

Supporting Information

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1. Experimental section

General procedures: All experiments were performed under dry argon gas using standard Schlenk techniques. Toluene, benzene, di-*n*-butylether and *n*-heptane were dried over Na/K respectively LiAlH₄ and stored under argon-atmosphere. C₆D₆ was dried over Na/K and stored over activated molecular sieve (3 Å). (Dipp₂NacNac)Ga was prepared according to literature procedure.^[1] SbCl₃ was sublimed prior to use, LiAlH₄, PH₃ and AsH₃ were used as purchased.

¹H, ¹³C and ³¹P NMR-spectra were recorded on a Bruker AV II 300 MHz and AV III HD 300 MHz relative to the tetramethylsilane standard. IR-spectra were recorded on a Bruker Alpha FT-IR with a diamond ATR (500-4000 cm⁻¹). Elemental analyses were performed on an ELEMENTAR vario Microcube and the content is reported in %. The TGA/DSC were performed on a DSC-TGA 3 from METTLER TOLEDO. X-ray crystallographic data were collected on a Bruker D8 Quest diffractometer using monochromatic Mo-Kα radiation (λ = 0.71073 Å) and a PHOTON 100 detector. Multi-scan and numerical absorption corrections were applied using the SADABS program.^[2,3] The solution of the structure was performed with intrinsic phasing with the SHELXT-2015 solution program, while for the structure refinement with full-matrix least-squares against *F*² the SHELXL-2015 or SHELXL-2018 packages were used, both within either the OLEX² or SHELXLE environments.^[4-7] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms at the carbon atoms were refined using the “riding model” approach with isotropic displacement parameters 1.2 times (1.5 times for terminal methyl groups) of that of the preceding carbon atom. More details regarding the refinements of individual structures are given in the next section. The hydrogen atoms at the Ga and Sb atoms were refined using appropriate distance restraints. CCDC 2053170 (**1**), 2053171 (**2**) 2053167 (**3**), 2053168 (**4**) and 2053169 (**5**) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Synthesis of (Dipp₂NacNac)GaH(PH₂) (1**).** A constant PH₃ gas flow was passed through a solution of 0.18 g (Dipp₂NacNac)Ga (0.37 mmol, 1 eq) in 10 mL toluene at -20 °C. The reaction was stopped after the former yellow solution was discoloured. Excess of PH₃ was removed from the solution and toluene was removed *in vacuo*. The obtained colourless solid was dissolved in 10 mL *n*-heptane and centrifugation to remove traces of insoluble contamination. Subsequently the solution was concentrated to 1 mL. Storage at -32 °C afforded colourless blocks of **1** in a yield of 0.095 g (0.18 mmol, 49%).

Elemental analysis calcd: for C₂₉H₄₄GaN₂P: C, 66.81; H, 8.51; N, 5.37. Found: C, 66.41; H, 8.427; N, 5.51. ¹H NMR (300 MHz, C₆D₆) δ (ppm) = 0.46 (d, 2H, PH₂, ¹J_{HP} = 175.5 Hz), 1.14

(d, 6H, CH(CH₃)₂, ²J_{HH} = 6.8 Hz), 1.17 (d, 6H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 1.29 (d, 6H, CH(CH₃)₂, ³J_{HH} = 6.8 Hz), 1.44 (d, 6H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 1.57 (s, 6H, β-CH₃), 3.31-3.43 (m, 4H, CH(CH₃)₂), 4.81 (s, 1H, γ-CH), 6.00 (d, 1H, GaH, ³J_{HP} = 25.4 Hz), 7.05-7.12 (m, 6H, Aryl-H). ¹³C{¹H} NMR (75.5 MHz, C₆D₆) δ (ppm) = 23.3, 24.2, 24.5, 24.6, 26.4, 28.2, 29.0 (C(CH₃)₃, CH(CH₃)₂), 96.0 (γ-CH), 124.3, 124.7, 127.2, 128.1, 141.3, 143.3, 144.9 (Aryl-C), 169.1 (NCCH₃). ³¹P{¹H} NMR (121.5 MHz, C₆D₆) δ (ppm) = -286.0 (s). ³¹P NMR (121.5 MHz, C₆D₆) δ (ppm) = -286.0 (td, ¹J_{PH} = 174.8 Hz, ²J_{PH} = 25.3 Hz). IR (ATR) ν (cm⁻¹) = 3034, 3023, 2959, 2923, 2865, 2283 (PH), 1828 (GaH), 1554, 1519, 1457, 1440, 1384, 1316, 1259, 1177, 1103, 1053, 1019, 934, 904, 866, 801, 795, 754, 713, 632, 600, 576, 521, 438.

Synthesis of (Dipp₂NacNac)GaH(AsH₂) (2). The synthesis of **2** was carried out similar to **1** with a constant AsH₃-gas flow at 0 °C. 0.137 g (Dipp₂NacNac)Ga (0.28 mmol) afforded 0.097 g of **2** (0.17 mmol, 61%) as colourless blocks from *n*-heptane at -32 °C.

Elemental analysis calcd.(%) for C₂₉H₄₄GaN₂As: C, 61.61; H, 7.85; N, 4.96. Found: C, 61.51; H, 8.021; N, 5.35. ¹H NMR (300 MHz, C₆D₆) δ (ppm) = -0.16 (s, 2H, AsH₂), 1.14 (d, 6H, CH(CH₃)₂, ²J_{HH} = 6.8 Hz), 1.17 (d, 6H, CH(CH₃)₂, ³J_{HH} = 6.7 Hz), 1.30 (d, 6H, CH(CH₃)₂, ³J_{HH} = 6.8 Hz), 1.43 (d, 6H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 1.57 (s, 6H, β-CH₃), 3.29-3.46 (m, 4H, CH(CH₃)₂), 4.82 (s, 1H, γ-CH), 6.33 (s, 1H, GaH), 7.05-7.12 (m, 6H, Aryl-H). ¹³C{¹H} NMR (75.5 MHz, C₆D₆) δ (ppm) = 23.4, 24.2, 24.6, 24.8, 26.4, 28.2, 29.1 (C(CH₃)₃, CH(CH₃)₂), 96.0 (γ-CH), 124.2, 124.7, 127.2, 128.1, 141.4, 143.1, 145.0 (Aryl-C), 169.1 (NCCH₃). IR (ATR) ν (cm⁻¹) = 3055, 3022, 2959, 2923, 2864, 2080 (AsH), 1823 (GaH), 1552, 1519, 1458, 1439, 1384, 1316, 1259, 1176, 1098, 1017, 934, 865, 795, 753, 713, 648, 614, 517, 437.

Synthesis of (Dipp₂NacNac)GaH(SbH₂) (3). The following synthesis was performed under exclusion of light. A solution of 2 g SbCl₃ in 10 mL *n*Bu₂O was added dropwise to a solution of 0.5 g LiAlH₄ in 70 mL *n*Bu₂O at -30 °C. Immediately, evolution of gas and formation of elemental antimony was observed. The formed gases SbH₃ and H₂ were removed *in vacuo* and passed through a cooling trap at -40 °C to remove traces of *n*Bu₂O. SbH₃ was collected in a second trap at -196°C. This cooling trap was separated after the reaction was stopped and connected to a schlenk tube with gas inlet pipe containing 0.183 g of (Dipp₂NacNac)Ga in 20 mL of toluene. The cooling trap was warmed to -78°C and the gas was passed through the schlenk tube at -50 °C. The reaction mixture was slowly warmed up while the reaction was completed after room temperature was reached. Toluene was removed *in vacuo* and the

remaining solid extracted with *n*-heptane and centrifuged. Colourless blocks of **3** were obtained at -32 °C in a yield of 0.166 g (0.27 mmol, 73%).

Elemental analysis calcd.(%) for C₂₉H₄₄GaN₂Sb C, 56.90; H, 7.25; N, 4.58. Found: C, 57.35; H, 7.102; N, 4.77. **¹H NMR** (300 MHz, C₆D₆) δ (ppm) = -1.50 (s, 2H, SbH₂), 1.13 (d, 6H, CH(CH₃)₂, ²J_{HH} = 6.8 Hz), 1.17 (d, 6H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 1.32 (d, 6H, CH(CH₃)₂, ³J_{HH} = 6.8 Hz), 1.41 (d, 6H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 1.58 (s, 6H, β-CH₃), 3.36 (hept, 4H, CH(CH₃)₂, ²J_{HH} = 6.8 Hz), 4.84 (s, 1H, γ-CH), 7.05-7.12 (m, 7H, GaH and Aryl-H). **¹³C{¹H} NMR** (75.5 MHz, C₆D₆) δ (ppm) = 23.5, 24.2, 24.8, 26.4, 28.2, 29.3 (C(CH₃)₃, CH(CH₃)₂), 96.2 (γ-CH), 124.2, 124.8, 127.2, 128.1, 141.8, 142.7, 145.3 (Aryl-C), 169.2 (NCCH₃). **IR** (ATR) ν (cm⁻¹) = 3066, 3056, 3020, 2960, 2923, 2865, 1845 (GaH), 1816 (SbH), 1552, 1520, 1458, 1437, 1383, 1317, 1231, 1177, 1101, 1054, 1018, 935, 864, 796, 757, 723, 714, 641, 605, 588, 522.0, 449, 431. **TGA**: decomposition at 273.70 °C.

Synthesis of {(Dipp₂NacNac)GaH}₂(AsH) (4). 0.07 g (0.12 mmol, 1 eq) of **2** were added to a solution of 0.06 g (Dipp₂NacNac)Ga (0.12 mmol, 1 eq) in 4 mL toluene. The solution was stirred over night and the solvent subsequently removed. The remaining colourless solid was extracted with *n*-heptane and centrifuged. Colourless blocks of **4** in a yield of 0.052 g (0.05 mmol, 41%) were obtained from benzene at 6 °C.

Elemental analysis calcd.(%) for C₅₈H₈₅Ga₂N₄As: C, 66.18; H, 8.14; N, 5.32. Found: C, 65.92, H, 7.567; N, 4.75. **¹H NMR** (300 MHz, C₆D₆) δ (ppm) = -2.10 (s, 1H, AsH), 0.96 (d, 12H, CH(CH₃)₂, ³J_{HH} = 6.7 Hz), 1.09 (d, 12H, CH(CH₃)₂, ³J_{HH} = 6.8 Hz), 1.17 (d, 12H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 1.26 (d, 12H, CH(CH₃)₂, ³J_{HH} = 6.9 Hz), 1.43 (s, 12H, β-CH₃), 3.11 (hept, 4H, CH(CH₃)₂, ³J_{HH} = 6.8 Hz), 3.39 (hept, 4H, CH(CH₃)₂, ³J_{HH} = 7.0 Hz), 4.73 (s, 2H, γ-CH), 6.01 (s, 2H, GaH), 6.98-7.04 (m, 8H, Aryl-H), 7.10-7.12 (m, 4H, Aryl-H). **¹³C{¹H} NMR** (75.5 MHz, C₆D₆) δ (ppm) = 23.7, 23.8, 24.3, 25.0, 27.5, 27.9, 29.3 (C(CH₃)₃, CH(CH₃)₂), 95.9 (γ-CH), 123.8, 124.3, 126.8, 18.1, 142.4, 143.1 144.8 (Aryl-C), 168.4 (NCCH₃). **IR** (ATR) = 3068, 2960, 2925, 2865, 2094 (AsH), 1861 (GaH), 1815, 1585, 1548, 1521, 1456, 1438, 1392, 1315, 1259, 1176, 1096, 1054, 1015, 935, 859, 796, 759, 718, 681, 643, 603, 588, 523, 454, 439.

Synthesis of {(Dipp₂NacNac)GaH}₂(SbH) (5). 0.093 g (0.15 mmol, 1 eq) of **3** was added to a solution of 0.06 g (Dipp₂NacNac)Ga (0.15 mmol, 1 eq) in 5 mL toluene. The solution was stirred over night and the solvent removed. The remaining yellow solid was extracted with *n*-heptane and centrifuged. Light yellow blocks of **5** in a yield of 0.09 g (0.08 mmol, 55%) were obtained from benzene at 6 °C.

Elemental analysis calcd.(%) for $C_{58}H_{85}Ga_2N_4Sb$: C, 63.36; H, 7.79; N, 5.10. Found: C, 62.73; H, 7.750; N, 5.23. **1H NMR** (300 MHz, C_6D_6) δ (ppm) = -4.62 (s, 1H, *SbH*), 0.94-1.01 (br, m, 12H, $CH(CH_3)_2$) 1.09 (d, 12H, $CH(CH_3)_2$, $^3J_{HH} = 6.7$ Hz), 1.18 (d, 12H, $CH(CH_3)_2$, $^3J_{HH} = 6.8$ Hz), 1.30-1.35 (br, m, 12H, $CH(CH_3)_2$), 1.47 (br, s, 12H, $\beta-CH_3$), 3.13 (hept, 4H, $CH(CH_3)_2$, $^3J_{HH} = 6.7$ Hz), 3.30-3.41 (br, m, 4H, $CH(CH_3)_2$), 4.75 (s, 2H, $\gamma-CH$), 6.43 (s, 2H, *GaH*), 7.01-7.07 (m, 8H, *Aryl-H*), 7.12-7.14 (m, 4H, *Aryl-H*). **$^{13}C\{^1H\}$ NMR** (75.5 MHz, C_6D_6) δ (ppm) = 23.9, 24.2, 24.3, 24.5, 24.9, 25.6, 27.4, 27.9, 28.4, 29.5 ($C(CH_3)_3$, $CH(CH_3)_2$), 96.0 ($\gamma-CH$), 123.8, 124.3, 124.7, 126.8, 142.6, 142.9, 145.0 (*Aryl-C*), 168.5 ($NCCH_3$). **IR** (ATR) ν (cm^{-1}) = 3058, 3013, 2960, 2924, 2865, 1891, 1852 (*GaH*), 1803 (*SbH*), 1584, 1548, 1519, 1437, 1392, 1313, 1252, 1175, 1098, 1055, 1016, 934, 858, 796, 758, 730, 669, 641, 598, 583, 521, 453, 437. **TGA** ($^{\circ}C$): 247.47.

2. Experimental spectra TGA

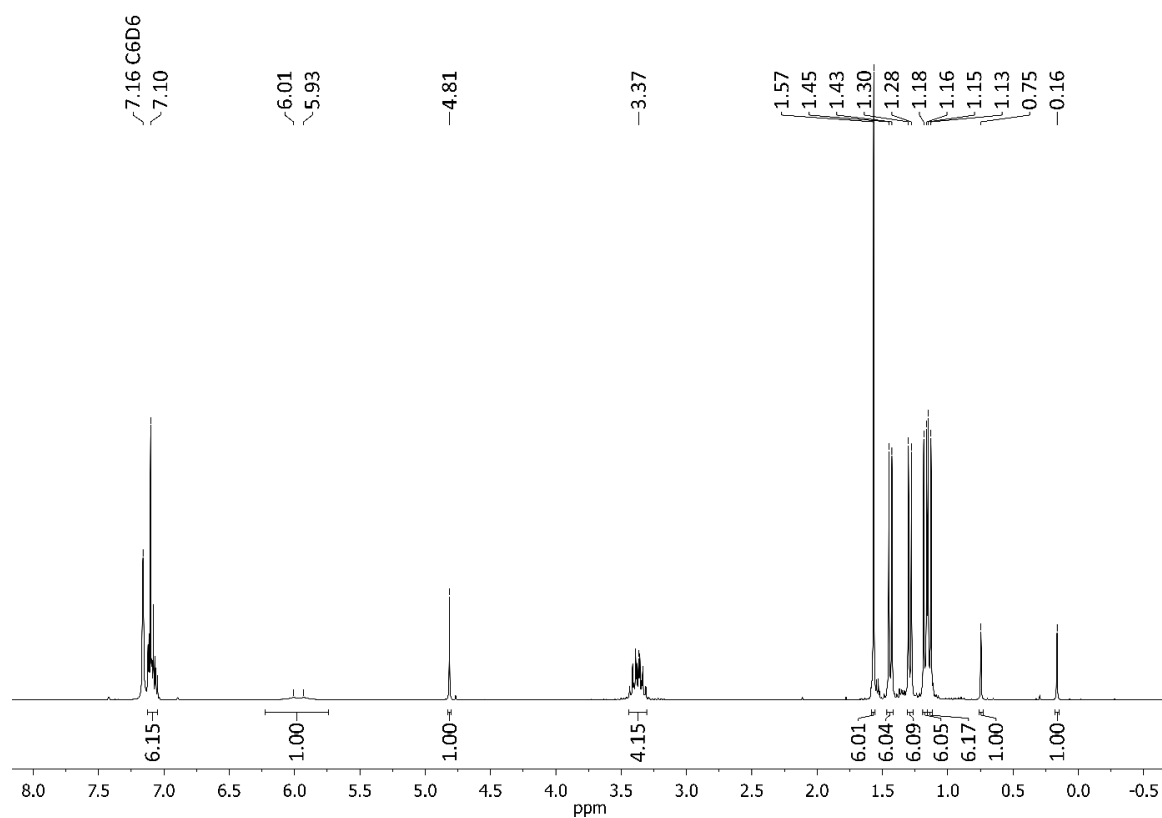


Figure S1. $^1\text{H-NMR}$ spectrum (300 MHz, C_6D_6 , 25 °C) of $(\text{Dipp}_2\text{NacNac})\text{GaH}(\text{PH}_2)$ (1).

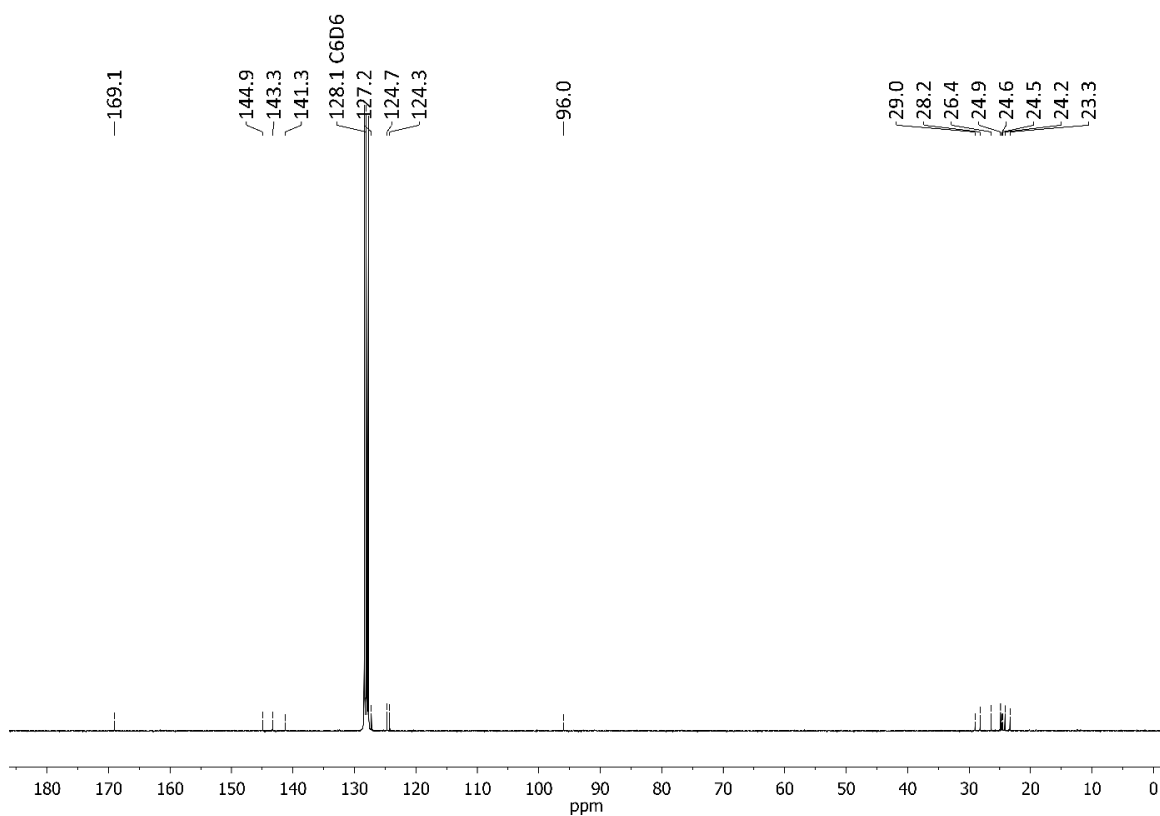


Figure S2. $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum (75.5 MHz, C_6D_6 , 25 °C) of $(\text{Dipp}_2\text{NacNac})\text{GaH}(\text{PH}_2)$ (1).

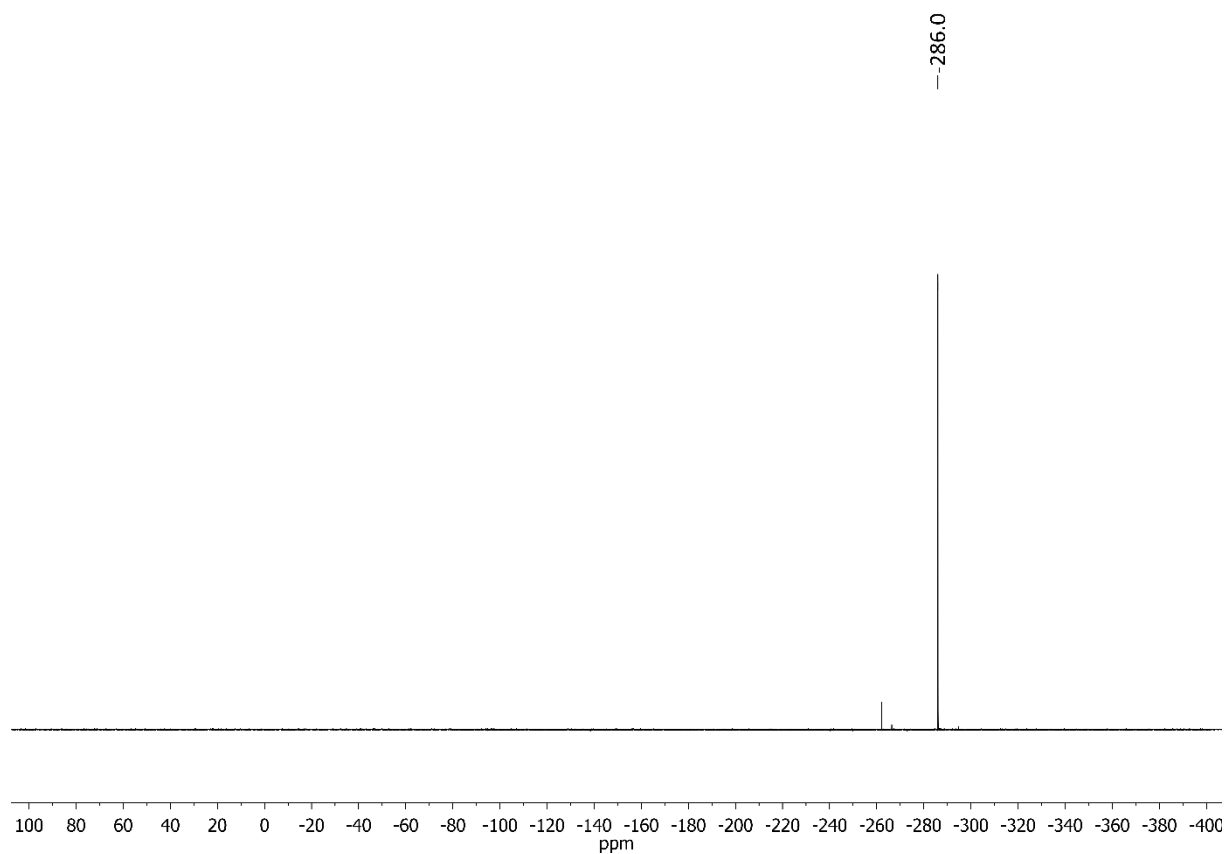


Figure S3. ^{31}P - $\{^1\text{H}\}$ -NMR spectrum (121.5 MHz, C_6D_6 , 25 °C) of $(\text{Dipp}_2\text{NacNac})\text{GaH}(\text{PH}_2)$ (**1**).

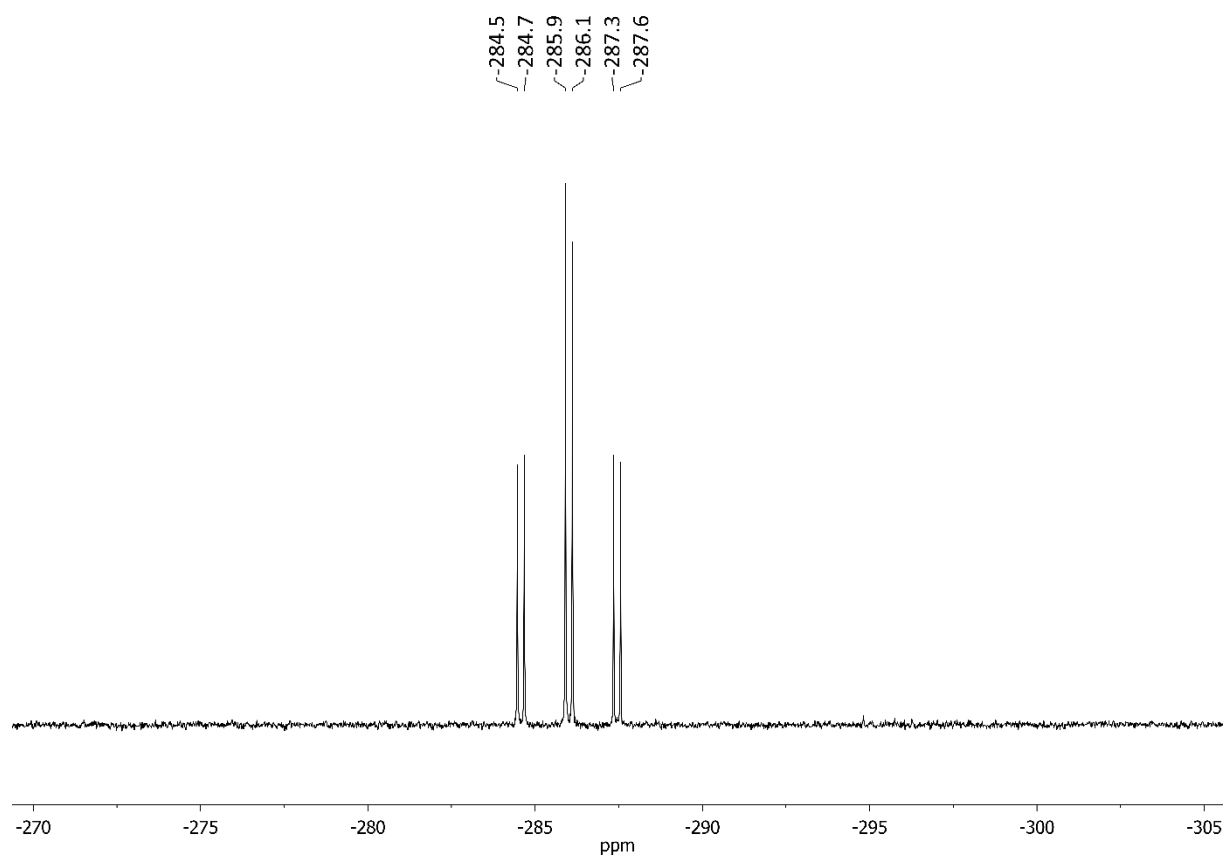


Figure S4. ^{31}P -NMR spectrum (121.5 MHz, C_6D_6 , 25 °C) of $(\text{Dipp}_2\text{NacNac})\text{GaH}(\text{PH}_2)$ (**1**).

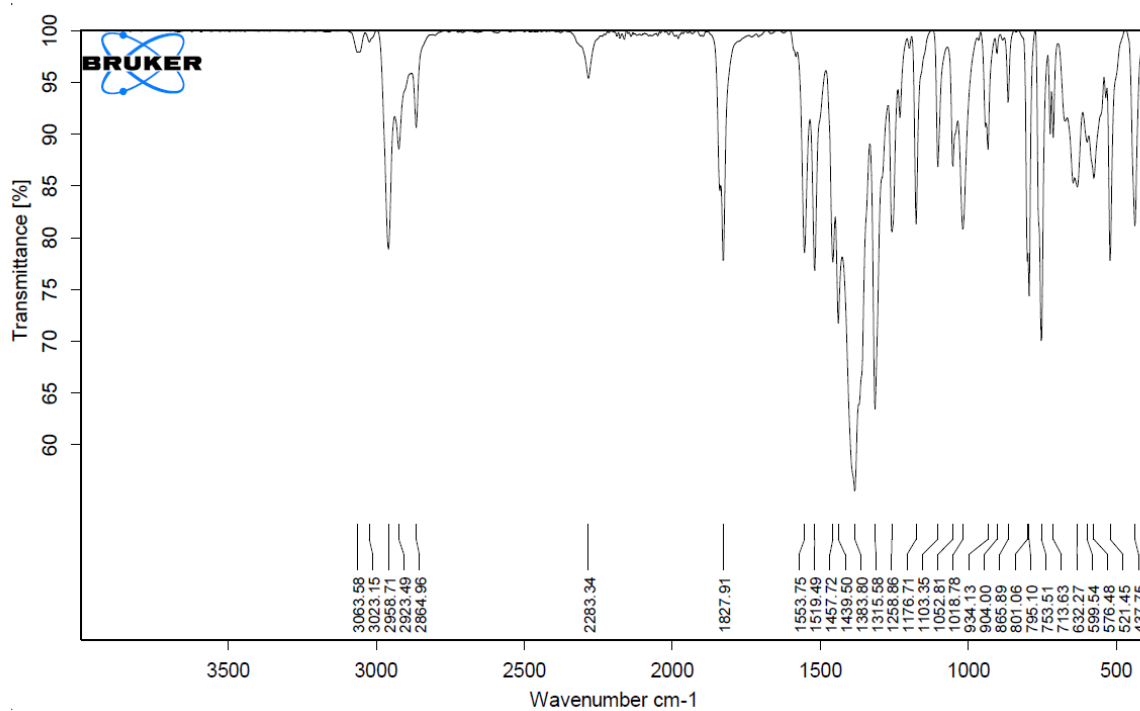


Figure S5. AT-IR spectrum of (Dipp₂NacNac)GaH(PH₂) (**1**).

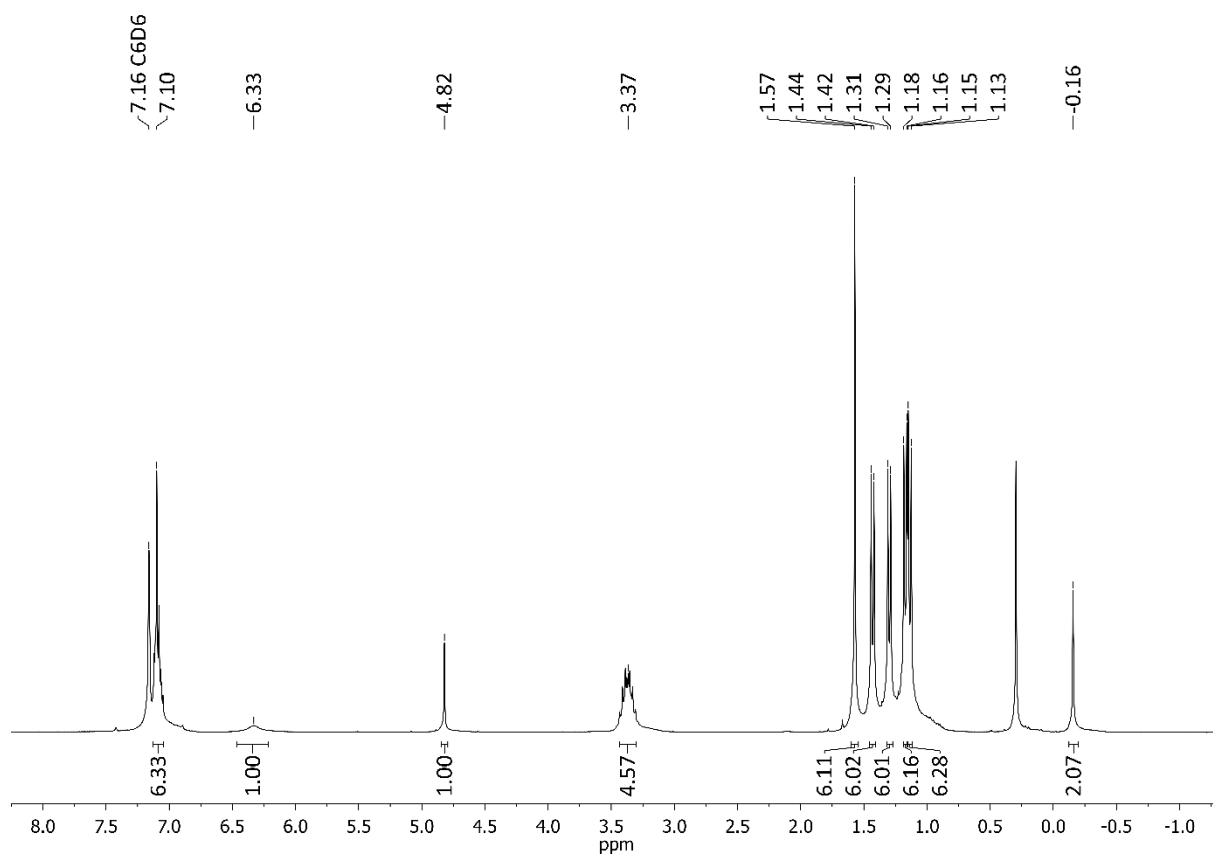


Figure S6. ¹H-NMR spectrum (300 MHz, C₆D₆, 25 °C) of (Dipp₂NacNac)GaH(AsH₂) (**2**).

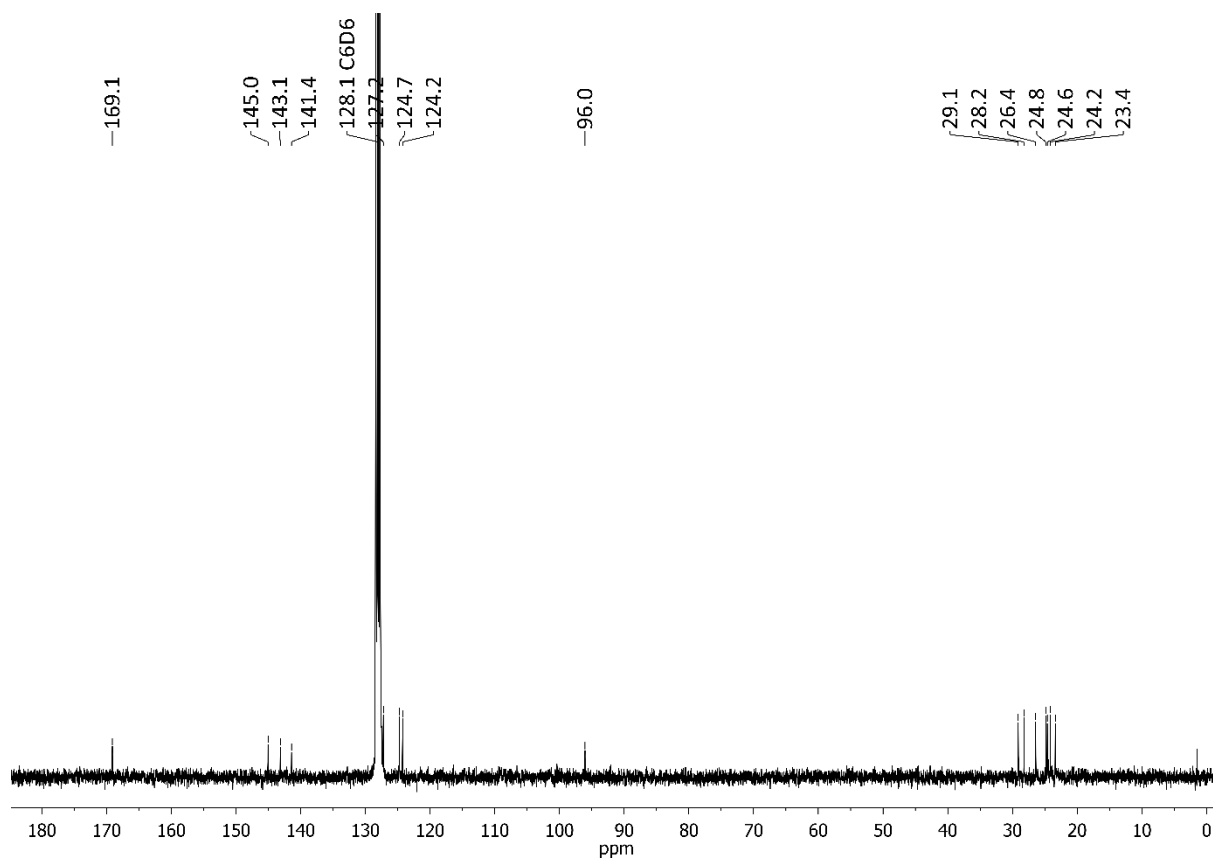


Figure S7. $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum (75.5 MHz, C_6D_6 , 25 °C) of $(\text{Dipp}_2\text{NacNac})\text{GaH}(\text{AsH}_2)$ (**2**).

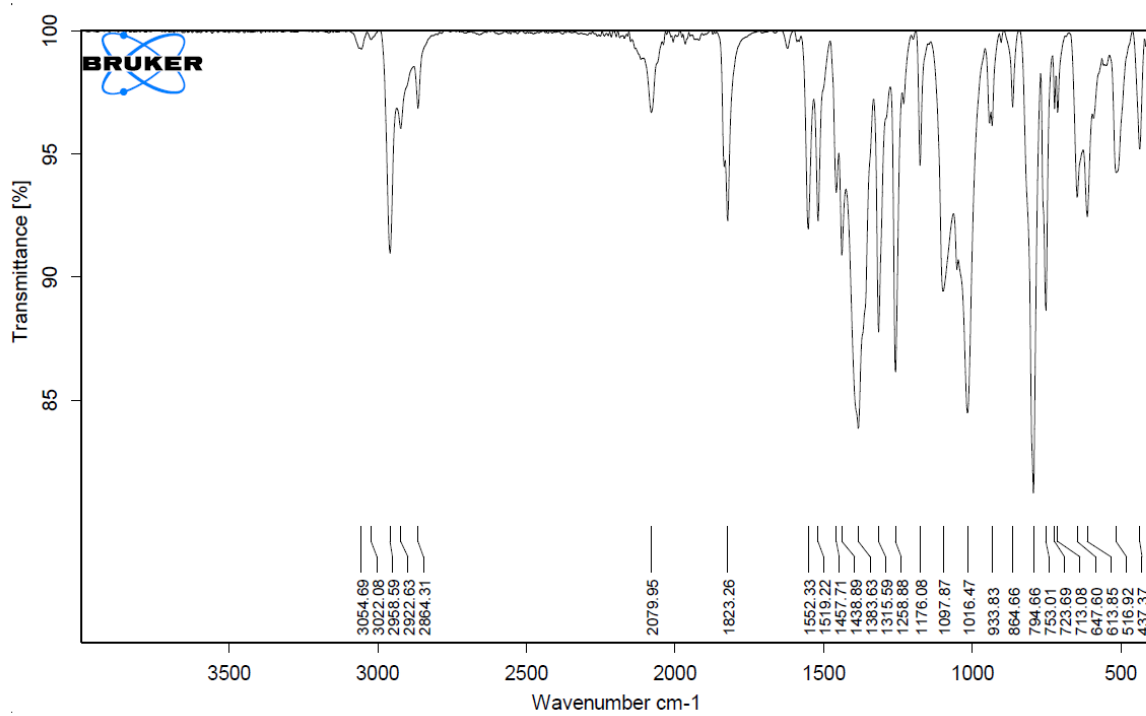


Figure S8. AT-IR spectrum of $(\text{Dipp}_2\text{NacNac})\text{GaH}(\text{AsH}_2)$ (**2**).

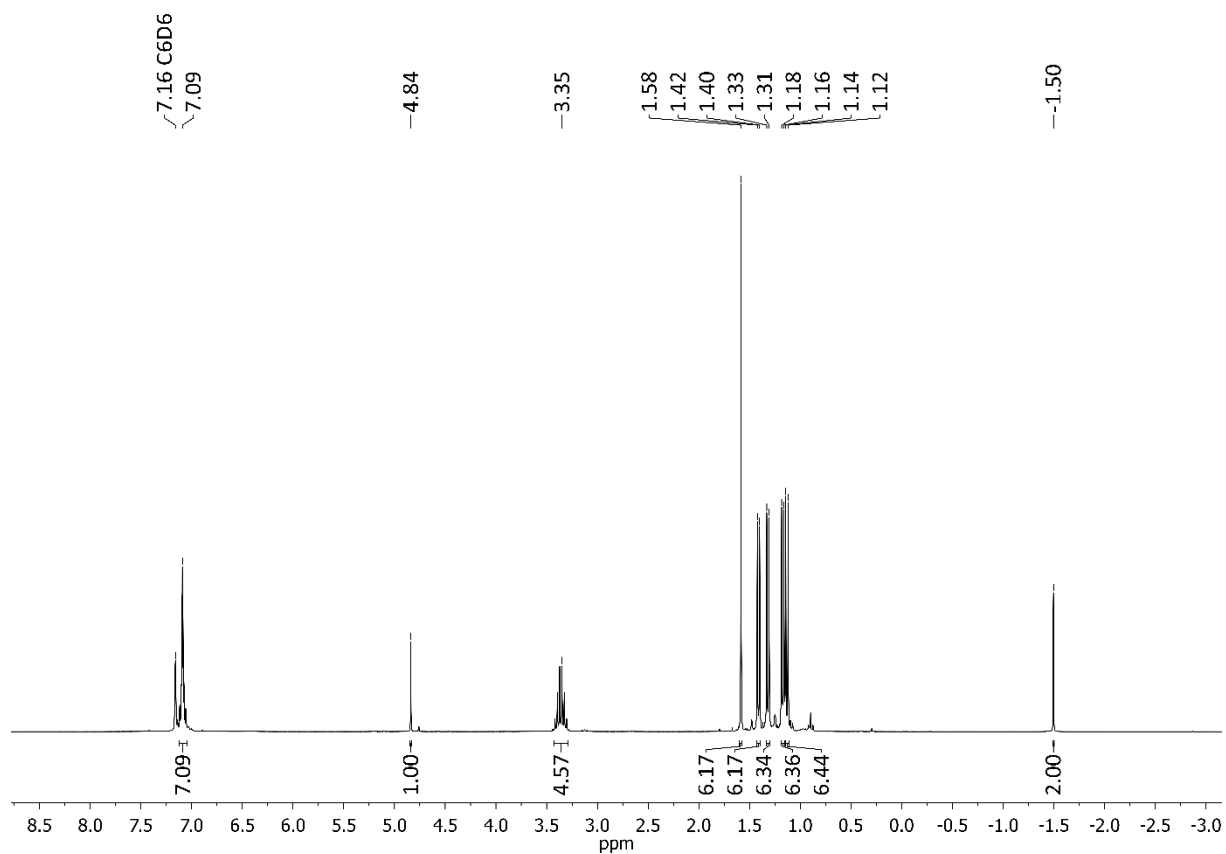


Figure S9. ^1H -NMR spectrum (300 MHz, C_6D_6 , 25 °C) of $(\text{Dipp}_2\text{NacNac})\text{GaH}(\text{SbH}_2)$ (**3**).

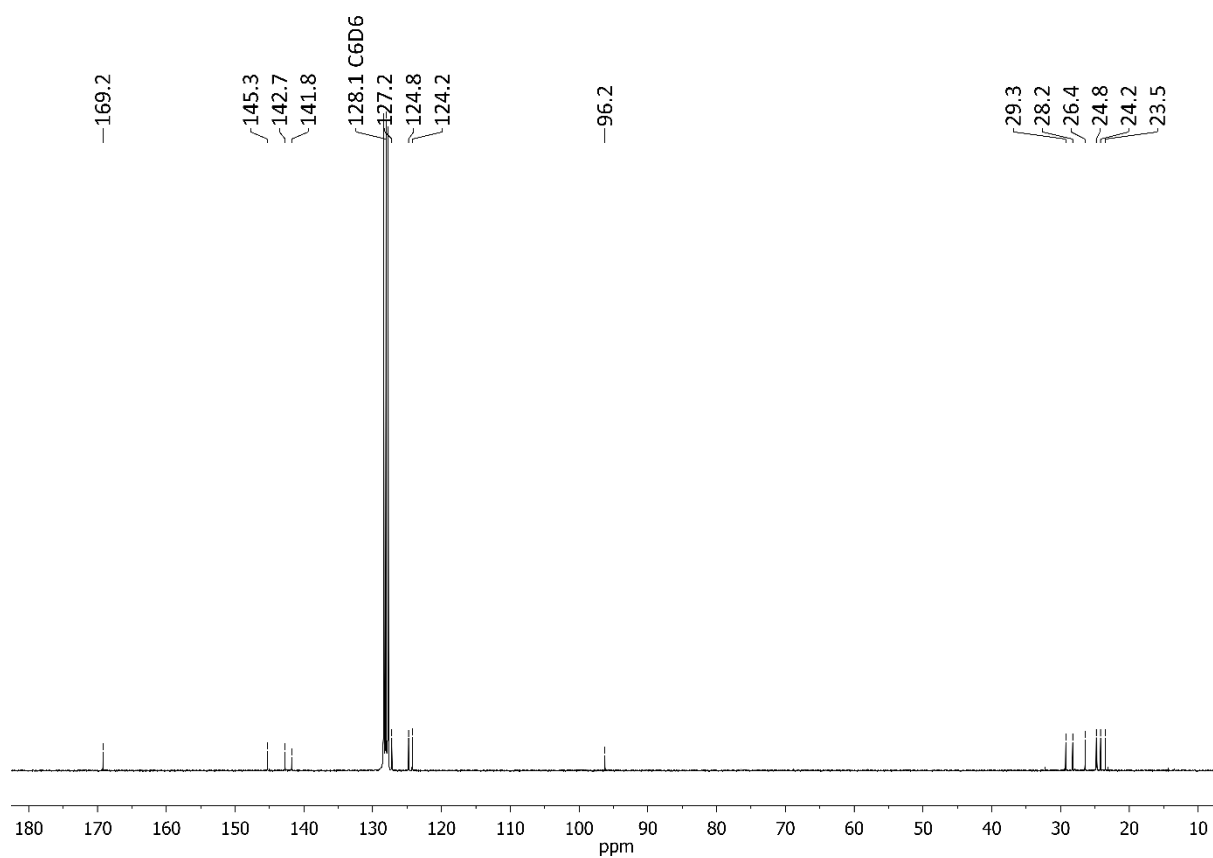


Figure S10. $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum (75.5 MHz, C_6D_6 , 25 °C) of $(\text{Dipp}_2\text{NacNac})\text{GaH}(\text{SbH}_2)$ (**3**)

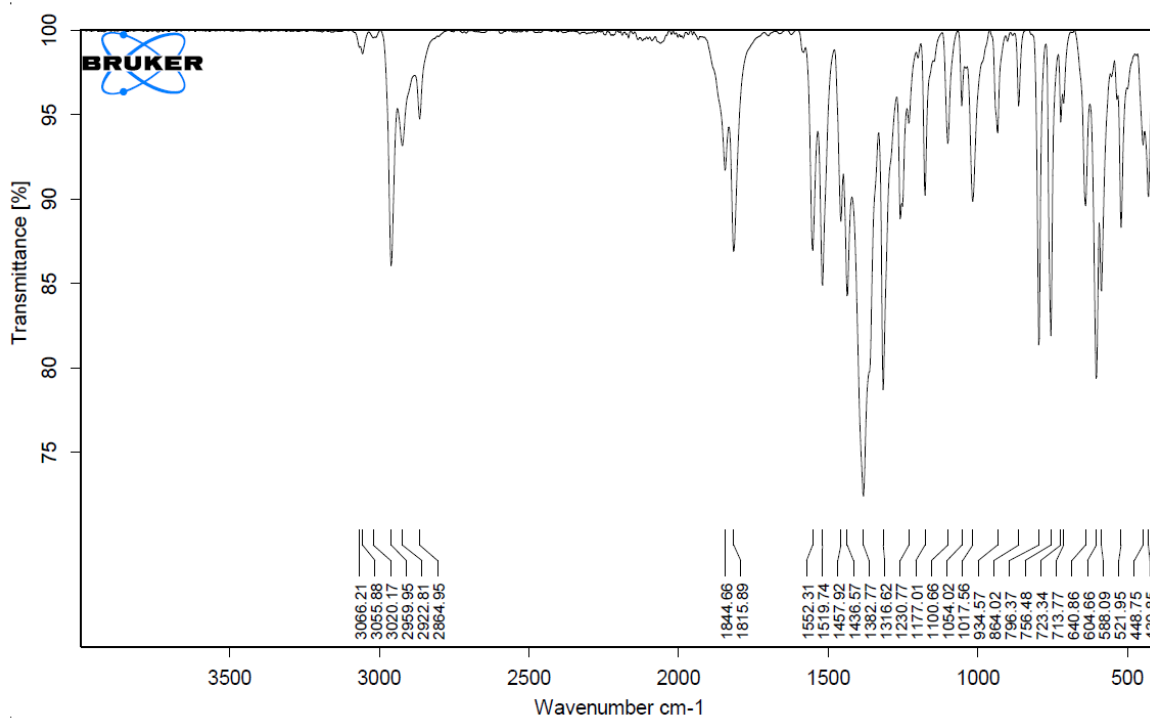


Figure S11. AT-IR spectrum of (Dipp₂NacNac)GaH(SbH₂) (**3**).

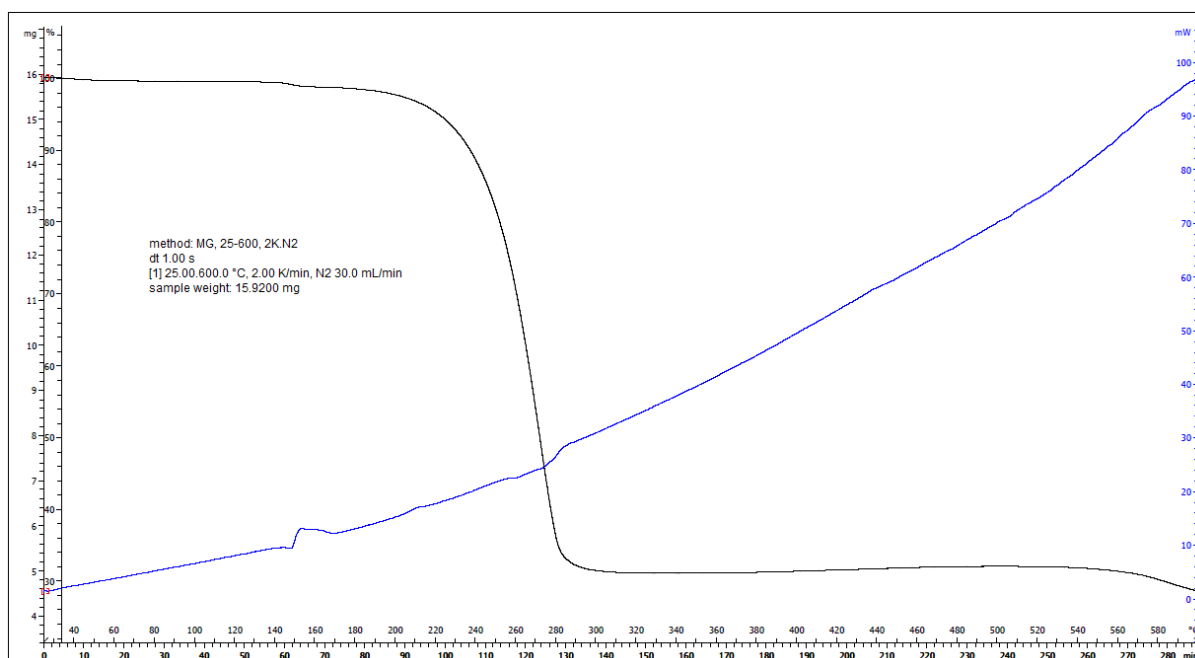


Figure S12. DSC-TGA of (Dipp₂NacNac)GaH(SbH₂) (**3**). Black: TGA; blue: DSC.

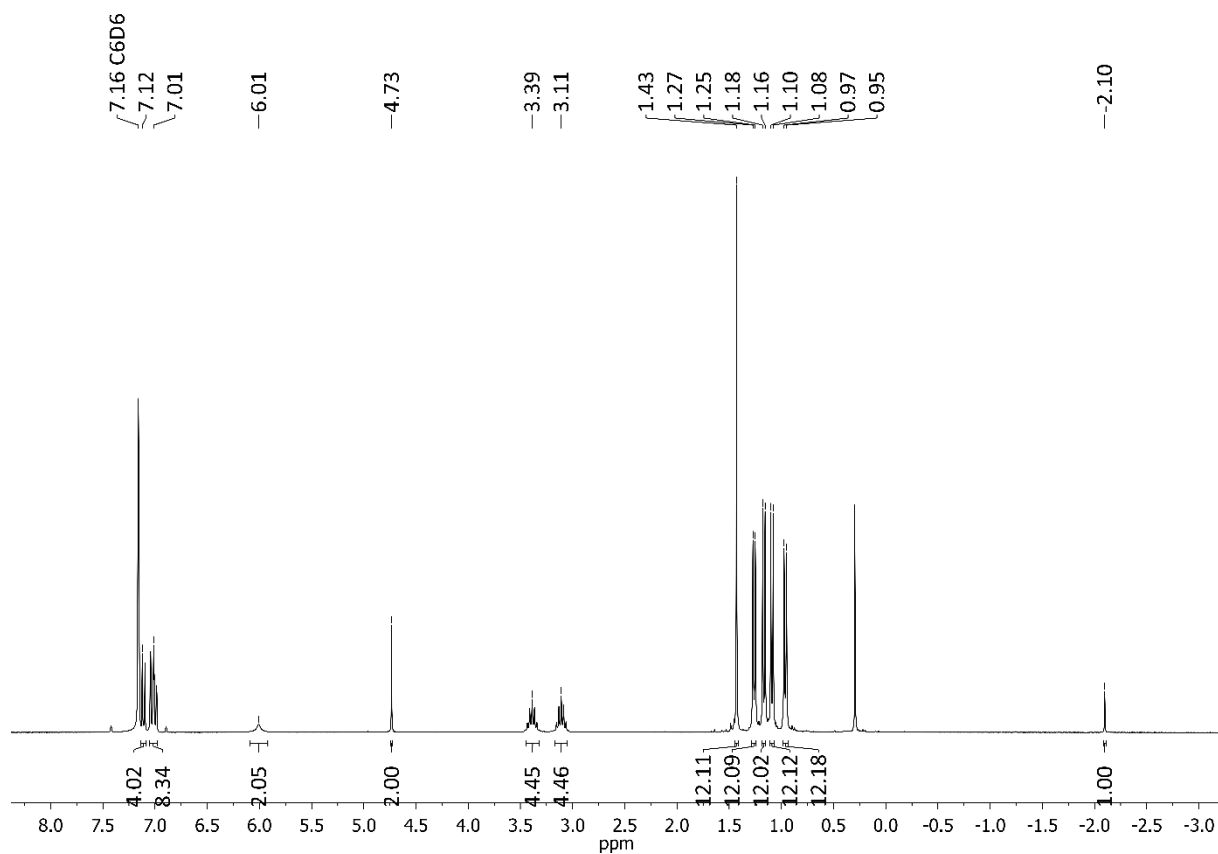


Figure S13. ^1H -NMR spectrum (300 MHz, C_6D_6 , 25 °C) of $[(\text{Dipp}_2\text{NacNac})\text{GaH}]_2(\text{AsH})$ (**4**).

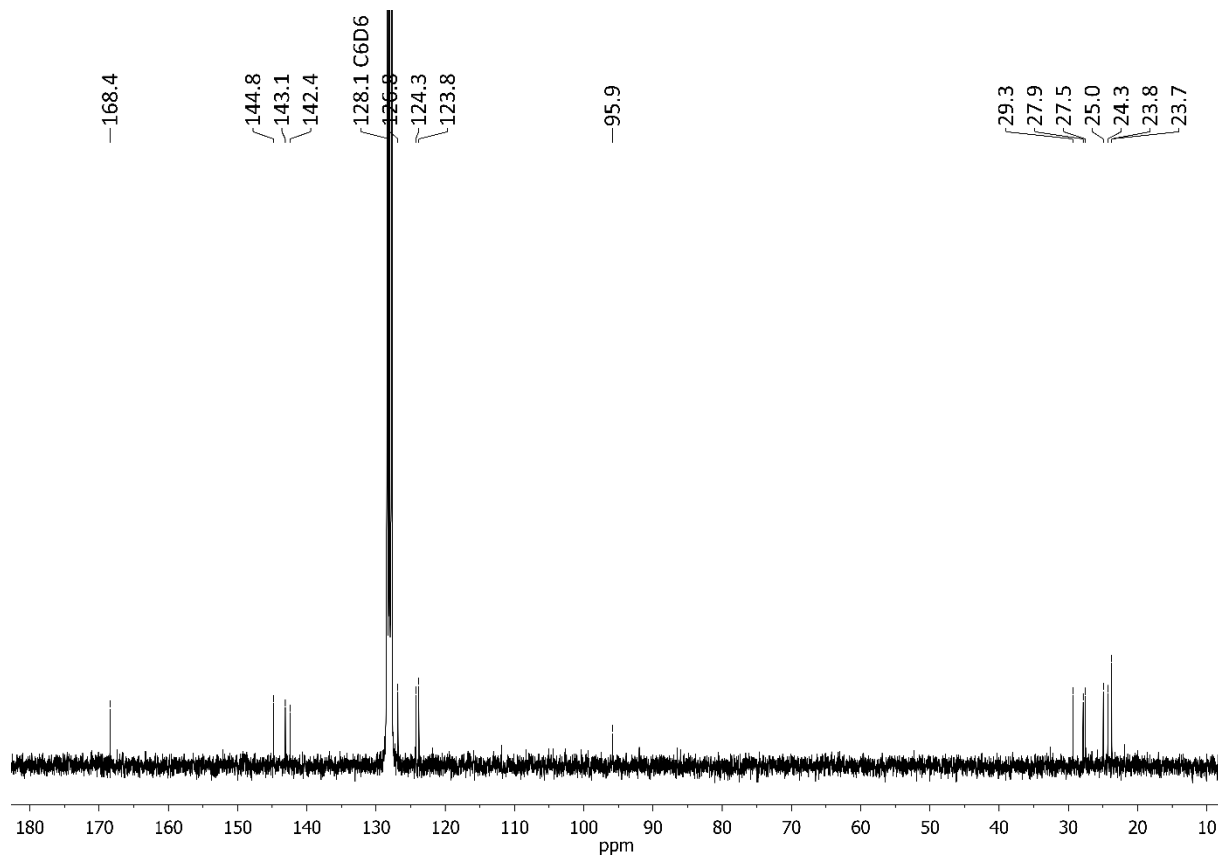


Figure S14. $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum (75.5 MHz, C_6D_6 , 25 °C) of $[(\text{Dipp}_2\text{NacNac})\text{GaH}]_2(\text{AsH})$ (**4**).

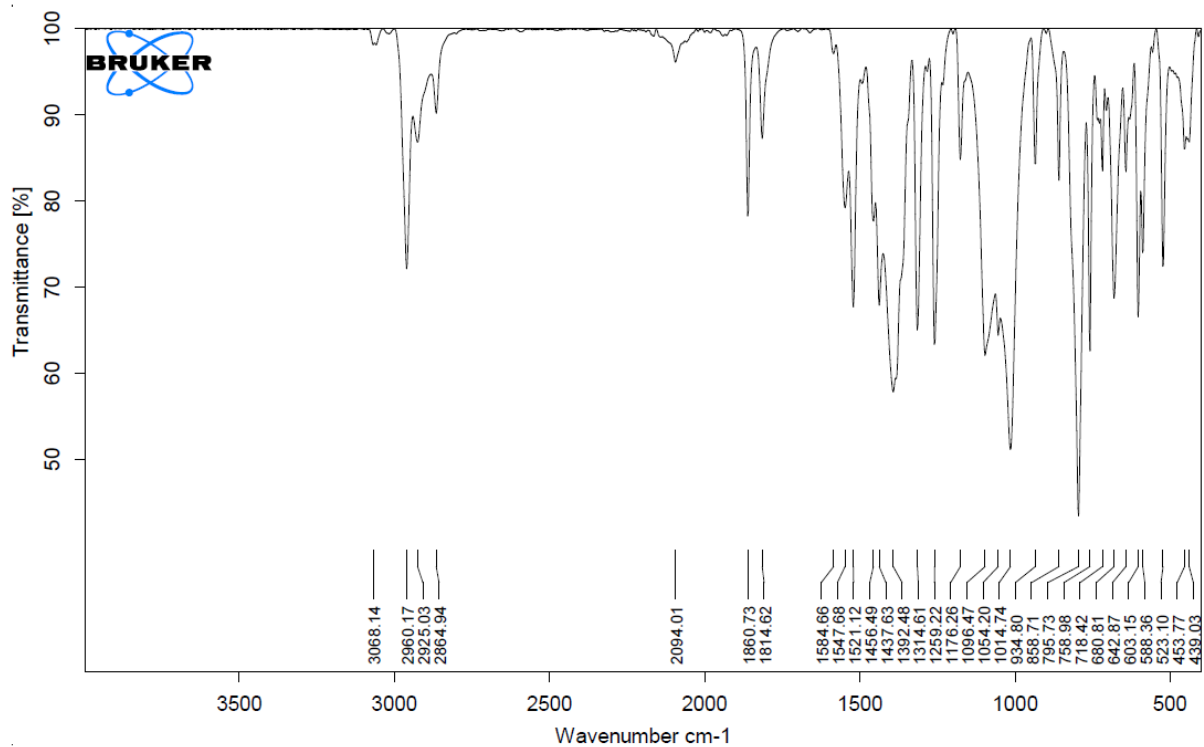


Figure S15. AT-IR spectrum of [(Dipp₂NacNac)GaH]₂AsH (4).

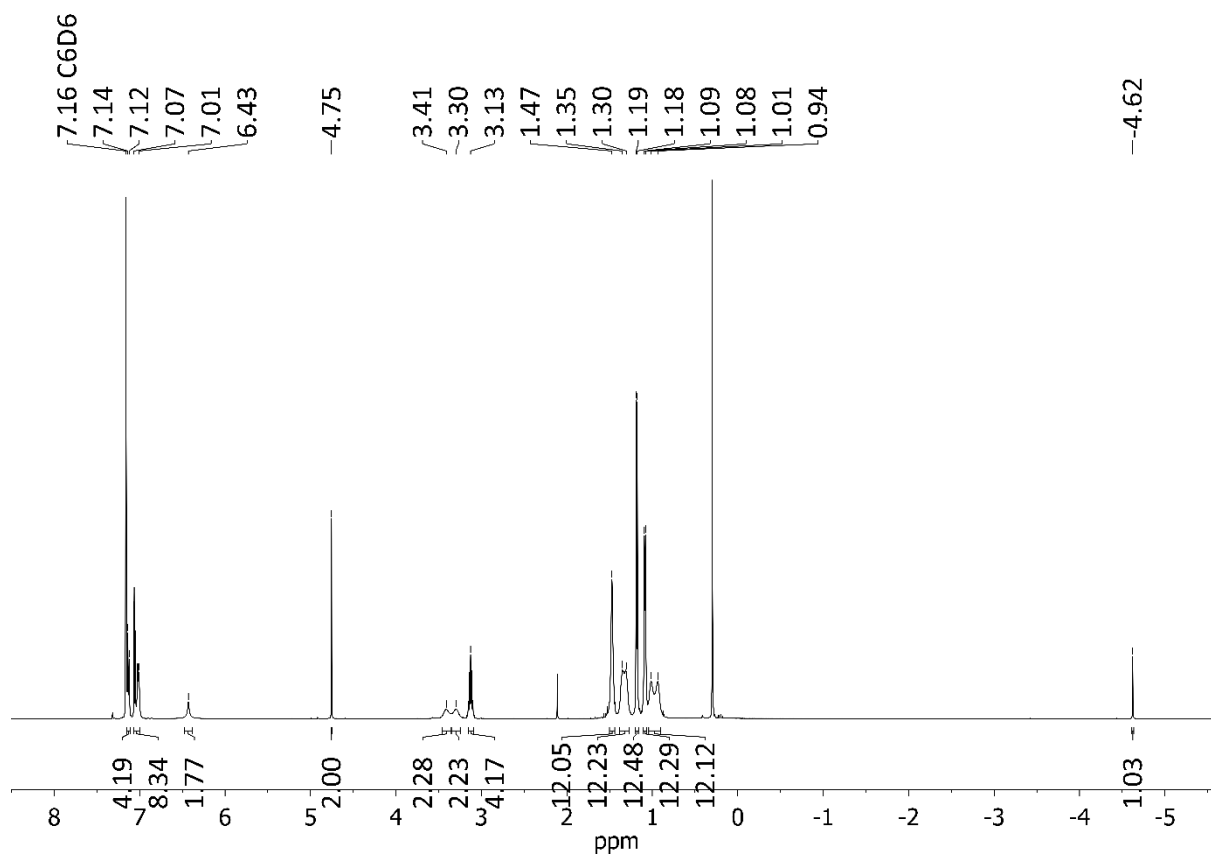


Figure S16. ¹H-NMR spectrum (300 MHz, C₆D₆, 25 °C) of [(Dipp₂NacNac)GaH]₂(SbH) (5).

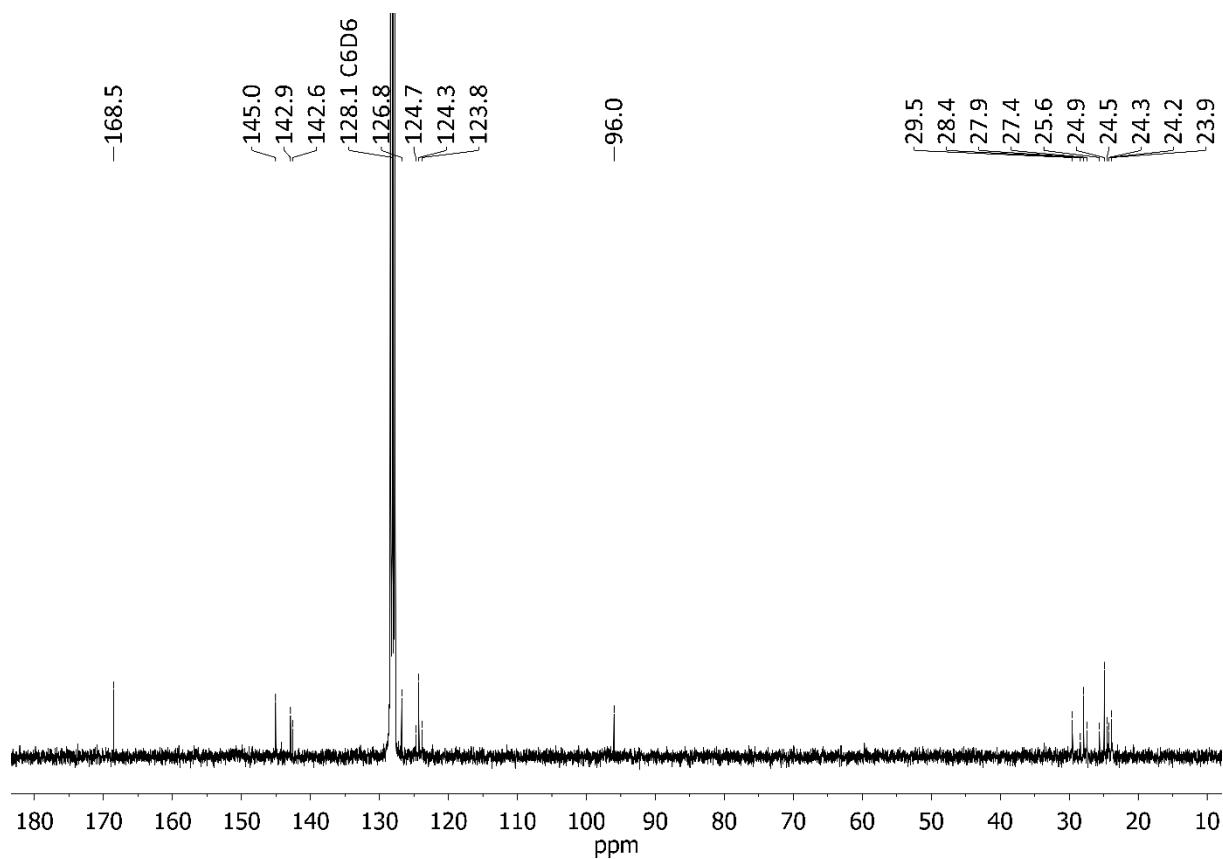


Figure S17. ^{13}C - $\{^1\text{H}\}$ -NMR spectrum (75.5 MHz, C_6D_6 , 25 °C) of $[(\text{Dipp}_2\text{NacNac})\text{GaH}]_2(\text{SbH})$ (**5**).

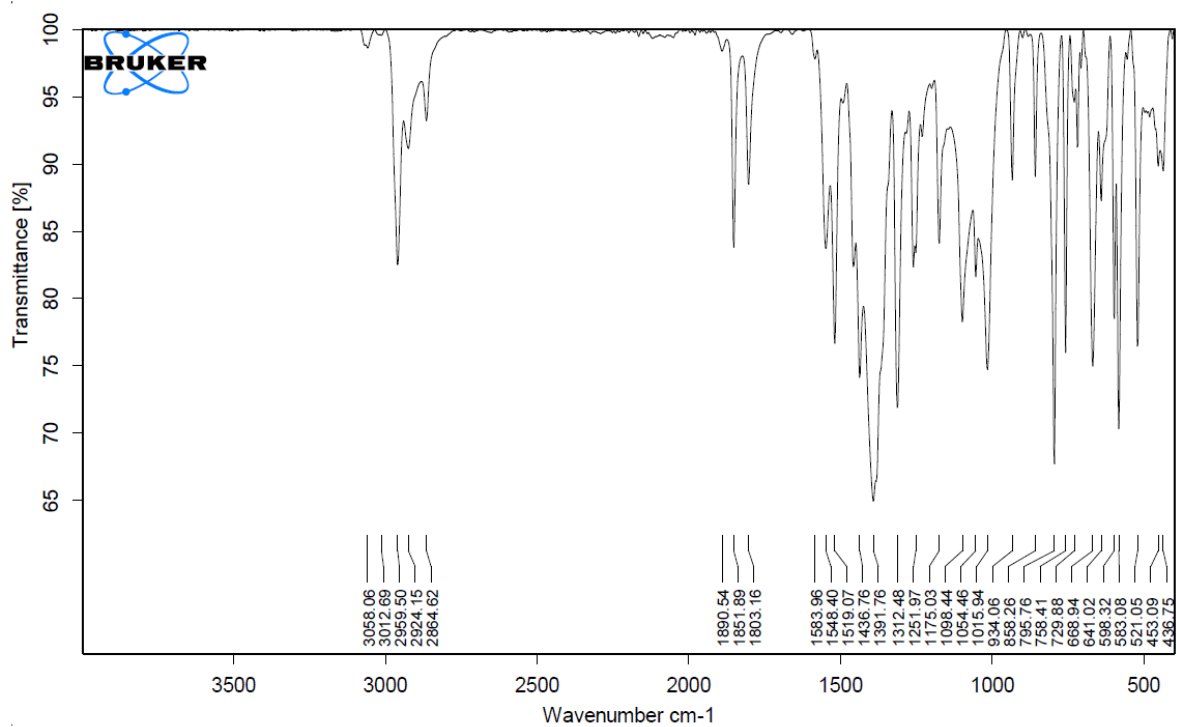


Figure S18. AT-IR spectrum of $[(\text{Dipp}_2\text{NacNac})\text{GaH}]_2(\text{SbH})$ (**5**).

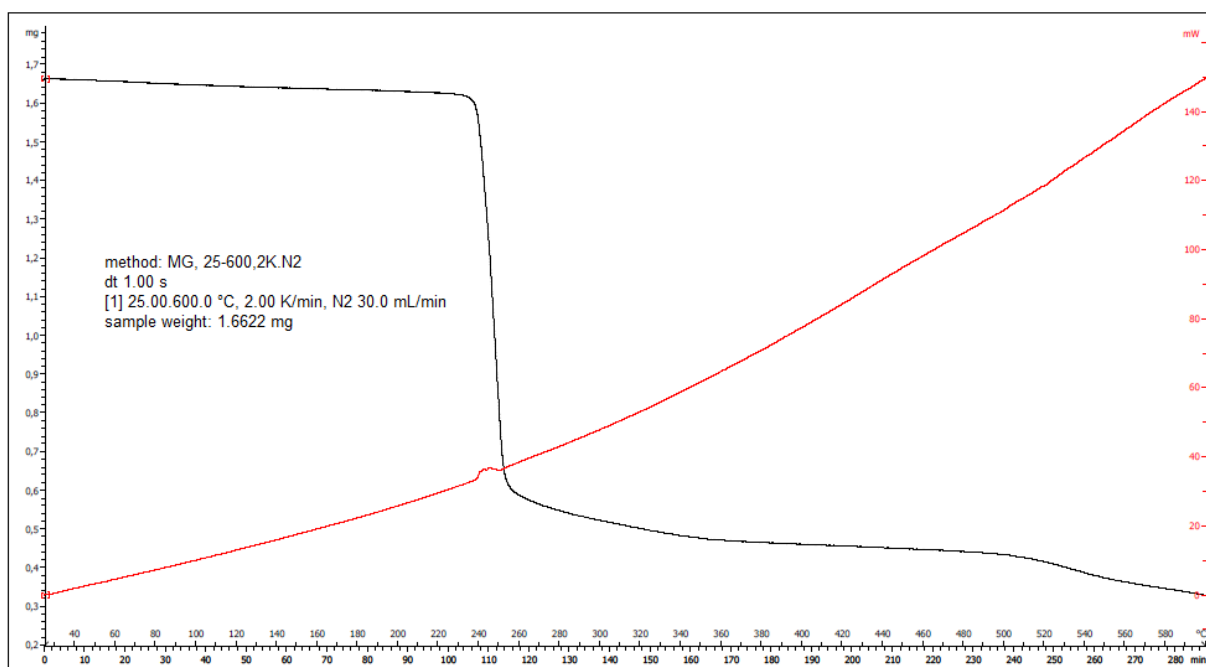


Figure S19. DSC-TGA of $[(\text{Dipp}_2\text{NacNac})\text{GaH}]_2(\text{SbH})$ (**5**). Black: TGA; red: DSC.

3. Crystallographic details

Refinement of 2 and 3: both crystal structures exhibit a mild positional disorder of As and Sb atoms respectively, which is justified by different positions of the attached hydrogen atoms making an angle between the disordered $M-H$ ($M = \text{As}, \text{Sb}$) species close to 90° and which leads to essentially identical configuration of the molecule. The distance between the disordered atoms equals 0.387(14) and 0.496(12) Å (two symmetry independent molecules in the As compound) or 0.116(2) Å (the Sb compound). It should be noted that in case of compound **1** the phosphorus atoms were found to describe the corresponding electron density peaks not fully satisfactorily even if various disorder models were applied. However, the other analytical techniques (NMR, IR, elemental analyses) show strong evidence of the high purity of the compound. So far the best model was obtained by using a single phosphorus atom at the highest density peak. Further investigation and a better model will be reported elsewhere.

Refinement of 4 and 5: Both compounds crystallize in the space group $P1$ forming pseudo-merohedrally twinned crystals so that the apparent space group is $C2$. The compounds contain two symmetry independent molecules in the unit cell. The molecules in each case contain a non-crystallographic inversion centre, which results in the disorder of the Ga–Sb–Ga and Ga–As–Ga parts (in case of the Sb compound the disorder in one of the two symmetry independent molecules is resolved via twin refinement). Interestingly, although the Checkcif algorithm suggested a strong evidence of pseudosymmetry and a tentative space group $C2/c$, a corresponding refinement led to very poor models and much higher residual electron density. Although a 2-fold rotation, an inversion center and a c -glide plane correspond very well to the atom coordinates, the different occupancies of the disordered As/Sb and Ga atoms destroy the corresponding symmetry elements. Inspection of the reciprocal space clearly shows that there are very strong reflections present which are against the c -glide plane extinction condition. It should be noted that the structure model of compound **4** contains four residual peaks of a yet unknown origin with a magnitude of 1.08...1.44 e/Å at the distances of 2.26...2.40 Å from Ga2A, Ga2B, Ga4A, Ga4B and lying approximately within the planes of Ga–As–Ga, which could not be unambiguously assigned to any plausible atom (a few attempts led to an unstable refinement with unphysical isotropic displacement parameters). Interestingly, a compound **5** could also be obtained either with similar peaks or without them depending on yet not identified conditions. More details will be reported elsewhere.

Table S1: Crystallographic data of compounds **1-3**.

| | 1 | 2 | 3 |
|----------------------------|--|---|---|
| Empirical formula | C ₂₉ H ₄₄ GaN ₂ P | C ₂₉ H ₄₄ GaN ₂ As | C ₂₉ H ₄₄ GaN ₂ Sb |
| M [g·mol ⁻¹] | 521.35 | 565.30 | 612.13 |
| Crystal colour and habitus | colourless block | colourless plate | colourless block |
| Crystal size [mm] | 0.490 x 0.210 x 0.204 | 0.454 x 0.219 x 0.064 | 0.426 x 0.407 x 0.346 |
| T [K] | 100 | 100 | 100 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group (No.) | $P2_1/c$ (14) | $P2_1/c$ (14) | $P2_1/c$ (14) |
| a [Å] | 18.1045(11) | 18.1546(10) | 17.1395(9) |
| b [Å] | 9.6018(6) | 9.6556(5) | 10.0131(5) |
| c [Å] | 33.3947(19) | 33.4172(19) | 18.1242(9) |
| β [°] | 90.8880(10) | 91.133(2) | 105.326(2) |
| V [Å ³] | 5804.5(6) | 5856.7(6) | 2999.9(3) |

| | | | |
|--|-----------------|-----------------|----------------|
| <i>Z</i> | 8 | 8 | 4 |
| <i>D</i> _{calc} [g•cm ⁻³] | 1.193 | 1.282 | 1.355 |
| μ [mm ⁻¹] | 1.021 | 2.079 | 1.816 |
| F(000) | 2224.0 | 2366.3 | 1256.0 |
| 2 θ range for data collection [°] | 4.414 to 59.328 | 4.392 to 61.184 | 4.66 to 59.462 |
| Reflections collected | 140725 | 156482 | 96904 |
| Independent reflections | 16395 | 17991 | 8511 |
| <i>R</i> _{int} , <i>R</i> _{σ} | 0.0386, 0.0236 | 0.0396, 0.0231 | 0.0329, 0.0168 |
| Data/restraints/parameters | 16395/6/640 | 17991/12/664 | 8511/1/329 |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>), all data] | 0.0389, 0.0526 | 0.0300, 0.0420 | 0.0229, 0.0300 |
| <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>), all data] | 0,0945, 0.1008 | 0,0617, 0.0653 | 0.0516, 0.0540 |
| <i>S</i> (all data) | 1.049 | 1.044 | 1.037 |
| $\Delta\rho$ _{final} (max/min) [e•Å ⁻³] | 1.43/-0.67 | 0.47/-0.34 | 0.48/-0.39 |

Table S2: Crystallographic data of compounds **4** and **5**.

| | 4 | 5 |
|--|--|--|
| Empirical formula | C ₅₈ H ₈₅ AsGa ₂ N ₄ | C ₅₈ H ₈₅ SbGa ₂ N ₄ |
| <i>M</i> [g•mol ⁻¹] | 1052.65 | 1099.48 |
| Crystal colour and habitus | colourless block | yellow block |
| Crystal size [mm] | 0.292 × 0.213 × 0.116 | 0.215 × 0.212 × 0.136 |
| <i>T</i> [K] | 100 | 100 |
| Crystal system (No.) | <i>P</i> 1 (1) | <i>P</i> 1 (1) |
| Space group | Triclinic | Triclinic |
| <i>a</i> [Å] | 14.2902(12) | 14.3990(7) |
| <i>b</i> [Å] | 14.2980(12) | 14.4137(7) |
| <i>c</i> [Å] | 14.8863(12) | 14.9394(7) |
| α [°] | 85.241(2) | 85.495(2) |
| β [°] | 85.225(2) | 85.477(2) |
| γ [°] | 64.920(2) | 64.209(2) |
| <i>V</i> [Å ³] | 2741.4(4) | 2779.6(2) |
| <i>Z</i> | 2 | 2 |
| <i>D</i> _{calc} [g•cm ⁻³] | 1.275 | 1.314 |
| μ [mm ⁻¹] | 1.621 | 1.484 |
| F(000) | 1112.0 | 1148.0 |
| 2 θ range for data collection [°] | 4.070 to 63.166 | 4.522 to 63.182 |
| Reflections collected | 183469 | 96707 |
| Independent reflections | 36653 | 35068 |
| <i>R</i> _{int} , <i>R</i> _{σ} | 0.0312, 0.0249 | 0.0351, 0.0515 |
| Data/restraints/parameters | 36653/187/1295 | 35068/105/1278 |
| <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>), all data] | 0.0247, 0.0276 | 0.0316, 0.0400 |
| <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>), all data] | 0.0591, 0.0606 | 0.0562, 0.0588 |
| <i>S</i> (all data) | 1.017 | 0.997 |
| $\Delta\rho$ _{final} (max/min) [e•Å ⁻³] | 1.45/-0.32 | 0.56/-0.58 |

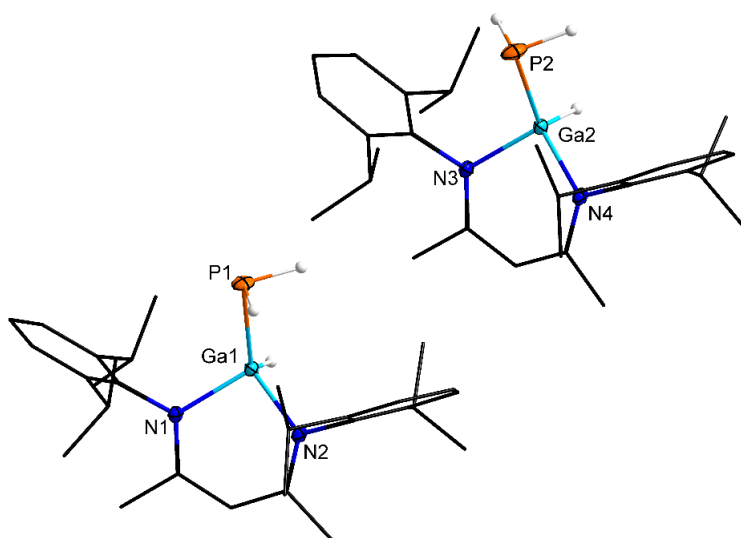


Figure S20: Both independent molecules in the unit cell of compound **1**. All hydrogen atoms on carbon are omitted for clarity. Carbon atoms are shown in the *wires and stick* model. Thermal ellipsoids represent a 50% probability level.

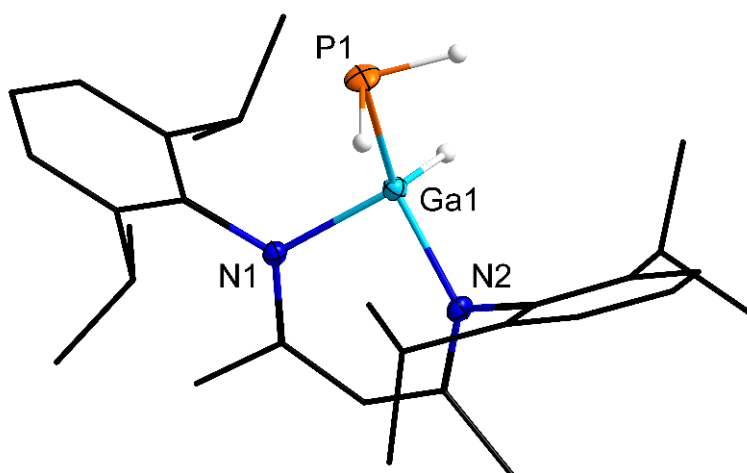


Figure S21: Molecular structure of **1**. Disordered parts are omitted for clarity.

Table S3: Bond length (Å) for **1**.

| | | | | | | |
|-----|-----|------------|--|-----|-----|----------|
| Ga1 | N2 | 1.9541(14) | | C42 | C43 | 1.510(2) |
| Ga1 | N1 | 1.9577(14) | | C44 | C45 | 1.409(2) |
| Ga1 | P1 | 2.3442(5) | | C45 | N4 | 1.326(2) |
| Ga2 | N3 | 1.9542(14) | | C45 | C46 | 1.511(2) |
| Ga2 | N4 | 1.9548(14) | | C47 | C48 | 1.404(2) |
| Ga2 | P2 | 2.3387(5) | | C47 | C52 | 1.411(2) |
| C1 | C2 | 1.532(3) | | C47 | N4 | 1.447(2) |
| C2 | C5 | 1.516(2) | | C48 | C49 | 1.397(2) |
| C2 | C3 | 1.535(3) | | C48 | C53 | 1.522(3) |
| C20 | C21 | 1.375(3) | | C49 | C50 | 1.378(3) |

| | | | | | | |
|-----|-----|----------|--|-----|-----|----------|
| C20 | C19 | 1.401(2) | | C50 | C51 | 1.380(3) |
| C21 | C22 | 1.379(3) | | C51 | C52 | 1.397(2) |
| C22 | C23 | 1.395(2) | | C52 | C56 | 1.516(3) |
| C23 | C18 | 1.405(2) | | C53 | C55 | 1.531(3) |
| C23 | C27 | 1.516(3) | | C53 | C54 | 1.531(3) |
| C24 | C19 | 1.514(3) | | C56 | C58 | 1.523(3) |
| C24 | C25 | 1.527(3) | | C56 | C57 | 1.526(3) |
| C24 | C26 | 1.531(3) | | N1 | C13 | 1.333(2) |
| C27 | C28 | 1.524(4) | | N1 | C4 | 1.438(2) |
| C27 | C29 | 1.528(3) | | N2 | C16 | 1.329(2) |
| C30 | C31 | 1.533(3) | | N2 | C18 | 1.445(2) |
| C31 | C34 | 1.519(2) | | C4 | C5 | 1.406(2) |
| C31 | C32 | 1.536(2) | | C4 | C9 | 1.409(2) |
| C33 | C34 | 1.408(2) | | C5 | C6 | 1.399(2) |
| C33 | C38 | 1.412(2) | | C6 | C7 | 1.382(3) |
| C33 | N3 | 1.441(2) | | C7 | C8 | 1.385(3) |
| C34 | C35 | 1.399(2) | | C8 | C9 | 1.395(2) |
| C35 | C36 | 1.382(3) | | C9 | C10 | 1.517(2) |
| C36 | C37 | 1.383(3) | | C10 | C11 | 1.532(3) |
| C37 | C38 | 1.393(2) | | C10 | C12 | 1.534(3) |
| C38 | C39 | 1.516(2) | | C13 | C15 | 1.399(2) |
| C39 | C40 | 1.530(3) | | C13 | C14 | 1.511(2) |
| C39 | C41 | 1.537(3) | | C15 | C16 | 1.404(2) |
| C42 | N3 | 1.329(2) | | C16 | C17 | 1.508(2) |
| C42 | C44 | 1.402(2) | | C18 | C19 | 1.406(2) |

Table S4: Bond angles (°) for **1**.

| | | | | | | | | |
|-----|-----|-----|------------|--|-----|-----|-----|------------|
| N2 | Ga1 | N1 | 95.20(6) | | C50 | C49 | C48 | 121.26(18) |
| N2 | Ga1 | P1 | 114.13(4) | | C49 | C50 | C51 | 119.95(17) |
| N1 | Ga1 | P1 | 111.07(4) | | C50 | C51 | C52 | 121.41(18) |
| N3 | Ga2 | N4 | 95.79(6) | | C51 | C52 | C47 | 117.94(17) |
| N3 | Ga2 | P2 | 107.35(4) | | C51 | C52 | C56 | 119.54(17) |
| N4 | Ga2 | P2 | 113.56(4) | | C47 | C52 | C56 | 122.49(15) |
| C5 | C2 | C1 | 110.14(15) | | C48 | C53 | C55 | 110.77(18) |
| C5 | C2 | C3 | 112.35(16) | | C48 | C53 | C54 | 112.01(17) |
| C1 | C2 | C3 | 110.58(17) | | C55 | C53 | C54 | 109.61(17) |
| C21 | C20 | C19 | 121.27(19) | | C52 | C56 | C58 | 112.69(17) |
| C20 | C21 | C22 | 120.00(17) | | C52 | C56 | C57 | 110.60(16) |
| C21 | C22 | C23 | 121.44(19) | | C58 | C56 | C57 | 109.81(18) |
| C22 | C23 | C18 | 117.98(18) | | C13 | N1 | C4 | 120.92(13) |
| C22 | C23 | C27 | 120.11(17) | | C13 | N1 | Ga1 | 118.38(11) |
| C18 | C23 | C27 | 121.91(16) | | C4 | N1 | Ga1 | 120.09(10) |
| C19 | C24 | C25 | 112.40(18) | | C16 | N2 | C18 | 120.94(14) |
| C19 | C24 | C26 | 110.46(18) | | C16 | N2 | Ga1 | 118.52(11) |
| C25 | C24 | C26 | 110.15(19) | | C18 | N2 | Ga1 | 119.91(11) |
| C23 | C27 | C28 | 111.6(2) | | C42 | N3 | C33 | 122.32(14) |
| C23 | C27 | C29 | 112.69(19) | | C42 | N3 | Ga2 | 120.31(11) |
| C28 | C27 | C29 | 109.46(19) | | C33 | N3 | Ga2 | 117.36(10) |
| C34 | C31 | C30 | 111.65(15) | | C45 | N4 | C47 | 122.04(14) |
| C34 | C31 | C32 | 110.66(15) | | C45 | N4 | Ga2 | 120.52(11) |
| C30 | C31 | C32 | 110.70(16) | | C47 | N4 | Ga2 | 116.97(11) |
| C34 | C33 | C38 | 120.69(15) | | C5 | C4 | C9 | 121.03(15) |
| C34 | C33 | N3 | 119.39(15) | | C5 | C4 | N1 | 119.51(15) |
| C38 | C33 | N3 | 119.69(15) | | C9 | C4 | N1 | 119.42(14) |
| C35 | C34 | C33 | 118.68(16) | | C6 | C5 | C4 | 118.39(16) |
| C35 | C34 | C31 | 118.89(16) | | C6 | C5 | C2 | 119.27(15) |
| C33 | C34 | C31 | 122.41(15) | | C4 | C5 | C2 | 122.33(15) |

| | | | | | | | | |
|-----|-----|-----|------------|--|-----|-----|-----|------------|
| C36 | C35 | C34 | 120.98(17) | | C7 | C6 | C5 | 121.07(16) |
| C35 | C36 | C37 | 119.76(17) | | C6 | C7 | C8 | 119.94(16) |
| C36 | C37 | C38 | 121.68(17) | | C7 | C8 | C9 | 121.21(17) |
| C37 | C38 | C33 | 118.18(16) | | C8 | C9 | C4 | 118.35(16) |
| C37 | C38 | C39 | 118.70(16) | | C8 | C9 | C10 | 119.40(16) |
| C33 | C38 | C39 | 123.09(16) | | C4 | C9 | C10 | 122.24(16) |
| C38 | C39 | C40 | 112.11(16) | | C9 | C10 | C11 | 111.76(16) |
| C38 | C39 | C41 | 109.81(16) | | C9 | C10 | C12 | 110.54(17) |
| C40 | C39 | C41 | 110.06(17) | | C11 | C10 | C12 | 109.36(16) |
| N3 | C42 | C44 | 123.47(15) | | N1 | C13 | C15 | 123.51(15) |
| N3 | C42 | C43 | 119.60(15) | | N1 | C13 | C14 | 119.18(15) |
| C44 | C42 | C43 | 116.92(15) | | C15 | C13 | C14 | 117.30(15) |
| C42 | C44 | C45 | 128.24(15) | | C13 | C15 | C16 | 128.14(16) |
| N4 | C45 | C44 | 123.49(15) | | N2 | C16 | C15 | 123.17(16) |
| N4 | C45 | C46 | 120.38(15) | | N2 | C16 | C17 | 119.91(15) |
| C44 | C45 | C46 | 116.13(15) | | C15 | C16 | C17 | 116.92(15) |
| C48 | C47 | C52 | 121.12(15) | | C23 | C18 | C19 | 121.35(15) |
| C48 | C47 | N4 | 119.59(15) | | C23 | C18 | N2 | 118.61(15) |
| C52 | C47 | N4 | 119.08(15) | | C19 | C18 | N2 | 119.94(15) |
| C49 | C48 | C47 | 118.31(17) | | C20 | C19 | C18 | 117.93(17) |
| C49 | C48 | C53 | 118.82(16) | | C20 | C19 | C24 | 119.43(17) |
| C47 | C48 | C53 | 122.86(15) | | C18 | C19 | C24 | 122.61(15) |

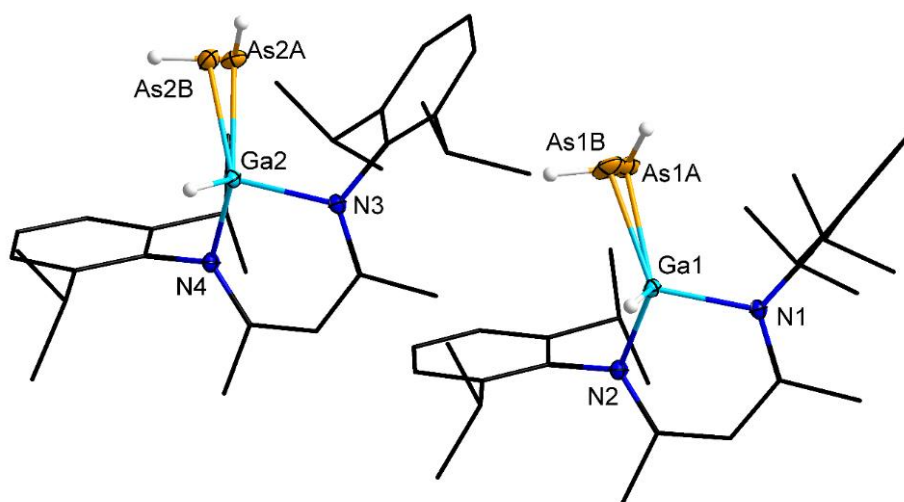


Figure S22: Both independent molecules in the unit cell of compound **2**. All hydrogen atoms on carbon are omitted for clarity. Carbon atoms are shown in the *wires and stick* model. Thermal ellipsoids represent a 50% probability level. Arsenic atoms were refined with split positions 0.91 : 0.09 (As1A, As1B) and 0.87 : 0.13 (As2A, As2B).

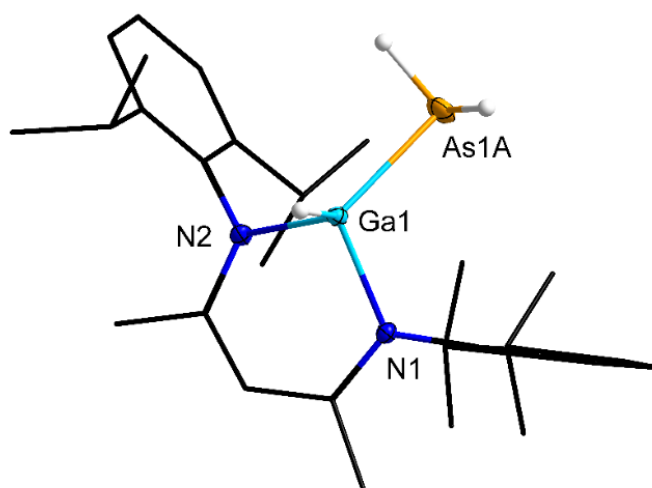


Figure S23: Molecular structure of **2**. Disordered parts are omitted for clarity.

Table S5: Bond length (Å) for **2**.

| | | | | | | |
|-----|------|------------|--|-----|-----|------------|
| Ga1 | N2 | 1.9567(11) | | C42 | C44 | 1.4016(18) |
| Ga1 | N1 | 1.9582(11) | | C42 | C43 | 1.5077(19) |
| Ga1 | As1B | 2.401(7) | | C44 | C45 | 1.4078(18) |
| Ga1 | As1A | 2.4163(6) | | C45 | N4 | 1.3259(17) |
| Ga2 | N4 | 1.9585(11) | | C45 | C46 | 1.5085(19) |
| Ga2 | N3 | 1.9590(11) | | C47 | C52 | 1.406(2) |
| Ga2 | As2B | 2.373(3) | | C47 | C48 | 1.4065(19) |
| Ga2 | As2A | 2.4218(6) | | C47 | N4 | 1.4461(16) |
| C1 | C2 | 1.534(2) | | C48 | C49 | 1.397(2) |
| C2 | C5 | 1.5184(19) | | C48 | C53 | 1.517(2) |
| C2 | C3 | 1.535(2) | | C49 | C50 | 1.379(2) |

| | | | | | | |
|-----|-----|------------|--|-----|-----|------------|
| C20 | C21 | 1.378(2) | | C50 | C51 | 1.381(2) |
| C20 | C19 | 1.399(2) | | C51 | C52 | 1.3974(19) |
| C21 | C22 | 1.377(2) | | C52 | C56 | 1.521(2) |
| C22 | C23 | 1.394(2) | | C53 | C55 | 1.531(3) |
| C23 | C18 | 1.4079(19) | | C53 | C54 | 1.532(2) |
| C23 | C27 | 1.518(2) | | C56 | C58 | 1.523(2) |
| C24 | C19 | 1.516(2) | | C56 | C57 | 1.525(2) |
| C24 | C25 | 1.526(2) | | N1 | C13 | 1.3326(17) |
| C24 | C26 | 1.532(2) | | N1 | C4 | 1.4394(17) |
| C27 | C28 | 1.520(3) | | N2 | C16 | 1.3283(17) |
| C27 | C29 | 1.526(3) | | N2 | C18 | 1.4438(17) |
| C30 | C31 | 1.532(2) | | C4 | C5 | 1.4074(18) |
| C31 | C34 | 1.5184(19) | | C4 | C9 | 1.4082(18) |
| C31 | C32 | 1.539(2) | | C5 | C6 | 1.3949(19) |
| C33 | C34 | 1.4078(18) | | C6 | C7 | 1.383(2) |
| C33 | C38 | 1.4110(19) | | C7 | C8 | 1.385(2) |
| C33 | N3 | 1.4394(16) | | C8 | C9 | 1.3973(19) |
| C34 | C35 | 1.3969(19) | | C9 | C10 | 1.5189(19) |
| C35 | C36 | 1.388(2) | | C10 | C12 | 1.529(2) |
| C36 | C37 | 1.383(2) | | C10 | C11 | 1.532(2) |
| C37 | C38 | 1.3933(19) | | C13 | C15 | 1.4018(19) |
| C38 | C39 | 1.5218(18) | | C13 | C14 | 1.5054(19) |
| C39 | C40 | 1.531(2) | | C15 | C16 | 1.4065(19) |
| C39 | C41 | 1.535(2) | | C16 | C17 | 1.5067(19) |
| C42 | N3 | 1.3303(17) | | C18 | C19 | 1.399(2) |

Table S6: Bond angles (°) for **2**.

| | | | | | | | | |
|-----|-----|------|------------|--|-----|-----|-----|------------|
| N2 | Ga1 | N1 | 95.22(5) | | C49 | C48 | C53 | 118.91(13) |
| N2 | Ga1 | As1B | 113.85(17) | | C47 | C48 | C53 | 122.97(12) |
| N1 | Ga1 | As1B | 117.7(3) | | C50 | C49 | C48 | 121.24(14) |
| N2 | Ga1 | As1A | 112.92(4) | | C49 | C50 | C51 | 120.13(14) |
| N1 | Ga1 | As1A | 109.25(5) | | C50 | C51 | C52 | 121.04(14) |
| N4 | Ga2 | N3 | 95.68(5) | | C51 | C52 | C47 | 118.26(13) |
| N4 | Ga2 | As2B | 114.48(7) | | C51 | C52 | C56 | 118.99(13) |
| N3 | Ga2 | As2B | 116.2(3) | | C47 | C52 | C56 | 122.73(12) |
| N4 | Ga2 | As2A | 113.45(3) | | C48 | C53 | C55 | 110.91(15) |
| N3 | Ga2 | As2A | 105.20(6) | | C48 | C53 | C54 | 112.36(13) |
| C5 | C2 | C1 | 110.33(12) | | C55 | C53 | C54 | 109.36(14) |
| C5 | C2 | C3 | 112.03(12) | | C52 | C56 | C58 | 112.40(13) |
| C1 | C2 | C3 | 110.49(13) | | C52 | C56 | C57 | 110.93(12) |
| C21 | C20 | C19 | 120.99(15) | | C58 | C56 | C57 | 109.79(14) |
| C22 | C21 | C20 | 120.00(14) | | C13 | N1 | C4 | 121.31(11) |
| C21 | C22 | C23 | 121.57(15) | | C13 | N1 | Ga1 | 118.37(9) |
| C22 | C23 | C18 | 117.72(14) | | C4 | N1 | Ga1 | 119.66(8) |
| C22 | C23 | C27 | 120.21(14) | | C16 | N2 | C18 | 121.34(11) |
| C18 | C23 | C27 | 122.07(13) | | C16 | N2 | Ga1 | 118.46(9) |
| C19 | C24 | C25 | 112.64(14) | | C18 | N2 | Ga1 | 119.65(8) |
| C19 | C24 | C26 | 110.57(14) | | C42 | N3 | C33 | 123.00(11) |
| C25 | C24 | C26 | 110.06(14) | | C42 | N3 | Ga2 | 120.22(9) |
| C23 | C27 | C28 | 111.52(16) | | C33 | N3 | Ga2 | 116.77(8) |
| C23 | C27 | C29 | 112.71(15) | | C45 | N4 | C47 | 122.42(11) |
| C28 | C27 | C29 | 109.60(15) | | C45 | N4 | Ga2 | 120.51(9) |
| C34 | C31 | C30 | 111.39(12) | | C47 | N4 | Ga2 | 116.60(8) |
| C34 | C31 | C32 | 110.50(12) | | C5 | C4 | C9 | 120.97(12) |
| C30 | C31 | C32 | 110.72(12) | | C5 | C4 | N1 | 119.59(12) |

| | | | | | | | | |
|-----|-----|-----|------------|--|-----|-----|-----|------------|
| C34 | C33 | C38 | 120.84(12) | | C9 | C4 | N1 | 119.35(11) |
| C34 | C33 | N3 | 119.24(12) | | C6 | C5 | C4 | 118.44(12) |
| C38 | C33 | N3 | 119.62(11) | | C6 | C5 | C2 | 119.39(12) |
| C35 | C34 | C33 | 118.56(13) | | C4 | C5 | C2 | 122.15(12) |
| C35 | C34 | C31 | 119.04(12) | | C7 | C6 | C5 | 121.32(13) |
| C33 | C34 | C31 | 122.39(12) | | C6 | C7 | C8 | 119.68(13) |
| C36 | C35 | C34 | 121.12(13) | | C7 | C8 | C9 | 121.31(13) |
| C37 | C36 | C35 | 119.52(13) | | C8 | C9 | C4 | 118.27(12) |
| C36 | C37 | C38 | 121.69(13) | | C8 | C9 | C10 | 119.21(12) |
| C37 | C38 | C33 | 118.22(12) | | C4 | C9 | C10 | 122.48(12) |
| C37 | C38 | C39 | 118.39(12) | | C9 | C10 | C12 | 110.72(13) |
| C33 | C38 | C39 | 123.36(12) | | C9 | C10 | C11 | 111.84(13) |
| C38 | C39 | C40 | 112.49(12) | | C12 | C10 | C11 | 109.22(13) |
| C38 | C39 | C41 | 109.53(12) | | N1 | C13 | C15 | 123.35(12) |
| C40 | C39 | C41 | 110.12(12) | | N1 | C13 | C14 | 119.40(12) |
| N3 | C42 | C44 | 123.48(12) | | C15 | C13 | C14 | 117.24(12) |
| N3 | C42 | C43 | 119.47(12) | | C13 | C15 | C16 | 128.19(12) |
| C44 | C42 | C43 | 117.05(12) | | N2 | C16 | C15 | 123.18(12) |
| C42 | C44 | C45 | 128.40(12) | | N2 | C16 | C17 | 119.79(12) |
| N4 | C45 | C44 | 123.45(12) | | C15 | C16 | C17 | 117.03(12) |
| N4 | C45 | C46 | 120.11(12) | | C19 | C18 | C23 | 121.46(13) |
| C44 | C45 | C46 | 116.44(12) | | C19 | C18 | N2 | 120.03(12) |
| C52 | C47 | C48 | 121.21(12) | | C23 | C18 | N2 | 118.37(12) |
| C52 | C47 | N4 | 119.21(12) | | C18 | C19 | C20 | 118.22(13) |
| C48 | C47 | N4 | 119.37(12) | | C18 | C19 | C24 | 122.70(12) |
| C49 | C48 | C47 | 118.11(13) | | C20 | C19 | C24 | 119.07(13) |

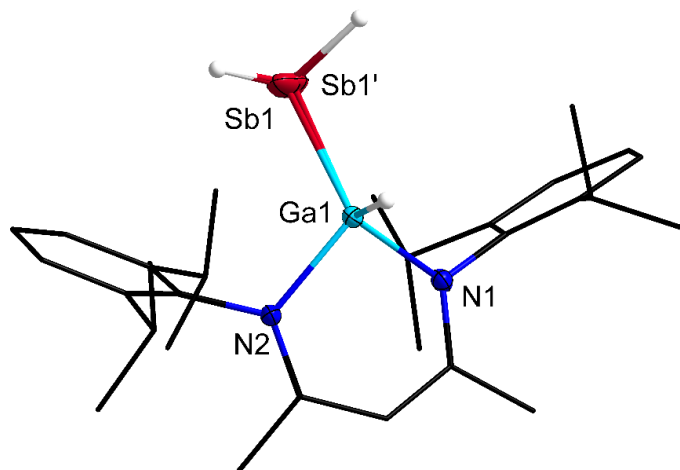


Figure S24: Molecular structure of **2**. All hydrogen atoms on carbon are omitted for clarity. Carbon atoms are shown in the *wires and stick* model. Thermal ellipsoids represent a 50% probability level. Antimony atoms were refined with split positions 0.5 : 0.5.

Table S7: Bond length (Å) for **3**.

| | | | | | | |
|-----|------|------------|--|-----|-----|----------|
| Sb1 | Ga1 | 2.6189(19) | | C27 | C29 | 1.524(2) |
| Ga1 | N2 | 1.9656(11) | | C27 | C28 | 1.537(2) |
| Ga1 | N1 | 1.9565(12) | | C6 | C11 | 1.405(2) |
| Ga1 | Sb1' | 2.600(2) | | C6 | C7 | 1.404(2) |
| N2 | C3 | 1.3215(17) | | C20 | C21 | 1.381(2) |
| N2 | C18 | 1.4387(17) | | C11 | C15 | 1.516(2) |

| | | | | | | |
|-----|-----|------------|--|-----|-----|----------|
| N1 | C1 | 1.3330(17) | | C11 | C10 | 1.394(2) |
| N1 | C6 | 1.4420(17) | | C12 | C7 | 1.516(2) |
| C3 | C2 | 1.4050(19) | | C12 | C13 | 1.533(2) |
| C3 | C5 | 1.5074(19) | | C12 | C14 | 1.534(2) |
| C1 | C2 | 1.4002(19) | | C22 | C21 | 1.380(2) |
| C1 | C4 | 1.5054(19) | | C7 | C8 | 1.398(2) |
| C18 | C19 | 1.404(2) | | C24 | C25 | 1.529(2) |
| C18 | C23 | 1.406(2) | | C24 | C26 | 1.530(2) |
| C19 | C20 | 1.396(2) | | C8 | C9 | 1.374(3) |
| C19 | C24 | 1.517(2) | | C15 | C16 | 1.518(2) |
| C23 | C27 | 1.525(2) | | C15 | C17 | 1.523(3) |
| C23 | C22 | 1.398(2) | | C10 | C9 | 1.382(3) |

Table S8: Bond angles (°) for **3**.

| | | | | | | | | |
|-----|-----|------|------------|--|-----|-----|-----|------------|
| N2 | Ga1 | Sb1 | 112.49(6) | | C23 | C27 | C28 | 110.73(13) |
| N2 | Ga1 | Sb1' | 110.74(6) | | C29 | C27 | C23 | 112.93(14) |
| N1 | Ga1 | Sb1 | 111.89(5) | | C29 | C27 | C28 | 109.00(14) |
| N1 | Ga1 | N2 | 94.34(5) | | C11 | C6 | N1 | 118.66(13) |
| N1 | Ga1 | Sb1' | 114.08(5) | | C7 | C6 | N1 | 119.93(13) |
| C3 | N2 | Ga1 | 120.36(9) | | C7 | C6 | C11 | 121.39(13) |
| C3 | N2 | C18 | 122.82(11) | | C21 | C20 | C19 | 120.96(15) |
| C18 | N2 | Ga1 | 116.45(8) | | C6 | C11 | C15 | 121.55(13) |
| C1 | N1 | Ga1 | 119.34(9) | | C10 | C11 | C6 | 118.07(15) |
| C1 | N1 | C6 | 119.46(11) | | C10 | C11 | C15 | 120.38(15) |
| C6 | N1 | Ga1 | 120.67(9) | | C7 | C12 | C13 | 108.94(13) |
| N2 | C3 | C2 | 123.13(13) | | C7 | C12 | C14 | 113.72(15) |
| N2 | C3 | C5 | 120.09(12) | | C13 | C12 | C14 | 110.05(14) |
| C2 | C3 | C5 | 116.78(12) | | C21 | C22 | C23 | 121.24(15) |
| N1 | C1 | C2 | 123.64(12) | | C6 | C7 | C12 | 122.12(13) |
| N1 | C1 | C4 | 119.45(12) | | C8 | C7 | C6 | 117.89(15) |
| C2 | C1 | C4 | 116.90(12) | | C8 | C7 | C12 | 119.84(14) |
| C1 | C2 | C3 | 127.72(13) | | C19 | C24 | C25 | 110.22(15) |
| C19 | C18 | N2 | 118.69(12) | | C19 | C24 | C26 | 112.64(14) |
| C19 | C18 | C23 | 121.79(13) | | C25 | C24 | C26 | 110.92(15) |
| C23 | C18 | N2 | 119.29(12) | | C22 | C21 | C20 | 120.28(14) |
| C18 | C19 | C24 | 122.03(13) | | C9 | C8 | C7 | 121.31(16) |
| C20 | C19 | C18 | 117.98(14) | | C11 | C15 | C16 | 112.99(15) |
| C20 | C19 | C24 | 119.93(14) | | C11 | C15 | C17 | 111.42(15) |
| C18 | C23 | C27 | 122.49(12) | | C16 | C15 | C17 | 109.57(16) |
| C22 | C23 | C18 | 117.60(14) | | C9 | C10 | C11 | 121.10(16) |
| C22 | C23 | C27 | 119.87(13) | | C8 | C9 | C10 | 120.09(15) |

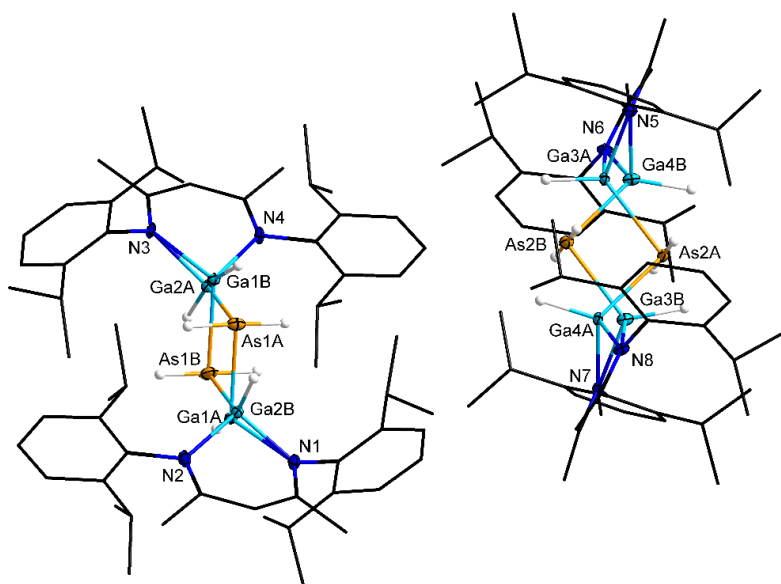


Figure S25: Both independent molecules in the unit cell of compound **4**. All hydrogen atoms on carbon are omitted for clarity. Carbon atoms are shown in the *wires and stick* model. Thermal ellipsoids represent a 50% probability level. Arsenic atoms were refined with split positions 0.9 : 0.1 (As1A, As1B) and 0.7 : 0.3 (As2A, As2B).

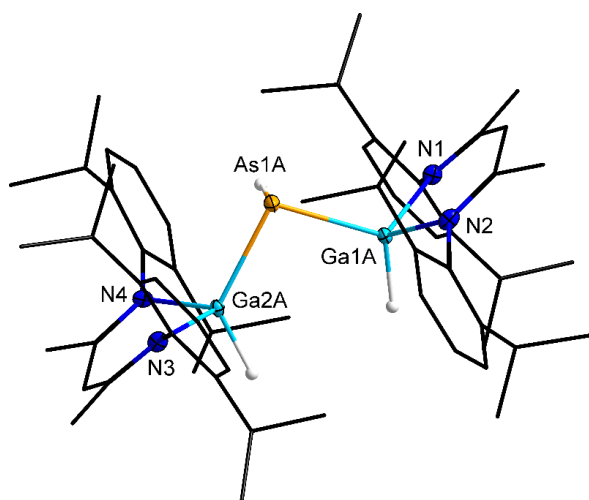


Figure S26: Molecular structure of **4**. Disordered parts are omitted for clarity.

Table S9: Bond length (Å) for **4**.

| | | | | | | |
|----|-----|----------|--|-----|-----|-----------|
| C1 | N1 | 1.293(7) | | C67 | C68 | 1.414(9) |
| C1 | C2 | 1.441(7) | | C68 | C69 | 1.365(9) |
| C1 | C4 | 1.551(7) | | C69 | C73 | 1.525(8) |
| C2 | C3 | 1.446(7) | | C70 | C72 | 1.528(9) |
| C3 | N2 | 1.296(7) | | C70 | C71 | 1.569(9) |
| C3 | C5 | 1.530(7) | | C73 | C75 | 1.507(10) |
| C6 | C11 | 1.385(8) | | C73 | C74 | 1.537(8) |

| | | | | | | |
|-----|-----|-----------|--|------|------|-----------|
| C6 | C7 | 1.402(8) | | C76 | C81 | 1.366(8) |
| C6 | N1 | 1.471(7) | | C76 | N6 | 1.409(7) |
| C7 | C8 | 1.422(7) | | C76 | C77 | 1.469(7) |
| C7 | C12 | 1.515(8) | | C77 | C78 | 1.328(9) |
| C8 | C9 | 1.347(10) | | C77 | C82 | 1.543(9) |
| C9 | C10 | 1.349(11) | | C78 | C79 | 1.364(10) |
| C10 | C11 | 1.464(8) | | C79 | C80 | 1.425(9) |
| C11 | C15 | 1.476(9) | | C80 | C81 | 1.373(8) |
| C12 | C13 | 1.528(9) | | C81 | C85 | 1.544(9) |
| C12 | C14 | 1.559(9) | | C82 | C83 | 1.539(9) |
| C15 | C16 | 1.477(10) | | C82 | C84 | 1.574(9) |
| C15 | C17 | 1.541(9) | | C85 | C86 | 1.484(10) |
| C18 | C23 | 1.343(8) | | C85 | C87 | 1.570(9) |
| C18 | C19 | 1.444(6) | | C88 | C89 | 1.350(8) |
| C18 | N2 | 1.479(6) | | C88 | N7 | 1.372(7) |
| C19 | C20 | 1.424(7) | | C88 | C91 | 1.495(8) |
| C19 | C24 | 1.496(9) | | C89 | C90 | 1.345(9) |
| C20 | C21 | 1.335(10) | | C90 | N8 | 1.378(7) |
| C21 | C22 | 1.402(10) | | C90 | C92 | 1.502(8) |
| C22 | C23 | 1.447(8) | | C93 | C94 | 1.373(8) |
| C23 | C27 | 1.511(8) | | C93 | N8 | 1.418(7) |
| C24 | C26 | 1.486(9) | | C93 | C98 | 1.439(7) |
| C24 | C25 | 1.577(9) | | C94 | C95 | 1.383(8) |
| C27 | C29 | 1.488(10) | | C94 | C99 | 1.550(8) |
| C27 | C28 | 1.513(10) | | C95 | C96 | 1.436(9) |
| C30 | N3 | 1.293(8) | | C96 | C97 | 1.365(10) |
| C30 | C31 | 1.451(7) | | C97 | C98 | 1.358(9) |
| C30 | C33 | 1.531(7) | | C98 | C102 | 1.548(8) |
| C31 | C32 | 1.447(6) | | C99 | C100 | 1.471(10) |
| C32 | N4 | 1.286(7) | | C99 | C101 | 1.558(9) |
| C32 | C34 | 1.520(7) | | C102 | C103 | 1.530(10) |
| C35 | C36 | 1.385(8) | | C102 | C104 | 1.544(9) |
| C35 | C40 | 1.396(8) | | C105 | N7 | 1.398(7) |
| C35 | N3 | 1.467(7) | | C105 | C110 | 1.425(7) |
| C36 | C37 | 1.435(7) | | C105 | C106 | 1.431(7) |
| C36 | C41 | 1.516(9) | | C106 | C107 | 1.346(9) |
| C37 | C38 | 1.343(10) | | C106 | C111 | 1.529(8) |
| C38 | C39 | 1.367(10) | | C107 | C108 | 1.419(10) |
| C39 | C40 | 1.433(8) | | C108 | C109 | 1.403(10) |
| C40 | C44 | 1.482(9) | | C109 | C110 | 1.349(8) |
| C41 | C42 | 1.509(9) | | C110 | C114 | 1.557(8) |
| C41 | C43 | 1.564(9) | | C111 | C112 | 1.493(9) |
| C44 | C46 | 1.519(10) | | C111 | C113 | 1.538(9) |
| C44 | C45 | 1.527(10) | | C114 | C116 | 1.534(9) |
| C47 | C52 | 1.376(8) | | C114 | C115 | 1.543(9) |
| C47 | C48 | 1.442(7) | | N1 | Ga2B | 1.919(9) |
| C47 | N4 | 1.463(6) | | N1 | Ga1A | 1.994(5) |
| C48 | C49 | 1.418(7) | | N2 | Ga2B | 1.891(9) |
| C48 | C53 | 1.486(8) | | N2 | Ga1A | 1.992(5) |
| C49 | C50 | 1.338(9) | | N3 | Ga2A | 1.990(4) |
| C50 | C51 | 1.389(8) | | N3 | Ga1B | 2.058(9) |
| C51 | C52 | 1.436(8) | | N4 | Ga2A | 1.976(4) |
| C52 | C56 | 1.494(9) | | N4 | Ga1B | 2.070(9) |
| C53 | C55 | 1.504(8) | | N5 | Ga4B | 1.983(5) |
| C53 | C54 | 1.570(9) | | N5 | Ga3A | 2.010(5) |
| C56 | C57 | 1.500(10) | | N6 | Ga4B | 1.980(5) |
| C56 | C58 | 1.535(9) | | N6 | Ga3A | 2.023(5) |
| C59 | C60 | 1.342(8) | | N7 | Ga4A | 1.991(5) |
| C59 | N5 | 1.373(7) | | N7 | Ga3B | 2.022(6) |

| | | | | | | |
|-----|-----|-----------|--|------|------|------------|
| C59 | C62 | 1.484(8) | | N8 | Ga4A | 1.975(5) |
| C60 | C61 | 1.358(9) | | N8 | Ga3B | 2.038(6) |
| C61 | N6 | 1.366(7) | | Ga1A | As1A | 2.4434(10) |
| C61 | C63 | 1.500(8) | | Ga2A | As1A | 2.4263(11) |
| C64 | N5 | 1.405(7) | | As1B | Ga2B | 2.443(10) |
| C64 | C69 | 1.425(7) | | As1B | Ga1B | 2.457(10) |
| C64 | C65 | 1.433(7) | | Ga3A | As2A | 2.4409(12) |
| C65 | C66 | 1.320(8) | | Ga4A | As2A | 2.4302(12) |
| C65 | C70 | 1.575(9) | | Ga3B | As2B | 2.446(3) |
| C66 | C67 | 1.412(10) | | Ga4B | As2B | 2.429(3) |

Table S10: Bond angles (°) for **4**.

| | | | | | | | | |
|-----|-----|-----|----------|--|------|------|------|----------|
| N1 | C1 | C2 | 126.1(5) | | C76 | C81 | C80 | 120.5(5) |
| N1 | C1 | C4 | 122.3(4) | | C76 | C81 | C85 | 121.6(5) |
| C2 | C1 | C4 | 111.5(5) | | C80 | C81 | C85 | 117.9(5) |
| C1 | C2 | C3 | 123.1(5) | | C83 | C82 | C77 | 109.7(6) |
| N2 | C3 | C2 | 125.2(5) | | C83 | C82 | C84 | 109.5(5) |
| N2 | C3 | C5 | 122.9(4) | | C77 | C82 | C84 | 108.1(6) |
| C2 | C3 | C5 | 112.0(5) | | C86 | C85 | C81 | 110.9(5) |
| C11 | C6 | C7 | 124.5(5) | | C86 | C85 | C87 | 108.3(6) |
| C11 | C6 | N1 | 117.4(5) | | C81 | C85 | C87 | 110.1(5) |
| C7 | C6 | N1 | 118.1(5) | | C89 | C88 | N7 | 122.3(5) |
| C6 | C7 | C8 | 117.0(5) | | C89 | C88 | C91 | 120.2(5) |
| C6 | C7 | C12 | 124.9(5) | | N7 | C88 | C91 | 117.4(5) |
| C8 | C7 | C12 | 118.2(5) | | C90 | C89 | C88 | 132.6(6) |
| C9 | C8 | C7 | 121.0(6) | | C89 | C90 | N8 | 122.0(5) |
| C8 | C9 | C10 | 121.0(6) | | C89 | C90 | C92 | 120.2(5) |
| C9 | C10 | C11 | 122.6(6) | | N8 | C90 | C92 | 117.7(5) |
| C6 | C11 | C10 | 113.8(5) | | C94 | C93 | N8 | 121.9(4) |
| C6 | C11 | C15 | 125.8(5) | | C94 | C93 | C98 | 119.5(5) |
| C10 | C11 | C15 | 120.4(5) | | N8 | C93 | C98 | 118.6(5) |
| C7 | C12 | C13 | 111.2(5) | | C93 | C94 | C95 | 120.1(5) |
| C7 | C12 | C14 | 112.2(5) | | C93 | C94 | C99 | 121.3(5) |
| C13 | C12 | C14 | 108.5(5) | | C95 | C94 | C99 | 118.5(5) |
| C11 | C15 | C16 | 114.0(5) | | C94 | C95 | C96 | 119.6(5) |
| C11 | C15 | C17 | 111.3(5) | | C97 | C96 | C95 | 119.4(6) |
| C16 | C15 | C17 | 112.3(6) | | C98 | C97 | C96 | 121.2(6) |
| C23 | C18 | C19 | 124.1(4) | | C97 | C98 | C93 | 119.9(5) |
| C23 | C18 | N2 | 119.0(4) | | C97 | C98 | C102 | 121.0(5) |
| C19 | C18 | N2 | 116.8(4) | | C93 | C98 | C102 | 119.1(5) |
| C20 | C19 | C18 | 115.1(5) | | C100 | C99 | C94 | 110.4(5) |
| C20 | C19 | C24 | 120.8(5) | | C100 | C99 | C101 | 109.6(6) |
| C18 | C19 | C24 | 124.1(4) | | C94 | C99 | C101 | 109.7(5) |
| C21 | C20 | C19 | 123.0(5) | | C103 | C102 | C104 | 109.7(6) |
| C20 | C21 | C22 | 120.2(5) | | C103 | C102 | C98 | 109.9(6) |
| C21 | C22 | C23 | 120.5(6) | | C104 | C102 | C98 | 110.6(5) |
| C18 | C23 | C22 | 117.0(5) | | N7 | C105 | C110 | 120.4(5) |
| C18 | C23 | C27 | 125.6(5) | | N7 | C105 | C106 | 121.4(4) |
| C22 | C23 | C27 | 117.3(5) | | C110 | C105 | C106 | 118.2(5) |
| C26 | C24 | C19 | 114.8(6) | | C107 | C106 | C105 | 119.2(5) |
| C26 | C24 | C25 | 108.4(5) | | C107 | C106 | C111 | 120.9(5) |
| C19 | C24 | C25 | 109.6(5) | | C105 | C106 | C111 | 119.9(5) |
| C29 | C27 | C23 | 112.8(6) | | C106 | C107 | C108 | 122.7(6) |
| C29 | C27 | C28 | 112.4(6) | | C109 | C108 | C107 | 117.6(6) |
| C23 | C27 | C28 | 114.6(5) | | C110 | C109 | C108 | 121.3(6) |
| N3 | C30 | C31 | 124.3(5) | | C109 | C110 | C105 | 121.0(5) |
| N3 | C30 | C33 | 122.3(5) | | C109 | C110 | C114 | 119.4(5) |
| C31 | C30 | C33 | 113.3(5) | | C105 | C110 | C114 | 119.6(5) |

| | | | | | | | | |
|-----|-----|-----|----------|--|------|------|------|------------|
| C32 | C31 | C30 | 123.5(5) | | C112 | C111 | C106 | 111.5(5) |
| N4 | C32 | C31 | 124.5(5) | | C112 | C111 | C113 | 110.9(5) |
| N4 | C32 | C34 | 122.7(4) | | C106 | C111 | C113 | 108.2(5) |
| C31 | C32 | C34 | 112.7(5) | | C116 | C114 | C115 | 109.8(5) |
| C36 | C35 | C40 | 123.9(5) | | C116 | C114 | C110 | 109.9(6) |
| C36 | C35 | N3 | 118.0(5) | | C115 | C114 | C110 | 111.0(5) |
| C40 | C35 | N3 | 118.1(5) | | C1 | N1 | C6 | 117.6(4) |
| C35 | C36 | C37 | 117.9(5) | | C1 | N1 | Ga2B | 113.7(4) |
| C35 | C36 | C41 | 123.4(5) | | C6 | N1 | Ga2B | 128.0(4) |
| C37 | C36 | C41 | 118.7(5) | | C1 | N1 | Ga1A | 124.5(4) |
| C38 | C37 | C36 | 119.2(6) | | C6 | N1 | Ga1A | 117.3(4) |
| C37 | C38 | C39 | 122.4(6) | | C3 | N2 | C18 | 117.6(4) |
| C38 | C39 | C40 | 121.5(6) | | C3 | N2 | Ga2B | 114.9(4) |
| C35 | C40 | C39 | 115.0(6) | | C18 | N2 | Ga2B | 126.4(4) |
| C35 | C40 | C44 | 123.9(5) | | C3 | N2 | Ga1A | 125.2(4) |
| C39 | C40 | C44 | 121.1(5) | | C18 | N2 | Ga1A | 116.8(4) |
| C42 | C41 | C36 | 112.1(5) | | C30 | N3 | C35 | 116.9(4) |
| C42 | C41 | C43 | 111.7(5) | | C30 | N3 | Ga2A | 118.3(3) |
| C36 | C41 | C43 | 112.7(5) | | C35 | N3 | Ga2A | 123.9(4) |
| C40 | C44 | C46 | 112.5(6) | | C30 | N3 | Ga1B | 128.2(4) |
| C40 | C44 | C45 | 112.6(6) | | C35 | N3 | Ga1B | 114.5(4) |
| C46 | C44 | C45 | 110.4(6) | | C32 | N4 | C47 | 117.4(4) |
| C52 | C47 | C48 | 123.8(4) | | C32 | N4 | Ga2A | 119.1(4) |
| C52 | C47 | N4 | 119.9(4) | | C47 | N4 | Ga2A | 122.9(4) |
| C48 | C47 | N4 | 116.3(5) | | C32 | N4 | Ga1B | 128.1(4) |
| C49 | C48 | C47 | 115.5(5) | | C47 | N4 | Ga1B | 113.9(4) |
| C49 | C48 | C53 | 121.2(5) | | C59 | N5 | C64 | 118.9(5) |
| C47 | C48 | C53 | 123.3(4) | | C59 | N5 | Ga4B | 112.8(4) |
| C50 | C49 | C48 | 122.6(5) | | C64 | N5 | Ga4B | 126.9(4) |
| C49 | C50 | C51 | 120.3(5) | | C59 | N5 | Ga3A | 123.4(4) |
| C50 | C51 | C52 | 121.8(5) | | C64 | N5 | Ga3A | 117.3(4) |
| C47 | C52 | C51 | 115.7(5) | | C61 | N6 | C76 | 119.7(5) |
| C47 | C52 | C56 | 123.4(5) | | C61 | N6 | Ga4B | 111.7(4) |
| C51 | C52 | C56 | 120.9(5) | | C76 | N6 | Ga4B | 125.7(4) |
| C48 | C53 | C55 | 115.7(5) | | C61 | N6 | Ga3A | 122.2(4) |
| C48 | C53 | C54 | 108.8(5) | | C76 | N6 | Ga3A | 118.1(3) |
| C55 | C53 | C54 | 110.2(5) | | C88 | N7 | C105 | 118.8(5) |
| C52 | C56 | C57 | 114.5(6) | | C88 | N7 | Ga4A | 114.7(4) |
| C52 | C56 | C58 | 111.3(6) | | C105 | N7 | Ga4A | 125.4(4) |
| C57 | C56 | C58 | 111.6(6) | | C88 | N7 | Ga3B | 124.8(4) |
| C60 | C59 | N5 | 122.5(5) | | C105 | N7 | Ga3B | 115.8(3) |
| C60 | C59 | C62 | 119.5(5) | | C90 | N8 | C93 | 118.5(5) |
| N5 | C59 | C62 | 117.9(5) | | C90 | N8 | Ga4A | 114.9(4) |
| C59 | C60 | C61 | 132.4(6) | | C93 | N8 | Ga4A | 124.5(4) |
| C60 | C61 | N6 | 123.5(5) | | C90 | N8 | Ga3B | 124.5(4) |
| C60 | C61 | C63 | 118.8(5) | | C93 | N8 | Ga3B | 116.8(4) |
| N6 | C61 | C63 | 117.5(6) | | N2 | Ga1A | N1 | 93.3(2) |
| N5 | C64 | C69 | 121.7(5) | | N2 | Ga1A | As1A | 111.33(15) |
| N5 | C64 | C65 | 120.5(5) | | N1 | Ga1A | As1A | 115.55(15) |
| C69 | C64 | C65 | 117.9(5) | | N4 | Ga2A | N3 | 92.95(19) |
| C66 | C65 | C64 | 121.9(5) | | N4 | Ga2A | As1A | 111.39(15) |
| C66 | C65 | C70 | 119.7(5) | | N3 | Ga2A | As1A | 116.00(15) |
| C64 | C65 | C70 | 118.4(5) | | Ga2A | As1A | Ga1A | 97.56(4) |
| C65 | C66 | C67 | 121.0(5) | | Ga2B | As1B | Ga1B | 97.5(3) |
| C66 | C67 | C68 | 118.3(6) | | N3 | Ga1B | N4 | 88.3(4) |
| C69 | C68 | C67 | 121.6(6) | | N3 | Ga1B | As1B | 117.6(4) |
| C68 | C69 | C64 | 119.3(5) | | N4 | Ga1B | As1B | 112.2(4) |
| C68 | C69 | C73 | 120.3(5) | | N2 | Ga2B | N1 | 99.0(4) |
| C64 | C69 | C73 | 120.4(5) | | N2 | Ga2B | As1B | 108.9(4) |

| | | | | | | | | |
|-----|-----|-----|----------|--|------|------|------|------------|
| C72 | C70 | C71 | 108.5(5) | | N1 | Ga2B | As1B | 113.9(4) |
| C72 | C70 | C65 | 111.3(5) | | N5 | Ga3A | N6 | 93.5(2) |
| C71 | C70 | C65 | 109.7(5) | | N5 | Ga3A | As2A | 115.57(15) |
| C75 | C73 | C69 | 112.0(6) | | N6 | Ga3A | As2A | 111.59(15) |
| C75 | C73 | C74 | 109.1(6) | | N8 | Ga4A | N7 | 94.3(2) |
| C69 | C73 | C74 | 108.5(5) | | N8 | Ga4A | As2A | 109.55(16) |
| C81 | C76 | N6 | 122.6(4) | | N7 | Ga4A | As2A | 114.48(14) |
| C81 | C76 | C77 | 118.8(5) | | Ga4A | As2A | Ga3A | 97.38(4) |
| N6 | C76 | C77 | 118.5(5) | | N7 | Ga3B | N8 | 91.5(2) |
| C78 | C77 | C76 | 119.2(6) | | N7 | Ga3B | As2B | 115.61(18) |
| C78 | C77 | C82 | 122.4(6) | | N8 | Ga3B | As2B | 110.53(18) |
| C76 | C77 | C82 | 118.4(5) | | N6 | Ga4B | N5 | 95.6(2) |
| C77 | C78 | C79 | 122.1(6) | | N6 | Ga4B | As2B | 107.46(18) |
| C78 | C79 | C80 | 119.5(6) | | N5 | Ga4B | As2B | 113.03(19) |
| C81 | C80 | C79 | 119.7(6) | | Ga4B | As2B | Ga3B | 97.63(11) |

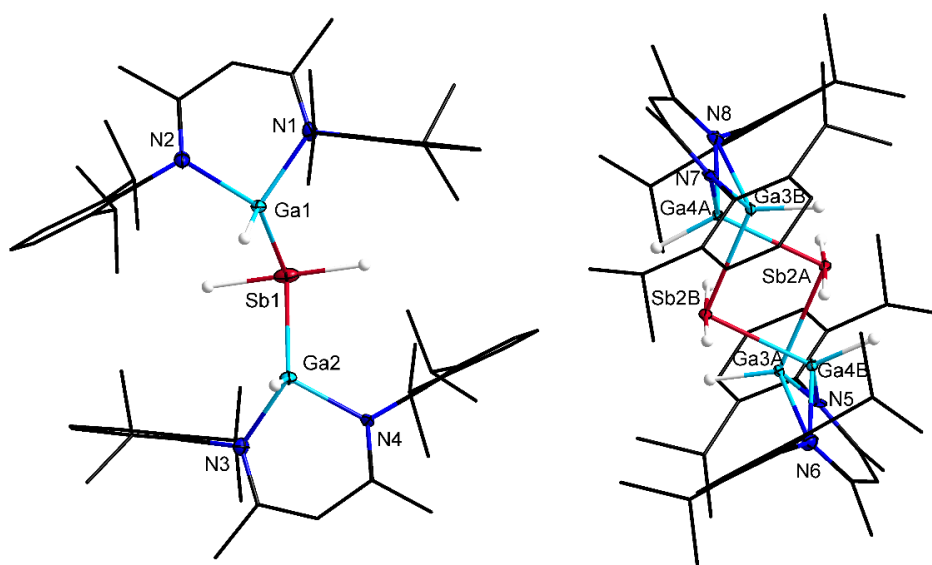


Figure S27: Both independent molecules in the unit cell of compound **5**. All hydrogen atoms on carbon are omitted for clarity. Carbon atoms are shown in the *wires and stick* model. Thermal ellipsoids represent a 50% probability level. Antimony atoms were refined with split positions 0.65 : 0.35.

Table S11: Bond length (Å) for **5**.

| | | | | | | |
|-----|-----|-----------|--|-----|-----|-----------|
| C1 | N1 | 1.344(10) | | C65 | C66 | 1.321(12) |
| C1 | C2 | 1.401(11) | | C65 | C70 | 1.570(11) |
| C1 | C4 | 1.500(11) | | C66 | C67 | 1.441(14) |
| C2 | C3 | 1.422(11) | | C67 | C68 | 1.387(14) |
| C3 | N2 | 1.332(9) | | C68 | C69 | 1.395(12) |
| C3 | C5 | 1.484(11) | | C69 | C73 | 1.519(11) |
| C6 | C11 | 1.375(11) | | C70 | C71 | 1.501(13) |
| C6 | C7 | 1.412(12) | | C70 | C72 | 1.550(12) |
| C6 | N1 | 1.490(9) | | C73 | C75 | 1.527(14) |
| C7 | C8 | 1.394(12) | | C73 | C74 | 1.540(12) |
| C7 | C12 | 1.508(13) | | C76 | N6 | 1.379(11) |
| C8 | C9 | 1.384(15) | | C76 | C81 | 1.412(11) |
| C9 | C10 | 1.314(15) | | C76 | C77 | 1.448(10) |
| C10 | C11 | 1.466(11) | | C77 | C78 | 1.343(13) |

| | | | | | | |
|-----|-----|-----------|--|------|------|------------|
| C11 | C15 | 1.461(13) | | C77 | C82 | 1.536(12) |
| C12 | C13 | 1.537(12) | | C78 | C79 | 1.374(13) |
| C12 | C14 | 1.545(13) | | C79 | C80 | 1.415(13) |
| C15 | C17 | 1.505(13) | | C80 | C81 | 1.377(12) |
| C15 | C16 | 1.559(12) | | C81 | C85 | 1.541(11) |
| C18 | C23 | 1.384(12) | | C82 | C84 | 1.535(14) |
| C18 | C19 | 1.407(12) | | C82 | C83 | 1.541(12) |
| C18 | N2 | 1.497(10) | | C85 | C87 | 1.522(12) |
| C19 | C20 | 1.420(12) | | C85 | C86 | 1.546(11) |
| C19 | C24 | 1.509(12) | | C88 | N7 | 1.306(11) |
| C20 | C21 | 1.345(14) | | C88 | C89 | 1.394(11) |
| C21 | C22 | 1.386(13) | | C88 | C91 | 1.530(11) |
| C22 | C23 | 1.433(11) | | C89 | C90 | 1.354(12) |
| C23 | C27 | 1.495(12) | | C90 | N8 | 1.335(10) |
| C24 | C26 | 1.529(11) | | C90 | C92 | 1.555(11) |
| C24 | C25 | 1.531(12) | | C93 | N8 | 1.393(11) |
| C27 | C28 | 1.514(14) | | C93 | C94 | 1.404(11) |
| C27 | C29 | 1.527(12) | | C93 | C98 | 1.445(10) |
| C30 | N3 | 1.340(10) | | C94 | C95 | 1.370(11) |
| C30 | C31 | 1.422(10) | | C94 | C99 | 1.548(11) |
| C30 | C33 | 1.499(11) | | C95 | C96 | 1.423(12) |
| C31 | C32 | 1.452(10) | | C96 | C97 | 1.410(13) |
| C32 | N4 | 1.318(9) | | C97 | C98 | 1.349(12) |
| C32 | C34 | 1.482(10) | | C98 | C102 | 1.530(11) |
| C35 | C36 | 1.369(12) | | C99 | C101 | 1.517(12) |
| C35 | C40 | 1.397(11) | | C99 | C100 | 1.543(11) |
| C35 | N3 | 1.481(10) | | C102 | C103 | 1.492(14) |
| C36 | C37 | 1.413(12) | | C102 | C104 | 1.530(12) |
| C36 | C41 | 1.510(13) | | C105 | N7 | 1.406(10) |
| C37 | C38 | 1.401(14) | | C105 | C110 | 1.410(10) |
| C38 | C39 | 1.284(15) | | C105 | C106 | 1.441(11) |
| C39 | C40 | 1.446(11) | | C106 | C107 | 1.389(12) |
| C40 | C44 | 1.477(13) | | C106 | C111 | 1.529(12) |
| C41 | C42 | 1.530(11) | | C107 | C108 | 1.352(15) |
| C41 | C43 | 1.545(13) | | C108 | C109 | 1.467(13) |
| C44 | C45 | 1.489(13) | | C109 | C110 | 1.332(12) |
| C44 | C46 | 1.554(13) | | C110 | C114 | 1.569(12) |
| C47 | C52 | 1.362(12) | | C111 | C112 | 1.508(14) |
| C47 | C48 | 1.412(12) | | C111 | C113 | 1.519(11) |
| C47 | N4 | 1.492(10) | | C114 | C116 | 1.492(14) |
| C48 | C49 | 1.414(11) | | C114 | C115 | 1.580(12) |
| C48 | C53 | 1.471(12) | | N1 | Ga1 | 1.982(7) |
| C49 | C50 | 1.346(13) | | N2 | Ga1 | 1.981(7) |
| C50 | C51 | 1.358(13) | | N3 | Ga2 | 1.977(7) |
| C51 | C52 | 1.447(12) | | N4 | Ga2 | 1.975(7) |
| C52 | C56 | 1.511(12) | | N5 | Ga4B | 1.979(6) |
| C53 | C54 | 1.522(12) | | N5 | Ga3A | 2.013(7) |
| C53 | C55 | 1.544(11) | | N6 | Ga4B | 1.970(7) |
| C56 | C57 | 1.524(13) | | N6 | Ga3A | 2.038(7) |
| C56 | C58 | 1.557(13) | | N7 | Ga4A | 1.999(6) |
| C59 | N5 | 1.330(11) | | N7 | Ga3B | 2.041(7) |
| C59 | C60 | 1.401(12) | | N8 | Ga4A | 1.975(7) |
| C59 | C62 | 1.518(13) | | N8 | Ga3B | 2.071(7) |
| C60 | C61 | 1.379(12) | | Ga1 | Sb1 | 2.6142(8) |
| C61 | N6 | 1.330(11) | | Ga2 | Sb1 | 2.5961(8) |
| C61 | C63 | 1.546(11) | | Ga3A | Sb2A | 2.6281(11) |
| C64 | N5 | 1.395(10) | | Ga4A | Sb2A | 2.6194(12) |
| C64 | C69 | 1.417(11) | | Ga3B | Sb2B | 2.6266(15) |
| C64 | C65 | 1.449(10) | | Ga4B | Sb2B | 2.6118(16) |

Table S12: Bond angles (°) for **5**.

| | | | | | | | | |
|-----|-----|-----|----------|--|------|------|------|----------|
| N1 | C1 | C2 | 121.4(7) | | C81 | C76 | C77 | 118.8(7) |
| N1 | C1 | C4 | 122.0(7) | | C78 | C77 | C76 | 119.6(7) |
| C2 | C1 | C4 | 116.5(7) | | C78 | C77 | C82 | 120.3(7) |
| C1 | C2 | C3 | 129.8(7) | | C76 | C77 | C82 | 120.1(8) |
| N2 | C3 | C2 | 121.0(7) | | C77 | C78 | C79 | 123.1(8) |
| N2 | C3 | C5 | 123.0(7) | | C78 | C79 | C80 | 117.4(8) |
| C2 | C3 | C5 | 116.0(7) | | C81 | C80 | C79 | 122.8(8) |
| C11 | C6 | C7 | 124.5(7) | | C80 | C81 | C76 | 118.2(7) |
| C11 | C6 | N1 | 116.9(7) | | C80 | C81 | C85 | 120.8(7) |
| C7 | C6 | N1 | 118.7(7) | | C76 | C81 | C85 | 121.0(7) |
| C8 | C7 | C6 | 117.6(8) | | C84 | C82 | C77 | 108.7(7) |
| C8 | C7 | C12 | 119.0(8) | | C84 | C82 | C83 | 110.7(8) |
| C6 | C7 | C12 | 123.4(8) | | C77 | C82 | C83 | 112.2(8) |
| C9 | C8 | C7 | 119.3(9) | | C87 | C85 | C81 | 111.2(7) |
| C10 | C9 | C8 | 122.8(8) | | C87 | C85 | C86 | 111.2(7) |
| C9 | C10 | C11 | 121.8(8) | | C81 | C85 | C86 | 107.2(7) |
| C6 | C11 | C15 | 125.9(7) | | N7 | C88 | C89 | 125.5(7) |
| C6 | C11 | C10 | 114.1(8) | | N7 | C88 | C91 | 118.3(7) |
| C15 | C11 | C10 | 120.0(8) | | C89 | C88 | C91 | 116.1(7) |
| C7 | C12 | C13 | 110.9(7) | | C90 | C89 | C88 | 127.7(7) |
| C7 | C12 | C14 | 112.7(8) | | N8 | C90 | C89 | 126.5(7) |
| C13 | C12 | C14 | 107.8(7) | | N8 | C90 | C92 | 117.5(7) |
| C11 | C15 | C17 | 112.5(7) | | C89 | C90 | C92 | 116.0(7) |
| C11 | C15 | C16 | 113.6(8) | | N8 | C93 | C94 | 121.3(6) |
| C17 | C15 | C16 | 109.8(7) | | N8 | C93 | C98 | 120.1(6) |
| C23 | C18 | C19 | 123.7(7) | | C94 | C93 | C98 | 118.5(7) |
| C23 | C18 | N2 | 117.5(7) | | C95 | C94 | C93 | 120.0(7) |
| C19 | C18 | N2 | 118.8(7) | | C95 | C94 | C99 | 118.9(7) |
| C18 | C19 | C20 | 117.6(8) | | C93 | C94 | C99 | 121.1(7) |
| C18 | C19 | C24 | 124.4(7) | | C94 | C95 | C96 | 122.3(7) |
| C20 | C19 | C24 | 117.9(7) | | C97 | C96 | C95 | 116.4(7) |
| C21 | C20 | C19 | 119.7(8) | | C98 | C97 | C96 | 123.0(8) |
| C20 | C21 | C22 | 122.6(8) | | C97 | C98 | C93 | 119.7(7) |
| C21 | C22 | C23 | 120.2(8) | | C97 | C98 | C102 | 121.3(7) |
| C18 | C23 | C22 | 116.1(7) | | C93 | C98 | C102 | 119.0(7) |
| C18 | C23 | C27 | 124.7(7) | | C101 | C99 | C100 | 110.1(7) |
| C22 | C23 | C27 | 119.1(7) | | C101 | C99 | C94 | 111.8(7) |
| C19 | C24 | C26 | 113.7(8) | | C100 | C99 | C94 | 107.5(6) |
| C19 | C24 | C25 | 111.5(7) | | C103 | C102 | C98 | 110.4(7) |
| C26 | C24 | C25 | 106.7(7) | | C103 | C102 | C104 | 111.7(8) |
| C23 | C27 | C28 | 112.1(8) | | C98 | C102 | C104 | 112.5(7) |
| C23 | C27 | C29 | 112.8(8) | | N7 | C105 | C110 | 121.4(7) |
| C28 | C27 | C29 | 110.3(8) | | N7 | C105 | C106 | 120.4(6) |
| N3 | C30 | C31 | 121.8(7) | | C110 | C105 | C106 | 118.2(7) |
| N3 | C30 | C33 | 121.5(7) | | C107 | C106 | C105 | 118.4(8) |
| C31 | C30 | C33 | 116.7(6) | | C107 | C106 | C111 | 121.0(8) |
| C30 | C31 | C32 | 127.5(7) | | C105 | C106 | C111 | 120.6(7) |
| N4 | C32 | C31 | 120.8(7) | | C108 | C107 | C106 | 123.2(9) |
| N4 | C32 | C34 | 123.2(7) | | C107 | C108 | C109 | 118.0(8) |
| C31 | C32 | C34 | 116.1(6) | | C110 | C109 | C108 | 120.0(8) |
| C36 | C35 | C40 | 124.9(8) | | C109 | C110 | C105 | 122.1(8) |
| C36 | C35 | N3 | 117.7(7) | | C109 | C110 | C114 | 118.4(7) |
| C40 | C35 | N3 | 117.4(7) | | C105 | C110 | C114 | 119.4(7) |
| C35 | C36 | C37 | 117.3(8) | | C112 | C111 | C113 | 110.9(8) |
| C35 | C36 | C41 | 123.8(8) | | C112 | C111 | C106 | 111.8(8) |

| | | | | | | | | |
|-----|-----|-----|----------|--|------|------|------|------------|
| C37 | C36 | C41 | 118.8(8) | | C113 | C111 | C106 | 108.6(7) |
| C38 | C37 | C36 | 118.8(9) | | C116 | C114 | C110 | 110.4(8) |
| C39 | C38 | C37 | 122.1(8) | | C116 | C114 | C115 | 111.0(7) |
| C38 | C39 | C40 | 123.1(8) | | C110 | C114 | C115 | 110.2(7) |
| C35 | C40 | C39 | 113.7(8) | | C1 | N1 | C6 | 117.2(6) |
| C35 | C40 | C44 | 123.8(7) | | C1 | N1 | Ga1 | 125.0(5) |
| C39 | C40 | C44 | 122.4(7) | | C6 | N1 | Ga1 | 117.2(5) |
| C36 | C41 | C42 | 111.4(7) | | C3 | N2 | C18 | 117.5(7) |
| C36 | C41 | C43 | 112.5(8) | | C3 | N2 | Ga1 | 125.6(6) |
| C42 | C41 | C43 | 110.9(8) | | C18 | N2 | Ga1 | 116.7(5) |
| C40 | C44 | C45 | 113.4(7) | | C30 | N3 | C35 | 116.2(6) |
| C40 | C44 | C46 | 112.5(8) | | C30 | N3 | Ga2 | 119.3(5) |
| C45 | C44 | C46 | 109.3(8) | | C35 | N3 | Ga2 | 123.5(5) |
| C52 | C47 | C48 | 124.6(7) | | C32 | N4 | C47 | 116.2(6) |
| C52 | C47 | N4 | 117.7(7) | | C32 | N4 | Ga2 | 120.8(5) |
| C48 | C47 | N4 | 117.7(7) | | C47 | N4 | Ga2 | 122.2(5) |
| C47 | C48 | C49 | 115.8(8) | | C59 | N5 | C64 | 120.2(7) |
| C47 | C48 | C53 | 123.8(7) | | C59 | N5 | Ga4B | 111.2(5) |
| C49 | C48 | C53 | 120.4(8) | | C64 | N5 | Ga4B | 127.1(5) |
| C50 | C49 | C48 | 120.9(8) | | C59 | N5 | Ga3A | 123.0(5) |
| C49 | C50 | C51 | 122.5(8) | | C64 | N5 | Ga3A | 116.5(5) |
| C50 | C51 | C52 | 120.0(8) | | C61 | N6 | C76 | 121.0(7) |
| C47 | C52 | C51 | 115.9(8) | | C61 | N6 | Ga4B | 110.1(6) |
| C47 | C52 | C56 | 123.7(7) | | C76 | N6 | Ga4B | 126.6(6) |
| C51 | C52 | C56 | 120.3(8) | | C61 | N6 | Ga3A | 121.4(6) |
| C48 | C53 | C54 | 112.5(7) | | C76 | N6 | Ga3A | 117.6(5) |
| C48 | C53 | C55 | 114.0(7) | | C88 | N7 | C105 | 121.1(7) |
| C54 | C53 | C55 | 109.4(7) | | C88 | N7 | Ga4A | 113.3(5) |
| C52 | C56 | C57 | 112.6(8) | | C105 | N7 | Ga4A | 124.5(5) |
| C52 | C56 | C58 | 111.8(8) | | C88 | N7 | Ga3B | 124.6(5) |
| C57 | C56 | C58 | 109.5(8) | | C105 | N7 | Ga3B | 113.9(5) |
| N5 | C59 | C60 | 125.5(8) | | C90 | N8 | C93 | 121.1(7) |
| N5 | C59 | C62 | 119.0(7) | | C90 | N8 | Ga4A | 112.5(6) |
| C60 | C59 | C62 | 115.4(8) | | C93 | N8 | Ga4A | 124.7(5) |
| C61 | C60 | C59 | 127.0(8) | | C90 | N8 | Ga3B | 122.5(6) |
| N6 | C61 | C60 | 127.0(7) | | C93 | N8 | Ga3B | 116.1(5) |
| N6 | C61 | C63 | 118.3(7) | | N2 | Ga1 | N1 | 93.6(3) |
| C60 | C61 | C63 | 114.5(8) | | N2 | Ga1 | Sb1 | 112.2(2) |
| N5 | C64 | C69 | 121.9(6) | | N1 | Ga1 | Sb1 | 114.4(2) |
| N5 | C64 | C65 | 120.3(7) | | N4 | Ga2 | N3 | 92.8(3) |
| C69 | C64 | C65 | 117.9(7) | | N4 | Ga2 | Sb1 | 110.8(2) |
| C66 | C65 | C64 | 121.4(8) | | N3 | Ga2 | Sb1 | 116.33(19) |
| C66 | C65 | C70 | 119.8(7) | | Ga2 | Sb1 | Ga1 | 95.67(3) |
| C64 | C65 | C70 | 118.7(7) | | N5 | Ga3A | N6 | 93.9(3) |
| C65 | C66 | C67 | 121.5(8) | | N5 | Ga3A | Sb2A | 113.49(18) |
| C68 | C67 | C66 | 117.7(8) | | N6 | Ga3A | Sb2A | 111.4(2) |
| C67 | C68 | C69 | 122.2(9) | | N8 | Ga4A | N7 | 95.5(3) |
| C68 | C69 | C64 | 119.3(8) | | N8 | Ga4A | Sb2A | 107.5(2) |
| C68 | C69 | C73 | 119.5(8) | | N7 | Ga4A | Sb2A | 114.16(19) |
| C64 | C69 | C73 | 121.2(7) | | Ga4A | Sb2A | Ga3A | 94.58(4) |
| C71 | C70 | C72 | 110.7(7) | | N7 | Ga3B | N8 | 91.4(3) |
| C71 | C70 | C65 | 109.9(7) | | N7 | Ga3B | Sb2B | 114.53(19) |
| C72 | C70 | C65 | 111.8(7) | | N8 | Ga3B | Sb2B | 109.73(19) |
| C69 | C73 | C75 | 111.8(8) | | N6 | Ga4B | N5 | 97.1(3) |
| C69 | C73 | C74 | 109.0(7) | | N6 | Ga4B | Sb2B | 104.8(2) |
| C75 | C73 | C74 | 109.2(8) | | N5 | Ga4B | Sb2B | 112.1(2) |
| N6 | C76 | C81 | 122.1(7) | | Ga4B | Sb2B | Ga3B | 95.14(5) |
| N6 | C76 | C77 | 119.1(7) | | | | | |

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