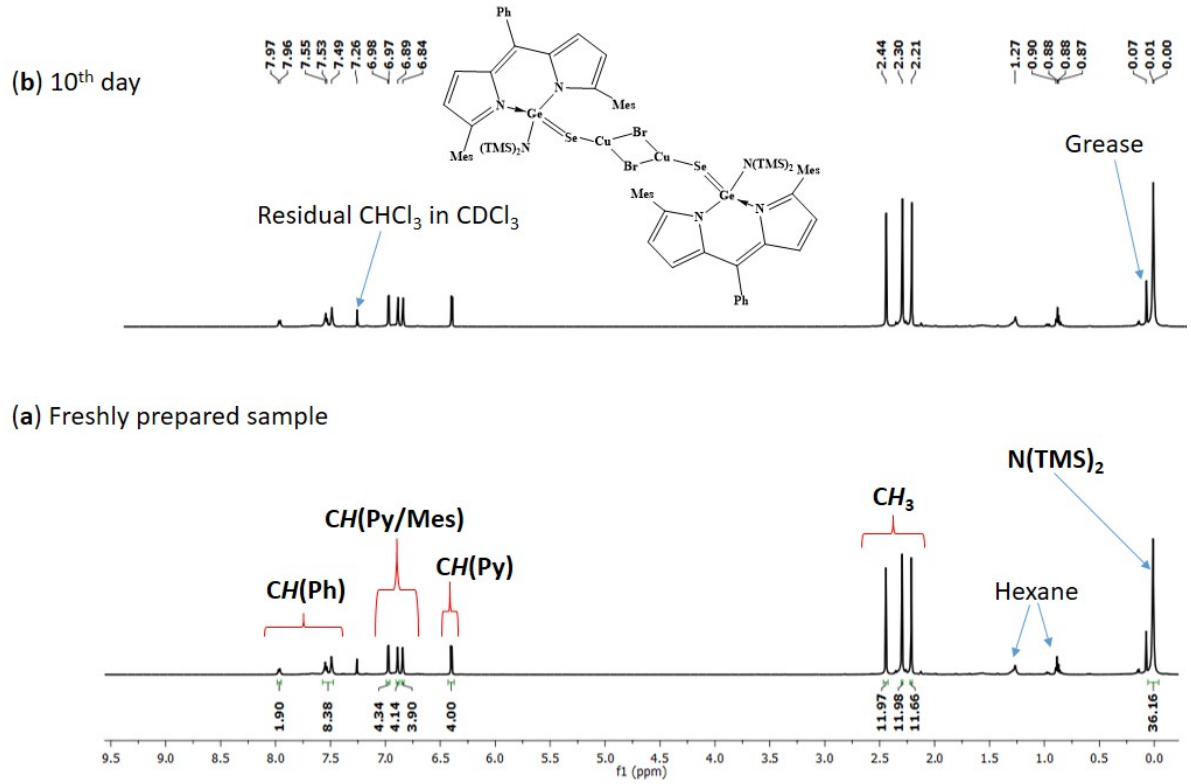


**Figure S71. Stability of compound 18 in water**

Around 10 mg of a freshly prepared sample of compound **18** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S71 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded every 4 h. Up to 12 h, we did not see any decomposition; the $^1H$ NMR spectrum recorded after 12 h [Figure S71 (**b**)] from the addition of exactly matches that of the freshly prepared sample [Figure S71 (**a**)].

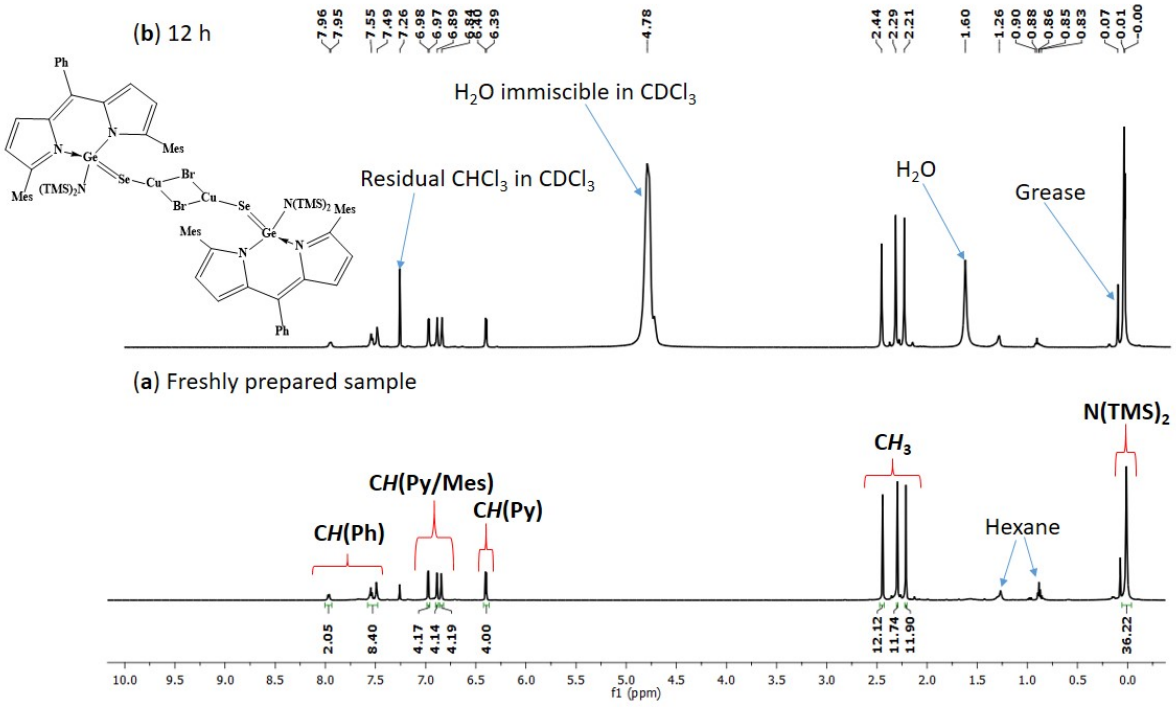


**Figure S72. $^{29}$Si NMR spectrum of compound 18**

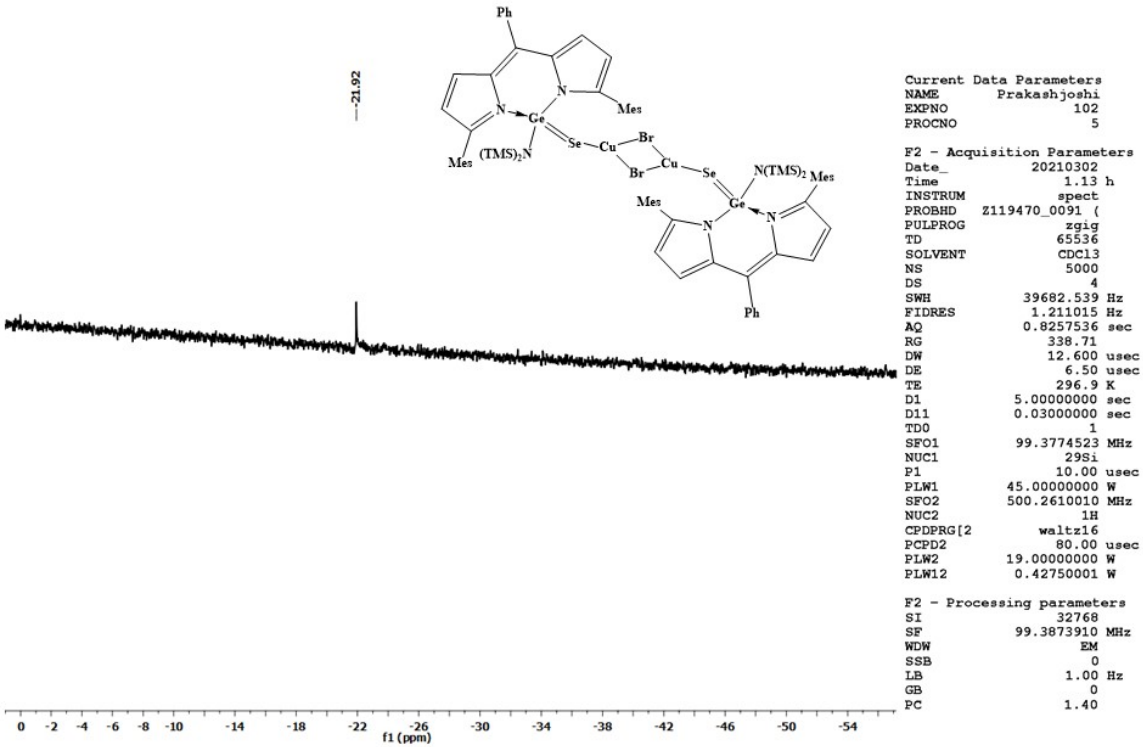



**Figure S73. $^{77}$Se NMR spectrum of compound 18**

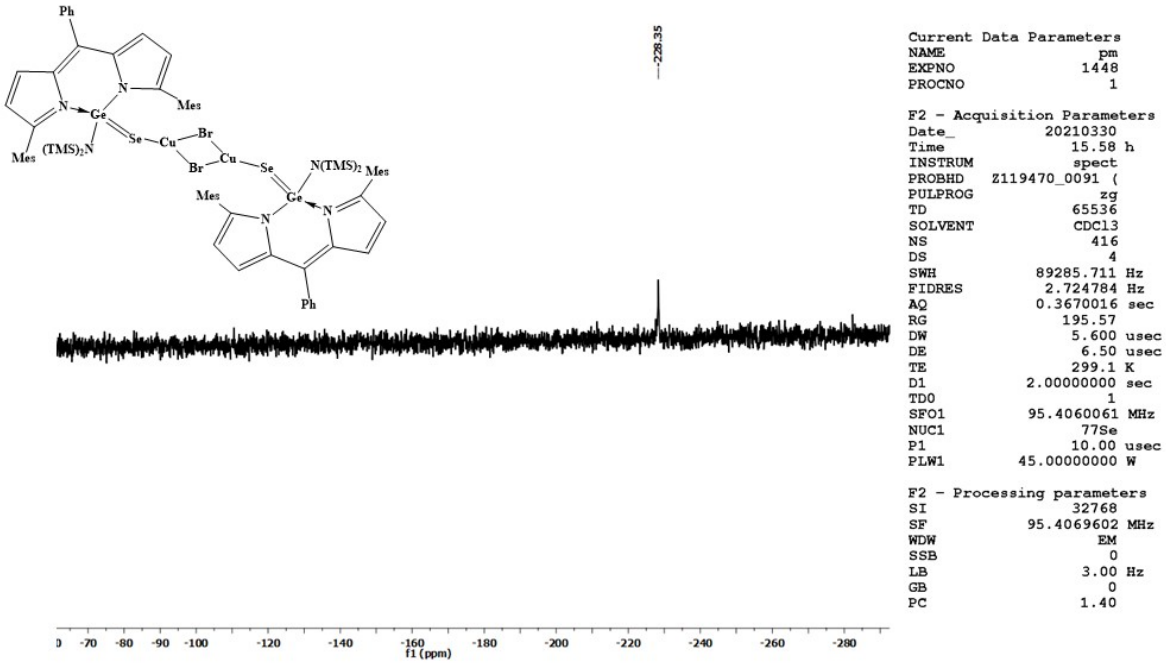


**Figure S74. $^{1}$H NMR spectrum of compound 19**

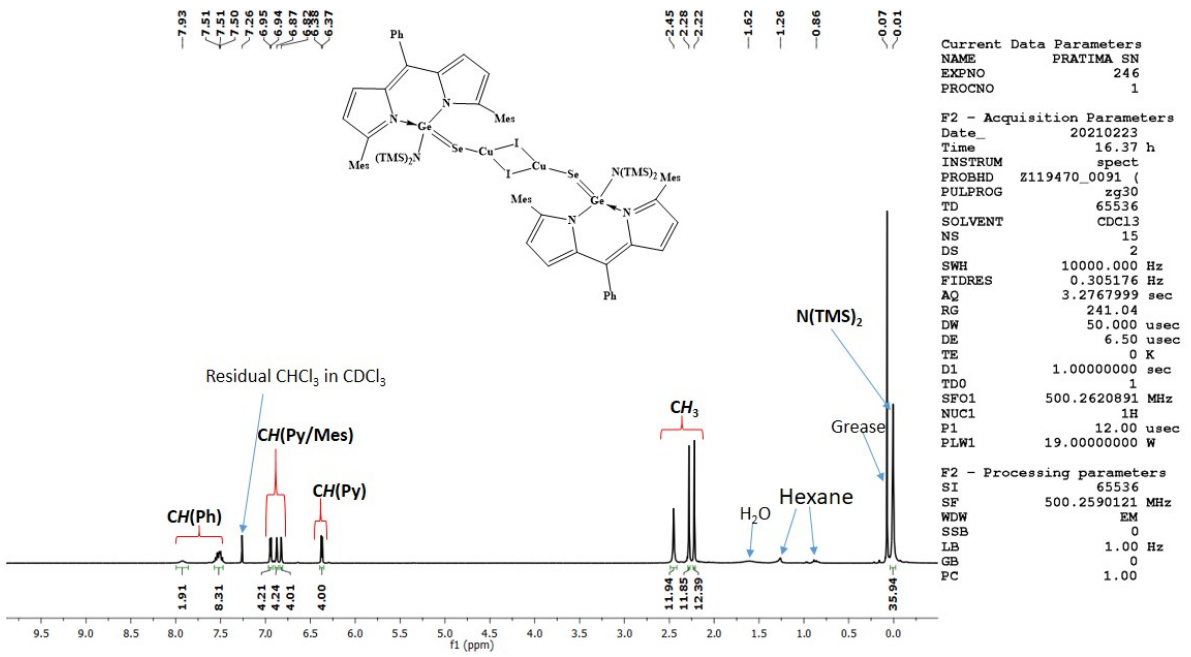



**Figure S75. $^{13}$C NMR spectrum of compound 19**

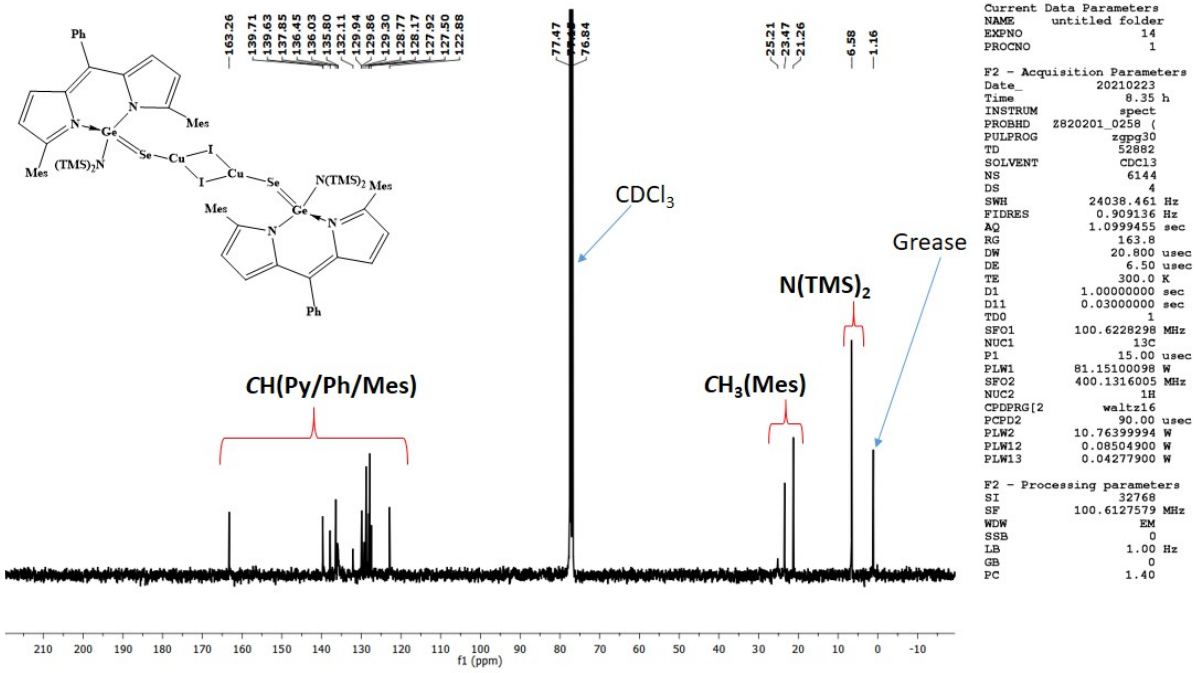


**Figure S76. Air stability of compound 19**

In an open vial, ~250 mg of a freshly prepared sample of compound **19** was kept at room temperature. Then, ~10 mg of the compound was taken in an NMR tube, dissolved in normal (non-dried) $CDCl_3$ (0.5 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S76 (**a**)]; this operation was carried out daily/after every 24 h. Up to 10 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 10$^{th}$ day [Figure S76 (**b**)] exactly matches that of the freshly prepared sample [Figure S76 (**a**)].

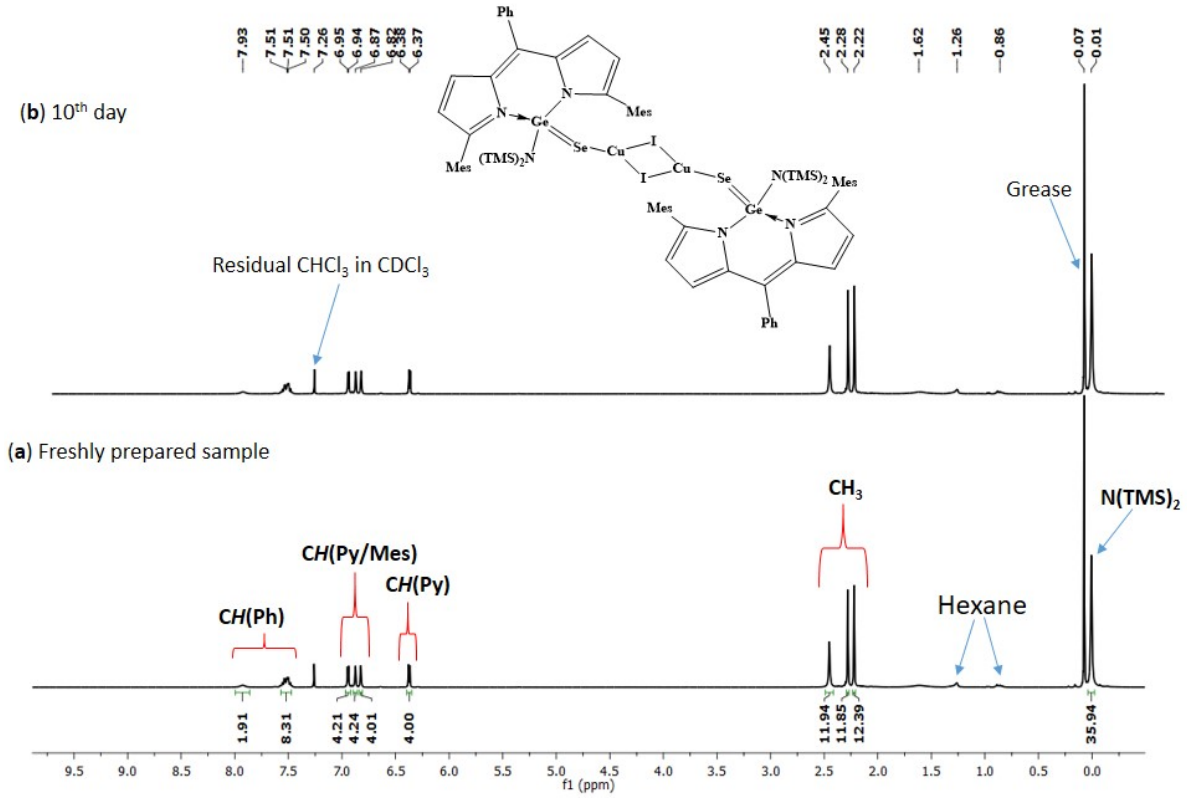


**Figure S77. Stability of compound 19 in water**

Around 10 mg of a freshly prepared sample of compound **19** was dissolved in normal $CDCl_3$ (0.4 mL), and its $^1H$ NMR spectrum was recorded (in a 500 MHz instrument) [Figure S77 (**a**)]. Then, water (0.1 mL) was added and mixed well by shaking, kept at room temperature, and its $^1H$ NMR spectrum was recorded daily. Up to 2 days, we did not see any decomposition; the $^1H$ NMR spectrum recorded on the 2nd day [Figure S77 (**b**)] exactly matches that of the freshly prepared sample [Figure S77 (**a**)].

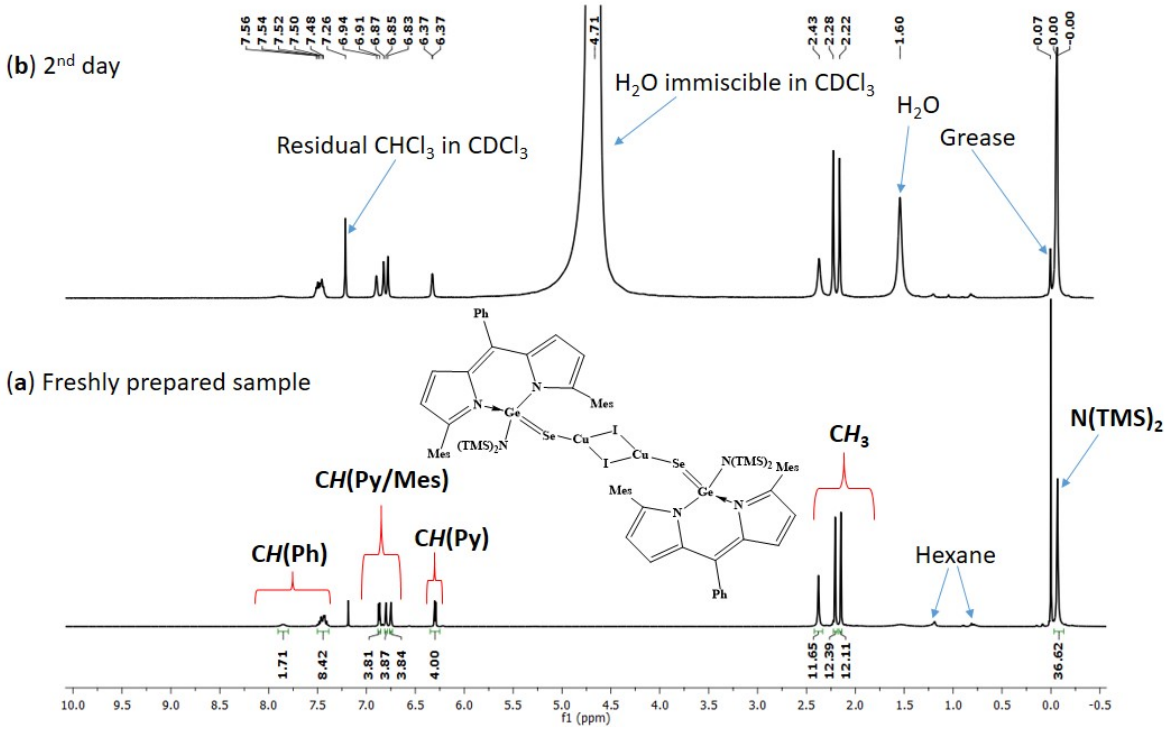


**Figure S78. $^{29}$Si NMR spectrum of compound 19**

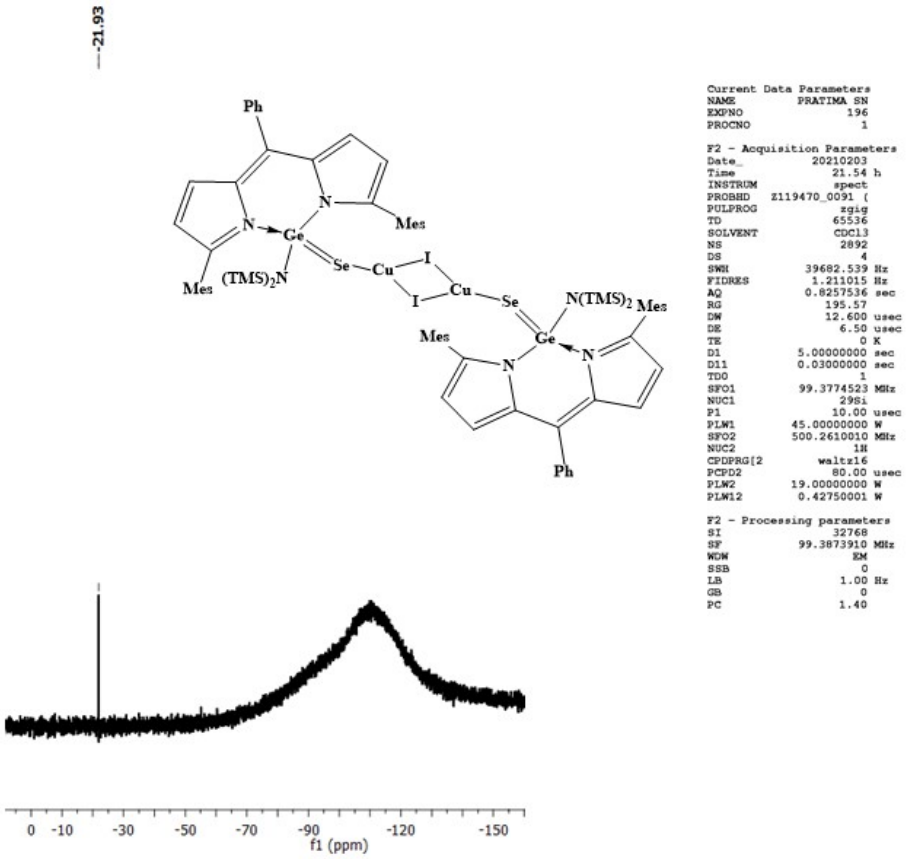



**Figure S79. $^{77}$Se NMR spectrum of compound 19**

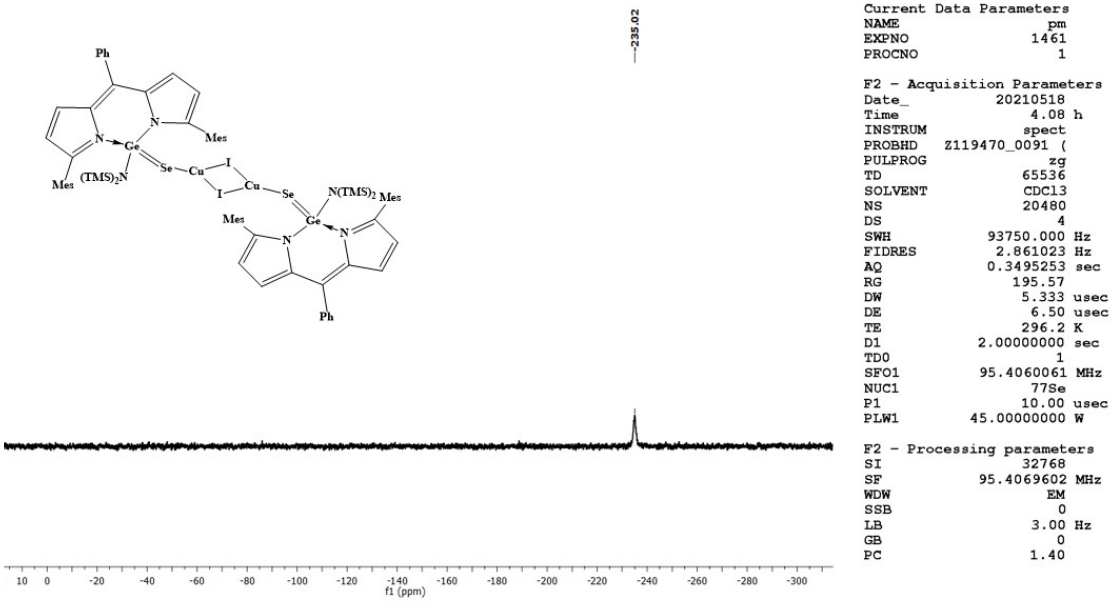


**Figure S80. IR spectrum of compound 6**

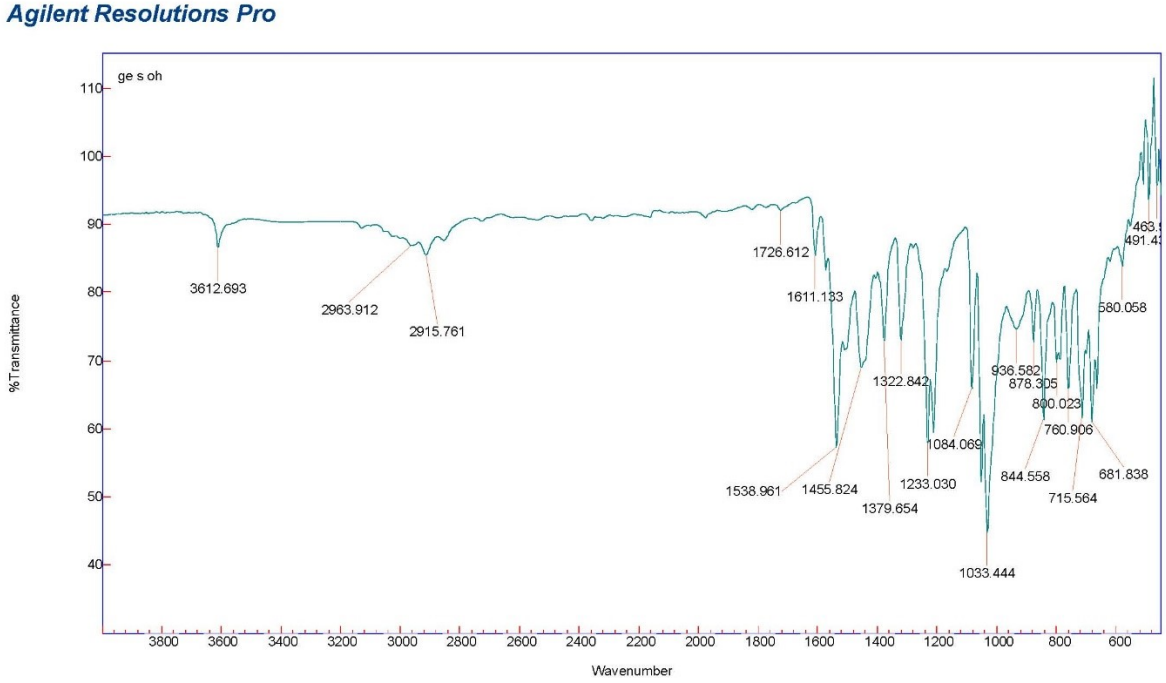



**Figure S81. IR spectrum of compound 7**

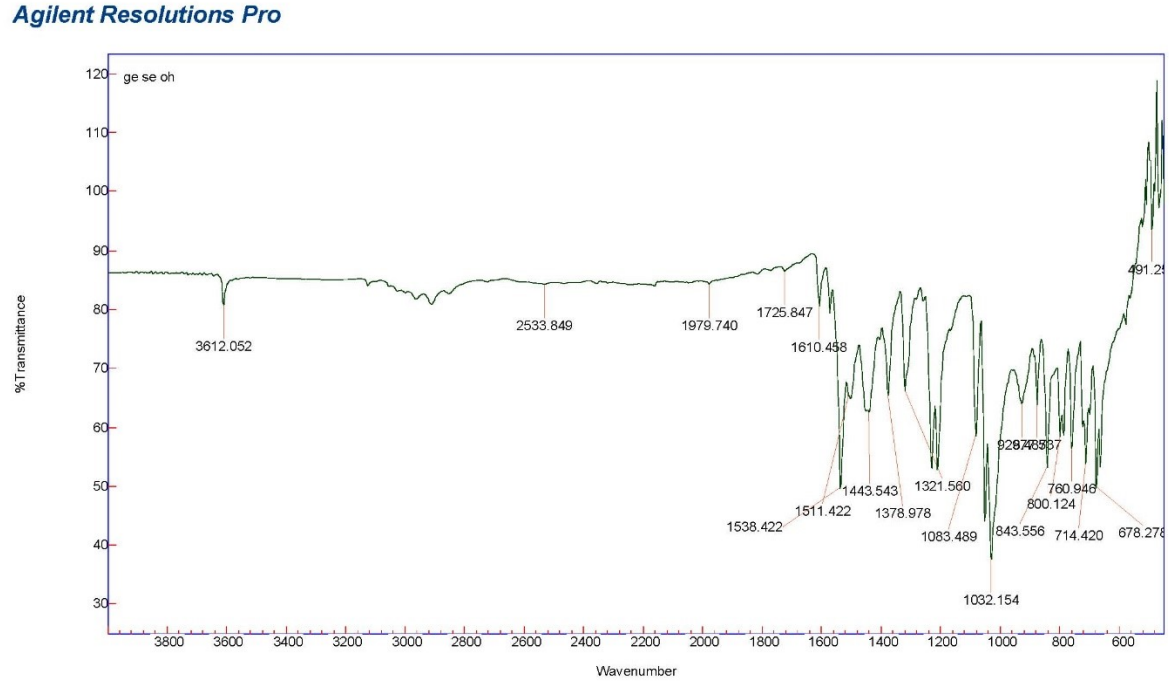


**Table S2. $^{77}$Se NMR spectroscopic data of germaselenocarbonyl compounds containing Ge=Se bonds**

| Compound | $^{77}$Se Resonance, $\delta$ in ppm | Reference |
|---|---|---|
| [Tbt(Tip)Ge(Se)] (**vii**) | 940.6 | S1 |
| [($^t$Bu)$_2$ATIGe(Se)Ph] (**xiii**) | -216.97 | S2 |
| [{HC(CMe)(N(2,6-$^i$Pr$_2$C$_6$H$_3$))$_2$}Ge(Se)OH] (**xiv**) | -439.8 | S3 |
| [(R)$_2$ATIGe(Se)O$^t$Bu] (R = $^t$Bu (**xv**), $^i$Bu (**xvi**) | -77.76 (**xv**), -285.10 (**xvi**) | S4 |
| [(R)$_2$ATIGe(Se)N(TMS)$_2$] (R = $^t$Bu (**xvii**), $^i$Bu (**xviii**)) | -36.76 (**xvii**), -183.31 (**xviii**) | S5 |
| [DPMGe(Se)Ph] (**4**) | -386 | This work |
| [DPMGe(Se)OH] (**7**) | -340 | This work |
| [DPMGe(Se)OEt] (**10**) | -379 | This work |
| [DPMGe(Se)N(TMS)$_2$] (**13**) | -178 | This work |
| [(DPMGe(Se)(N(TMS)$_2$)→CuCl] (**15**) | -237 | This work |
| [(DPMGe(Se)(N(TMS)$_2$)→CuBr]$_2$(**18**) | -228 | This work |
| [(DPMGe(Se)(N(TMS)$_2$)→CuI]$_2$ (**19**) | -235 | This work |

**Table S3. UV-vis spectroscopic data of germacarbonyl compounds 3-4, 6-7, 9-10, 12-13, and copper(I) complexes 14, 18, and 19**

| Compounds | $\lambda_{max}$ (nm) | $\varepsilon$ ($m^{-1}cm^{-1}$, br) |
|---|---|---|
| DPMGe(S)Ph (**3**) | 507 | 54520 |
| DPMGe(Se)Ph (**4**) | 506 | 51460 |
| DPMGe(S)OH (**6**) | 511 | 56920 |
| DPMGe(Se)OH (**7**) | 508 | 72020 |
| DPMGe(S)OEt (**9**) | 512 | 58240 |
| DPMGe(Se)OEt (**10**) | 510 | 59000 |
| DPMGe(S)N(TMS)$_2$ (**12**) | 514 | 36680 |
| DPMGe(Se)N(TMS)$_2$(**13**) | 523 | 45980 |
| [(DPMGe(S)N(TMS)$_2$→CuCl] (**14**) | 511 | 74000 |
| [(DPMGe(Se)N(TMS)$_2$→CuBr]$_2$ (**18**) | 513 | 89800 |
| [(DPMGe(Se)N(TMS)$_2$→CuI]$_2$ (**19**) | 514 | 109000 |

**Figure S82. UV-vis spectra of thiogermacarbonyl compounds 3, 6, 9, and 12**

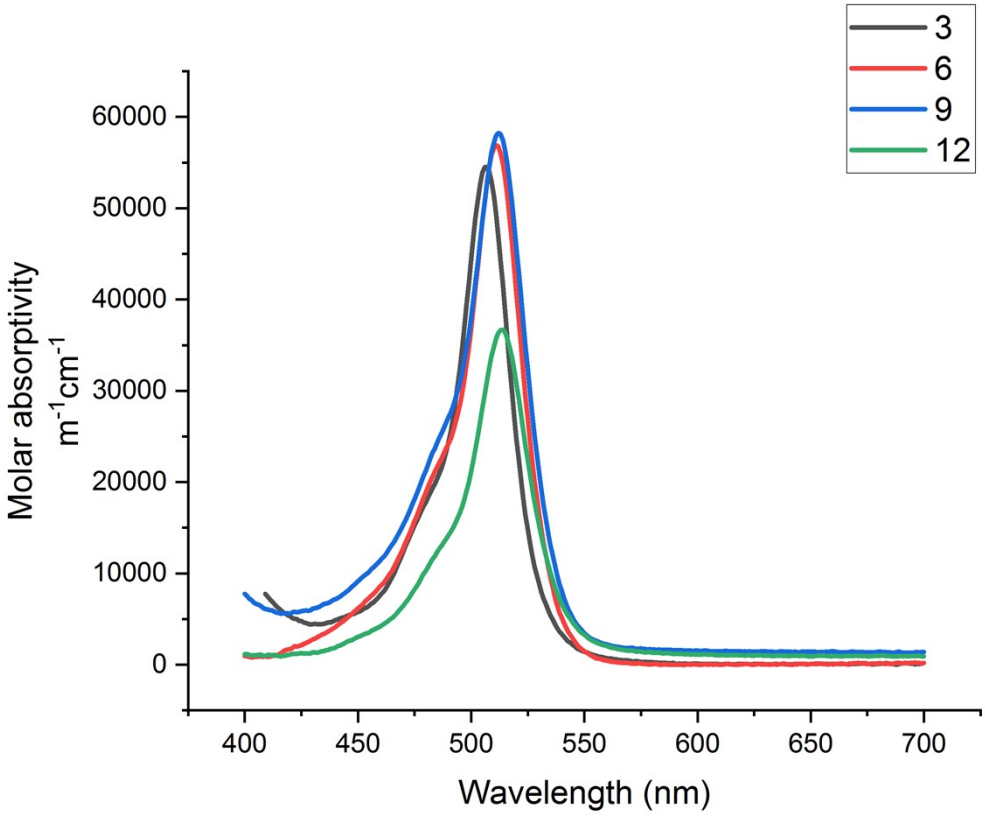



**Figure S83. UV-vis spectra of selenogermacarbonyl compounds 4, 7, 10, and 13**

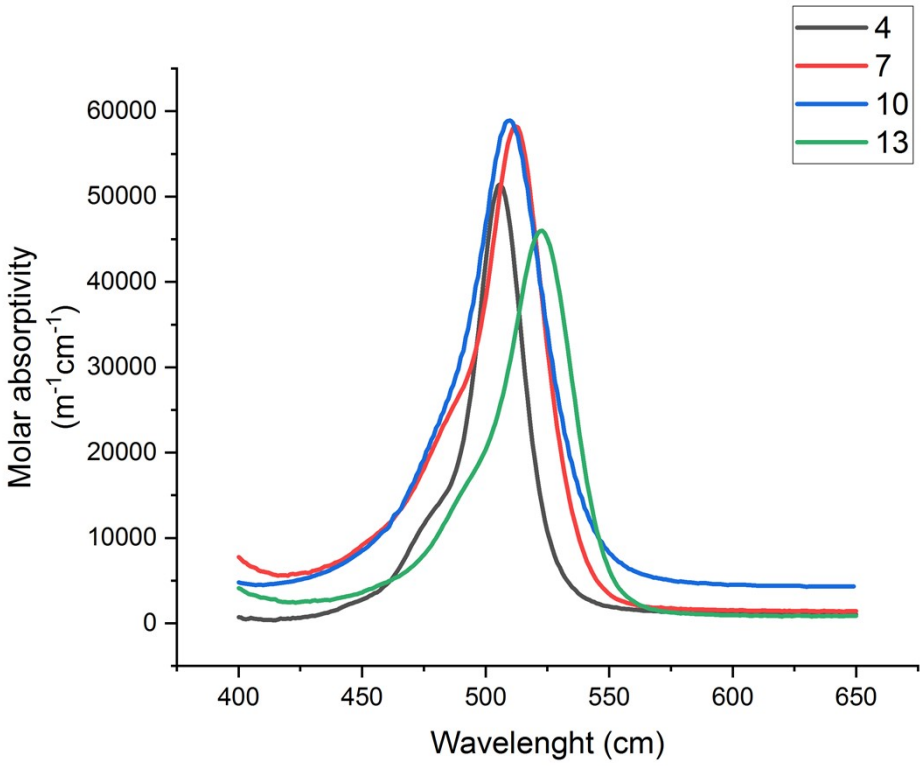
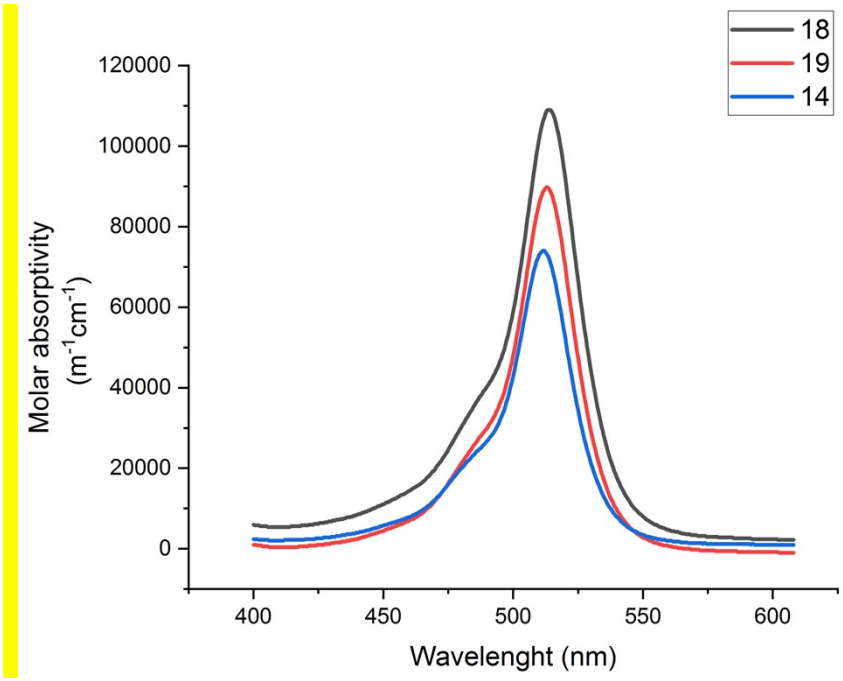


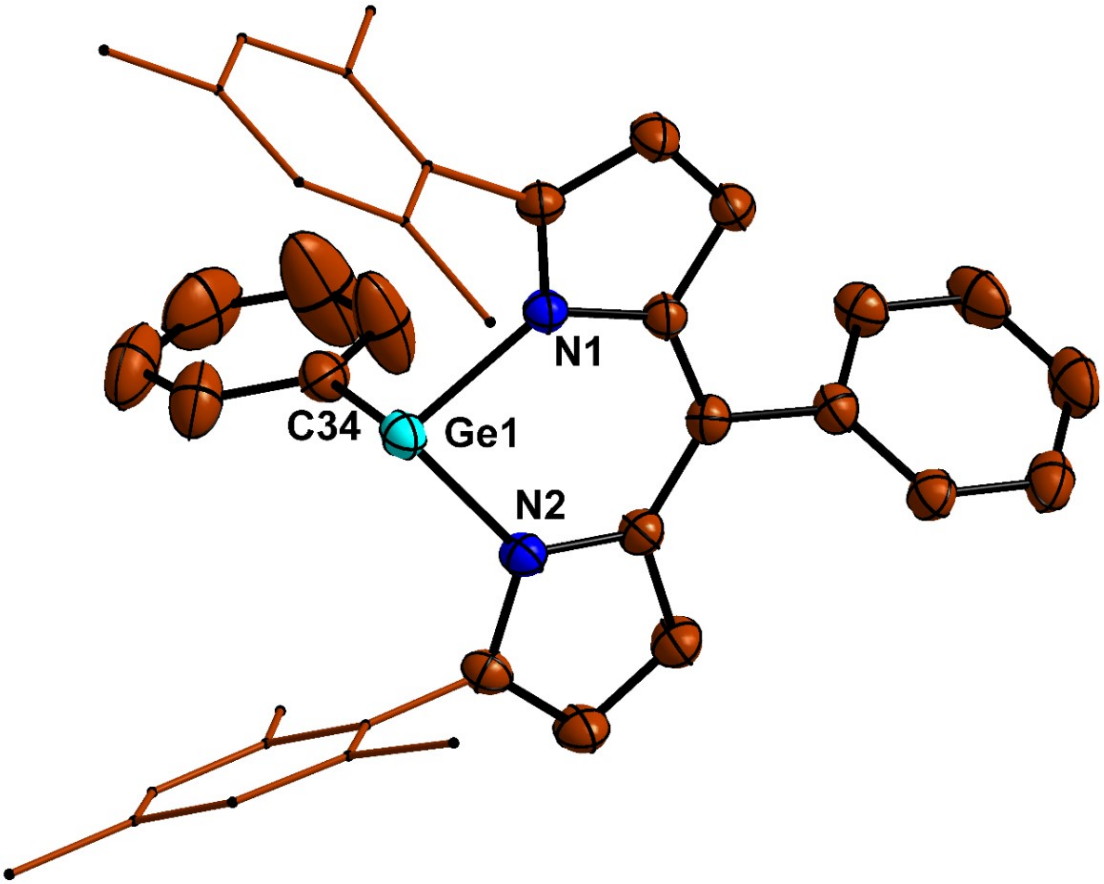

**Figure S84. UV-visible spectra of copper(I) complexes 14, 18, and 19**




**X-ray crystal structure determination of compounds 2-4, 9, 11-14, 16-17, and 19**

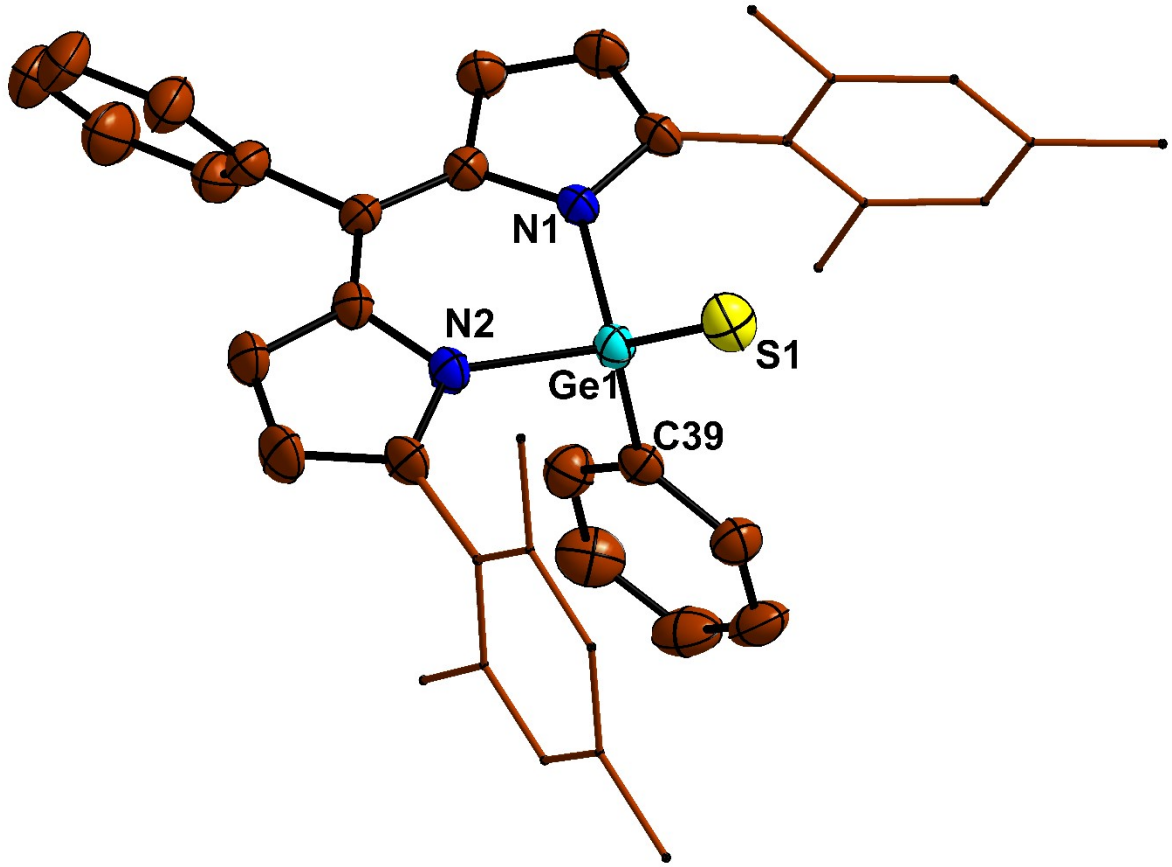
Single crystal X-ray diffraction data of compounds **2-4**, **9**, **11-14**, **16-17**, and **19** were collected using a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer (Tables S1, S2, and S3).[S4] The crystals were covered with Paratone-N and mounted on a glass capillary. The data were collected using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). The integration of data was performed using SAINT. Empirical absorption correction was applied using SADABS.[S5]Structural solutions were accomplished by direct methods and refined by full-matrix least-squares on $F^2$ using either SHELXTL[S6] or SHELXL-2013 incorporated in OLEX2. All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were fixed according to a riding model and were refined isotropically. Important crystallographic data are provided in Tables S1, S2, and S3. [S7]

**Figure S85. Molecular structure of compound 2**



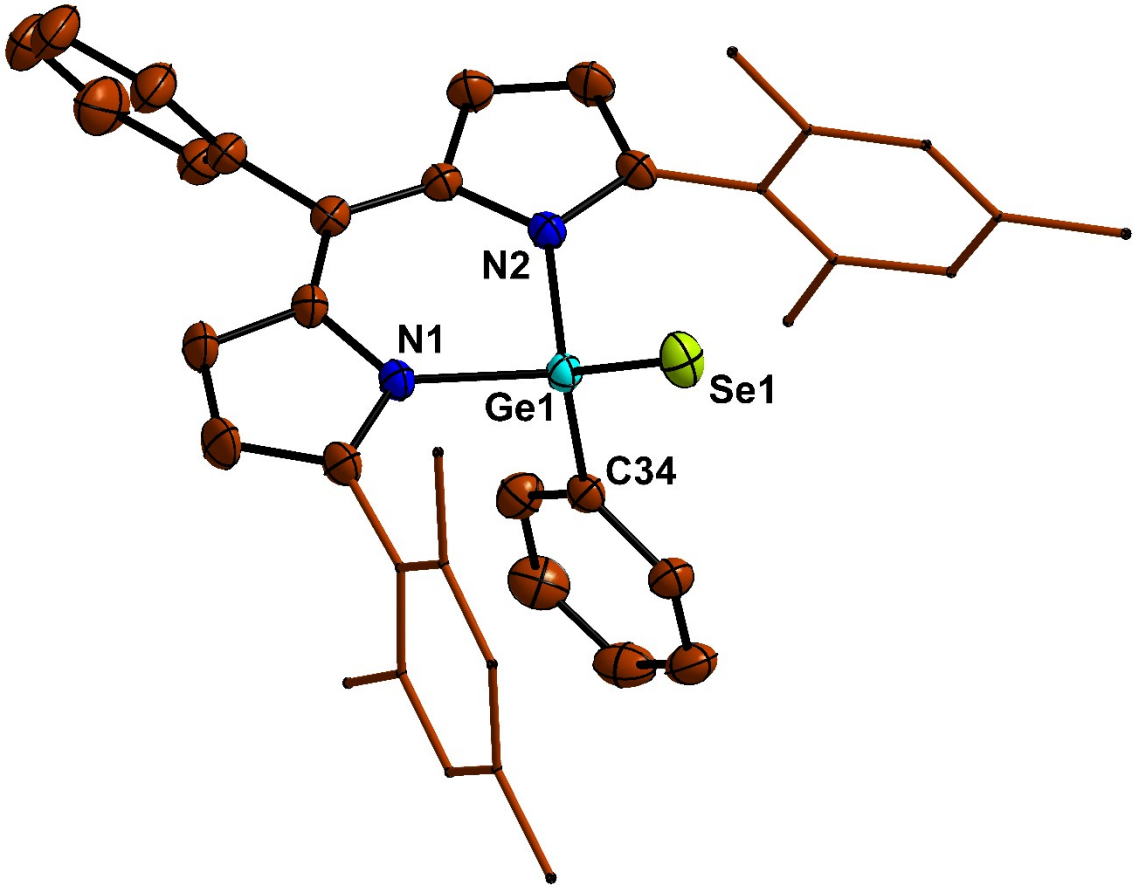

Molecular structure of DPMGePh (**2**). All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Ge(1)−N(1) 2.001(2), Ge(1)−N(2) 2.016(2), Ge(1)−C(34) 2.001(2); C(34)−Ge(1)−N(1) 97.13(8), C(34)−Ge(1)−N(2) 93.96(8), N(1)−Ge(1)−N(2) 86.55(6). Data collection temperature: 302 K.

**Figure S86. Molecular structure of compound 3**



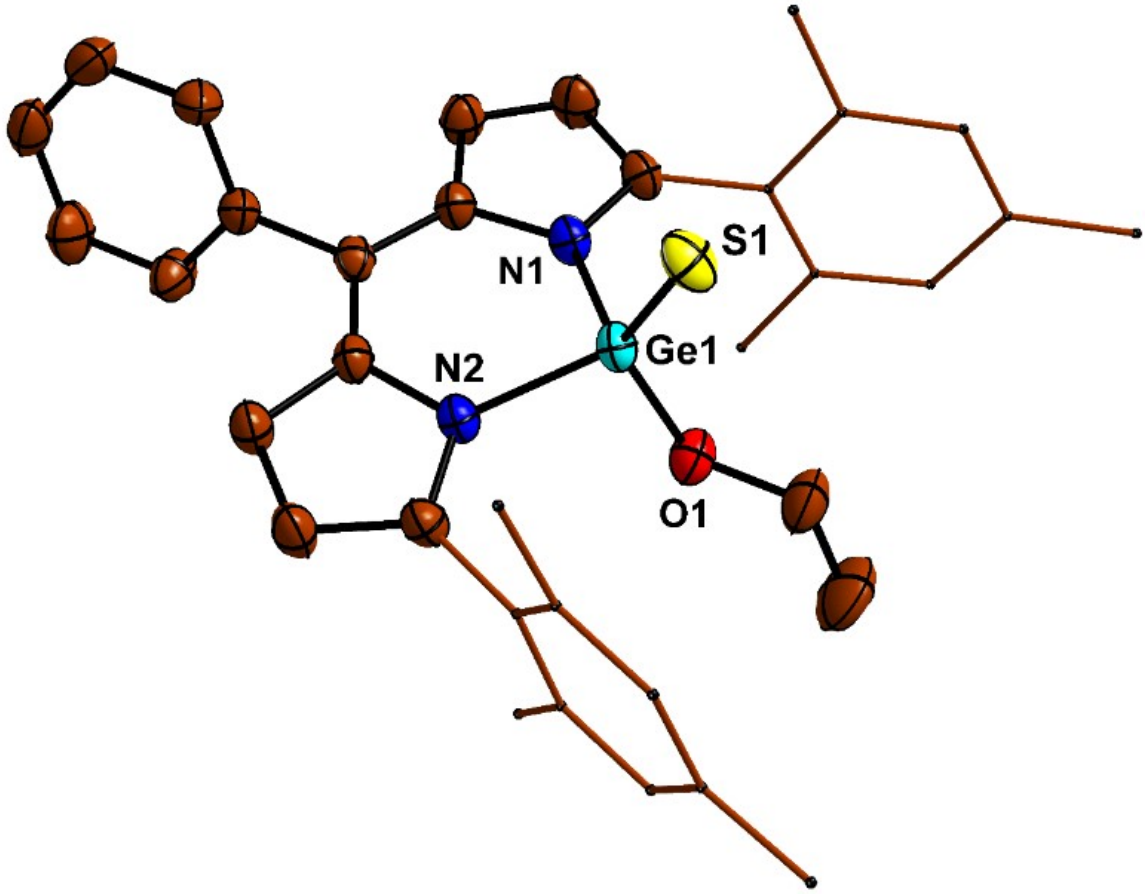

Molecular structure of DPMGe(S)Ph (**3**). All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Ge(1)−S(1) 2.052(2), Ge(1)−N(1) 1.946(5), Ge(1)−N(2) 1.943(4), Ge(1)−C(39) 1.928(6); C(39)−Ge(1)−N(1) 102.6(2), C(39)−Ge(1)−N(2) 102.8(2), N(1)−Ge(1)−N(2) 92.17(2), C(39)-Ge(1)-S(1) 122.31(2). Data collection temperature: 273 K.

**Figure S87. Molecular structure of compound 4**



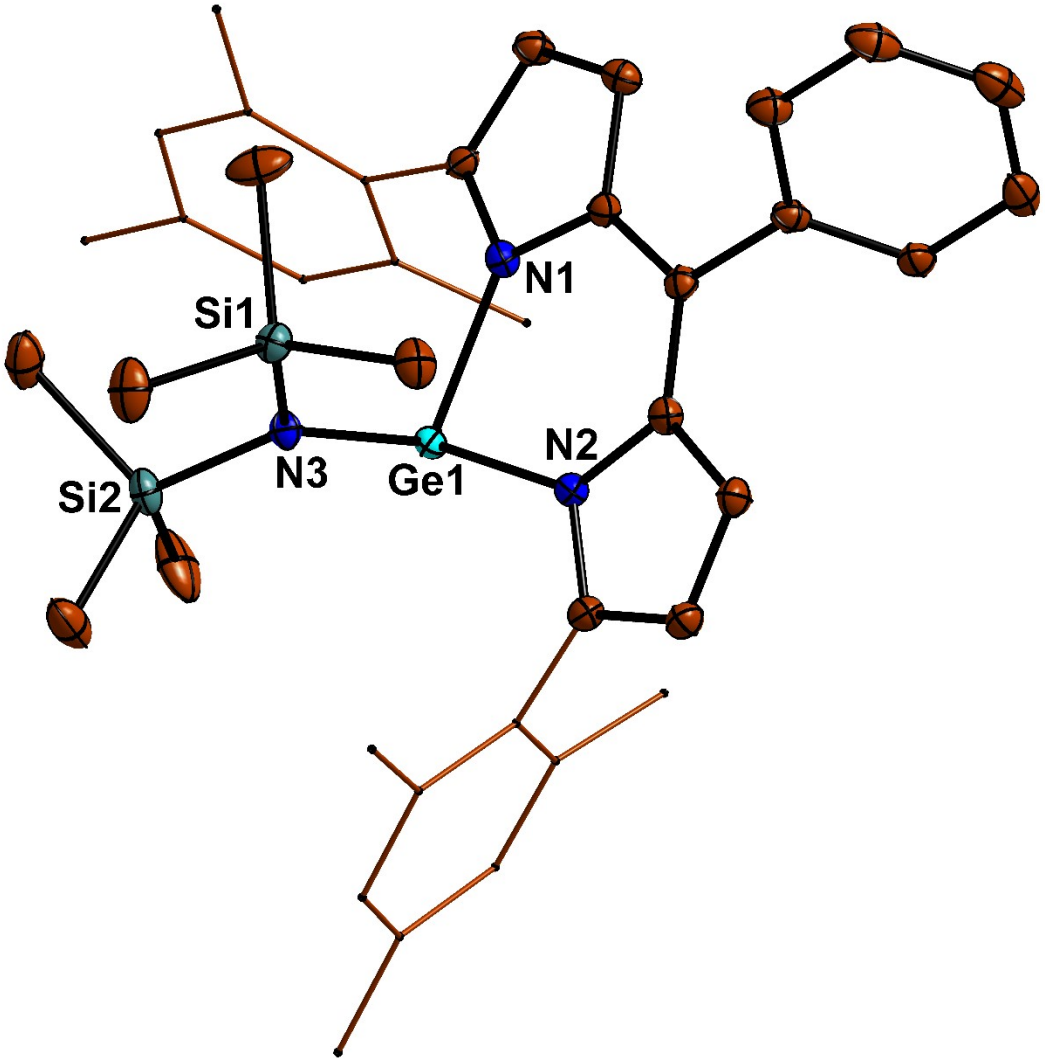

Molecular structure of DPMGe(Se)Ph (**4**). All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Ge(1)−Se(1) 2.195(3), Ge(1)−N(1) 1.942(1), Ge(1)−N(2) 1.946(1), Ge(1)−C(34) 1.933(2); C(34)−Ge(1)−N(1) 102.89(6), C(34)−Ge(1)−N(2) 102.89(6), N(1)−Ge(1)−N(2) 92.31(5), C(34)-Ge(1)-Se(1) 121.13(5). Data collection temperature: 302 K.

**Figure S88. Molecular structure of compound 9**



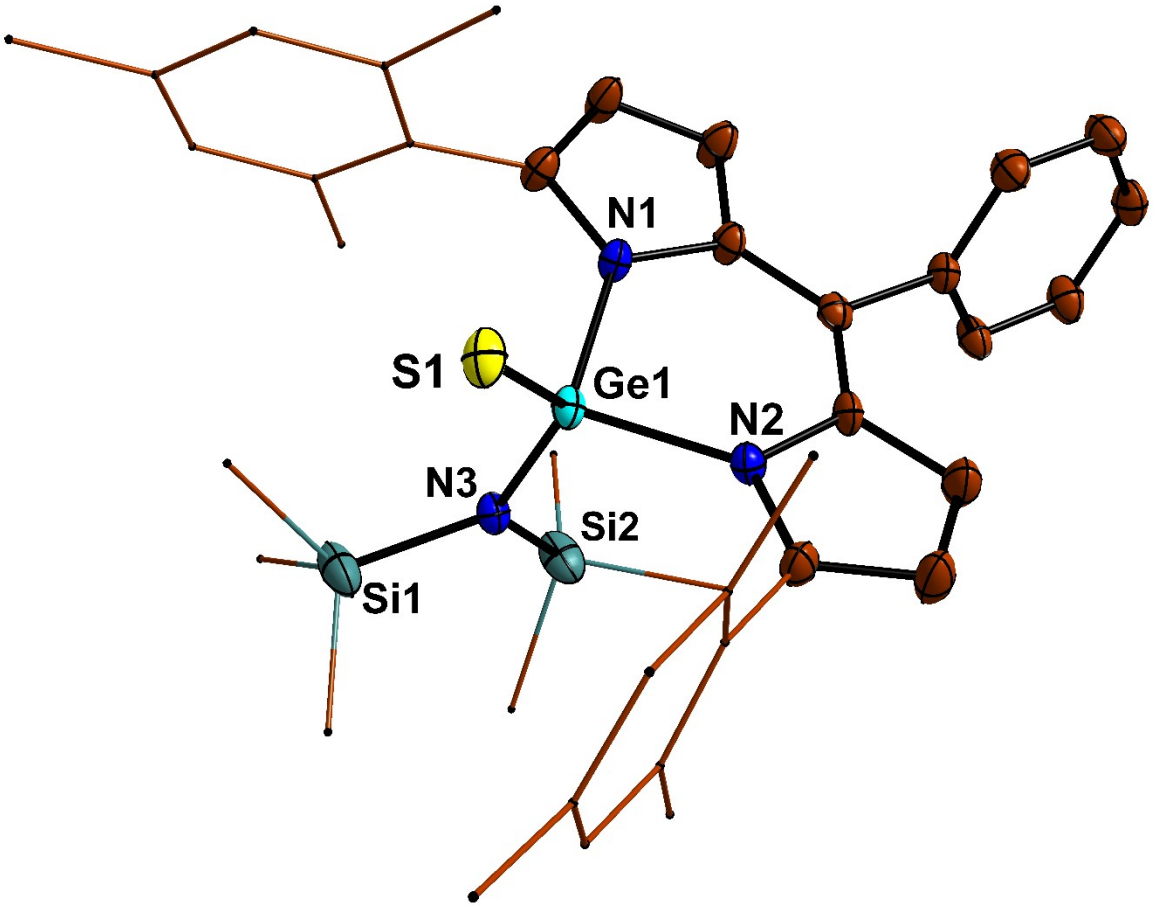

Molecular structure of DPMGe(S)OEt (**9**). All hydrogen atoms were omitted for clarity, and thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Ge(1)−S(1) 2.058(5) Ge(1)−O(1) 1.751(2), Ge(1)−N(1) 1.914(2), Ge(1)−N(2) 1.915(2); O(1)−Ge(1)−N(1) 102.74(6), O1(1)−Ge(1)−N(2) 100.60(7) N(1)−Ge(1)−N(2) 93.05(6). Data collection temperature: 273 K.

**Figure S89. Molecular structure of compound 11**



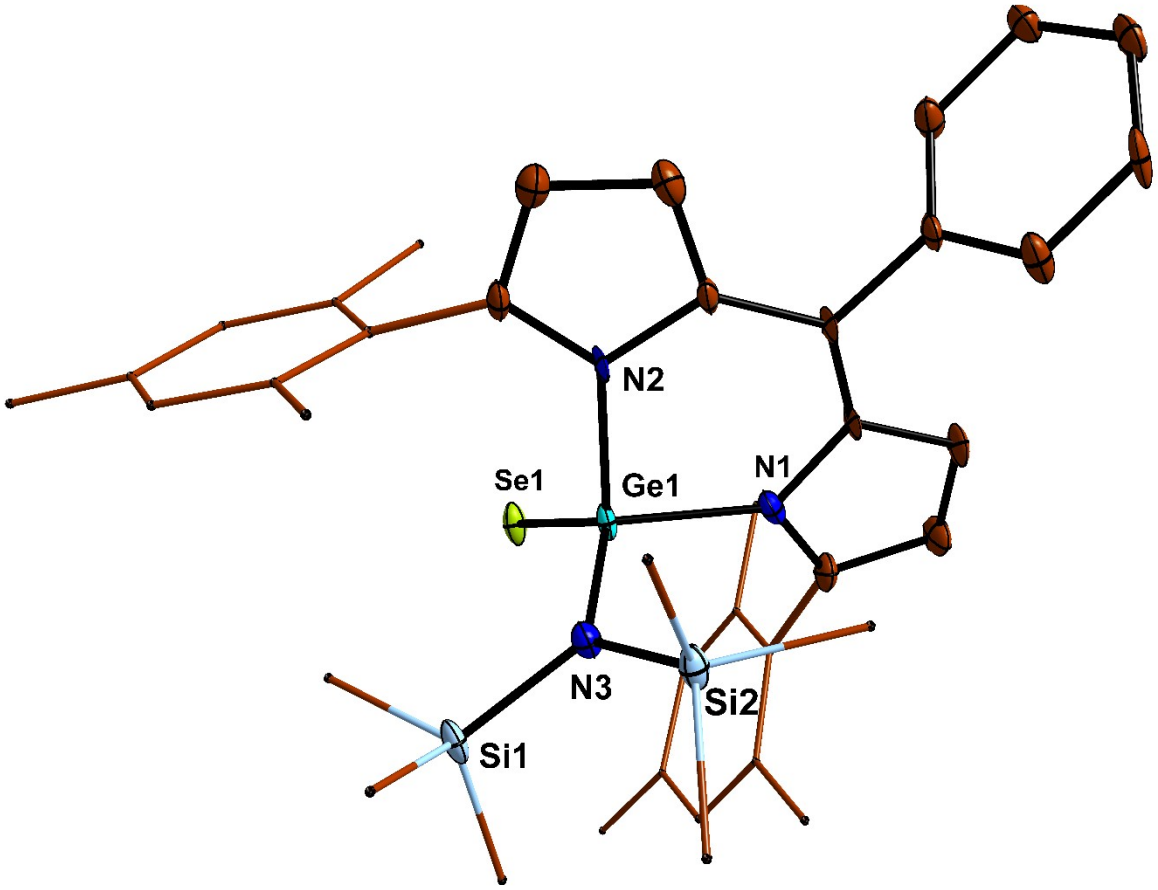

Molecular structure of DPMGeN(TMS)$_2$ (**11**). All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ge(1)−N(1) 2.042(2), Ge(1)−N(2) 2.025(2), Ge(1)−N(3) 1.924(2); N(3)−Ge(1)−N(1) 100.98(8), N(3)−Ge(1)−N(2) 100.03(8) N(1)−Ge(1)−N(2) 86.02(8). Data collection temperature: 100 K.

**Figure S90. Molecular structure of compound 12**



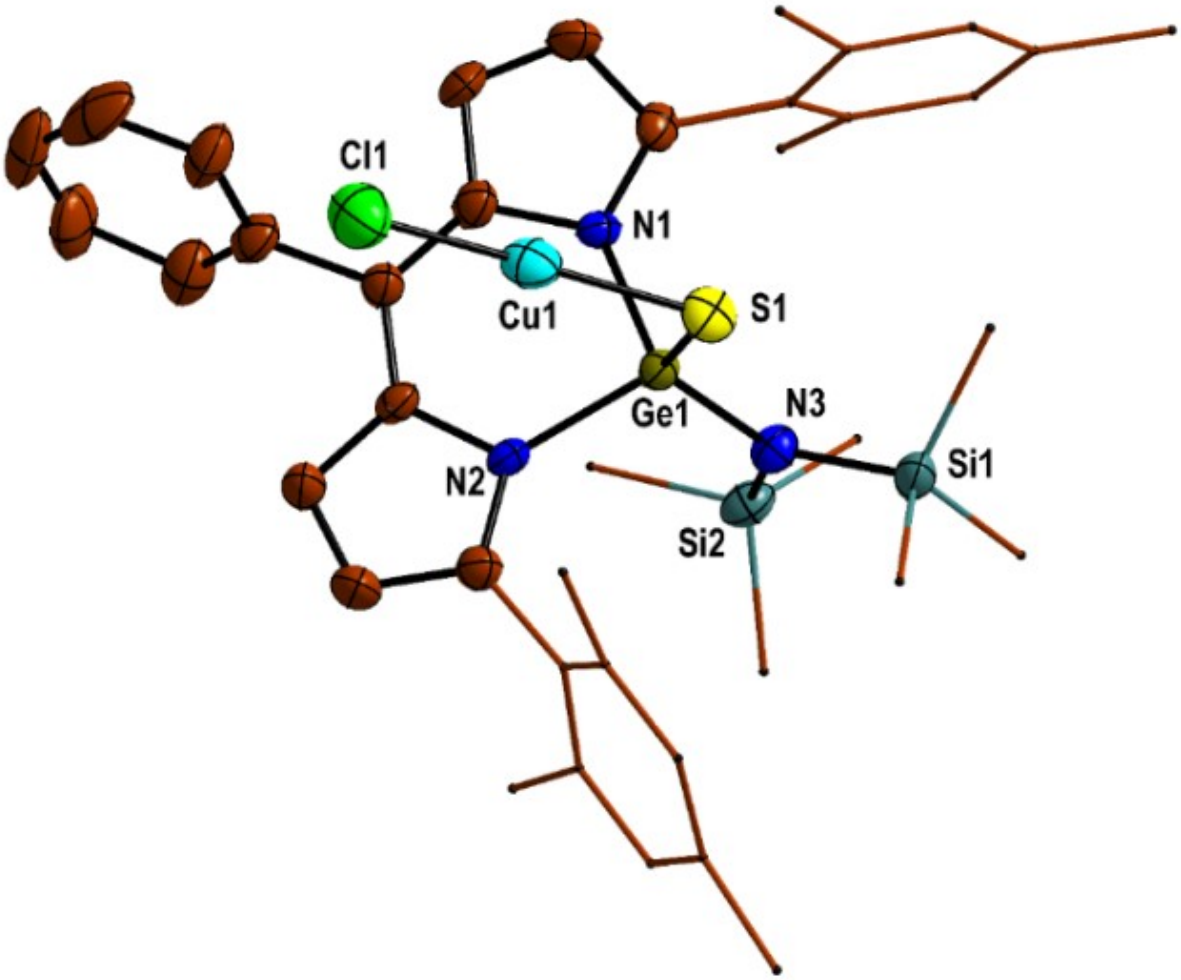

Molecular structure of DPMGe(S)N(TMS)$_2$ (**12**). All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ge(1)−S(1) 2.062(1), Ge(1)−N(1) 1.951(4), Ge(1)−N(2) 1.953(3), Ge(1)−N(3) 1.843(3); N(3)−Ge(1)−N(1) 105.91(2), N(3)−Ge(1)−N(2) 107.46(2), N(1)−Ge(1)−N(2) 92.75(2). Data collection temperature: 100 K.

**Figure S91. Molecular structure of compound 13**



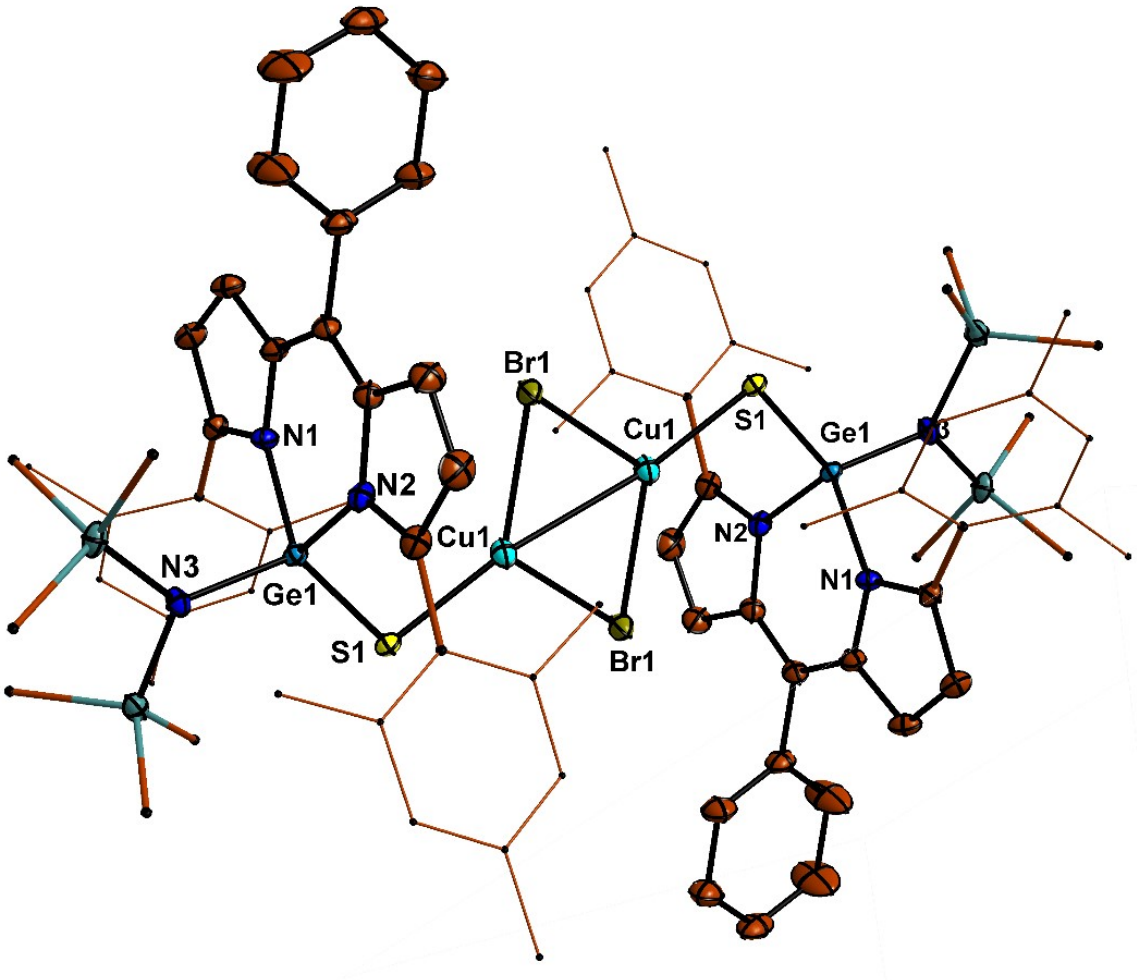

Molecular structure of DPMGe(Se)N(TMS)$_2$ (**13**). All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ge(1)−Se(1) 2.194(1), Ge(1)−N(1) 1.951(7), Ge(1)−N(2) 1.953(7), Ge(1)−N(3) 1.837(7); N(3)−Ge(1)−N(1) 108.1(3), N(3)−Ge(1)−N(2) 104.5(3), N(1)−Ge(1)−N(2) 92.9(3). Data collection temperature: 100 K.

**Figure S92. Molecular structure of compound 14**



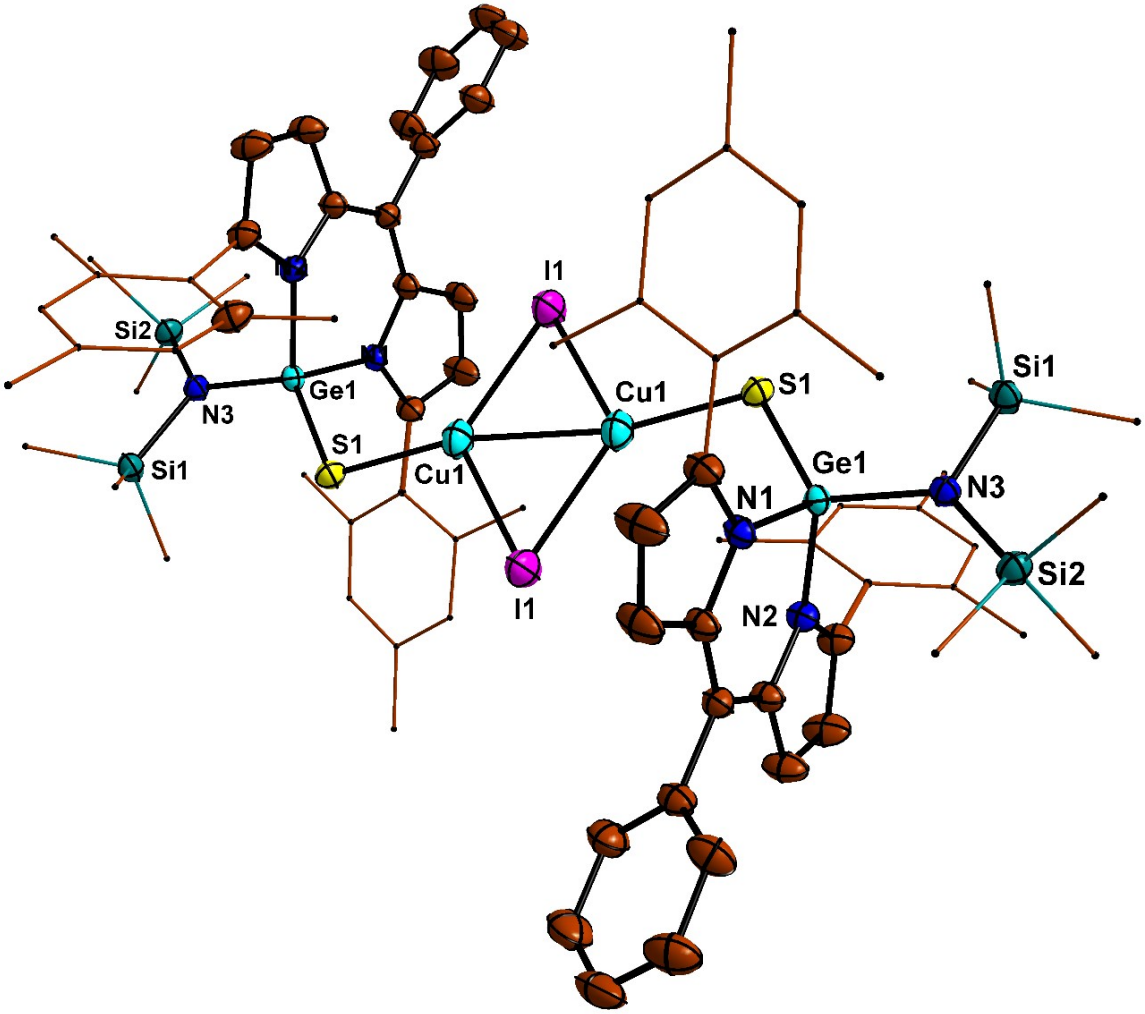

Molecular structure of [(DPMGe(S)N(TMS)$_2$)→CuCl] (**14**). All hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ge(1)−S(1) 2.132(7), Ge(1)−N(1) 1.934(1), Ge(1)−N(2) 1.938(1), Ge(1)−N(3) 1.831(1), S(1)−Cu(1) 2.143(8), Cu(1)−Cl(1) 2.087(2); N(3)−Ge(1)−N(1) 112.2(5), N(3)−Ge(1)−N(2) 112.0(5), N(1)−Ge(1)−N(2) 96.6(4), N(3)-Ge(1)-S(1) 116.30(4), S(1)-Cu(1)-Cl(1) 178.04(2). Data collection temperature: 100 K.

**Figure S93. Molecular structure of compound 16**



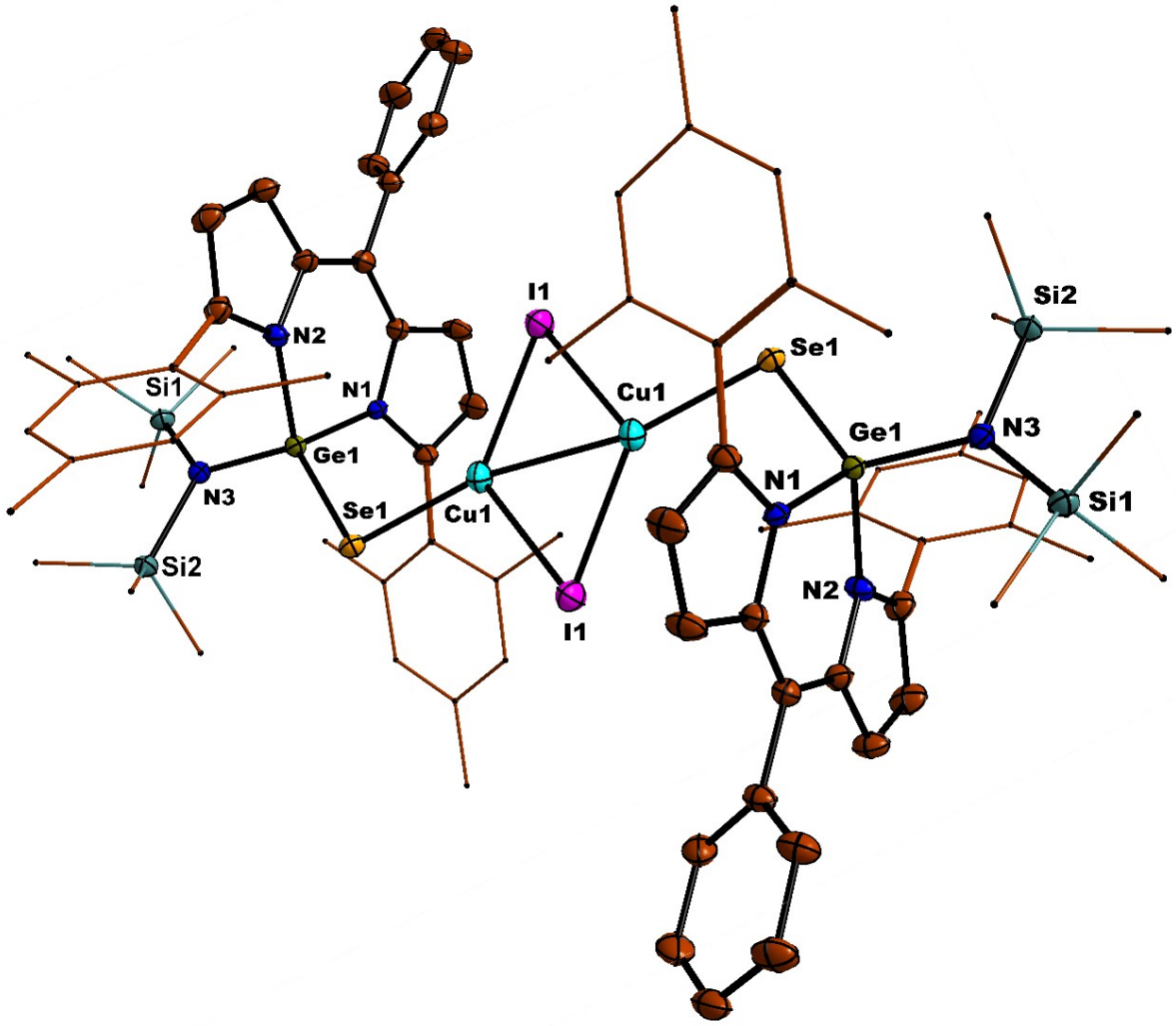

Molecular structure of $[(DPMGe(S)N(TMS)_2)\rightarrow CuBr]_2$ (**16**). All hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ge(1)−S(1) 2.101(7), Ge(1)−N(1) 1.936(2), Ge(1)−N(2) 1.931(2), Ge(1)−N(3) 1.838(2), S(1)−Cu(1) 2.212(8), Cu(1)−Br(1) 2.458(5), Cu1-Cu1 2.725(5); N(3)−Ge(1)−N(1) 103.47(9), N(3)−Ge(1)−N(2) 110.32(9), N(1)−Ge(1)−N(2) 95.13(9), Ge(1)-S(1)-Cu(1) 103.31(3), Br(1)-Cu(1)-Br(1) 111.85(2), S(1)-Cu(1)-Br(1) 132.92(2). Data collection temperature: 100 K. Symmetry transformation used to generate equivalent atoms: -x, 1-y, 2-z.

**Figure S94. Molecular structure of compound 17**




Molecular structure of $[(DPMGe(S)N(TMS)_2)\rightarrow CuI]_2$ (**17**). All hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ge(1)−S(1) 2.103(8), Ge(1)−N(1) 1.932(2), Ge(1)−N(2) 1.934(2), Ge(1)−N(3) 1.848(2), S(1)−Cu(1) 2.241(9), Cu(1)−I(1) 2.568(6), Cu1-Cu1 2.699(8); N(3)−Ge(1)−N(1) 110.77(1), N(3)−Ge(1)−N(2) 105.93(1), N(1)−Ge(1)−N(2) 94.84(9), Ge(1)-S(1)-Cu(1) 106.51(3), S(1)-Cu(1)-I(1) 133.54(3). Data collection temperature: 278 K. Symmetry transformation used to generate equivalent atoms: 1-x, 1-y, 1-z.

**Figure S95. Molecular structure of compound 19**




Molecular structure of $[(DPMGe(Se)N(TMS)_2)\rightarrow CuI]_2$ (**19**). All hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg): Ge(1)−Se(1) 2.234(6), Ge(1)−N(1) 1.928(2), Ge(1)−N(2) 1.931(3), Ge(1)−N(3) 1.853(3), Se(1)−Cu(1) 2.349(5), Cu(1)−I(1) 2.566(5), Cu1-Cu1 2.581(8); N(3)−Ge(1)−N(1) 110.98(2), N(3)−Ge(1)−N(2) 105.98(2), N(1)−Ge(1)−N(2) 94.50 (1), Ge(1)-Se(1)-Cu(1) 102.18(2), I(1)-Cu(1)-I(1) 120.47(2), Se(1)-Cu(1)-I(1) 133.05(2). Data collection temperature: 100 K. Symmetry transformation used to generate equivalent atoms: 1-x, 1-y, 1-z.

**Table S4. Crystal data and structure refinement for DPMGePh (2), DPMGe(S)Ph (3), DPMGe(Se)Ph (4), and DPMGe(S)OEt (9)**

| | **DPMGePh (2)** | **DPMGe(S)Ph (3)** | **DPMGe(Se)Ph (4)** | **DPMGe(S)OEt (9)** |
|---|---|---|---|---|
| Empirical formula | $C_{39}H_{36}GeN_2$ | $C_{39}H_{36}GeN_2S$ | $C_{39}H_{36}GeN_2Se$ | $C_{35}H_{36}GeN_2OS$ |
| Formula weight | 605.31 | 637.37 | 684.27 | 605.33 |
| Temperature, K | 302(2) | 273.15 | 302(2) | 273(2) |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| $a$, Å | 15.0811(6) | 7.995(5) | 8.0415(3) | 14.9611(5) |
| $b$, Å | 11.4764(4) | 21.180(1) | 21.2170(8) | 14.0451(5) |
| $c$, Å | 18.5521(7) | 19.615(1) | 19.7259(7) | 15.5244(6) |
| $\alpha$, deg | 90 | 90 | 90 | 90 |
| $\beta$, deg | 90.19 | 99.409(3) | 99.617(1) | 107.287(1) |
| $\gamma$, deg | 90 | 90 | 90 | 90 |
| Volume, Å$^3$ | 3210.9(2) | 3276.8(4) | 3318.3(2) | 3114.79(2) |
| $Z$ | 4 | 4 | 4 | 4 |
| Density (calcd), mg/m$^3$ | 1.252 | 1.292 | 1.370 | 1.290 |
| Absorption coefficient, mm$^{-1}$ | 0.983 | 1.028 | 2.049 | 1.080 |
| $F$(000) | 1264 | 1328 | 1400 | 1264 |
| Crystal size, mm$^3$ | 0.28 x 0.15 x 0.11 | 0.18 x 0.16 x 0.11 | 0.24 x 0.18 x 0.12 | 0.20 x 0.18 x 0.16 |
| $\theta$ range for data | 2.087 to 28.293 | 4.628 to 56.682 | 2.187 to 28.294 | 1.997 to 28.297 |

| collection, deg | | | | |
|---|---|---|---|---|
| Limiting indices | -20 ≤ h ≤ 20,<br>-15 ≤ k ≤ 15,<br>-24 ≤ l ≤ 24 | -10 ≤ h ≤ 10,<br>-28 ≤ k ≤ 28,<br>-26 ≤ l ≤ 26 | -10 ≤ h ≤ 10,<br>-28 ≤ k ≤ 28,<br>-26 ≤ l ≤ 26 | -19 ≤ h ≤ 19,<br>-18 ≤ k ≤ 18,<br>-20 ≤ l ≤ 20 |
| No. of reflection collected | 157823 | 102855 | 171359 | 89570 |
| No. of independent reflection | 7970<br>[$R_{(int)}$ = 0.0854] | 8110<br>[$R_{(int)}$ = 0.0576] | 8248<br>[$R_{(int)}$ = 0.0562] | 7753<br>[$R_{(int)}$ = 0.0612] |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| No. of data /restraints/ parameters | 7970 / 0 / 385 | 8110 / 0 / 392 | 8235 / 0 / 394 | 7735 / 0 / 368 |
| Goodness-of-fit on $F^2$ | 0.938 | 1.141 | 1.045 | 0.787 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1$ = 0.0383,<br>$wR_2$ = 0.1272 | $R_1$ = 0.0887,<br>$wR_2$ = 0.2482 | $R_1$ = 0.0311,<br>$wR_2$ = 0.0.0689 | $R_1$ = 0.0321,<br>$wR_2$ = 0.1036 |
| $R$ indices (all data) | $R_1$ = 0.0523,<br>$wR_2$ = 0.1336 | $R_1$ = 0.0953,<br>$wR_2$ = 0.2521 | $R_1$ = 0.0406,<br>$wR_2$ = 0.0708 | $R_1$ = 0.0457,<br>$wR_2$ = 0.1130 |
| Largest diff peak and hole, e Å$^{-3}$ | 0.399 and -0.433 | 2.50 and -0.98 | 0.439 and -0.462 | 0.309 and -0.299 |

**Table S5. Crystal data and structure refinement for DPMGeN(TMS)$_2$ (11), DPMGe(S)N(TMS)$_2$ (12), and DPMGe(Se)N(TMS)$_2$ (13)**

| | **DPMGeN(TMS)$_2$ (11)** | **DPMGe(S)N(TMS)$_2$ (12)** | **DPMGe(Se)N(TMS)$_2$ (13)** |
|---|---|---|---|
| Empirical formula | $C_{39}H_{49}GeN_3Si_2$ | $C_{39}H_{49}GeN_3SSi_2$ | $C_{39}H_{49}GeN_3SeSi_2$ |
| Formula weight | 688.60 | 742.74 | 767.56 |

| Temperature, K | 100(2) | 100(2) | 100(2) |
|---|---|---|---|
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/n$ | $P$-1 | $P$-1 |
| $a$, Å | 13.302(2) | 8.769(1) | 8.966(6) |
| $b$, Å | 9.776(16) | 11.382(2) | 11.294(8) |
| $c$, Å | 28.456(4) | 21.887(4) | 19.906(2) |
| $\alpha$, deg | 90 | 76.889(8) | 86.969(4) |
| $\beta$, deg | 93.91 | 86.438(8) | 77.252(4) |
| $\gamma$, deg | 90 | 72.957(8) | 73.433(4) |
| Volume, Å$^3$ | 3691.8(1) | 2034.3(6) | 1884.5(2) |
| $Z$ | 4 | 2 | 2 |
| Density (calcd), mg/m$^3$ | 1.239 | 1.245 | 1.353 |
| Absorption coefficient, mm$^{-1}$ | 0.925 | 0.895 | 1.873 |
| $F$(000) | 1456 | 808 | 796 |
| Crystal size, mm$^3$ | 0.15 x 0.12 x 0.10 | 0.16 x 0.11 x 0.08 | 0.20 x 0.15 x 0.10 |
| $\theta$ range for data collection, deg | 2.203 to 28.283 | 1.947 to 28.276 | 1.88 to 26.47 |
| Limiting indices | $-17 \le h \le 17$,<br>$-13 \le k \le 13$,<br>$-37 \le l \le 37$ | $-11 \le h \le 11$,<br>$-15 \le k \le 15$,<br>$-29 \le l \le 29$ | $-11 \le h \le 11$,<br>$-14 \le k \le 14$,<br>$-24 \le l \le 24$ |
| No. of reflection collected | 55515 | 59248 | 45430 |
| No. of independent reflection | 9127<br>[$R_{(int)} = 0.088$] | 10058<br>[$R_{(int)} = 0.0896$] | 7711<br>[$R_{(int)} = 0.0889$] |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| No. of data | 9127 / 0 / 418 | 10058 / 0 / 455 | 7711 / 0 / 415 |

| /restraints/ parameters | | | |
|---|---|---|---|
| Goodness-of-fit on $F^2$ | 1.123 | 1.045 | 1.069 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1 = 0.0507$, $wR_2 = 0.1478$ | $R_1 = 0.0751$, $wR_2 = 0.1963$ | $R_1 = 0.0903$, $wR_2 = 0.2538$ |
| $R$ indices (all data) | $R_1 = 0.0650$, $wR_2 = 0.1643$ | $R_1 = 0.1019$, $wR_2 = 0.2224$ | $R_1 = 0.1096$, $wR_2 = 0.2706$ |
| Largest diff peak and hole, e Å$^{-3}$ | 0.864 and -0.652 | 1.991 and -1.255 | 4.64 and -2.36 |

**Table S6. Crystal data and structure refinement for [(DPMGe(S)N(TMS)$_2$)→CuCl] (14) [(DPMGe(S)N(TMS)$_2$)→CuBr]$_2$ (16), [(DPMGe(S)N(TMS)$_2$)→CuI]$_2$ (17), and [(DPMGe(Se)N(TMS)$_2$)→CuI]$_2$ (19)**

| | **[(DPMGe(S)N(TMS)$_2$)→CuCl] (14)** | **[(DPMGe(S)N(TMS)$_2$)→CuBr]$_2$ (16)** | **[(DPMGe(S)N(TMS)$_2$)→CuI]$_2$ (17)** | **[(DPMGe(Se)N(TMS)$_2$)→CuI]$_2$ (19)** |
|---|---|---|---|---|
| Empirical formula | $C_{39}H_{49}ClCuGeN_3SSi_2$ | $C_{84}H_{112}Br_2Cu_2Ge_2N_6S_2Si_4$ | $C_{78}H_{98}I_2Cu_2Ge_2N_6S_2Si_4$ | $C_{78}H_{98}Cu_2Ge_2I_2N_6Se_2Si_4$ |
| Formula weight | 819.66 | 1814.40 | 1822.22 | 1916.02 |
| Temperature, K | 100 | 100 | 278 | 100 |
| Wavelength, Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | *P*-1 | *P*-1 | $P2_1/c$ | $P2_1/c$ |
| *a*, Å | 10.915(3) | 12.3707(4) | 13.947(2) | 13.7954(7) |
| *b*, Å | 12.011(3) | 12.4183(4) | 12.306(2) | 12.2314(6) |

| | | | | |
|---|---|---|---|---|
| $c$, Å | 17.769(4) | 16.7015(5) | 23.936(4) | 23.9124(1) |
| $\alpha$, deg | 83.360(1) | 89.009(1) | 90 | 90 |
| $\beta$, deg | 76.387(1) | 74.715(1) | 90.327(6) | 90.032(2) |
| $\gamma$, deg | 69.278(1) | 61.241(1) | 90 | 90 |
| Volume, Å$^3$ | 2116.37(9) | 2151.41(1) | 4107.9(1) | 4034.9(3) |
| $Z$ | 2 | 1 | 2 | 2 |
| Density (calcd), mg/m$^3$ | 1.286 | 1.400 | 1.473 | 1.577 |
| Absorption coefficient, mm$^{-1}$ | 1.411 | 2.258 | 2.140 | 3.029 |
| $F$(000) | 852 | 938 | 1848 | 1920 |
| Crystal size, mm$^3$ | 0.28 x 0.14 x 0.11 | 0.20 x 0.15 x 0.10 | 0.18 x 0.16 x 0.11 | 0.19 x 0.16 x 0.14 |
| $\theta$ range for data collection, deg | 1.31 to 28.21 | 1.39 to 28.32 | 1.7 to 28.50 | 1.476 to 26.454 |
| Limiting indices | $-14 \le h \le 14$,<br>$-15 \le k \le 15$,<br>$-23 \le l \le 23$ | $-16 \le h \le 16$,<br>$-16 \le k \le 16$,<br>$-22 \le l \le 22$ | $-18 \le h \le 18$,<br>$-16 \le k \le 16$,<br>$-31 \le l \le 22$ | $-17 \le h \le 17$,<br>$-15 \le k \le 15$,<br>$-29 \le l \le 29$ |
| No. of reflection collected | 66778 | 73718 | 159619 | 106855 |
| No. of independent reflection | 10373<br>[$R_{(int)}$ = 0.0407] | 10700<br>[$R_{(int)}$ = 0.0532] | 10306<br>[$R_{(int)}$ = 0.0512] | 7753<br>[$R_{(int)}$ = 0.0612] |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |

| | | | | |
|---|---|---|---|---|
| No. of data /restraints/ parameters | 10373 / 0 / 479 | 10700 / 0 / 473 | 10306 / 0 / 445 | 8305 / 0 / 445 |
| Goodness-of-fit on $F^2$ | 1.041 | 1.044 | 1.078 | 1.039 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1 = 0.0270$, $wR_2 = 0.0643$ | $R_1 = 0.0342$, $wR_2 = 0.0821$ | $R_1 = 0.0363$, $wR_2 = 0.0831$ | $R_1 = 0.0316$, $wR_2 = 0.1179$ |
| $R$ indices (all data) | $R_1 = 0.0345$, $wR_2 = 0.0684$ | $R_1 = 0.0444$, $wR_2 = 0.0888$ | $R_1 = 0.0564$, $wR_2 = 0.0934$ | $R_1 = 0.0369$, $wR_2 = 0.1244$ |
| Largest diff peak and hole, e Å$^{-3}$ | 0.46 and -0.34 | 1.41 and -0.84 | 0.78 and -0.79 | 0.309 and -0.299 |

**Computational details**

GAUSSIAN-09 was used for carrying out theoretical calculations.[S10] The geometries of compounds **3**, **4**, **12**, **13**, **18**, **xvii**, **xviii**, LGe(S)N(TMS)$_2$ (**xx**), LGe(Se)N(TMS)$_2$ (**xxi**), CuCl, CuBr, and CuI were optimized at the B3LYP level of theory using LANL2DZ basis set having Effective Core Potential (ECP) for the core electrons of germanium, selenium, copper, bromine, and iodine atoms; 6-31G** basis set for rest of the elements (L = amidinate). For the geometry optimizations of compounds **3**, **4**, **12**, **13**, **xvii**, and **xviii**, coordinates obtained from single crystal X-ray diffraction studies were used. For compounds **18**, **xx**, **xxi**, CuCl, CuBr, and CuI, coordinates were obtained by modeling their structures (using GaussView 5). The frequency calculations were carried out on the optimized geometries to characterize the stationary points as minima. The same level of theory and basis sets were used for performing the AOMix[S11-S12] and Weinhold's Natural Bond Orbital (NBO)[S13-S14] calculations on the optimized geometries. TD-DFT [S15] calculations were carried out on the optimized geometries of compounds **12**, **13**, and **18** using toluene as a solvent with the aforementioned level of theory and basis sets. Chemcraft (http://www.chemcraftprog.com) software was used for the visualization of Gaussian outputs.

**Table S7.** NPA charges of germanium and chalcogen atoms in dipyrrinate, aminotroponiminate, and amidinate ligand stabilized thio- and selenogermaamides.

| S. No. | Compound | WBI of Ge=E | NPA Charge | | |
|---|---|---|---|---|---|
| | | | Ge | S | Se |
| 1. | DPMGe=S(N(TMS)$_2$) **12** | 1.419 | 1.852 | -0.826 | ---- |
| 2. | ATIGe=S(N(TMS)$_2$) (**xviii**) | 1.408 | 1.852 | -0.836 | ---- |
| 3. | LGe=S(N(TMS)$_2$) (**xx**) | 1.429 | 1.803 | -0.827 | ---- |
| | | | | | |
| 4. | DPMGe=Se(N(TMS)$_2$) **13** | 1.439 | 1.702 | ---- | -0.685 |
| 5. | ATIGe=Se(N(TMS)$_2$) (**xvii**) | 1.424 | 1.710 | ---- | -0.701 |
| 6. | LGe=Se(N(TMS)$_2$) (**xxi**) | 1.443 | 1.659 | ---- | -0.693 |

DPM = dipyirrinate, ATI = aminotroponiminate, L = amidinate

**Table S8.** The HOMO of dipyrrinate, aminotroponiminate, and amidinate ligand stabilized thio- and selenogermaamides along with the percentage contributions of germanium and E atoms (E = S, Se)

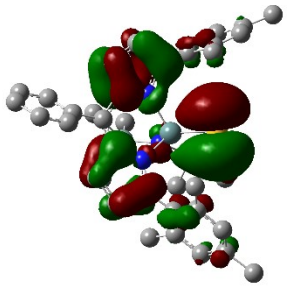
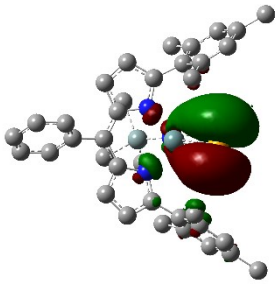
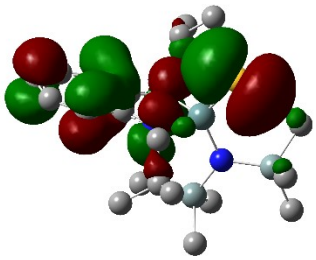
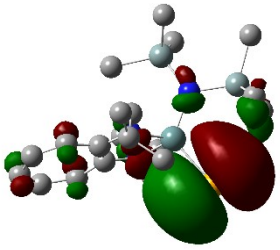
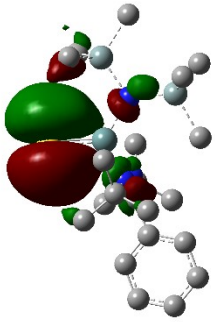
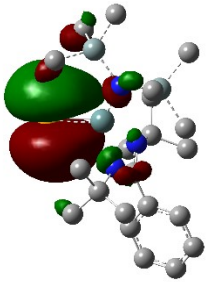
| 1. DPMGe(S)N(TMS)$_2$ **12** | 4. DPMGe(Se)N(TMS)$_2$ **13** |
|---|---|
|  |  |
| ε = -0.18514 a.u.<br>Ge: 6.37%, S: 80.64% | ε = -0.17427 a.u.<br>Ge: 6.90%, Se: 83.27% |
| | |
| 2. ATIGe(S)N(TMS)$_2$ (**xviii**) | ATIGe(Se)N(TMS)$_2$ (**xvii**) |
|  |  |
| ε = -0.18739 a.u.<br>Ge: 6.20%, S: 79.97% | ε = -0.17750 a.u.<br>Ge: 7.21%, Se: 84.10% |
| | |
| 3. LGe(S)N(TMS)$_2$ (**xx**) | 6. LGe(Se)N(TMS)$_2$ (**xxi**) |
|  |  |
| HOMO (ε = -0.19305 a.u.)<br>Ge: 7.84%, S: 84.83% | HOMO (ε = -0.18257 a.u.)<br>Ge: 8.27%, Se: 86.25% |

**Table S9.** WBI of the Ge=E bond and NPA charges of chalcogen (E) atoms in compounds **12** and **13**

| Compounds | WBI of Ge=E | E | NPA charges |
|---|---|---|---|
| **12** | 1.419 | S | -0.826 |
| **13** | 1.439 | Se | -0.685 |

**Table S10.** NPA charges of copper and halogen atoms in copper halides

| Compounds | NPA Charges | |
|---|---|---|
| | Cu | X (X = Cl, Br, I) |
| CuCl | 0.624 | -0.624 |
| CuBr | 0.553 | -0.553 |
| CuI | 0.506 | -0.506 |

**Coordinates of the optimized geometries of compounds 3, 4, 12, 13, 18, xvii, xviii, xx, xxi, CuCl, CuBr, and CuI**

Compound **3**

| | | | |
|---|---|---|---|
| Ge | 0.02719600 | -0.52710300 | -0.27954600 |
| S | 0.09092600 | -1.84405700 | -1.90401300 |
| N | 1.38794600 | 0.92259500 | -0.25008600 |
| N | -1.47671100 | 0.77306100 | -0.25905100 |
| C | 3.45853500 | -0.54006100 | -0.37388100 |
| C | 0.06313300 | -1.16334500 | 1.57691300 |
| C | 3.96430800 | -1.19971000 | 0.76808200 |
| C | 1.12816800 | 2.29606700 | -0.12193500 |
| C | 0.11927500 | -2.54122300 | 1.82810900 |
| H | 0.14451500 | -3.23384300 | 0.99082800 |
| C | -0.15053000 | 2.87739100 | -0.11493700 |
| C | 2.73844600 | 0.75224300 | -0.22624800 |
| C | -2.79967800 | 0.47134400 | -0.36431200 |
| C | 3.75059000 | -1.02696200 | -1.66741600 |
| C | -0.23052400 | 4.36694600 | -0.01809500 |
| C | 0.03053600 | -0.27619600 | 2.66525500 |
| H | -0.01243800 | 0.79695000 | 2.49512300 |
| C | -1.36077600 | 2.17097400 | -0.20275300 |
| C | 4.95611500 | -2.90698500 | -0.67274500 |
| C | -2.66768300 | 2.72371500 | -0.28350000 |
| H | -2.89510600 | 3.77923600 | -0.28479300 |
| C | 3.75862800 | -0.64816300 | 2.16061300 |
| H | 4.18482700 | 0.35648100 | 2.26137300 |
| H | 4.23869100 | -1.29046100 | 2.90360400 |
| H | 2.69864300 | -0.57339100 | 2.41876600 |
| C | 4.69368500 | -2.37941500 | 0.59433100 |
| H | 5.07399900 | -2.89313200 | 1.47450400 |
| C | -3.55459300 | 1.66932400 | -0.37690500 |
| H | -4.63164200 | 1.71170300 | -0.45826600 |
| C | -3.79705800 | -1.55879400 | 0.71842900 |
| C | 0.14182700 | -3.02305700 | 3.13924200 |
| H | 0.18508200 | -4.09341900 | 3.32103000 |
| C | -4.62044300 | -3.41718600 | -0.63878600 |
| C | -4.24693200 | -2.71490300 | -1.78763800 |
| H | -4.43460300 | -3.15406700 | -2.76476600 |
| C | -3.25365900 | -0.74594100 | -2.99809900 |
| H | -3.70453800 | -1.23458700 | -3.86606300 |
| H | -2.16510800 | -0.76299300 | -3.12488800 |
| H | -3.57600200 | 0.30066200 | -2.99060500 |
| C | -3.63513100 | -1.46050500 | -1.72490000 |
| C | -4.39965400 | -2.81517200 | 0.60235200 |
| H | -4.71425000 | -3.32937400 | 1.50783600 |
| C | 0.05294900 | -0.75625600 | 3.97636600 |
| H | 0.02749100 | -0.06019100 | 4.81057200 |
| C | 0.10855500 | -2.13225500 | 4.21361000 |
| H | 0.12583500 | -2.50708300 | 5.23337700 |
| C | -0.83543900 | 4.97789500 | 1.09166300 |
| H | -1.23790100 | 4.35856800 | 1.88724700 |

| | | | |
|---|---|---|---|
| C | 2.37399700 | 2.96870100 | 0.00206300 |
| H | 2.49437500 | 4.03441700 | 0.12741700 |
| C | -3.38014400 | -0.89455700 | -0.45589200 |
| C | 3.36682400 | 2.01116700 | -0.06785000 |
| H | 4.43661000 | 2.15936100 | -0.02331600 |
| C | 4.49092500 | -2.20573400 | -1.78780600 |
| H | 4.70852000 | -2.58423100 | -2.78389600 |
| C | 0.29386500 | 5.17695800 | -1.03772200 |
| H | 0.75240800 | 4.71164300 | -1.90454100 |
| C | -3.63648800 | -0.93220500 | 2.08490200 |
| H | -4.05816600 | 0.07857300 | 2.11410300 |
| H | -2.58511300 | -0.85047300 | 2.37551600 |
| H | -4.14598600 | -1.53086700 | 2.84461700 |
| C | -0.38735800 | 7.16566300 | 0.16088900 |
| H | -0.44804500 | 8.24778100 | 0.22994800 |
| C | 0.21046300 | 6.56660800 | -0.94956600 |
| H | 0.61088100 | 7.18044600 | -1.75102200 |
| C | -5.23779700 | -4.79184000 | -0.73806000 |
| H | -5.86260500 | -5.01594200 | 0.13187300 |
| H | -4.46288200 | -5.56670200 | -0.79244200 |
| H | -5.85570500 | -4.88984300 | -1.63612000 |
| C | 3.28526400 | -0.30366000 | -2.90747800 |
| H | 3.79769500 | -0.68815900 | -3.79353000 |
| H | 3.47506000 | 0.77322600 | -2.84497500 |
| H | 2.20824300 | -0.45015400 | -3.04742600 |
| C | -0.90767200 | 6.36802600 | 1.18183200 |
| H | -1.36970800 | 6.82681200 | 2.05107700 |
| C | 5.71201700 | -4.20440500 | -0.83303400 |
| H | 6.38346300 | -4.38577000 | 0.01179100 |
| H | 6.30879900 | -4.21025900 | -1.75042700 |
| H | 5.02162800 | -5.05526400 | -0.89044900 |

Compound **4**

| | | | |
|---|---|---|---|
| Ge | -0.43553200 | -0.00431300 | -0.15697300 |

| | | | |
|---|---|---|---|
| Se | -1.95996100 | -0.02555000 | -1.84654400 |
| N | 0.92137100 | 1.44933300 | -0.18983300 |
| N | 0.95309100 | -1.42723800 | -0.17732500 |
| C | -0.98482500 | -0.01263900 | 1.72846500 |
| C | -2.34895300 | -0.01665400 | 2.05080600 |
| H | -3.08542000 | -0.01638000 | 1.25108600 |
| C | -1.26706500 | 3.86203400 | 0.88036300 |
| C | 2.34000300 | -1.22063500 | -0.10498300 |
| C | 0.67596000 | 2.78565800 | -0.28612300 |
| C | 2.31473100 | 1.27154500 | -0.18874700 |
| C | 2.97203800 | 0.03274400 | -0.12655300 |
| C | -0.04171600 | -0.01379000 | 2.76946700 |
| H | 1.02209700 | -0.01281700 | 2.54482300 |
| C | -0.58683800 | -3.44982400 | -0.24061700 |
| C | -1.24462400 | 3.75863800 | -1.56774000 |
| C | 0.73283100 | -2.77097400 | -0.14667800 |
| C | -2.76255100 | -0.02029300 | 3.38535400 |
| H | -3.82292800 | -0.02271800 | 3.62231000 |
| C | -2.49214700 | 4.53268700 | 0.81524800 |
| H | -2.96133300 | 4.85477400 | 1.74228400 |
| C | -1.23168200 | -3.90314800 | 0.93164100 |
| C | 2.92173100 | 2.55202300 | -0.29424000 |
| H | 3.98555900 | 2.73158100 | -0.33623500 |
| C | 4.46674100 | 0.04962500 | -0.08987500 |
| C | -1.11388700 | -3.76756100 | -1.51231400 |
| C | -0.66069700 | 3.43640000 | -0.32213200 |
| C | -2.46683100 | 4.43537000 | -1.57909600 |
| H | -2.92160400 | 4.67214700 | -2.53822900 |
| C | 1.90560400 | 3.48507100 | -0.34772900 |
| H | 1.99256700 | 4.55933200 | -0.43031100 |
| C | -3.11714700 | 4.81418200 | -0.40192100 |
| C | -1.81670300 | -0.02048800 | 4.41204700 |
| H | -2.13864000 | -0.02336200 | 5.44985800 |
| C | -2.43914300 | -4.59646900 | 0.80947400 |
| H | -2.94100300 | -4.93446100 | 1.71341500 |
| C | -0.58747100 | 3.37945000 | -2.87229900 |
| H | 0.47896300 | 3.62706700 | -2.88065300 |
| H | -1.06369500 | 3.89753100 | -3.70917400 |
| H | -0.68374800 | 2.30069600 | -3.04254500 |
| C | -0.60645400 | 3.64608000 | 2.22276000 |
| H | -1.15218300 | 4.17389200 | 3.00933600 |
| H | 0.42528500 | 4.01485000 | 2.22377300 |
| H | -0.56977700 | 2.58797900 | 2.49584600 |
| C | 2.96910400 | -2.49102400 | -0.00724900 |
| H | 4.03375300 | -2.65102200 | 0.07497000 |
| C | -3.00788100 | -4.87779300 | -0.43543200 |
| C | -2.31909400 | -4.47144600 | -1.58083000 |
| H | -2.72878000 | -4.70748000 | -2.56022700 |
| C | -0.45367900 | -0.01738100 | 4.10350500 |
| H | 0.28528800 | -0.01849500 | 4.90034800 |

| | | | |
|---|---|---|---|
| C | 5.14694400 | 0.61993600 | 0.99744100 |
| H | 4.57799600 | 1.04337600 | 1.81940200 |
| C | -0.63237600 | -3.68670300 | 2.30252200 |
| H | 0.36052800 | -4.14418300 | 2.38136900 |
| H | -1.26653900 | -4.13047200 | 3.07445400 |
| H | -0.51533800 | -2.62528700 | 2.53619000 |
| C | -0.40850900 | -3.36652300 | -2.78493300 |
| H | -0.81859900 | -3.91023200 | -3.64040200 |
| H | 0.66657400 | -3.56899500 | -2.73638200 |
| H | -0.54305800 | -2.29443700 | -2.97027000 |
| C | 1.97241700 | -3.44627200 | -0.03739300 |
| H | 2.08020900 | -4.52100300 | 0.00380000 |
| C | 5.21129300 | -0.50273200 | -1.14385400 |
| H | 4.69216200 | -0.93587500 | -1.99306000 |
| C | -4.45991300 | 5.50368200 | -0.44535800 |
| H | -5.27508100 | 4.77101100 | -0.49549800 |
| H | -4.55134900 | 6.14884700 | -1.32476800 |
| H | -4.62612100 | 6.11628300 | 0.44594400 |
| C | 6.54145300 | 0.63118300 | 1.03194500 |
| H | 7.05433900 | 1.06720700 | 1.88422000 |
| C | 7.27412700 | 0.08355500 | -0.02287400 |
| H | 8.35975500 | 0.09677400 | 0.00286400 |
| C | 6.60568200 | -0.48047100 | -1.11123500 |
| H | 7.16892100 | -0.90219900 | -1.93849700 |
| C | -4.33410100 | -5.59217500 | -0.54031100 |
| H | -4.51652400 | -6.23114600 | 0.32909200 |
| H | -4.38406300 | -6.21555300 | -1.43847900 |
| H | -5.16195900 | -4.87442300 | -0.59804400 |

Compound **12**

| | | | |
|---|---|---|---|
| Ge | -0.31151400 | 0.24328100 | -0.24499400 |
| S | -1.38950600 | 1.04105700 | -1.85662600 |
| Si | 0.11579800 | 0.06507700 | 3.00237900 |
| Si | -2.44259300 | 1.26050500 | 1.85304900 |
| N | -0.83406200 | 0.47811900 | 1.54215400 |
| N | 1.61634400 | 0.70525600 | -0.43340700 |
| N | 0.06634200 | -1.71160000 | -0.39577500 |
| C | 2.55113600 | -1.60427600 | -0.29154600 |
| C | -2.28417400 | -2.61594800 | -0.82057900 |
| C | -2.62082400 | -2.47396500 | -2.18718400 |
| C | -3.29570500 | -2.84811300 | 0.13606900 |
| C | 2.67830800 | -0.21536100 | -0.44789400 |
| C | 3.81039800 | -2.40805100 | -0.24793300 |
| C | 1.33129800 | -2.29739400 | -0.21769600 |
| C | -0.84958000 | -2.72212300 | -0.44363700 |
| C | 1.40246400 | 3.21467200 | -0.91579300 |
| C | 1.15601300 | 4.06685100 | 0.17898900 |
| C | -4.63100300 | -2.86057400 | -0.27747800 |
| H | -5.40754600 | -3.02444600 | 0.46627800 |
| C | 2.13735400 | 1.93396100 | -0.72526700 |
| C | 1.15493500 | -3.70038100 | -0.08385400 |
| H | 1.94918700 | -4.41510200 | 0.07086600 |
| C | 6.18351000 | -3.91086200 | -0.17444100 |
| H | 7.10043300 | -4.49214400 | -0.14550100 |
| C | -3.96949000 | -2.49919800 | -2.55144700 |
| H | -4.22549300 | -2.38389500 | -3.60210700 |
| C | -4.99099200 | -2.67453600 | -1.61491300 |
| C | 4.07379700 | -3.37612200 | -1.23106200 |
| H | 3.35673000 | -3.53116100 | -2.03084100 |
| C | -0.19429400 | -3.95837300 | -0.22651100 |
| H | -0.68772000 | -4.92008700 | -0.22845500 |
| C | 0.55553200 | 5.30957600 | -0.04723400 |
| H | 0.36461300 | 5.96110200 | 0.80257400 |
| C | -2.96348400 | -3.08438700 | 1.58995900 |
| H | -2.38818300 | -4.00643200 | 1.73144400 |
| H | -3.87448300 | -3.16754500 | 2.18898800 |
| H | -2.36156300 | -2.26913700 | 1.99698900 |
| C | 4.75657500 | -2.19902600 | 0.76878100 |
| H | 4.55981900 | -1.45528600 | 1.53395000 |
| C | 1.10717400 | 3.64534900 | -2.22977100 |
| C | 0.51052700 | 4.89577700 | -2.40613700 |
| H | 0.27165600 | 5.21954700 | -3.41662200 |
| C | -1.56444600 | -2.32165600 | -3.25392800 |
| H | -0.75826300 | -3.05335200 | -3.13232900 |
| H | -1.12452700 | -1.31939500 | -3.20855900 |
| H | -1.99956700 | -2.45816100 | -4.24766000 |
| C | 5.25458600 | -4.11730300 | -1.19625100 |
| H | 5.44938300 | -4.85393100 | -1.97014300 |
| C | 5.93029300 | -2.95178100 | 0.80801400 |
| H | 6.64661100 | -2.78763500 | 1.60768400 |

| | | | |
|---|---|---|---|
| C | 1.55226300 | 3.66990300 | 1.57989300 |
| H | 1.35239300 | 4.47915200 | 2.28722100 |
| H | 2.61789400 | 3.42156500 | 1.64292700 |
| H | 0.99229000 | 2.79182600 | 1.90912000 |
| C | 3.53810300 | 1.82064500 | -0.89083600 |
| H | 4.19079100 | 2.64822700 | -1.13070400 |
| C | 3.87660500 | 0.49257900 | -0.72484800 |
| H | 4.85425300 | 0.04416000 | -0.81847600 |
| C | 0.21165000 | 5.73761600 | -1.33125500 |
| C | -6.44102200 | -2.65234700 | -2.03488900 |
| H | -7.06867400 | -3.22258400 | -1.34340200 |
| H | -6.57396300 | -3.06792700 | -3.03861300 |
| H | -6.82656000 | -1.62540300 | -2.05586300 |
| C | 1.40216500 | 2.78196400 | -3.43194700 |
| H | 1.22571800 | 3.33582900 | -4.35793000 |
| H | 0.74791200 | 1.90287900 | -3.42795000 |
| H | 2.43910500 | 2.43002800 | -3.43901300 |
| C | -0.47092800 | 7.06613800 | -1.55374000 |
| H | -0.15988600 | 7.52291000 | -2.49852700 |
| H | -0.25184100 | 7.77091000 | -0.74594100 |
| H | -1.56057500 | 6.94515100 | -1.59576600 |
| C | 1.97868600 | -0.14297200 | 2.73904900 |
| H | 2.22848400 | -1.08086000 | 2.24031800 |
| H | 2.41959200 | -0.18426900 | 3.74294700 |
| H | 2.45487900 | 0.68056700 | 2.20334400 |
| C | -3.78594500 | 0.96808100 | 0.56379100 |
| H | -3.61424500 | 1.51994100 | -0.35956100 |
| H | -4.72725000 | 1.30886600 | 1.01637300 |
| H | -3.90796600 | -0.08591300 | 0.30146300 |
| C | -3.23955600 | 0.54986100 | 3.43142500 |
| H | -3.56685300 | -0.48110700 | 3.25982200 |
| H | -4.14378900 | 1.14149700 | 3.62162800 |
| H | -2.64678800 | 0.56533100 | 4.34683200 |
| C | 0.02552300 | 1.42304500 | 4.33238200 |
| H | 0.60676500 | 2.30298500 | 4.04139100 |
| H | 0.48473500 | 1.02120200 | 5.24430100 |
| H | -0.97642400 | 1.76251100 | 4.59642100 |
| C | -2.21682800 | 3.12910100 | 2.03586700 |
| H | -1.55946300 | 3.40346200 | 2.86610400 |
| H | -3.18727300 | 3.61124900 | 2.20432300 |
| H | -1.79296900 | 3.54889800 | 1.11757800 |
| C | -0.41996000 | -1.57142800 | 3.79674800 |
| H | -1.46116300 | -1.57927700 | 4.12852300 |
| H | 0.20817100 | -1.75884400 | 4.67643300 |
| H | -0.27706000 | -2.41202500 | 3.10977500 |

Compound **13**

| | | | |
|---|---|---|---|
| Ge | 0.26523500 | 0.19859100 | -0.13923100 |
| Si | -0.29903800 | -0.06396900 | 3.08289800 |
| Si | 2.35261400 | 1.06021300 | 2.08473500 |
| N | -0.16737400 | -1.74371800 | -0.36048700 |
| N | -1.64359700 | 0.72850200 | -0.38262900 |
| N | 0.72602400 | 0.36139500 | 1.67493600 |
| C | -2.72959700 | -0.16216000 | -0.45882500 |
| C | -1.35924800 | 3.24947600 | -0.78759000 |
| C | -2.12369300 | 1.97866700 | -0.65974200 |
| C | -0.45369200 | 5.27618700 | 0.17896200 |
| H | -0.23986200 | 5.87783300 | 1.05948600 |
| C | -3.93444100 | -2.32151900 | -0.33853800 |
| C | 3.75211000 | 0.71416900 | 0.86964600 |
| H | 3.82298000 | -0.33649500 | 0.57688900 |
| H | 3.68023700 | 1.30510100 | -0.04278700 |
| H | 4.68270100 | 0.97648700 | 1.39137500 |
| C | -0.44443900 | 4.98703900 | -2.19823600 |
| H | -0.20866300 | 5.35796400 | -3.19307200 |
| C | -1.45619600 | -2.28948100 | -0.22708300 |
| C | -1.07102600 | 3.74457200 | -2.08090900 |
| C | -3.89814000 | 0.58427300 | -0.75933800 |
| H | -4.88308100 | 0.16454100 | -0.89822800 |
| C | 2.53595400 | -2.62116500 | -2.09277300 |
| C | -6.35107600 | -3.75553700 | -0.36049900 |
| H | -7.28461000 | -4.31044300 | -0.36833500 |
| C | -0.11120700 | 5.76253300 | -1.08423000 |
| C | -2.15485800 | -0.20765700 | 2.74423900 |
| H | -2.58703100 | 0.64315900 | 2.21424600 |
| H | -2.41259700 | -1.12535600 | 2.21365300 |
| H | -2.63184100 | -0.26049200 | 3.73103200 |
| C | 4.48214200 | -3.07456000 | -0.13212300 |
| H | 5.23295700 | -3.26551300 | 0.63130100 |
| C | -3.51964400 | 1.90597200 | -0.87787800 |
| H | -4.14193700 | 2.75724900 | -1.11552900 |
| C | -1.08306200 | 4.03853700 | 0.34669900 |
| C | 2.16143800 | -2.73640100 | -0.73362200 |
| C | 3.89090300 | -2.70313800 | -2.42367800 |
| H | 4.17681900 | -2.60696700 | -3.46853700 |
| C | -1.40538300 | 2.95845800 | -3.32541300 |
| H | -0.80399200 | 2.04364900 | -3.36463800 |
| H | -2.46097600 | 2.66908400 | -3.35667300 |
| H | -1.18848500 | 3.54575600 | -4.22164200 |
| C | 3.13885000 | -3.00410400 | 0.24845200 |
| C | 4.88154400 | -2.91232500 | -1.46137500 |
| C | 0.71437400 | -2.78597200 | -0.39415400 |
| C | -2.65020600 | -1.55671000 | -0.32821600 |
| C | -6.10038100 | -2.81951500 | 0.64452700 |
| H | -6.83547900 | -2.64694600 | 1.42516300 |
| C | -1.33184000 | -3.69880900 | -0.10580000 |
| H | -2.15407000 | -4.38783800 | 0.01557400 |

| | | | |
|---|---|---|---|
| C | -1.48435300 | 3.58535600 | 1.72860100 |
| H | -0.93427800 | 2.68860800 | 2.02079900 |
| H | -1.27664900 | 4.36144800 | 2.47000100 |
| H | -2.55289000 | 3.34694900 | 1.77973000 |
| C | -4.90495400 | -2.10077300 | 0.65255200 |
| H | -4.71057800 | -1.37552800 | 1.43578100 |
| C | -4.19565300 | -3.26622100 | -1.34473100 |
| H | -3.45906400 | -3.43052500 | -2.12469000 |
| C | 1.51234200 | -2.43982200 | -3.18678100 |
| H | 0.67100600 | -3.13170800 | -3.07178300 |
| H | 1.11664000 | -1.41813100 | -3.17266400 |
| H | 1.96364900 | -2.61407300 | -4.16729400 |
| C | 0.60387400 | 7.08279200 | -1.24425500 |
| H | 0.41193700 | 7.74901700 | -0.39777000 |
| H | 1.68937900 | 6.93564600 | -1.30532000 |
| H | 0.29551300 | 7.59714300 | -2.15991000 |
| C | 0.15405500 | -1.74227300 | 3.83963900 |
| H | 0.01175600 | -2.55294800 | 3.11739100 |
| H | 1.18028000 | -1.79709200 | 4.21009000 |
| H | -0.51363100 | -1.93988600 | 4.68740600 |
| C | 2.20860300 | 2.93459000 | 2.28501300 |
| H | 1.84819100 | 3.38710000 | 1.35535400 |
| H | 1.52699600 | 3.22759400 | 3.08909800 |
| H | 3.19220600 | 3.36633400 | 2.50573800 |
| C | 0.01142000 | -4.00087600 | -0.21098500 |
| H | 0.47240000 | -4.97857800 | -0.21004300 |
| C | 3.02619600 | 0.29353600 | 3.69347500 |
| H | 2.38652100 | 0.32665800 | 4.57594300 |
| H | 3.31656900 | -0.74913200 | 3.52722000 |
| H | 3.94427000 | 0.84168300 | 3.93986800 |
| C | -5.39788900 | -3.97292200 | -1.35738700 |
| H | -5.59007400 | -4.69156800 | -2.14862900 |
| C | 2.75977400 | -3.22215100 | 1.69355300 |
| H | 2.16889800 | -4.13606000 | 1.82480500 |
| H | 3.65079600 | -3.31201800 | 2.32103400 |
| H | 2.15574800 | -2.39633300 | 2.07509200 |
| C | -0.22880800 | 1.25251900 | 4.45622900 |
| H | 0.76476500 | 1.60563600 | 4.73299400 |
| H | -0.82780800 | 2.12828300 | 4.18970300 |
| H | -0.68180800 | 0.81557900 | 5.35504000 |
| C | 6.34093800 | -2.95161400 | -1.84624300 |
| H | 6.48006400 | -3.37141900 | -2.84733700 |
| H | 6.77022900 | -1.94201600 | -1.85572700 |
| H | 6.92708000 | -3.54877000 | -1.14113300 |
| Se | 1.51433700 | 1.08423300 | -1.83592200 |

Compound **18**

| | | | |
|---|---|---|---|
| Br | -0.79248500 | -1.84170300 | -0.08794100 |
| Ge | -5.15092000 | 0.13325600 | -0.00439200 |
| Cu | -1.52659700 | 0.55626000 | 0.39527800 |
| Si | -8.26099100 | -0.78979600 | -0.32350700 |
| Si | -7.60630500 | 2.17467500 | 0.00526000 |
| N | -4.66475100 | -0.79400200 | -1.67436100 |
| N | -4.83443900 | -1.43961000 | 1.13418900 |
| N | -6.99062100 | 0.47148400 | -0.11714000 |
| C | -4.44159200 | -3.08207700 | -0.70470900 |
| C | -4.16436800 | -4.51747800 | -1.01722000 |
| C | -2.93582500 | -4.89022300 | -1.58599700 |
| H | -2.18205600 | -4.13032100 | -1.76677000 |
| C | -2.67457500 | -6.23128400 | -1.86761100 |
| H | -1.71503100 | -6.51095100 | -2.29237500 |
| C | -3.63406300 | -7.20916700 | -1.59666000 |
| H | -3.42804700 | -8.25177600 | -1.82111700 |
| C | -4.85633800 | -6.84403500 | -1.02922300 |
| H | -5.60690500 | -7.59946200 | -0.81530800 |
| C | -5.11870600 | -5.50633900 | -0.73225500 |
| H | -6.06810300 | -5.22234600 | -0.28889700 |
| C | -4.54471900 | -2.72731000 | 0.64728500 |
| C | -4.28394100 | -3.57098600 | 1.75411100 |
| H | -4.00642900 | -4.61175900 | 1.68412800 |
| C | -4.39442100 | -2.79953900 | 2.89481800 |
| H | -4.23661200 | -3.10411300 | 3.91964400 |
| C | -4.71366700 | -1.48276700 | 2.50019300 |
| C | -4.81676300 | -0.34950700 | 3.46176200 |
| C | -3.63170400 | 0.22379100 | 3.97340300 |
| C | -2.25731100 | -0.25141100 | 3.56709400 |
| H | -1.88534600 | -1.00353600 | 4.27564000 |
| H | -2.23851700 | -0.70839400 | 2.57652200 |
| H | -1.54541500 | 0.57812500 | 3.56480500 |
| C | -3.73428500 | 1.23934100 | 4.93004900 |
| H | -2.81890000 | 1.69370200 | 5.30282000 |
| C | -4.96426800 | 1.68177300 | 5.41851400 |
| C | -6.12042600 | 1.05181500 | 4.94816400 |
| H | -7.08907500 | 1.34609900 | 5.34596500 |
| C | -6.06790700 | 0.03740600 | 3.98904100 |
| C | -7.33758100 | -0.66107200 | 3.57170700 |
| H | -7.51937200 | -0.53947000 | 2.50312500 |
| H | -7.28759000 | -1.73713900 | 3.77484300 |
| H | -8.20032500 | -0.25701400 | 4.10790000 |
| C | -5.04579600 | 2.81003900 | 6.41868500 |
| H | -5.91887200 | 2.70691400 | 7.07059200 |
| H | -4.15230100 | 2.85216800 | 7.04893500 |
| H | -5.13117300 | 3.77872000 | 5.91063100 |
| C | -4.53390500 | -2.19024700 | -1.78636400 |
| C | -4.39135900 | -2.50992100 | -3.15897100 |
| H | -4.27067900 | -3.50811800 | -3.55193000 |
| C | -4.39146100 | -1.31913200 | -3.86182400 |

| | | | |
|---|---|---|---|
| H | -4.26079900 | -1.17837300 | -4.92552000 |
| C | -4.53879900 | -0.26628300 | -2.93333500 |
| C | -4.43790400 | 1.17359700 | -3.30678400 |
| C | -3.18019400 | 1.81435500 | -3.23727000 |
| C | -3.07557600 | 3.14321700 | -3.66146700 |
| H | -2.10929200 | 3.63636000 | -3.58413900 |
| C | -4.16086000 | 3.84342000 | -4.19011000 |
| C | -5.37616000 | 3.16478300 | -4.32202500 |
| H | -6.22753500 | 3.67533900 | -4.76660200 |
| C | -5.53191200 | 1.84172500 | -3.90046800 |
| C | -6.85596500 | 1.14857700 | -4.10087300 |
| H | -7.57635100 | 1.81361100 | -4.58513700 |
| H | -6.75490600 | 0.25352500 | -4.72466000 |
| H | -7.27842400 | 0.82557300 | -3.14860500 |
| C | -4.02923400 | 5.29043800 | -4.60030100 |
| H | -3.01683500 | 5.51767700 | -4.94782300 |
| H | -4.73095000 | 5.54720400 | -5.39988100 |
| H | -4.23918000 | 5.95698900 | -3.75454600 |
| C | -1.92910200 | 1.08549600 | -2.81475500 |
| H | -1.45685400 | 0.60934900 | -3.68474300 |
| H | -1.20104100 | 1.77373400 | -2.37881600 |
| H | -2.11992300 | 0.29598200 | -2.08635700 |
| C | -6.40175300 | 3.52712500 | -0.51717000 |
| H | -5.63709600 | 3.74353400 | 0.22904500 |
| H | -5.89542800 | 3.31866700 | -1.46263900 |
| H | -7.00969600 | 4.43091000 | -0.65922500 |
| C | -8.14882900 | 2.55427100 | 1.77644600 |
| H | -8.97683700 | 1.92761900 | 2.11877300 |
| H | -7.31539500 | 2.42302000 | 2.47407500 |
| H | -8.47326300 | 3.59983800 | 1.84292300 |
| C | -9.07505300 | 2.44618500 | -1.17383000 |
| H | -8.73071100 | 2.48375100 | -2.21202200 |
| H | -9.89591200 | 1.73016100 | -1.11927200 |
| H | -9.49157500 | 3.43389200 | -0.94002500 |
| C | -7.75639400 | -2.53506600 | 0.20082800 |
| H | -7.07542800 | -2.99623400 | -0.51659800 |
| H | -7.31960500 | -2.61144000 | 1.19779500 |
| H | -8.67944000 | -3.12804100 | 0.19583800 |
| C | -8.83521500 | -1.01382100 | -2.11591300 |
| H | -9.27852900 | -0.11854700 | -2.55815000 |
| H | -8.01871600 | -1.34548400 | -2.76481500 |
| H | -9.60076300 | -1.79977800 | -2.12930800 |
| C | -9.81049700 | -0.42591000 | 0.71743200 |
| H | -9.61710800 | -0.52063400 | 1.78910900 |
| H | -10.27283300 | 0.54742000 | 0.54735700 |
| H | -10.55539200 | -1.18769500 | 0.45538600 |
| Br | 0.72796700 | 1.77452900 | 0.65222500 |
| Ge | 5.11118700 | -0.11868800 | -0.02424000 |
| Cu | 1.45187900 | -0.60443700 | 0.11997100 |
| Si | 8.25748700 | 0.66205100 | -0.27625800 |

| | | | |
|---|---|---|---|
| Si | 7.33091300 | -2.28094000 | -0.53491500 |
| N | 4.87367500 | 0.85547400 | 1.67481700 |
| N | 4.65724200 | 1.43142700 | -1.15857600 |
| N | 6.92148600 | -0.53477600 | -0.22704800 |
| C | 4.43716600 | 3.10478400 | 0.68499900 |
| C | 4.16570600 | 4.54326200 | 0.99523400 |
| C | 2.96960500 | 4.91500200 | 1.62832700 |
| H | 2.23332900 | 4.15257300 | 1.86408800 |
| C | 2.71827800 | 6.25853200 | 1.90911900 |
| H | 1.78391800 | 6.53854500 | 2.38656200 |
| C | 3.65558400 | 7.23740600 | 1.57235900 |
| H | 3.45720600 | 8.28166700 | 1.79610700 |
| C | 4.84627800 | 6.87133300 | 0.94158900 |
| H | 5.57956400 | 7.62776300 | 0.67710800 |
| C | 5.09896900 | 5.53112300 | 0.64677600 |
| H | 6.02417800 | 5.24427900 | 0.15602600 |
| C | 4.38837200 | 2.72057000 | -0.66136000 |
| C | 4.01620800 | 3.54802700 | -1.74714500 |
| H | 3.72820500 | 4.58472400 | -1.66063500 |
| C | 4.05413300 | 2.77059300 | -2.88864700 |
| H | 3.81036100 | 3.06343000 | -3.89999300 |
| C | 4.43690100 | 1.46648700 | -2.51284600 |
| C | 4.54735000 | 0.34438900 | -3.48552400 |
| C | 3.42122700 | -0.45510300 | -3.77447300 |
| C | 2.06505900 | -0.20419700 | -3.15977000 |
| H | 1.41263500 | 0.28591800 | -3.89463600 |
| H | 2.10594000 | 0.44074200 | -2.28091100 |
| H | 1.58459000 | -1.13995300 | -2.86422500 |
| C | 3.54061400 | -1.45815000 | -4.74482900 |
| H | 2.67697200 | -2.08804400 | -4.94668000 |
| C | 4.71616500 | -1.65775700 | -5.46818900 |
| C | 5.78716000 | -0.78822300 | -5.23271900 |
| H | 6.69491400 | -0.88734100 | -5.82414900 |
| C | 5.71949900 | 0.21765600 | -4.26731700 |
| C | 6.85730700 | 1.20348600 | -4.14317900 |
| H | 7.11623100 | 1.41060400 | -3.10434100 |
| H | 6.59104700 | 2.16421100 | -4.60114600 |
| H | 7.75330000 | 0.83495300 | -4.64932900 |
| C | 4.83242100 | -2.77604300 | -6.47588000 |
| H | 5.48573600 | -2.49992300 | -7.30958800 |
| H | 3.85542300 | -3.05101900 | -6.88427800 |
| H | 5.25755400 | -3.67552800 | -6.01339600 |
| C | 4.68878300 | 2.24862300 | 1.76578100 |
| C | 4.67505600 | 2.60557100 | 3.13642100 |
| H | 4.55091500 | 3.61029200 | 3.51118300 |
| C | 4.79836600 | 1.43912200 | 3.86524900 |
| H | 4.78775200 | 1.32337200 | 4.93976900 |
| C | 4.89585500 | 0.36405600 | 2.95476800 |
| C | 4.90276900 | -1.05748600 | 3.40432100 |
| C | 3.67075200 | -1.72440400 | 3.58744100 |

| | | | |
|---|---|---|---|
| C | 3.67823400 | -3.01587900 | 4.12638600 |
| H | 2.72808900 | -3.53200400 | 4.24492800 |
| C | 4.85486800 | -3.64674000 | 4.53194700 |
| C | 6.05435300 | -2.93985300 | 4.40462500 |
| H | 6.98192100 | -3.39726700 | 4.74201800 |
| C | 6.09967200 | -1.65817700 | 3.85221900 |
| C | 7.42116600 | -0.94185700 | 3.73656900 |
| H | 8.22323900 | -1.51741700 | 4.20664100 |
| H | 7.39293400 | 0.04637800 | 4.20867300 |
| H | 7.68566700 | -0.78806000 | 2.68826800 |
| C | 4.83636100 | -5.05342400 | 5.08030400 |
| H | 3.88573700 | -5.27940300 | 5.57263700 |
| H | 5.64224600 | -5.21344400 | 5.80341600 |
| H | 4.96912600 | -5.78827500 | 4.27650500 |
| C | 2.34151500 | -1.06520700 | 3.30998800 |
| H | 1.95165600 | -0.59749000 | 4.22398300 |
| H | 1.60471800 | -1.80052600 | 2.97639200 |
| H | 2.39788200 | -0.28519400 | 2.54992000 |
| C | 6.69406500 | -3.43821800 | 0.81032400 |
| H | 5.61950500 | -3.37218000 | 0.98560100 |
| H | 7.20762600 | -3.26578100 | 1.76031800 |
| H | 6.91860600 | -4.46566700 | 0.49614200 |
| C | 6.69782600 | -2.83200700 | -2.22296200 |
| H | 7.12617400 | -2.23037500 | -3.03029100 |
| H | 5.60944600 | -2.76474000 | -2.29653400 |
| H | 6.98417800 | -3.87718100 | -2.39378000 |
| C | 9.20595300 | -2.59046800 | -0.53923800 |
| H | 9.72841700 | -2.22462800 | 0.34870800 |
| H | 9.72296000 | -2.21485900 | -1.42353100 |
| H | 9.31582100 | -3.68219900 | -0.54157800 |
| C | 7.68337500 | 2.46273600 | -0.34261400 |
| H | 7.12440000 | 2.76177400 | 0.54715100 |
| H | 7.09728400 | 2.72283900 | -1.22639000 |
| H | 8.59924400 | 3.06671400 | -0.36455000 |
| C | 9.38230000 | 0.62517000 | 1.25053900 |
| H | 9.74251600 | -0.36939700 | 1.52446000 |
| H | 8.88815600 | 1.05797000 | 2.12548600 |
| H | 10.26328800 | 1.24345500 | 1.03568500 |
| C | 9.38010600 | 0.40918700 | -1.79473900 |
| H | 8.91970600 | -0.18924800 | -2.58397600 |
| H | 10.32253100 | -0.07025800 | -1.51575300 |
| H | 9.62831000 | 1.38546000 | -2.22681200 |
| Se | -3.61913900 | 1.79785200 | 0.58302000 |
| Se | 3.53050800 | -1.82866300 | -0.23827400 |

Compound **xviii**

| | | | |
|---|---|---|---|
| Ge | 0.27171100 | -0.21873200 | -0.83214000 |
| S | 0.68886400 | -0.62307000 | -2.85653400 |
| Si | 1.43880400 | 0.24432000 | 2.15135300 |
| Si | 3.28855200 | -0.59771700 | -0.19215000 |
| N | -0.92903400 | 1.31458900 | -0.71259900 |
| N | -1.21956000 | -1.12413200 | 0.01167400 |
| N | 1.64037700 | -0.20523300 | 0.43912100 |
| C | -2.16416200 | 1.03119000 | -0.26722600 |
| C | -3.19668200 | 1.99759300 | -0.26027100 |
| H | -2.89814000 | 2.96442500 | -0.64422500 |
| C | -4.51893500 | 1.94832200 | 0.16582800 |
| H | -5.06756700 | 2.87737800 | 0.02358100 |
| C | -5.23318000 | 0.91328500 | 0.76600900 |
| H | -6.26470600 | 1.11532400 | 1.03879900 |
| C | -4.73458600 | -0.35320300 | 1.05428400 |
| H | -5.42910000 | -1.03373600 | 1.54297800 |
| C | -3.48133600 | -0.90262600 | 0.79917200 |
| H | -3.38660100 | -1.93398700 | 1.11372500 |
| C | -2.32104700 | -0.37444000 | 0.18971500 |
| C | -0.55517400 | 2.53039200 | -1.45072200 |
| H | -1.44134100 | 3.00956500 | -1.87945300 |
| H | 0.04298400 | 2.18210300 | -2.30086100 |
| C | -1.11487400 | -2.51784400 | 0.45833800 |
| H | -1.46163000 | -2.58239400 | 1.49893600 |
| H | -0.04694900 | -2.76073600 | 0.47824300 |
| C | 0.26929600 | 3.55409800 | -0.64420100 |
| H | 1.10903800 | 3.00582200 | -0.19737700 |
| C | -1.85046100 | -3.57487000 | -0.40221200 |
| H | -2.88106200 | -3.23140600 | -0.55974500 |
| C | -0.53072700 | 4.21981400 | 0.48309100 |
| H | -1.35348400 | 4.82191700 | 0.07696400 |
| H | 0.10696100 | 4.89254500 | 1.06653700 |
| H | -0.95823900 | 3.48705400 | 1.17384900 |
| C | 0.84551200 | 4.60486500 | -1.60528300 |
| H | 0.04469600 | 5.16091900 | -2.10837800 |
| H | 1.46861200 | 4.14232100 | -2.37730100 |
| H | 1.46179600 | 5.33069200 | -1.06532100 |
| C | -1.90196100 | -4.89910100 | 0.37566300 |
| H | -2.41466600 | -5.67059000 | -0.20712200 |
| H | -2.42903400 | -4.79580600 | 1.33149500 |
| H | -0.89128100 | -5.26730900 | 0.59003100 |
| C | -1.19972000 | -3.76602600 | -1.77695400 |
| H | -0.18267600 | -4.16333600 | -1.67449000 |
| H | -1.12496000 | -2.82941300 | -2.33485100 |
| H | -1.77692700 | -4.47996300 | -2.37449100 |
| C | -0.35038100 | 0.57257000 | 2.68015500 |
| H | -0.85366700 | 1.34357100 | 2.09351400 |
| H | -0.30688600 | 0.93292900 | 3.71541800 |
| H | -0.97519100 | -0.32435200 | 2.67957200 |
| C | 2.36039400 | 1.85545200 | 2.54655300 |

| | | | |
|---|---|---|---|
| H | 3.40273700 | 1.85961000 | 2.21873500 |
| H | 2.35234600 | 2.03940700 | 3.62778900 |
| H | 1.86288800 | 2.70632900 | 2.06820800 |
| C | 2.01113800 | -1.13736300 | 3.31874600 |
| H | 1.58903400 | -2.10290700 | 3.01808300 |
| H | 1.64778900 | -0.92259200 | 4.33103000 |
| H | 3.09495500 | -1.25030500 | 3.37723400 |
| C | 3.86757400 | 0.73694500 | -1.39727600 |
| H | 3.21229300 | 0.79571900 | -2.26976000 |
| H | 4.88251000 | 0.51493900 | -1.74831900 |
| H | 3.89320400 | 1.71972900 | -0.91180700 |
| C | 4.60193800 | -0.68376800 | 1.17947300 |
| H | 4.66293500 | 0.18159400 | 1.84337100 |
| H | 5.56655800 | -0.75692000 | 0.66155400 |
| H | 4.50382000 | -1.58280300 | 1.79413500 |
| C | 3.33394300 | -2.31539200 | -0.97671700 |
| H | 3.02476300 | -3.07929900 | -0.25315500 |
| H | 4.36135100 | -2.55096000 | -1.28085200 |
| H | 2.69136400 | -2.38490600 | -1.85646800 |

Compound **xvii**

| | | | |
|---|---|---|---|
| Ge | 0.26119100 | -0.19264200 | -0.61812000 |
| Se | 0.78378200 | -0.68579000 | -2.79954600 |
| Si | 1.27444200 | 0.46693200 | 2.38001700 |
| Si | 3.26998600 | -0.41823300 | 0.17972100 |
| N | -1.22082900 | -1.12015200 | 0.21745400 |
| N | -1.01295100 | 1.28830300 | -0.62784900 |
| N | 1.57498400 | -0.06626300 | 0.70426400 |
| C | -2.36812400 | -0.42201000 | 0.29024500 |
| C | -3.53494800 | -0.98075400 | 0.85870300 |
| H | -3.40944200 | -1.99078800 | 1.22655200 |
| C | -4.82719000 | -0.48668500 | 1.01389900 |
| H | -5.51541400 | -1.18055900 | 1.49253600 |
| C | -5.36932400 | 0.73810500 | 0.63821200 |
| H | -6.42393800 | 0.89852800 | 0.84126500 |
| C | -4.67127000 | 1.78142100 | 0.03313600 |
| H | -5.25422700 | 2.67490600 | -0.18167000 |
| C | -3.33064400 | 1.87855500 | -0.32061300 |
| H | -3.05742300 | 2.84257200 | -0.72929700 |
| C | -2.25488500 | 0.96446100 | -0.23012000 |
| C | -1.06767000 | -2.46743400 | 0.77900800 |
| H | -1.47753900 | -2.46799200 | 1.79829600 |
| H | 0.00852200 | -2.64229500 | 0.88441500 |
| C | -0.66167300 | 2.49316400 | -1.39528100 |
| H | -1.54676500 | 2.90930700 | -1.88717500 |
| H | -0.00518900 | 2.14557800 | -2.20190700 |
| C | -1.68666800 | -3.63587400 | -0.02844900 |
| H | -2.71387300 | -3.35986900 | -0.29920500 |
| C | 0.06943700 | 3.58824200 | -0.59272400 |
| H | 0.91202600 | 3.10235400 | -0.08326600 |
| C | -0.91894400 | -3.92858900 | -1.32263700 |
| H | -0.84505300 | -3.05147000 | -1.97039900 |
| H | -1.41258600 | -4.72959200 | -1.88351100 |
| H | 0.10363100 | -4.25871100 | -1.10276600 |
| C | -1.74702000 | -4.88038200 | 0.87136400 |
| H | -2.17093900 | -5.73055300 | 0.32810000 |
| H | -2.36006800 | -4.71386700 | 1.76496800 |
| H | -0.74351100 | -5.17139200 | 1.20508500 |
| C | -0.81584800 | 4.25716500 | 0.46697400 |
| H | -1.64479800 | 4.80354800 | -0.00061600 |
| H | -0.23944700 | 4.98158100 | 1.05244600 |
| H | -1.24213800 | 3.53177200 | 1.16607400 |
| C | 0.64061900 | 4.62854300 | -1.56826000 |
| H | 1.31944700 | 4.16771900 | -2.29284100 |
| H | 1.19675900 | 5.40292700 | -1.03046600 |
| H | -0.16100500 | 5.12619200 | -2.12803300 |
| C | -0.54786500 | 0.75769600 | 2.80656600 |
| H | -1.05055700 | 1.47409000 | 2.15427200 |
| H | -0.56478800 | 1.17725400 | 3.82010500 |
| H | -1.13962300 | -0.16093100 | 2.83108400 |
| C | 2.12278700 | 2.12844700 | 2.72575000 |

| | | | |
|---|---|---|---|
| H | 3.17544700 | 2.15745900 | 2.43427100 |
| H | 2.06878800 | 2.36420300 | 3.79555600 |
| H | 1.61202900 | 2.93511500 | 2.18862100 |
| C | 1.83467900 | -0.83063300 | 3.64550200 |
| H | 1.48038100 | -1.82924700 | 3.36611200 |
| H | 1.39667500 | -0.58926700 | 4.62161000 |
| H | 2.91653800 | -0.88478600 | 3.77642800 |
| C | 3.86750900 | 0.89987200 | -1.03397700 |
| H | 3.26116800 | 0.91103200 | -1.94319700 |
| H | 4.90712800 | 0.70408400 | -1.32293000 |
| H | 3.83257000 | 1.89656600 | -0.57857300 |
| C | 3.42394200 | -2.15565800 | -0.54384300 |
| H | 3.06870600 | -2.90656600 | 0.17211200 |
| H | 4.48076100 | -2.37072800 | -0.74523500 |
| H | 2.86710100 | -2.27020100 | -1.47570300 |
| C | 4.50339300 | -0.41426000 | 1.62589100 |
| H | 4.49123700 | 0.47120000 | 2.26474300 |
| H | 5.49853200 | -0.46429200 | 1.16634900 |
| H | 4.40200100 | -1.29882800 | 2.26071500 |

LGe=S(N(TMS)$_2$) (**xx**)
(L = Amidinate)

| | | | |
|---|---|---|---|
| C | 1.67257900 | 0.00596700 | -0.05650000 |
| C | 3.14079800 | 0.00203200 | 0.22052700 |
| C | 3.60620700 | -0.10158100 | 1.53900600 |
| H | 2.89513100 | -0.18170100 | 2.35490700 |
| C | 4.97642400 | -0.09431500 | 1.79993700 |
| H | 5.32814100 | -0.17303900 | 2.82429500 |
| C | 5.89135500 | 0.01444100 | 0.75031300 |
| H | 6.95762300 | 0.01939700 | 0.95583900 |
| C | 5.43151700 | 0.11634100 | -0.56357000 |
| H | 6.13742100 | 0.19947000 | -1.38444100 |
| C | 4.06136700 | 0.11138500 | -0.83081700 |
| H | 3.70515700 | 0.18722000 | -1.85305400 |
| C | 1.22928300 | 2.54549000 | -0.22237700 |
| C | 2.13563100 | 2.99111500 | 0.94021200 |
| H | 1.70385600 | 2.71392700 | 1.90696500 |
| H | 2.23558700 | 4.08104900 | 0.91683000 |
| H | 3.13752200 | 2.56479600 | 0.87296000 |
| C | 1.88069000 | 2.89176400 | -1.57749300 |
| H | 2.86957900 | 2.43485900 | -1.66807400 |
| H | 2.00452900 | 3.97642700 | -1.66769400 |
| H | 1.25557300 | 2.53990100 | -2.40276800 |
| C | -0.11818300 | 3.28371600 | -0.11112000 |
| H | -0.78419100 | 3.01448500 | -0.93665500 |
| H | 0.04599800 | 4.36441700 | -0.15317100 |
| H | -0.62050900 | 3.04959200 | 0.83213200 |
| C | 1.25839900 | -2.50794200 | -0.45850000 |
| C | 2.05151100 | -2.66774800 | -1.77209300 |
| H | 1.51316700 | -2.19510600 | -2.59852200 |
| H | 2.18266200 | -3.73069300 | -2.00197600 |
| H | 3.04541100 | -2.21976300 | -1.69607800 |
| C | 2.04351800 | -3.10010500 | 0.72688100 |
| H | 3.02399800 | -2.63626500 | 0.84621200 |
| H | 2.19961000 | -4.17077400 | 0.55886400 |
| H | 1.48703200 | -2.98439100 | 1.66240800 |
| C | -0.07934300 | -3.25916700 | -0.59162900 |
| H | -0.68807100 | -3.14538600 | 0.31041400 |
| H | 0.10916400 | -4.32590000 | -0.74359400 |
| H | -0.65172500 | -2.89227000 | -1.44873000 |
| C | -0.17400800 | -0.07138800 | 2.75157100 |
| H | 0.45328300 | -0.86907900 | 2.34957100 |
| H | -0.22505000 | -0.19843800 | 3.83956700 |
| H | 0.30879500 | 0.88775200 | 2.54980700 |
| C | -2.83860900 | 1.27003000 | 3.00289200 |

| | | | |
|---|---|---|---|
| H | -2.60415000 | 2.23957500 | 2.54962100 |
| H | -2.49109800 | 1.30178400 | 4.04251400 |
| H | -3.92471900 | 1.16544000 | 3.02427600 |
| C | -2.62753100 | -1.81482800 | 2.67360900 |
| H | -3.64341500 | -2.01913500 | 2.32561200 |
| H | -2.63770700 | -1.86262700 | 3.76932600 |
| H | -1.98969300 | -2.63163800 | 2.31719100 |
| C | -3.98552800 | -1.50038000 | -1.47130800 |
| H | -3.24362400 | -1.60284400 | -2.26713600 |
| H | -4.97894600 | -1.47540600 | -1.93513900 |
| H | -3.93999900 | -2.39115300 | -0.83417000 |
| C | -3.90146600 | 1.62179400 | -1.51870400 |
| H | -3.73568300 | 2.52394000 | -0.91835800 |
| H | -4.92553700 | 1.67011400 | -1.90887300 |
| H | -3.21141000 | 1.63322600 | -2.36484600 |
| C | -5.12253300 | 0.16000800 | 0.79719100 |
| H | -5.10910900 | -0.59790100 | 1.58414100 |
| H | -6.04327200 | 0.00478800 | 0.22073600 |
| H | -5.20411900 | 1.14361900 | 1.26773200 |
| Ge | -0.63456400 | 0.02878300 | -0.83815500 |
| N | 0.90546400 | -1.08235000 | -0.23019200 |
| N | 0.90545000 | 1.09831000 | -0.16676500 |
| N | -2.07533300 | 0.02391800 | 0.32825000 |
| S | -0.86591600 | 0.06149100 | -2.92961900 |
| Si | -3.70292900 | 0.07027400 | -0.46243200 |
| Si | -1.94907400 | -0.13999500 | 2.09879000 |

LGe=Se(N(TMS)$_2$) (**xxi**)
(L = Amidinate)

| | | | |
|---|---|---|---|
| C | 1.72731000 | 0.09225100 | -0.00949100 |
| C | 3.20517300 | 0.31276800 | -0.02301700 |
| C | 3.72419800 | 1.61438400 | 0.02137100 |
| H | 3.04716100 | 2.46129800 | 0.06774700 |
| C | 5.10397200 | 1.81878200 | -0.00146500 |
| H | 5.49728200 | 2.83040700 | 0.03166800 |
| C | 5.97472100 | 0.72884800 | -0.06746600 |
| H | 7.04843500 | 0.89013500 | -0.08489200 |
| C | 5.46126100 | -0.56847000 | -0.11042100 |
| H | 6.13290700 | -1.42021000 | -0.16009300 |
| C | 4.08159200 | -0.77929900 | -0.08915900 |
| H | 3.68309200 | -1.78830200 | -0.11894600 |
| C | 1.26280800 | -0.14133300 | -2.54038600 |
| C | 2.16864800 | 1.00352100 | -3.03118100 |
| H | 1.73430800 | 1.98020300 | -2.79614100 |
| H | 2.27271000 | 0.93524800 | -4.11885900 |
| H | 3.16908400 | 0.95556600 | -2.59879300 |
| C | 1.90919800 | -1.50824100 | -2.84666400 |
| H | 2.90562500 | -1.58218700 | -2.40370500 |
| H | 2.01513200 | -1.63700500 | -3.92927900 |
| H | 1.29052400 | -2.32067700 | -2.45549800 |
| C | -0.08951900 | -0.05023700 | -3.27233200 |
| H | -0.75470300 | -0.86706300 | -2.97568500 |
| H | 0.06761400 | -0.12334900 | -4.35239600 |
| H | -0.58926400 | 0.89998800 | -3.06200400 |
| C | 1.31490200 | -0.18303100 | 2.52289200 |
| C | 2.10416500 | -1.48865400 | 2.75166200 |
| H | 1.56697900 | -2.33899600 | 2.32243300 |
| H | 2.23013600 | -1.66160200 | 3.82595500 |
| H | 3.10014500 | -1.43766800 | 2.30528400 |
| C | 2.10731300 | 1.02596900 | 3.05512200 |
| H | 3.08513700 | 1.11902100 | 2.57954900 |
| H | 2.27050300 | 0.90583800 | 4.13111100 |
| H | 1.55419400 | 1.95783500 | 2.90156800 |
| C | -0.02288100 | -0.27177000 | 3.28060800 |
| H | -0.63175600 | 0.62180400 | 3.11308300 |
| H | 0.16554400 | -0.35913500 | 4.35459600 |
| H | -0.59527900 | -1.14952600 | 2.96641300 |
| C | -0.01275600 | 2.95872400 | -0.00221900 |
| H | 0.59915700 | 2.55869700 | 0.80769100 |
| H | -0.03256300 | 4.05053000 | 0.09884800 |
| H | 0.46841900 | 2.72168400 | -0.95398700 |
| C | -2.65162800 | 3.26208400 | -1.37350500 |

| | | | |
|---|---|---|---|
| H | -2.43252200 | 2.76704600 | -2.32606300 |
| H | -2.25702800 | 4.28329700 | -1.43688600 |
| H | -3.73601600 | 3.33622400 | -1.27710200 |
| C | -2.47834500 | 3.01662000 | 1.72342300 |
| H | -3.50822000 | 2.71313800 | 1.92846500 |
| H | -2.44701900 | 4.11287400 | 1.73997100 |
| H | -1.86108800 | 2.65980700 | 2.55575500 |
| C | -4.00967800 | -1.05749900 | 1.53370700 |
| H | -3.31478300 | -1.88921700 | 1.67448800 |
| H | -5.02650900 | -1.46794800 | 1.51531400 |
| H | -3.93716400 | -0.39182100 | 2.40144800 |
| C | -3.89976900 | -1.22708400 | -1.58206700 |
| H | -3.68335700 | -0.67496100 | -2.50396800 |
| H | -4.94561100 | -1.55423900 | -1.63296000 |
| H | -3.26618000 | -2.11606200 | -1.55133800 |
| C | -5.02747300 | 1.19308900 | -0.22404900 |
| H | -4.99055500 | 2.00603700 | 0.50494800 |
| H | -5.97350400 | 0.66157800 | -0.06111800 |
| H | -5.07581000 | 1.62943100 | -1.22532800 |
| Ge | -0.60421600 | -0.61603600 | 0.00418100 |
| N | 0.96176500 | -0.01921600 | 1.08758200 |
| N | 0.94928500 | -0.03018700 | -1.09335000 |
| N | -2.00481700 | 0.59768200 | -0.03684700 |
| Si | -3.66607500 | -0.12204900 | -0.06966300 |
| Si | -1.80903300 | 2.36876100 | 0.07177600 |
| Se | -0.88004900 | -2.89308800 | 0.06004300 |

| | | | |
|---|---|---|---|
| Cu | 0.00000000 | 0.00000000 | 0.78294800 |
| Cl | 0.00000000 | 0.00000000 | -1.33561700 |

CuBr

| | | | |
|---|---|---|---|
| Br | 0.00000000 | 0.00000000 | 1.03518400 |
| Cu | 0.00000000 | 0.00000000 | -1.24935900 |

CuI

| | | | |
|---|---|---|---|
| Cu | 0.00000000 | 0.00000000 | -1.57568400 |
| I | 0.00000000 | 0.00000000 | 0.86216700 |

## Supporting references

1. T. Matsumoto, N. Tokitoh and R. Okazaki, *Angew. Chem. Int. Ed*., 1994, **33**, 2316–2317.
2. D. Yadav, R. K. Siwatch, G. Mukherjee, G. Rajaraman and S. Nagendran, *Inorg. Chem.*, 2014, **53**, 10054–10059.
3. L. W. Pineda, V. Jancik, R. B. Oswald and H. W. Roesky, *Organometallics*, 2006, **25**, 2384–2387.
4. R. K. Siwatch and S. Nagendran, *Organometallics*, 2012, **31**, 3389–3394.
5. R. K. Siwatch, S. Karwasara, M. K. Sharma, S. Mondal, G. Mukherjee, G. Rajaraman and S. Nagendran, *Organometallics*, 2016, **35**, 429–438.
6. SMART, Bruker Molecular Analysis Research Tool, Version 5.618, Bruker AXS, Madison, WI (2000).
7. SAINT-NT, Version 6.04; Bruker AXS, WI (2001).
8. SHELXTL-NT, Version 6.10, Bruker AXS, Madison, WI (2000).
9. CCDC 2116996 (**2**), 2116997 (**3**), 2116998 (**4**), 2117002 (**9**), 2116999 (**11**), 2117005 (**12**), 2117004 (**13**), 2117001 (**14**), 2117000 (**16**), 2117006 (**17**), and 2117003 (**19**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
10. 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 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2013.

11. S. I. Gorelsky, AOMix: Program for Molecular Orbital Analysis, http://www.sg-chem.net/, version X.X, 2019.
12. S. I. Gorelsky, A. B. P. Lever, *J. Organomet. Chem.* 2001, **635**, 187-196.
13. F. Wheinhold and C. Landis, Valency and Bonding; Cambridge: Cambridge, 2005.
14. (a) A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.* 1988, **88**, 899. (b) E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold, NBO Version 3.1.
15. R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.* 1998, **109**, 8218.