Supporting Information

Donor–acceptor-stabilised germanium analogues of acid chloride, ester, and acyl pyrrole compounds: synthesis and reactivity

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1. Experimental Section

All the manipulations were performed using either standard Schlenk or glove box [Jacomex GP(Concept)-T2] techniques. Germylenes **G1**, **G2**, and **G5** were synthesized by following literature procedures.[S1-S3] Solvents were dried using conventional methods. $B(C_6F_5)_3$ and N_2O (99.99% purity) were purchased from Sigma Aldrich and Sigma gases, respectively, and used without further purification. ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{29}Si NMR spectra were recorded on a 300/400 MHz Bruker Topspin spectrometer. The chemical shifts δ are reported in ppm and are referenced internally with respect to the residual solvent (^{1}H NMR) and solvent (^{13}C NMR) resonances. For ^{11}B, ^{19}F, and ^{29}Si NMR spectroscopic studies, $BF_3{\cdot}Et_2O$, $CFCl_3$, and $(CH_3)_4Si$ were used as external references, respectively. Melting points were recorded using Unitech Sales digital melting point apparatus by sealing the samples in glass capillaries, and the reported melting points are uncorrected. Elemental analyses were carried out using a Perkin-Elmer CHN analyzer.

General synthetic route for amidogermylenes (*i*-Bu)$_2$ATIGeN(H)Ph (G3) and (*i*-Bu)$_2$ATIGeN(Me)Ph (G4).

To a solution of (*i*-Bu)$_2$ATIGeCl (**G1**) in hexane (15 mL), lithium salt LiN(H)Ph for **G3** / LiN(Me)Ph for **G4** was added at -40 °C with stirring. The reaction mixture was then slowly brought to room temperature and stirred for 6 h. It was filtered using a G4 frit containing celite. Removal of hexane from the filtrate gave an analytically pure sample of amidogermylene as a red pasty material.

Data for compound G3: Compound **G1** (2 g, 5.89 mmol), LiN(H)Ph (0.60 g, 6.0 mmol), Yield: 2.31 g, 99%. Anal. Calcd for $C_{21}H_{29}GeN_3$ (M = 396.12): C, 63.67; H, 7.38; N, 10.61. Found: C, 63.10; H, 7.90; N, 10.35. ^{1}H NMR (300 MHz, C_6D_6): δ 0.87 (d, $^{3}J_{HH}$ = 6.9, 6H, CH(CH_3)$_2$), 0.96 (d, $^{3}J_{HH}$ = 6.6, 6H, CH(CH_3)$_2$), 2.14–2.23 (m, 2H, CH(CH$_3$)$_2$), 3.18 (dd,

$^3J_{HH}$ = 13.5, 6.0, 2H, CH_2), 3.29 (dd, $^3J_{HH}$ = 13.5, 8.1, 2H, CH_2), 4.24 (s, 1H, N*H*), 6.27 (t, $^3J_{HH}$ = 8.4, 1H, CH_{Ar}), 6.37 (d, $^3J_{HH}$ = 11.4, 2H, CH_{Ar}), 6.77-6.86 (m, 3H, CH_{Ar}), 7.01 (d, $^3J_{HH}$ = 7.5, 2H, CH_{ring}), 7.30 (d, $^3J_{HH}$ = 7.8 Hz, 2H, CH_{ring}). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 20.89 (CH(*C*H_3)$_2$), 20.96 (CH(*C*H_3)$_2$), 27.65 (*C*H(CH$_3$)$_2$), 53.80 (*C*H$_2$), 113.82, 115.91, 116.18, 119.44, 129.29, 136.34, 152.53, 160.72.

Data for compound G4: Compound **G1** (2 g, 5.89 mmol), LiN(Me)Ph (0.68 g, 6.0 mmol), Yield: 2.44 g, 99%. Anal. Calcd for $C_{22}H_{31}GeN_3$ (*M* = 410.14): C, 64.43; H, 7.62; N, 10.25. Found: C, 64.05; H, 7.38; N, 10.52. ^1H NMR (300 MHz, C_6D_6): δ 0.83 (d, $^3J_{HH}$ = 6.6, 6H, CH(C*H*$_3$)$_2$), 0.92 (d, $^3J_{HH}$ = 6.6, 6H, CH(C*H*$_3$)$_2$), 2.08–2.21 (m, 2H, C*H*(CH$_3$)$_2$), 2.90 (s, 3H, NC*H*$_3$), 3.14 (dd, $^3J_{HH}$ = 13.5, 6.0, 2H, CH_2), 3.26 (dd, $^3J_{HH}$ = 13.5, 7.8, 2H, CH_2), 6.23 (t, $^3J_{HH}$ = 9.3, 1H, CH_{Ar}), 6.33 (d, $^3J_{HH}$ = 11.4, 2H, CH_{Ar}), 6.42 (d, $^3J_{HH}$ = 7.8, 1H, CH_{Ar}), 6.73-6.85 (m, 4H, CH_{ring}), 6.98 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH_{ring}). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 20.79 (CH(*C*H_3)$_2$), 20.92 (CH(*C*H_3)$_2$), 27.61 (*C*H(CH$_3$)$_2$), 53.78 (*C*H$_2$), 113.80, 115.94, 116.21, 119.42, 129.25, 136.30, 152.44, 160.70.

General synthetic route for germanium *μ*-oxo dimers {(*i*-Bu)$_2$ATIGe(Y)(*μ*-O)}$_2$ [Y = Cl (D1), OSiPh$_3$ (D2), N(H)Ph (D3), N(Me)Ph (D4), NC$_4$H$_4$ (D5)].

N_2O gas was passed into the solution of germylene (**G1**-**G5**) in THF (30 mL) and the reaction mixture was heated at 60 °C for 2 h. Removal of THF from the reaction mixture afforded germanium *μ*-oxo dimer (**D1**-**D5**) as a yellow solid. This solid was washed with hexane and dried *in vacuo* to result in an analytically pure sample of germanium *μ*-oxo dimer (**D1**-**D5**).

Synthesis of compound D1: Compound **G1** (2 g, 5.89 mmol), Yield: 1.25 g, 60%. Mp: 122 °C. Anal. Calcd for $C_{30}H_{46}Cl_2Ge_2N_4O_2$ (*M* = 710.90): C, 50.69; H, 6.52; N, 7.88. Found: C, 50.39; H, 6.30; N, 7.50. ^1H NMR (300 MHz, $CDCl_3$): *δ* 0.99 (d, $^3J_{HH}$ = 6.0 Hz, 24H, CH(C*H*$_3$)$_2$), 2.31-2.45 (m, 4H, C*H*(CH$_3$)$_2$), 3.87 (d, $^3J_{HH}$ = 7.8 Hz, 8H, CH_2), 7.06 (t, $^3J_{HH}$ =

9.0 Hz, 2H, C*H*), 7.24 (d, $^{3}J_{HH}$ = 11.7 Hz, 4H, C*H*), 7.57 (t, $^{3}J_{HH}$ = 10.2 Hz, 4H, C*H*). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 20.85 ($CH(CH_3)_2$), 27.48 ($CH(CH_3)_2$), 53.26 (CH_2), 118.22 (C_4), 126.90 ($C_{2,6}$), 138.67 ($C_{3,5}$), 155.08 ($C_{1,7}$).

Synthesis of compound D2: Compound **G2** (1 g, 1.72 mmol), Yield: 1.02 g, 99%. Mp: 104 °C. The data for this compound matches with the literature report.[S2]

Synthesis of compound D3: Compound **G3** (1.5 g, 3.78 mmol), Yield: 1.54 g, 99%. Mp: 109 °C. Anal. Calcd for $C_{42}H_{58}Ge_2N_6O_2$ (M = 824.23): C, 61.20; H, 7.09; N, 10.20. Found: C, 60.95; H, 6.90; N, 10.35. ^{1}H NMR (300 MHz, C_6D_6): δ 0.87 (d, 12H, $^{3}J_{HH}$ = 6.0 Hz, $CH(CH_3)_2$), 0.96 (d, 12H, $^{3}J_{HH}$ = 6.0 Hz, $CH(CH_3)_2$), 2.14–2.23 (m, 4H, $CH(CH_3)_2$), 3.15-3.21 (dd, 4H, $^{3}J_{HH}$ = 12.0, 6.3 Hz, CH_2), 3.26-3.33 (dd, $^{3}J_{HH}$ = 12.0, 6.3 Hz, 4H, CH_2), 4.24 (s, 2H, N*H*), 6.27 (t, 2H, $^{3}J_{HH}$ = 9.3 Hz, CH_{Ar}), 6.37 (d, 4H, $^{3}J_{HH}$ = 10.4 Hz, CH_{Ar}), 6.46 (t, 2H, $^{3}J_{HH}$ = 7.5 Hz, CH_{Ar}), 6.77-6.86 (m, 4H, CH_{ring}), 7.01 (d, 4H, $^{3}J_{HH}$ = 7.5 Hz, CH_{Ar}),7.17 (t, $^{3}J_{HH}$ = 8.1 Hz, 2H, CH_{ring}), 7.25 (t, 4H, $^{3}J_{HH}$ = 7.9 Hz, CH_{ring}). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 21.15 ($CH(CH_3)_2$), 21.21 ($CH(CH_3)_2$), 21.26 ($CH(CH_3)_2$), 27.38 ($CH(CH_3)_2$), 27.75 ($CH(CH_3)_2$), 52.88 (CH_2), 53.20 (CH_2), 114.68, 114.77, 116.72, 117.15, 118.04, 119.03, 121.07, 121.17, 128.39, 136.34, 149.21, 155.17.

Synthesis of compound D4: Compound **G4** (1.2 g, 2.92 mmol), Yield: 1.23 g, 99%. Mp: 113 °C. Anal. Calcd for $C_{44}H_{62}Ge_2N_6O_2$ (M = 852.28): C, 62.01; H, 7.33; N, 9.86. Found: C, 62.23; H, 7.19; N, 9.75. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (d, $^{3}J_{HH}$ = 6.9 Hz, 24H, $CH(CH_3)_2$), 2.18–2.29 (m, 4H, $CH(CH_3)_2$), 2.69 (s, 6H, CH_3), 3.33 (dd, $^{3}J_{HH}$ = 13.2, 6.9 Hz, 4H, CH_2), 3.79 (dd, $^{3}J_{HH}$ = 13.2, 7.5 Hz, 4H, CH_2), 6.48-6.55 (m, 2H, CH_{Ar}), 6.61 (t, $^{3}J_{HH}$ = 9.3 Hz, 2H, CH_{Ar}), 6.76-6.84 (m, 12H, CH_{ring}), 7.17-7.28 (m, 4H, CH_{ring}). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 21.20 ($CH(CH_3)_2$), 27.71 ($CH(CH_3)_2$), 35.23 (CH_3), 53.93 (CH_2), 114.35, 117.13, 118.46, 120.64, 127.72, 135.99, 153.16, 154.99.

Synthesis of compound D5: Compound **G5** (2 g, 5.40 mmol), Yield: 2.04 g, 98%. Mp: 107 °C. Anal. Calcd for $C_{38}H_{54}Ge_2N_6O_2$ (M = 772.15): C, 59.11; H, 7.05; N, 10.88. Found: C, 58.80; H, 6.80; N, 10.70. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.76 (d, $^3J_{HH}$ = 6.6 Hz, 12H, CH(CH_3)$_2$), 0.89 (d, $^3J_{HH}$ = 4.2 Hz, 12H, CH(CH_3)$_2$), 2.23–2.35 (m, 4H, CH(CH$_3$)$_2$), 3.69 (dd, $^3J_{HH}$ = 13.5, 7.5 Hz, 4H, CH_2), 3.83 (dd, $^3J_{HH}$ = 14.1, 8.1 Hz, 4H, CH_2), 6.11 (s, 4H, C$H_{pyrrole}$), 6.69 (s, 4H, C$H_{pyrrole}$), 6.74 (t, $^3J_{HH}$ = 9.6 Hz, 2H, CH_{ring}), 6.95–7.04 (m, 4H, CH_{ring}), 7.34 (t, $^3J_{HH}$ = 10.5 Hz, 4H, CH_{ring}). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 20.65 (CH(*C*H$_3$)$_2$), 21.06 (CH(*C*H$_3$)$_2$), 27.41 (*C*H(CH$_3$)$_2$), 53.43 (*C*H$_2$), 108.40 (pyrrole), 115.60, 122.54 (pyrrole), 123.95, 137.02, 155.28.

General route for the synthesis of donor-acceptor stabilized germaacid chloride (*i*-Bu)$_2$ATIGe(O)(Cl)→B(C$_6$F$_5$)$_3$ (1), germaester (*i*-Bu)$_2$ATIGe(O)(OSiPh$_3$)→B(C$_6$F$_5$)$_3$ (2), and *N*-germaacyl pyrrole (*i*-Bu)$_2$ATIGe(O)(NC$_4$H$_4$)→B(C$_6$F$_5$)$_3$ (3).

A solution of $B(C_6F_5)_3$ in toluene (5 mL) was transfered to a solution of germanium μ-oxo dimer (**D1**, **D2**, and **D5**) in toluene (30 mL) at room temperature, stirred for 2 h, and the solvent was removed under vacuum to afford an analytically pure sample of the desired germanium compound (**1**, **2**, and **3**, respectively). Single crystals of these compounds (**1**, **2**, and **3**) suitable for X-ray diffraction studies were grown by cooling their saturated solutions in dichloromethane at -40 °C.

Synthesis of compound 1: Compound **D1** (1.0 g, 1.40 mmol) and $B(C_6F_5)_3$ (1.44 g, 2.80 mmol). Yield: 2.41 g, 99%. Mp: 131 °C. Anal. Calcd for $C_{33}H_{23}BClF_{15}GeN_2O$ (M = 867.43): C, 45.69; H, 2.67; N, 3.23 Found: C, 45.52; H, 2.55; N, 3.35. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.97 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$), 2.17-2.27 (m, 2H, CH(CH$_3$)$_2$), 3.48-3.59 (m, 2H, CH_2), 7.36-7.45 (m, 3H, CH), 7.80 (t, $^3J_{HH}$ = 12.0 Hz, 2H, CH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 20.37 (CH(*C*H$_3$)$_2$), 20.59 (*C*H(CH$_3$)$_2$), 27.59

(*C*H(CH$_3$)$_2$), 53.45 (*C*H$_2$), 120.36 (*C*$_4$), 131.23 (*C*$_{2,6}$), 135.53 (*C*F), 138.00 (*C*F), 140.54 (*C*$_{3,5}$), 146.68 (*C*F), 149.11 (*C*F), 155.78 (*C*$_{1,7}$). ^{19}F{^{1}H} NMR (282 MHz, C$_6$D$_6$): δ -133.14 (dd, $^3J_{FF}$ = 23.2, 6.9 Hz, 6F, *ortho*-C$_6$*F*$_5$), -159.45 (t, $^3J_{FF}$ = 20.6 Hz, 3F, *para*-C$_6$*F*$_5$), -164.74 (m, 6F, *meta*-C$_6$*F*$_5$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.46 (s).

Synthesis of compound 2: Compound **D2** (1.0 g, 0.84 mmol) and B(C$_6$F$_5$)$_3$ (0.86 g, 1.68 mmol). Yield: 1.84 g, 99%. Mp: 125 °C. Anal. Calcd for C$_{51}$H$_{38}$BF$_{15}$GeN$_2$O$_2$Si (M = 1107.37): C, 55.32; H, 3.46; N, 2.53 Found: C, 55.56; H, 3.25; N, 2.23. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.62 (d, $^3J_{HH}$ = 7.2 Hz, 6H, CH(C*H*$_3$)$_2$), 0.65 (d, $^3J_{HH}$ = 6.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.89-1.95 (m, 2H, C*H*(CH$_3$)$_2$), 3.11 (dd, $^3J_{HH}$ = 16.0, 8.0 Hz, 2H, C*H*$_2$), 3.26 (dd, $^3J_{HH}$ = 16.0, 8.0 Hz, 2H, C*H*$_2$), 7.09 (d, $^3J_{HH}$ = 12.0, 2H, C*H*), 7.28 (t, $^3J_{HH}$ = 6.8 Hz, 5H, C*H*), 7.38 (t, $^3J_{HH}$ = 8.0 Hz, 2H, C*H*), 7.52 (d, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*), 7.62 (t, $^3J_{HH}$ = 10.4 Hz, 2H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 19.79 (CH(*C*H$_3$)$_2$), 20.10 (CH(*C*H$_3$)$_2$), 27.75 (*C*H(CH$_3$)$_2$), 52.70 (*C*H$_2$), 119.41 (*C*$_4$), 127.79 (*C*$_{2,6}$), 130.25 (*C*$_{Ar}$), 134.34 (*C*$_{Ar}$), 135.13 (*C*$_{Ar}$), 136.02 (*C*$_{3,5}$), 137.86 (*C*F), 139.60 (*C*F), 146.89 (*C*F), 150.57 (*C*F), 155.30 (*C*$_{1,7}$). ^{19}F{^{1}H} NMR (282 MHz, CDCl$_3$): δ -132.31 (d, $^3J_{FF}$ = 16.92 Hz, 6F, *ortho*-C$_6$*F*$_5$), -159.75 (t, $^3J_{FF}$ = 20.70 Hz, 3F, *para*-C$_6$*F*$_5$), -165.05 (d, 6F, $^3J_{FF}$ = 24.27 Hz, *meta*-C$_6$*F*$_5$). ^{11}B{^{1}H} NMR (128 MHz, CDCl$_3$): δ -2.61 (s). ^{29}Si{^{1}H} NMR (79 MHz, CDCl$_3$): δ -13.62 (s).

Synthesis of compound 3: Compound **D5** (2.0 g, 2.59 mmol) and B(C$_6$F$_5$)$_3$ (2.65 g, 5.18 mmol). Yield: 4.60 g, 99%. Mp: 129 °C. Anal. Calcd for C$_{37}$H$_{27}$BF$_{15}$GeN$_3$O (M = 898.06): C, 49.48; H, 3.03; N, 4.68 Found: C, 49.29; H, 3.31; N, 3.36. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.76 (d, $^3J_{HH}$ = 6.4 Hz, 6H, CH(C*H*$_3$)$_2$), 0.81 (d, $^3J_{HH}$ = 8.0 Hz, 6H, CH(C*H*$_3$)$_2$), 1.73-1.83 (m, 2H, C*H*(CH$_3$)$_2$), 3.36-3.47 (m, 4H, C*H*$_2$), 6.43 (s, 2H, Py), 6.98 (s, 2H, Py), 7.36 (d, $^3J_{HH}$ = 11.6 Hz, 2H, C*H*), 7.42 (t, $^3J_{HH}$ = 9.2 Hz, 1H, C*H*), 7.80 (t, $^3J_{HH}$ = 10.0 Hz, 2H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 20.33 (CH(*C*H$_3$)$_2$), 20.41 (CH(*C*H$_3$)$_2$), 29.16 (*C*H(CH$_3$)$_2$), 54.48

(CH_2), 113.68 (Py), 119.90 (C_4), 124.30 (Py), 130.84 ($C_{2,6}$), 135.97 (*C*F), 139.27 (*C*F), 140.31 ($C_{3,5}$), 147.22 (*C*F), 150.40 (*C*F), 156.25 ($C_{1,7}$). $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ -133.09 (dd, $^3J_{FF}$ = 25.66, 24.53 Hz, 6F, *ortho*-C_6F_5), -159.77 (t, $^3J_{FF}$ = 20.30 Hz, 3F, *para*-C_6F_5), -164.83 (m, 6F, *meta*-C_6F_5). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -2.72 (s).

General synthetic route for the isolation of donor-acceptor stabilized germaynone (*i*-Bu)$_2$ATIGe(O)(CCPh)→B(C_6F_5)$_3$ (4), germaester (*i*-Bu)$_2$ATIGe(O)(O*t*-Bu)→B(C_6F_5)$_3$ (5), and germaimine (*i*-Bu)$_2$ATIGe=N($SiMe_3$)($OSiMe_3$)→B(C_6F_5)$_3$ (9).

A solution of germaacid chloride **1** in toluene (10 mL) was transfered to a suspension/solution of lithium/potassium salt [lithium phenylacetylide (for compound **4**), potassium *t*-butoxide (for compound **5**), and lithium bis-trimethylsilyl amide (for compound **9**)] in toluene (10 mL) at 0 °C. The reaction mixture was then stirred for overnight at room temperature and filtered through a G4 frit containing celite. Removal of the solvent from the filtrate gave an analytically pure sample of the germanium compound [germaynone [(*i*-Bu)$_2$ATIGe(O)(CCPh)→B(C_6F_5)$_3$] (**4**), germaester [(*i*-Bu)$_2$ATIGe(O)(O^{t}Bu)→B(C_6F_5)$_3$] (**5**), and germaimine [(*i*-Bu)$_2$ATIGe=N($SiMe_3$)($OSiMe_3$)→B(C_6F_5)$_3$] (**9**)]. Single crystals of these compounds suitable for X-ray diffraction studies were grown from their saturated solutions in dichloromethane at -40 °C.

General synthetic route for the isolation of donor-acceptor stabilized germaketones (*i*-Bu)$_2$ATIGe(O)(X)→B(C_6F_5)$_3$ [X = Ph (6), X = Me (7)].

A solution of germaacid chloride **1** in toluene (20 mL) was treated with the lithium salt [phenyl lithium (1.9 M in dibutylether) (for compound **6**) and methyl lithium (1.6 M in diethyl ether) (for compound **7**)] at 0 °C. The reaction mixture was then stirred for overnight at room temperature and filtered through a G4 frit containing celite. Removal of the solvent from the filtrate gave an analytically pure sample of germaketone {[(*i*-

Bu)$_2$ATIGe(O)(Ph)→B(C_6F_5)$_3$] (**6**) and [(*i*-Bu)$_2$ATIGe(O)(Me)→B(C_6F_5)$_3$] (**7**)}. Single crystals of these compounds suitable for X-ray diffraction studies were grown from their saturated solutions in dichloromethane at -40 °C.

Synthesis of compound 4: Compound **1** (0.5 g, 0.58 mmol), LiCCPh (68 mg, 0.63 mmol). Yield: 0.48 g, 90%. Mp: 141 °C. Anal. Calcd for $C_{41}H_{28}BF_{15}GeN_2O$ (M = 933.10): C, 52.77; H, 3.02; N, 3.00 Found: C, 52.29; H, 3.15; N, 3.11. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06-1.10 (q, 12H, CH(CH_3)$_2$), 2.40-2.49 (m, 2H, CH(CH$_3$)$_2$), 3.53 (dd, $^3J_{HH}$ = 15.3, 9.0 Hz, 2H, CH_2), 3.76 (dd, $^3J_{HH}$ = 14.1, 7.8 Hz, 2H, CH_2), 6.87 (t, $^3J_{HH}$ = 9.3, 1H, CH), 6.99 (s, $^3J_{HH}$ = 11.4, 2H, CH), 7.25-7.33 (m, 3H, CH), 7.37-7.44 (m, 4H, CH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 20.43 (CH(*C*H$_3$)$_2$), 20.59 (CH(*C*H$_3$)$_2$), 27.37 (*C*H(CH$_3$)$_2$), 53.21 (*C*H$_2$), 109.11, 118.70, 120.14(*C*$_4$), 125.30, 128.25, 128.58, 129.04, 131.81 (*C*$_{2,6}$), 135.11 (*C*F), 138.55 (*C*F), 139.69 (*C*$_{3,5}$), 146.57 (*C*F), 149.66 (*C*F), 157.40 (*C*$_{1,7}$). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ -133.62 (d, $^3J_{FF}$ = 24.81 Hz, 6F, *ortho*-C$_6$*F*$_5$), -160.74 (t, $^3J_{FF}$ = 20.30 Hz, 3F, *para*-C$_6$*F*$_5$), -165.39 (m, 6F, *meta*-C$_6$*F*$_5$). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -2.79 (s).

Synthesis of compound 5 Compound **1** (0.5 g, 0.58 mmol), KO*t*-Bu (65 mg, 0.59 mmol). Yield: 0.42 g, 81%. Mp: 147 °C. Anal. Calcd for $C_{37}H_{32}BF_{15}GeN_2O_2$ (M = 905.09): C, 49.10; H, 3.56; N, 3.10 Found: C, 49.27; H, 3.39; N, 3.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (d, $^3J_{HH}$ = 6.0 Hz, 12H, CH(CH_3)$_2$), 1.51 (s, 9H, C(CH_3)$_3$), 2.34-2.40 (m, 2H, CH(CH$_3$)$_2$), 3.54 (dd, $^3J_{HH}$ = 14.4, 6.8 Hz, 2H, CH_2), 3.67 (dd, $^3J_{HH}$ = 14.0, 7.6 Hz, 2H, CH_2), 6.88 (t, $^3J_{HH}$ = 9.2 Hz, 1H, CH), 6.97 (d, $^3J_{HH}$ = 11.2 Hz, 2H, CH), 7.39 (t, $^3J_{HH}$ = 10.4 Hz, 2H, CH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 20.79 (CH(*C*H$_3$)$_2$), 20.82 (CH(*C*H$_3$)$_2$), 27.33 (*C*H(CH$_3$)$_2$), 32.23 (*C*(*C*H$_3$)$_3$), 52.56 (*C*H$_2$), 118.34 (*C*$_4$), 128.21 (*C*$_{2,6}$), 129.02, 134.85 (*C*F), 138.14 (*C*F), 139.28 (*C*$_{3,5}$), 146.04 (*C*F), 149.29 (*C*F), 155.59 (*C*$_{1,7}$). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -132.30

(d, $^{3}J_{FF}$ = 22.18 Hz, 6F, *ortho*-C_6F_5), -159.73 (t, $^{3}J_{FF}$ = 21.80 Hz, 3F, *para*-C_6F_5), -165.04 (t, $^{3}J_{FF}$ = 19.55 Hz, 6F, *meta*-C_6F_5). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ -2.44 (s).

Synthesis of compound 6: Compound **1** (0.5 g, 0.58 mmol), PhLi (0.3 mL, 1.9 M in dibutylether). Yield: 0.45 g, 87%. Mp: 131 °C. Anal. Calcd for $C_{39}H_{28}BF_{15}GeN_2O$ (M = 909.08): C, 51.53; H, 3.10; N, 3.08 Found: C, 51.40; H, 3.19; N, 2.89. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.70 (d, $^{3}J_{HH}$ = 7.5 Hz, 6H, CH(CH_3)$_2$), 0.81 (d, $^{3}J_{HH}$ = 6.3 Hz, 6H, CH(CH_3)$_2$), 1.78-1.91 (m, 2H, CH(CH$_3$)$_2$), 3.34-3.45 (m, 4H, CH_2), 7.18 (d, $^{3}J_{HH}$ = 11.1 Hz, 2H, CH), 7.25 (t, $^{3}J_{HH}$ = 5.7 Hz, 1H, CH), 7.52-7.67 (m, 4H, CH), 7.86 (d, $^{3}J_{HH}$ = 5.4 Hz, 2H, CH). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 20.38 (CH(*C*H$_3$)$_2$), 20.53 (CH(*C*H$_3$)$_2$), 28.27 (*C*H(CH$_3$)$_2$), 53.64 (*C*H$_2$), 118.73 (C_4), 128.37, 129.17 ($C_{2,6}$), 133.01, 134.82 (*C*F), 135.18, 138.08 (*C*F), 139.46 ($C_{3,5}$), 146.13 (*C*F), 149.39 (*C*F), 157.65 ($C_{1,7}$). $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$): δ -133.65 (d, $^{3}J_{FF}$ = 24.25 Hz, 6F, *ortho*-C_6F_5), -160.67 (t, $^{3}J_{FF}$ = 21.15 Hz, 3F, *para*-C_6F_5), -165.26 (m, 6F, *meta*-C_6F_5). $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$): δ -3.12 (s).

Synthesis of compound 7: Compound **1** (0.3 g, 0.35 mmol), MeLi (0.21 mL, 1.6 M in diethyl ether). Yield: 0.27 g, 92%. Mp: 126 °C. Anal. Calcd for $C_{34}H_{26}BF_{15}GeN_2O$ (M = 847.01): C, 48.21; H, 3.09; N, 3.31 Found: C, 48.05; H, 2.96; N, 3.09. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (d, $^{3}J_{HH}$ = 6.0 Hz, 6H, CH(CH_3)$_2$), 0.98 (d, $^{3}J_{HH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$), 0.98 (d, $^{3}J_{HH}$ = 6.4 Hz, 6H, CH(CH_3)$_2$), 1.25 (s, 3H, CH_3), 2.07-2.11 (m, 2H, CH(CH$_3$)$_2$), 3.35 (dd, $^{3}J_{HH}$ = 23.2, 14.0 Hz, 2H, CH_2), 3.48 (dd, $^{3}J_{HH}$ = 14.1, 5.2 Hz, 2H, CH_2), 7.06 (d, $^{3}J_{HH}$ = 10.2, 2H, CH), 7.20 (t, $^{3}J_{HH}$ = 9.6 Hz, 1H, CH), 7.57 (t, $^{3}J_{HH}$ = 9.6 Hz, 2H, CH). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ 20.37 (CH(*C*H$_3$)$_2$), 20.65 (CH(*C*H$_3$)$_2$), 27.07 (*C*H(CH$_3$)$_2$), 53.23 (*C*H$_2$), 118.66 (C_4), 128.77 ($C_{2,6}$), 134.73 (*C*F), 138.17 (*C*F), 139.31 ($C_{3,5}$), 146.04 (*C*F), 149.18 (*C*F), 157.35 ($C_{1,7}$). $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$): δ -134.29 (d, $^{3}J_{FF}$ = 19.74 Hz,

6F, *ortho*-C_6F_5), -160.83 (t, $^3J_{FF}$ = 20.30 Hz, 3F, *para*-C_6F_5), -165.33 (m, 6F, *meta*-C_6F_5). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ -3.31 (s).

Synthesis of compound 9: Compound **1** (0.2 g, 0.23 mmol), $LiN(TMS)_2$ (39 mg, 0.24 mmol). Yield: 0.22 g, 96%. Mp: 118 °C. Anal. Calcd for $C_{39}H_{41}BF_{15}GeN_3OSi_2$ (M = 992.36): C, 47.20; H, 4.16; N, 4.23 Found: C, 47.31; H, 3.98; N, 4.06. ^1H NMR (300 MHz, C_6D_6): δ 0.38 (s, 9H, $Si(CH_3)_3$), 0.49 (s, 9H, $Si(CH_3)_3$), 0.90-0.93 (q, 12H, $CH(CH_3)_2$), 2.19-2.32 (m, 2H, $CH(CH_3)_2$), 3.27 (dd, $^3J_{HH}$ = 13.2, 6.0 Hz, 2H, CH_2), 3.46 (dd, $^3J_{HH}$ = 13.8, 7.8 Hz, 2H, CH_2), 6.21 (t, $^3J_{HH}$ = 8.4 Hz, 1H, C*H*), 6.40 (t, $^3J_{HH}$ = 11.1 Hz, 2H, C*H*), 6.68 (t, $^3J_{HH}$ = 9.9 Hz, 2H, C*H*).

Synthesis of compounds 2 and 3 from compound 1.

A solution of germaacid chloride **1** (0.3 g, 0.34 mmol) in toluene (10 mL) was transfered to a solution of the lithium salt [lithium triphenylsiloxide (97 mg, 0.34 mmol) (for compound **2**) and lithium pyrrol-1-ide (26 mg, 0.34 mmol) (for compound **3**)] in toluene (10 mL) at 0 °C. The reaction mixture was then brought to room temparature and stirred overnight. It was filtered using a G4 frit containing celite. Removal of solvent from the filtrate gave a yellow solid, which was washed with hexane (2 mL) and dried in *vacuo* to get a pure sample of the germanium compound [**2** (0.320 mg, 84%) and **3** (0.282 mg, 91%)].

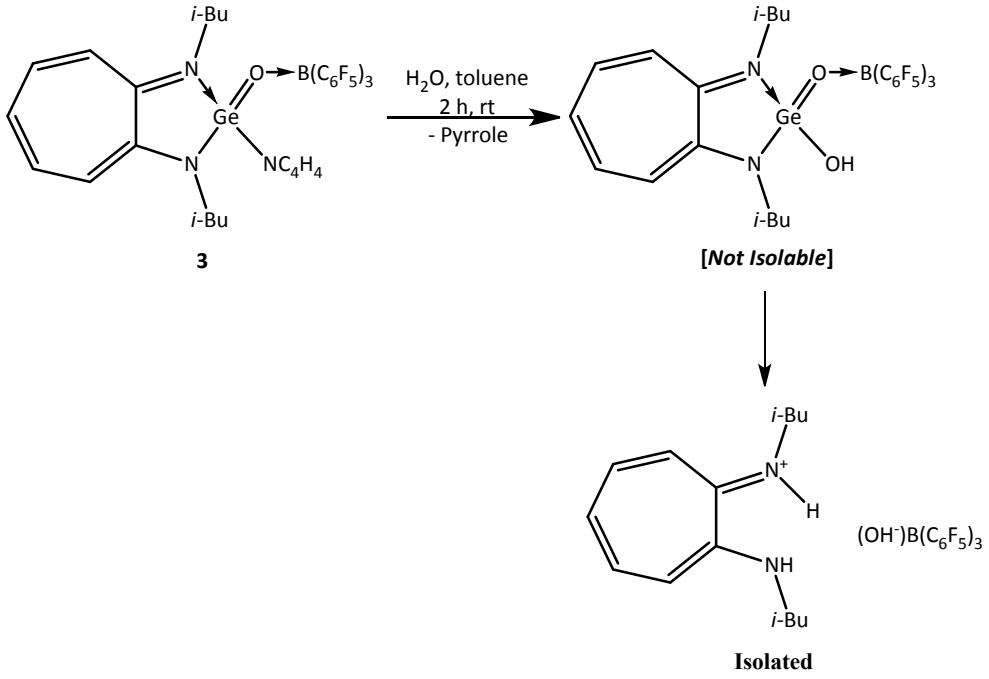
Conversion of compound 2/5 to compound 1.

To a toluene solution (20 mL) of compound **2** (0.3 g, 0.35 mmol), TMSCl (46 μL, 0.36 mmol) was added at 0 °C. The reaction mixture was stirred for 2 h at room temperature and all the volatiles were removed under reduced pressure. The resultant solid was washed with hexane and finally dried *in vacuo* to get an analytically pure sample of compound **1** in 86% yield (Note: Using the same procedure and starting from compound **5** instead of **2**, compound **1** can be isolated).

Synthesis of compound 10.

To a toluene (10 mL) solution of compound **3** (0.5 g, 0.56 mmol), thiophenol (57 μL, 0.56 mmol) was added at room temperature. The resulting solution was then stirred for 6 h, and the solvent was removed under reduced pressure to get an analytically pure sample of compound **10**. Single crystals of compound **10** suitable for X-ray diffraction studies were grown from its toluene solution at -40 °C. Yield: 0.52 g, 99%. Mp: 135 °C. Anal. Calcd for $C_{39}H_{28}BF_{15}GeN_2OS$ (M = 941.14): C, 49.77; H, 3.00; N, 2.98. Found: C, 50.02; H, 2.67; N, 3.51. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.74 (d, $^3J_{HH}$ = 6.6 Hz, 6H, $CH(CH_3)_2$), 0.93 (d, $^3J_{HH}$ = 6.6 Hz, 6H, $CH(CH_3)_2$), 2.04-2.13 (m, 2H, $CH(CH_3)_2$), 3.41 (dd, $^3J_{HH}$ = 14.1, 6.6 Hz, 2H, CH_2), 3.55 (dd, $^3J_{HH}$ = 14.1, 8.4 Hz, 2H, CH_2), 6.95-7.03 (m, 5H, C*H*), 7.10-7.18 (m, 3H, C*H*), 7.52 (t, $^3J_{HH}$ = 10.2, 2H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 19.81 ($CH(CH_3)_2$), 20.53 ($CH(CH_3)_2$), 27.56 ($CH(CH_3)_2$), 52.82 (CH_2), 118.62 (C_4), 125.62 (Ph), 128.86 (Ph), 129.01 (Ph), 129.07 ($C_{2,6}$), 135.08 (*C*F), 135.48 (Ph), 139.34 (*C*F), 140.76 ($C_{3,5}$), 146.83 (*C*F), 149.83 (*C*F), 156.57 ($C_{1,7}$). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ -132.91 (dd, $^3J_{FF}$ = 27.63, 10.99 Hz, 6F, *ortho*-C_6F_5), -160.40 (t, $^3J_{FF}$ = 21.43 Hz, 3F, *para*-C_6F_5), -165.37 (m, 6F, *meta*-C_6F_5). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ -2.73 (s).

Scheme for the attempted synthesis of germacarboxylic Acid.



Scheme S1. Reaction of compound **3** with water.

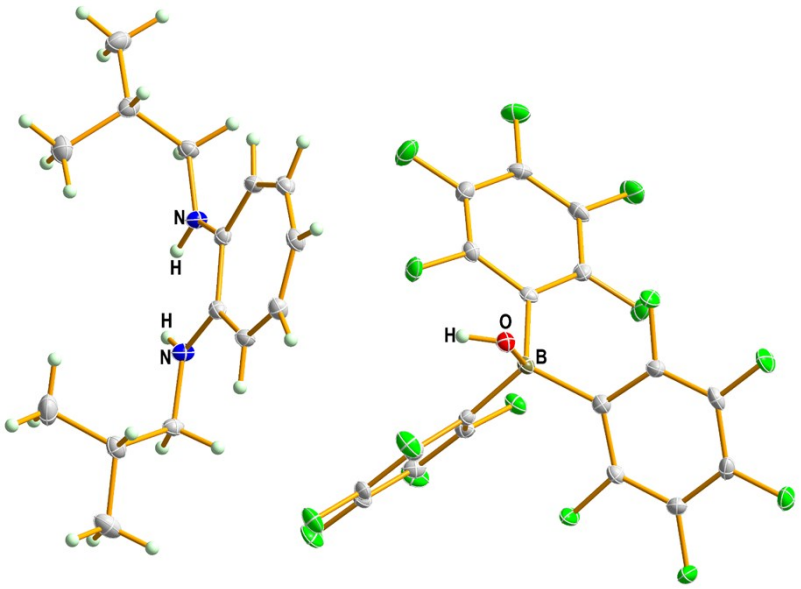


Figure S0. Molecular structure of the isolated ATI ligand salt $[ATIH]^{+}[(OH)(B(C_6F_5)_3)]^{-}$.

2. NMR Spectra of Compounds D1, D3-D5, 1-7, 9, and 10

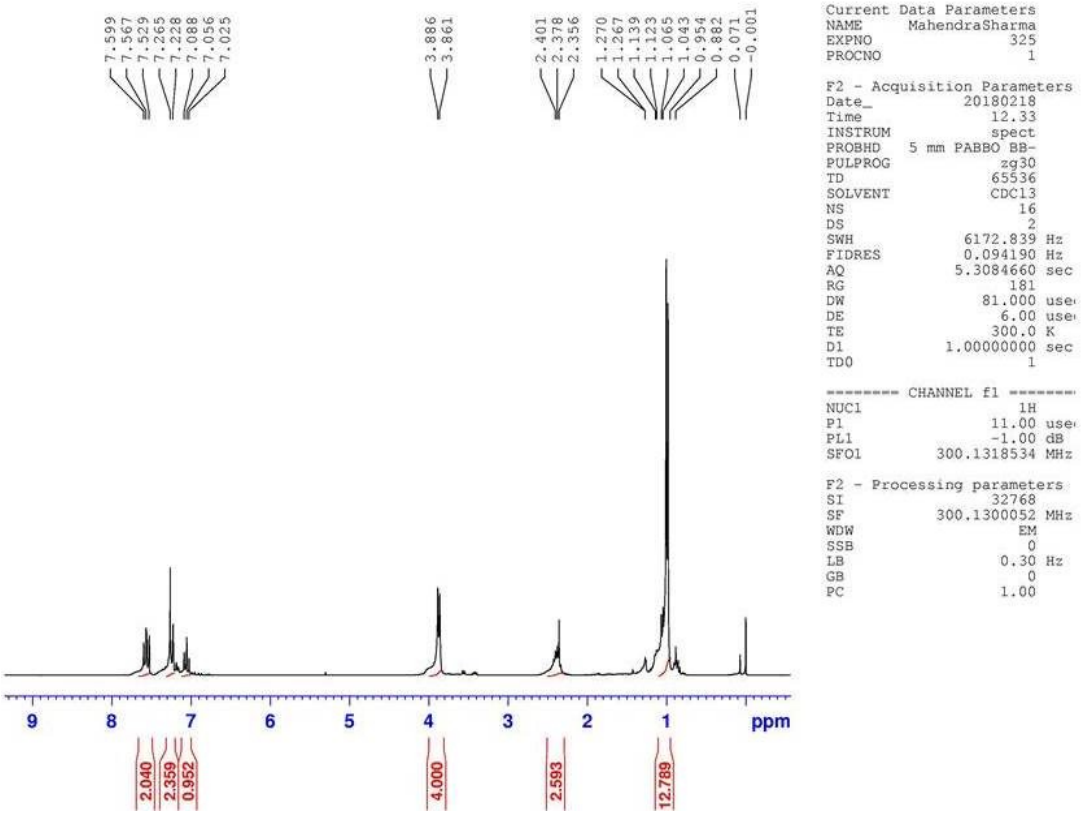


Figure S1. ^{1}H NMR spectrum of compound **D1** in $CDCl_3$ at 300 K.

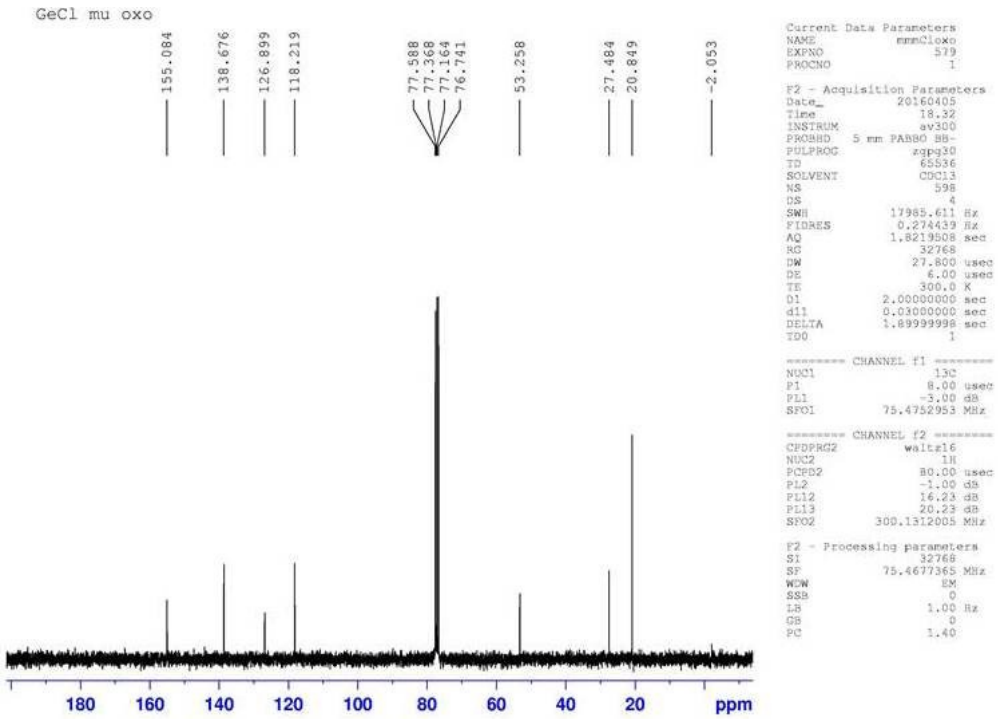


Figure S2. ^{13}C NMR spectrum of compound **D1** in $CDCl_3$ at 300 K.

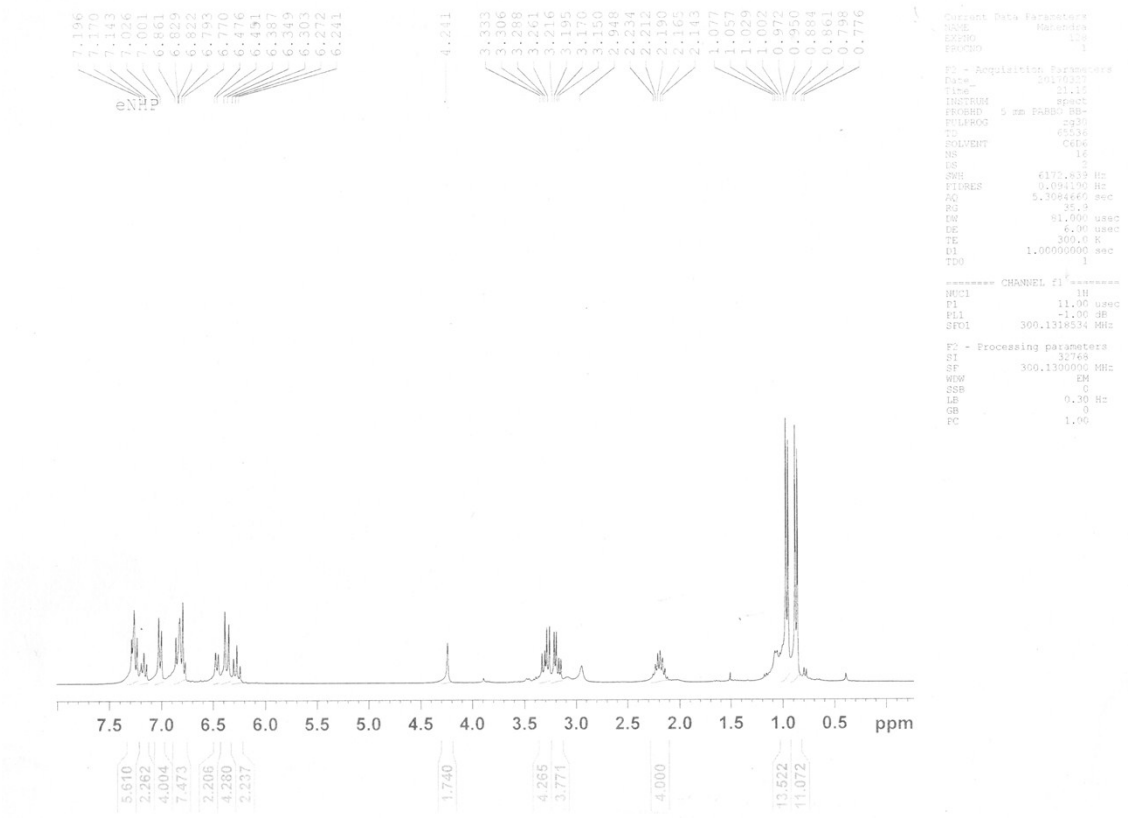


Figure S3. ^{1}H NMR spectrum of compound **D3** in $CDCl_3$ at 300 K.

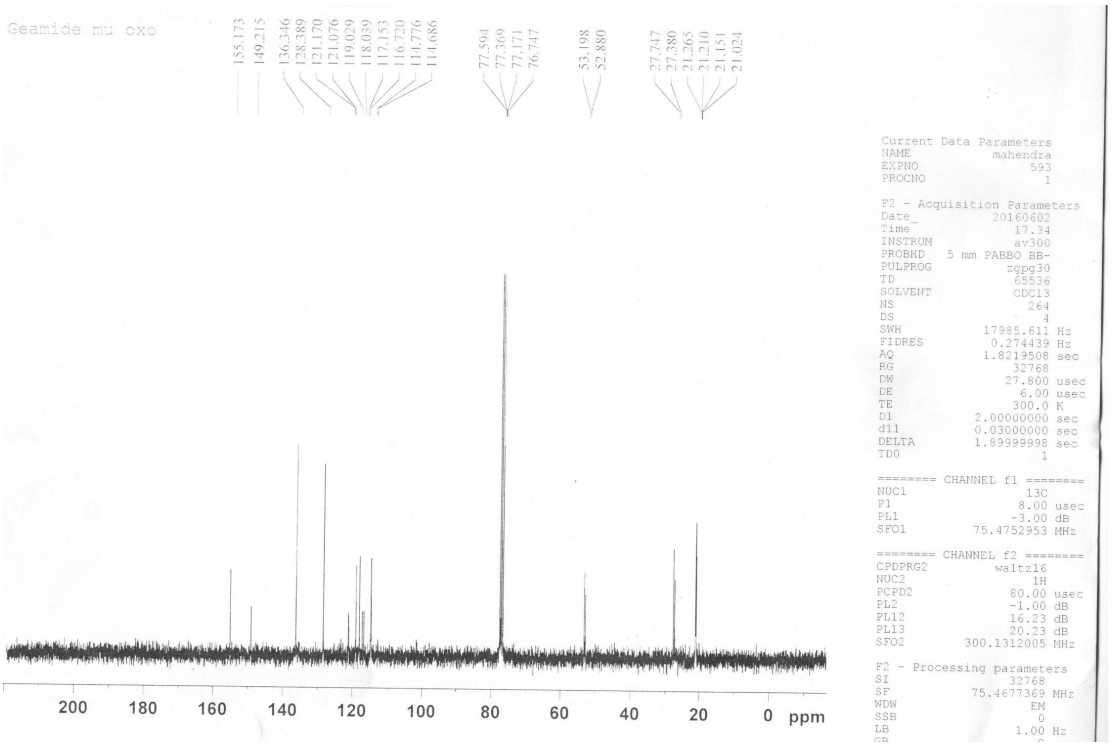


Figure S4. ^{13}C NMR spectrum of compound **D3** in $CDCl_3$ at 300 K.

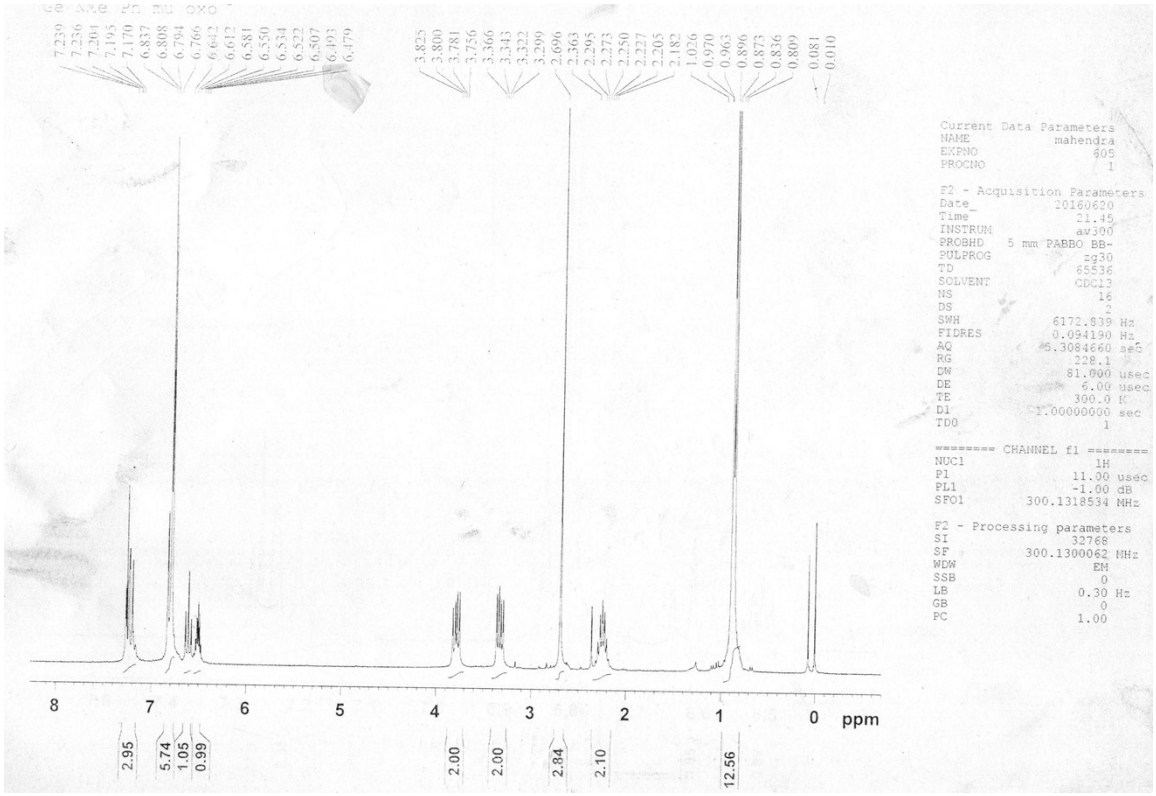


Figure S5. ^{1}H NMR spectrum of compound **D4** in $CDCl_3$ at 300 K.

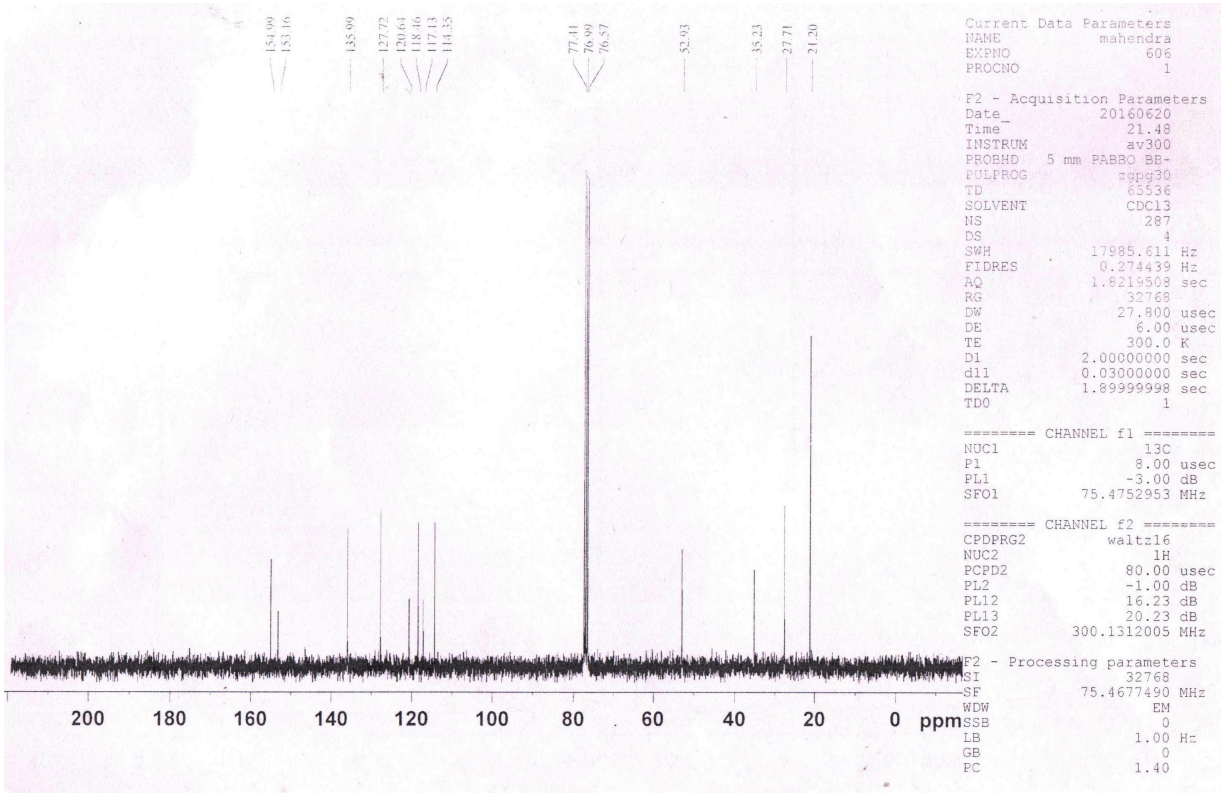


Figure S6. ^{13}C NMR spectrum of compound **D4** in $CDCl_3$ at 300 K.

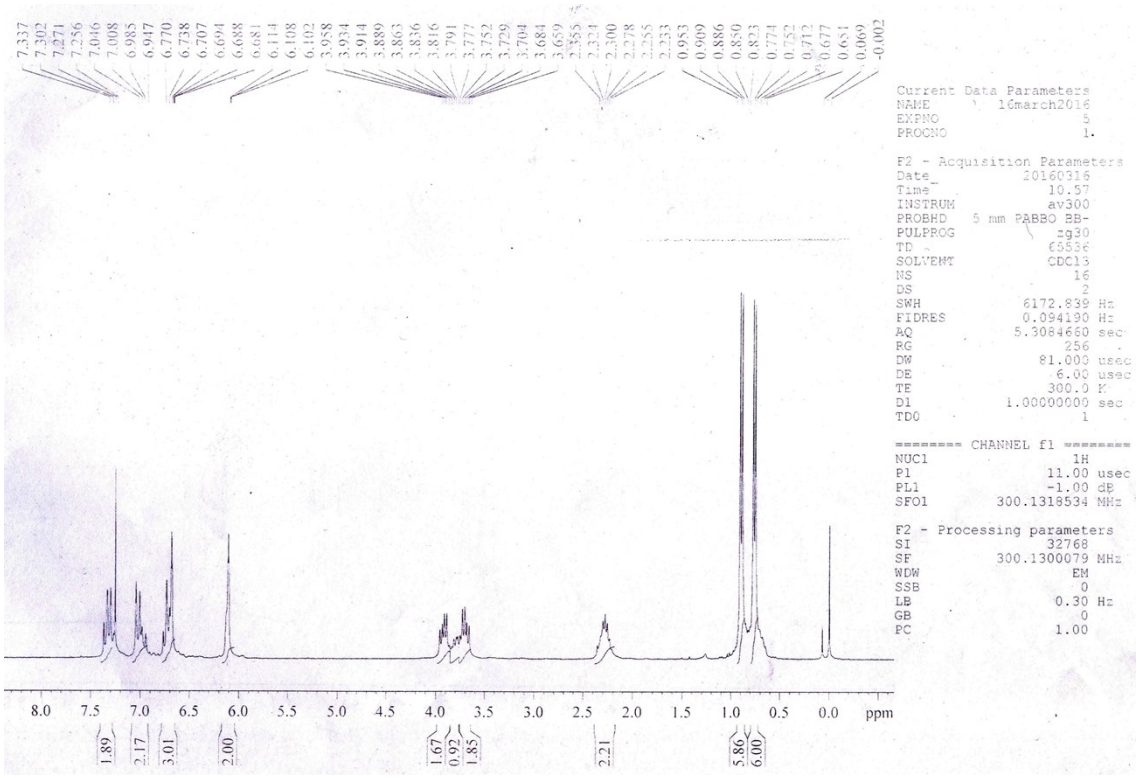


Figure S7. ^{1}H NMR spectrum of compound **D5** in $CDCl_3$ at 300 K.

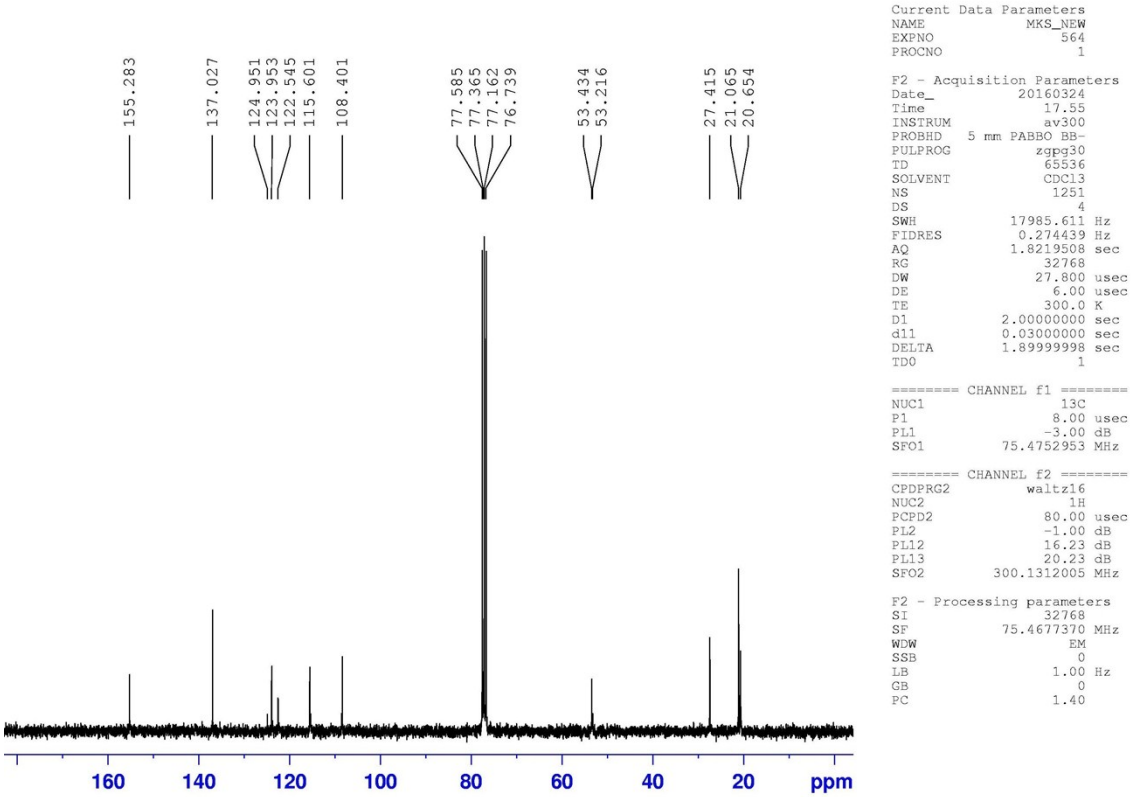


Figure S8. ^{13}C NMR spectrum of compound **D5** in $CDCl_3$ at 300 K.

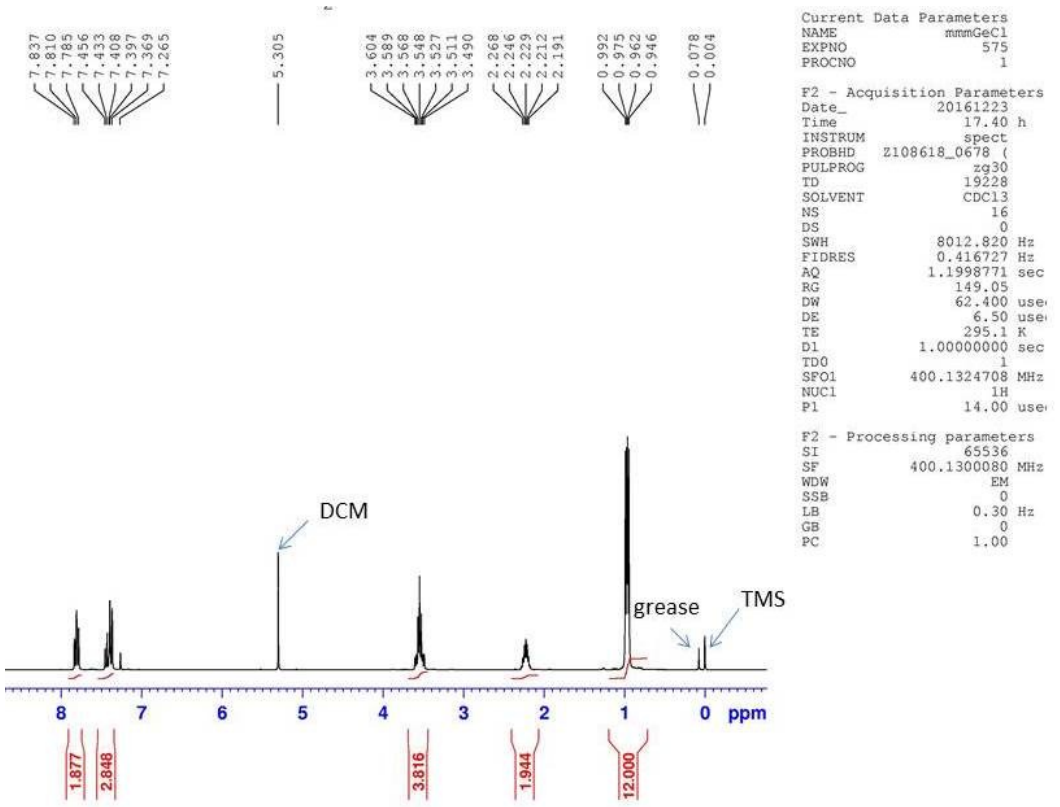


Figure S9. ^{1}H NMR spectrum of compound **1** in $CDCl_3$ at 300 K.

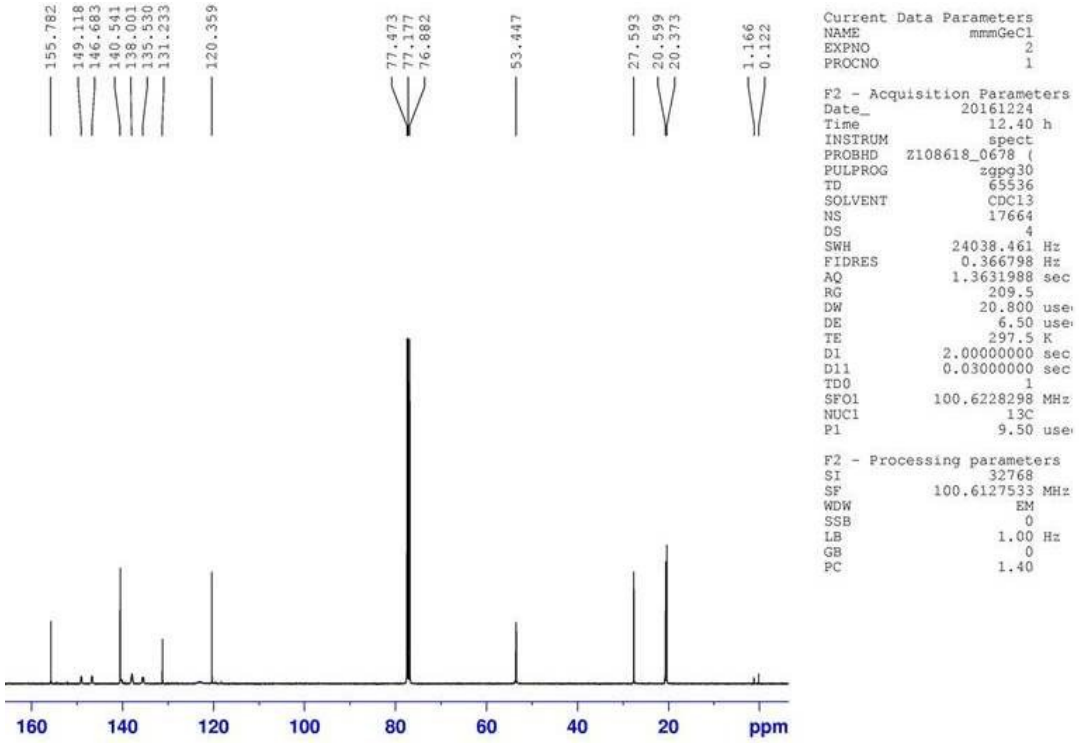


Figure S10. ^{13}C NMR spectrum of compound **1** in $CDCl_3$ at 300 K.

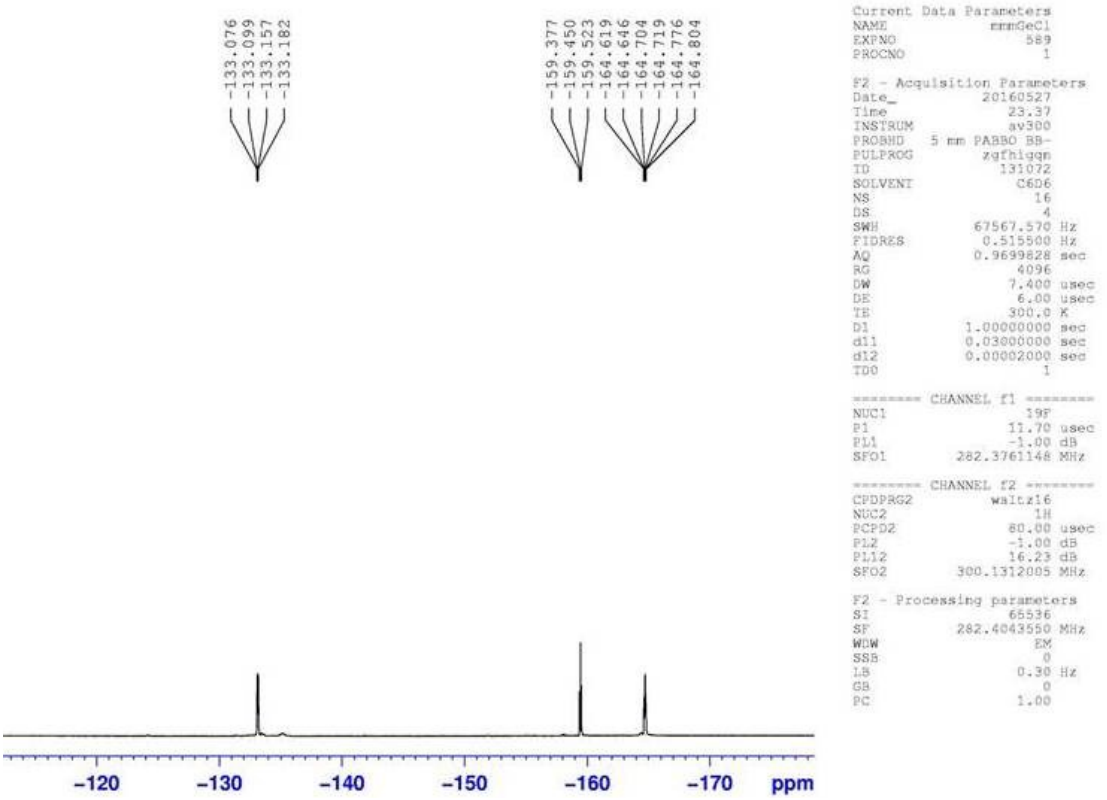



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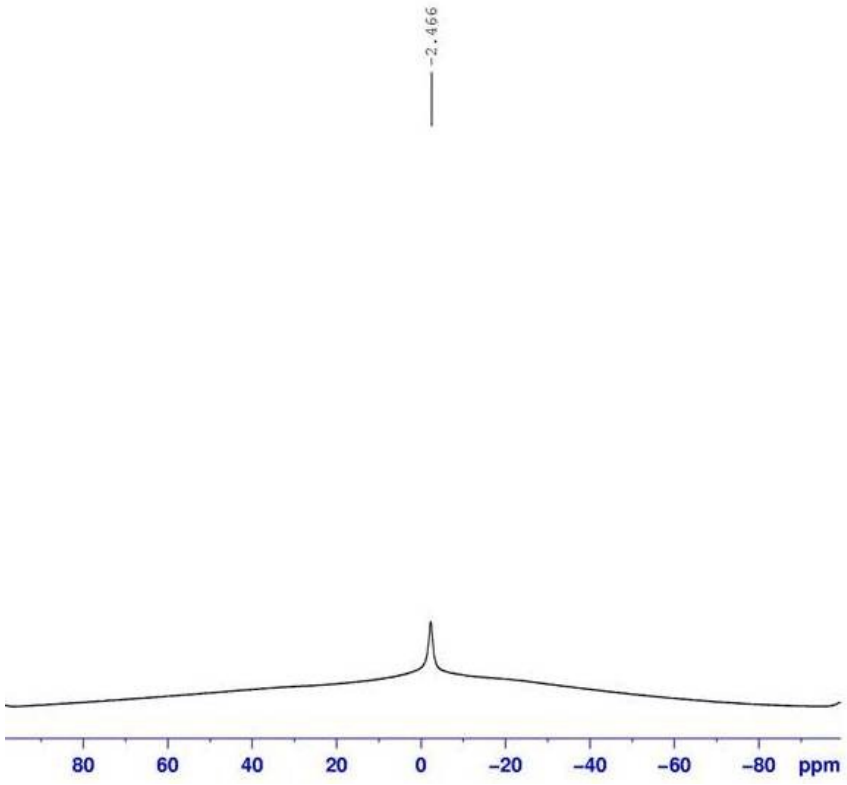
Figure S11. ^{19}F NMR spectrum of compound **1** in $CDCl_3$ at 300 K.

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NUC1                      11B
P1                     8.88 use

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Figure S12. ^{11}B NMR spectrum of compound **1** in $CDCl_3$ at 300 K.

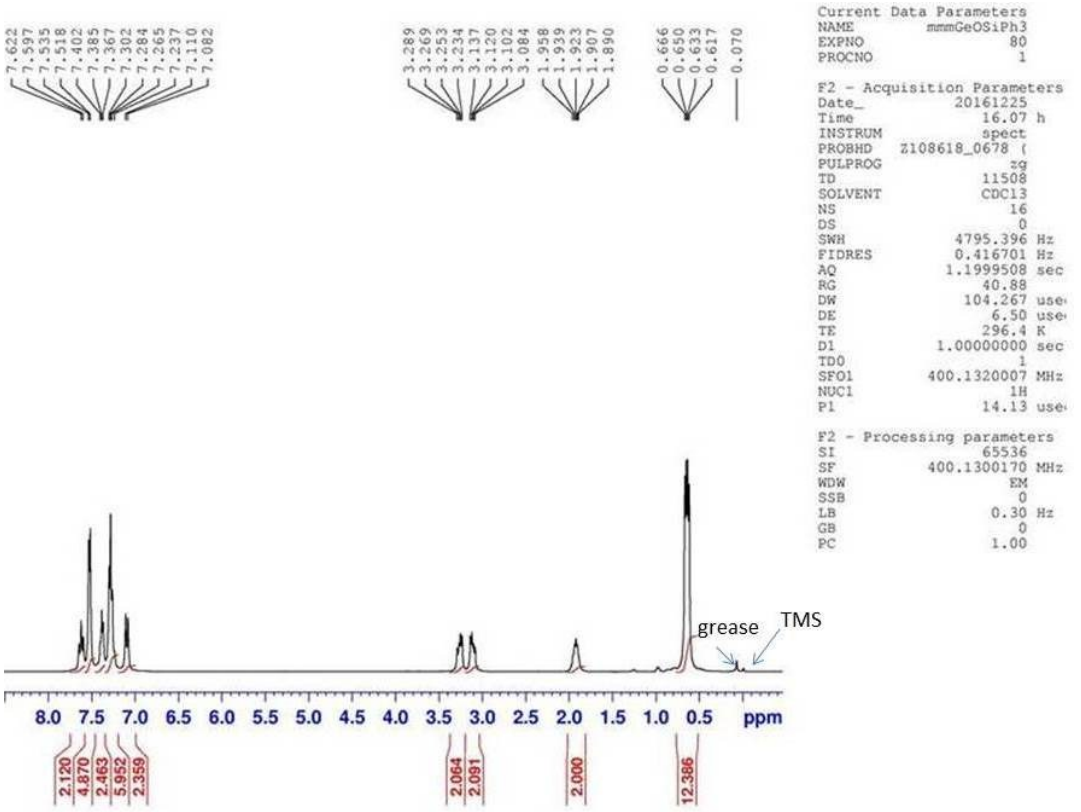


Figure S13. ^{1}H NMR spectrum of compound **2** in $CDCl_3$ at 300 K.

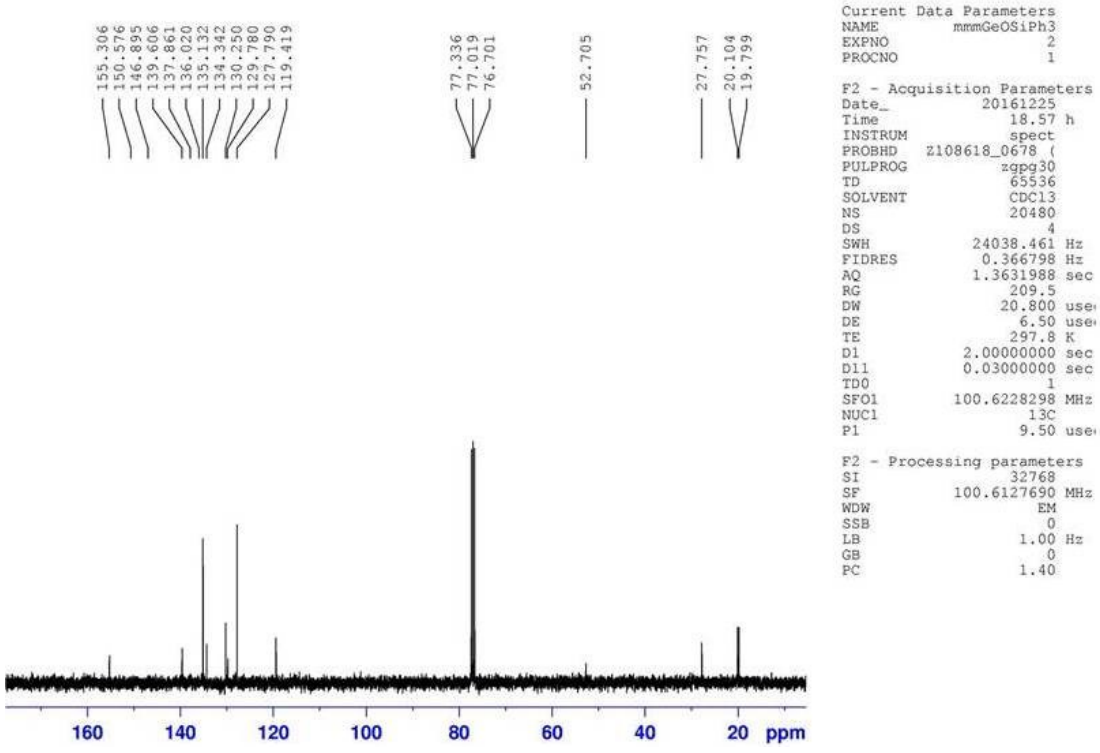


Figure S14. ^{13}C NMR spectrum of compound **2** in $CDCl_3$ at 300 K.

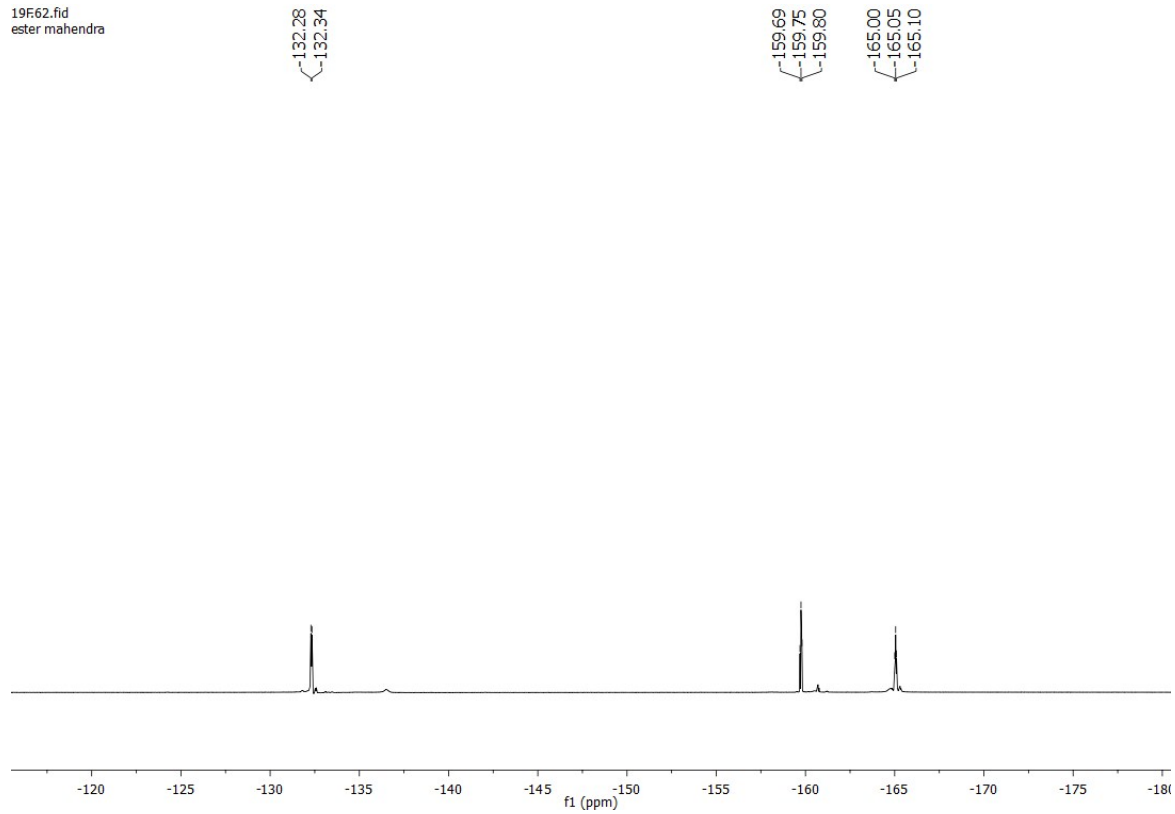


Figure S15. ^{19}F NMR spectrum of compound **2** in $CDCl_3$ at 300 K.

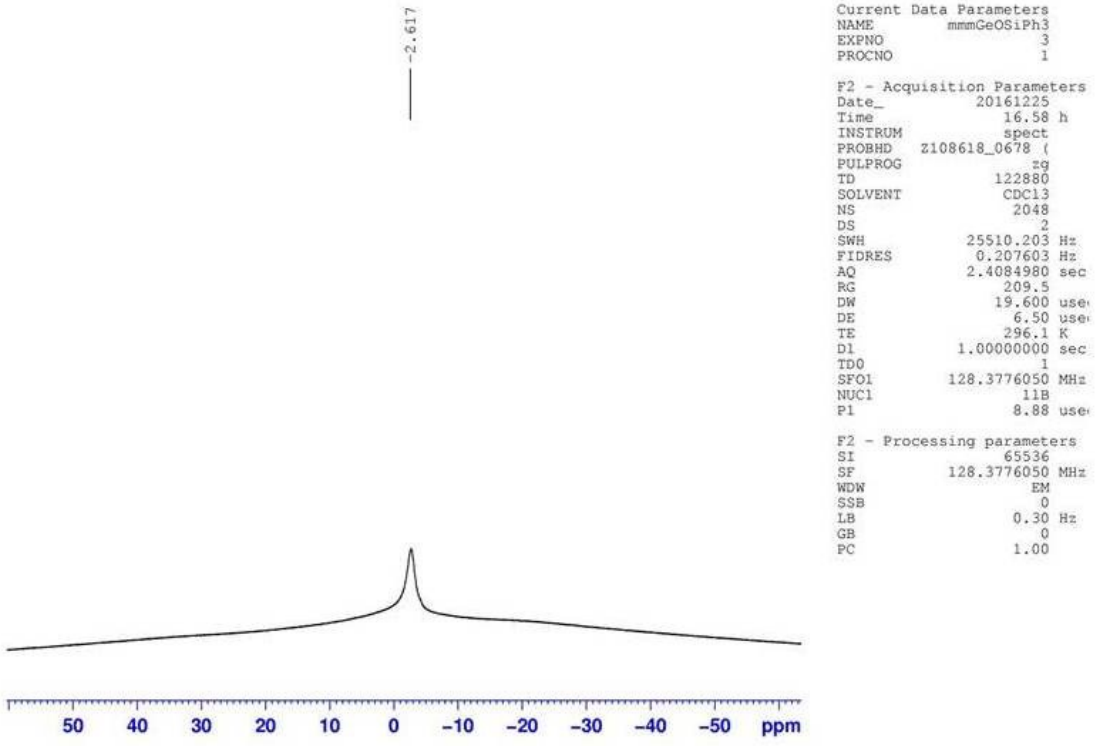


Figure S16. ^{11}B NMR spectrum of compound **2** in $CDCl_3$ at 300 K.

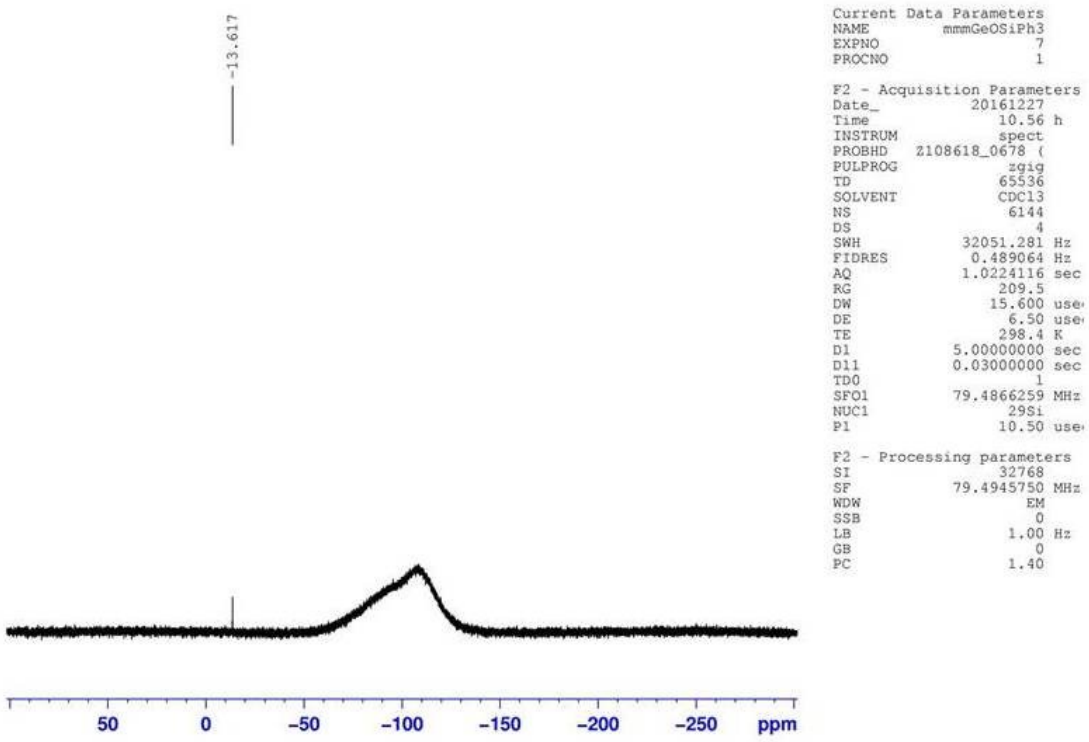


Figure S17. ^{29}Si NMR spectrum of compound **2** in $CDCl_3$ at 300 K.

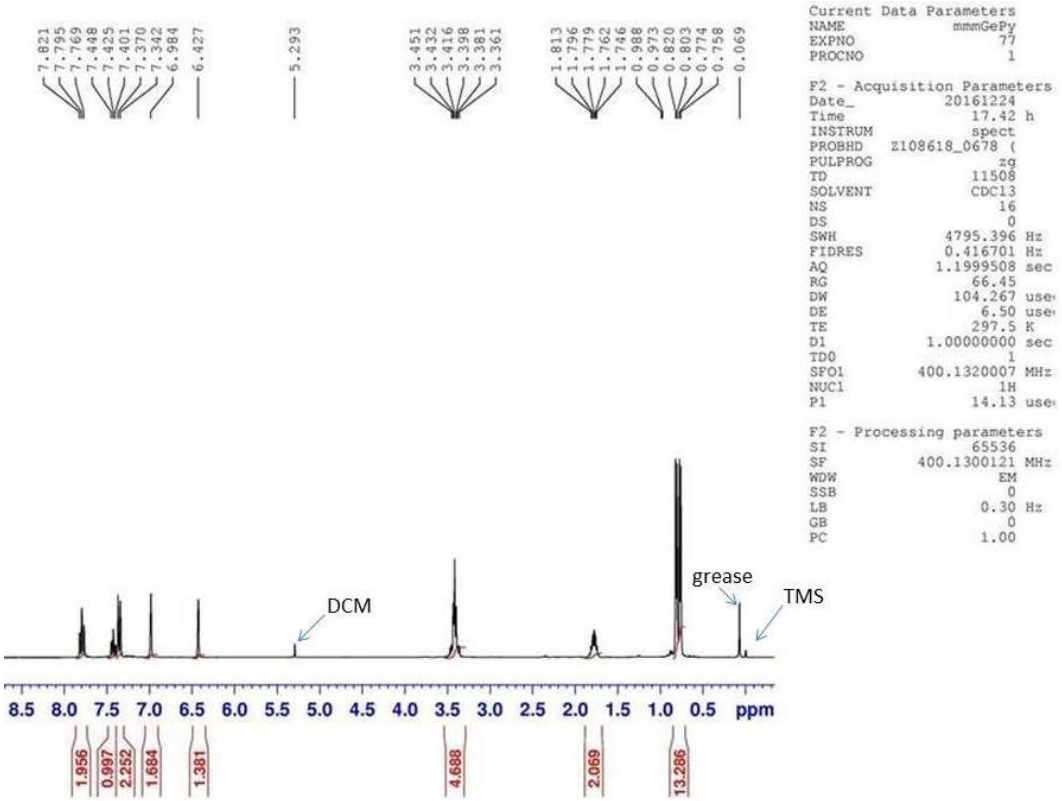


Figure S18. ^{1}H NMR spectrum of compound **3** in $CDCl_3$ at 300 K.

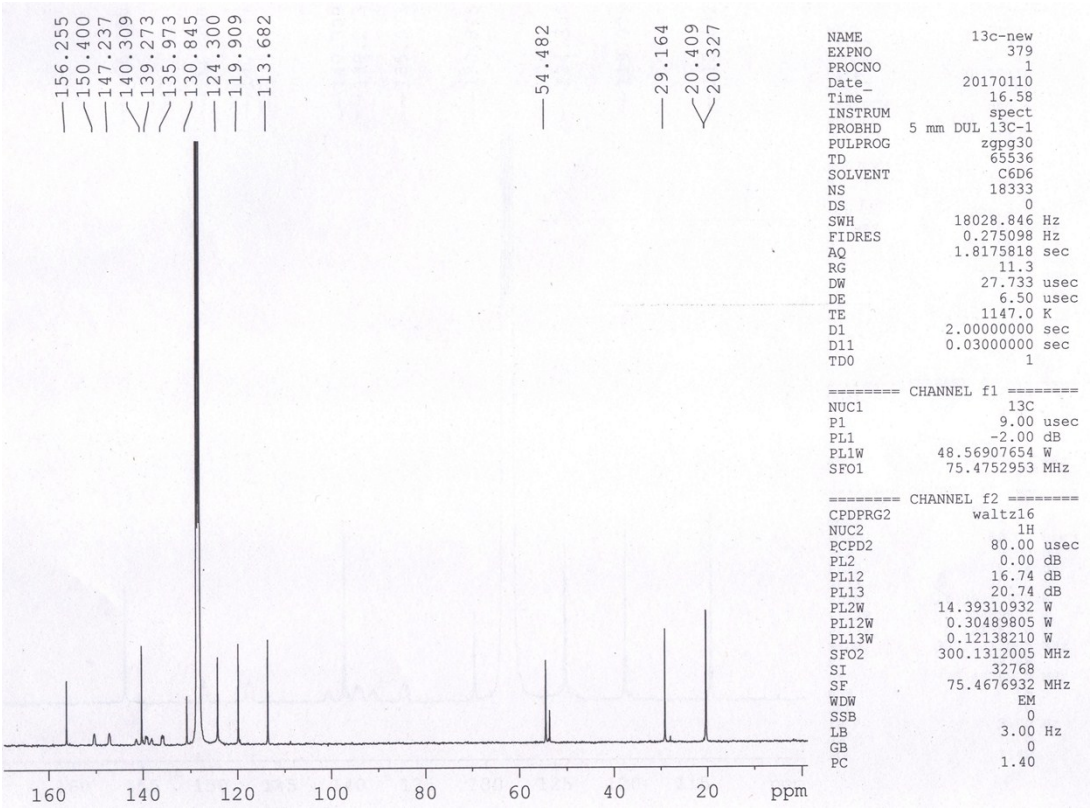


Figure S19. ^{13}C NMR spectrum of compound **3** in C_6D_6 at 300 K.

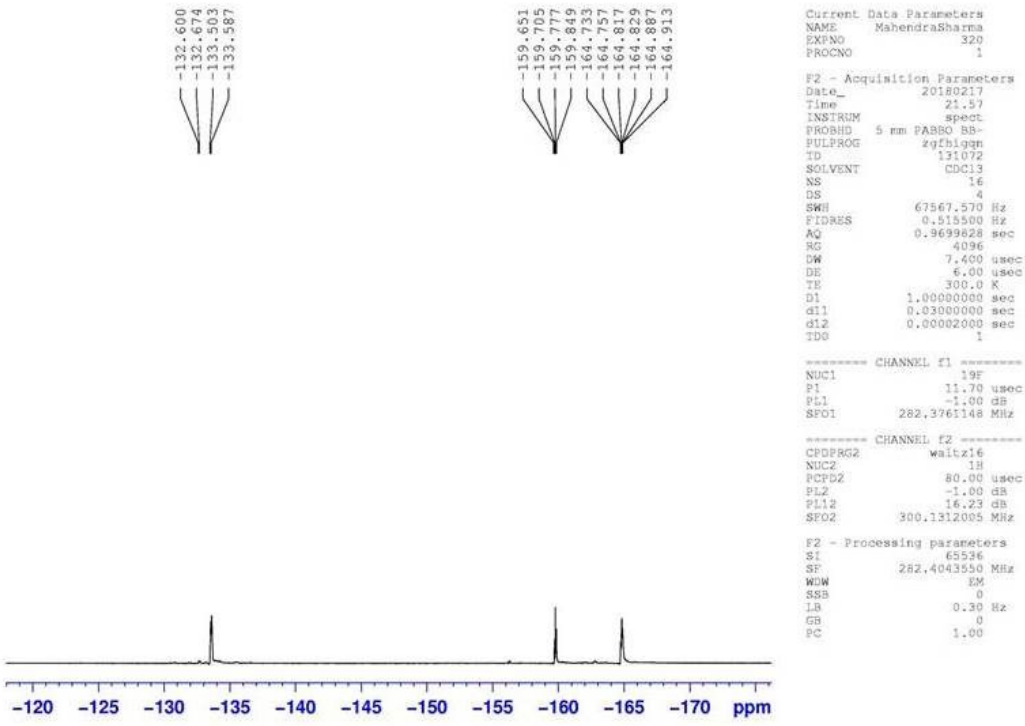


Figure S20. ^{19}F NMR spectrum of compound **3** in $CDCl_3$ at 300 K.

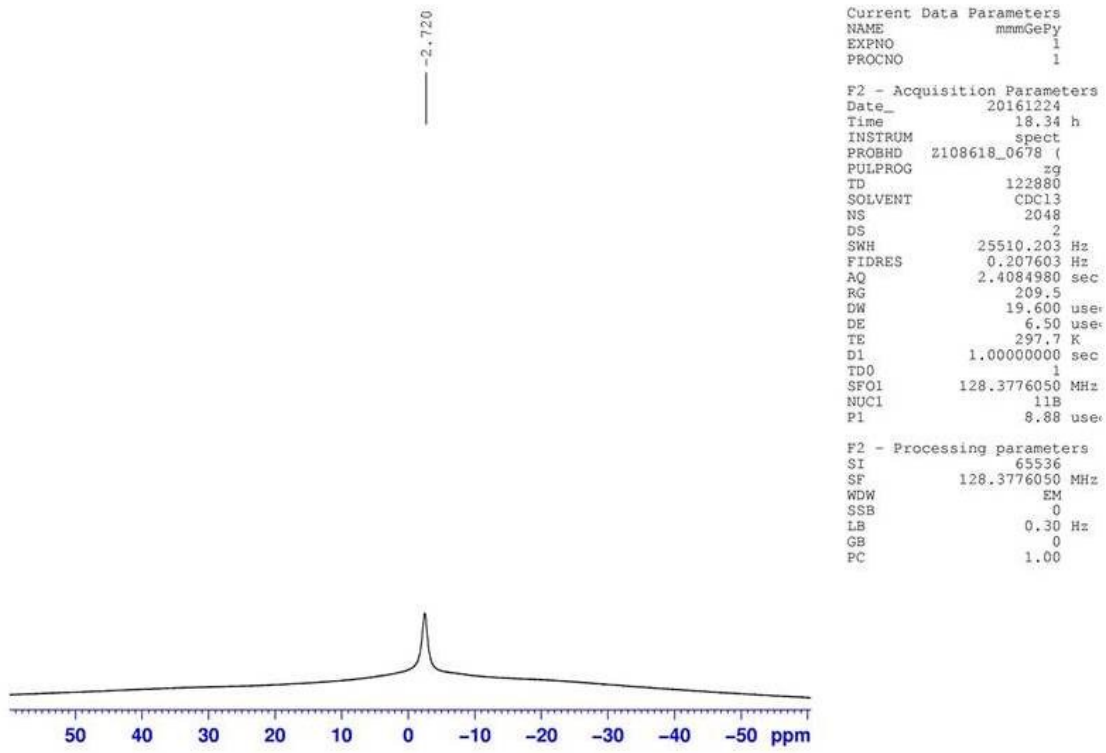


Figure S21. ^{11}B NMR spectrum of compound **3** in $CDCl_3$ at 300 K.

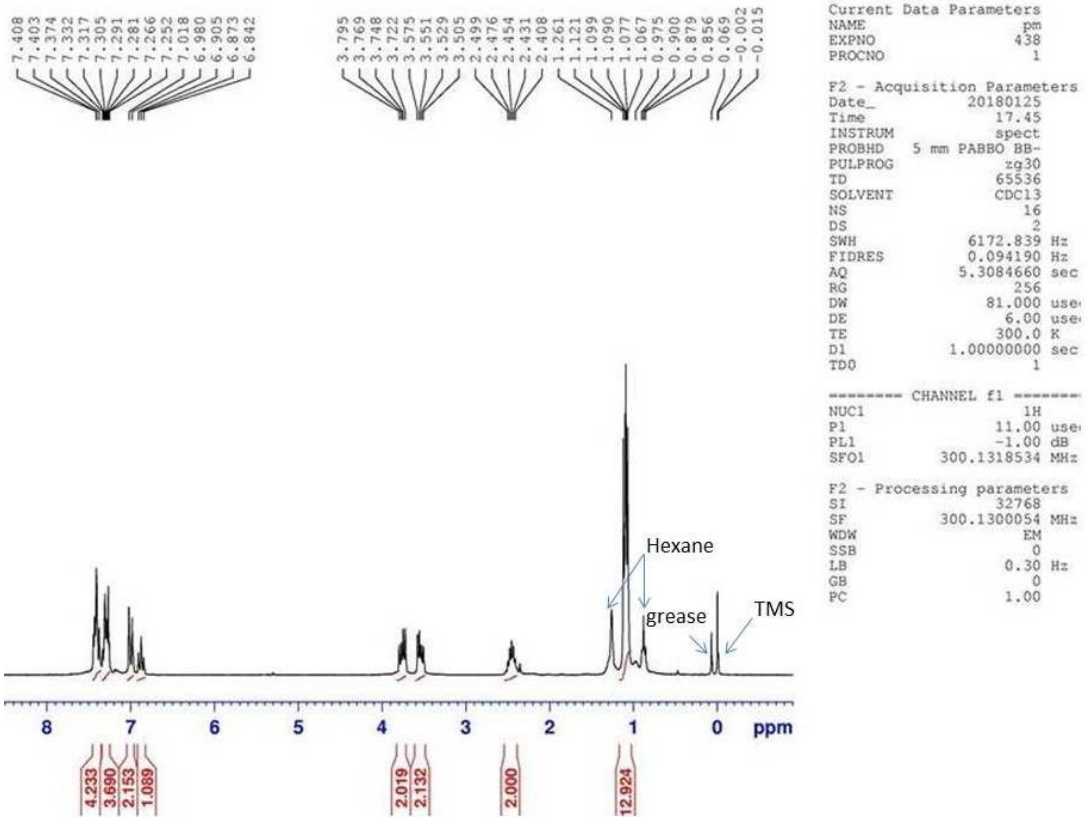


Figure S22. ^{1}H NMR spectrum of compound **4** in $CDCl_3$ at 300 K.

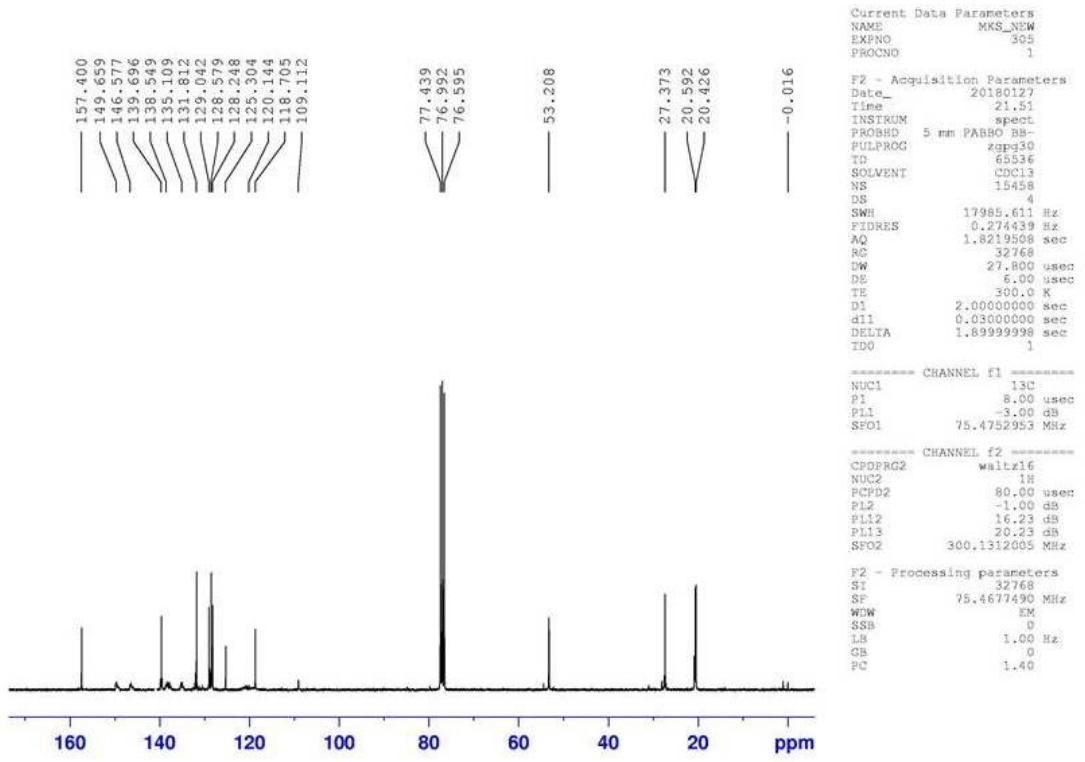


Figure S23. ^{13}C NMR spectrum of compound **4** in $CDCl_3$ at 300 K.

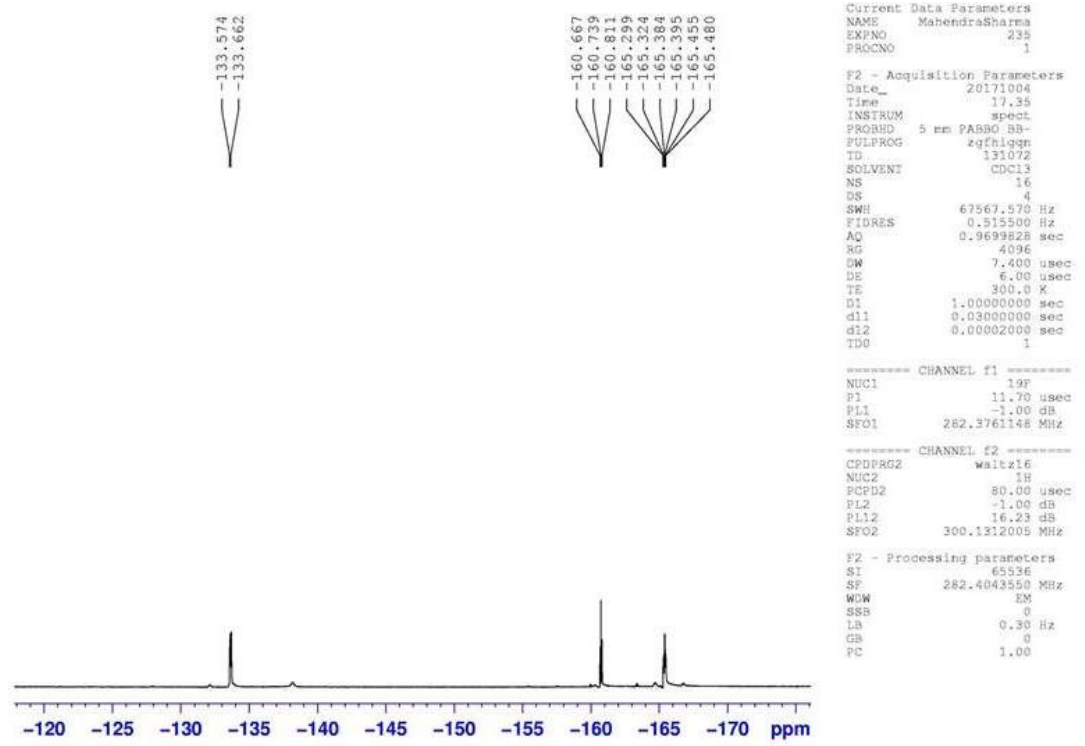


Figure S24. ^{19}F NMR spectrum of compound **4** in $CDCl_3$ at 300 K.

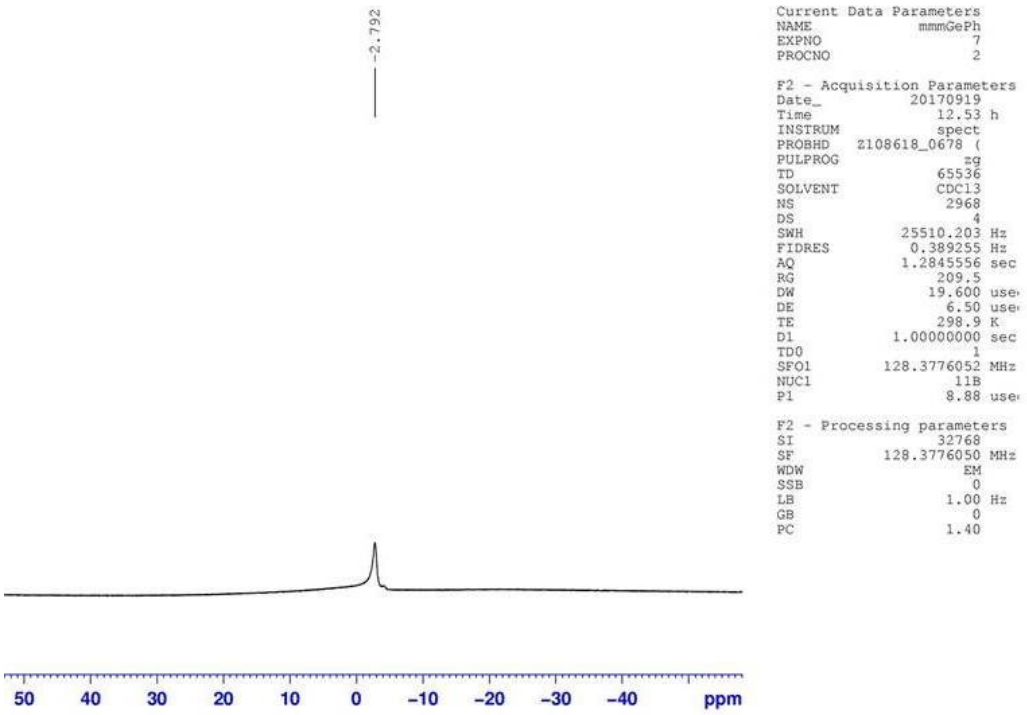


Figure S25. ^{11}B NMR spectrum of compound **4** in $CDCl_3$ at 300 K.

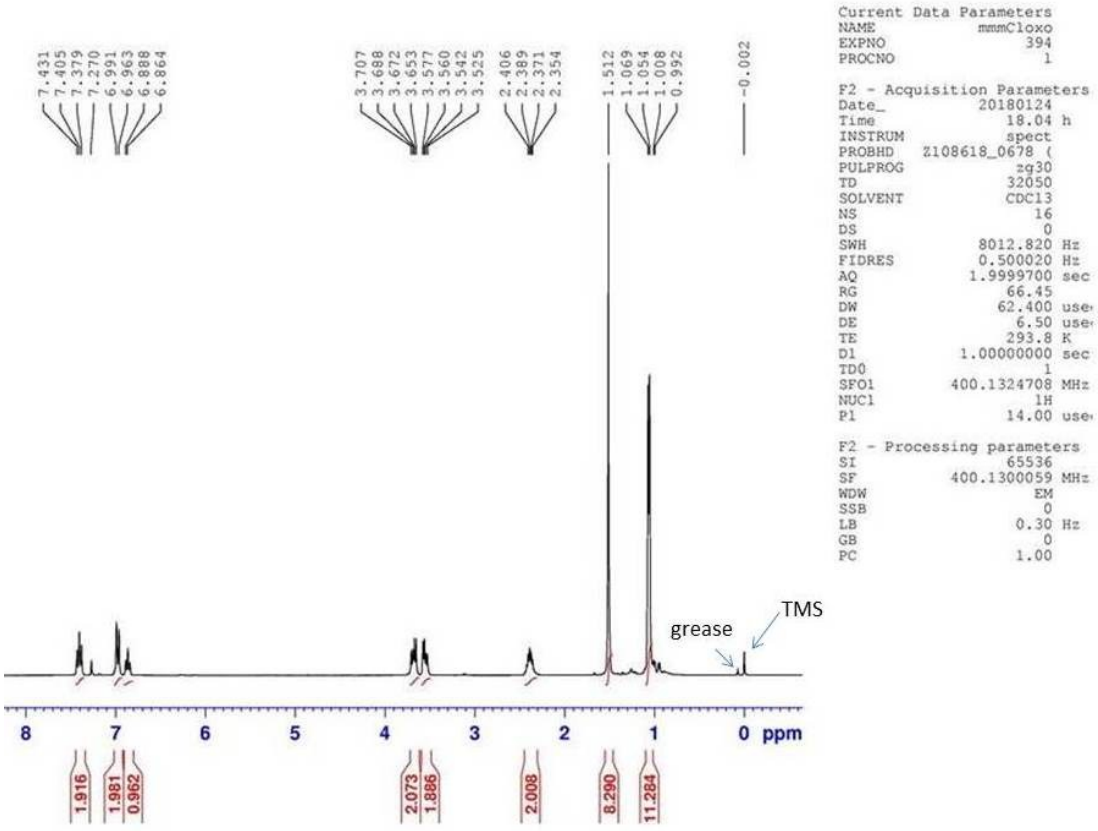


Figure S26. ^{1}H NMR spectrum of compound **5** in $CDCl_3$ at 300 K.

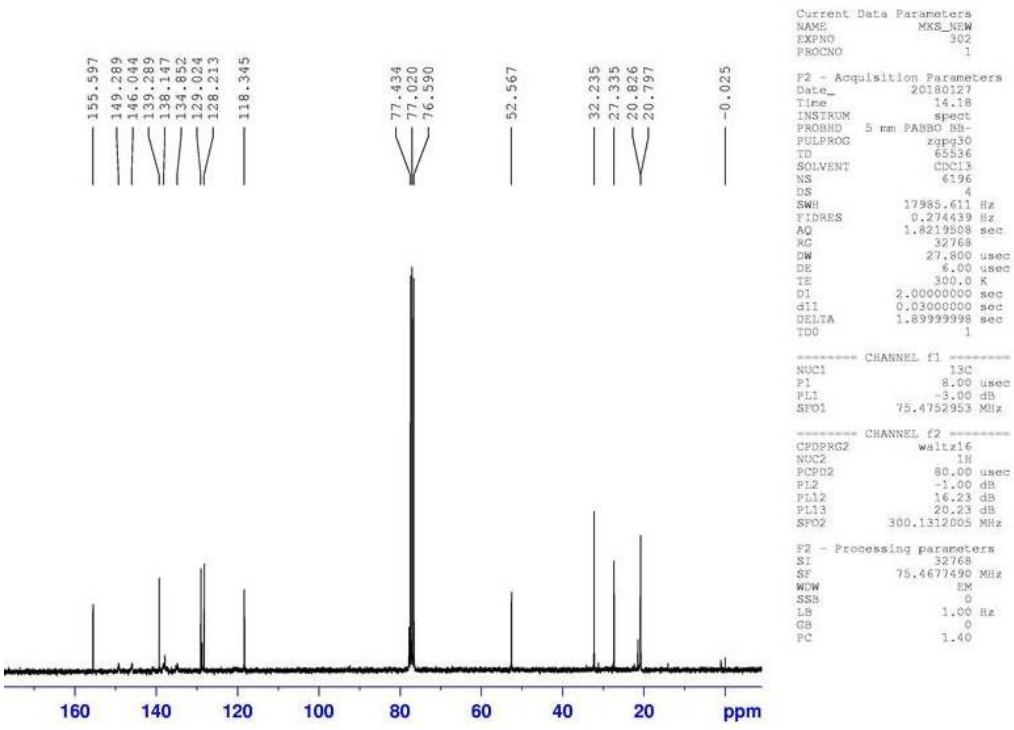


Figure S27. ^{13}C NMR spectrum of compound **5** in $CDCl_3$ at 300 K.

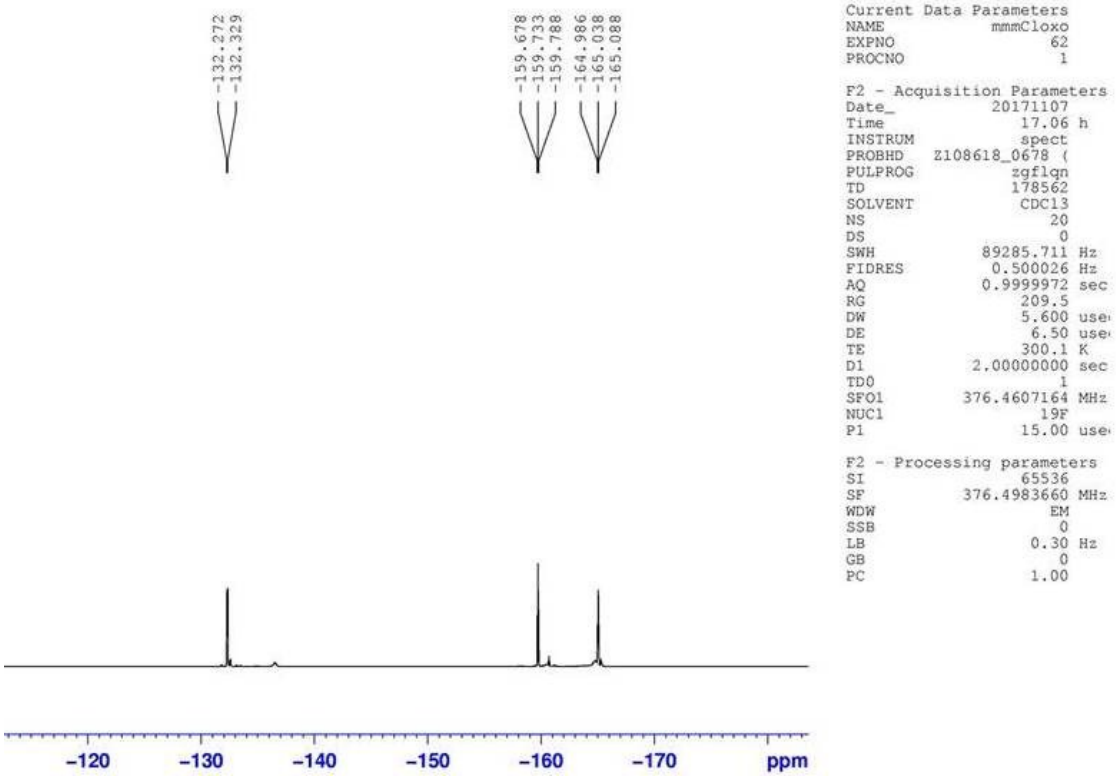


Figure S28. ^{19}F NMR spectrum of compound **5** in $CDCl_3$ at 300 K.

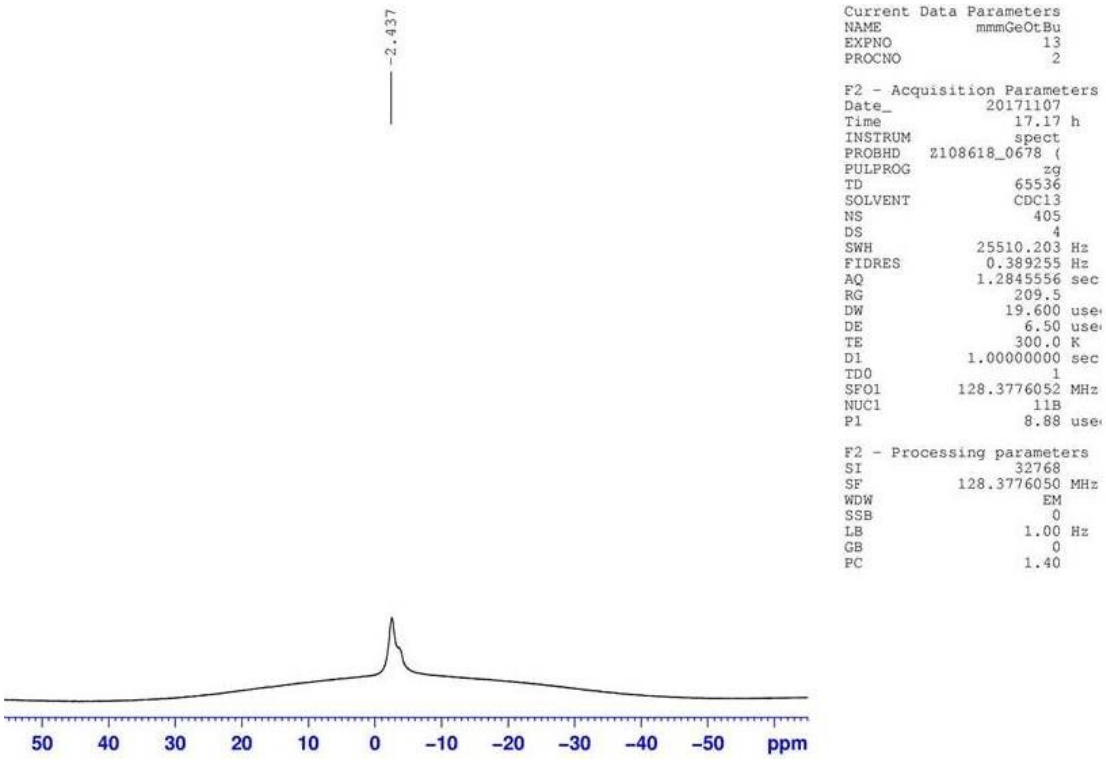


Figure S29. ^{11}B NMR spectrum of compound **5** in $CDCl_3$ at 300 K.

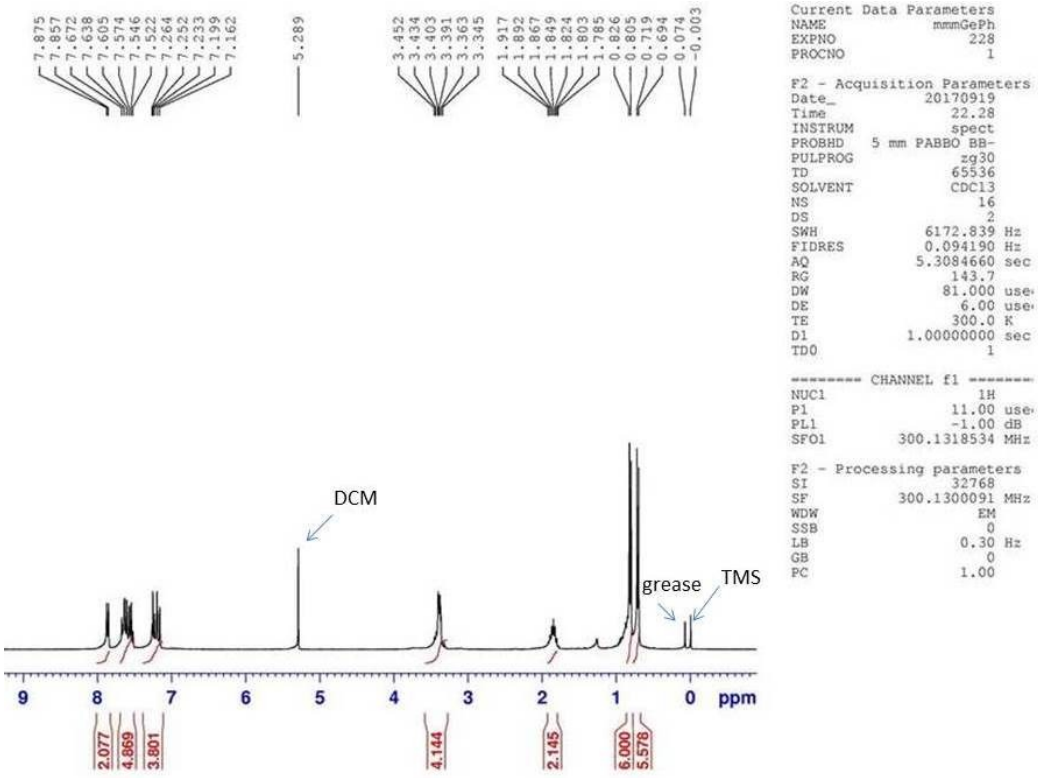


Figure S30. ^{1}H NMR spectrum of compound **6** in $CDCl_3$ at 300 K.

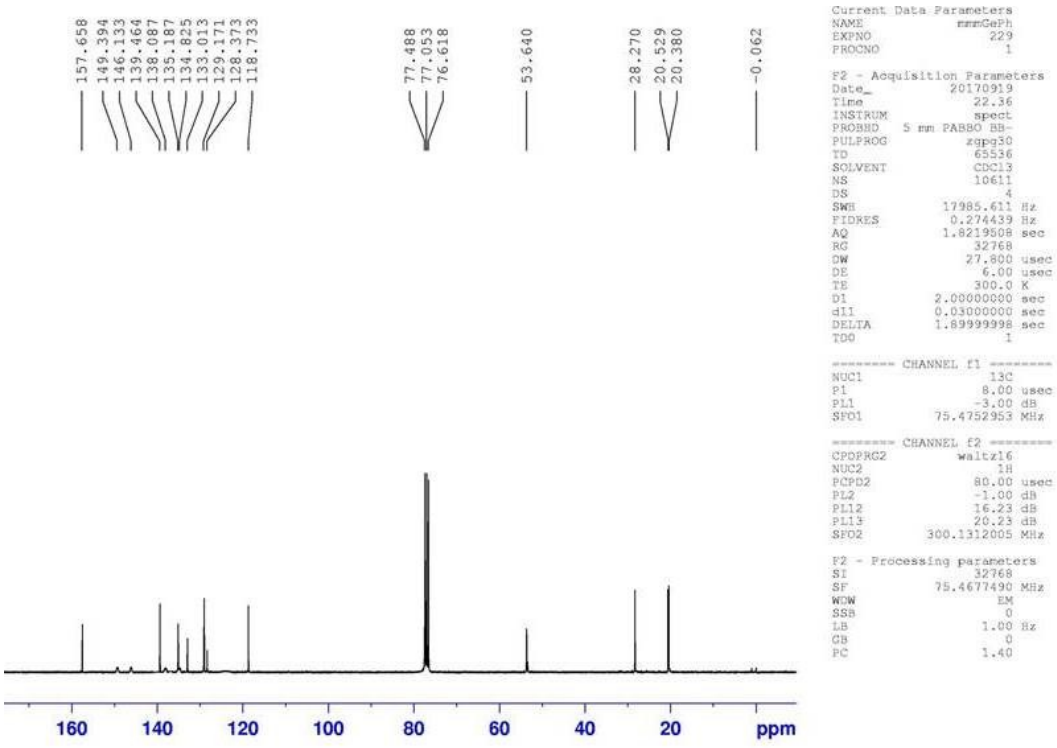


Figure S31. ^{13}C NMR spectrum of compound **6** in $CDCl_3$ at 300 K.

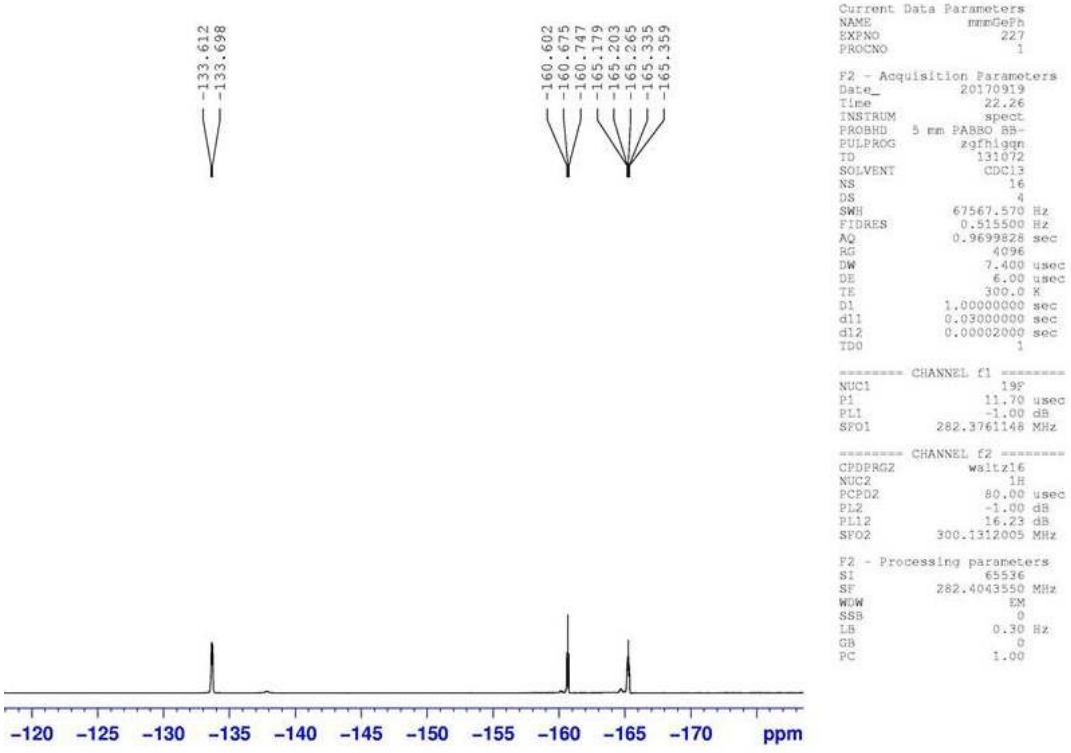


Figure S32. ^{19}F NMR spectrum of compound **6** in $CDCl_3$ at 300 K.

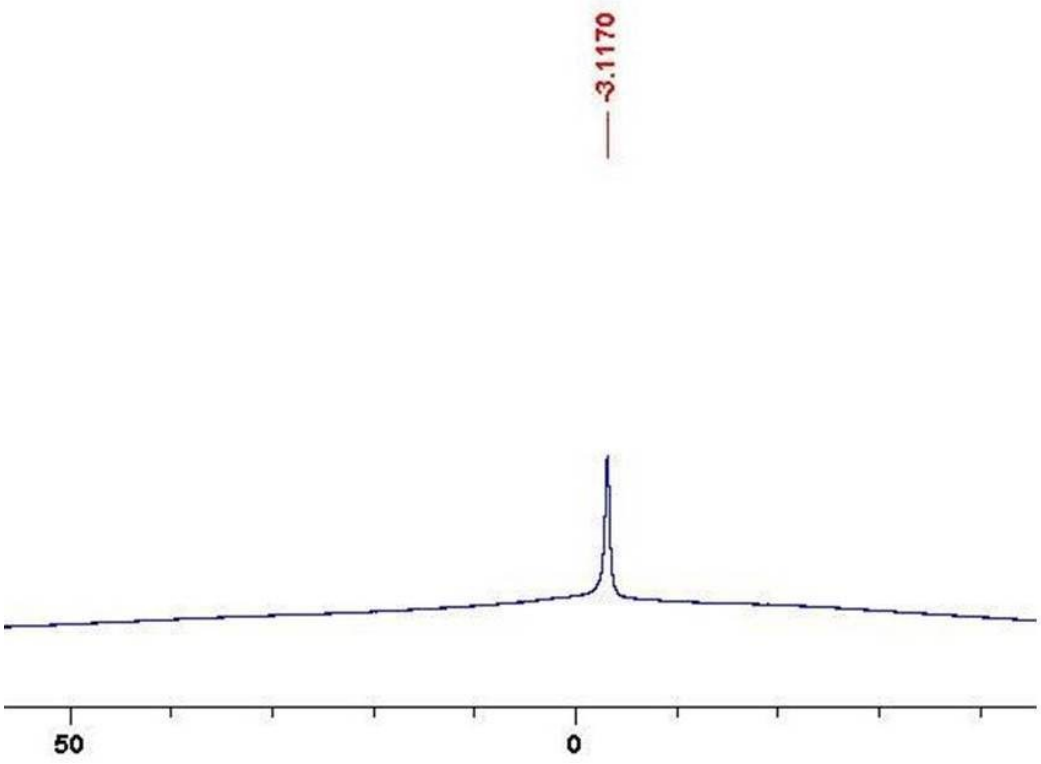


Figure S33. ^{11}B NMR spectrum of compound **6** in $CDCl_3$ at 300 K.

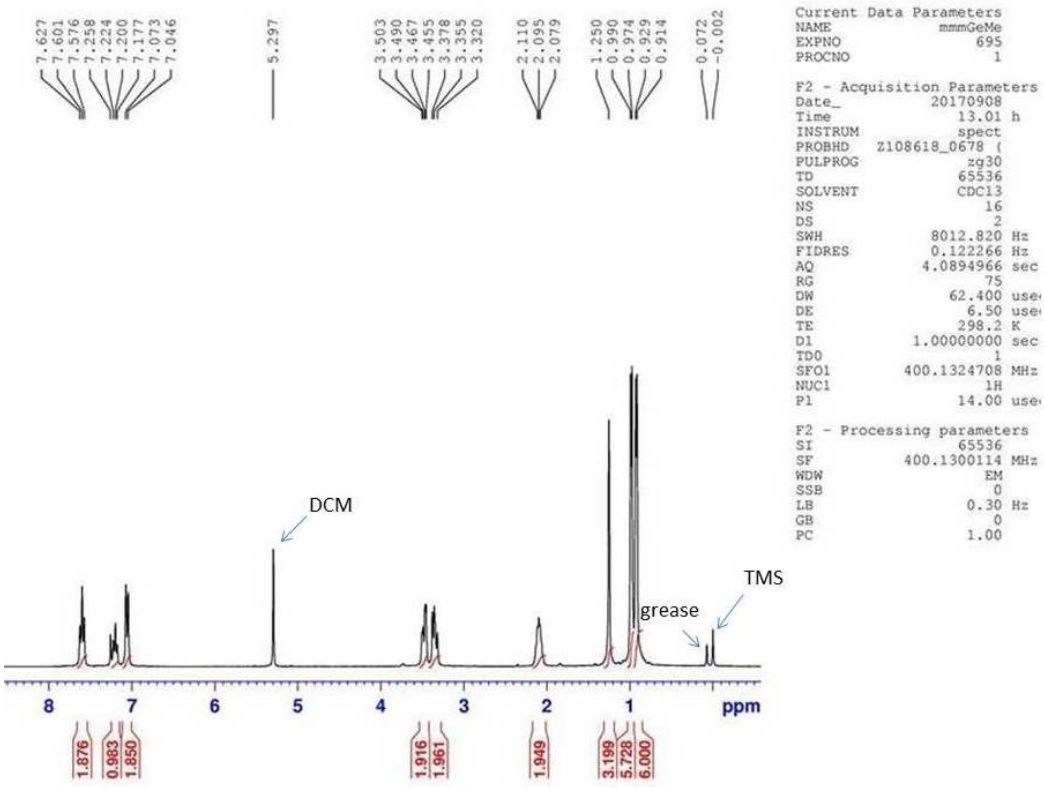


Figure S34. ^{1}H NMR spectrum of compound **7** in $CDCl_3$ at 300 K.

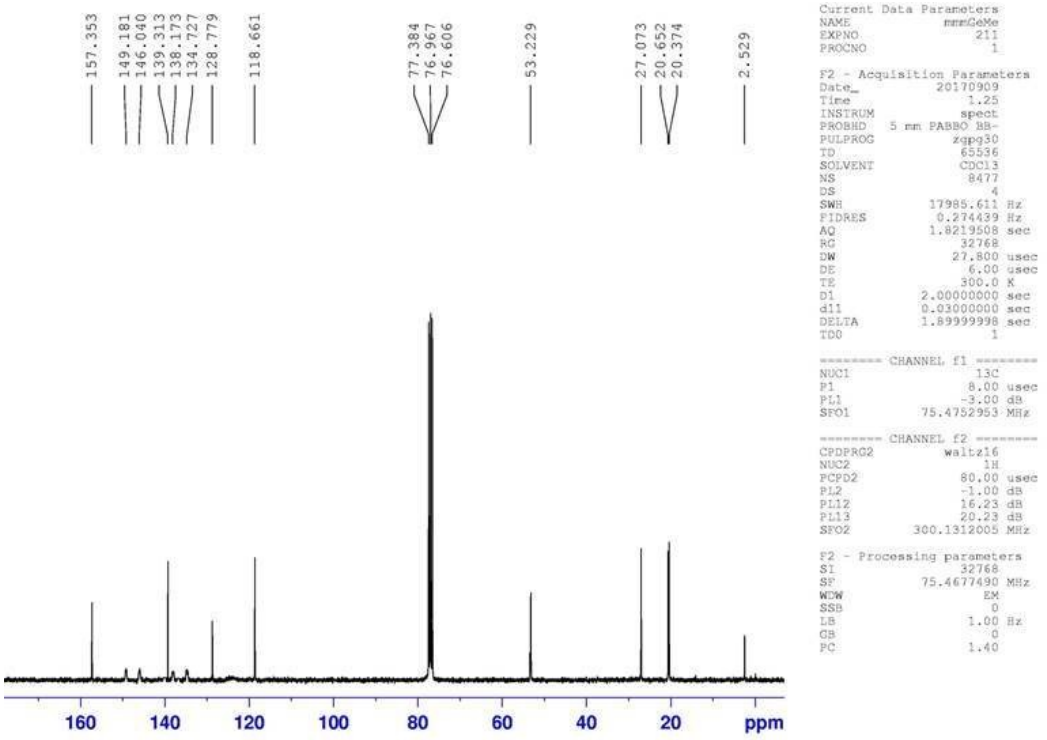


Figure S35. ^{13}C NMR spectrum of compound **7** in $CDCl_3$ at 300 K.

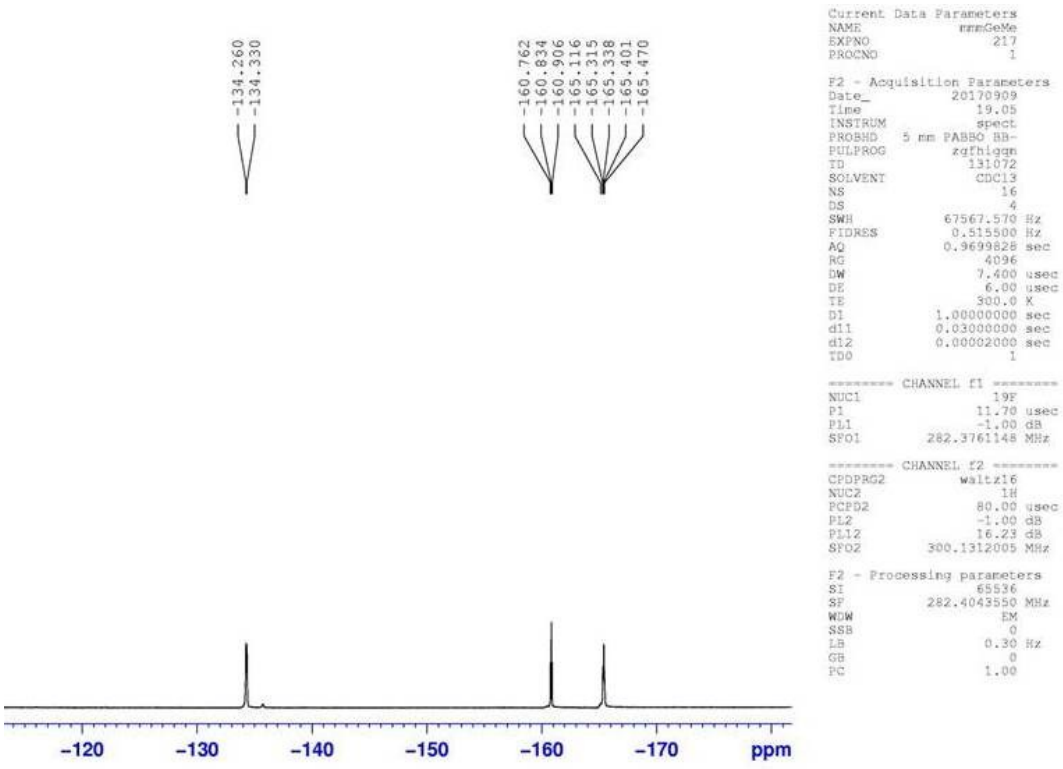


Figure S36. ^{19}F NMR spectrum of compound **7** in $CDCl_3$ at 300 K.

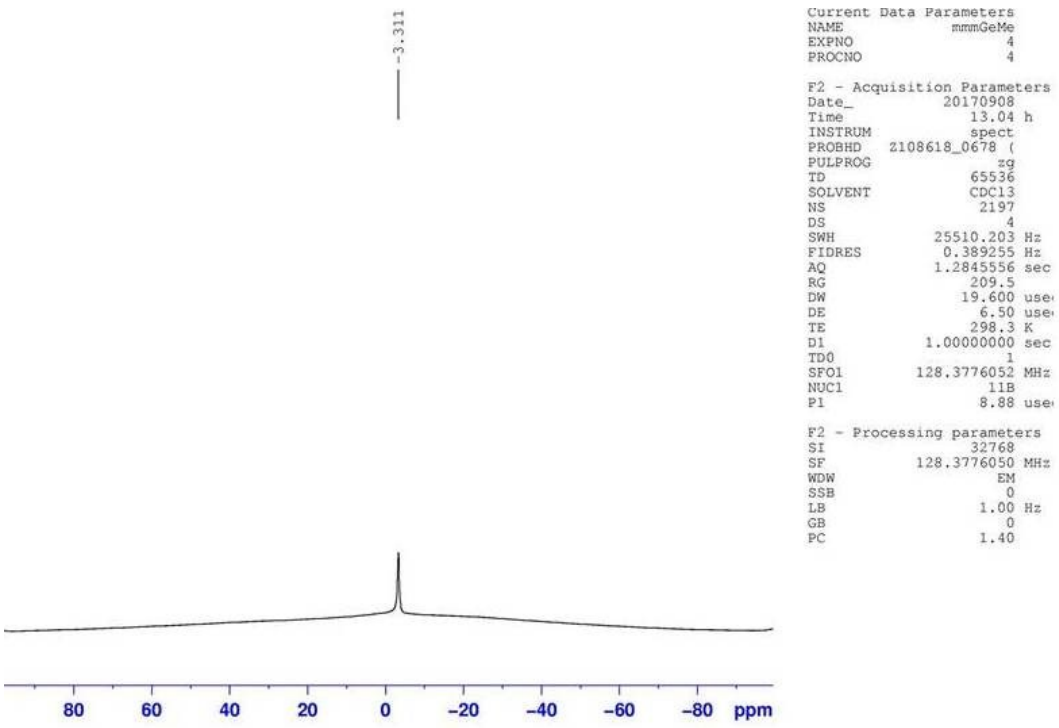


Figure S37. ^{11}B NMR spectrum of compound **7** in $CDCl_3$ at 300 K.

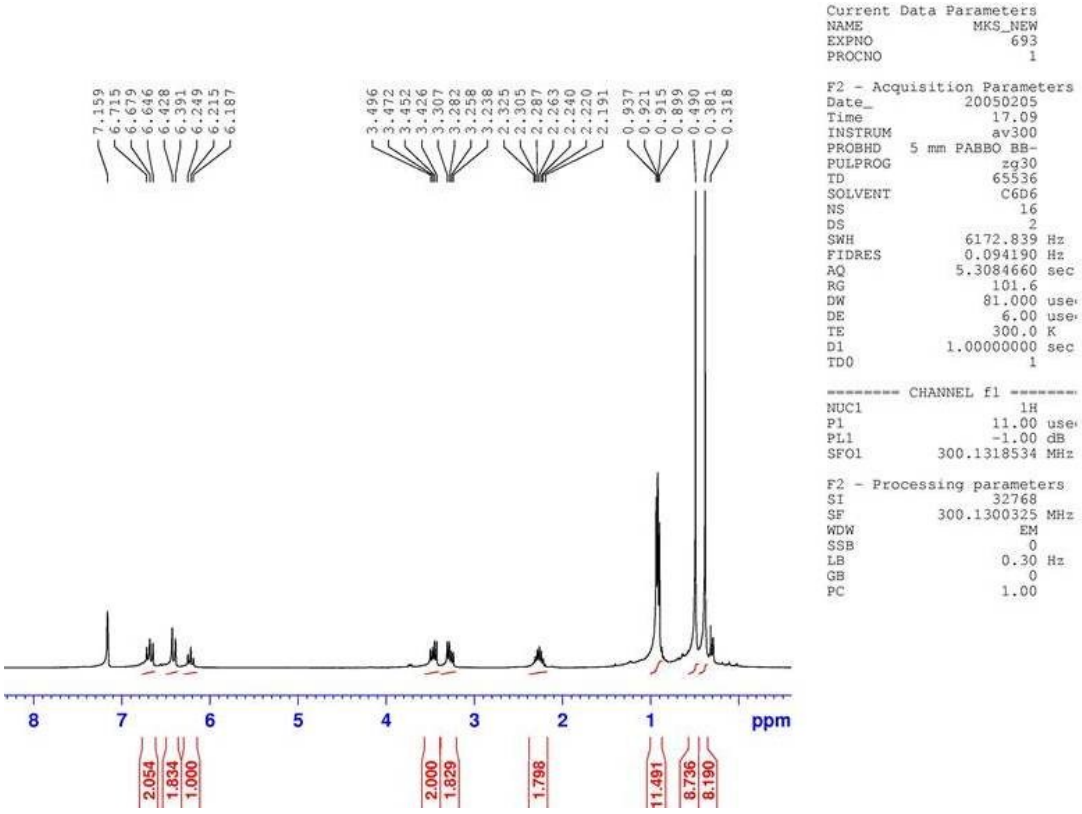


Figure S38. ^{1}H NMR spectrum of compound **9** in $CDCl_3$ at 300 K.

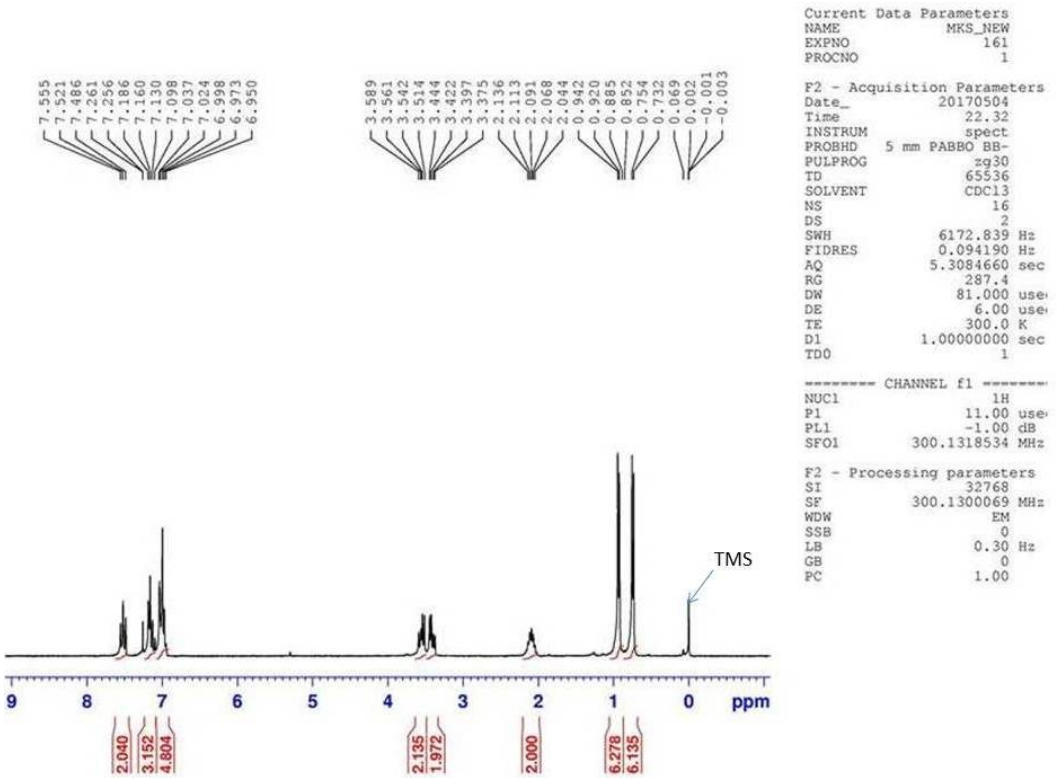


Figure S39. ^{1}H NMR spectrum of compound **10** in $CDCl_3$ at 300 K.

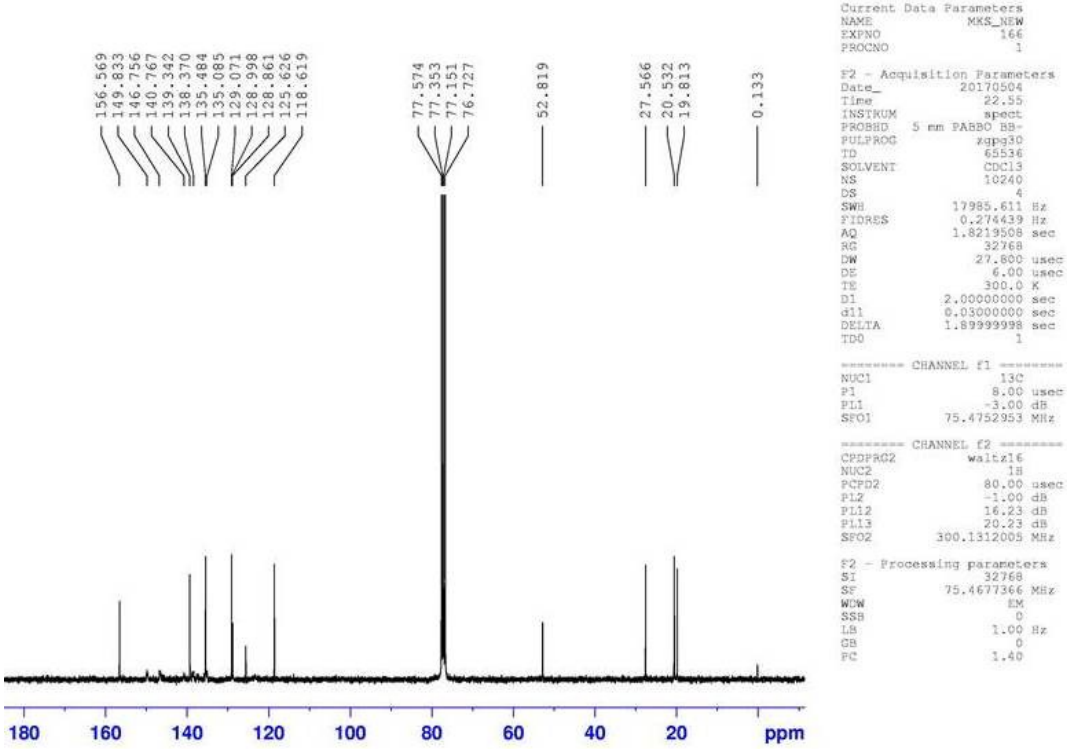


Figure S40. ^{13}C NMR spectrum of compound **10** in $CDCl_3$ at 300 K.

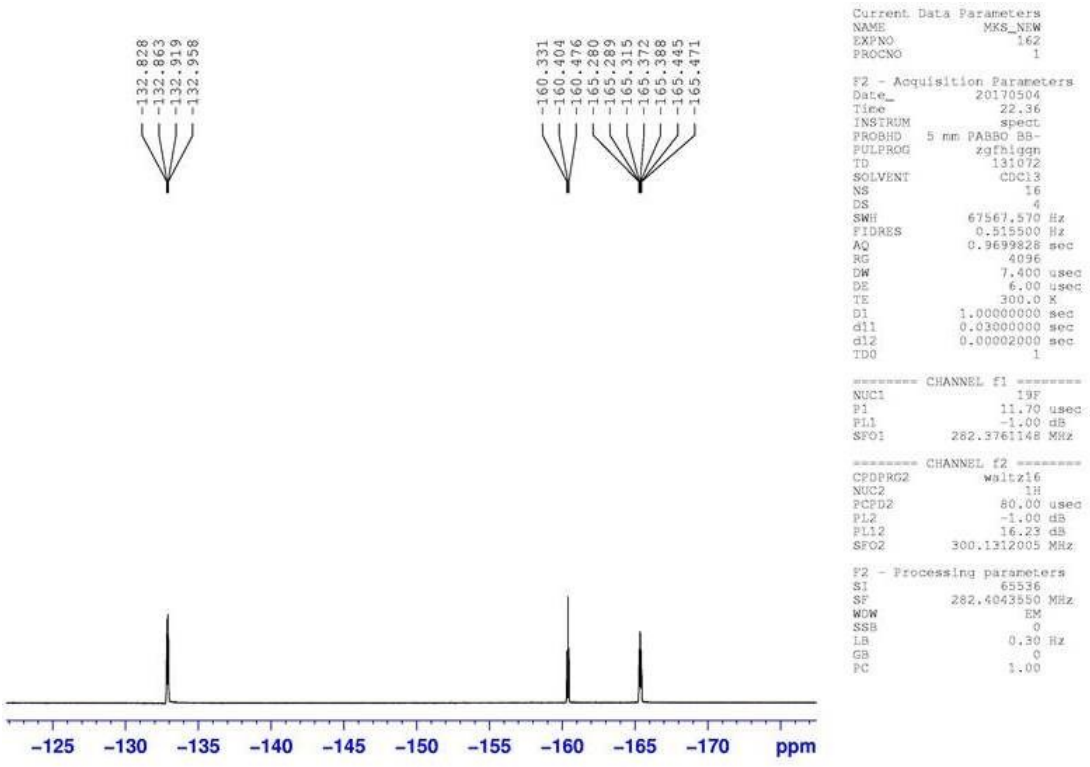


Figure S41. ^{19}F NMR spectrum of compound **10** in $CDCl_3$ at 300 K.

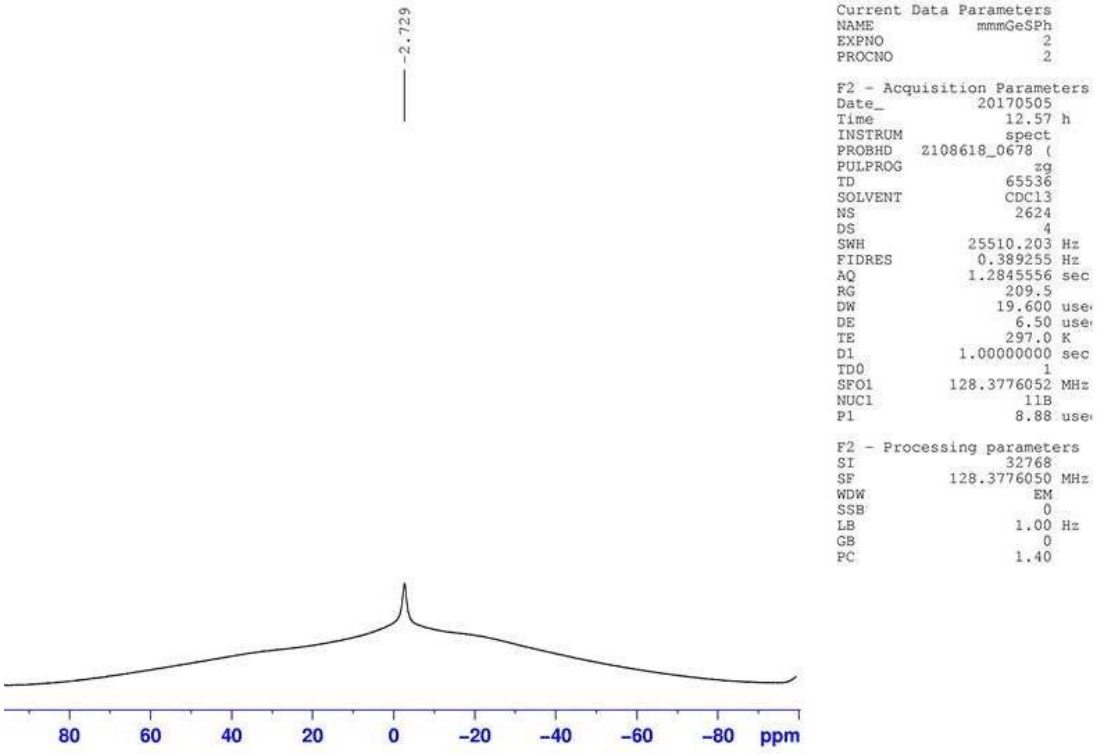


Figure S42. ^{11}B NMR spectrum of compound **10** in $CDCl_3$ at 300 K.

3. NMR Spectra of the Products Obtained from the Reactions of Compounds D1, D2, and D5 with BF_3, $GeCl_2$, and $SnCl_2$ (that include Figures S43-S51)*

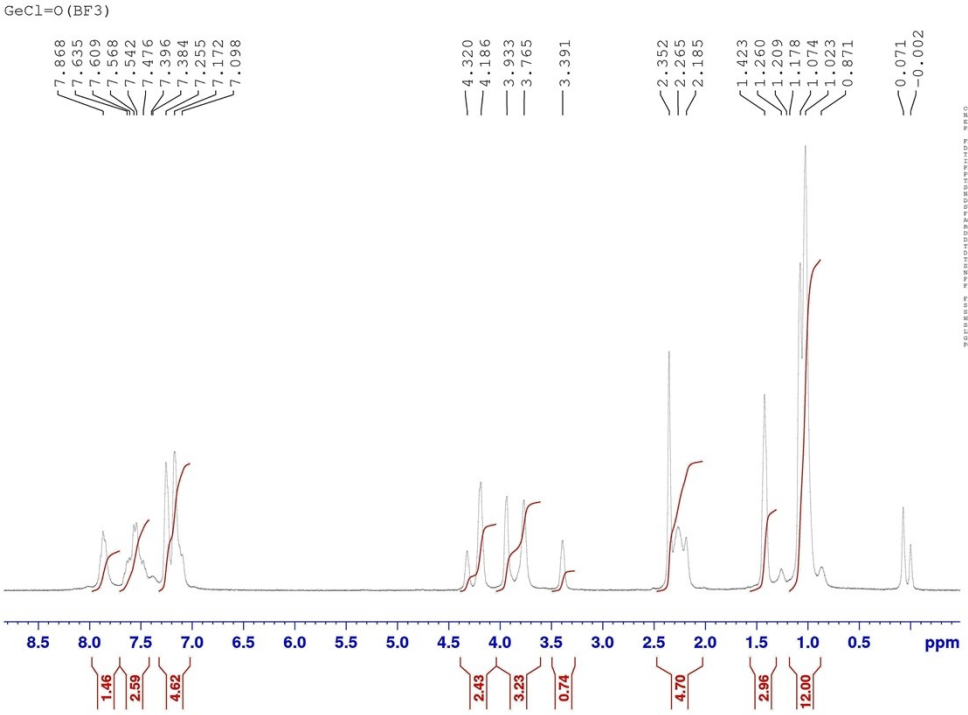


Figure S43. ^{1}H NMR spectrum of the product obtained from the reaction of **D1** with BF_3.

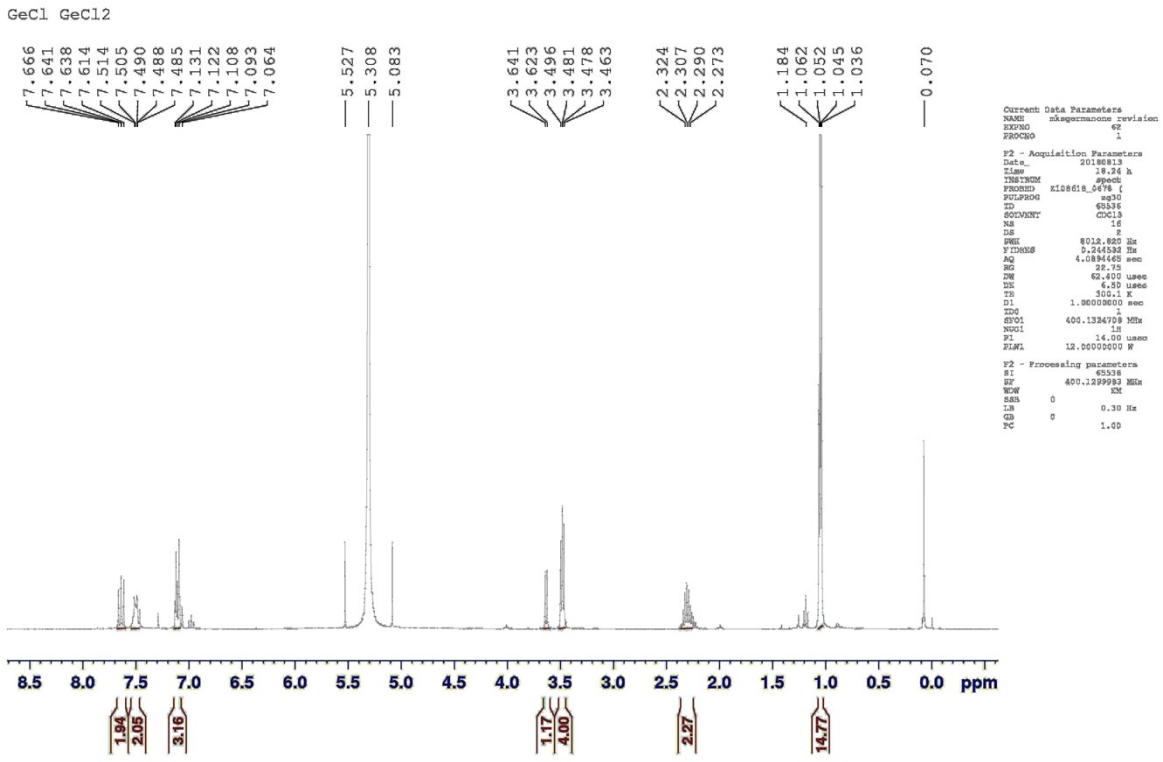


Figure S44. ^{1}H NMR spectrum of the product obtained from the reaction of **D1** with $GeCl_2$.

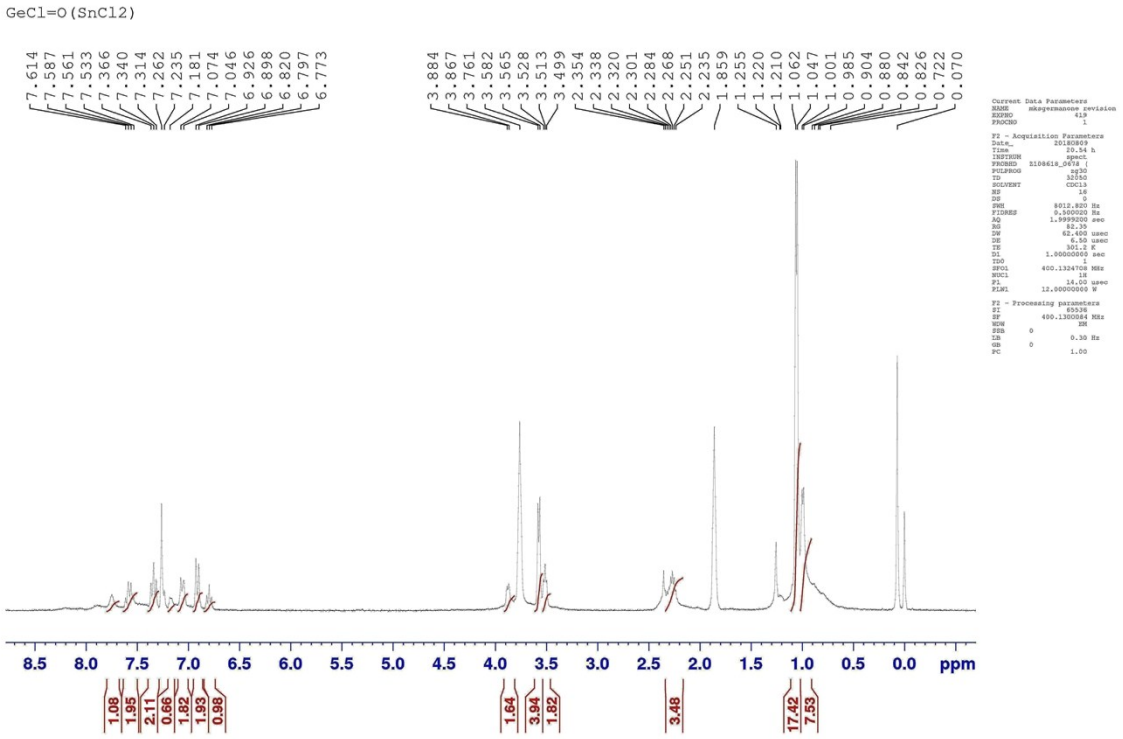


Figure S45. ^{1}H NMR spectrum of the product obtained from the reaction of **D1** with $SnCl_2$.

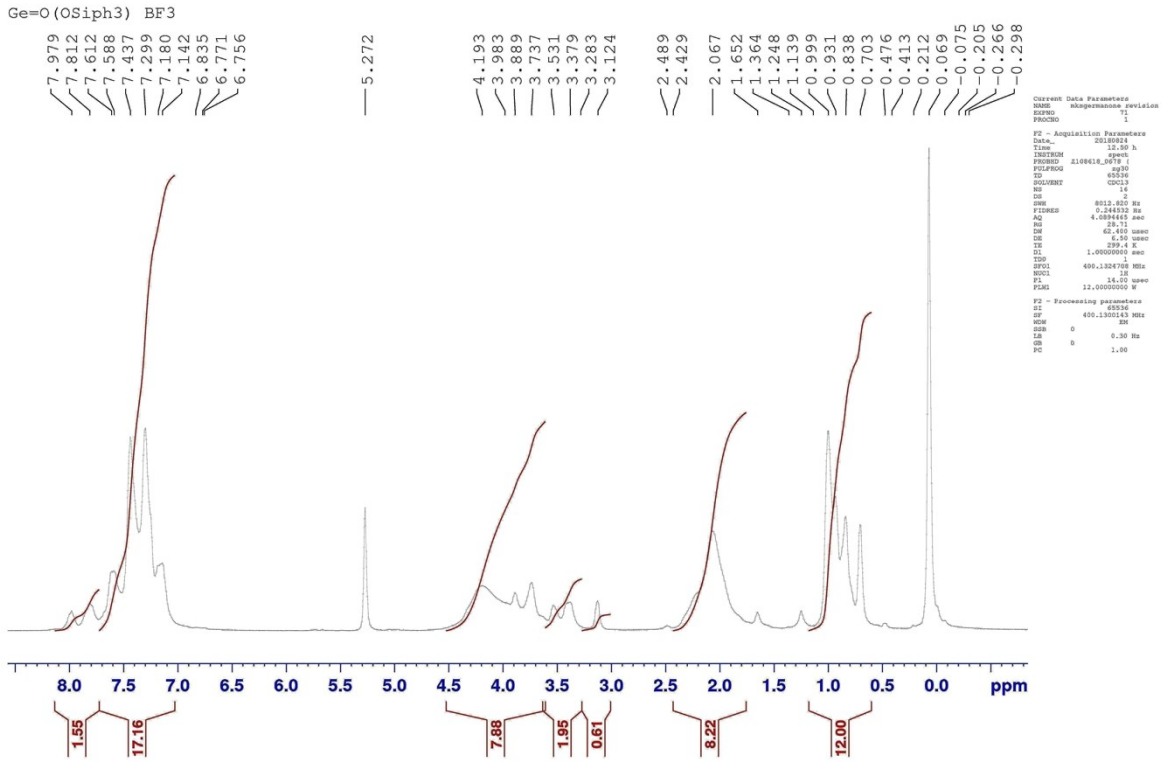


Figure S46. ^{1}H NMR spectrum of the product obtained from the reaction of **D2** with BF_3.

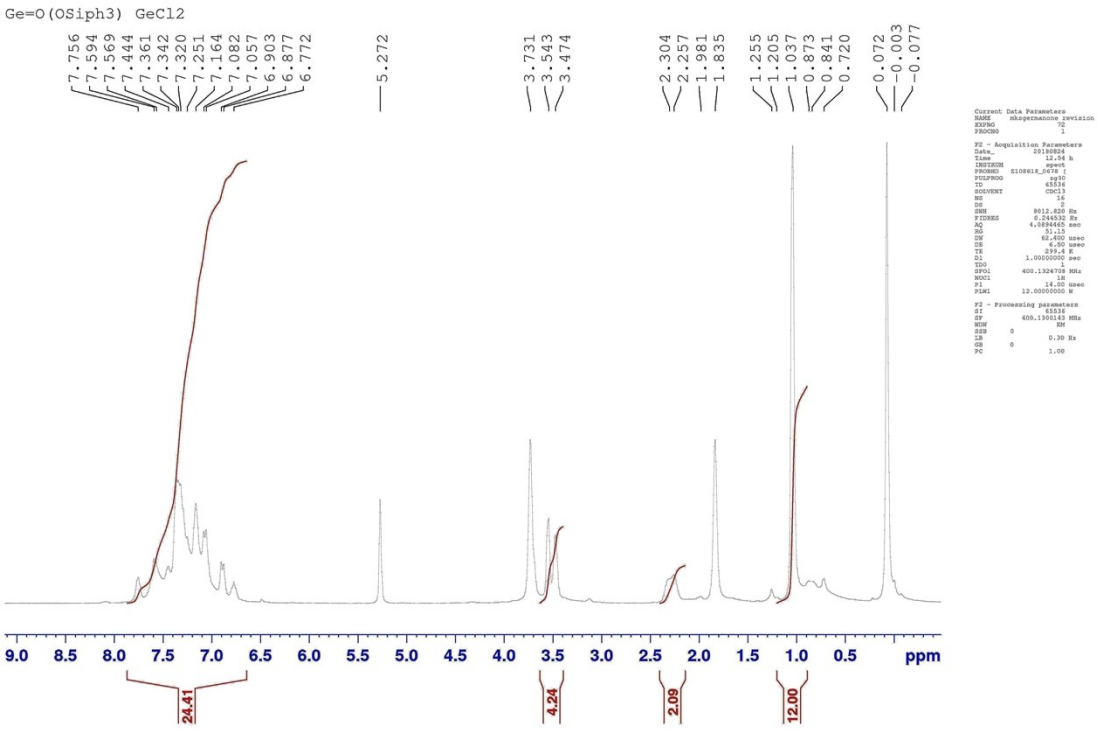


Figure S47. ^{1}H NMR spectrum of the product obtained from the reaction of **D2** with $GeCl_2$.

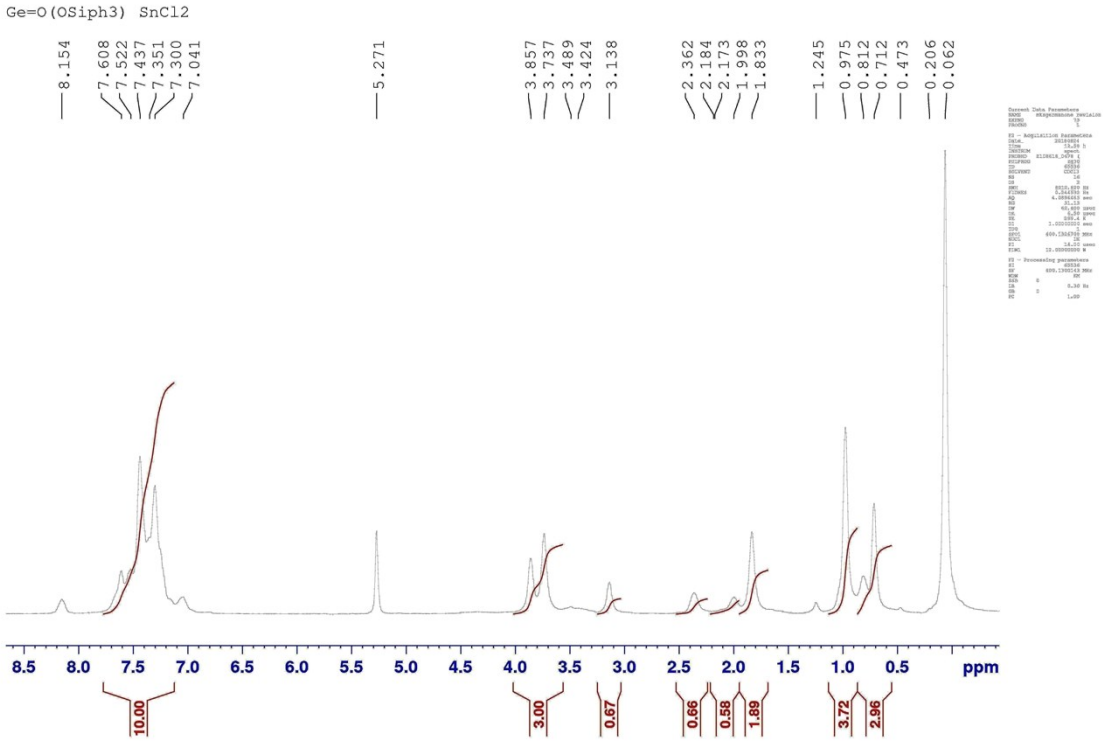


Figure S48. ^{1}H NMR spectrum of the product obtained from the reaction of **D2** with $SnCl_2$.

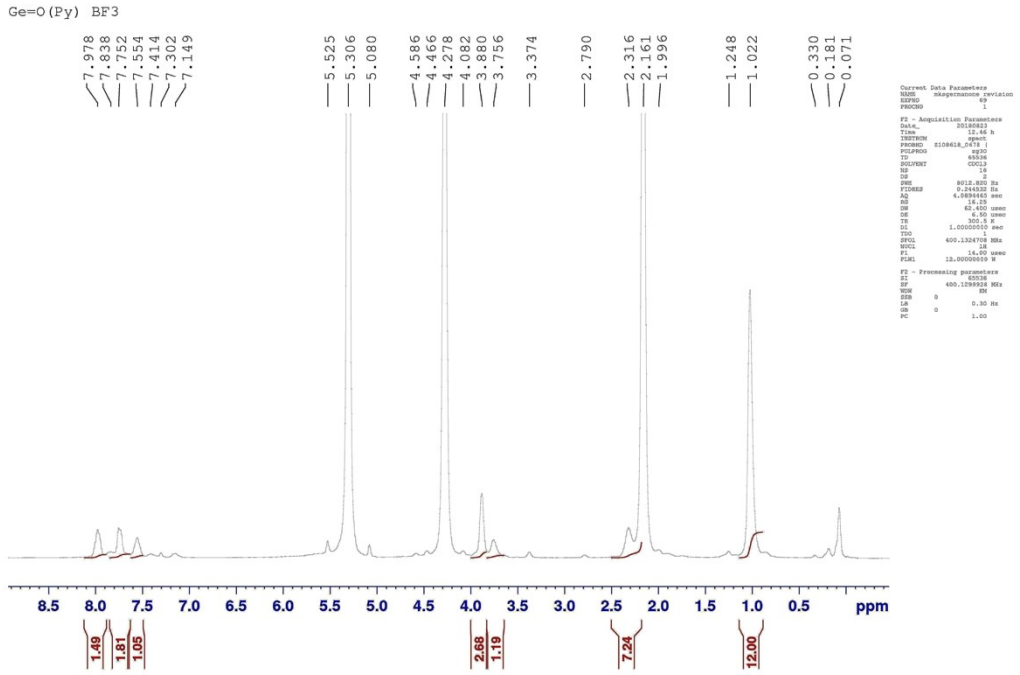


Figure S49. ^{1}H NMR spectrum of the product obtained from the reaction of **D5** with BF_3.

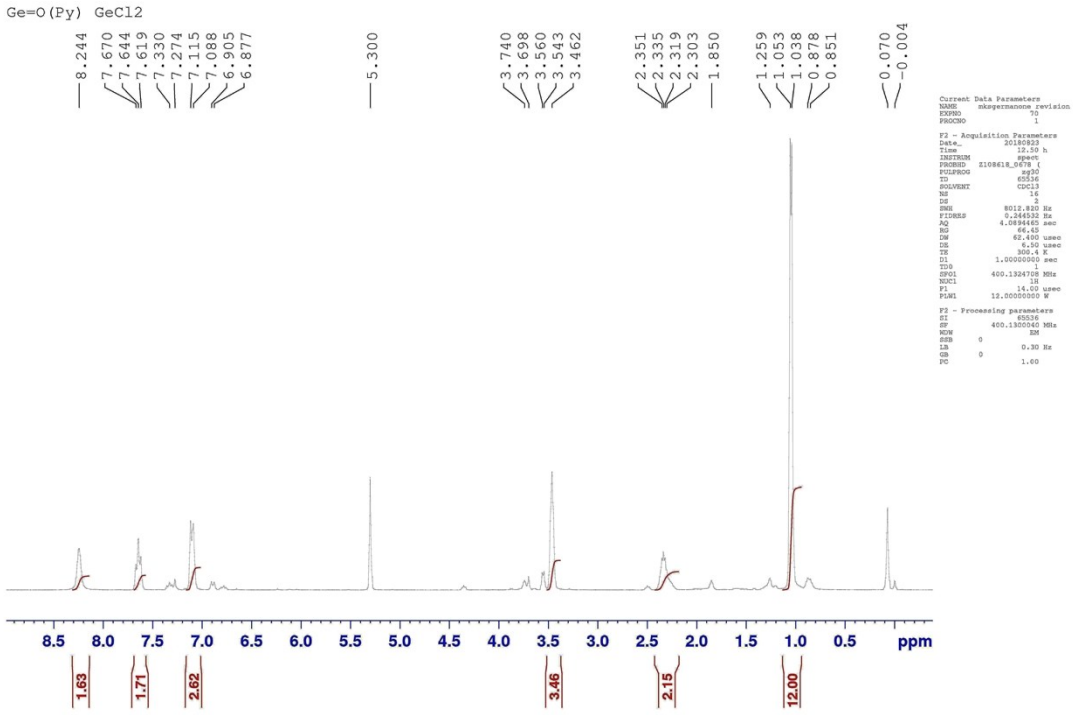


Figure S50. ^{1}H NMR spectrum of the product obtained from the reaction of **D5** with $GeCl_2$.

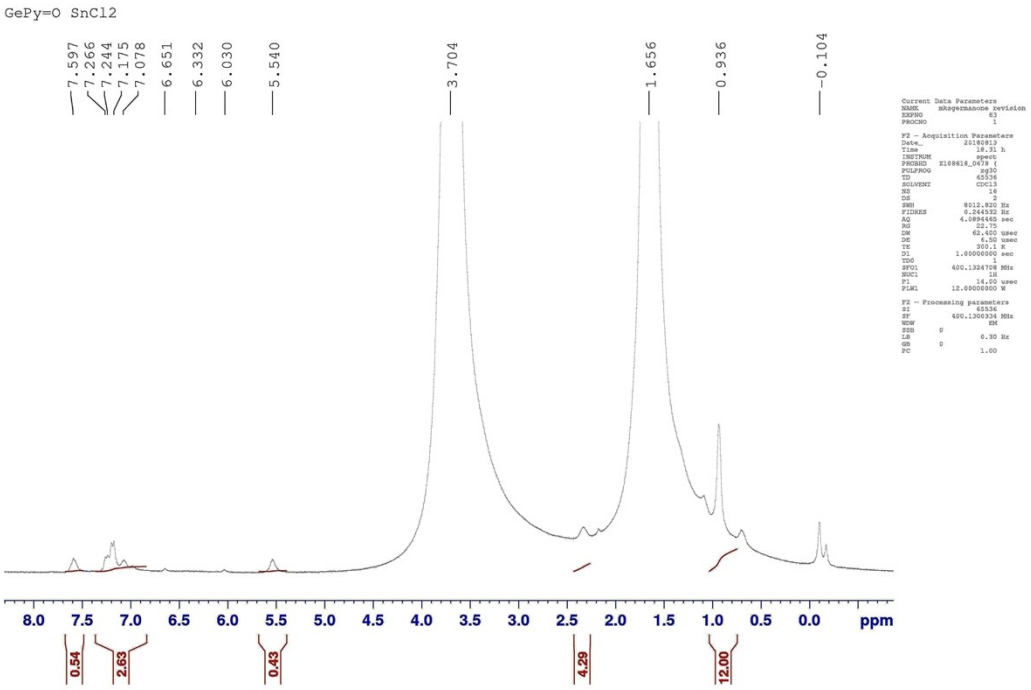


Figure S51. ^{1}H NMR spectrum of the product obtained from the reaction of **D5** with $SnCl_2$.

*****_Most of the products had solubility issues in $CDCl_3$. Therefore, to enhance the solubility, solvents, such as CH_2Cl_2 and/or THF was/were added to the NMR samples; the solvent peak(s) can be seen in their ^{1}H NMR spectra (vide supra). Even this addition [of high polar solvent(s)] did not help to improve the solubility of these products._

4. UV-vis Spectra of Compounds 1, 2, and 10

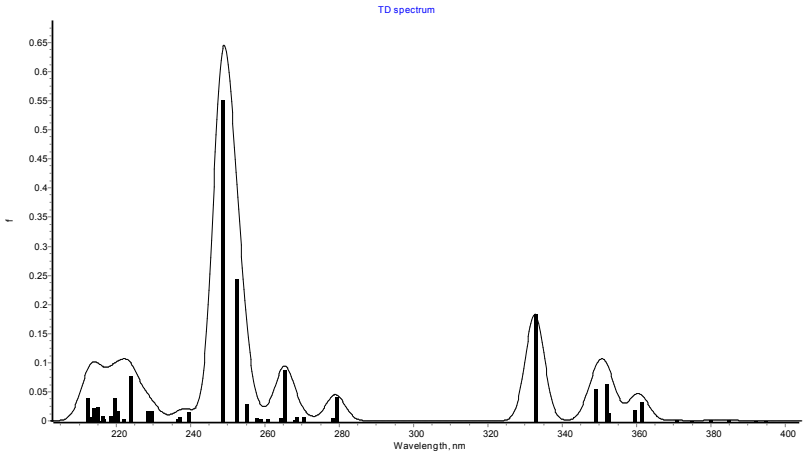
Table S1. Observed and calculated transitions for compounds **1**, **2**, and **10**.

Compound **1**			
Transition	Origin of transition (percentage contribution)	λ_{max} (ε) (obsd)	λ_{max} (f) (calcd)
$\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-1 → LUMO+1 (94)	420 (10913)	384.69 (0.0012)
$\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO → LUMO+1 (4)		
$\pi_{(ATI)} \rightarrow \pi^*_{(ATI)}$	HOMO-9 → LUMO (4)	352 (10410)	332.7 (0.1831)
$\sigma_{(C_6F_5)} + nb_{(O)} \rightarrow \pi^*_{(ATI)}$	HOMO-8 → LUMO (6)		
$\sigma_{(C_6F_5)} + nb_{(O)} \rightarrow \pi^*_{(ATI)}$	HOMO-7 → LUMO (3)		
$\pi_{(ATI)} \rightarrow \pi^*_{(ATI)}$	HOMO-6 → LUMO+1 (85)		
$\pi_{(ATI)} \rightarrow \pi^*_{(ATI)}$	HOMO-9 → LUMO (45)	285 (9926)	248.46 (0.5505)
$\sigma_{(C_6F_5)} + nb_{(O)} \rightarrow \pi^*_{(ATI)}$	HOMO-8 → LUMO (16)		
$\sigma_{(C_6F_5)} + nb_{(O)} \rightarrow \pi^*_{(ATI)}$	HOMO-7 → LUMO (3)		
$\pi_{(ATI)} \rightarrow \pi^*_{(ATI)}$	HOMO-6 → LUMO+1 (7)		
$\pi_{(C_6F_5)} \rightarrow \sigma^*_{(Ge\text{-}Cl)}$	HOMO-6 → LUMO+2 (7)		
$\pi_{(C_6F_5)} \rightarrow \sigma^*_{(Ge\text{-}Cl)}$	HOMO-5 → LUMO+2 (3)		
$\pi_{(C_6F_5)} \rightarrow \sigma^*_{(Ge\text{-}Cl)}$	HOMO-4 → LUMO+2 (10)		
Compound **2**			
$\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-4 → LUMO (18)	420 (11236)	381.49 (0.0084)
$\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-3 → LUMO (10)		
$\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-1 → LUMO (48)		
$\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO → LUMO (22)		
$\sigma_{[B\text{-}C(C_6F_5)]} + nb_{(O)} \rightarrow \pi^*_{(ATI)}$	HOMO-14→ LUMO (2)	351 (10620)	338.83 (0.0725)
$\pi_{(ATI)} + \pi_{(C_6F_5)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-8 → LUMO+1 (11)		
$\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-7 → LUMO+1 (14)		
$\pi_{(ATI)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-5 → LUMO (2)		
$\pi_{(ATI)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-5 → LUMO+1 (35)		

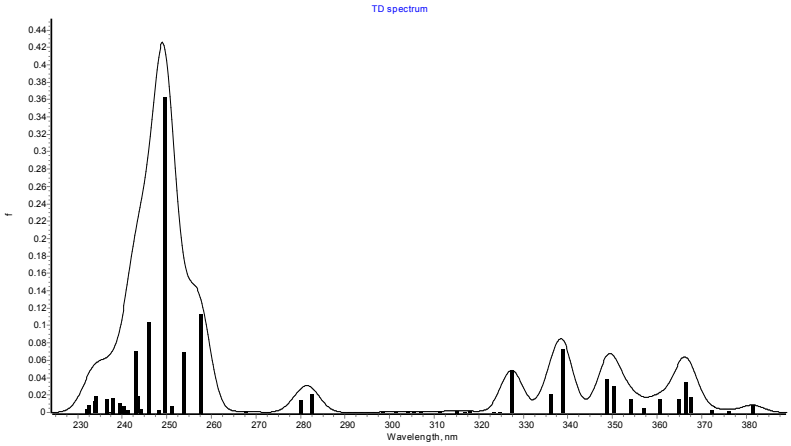
$\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-4 → LUMO+1 (6)		
$\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-3 → LUMO+1 (23)		
$\sigma_{(C_6F_5)} + \sigma_{[C\text{-}F(C_6F_5)]} + \sigma_{[Si\text{-}C(C_6F_5)]} \rightarrow \pi^*_{(ATI)}$	HOMO-16 → LUMO (22)	285 (11186)	249.32 (0.3625)
$\pi_{(ATI)} + \sigma_{[B\text{-}C(C_6F_5)]} \rightarrow \pi^*_{(ATI)}$	HOMO-15 → LUMO (4)		
$\pi_{(ATI)} + \sigma_{[B\text{-}C(C_6F_5)]} \rightarrow \pi^*_{(ATI)}$	HOMO-15 → LUMO+1 (21)		
$\sigma_{[B\text{-}C(C_6F_5)]} + nb_{(O)} \rightarrow \pi^*_{(ATI)}$	HOMO-14 → LUMO (34)		
$\sigma_{[B\text{-}C(C_6F_5)]} + nb_{(O)} \rightarrow \pi^*_{(ATI)}$	HOMO-14 → LUMO+1 (4)		
$\sigma_{[B\text{-}C(C_6F_5)]} + nb_{(O)} + \pi_{(C_6F_5)}) \rightarrow \pi^*_{(ATI)}$	HOMO-13 → LUMO (2)		
$\pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-3 → LUMO+1 (3)		
Compound **10**			
$n_{(F)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO → LUMO (99)	420 (12773)	381.51 (0.0001)
$n_{(F)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-4 → LUMO (26)	--	369.88 (0.0708)
$n_{(F)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-3 → LUMO (3)		
$n_{(F)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-2 → LUMO (14)		
$n_{(F)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-1 → LUMO (52)		
$\sigma_{[B\text{-}C(C_6F_5)]} + \sigma_{[C\text{-}C(C_6F_5)]} + n_{(O)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-11 → LUMO (5)	353 (14176)	344.27 (0.1584)
$n_{(S)} + n_{(O)} + \sigma_{[B\text{-}C(C_6F_5)]} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-8 → LUMO (2)		
$n_{(F)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-5 → LUMO+1 (4)		
$n_{(F)} + \pi_{(C_6F_5)} \rightarrow \pi^*_{(ATI)}$	HOMO-4 → LUMO+1 (84)		
$\pi_{(ATI)} \rightarrow \pi^*_{(ATI)}$	HOMO-12 → LUMO (4)	287 (28993)	250.24 (0.4643)

Figure S52. UV-vis spectra (calculated through DFT analysis) of compounds **1** (a), **2** (b), and **10** (c).

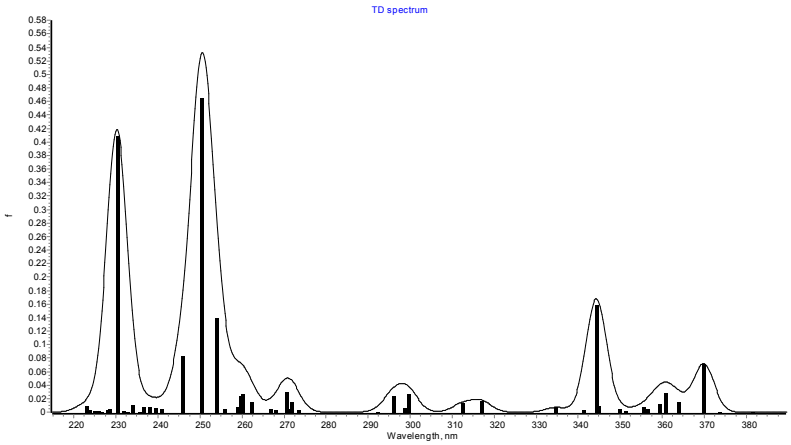
(a)



(b)



(c)



5. Molecular Structure Determination of Compounds D1, D3-D5, 1-7, 9, and 10

Single crystal X-ray diffraction data for compounds **D1, D3-D5, 1-7**, **9**, and **10** were collected using a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer (Tables S2-S5).[S4] The crystals were covered with Paratone-N and mounted on a glass capillary. The data were collected either at room temperatures or at a low temperature (under a steady flow of cold dinitrogen) using Mo Kα radiation (λ = 0.71073 Å). Integration of data was performed using SAINT. Empirical absorption correction was applied using SADABS.[S5] Structure 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.[S7] All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were fixed according to a riding model and were refined isotropically. In compound **4**, a solvent molecule (dichloromethane) is disordered. In compound **9**, large regions of diffused electron density that could not be modelled (disordered solvents) were removed from the refinement using SQUEEZE function in PLATON.

Table S2. Crystal data and structure refinement parameters for compounds **D1** and **D3-D5**.

	D1	**D3**	**D4**	**D5**
Empirical formula	$C_{30}H_{46}Cl_2Ge_2N_4O_2$	$C_{42}H_{58}Ge_2N_6O_2$	$C_{44}H_{62}Ge_2N_6O_2$	$C_{52}H_{70}Ge_2N_6O_2$
Formula weight	710.83	824.16	852.22	956.36
Temperature, K	293(2)	293(2)	293(2)	273(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\ 2_1/n$	$P\bar{1}$	$P\ 2_1/n$
Unit cell dimensions	a = 8.2234(14) Å b = 10.4654(17) Å c = 11.0901(19) Å α = 105.331(3)° β = 105.474(3)° γ = 104.265(3)°	a = 9.571(4) Å b = 13.665(7) Å c = 15.943(7) Å β = 91.027(14)°	a = 12.9207(10) Å b = 12.9316(11) Å c = 14.5928(12) Å α = 69.9910(10)° β = 89.472(2)° γ = 71.2250(10)°	a = 10.595(4) Å b = 15.635(5) Å c = 14.875(5) Å β = 92.261(6)°
Volume, Å^3	833.9(2)	2084.7(16)	2155.2(3)	2462.1(14)
Z	1	2	2	2
Density (calculated), g/cm^3	1.416	1.313	1.313	1.290
Absorption coefficient, mm^{-1}	1.995	1.483	1.437	1.266
F(000)	368.0	864.0	1140	1008.0
Crystal size, mm^3	0.421 x 0.413 x 0.380	0.350 x 0.265 x 0.157	0.350 x 0.255 x 0.159	0.431 x 0.403 x 0.390
θ range for data collection, °	2.15 to 25.00	1.96 to 25.00	1.49 to 25.00	1.89 to 25.00

Limiting indices	-9 ≤ h ≤ 9, -12≤ k ≤ 10, -13 ≤ l ≤ 11	-11 ≤ h ≤ 10, -16 ≤ k ≤ 6, -15 ≤ l ≤ 17	-15 ≤ h ≤ 10, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17	-12 ≤ h ≤ 12, -18 ≤ k ≤ 10, -15 ≤ l ≤ 17
Reflections collected	4407	4960	11344	10217
Independent reflections	2943 [$R_{(int)}$ = 0.0208]	3667 [$R_{(int)}$ = 0.0270]	7473 [$R_{(int)}$ = 0.0165]	4312 [$R_{(int)}$ = 0.0578]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
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
Data /restraints/ parameter	2892 / 0 / 185	2853 / 0 / 239	7473 / 0 / 497	4312 / 0 / 285
Goodness-of-fit on F^2	1.049	1.122	1.110	0.937
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0316, wR_2 = 0.0776	R_1 = 0.0554, wR_2 = 0.1524	R_1 = 0.0289, wR_2 = 0.0807	R_1 = 0.0454, wR_2 = 0.0923
R indices (all data)	R_1 = 0.0360, wR_2 = 0.0798	R_1 = 0.0791, wR_2 = 0.1912	R_1 = 0.0349, wR_2 = 0.0943	R_1 = 0.0700, wR_2 = 0.0992
Largest diff. peak and hole, eÅ^{-3}	0.300 and -0.415	0.626 and -0.870	0.425 and -0.327	0.604 and -0.401

Table S3. Crystal data and structure refinement parameters for compounds **1**, **2**, **3**, and **4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{33}H_{23}BClF_{15}GeN_2O{\cdot}CH_2Cl_2$	$C_{51}H_{38}BF_{15}GeN_2O_2Si$	$C_{37}H_{27}BF_{15}GeN_3O{\cdot}CH_2Cl_2$	$C_{42}H_{30}BClF_{15}GeN_2O$
Formula weight	952.33	1107.35	982.96	982.55
Temperature, K	100(2)	100(2)	100(2)	100(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 11.7309(18) Å b = 13.344(2) Å c = 13.627(2) Å α = 62.827(3)° β = 73.967(3)° γ = 81.201(3)°	a = 11.6250(11) Å b = 15.0956(14) Å c = 15.2052(14) Å α = 82.564(2)° β = 69.443(2)° γ = 69.8390(10)°	a = 12.436(2) Å b = 12.462(2) Å c = 15.186(3) Å α = 106.723(4)° β = 96.368(3)° γ = 115.028(3)°	a = 11.7566(13) Å b = 13.7449(15) Å c = 13.7689(15) Å α = 65.642(3)° β = 74.276(3)° γ = 74.609(3)°
Volume, Å^3	1823.0(5)	2345.2(4)	1967.6(6)	1920.9(4)
Z	2	2	2	2
Density (calculated), g/cm^3	1.735	1.568	1.659	1.699
Absorption coefficient, mm^{-1}	1.171	0.783	1.023	0.980
F(000)	948	1120.0	984.0	986.0
Crystal size, mm^3	0.421 x 0.413 x 0.381	0.421 x 0.403 x 0.380	0.451 x 0.443 x 0.410	0.18 x 0.16 x 0.13
θ range for data	1.73 to 24.99	1.43 to 25.00	1.45 to 25.00	1.828 to 26.679

collection, °				
Limiting indices	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -16 ≤ l ≤ 14	-13 ≤ h ≤ 13, -17 ≤ k ≤ 17, -18 ≤ l ≤ 9	-14 ≤ h ≤ 14, -13 ≤ k ≤ 14, -14 ≤ l ≤ 18	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -17 ≤ l ≤ 17
Reflections collected	9590	12248	9788	34134
Independent reflections	6318 [$R_{(int)}$ = 0.0265]	8104 [$R_{(int)}$ = 0.0168]	6771 [$R_{(int)}$ = 0.0363]	8074 [$R_{(int)}$ = 0.1800]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
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
Data /restraints/ parameter	6318 / 0 / 518	8104 / 0 / 662	6771 / 0 / 554	8074 / 0 / 572
Goodness-of-fit on F^2	1.088	1.189	0.974	1.053
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0463, wR_2 = 0.1182	R_1 = 0.0332, wR_2 = 0.0969	R_1 = 0.0560, wR_2 = 0.1319	R_1 = 0.0517, wR_2 = 0.1220
R indices (all data)	R_1 = 0.0580, wR_2 = 0.1384	R_1 = 0.0389, wR_2 = 0.1169	R_1 = 0.0897, wR_2 = 0.1500	R_1 = 0.0643, wR_2 = 0.1307
Largest diff. peak and hole, eÅ^{-3}	0.704 and -0.641	0.653 and -0.512	1.136 and -0.759	0.889 and -1.407

Table S4. Crystal data and structure refinement parameters for compounds **5**-**7**, and **10**.

	5	**6**	**7**	**10**
Empirical formula	$C_{37}H_{32}BF_{15}GeN_2O_2$	$C_{40}H_{30}BCl_2F_{15}GeN_2O$	$C_{35}H_{28}BCl_2F_{15}GeN_2O$	$C_{39}H_{28}BF_{15}GeN_2OS$
Formula weight	905.07	993.98	931.91	941.11
Temperature, K	100(2)	100(2)	100(2)	100(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P\,2_1/n$	$P\bar{1}$	$P\,2_12_12_1$	$P\,2_1/c$
Unit cell dimensions	a = 11.415(3) Å b = 38.762(14) Å c = 17.556(6) Å β = 96.277(8)°	a = 12.501(3) Å b = 12.739(3) Å c = 15.229(4) Å α = 97.161(8)° β = 106.180(8)° γ = 115.904(7)°	a = 12.1298(9) Å b = 15.8356(12) Å c = 19.4206(15) Å	a = 15.032(14) Å b = 11.229(12) Å c = 23.30(2) Å β = 104.94(4)°
Volume, Å^3	7722(4)	2008.1(8)	3730.4(5)	3800(6)
Z	8	2	4	4
Density (calculated), g/cm^3	1.557	1.644	1.659	1.645
Absorption coefficient, mm^{-1}	0.902	1.002	1.073	0.971
F(000)	3648.0	996.0	1864.0	3032
Crystal size, mm^3	0.20 x 0.18 x 0.17	0.20 x 0.15 x 0.13	0.18 x 0.17 x 0.14	0.471 x 0.433 x 0.380
θ range for data collection,°	1.961 to 28.355	1.915 to 26.776	2.361 to 28.563	1.81 to 24.99°

Limiting indices	-15 ≤ h ≤ 15, -51 ≤ k ≤ 51, -23 ≤ l ≤ 23	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19	-10 ≤ h ≤ 16, -20 ≤ k ≤ 21, -26 ≤ l ≤ 24	-17 ≤ h ≤ 17, -13 ≤ k ≤ 13, -27 ≤ l ≤ 27
Reflections collected	253267	60329	34274	39248
Independent reflections	19194 [$R_{(int)}$ = 0.1875]	8483 [$R_{(int)}$ = 0.1897]	9489 [$R_{(int)}$ = 0.1125]	6692 [$R_{(int)}$ = 0.0732]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
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
Data /restraints/ parameter	19194 / 0 / 1059	8483 / 0 / 563	9489 / 0 / 519	6692 / 0 / 545
Goodness-of-fit on F^2	1.047	0.824	1.069	1.080
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0560, wR_2 = 0.0962	R_1 = 0.0434, wR_2 = 0.1120	R_1 = 0.0373, wR_2 = 0.0892	R_1 = 0.0493, wR_2 = 0.1164
R indices (all data)	R_1 = 0.1042, wR_2 = 0.1068	R_1 = 0.0498, wR_2 = 0.1187	R_1 = 0.0446, wR_2 = 0.0932	R_1 = 0.0803, wR_2 = 0.1338
Largest diff. peak and hole, eÅ^{-3}	0.695 and -0.495	1.558 and -1.154	0.521 and -0.704	1.583 and -0.593

Table S5. Crystal data and structure refinement parameters for compounds **9**.

	9
Empirical formula	$C_{39}H_{41}BF_{15}GeN_3OSi_2$
Formula weight	992.35
Temperature, K	100(2)
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 11.6826(7) Å b = 12.4053(8) Å c = 17.1901(11) Å α = 83.572(2)° β = 87.402(2)° γ = 73.342(2)°
Volume, Å^3	2371.5(3)
Z	2
Density (calculated), g/cm^3	1.390
Absorption coefficient, mm^{-1}	0.788
F(000)	1008.0
Crystal size, mm^3	0.17 x 0.15 x 0.14
θ range for data collection,°	1.991 to 32.561
Limiting indices	-17 ≤ h ≤ 16, -18 ≤ k ≤ 17, -24 ≤ l ≤ 26
Reflections collected	62263

Independent reflections	15738 [$R_{(int)}$ = 0.1647]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data /restraints/ parameter	15738 / 0 / 569
Goodness-of-fit on F^2	1.022
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0480, wR_2 = 0.1174
R indices (all data)	R_1 = 0.0617, wR_2 = 0.1253
Largest diff. peak and hole, eÅ^{-3}	0.915 and -1.854

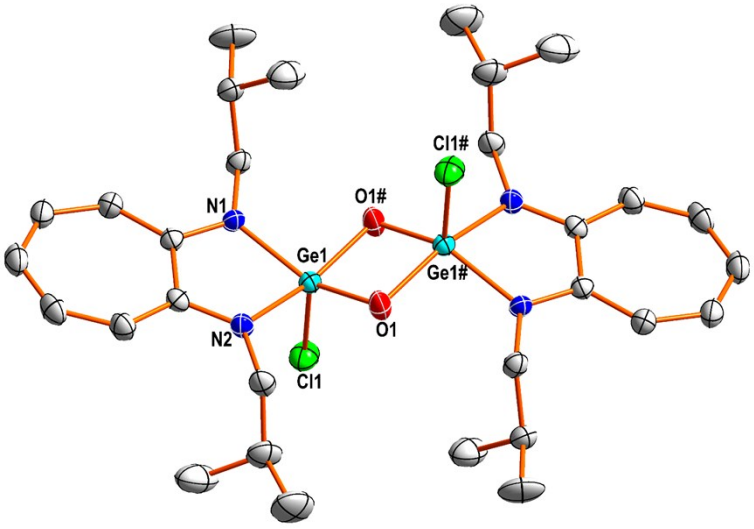


Figure S53. Molecular structure of μ-oxo dimer **D1** with thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-O1 1.822(2), Ge1-O1# 1.789(2), Ge1-Cl1 2.200(8), Ge1-N1 1.912(2), Ge1-N2 1.950(2); O1#-Ge1-O1 83.27(8), O1-Ge1-N1 93.71(8), O1#-Ge1-N2 91.39(8), O1-Ge1-N2 162.00(1), O1-Ge1-Cl1 98.72(7), O1#-Ge1-Cl1 110.38(8), N2-Ge1-N1 81.12(9), N1-Ge1-Cl1 103.58(7), N2-Ge1-Cl1 99.26(7). #Symmetry transformation used to generate equivalent atoms: -x+1, -y, -z+1. Data collection temperature: 293 K.

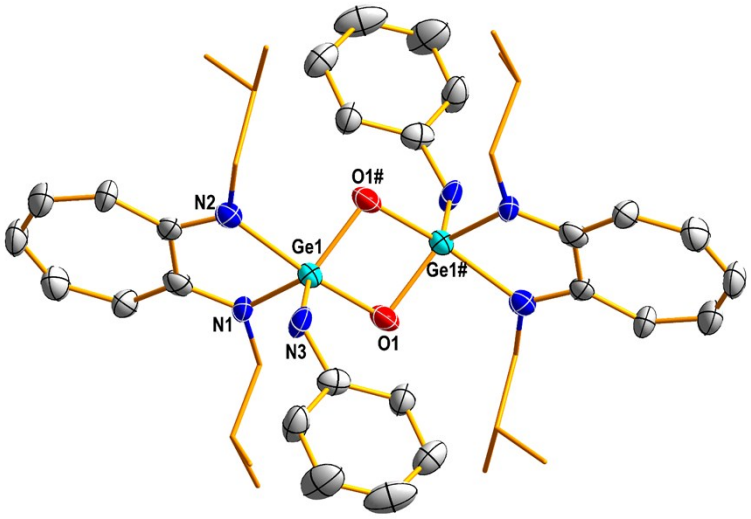


Figure S54. Molecular structure of μ-oxo dimer **D3** with thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-O1 1.807(3), Ge1-O1# 1.823(5), Ge1-N3 1.864(4), Ge1-N1 1.920(5), Ge1-N2 1.983(5); O1#-Ge1-O1 83.40(2), O1-Ge1-N1 131.40(2), O1#-Ge1-N2 165.93(2), O1-Ge1-N2 90.40(2), O1-Ge1-N3 117.1(2), O1#-Ge1-N3 103.7(2), N2-Ge1-N1 90.3(2), N1-Ge1-N3 110.45(2), N2-Ge1-N3 90.30(2). #Symmetry transformation used to generate equivalent atoms: -x+1, -y+1, -z+1. Data collection temperature: 293 K.

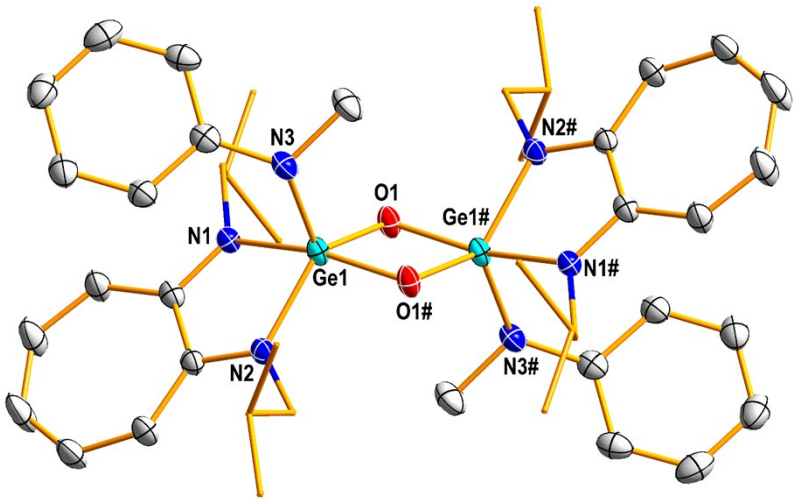


Figure S55. Molecular structure of μ-oxo dimer **D4** with thermal ellipsoids at the 30% probability level. Two molecules present in the asymmetric unit, only one is shown here. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-O1 1.801(2), Ge1-O1# 1.836(2), Ge1-N3 1.875(2), Ge1-N1 1.978(2), Ge1-N2 1.925(2); O1#-Ge1-O1 83.72(7), O1-Ge1-N1 90.38(7), O1#-Ge1-N2 94.57(7), O1-Ge1-N2 130.71(8), O1-Ge1-N3 113.28(8), O1#-Ge1-N3 99.05(8), N2-Ge1-N1 79.66(7), N1-Ge1-N3 94.95(8), N2-Ge1-N3 115.59(8). #Symmetry transformations used to generate equivalent atoms: -x+1, -y+1, -z+1; -x, -y+1, -z. Data collection temperature: 293 K.

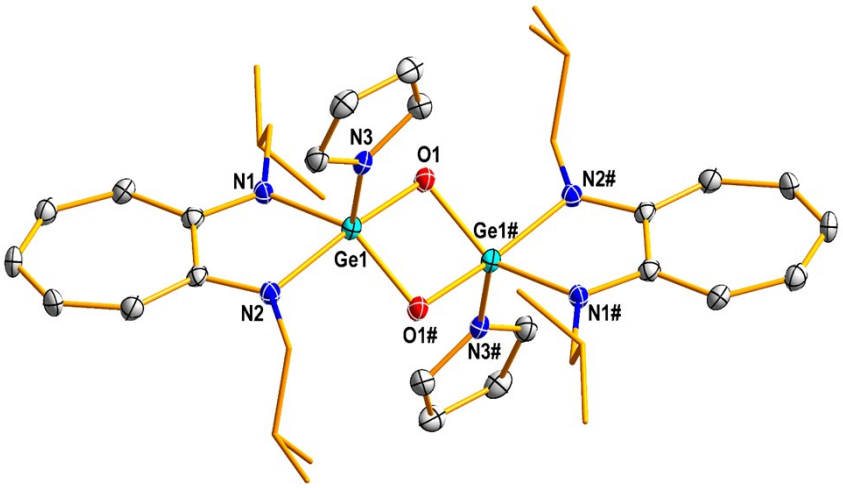


Figure S56. Molecular structure of μ-oxo dimer **D5** with thermal ellipsoids at the 30% probability level. All hydrogen atoms and toluene are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-O1 1.801(2), Ge1-O1# 1.848(2), Ge1-N3 1.892(3), Ge1-N1 1.920(3), Ge1-N2 1.966(3); O1#-Ge1-O1 83.81(1), O1-Ge1-N1 136.46(1), O1#-Ge1-N2 167.76(1), O1-Ge1-N2 91.41(1), O1-Ge1-N3 115.24(1), O1#-Ge1-N3 97.29(1), N2-Ge1-N1 80.80(1), N1-Ge1-N3 108.11(1), N2-Ge1-N3 94.94(1). $^{\#}$Symmetry transformation used to generate equivalent atoms: -x, -y+2, -z. Data collection temperature: 273 K.

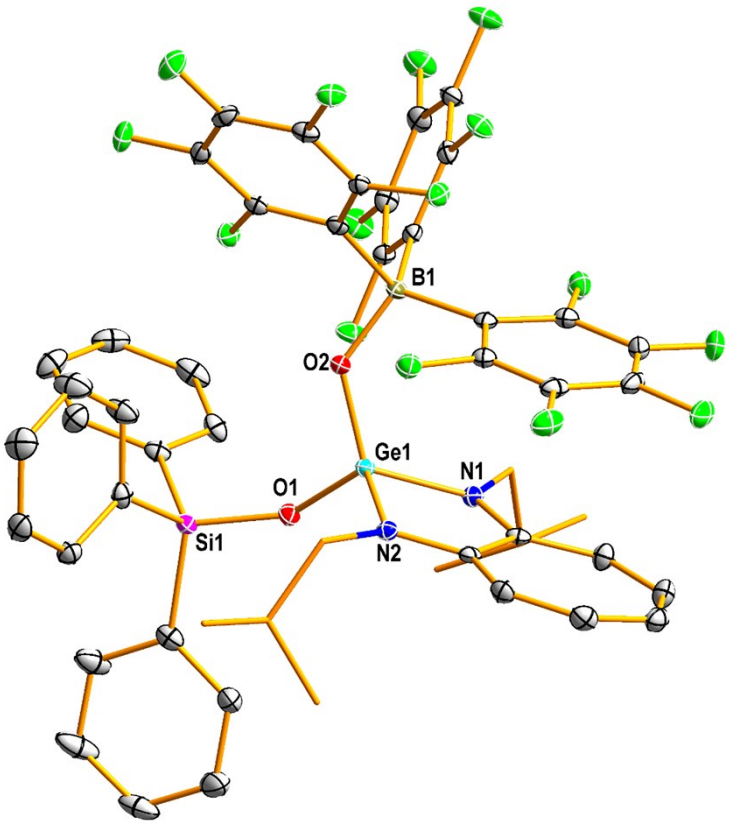


Figure S57. Molecular structure of germaester **2** with thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-O2 1.696(2), O2-B1 1.497(3), Ge1-O1 1.719(2), Ge1-N1 1.847(2), Ge1-N2 1.849(2); O2-Ge1-N1 120.05(8), O2-Ge1-N2 113.29(8), O2-Ge1-O1 111.43(8), B1-O2-Ge1 130.94(2), N2-Ge1-N1 87.34(8), N1-Ge1-O1 110.46(8), N2-Ge1-O1 112.20(8). Data collection temperature: 100 K.

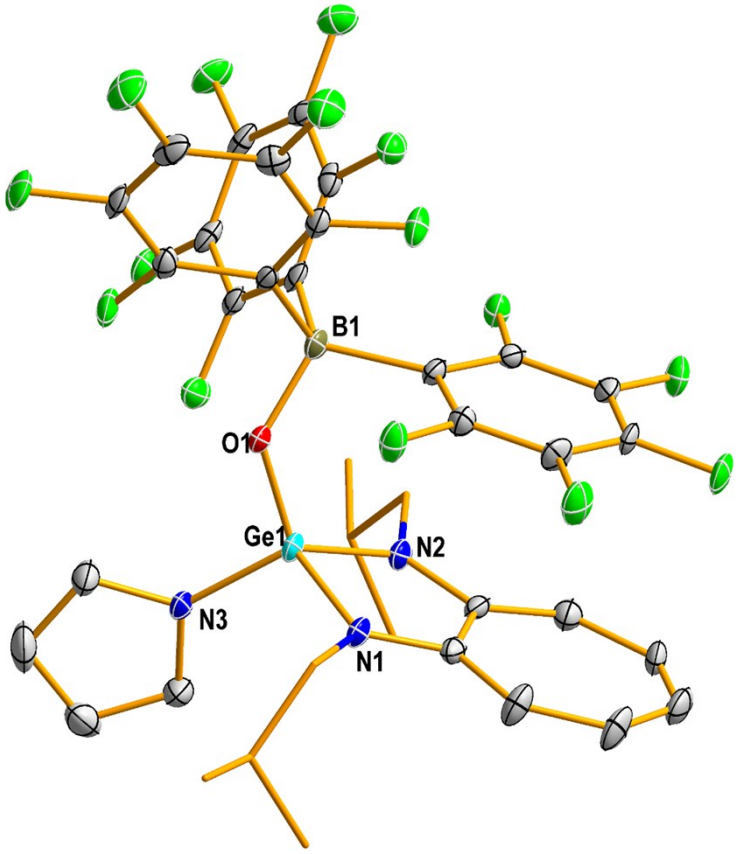


Figure S58. Molecular structure of *N*-germaacyl pyrrole **3**·CH_2Cl_2 with thermal ellipsoids at the 50% probability level. All hydrogen atoms and a solvent molecule (CH_2Cl_2) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-O1 1.695(3), O1-B1 1.494(6), Ge1-N3 1.819(4), Ge1-N1 1.836(4), Ge1-N2 1.851(4); O1-Ge1-N1 114.37(2), O1-Ge1-N2 120.92(2), O1-Ge1-N3 108.17(2), B1-O1-Ge1 129.0(3), N2-Ge1-N1 87.67(2), N1-Ge1-N3 110.33(2), N2-Ge1-N3 113.92(2). Data collection temperature: 100 K.

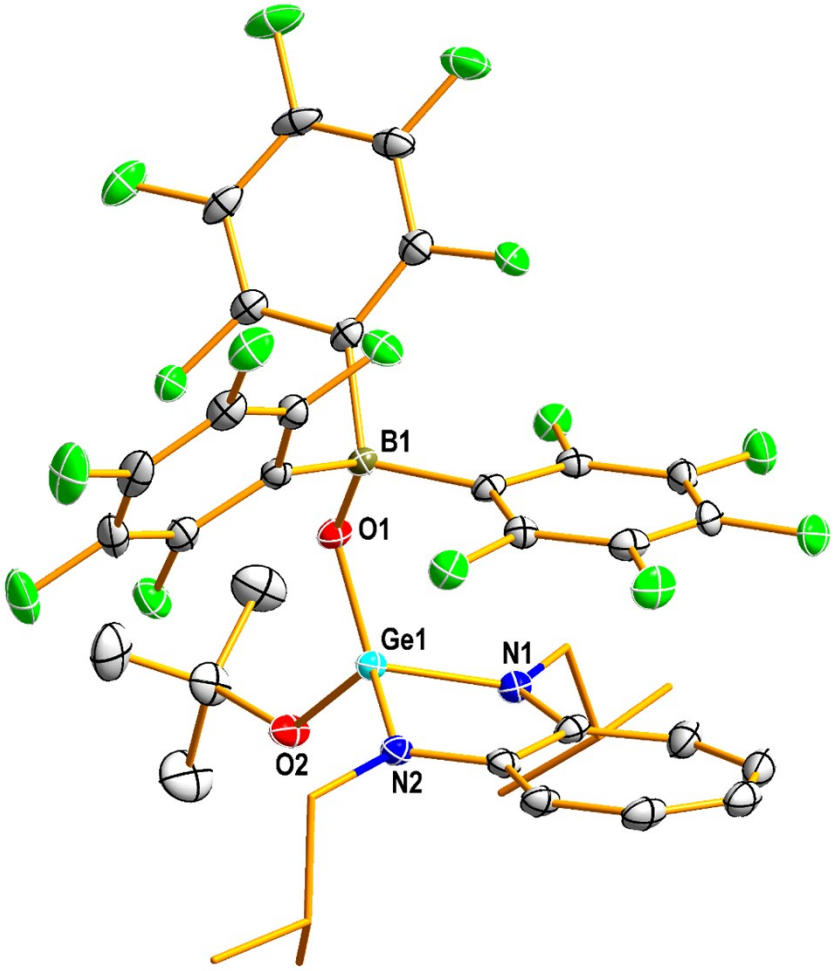


Figure S59. Molecular structure of germaester **5** with thermal ellipsoids at the 50% probability level. Two molecules present in the asymmetric unit, only one is shown here. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-O1 1.712(2), O1-B1 1.505(3), Ge1-O2 1.724(2), Ge1-N1 1.851(3), Ge1-N2 1.849(2); O1-Ge1-N1 115.42(1), O1-Ge1-N2 117.18(1), O1-Ge1-O2 113.62(9), B1-O1-Ge1 128.80(2), N2-Ge1-N1 86.79(1), N1-Ge1-O2 110.08(1), N2-Ge1-O2 110.87(1). Data collection temperature: 100 K.

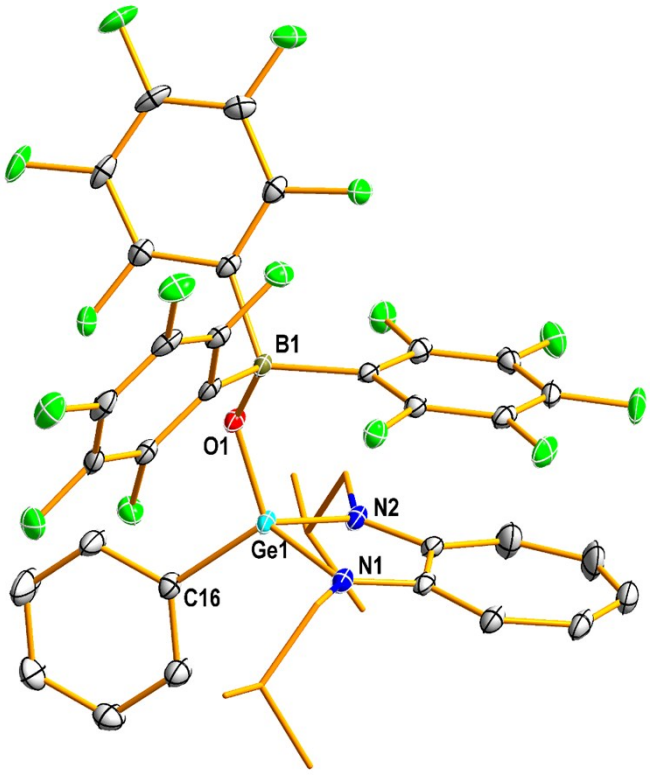


Figure S60. Molecular structure of germanone **6** with thermal ellipsoids at the 50% probability level. All hydrogen atoms and a solvent molecule (CH_2Cl_2) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-O1 1.720(2), O1-B1 1.481(3), Ge1-C16 1.914(2), Ge1-N1 1.866(2), Ge1-N2 1.861(2); O1-Ge1-N1 117.05(8), O1-Ge1-N2 111.42(9), O1-Ge1-C16 110.66(9), B1-O1-Ge1 131.26(2), N2-Ge1-N1 86.21(9), N1-Ge1-C16 117.70(1), N2-Ge1-C16 111.34(1). Data collection temperature: 100 K.

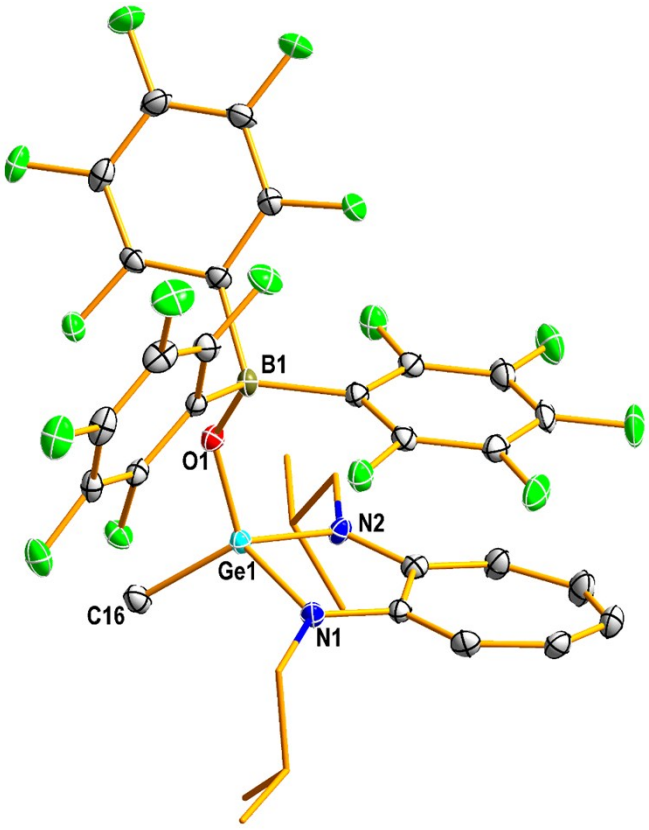


Figure S61. Molecular structure of germanone **7** with thermal ellipsoids at the 50% probability level. All hydrogen atoms and a solvent molecule (CH_2Cl_2) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-O1 1.716(2), O1-B1 1.475(4), Ge1-C16 1.901(3), Ge1-N1 1.859(3), Ge1-N2 1.867(3); O1-Ge1-N1 118.29(2), O1-Ge1-N2 108.96(1), O1-Ge1-C16 110.17(2), B1-O1-Ge1 133.7(2), N2-Ge1-N1 85.43(1), N1-Ge1-C16 114.15(2), N2-Ge1-C16 118.09(15). Data collection temperature: 100 K.

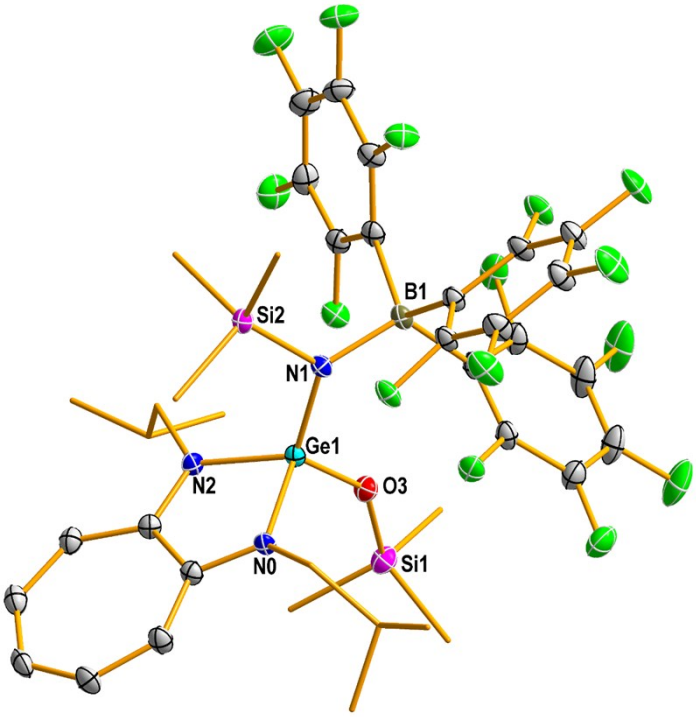


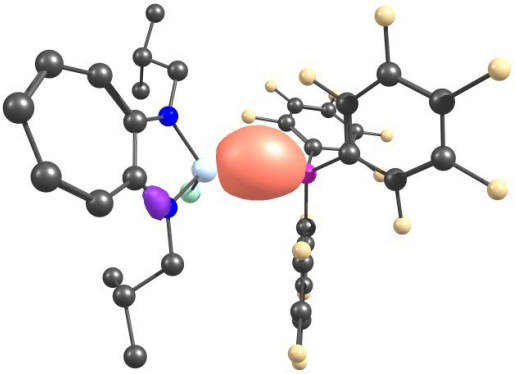
Figure S62. Molecular structure of germaimine **9** with thermal ellipsoids at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-N1 1.782(1), N1-B1 1.592(3), Ge1-O3 1.734(2), Ge1-N2 1.874(2), Ge1-N0 1.869(2); O3-Ge1-N1 115.16(8), O3-Ge1-N2 108.79(8), O3-Ge1-N0 107.83(8), B1-N1-Ge1 124.06(2), N2-Ge1-N0 86.14(8). Data collection temperature: 100 K.

6. Computational Details

GAUSSIAN-09 programs were used for carrying out theoretical calculations.[S8] The geometries of compounds **1, 2**, **3,** and **10** were optimized at the B3LYP level of theory using LANL2DZ basis set having Effective Core Potential (ECP) for core electrons of germanium and silicon atoms, and 6-31+G** basis set for rest of the elements. For geometry optimizations coordinates obtained from single crystal X-ray diffraction studies were used. The frequency calculations were carried on the optimized geometries to characterize the stationary points as minima. The same level of theory and LANL2DZ/6-31G** basis sets were used for performing the Weinhold's Natural Bond Orbital (NBO) calculations on the optimized geometries.[S9-S10] TDDFT[S11] calculations were carried out on the optimized geometries using toluene as a solvent with the aforementioned level of theory and LANL2DZ/6-31G** basis sets. Chemcraft (http://www.chemcraftprog.com) was used for the visualization of Gaussian outputs and plotting the NBO interactions. EDA calculations were performed using a LANL2DZ basis set for germanium and silicon atoms, and a 6-31G* basis set for rest of the atoms. These calculations were performed by treating Y-Ge=O→$B(C_6F_5)_3$ (Y = Cl **1**, $OSiPh_3$ **2**, NC_4H_4 **3**, SPh **10**) as one fragment and ATI ligand as other fragment. The interaction energy of the two fragments can be represented as: $\Delta E_{int} = \Delta E_{Steric} + \Delta E_{orb}$.

Table S6. Nature of Ge-O and O→B bonds in compounds **1**, **2**, **3**, and **10**.

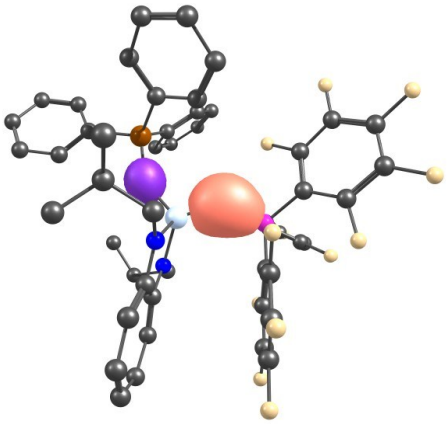
Compound	Bond	Orbitals	Ionicity	% Contribution	WBI
1	**Ge-O**	$sp^{2.59}$ (Ge) and $sp^{1.62}$ (O)	0.72	14.05% (Ge) and 85.95% (O)	0.76
	B-O	$sp^{3.93}$ (B) and $sp^{0.72}$ (O)	0.65	17.73% (B) and 82.27% (O)	0.63
2	**Ge-O**	$sp^{2.53}$ (Ge) and $sp^{2.89}$ (O)	0.71	14.67% (Ge) and 85.33% (O)	0.70
	B-O	$sp^{3.75}$ (B) and $sp^{0.90}$ (O)	0.63	18.35% (B) and 81.65% (O)	0.66
3	**Ge-O**	$sp^{2.43}$ (Ge) and $sp^{2.57}$ (O)	0.70	15.01% (Ge) and 84.99% (O)	0.74
	B-O	$sp^{3.84}$ (B) and $sp^{0.86}$ (O)	0.64	18.12% (B) and 81.88% (O)	0.65
10	**Ge-O**	sp^{2} (Ge) and $sp^{2.66}$ (O)	0.68	15.79% (Ge) and 84.21% (O)	0.74
	B-O	$sp^{3.87}$ (B) and $sp^{0.85}$ (O)	0.64	17.85% (B) and 82.15% (O)	0.63



Compound **1**

HOMO-128 (MO number: 74)

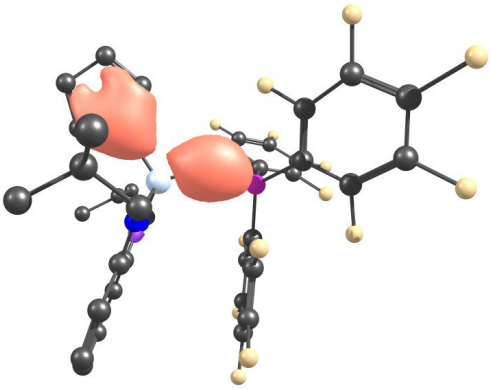
Contributions of Ge, O, and B to this MO are 4.54%, 86.49%, and 0.33%, respectively.



Compound **2**

HOMO-172 (MO number: 89)

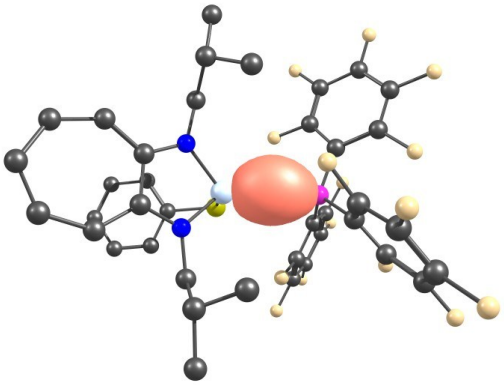
Contributions of Ge, O, and B to this MO are 3.04%, 79.24%, and 0.91%, respectively.



Compound **3**

HOMO-137 (MO number: 74)

Contributions of Ge, O, and B to this MO are 3.27%, 51.36%, and 0.21%, respectively.

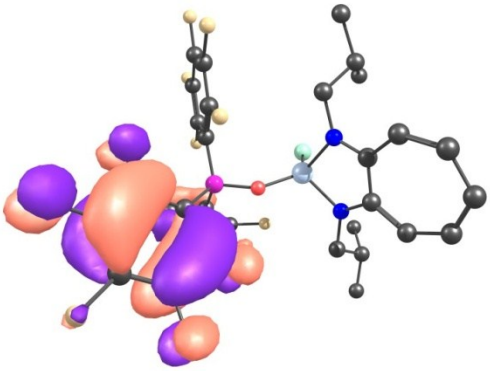


Compound **10**

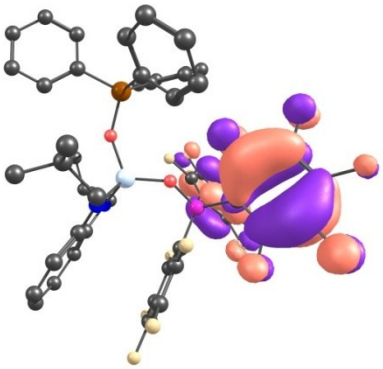
HOMO-142 (MO number: 80)

Contributions of Ge, O, and B to this MO are 3.90%, 88.75%, and 1.01%, respectively.

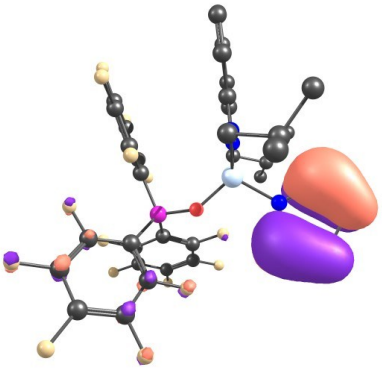
Figure S63. Molecular orbital of compounds **1**, **2**, **3**, and **10** that shows the Ge-O bond. Atomic contributions were calculated using AOMix software.



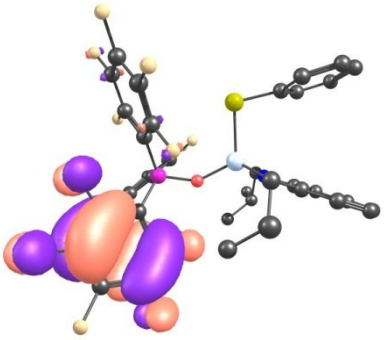
Compound **1** (ε = -0.22124 a.u.)



Compound **2** (ε = -0.22103 a.u.)

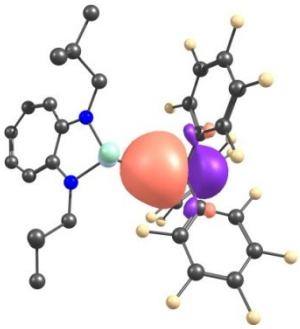


Compound **3** (ε = -0.22059 a.u.)

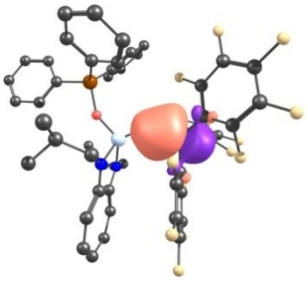


Compound **10** (ε = -0.22064 a.u.)

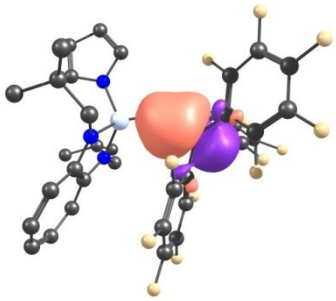
Figure S64. Pictorial representation of HOMOs of (a) compounds **1**, **2**, and **10** that are primarily localized on a phenyl ring of the $B(C_6F_5)_3$ moiety and (b) compound **3** that is mainly localized on the pyrrole ring.



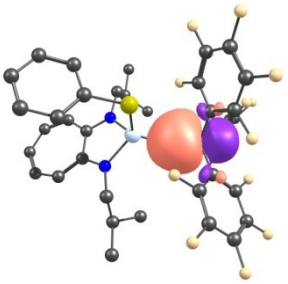
(a) $sp^{0.29}$(O)-$sp^{4.39}$(B); 280.3 kcal/mol



(b) $sp^{0.42}$(O)-$sp^{4.11}$(B); 315.6 kcal/mol

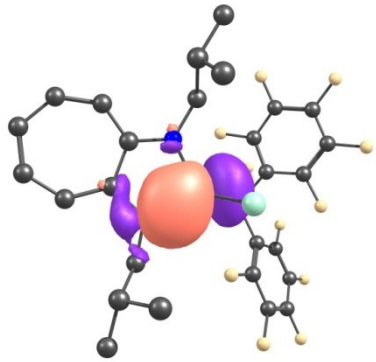


(c) $sp^{0.32}$(O)-$sp^{4.24}$(B); 296.3 kcal/mol

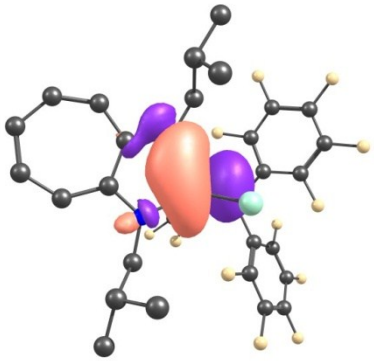


(d) $sp^{0.32}$(O)-$sp^{4.41}$(B); 294.6 kcal/mol

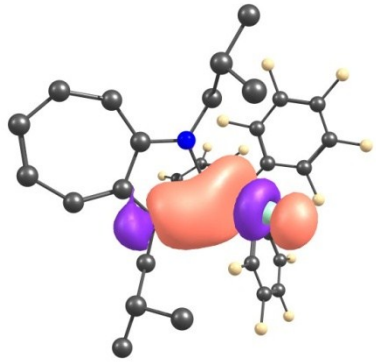
Figure S65. Pictorial representation of NBO donor-acceptor interactions between: sp^x orbital of oxygen and sp^y orbital of boron in compounds **1** (a; x = 0.29 and y = 4.39), **2** (b; x = 0.42 and y = 4.11), **3** (c; x = 0.32 and y = 4.24), and **10** (d; x = 0.32 and y = 4.41).



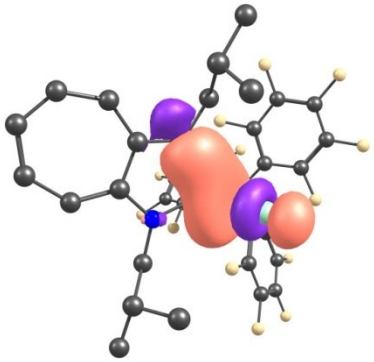
(a) $sp^{3.07}(N_4)$- p(Ge); 159.4 kcal/mol



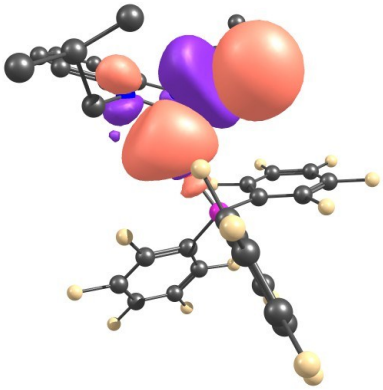
(b) $sp^{3.21}(N_5)$- p(Ge); 50.0 kcal/mol



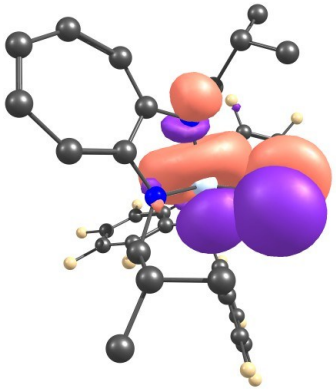
(c) $sp^{3.07}(N_4)$-σ^*(Ge-Cl); 41.1 kcal/mol



(d) $sp^{3.21}$ (N_5)-σ^*(Ge-Cl); 26.8 kcal/mol

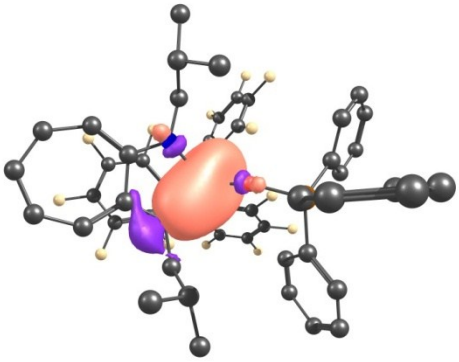


(e) s(Cl)- π^*(Ge-N_4); 13.12 kcal/mol

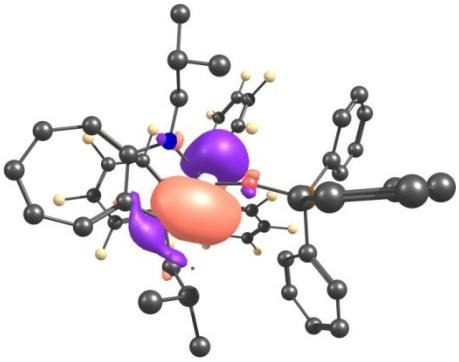


(f) p(Cl)- π^*(Ge-N_5); 5.42 kcal/mol

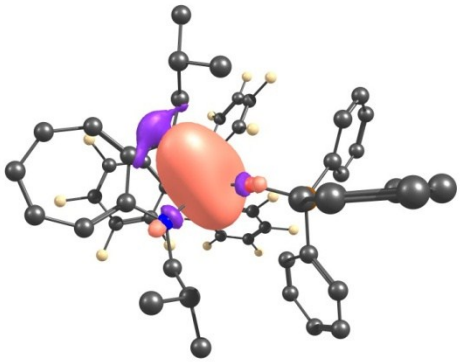
Figure S66. Pictorial representation of NBO donor-acceptor interactions in compound **1** between: sp^x (x = 3.07, 3.21) hybrid orbitals of N_{ATI} atoms and vacant p orbital of germanium atom (a-b), sp^x (x=3.07, 3.21) hybrid orbitals of N_{ATI} atoms and σ^* orbital of Ge-Cl bond (c-d), and s or p orbital of chlorine atom and π^* orbitals of Ge-N_{ATI} bonds (e-f).



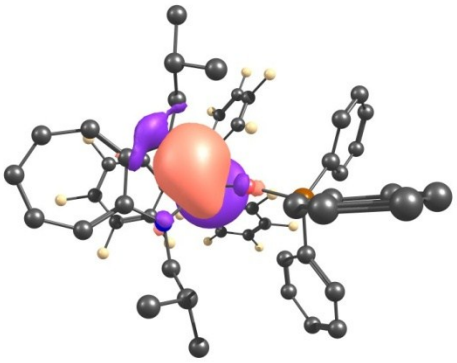
(a) $sp^{3.22}(N_6)$- s(Ge); 126.2 kcal/mol



(b) $sp^{3.22}(N_6)$- p(Ge); 87.2 kcal/mol

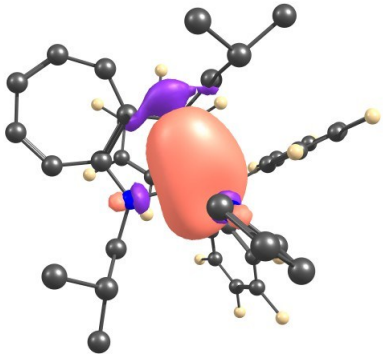


(c) $sp^{3.11}(N_7)$- s(Ge); 134.3 kcal/mol

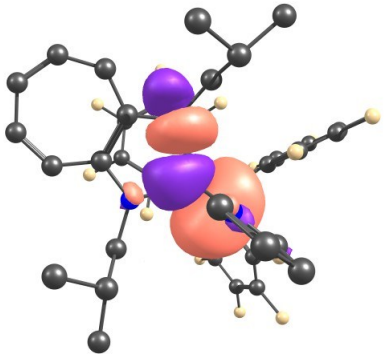


(d) $sp^{3.11}(N_7)$- p(Ge); 49.2 kcal/mol

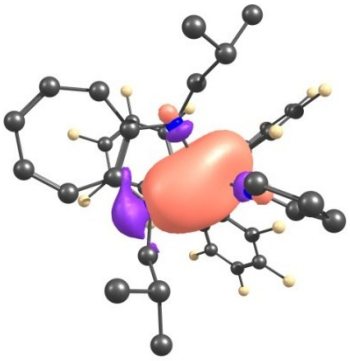
Figure S67. Pictorial representation of NBO donor-acceptor interactions between sp^x (x = 3.22, 3.11) hybrid orbitals of N_{ATI} atoms and vacant *s* or *p* orbital of germanium atom in compound **2**.



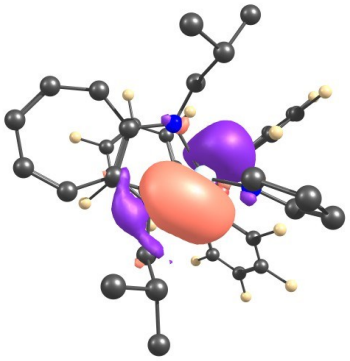
(a) $sp^{3.20}(N_{18})$- s(Ge); 141.3 kcal/mol



(b) $sp^{3.20}(N_{18})$- p(Ge); 51.1 kcal/mol

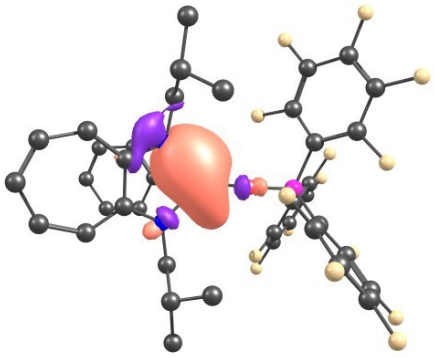


(c) $sp^{3.29}(N_{20})$- s(Ge); 126.2 kcal/mol

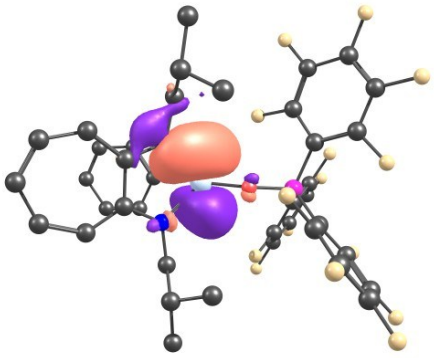


(d) $sp^{3.29}(N_{20})$- p(Ge); 90.1 kcal/mol

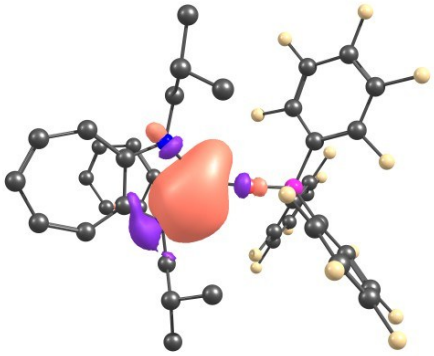
Figure S68. Pictorial representation of NBO donor-acceptor interactions between sp^x (x = 3.20, 3.29) hybrid orbitals of N_{ATI} atoms and vacant *s* or *p* orbital of germanium atom in compound **3**.



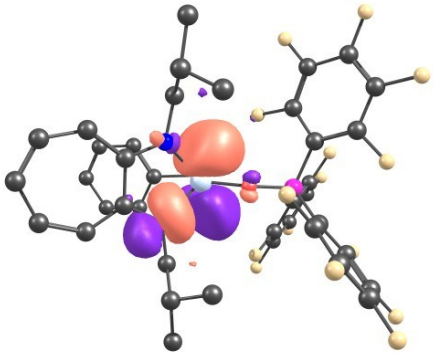
(a) $sp^{3.11}(N_4)$-$sp^{1.45}$(Ge); 117.9 kcal/mol



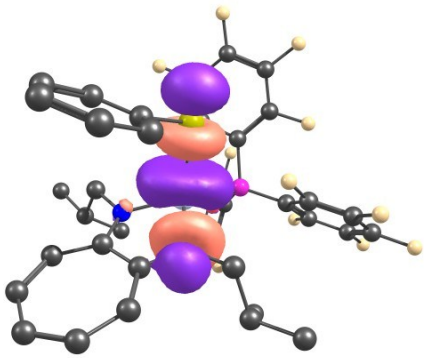
(b) $sp^{3.11}(N_4)$-p(Ge); 49.8 kcal/mol



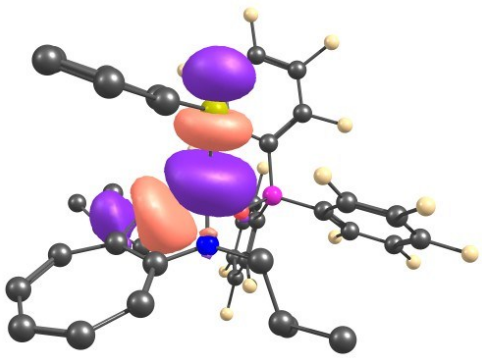
(c) $sp^{3.09}(N_5)$- $sp^{1.45}$(Ge); 114.6 kcal/mol



(d) $sp^{3.09}(N_5)$- p(Ge); 46.7 kcal/mol



(e) $sp^{3.11}(N_4)$-σ^*(Ge-S); 13.8 kcal/mol



(f) $sp^{3.09}(N_5)$-σ^*(Ge-S); 15.6 kcal/mol

Figure S69. Pictorial representation of NBO donor-acceptor interactions in compound **10** between sp^x (x = 3.11, 3.09) hybrid orbitals of N_{ATI} atoms and $sp^{1.45}$ or p orbital of germanium atom (a-d); sp^x (x = 3.11, 3.09) hybrid orbitals of N_{ATI} atoms and σ^* orbital of Ge-S bond (e-f).

Table S7. EDA analysis on compounds **1**, **2**, **3**, and **10**.

Compound	EDA* {$YGe(O)B(C_6F_5)_3$ + ATI ligand}		
	ΔE_{int} (kcal/mol)	ΔE_{steric} (kcal/mol)	ΔE_{orb} (kcal/mol)
(i-Bu)$_2$ATIGe(O)(Cl)→$B(C_6F_5)_3$ (**1**)	-292.71	169.09	-461.80
(i-Bu)$_2$ATIGe(O)($OSiPh_3$)→$B(C_6F_5)_3$ (**2**)	-281.32	177.98	-459.30
(i-Bu)$_2$ATIGe(O)(NC_4H_4)→$B(C_6F_5)_3$ (**3**)	-285.87	220.73	-506.60
(i-Bu)$_2$ATIGe(O)(SPh)→$B(C_6F_5)_3$ (**10**)	-275.40	156.50	-431.90
*E_{orb} = orbital energy, E_{int} = interaction energy, E_{steric} = steric energy, and $E_{int} = E_{steric} + E_{orb}$			

7. Coordinates of the Optimized Geometries of:

Compound 1

32	1.592574000	-0.292617000	-0.675109000
17	1.480681000	0.047977000	-2.809223000
8	0.133735000	-0.284471000	0.158427000
7	2.642805000	-1.749925000	-0.128398000
7	2.963754000	0.798408000	0.009724000
5	-1.309502000	0.156465000	0.130329000
9	-0.873294000	-2.254281000	1.702717000
9	-1.572119000	-2.722124000	4.232849000
9	-2.953567000	-0.839075000	5.671054000
9	-3.608000000	1.544284000	4.490176000
9	-2.906867000	2.058262000	1.976713000
9	-0.512386000	-2.222873000	-1.693188000
9	-2.201217000	-3.830310000	-2.937911000
9	-4.912454000	-3.423861000	-2.796687000
9	-5.878588000	-1.315743000	-1.331003000
9	-4.194867000	0.331482000	-0.054436000
9	0.000247000	2.352493000	1.508156000
9	0.155153000	4.913534000	0.763502000
9	-1.043646000	5.764433000	-1.551418000
9	-2.390799000	3.959069000	-3.111738000
9	-2.548882000	1.406082000	-2.414105000
6	3.698935000	-1.367755000	0.634017000
6	4.536176000	-2.323391000	1.243808000
1	4.292203000	-3.349813000	1.003743000
6	5.629018000	-2.189623000	2.098666000
1	6.080037000	-3.132777000	2.398702000

6	6.213481000	-1.042868000	2.632162000
1	7.057934000	-1.185070000	3.300076000
6	5.802862000	0.268432000	2.401598000
1	6.356446000	1.038584000	2.933913000
6	4.783178000	0.753580000	1.585044000
1	4.679723000	1.831081000	1.604416000
6	3.854395000	0.097505000	0.753414000
6	2.198298000	-3.155792000	-0.243026000
1	1.140642000	-3.133713000	-0.511046000
1	2.248969000	-3.613155000	0.751996000
6	2.945328000	2.271764000	-0.081451000
1	2.868825000	2.691972000	0.928920000
1	2.015871000	2.543350000	-0.590135000
6	2.962618000	-4.017727000	-1.273343000
1	4.031167000	-4.012310000	-1.016659000
6	4.124875000	2.914538000	-0.848164000
1	5.062455000	2.639469000	-0.348234000
6	2.821390000	-3.483670000	-2.705479000
1	3.365220000	-4.126816000	-3.405372000
1	3.222380000	-2.470887000	-2.807642000
1	1.770745000	-3.462830000	-3.016478000
6	2.454764000	-5.465099000	-1.166948000
1	1.389432000	-5.525549000	-1.418939000
1	2.584066000	-5.871185000	-0.156936000
1	2.996940000	-6.115077000	-1.861061000
6	4.217473000	2.439357000	-2.304074000
1	3.313923000	2.701853000	-2.865557000
1	4.349238000	1.355670000	-2.375181000

1	5.070303000	2.913071000	-2.801598000
6	3.979350000	4.443181000	-0.767046000
1	4.819985000	4.935556000	-1.266027000
1	3.949501000	4.797177000	0.269557000
1	3.058961000	4.778467000	-1.259429000
6	-1.807770000	-0.049633000	1.703150000
6	-1.524586000	-1.256431000	2.354726000
6	-1.888919000	-1.539613000	3.668572000
6	-2.592474000	-0.589656000	4.401679000
6	-2.920930000	0.618269000	3.797159000
6	-2.531617000	0.859358000	2.479198000
6	-2.263964000	-0.851166000	-0.776807000
6	-1.840705000	-1.934485000	-1.543085000
6	-2.696666000	-2.801852000	-2.221706000
6	-4.069101000	-2.601957000	-2.152793000
6	-4.554226000	-1.531734000	-1.405130000
6	-3.655963000	-0.698454000	-0.746989000
6	-1.316354000	1.730699000	-0.385159000
6	-0.628494000	2.700599000	0.355410000
6	-0.530206000	4.041146000	-0.002710000
6	-1.135466000	4.478621000	-1.177610000
6	-1.818862000	3.558831000	-1.963240000
6	-1.888441000	2.222154000	-1.562382000

Compound 2

32	0.715521000	0.902006000	-0.110170000
14	3.451133000	-0.881906000	0.113175000
8	2.353489000	0.384133000	-0.251803000
8	-0.357514000	-0.348396000	0.330123000
5	-1.825354000	-0.616478000	0.121196000
7	0.629510000	2.402154000	1.033303000
7	0.270434000	2.099274000	-1.492943000
9	-0.394524000	-3.092946000	0.620068000
9	-4.437085000	-1.476973000	-0.828933000
9	-4.827477000	-2.651686000	3.745878000
9	-4.282879000	-0.709578000	2.025618000
9	0.155481000	-1.398896000	-2.115929000
9	-2.023698000	0.922733000	2.593077000
9	-3.260975000	1.107687000	-2.011372000
9	-3.036236000	-3.514708000	-4.832778000
9	-0.965554000	-5.019412000	2.371891000
9	-4.482862000	3.419075000	-1.571862000
9	-3.237132000	3.266664000	2.992623000
9	-3.190569000	-4.837943000	3.967806000
9	-0.455161000	-2.750080000	-4.313684000
9	-5.017667000	-2.855571000	-3.053675000
9	-4.507019000	4.547061000	0.926508000
6	3.196065000	-2.363751000	-1.019618000
6	-3.398936000	-1.733642000	2.077163000
6	-3.412478000	-1.784068000	-1.659780000
6	-0.079319000	3.328550000	-1.028835000
6	-2.116374000	-1.367244000	-1.333338000

6	-1.486427000	-2.906833000	1.401652000
6	-3.258514000	1.555547000	-0.730339000
6	-1.155790000	-1.737143000	-2.274087000
6	-2.897907000	-3.856584000	3.099144000
6	-2.626110000	0.834647000	0.286002000
6	-0.589111000	5.938808000	0.744024000
1	-0.649385000	6.672583000	1.544617000
6	0.919613000	2.274116000	2.474316000
1	0.619791000	1.261921000	2.761436000
1	0.274556000	2.946732000	3.048251000
6	-0.641398000	4.292205000	-1.886874000
1	-0.782546000	3.955823000	-2.905780000
6	-3.267521000	2.704478000	1.768381000
6	-1.054596000	6.361578000	-0.501288000
1	-1.442362000	7.373852000	-0.565499000
6	5.139228000	-0.100805000	-0.220152000
6	-1.437132000	-2.446316000	-3.443064000
6	4.414238000	-1.418474000	2.770081000
1	5.395715000	-1.183284000	2.367251000
6	-0.067267000	4.709063000	1.132983000
1	0.211371000	4.664713000	2.177370000
6	3.279698000	-1.342487000	1.940754000
6	-3.912862000	3.359647000	0.723656000
6	0.171089000	1.726204000	-2.918552000
1	-0.834965000	1.969352000	-3.280519000
1	0.260600000	0.640520000	-2.972723000
6	-2.743613000	-2.832794000	-3.713574000
6	-3.722841000	-2.743941000	2.983397000

6	3.388978000	-3.363594000	-3.239230000
1	3.680201000	-3.279265000	-4.282648000
6	4.305239000	-1.792793000	4.112943000
1	5.196107000	-1.847967000	4.732781000
6	-3.902500000	2.779642000	-0.538107000
6	0.867964000	2.095996000	-5.298609000
1	1.612232000	2.531424000	-5.973261000
1	-0.107011000	2.529423000	-5.550225000
1	0.819802000	1.020565000	-5.508328000
6	-2.643440000	1.485075000	1.526443000
6	0.158827000	3.511675000	0.421013000
6	-3.745729000	-2.496140000	-2.806964000
6	5.309691000	1.294607000	-0.223980000
1	4.446816000	1.937206000	-0.073093000
6	1.249135000	2.354554000	-3.831963000
1	1.258900000	3.440453000	-3.669236000
6	2.462354000	-4.656133000	-1.417270000
1	2.027993000	-5.577002000	-1.038511000
6	-1.768100000	-3.940221000	2.292340000
6	2.644304000	-3.570146000	-0.556032000
1	2.347370000	-3.668923000	0.483401000
6	3.569292000	-2.282374000	-2.375198000
1	4.014182000	-1.368030000	-2.760690000
6	-2.263107000	-1.749978000	1.261596000
6	2.026099000	-1.647242000	2.506879000
1	1.128496000	-1.605668000	1.896711000
6	7.535005000	-0.335590000	-0.638317000
1	8.396974000	-0.976147000	-0.803834000

6	-1.075216000	5.599956000	-1.665080000
1	-1.492517000	6.087299000	-2.543244000
6	2.571472000	2.169190000	4.353503000
1	3.621982000	2.259899000	4.647493000
1	2.245408000	1.152613000	4.594696000
1	1.991900000	2.869824000	4.968228000
6	3.053454000	-2.094859000	4.655808000
1	2.966240000	-2.389622000	5.697984000
6	2.832286000	-4.553897000	-2.760157000
1	2.687803000	-5.396003000	-3.431334000
6	6.274059000	-0.904168000	-0.435038000
1	6.175087000	-1.987026000	-0.455295000
6	2.403349000	2.475445000	2.856728000
1	2.983496000	1.734215000	2.293839000
6	7.683954000	1.054350000	-0.635023000
1	8.662413000	1.498656000	-0.795821000
6	6.567123000	1.869716000	-0.429830000
1	6.675156000	2.951213000	-0.432894000
6	1.913376000	-2.018185000	3.850250000
1	0.936697000	-2.255144000	4.263226000
6	2.951845000	3.866906000	2.511669000
1	2.836584000	4.105722000	1.449401000
1	4.020578000	3.917273000	2.745372000
1	2.454005000	4.651273000	3.095735000
6	2.651906000	1.815847000	-3.519719000
1	2.705193000	0.738804000	-3.717951000
1	2.931202000	1.972654000	-2.474394000
1	3.400862000	2.309796000	-4.147959000

Compound 3

32	1.276264000	0.239844000	-1.143703000
9	-0.867076000	1.696616000	2.665637000
9	-2.426953000	4.635126000	-1.221747000
9	-3.722661000	0.349442000	1.872465000
9	-0.848195000	2.510892000	-1.265944000
9	0.059912000	-2.621475000	0.853274000
9	0.568684000	1.084279000	4.806669000
9	1.787205000	-1.359410000	5.035869000
9	-4.294673000	-2.294169000	-3.228358000
9	-2.600600000	-2.388834000	1.951326000
9	-4.678826000	4.694567000	0.344555000
9	-5.296784000	2.515786000	1.891233000
9	1.515476000	-3.192976000	3.012800000
9	-2.583594000	-0.426043000	-2.401182000
9	-5.197400000	-4.224437000	-1.502268000
9	-4.320992000	-4.225546000	1.093313000
8	-0.357144000	-0.113615000	-0.890341000
7	2.296369000	1.239501000	0.078593000
7	1.472636000	0.809783000	-2.875865000
7	2.459778000	-1.175244000	-0.778561000
5	-1.361984000	-0.141092000	0.230017000
6	0.417730000	0.163764000	3.836326000
6	-0.531580000	-0.446465000	1.640567000
6	1.042162000	-1.071301000	3.956720000
6	-2.226139000	1.276399000	0.272762000
6	3.358501000	-0.889434000	0.192446000
6	0.136212000	-1.665585000	1.813247000

6	-1.960448000	2.421708000	-0.477439000
6	0.900451000	-1.997307000	2.927349000
6	-0.337169000	0.449613000	2.696091000
6	-3.376951000	1.378474000	1.063437000
6	-3.873878000	-3.292157000	0.233485000
6	-2.949369000	-1.366984000	-1.494878000
6	-2.758243000	3.566153000	-0.471935000
6	3.270780000	0.506371000	0.684392000
6	2.251438000	-2.490615000	-1.417829000
1	1.168946000	-2.610022000	-1.525654000
1	2.569006000	-3.291276000	-0.743623000
6	1.946341000	2.638158000	0.409413000
1	2.227439000	2.859373000	1.442888000
1	0.856905000	2.703760000	0.375678000
6	-2.963020000	-2.320972000	0.648069000
6	-3.858225000	-2.317600000	-1.954781000
6	0.456094000	0.860210000	-3.828985000
1	-0.560658000	0.625648000	-3.551831000
6	-3.897193000	3.603814000	0.322645000
6	-4.207637000	2.493880000	1.104073000
6	5.644375000	-0.765571000	2.470894000
1	6.441942000	-0.966093000	3.180020000
6	-2.443843000	-1.329819000	-0.189327000
6	5.114096000	0.520714000	2.460995000
1	5.554046000	1.219583000	3.168737000
6	4.264259000	-1.861467000	0.664181000
1	4.178387000	-2.822242000	0.173787000
6	5.244910000	-1.820309000	1.650873000

1	5.774336000	-2.759161000	1.795748000
6	2.914786000	-2.641204000	-2.804076000
1	2.549784000	-1.818911000	-3.433022000
6	4.093434000	1.063879000	1.679902000
1	3.899439000	2.107696000	1.887638000
6	-4.323177000	-3.295911000	-1.082185000
6	4.063225000	3.743999000	-0.549022000
1	4.421839000	4.458148000	-1.297497000
1	4.511674000	2.772542000	-0.782199000
1	4.446344000	4.071745000	0.425816000
6	2.529058000	3.691805000	-0.557523000
1	2.203657000	3.417236000	-1.569272000
6	1.922068000	5.063240000	-0.221266000
1	2.193640000	5.380454000	0.793721000
1	0.829803000	5.048228000	-0.292279000
1	2.290113000	5.825112000	-0.915666000
6	2.409181000	1.429710000	-4.822210000
1	3.139074000	1.736410000	-5.559259000
6	2.669945000	1.158349000	-3.499914000
1	3.599721000	1.187169000	-2.950029000
6	1.006572000	1.238596000	-5.029802000
1	0.464500000	1.371442000	-5.955926000
6	2.451608000	-3.965052000	-3.433415000
1	2.870286000	-4.079923000	-4.438269000
1	1.360695000	-4.011914000	-3.519397000
1	2.780462000	-4.825204000	-2.836459000
6	4.446779000	-2.555777000	-2.756447000
1	4.793371000	-1.619175000	-2.307709000

1	4.860950000	-2.606311000	-3.768654000
1	4.874980000	-3.389436000	-2.185105000

Compound 10

32	-1.379669000	0.089882000	-0.091164000
8	0.247342000	0.119047000	0.365025000
16	-1.752104000	-0.329247000	-2.269000000
7	-2.416681000	1.542955000	0.561173000
7	-2.522609000	-0.982154000	0.984809000
5	1.682855000	-0.035259000	-0.109753000
9	4.367734000	1.165964000	0.810593000
9	5.173569000	3.657441000	0.410280000
9	3.635259000	5.429083000	-1.005641000
9	1.223975000	4.596443000	-2.027214000
9	0.393527000	2.089625000	-1.666727000
9	3.058601000	0.545527000	-2.826413000
9	3.007413000	-1.033599000	-4.950364000
9	1.711945000	-3.445855000	-4.887244000
9	0.444546000	-4.231273000	-2.579096000
9	0.478388000	-2.668966000	-0.418641000
9	1.409677000	0.645220000	2.741991000
9	2.563073000	-0.548042000	4.820989000
9	4.330487000	-2.610708000	4.447800000
9	4.906165000	-3.443062000	1.899342000
9	3.774620000	-2.280446000	-0.200822000
6	-3.527053000	1.150342000	1.229047000
6	-4.519033000	2.078868000	1.607517000
1	-4.309023000	3.100032000	1.318671000

6	-5.726837000	1.926971000	2.286138000
1	-6.277962000	2.853643000	2.430916000
6	-6.327808000	0.779387000	2.798075000
1	-7.281332000	0.903521000	3.302916000
6	-5.820408000	-0.515409000	2.709921000
1	-6.435994000	-1.295111000	3.153203000
6	-4.638325000	-0.976510000	2.134843000
1	-4.506599000	-2.047473000	2.211402000
6	-3.585848000	-0.305703000	1.476452000
6	-2.146240000	2.951085000	0.213967000
1	-3.034073000	3.372977000	-0.276111000
1	-1.354353000	2.946972000	-0.537136000
6	-2.390036000	-2.447982000	1.079374000
1	-3.331774000	-2.908799000	0.753625000
1	-1.630577000	-2.745835000	0.353756000
6	-1.712549000	3.857079000	1.391656000
1	-2.507957000	3.854069000	2.148417000
6	-1.983279000	-2.995401000	2.468173000
1	-2.741959000	-2.693287000	3.202408000
6	-0.426274000	3.369441000	2.069372000
1	0.418474000	3.378275000	1.373062000
1	-0.520915000	2.350784000	2.453253000
1	-0.172586000	4.022180000	2.911295000
6	-1.565654000	5.295710000	0.868801000
1	-1.283344000	5.972071000	1.681867000
1	-2.499273000	5.670330000	0.431935000
1	-0.787187000	5.358919000	0.099400000
6	-0.630647000	-2.449178000	2.940455000

1	0.171028000	-2.736452000	2.252993000
1	-0.387252000	-2.847751000	3.930951000
1	-0.632685000	-1.357911000	3.011793000
6	-1.975900000	-4.531452000	2.400879000
1	-2.952427000	-4.933853000	2.105394000
1	-1.720983000	-4.957274000	3.376519000
1	-1.231901000	-4.888439000	1.678893000
6	-3.551697000	-0.448897000	-2.303511000
6	-4.334451000	0.701227000	-2.480671000
1	-3.853710000	1.671996000	-2.550089000
6	-5.723407000	0.591259000	-2.589407000
1	-6.323233000	1.485738000	-2.731607000
6	-6.336768000	-0.663728000	-2.532041000
1	-7.415542000	-0.747436000	-2.625601000
6	-5.555811000	-1.812095000	-2.370217000
1	-6.025006000	-2.791461000	-2.341530000
6	-4.166785000	-1.708618000	-2.256814000
1	-3.556847000	-2.600041000	-2.148646000
6	2.295355000	1.490811000	-0.350113000
6	3.521927000	1.967478000	0.123445000
6	3.985809000	3.268445000	-0.084158000
6	3.212757000	4.171156000	-0.804221000
6	1.991961000	3.744711000	-1.317314000
6	1.580170000	2.437835000	-1.084771000
6	1.728513000	-0.946459000	-1.498595000
6	2.369109000	-0.611924000	-2.696909000
6	2.376188000	-1.426749000	-3.830493000
6	1.724914000	-2.654329000	-3.804026000

6	1.084283000	-3.046895000	-2.633801000
6	1.107750000	-2.197957000	-1.534395000
6	2.463472000	-0.791667000	1.143956000
6	2.236705000	-0.393883000	2.466692000
6	2.841408000	-0.980393000	3.575152000
6	3.742266000	-2.024068000	3.392369000
6	4.026055000	-2.444826000	2.098793000
6	3.396041000	-1.825428000	1.019123000

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