# Supporting Information

*for*

## Access to diverse germylenes and a six-membered dialane with a flexible *β*-diketiminate

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**1. General Experimental Information.** All manipulations and experiments including NMR sample preparation were carried out under an inert atmosphere of argon applying standard Schlenk techniques or in a Glove box. The solvents used were purified by an MBRAUN solvent purification system as MB SPS-800. All chemicals purchased from Sigma Aldrich were used without further purification. Ligand **L** was prepared according to the literature procedure.[S1] $^1$H, $^{13}$C and $^{27}$Al NMR spectra were recorded in $C_6D_6$ or $CDCl_3$ using a Bruker Avance DPX 200 or a Bruker Avance DRX 500 spectrometer and were referenced to external SiMe$_4$. HRMS and LC-mass spectra were obtained using a Q Exactive Thermo Scientific and an Agilent Technologies 6120. Elemental analyses were performed at the CSIR-National Chemical Laboratory, Pune. Melting points were measured in a sealed glass tube on a Stuart SMP-30 melting point apparatus and were uncorrected.

**2. Synthesis and characterization of compound 1**

A solution of *n*-BuLi in *n*–hexane (3.93 mL, 6.29 mmol, 1.6 M) was added drop wise to a stirred solution of **L** (2,6-diisopropyl-N-((2Z,4E)-4-((pyridin-2-ylmethyl)imino)pent-2-en-2-yl)aniline) (2.0 g, 5.72 mmol, in THF 20 mL) at –78 °C, over a period of 10 min. The suspension was allowed to warm up to room temperature and stirred for 8 h. Next, the solution of GeCl$_2$·dioxane (1.39 g, 6.0 mmol) in THF was added drop by drop to the above suspension at –30 °C via cannula. The reaction mixture was further warmed to room temperature and stirred for another 15 h. Subsequently, all volatiles were removed in vacuo and the residue was extracted into toluene (30 mL). The resultant toluene solvent was concentrated to 10–12 mL and stored at –30 °C in a freezer, which afforded colorless crystals of **1** within one day. Yield: 2.57 g (98.4%). M.p.: 218 °C. Anal. Calcd: C, 60.10; H, 7.24; N, 9.14. Found: C, 59.89; H, 6.59; N, 8.89. $^1$H NMR (400 MHz, $C_6D_6$, 25 °C): $\delta$ 8.38 (d, J = 4.9 Hz, 1H), 7.18 (d, J = 4.9 Hz, 2H), 7.05 (dd, J = 12.4, 4.9 Hz, 3H), 6.59 (dd, J = 8.1, 5.4 Hz, 1H), 5.21 (s, 1H), 4.78 (s, 2H), 4.01 – 3.87 (m, 1H), 2.81 (hept, J = 6.9 Hz, 1H), 1.82 (s, 3H),

1.62 (s, 3H), 1.54 (d, J = 6.6 Hz, 3H), 1.23 (d, J = 6.9 Hz, 3H), 1.02 (dd, J = 11.3, 6.9 Hz, 6H)

ppm. $^{13}$C NMR (100.56 MHz, $C_6D_6$, 25 °C); $\delta$ 166.09, 163.71, 158.65, 149.79, 146.77, 144.42, 140.18, 136.36, 125.13, 124.00, 122.14, 121.96, 102.50, 54.98, 28.53, 28.42, 27.42, 25.09, 24.09, 23.99, 22.94, 22.47 ppm. LC-MS: Calcd: 456.59, found: 456.1696.
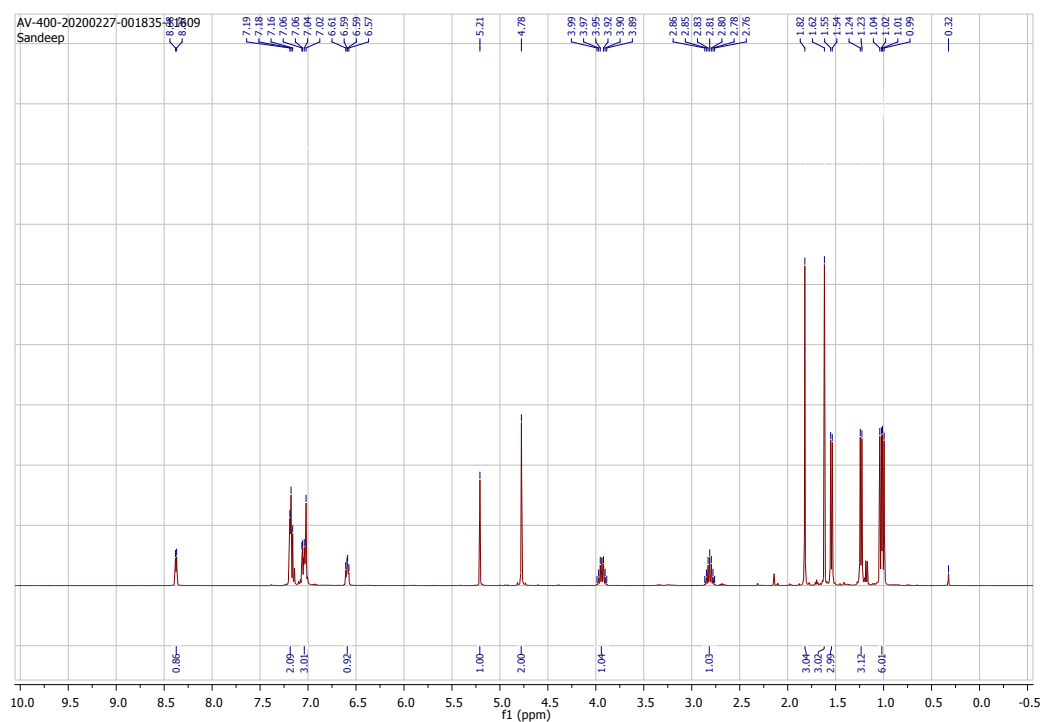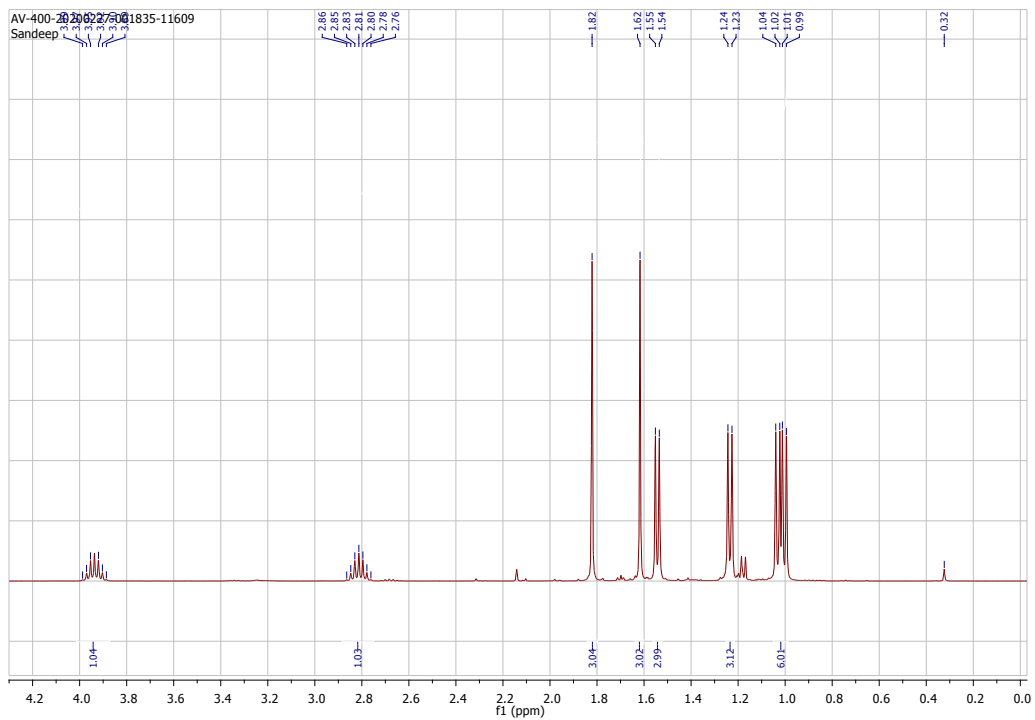


Figure S1. $^1$H NMR of **1**

3.92
3.91
3.90
3.89
3.88
3.87

2.86
2.85
2.83
2.81
2.80
2.78
2.76

1.82

1.62
1.55
1.54

1.24
1.23

1.04
1.02
1.01
0.99

0.32

1.04

1.03

3.04

3.02
2.99

3.12

6.01

f1 (ppm)

Figure S2. $^1$H NMR of **1**(zoom in)

166.88
163.72
158

149.79
146.77
144.42
140.18
136.36

128.30
128.06
127.82
125.13
124.00
122.14
121.96

102.50
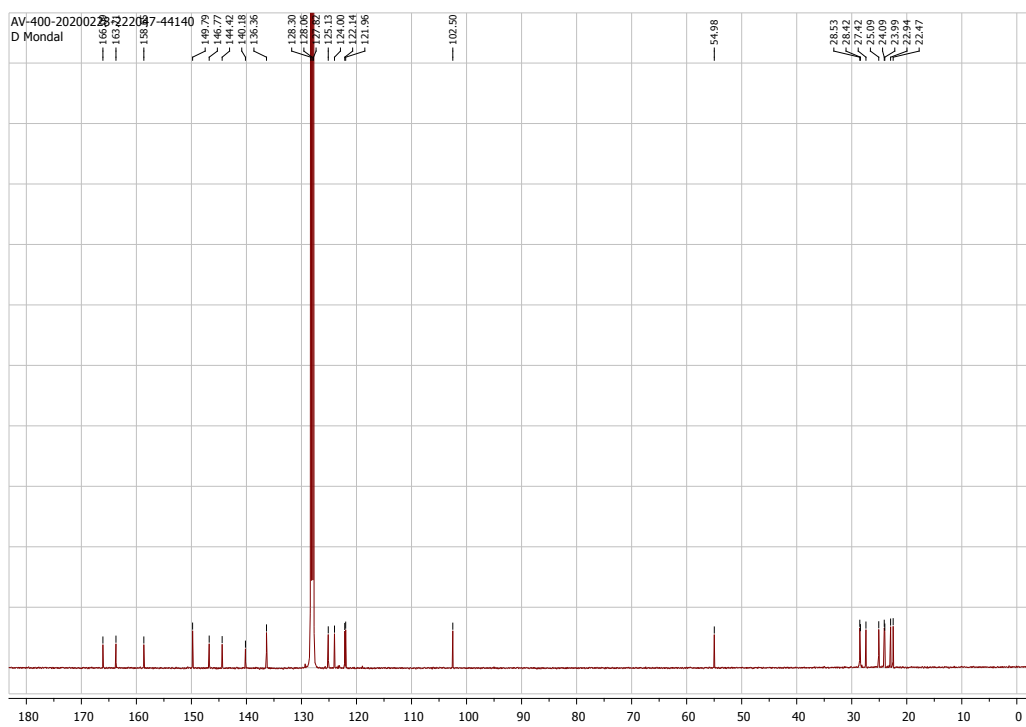
54.98

28.53
28.42
27.42
25.09
24.09
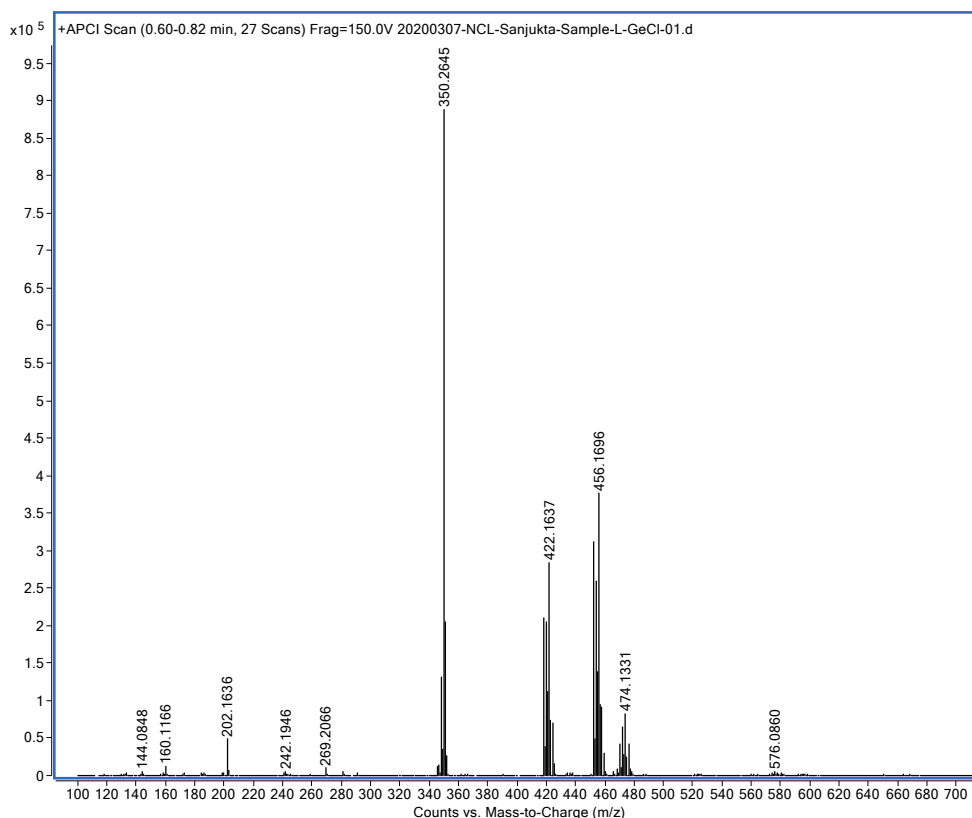23.99
22.94
22.47

Figure S3. $^{13}$C NMR of compound **1**

Figure S4. LC-MS of compound **1**

### 3. Synthesis and characterization of compound 2 and 3.

To a stirred solution of **1** (0.457 g, 1.0 mmol, in THF 10 mL) at −78 °C was added drop wise GeCl$_2$·dioxane in THF (0.243 g, 1.05 mmol) over a period of 5 min. The solution was allowed to come to room temperature and stirred for 15 h. All volatiles were removed under reduced pressure and the residue was washed with *n*-pentane (5 mL), and extracted with toluene of about 15 mL. The solvent was concentrated to 5 to 8 mL and stored at −30 °C in a freezer overnight to afford colorless crystals of **2** suitable for X-ray analysis. Yield: 0.13 g (46 %). M.p.: 186 °C. Anal. Calcd.: C, 47.30; H, 3.97; N, 10.03. Found: C, 46.72; H, 3.46; N, 9.47. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta$ 8.22 (d, $J$ = 5.8 Hz, 1H), 7.75 (t, $J$ = 8.6 Hz, 1H), 7.50 (d, $J$ = 8.5 Hz, 1H), 6.98 (t, $J$ = 6.5 Hz, 1H), 5.91 (s, 1H), 2.40 (s, 3H), 2.34 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$, 25 °C); $\delta$ 151.50, 143.39, 141.10, 140.23, 130.07, 126.67, 118.23, 117.87, 116.01, 15.10, 13.23 ppm. LC-MS: Calcd: 279.30, found: 279.0006.

The undissolved part remained in toluene was further extracted with THF (2 × 10 mL) and stored at −30 °C in a freezer overnight to grow the suitable colorless crystals for X-ray analysis of compound **3**. The low solubility of **3** in most of the organic solvents prevents NMR spectroscopic measurement. M.p.: 145 °C Anal. Calcd.: C, 44.93; H, 5.97; N, 4.37. Found: C, 44.26; H, 5.31; N, 4.68.
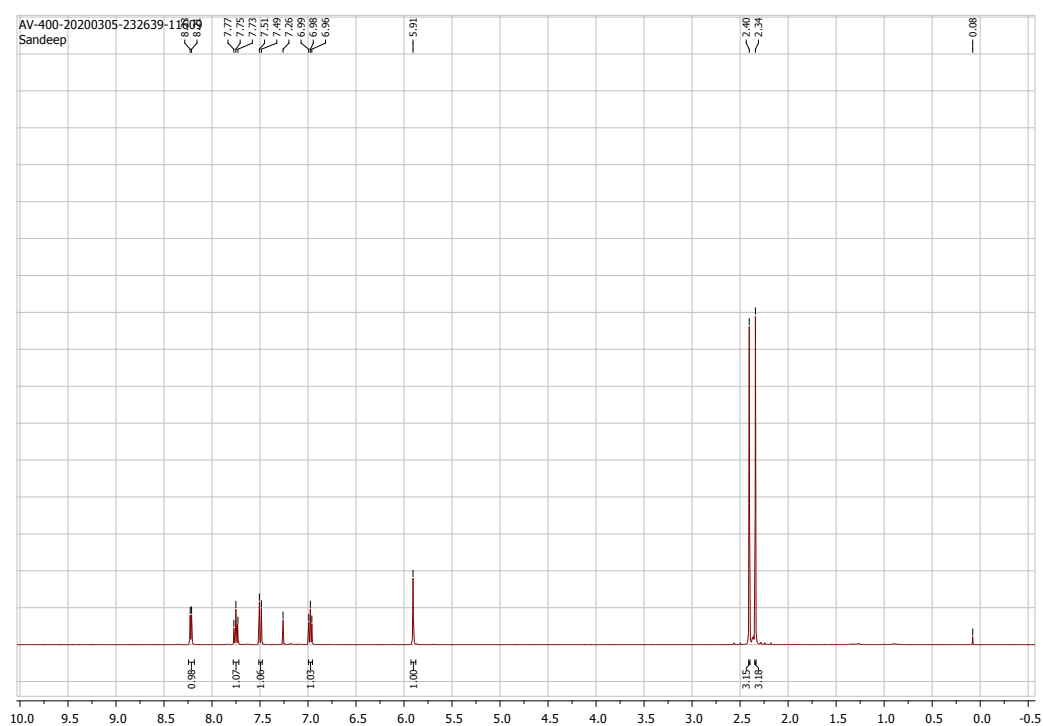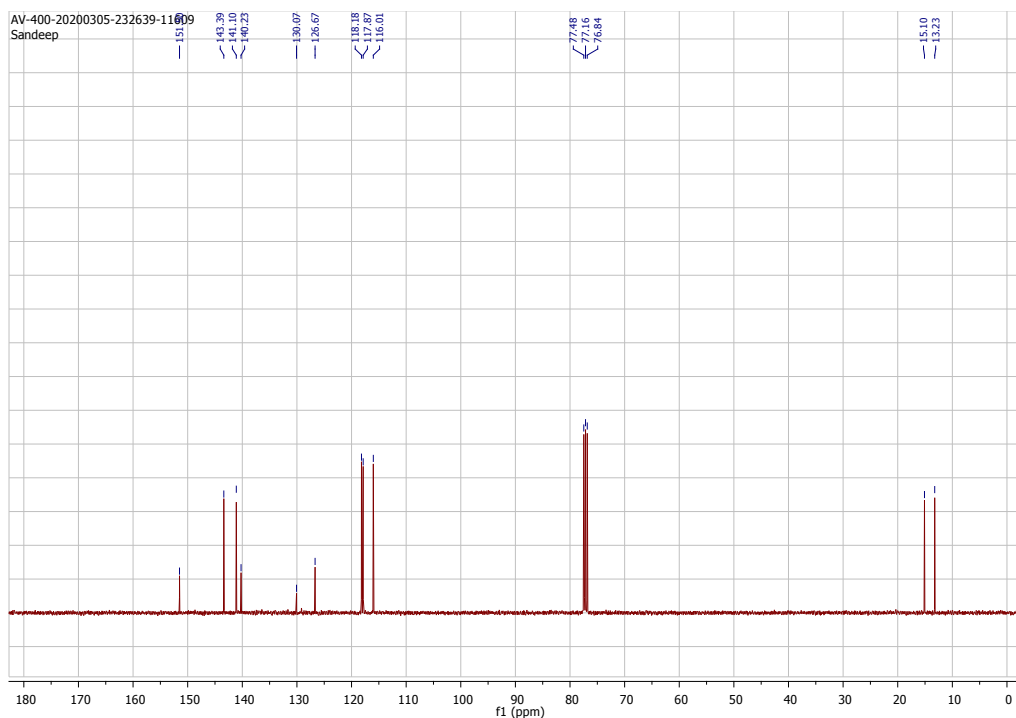


Figure S5. $^1$H NMR of compound **2**

Figure S6. $^{13}$C NMR of compound **2**



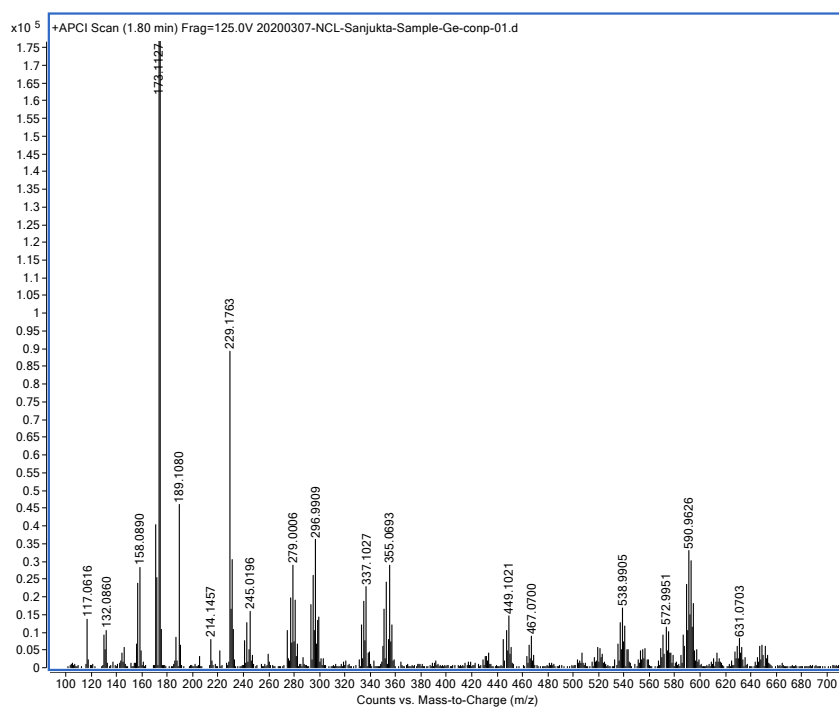Figure S7. LC-MS of compound **2**

## 4. Synthesis and characterization of compound 4.

To a stirred solution of **1** (0.457 g, 1.0 mmol) in THF (10 mL) at –78 °C was added drop wise

AlCl$_3$ (0.140 g, 1.05 mmol, THF 10 mL) over a period of 5 min. The solution was warmed to

room temperature and stirred for 15 h. All volatiles were removed under reduced pressure and extracted with *n*-heaxne (2 × 15 mL). The solvent was reduced to 5 mL and stored at −30 °C in a freezer overnight to obtain the yellow crystals of **4** suitable for X-ray analysis. Yield: 0.42 g (94.67 %). M.p.: 267 °C. Anal. Calcd: C, 61.18; H, 7.40; N, 9.35. Found: C, 61.42; H, 6.70; N, 8.56. $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): δ 8.89 (d, *J* = 4.6 Hz, 1H), 7.85 (t, *J* = 8.5 Hz, 1H), 7.39 (t, *J* = 6.4 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.24 −7.20 (m, 1H), 7.18 (d, *J* = 7.0 Hz, 1H), 7.13 (d, *J* = 7.1 Hz, 2H), 5.30 (s, 1H), 4.88 (s, 2H), 3.22 (dq, *J* = 13.6, 6.8 Hz, 2H), 2.30 (s, 3H), 1.76 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 6H), 1.13 (d, *J* = 6.9 Hz, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$, 25 °C): δ 171.25, 166.44, 154.52, 147.91, 145.18, 143.65, 139.57, 138.01, 129.17, 128.36, 126.12, 125.43, 123.66, 123.42, 121.02, 99.87, 50.89, 28.29, 25.38, 24.92, 24.60, 24.04 ppm. HRMS: Calcd.: 446.1705, found: 446.2590.
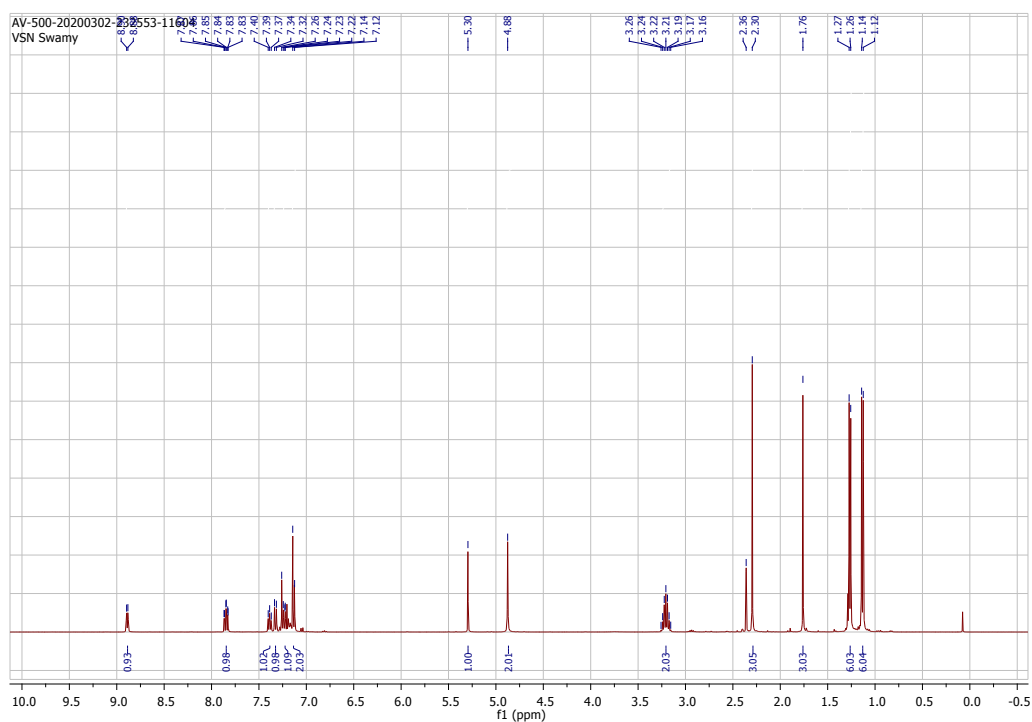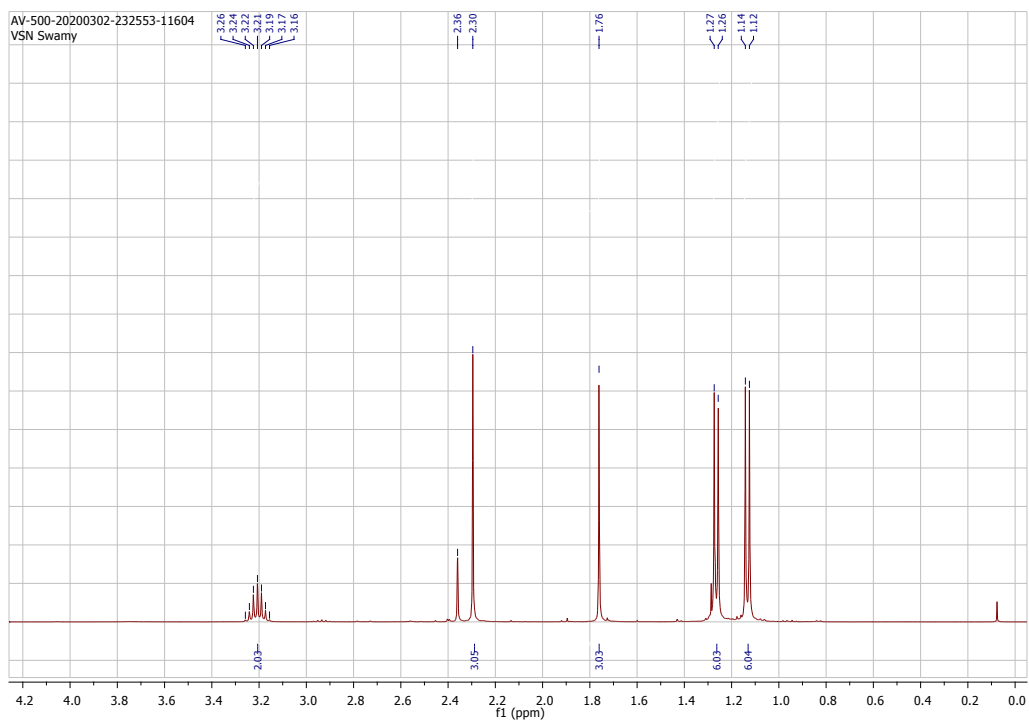


Figure S8. $^1$H NMR of compound **4**

Figure S9. ¹H NMR of compound **4** (zoom in)
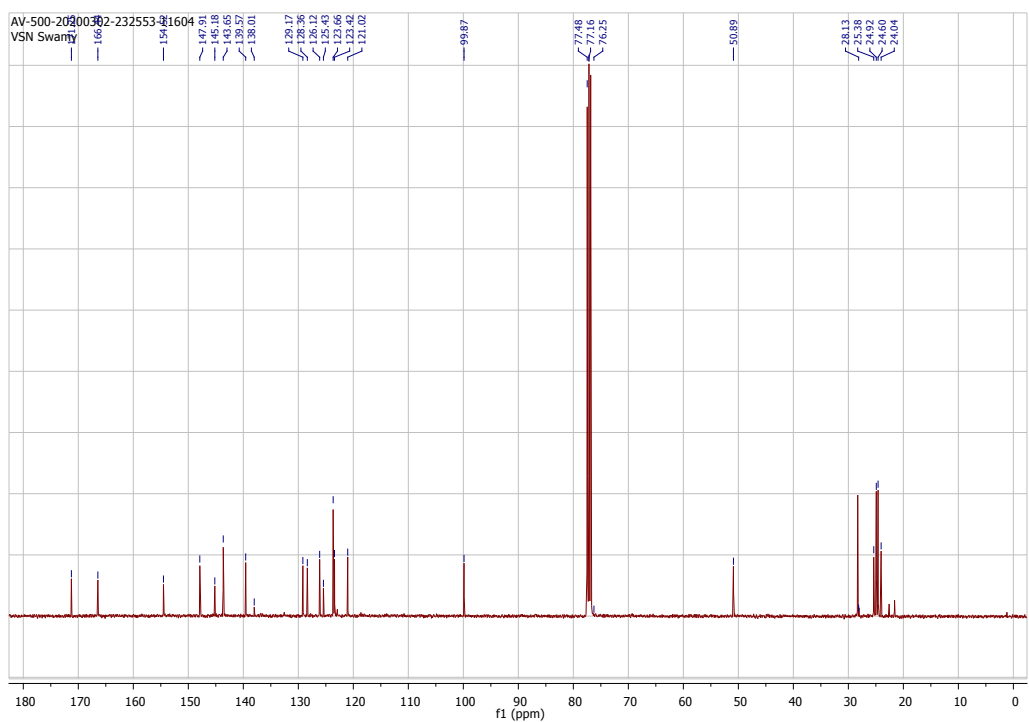
Figure S10. ¹³C NMR of compound **4**

446.2590
R=51207
$C_{23} H_{31} N_3 Al Cl_2$ = 446.1705
198.3363 ppm

447.2618
R=46800
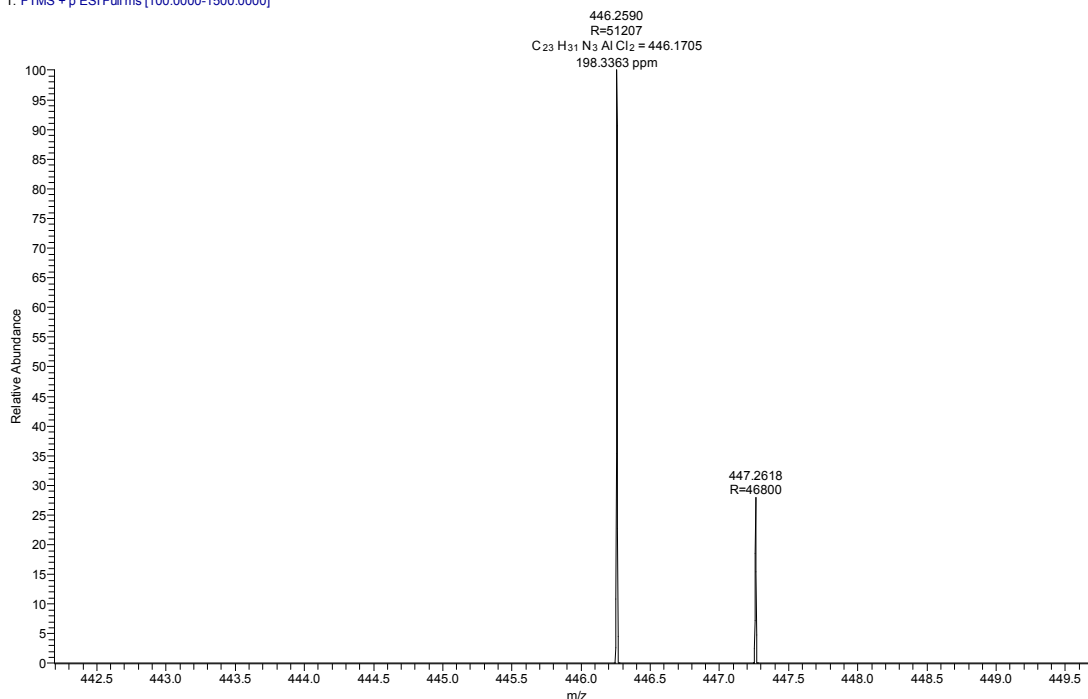
Figure S11. HRMS of compound **4**

## 5. Synthesis and characterization of compound 5

A toluene solution of $AlH_3 \cdot NMe_2Et$ (4.80 mL, 2.40 mmol, 0.5 M) was cooled down to −78 °C and was added drop by drop to a stirred solution of the toluene solution (10 mL) of the ligand **L** (0.70 g, 2.00 mmol), *via* cannula at −78 °C. The reaction mixture was allowed to warm to room temperature and left for stirring overnight. The solution was removed under reduced pressure and washed the residue with *n*-hexane (2 × 10 mL) and extracted with toluene (20 mL). The toluene was reduced to 10 mL and *n*-hexane (4 mL) was added to it drop by drop till the solution becomes turbid. The solution was kept at −30 °C in a freezer for two days to obtain colorless crystals of **5**. Yield: 1.26 g (84%). M.p.: 234 °C. Anal. Calcd: C, 61.67; H, 6.12; N, 19.62. Found: C, 62.05; H, 7.02; N, 19.87. HRMS: Calcd: 750.45, found: 375.2787 (Half fragment). IR (Nujol, mull, cm$^{-1}$): 1693 and 1743 (Al–H). The clean resonance for the $^1$H NMR could not be observed due to the insolubility of **5** in common organic solvents and also could be due to the partial decomposition into an unidentified mixture within a few days at room temperature.
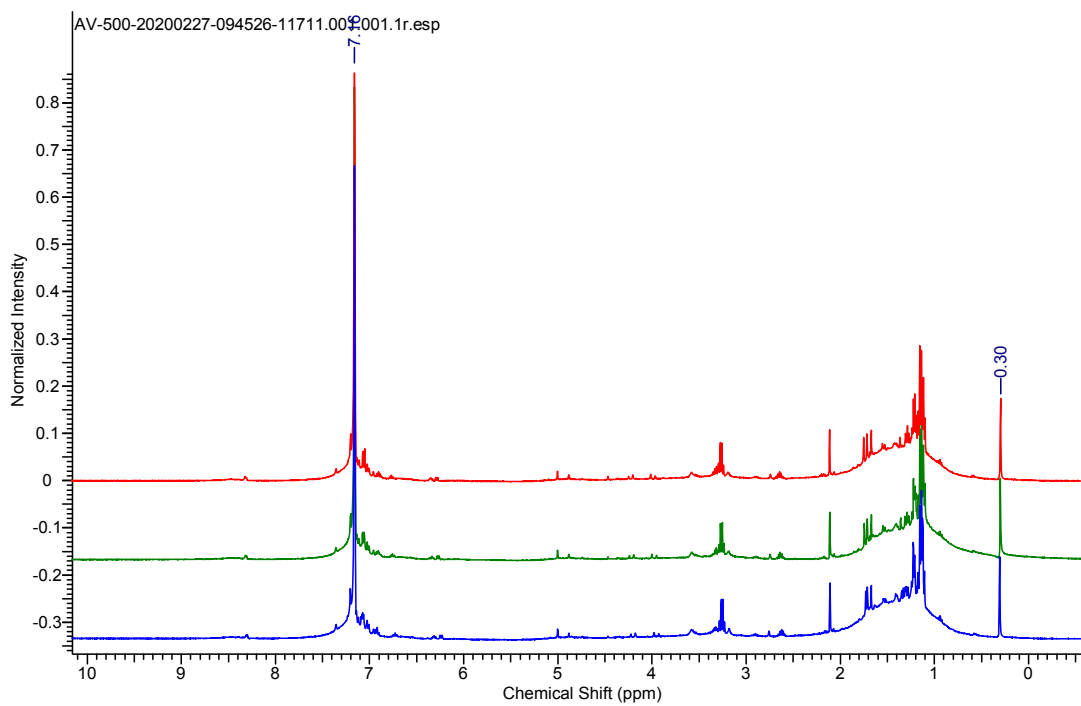
Figure S12. Variable temperature NMR of **5** in $C_6D_6$
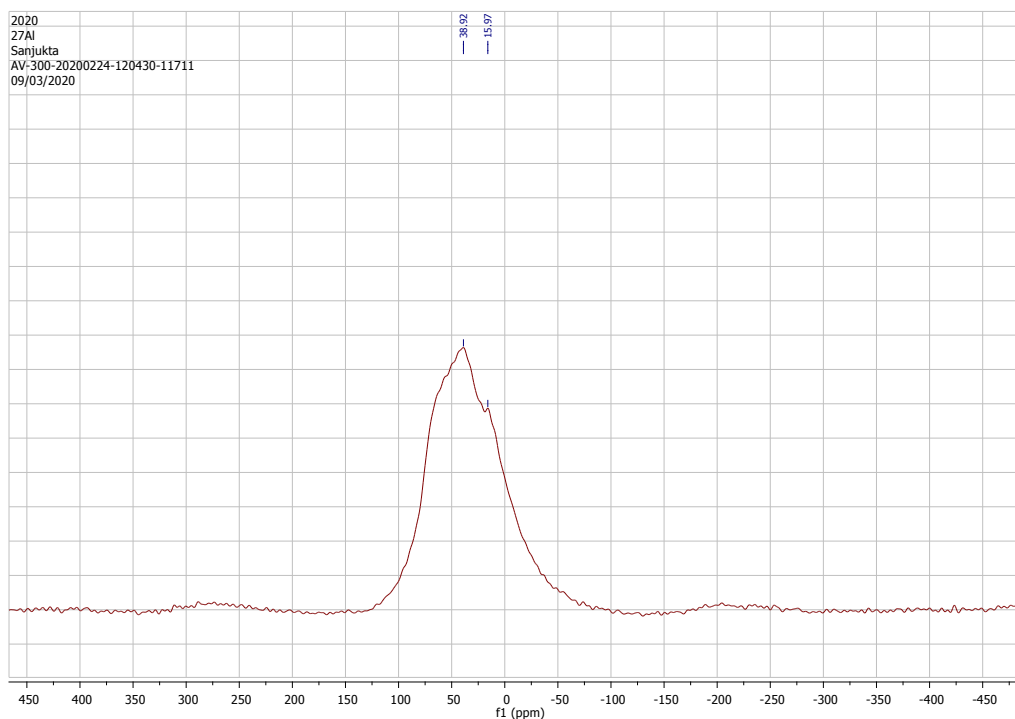


Figure S13. $^{27}Al$ NMR of compound **5**

L-AlH3_200227151010 #242 RT: 1.30 AV: 1 NL: 5.31E6
T: FTMS + p ESI Full ms [100.0000-1500.0000]

376.2736
R=56307
C 22 H 43 N 3 Al = 376.3267
-141.1159 ppm

378.2896
R=56102

380.3050
R=53702

375.2787
R=51602
C 22 H 42 N 3 Al = 375.3189
-107.1397 ppm

379.1093
R=55002

377.2772
R=45200

374.3160
R=48100
C 22 H 41 N 3 Al = 374.3110
13.2810 ppm

Relative Abundance

m/z
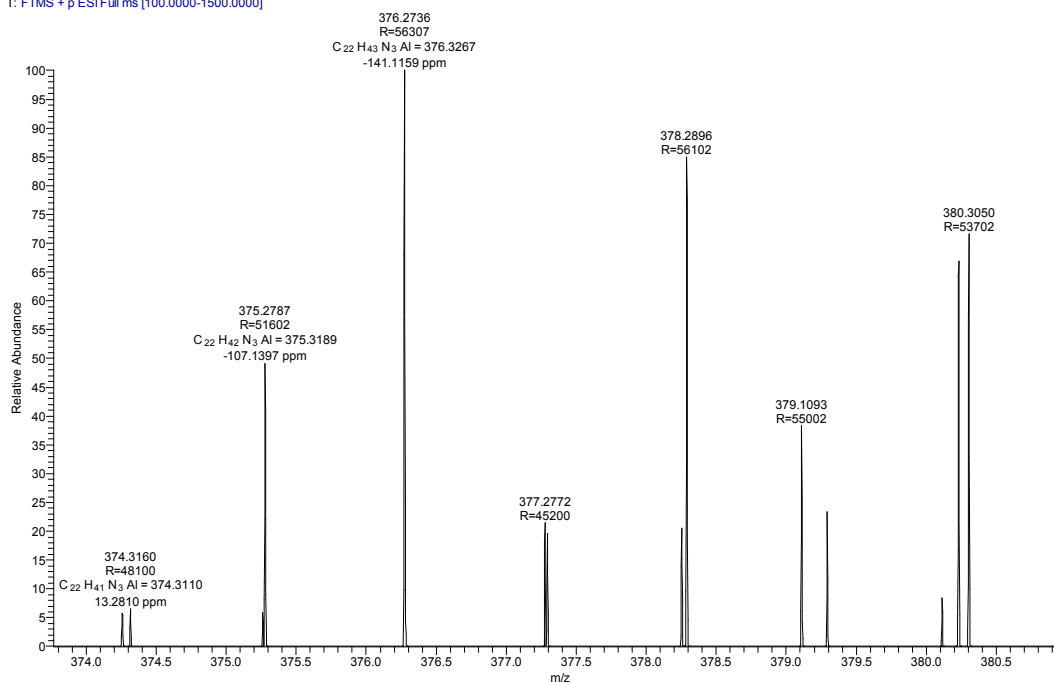
Figure S14. HRMS of compound **5**

## 6. Crystallographic data for the structural analysis of compounds 1-5

Good quality single crystals suitable for single-crystal X-ray diffraction analysis were selected using Leica polarizing microscope (S8 APO) and then mounted in the diffractometer. The X-ray intensity data for each compound were measured on a Bruker II CCD diffractometer with graphite-monochromatized (MoK$_\alpha$= 0.71073 Å) radiation at 100-150(2) K. The intensity measurements were carried out with Mo fine focus sealed tube diffraction source (Mo-Kα = 0.71073 Å) and the generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from a total of 36 frames (matrix, three runs, each run comprised of 12 frames). The full intensity data were collected using an optimized strategy that consisted of different sets of $\omega$, $\varphi$ and 2$\theta$ with 0.5° width keeping the sample-to-detector distance fixed at 5.00 cm with varying exposure time (10-20 Sec) depending on the diffraction power of the crystals. The whole process of X-ray data acquisition (unit–cell measurements and data collection) was controlled and monitored by the APEX2 program suite of Bruker-AXS.[S2] The complete data sets were corrected for Lorentz-

polarization and absorption effects (multi-scan method) by using SAINT[S3] and SADABS[S4] programs with the transmission coefficients. Using the APEX3[S5] program suite, the structure was solved with the ShelXS-97[S6] structure solution program, using direct methods. The model was refined with a version of ShelXL-2013[S7] using Least Squares minimization based on $F^2$. All non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were refined isotropically by placing them in a geometrically idealized position and constrained to ride on their parent atoms. An ORTEP III[S8] views of all the molecules were drawn at the 50% probability displacement ellipsoids, and H atoms are shown as small spheres of arbitrary radii.

The crystal structure of compound **1** belongs to monoclinic $P2_1/n$ space group whereas crystal structure of compounds **2**, **3** and **5** crystallized in the triclinic centrosymmetric $P$-1 space group comprising one molecule in the asymmetric unit. On the other hand crystal structure of compound **4** belongs to monoclinic $P2_1/c$ space group containing one molecule of the complex along with two molecules of solvent benzene moiety. Both solvent molecules have 0.75% occupancy in the crystal structure. In the crystal structure of compound **5**, both pyridine rings displays disorder over two positions which has been restrained to equal occupancies (50:50) using PART instructions during refinement. Further, the crystal structure contained the highly disordered THF (tetrahydrofuran) solvent molecule, which has been squeezed for better convergence. The PLATON/SQUEEZE was used to correct the diffraction data for the contribution from disordered lattice solvent (THF) molecules. The solvent accessible void volume per unit cell was 281 $A^3$ (12%) and Electron Count/unit Cell was 59 e/$Å^{-3}$, estimated by PLATON. This electron count corresponds to one and half (1.5) disordered THF molecules per unit cell (0.75 occupancy in the asymmetric unit). However, they have been included in SFAC and UNIT instructions to compute the correct molecular formula, formula weight, crystal density, etc.

Table 1.Crystallographic data for compounds **1-5**.

| Crystal data | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Chemical formula | $C_{23}H_{30}Cl_1Ge_1N_3$ | $C_{11}H_{11}Cl_1Ge_1N_2$ | $C_{12}H_{19}Cl_2Ge_1N_1$ | $C_{23}H_{30}Al_1Cl_2N_3 2 (C_6H_6)$ | $C_{46}H_{58}Al_2N_6$ |
| Formula weight,$(M_r)$ | 456.54 | 279.28 | 320.77 | 602.60 | 748.94 |
| Crystal system, space group | Monoclinic, $P2_1/n$ | Triclinic, $P$-1 | Triclinic, $P$-1 | Monoclinic, $P2_1/c$ | Triclinic, $P$-1 |
| Temperature (K) | 105(2) | 100(2) | 296(2) | 100(2) | 100(2) |
| $a$, (Å) $b$, (Å) $c$ (Å) | 10.7669(4), 11.2877(4), 18.6038(7) | 7.9051(3), 8.8862(4), 9.0373(4) | 8.8999(6), 9.3908(7), 9.8279(7) | 17.2631(13), 10.6231(7), 18.1589(13) | 8.8257(6), 15.7134(10), 17.6385(11) |
| $\alpha$, (°) $\beta$, (°) $\gamma$ (°) | 90, 96.881(2), 90 | 67.589(2), 74.175(2), 77.444(2) | 91.216(2), 109.977(2), 110.198(2) | 90, 103.330(3), 90 | 82.476(2), 76.292(2), 75.862(2) |
| $V$ (Å$^3$) | 2244.70(14 | 560.04(4) | 715.42 (9) | 3240.4(4) | 2297.5(3) |
| $Z$ | 4 | 2 | 2 | 4 | 2 |
| $D_{calc}$ (g cm$^{-3}$) | 1.351 | 1.656 | 1.489 | 1.235 | 1.167 |
| $\mu$(mm$^{-1}$) | 0.098 | 2.939 | 2.490 | 0.256 | 0.105 |
| $F(000)$ | 952 | 280 | 328 | 1280 | 868 |
| Crystal size (mm) | 0.36×0.28×0.16 | 0.36×0.28×0.16 | 0.38×0.28×0.16 | 0.32×0.28×0.12 | 0.36×0.26×0.16 |
| Absorption correction | multi-scan | multi-scan | multi-scan | multi-scan | multi-scan |
| $T_{min}$, $T_{max}$ | 0.578, 0.787 | 0.334, 0.589 | 0.451, 0.691 | 0.921, 0.970 | 0.978, 0.991 |
| Total reflns. | 33365 | 8276 | 26002 | 140823 | 95322 |
| Independent reflns. | 3954 | 1979 | 2523 | 5699 | 8597 |
| Obs.reflns. | 3576 | 1928 | 2355 | 4941 | 7467 |
| $R_{int}$ | 0.0383 | 0.0292 | 0.0445 | 0.0788 | 0.0649 |
| $R_{sig}$ | 0.0205 | 0.0230 | 0.0206 | 0.0211 | 0.0312 |
| $2\theta_{max}$(°) | 50 | 50 | 50 | 50 | 51.23 |
| $R[F^2> 2\sigma(F^2)]$, $wR2[F^2> 2\sigma(F^2)]$ | 0.0249, 0.0674, | 0.0178, 0.0451 | 0.0169, 0.0383 | 0.0323, 0.0793 | 0.0485, 0.1112 |
| $R$(all data), $wR2$(all data) | 0.0292, 0.0595 | 0.0183, 0.0454 | 0.0206, 0.0399 | 0.0406, 0.0862 | 0.0594, 0.1165 |
| goodness-of-fit ($S$) | 1.038 | 1.082 | 1.061 | 1.052 | 1.073 |
| No. of parameters No. of restraints | 260, 0 | 139, 0 | 222 | 377 0 | 626 12 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.732, -0.964 | 0.288, -0.263 | 0.338, −0.220 | 0.856, −0.224 | 0.681, −0.241 |
| CCDC Nos. | 2000072 | 2000154 | 2000073 | 2000071 | 2002736 |
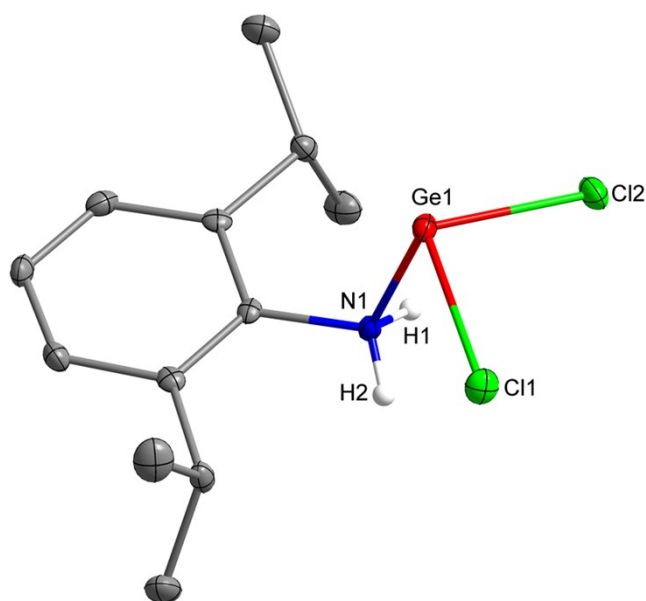
Figure S15. Molecular structure of compound **3** with anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and bond angles (°):Cl1 Ge1 2.2744(4), Cl2 Ge1 2.2793(4), Ge1 N1 2.1674(14); N1 Ge1 Cl1 90.63(4), N1 Ge1 Cl2 90.78(4), Cl1 Ge1 Cl2 95.903(16).

## 7. Details of theoretical calculations

All the geometry optimization in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 7.1 suite of programs,[S9] using the PBE functional.[S10] The TZVP[S11] basis set has been employed. The resolution of identity (RI),[S12] along with the multipole accelerated resolution of identity (marij)[S13] approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Dispersion correction (disp3) and solvent correction were incorporated with optimization calculations using the COSMO model,[S14] with toluene ($\varepsilon = 2.38$) as the solvent. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima. The single point energy calculation of all the PBE/TZVP optimized compounds have been performed with M06-2X/6-311+G(d) level of theory using Gaussian09[S15] software packages.

The nature of germanium-ligand and aluminium-ligand interaction in compound **2** and compound **5** was investigated with the natural bond orbitals (NBO) analysis procedures as implemented in the Gaussian 09 program. The analyses was performed at the PBE/TZVP optimized geometry using the M06-2X density functional together with the all electron 6-311+g(d) basis set. In order to gain insight into the interaction of the carbon and nitrogen donor ligand with the central germanium and aluminium atom, the intermolecular charge transfer in the complex has been analysed with the natural bond orbital (NBO) analysis. The energetic estimate of donor (i) – acceptor (j) orbital interactions can be obtained by the second order perturbation theory analysis of the Fock matrix in the NBO basis. The donor–acceptor interaction energy E(2) is given by

$$E(2) = \Delta E(i,j) = q(i,j)F(i,j)2/\{\varepsilon(i) - \varepsilon(j)\}$$

where q(i) is the donor orbital occupancy, $\varepsilon(i)$ and $\varepsilon(j)$ are the diagonal elements (orbital energies), and F(i,j) is the off-diagonal NBO Fock matrix element. In the present investigation, the important interactions between the central germanium and aluminium with the ligands have been analyzed. With the NBO analysis we have also performed NLMO and WBI bond order analysis.



| HOMO | LUMO |

Figure S16. HOMO and LUMO of Compound **1.** HOMO-LUMO energy gap 6.48 eV
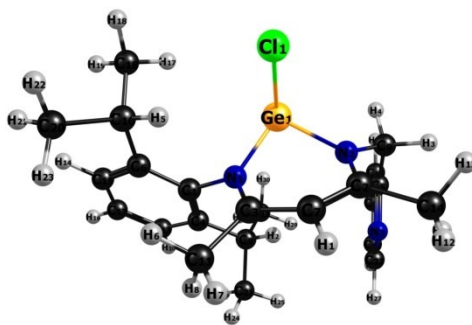
Figure S17. PBE/TZVP optimized geometry of compound **1.** Bond lengths (Å) and bond angles (°) Ge1-Cl1 2.31; Ge1-N1 1.99; Ge1-N2 1.98; N1-Ge1-N2 88.0; N1-Ge1-Cl1 94.8; N2-Ge1-Cl1 95.0.



HOMO                    LUMO

Figure S18. HOMO and LUMO of Compound **2.** HOMO-LUMO energy gap 5.48 eV.
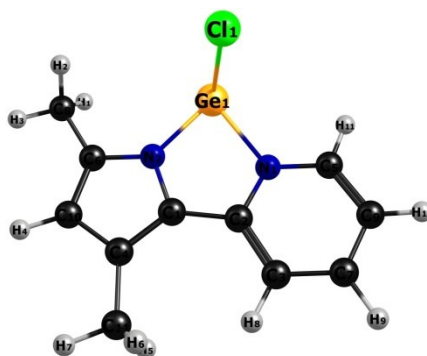


Figure S19.PBE/TZVP optimized geometry of compound **2**. Bond lengths (Å) and bond angles (°) Ge1-Cl1 2.29; Ge1-N1 2.12; Ge1-N2 1.99; N2-C5 1.39; N1-C4 1.37; C4-C5 1.42; N1-Ge1-Cl1 92.9; N2-Ge1-Cl1 96.2; N1-Ge1-N2 78.1.

Table S1. Results of the NBO analysis for the compound **2** computed at the M06-2X/6-311+G(d) Level of Theory: natural occupation and natural charges at germanium (Q in e), stabilization energies ($\Delta E(2)$ in kcal/mol) associated with the most important donor-acceptor interactions, WBI and NLMO bond orders

| Compound | Ge natural occupation | | | | $Q_{NBO}$ | charge transfer | | | | bond order | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4s | 4p | 4d | 5s | | donor | occu | acceptor | occu | E(2) | WBI | NLMO |
| **2** | 1.70 | 1.20 | 0.01 | 0.01 | 1.08 | N3 | 1.77 | Ge1 | 0.22 | 61.8 | 0.35 | 0.38 |
| | | | | | | N4 | 1.73 | Ge1 | 0.27 | 84.0 | 0.45 | 0.48 |
| | | | | | | Cl2 | 1.63 | Ge1 | 0.44 | 178.6 | 0.71 | 0.59 |



(**a**)          (**b**)          (**c**)
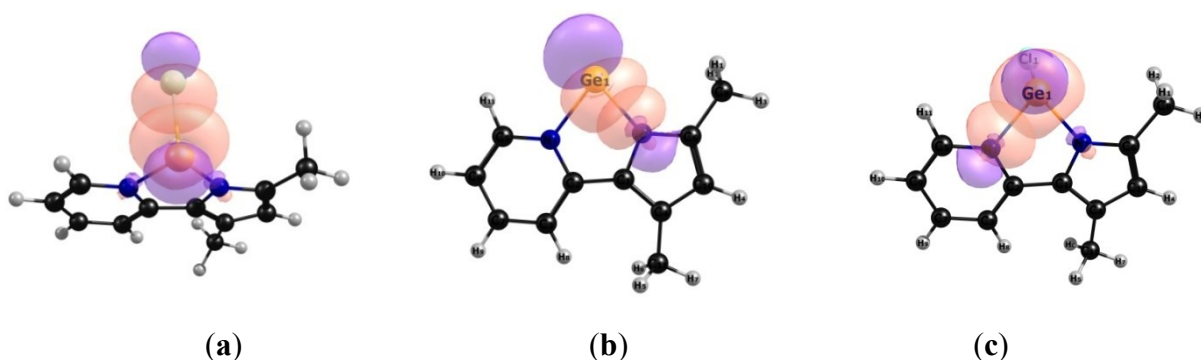
Figure S20.Selective natural bonding orbital interaction in compound **2. (a)** LP (4)Cl→ LP*(2) Ge, (**b**) LP (1) N→LP*(4) Ge, (**c**) LP (1) N→LP*(3) Ge.
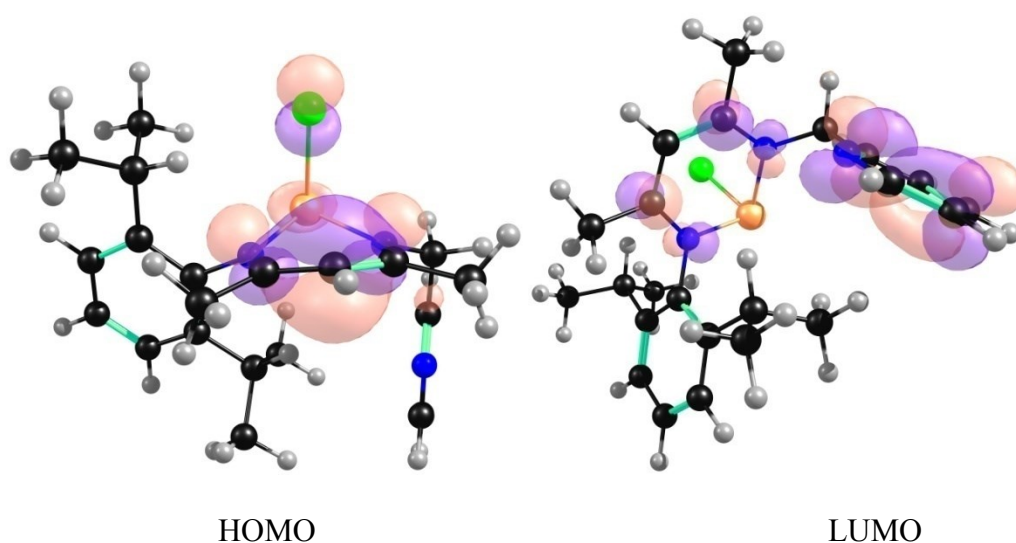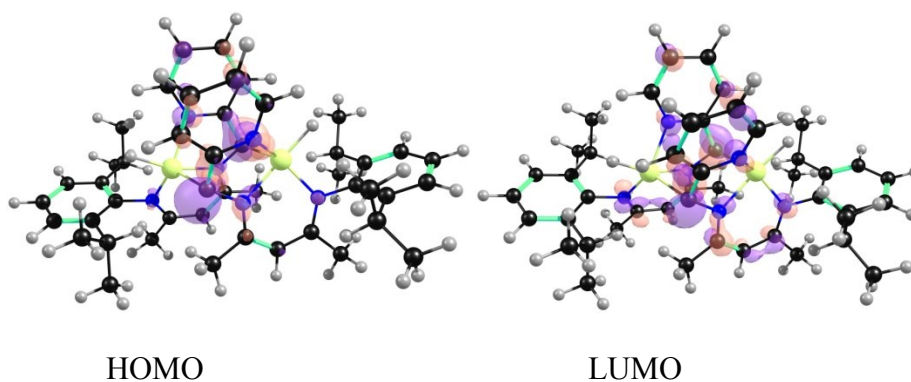


HOMO          LUMO
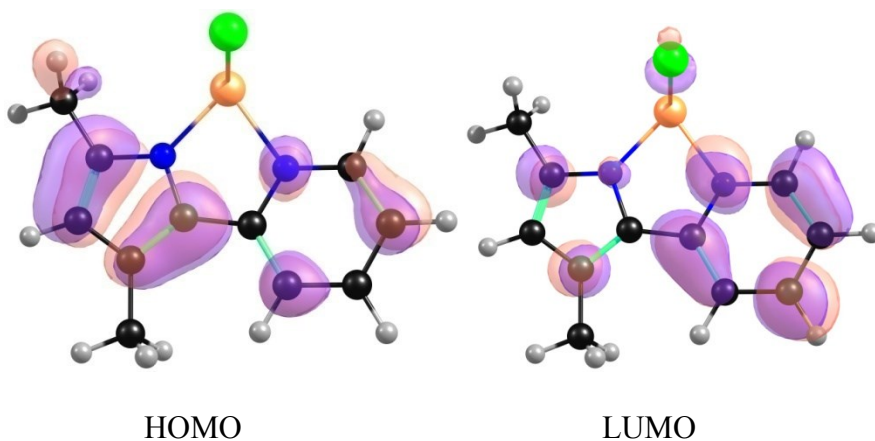
Figure S21. HOMO and LUMO of Compound **5** with a HOMO-LUMO energy gap 2.72 eV.
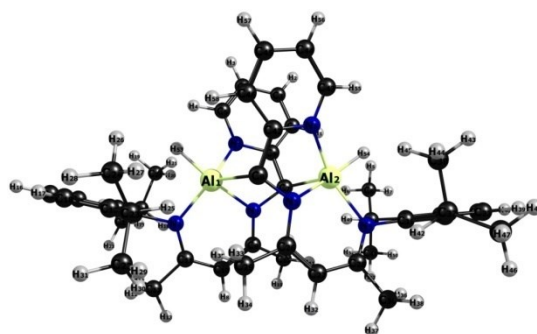
Figure S22. PBE/TZVP optimized geometry of compound **5**. Bond lengths (Å) and bond angles (°) Al1-N2 1.99; AL1-C8 2.22; Al1-H53 1.62; Al1-N1 1.97; Al1-N4 1.93; Al2-N3 2.17; Al2-C7 2.00; Al2-H54 1.61; Al2-N6 2.06; Al2-N5 2.00; N3-C8 1.45; N2-C7 1.32

Table S2.Results of the NBO analysis for the compound **5** computed at the M06-2X/6-311+G(d) Level of Theory: natural occupation and natural charges at aluminium (Q in e), stabilization energies ($\Delta E(2)$ in kcal/mol) associated with the most important donor-acceptor interactions, WBI and NLMO bond orders.

| Compound | Al natural occupation | | | | $Q_{NBO}$ | charge transfer | | | | bond order | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3s | 3p | 3d | 4s | | donor | occu. | acceptor | occu | E(2) | WBI | NLMO |
| Al15 | 0.54 | 0.80 | 0.02 | 0.01 | 1.64 | N1 | 1.82 | Al15 | 0.21 | 60.2 | 0.26 | 0.36 |
| | | | | | | N17 | 1.82 | Al15 | 0.31 | 89.4 | 0.24 | 0.35 |
| | | | | | | N19 | 1.80 | Al15 | 0.31 | 58.5 | 0.30 | 0.39 |
| **5** | | | | | | C22 | 1.69 | Al15 | 0.31 | 25.7 | 0.37 | 0.44 |
| | | | | | | | | | | | | |
| Al16 | 0.58 | 0.80 | 0.02 | 0.01 | 1.59 | N18 | 1.80 | Al16 | 0.39 | 33.0 | 0.21 | 0.29 |
| | | | | | | N20 | 1.82 | Al16 | 0.17 | 50.8 | 0.24 | 0.34 |
| | | | | | | N104 | 1.84 | Al16 | 0.25 | 34.5 | 0.21 | 0.30 |
| | | | | | | C21 | 1.64 | Al16 | 0.39 | 134.1 | 0.53 | 0.60 |

**(I) Further Analysis of Compound 2.** The difference in donation between the pyrrole and pyridine nitrogen donors can be ascribed to the nature of the donor atom and to the Ge−N

bond distance. In compound **2**, the two Ge–N bond distances for pyrrole and the pyridine ligands are 1.98 Å and 2.07 Å and the N1–Ge1–N2 bond angle is 78.7°, which is consistent with the X-ray crystal data. In the above explained bonding interaction, the lone pair on the nitrogen and chloride donors, with an occupancy of more than 1.60e, have interactions with the Ge with occupancies less than 0.5e, which indicates strong donor-acceptor interactions between ligands and the metal centre. We have also computed the NLMO and WBI bond orders (Table S1) analysis, the values (~0.4 for Ge-N and ~0.7 for Ge-Cl) of which suggest that the Ge-Cl bond has some covalent character but in Ge-N bonds there are ionic or dative type interactions present. Furthermore, DFT calculations reveal that in **2**, both the HOMO and LUMO are localized over the five and six membered rings and both of them are pi in nature. The HOMO−LUMO energy gap for **1** has been determined to be 5.48 eV.

**(II) Analysis of Compound 5.** The NBO analysis of **5** revealed that the contribution of the 3d orbital of the Al centre towards the bonding is very small: the natural occupation in the 3d shell of the two Al centres is equal to 0.02; thus the total 3d population is distinctly smaller than that required for a formal $sp^3d$ hybridization (ESI, Table S2). A stabilizing electronic effect responsible for the formation of chemical bonds is the transfer of charge from the ligands to the metal ion. The NBO charges of the two Al atoms are 1.59e and 1.64e. The dominant ionic character of the Al−ligand bonds is also evident in the localized Lewis-like description of the bonding pattern. In the Lewis structure of **5**, no localized electron pair for bonding between the Al and the coordinated ligands was found. From the NBO data, the "non-Lewis" occupancy suggests that large charge-transfer interactions take place where the ligand lone-pair orbital effectively donates its electron density to an unoccupied orbital on the metal. From the NBO analysis, the second order perturbation energy for the two Al centres with the surrounding ligands span between 25.7 kcal/mol and 134.2 kcal/mol. The interactions energies of one of the Al centres with one carbon donor and three nitrogen donor

ligands are 25.7 kcal/mol, 60.2 kcal/mol, 58.5 kcal/mol and 89.4 kcal/mol respectively (Table S2 and Figure S25). On the other hand, the interaction energies of the other Al centre with the same donor ligands are 134.2 kcal/mol, 34.5 kcal/mol, 50.8 kcal/mol and 33.1 kcal/mol respectively (Table S2 and Figure S25). It has been observed that for the penta-coordinated neutral Al complex, the donation of one of the nitrogen atoms is generally higher than the donation from the other nitrogen atoms. The difference in donation can be ascribed to the nature of the donor atom and to the Al−N bond distance. In the compound **5**, the two Al–N bond distances in the six membered ring are larger (1.99 Å and 2.17 Å) than for the other two Al-N bonds (1.93 and 2.00 Å). This is consistent with the crystal structure. In all the cases, the lone pair on the nitrogen and carbon donors, with an occupancy of more than 1.70e, has interactions with the Al with occupancies less than 0.3e, which indicates strong donor-acceptor interactions between ligands and the metal centre. We have also computed the NLMO and WBI bond orders (Table S2) that further confirm these results. It has been found that the NLMO and WBI bond orders are low (>0.4), which indicate that the covalent bonding of the Al with the coordinated ligand is weak. Only in the case of Al-H does the bond order (~0.7) indicate covalency.
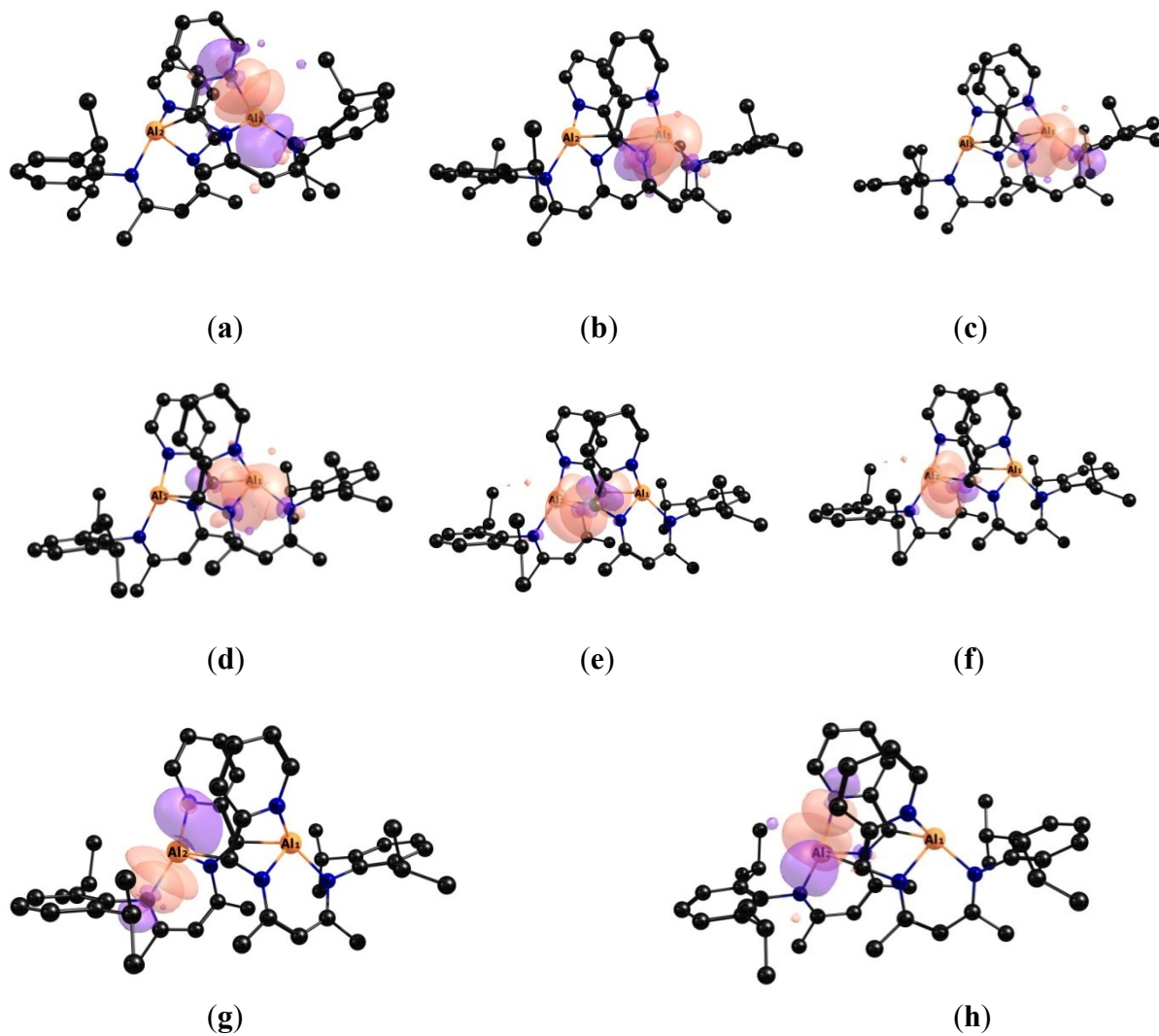
Figure S23. Selective natural bonding orbital interaction in compound **5** . **(a)**LP (1) N→ LP*(2) Al,**(b)** LP (1) N→ LP*(1)Al,**(c)**LP (1) N→ LP*(1)Al,**(d)**LP (1) C→ LP*(1)Al,**(e)**LP (1) C→ LP*(1)Al,**(f)** LP (1) N→LP*(1)Al,**(g)** LP (1) N→ LP*(3)Al,**(h)** LP (1) N→ LP*(2)Al.

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T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. E. Heyd, K. N. B. Kudin, V. N. Staroverov, R. Kobayashi, J. 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, D. J. Fox, Gaussian, Inc., *Wallingford CT*, **2009**.

**PBE/TZVP optimized geometries for all the compounds**

**Compound 1**

| | | | |
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| N | 4.96126800 | 7.35540400 | 13.75261200 |
| N | 2.18455300 | 7.05074900 | 13.77791600 |
| C | 5.37809300 | 8.38066600 | 9.81854500 |
| C | 4.84130400 | 8.62752800 | 14.12127000 |
| C | 5.35008200 | 9.61576600 | 11.89842900 |
| C | 4.09910600 | 8.15254100 | 9.29381800 |
| C | 2.89592000 | 6.05099700 | 14.31058500 |
| C | 6.51193200 | 8.48191600 | 8.99700900 |
| C | 5.17502300 | 9.69195800 | 13.27590700 |
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| C | 2.87030500 | 7.97961400 | 10.18313900 |
| H | 3.16431100 | 8.06280400 | 11.13544200 |
| C | 4.37620000 | 6.26964000 | 14.55198500 |
| H | 4.51511400 | 6.47123800 | 15.51093700 |
| H | 4.85880500 | 5.42938400 | 14.34918700 |
| C | 7.90872900 | 8.67008200 | 9.56440100 |
| H | 7.81932700 | 8.85858700 | 10.54256100 |
| C | 5.28221800 | 10.89353400 | 11.10552100 |
| H | 6.05393000 | 10.94568300 | 10.50377500 |
| H | 5.29377900 | 11.65906500 | 11.71724100 |
| H | 4.45559700 | 10.90843300 | 10.57950100 |
| C | 0.21964300 | 5.68809800 | 13.93989600 |
| H | -0.71403100 | 5.59418400 | 13.79509300 |
| C | 3.96851100 | 8.05941800 | 7.90636700 |
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| C | 4.28267800 | 8.98500900 | 15.47418200 |
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| H | 7.07007600 | 8.43642700 | 7.03514700 |
| C | 2.31356200 | 4.85551700 | 14.67887300 |
| H | 2.84078000 | 4.16177500 | 15.05658000 |

| | | | |
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| H | 4.95373500 | 8.11924300 | 6.13936100 |
| C | 8.73381800 | 7.38847700 | 9.40629900 |
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| H | 9.63174500 | 7.53115300 | 9.77237100 |
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| C | 8.62889200 | 9.86206300 | 8.91962000 |
| H | 8.74033100 | 9.69613400 | 7.96048300 |
| H | 9.50884600 | 9.97606900 | 9.33648300 |
| H | 8.09739900 | 10.67477800 | 9.05020200 |
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| H | 2.22238900 | 9.95123600 | 10.09005100 |
| H | 1.05422700 | 8.93760100 | 10.50008100 |
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| H | 2.92924600 | 5.91588400 | 10.21934000 |

## Compound 2

| | | | |
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| C | 7.03940000 | 3.68830000 | 5.64720000 |
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| C | 7.55360000 | 4.21770000 | 6.83890000 |
| C | 8.65850000 | 7.46440000 | 1.39910000 |
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| H | 8.13493628 | 4.76855303 | 0.41622484 |
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| H | 6.44646996 | 2.79789332 | 5.66978133 |
| H | 7.36969533 | 3.73280058 | 7.77482287 |
| H | 8.70404445 | 5.77661467 | 7.68609168 |

## Compound 5

| | | | |
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| C | 6.75803600 | 5.91722000 | 0.38860700 |

| | | | |
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| H | 9.00980200 | 8.48569900 | 0.54015600 |
| C | 4.27543900 | 3.38679800 | 5.01223500 |
| H | 4.67643900 | 3.06471300 | 4.04101400 |
| H | 3.81219200 | 4.37662400 | 4.88284800 |
| H | 3.48015400 | 2.68613600 | 5.30926700 |
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| Al | 8.36774900 | 4.34622600 | 4.36934500 |
| N | 8.05103300 | 7.35865900 | 4.66358500 |
| N | 10.02915300 | 5.44014400 | 4.98933500 |
| N | 9.80477300 | 9.61271900 | 4.79057500 |
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| | | | |
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| H | 11.71858900 | 6.66877100 | 7.63630200 |
| H | 11.14798700 | 7.68349900 | 6.28587800 |
| C | 8.64360500 | 3.15999000 | 8.58941800 |
| H | 7.60084500 | 2.82453400 | 8.66621700 |
| H | 8.88830000 | 3.80180300 | 9.44473800 |
| H | 9.26940400 | 2.25633600 | 8.65470900 |
| C | 7.61920200 | 2.20680600 | 6.18876400 |
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| C | 7.67881400 | -0.20942400 | 6.23319400 |
| H | 8.23944000 | -1.14642100 | 6.24087400 |
| C | 6.28511300 | -0.24704900 | 6.24938100 |
| H | 5.76335000 | -1.20560400 | 6.28826900 |
| C | 5.56120900 | 0.94211500 | 6.19479000 |
| H | 4.46999300 | 0.90594200 | 6.17773000 |
| C | 6.20745300 | 2.18404900 | 6.14390200 |
| C | 9.89006900 | 1.02133800 | 6.06413700 |
| H | 10.25350200 | 2.01228000 | 6.37225100 |
| C | 10.28170700 | 0.84228500 | 4.58513200 |
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| H | 11.37237600 | 0.92001500 | 4.45704500 |
| H | 9.80730100 | 1.60724000 | 3.95419300 |
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| C | 4.84696600 | 3.87990300 | 7.43257200 |
| H | 4.16897900 | 3.10782800 | 7.82901600 |
| H | 4.28362900 | 4.82293800 | 7.36013700 |
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| H | 7.42483900 | 3.21619000 | 3.66703800 |
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| N | 9.63009300 | 4.34841900 | 2.76491500 |
| C | 9.48025100 | 3.58972600 | 1.65994300 |
| H | 8.78523800 | 2.75187600 | 1.76154300 |
| C | 10.14732900 | 3.86325100 | 0.47727500 |
| H | 10.02253300 | 3.20615600 | -0.38346900 |
| C | 10.97082300 | 5.00934000 | 0.41206600 |
| H | 11.49398900 | 5.25885100 | -0.51276500 |
| C | 11.10438700 | 5.81519200 | 1.52879600 |
| H | 11.70465600 | 6.72582300 | 1.52065800 |