

Synthesis of a Dimeric Phosphine-Stabilized Phosphidogermanium(I)- Amidogermanium(II) Derivative

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Supporting Information

1. Experimental Procedure
2. Selected NMR Spectra
3. References

1. Experimental Section

General Procedures. All chemical manipulations were performed using standard Schlenk techniques, under an atmosphere of argon gas. The solvents used were purified by the MBRAUN solvent purification system. Compound **1** was prepared by methods outlined in the literature.¹ The ¹H, ¹³C, ²⁹Si and ³¹P NMR spectra were recorded in deuterated benzene (C₆D₆) on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe₄ for ¹H, ¹³C and ²⁹Si and 85% H₃PO₄ for ³¹P. Elemental analyses were performed by Nanyang Technological University, Division of Chemistry and Biological Chemistry. Melting points were measured in sealed glass tubes and were uncorrected.

Synthesis of [L{(Ar)(Ph₂P)N}Si:→GeCl₂] (2**).** Toluene (20 mL) was added to a mixture of [L{(Ar)(Ph₂P)N}Si:] (**1**) (0.62 g, 1.00 mmol) and GeCl₂.dioxane (0.23 g, 1.00 mmol) and stirred for 16 hours at ambient temperature. The resulting orange mixture was filtered and concentrated to ca. 10 mL to afford compound **2** as colourless crystals. Yield: 0.27 g (31.6 %). Mp. 213.7 °C (decomposed). Elemental analysis calcd for C₄₆H₅₈Cl₂GeN₃PSi (**2**.C₇H₈): C, 64.56; H, 6.84; N, 4.91. Found: C, 64.54; H, 6.55; N, 5.11. ¹H NMR (399.5 MHz, C₆D₆, 23.3 °C): δ 0.23 (d, ²J_{HH} = 6.4 Hz, 6H, CH(CH₃)₂), 1.24 (s, 18H, *t*Bu), 1.29 (d, ²J_{HH} = 6.4 Hz, 6H, CH(CH₃)₂), 3.52 (br, 2H, CH(CH₃)₂), 6.83 – 7.01 (m, 8H, Ph), 7.03 – 7.12 (m, 4H, Ph), 7.29 (d, 1H, ³J_{HH} = 7.7 Hz, Ph), 7.50 (m, 4H, Ph), 8.54 (d, 1H, ³J_{HH} = 7.7 Hz, Ph). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 24.9 °C): δ 23.92, 24.05 (CH(CH₃)₂), 28.41 (CH(CH₃)₂), 31.95, 55.62 (*t*Bu), 125.11, 126.60, 127.24, 128.38, 128.45, 129.91, 130.30, 130.59, 133.70, 135.34 (d, ²J_{C-P} = 21.9 Hz), 104.59, 147.33 (Ar). ³¹P{¹H} NMR (160.2 MHz, C₆D₆, 24.9 °C): δ 44.90. ²⁹Si{¹H} NMR (79.4 MHz, C₆D₆, 24.9 °C): δ -12.85 (d, ²J_{SiP} = 43.1 Hz). The Si NMR signal is relatively weak due to quadrupolar broadening with the germanium nucleus (*I* = 9/2).

Synthesis of [:Ge(Cl){N(Ar)PPh₂}(Ph₂P)Ge:]₂ (3**).** The mother liquor from the synthesis of **2** was concentrated to ca. 5mL to afford **3** as orange crystals. Yield: 0.07 g (4.9 %). Mp. 183.5 °C (decomposed). Elemental analysis calcd for C₇₂H₇₄Cl₂Ge₄N₂P₄: C, 59.51; H, 5.14; N, 1.93. Found: C, 59.37; H, 5.02; N, 1.87. ³¹P{¹H} CP-MAS NMR: δ -14.03, 103.63.

Synthesis of [L(PPh₂)Si=NAr] (6**).** C₆D₆ (0.4 mL) was added to **1** (31 mg) in an NMR tube. The resulting solution was heated to 80 °C for 16 hours and monitored periodically by ³¹P{¹H} NMR. All volatiles were removed and hexane (1.0 mL) was added. The resulting mixture was filtered and concentrated to afford **6** as yellow crystals. Yield: 29 mg (93.5 %). Mp. 212.9 °C (decomposed). Elemental analysis calcd for C₃₉H₅₀N₃PSi: C, 75.56; H, 8.13; N, 6.78. Found: C, 75.24; H, 8.01; N, 6.64. ¹H NMR (399.5 MHz, C₆D₆, 23.3 °C): δ 1.01 (s, 18H, *t*Bu), 1.45 (d, ³J_{HH} = 7.30 Hz, 12H, CH(CH₃)₂), 4.23 (sept, ³J_{HH} = 7.30 Hz, 2H, CH(CH₃)₂), 6.84 – 6.90 (m, 4H, Ph), 7.01 – 7.11 (m, 8H, Ph), 7.37 (d, ³J_{HH} = 7.75 Hz, 2H, Ph), 7.96 – 8.00 (m, 4H, Ph). ¹³C{¹H} NMR (99.5 MHz, C₆D₆, 24.9 °C): δ 28.40, 23.30 (CH(CH₃)₂), 31.25, 41.52 (*t*Bu), 123.33, 128.11,

128.71, 131.08, 131.29, 148.22, 150.67 (Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (160.2 MHz, C_6D_6 , 24.9 °C): δ -53.56. $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.4 MHz, C_6D_6 , 24.9 °C): δ -77.70 (d, $J_{\text{SiP}} = 10.6$ Hz).

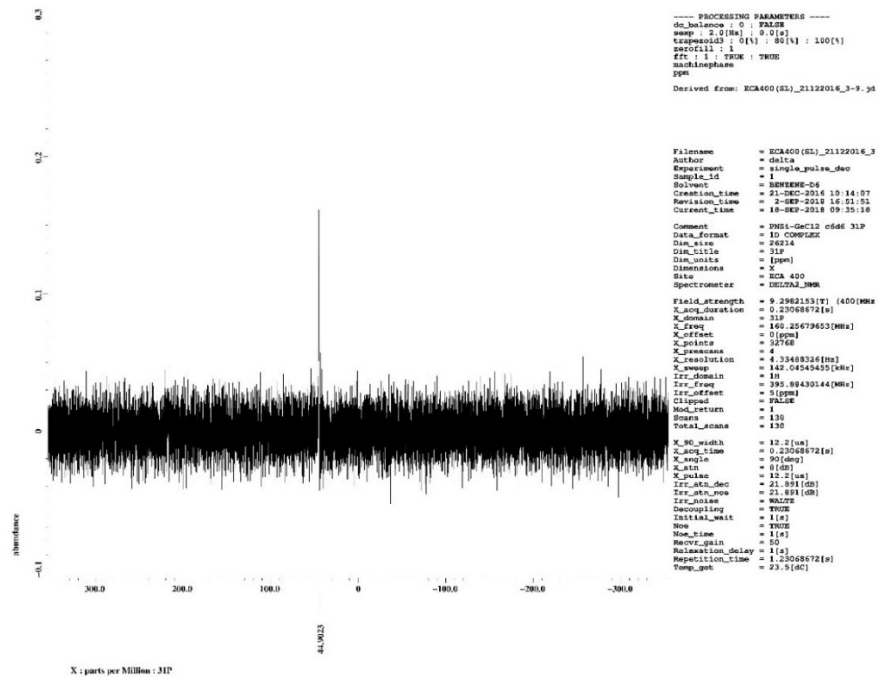
Synthesis of [$\{\text{Ph}_2\text{PN}(\text{Ar})\text{GeCl}\}\{\text{Ph}_2\text{PGeCl}\}$] (7). Toluene (20 mL) was added to a mixture of **3** (0.58 g, 0.40 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.41 g, 0.80 mmol) at room temperature and stirred for 16 hours. The insoluble precipitate was filtered, and the filtrate was concentrated to obtain **7** as colourless crystalline solid. Yield: 0.03g (9.8 %) Mp. 194.5 °C. Elemental analysis calcd for $\text{C}_{36}\text{H}_{37}\text{Cl}_2\text{Ge}_2\text{NP}_2$: C, 56.76; H, 4.90; N, 1.84. Found: C, 56.47; H, 4.78; N, 1.76. ^1H NMR (399.5 MHz, C_6D_6 , 23.3 °C) shows two geometric isomers (*cis* and *trans*). *1st set*: δ -0.057 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.46 (d, $^3J_{\text{HH}} = 6.4$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.66 (d, 3H, $\text{CH}(\text{CH}_3)_2$, overlapping with the 2nd set), 2.30 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 4.40 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 6.79 – 7.13 (m, Ph, overlapping with the 2nd set), 7.44 – 8.03 (m, Ph, overlapping with the 2nd set). *2nd set*: δ 0.51 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 0.63 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.43 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.47 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 4.10 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 4.18 (sept, $^3J_{\text{HH}} = 6.8$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 6.79 – 7.13 (m, Ph, overlapping with the 1st set), 7.44 – 8.03 (m, Ph, overlapping with the 1st set). $^{31}\text{P}\{^1\text{H}\}$ NMR (160.2 MHz, C_6D_6 , 24.9 °C) shows two geometric isomers (*cis* and *trans*). *1st set*: δ 88.6 ppm, $^3J_{\text{PP}} = 34.7$ Hz (Ph_2PGeCl), -19.3 ppm, $^3J_{\text{PP}} = 34.7$ Hz ($\text{Ph}_2\text{PN}(\text{Ar})\text{GeCl}$); *2nd set*: δ 96.7 ppm, $^3J_{\text{PP}} = 30.3$ Hz (Ph_2PGeCl), -27.1 ppm, $^3J_{\text{PP}} = 30.3$ Hz ($\text{Ph}_2\text{PN}(\text{Ar})\text{GeCl}$).

X-ray Data Collection and Structural Refinement. Intensity data for compounds **2**, **3**, **6** and **7** were collected using a Bruker APEX II diffractometer. The crystals of **2**, **3**, **6** and **7** were measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .² All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations.

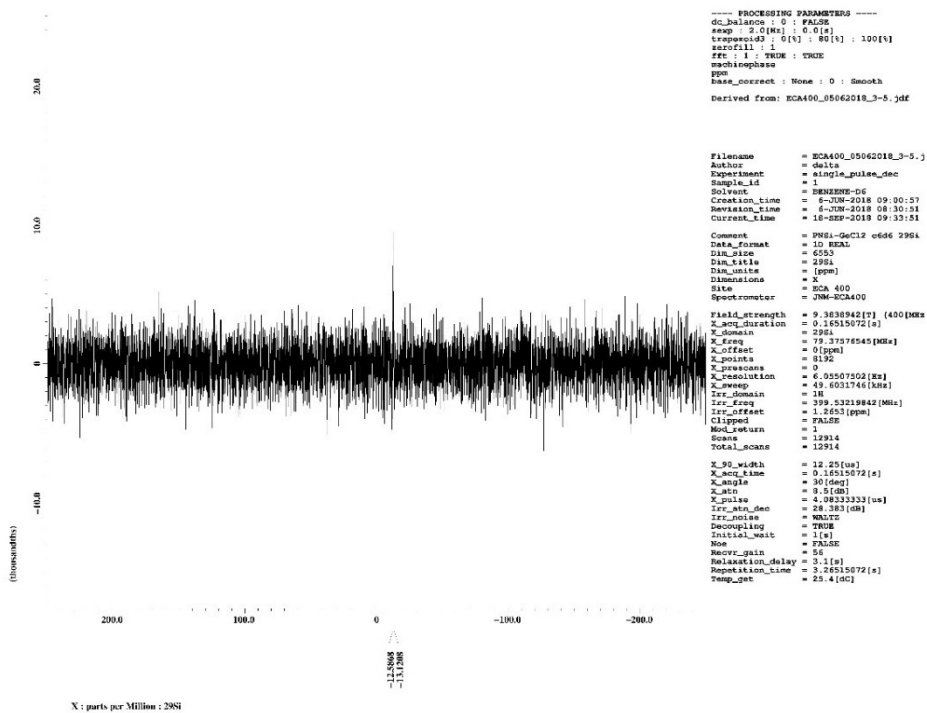
Table S1: Crystallographic data for compounds 2, 3, 6 and 7

	2	3	6	7
CCDC Number	1879740	1879742	1879741	1879744
Formula	C ₄₆ H ₅₈ Cl ₂ GeN ₃ PSi	C ₄₃ H ₄₅ ClGe ₂ NP ₂	C ₃₉ H ₅₀ N ₃ PSi	C ₃₆ H ₃₇ Cl ₂ Ge ₂ NP ₂
<i>M_r</i>	855.50	818.37	619.88	761.68
Color	Colourless	orange	orange	colorless
Crystal System	Triclinic	monoclinic	monoclinic	triclinic
Space Group	<i>P</i> -1	<i>P</i> 1 21/ <i>n</i> 1	<i>P</i> 1 21/ <i>n</i> 1	<i>P</i> -1
<i>a</i> /Å	11.09490(10)	11.7897(2)	17.5974(4)	10.8060(5)
<i>b</i> /Å	12.63690(10)	16.3455(2)	13.0761(4)	16.9006(7)
<i>c</i> /Å	17.6502(2)	20.0346(3)	31.5626(8)	20.7677(9)
<i>α</i> /deg	78.2671(5)	90	90	66.7498(13)
<i>β</i> /deg	89.0480(5)	103.3601(8)	103.6919(8)	89.8652(15)
<i>γ</i> /deg	65.4174(5)	90	90	81.2991(16)
<i>V</i> / Å ³	2196.90(4)	3756.35(10)	7056.3(3)	3437.8(3)
<i>Z</i>	2	4	8	4
<i>d</i> _{calcd} /g cm ⁻³	1.293	1.447	1.167	1.472
<i>μ</i> / mm ⁻¹	2.933	3.668	0.143	2.024
<i>F</i> (000)	900	1684	2672	1552
Crystal Size/mm ³	0.120 x 0.220 x 0.300	0.010 x 0.020 x 0.040	0.160 x 0.200 x 0.220	0.140 x 0.220 x 0.260
Index Range	-13<= <i>h</i> <=13	-13<= <i>h</i> <=13	-25<= <i>h</i> <=24	-15<= <i>h</i> <=15
	-14<= <i>k</i> <=14	-19<= <i>k</i> <=19	-18<= <i>k</i> <=18	-24<= <i>k</i> <=22
	-21<= <i>l</i> <=20	-23<= <i>l</i> <=23	-45<= <i>l</i> <=45	-30<= <i>l</i> <=0
No. of reflections	20072	70144	203092	22757
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> >2σ(<i>I</i>)]	0.0380, 0.0987	0.0527, 0.1389	0.0495, 0.1071	0.0707, 0.1694
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0411, 0.1019	0.0655, 0.1505	0.0763, 0.1237	0.1224, 0.2075
GOF, <i>F</i> ²	1.025	1.038	1.055	1.014
No. of data/ restraints/ param	7569 / 0 / 498	6637 / 0 / 447	22474 / 0 / 813	22757 / 0 / 783
Largest diff peak, hole/ eÅ ⁻³	0.810, -0.698	2.358, -0.847	1.144, -0.398	1.880, -1.638

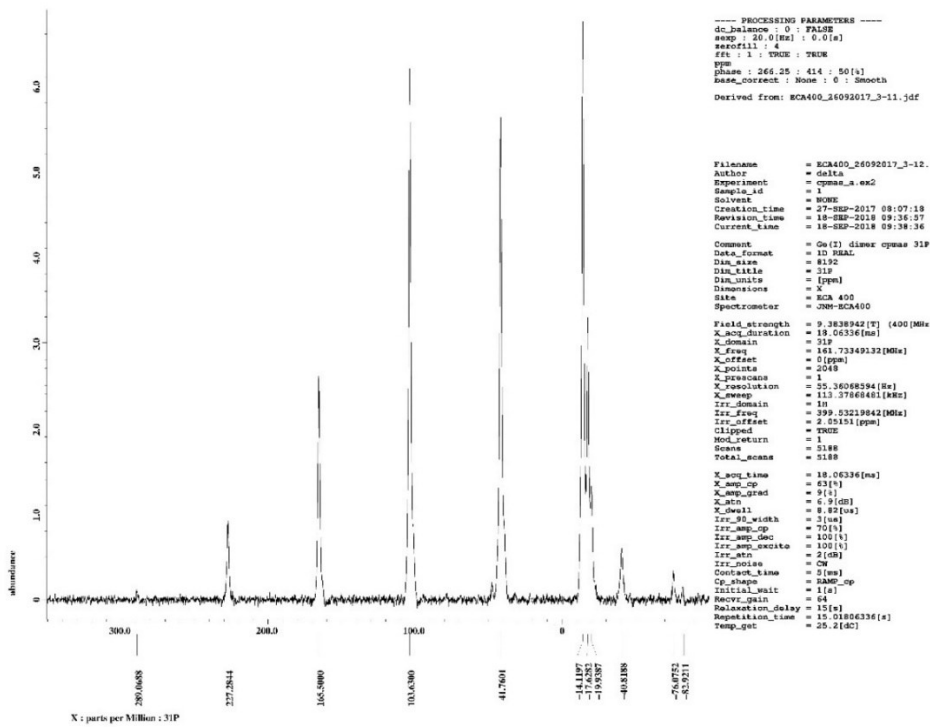
2. NMR Spectra



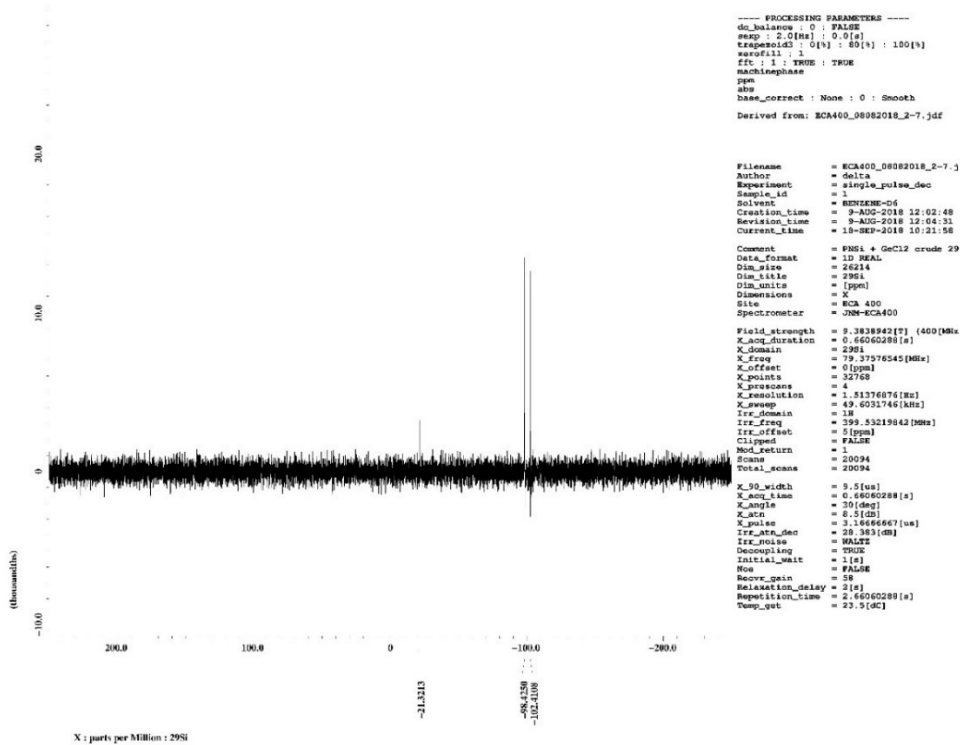
(a) ^{31}P NMR spectrum of compound **2**



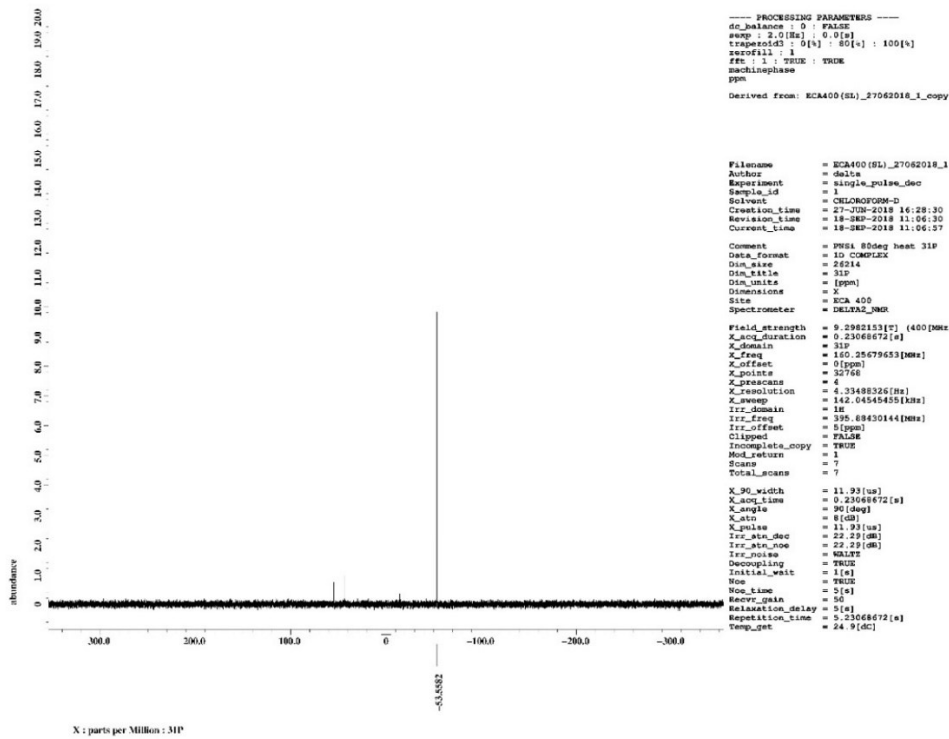
(b) ^{29}Si NMR spectrum of compound **2**.



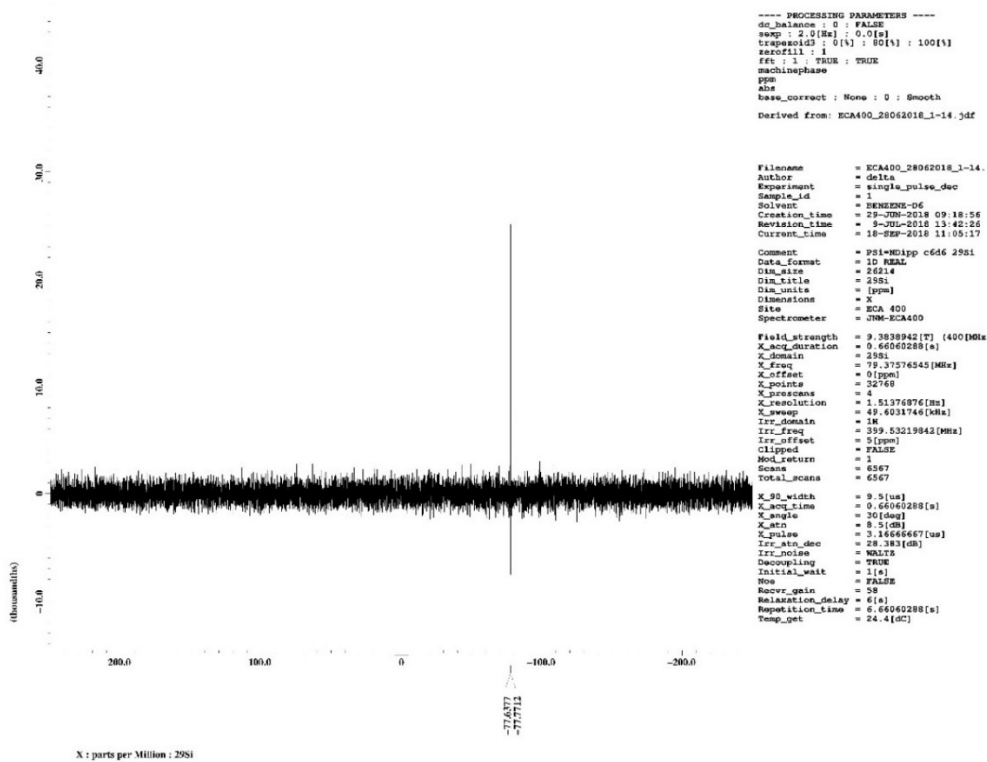
(c) ^{31}P CPMAS NMR spectrum of compound **3**



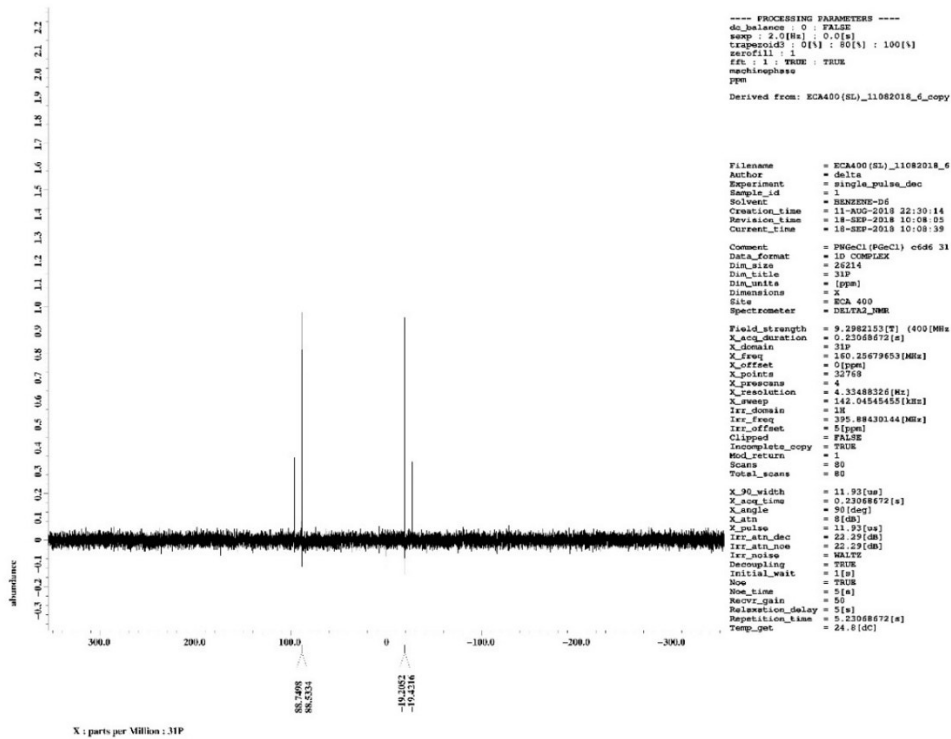
(d) ^{29}Si NMR spectrum of mother liquor from compound **3** showing presence of compounds **4** and **5**



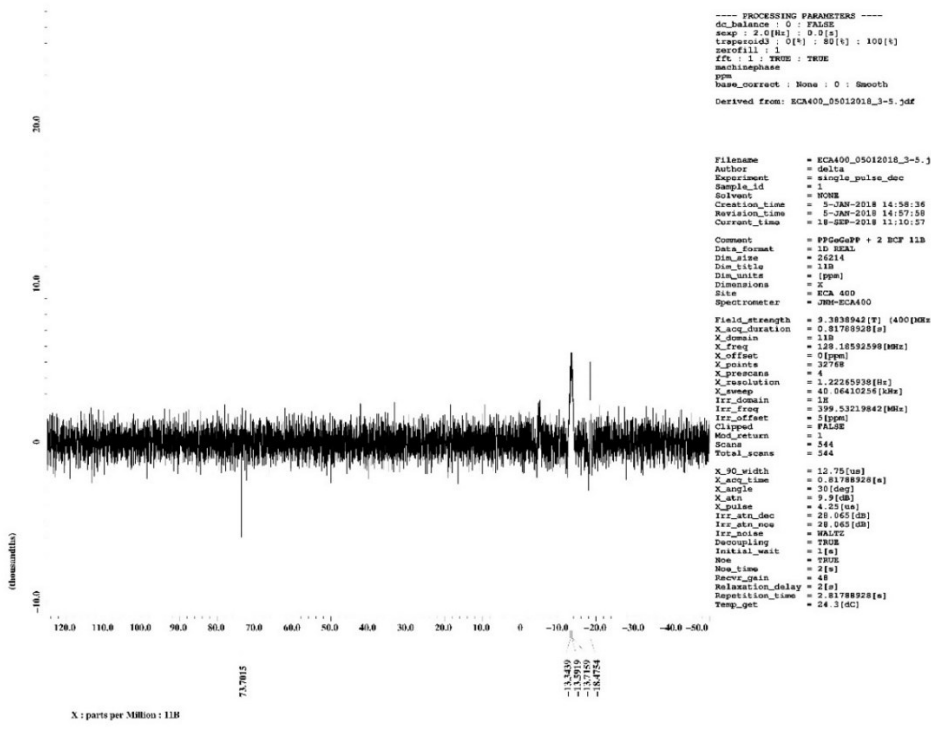
(e) ^{31}P NMR spectrum of compound 6



(f) ^{29}Si NMR spectrum of compound 6



(g) ^{31}P NMR spectrum of compound 7



(h) ^{11}B NMR spectrum of crude reaction mixtures from the reaction of **3** and $\text{B}(\text{C}_6\text{F}_5)_3$ showing unknown 4-coordinate boron compounds

3. References

1. Khan, S.; Pal, S.; Kathewad, N.; Purushothaman, I.; De, S.; Parameswaran, P. *Chem. Commun.* **2016**, 52, 3880 – 3882.
2. Sheldrick, G. M. SHELXL-97; Universität Göttingen: Göttingen, Germany, **1997**.