Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Reaction of an Arsinoamide with Chloro Tetrylenes: Substitution and As-N Bond Insertion

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Content

1. Experimental Section

All manipulations of air- and moisture-sensitive materials were performed under inert atmosphere by using either a double-manifold Schlenk line or an argon-filled MBraun glovebox. All the solvents were dried from a MBraun solvent purification system (SPS-800), degassed, and stored under vacuum over $LiAlH_4$. Deuterated solvents were obtained from Aldrich GmbH (99 atom % D) and were degassed, dried, and stored under vacuum in the presence of Na/K alloy. IR spectra were obtained on a Bruker Tensor 37 instrument. NMR spectra were recorded with a Bruker Avance II 300 MHz or Avance III 400 MHz NMR spectrometer. Chemical shifts are referenced to the residual protio solvent (^1H) or the deuterated solvent ($^{13}C\{^1H\}$), and are reported relative to tetramethylsilane (^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$). Elemental analyses were carried out with an Elementar Vario micro cube.

[(Mes_2AsNPh){Li(OEt_2)$_2$}],[1] [**L**SiCl] (**L** = PhC(^{t}BuN)$_2$)[2] and [**L**GeCl][3] were prepared according to the literature procedures. The other chemicals were purchased from abcr, Acros Organics, Alfa Aesar and Sigma Aldrich and used without further purification.

[**L**Si(=NPh)(AsMes_2)] (**1**)

Toluene (20 mL) was condensed onto a mixture of [**L**SiCl] (0.118 g, 0.400 mmol) and [(Mes_2AsNPh){Li(OEt_2)$_2$}] (0.224 g, 0.400 mmol), and the reaction mixture was stirred at room temperature overnight (16-18h). The white precipitate that formed was removed by filtration and the target compound was isolated after removing toluene under vacuum and washing the solid residue with cold *n*-pentane (3×5 mL). Crystals of compound **1** were obtained from a mixture of *n*-pentane/diethyl ether (v/v=1:1) after storage at -30 ºC overnight. Yield: 0.163 g (0.246 mmol), 61%.

^1H NMR (300 MHz, C_6D_6, 298 K): δ(ppm) = 7.49-7.44 (m, 2H, *m-H* Ph), 7.34-7.30 (m, 1H, *p-H* Ph), 7.23-7.20 (m, 2H, *o-H* Ph), 7.01-6.83 (m, 5H, Ph), 6.78 (s, 4H, Ar-C*H* Mes), 2.83 (s, 12H, *o*-CH_3 Mes), 2.09 (s, 6H, *p*-CH_3 Mes), 0.99 (s, 18H, ^{t}Bu).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 298 K): δ(ppm) = 176.0 (N*C*N), 153.7 (C_{arom}), 143.6 (C_{arom}), 137.4 (C_{arom}), 136.4 (C_{arom}), 131.1 (C_{arom}), 130.6 (C_{arom}), 129.7 (C_{arom}), 129.2 (C_{arom}), 128.9 (C_{arom}), 127.9 (C_{arom}), 124.1 (C_{arom}), 115.3 (C_{arom}), 55.0 (^{t}Bu-*C*), 31.1 (^{t}Bu-*C*H_3), 25.5 (*o*-*C*H_3 Mes), 20.9 (*p*-*C*H_3 Mes).

$^{29}Si\{^1H\}$ NMR (59 MHz, C_6D_6, 298 K): δ(ppm) = -68.9.

IR (ATR, cm^{-1}): 2965(m), 2920(w), 2868(w), 1645(w), 1588(s), 1527(s), 1491(m), 1468(m), 1448(m), 1390(m), 1364(s), 1282(m), 1200(m), 1068(m), 1023(m), 920(w), 886(w), 847(s), 799(w), 697(vs), 616(m), 584(w), 552(w), 501(s), 433(w).

Anal. calcd. (%) for [$C_{39}H_{50}AsN_3Si$] (663.86): C, 70.56; H, 7.59; N, 6.33. Found: C, 70.01; H, 7.28; N, 6.18.

[**L**Ge(Mes$_2$AsNPh)] (**2**)

Toluene (20 mL) was condensed onto a mixture of [**L**GeCl] (0.136 g, 0.400 mmol) and [(Mes$_2$AsNPh){Li(OEt$_2$)$_2$}] (0.224 g, 0.400 mmol). The colour of the reaction mixture gradually changed from light yellow to colourless. The reaction mixture was stirred overnight (16-18h) at room temperature and then filtered. After removal of all the volatiles from the filtrate under vacuum, the obtained residue was dissolved in a minimum amount of *n*-pentane. Crystals of compound **2** were obtained by storing overnight the *n*-pentane solution at -30 °C. Yield: 0.178 g (0.251 mmol), 63%.

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ(ppm) = 7.79-7.77 (m, 2H, *m-H* Ph), 7.34-7.29 (m, 2H, *o-H* Ph), 7.22-7.16 (m, 1H, *p-H* Ph), 6.98-6.86 (m, 5H, Ph), 6.75 (s, 4H, Ar-C*H* Mes), 2.65 (s, 12H, *o*-C*H*$_3$ Mes), 2.11 (s, 6H, *p*-C*H*$_3$ Mes), 0.96 (s, 18H, ^{t}Bu).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ(ppm) = 167.4 (N*C*N), 155.7 (C_{arom}), 142.5 (C_{arom}), 139.9 (C_{arom}), 137.8 (C_{arom}), 136.3 (C_{arom}), 130.2 (C_{arom}), 129.0 (C_{arom}), 128.5 (C_{arom}), 128.1 (C_{arom}), 127.2 (C_{arom}), 125.8 (C_{arom}), 120.7 (C_{arom}), 53.0 (^{t}Bu-*C*), 31.8 (^{t}Bu-*C*H$_3$), 23.1 (*o*-*C*H$_3$ Mes), 21.0 (*p*-*C*H$_3$ Mes).

IR (ATR, cm^{-1}): 3063(w), 2959(m), 2920(m), 2864(w), 1587(m), 1478(m), 1458(m), 1419(vs), 1360(m), 1250(m), 1203(vs), 1177(m), 1061(m), 1017(m), 924(w), 896(w), 849(vs), 784(vs), 747(w), 722(s), 710(s), 695(vs), 604(m), 575(m), 545(m), 517(s), 479(m).

Anal. calcd. (%) for [$C_{39}H_{50}AsN_3Ge$] (708.40): C, 66.12; H, 7.11; N, 5.93. Found: C, 66.07; H, 6.85; N, 5.74.

[{Mes$_2$As}(Cl)Ge(μ-NPh)]$_2$ (**3**)

Toluene (20 mL) was condensed onto a mixture of GeCl$_2$·dioxane (0.093 g, 0.400 mmol) and [(Mes$_2$AsNPh){Li(OEt$_2$)$_2$}] (0.224 g, 0.400 mmol), and the reaction mixture was stirred overnight (16-18h) at room temperature. The white precipitate that formed was removed by filtration and the target compound was obtained after removing all the volatiles under vacuum and subsequently washing the residue with cold *n*-pentane (3×5 mL). Crystals of compound **3** were obtained from a mixture of diethyl ether and *n*-pentane (1:1) after storage at -30 °C for 3 days. Yield: 0.074 g (0.072 mmol), 36%.

^{1}H NMR (300 MHz, d_8-THF, 298 K): δ(ppm) = 6.81-6.76 (m, 4H, *m-H* Ph), 6.73 (s, 8H, Ar-C*H* Mes), 6.66-6.61 (m, 2H, *p-H* Ph), 6.52-6.49 (m, 4H, *o-H* Ph), 2.23 (s, 24H, *o*-CH_3 Mes), 2.22 (s, 12H, *p*-CH_3 Mes).

^{13}C{^{1}H} NMR (75 MHz, d_8-THF, 298 K): δ(ppm) = 153.0 (C_{arom}), 142.8 (C_{arom}), 139.2 (C_{arom}), 138.0 (C_{arom}), 130.6 (C_{arom}), 128.6 (C_{arom}), 126.0 (C_{arom}), 122.0 (C_{arom}), 23.2 (*o*-CH$_3$ Mes), 21.0 (*p*-CH$_3$ Mes).

IR (ATR, cm^{-1}): 3019(w), 2969(m), 2916(m), 2856(w), 1588(m), 1464(s), 1442(s), 1403(m), 1375(m), 1284(m), 1220(vs), 1074(w), 1024(m), 892(m), 852(vs), 778(vs), 709(s), 686(vs), 610(m), 582(m), 549(m), 503(s).

Anal. calcd. (%) for [$C_{24}H_{27}AsClGeN$]$_2$(1024.98): C, 56.25; H, 5.31; N, 2.73. Found: C, 56.31; H, 5.36; N, 2.90.

[(Mes$_2$AsNPh)$_2$Ge] (**4**)

Toluene (20 mL) was condensed onto a mixture of GeCl$_2$·dioxane (0.093 g, 0.400 mmol) and [(Mes$_2$AsNPh){Li(OEt$_2$)$_2$}] (0.448 g, 0.800 mmol), and the reaction mixture was stirred overnight (16-18h) at room temperature. The white precipitate that formed was removed by filtration and compound **4** was obtained as a yellow solid after removing all the volatiles under vacuum and subsequently washing the residue with cold *n*-pentane (5 mL). Crystals of compound **4** were obtained by storing a concentrated solution in *n*-heptane at -30 °C overnight. Yield: 0.307 g (0.348 mmol), 87%.

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ(ppm) = 6.99-6.94 (m, 4H, Ph), 6.86-6.77 (m, 6H, Ph), 6.63 (s, 8H, Ar-C*H* Mes), 2.39 (s, 24H, *o*-CH_3 Mes), 2.07 (s, 12H, *p*-CH_3 Mes).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ(ppm) = 152.8 (C_{arom}), 142.4 (C_{arom}), 138.6 (C_{arom}), 137.7 (C_{arom}), 130.4 (C_{arom}), 128.5 (C_{arom}), 125.7 (C_{arom}), 121.9 (C_{arom}), 23.2 (*o*-CH$_3$ Mes), 20.9 (*p*-CH$_3$ Mes).

IR (ATR, cm^{-1}): 3019(w), 2970(w), 2948(w), 2916(w), 1586(m), 1463(m), 1442(m), 1375(w), 1285(w), 1221(s), 1075(w), 1026(m), 892(m), 850(s), 779(vs), 709(s), 687(vs), 612(w), 581(w), 547(w), 504(s).

Anal. calcd. (%) for [$C_{48}H_{54}As_2GeN_2$] (881.45): C, 65.41; H, 6.18; N, 3.18. Found: C, 65.65; H, 6.07; N, 3.12.

2. NMR Spectra

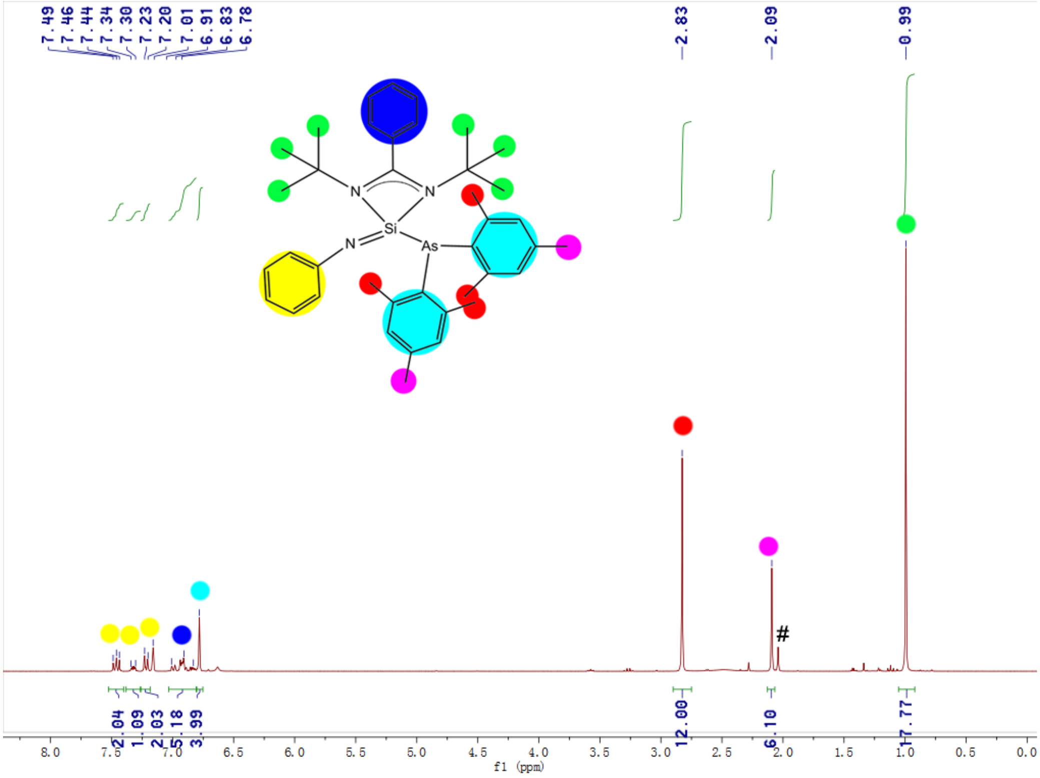

*Figure S1. ^{1}H NMR spectrum of compound **1** (300 MHz, C_6D_6, 298K) (# stands for solvent peak).*

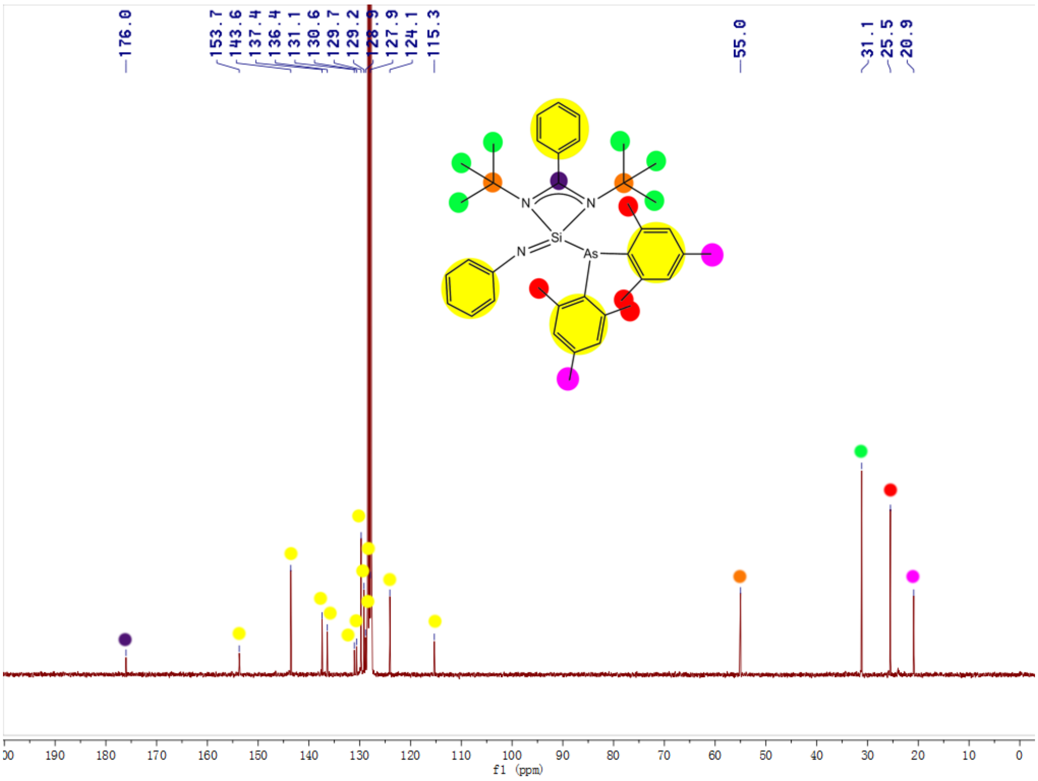

*Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** (75 MHz, C_6D_6, 298K).*

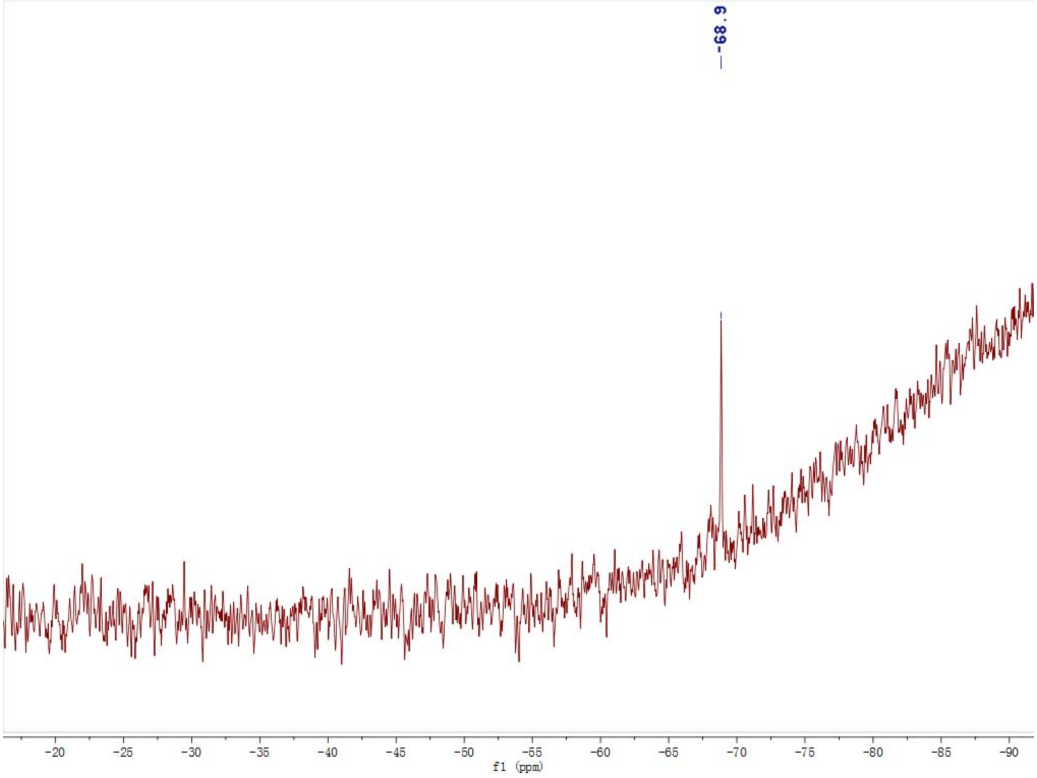

*Figure S3. ^{29}Si NMR spectrum of compound **1** (59.6 MHz, C_6D_6, 298K).*

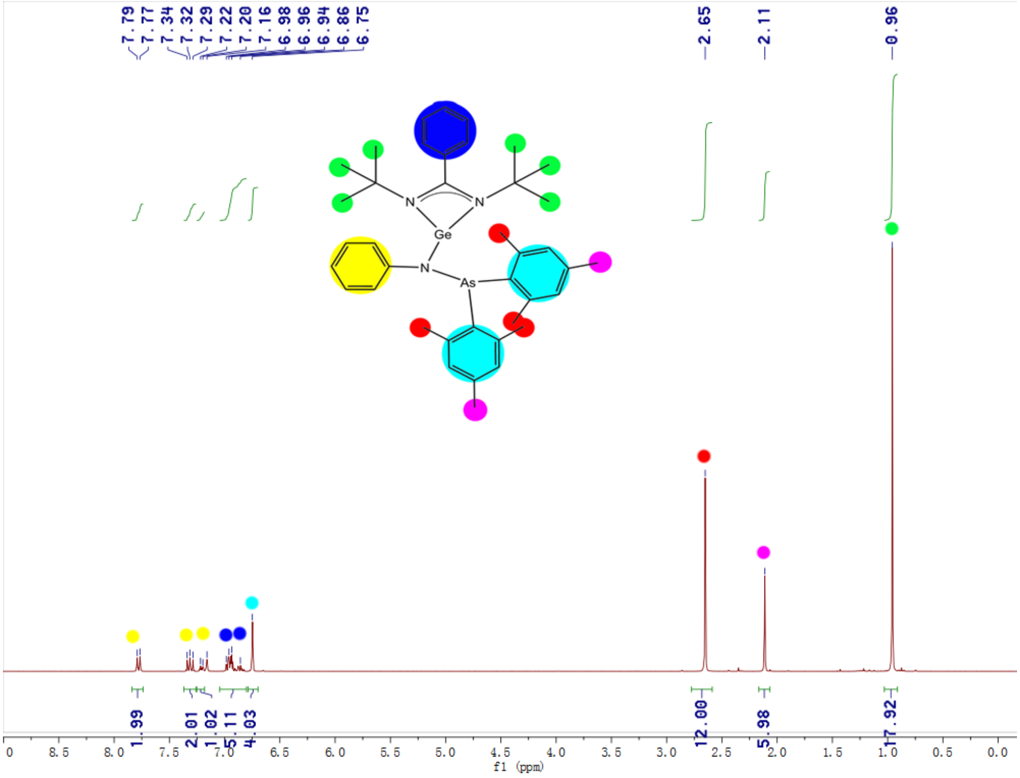

*Figure S4. ^{1}H NMR spectrum of compound **2** (300 MHz, C_6D_6, 298K).*

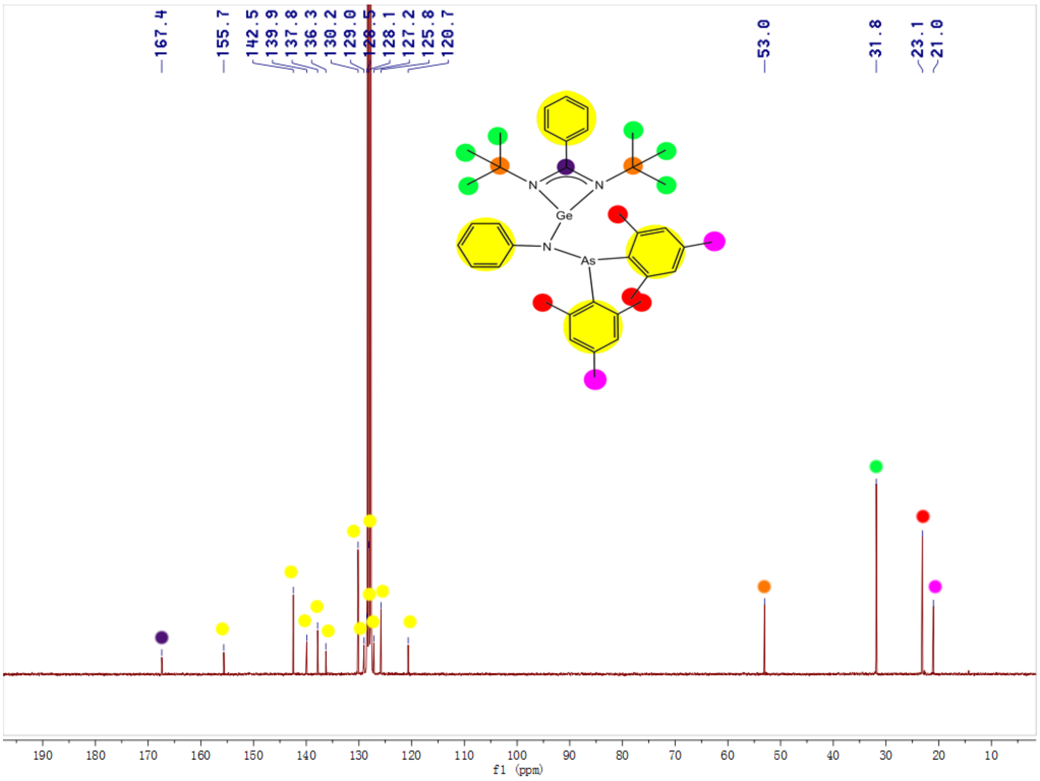

*Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** (75 MHz, C_6D_6, 298K).*

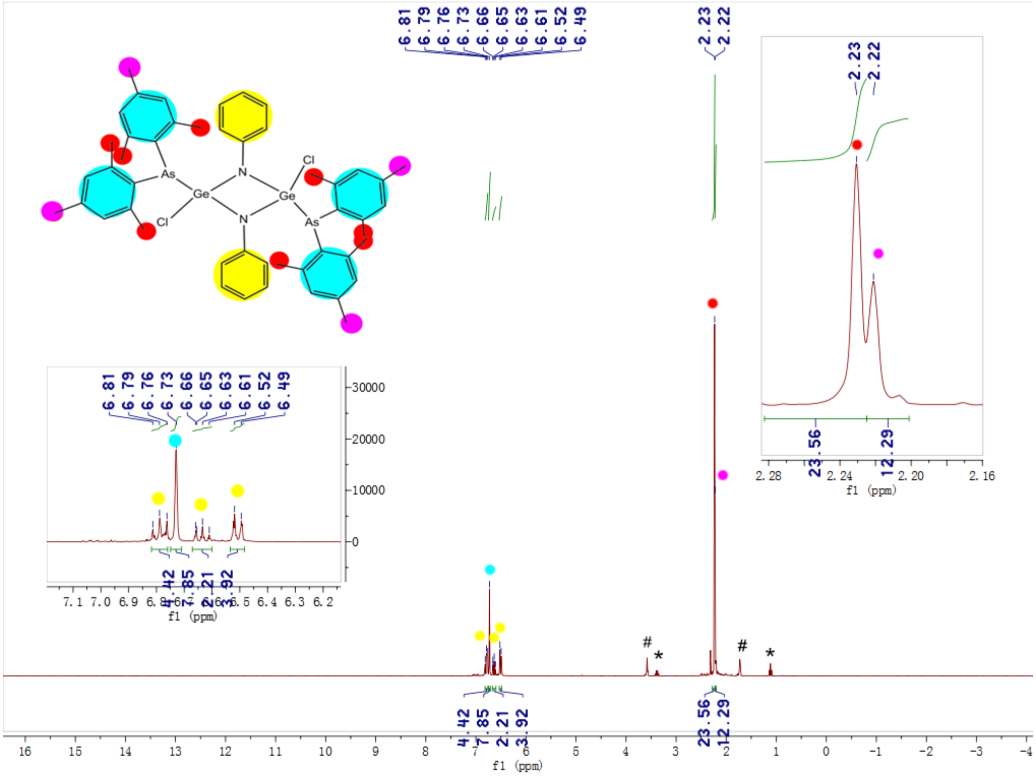

*Figure S6. ^{1}H NMR spectrum of compound **3** (300 MHz, d_8-THF, 298K) (# stands for d_8-THF peaks; * stands for diethyl ether peaks).*

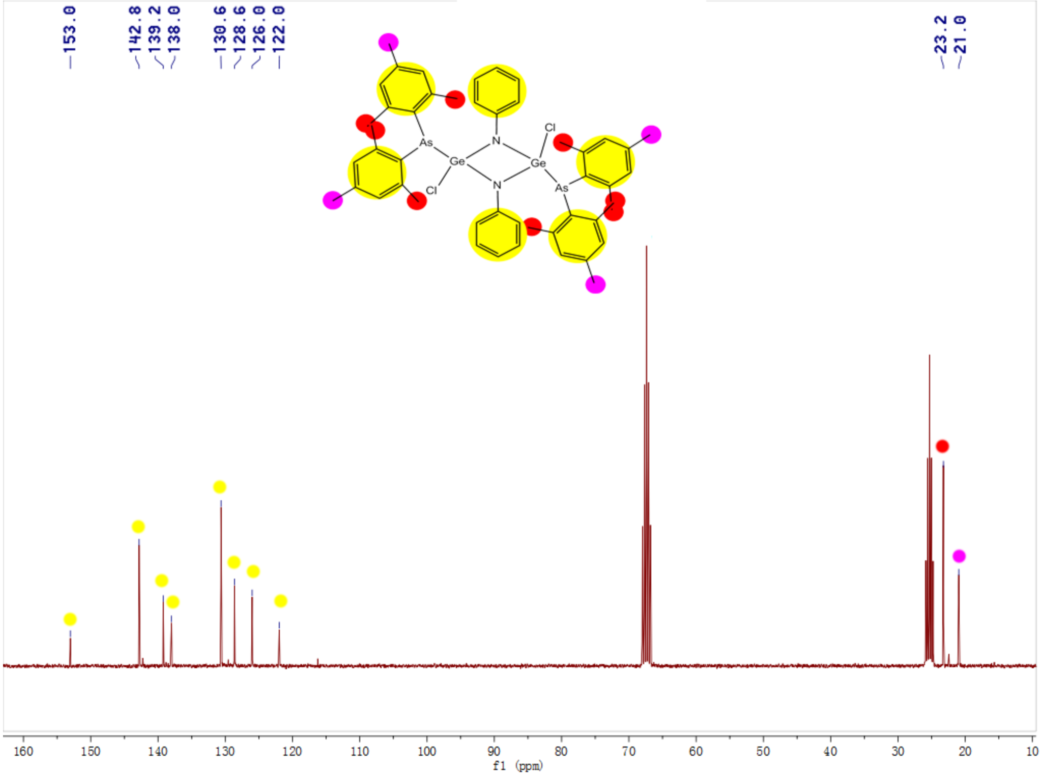

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of compound ***3*** *(75 MHz, d_8-THF, 298K).*

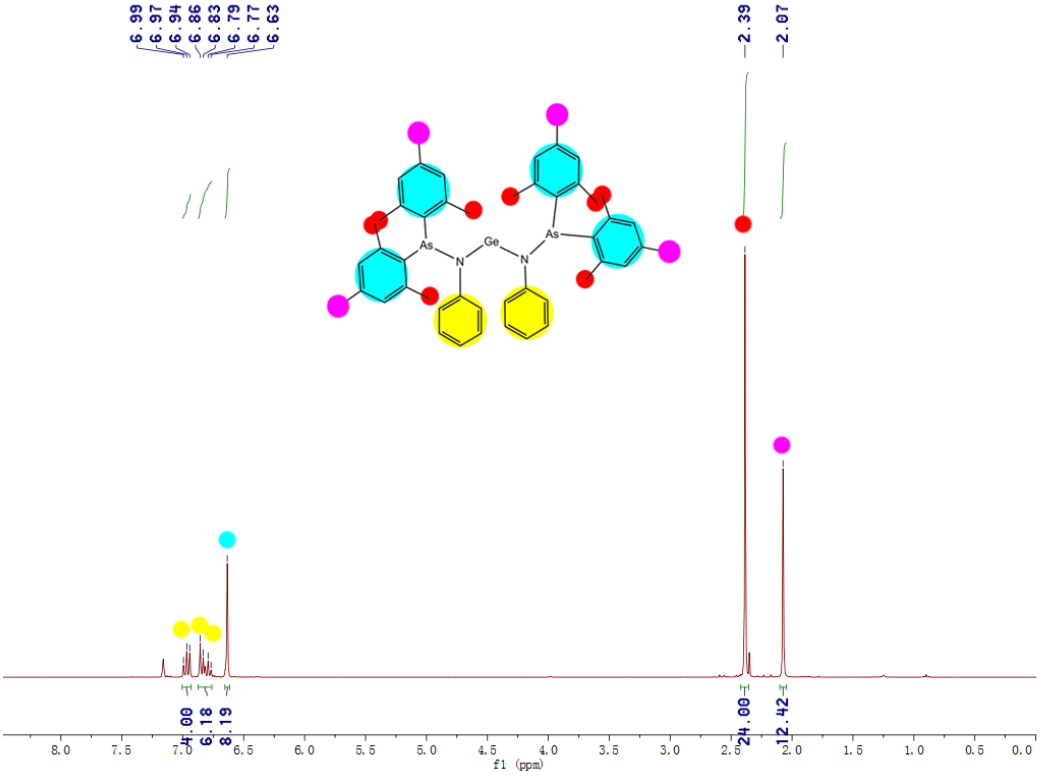

Figure S8. ^{1}H NMR spectrum of compound ***4*** *(300 MHz, C_6D_6, 298K).*

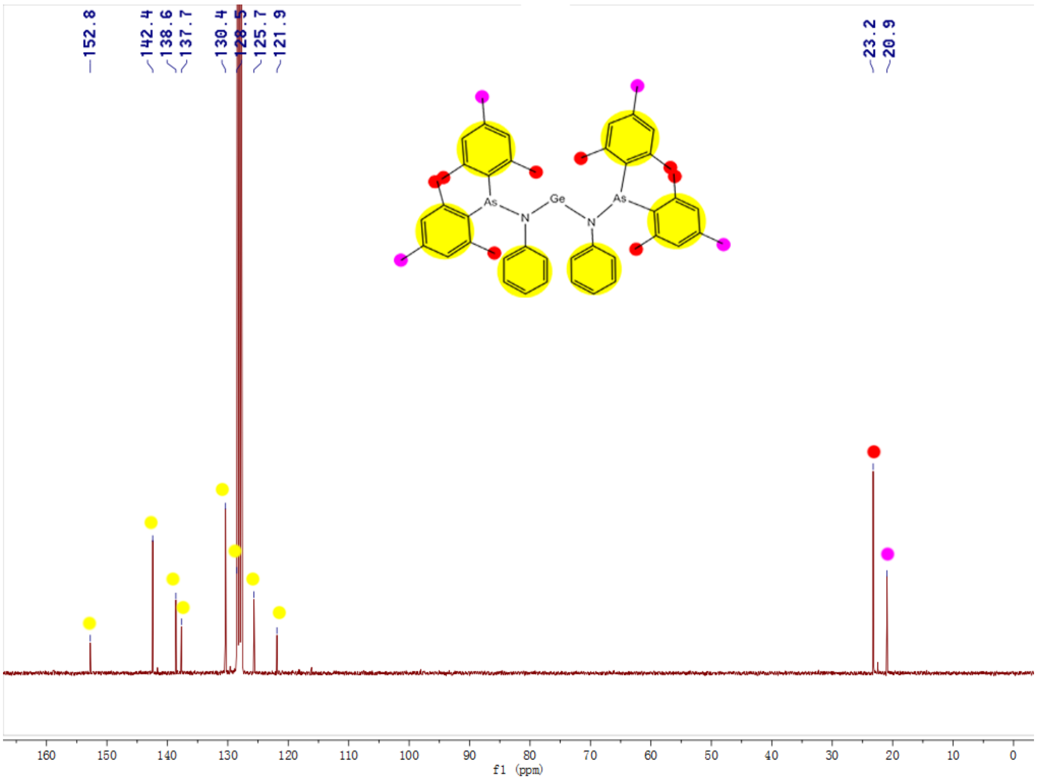

*Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4** (75 MHz, C_6D_6, 298K).*

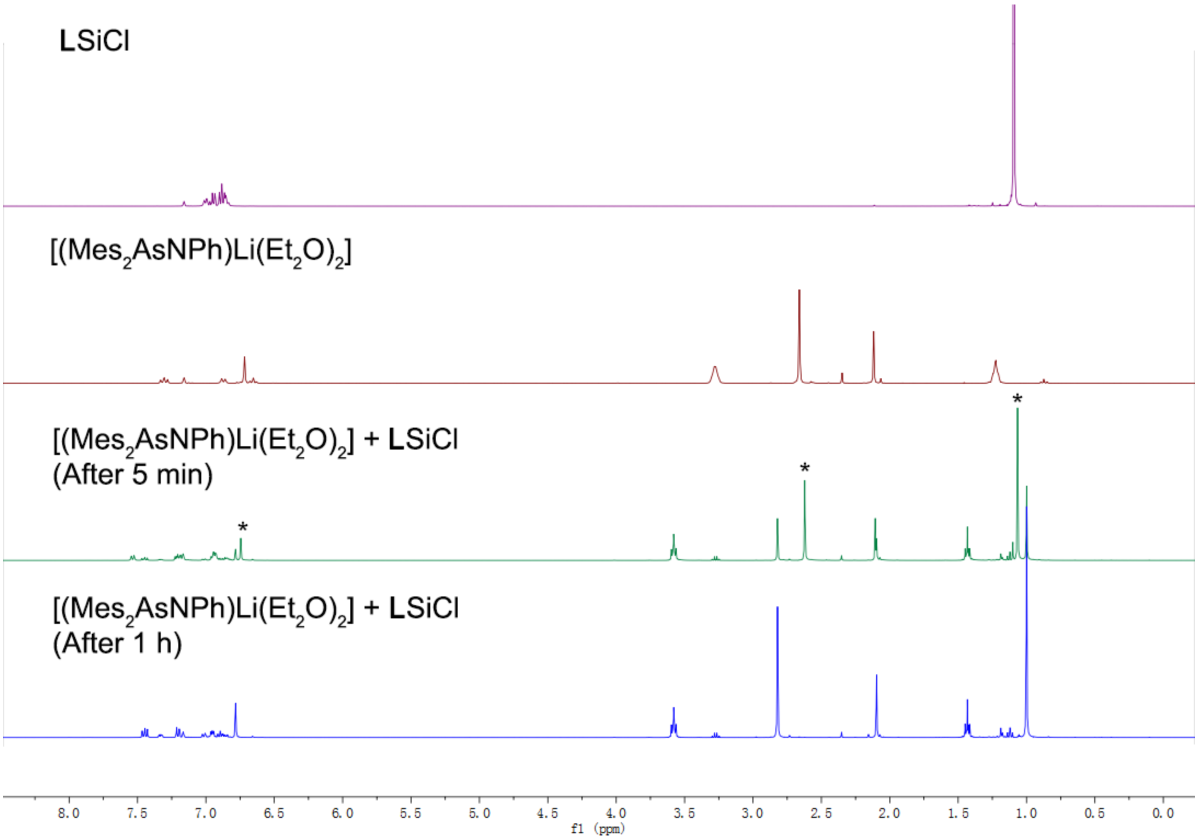

*Figure S10. ^{1}H NMR (400 MHz, C_6D_6, 298K) monitoring of the formation of **1** and comparison with the starting material. The signals with the asterisk correspond to an intermediate species that disappears over 1 h at room temperature.*

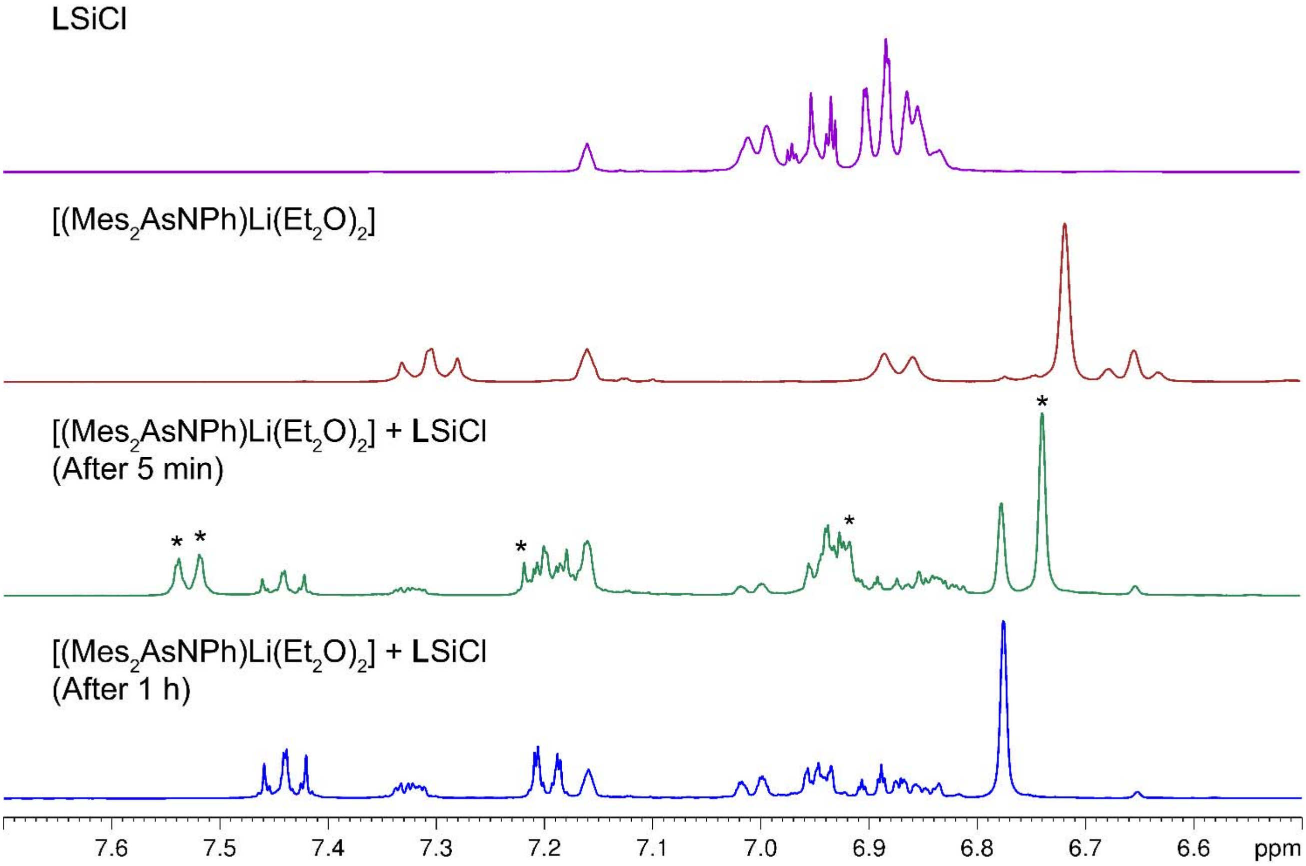

Figure S11. Detail of the aromatic region of the ^{1}H NMR (400 MHz, C_6D_6, 298K) monitoring of the formation of ***1*** *and comparison with the starting material. The signals with the asterisk correspond to an intermediate species that disappears over 1 h at room temperature.*

3. IR spectra

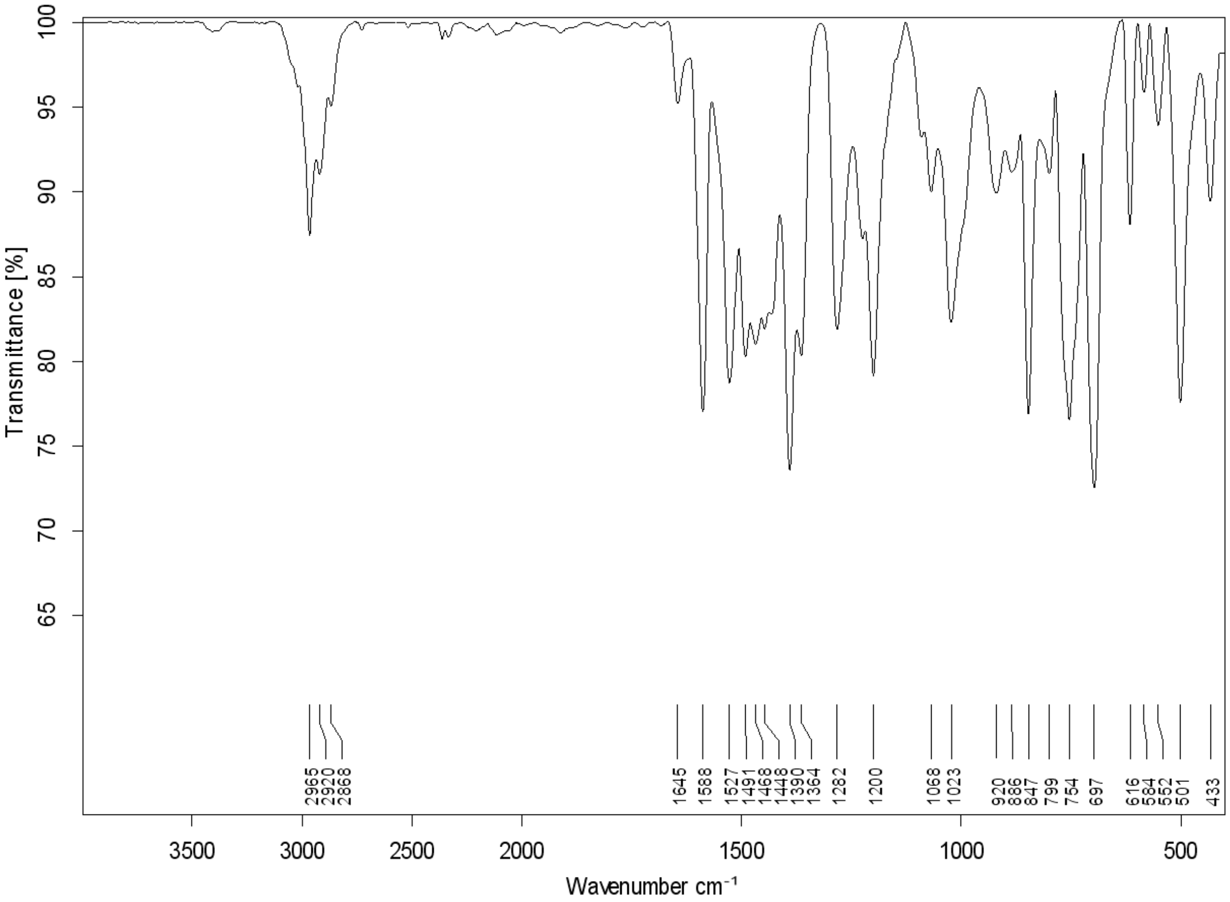

Figure S12. IR spectrum of compound ***1****.*

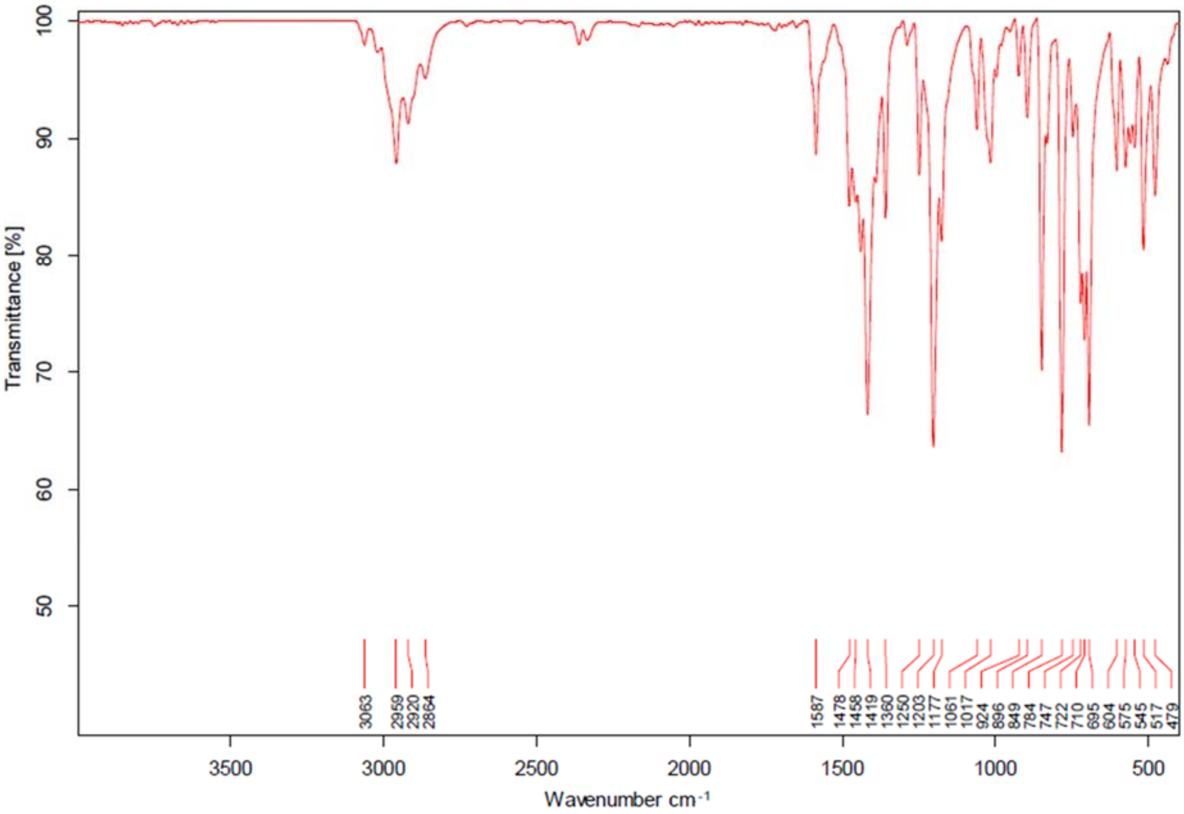

*Figure S13. IR spectrum of compound **2**.*

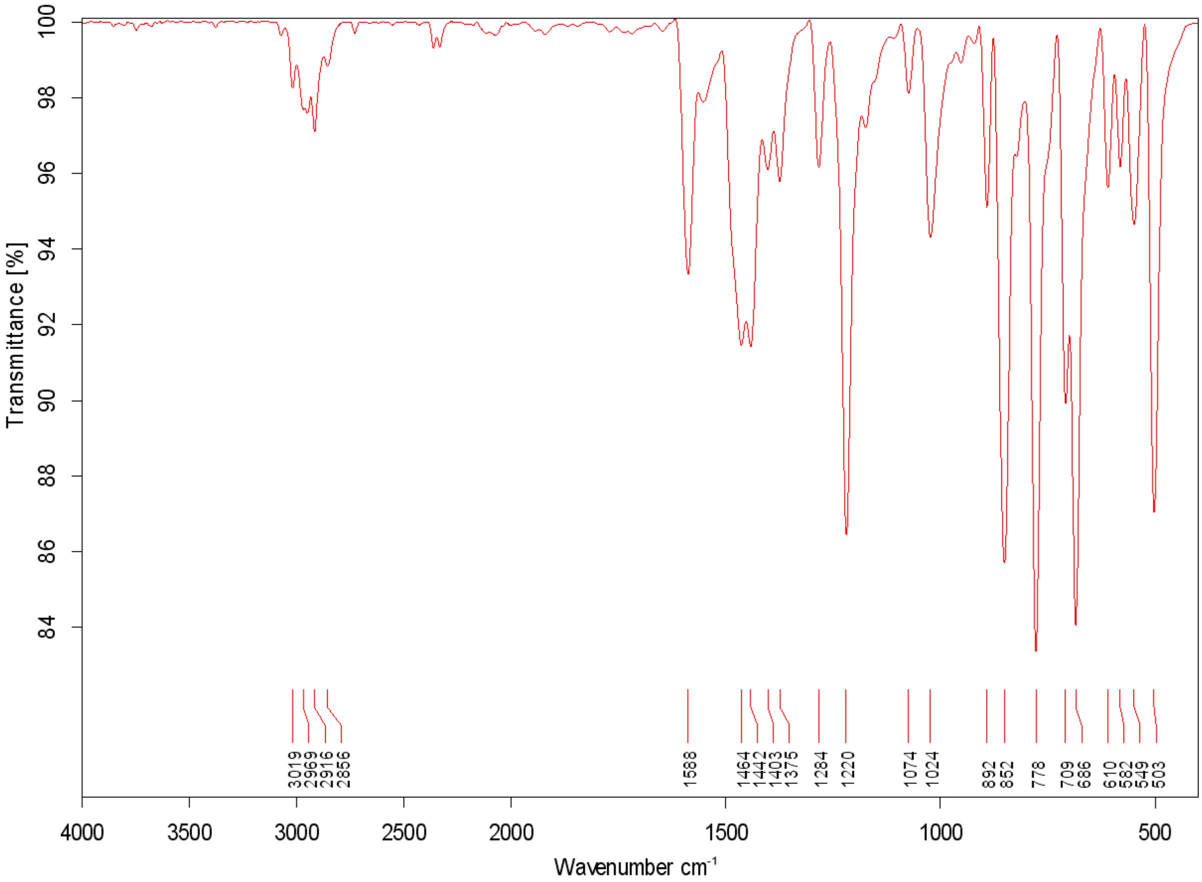

*Figure S14. IR spectrum of compound **3**.*

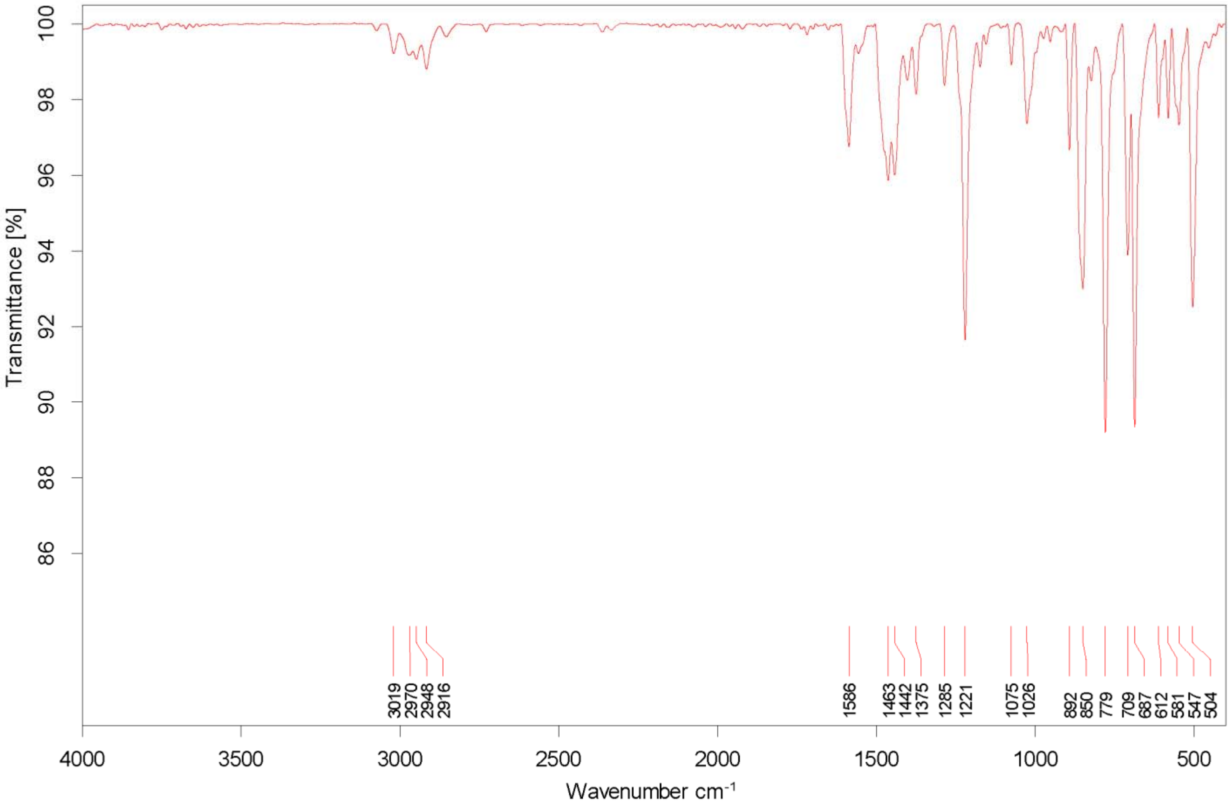

*Figure S15. IR spectrum of compound **4**.*

4. Crystallographic Investigations

A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fibre or a mylar loop. The crystal was transferred directly to the cold stream of a STOE IPDS 2 (150 or 210 K) or STADIVARI (100 K) diffractometer.

All structures were solved by using the program SHELXS/T[4] and Olex2.[5] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 by using the program SHELXL.[4] In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond distances and angles have been deposited as supporting information.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC- 1922573-1922576. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Table S1: Crystal data, data collection and refinement for compounds 1, 2, 3 and 4.

	1	**2**	**3**	**4**
Empirical formula	$C_{39}H_{50}AsN_3Si$	$C_{39}H_{50}AsGeN_3$	$C_{53}H_{66}As_2Cl_2Ge_2N_2$	$C_{48}H_{54}As_2GeN_2$
Formula weight	663.83	708.33	1096.99	881.36
Temperature/K	150	150	100	210
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	*P*2₁/*c*	*P*-1	*P*2₁/*c*	*C*2/*c*
a/Å	16.8814(4)	9.1929(5)	12.3661(12)	13.0143(7)
b/Å	12.7921(3)	12.0657(7)	8.5420(5)	18.0257(7)
c/Å	18.4683(5)	16.2153(9)	24.170(2)	19.1618(10)
α/°		91.416(5)		
β/°	116.297(2)	91.029(4)	98.891(7)	107.787(4)
γ/°		93.834(4)		
V/Å^3	3575.46(16)	1793.66(17)	2522.4(4)	4280.3(4)
Z	4	2	2	4
ρ_{calc}g/cm^3	1.233	1.312	1.444	1.368
μ/mm^{-1}	1.015	1.800	2.636	2.284
F(000)	1408.0	740.0	1124.0	1816.0
Crystal size/mm^3	0.393 × 0.324 × 0.213	0.48 × 0.378 × 0.269	0.174 × 0.09 × 0.044	0.204 × 0.151 × 0.073
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Index ranges	$-23 \le h \le 23$, $-17 \le k \le 15$, $-23 \le l \le 25$	$-12 \le h \le 12$, $-16 \le k \le 16$, $-22 \le l \le 19$	$-16 \le h \le 16$, $-11 \le k \le 10$, $-32 \le l \le 33$	$-18 \le h \le 17$, $-22 \le k \le 24$, $-25 \le l \le 26$
Reflections collected	28628	18292	14593	14395
Independent reflections	9644 [R_{int} = 0.0350, R_{sigma} = 0.0365]	9516 [R_{int} = 0.0293, R_{sigma} = 0.0720]	6191 [R_{int} = 0.0475, R_{sigma} = 0.0838]	5950 [R_{int} = 0.0352, R_{sigma} = 0.0441]
GOOF	1.014	0.879	0.983	0.996
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0432, wR_2 = 0.1126	R_1 = 0.0278, wR_2 = 0.0555	R_1 = 0.0515, wR_2 = 0.1103	R_1 = 0.0425, wR_2 = 0.0986
Final *R* indexes [all data]	R_1 = 0.0612, wR_2 = 0.1222	R_1 = 0.0541, wR_2 = 0.0577	R_1 = 0.1009, wR_2 = 0.1291	R_1 = 0.0629, wR_2 = 0.1053
Largest diff. peak/hole / e Å^{-3}	0.91/-0.43	0.40/-0.42	0.80/-0.86	0.95/-0.74

ORTEP-Plots of solid-state structures

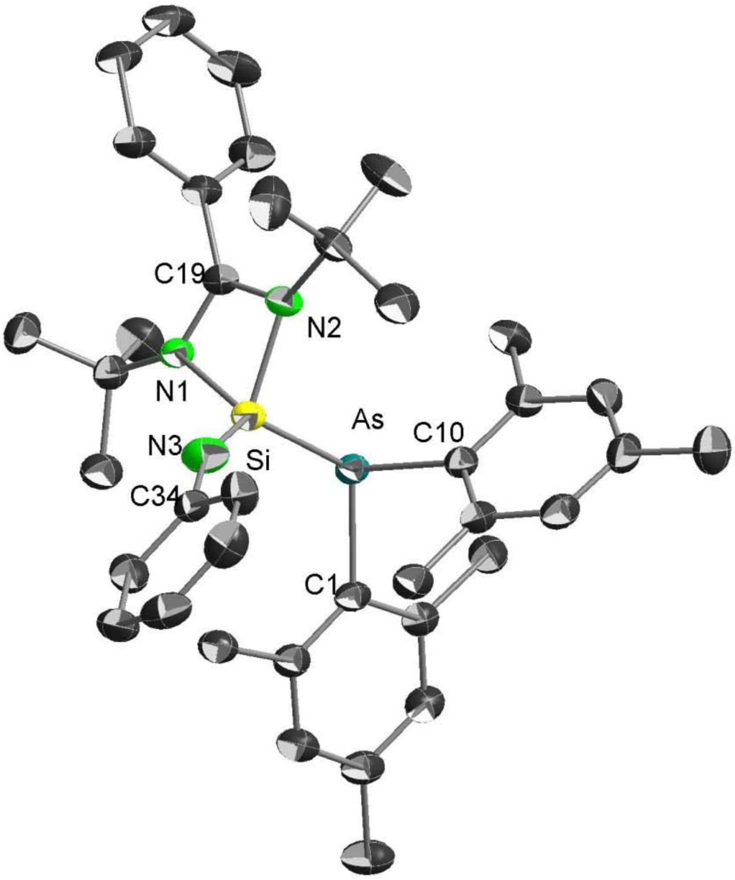

Figure S16. Molecular structure of ***1*** *in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. . Selected bond lengths [Å] and angles [°]: As-Si 2.3948(6), As-C1 1.991(2), As-C10 1.978(2), Si-N1 1.840(2), Si-N2 1.833(2), Si-N3 1.570(2), Si-C19 2.290(2), N3-C34 1.351(3); C10-As-C1 99.72(8), C1-As-Si 118.96(6), C10-As-Si 100.28(6), N2-Si-N1 71.63(8), N1-Si-As 99.40(6), N2-Si-As 98.02(6), N3-Si-As 133.76(8), N3-Si-N1 117.25(10), C34-N3-Si 161.3(2).*

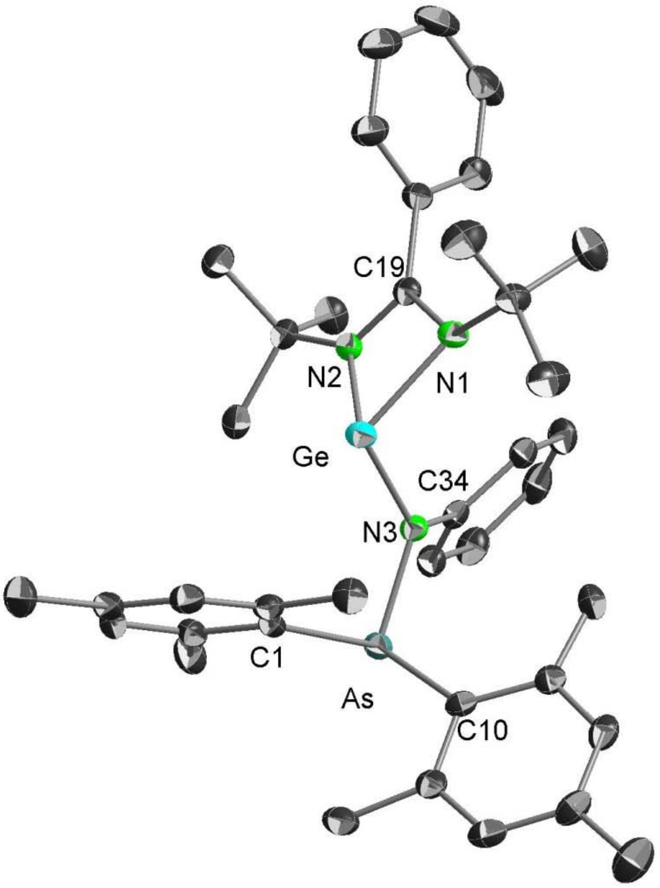

*Figure S17. Molecular structure of **2** in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths [Å] and angles [°]: As-N3 1.883(2), As-C1 1.976(2), As-C10 1.984(2), Ge-N1 2.067(2), Ge-N2 1.999(1), Ge-N3 1.914(1), Ge-C19 2.475(2), N3-C34 1.427(2); C1-As-C10 103.56(7), N2-Ge-N1 64.13(6), N3-Ge-N1 105.04(6), N3-Ge-N2 98.70(6), As-N3-Ge 120.36(8), C34-N3-Ge 122.75(11), C34-N3-As 113.13(11).*

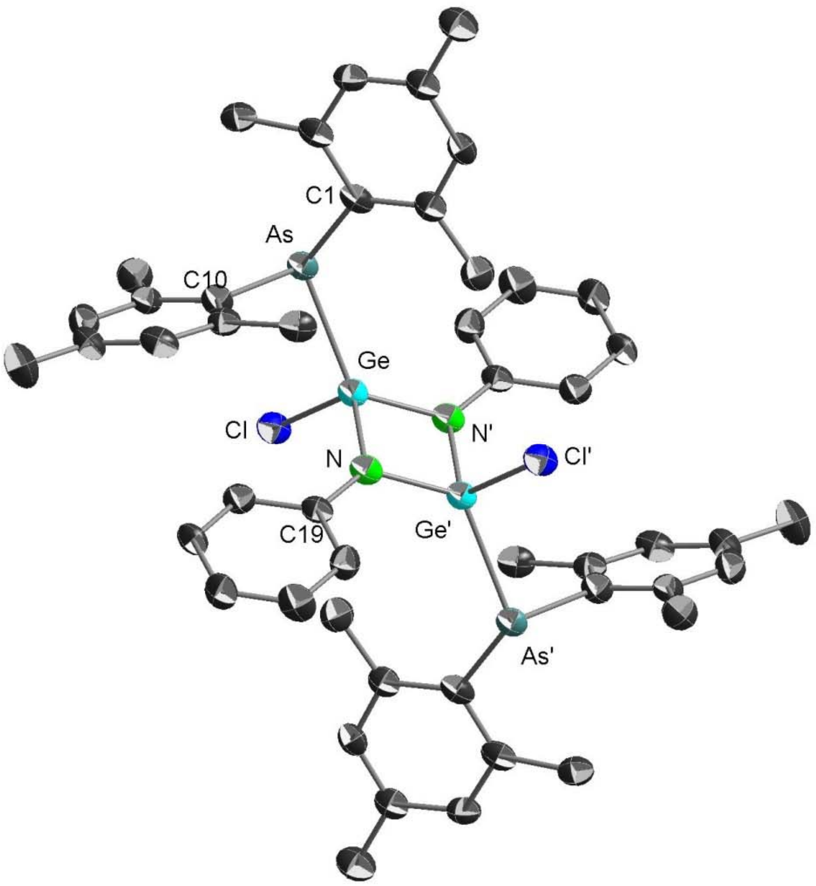

Figure S18. Molecular structure of ***3*** *in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths [Å] and angles [°]: As-Ge 2.4316(7), As-C1 1.976(4), As-C10 1.979(4), Ge-Cl 2.199(1), Ge-N 1.853(3), Ge-N' 1.842(4), N-C19 1.396(5); C1-As-C10 102.2(2), N-Ge-As 126.16(11), N'-Ge-As 134.06(11), N-Ge-Cl 107.88(11), N-Ge-N' 83.7(2), Ge-N-Ge' 96.3(2), C19-N-Ge 128.9(3), C19-N-Ge' 133.2(3), Cl-Ge-As 94.62(4).*

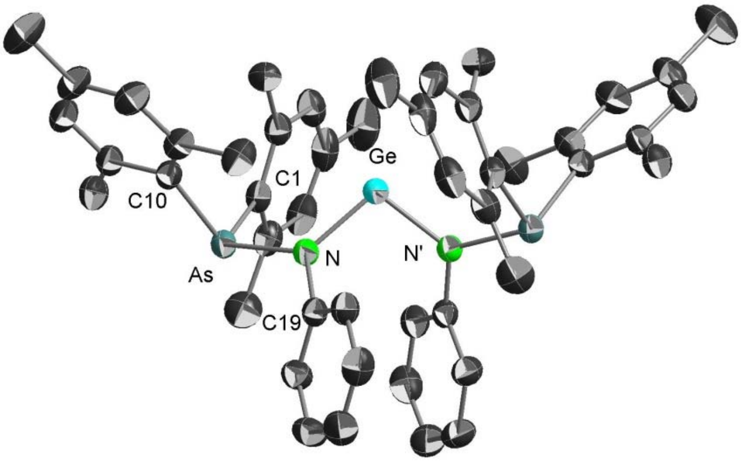

*Figure S19. Molecular structure of **4** in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths [Å] and angles [°]: As-N 1.880(2), As-C1 1.991(3), As-C10 1.979(3), Ge-N 1.879(2), N-C19 1.424(3); C10-As-C1 102.63(11), N-Ge-N' 101.27(13), Ge-N-As 121.90(11), N-As-C1 96.63(10), N-As-C10 109.50(10), C19-N-As 115.4(2), C19-N-Ge 122.2(2).*

5. Computational Details

The quantum chemical RI-DFT calculations of the molecules **1**, **2**, [**L**Ge(=NPh)(AsMes$_2$)] and [**L**Si(Mes$_2$AsNPh)] were performed by means of the program system TURBOMOLE using the RI-BP86 functional [6-11] without the constraint of symmetry. The basis sets for Si, Ge, As, C, H and N were of def-SV(P) quality.[12,13] The partial charges and shared electron numbers (SEN) as reliable measures of bond strength were obtained from Ahlrichs-Heinzmann population analysis based on occupation numbers (Table S2).[14] The localisation of MOs was performed using the method of Pipek and Mezey.[15] The results summarizing the LMOs of the bonds of interest are given in Figure S20.

Table S2: Results of the quantum chemical calculations

	E$_{tot}$/hartree	Energy difference/ kJ·mol^{-1}	(SEN(E=N)	SEN(E-N)	SEN(As-E)	SEN(As-N)
1	-4204.644103	0	1.62	-	0.92	-
[**L**Si(Mes$_2$AsNPh)]	-4204.625537	+48.7	-	1.19	-	0.89
[**L**Ge(=NPh)(AsMes$_2$)]	-5992.204463	+51.6	1.41	-	0.83	-
2	-5992.224099	0	-	1.02	-	0.91

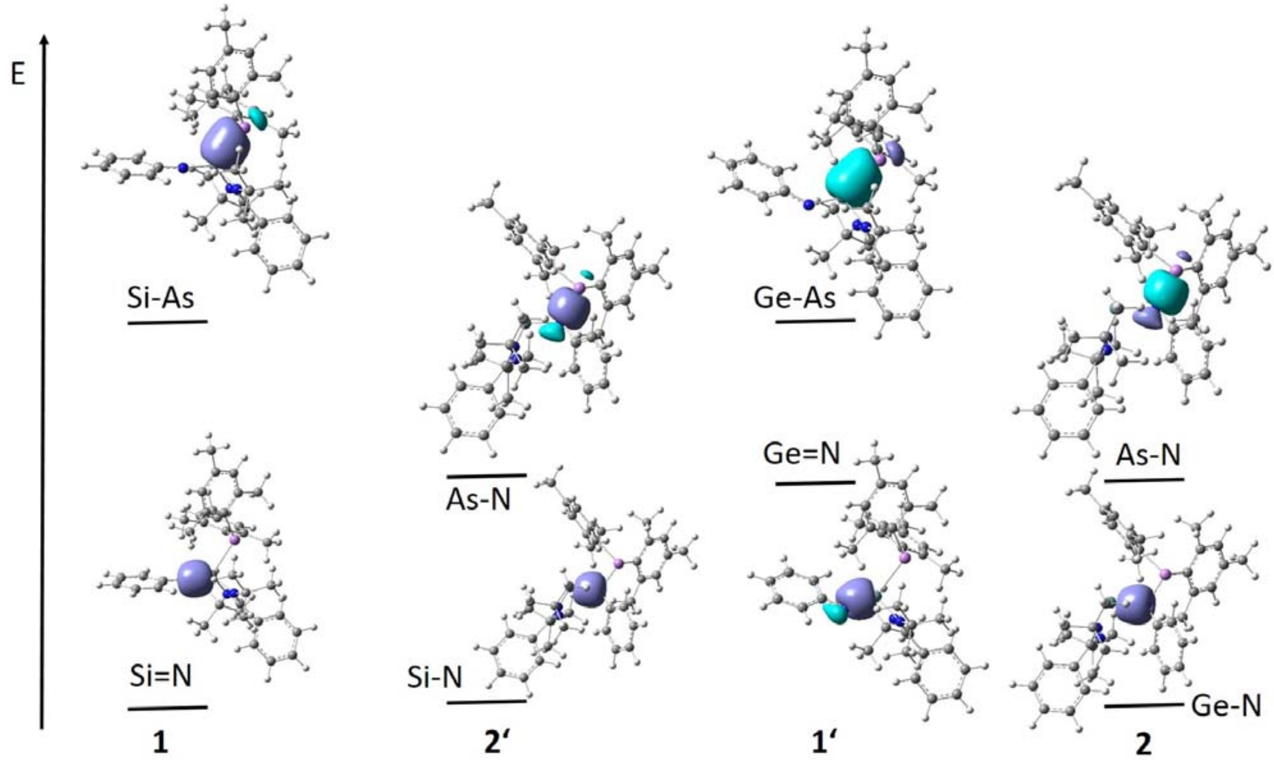

*Figure S20. LMO diagram of the bonds of interest of the molecules **1**, **2**, [**L**Ge(=NPh)(AsMes$_2$)], and [LSi(Mes$_2$AsNPh)].*

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