Electronic Supplementary Information For

A germanimidoyl chloride: Synthesis, characterization and reactivity

By Tong Li,[a†] Li Zhang,[b†] Yuhao He,[a] Yizhen Chen,[a] Dongmin Wang,[a] Jingjing Liu[a*] and Gengwen Tan[a,c*]Corresponding authors: Jingjing Liu: jjliu@suda.edu.cn; Gengwen Tan: gwtan@suda.edu.cn;

Content

Experimental Section

General considerations: All experiments were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in a N_2 filled-glove box. Solvents were dried by standard methods and stored in activated 4 Å molecule sieve in the glovebox. The NMR spectra were recorded on Bruker spectrometers (AV400) referenced to residual solvent signals as internal standards. The solutions of samples in the deuterated solvent were sealed off in a NMR tube under vacuum for measurements. Element analyses were performed on an Elementar Vario EL III instrument. For the single crystal X-ray structure analyses the crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data for all compounds were collected on a Bruker D8 CMOS detector at low temperatures. The structures were solved by direct methods and all refined on F^2 with the SHELX-2014/3 software package.[1] The positions of the H atoms were calculated and considered isotropically according to a riding model. Platon SQUEEZE was used to remove the highly disordered solvent molecules in the crystal lattices.[2] Commercially available reagents were purchased from Energy Chemical and used as received. M^{s}Fluind$^{t\mathrm{Bu}}$-GeCl (**1**),[3] mesitylazide,[4] 1-azido-4-(tert-butyl)benzene[4] and 3,5-di-*tert*-phenyl lithium[5] were synthesized according to reported procedures.

Synthesis of M^{s}Fluind$^{t\mathrm{Bu}}$-Ge(Cl)=NMes (2)

To a solution of M^{s}Fluind$^{t\mathrm{Bu}}$-GeCl (**1**) (1.69 g, 2.00 mmol) in THF (30 mL), Mes-N_3 (0.36 g, 2.20 mmol) was added at room temperature. The suspension was stirred for 16 h and turned clear gradually. The color changed from yellow to orange red. The solvent was removed under vacuum, and the residue was washed with *n*-hexane (10 mL) to give an orange red powder (1.42 g, 73%). Orange crystals of **2** suitable for X-ray diffraction were obtained from THF/*n*-hexane solution at room temperature. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = 1.29 (s, 36H, C(C$\underline{H}_3$)$_3$), 1.54 (s, 12H, C(C$\underline{H}_3$)$_2$), 1.60 (s, 6H, Mes-C$\underline{H}_3$), 2.12 (s, 3H, Mes-C$\underline{H}_3$), 2.49 (s, 4H, CC$\underline{H}_2$C(CH$_3$)$_2$), 6.70 (s, 2H, Ar-$\underline{H}$), 7.18 (m, 4H, Ar-$\underline{H}$), 7.25 (m, 4H, Ar-$\underline{H}$), 7.36 (m, 4H, Ar-$\underline{H}$), 7.46 (s, 1H, Ar-$\underline{H}$) ppm. ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ = 21.0 (Mes-$\underline{C}$H$_3$), 21.8 (Mes-$\underline{C}$H$_3$), 23.1 (C($\underline{C}$H$_3$)$_3$), 31.7 ($\underline{C}$(CH$_3$)$_3$), 35.1 (C($\underline{C}$H$_3$)$_2$), 43.0 ($\underline{C}$(CH$_3$)$_2$), 58.3 (C$\underline{C}$H$_2$C(CH$_3$)$_2$), 64.9 ($\underline{C}$CH$_2$C(CH$_3$)$_2$), 120.0, 120.7, 122.5, 126.0, 127.9, 128.2, 130.4, 131.2, 131.9, 147.3, 148.5, 150.8, 155.4, 155.8 ppm. Elemental analysis for $C_{65}H_{76}ClGeN$ (%): Cacld: C

79.71, H 7.82, N 1.43; Found: C 79.36, H 7.45, N 1.65.

Synthesis of M^{s}Fluind^{tBu}-Ge(Cl)N$_4$Ar$_2$ (3)

To a solution of **1** (0.85 g, 1.00 mmol) in THF (30 mL), 1-azido-4-(*tert*- butyl)benzene (ArN_3) (0.44 g, 2.50 mmol) was added at room temperature. The yellow suspension was stirred for 16 h and turned clear gradually. The solvent was removed under vacuum, and the residue was washed with *n*-hexane (10 mL) to give a light yellow powder (0.77 g, 65%). Colorless crystals of **3** suitable for X-ray diffraction were obtained from THF/*n*-hexane solution at room temperature. ^{1}H NMR (THF-d_8, 400 MHz, 298 K): δ = 1.03 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.16 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.29 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.58 (s, 6H, C(C$\underline{H}_3$)$_2$), 1.60 (s, 6H, C(C$\underline{H}_3$)$_2$), 2.16 (s, 2H, CC$\underline{H}_2$C(CH$_3$)$_2$), 2.33 (s, 2H, CC$\underline{H}_2$C(CH$_3$)$_2$), 6.43-6.46 (m, 4H, Ar-$\underline{H}$), 6.79 (s, 2H, Ar-$\underline{H}$), 6.96-7.08 (m, 10H, Ar-$\underline{H}$), 7.23-7.26 (m, 2H, Ar-$\underline{H}$), 7.46-7.49 (m, 2H, Ar-$\underline{H}$), 8.02 (s, 1H, Ar-$\underline{H}$) ppm. ^{13}C NMR (THF-d_8, 100 MHz, 298 K): δ = 31.7 (C($\underline{C}$H$_3$)$_3$), 31.8 ($\underline{C}$(CH$_3$)$_3$), 32.1 (C($\underline{C}$H$_3$)$_3$), 32.3 (C($\underline{C}$H$_3$)$_3$), 32.9 ($\underline{C}$(CH$_3$)$_3$), 34.6 ($\underline{C}$(CH$_3$)$_3$), 35.0 (C($\underline{C}$H$_3$)$_2$), 35.3 (C($\underline{C}$H$_3$)$_2$), 42.1 ($\underline{C}$(CH$_3$)$_2$), 42.2 ($\underline{C}$(CH$_3$)$_2$), 64.2 (C$\underline{C}$H$_2$C(CH$_3$)$_2$), 64.6 (C$\underline{C}$H$_2$C(CH$_3$)$_2$), 68.0 ($\underline{C}$CH$_2$C(CH$_3$)$_2$), 68.8 ($\underline{C}$CH$_2$C(CH$_3$)$_2$), 116.9, 117.0, 117.7, 119.7, 119.8, 119,8, 119.9, 120.6, 124.7, 124.9, 125.0, 125.4, 125.5, 126.1, 126.4, 137.6, 137.7, 137.9, 138.4, 141.8, 144.7, 149.9, 150.2, 150.7, 152.5, 156.4, 160.4, 161.5 ppm. Elemental analysis for $C_{76}H_{91}ClGeN_4$ (%): Cacld: C 78.11, H 7.85, N 4.79; Found: C 78.55, H 7.39, N 4.96.

Synthesis of [M^{s}Fluind^{tBu}-GeN$_4$Ar$_2$][BAr$^{F}_4$] (4)

C_6H_5F (15 mL) was added to a mixture of **3** (0.24 g, 0.20 mmol) and NaBAr$^{F}_4$ (0.18 g, 0.20 mmol). After stirring for 16 h, the reaction mixture was filtered. The volatiles in the filtrate was removed under vacuum, and the residue was washed with *n*-hexane to give a red powder (0.22 g, 55%). Red crystals of **4** suitable for X-ray diffraction were obtained from C_6H_5F/*n*-hexane solution at room temperature. ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ = 0.98 (s, 36H, C(C$\underline{H}_3$)$_3$), 1.36 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.80 (s, 12H, C(C$\underline{H}_3$)$_2$), 2.67 (s, 4H, CC$\underline{H}_2$C(CH$_3$)$_2$), 6.20-6.22 (m, 4H, Ar-$\underline{H}$), 6.92 (s, 2H, Ar-$\underline{H}$), 6.94 (s, 2H, Ar-$\underline{H}$), 7.03-7.04 (m, 4H, Ar-$\underline{H}$), 7.12-7.18 (m, 8H, Ar-$\underline{H}$), 7.58 (s, 4H, Ar-$\underline{H}$), 7.75 ((m, 8H, Ar-$\underline{H}$), 7.93 (s, 1H, Ar-$\underline{H}$) ppm. ^{11}B NMR (CD_2Cl_2, 128 MHz, 298 K): δ = –6.6 ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz, 298 K): δ = 31.1 (C($\underline{C}$H$_3$)$_3$), 31.4 ($\underline{C}$(CH$_3$)$_3$), 33.1 (C($\underline{C}$H$_3$)$_3$), 35.0 ($\underline{C}$(CH$_3$)$_3$), 35.3 (C($\underline{C}$H$_3$)$_2$), 45.1

($\underline{C}(CH_3)_2$), 55.0 ($C\underline{C}H_2C(CH_3)_2$), 64.0 ($\underline{C}CH_2C(CH_3)_2$), 117.9, 118.7, 121.4, 121.9, 123.7, 126.4, 127.0, 127.6, 129.3, 135.2, 137.7, 138.4, 150.6, 151.3, 151.4, 154.1, 158.5, 162.1 (q, B-C, $^1J_{BC}$ = 50 Hz) ppm. ^{19}F NMR (CD_2Cl_2, 376 MHz, 298 K): δ = –62.8 ppm. Elemental analysis for $C_{108}H_{103}BF_{24}GeN_4$ (%): Cacld: C 64.98, H 5.20, N 2.81; Found: C 64.21, H 5.36, N 3.25.

Synthesis of M^{s}Fluind^{tBu}-Ge(Ar')=NMes (5)

THF (15 mL) was added to a Schlenk containing **2** (0.98 g, 1.00 mmol) and 3,5-di-*tert*-phenyl lithium (Ar'Li) (0.21 g, 1.01 mmol). The reaction mixture was stirred for 16 h at room temperature and filtered afterwards. The volatiles in the filtrate was removed under vacuum, and the residue was washed with *n*-hexane (10 mL) to give an orange powder (0.74 g, 65%). Orange crystals of **5** suitable for X-ray diffraction were grown from THF/*n*-hexane solution at room temperature. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 0.98 (s, 36H, C(C$\underline{H}_3$)$_3$), 1.19 (s, 6H, Mes-C$\underline{H}_3$), 1.23 (s, 18H, C(C$\underline{H}_3$)$_3$), 1.67 (s, 12H, C(C$\underline{H}_3$)$_2$), 2.16 (s, 3H, Mes-C$\underline{H}_3$), 2.37 (s, 4H, CC$\underline{H}_2$C(CH$_3$)$_2$), 6.38 (s, 2H, Ar-$\underline{H}$), 6.79 (m, 4H, Ar-$\underline{H}$), 6.95 (m, 5H, Ar-$\underline{H}$), 7.08 (m, 5H, Ar-$\underline{H}$), 7.24 (s, 1H, Ar-$\underline{H}$), 7.55 (s, 1H, Ar-$\underline{H}$) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 19.9 (Mes-$\underline{C}$H$_3$), 20.9 (Mes-$\underline{C}$H$_3$), 31.6 (C($\underline{C}$H$_3$)$_3$), 31.7 ($\underline{C}$(CH$_3$)$_3$), 33.3 (C($\underline{C}$H$_3$)$_3$), 34.7 ($\underline{C}$(CH$_3$)$_3$), 34.9 (C($\underline{C}$H$_3$)$_2$), 42.5 ($\underline{C}$(CH$_3$)$_2$), 58.3 ($C\underline{C}H_2C(CH_3)_2$), 65.4 ($\underline{C}CH_2C(CH_3)_2$), 119.4, 119.6, 121.9, 124.7, 124.8, 127.2, 127.6, 127.9, 130.8, 132.3, 141.6, 148.3, 148.6, 149.5, 149.7, 154.7 ppm. Elemental analysis for $C_{79}H_{97}GeN$ (%): Cacld: C 83.73, H 8.63, N 1.24; Found: C 84.11, H 8.41, N 1.86.

Synthesis of M^{s}Fluind^{tBu}-Ge(Me)$_2$-N(Mes)Li(thf) (6)

Methyllithium (0.55 mL, 1.10 mmol, 2 M in THF) was added to a pre-cooled (–30 °C) solution of **2** (0.49 g, 0.50 mmol) in THF (15 mL) *via* syringe. The suspension was allowed to warm up to room temperature and stirred for 16 h. The color changed from orange to light yellow. The mixture was filtered and the filtrate was concentrated to 2 mL and stored at –30 °C to yield a yellow powder (0.32 g, 60%). Yellow crystals of **6** suitable for X-ray diffraction were obtained from THF solution by layering *n*-hexane at room temperature. ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ = –0.54 (s, 6H, Ge(C$\underline{H}_3$)$_2$), 1.24 (br, 4H, C$\underline{H}_2$CH$_2$O), 1.35 (s, 36H, C(C$\underline{H}_3$)$_3$), 1.57 (s, 12H, C(C$\underline{H}_3$)$_2$), 1.79 (s, 6H, Mes-C$\underline{H}_3$), 2.33 (s, 3H, Mes-C$\underline{H}_3$), 2.42 (s, 4H, CC$\underline{H}_2$C(CH$_3$)$_2$), 3.16 (br, 4H, CH$_2$C$\underline{H}_2$O), 6.63 (s, 2H, Ar-$\underline{H}$), 7.16 (m, 5H,

Ar-*H*), 7.52 (m, 8H, Ar-*H*) ppm. ^{13}C NMR (C_6D_6, 100 MHz, 298 K): δ = 8.4 (Ge(*C*H_3)$_2$), 14.4 (Mes-C(*C*H_3)$_3$), 23.1 (Mes-C(*C*H_3)$_3$), 23.4 (C(*C*H_3)$_3$), 25.36 (*C*H_2CH$_2$O), 31.8 (*C*(CH$_3$)$_3$), 32.9 (C(*C*H_3)$_2$), 35.2 (*C*(CH$_3$)$_2$), 44.6 (C*C*H$_2$C(CH$_3$)$_2$), 64.1 (*C*CH$_2$C(CH$_3$)$_2$), 68.36 (CH$_2$*C*H$_2$O), 116.6, 118.23, 119.7, 124.7, 124.9, 129.8, 137.9, 149.8, 149.9, 150.7, 155.7, 157.0, 157.1, 157.9 ppm. Elemental analysis for $C_{71}H_{90}GeNOLi$ (%): Cacld: C 80.98, H 8.61, N 1.33; Found: C 81.36, H 8.22, N 1.83.

Table S1. Crystal data and refinement of 2-4

	2	**3**	**4**
formula	$C_{65}H_{76}ClGeN$	$C_{76}H_{91}ClGeN_4$	$C_{117}H_{124}BF_{24}GeN_4$
formula weight	979.30	1168.56	2125.59
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	P-1	P-1
a/Å	15.0823(10)	10.4216(10)	10.8141(5)
b/Å	26.4574(17)	17.8327(16)	19.1127(10)
c/Å	14.7964(10)	21.2462(16)	27.1321(15)
α/deg		86.176(4)	93.952(2)
β/deg	108.586(3)	82.097(4)	96.523(2)
γ/deg		76.433(5)	96.935(2)
V/Å^3	5596.4(6)	3799.4(6)	5511.3(5)
Z	4	2	2
ρ_{calcd}/g·cm^{-3}	1.162	1.021	1.281
μ/mm^{-1}	0.963	0.760	0.736
F(000)	2088	1248	2214
crystal size/mm^3	0.15 × 0.12 × 0.1	0.16 × 0.14 × 0.12	0.2 × 0.18 × 0.16
θ range/deg	2.689–54.448	2.824–54.108	2.033–53.989
index ranges	$-18 \le h \le 18$	$-12 \le h \le 12$	$-13 \le h \le 12$
	$-31 \le k \le 26$	$-21 \le k \le 21$	$-23 \le k \le 23$
	$-17 \le l \le 16$	$-25 \le l \le 24$	$-32 \le l \le 32$
collected data	72960	58815	98139
unique data	10335	13849	20104
	(R_{int} = 0.0969)	(R_{int} = 0.0587)	(R_{int} = 0.0457)
completeness to θ	99.9%	99.3%	99.6%
data/restraints/parameters	10335/115/642	13849/0/761	20104/409/1482
GOF on F^2	1.022	1.067	1.026
final R indices[$I>2\sigma(I)$]	R_1 = 0.0746	R_1 = 0.0431	R_1 = 0.0540
	wR_2 = 0.1972	wR_2 = 0.1179	wR_2 = 0.1466
R indices (all data)	R_1 = 0.1290	R_1 = 0.0563	R_1 = 0.0601
	wR_2 = 0.2277	wR_2 = 0.1250	wR_2 = 0.1512
Largest diff peak/hole (e·Å^{-3})	0.99/–0.77	0.25/–0.61	0.99/–0.72

Table S2. Crystal data and refinement of 5-6

	5	**6**
formula	$C_{79}H_{97}GeN$	$C_{71}H_{90}GeLiNO$
formula weight	1133.16	1052.96
crystal system	triclinic	triclinic
space group	*P*-1	*P*-1
a/Å	10.9718(8)	12.7185(7)
b/Å	11.2149(9)	15.0410(9)
c/Å	27.474(2)	17.9978(10)
α/deg	93.954(4)	82.265(3)
β/deg	91.347(4)	73.454(2)
γ/deg	97.621(4)	80.240(2)
V/Å^3	3340.9(5)	3239.0(3)
Z	2	2
ρ_{calcd}/g·cm^{-3}	1.126	1.080
μ/mm^{-1}	0.606	0.609
F(000)	1220	1132
crystal size/mm^3	0.18 × 0.14 × 0.12	0.2 × 0.14 × 0.13
θ range/deg	3.468–54.008	2.237–54.075
index ranges	$-12 \le h \le 13$	$-15 \le h \le 15$
	$-13 \le k \le 13$	$-18 \le k \le 18$
	$-33 \le l \le 32$	$-21 \le l \le 21$
collected data	60392	56006
unique data	12214	11882
	(R_{int} = 0.0647)	(R_{int} = 0.0587)
completeness to *θ*	99.6%	99.7%
data/restraints/parameters	12214/382/823	11882/126/715
GOF on F^2	1.056	1.042
final *R* indices[$I>2\sigma(I)$]	R_1 = 0.0576	R_1 = 0.0446
	wR_2 = 0.1529	wR_2 = 0.1155
R indices (all data)	R_1 = 0.0774	R_1 = 0.0608
	wR_2 = 0.1641	wR_2 = 0.1235
Largest diff peak/hole (e·Å^{-3})	0.61/–0.60	0.37/–0.66

Computational details

All of the calculations were performed with the Gaussian 09 program.[6] All the geometry optimizations were performed with the ωB97XD functional[7] in conjunction with a 6-31G(d) basis set[8] in the gas phase. Besides, the natural bond orbital (NBO) analysis[9] was obtained at the same level. The quantum theory of atoms in molecules (QTAIM) analyses were performed using Multiwfn (Version 3.8).[10] The wavefunction files for QTAIM were obtained from Gaussian 16 at theωB97XD/6-31G(d) level of theory.

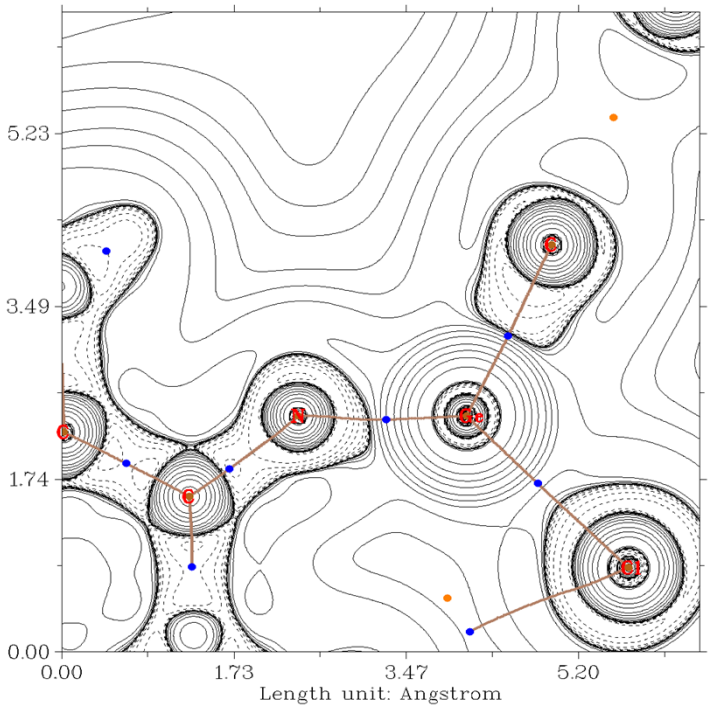

Fig. S1 Contour line diagrams of the Laplacian distribution $\nabla^2\rho(r)$ in the C-Ge-N plane of **2**.

Coordinates of the studied molecule

2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	32	0	-0.763279	-0.392135	-0.487910
2	17	0	-2.903375	-0.892185	-0.397720
3	7	0	0.526779	-0.798022	-1.481105
4	6	0	-0.430456	0.758428	1.002929
5	6	0	-0.688430	2.130086	0.997149
6	6	0	-0.538580	2.900541	2.145414
7	6	0	-0.143157	2.312017	3.342181
8	1	0	-0.061546	2.905425	4.251022
9	6	0	0.151544	0.954932	3.355427
10	6	0	0.041650	0.195739	2.189580
11	6	0	-1.247316	4.407948	0.403899
12	1	0	-0.655758	5.152337	-0.136710
13	1	0	-2.296548	4.697272	0.291630
14	6	0	-0.860675	4.363708	1.912734
15	6	0	0.358132	5.249630	2.210801
16	1	0	0.658427	5.166558	3.261555
17	1	0	1.216871	4.965447	1.593603
18	1	0	0.127219	6.301671	2.007681
19	6	0	-2.040337	4.804649	2.792411
20	1	0	-1.789126	4.735192	3.857054
21	1	0	-2.313505	5.844388	2.577826
22	1	0	-2.918088	4.174293	2.611723
23	6	0	0.617664	-1.318504	3.968284
24	1	0	-0.243678	-1.895401	4.319605
25	1	0	1.514835	-1.854884	4.289312
26	6	0	0.552148	0.120383	4.557612
27	6	0	-0.530056	0.204604	5.646111
28	1	0	-0.295523	-0.475845	6.473062
29	1	0	-0.603251	1.218629	6.055855
30	1	0	-1.511191	-0.068818	5.242991
31	6	0	1.892542	0.573171	5.155528
32	1	0	2.147463	-0.041555	6.026416
33	1	0	2.709463	0.487245	4.434602
34	1	0	1.840428	1.617516	5.484009
35	6	0	-1.029527	2.994632	-0.211110
36	6	0	0.098912	2.903536	-1.231549
37	6	0	1.426828	3.234514	-1.061651
38	1	0	1.756694	3.640491	-0.109543

39	6	0	2.345453	3.030712	-2.099313
40	6	0	1.874403	2.478712	-3.296340
41	1	0	2.561707	2.295075	-4.114648
42	6	0	0.540292	2.112398	-3.464618
43	1	0	0.216604	1.651382	-4.393108
44	6	0	-0.350081	2.334240	-2.427332
45	6	0	-1.784575	2.054316	-2.290809
46	6	0	-2.706621	1.489622	-3.166639
47	1	0	-2.400174	1.135501	-4.146831
48	6	0	-4.035753	1.406269	-2.774438
49	1	0	-4.750510	0.971311	-3.467119
50	6	0	-4.478502	1.851221	-1.516941
51	6	0	-3.530172	2.379896	-0.638794
52	1	0	-3.813554	2.705380	0.357093
53	6	0	-2.201661	2.471753	-1.022798
54	6	0	0.550923	-1.222148	2.410690
55	6	0	1.908804	-1.486716	1.749109
56	6	0	3.104168	-0.802545	1.913804
57	1	0	3.112680	0.118401	2.484591
58	6	0	4.285240	-1.298353	1.348228
59	6	0	4.208937	-2.469772	0.579853
60	1	0	5.109648	-2.874357	0.127975
61	6	0	3.006284	-3.125934	0.354533
62	1	0	2.972805	-4.007118	-0.279080
63	6	0	1.854063	-2.633134	0.952939
64	6	0	0.480246	-3.138492	0.951288
65	6	0	-0.105661	-4.216540	0.302703
66	1	0	0.467276	-4.835743	-0.381089
67	6	0	-1.446787	-4.493429	0.546877
68	1	0	-1.894951	-5.344076	0.041791
69	6	0	-2.232404	-3.711611	1.407287
70	6	0	-1.626425	-2.618016	2.033706
71	1	0	-2.196973	-1.964353	2.685977
72	6	0	-0.290433	-2.330414	1.795271
73	6	0	0.934085	-1.689077	-2.442962
74	6	0	2.316564	-1.661955	-2.751307
75	6	0	2.831490	-2.570463	-3.664928
76	1	0	3.898505	-2.546828	-3.882998
77	6	0	2.021994	-3.506729	-4.314375
78	6	0	0.661206	-3.498785	-4.026933
79	1	0	0.005633	-4.205892	-4.532916
80	6	0	0.101874	-2.608874	-3.109281
81	6	0	3.188501	-0.639204	-2.082653
82	1	0	2.974549	0.356857	-2.483276

83	1	0	2.978977	-0.586210	-1.011941
84	1	0	4.251208	-0.858960	-2.231007
85	6	0	2.614790	-4.487500	-5.295056
86	1	0	1.837800	-5.091755	-5.773766
87	1	0	3.173750	-3.974047	-6.086142
88	1	0	3.312776	-5.174677	-4.801237
89	6	0	-1.370111	-2.611866	-2.834366
90	1	0	-1.587082	-2.911442	-1.801268
91	1	0	-1.794759	-1.607282	-2.956875
92	1	0	-1.901915	-3.295073	-3.503303
93	6	0	3.815574	3.396937	-1.868449
94	6	0	3.939375	4.925424	-1.725699
95	1	0	3.325622	5.300011	-0.899153
96	1	0	4.980304	5.209122	-1.529162
97	1	0	3.613023	5.429960	-2.641727
98	6	0	4.303587	2.720213	-0.572968
99	1	0	3.810049	3.130388	0.314444
100	1	0	4.098592	1.645174	-0.597569
101	1	0	5.382574	2.867387	-0.445307
102	6	0	4.722669	2.938257	-3.018236
103	1	0	4.455115	3.419138	-3.965450
104	1	0	5.760999	3.207623	-2.795993
105	1	0	4.681485	1.852322	-3.156334
106	6	0	-5.960989	1.720407	-1.147363
107	6	0	-6.384556	0.240522	-1.217098
108	1	0	-5.806876	-0.363318	-0.509700
109	1	0	-7.447602	0.140501	-0.967646
110	1	0	-6.234613	-0.181134	-2.215850
111	6	0	-6.804803	2.544178	-2.138797
112	1	0	-6.678900	2.193056	-3.168076
113	1	0	-7.869312	2.467786	-1.887574
114	1	0	-6.520014	3.601577	-2.107589
115	6	0	-6.251563	2.229740	0.271059
116	1	0	-5.697313	1.660114	1.025296
117	1	0	-6.000413	3.290644	0.382292
118	1	0	-7.319106	2.118266	0.489568
119	6	0	5.650309	-0.638903	1.584954
120	6	0	6.506067	-1.586233	2.448903
121	1	0	6.660659	-2.550070	1.952719
122	1	0	7.490585	-1.143454	2.642443
123	1	0	6.020391	-1.778605	3.411912
124	6	0	5.527893	0.702548	2.321284
125	1	0	4.900725	1.411634	1.771348
126	1	0	5.108906	0.577550	3.326286

127	1	0	6.520412	1.152034	2.434957
128	6	0	6.369899	-0.391232	0.245637
129	1	0	6.567068	-1.323712	-0.292159
130	1	0	5.776433	0.252918	-0.409210
131	1	0	7.335575	0.096991	0.422455
132	6	0	-3.699522	-4.088676	1.648341
133	6	0	-4.436274	-3.035551	2.488040
134	1	0	-4.005564	-2.939318	3.491098
135	1	0	-4.417345	-2.052313	2.005332
136	1	0	-5.484080	-3.331053	2.609554
137	6	0	-4.443071	-4.232574	0.306575
138	1	0	-4.405763	-3.299455	-0.263500
139	1	0	-4.017257	-5.024930	-0.316915
140	1	0	-5.494220	-4.486439	0.487212
141	6	0	-3.744884	-5.432294	2.401668
142	1	0	-4.783263	-5.729353	2.591571
143	1	0	-3.265851	-6.230958	1.825338
144	1	0	-3.227743	-5.356704	3.364596

Selected NMR spectra

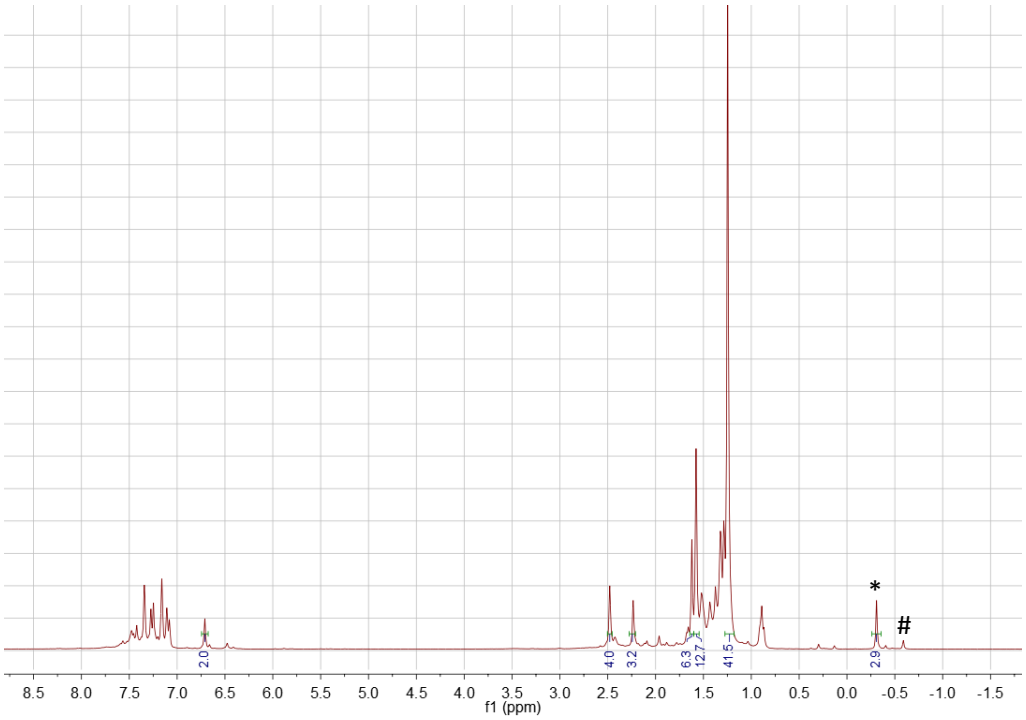

Fig. S2 ^{1}H NMR spectrum in C_6D_6 solution at 298 K of the product from the reaction of **2** with MeLi (1:1 ratio). * The proton signal for the Ge-CH_3 group in M^{s}Fluind^{tBu}-Ge(Me)=NMes; # The proton signal for the Ge-$(CH_3)_2$ moiety in **6**.

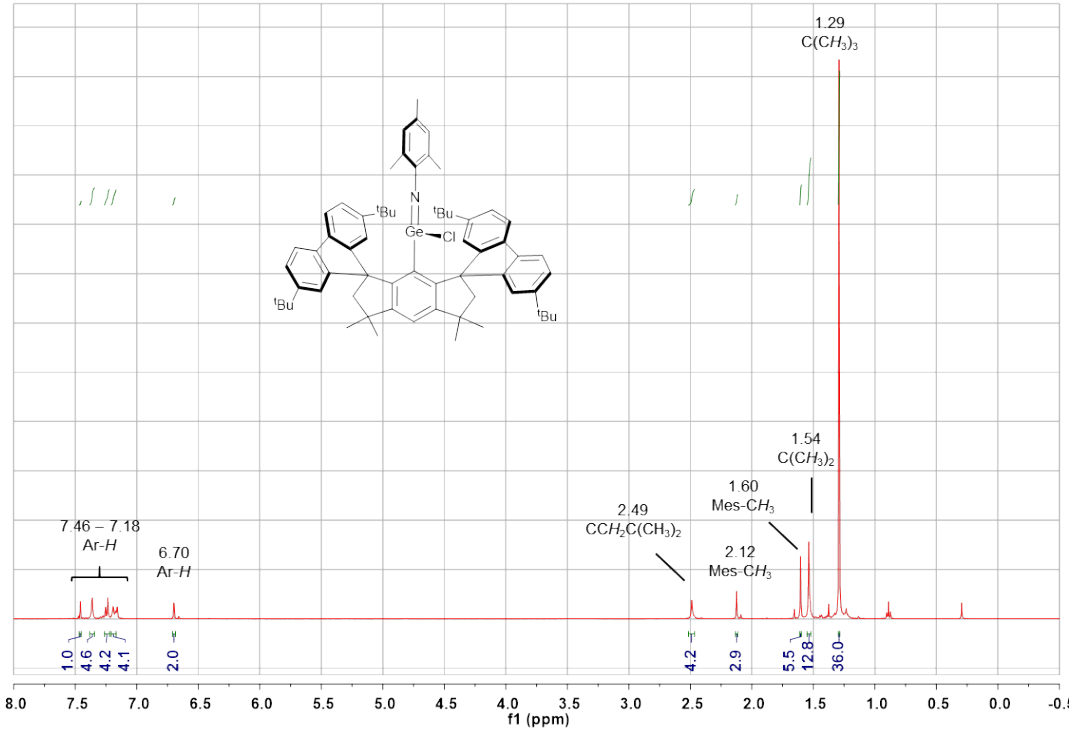

Fig. S3 ^{1}H NMR spectrum of **2** in C_6D_6 at 298 K.

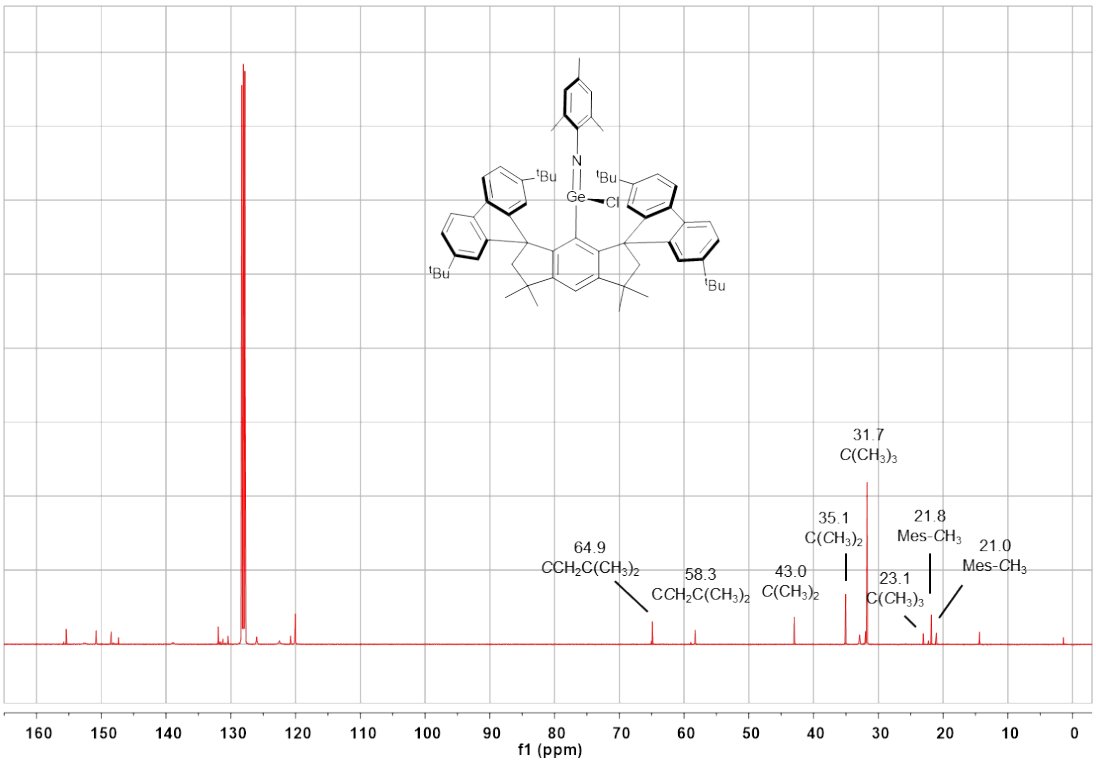

Fig. S4 $^{13}C\{^{1}H,^{13}C\}$ NMR spectrum of **2** in C_6D_6 at 298 K.

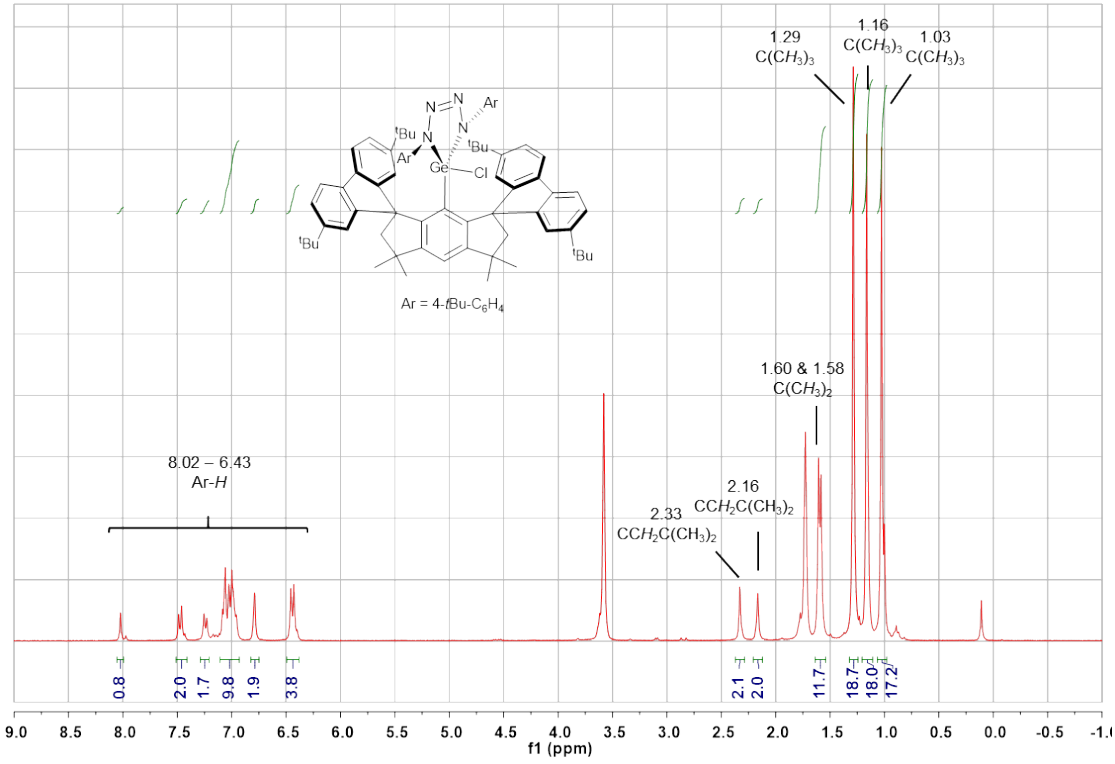

Fig. S5 ^{1}H NMR spectrum of **3** in THF-d_8 at 298 K.

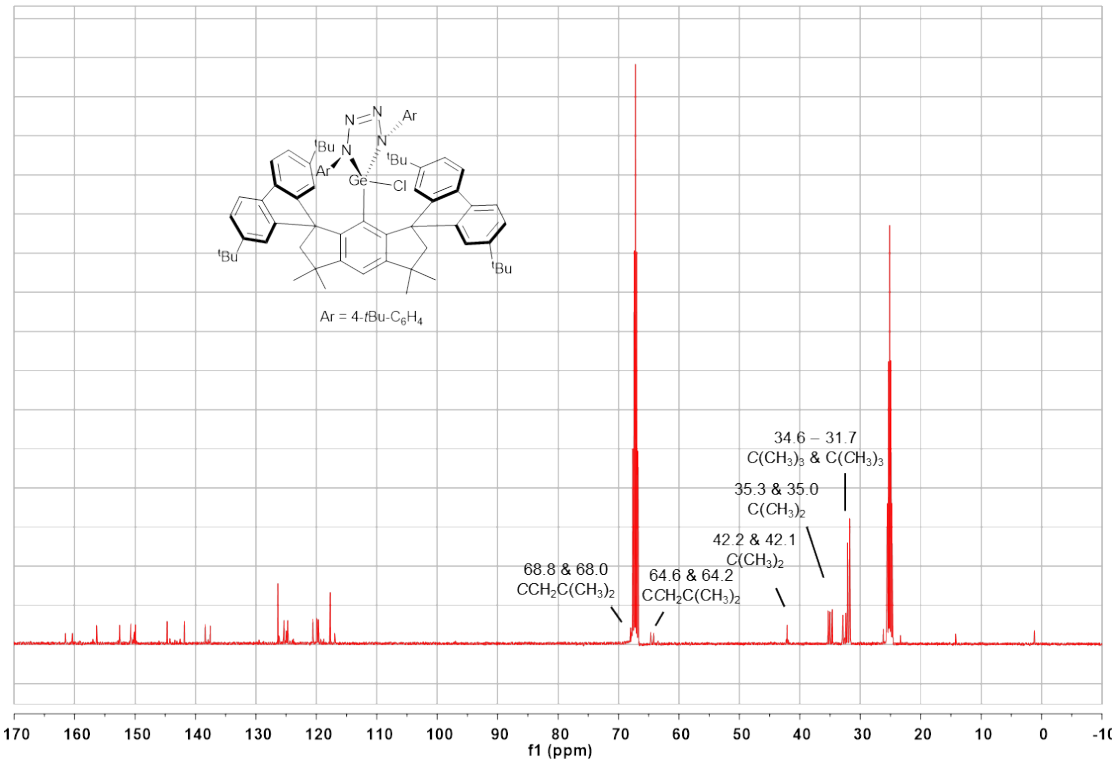

Fig. S6 $^{13}C\{^{1}H,^{13}C\}$ NMR spectrum of **3** in THF-d_8 at 298 K.

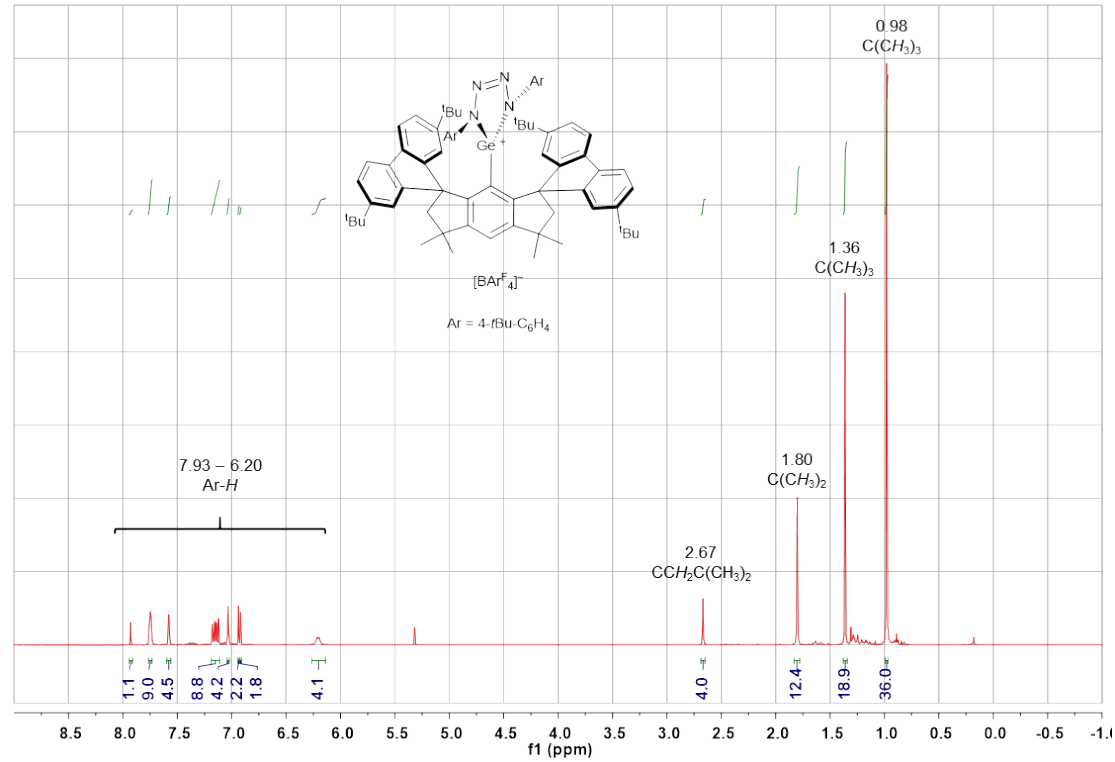

Fig. S7 ^{1}H NMR spectrum of **4** in CD_2Cl_2 at 298 K.

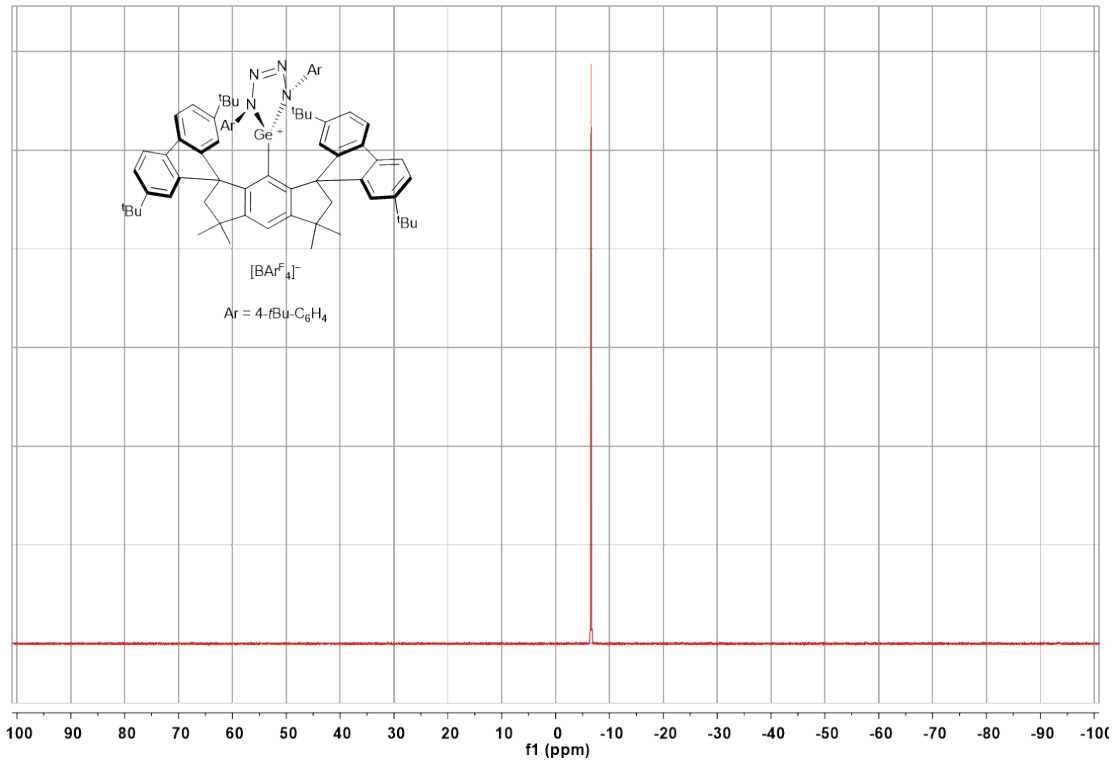

Fig. S8 ^{11}B NMR spectrum of **4** in CD_2Cl_2 at 298 K.

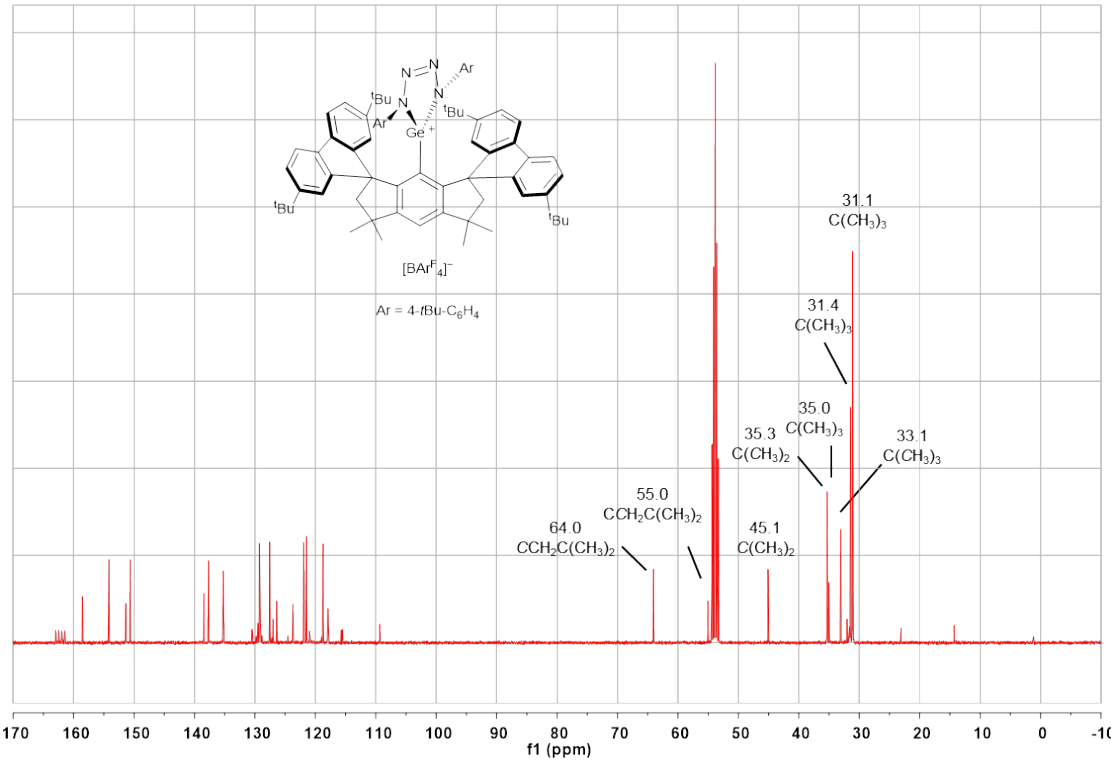

Fig. S9 ^{13}C{^{1}H,^{13}C} NMR spectrum of **4** in CD_2Cl_2 at 298 K.

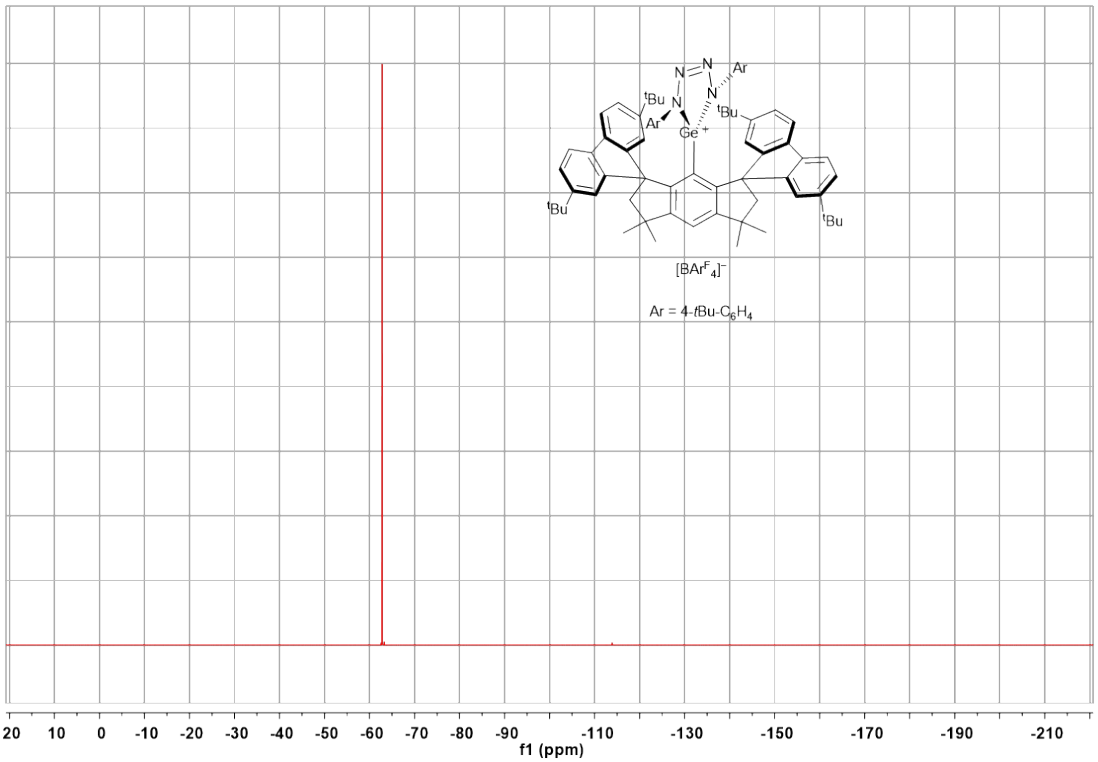

Fig. S10 ^{19}F NMR spectrum of **4** in CD_2Cl_2 at 298 K.

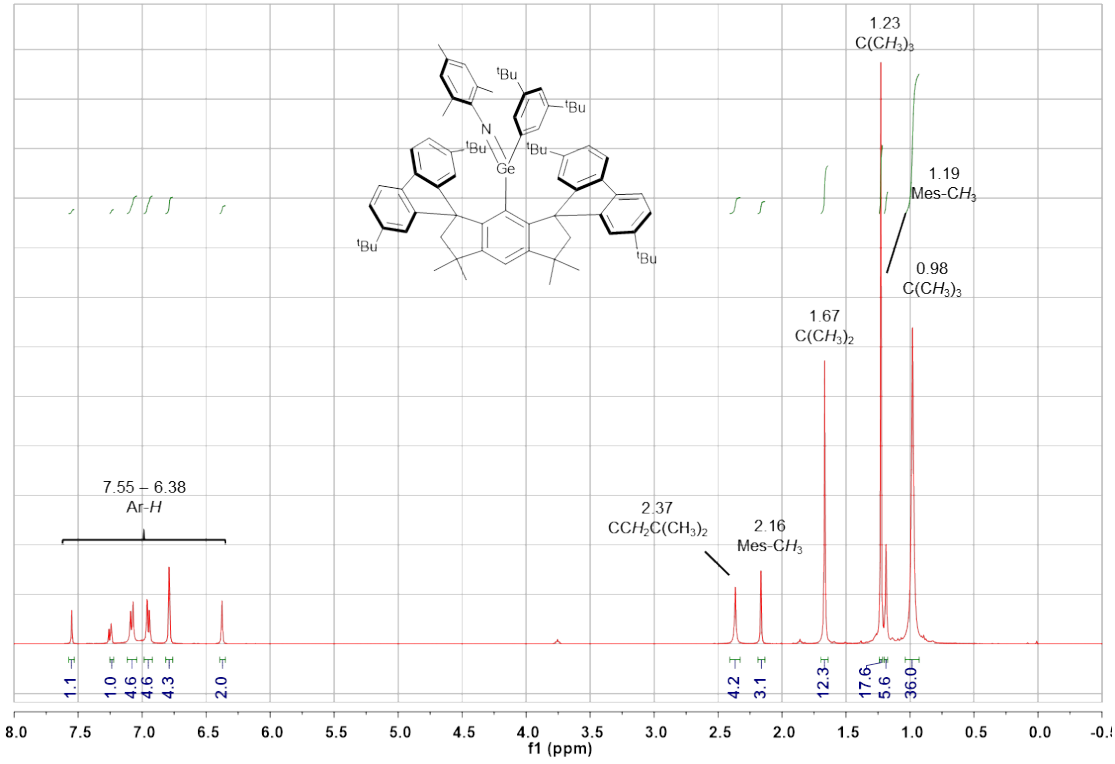

Fig. S11 ^1H NMR spectrum of **5** in $CDCl_3$ at 298 K.

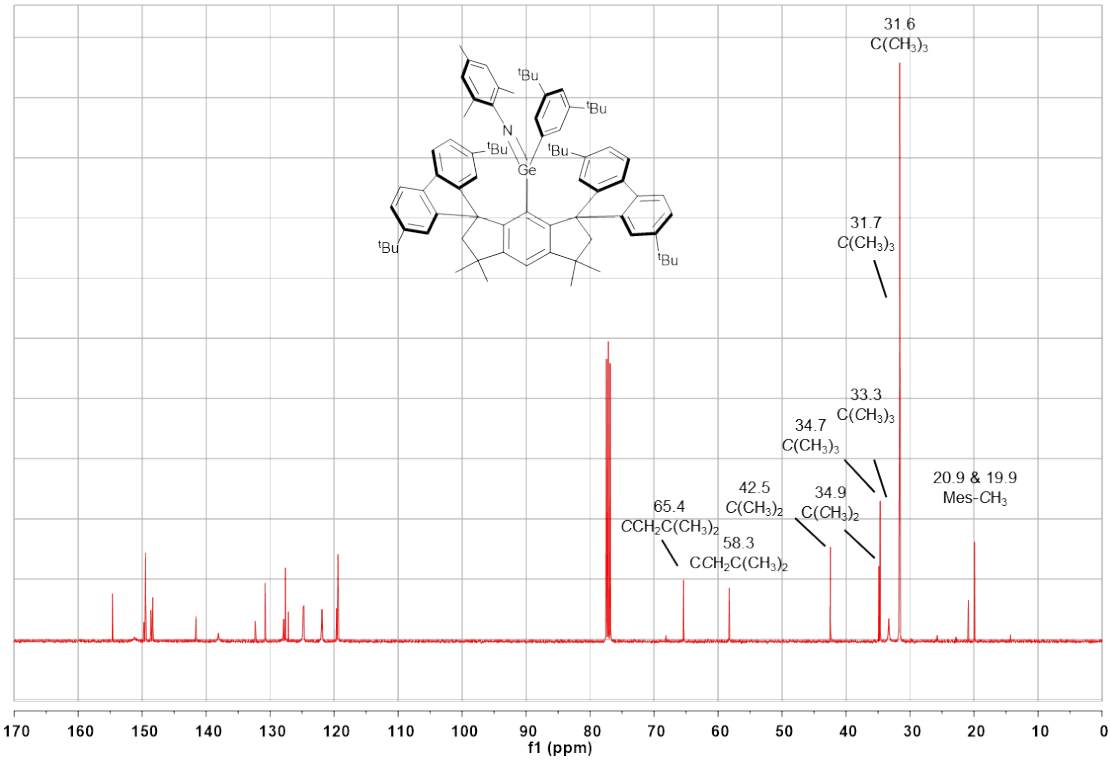

Fig. S12 $^{13}C\{^{1}H,^{13}C\}$ NMR spectrum of **5** in $CDCl_3$ at 298 K.

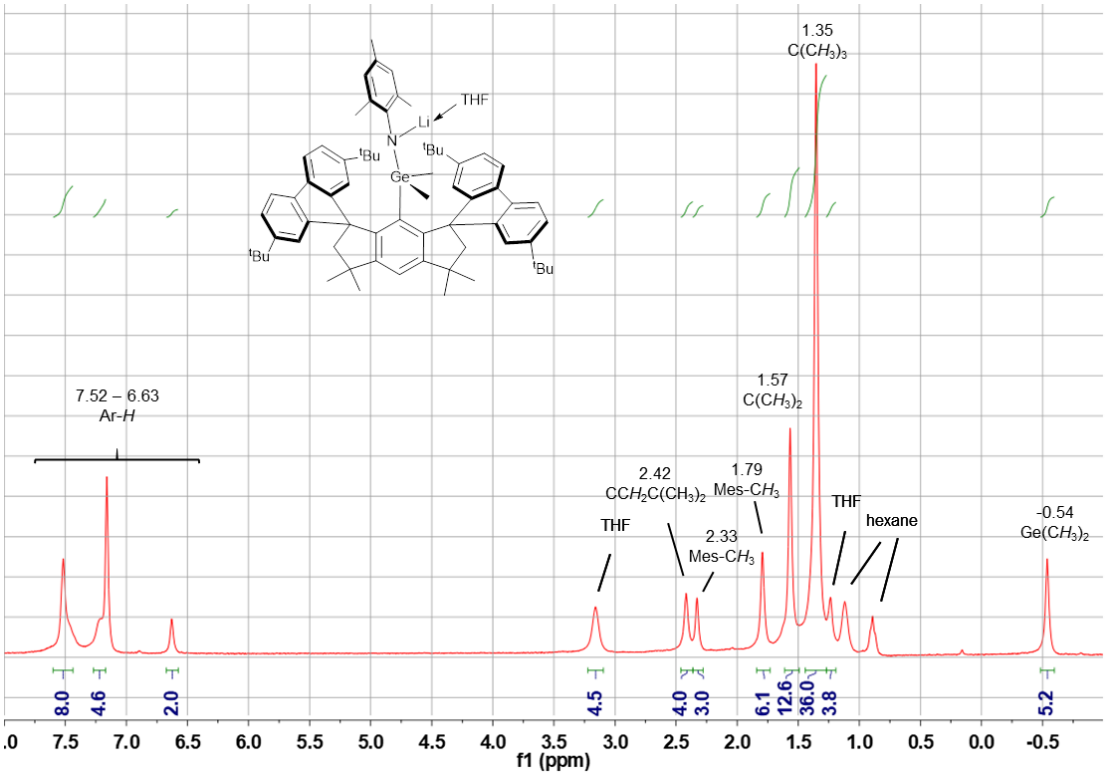

Fig. S13 ^{1}H NMR spectrum of **6** in C_6D_6 at 298 K.

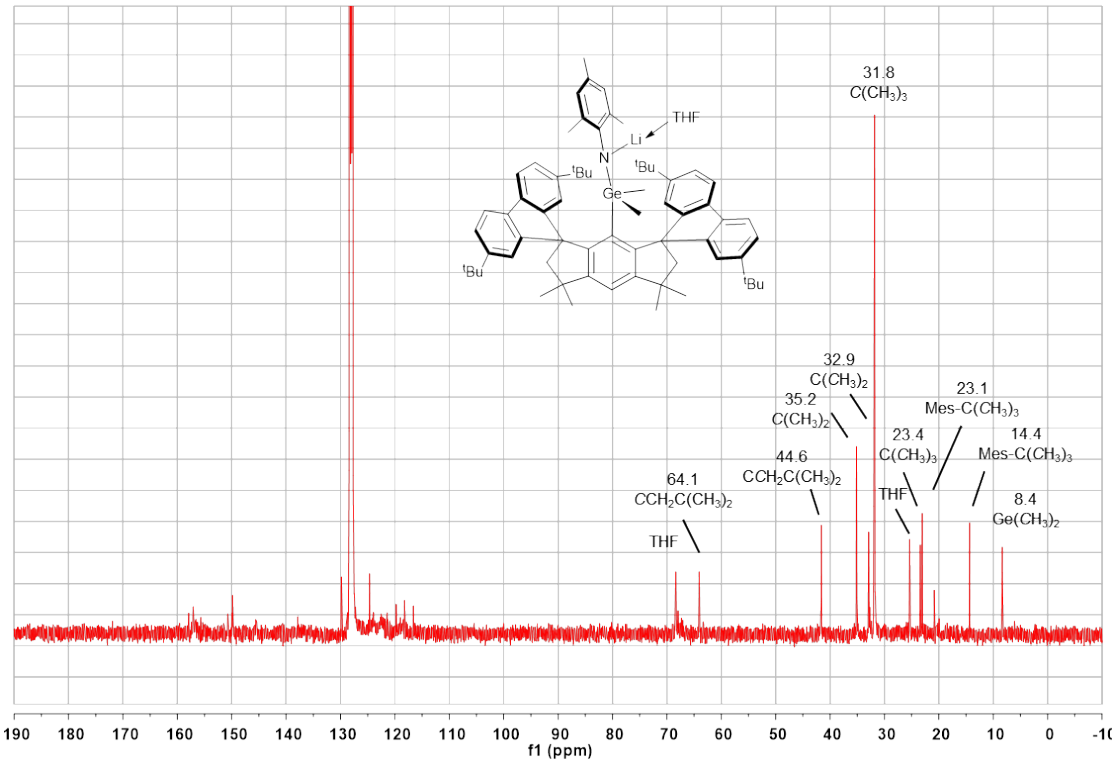

Fig. S14 $^{13}C\{^{1}H,^{13}C\}$ NMR spectrum of **6** in C_6D_6 at 298 K.

References

1 G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

2 A. Spek, *Acta Cryst.*, 2015, **C71**, 9-18.

3 Y. He, C. Dai, D. Wang, J. Zhu and G. Tan, *J. Am. Chem. Soc.*, 2022, **144**, 5126–5135.

4 D. Xin, A. Qin and B. Z. Tang, *Polymer Chemistry*, 2019, **10**, 4271-4278.

5 T. Heitkemper, L. Naß and C. P. Sindlinger, *Dalton Trans.*, 2020, **49**, 2706-2714.

6 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F.Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A.Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision C.01, Gaussian, Inc.: Wallingford CT., 2019.

7 J. D. Chai and M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615−6620.

8 R. Ditchfield, W. J. Hehre and J. A Pople, Self-consistent molecular-orbital methods. IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules, *J. Chem. Phys.*, 1971, **54**, 724−728.

9 Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.*1988, **88**, 899−926.

10 Lu, T.; Chen, F., Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580-592.