Electronic Supplementary Material (ESI) for

An α-diiminato germylene family: syntheses, structures, and reactivity towards C-C coupled digermylene and digermylene oxide

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A. General remarks

All manipulations were carried out under an atmosphere of purified nitrogen or argon using standard Schlenk lines and glovebox techniques. Glass wares were heatdried and cooled down under vacuum. Hexane was deoxygenated and then refluxed over NaH, another solvents were dried over sodium/benzophenone, distilled and deoxygenated. The solid reactants were weighed in the glove box, and liquid reagents were added with syringe or drip funnel under inert atmosphere. K[^{s}Bu$_3$BH], $AlCl_3$ and K were purchased from Arcos. The starting materials α-diimine,[1] $GeCl_2$•dioxane,[2] KN(Si^{t}BuMe$_2$)$_2$,[3] and NHC[4] (NHC = [HCN-^{t}Bu)$_2$C:]) were prepared according to the literature procedures. Potassium was treated under vigorous stirring and refluxing in hexane under argon, and then cooled rapidly to form potassium grains. The ultra-fine potassium chips was screened and used for the reduction reactions.

The solution ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Zhongke WNMR-1 400 and ECZ 400R. Chemical shifts of the deuterated solvents in ^{1}H NMR data: C_6D_6, 7.16 ppm; $CDCl_3$, 7.26 ppm. ^{13}C{^{1}H} NMR: C_6D_6, 128.06 ppm; $CDCl_3$, 77.16 ppm. ^{27}Al{^{1}H} NMR spectra was recorded on ECZ 600R. The following abbreviations were used to describe peak patterns when appropriate: s = singlet, d = doublet, t = triplet, m = multiplet, sept = septet. Elemental analysis (C, H, N) was performed with 0.05 mL tin-capsules on a Perkin-Elmer 2400 CHN elemental analyze. Melting points were measured in sealed glass capillaries on TD-V20G melting point apparatus under nitrogen.

The single-crystal X-ray diffractions were performed on Bruker D8 VENTURE PHOTON II diffractometer (compounds **4**, **5**, **6**, **6a** and **7** at 150 K, compounds **2** and **7a** at 90 K and 153 K, respectively) with a Ga-target Liquid X-ray source (λ = 1.34138 Å). Compound **3** was measured on Bruker D8 Quest at 153 K with a Mo-Kα X-ray source (λ = 0.71073 Å). By using Olex2,[5] the structures were solved by direct methods with SHELXT and refined by full-matrix least-squares techniques against F^2 using SHELXL-2014 programs.[6] All thermal displacement parameters were refined anisotropically for non-hydrogen atoms and isotropically for H atoms. The graphical representation of the molecular structures was carried out using Ortep32. Crystal data, details of data collections and refinements can be showed in Table S1-S8.

B. Crystal structures of 6a and 7a, crystallographic data for complexes 2-5, 6/6a and 7/7a

Crystal structure of 6a (the structure of its enantiomer is not shown.)

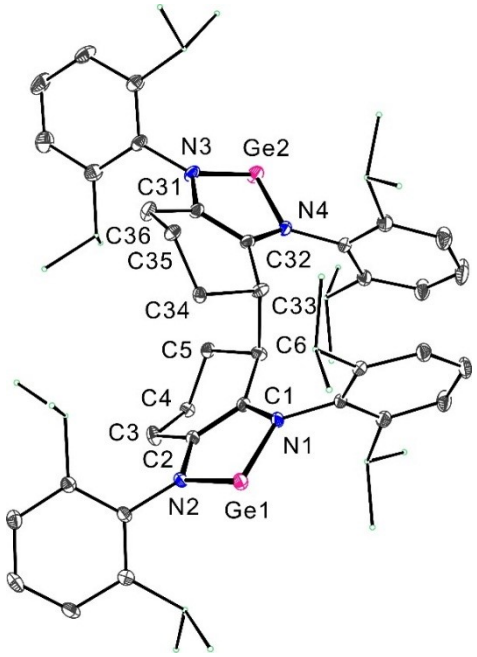

Figure S1. Molecular structure of **6a**. Thermal ellipsoids are drawn at the 30% probability level (except the C atoms of the ^{i}Pr groups). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1-N1 1.8740(12), Ge1-N2 1.8563(12), Ge2-N3 1.8608(13), Ge2-N4 1.8765(12), N1-C1 1.4053(18), N2-C2 1.3959(19), C1-C2 1.362(2), N1-C7 1.4377(18), N2-C19 1.4429(18), C1-C6 1.518(2), C2-C3 1.500(2), C6-C33 1.581(2), C3-C4 1.480(3), C5-C4 1.522(6), C6-C5 1.607(5), N1-Ge1-N2 83.88(5), N3-Ge2-N4 83.62(5).

Crystal structure of 7a

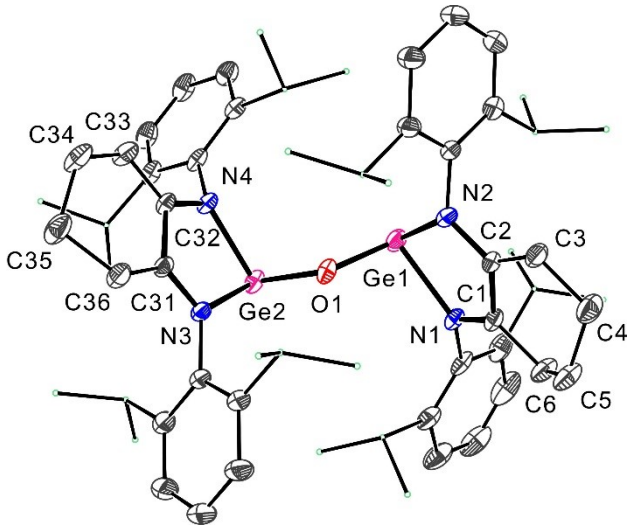

Figure S2. Molecular structure of **7a**. Thermal ellipsoids are drawn at the 30% probability level (except the C atoms of the ^{i}Pr groups). All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge1-O1 1.807(2), Ge2-O1 1.8143(19), Ge1-N1 2.090(2), Ge1-N2 1.981(2), Ge2-N3 2.076(2), Ge2-N4 1.984(2), N1-C1 1.305(3), N2-C2 1.369(3), C1-C2 1.468(4), N1-C7 1.453(3), N2-C19 1.437(4), C1-C6 1.478(3), C2-C3 1.373(4), C3-C4 1.503(4), C5-C4 1.505(4), C6-C5 1.493(4), N3-C31 1.310(3), N4-C32 1.372(3), C32-C31 1.466(3), C32-C33 1.370(4), C33-C34 1.482(4), C34-C35 1.487(5), C36-C35 1.510(4), N1-Ge1-N2 78.42(9), N3-Ge2-N4 78.73(9), Ge1-O1-Ge2 121.17(11).

Crystallographic data for compound 2

Identification code	Compound 2
Empirical formula	$C_{30}H_{41}ClGeN_2$
Formula weight	537.69
Temperature/K	90.0
Crystal system	monoclinic
Space group	P21/c
a/Å	17.622(7)
b/Å	10.372(3)
c/Å	17.159(7)
α/°	90
β/°	117.354(11)
γ/°	90
Volume/Å^3	2785.5(19)
Z	4
ρcalcg/cm^3	1.282
μ/mm^{-1}	1.685
F(000)	1136.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	4.912 to 110.132
Index ranges	-21 ≤ h ≤ 21, -12 ≤ k ≤ 12, -20 ≤ l ≤ 20
Reflections collected	39101
Independent reflections	5298 [R_{int} = 0.0590, R_{sigma} = 0.0369]
Data/restraints/parameters	5298/38/315
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0435, wR_2 = 0.1082
Final R indexes [all data]	R_1 = 0.0601, wR_2 = 0.1161
Largest diff. peak/hole / e Å^{-3}	0.94/-0.83

Table S1. Bond lengths [Å] and angles [°] for compound **2**

Ge1-Cl1	2.3140(10)	C20-C28	1.518(5)
Ge1-N1	1.904(2)	C20-C21	1.396(4)
Ge1-N2	2.062(2)	C24-C25	1.517(4)
N1-C1	1.383(4)	C24-C23	1.395(4)
N1-C7	1.438(3)	C11-C10	1.378(4)
N2-C19	1.450(4)	C6-C5	1.487(4)
N2-C2	1.297(4)	C16-C17	1.527(5)
C1-C2	1.461(4)	C16-C18	1.518(4)
C1-C6	1.364(4)	C25-C27	1.517(5)

C7-C8	1.396(4)	C25-C26	1.525(4)
C7-C12	1.404(4)	C13-C14	1.518(4)
C8-C9	1.396(4)	C13-C15	1.522(5)
C8-C16	1.509(4)	C5-C4	1.482(5)
C19-C20	1.398(4)	C28-C30	1.532(5)
C19-C24	1.407(5)	C28-C29	1.534(5)
C12-C11	1.396(4)	C23-C22	1.375(5)
C12-C13	1.524(4)	C21-C22	1.378(5)
C9-C10	1.377(4)	C3-C4	1.440(5)
C2-C3	1.492(4)	C1-C2-C3	118.3(3)
N1-Ge1-Cl1	99.84(8)	C19-C20-C28	124.7(3)
N1-Ge1-N2	80.12(9)	C21-C20-C19	116.8(3)
N2-Ge1-Cl1	91.48(8)	C21-C20-C28	118.5(3)
C1-N1-Ge1	117.02(17)	C19-C24-C25	122.5(3)
C1-N1-C7	117.8(2)	C23-C24-C19	117.4(3)
C7-N1-Ge1	122.77(17)	C23-C24-C25	120.1(3)
C19-N2-Ge1	122.44(18)	C10-C11-C12	120.9(3)
C2-N2-Ge1	113.91(19)	C1-C6-C5	123.1(3)
C2-N2-C19	123.6(2)	C9-C10-C11	120.3(3)
N1-C1-C2	112.8(2)	C8-C16-C17	112.0(2)
C6-C1-N1	127.1(3)	C8-C16-C18	111.1(3)
C6-C1-C2	120.0(3)	C18-C16-C17	110.8(3)
C8-C7-N1	119.8(2)	C24-C25-C27	113.2(3)
C8-C7-C12	121.6(2)	C24-C25-C26	110.3(3)
C12-C7-N1	118.6(3)	C27-C25-C26	110.7(3)
C7-C8-C16	121.8(2)	C14-C13-C12	112.3(3)
C9-C8-C7	118.1(3)	C14-C13-C15	111.2(3)
C9-C8-C16	120.0(3)	C15-C13-C12	111.0(3)
C20-C19-N2	120.0(3)	C4-C5-C6	113.1(3)
C20-C19-C24	122.8(3)	C20-C28-C30	110.7(3)
C24-C19-N2	117.1(3)	C20-C28-C29	112.3(3)
C7-C12-C13	122.4(2)	C30-C28-C29	109.5(3)
C11-C12-C7	118.0(3)	C22-C23-C24	120.9(3)
C11-C12-C13	119.5(3)	C22-C21-C20	121.6(3)
C10-C9-C8	121.0(3)	C23-C22-C21	120.4(3)
N2-C2-C1	115.3(2)	C4-C3-C2	112.7(3)
N2-C2-C3	126.0(3)	C3-C4-C5	117.4(3)

Crystallographic data for compound 3

Identification code	Compound 3
Empirical formula	$C_{30}H_{42}N_2Ge$
Formula weight	503.24
Temperature/K	153.15
Crystal system	monoclinic
Space group	C2/c
a/Å	31.977(6)
b/Å	11.392(2)
c/Å	18.293(4)
α/°	90
β/°	121.120(7)
γ/°	90
Volume/Å^3	5704(2)
Z	8
ρcalcg/cm^3	1.172
μ/mm^{-1}	1.093
F(000)	2144.0
Crystal size/mm^3	0.16 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.202 to 52.944
Index ranges	-36 ≤ h ≤ 39, -14 ≤ k ≤ 14, -22 ≤ l ≤ 22
Reflections collected	34671
Independent reflections	5831 [R_{int} = 0.0390, R_{sigma} = 0.0250]
Data/restraints/parameters	5831/672/306
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0649, wR_2 = 0.1528
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1599
Largest diff. peak/hole / e Å^{-3}	2.29/-2.29

Table S2. Bond lengths [Å] and angles [°] for compound **3**

Ge1-N1	1.868(3)	C12-C16	1.520(5)
Ge1-N2	1.869(3)	C13-C14	1.532(5)
N1-C1	1.383(5)	C13-C15	1.527(5)
N1-C7	1.442(4)	C16-C17	1.522(6)
C1-C2	1.360(5)	C16-C18	1.535(5)
C1-C6	1.496(5)	C19-C20	1.402(6)
N2-C2	1.384(5)	C19-C24	1.405(6)
N2-C19	1.438(5)	C20-C21	1.393(6)

C2-C3	1.498(5)	C20-C28	1.527(6)
C3-C4	1.487(6)	C21-C22	1.379(6)
C6-C5	1.516(6)	C22-C23	1.388(6)
C7-C8	1.404(5)	C23-C24	1.396(6)
C7-C12	1.406(5)	C24-C25	1.518(6)
C8-C9	1.397(5)	C25-C26	1.520(6)
C8-C13	1.526(5)	C25-C27	1.525(6)
C9-C10	1.390(5)	C28-C29	1.521(7)
C10-C11	1.382(5)	C28-C30	1.524(6)
C11-C12	1.397(5)	C4-C5	1.370(6)
N1-Ge1-N2	83.08(12)	C8-C13-C14	111.2(3)
C1-N1-Ge1	114.7(2)	C8-C13-C15	111.0(3)
C1-N1-C7	122.5(3)	C15-C13-C14	111.0(3)
C7-N1-Ge1	122.7(2)	C12-C16-C17	111.2(3)
N1-C1-C6	122.4(3)	C12-C16-C18	111.1(3)
C2-C1-N1	113.9(3)	C17-C16-C18	110.6(3)
C2-C1-C6	123.8(4)	C20-C19-N2	118.7(3)
C2-N2-Ge1	114.6(2)	C20-C19-C24	121.9(4)
C2-N2-C19	121.8(3)	C24-C19-N2	119.4(3)
C19-N2-Ge1	123.6(2)	C19-C20-C28	122.0(4)
C1-C2-N2	113.8(3)	C21-C20-C19	117.5(4)
C1-C2-C3	124.1(4)	C21-C20-C28	120.5(4)
N2-C2-C3	122.1(3)	C22-C21-C20	121.6(4)
C4-C3-C2	111.2(3)	C21-C22-C23	120.2(4)
C1-C6-C5	109.7(3)	C22-C23-C24	120.5(4)
C8-C7-N1	118.6(3)	C19-C24-C25	122.0(4)
C8-C7-C12	121.2(3)	C23-C24-C19	118.2(4)
C12-C7-N1	120.0(3)	C23-C24-C25	119.8(4)
C7-C8-C13	122.3(3)	C24-C25-C26	111.5(4)
C9-C8-C7	118.1(3)	C24-C25-C27	112.0(3)
C9-C8-C13	119.6(3)	C26-C25-C27	110.7(4)
C10-C9-C8	121.3(4)	C29-C28-C20	110.8(4)
C11-C10-C9	119.8(3)	C29-C28-C30	111.2(4)
C10-C11-C12	120.9(4)	C30-C28-C20	111.8(4)
C7-C12-C16	122.1(3)	C5-C4-C3	120.4(4)
C11-C12-C7	118.5(3)	C4-C5-C6	120.9(4)
C11-C12-C16	119.4(3)		

Crystallographic data for compound 4

Identification code	Compound 4
Empirical formula	$C_{30}H_{40}GeN_2$
Formula weight	501.23
Temperature/K	150.15
Crystal system	triclinic
Space group	P-1
a/Å	8.9419(5)
b/Å	11.8530(7)
c/Å	13.4458(7)
α/°	101.563(2)
β/°	90.578(2)
γ/°	98.666(2)
Volume/Å^3	1379.04(13)
Z	2
ρcalcg/cm^3	1.207
μ/mm^{-1}	1.130
F(000)	532.0
Crystal size/mm^3	0.25 × 0.23 × 0.2
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	3.094 to 51.384
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	21154
Independent reflections	5236 [R_{int} = 0.0590, R_{sigma} = 0.0490]
Data/restraints/parameters	5236/0/306
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.1080
Final R indexes [all data]	R_1 = 0.0602, wR_2 = 0.1180
Largest diff. peak/hole / e Å^{-3}	0.44/-0.74

Table S3. Bond lengths [Å] and angles [°] for compound **4**

Ge1-N1	1.855(2)	C24-C25	1.512(4)
Ge1-N2	1.856(2)	C16-C17	1.527(4)
N1-C7	1.443(3)	C16-C18	1.512(5)
N1-C1	1.406(3)	C3-C4	1.490(4)
N2-C19	1.436(3)	C6-C5	1.507(4)
N2-C2	1.404(3)	C11-C10	1.391(4)
C19-C24	1.415(4)	C23-C22	1.380(4)
C19-C20	1.399(4)	C10-C9	1.372(4)

C2-C1	1.473(3)	C13-C15	1.533(4)
C2-C3	1.348(4)	C13-C14	1.519(4)
C7-C8	1.406(4)	C20-C21	1.396(4)
C7-C12	1.404(4)	C20-C28	1.516(4)
C1-C6	1.336(4)	C22-C21	1.373(5)
C8-C16	1.518(4)	C25-C26	1.539(4)
C8-C9	1.394(4)	C25-C27	1.519(4)
C12-C11	1.387(4)	C4-C5	1.517(4)
C12-C13	1.527(4)	C28-C30	1.525(6)
C24-C23	1.395(4)	C28-C29	1.529(5)
N1-Ge1-N2	85.64(9)	C23-C24-C25	120.9(3)
C7-N1-Ge1	124.60(18)	C8-C16-C17	112.4(2)
C1-N1-Ge1	115.36(17)	C18-C16-C8	111.1(3)
C1-N1-C7	120.0(2)	C18-C16-C17	109.9(3)
C19-N2-Ge1	126.08(18)	C2-C3-C4	120.3(3)
C2-N2-Ge1	115.08(16)	C1-C6-C5	120.2(3)
C2-N2-C19	118.2(2)	C12-C11-C10	120.8(3)
C24-C19-N2	118.3(2)	C22-C23-C24	121.3(3)
C20-C19-N2	120.4(2)	C9-C10-C11	120.0(3)
C20-C19-C24	121.3(2)	C12-C13-C15	111.9(3)
N2-C2-C1	112.2(2)	C14-C13-C12	111.2(3)
C3-C2-N2	126.9(2)	C14-C13-C15	110.5(3)
C3-C2-C1	120.8(3)	C19-C20-C28	121.8(3)
C8-C7-N1	119.6(2)	C21-C20-C19	118.5(3)
C12-C7-N1	119.0(2)	C21-C20-C28	119.6(3)
C12-C7-C8	121.4(2)	C21-C22-C23	120.5(3)
N1-C1-C2	111.5(2)	C10-C9-C8	121.5(3)
C6-C1-N1	127.3(2)	C22-C21-C20	120.8(3)
C6-C1-C2	121.2(2)	C24-C25-C26	109.6(3)
C7-C8-C16	121.9(2)	C24-C25-C27	113.8(3)
C9-C8-C7	117.7(3)	C27-C25-C26	110.1(3)
C9-C8-C16	120.4(3)	C3-C4-C5	114.3(3)
C7-C12-C13	121.6(2)	C6-C5-C4	113.5(3)
C11-C12-C7	118.4(3)	C20-C28-C30	109.8(3)
C11-C12-C13	120.0(2)	C20-C28-C29	112.1(3)
C19-C24-C25	121.4(2)	C30-C28-C29	110.8(3)
C23-C24-C19	117.5(3)		

Crystallographic data for compound 5

Identification code	Compound 5

Empirical formula	$C_{81}H_{106}Al_4Cl_{14}Ge_2N_4$
Formula weight	1885.09
Temperature/K	150.15
Crystal system	monoclinic
Space group	C2/c
a/Å	23.395(3)
b/Å	10.6792(12)
c/Å	37.715(4)
α/°	90
β/°	96.837(4)
γ/°	90
Volume/Å^3	9356.0(18)
Z	4
ρcalcg/cm^3	1.338
μ/mm^{-1}	1.122
F(000)	3896.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	3.506 to 51.416
Index ranges	-28 ≤ h ≤ 28, -13 ≤ k ≤ 13, -45 ≤ l ≤ 45
Reflections collected	49758
Independent reflections	8863 [R_{int} = 0.0513, R_{sigma} = 0.0348]
Data/restraints/parameters	8863/0/485
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0414, wR_2 = 0.1261
Final R indexes [all data]	R_1 = 0.0460, wR_2 = 0.1313
Largest diff. peak/hole / e Å^{-3}	0.61/-1.05

Table S4. Bond lengths [Å] and angles [°] for compound **5**

Ge1-N1	1.9123(19)	C13-C14	1.526(3)
Ge1-N2	1.9180(19)	C13-C15	1.534(4)
Cl1-Al1	2.1066(11)	C16-C17	1.529(4)
Al1-Cl2	2.0960(12)	C16-C18	1.529(3)
Al1-Cl3	2.1142(11)	C19-C20	1.402(3)
Al1-Cl4	2.2749(10)	C19-C24	1.402(3)
N1-C1	1.351(3)	C20-C21	1.402(3)
N1-C7	1.449(3)	C20-C28	1.518(3)
C1-C2	1.455(3)	C21-C22	1.374(4)
C1-C6	1.418(3)	C22-C23	1.384(4)

Al2-Cl4	2.2560(10)	C23-C24	1.400(3)
Al2-Cl5	2.1048(11)	C24-C25	1.522(3)
Al2-Cl6	2.0939(10)	C25-C26	1.533(4)
Al2-Cl7	2.1087(10)	C25-C27	1.524(3)
N2-C2	1.351(3)	C28-C29	1.518(4)
N2-C19	1.457(3)	C28-C30	1.526(5)
C2-C3	1.412(3)	C31-C32	1.395(5)
C3-C4	1.457(4)	C31-C36	1.393(4)
C4-C5	1.473(4)	C31-C37	1.503(5)
C5-C6	1.469(4)	C32-C33	1.385(5)
C7-C8	1.401(3)	C33-C34	1.368(5)
C7-C12	1.401(3)	C34-C35	1.376(5)
C8-C9	1.396(3)	C35-C36	1.383(5)
C8-C16	1.525(3)	C38-C39	1.384(4)
C9-C10	1.384(4)	C38-C391	1.384(4)
C10-C11	1.383(4)	C39-C40	1.378(5)
C11-C12	1.401(3)	C40-C41	1.392(4)
C12-C13	1.525(3)	C41-C42	1.505(7)
N1-Ge1-N2	82.32(8)	C11-C12-C7	117.2(2)
Cl1-Al1-Cl3	113.49(5)	C11-C12-C13	121.1(2)
Cl1-Al1-Cl4	100.86(4)	C12-C13-C14	112.7(2)
Cl2-Al1-Cl1	114.20(5)	C12-C13-C15	111.3(2)
Cl2-Al1-Cl3	113.81(5)	C14-C13-C15	110.1(2)
Cl2-Al1-Cl4	107.51(5)	C8-C16-C17	110.4(2)
Cl3-Al1-Cl4	105.51(4)	C8-C16-C18	112.5(2)
C1-N1-Ge1	115.49(15)	C17-C16-C18	111.5(2)
C1-N1-C7	121.85(18)	C20-C19-N2	118.4(2)
C7-N1-Ge1	122.63(14)	C20-C19-C24	122.9(2)
N1-C1-C2	113.59(19)	C24-C19-N2	118.7(2)
N1-C1-C6	126.1(2)	C19-C20-C21	117.2(2)
C6-C1-C2	120.3(2)	C19-C20-C28	122.6(2)
Cl5-Al2-Cl4	104.89(4)	C21-C20-C28	120.2(2)
Cl5-Al2-Cl7	113.05(5)	C22-C21-C20	121.1(2)
Cl6-Al2-Cl4	105.57(4)	C21-C22-C23	120.5(2)
Cl6-Al2-Cl5	116.67(5)	C22-C23-C24	121.1(2)
Cl6-Al2-Cl7	111.53(5)	C19-C24-C25	121.8(2)
Cl7-Al2-Cl4	103.73(4)	C23-C24-C19	117.1(2)
C2-N2-Ge1	115.71(15)	C23-C24-C25	121.1(2)
C2-N2-C19	121.77(18)	C24-C25-C26	111.1(2)
C19-N2-Ge1	122.46(14)	C24-C25-C27	112.7(2)
N2-C2-C1	112.87(19)	C27-C25-C26	111.1(2)

N2-C2-C3	126.6(2)	C20-C28-C30	110.4(3)
C3-C2-C1	120.6(2)	C29-C28-C20	111.8(2)
C2-C3-C4	119.1(2)	C29-C28-C30	110.4(3)
Al2-Cl4-Al1	110.82(4)	C32-C31-C37	121.8(3)
C3-C4-C5	117.2(3)	C36-C31-C32	117.6(3)
C6-C5-C4	115.9(3)	C36-C31-C37	120.5(3)
C1-C6-C5	117.8(2)	C33-C32-C31	120.9(3)
C8-C7-N1	118.4(2)	C34-C33-C32	120.6(3)
C12-C7-N1	118.43(19)	C33-C34-C35	119.5(3)
C12-C7-C8	123.1(2)	C34-C35-C36	120.6(3)
C7-C8-C16	122.0(2)	C35-C36-C31	120.9(3)
C9-C8-C7	117.3(2)	C391-C38-C39	119.4(5)
C9-C8-C16	120.7(2)	C40-C39-C38	120.0(3)
C10-C9-C8	120.7(2)	C39-C40-C41	121.6(3)
C11-C10-C9	120.9(2)	C401-C41-C40	117.3(4)
C10-C11-C12	120.7(2)	C401-C41-C42	121.3(2)
C7-C12-C13	121.7(2)	C40-C41-C42	121.3(2)

Crystallographic data for compound 6

Identification code	Compound 6
Empirical formula	$C_{60}H_{82}Ge_2N_4$
Formula weight	1004.47
Temperature/K	150.15
Crystal system	monoclinic
Space group	P21/n
a/Å	12.8471(7)
b/Å	12.1217(7)
c/Å	18.1718(9)
α/°	90
β/°	104.017(2)
γ/°	90
Volume/Å^3	2745.6(3)
Z	2
ρcalcg/cm^3	1.215
μ/mm^{-1}	1.135
F(000)	1068.0
Crystal size/mm^3	0.3 × 0.25 × 0.2
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	3.516 to 51.532
Index ranges	$-15 \le h \le 15$, $-14 \le k \le 13$, $-22 \le l \le 21$

Reflections collected	35478
Independent reflections	5223 [R_{int} = 0.1508, R_{sigma} = 0.0859]
Data/restraints/parameters	5223/0/306
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0549, wR_2 = 0.1265
Final R indexes [all data]	R_1 = 0.1059, wR_2 = 0.1460
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.78

Table S5. Bond lengths [Å] and angles [°] for compound **6**

Ge1-N1	1.878(3)	C7-C8	1.410(5)
Ge1-N2	1.863(3)	C8-C16	1.534(5)
N1-C1	1.404(5)	C8-C9	1.407(5)
N1-C7	1.451(4)	C28-C30	1.533(6)
N2-C2	1.391(4)	C28-C29	1.503(7)
N2-C19	1.440(4)	C16-C18	1.530(6)
C12-C13	1.521(5)	C16-C17	1.533(6)
C12-C7	1.403(5)	C19-C24	1.412(5)
C12-C11	1.406(5)	C10-C11	1.363(6)
C1-C2	1.359(5)	C10-C9	1.373(6)
C1-C6	1.512(5)	C4-C3	1.505(5)
C5-C4	1.542(5)	C22-C23	1.373(6)
C5-C6	1.535(5)	C22-C21	1.374(6)
C2-C3	1.492(5)	C6-C61	1.547(7)
C20-C28	1.522(5)	C23-C24	1.393(5)
C20-C19	1.397(5)	C24-C26	1.517(6)
C20-C21	1.411(5)	C26-C25	1.523(7)
C13-C15	1.529(5)	C26-C27	1.504(6)
C13-C14	1.529(6)	C6-C6’	1.548
N2-Ge1-N1	83.97(13)	C9-C8-C16	117.8(3)
C1-N1-Ge1	114.0(2)	C20-C28-C30	111.0(3)
C1-N1-C7	124.0(3)	C29-C28-C20	111.7(4)
C7-N1-Ge1	122.0(2)	C29-C28-C30	111.9(4)
C2-N2-Ge1	113.7(2)	C18-C16-C8	110.0(4)
C2-N2-C19	121.0(3)	C18-C16-C17	109.7(3)
C19-N2-Ge1	124.8(2)	C17-C16-C8	113.3(3)
C7-C12-C13	123.3(3)	C20-C19-N2	119.4(3)
C7-C12-C11	117.6(3)	C20-C19-C24	121.9(3)
C11-C12-C13	119.0(3)	C24-C19-N2	118.6(3)
N1-C1-C6	126.5(3)	C11-C10-C9	120.6(4)
C2-C1-N1	112.9(3)	C3-C4-C5	116.7(3)
C2-C1-C6	120.4(3)	C10-C11-C12	121.6(4)

C6-C5-C4	114.9(3)	C23-C22-C21	120.3(3)
N2-C2-C3	122.5(3)	C1-C6-C5	106.7(3)
C1-C2-N2	115.4(3)	C1-C6-C61	113.6(3)
C1-C2-C3	121.9(3)	C5-C6-C61	112.0(4)
C19-C20-C28	122.0(3)	C2-C3-C4	112.9(3)
C19-C20-C21	117.9(3)	C22-C23-C24	122.1(4)
C21-C20-C28	120.1(4)	C19-C24-C26	122.0(3)
C12-C13-C15	112.9(3)	C23-C24-C19	117.0(4)
C12-C13-C14	109.8(3)	C23-C24-C26	120.9(3)
C14-C13-C15	110.1(3)	C22-C21-C20	120.7(4)
C12-C7-N1	119.7(3)	C10-C9-C8	120.8(4)
C12-C7-C8	121.3(3)	C24-C26-C25	111.6(4)
C8-C7-N1	118.8(3)	C27-C26-C24	111.5(4)
C7-C8-C16	124.2(3)	C27-C26-C25	111.4(4)
C9-C8-C7	117.9(4)		

Crystallographic data for compound 6a

Identification code	Compound 6a
Empirical formula	$C_{60}H_{82}Ge_2N_4$
Formula weight	1004.47
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	13.3724(9)
b/Å	14.6460(9)
c/Å	15.5895(11)
α/°	93.181(3)
β/°	92.200(3)
γ/°	114.758(3)
Volume/Å^3	2761.9(3)
Z	2
ρcalcg/cm^3	1.208
μ/mm^{-1}	1.108
F(000)	1068.0
Crystal size/mm^3	0.2 × 0.18 × 0.15
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	4.95 to 110.012
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19
Reflections collected	61048
Independent reflections	10496 [R_{int} = 0.0471, R_{sigma} = 0.0304]

Data/restraints/parameters	10496/6/647
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0281, wR_2 = 0.0724
Final R indexes [all data]	R_1 = 0.0335, wR_2 = 0.0752
Largest diff. peak/hole / e $Å^{-3}$	0.29/-0.39

Table S6. Bond lengths [Å] and angles [°] for compound **6a**

Ge1-N1	1.8740(12)	C50-C51	1.397(2)
Ge1-N2	1.8563(12)	C13-C15	1.538(2)
Ge2-N4	1.8765(12)	C13-C14	1.531(2)
Ge2-N3	1.8608(13)	C11-C10	1.377(2)
N1-C7	1.4377(18)	C3-C4	1.480(3)
N1-C1	1.4053(18)	C3-C4A	1.608(4)
N4-C32	1.3991(19)	C25-C26	1.536(2)
N4-C49	1.4388(19)	C25-C27	1.533(2)
N3-C31	1.3944(19)	C23-C22	1.385(2)
N3-C37	1.4434(19)	C9-C10	1.384(2)
N2-C19	1.4429(18)	C54-C55	1.525(2)
N2-C2	1.3959(19)	C54-C53	1.390(2)
C31-C32	1.359(2)	C21-C22	1.376(2)
C31-C36	1.502(2)	C16-C18	1.528(2)
C7-C12	1.411(2)	C16-C17	1.534(2)
C7-C8	1.420(2)	C55-C56	1.522(2)
C19-C24	1.406(2)	C55-C57	1.534(3)
C19-C20	1.408(2)	C33-C34A	1.511(3)
C32-C33	1.514(2)	C33-C34	1.676(6)
C12-C13	1.530(2)	C58-C60	1.533(2)
C12-C11	1.395(2)	C58-C59	1.529(2)
C1-C2	1.362(2)	C36-C35A	1.556(3)
C1-C6	1.518(2)	C36-C35	1.477(5)
C2-C3	1.500(2)	C43-C44	1.525(2)
C37-C42	1.405(2)	C43-C45	1.533(2)
C37-C38	1.405(2)	C38-C39	1.394(2)
C24-C25	1.525(2)	C38-C46	1.522(2)
C24-C23	1.392(2)	C51-C52	1.382(3)
C8-C9	1.388(2)	C28-C29	1.534(3)
C8-C16	1.528(2)	C28-C30	1.526(3)
C42-C43	1.518(2)	C41-C40	1.376(3)
C42-C41	1.394(2)	C53-C52	1.381(3)
C49-C50	1.408(2)	C39-C40	1.381(3)
C49-C54	1.416(2)	C46-C48	1.525(3)

C6-C33	1.581(2)	C46-C47	1.538(3)
C6-C5	1.607(5)	C5-C4	1.522(6)
C6-C5A	1.512(5)	C34A-C35A	1.515(4)
C20-C21	1.399(2)	C35-C34	1.509(8)
C20-C28	1.523(2)	C4A-C5A	1.504(6)
C50-C58	1.525(2)		
N2-Ge1-N1	83.88(5)	C51-C50-C58	118.05(14)
N3-Ge2-N4	83.62(5)	C12-C13-C15	111.51(13)
C7-N1-Ge1	121.67(9)	C12-C13-C14	111.49(13)
C1-N1-Ge1	114.19(9)	C14-C13-C15	109.32(14)
C1-N1-C7	122.92(12)	C10-C11-C12	121.68(14)
C32-N4-Ge2	114.26(9)	C2-C3-C4A	108.82(16)
C32-N4-C49	122.97(12)	C4-C3-C2	109.27(16)
C49-N4-Ge2	121.37(10)	C24-C25-C26	112.52(14)
C31-N3-Ge2	114.26(10)	C24-C25-C27	110.26(14)
C31-N3-C37	120.49(13)	C27-C25-C26	110.13(14)
C37-N3-Ge2	125.05(10)	C22-C23-C24	121.30(15)
C19-N2-Ge1	124.73(10)	C10-C9-C8	121.61(15)
C2-N2-Ge1	114.24(9)	C49-C54-C55	122.02(14)
C2-N2-C19	120.79(12)	C53-C54-C49	118.50(15)
N3-C31-C36	120.26(13)	C53-C54-C55	119.21(14)
C32-C31-N3	114.59(13)	C22-C21-C20	121.30(15)
C32-C31-C36	125.01(14)	C8-C16-C17	109.78(13)
C12-C7-N1	119.96(13)	C18-C16-C8	113.41(14)
C12-C7-C8	120.56(13)	C18-C16-C17	109.83(14)
C8-C7-N1	119.27(13)	C54-C55-C57	109.23(15)
C24-C19-N2	119.23(13)	C56-C55-C54	112.92(14)
C24-C19-C20	121.40(14)	C56-C55-C57	110.65(14)
C20-C19-N2	119.34(13)	C32-C33-C6	112.19(12)
N4-C32-C33	123.77(13)	C32-C33-C34	107.3(2)
C31-C32-N4	113.24(13)	C6-C33-C34	101.4(3)
C31-C32-C33	122.83(14)	C34A-C33-C32	108.70(15)
C7-C12-C13	124.67(13)	C34A-C33-C6	120.04(17)
C11-C12-C7	118.17(13)	C11-C10-C9	119.62(14)
C11-C12-C13	117.14(13)	C50-C58-C60	111.32(14)
N1-C1-C6	123.89(12)	C50-C58-C59	111.48(14)
C2-C1-N1	112.93(13)	C59-C58-C60	110.76(15)
C2-C1-C6	122.97(13)	C21-C22-C23	119.96(15)
N2-C2-C3	120.58(13)	C31-C36-C35A	109.74(14)
C1-C2-N2	114.70(13)	C35-C36-C31	110.5(2)
C1-C2-C3	124.59(14)	C42-C43-C44	110.84(14)

C42-C37-N3	119.24(14)	C42-C43-C45	111.58(15)
C42-C37-C38	121.53(14)	C44-C43-C45	110.17(15)
C38-C37-N3	119.22(14)	C37-C38-C46	122.80(15)
C19-C24-C25	122.47(13)	C39-C38-C37	118.03(15)
C23-C24-C19	118.11(14)	C39-C38-C46	119.16(16)
C23-C24-C25	119.37(14)	C52-C51-C50	121.60(16)
C7-C8-C16	122.11(13)	C20-C28-C29	111.99(15)
C9-C8-C7	118.16(14)	C20-C28-C30	110.94(17)
C9-C8-C16	119.43(14)	C30-C28-C29	110.01(17)
C37-C42-C43	123.01(14)	C40-C41-C42	121.29(16)
C41-C42-C37	117.85(15)	C52-C53-C54	121.47(16)
C41-C42-C43	119.13(15)	C40-C39-C38	121.00(17)
C50-C49-N4	120.09(13)	C41-C40-C39	120.23(16)
C50-C49-C54	120.52(14)	C38-C46-C48	110.40(17)
C54-C49-N4	119.16(13)	C38-C46-C47	112.06(17)
C1-C6-C33	112.72(12)	C48-C46-C47	109.85(19)
C1-C6-C5	107.2(2)	C53-C52-C51	119.55(16)
C33-C6-C5	105.8(2)	C4-C5-C6	112.3(3)
C5A-C6-C1	110.3(2)	C33-C34A-C35A	112.5(2)
C5A-C6-C33	121.2(2)	C34A-C35A-C36	111.9(2)
C19-C20-C28	122.56(14)	C3-C4-C5	106.5(3)
C21-C20-C19	117.92(14)	C36-C35-C34	106.4(4)
C21-C20-C28	119.52(14)	C35-C34-C33	112.3(5)
C49-C50-C58	123.68(14)	C5A-C4A-C3	110.7(3)
C51-C50-C49	118.24(14)	C4A-C5A-C6	112.5(3)

Crystallographic data for compound 7

Identification code	Compound 7
Empirical formula	$C_{120}H_{164}Ge_4N_8O_2$
Formula weight	2040.94
Temperature/K	150(2)
Crystal system	orthorhombic
Space group	P212121
a/Å	13.4853(5)
b/Å	24.7376(13)
c/Å	34.1042(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	11377.0(9)

Z	4
ρcalcg/cm^3	1.192
μ/mm^{-1}	1.089
F(000)	4336.0
Crystal size/mm^3	0.15 × 0.13 × 0.10
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	3.838 to 109.822
Index ranges	-16 ≤ h ≤ 14, -30 ≤ k ≤ 30, -41 ≤ l ≤ 40
Reflections collected	142714
Independent reflections	21579 [R_{int} = 0.0814, R_{sigma} = 0.0511]
Data/restraints/parameters	21579/16/1270
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0365, wR_2 = 0.0909
Final R indexes [all data]	R_1 = 0.0441, wR_2 = 0.0950
Largest diff. peak/hole / e Å^{-3}	0.31/-0.51
Flack parameter	0.036(10)

Table S7. Bond lengths [Å] and angles [°] for compound **7**

Ge1-O1	1.813(2)	C97-C102	1.414(7)
Ge1-N1	2.011(3)	C39-C40	1.369(7)
Ge1-N2	2.044(3)	C58-C60	1.518(6)
Ge2-O1	1.808(3)	C58-C59	1.528(7)
Ge2-N4	2.030(3)	C73-C74	1.530(6)
Ge2-N3	2.047(3)	C73-C75	1.531(7)
Ge3-O2	1.817(3)	C6-C5	1.473(7)
Ge3-N6	2.008(3)	C118-C110	1.516(7)
Ge3-N5	2.055(3)	C118-C120	1.523(7)
Ge4-O2	1.811(3)	C118-C119	1.532(7)
Ge4-N7	2.026(3)	C8-C9	1.402(6)
Ge4-N8	2.036(4)	C8-C13	1.522(7)
N1-C1	1.347(5)	C9-C10	1.364(7)
N1-C7	1.439(5)	C53-C52	1.391(7)
N5-C61	1.311(5)	C102-C101	1.394(7)
N5-C67	1.435(5)	C102-C103	1.496(7)
N3-C31	1.339(5)	C80-C81	1.392(6)
N3-C37	1.436(5)	C80-C79	1.406(6)
N2-C2	1.325(5)	C11-C10	1.375(7)
N2-C19	1.440(5)	C109-C110	1.407(7)
N4-C32	1.328(5)	C109-C114	1.413(6)
N4-C49	1.448(5)	C16-C18	1.521(6)
C49-C54	1.403(6)	C16-C17	1.524(7)

C49-C50	1.406(6)	C51-C52	1.377(7)
N6-C62	1.362(5)	C110-C111	1.401(6)
N6-C79	1.436(5)	C65-C64	1.493(7)
N7-C91	1.359(6)	C65-C66	1.512(7)
N7-C97	1.423(6)	C79-C84	1.410(6)
C1-C6	1.399(5)	C72-C71	1.391(6)
C1-C2	1.467(5)	C72-C76	1.520(7)
C37-C38	1.404(6)	C46-C47	1.529(6)
C37-C42	1.414(6)	C46-C48	1.533(7)
N8-C92	1.330(5)	C84-C83	1.394(7)
N8-C109	1.446(5)	C84-C85	1.524(7)
C19-C24	1.406(5)	C81-C82	1.375(7)
C19-C20	1.408(5)	C92-C93	1.425(7)
C2-C3	1.456(6)	C92-C91	1.460(6)
C61-C66	1.459(6)	C69-C70	1.377(7)
C61-C62	1.464(5)	C43-C44	1.513(7)
C32-C33	1.445(5)	C43-C45	1.536(6)
C32-C31	1.457(5)	C91-C96	1.416(7)
C31-C36	1.424(5)	C40-C41	1.383(7)
C24-C23	1.406(6)	C64-C63	1.473(7)
C24-C25	1.524(5)	C36-C35	1.453(8)
C50-C51	1.389(6)	C36-C35A	1.536(19)
C50-C58	1.528(6)	C111-C112	1.382(9)
C38-C39	1.400(6)	C103-C105	1.507(7)
C38-C46	1.516(6)	C103-C104	1.550(8)
C55-C56	1.519(6)	C114-C113	1.401(8)
C55-C54	1.526(6)	C114-C115	1.512(9)
C55-C57	1.530(6)	C82-C83	1.374(8)
C54-C53	1.387(6)	C85-C87	1.512(8)
C20-C21	1.392(6)	C85-C86	1.525(8)
C20-C28	1.527(6)	C13-C14	1.524(7)
C67-C68	1.403(6)	C13-C15	1.527(8)
C67-C72	1.403(6)	C93-C94	1.445(8)
C23-C22	1.382(6)	C34-C35A	1.435(19)
C7-C12	1.402(6)	C34-C35	1.475(11)
C7-C8	1.402(6)	C76-C77	1.505(14)
C25-C27	1.523(5)	C76-C78A	1.506(13)
C25-C26	1.528(6)	C76-C77A	1.526(14)
C62-C63	1.390(6)	C76-C78	1.572(13)
C33-C34	1.473(6)	C71-C70	1.380(8)
C88-C80	1.509(6)	C96-C95	1.441(8)

C88-C89	1.527(7)	C98-C99	1.382(9)
C88-C90	1.528(7)	C98-C106	1.502(9)
C42-C41	1.392(6)	C113-C112	1.373(10)
C42-C43	1.518(7)	C3-C4	1.483(7)
C12-C11	1.404(6)	C101-C100	1.398(9)
C12-C16	1.510(6)	C99-C100	1.362(10)
C28-C29	1.514(7)	C4-C5	1.457(8)
C28-C30	1.545(6)	C106-C108	1.522(10)
C21-C22	1.375(6)	C106-C107	1.536(10)
C68-C69	1.402(6)	C115-C117	1.523(9)
C68-C73	1.516(6)	C115-C116	1.541(9)
C97-C98	1.412(6)	C94-C95	1.442(9)
O1-Ge1-N1	100.15(13)	C60-C58-C50	111.8(4)
O1-Ge1-N2	93.85(12)	C60-C58-C59	110.9(4)
N1-Ge1-N2	78.71(12)	C50-C58-C59	112.5(4)
O1-Ge2-N4	94.40(13)	C68-C73-C74	112.8(4)
O1-Ge2-N3	100.48(13)	C68-C73-C75	108.9(4)
N4-Ge2-N3	78.42(12)	C74-C73-C75	110.9(4)
O2-Ge3-N6	99.97(14)	C1-C6-C5	121.9(4)
O2-Ge3-N5	94.53(13)	C110-C118-C120	112.3(4)
N6-Ge3-N5	78.52(13)	C110-C118-C119	110.4(4)
O2-Ge4-N7	99.73(14)	C120-C118-C119	110.1(5)
O2-Ge4-N8	94.99(14)	C7-C8-C9	118.3(4)
N7-Ge4-N8	78.82(14)	C7-C8-C13	122.4(4)
Ge2-O1-Ge1	120.94(16)	C9-C8-C13	119.3(4)
Ge4-O2-Ge3	119.60(17)	C10-C9-C8	121.6(4)
C1-N1-C7	119.5(3)	C54-C53-C52	122.0(4)
C1-N1-Ge1	116.5(3)	C101-C102-C97	117.1(5)
C7-N1-Ge1	121.1(2)	C101-C102-C103	120.7(5)
C61-N5-C67	123.4(3)	C97-C102-C103	122.1(4)
C61-N5-Ge3	115.9(2)	C81-C80-C79	117.5(4)
C67-N5-Ge3	120.5(2)	C81-C80-C88	120.7(4)
C31-N3-C37	118.8(3)	C79-C80-C88	121.7(4)
C31-N3-Ge2	115.5(2)	C10-C11-C12	121.2(4)
C37-N3-Ge2	122.3(3)	C110-C109-C114	121.3(4)
C2-N2-C19	121.6(3)	C110-C109-N8	120.1(4)
C2-N2-Ge1	115.8(2)	C114-C109-N8	118.5(5)
C19-N2-Ge1	122.2(2)	C9-C10-C11	119.9(4)
C32-N4-C49	120.6(3)	C12-C16-C18	113.3(4)
C32-N4-Ge2	116.4(3)	C12-C16-C17	111.8(4)
C49-N4-Ge2	122.0(2)	C18-C16-C17	110.0(4)

C54-C49-C50	121.4(4)	C52-C51-C50	120.6(4)
C54-C49-N4	120.3(3)	C111-C110-C109	118.3(5)
C50-C49-N4	118.3(4)	C111-C110-C118	119.7(5)
C62-N6-C79	116.1(3)	C109-C110-C118	121.9(4)
C62-N6-Ge3	116.3(2)	C64-C65-C66	112.5(4)
C79-N6-Ge3	125.3(3)	C80-C79-C84	121.5(4)
C91-N7-C97	121.0(4)	C80-C79-N6	119.9(4)
C91-N7-Ge4	115.8(3)	C84-C79-N6	118.5(4)
C97-N7-Ge4	121.0(3)	C21-C22-C23	120.0(4)
N1-C1-C6	126.8(4)	C71-C72-C67	118.4(4)
N1-C1-C2	114.0(3)	C71-C72-C76	120.1(4)
C6-C1-C2	118.8(4)	C67-C72-C76	121.5(4)
C38-C37-C42	121.3(4)	C38-C46-C47	112.6(4)
C38-C37-N3	119.9(4)	C38-C46-C48	110.2(4)
C42-C37-N3	118.9(4)	C47-C46-C48	110.4(4)
C92-N8-C109	120.6(4)	C83-C84-C79	117.7(4)
C92-N8-Ge4	116.2(3)	C83-C84-C85	121.1(4)
C109-N8-Ge4	122.4(3)	C79-C84-C85	121.1(4)
C24-C19-C20	121.4(4)	C82-C81-C80	121.7(4)
C24-C19-N2	119.7(3)	N8-C92-C93	126.1(4)
C20-C19-N2	118.8(3)	N8-C92-C91	115.0(4)
N2-C2-C3	125.5(4)	C93-C92-C91	118.8(4)
N2-C2-C1	114.8(3)	C51-C52-C53	119.7(4)
C3-C2-C1	119.4(3)	C70-C69-C68	121.7(5)
N5-C61-C66	125.9(4)	C44-C43-C42	111.8(4)
N5-C61-C62	115.3(3)	C44-C43-C45	110.8(4)
C66-C61-C62	118.7(3)	C42-C43-C45	111.7(4)
N4-C32-C33	125.4(4)	N7-C91-C96	126.1(4)
N4-C32-C31	115.0(3)	N7-C91-C92	114.2(4)
C33-C32-C31	119.6(3)	C96-C91-C92	119.6(4)
N3-C31-C36	125.9(4)	C39-C40-C41	120.4(4)
N3-C31-C32	114.7(3)	C40-C41-C42	120.9(4)
C36-C31-C32	119.3(3)	C63-C64-C65	111.8(4)
C19-C24-C23	117.5(4)	C31-C36-C35	120.0(4)
C19-C24-C25	122.4(3)	C31-C36-C35A	114.5(10)
C23-C24-C25	120.0(3)	C112-C111-C110	120.4(6)
C51-C50-C49	118.9(4)	C102-C103-C105	113.5(5)
C51-C50-C58	119.4(4)	C102-C103-C104	110.7(4)
C49-C50-C58	121.7(4)	C105-C103-C104	109.0(4)
C39-C38-C37	117.8(4)	C113-C114-C109	117.8(6)
C39-C38-C46	119.5(4)	C113-C114-C115	119.6(5)

C37-C38-C46	122.6(4)	C109-C114-C115	122.6(5)
C56-C55-C54	112.0(3)	C61-C66-C65	116.0(4)
C56-C55-C57	110.4(4)	C83-C82-C81	120.0(4)
C54-C55-C57	110.7(3)	C87-C85-C84	113.0(5)
C53-C54-C49	117.4(4)	C87-C85-C86	110.8(5)
C53-C54-C55	120.0(4)	C84-C85-C86	110.8(5)
C49-C54-C55	122.6(3)	C8-C13-C14	112.2(4)
C21-C20-C19	118.4(4)	C8-C13-C15	111.7(5)
C21-C20-C28	119.8(4)	C14-C13-C15	110.7(5)
C19-C20-C28	121.8(4)	C92-C93-C94	119.9(5)
C68-C67-C72	121.1(4)	C35A-C34-C33	120.0(9)
C68-C67-N5	120.2(4)	C33-C34-C35	113.4(5)
C72-C67-N5	118.7(4)	C62-C63-C64	121.6(4)
C22-C23-C24	121.4(4)	C77-C76-C72	110.0(8)
C12-C7-C8	120.7(4)	C78A-C76	-C72
C12-C7-N1	120.6(3)	C78A-C76	-C77A
C8-C7-N1	118.7(4)	C72-C76-C77A	112.2(9)
C27-C25-C24	112.5(4)	C77-C76-C78	108.7(9)
C27-C25-C26	110.4(4)	C72-C76-C78	111.2(7)
C24-C25-C26	110.4(3)	C70-C71-C72	121.5(4)
N6-C62-C63	126.1(4)	C91-C96-C95	121.0(5)
N6-C62-C61	113.7(3)	C82-C83-C84	121.4(5)
C63-C62-C61	120.1(4)	C99-C98-C97	119.1(6)
C32-C33-C34	117.4(4)	C99-C98-C106	118.5(5)
C80-C88-C89	111.5(4)	C97-C98-C106	122.4(5)
C80-C88-C90	112.1(4)	C112-C113-C114	121.0(5)
C89-C88-C90	110.0(4)	C2-C3-C4	116.5(4)
C41-C42-C37	118.1(4)	C69-C70-C71	119.4(4)
C41-C42-C43	119.5(4)	C113-C112-C111	121.0(5)
C37-C42-C43	122.4(4)	C102-C101-C100	121.0(6)
C7-C12-C11	118.4(4)	C100-C99-C98	120.5(6)
C7-C12-C16	122.0(4)	C5-C4-C3	115.2(5)
C11-C12-C16	119.6(4)	C98-C106-C108	112.4(7)
C29-C28-C20	112.7(4)	C98-C106-C107	110.9(6)
C29-C28-C30	109.6(4)	C108-C106-C107	111.4(5)
C20-C28-C30	111.1(4)	C114-C115-C117	113.7(6)
C22-C21-C20	121.3(4)	C114-C115-C116	112.4(6)
C69-C68-C67	117.9(4)	C117-C115-C116	110.0(6)
C69-C68-C73	119.3(4)	C95-C94-C93	118.0(6)
C67-C68-C73	122.7(3)	C4-C5-C6	117.0(4)
C98-C97-C102	121.2(4)	C96-C95-C94	118.8(5)

C98-C97-N7	118.5(4)	C36-C35-C34	116.0(6)
C102-C97-N7	120.3(4)	C99-C100-C101	121.0(6)
C40-C39-C38	121.4(4)	C34-C35A-C36	113.4(14)

Crystallographic data for compound 7a

Identification code	Compound 7a
Empirical formula	$C_{66}H_{96}Ge_2N_4O$
Formula weight	1106.64
Temperature/K	153.0
Crystal system	triclinic
Space group	P-1
a/Å	12.930(5)
b/Å	15.925(8)
c/Å	17.049(8)
α/°	73.279(18)
β/°	85.825(19)
γ/°	71.002(18)
Volume/Å^3	3178(3)
Z	2
ρcalcg/cm^3	1.156
μ/mm^{-1}	0.997
F(000)	1184.0
Crystal size/mm^3	0.2 × 0.18 × 0.15
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	4.71 to 107.88
Index ranges	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected	62124
Independent reflections	11632 [R_{int} = 0.0687, R_{sigma} = 0.0487]
Data/restraints/parameters	11632/2/676
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0448, wR_2 = 0.1070
Final R indexes [all data]	R_1 = 0.0698, wR_2 = 0.1187
Largest diff. peak/hole / e Å^{-3}	0.56/-0.56

Table S8. Bond lengths [Å] and angles [°] for compound **7a**

Ge2-O1	1.8143(19)	C55-C56	1.523(4)
Ge2-N4	1.984(2)	C55-C57	1.535(4)
Ge2-N3	2.076(2)	C33-C34	1.482(4)
Ge1-O1	1.807(2)	C53-C52	1.371(4)
Ge1-N1	2.090(2)	C12-C13	1.509(5)

Ge1-N2	1.981(2)	C12-C11	1.405(4)
N4-C32	1.372(3)	C8-C9	1.407(5)
N4-C49	1.437(3)	C8-C16	1.505(6)
N3-C31	1.310(3)	C36-C35	1.510(4)
N3-C37	1.438(3)	C3-C4	1.503(4)
N1-C1	1.305(3)	C42-C43	1.518(5)
N1-C7	1.453(3)	C42-C41	1.392(4)
N2-C2	1.369(3)	C58-C60	1.524(5)
N2-C19	1.437(4)	C58-C59	1.528(4)
C32-C31	1.466(3)	C51-C52	1.378(5)
C32-C33	1.370(4)	C6-C5	1.493(4)
C1-C2	1.468(4)	C23-C22	1.378(5)
C1-C6	1.478(3)	C34-C35	1.487(5)
C49-C54	1.403(4)	C5-C4	1.505(4)
C49-C50	1.415(4)	C22-C21	1.378(5)
C2-C3	1.373(4)	C43-C44	1.519(5)
C31-C36	1.469(4)	C43-C45	1.509(6)
C54-C55	1.522(4)	C39-C40	1.375(5)
C54-C53	1.401(4)	C20-C21	1.395(5)
C7-C12	1.389(4)	C20-C28	1.524(5)
C7-C8	1.394(4)	C13-C15	1.515(5)
C46-C38	1.512(4)	C13-C14	1.533(5)
C46-C47	1.533(4)	C11-C10	1.359(6)
C46-C48	1.534(4)	C41-C40	1.377(5)
C50-C58	1.524(4)	C9-C10	1.370(6)
C50-C51	1.393(4)	C16-C17	1.537(6)
C24-C19	1.400(4)	C16-C18	1.549(6)
C24-C25	1.516(4)	C28-C29	1.494(7)
C24-C23	1.392(4)	C28-C30	1.509(7)
C37-C38	1.404(4)	C66-C65	1.589(15)
C37-C42	1.411(4)	C61-C62	1.503(11)
C38-C39	1.396(4)	C63-C64	1.507(12)
C19-C20	1.408(4)	C63-C62	1.397(11)
C25-C27	1.527(4)	C64-C65	1.447(9)
C25-C26	1.529(4)	C20-C19-N2	118.8(3)
O1-Ge2-N4	101.38(9)	C24-C25-C27	112.7(2)
O1-Ge2-N3	92.74(9)	C24-C25-C26	110.3(3)
N4-Ge2-N3	78.73(9)	C27-C25-C26	109.6(3)
O1-Ge1-N1	98.00(9)	C54-C55-C56	113.6(2)
O1-Ge1-N2	96.87(10)	C54-C55-C57	110.5(2)
N2-Ge1-N1	78.42(9)	C56-C55-C57	109.6(3)

Ge1-O1-Ge2	121.17(11)	C32-C33-C34	123.0(2)
C32-N4-Ge2	116.91(16)	C52-C53-C54	121.4(3)
C32-N4-C49	119.27(19)	C7-C12-C13	122.8(3)
C49-N4-Ge2	119.54(16)	C7-C12-C11	117.6(3)
C31-N3-Ge2	115.40(17)	C11-C12-C13	119.6(3)
C31-N3-C37	122.0(2)	C7-C8-C9	117.6(4)
C37-N3-Ge2	122.52(17)	C7-C8-C16	122.5(3)
C1-N1-Ge1	114.86(18)	C9-C8-C16	119.9(3)
C1-N1-C7	120.6(2)	C31-C36-C35	114.0(2)
C7-N1-Ge1	123.49(16)	C2-C3-C4	121.8(3)
C2-N2-Ge1	117.77(19)	C37-C42-C43	122.0(3)
C2-N2-C19	119.0(2)	C41-C42-C37	117.4(3)
C19-N2-Ge1	121.61(17)	C41-C42-C43	120.6(3)
N4-C32-C31	113.8(2)	C50-C58-C60	112.7(3)
C33-C32-N4	127.3(2)	C50-C58-C59	110.8(3)
C33-C32-C31	118.9(2)	C60-C58-C59	111.6(3)
N1-C1-C2	116.0(2)	C52-C51-C50	121.2(3)
N1-C1-C6	125.0(3)	C53-C52-C51	120.2(3)
C2-C1-C6	118.8(2)	C1-C6-C5	113.5(3)
C54-C49-N4	120.1(2)	C22-C23-C24	121.3(3)
C54-C49-C50	120.9(2)	C33-C34-C35	112.9(3)
C50-C49-N4	118.8(3)	C6-C5-C4	111.1(3)
N2-C2-C1	112.9(2)	C21-C22-C23	119.7(3)
N2-C2-C3	127.1(3)	C42-C43-C44	113.4(3)
C3-C2-C1	119.8(2)	C45-C43-C42	111.0(4)
N3-C31-C32	115.2(2)	C45-C43-C44	111.3(4)
N3-C31-C36	125.4(2)	C3-C4-C5	112.2(3)
C32-C31-C36	119.4(2)	C40-C39-C38	121.6(3)
C49-C54-C55	121.9(2)	C19-C20-C28	122.3(3)
C53-C54-C49	118.0(3)	C21-C20-C19	117.9(3)
C53-C54-C55	120.0(3)	C21-C20-C28	119.8(3)
C12-C7-N1	119.7(3)	C12-C13-C15	112.1(3)
C12-C7-C8	121.9(3)	C12-C13-C14	112.0(3)
C8-C7-N1	118.4(3)	C15-C13-C14	110.7(3)
C38-C46-C47	111.5(2)	C10-C11-C12	121.8(4)
C38-C46-C48	111.2(3)	C40-C41-C42	121.8(3)
C47-C46-C48	110.6(2)	C10-C9-C8	121.4(4)
C49-C50-C58	122.5(2)	C39-C40-C41	119.8(3)
C51-C50-C49	118.2(3)	C34-C35-C36	111.7(3)
C51-C50-C58	119.2(3)	C8-C16-C17	111.6(4)
C19-C24-C25	121.8(2)	C8-C16-C18	110.9(4)

C23-C24-C19	118.5(3)	C17-C16-C18	110.4(4)
C23-C24-C25	119.7(3)	C22-C21-C20	121.5(3)
C38-C37-N3	120.4(2)	C11-C10-C9	119.7(3)
C38-C37-C42	121.8(2)	C29-C28-C20	113.0(3)
C42-C37-N3	117.7(2)	C29-C28-C30	110.2(4)
C37-C38-C46	123.1(2)	C30-C28-C20	111.9(5)
C39-C38-C46	119.4(3)	C62-C63-C64	110.3(10)
C39-C38-C37	117.5(3)	C65-C64-C63	119.8(12)
C24-C19-N2	120.1(3)	C63-C62-C61	112.9(9)
C24-C19-C20	121.1(3)	C64-C65-C66	115.7(15)

C. NMR spectra of 2-7

Compound 2

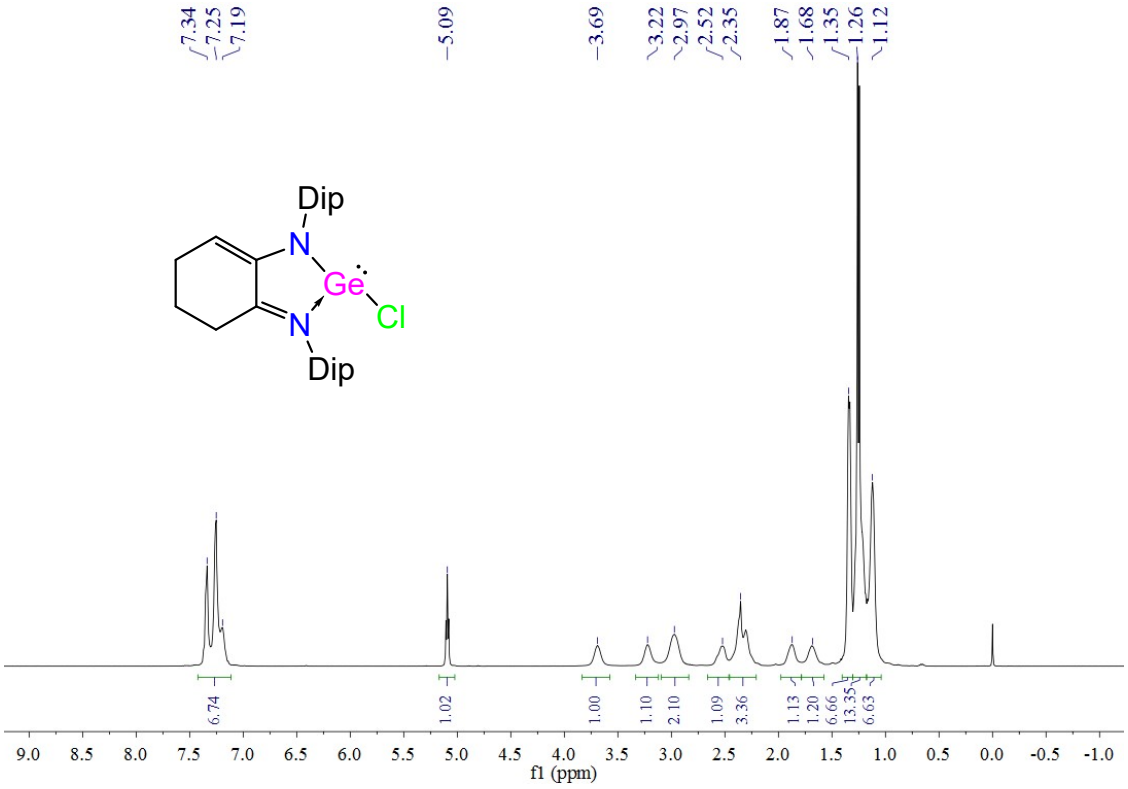

Figure S3. ^{1}H-NMR (400 MHz) spectrum of **2** in $CDCl_3$.

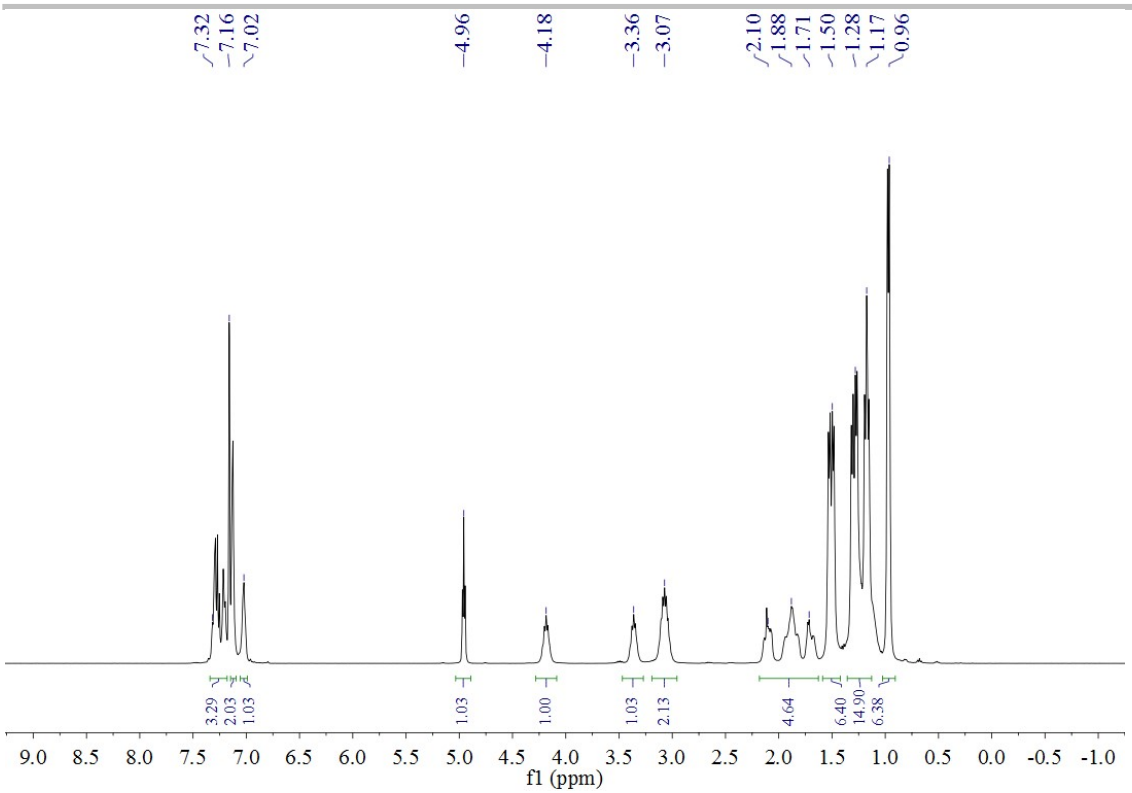

Figure S4. ^{1}H-NMR (400 MHz) spectrum of **2** in C_6D_6.

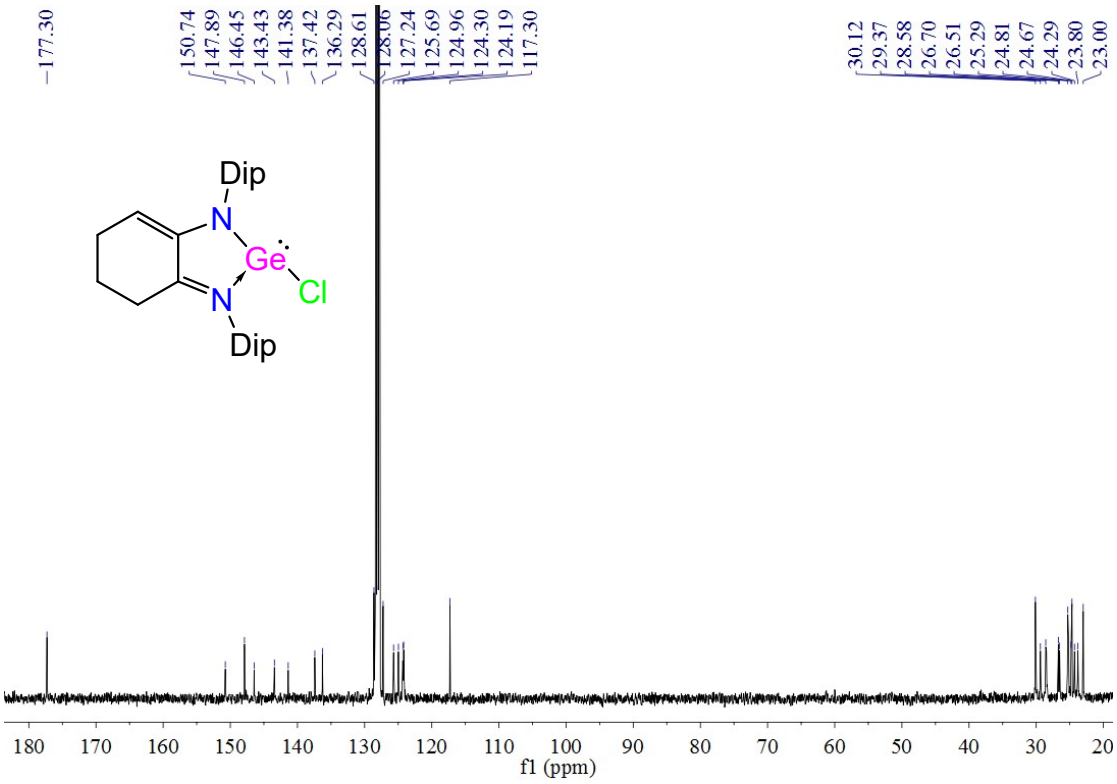

Figure S5. ^{13}C-NMR (100 MHz) spectrum of **2** in C_6D_6.

Compound 3

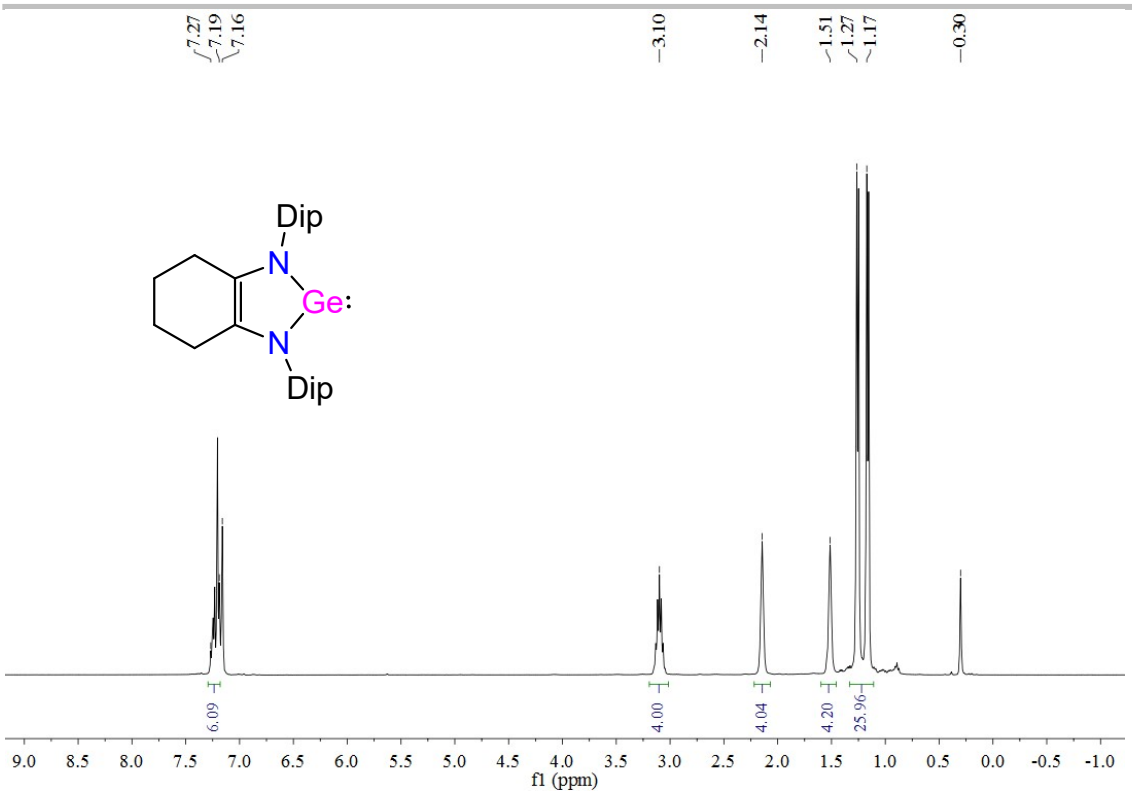

Figure S6. ^{1}H-NMR (400 MHz) spectrum of **3** in C_6D_6.

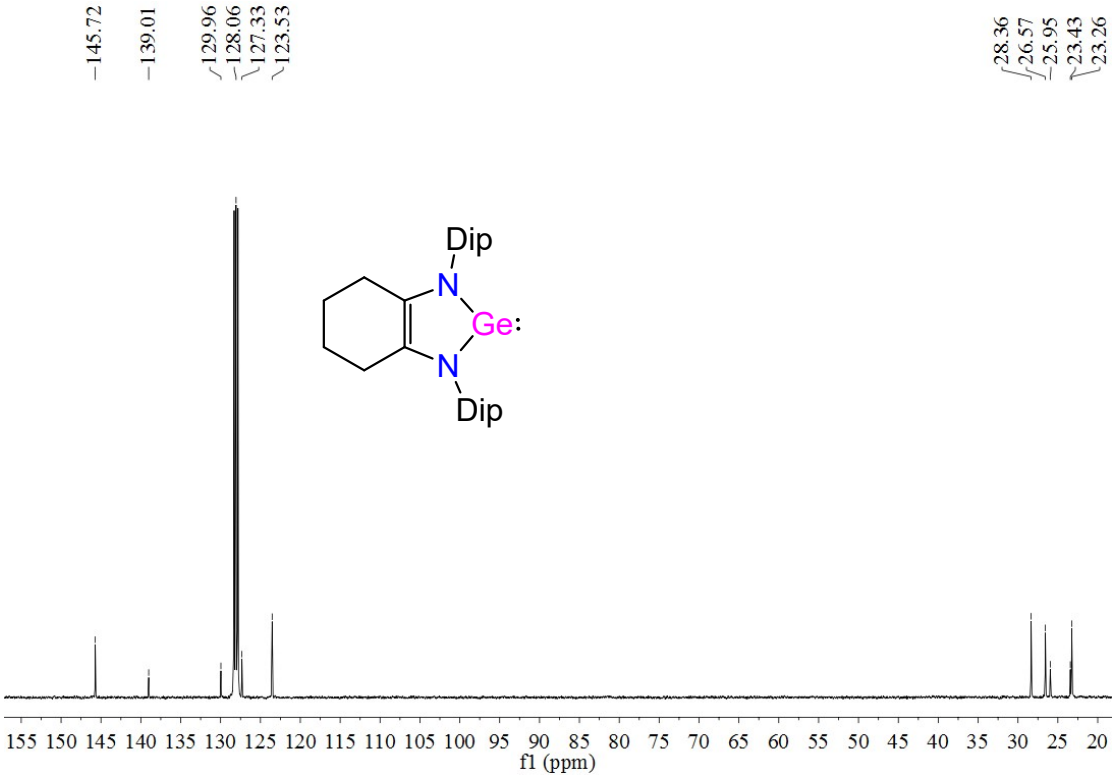

Figure S7. ^{13}C-NMR (100 MHz) spectrum of **3** in C_6D_6.

Compound 4

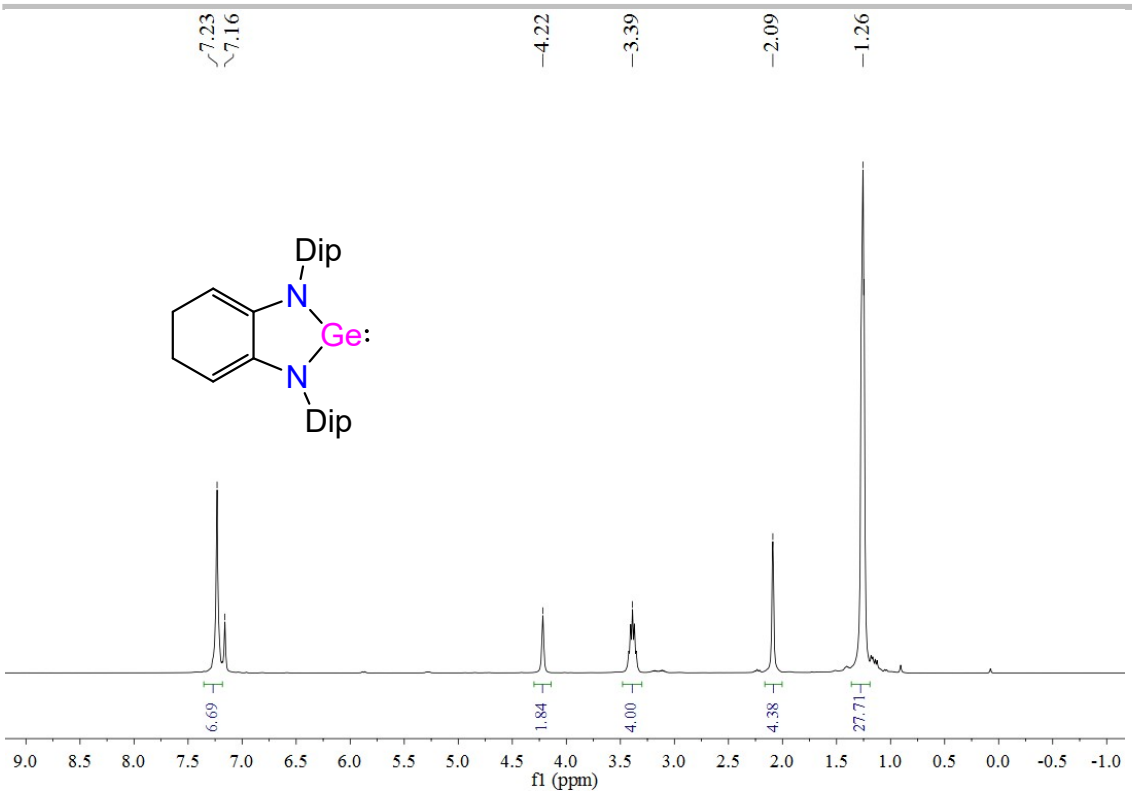

Figure S8. ^{1}H-NMR (400 MHz) spectrum of **4** in C_6D_6.

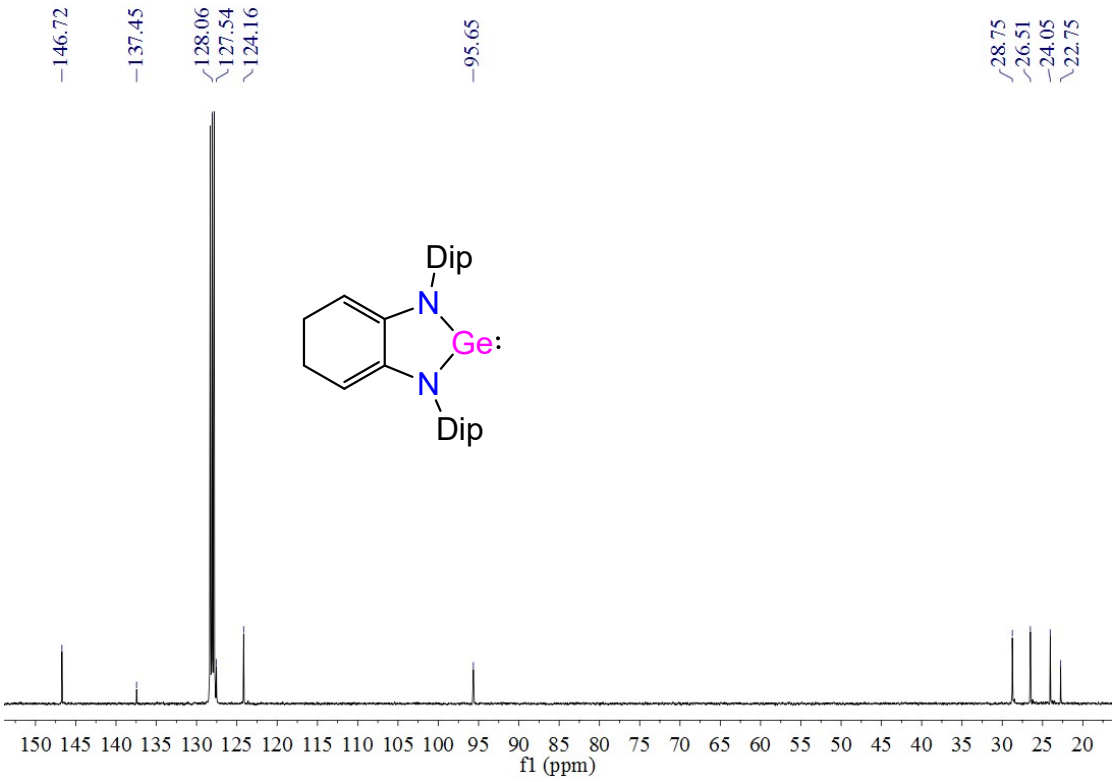

Figure S9. ^{13}C-NMR (100 MHz) spectrum of **4** in C_6D_6.

Compound 5

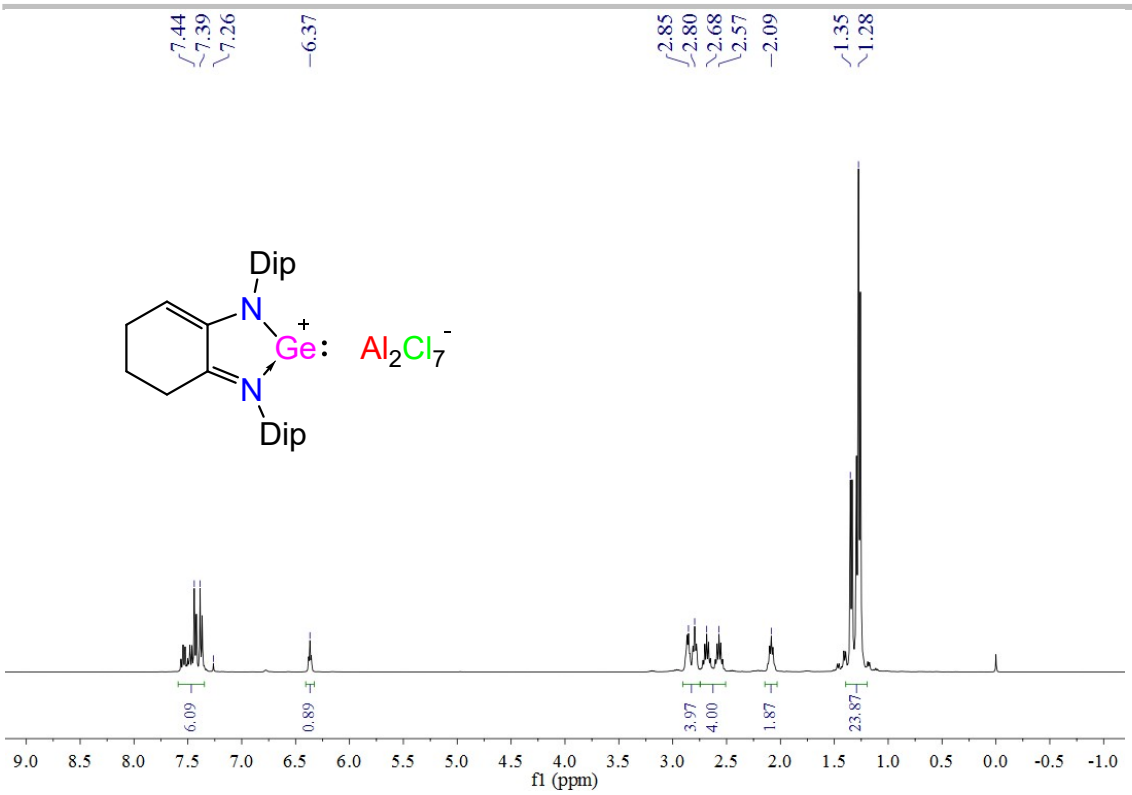

Figure S10. ^{1}H-NMR (400 MHz) spectrum of **5** in $CDCl_3$.

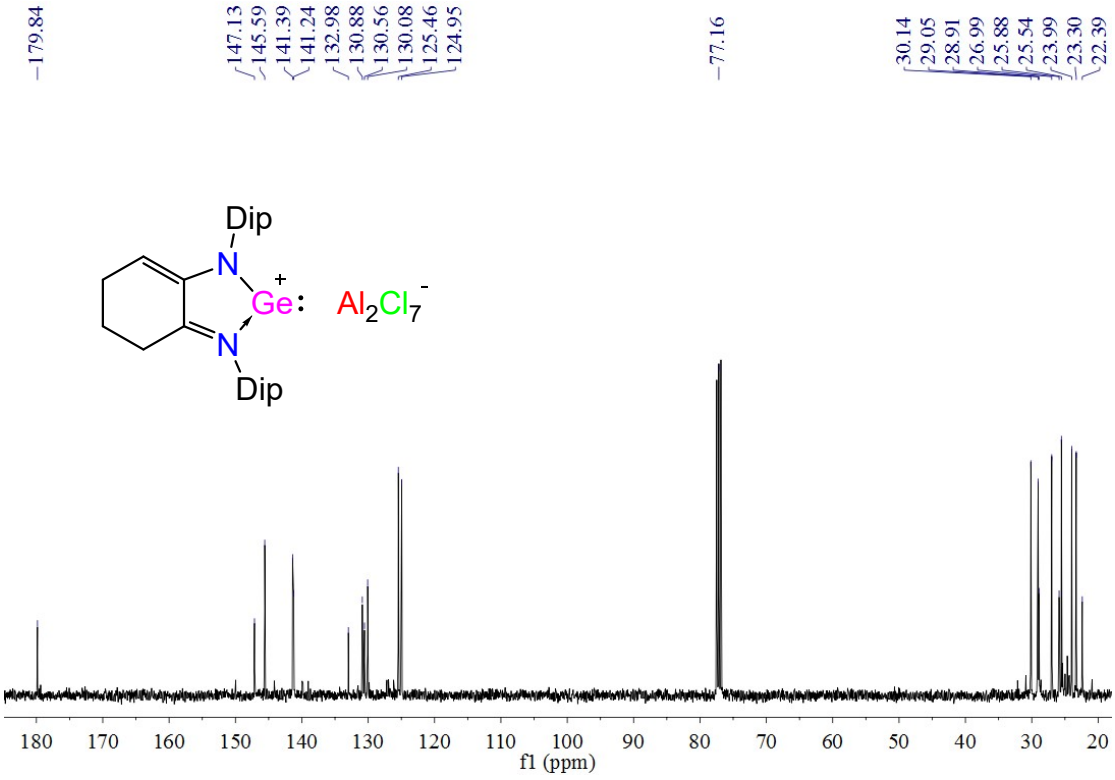

Figure S11. ^{13}C-NMR (100 MHz) spectrum of **5** in $CDCl_3$.

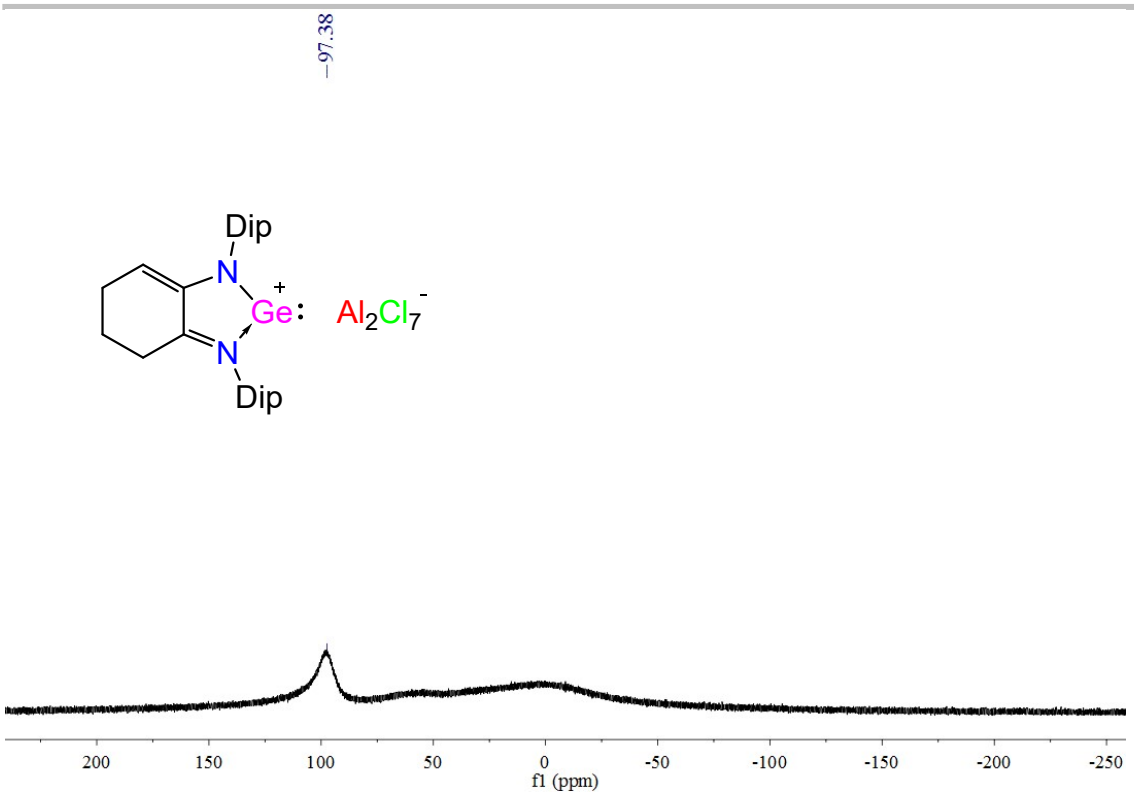

Figure S12. ^{27}Al-NMR (600 MHz) spectrum of **5** in $CDCl_3$.

Compound 6

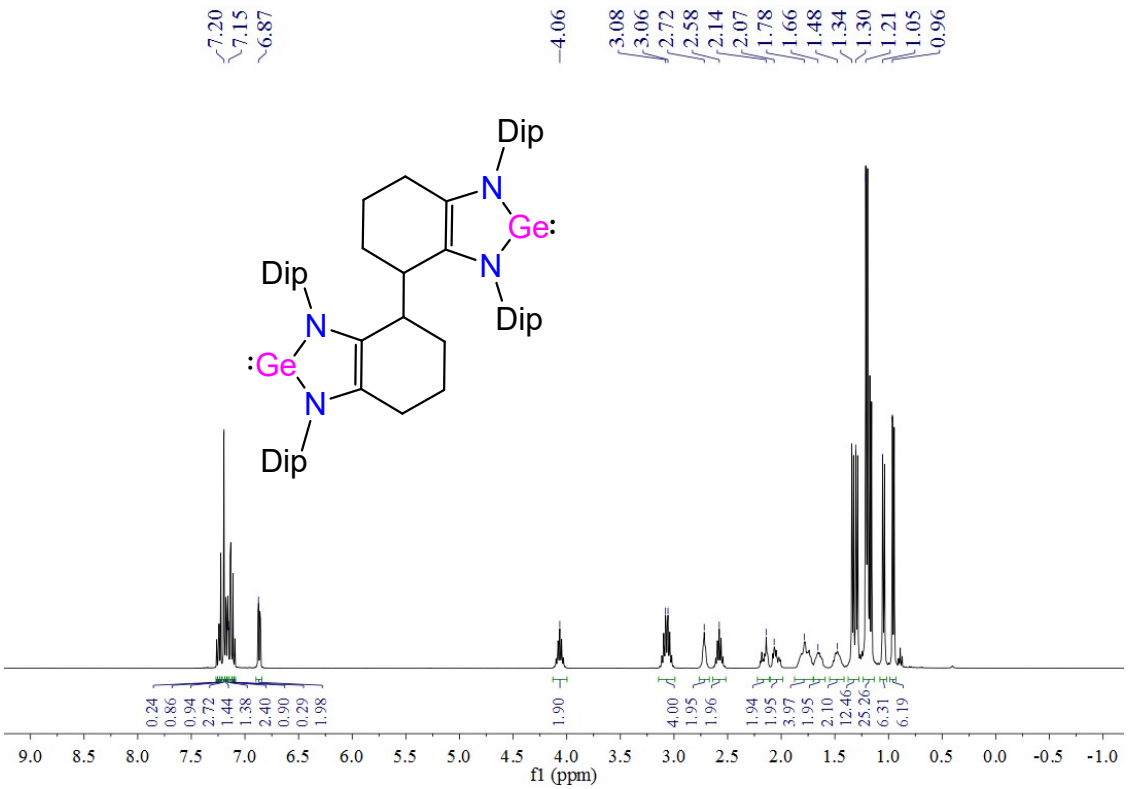

Figure S13. ^{1}H-NMR (400 MHz) spectrum of **6** in C_6D_6.

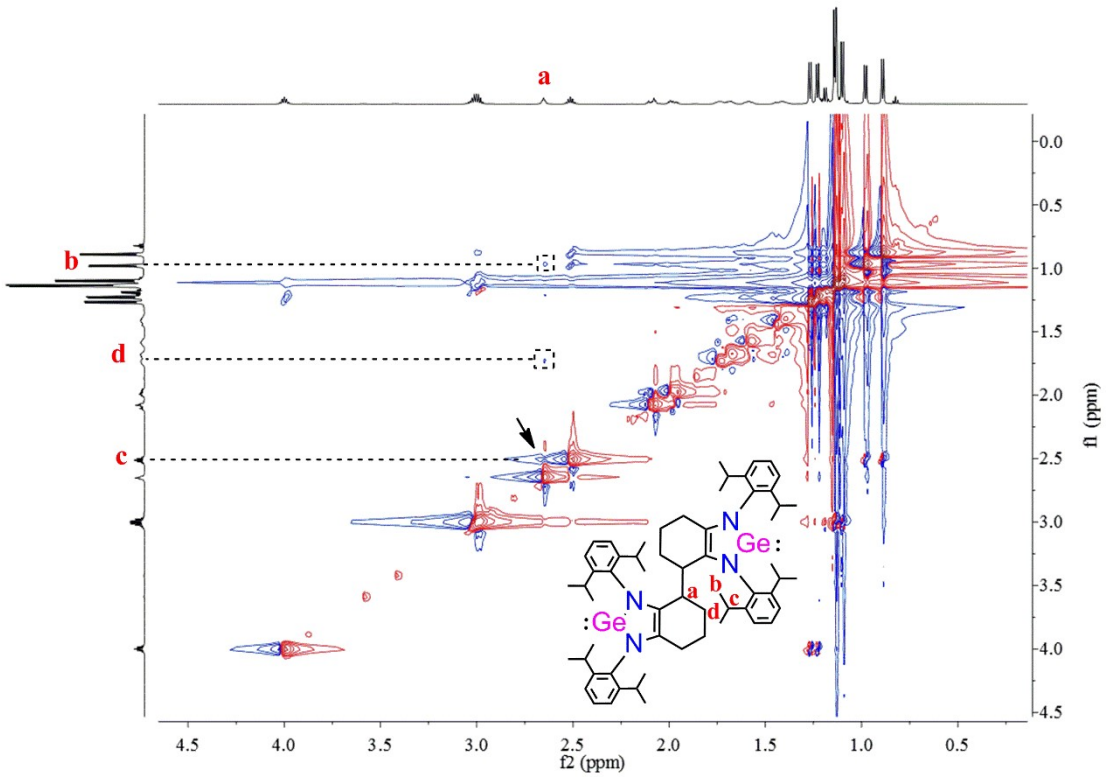

Figure S14. ^{1}H-^{1}H NOESY NMR (600 MHz) spectrum of **6** in C_6D_6.

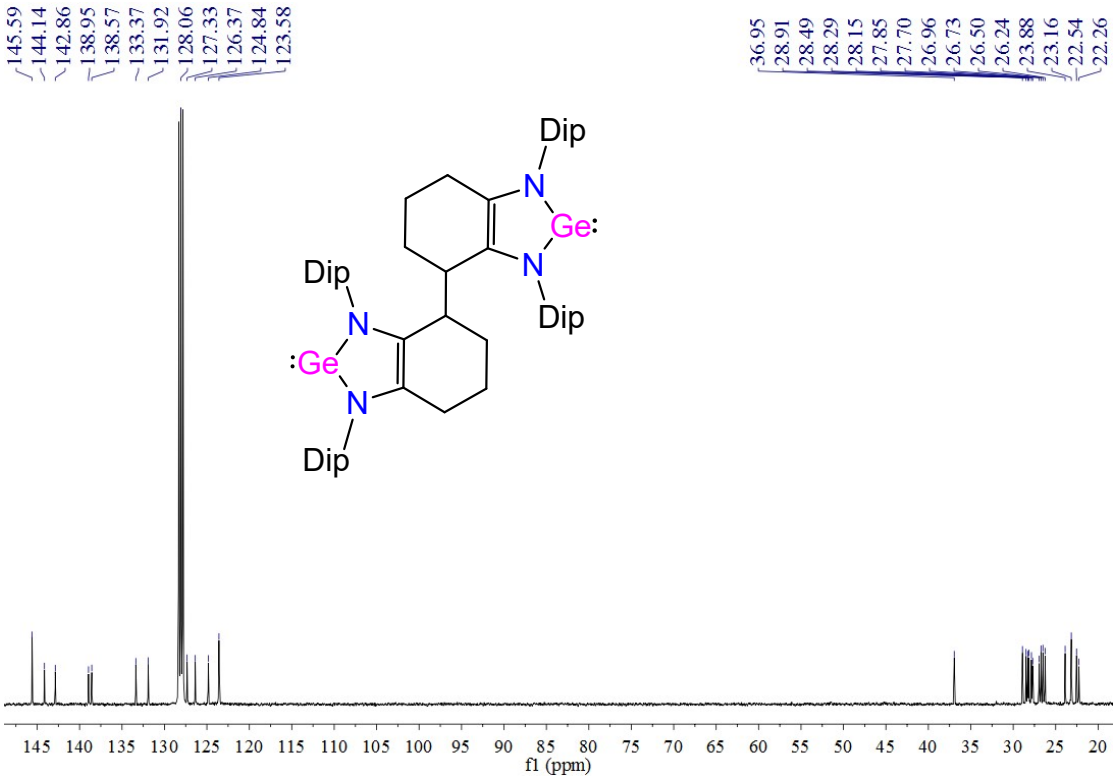

Figure S15. ^{13}C-NMR (100 MHz) spectrum of **6** in C_6D_6.

Compound 7

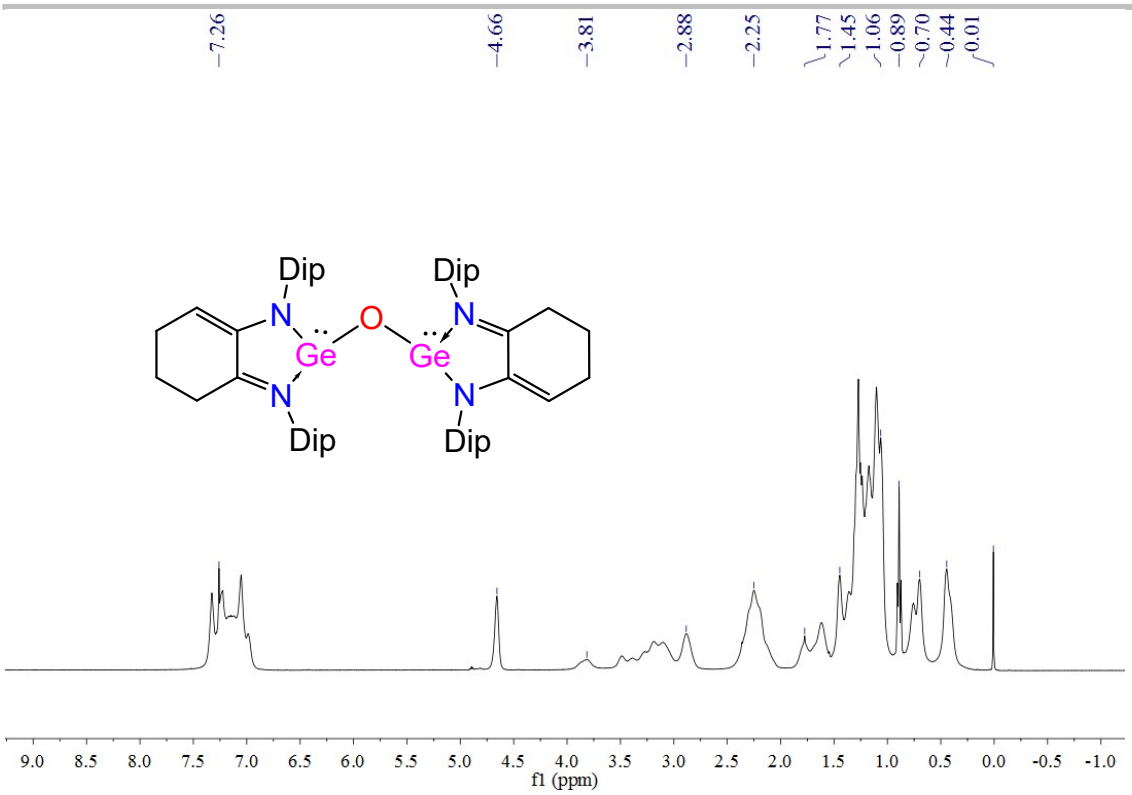

Figure S16. ^{1}H-NMR (400 MHz) spectrum of the mixture of conformational and *cis-trans* isomers of **7** in $CDCl_3$ at 298 K.

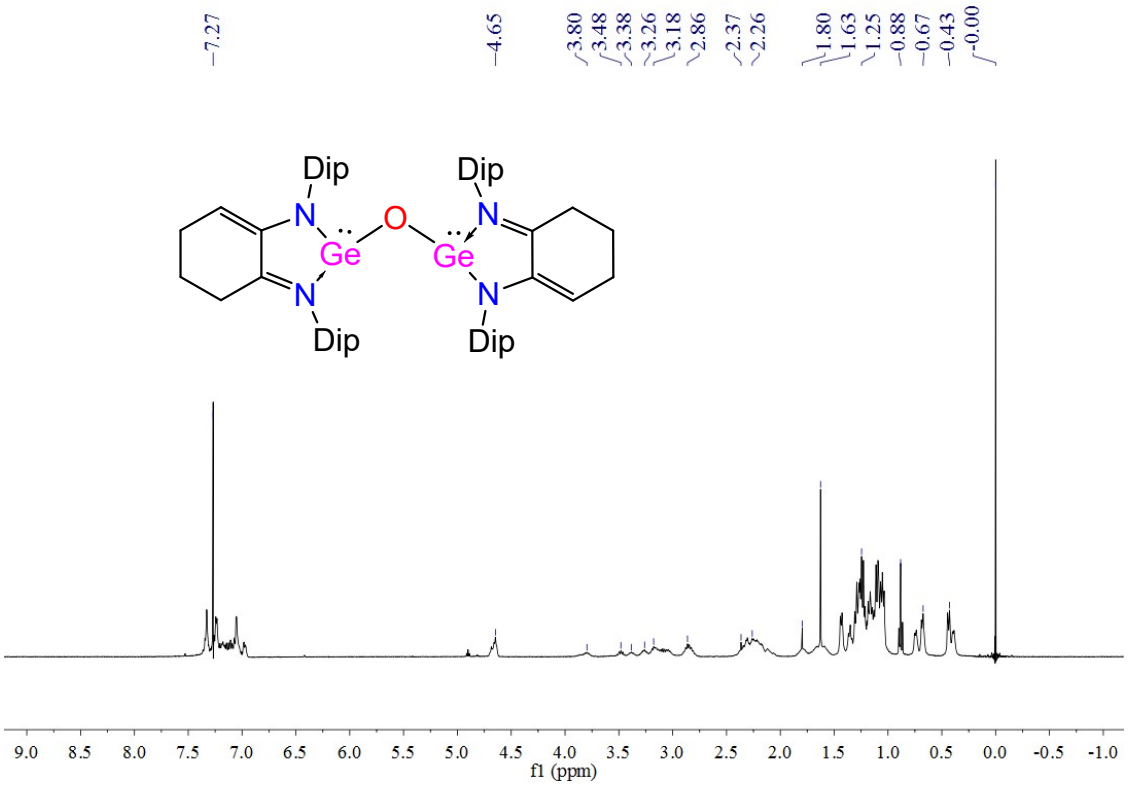

Figure S17. ^{1}H-NMR (400 MHz) spectrum of the mixture of conformational and *cis-trans* isomers of **7** in $CDCl_3$ at 273 K.

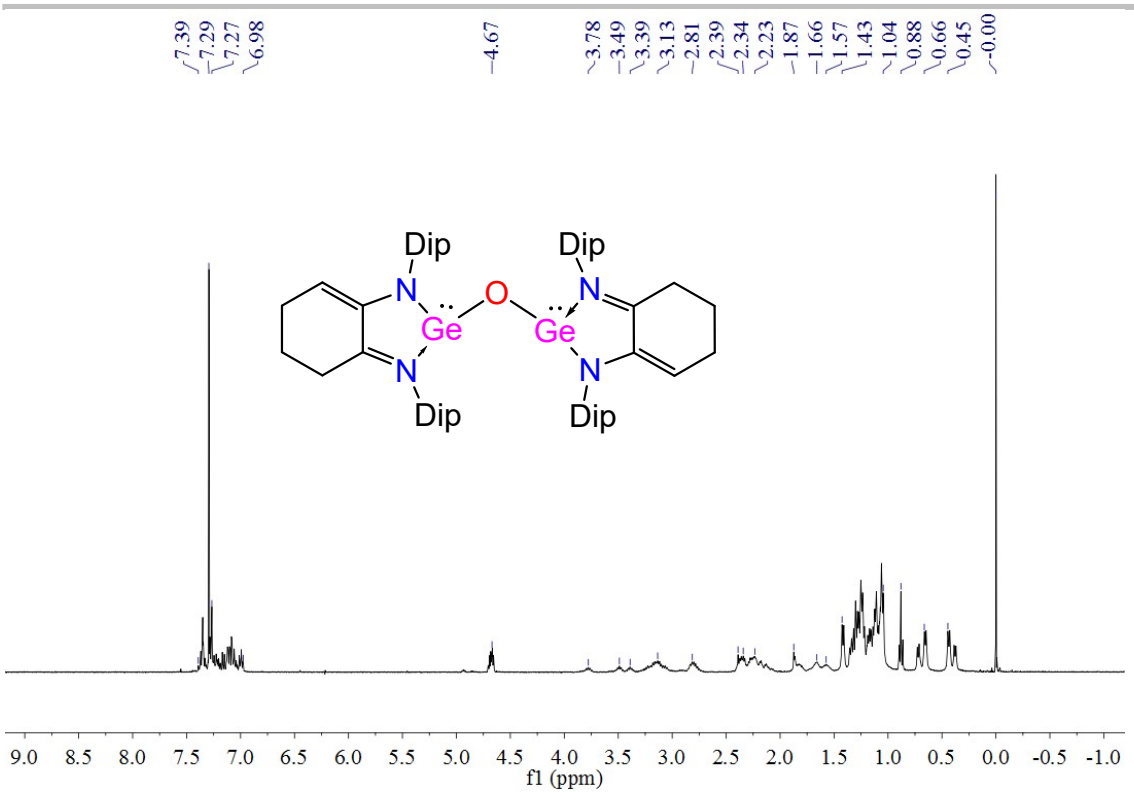

Figure S18. ^{1}H-NMR (400 MHz) spectrum of the mixture of conformational and *cis-trans* isomers of **7** in $CDCl_3$ at 223 K.

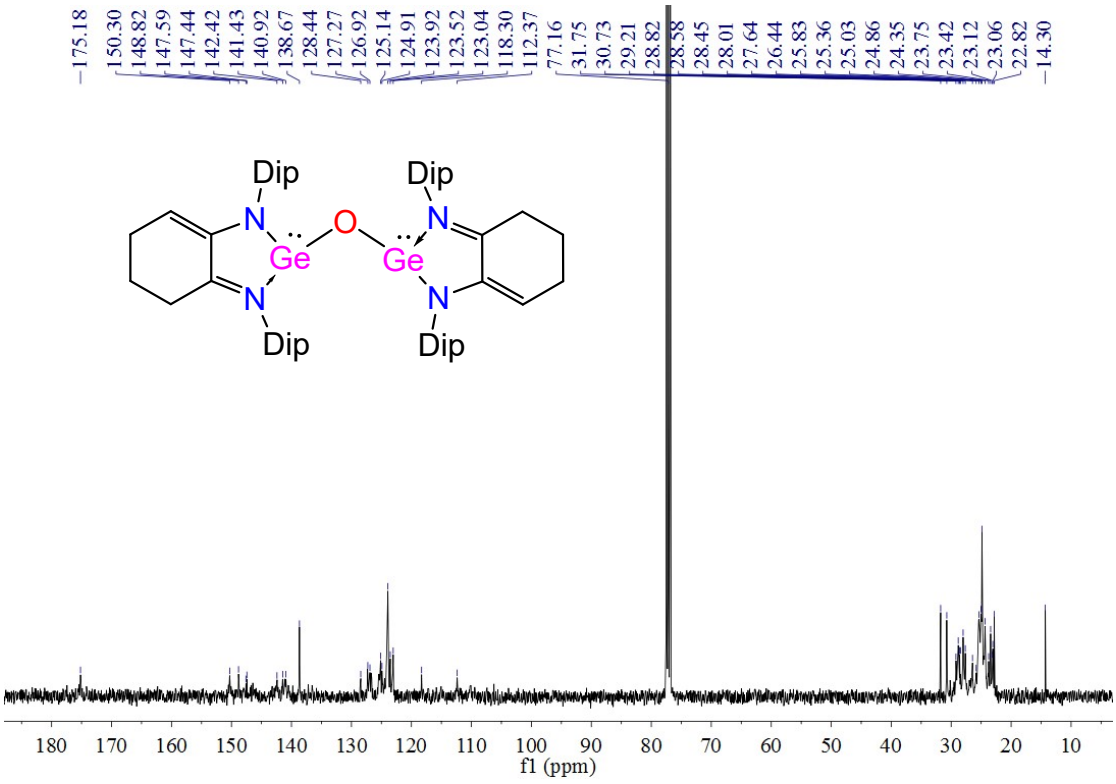

Figure S19. ^{13}C-NMR (100 MHz) spectrum of the mixture of conformational and *cis-trans* isomers of **7** in $CDCl_3$ at 298 K.

D. Computational details

The geometries of **3**, **4** and **5** were optimized by hybrid functional M06-2x[7] with the def2-TZVP basis set.[8] Table S9-S10 list the key geometries of **3**, **4**, **5** and **C-Ge**, and the optimized structures are in agreement with single-crystal XRD results of **3** and **4**. The observation of experimental structural feature of **5** deviating from the theoretical values.

Table S9. Key geometries in internal coordinates (R is bond length in Å, θ is bond angle in degrees °) of **3**, **4** and **5**.

Bond parameters	**3**		**4**		**5**	
	experiment	theory	experiment	theory	experiment	theory
R_{Ge1-N1}	1.868(3)	1.873	1.855(2)	1.863	1.9123(19)	2.004
R_{Ge1-N2}	1.869(3)	1.873	1.856(2)	1.864	1.9180(19)	1.839
R_{N1-C1}	1.383(5)	1.388	1.406(3)	1.397	1.351(3)	1.299
R_{N2-C2}	1.384(5)	1.388	1.404(3)	1.397	1.351(3)	1.398
R_{C1-C2}	1.360(5)	1.357	1.473(3)	1.478	1.455(3)	1.452
$\theta_{N(1)-Ge(1)-N(2)}$	83.08(12)	83.1	85.64(9)	85.5	82.32(8)	83.2

Table S10. Part of NPA charges and NICS(1) of C_2N_2Ge-rings in **3**, **4**, **5** and **C-Ge**.

Atom	**3**	**4**	**5**	**C-Ge**
Ge	1.036	1.220	1.297	1.140
N1	-0.814	-0.869	-0.681	-0.829
N2	-0.814	-0.869	-0.892	-0.829
C1	0.110	0.121	0.446	0.119
C2	0.110	0.121	0.018	0.119
C_2N_2Ge	-0.372	-0.276	0.188	-0.280
NICS(1)	-4.657	-0.605	-2.220	-4.547

Table S11. The coordinates for DFT-calculated structures of **3**.

Atom	x	y	z
Ge	0.00007600	-0.00191900	-1.45635800
N	1.24282400	-0.01706300	-0.05455400
C	0.67814100	-0.01381500	1.21339000
N	-1.24284300	0.01648100	-0.05474800
C	-0.67829000	0.01626800	1.21327600
C	-1.51280400	0.05621700	2.45824100
H	-2.31732600	0.78750800	2.33991300
H	-2.00642400	-0.91201200	2.61007300
C	1.51257800	-0.05118600	2.45848800
H	2.00638800	0.91727200	2.60824400
H	2.31695500	-0.78288200	2.34169300
C	2.65971400	0.01548000	-0.20905700
C	3.36275200	-1.18092100	-0.40888200

C	4.73843800	-1.11281900	-0.61245700
H	5.29717000	-2.02457500	-0.78447100
C	5.40297500	0.10107600	-0.59661100
H	6.47277200	0.13552400	-0.75855600
C	4.69879000	1.27121000	-0.36321500
H	5.22867100	2.21543600	-0.34289500
C	3.32296300	1.25101600	-0.16144900
C	2.65583600	-2.52199400	-0.42449300
H	1.65944500	-2.37631800	-0.00216000
C	2.49188900	-3.02522000	-1.86072400
H	1.93822500	-2.30918600	-2.47061100
H	1.95737600	-3.97710700	-1.87751800
H	3.47019800	-3.17404800	-2.32395200
C	3.37190500	-3.56646200	0.43229600
H	4.34435000	-3.83213500	0.01395800
H	2.77697600	-4.47996600	0.48147900
H	3.53013800	-3.20402300	1.44911800
C	2.56167100	2.54445500	0.05692600
H	1.58982500	2.29381500	0.48667900
C	2.31387400	3.24539400	-1.28174800
H	3.26379900	3.50033500	-1.75737100
H	1.74682100	4.16688700	-1.13466400
H	1.75660600	2.60417500	-1.96720800
C	3.26840500	3.48628200	1.03151200
H	3.51424300	2.97968400	1.96615200
H	2.62524100	4.33732500	1.26102100
H	4.19375500	3.88288500	0.61014700
C	-2.65975500	-0.01599600	-0.20918500
C	-3.36267200	1.18037200	-0.40976200
C	-4.73840700	1.11232500	-0.61288000
H	-5.29708200	2.02402800	-0.78532100
C	-5.40308800	-0.10150200	-0.59612200
H	-6.47292800	-0.13590500	-0.75779600
C	-4.69901100	-1.27156800	-0.36215800
H	-5.22899900	-2.21572100	-0.34109200
C	-3.32313900	-1.25139800	-0.16057700
C	-2.56204500	-2.54473900	0.05902900
H	-1.59013100	-2.29374100	0.48843900
C	-2.31448900	-3.24720900	-1.27886700
H	-3.26450100	-3.50259800	-1.75408600
H	-1.74754000	-4.16860400	-1.13077900

H	-1.75722400	-2.60687300	-1.96514700
C	-3.26889700	-3.48538400	1.03468600
H	-3.51456300	-2.97774900	1.96880700
H	-2.62591200	-4.33633000	1.26506600
H	-4.19436200	-3.88223100	0.61379600
C	-2.65536100	2.52121200	-0.42698000
H	-1.65917500	2.37587200	-0.00403500
C	-2.49069400	3.02211500	-1.86396200
H	-1.93728500	2.30480200	-2.47257500
H	-1.95564100	3.97367200	-1.88209900
H	-3.46880500	3.17075000	-2.32766600
C	-3.37140500	3.56731600	0.42779300
H	-4.34352700	3.83276300	0.00855400
H	-2.77610900	4.48064300	0.47575600
H	-3.53027400	3.20662600	1.44514100
C	-0.64853100	0.40577600	3.66905800
H	-0.40592700	1.47270900	3.64040700
H	-1.20942000	0.22801100	4.58799800
C	0.64819400	-0.39799400	3.67004800
H	0.40563500	-1.46499500	3.64384300
H	1.20903800	-0.21807800	4.58859500

Table S12. The coordinates for DFT-calculated structures of **4**.

Atom	x	y	z
Ge	0.00068500	-0.04829500	-1.39085400
N	-1.26232800	0.01632100	-0.02257600
N	1.26522200	-0.08440300	-0.02234600
C	2.67536700	0.01042700	-0.20068100
C	0.74000700	0.01141100	1.26905500
C	-2.67570000	-0.01975000	-0.19648400
C	-0.73695800	-0.05310500	1.27048400
C	-3.32362100	-1.25145100	-0.35762400
C	-3.39142500	1.18723200	-0.18976800
C	3.26668400	1.26959700	-0.37049900
C	-2.55997300	-2.56028700	-0.31710800
H	-1.57126400	-2.35684000	0.09889200
C	1.42003200	0.19817400	2.40857000
H	2.49853200	0.29741900	2.39175100
C	-1.41695800	-0.20437600	2.41522500
H	-2.49620400	-0.29596000	2.40283900
C	-4.76365600	1.14180300	-0.40884300

H	-5.33518300	2.06100300	-0.42016600
C	4.63966100	1.32925700	-0.59416200
H	5.11414900	2.29091200	-0.74775800
C	-5.41321600	-0.06575100	-0.61266700
H	-6.48136300	-0.08218500	-0.78793400
C	-2.67683000	2.50850100	0.01607700
H	-1.75488000	2.29894000	0.56113900
C	3.44500400	-1.16260800	-0.18802500
C	5.40734400	0.17796900	-0.62220600
H	6.47341900	0.24194900	-0.79935100
C	-4.69859500	-1.25023600	-0.57899200
H	-5.21557100	-2.19049800	-0.72585400
C	4.81354900	-1.05652200	-0.41028500
H	5.42625900	-1.94892900	-0.41693700
C	2.44724300	2.54481200	-0.33556600
H	1.46293000	2.30001500	0.06838900
C	0.65978700	0.40121800	3.69262800
H	0.44872700	1.47300000	3.81421800
H	1.26966300	0.10671200	4.54768500
C	-0.65548300	-0.37311500	3.70382500
H	-0.44396600	-1.44097300	3.85445000
H	-1.26482400	-0.05570400	4.55102700
C	2.26096100	3.10396600	-1.74843300
H	3.22776900	3.36305000	-2.18642200
H	1.64308000	4.00378700	-1.73071100
H	1.78639100	2.37325000	-2.40722900
C	-3.22790400	-3.59027000	0.59390700
H	-3.37970800	-3.18489800	1.59502000
H	-2.60110400	-4.47996800	0.67414900
H	-4.19684600	-3.90595900	0.20323100
C	2.78897900	-2.51208700	0.02781900
H	1.86121500	-2.33792200	0.57554000
C	3.06094900	3.59735900	0.58782000
H	3.21609200	3.19360500	1.58911800
H	2.39734600	4.46037700	0.66372200
H	4.02120500	3.95348800	0.21077400
C	-3.48791800	3.49845100	0.85000000
H	-4.36737100	3.85521400	0.31068900
H	-2.87788400	4.37100900	1.08844600
H	-3.82053900	3.04709200	1.78563100
C	-2.38090100	-3.12198300	-1.72995100

H	-3.35299500	-3.33750700	-2.17971100
H	-1.80226900	-4.04747800	-1.70854700
H	-1.86792300	-2.41005000	-2.38028600
C	-2.30432500	3.12957500	-1.33306000
H	-1.68063500	2.45909500	-1.92818600
H	-1.76098400	4.06582200	-1.18999800
H	-3.20581100	3.34285100	-1.91222800
C	2.43594900	-3.15347500	-1.31703900
H	1.78638700	-2.50853600	-1.91255300
H	1.92832700	-4.10866400	-1.16837600
H	3.34328000	-3.33554800	-1.89789800
C	3.64503500	-3.46313400	0.86183200
H	4.53519800	-3.78616300	0.31883100
H	3.07262900	-4.35870600	1.10801800
H	3.96400800	-2.99368400	1.79329900

Table S13. The coordinates for DFT-calculated structures of **5**.

Atom	x	y	z
Ge	-2.37151500	-0.10732600	1.54257400
N	-1.51884300	-1.44176500	0.31487300
C	-1.01541100	-0.88490700	-0.74541000
N	-2.11881500	1.03366200	0.12218500
C	-1.30731100	0.52939900	-0.89841300
C	-0.87355500	1.19022500	-1.98892600
H	-1.18521200	2.22127400	-2.12810300
C	0.00849300	0.56959800	-3.01986300
H	0.75758600	1.30122300	-3.32972100
H	-0.60053200	0.36109200	-3.91046400
C	0.69344900	-0.69341900	-2.51999200
H	1.18499200	-1.21753300	-3.33756600
H	1.47768900	-0.40517100	-1.81752600
C	-0.28552800	-1.62338900	-1.81436800
H	-1.04030600	-2.01147600	-2.51296800
H	0.21632100	-2.49000500	-1.38141900
C	-1.59298300	-2.87822300	0.44779000
C	-2.65211500	-3.52568600	-0.20582800
C	-2.76916400	-4.90172600	-0.03915900
H	-3.58074900	-5.42878000	-0.52337000
C	-1.86110500	-5.60788800	0.72974300
H	-1.96934300	-6.67841900	0.84707600
C	-0.80400000	-4.94917900	1.33225500

H	-0.08319600	-5.51290600	1.90885100
C	-0.64155600	-3.57326500	1.20237100
C	0.51532000	-2.86615500	1.87212000
H	0.71929100	-1.94978100	1.31658000
C	1.80433100	-3.68570200	1.87506700
H	1.73392300	-4.55243500	2.53428300
H	2.62480200	-3.06658000	2.23836000
H	2.06275700	-4.03363700	0.87378500
C	0.13183300	-2.47811100	3.30273700
H	-0.75828500	-1.84504200	3.33212000
H	0.94518800	-1.93102900	3.77967400
H	-0.08156200	-3.37589500	3.88771200
C	-3.67800800	-2.78132700	-1.04144900
H	-3.25521200	-1.82342000	-1.35348400
C	-4.92837300	-2.49027000	-0.20846400
H	-5.36515100	-3.42311200	0.15355700
H	-5.67530500	-1.97101000	-0.81069400
H	-4.70500600	-1.87188000	0.66576400
C	-4.05586700	-3.52975800	-2.32026000
H	-3.17140500	-3.82649300	-2.88553900
H	-4.67147400	-2.88962000	-2.95362000
H	-4.63667800	-4.42732100	-2.10473000
C	-2.79161600	2.29026100	-0.07733600
C	-2.14647900	3.49298800	0.25426000
C	-2.81072800	4.68742400	-0.00067300
H	-2.32865000	5.62392400	0.24562400
C	-4.07382500	4.69806300	-0.56880800
H	-4.57231100	5.63880600	-0.76434000
C	-4.69787100	3.50539900	-0.88111400
H	-5.68869000	3.52080100	-1.31865900
C	-4.07533400	2.28179600	-0.64326700
C	-4.82478500	1.01106800	-0.99547300
H	-4.20051300	0.15490300	-0.73568400
C	-6.11868500	0.91087800	-0.18338900
H	-5.91166000	0.90870100	0.88875800
H	-6.66528600	-0.00002200	-0.42980700
H	-6.77463300	1.75730000	-0.39217400
C	-5.10643400	0.91749100	-2.49597600
H	-5.76703400	1.72172800	-2.82463600
H	-5.59341900	-0.03150700	-2.73152300
H	-4.18251800	0.98328300	-3.07303200

C	-0.79110300	3.49151500	0.92338600
H	-0.27249700	2.58610000	0.61032800
C	0.08717000	4.67864800	0.53777500
H	0.17080900	4.78090400	-0.54522100
H	1.09211000	4.53147900	0.93587100
H	-0.29454900	5.61550900	0.94827400
C	-0.96953500	3.44068200	2.44388700
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H	0.00052100	3.39409000	2.94105200
H	-1.54760300	2.56763200	2.75655900
Cl	4.11581200	-0.42719700	-2.98999700
Al	5.17029400	-0.34926700	-1.15721300
Cl	6.41446800	-2.01159000	-0.82275700
Al	2.58571000	1.26507500	1.00602800
Cl	5.92535200	1.54084700	-0.64873100
Cl	3.52544900	-0.71034200	0.47261400
Cl	3.75019500	2.35672000	2.35693300
Cl	2.14336000	2.20465600	-0.83799900
Cl	0.79598400	0.56391900	2.00615700

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