Supporting Information for:

Synthesis and reactivity of alkali metal aluminates bearing bis(organoamido)phosphane ligands

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Table of Contents:

1. Synthesis of prepared compounds

All air and moisture sensitive manipulations were carried out under an argon atmosphere using standard Schlenk tube technique. Solvents were dried using a Pure Solv–Innovative Technology equipment under argon gas atmosphere. Starting compounds [PhP(NH*t*Bu)N(*t*Bu)]AlMe$_2$,[23] PhP(NH*t*Bu)$_2$,[27a] *t*BuP(NH-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$[33] and Ph(O)P(NH*t*Bu)$_2$[42] were prepared according to the published procedures. Elemental analyses were performed on an LECO-CHNS-932 analyzer.

NMR spectroscopy

The NMR spectra were recorded on Bruker Avance 500 MHz spectrometer or Bruker Ultrashield 400 MHz, using 5 mm tunable broad-band probe. Appropriate chemical shifts in ^{1}H and ^{13}C NMR spectra were related to the residual signals of the solvents (C$_6$D$_6$: δ(^{1}H) = 7.16 ppm; δ(^{13}C) = 128.39 ppm, thf-d$_8$: δ(^{1}H) = 1.73 and 3.58 ppm; δ(^{13}C) = 25.37 and 67.57 ppm).

sc-XRD Crystallography

The X-ray data for crystals of **1-5**, **7**, **9**, **12-20** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoKa radiation (l = 0.71073 Å), a graphite monochromator, and the f and c scan mode. Data reductions were performed with DENZO-SMN.[S1] The absorption was corrected by integration methods.[S2] Structures were solved by direct methods (Sir92)[S3] and refined by full matrix least-square based on F^2 (SHELXL97)[S4]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors H$_{iso}$(H) = 1.2 U$_{eq}$(pivot atom) or of 1.5U$_{eq}$ for the methyl moiety with C-H = 0.96, 0.97, 0.98, and 0.93 Å for methyl, methylene, methine and hydrogen atoms in aromatic ring, respectively,

*R*int = å½*F*o2 - $F_{o,mean}$²½/å*F*o2, GOF = [å($w(F_o^2 - F_c^2)^2$)/($N_{diffrs} - N_{params}$)]^{½} for all data, $R(F)$ = å½½*F*o½ - ½*F*c½½/å½*F*o½for observed data, $wR(F^2)$ = [å($w(F_o^2 - F_c^2)^2$)/(å$w(F_o^2)^2$)]^{½} for all data.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 2247148-2247164. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

Synthesis of {[PhP(N*t*Bu)$_2$]AlMe$_2$}Li.OEt$_2$ (1) : Solution of *n*BuLi (2.8 mL, 1.6M, 4.4 mmol) in hexane was added to a stirred solution [PhP(NH*t*Bu)N(*t*Bu)]AlMe$_2$ (1.362 g, 4.4 mmol) in diethylether (10 mL) at -50 °C. The reaction mixture was slowly warmed to room temperature and stirred for additional 30 minutes. The solvent was removed by reduced pressure and the yellow oil was redissolved in hexane (5 mL). Storage at -30 °C for one day yielded yellow single crystals of **1** suitable for X-Ray diffraction analysis. Yield 1.424 g, 83 %. M. p. 60 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ = -0.69 (s, 3H, Al(C*H*$_3$)), -0.26 (s, 3H, Al(C*H*$_3$)), 0.60 (t, ^3J(^{1}H-^{1}H) = 7.0 Hz, 6H, OCH$_2$C*H*$_3$), 1.32 (s, 18H, C(C*H*$_3$)$_3$), 2.77 (q, ^3J(^{1}H-^{1}H) = 7.2 Hz, 6H, OC*H*$_2$CH$_3$), 7.00 (t, ^3J(^{1}H-^{1}H) = 7.6 Hz, 1H, *p*-Ar*H*), 7.13 (t, ^3J(^{1}H-^{1}H) = 7.6 Hz, 2H, *m*-Ar*H*), 7.93 (m, 2H, *o*-Ar*H*). ^{13}C{^{1}H} NMR (125.76 MHz, C$_6$D$_6$, 298 K): δ = -4.1, -1.7 (s broad, Al(*C*H$_3$)), 14.6 (s, OCH$_2$*C*H$_3$), 33.8 (s, C(*C*H$_3$)$_3$), 52.0 (d, ^2J(^{31}P-^{13}C) = 17.2 Hz, *C*(CH$_3$)$_3$), 65.2 (s, O*C*H$_2$CH$_3$), 128.8 (s, *p*-Ar*C*), 129.6 (d, ^2J(^{31}P-^{13}C) = 19.8 Hz, *o*-Ar*C*), 129.8 (d, ^3J(^{31}P-^{13}C) = 3.8 Hz, *m*-Ar*C*), 155.4 (d, ^1J(^{31}P-^{13}C) = 53.4 Hz, *ipso*-Ar*C*). ^{31}P{^{1}H} NMR (202.46 MHz, C$_6$D$_6$, 298 K): δ = 101.3 (s). ^{7}Li NMR (194.3 MHz, C$_6$D$_6$, 298 K): δ = -0.46 (s). Anal. Calc. for C$_{20}$H$_{39}$AlLiN$_2$OP (388.43): C 61.8, H 10.1, N 7.2; Found: C 61.7, H 10.0, N 7.2.

Synthesis of {[PhP(N*t*Bu)$_2$]AlMe$_2$}K (2): Solution of [PhP(NH*t*Bu)N(*t*Bu)]AlMe$_2$ (0.771 g, 2.5 mmol) in THF (20 mL) was added to elemental potassium (0.108 g, 2.8 mmol) at room temperature. After one hour of stirring the orange solution was filtrated from the residual potassium and the solvent was removed by reduced pressure, yielding **2** in a form of orange oil (yield 0.832 g, 96 %). The product was then redissolved in benzene (5 mL). Storage at 6 °C for one day yielded yellow single crystals suitable for X-Ray diffraction analysis. Yield of the crystalline material 0.182 g, 21 %. M. p. 158 °C with decomposition. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ = -0.71 (s, 3H, Al(C*H*$_3$)), -0.12 (s, 3H, Al(C*H*$_3$)), 1.43 (s, 18H, C(C*H*$_3$)$_3$), 6.98 (t, ^3J(^{1}H-^{1}H) = 7.0 Hz, 1H, *p*-Ar*H*), 7.14 (m, 2H, *m*-Ar*H*), 8.08 (m, 2H, *o*-Ar*H*). ^{13}C{^{1}H} NMR (125.76 MHz, C$_6$D$_6$, 298 K): δ = -2.3, 0.7 (s, Al(*C*H$_3$)), 34.4 (s, C(*C*H$_3$)$_3$), 51.7 (d, ^2J(^{31}P-^{13}C) = 17.0 Hz, *C*(CH$_3$)$_3$), 127.5 (s, *p*-Ar*C*), 128.8 (d, ^3J(^{31}P-^{13}C) = 3.1 Hz, *m*-Ar*C*), 130.0 (d, ^2J(^{31}P-^{13}C) = 19.7 Hz, *o*-Ar*C*), 160.2 (d, ^1J(^{31}P-^{13}C) = 56.8 Hz, *ipso*-ArC). ^{31}P{^{1}H} NMR (202.46 MHz, C$_6$D$_6$, 298 K): δ = 101.7 (s). Anal. Calc. for C$_{16}$H$_{29}$AlKN$_2$P (346.47): C 55.5, H 8.4, N 8.1; Found: C 55.6, H 8.6, N 8.0.

Synthesis of {[PhP(N*t*Bu)$_2$]AlH$_2$}Li.THF (3): Solution of PhP(NH*t*Bu)$_2$ (1.063 g, 4.2 mmol) in THF (10 mL) was added to a stirred suspension of LiAlH$_4$ (0.240 g, 6.3 mmol) in THF (10 mL). The stirring continued overnight and then the solvent was removed under reduced pressure. The product was extracted with toluene (20 mL) giving slightly yellow solution which was concentrated to the half of its volume. Storage at 6 °C for one day yielded colorless single crystals of **3** suitable for X-Ray diffraction analysis. Yield 0.544 g, 36 %. M. p. 132 °C with decomposition. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ = 1.16 (s broad, 4H, OCH$_2$C*H*$_2$), 1.47 (s, 18H, C(C*H*$_3$)$_3$), 3.10 (s broad, 4H, OC*H*$_2$CH$_2$), 4.76 (s broad, 2H, Al*H*$_2$), 7.08 (t, ^3J(^{1}H-^{1}H) = 7.3 Hz, 1H, *p*-Ar*H*), 7.38 (t, ^3J(^{1}H-^{1}H) = 7.5 Hz, 2H, *m*-Ar*H*), 8.22 (m, 2H, *o*-Ar*H*). ^{13}C{^{1}H} NMR (125.76 MHz, C$_6$D$_6$, 298 K): δ = 25.4 (s, OCH$_2$*C*H$_2$), 32.9 (d, ^3J(^{31}P-^{13}C) = 10.0 Hz, C(*C*H$_3$)$_3$), 52.0 (d, ^2J(^{31}P-^{13}C) = 15.5 Hz, *C*(CH$_3$)$_3$), 68.8 (s, O*C*H$_2$CH$_2$), 129.2 (s, Ar*C*), 130.0 (s, Ar*C*), 129.8 (d, ^2J(^{31}P-^{13}C) = 16.3 Hz, *o*-Ar*C*), 155.0 (d, ^1J(^{31}P-^{13}C) = 50.8 Hz, *ipso*-Ar*C*). ^{31}P{^{1}H} NMR (202.46 MHz, C$_6$D$_6$, 298 K): δ = 115.9 (s). ^{7}Li NMR (194.3 MHz, C$_6$D$_6$, 298 K): δ = 0.05 (s). Anal. Calc. for C$_{18}$H$_{33}$AlLiN$_2$OP (358.36): C 60.3, H 9.3, N 7.8; Found: C 60.4, H 9.4, N 7.7.

Synthesis of {[*t*BuP(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$]AlMe$_2$}Li.(OEt$_2$)$_2$ (4): Solution of *n*BuLi (0,94 mL, 1.6M, 1.5 mmol) in hexane was added to a stirred solution of *t*BuP(NH-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$ (0.665 g, 1.5 mmol) in hexane (10 mL) at 0 °C while stirring. The reaction mixture was slowly warmed to room temperature and a solution of AlMe$_3$ (0.75 mL, 2.0 M, 1.5 mmol) was added giving colorless suspension. The precipitate was filtrated off and redissolved in diethylether (10 mL). Storage at 6 °C for one day yielded colorless single crystals of **4** suitable for X-Ray diffraction analysis. Yield 0.432 g, 44%. M. p. 90 °C with decomposition. ^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K): δ = -0.70 (s, 3H, Al(C*H*$_3$)), -0.10 (s, 3H, Al(C*H*$_3$)), 0.85 (t, ^3J(^{1}H-^{1}H) = 6.8 Hz, 12H, OCH$_2$C*H*$_3$), 1.19 (d, ^3J(^{31}P-^{1}H) = 11.2 Hz, 9H, C(C*H*$_3$)$_3$), 1.45 (s broad, 18H, CH(C*H*$_3$)$_2$), 1.78 (s broad, 6H, CH(C*H*$_3$)$_2$), 3.00 (q, ^3J(^{1}H-^{1}H) = 6.8 Hz, 8H, OC*H*$_2$CH$_3$), 4.64 (s broad, 2H, C*H*(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (125.76 MHz, C$_6$D$_6$, 298 K): δ = -2.2, -6.0 (s broad, Al(*C*H$_3$)), 14.6 (s, OCH$_2$*C*H$_3$), 25.3 (s, CH(*C*H$_3$)$_2$), 25.7 (d, ^2J(^{31}P-^{13}C) = 19.4 Hz, C(*C*H$_3$)$_3$), 26.6 (s, CH(*C*H$_3$)$_2$), 26.8 (d, ^4J(^{31}P-^{13}C) = 7.3 Hz, *C*H(CH$_3$)$_2$), 27.1 (s, CH(*C*H$_3$)$_2$)), 27.9 (s, CH(*C*H$_3$)$_2$)), 29.2 (d, ^4J(^{31}P-^{13}C) = 18.5 Hz, *C*H(CH$_3$)$_2$), 39.2 (d, J(^{31}P-^{13}C) = 49.0 Hz, *C*(CH$_3$)$_3$), 66.2 (s, O*C*H$_2$CH$_3$), 119.9 (s, Ar*C*), 123.3 (s, Ar*C*), 124.5 (s, Ar*C*), 145.9 (d, J(^{31}P-^{13}C) = 25.6 Hz, Ar*C*), 149.2 (d, J(^{31}P-^{13}C) = 10.6 Hz, Ar*C*). ^{31}P{^{1}H} NMR (202.46 MHz, C$_6$D$_6$, 298 K): δ = 167.7. ^{7}Li NMR (194.3 MHz, C$_6$D$_6$, 298K): δ = -1.10. Anal. Calc. for C$_{38}$H$_{69}$AlLiN$_2$O$_2$P (650.86): C 70.1, H 10.7, N 4.3; Found: C 70.3, H 10.8, N 4.3.

Synthesis of {[Ph(O)P(N*t*Bu)$_2$]AlMe$_2$}Li.OEt$_2$ (5): Solution of *n*BuLi (1.4 mL, 1.6M, 2.2 mmol) in hexane was added to a stirred suspension of Ph(O)P(NH*t*Bu)$_2$ (0.602 g, 2.2 mmol) in diethylether (10 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for an additional hour.

Solution of $AlMe_3$ (1.1 mL, 2.0 M, 2.2 mmol) was added dropwise at room temperature and the reaction mixture was stirred for one additional hour. The solvent was removed under reduced pressure and the product was extracted with toluene (15 mL). The extract was concentrated to the half of its volume. Storage at -30 °C for one day yielded colorless single crystals of **5** suitable for X-Ray diffraction analysis. Yield 0.399 g, 44 %. M. p. 252 °C. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = -0.24 (s, 3H, Al(CH_3)), -0.02 (s, 3H, Al(CH_3)),0.98 (t, ^3J(^{1}H-^{1}H) = 7.0 Hz, 6H, OCH$_2$CH_3), 1.23 (s, 18H, C(CH_3)$_3$), 3.30 (q, ^3J(^{1}H-^{1}H) = 7.0 Hz, 6H, OCH_2CH$_3$), 7.14 (m, 3H, Ar*H*), 8.00 (m, 2H, *o*-Ar*H*). ^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6, 298 K): δ = -6.2, -4.5 (s broad, Al(*C*H$_3$)), 15.1 (s, OCH$_2$*C*H$_3$), 34.3 (d, ^3J(^{31}P-^{13}C) = 7.4 Hz, C(*C*H$_3$)$_3$), 51.0 (s, *C*(CH$_3$)$_3$), 66.0 (s, O*C*H$_2$CH$_3$), 128.7 (d, J(^{31}P-^{13}C) = 11.9 Hz, Ar*C*), 130.6 (s, Ar*C*), 132.8 (d, J(^{31}P-^{13}C) = 8.7 Hz, Ar*C*), 141.0 (d, ^1J(^{31}P-^{13}C) = 125.0 Hz, *ipso*-Ar*C*). ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6, 298 K): δ = 19.0 (s). ^{7}Li NMR (194.3 MHz, C_6D_6, 298 K): δ = 0.52 (s). Anal. Calc. for $C_{20}H_{39}AlLiN_2O_2P$ (404.43): C 59.4, H 9.7, N 6.9; Found: C 59.4, H 9.7, N 7.0.

Synthesis of {[Ph(S)P(N*t*Bu)$_2$]AlMe$_2$}Li (6): Solution of **1** (0.732 g, 1.9 mmol) in hexane (5 mL) was added to a stirred suspension of elemental sulfur (0.060 g, 1.9 mmol) in hexane (5 mL) at room temperature. A colorless precipitate appeared immediately, the suspension was stirred for 30 minutes. The colorless powder of **6** was filtrated off and dried in *vacuo*. Yield 0.463 g, 71 %. M. p. 205 °C. ^{1}H NMR (500 MHz, THF-d_8, 298 K): δ = -0.92 (s, 3H, Al(CH_3)), -0.86 (s, 3H, Al(CH_3)), 1.00 (s, 18H, C(CH_3)$_3$), 7.00-7.05 (m, 3H, Ar*H*), 8.22 (m, 2H, *o*-Ar*H*). ^{13}C{^{1}H} NMR (125.76 MHz, THF-d_8, 298 K): δ = -5.0 (s broad, Al(*C*H$_3$)), 33.9 (d, ^3J(^{31}P-^{13}C) = 8.3 Hz, C(*C*H$_3$)$_3$), 52.9 (s, *C*(CH$_3$)$_3$), 126.7 (d, ^3J(^{31}P-^{13}C) = 11.4 Hz, *m*-Ar*C*), 127.7 (d, ^4J(^{31}P-^{13}C) = 3.0 Hz, *p*-Ar*C*), 133.2 (d, ^2J(^{31}P-^{13}C) = 10.9 Hz, *o*-Ar*C*), 151.3 (d, ^1J(^{31}P-^{13}C) = 94.2 Hz, *ipso*-Ar*C*). ^{31}P{^{1}H} NMR (202.46 MHz, THF-d_8, 298 K): δ = 50.2 (s). ^{7}Li NMR (194.3 MHz, THF-d_8, 298 K): δ = -0.30 (s). Anal. Calc. for $C_{16}H_{29}AlLiN_2PS$ (346.38): C 55.5, H 8.4, N 8.1; Found: C 55.6, H 8.5, N 8.0.

Synthesis of {[Ph(Se)P(N*t*Bu)$_2$]AlMe$_2$}Li (7): Solution of **1** (0.609 g, 1.6 mmol) in hexane (10 mL) was added to a stirred suspension of elemental selenium (0.149 g, 1.6 mmol) in hexane (5 mL) at room temperature. The reaction mixture was heated to 60 °C for one day giving colorless suspension of **7**. The suspension was filtrated and the solid was extracted with toluene (10 mL). The solvent was removed under reduced pressure to give colorless powder of **7**. Yield 0.469 g, 76 %. X-Ray quality crystals were obtained from mixture toluene/hexane. M. p. 213 °C. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = -0.34 (s, 3H, Al(CH_3)), -0.04 (s, 3H, Al(CH_3)), 1.28 (s, 18H, C(CH_3)$_3$), 7.07-7.15 (m, 3H, Ar*H*), 8.53 (m very broad, 2H, *o*-Ar*H*). ^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6, 298 K): δ = -5.2, -4.5 (s broad, Al(*C*H$_3$)), 33.6 (d, ^3J(^{31}P-^{13}C) = 8.0 Hz, C(*C*H$_3$)$_3$), 52.9 (s, *C*(CH$_3$)$_3$), 131.7 (s, Ar*C*), 133.8 (s broad, Ar*C*), 141.9 (d, ^1J(^{31}P-^{13}C) = 87.6 Hz, *ipso*-Ar*C*). ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6, 298 K): δ = 49.9 (s, ^1J(^{77}Se-^{31}P) = 597 Hz). ^{7}Li NMR (194.3 MHz, C_6D_6, 298 K): δ = 0.90 (s). ^{77}Se NMR (95.38 MHz, C_6D_6, 298 K): δ = -64.0 (d, ^1J(^{77}Se-^{31}P) = 597 Hz). Anal. Calc. for $C_{16}H_{29}AlLiN_2PSe$ (393.27): C 48.9, H 7.4, N 7.1; Found: C 49.0, H 7.4, N 7.0.

Synthesis of {[Ph(Te)P(N*t*Bu)$_2$]AlMe$_2$}Li (8): Solution of **1** (0.599 g, 1.5 mmol) in toluene (10 mL) was added to a stirred suspension of elemental tellurium (0.236 g, 1.9 mmol) in toluene (5 mL) at room temperature. The reaction mixture was heated to 95 °C for three hours giving colorless solution. The solution was filtrated from the residual tellurium and concentrated to a third of its volume and overlayered with a little amount of hexane (1 mL). Storage at -30 °C for one day yielded colorless crystals of **8**. Yield 0.327 g, 48 %. M. p. 145 °C with decomposition. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = -0.35 (s, 3H, Al(CH_3)), -0.04 (s, 3H, Al(CH_3)), 1.28 (s, 18H, C(CH_3)$_3$), 7.03-7.15 (m, 3H, Ar*H*), 8.49 (m very broad, 2H, *o*-Ar*H*). ^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6, 298 K): δ = -4.8, -4.1 (s broad, Al(*C*H$_3$)), 33.4 (d, ^3J(^{31}P-^{13}C) = 7.8 Hz, C(*C*H$_3$)$_3$), 53.4 (d, ^2J(^{31}P-^{13}C) = 2.0 Hz,*C*(CH$_3$)$_3$), 132.0 (s, Ar*C*), 141.6 (d, ^1J(^{31}P-^{13}C) = 50.9 Hz, *ipso*-Ar*C*), *o,m*-Ar*C* not observed. ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6,

298 K): δ = 10.2 (s, $^{1}J(^{125}\text{Te-}^{31}\text{P})$ = 1501 Hz). ^{7}Li NMR (194.3 MHz, C_6D_6, 298 K): δ = 0.11 (s). ^{125}Te NMR (157.8 MHz, C_6D_6, 298 K): δ = -250.0 (d, $^{1}J(^{125}\text{Te-}^{31}\text{P})$ = 1501 Hz). Anal. Calc. for $C_{16}H_{29}AlLiN_2PTe$ (441.91): C 43.5, H 6.6, N; Found: C 43.6, H 6.7.

Synthesis of Bu_4N^+ {[Ph(Te)P(N*t*Bu)$_2$]AlMe$_2$}$^-$ (9): Solution of Bu_4NBr (0.387 g, 1.2 mmol) in THF (20 mL) was added to a solution of **8** (0.530 g, 1.2 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred for one week at room temperature giving yellow solution. The solvent was removed under reduced pressure and the product was extracted with three portions of toluene (3x30 mL). The extracts were combined and the solvent was removed under reduced pressure giving yellow powder of **9**. Yield 0.666 g, 82 %. X-Ray quality crystals were obtained from toluene. M. p. 147 °C. ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ = -0.84 (s, 3H, Al(CH_3)), -0.79 (s, 3H, Al(CH_3)), 1.00 (q, $^{3}J(^{1}\text{H-}^{1}\text{H})$ = 7.3 Hz, 12H, $CH_2CH_2CH_2CH_3$), 1.10 (s, 18H, C(CH_3)$_3$), 1.43 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.76 (m, 8H, $CH_2CH_2CH_2CH_3$), 3.44 (m, 8H, $CH_2CH_2CH_2CH_3$), 7.07-7.15 (m, 3H, Ar*H*), 8.31 (m, 2H, *o*-Ar*H*). ^{13}C{^{1}H} NMR (125.76 MHz, C_6D_6, 298 K): δ = -5.2, -3.3 (s, Al(CH_3)$_3$), 14.3 (s, $CH_2CH_2CH_2CH_3$), 20.8 (s, $CH_2CH_2CH_2CH_3$), 25.1 (s, $CH_2CH_2CH_2CH_3$), 33.7 (d, $^{3}J(^{31}\text{P-}^{13}\text{C})$ = 7.9 Hz, C(CH_3)$_3$), 52.3 (s, C(CH_3)$_3$), 59.7 (s, $CH_2CH_2CH_2CH_3$), 126.5 (d, $J(^{31}\text{P-}^{13}\text{C})$ = 11.1 Hz, Ar*C*), 128.8 (d, $J(^{31}\text{P-}^{13}\text{C})$ = 2.7 Hz, Ar*C*), 133.2 (s broad, Ar*C*), 151.2 (d, $^{1}J(^{31}\text{P-}^{13}\text{C})$ = 56.7 Hz, *ipso*-Ar*C*). ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6, 298 K): δ = 0.6 ($^{1}J(^{127}\text{Te-}^{31}\text{P})$ = 1502.0 Hz). ^{125}Te NMR (157.8 MHz, C_6D_6, 298 K): δ = -401.8 (d, $^{1}J(^{125}\text{Te-}^{31}\text{P})$ = 1626 Hz). Anal. Calc. for $C_{32}H_{65}AlN_3PTe$ (677.43): C 43.5, H 6.6, N 6.2; Found: C 43.6, H 6.7, N 6.2.

General procedure for Synthesis of compounds 10, 11 and 14-18: Solution of **1** in hexane was added to a stirred solution of the appropriate halide (GX) in hexane at room temperature. A precipitate of LiX was formed immediately. The reaction mixture was stirred for one day and then it was filtrated to give colorless solution. The solution was dried in *vacuo* to yield compounds **10**, **11** and **14-18** as colorless solids. Compounds **14-18** were recrystallized in hexane to obtain single crystals suitable for X-Ray diffraction analysis.

[Ph(Me)P(N*t*Bu)$_2$]AlMe$_2$ (10): **1**: (0.632 g, 1.6 mmol), hexane (10 mL); CH_3I: (0.231 g, 0.1 mL, 1.6 mmol), hexane (5 mL). Yield 0.498 g, 95 %. M. p. 106 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.13, -0.04 (s, 3H, Al(CH_3)), 1.03 (s, 18H, C(CH_3)$_3$), 1.52 (d, $^{2}J(^{31}\text{P-}^{1}\text{H})$ = 13.1 Hz, 3H, PCH_3), 7.02 (m, 3H, Ar*H*), 7.56 (s broad, 2H, *o*-Ar*H*) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ = -5.1 (s broad, Al(CH_3)), 18.8 (d, $^{1}J(^{31}\text{P-}^{13}\text{C})$ = 61.9 Hz, PCH_3), 34.0 (d, $^{3}J(^{31}\text{P-}^{13}\text{C})$ = 7.3 Hz, C(CH_3)$_3$), 51.1 (s, $C(CH_3)_3$), 128.9 (d, $J(^{31}\text{P-}^{13}\text{C})$ = 11.5 Hz, Ar*C*), 131.1 (s broad, Ar*C*), 131.8 (d, $J(^{31}\text{P-}^{13}\text{C})$ = 2.8 Hz, Ar*C*), 138.7 (d, $^{1}J(^{31}\text{P-}^{13}\text{C})$ = 86.7 Hz, *ipso*-Ar*C*) ppm. ^{31}P NMR (161.97 MHz, C_6D_6, 298 K): δ = 27.8 (q, $^{2}J_{PH}$ = 13.1 Hz) ppm. Anal. calcd. for $C_{17}H_{32}AlN_2P$ (322.40): C 63.3, H 10.0, N, 8.7; found C 63.3, H 10.0, N 8.8.

[Ph(Me$_3$Si)P(N*t*Bu)$_2$]AlMe$_2$ (11): **1**: (0.667 g, 1.7 mmol), hexane (10 mL); Me_3SiCl: (0.187 g, 0.22 mL, 1.7 mmol), hexane (5 mL). Yield 0.614 g, 94 %. M. p. 158 °C with decomposition. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.11, -0.03 (s, 3H, Al(CH_3)), 0.43 (d, $^{3}J(^{31}\text{P-}^{1}\text{H})$ = 6.6 Hz, 9H, Si(CH_3)$_3$), 1.10 (s, 18H, C(CH_3)$_3$), 7.08 (m, 3H, Ar*H*), 7.79 (m, 2H, *o*-Ar*H*) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ = -5.3, -2.4 (s broad, Al(CH_3)), 0.9 (d, $^{2}J(^{31}\text{P-}^{13}\text{C})$ = 11.9 Hz, Si(CH_3)$_2$), 34.9 (d, $^{3}J(^{31}\text{P-}^{13}\text{C})$ = 7.0 Hz, C(CH_3)$_3$), 51.2 (s, $C(CH_3)_3$), 129.2 (d, $J(^{31}\text{P-}^{13}\text{C})$ = 10.3 Hz, Ar*C*), 130.6 (d, $J(^{31}\text{P-}^{13}\text{C})$ = 12.4 Hz, Ar*C*), 131.9 (d, $J(^{31}\text{P-}^{13}\text{C})$ = 2.7 Hz, Ar*C*), 142.4 (d, $^{1}J(^{31}\text{P-}^{13}\text{C})$ = 46.1 Hz, *ipso*-Ar*C*) ppm. ^{31}P NMR (161.97 MHz, C_6D_6, 298 K): δ = 36.3 (s, $^{1}J(^{31}\text{P-}^{29}\text{Si})$ = 96.7 Hz) ppm. ^{29}Si NMR (99.33MHz, C_6D_6, 298 K): δ = -6.2 (d, $^{1}J(^{31}\text{P-}^{29}\text{Si})$ = 96.7 Hz) ppm. Anal. calcd. for $C_{19}H_{38}AlN_2PSi$ (380.56): C 60.0, H 10.1, N 7.4; found C 60.2, H 10.2, N 7.4.

{Ph[2,6-*i*Pr$_2$-C$_6$H$_3$(H)N(Ph)P]P(N*t*Bu)$_2$}AlMe$_2$ (14): 1: (0.834 g, 2.1 mmol), hexane (10 mL); PhP(Cl)N(H)Dipp: (0.687 g, 2.1 mmol), hexane (20 mL). Yield 0.584 g, 46 % (after recrystallization). M. p. 158 °C with decomposition. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ = -0.19, -0.06 (s, 3H, Al(CH_3)), 0.94 (d, ^3J(^{1}H-^{1}H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.04 (s, 9H, C(CH_3)$_3$), 1.13 (d, ^3J(^{1}H-^{1}H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.19 (s, 9H, C(CH_3)$_3$), 2.99 (sept, ^3J(^{1}H-^{1}H) = 6.8 Hz, 2H, CH(CH$_3$)$_2$), 4.41 (dd, ^2J(^{31}P-^{1}H) = 9.1 Hz, ^3J(^{31}P-^{1}H) = 6.8 Hz, 1H, NH), 6.87 (m, 2H, ArH), 6.93 (m, 1H ArH), 7.09 (m, 3H, ArH), 7.16 (m, 1H, ArH), 7.39 (m, 2H, ArH), 7.96 (m, 2H, *o*-ArH), 8.15 (m, 2H, *o*-ArH) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 298 K): δ = -4.6, -3.8 (s broad, Al(*C*H$_3$)), 23.8 (s, CH(*C*H$_3$)$_2$), 25.0 (d, J(^{31}P-^{13}C) = 2.9 Hz, CH(*C*H$_3$)$_2$), 29.3 (d, J(^{31}P-^{13}C) = 6.3 Hz, *C*H(CH$_3$)$_2$), 34.4 (dd, J(^{31}P-^{13}C) = 6.1 Hz, J(^{31}P-^{13}C) = 5.9 Hz, C(*C*H$_3$)$_3$), 34.6 (d, J(^{31}P-^{13}C) = 7.2 Hz, C(*C*H$_3$)$_3$), 50.8 (s, *C*(CH$_3$)$_3$), 52.4 (s, *C*(CH$_3$)$_3$), 124.4 (s, Ar*C*), 124.8 (s, Ar*C*), 129.2 (d, J(^{31}P-^{13}C) = 10.2 Hz, Ar*C*), 129.5 (d, J(^{31}P-^{13}C) = 3.3 Hz, Ar*C*), 129.6 (dd, J(^{31}P-^{13}C) = 5.4 Hz, J(^{31}P-^{13}C) = 2.7 Hz, Ar*C*), 130.7 (dd, J(^{31}P-^{13}C) = 16.1 Hz, J(^{31}P-^{13}C) = 4.2 Hz, Ar*C*), 132.1 (d, J(^{31}P-^{13}C) = 2.2 Hz, Ar*C*), 132.5 (dd, J(^{31}P-^{13}C) = 9.9 Hz, J(^{31}P-^{13}C) = 7.3 Hz, Ar*C*), 135.6 (dd, J(^{31}P-^{13}C) = 15.4 Hz, J(^{31}P-^{13}C) = 1.5 Hz, Ar*C*), 139.0 (dd, ^1J(^{31}P-^{13}C) = 55.4 Hz, ^2J(^{31}P-^{13}C) = 18.0 Hz, *ipso-Ph*P(N*t*Bu)$_2$), 140.0 (dd, ^nJ(^{31}P-^{13}C) = 14.6 Hz, J(^{31}P-^{13}C) = 1.4 Hz, Ar*C*), 141.4 (dd, J(^{31}P-^{13}C) = 3.0 Hz, J(^{31}P-^{13}C) = 1.5 Hz, Ar*C*) ppm. ^{31}P NMR (161.97 MHz, C$_6$D$_6$, 298 K): δ = 28.8 (d, ^1J(^{31}P-^{31}P) = 350 Hz), 42.6 (d, ^1J(^{31}P-^{31}P) = 350 Hz) ppm. Anal. calcd. for C$_{34}$H$_{52}$AlN$_3$P$_2$ (591.73): C 69.0, H 8.9, N 7.1; found C 69.1, H 9.0, 7.0.

[Ph(Ph$_2$P)P(N*t*Bu)$_2$]AlMe$_2$ (15): 1: (0.722 g, 1.9 mmol), hexane (10 mL); Ph$_2$PCl: (0.410 g, 0.33 mL, 1.9 mmol), hexane (5 mL). Yield 0.833 g, 91 %. M. p. 126 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ = -0.06 (d, ^3J(^{31}P-^{1}H) = 1.2 Hz, 3H, Al(CH_3)), -0.04 (d, ^3J(^{31}P-^{1}H) = 1.2 Hz, 3H, Al(CH_3)), 0.98 (s, 18H, C(CH_3)$_3$), 7.03 (m, 2H, ArH), 7.07-7.15 (m, 7H, ArH), 7.80 (m, 4H, *o*-ArH), 8.57 (m, 2H, *o*-ArH) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 298 K): δ = -5.8, -4.0 (s broad, Al(*C*H$_3$)), 34.2 (dd, ^3J(^{31}P-^{13}C) = 6.8 Hz, ^4J(^{31}P-^{13}C) = 1.8 Hz, C(*C*H$_3$)$_3$), 51.8 (s, *C*(CH$_3$)$_3$), 129.0 (d, J(^{31}P-^{13}C) = 9.6 Hz, Ar*C*), 129.5 (d, J(^{31}P-^{13}C) = 7.4 Hz, Ar*C*), 130.0 (s, Ar*C*), 131.9 (dd, ^1J(^{31}P-^{13}C) = 14.9 Hz, ^2J(^{31}P-^{13}C) = 4.4 Hz, *ipso-Ph*$_2$P), 132.4 (s, Ar*C*), 133.1 (dd, J(^{31}P-^{13}C) = 12.8 Hz, J(^{31}P-^{13}C) = 9.1 Hz, *ipso-Ph*$_2$P), 136.1 (dd, J(^{31}P-^{13}C) = 19.0 Hz, J(^{31}P-^{13}C) = 7.0 Hz, Ar*C*), 139.9 (dd, ^1J(^{31}P-^{13}C) = 66.1 Hz, ^2J(^{31}P-^{13}C) = 28.6 Hz, *ipso*-P(*Ph*)(N*t*Bu)$_2$) ppm. ^{31}P NMR (161.97 MHz, C$_6$D$_6$, 298 K): δ = -23.0 (d, ^1J(^{31}P-^{31}P) = 315.8 Hz, Ph$_2$*P*), 38.3 (d, ^1J(^{31}P-^{31}P) = 315.8 Hz, *P*(N*t*Bu)$_2$) ppm. Anal. calcd. for C$_{28}$H$_{39}$AlN$_2$P$_2$ (492.55): C 68.3, H 8.0, N 5.9; found C 68.4, H 8.0, N, 6.0.

{Ph[Ph(Cl)P]P(N*t*Bu)$_2$}AlMe$_2$ (16): 1: (0.783 g, 2.0 mmol), hexane (10 mL); *t*BuPCl$_2$: (0.361 g, 0.27 mL, 2.0 mmol), hexane (5 mL). Yield 0.863 g, 95 %. M. p. 117 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ = -0.59, -0.08 (s, 3H, Al(CH_3)), 1.09 (s, 9H, C(CH_3)$_3$), 1.12 (s, 9H, C(CH_3)$_3$), 7.01 (m, 3H, ArH), 7.10 (m, 1H, ArH), 7.20 (m, 2H, ArH), 7.91 (m, 2H, *o*-ArH), 8.10 (m, 2H, *o*-ArH) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C$_6$D$_6$, 298 K): δ = -5.9, -3.7 (s broad, Al(*C*H$_3$)), 34.4 (dd, ^3J(^{31}P-^{13}C) = 5.9 Hz, ^4J(^{31}P-^{13}C) = 5.9 Hz, C(*C*H$_3$)$_3$), 34.8 (d, ^3J(^{31}P-^{13}C) = 7.3 Hz, C(*C*H$_3$)$_3$), 51.6 (s, *C*(CH$_3$)$_3$), 52.1 (s, *C*(CH$_3$)$_3$), 129.2 (d, J(^{31}P-^{13}C) = 10.9 Hz, Ar*C*), 129.2 (dd, J(^{31}P-^{13}C) = 6.2 Hz, J(^{31}P-^{13}C) = 2.4 Hz, Ar*C*), 130.8 (d, J(^{31}P-^{13}C) = 2.8 Hz, Ar*C*), 132.7 (dd, J(^{31}P-^{13}C) = 9.8 Hz, J(^{31}P-^{13}C) = 7.5 Hz, Ar*C*), 132.8 (s, Ar*C*), 132.9 (dd, ^1J(^{31}P-^{13}C) = 20.3 Hz, ^2J(^{31}P-^{13}C) = 4.9 Hz, Ar*C*), 136.7 (dd, ^1J(^{31}P-^{13}C) = 61.6 Hz, ^2J(^{31}P-^{13}C) = 20.0 Hz, *ipso*-Ar*C*) ppm. ^{31}P NMR (161.97 MHz, C$_6$D$_6$, 298 K): δ = 40.1 (d, ^1J(^{31}P-^{31}P) = 337 Hz, *P*(N*t*Bu)$_2$), 58.9 (d, ^1J(^{31}P-^{31}P) = 337 Hz, *P*Ph) ppm. Anal. calcd. for C$_{22}$H$_{34}$AlClN$_2$P$_2$ (450.90): C 58.6, H 7.6, N 6.2; found C 58.7, H 7.7, N 6.2.

{Ph[*t*Bu(Cl)P]P(N*t*Bu)$_2$}AlMe$_2$ (17): 1: (0.560 g, 1.4 mmol), hexane (10 mL); *t*BuPCl$_2$: (1.44 mL, 1.4 mmol, 1 M solution in Et$_2$O), hexane (5 mL). Yield 0.559 g, 90 %. M. p. 117 °C. ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ = -0.15, -0.01 (s, 3H, Al(CH_3)), 1.07 (s, 9H, NC(CH_3)$_3$), 1.26 (s, 9H, NC(CH_3)$_3$), 1.47 (d, ^3J(^{31}P-^{1}H) = 14.1 Hz, 9H, PC(CH_3)$_3$), 6.99 (m, 3H, ArH), 8.12 (m, 2H, *o*-ArH) ppm. ^{13}C{^{1}H} NMR

(100.61 MHz, C_6D_6, 298 K): δ = -5.0, -3.3 (s broad, Al(*C*H$_3$)), 29.5 (dd, ^2J(^{31}P-^{13}C) = 14.6 Hz, ^3J(^{31}P-^{13}C) = 5.0 Hz, PC(*C*H$_3$)$_3$), 34.4 (dd, ^3J(^{31}P-^{13}C) = 5.8 Hz, ^4J(^{31}P-^{13}C) = 5.7 Hz, NC(*C*H$_3$)$_3$), 35.1 (d, ^3J(^{31}P-^{13}C) = 6.9 Hz, NC(*C*H$_3$)$_3$), 38.7 (dd, ^1J(^{31}P-^{13}C) = 41.6 Hz, ^2J(^{31}P-^{13}C) = 5.0 Hz, P*C*(CH$_3$)$_3$), 52.1 (d, ^2J(^{31}P-^{13}C) = 10.2 Hz, N*C*(CH$_3$)$_3$), 128.8 (d, J(^{31}P-^{13}C) = 10.6 Hz, Ar*C*), 132.7 (d, J(^{31}P-^{13}C) = 2.5 Hz, Ar*C*), 132.9 (dd, J(^{31}P-^{13}C) = 9.5 Hz, J(^{31}P-^{13}C) = 8.3 Hz, Ar*C*), 137.6 (dd, ^1J(^{31}P-^{13}C) = 57.5 Hz, ^2J(^{31}P-^{13}C) = 18.4 Hz, *ipso*-Ar*C*) ppm. ^{31}P NMR (161.97 MHz, C_6D_6, 298 K): δ = 38.0 (d, ^1J(^{31}P-^{31}P) = 371 Hz, *P*(N*t*Bu)$_2$), 92.1 (d, ^1J(^{31}P-^{31}P) = 371 Hz, *Pt*Bu) ppm. Anal. calcd. for $C_{20}H_{38}AlClN_2P_2$ (430.91): C 55.8, H 8.9, N 6.5; found C 55.8, H 9.0, N 6.5.

{Ph[Me$_2$(Cl)Si]P(N*t*Bu)$_2$}AlMe$_2$ (18): 1: (0.681 g, 1.8 mmol), hexane (10 mL); Me_2SiCl_2: (0.226 g, 0.21 mL, 1.8 mmol), hexane (5 mL). Yield 0.654 g, 93 %. M. p. 138 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.16, -0.02 (s, 3H, Al(C*H*$_3$)), 0.74 (d, ^3J(^{31}P-^{1}H) = 5.1 Hz, 6H, Si(C*H*$_3$)$_2$), 1.12 (s, 18H, C(C*H*$_3$)$_3$), 7.05 (m, 3H, Ar*H*), 7.56 (m, 2H, *o*-Ar*H*) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ = -5.6, -2.6 (s broad, Al(*C*H$_3$)), 3.6 (d, ^2J(^{31}P-^{13}C) = 15.4 Hz, ^1J(^{29}Si-^{13}C) = 54.5 Hz, Si(*C*H$_3$)$_2$), 34.9 (d, ^3J(^{31}P-^{13}C) = 7.0 Hz, C(*C*H$_3$)$_3$), 51.6 (s, *C*(CH$_3$)$_3$), 129.3 (d, J(^{31}P-^{13}C) = 11.3 Hz, Ar*C*), 130.8 (d, J(^{31}P-^{13}C) = 12.3 Hz, Ar*C*), 132.5 (d, J(^{31}P-^{13}C) = 3.2 Hz, Ar*C*), 139.9 (d, ^1J(^{31}P-^{13}C) = 55.8 Hz, *ipso*-Ar*C*) ppm. ^{31}P NMR (161.97 MHz, C_6D_6, 298 K): δ = 29.3 (s, ^1J(^{31}P-^{29}Si) = 117.6 Hz) ppm. ^{29}Si NMR (99.33MHz, C_6D_6, 298 K): δ = 15.1 (d, ^1J(^{31}P-^{29}Si) = 117.6 Hz) ppm. Anal. calcd. for $C_{18}H_{35}AlClN_2PSi$ (400.98): C 53.9, H 8.8, N 7.0; found C 54.0, H 8.9, N 6.9.

[Ph(Ph$_3$Sn)P(N*t*Bu)$_2$]AlMe$_2$ (12): Solution of **1** (0.562 g, 1.4 mmol) in toluene (5 mL) was added to a stirred solution of Ph_3SnCl (0.558 g, 1.4 mmol) in toluene (10 mL) at room temperature. The reaction mixture was stirred for one day and then it was filtrated to give colorless solution. The solution was dried in *vacuo* to yield compound **12** as colorless solid. X-Ray quality crystals were obtained from diethylether solution. Yield 0.618 g, 65 % (after recrystallization). M. p. 172 °C. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.06, 0.09 (s, 3H, Al(C*H*$_3$)), 1.06 (d, ^4J(^{31}P-^{1}H) = 1.2 Hz, 18H, C(C*H*$_3$)$_3$), 7.01 (m, 1H, Ar*H*), 7.07 (m, 2H, Ar*H*), 7.13 (m, 3H, Ar*H*), 7.20 (m, 6H, Ar*H*), 7.86 (d, ^3J(^{1}H-^{1}H) = 6.7 Hz, ^3J(Sn-^{1}H) = 47.6 Hz, 6H, *o*-C$_6$*H*$_5$Sn), 8.26 (m, 2H, *o*-C$_6$*H*$_5$) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ = -5.0, -3.1 (s broad, Al(*C*H$_3$)), 34.6 (d, ^3J(^{31}P-^{13}C) = 7.5 Hz, C(*C*H$_3$)$_3$), 51.8 (s, *C*(CH$_3$)$_3$), 129.4 (d, J(^{31}P-^{13}C) = 11.5 Hz, Ar*C*), 129.4 (s, Ar*C*), 129.6 (s, Ar*C*), 129.8 (s, Ar*C*), 130.1 (s, ^3J(Sn-^{13}C) = 11.3 Hz, *m*-*C*$_6$H$_5$Sn),130.6 (d, J(^{31}P-^{13}C) = 14.6 Hz, Ar*C*), 132.6 (d, J(^{31}P-^{13}C) = 13.2 Hz, Ar*C*), 132.4 (d, J(^{31}P-^{13}C) = 2.8 Hz, Ar*C*), 138.4 (d, ^3J(^{31}P-^{13}C) = 1.4 Hz, ^2J(Sn-^{13}C) = 34.6 Hz, Ar*C*), 140.1 (d, ^2J(^{31}P-^{13}C) = 13.7 Hz, ^1J(^{119}Sn-^{13}C) = 448 Hz, ^1J(^{117}Sn-^{13}C) = 422 Hz, *ipso*-*C*$_6$H$_5$Sn), 145.0 (d, ^1J(^{31}P-^{13}C) = 41.1 Hz, ^2J(^{119}Sn-^{13}C) = 221 Hz, ^2J(^{117}Sn-^{13}C) = 140 Hz, *ipso*-*C*$_6$H$_5$P) ppm. ^{31}P NMR (161.97 MHz, C_6D_6, 298 K): δ = 45.6 (s, ^1J(Sn-^{31}P) = 506 Hz) ppm. ^{119}Sn{^{1}H} NMR (186.4 MHz, C_6D_6, 298 K): δ = -200.1 (d, ^1J(^{119}Sn-^{31}P) = 506 Hz) ppm. Anal. calcd. for $C_{34}H_{44}AlN_2PSn$ (611.32): C 62.1, H 6.8, N 4.4; found C 62.2, H 6.9, N 4.4.

[Ph(Me$_3$Pb)P(N*t*Bu)$_2$]AlMe$_2$ (13): Solution of **1** (0.384 g, 1.0 mmol) in THF (5 mL) was added to a stirred solution of Me_3PbBr (0.328 g, 1.0 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred for one day and the volatiles were removed in *vacuo*. The solid was extracted with diethylether. The volatiles were removed in *vacuo* to yield compound **13** as colorless solid. X-Ray quality crystals were obtained from diethylether solution. Yield 0.509 g, 92 %. M. p. 170 °C with decomposition. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.15, -0.01 (s, 3H, Al(C*H*$_3$)), 1.09 (s, 18H, C(C*H*$_3$)$_3$), 1.10 (d, ^3J(^{31}P-^{1}H) = 3.4 Hz, ^2J(^{207}Pb-^{1}H) = 50.5 Hz, 9H, Pb(C*H*$_3$)$_3$), 7.07 (m, 3H, Ar*H*), 7.75 (m, 2H, *o*-Ar*H*) ppm. ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_6, 298 K): δ = -5.7, -4.8 (s broad, Al(*C*H$_3$)), 3.7 (d, ^2J(^{31}P-^{13}C) = 13.0 Hz, ^1J(^{207}Pb-^{13}C) = 143.8 Hz, Pb(*C*H$_3$)$_2$), 34.4 (d, ^3J(^{31}P-^{13}C) = 7.3 Hz, ^4J(^{207}Pb-^{13}C) = 7.2 Hz, C(*C*H$_3$)$_3$), 51.4 (s, *C*(CH$_3$)$_3$), 129.4 (d, J(^{31}P-^{13}C) = 11.0 Hz, Ar*C*), 130.5 (d, J(^{31}P-^{13}C) = 15.0 Hz, Ar*C*), 132.1 (d, J(^{31}P-^{13}C) = 2.7 Hz, Ar*C*), 145.1 (d, ^1J(^{31}P-^{13}C) = 25.6 Hz, *ipso*-Ar*C*) ppm. ^{31}P

NMR (161.97 MHz, C_6D_6, 298 K): δ = 47.1 (s, $^1J(^{207}Pb\text{-}^{31}P)$ = 290.0 Hz) ppm. ^{207}Pb NMR (104.61 MHz, C_6D_6, 298 K): δ = -106.4 (d-dc, $^1J(^{207}Pb\text{-}^{31}P)$ = 290.0 Hz, $^2J(^{207}Pb\text{-}^{1}H)$ = 50.5 Hz) ppm. Anal. calcd. for $C_{19}H_{38}AlN_2PPb$ (559.67): C 40.8, H 6.8, N 4.6; found C 40.9, H 6.9, N 4.6.

{Ph[Me$_2$(Cl)Ge]P(N*t*Bu)$_2$}AlMe$_2$ (19): Solution of **1** (0.449 g, 1.2 mmol) in toluene (5 mL) was added to a stirred solution of Me_2GeCl_2 (0.201 g, 0.13 mL, 1.2 mmol) in toluene (10 mL) at room temperature. The reaction mixture was stirred for one day and then it was filtrated to give colorless solution. The solution was dried in *vacuo* to yield compound **19** as colorless solid. X-Ray quality crystals were obtained from diethylether solution. Yield 0.469 g, 91 %. M. p. 244 °C. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = -0.17, -0.03 (s, 3H, Al(CH_3)), 0.96 (t, $^3J(^{31}P\text{-}^{1}H)$ = 4.4 Hz, 6H, Sn(CH_3)$_2$), 1.10 (s, 18H, C(CH_3)$_3$), 7.02 (m, 3H, Ar*H*), 7.95 (m, 3H, *o*-Ar*H*) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298 K): δ = -6.3, -4.1 (s broad, Al(*C*H$_3$)), 6.3 (d, $^2J(^{31}P\text{-}^{13}C)$ = 13.7 Hz, Si(*C*H$_3$)$_2$), 34.7 (d, $^3J(^{31}P\text{-}^{13}C)$ = 7.2 Hz, C(*C*H$_3$)$_3$), 51.7 (s, *C*(CH$_3$)$_3$), 129.5 (d, $J(^{31}P\text{-}^{13}C)$ = 12.0 Hz, Ar*C*), 130.8 (d, $J(^{31}P\text{-}^{13}C)$ = 12.8 Hz, Ar*C*), 132.8 (d, $J(^{31}P\text{-}^{13}C)$ = 2.8 Hz, Ar*C*), 139.7 (d, $^1J(^{31}P\text{-}^{13}C)$ = 57.1 Hz, *ipso*-Ar*C*) ppm. ^{31}P NMR (161.97 MHz, C_6D_6, 298 K): δ = 34.7 (s) ppm. Anal. calcd. for $C_{18}H_{35}AlClGeN_2P$ (445.53): C 48.5, H 7.9, N 6.3; found C 48.5, H 7.9, N 6.3.

{**[PhP(N*t*Bu)$_2$]AlMe$_2$}$_2$SnMe$_2$ (20):** Solution of **1** (0.489 g, 1.3 mmol) in toluene (5 mL) was added to a stirred solution of Me_2SnCl_2 (0.385 g, 1.3 mmol) in toluene (10 mL) at room temperature. The reaction mixture was stirred for one day and then it was filtrated to give colorless solution. The solution was dried in *vacuo* to yield compound **20** as colorless solid. X-Ray quality crystals were obtained from diethylether solution. Yield 0.770 g, 93 %. M. p. 126 °C with decomposition. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = -0.05, -0.03 (s, 6H, Al(CH_3)), 1.10 (s, 36H, C(CH_3)$_3$), 1.12 (t, $^3J(^{31}P\text{-}^{1}H)$ = 4.2 Hz, 6H, Sn(CH_3)$_2$), 7.04 (m, 6H, Ar*H*), 7.90 (m, 4H, *o*-Ar*H*) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, C_6D_6, 298 K): δ = -4.7, -3.1 (s broad, Al(*C*H$_3$)), -0.4 (t, $^2J(^{31}P\text{-}^{13}C)$ = 12.0 Hz, $^1J(^{119}Sn\text{-}^{13}C)$ = 218 Hz, $^1J(^{117}Sn\text{-}^{13}C)$ = 209 Hz, Sn(*C*H$_3$)$_2$), 34.5 (d, $^3J(^{31}P\text{-}^{13}C)$ = 4.1 Hz, C(*C*H$_3$)$_3$), 34.6 (d, $^3J(^{31}P\text{-}^{13}C)$ = 4.0 Hz, C(*C*H$_3$)$_3$), 51.2 (s, $^3J(Sn\text{-}^{13}C)$ = 7.0 Hz, *C*(CH$_3$)$_3$), 129.2 (m, Ar*C*), 131.3 (m, Ar*C*), 132.8 (s, Ar*C*), 141.6 (d, $^1J(^{31}P\text{-}^{13}C)$ = 36.9 Hz, $^2J(^{119}Sn\text{-}^{13}C)$ = 216 Hz, $^2J(^{117}Sn\text{-}^{13}C)$ = 139 Hz, *ipso*-Ar*C*) ppm. ^{31}P NMR (161.97 MHz, C_6D_6, 298 K): δ = 52.9 (s, $^1J(Sn\text{-}^{31}P)$ = 200 Hz) ppm. $^{119}Sn\{^1H\}$ NMR (186.4 MHz, C_6D_6, 298 K): δ = -131.1 (d, $^1J(Sn\text{-}^{31}P)$ = 200 Hz) ppm. Anal. calcd. for $C_{34}H_{44}AlN_2PSn$ (657.39): C 62.1, H 6.8; found C 62.2, H 6.9.

2. NMR spectra of prepared compounds

Spectroscopic characterization of {[PhP(N*t*Bu)$_2$]AlMe$_2$}Li.OEt$_2$ (1)

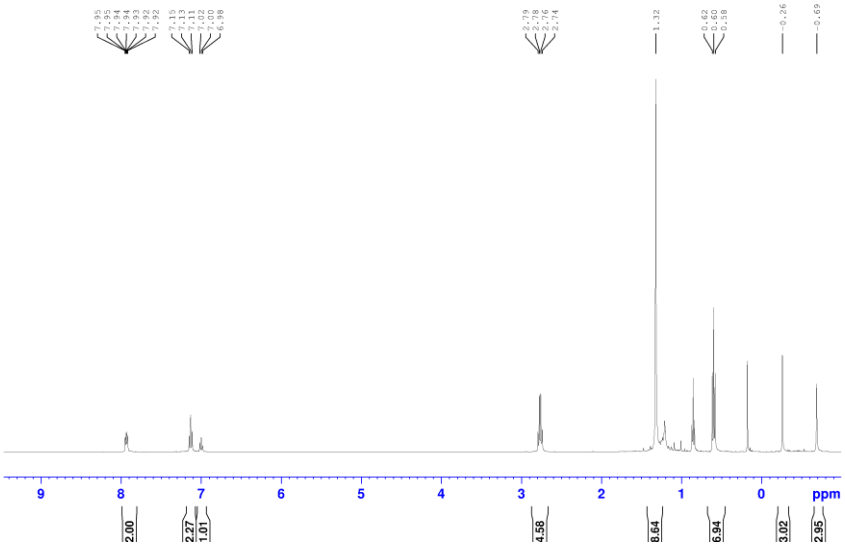


Fig. S1. ^{1}H NMR spectrum of **1**.

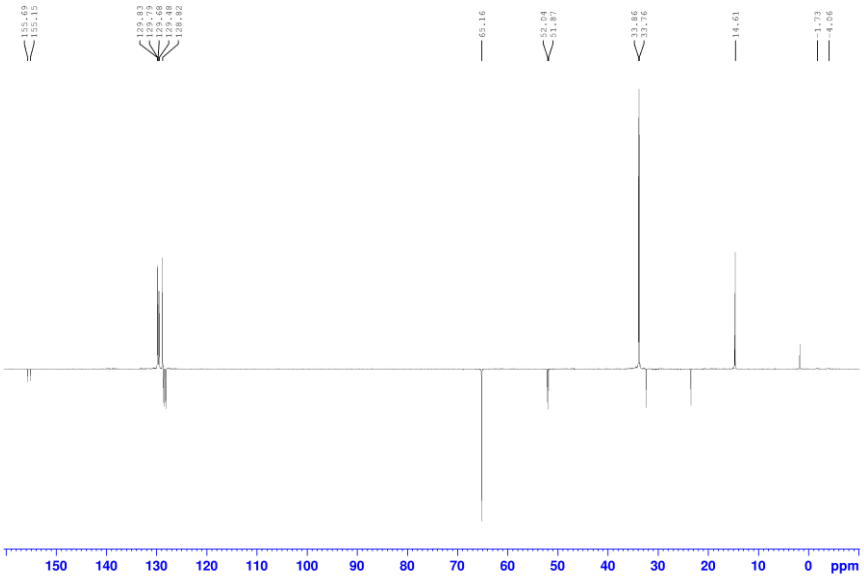


Fig. S2. ^{13}C{^{1}H} APT NMR spectrum of **1**.

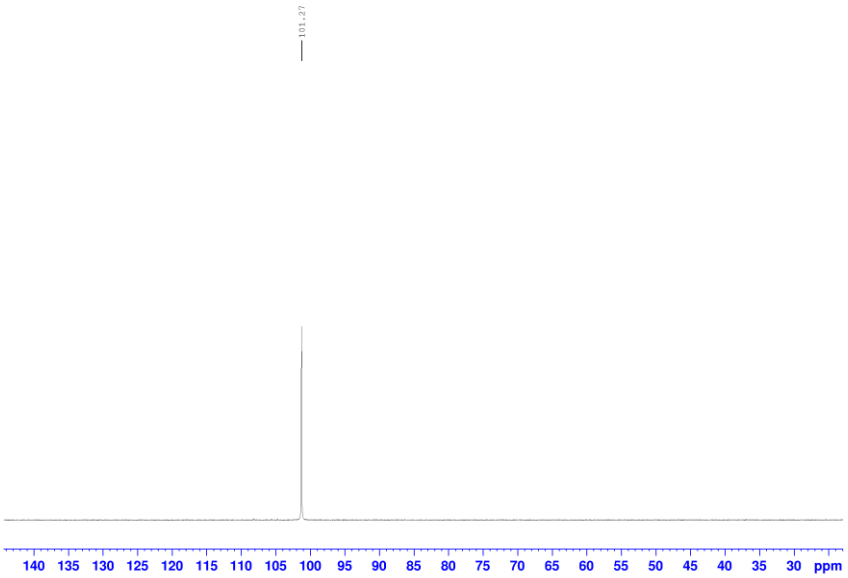


Fig. S3. ^{31}P NMR spectrum of **1**.

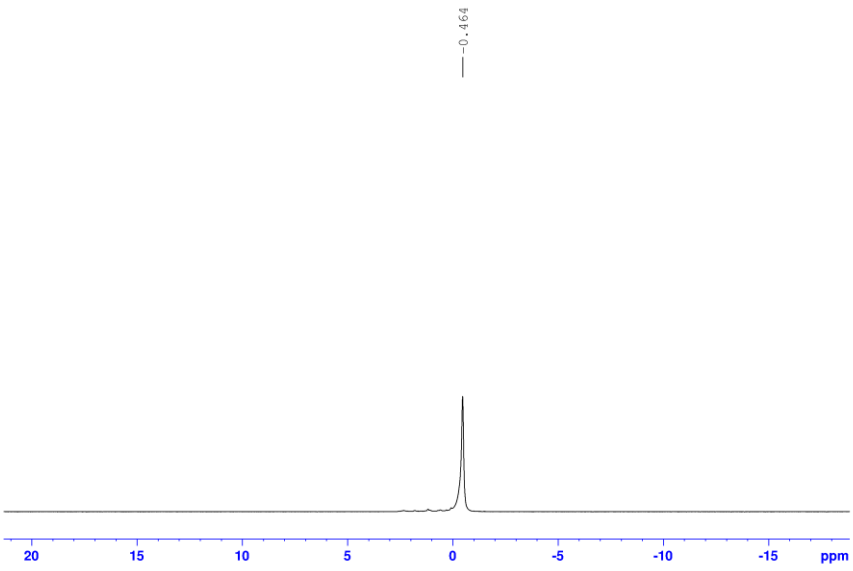


Fig. S4. ^{7}Li NMR spectrum of **1**.

Spectroscopic characterization of [PhP(N*t*Bu)$_2$AlMe$_2$]K (2).

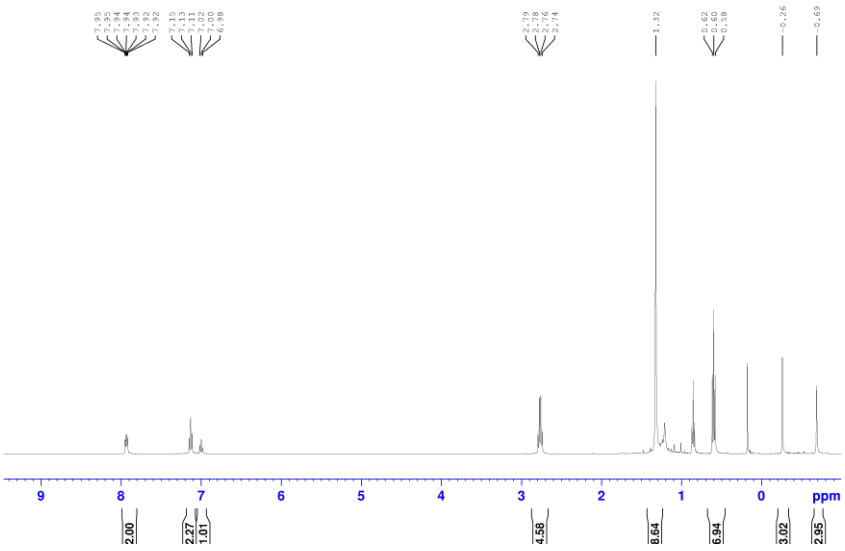


Fig. S5. ^{1}H NMR spectrum of **2**.

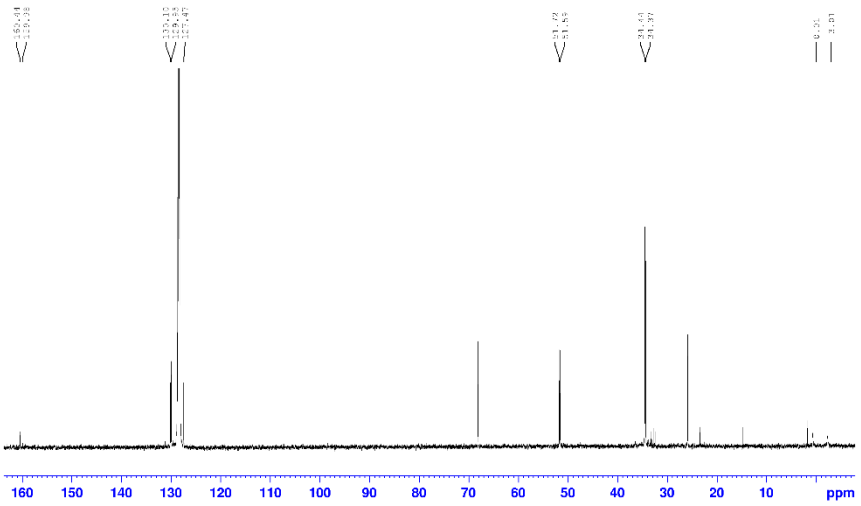


Fig. S6. ^{13}C{^{1}H} NMR spectrum of **2**.

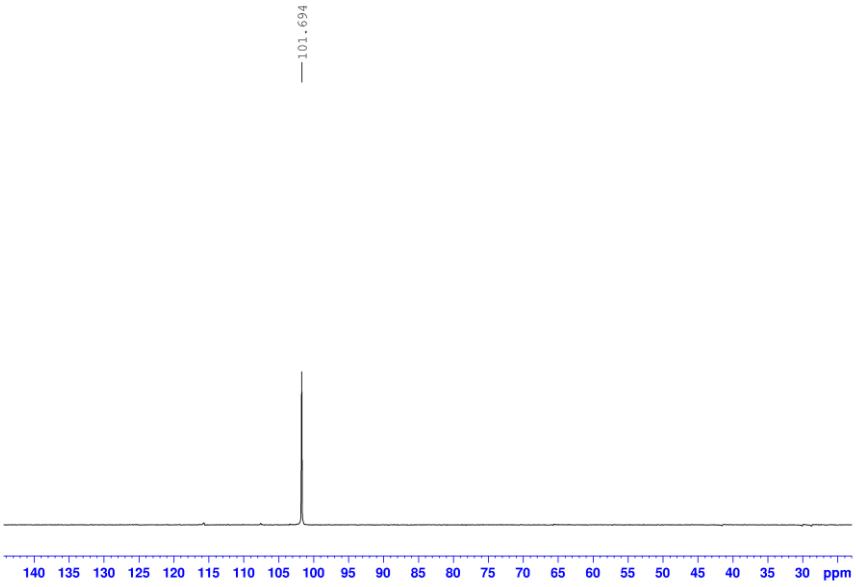


Fig. S7. ^{31}P NMR spectrum of **2**.

Spectroscopic characterization of [PhP(N*t*Bu)$_2$AlH$_2$]Li.THF (3).

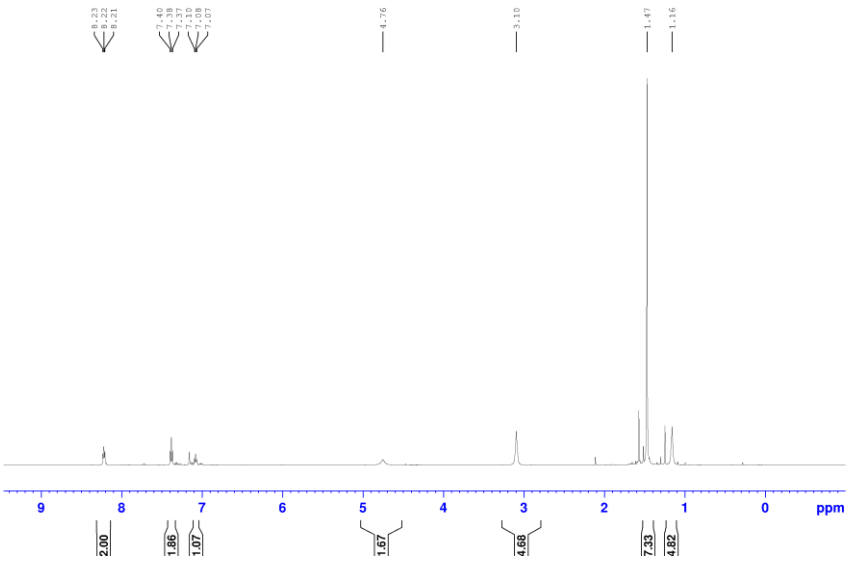


Fig. S8. ^{1}H NMR spectrum of **3**.

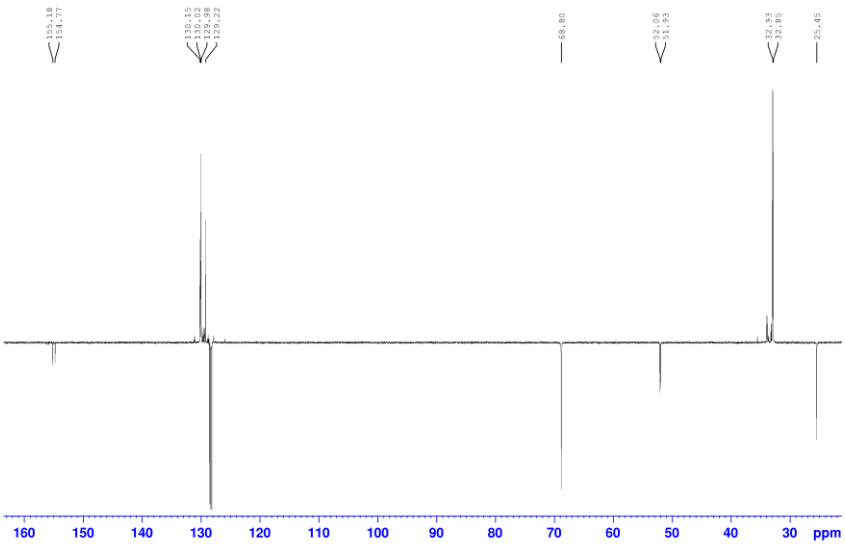


Fig. S9. $^{13}C\{^{1}H\}$ APT NMR spectrum of **3**.

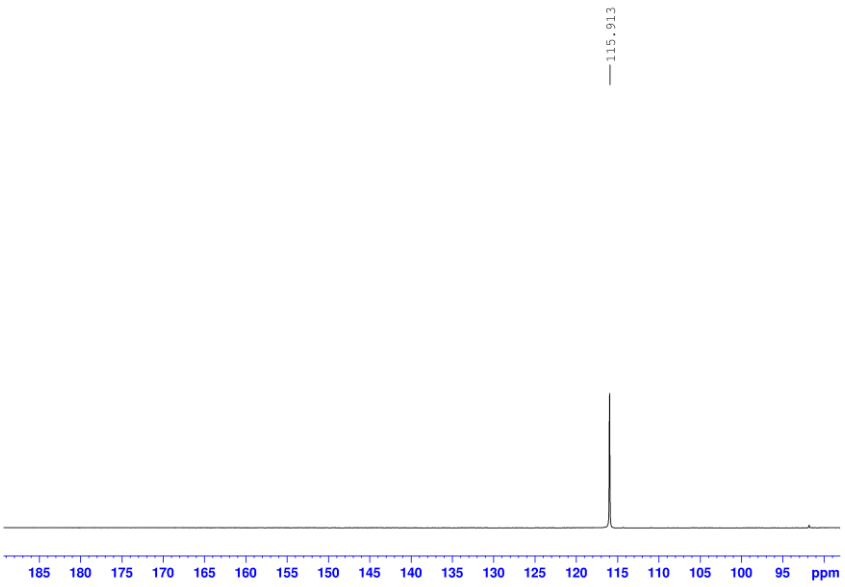


Fig. S10. ^{31}P NMR spectrum of **3**.

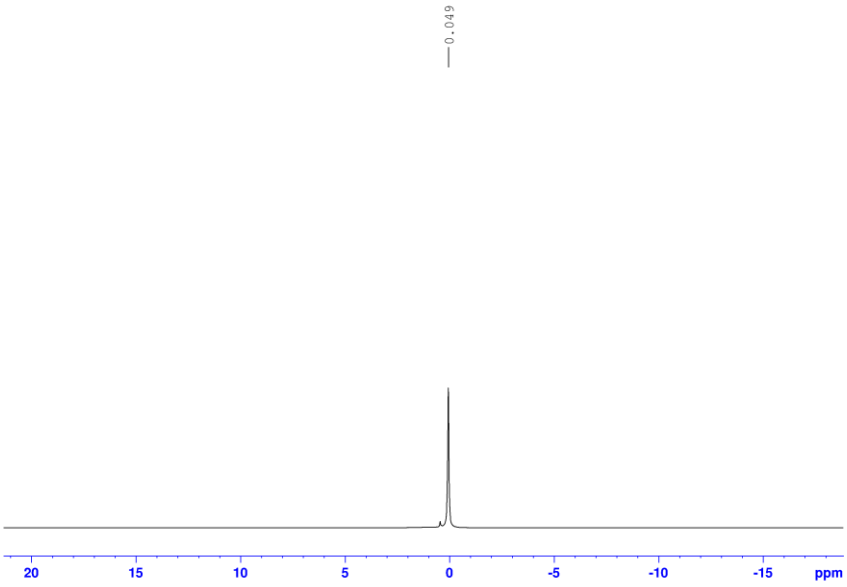


Fig. S11. ^{7}Li NMR spectrum of **3**.

Spectroscopic characterization of {[*t*BuP(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$]AlMe$_2$}Li.(OEt$_2$)$_2$ (4).

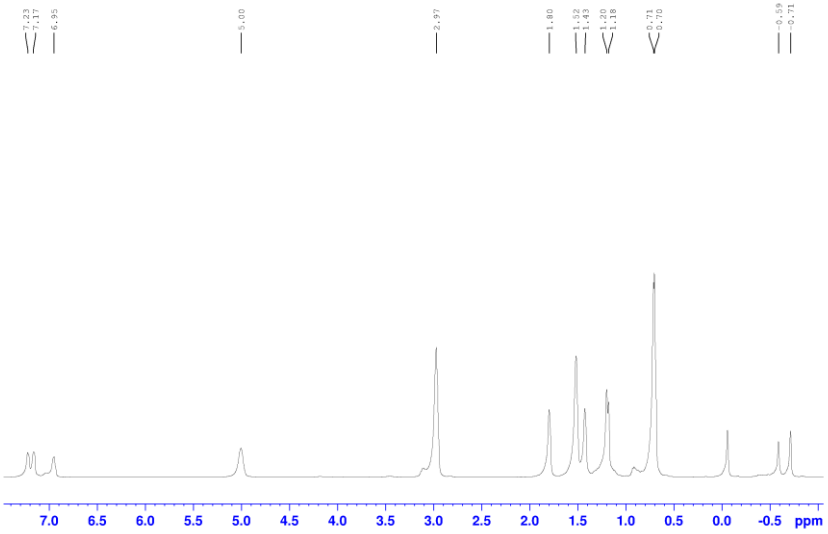


Fig. S12. ^{1}H NMR spectrum of **4**.

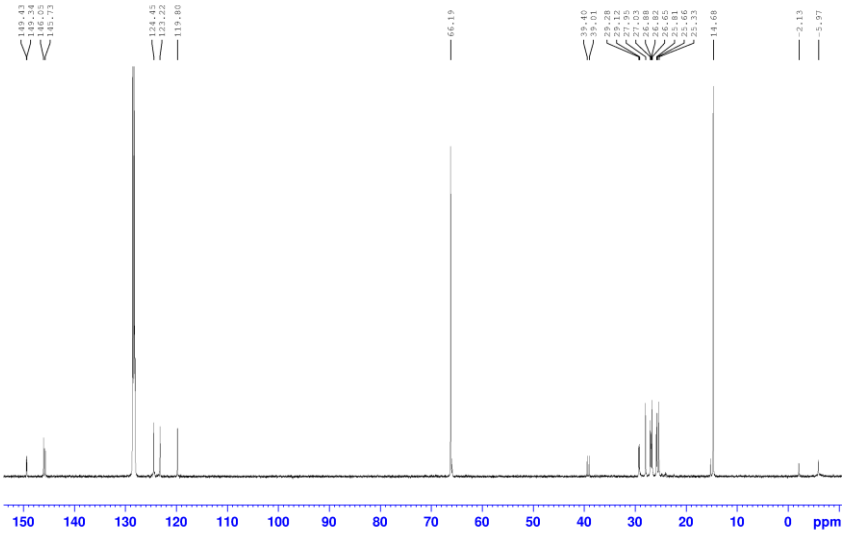


Fig. S13. $^{13}C\{^{1}H\}$ APT NMR spectrum of **4**.

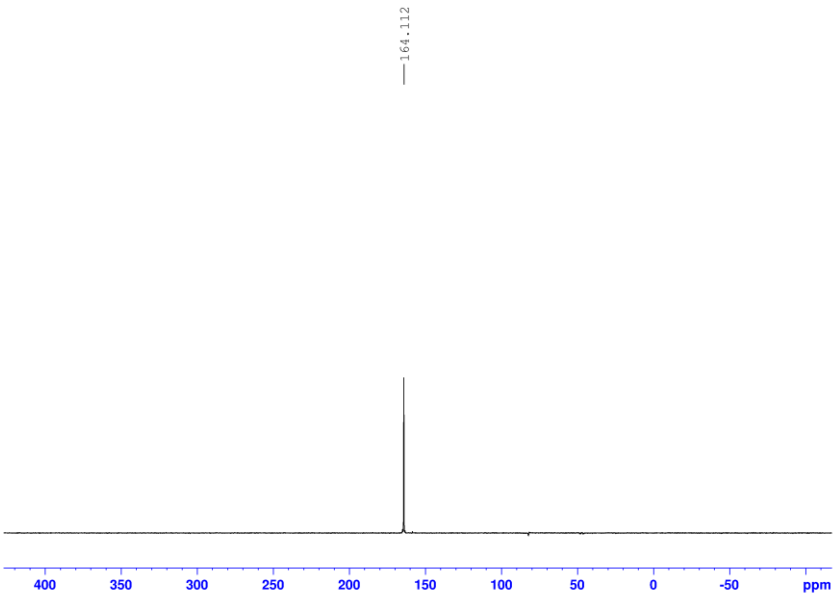


Fig. S14. ^{31}P NMR spectrum of **4**.

Spectroscopic characterization of {[Ph(O)P(N*t*Bu)$_2$]AlMe$_2$}Li.OEt$_2$ (5).

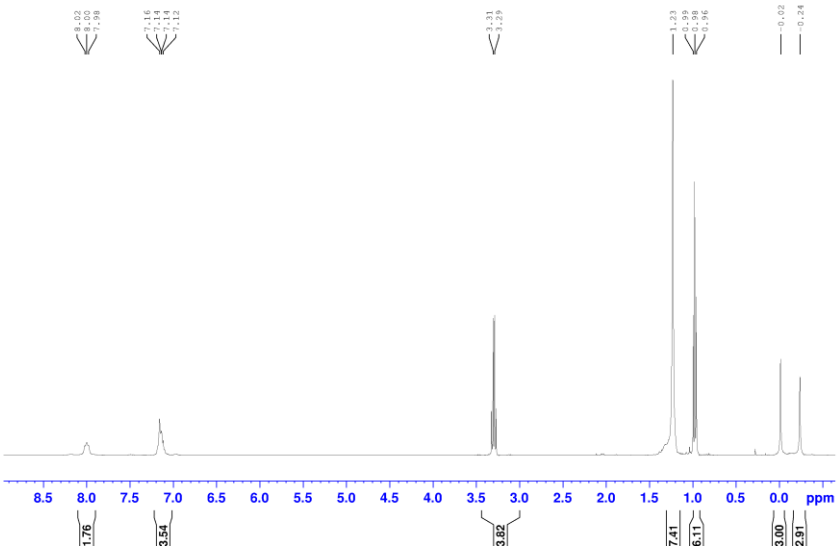


Fig. S15. ^{1}H NMR spectrum of **5**.

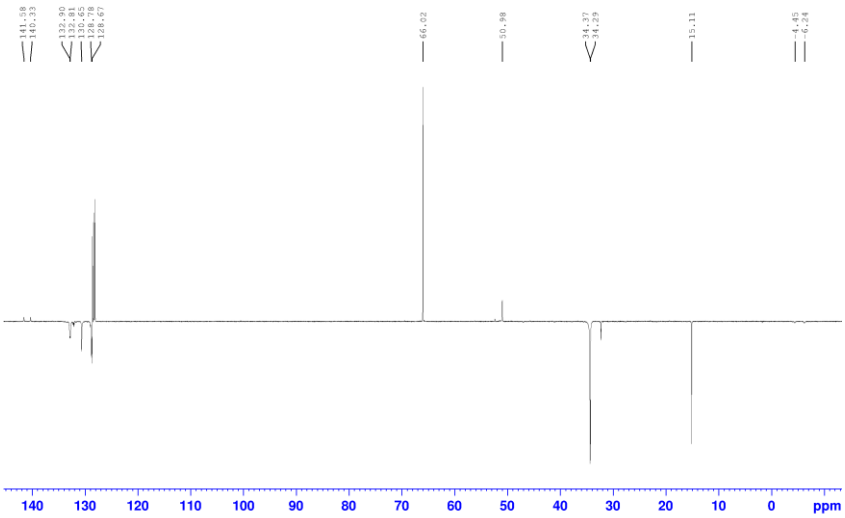


Fig. S16. ^{13}C{^{1}H} APT NMR spectrum of **5**.

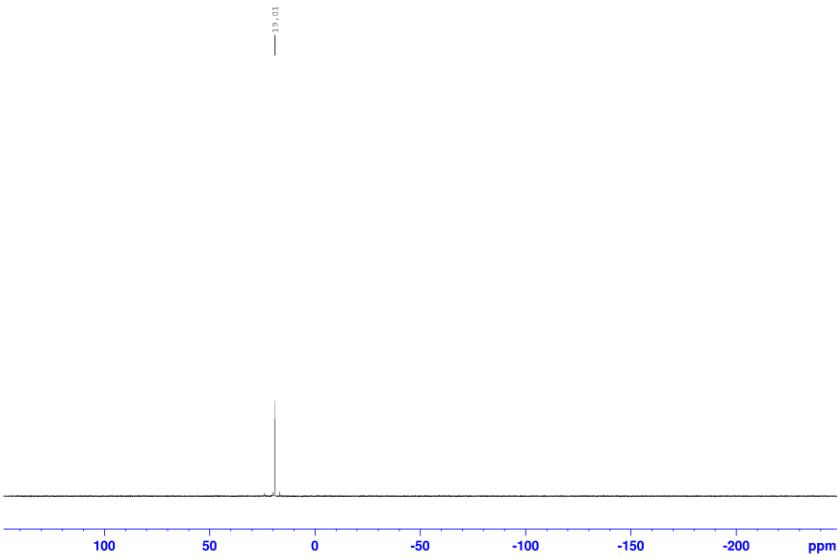


Fig. S17. ^{31}P NMR spectrum of **5**.

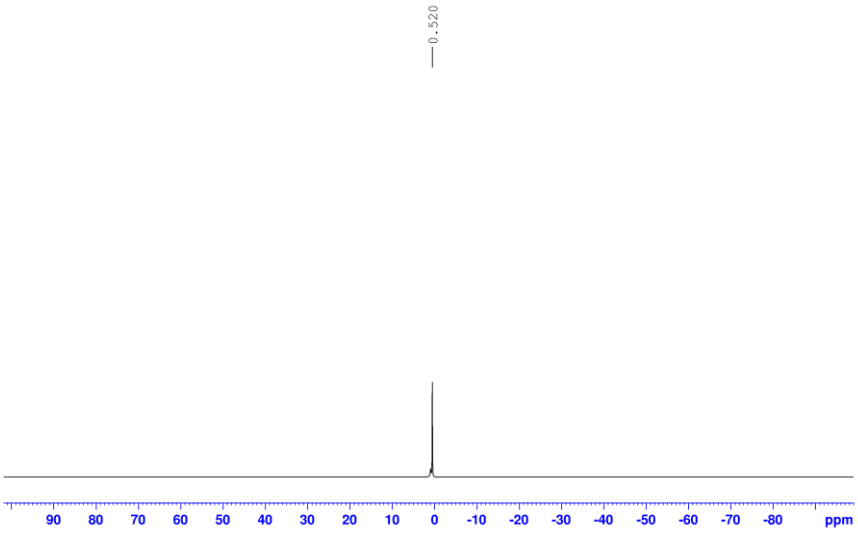


Fig. S18. ^{7}Li NMR spectrum of **5**.

Spectroscopic characterization of Synthesis of {[Ph(S)P(N*t*Bu)$_2$]AlMe$_2$}Li (6).

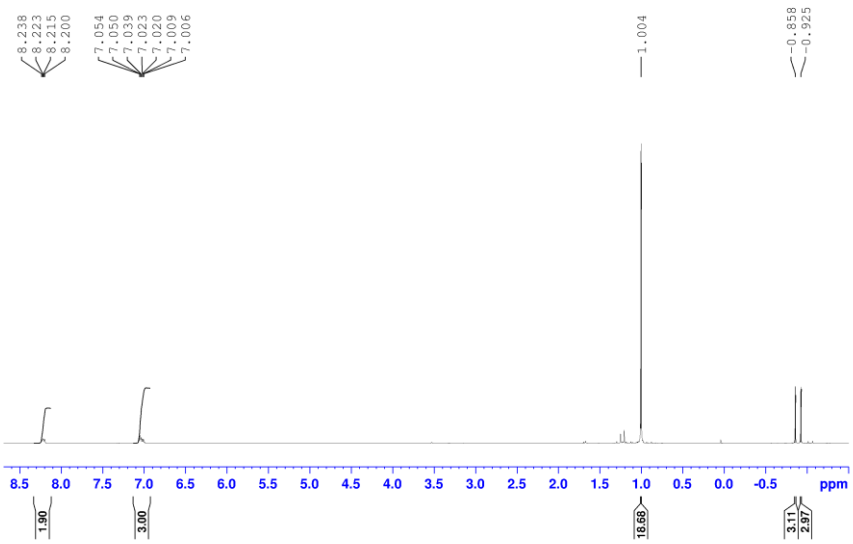


Fig. S19. ^{1}H NMR spectrum of **6**.

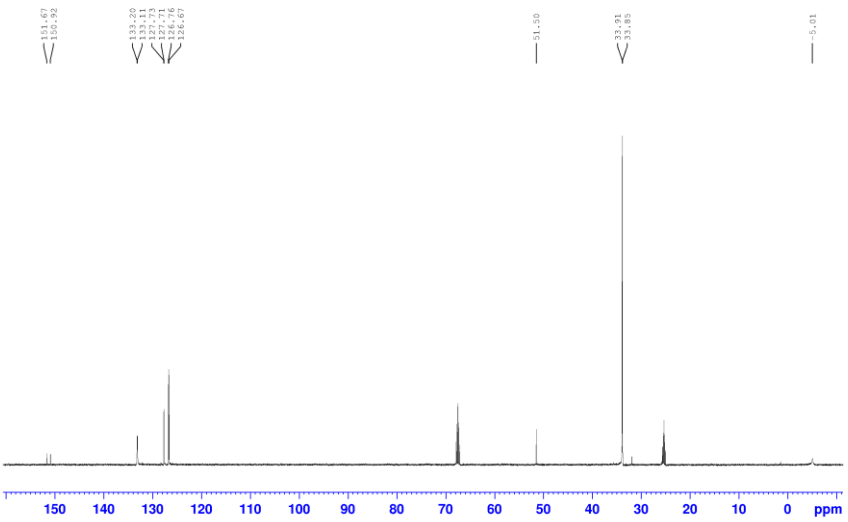


Fig. S20. ^{13}C{^{1}H} NMR spectrum of **6**.

Fig. S21. ^{31}P NMR spectrum of **6**.

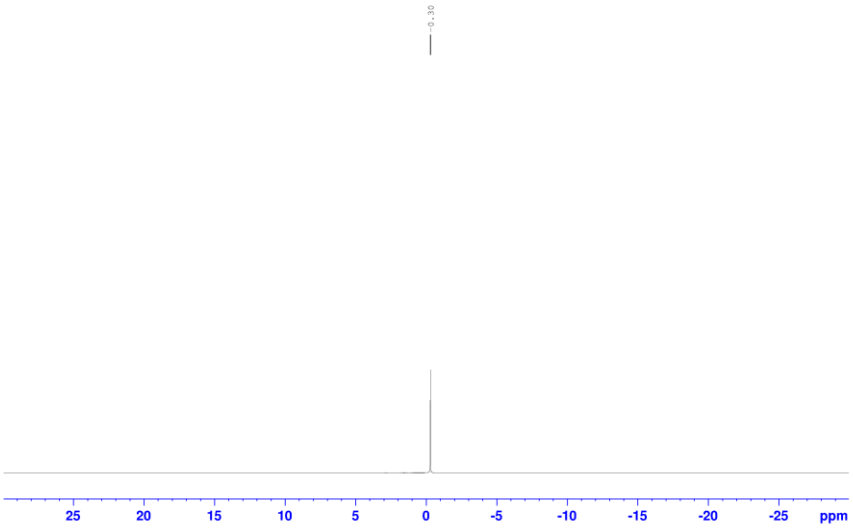


Fig. S22. ^{7}Li NMR spectrum of **6**.

Spectroscopic characterization of {[Ph(Se)P(N*t*Bu)$_2$]AlMe$_2$}Li (7).

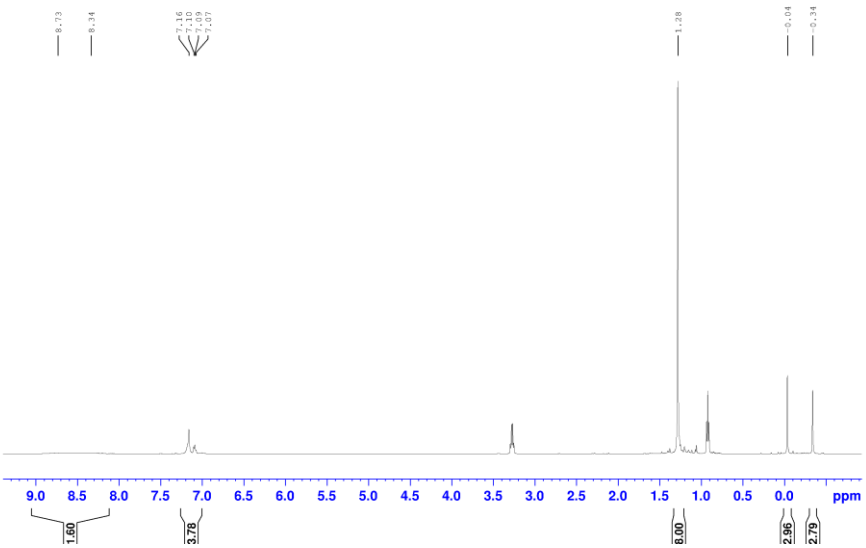


Fig. S23. ^{1}H NMR spectrum of **7**.

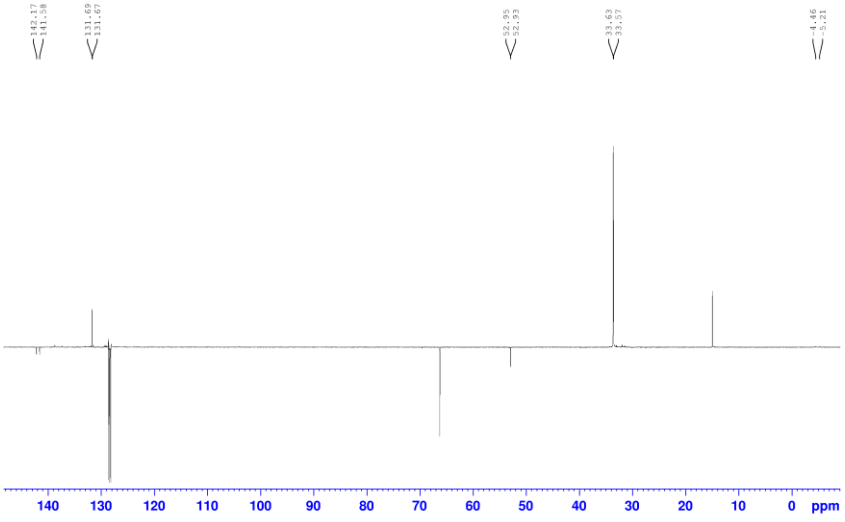


Fig. S24. ^{13}C{^{1}H} APT NMR spectrum of **7**.

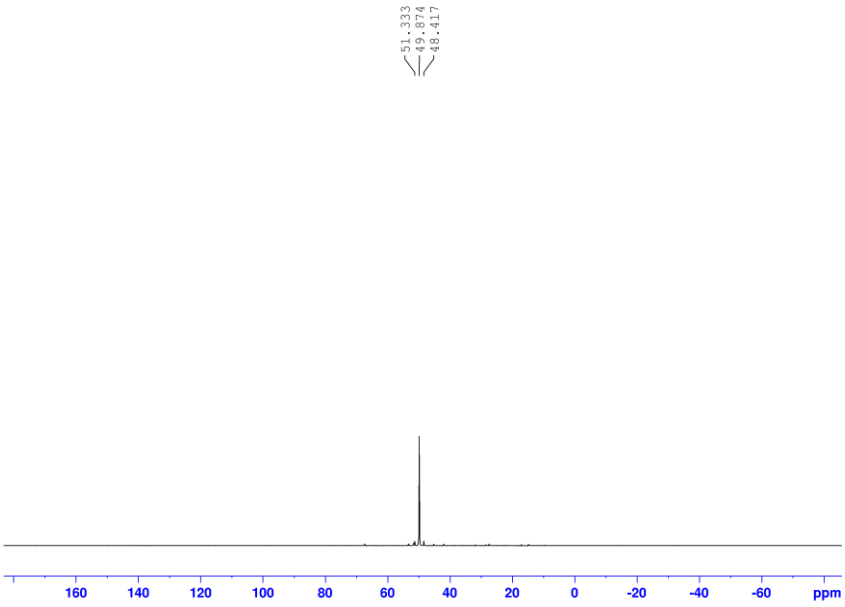


Fig. S25. ^{31}P NMR spectrum of **7**.

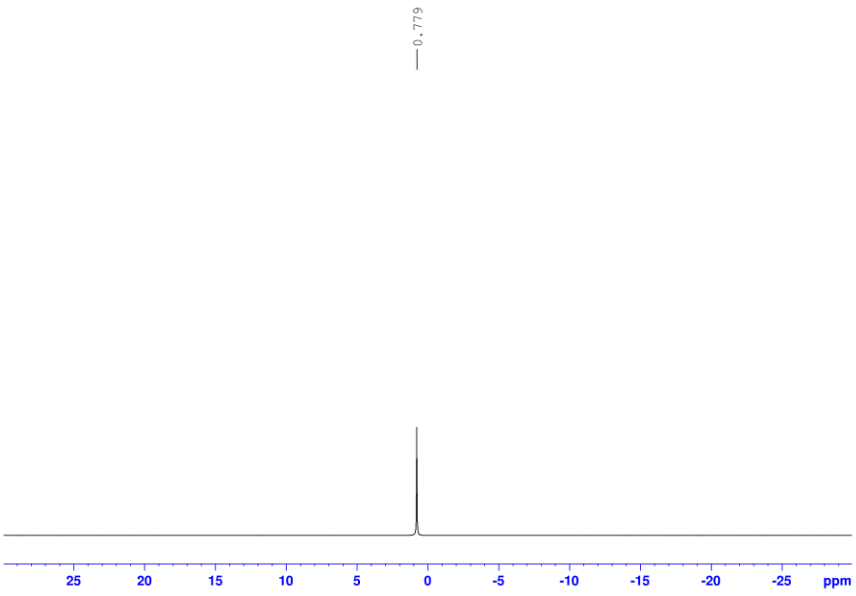


Fig. S26. ^{7}Li NMR spectrum of **7**.

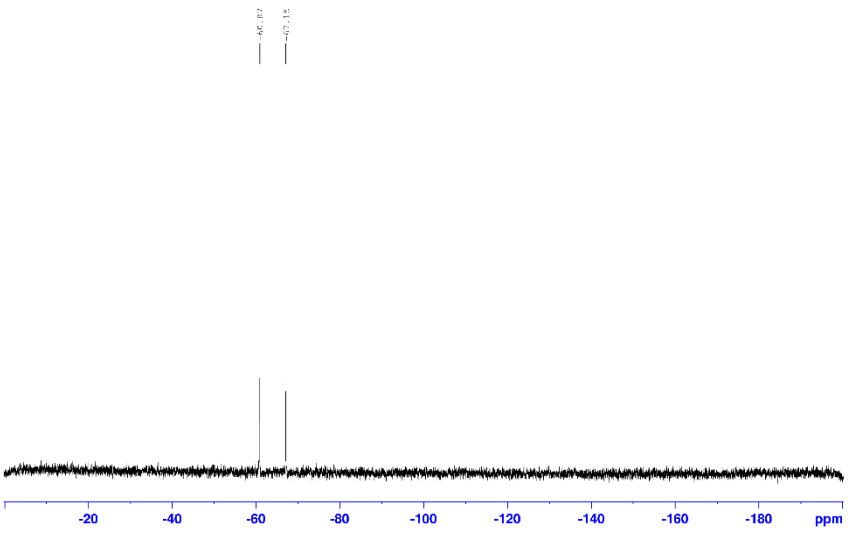


Fig. S27. ^{77}Se NMR spectrum of **7**.

Spectroscopic characterization of {[Ph(Te)P(N*t*Bu)$_2$]AlMe$_2$}Li (8).

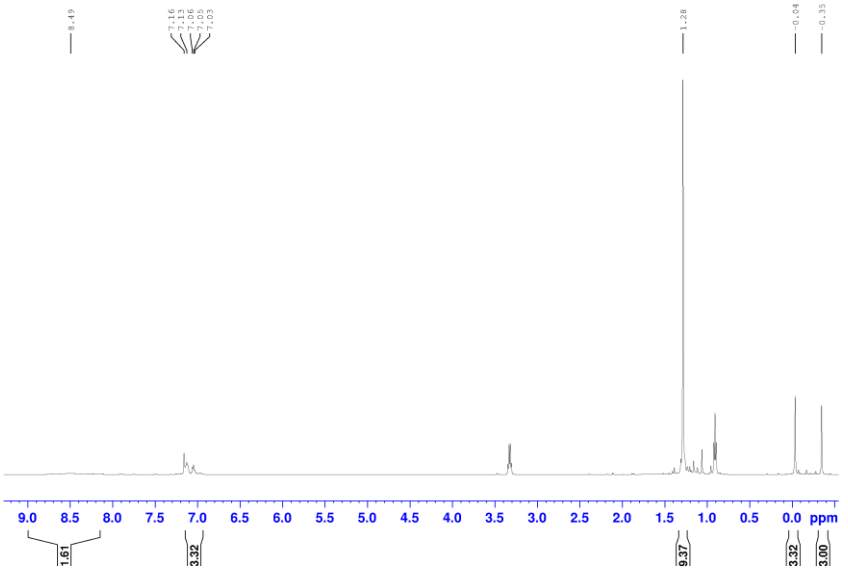


Fig. S28. ^{1}H NMR spectrum of **8**.

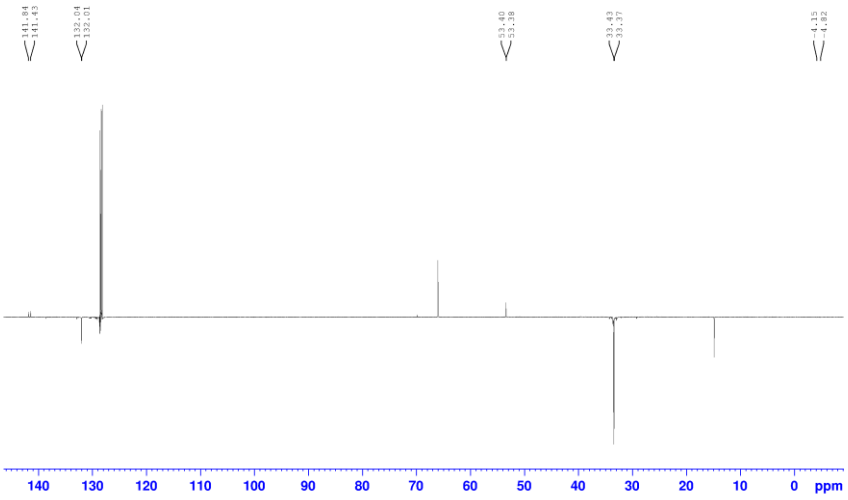


Fig. S29. $^{13}C\{^{1}H\}$ APT NMR spectrum of **8**.

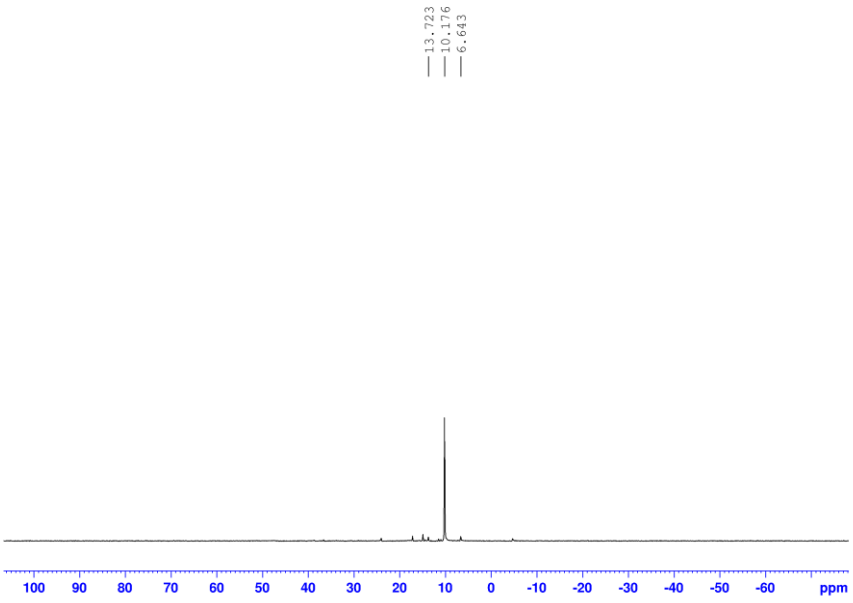


Fig. S30. ^{31}P NMR spectrum of **8**.

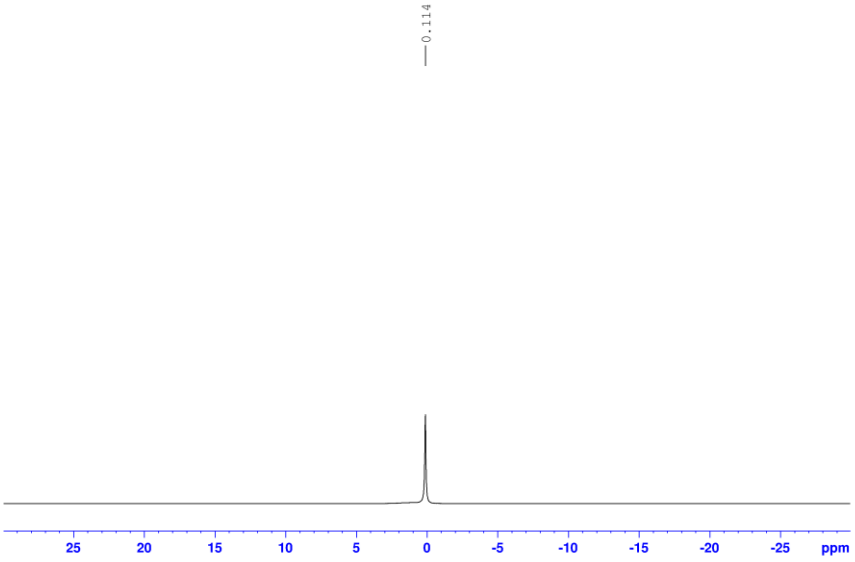


Fig. S31. ^{7}Li NMR spectrum of **8**.

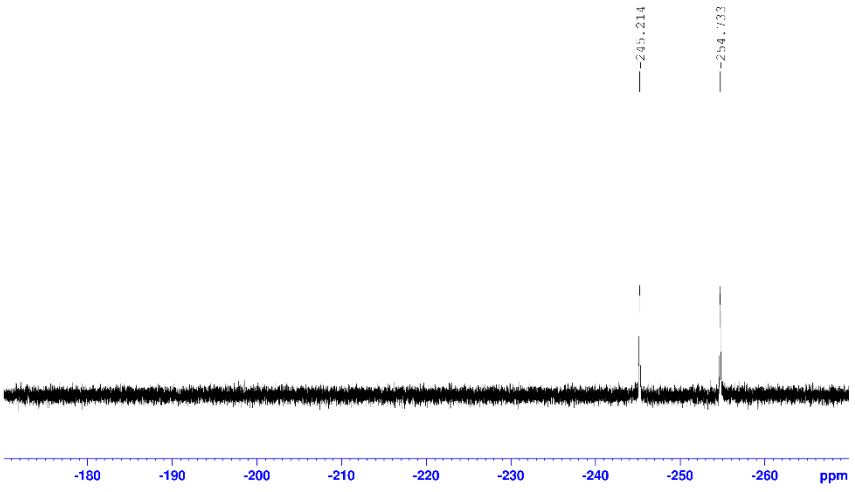


Fig. S32. ^{125}Te NMR spectrum of **8**.

Spectroscopic characterization of Bu_4N^+ {[Ph(Te)P(N*t*Bu)$_2$]AlMe$_2$}$^-$ (9).

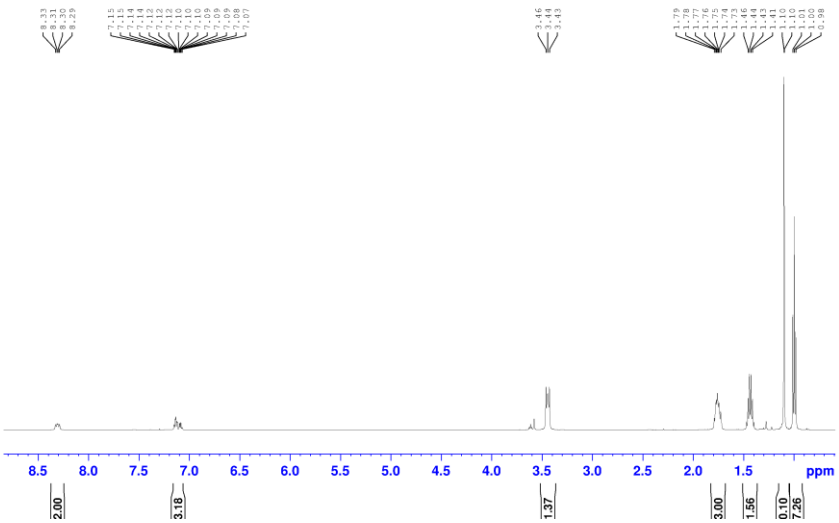


Fig. S33. ^{1}H NMR spectrum of **9**.

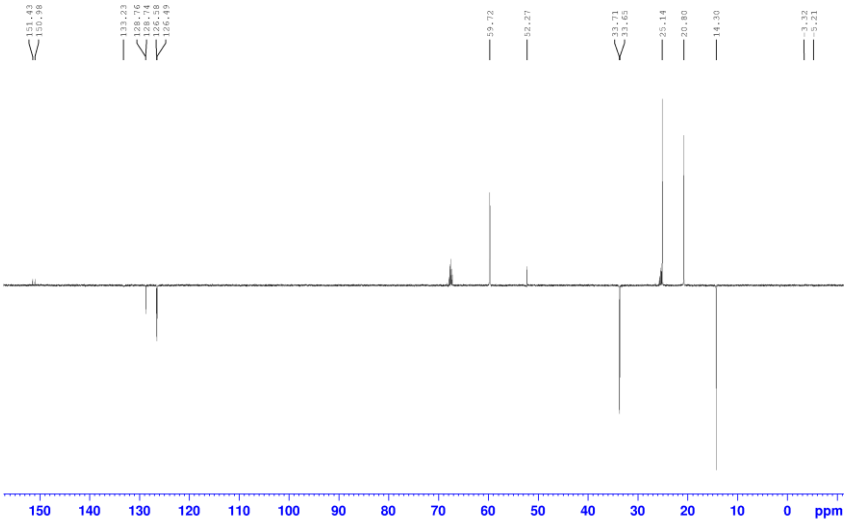


Fig. S34. ^{13}C{^{1}H} APT NMR spectrum of **9**.

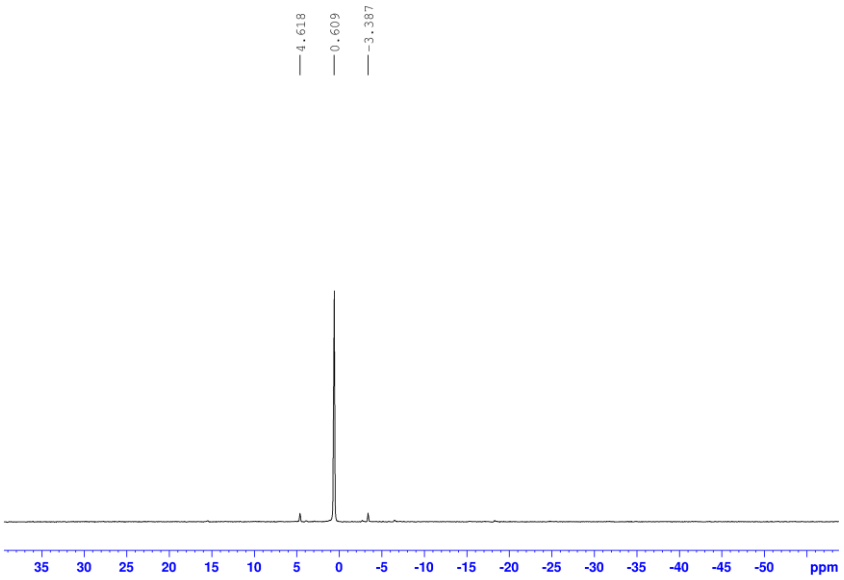


Fig. S35. ^{31}P NMR spectrum of **9**.

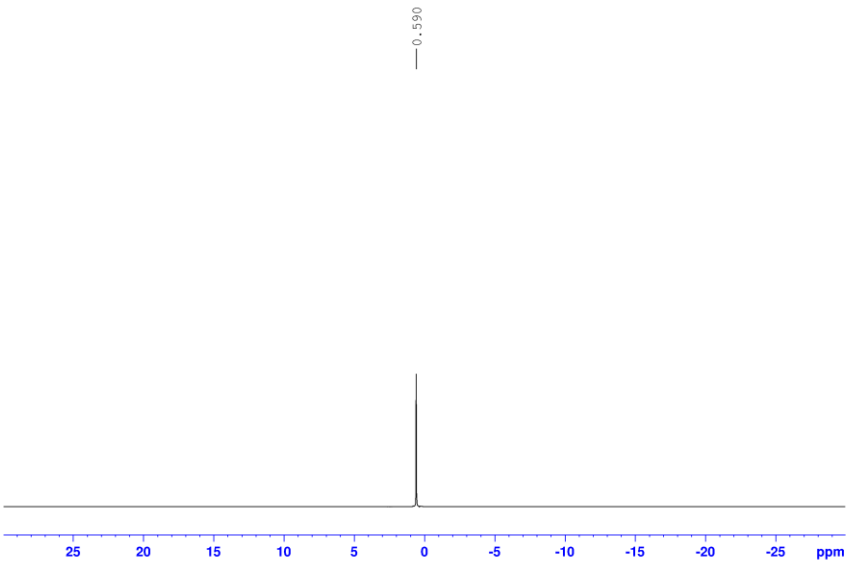


Fig. S36. ^{7}Li NMR spectrum of **9**.

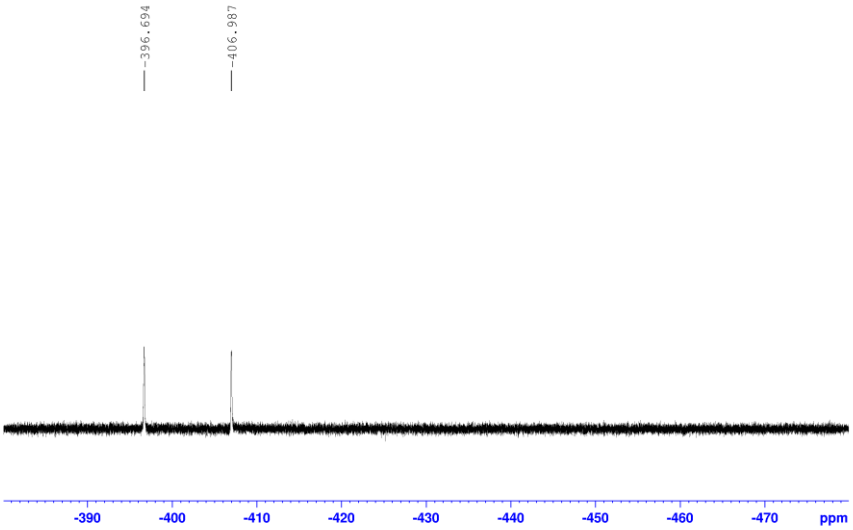


Fig. S37. ^{125}Te NMR spectrum of **9**.

Spectroscopic characterization of [Ph(Me)P(N*t*Bu)$_2$]AlMe$_2$ (10).

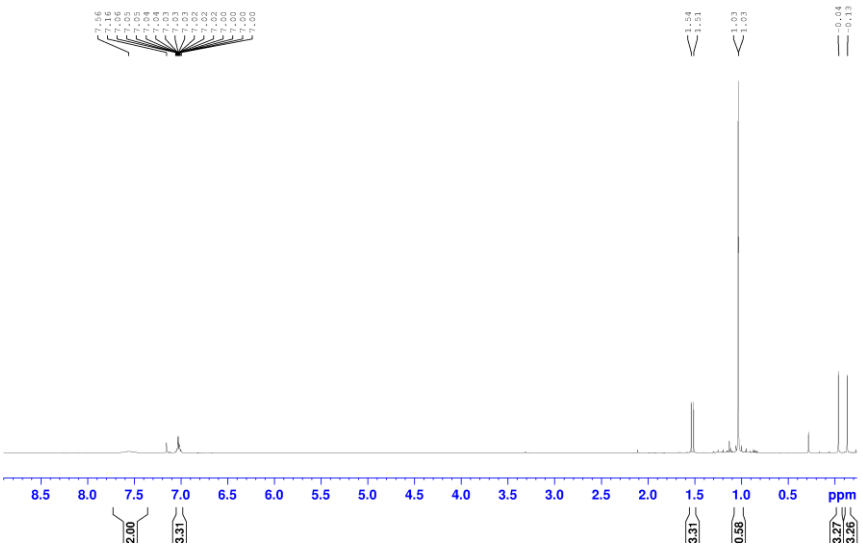


Fig. S38. ^{1}H NMR spectrum of **10**.

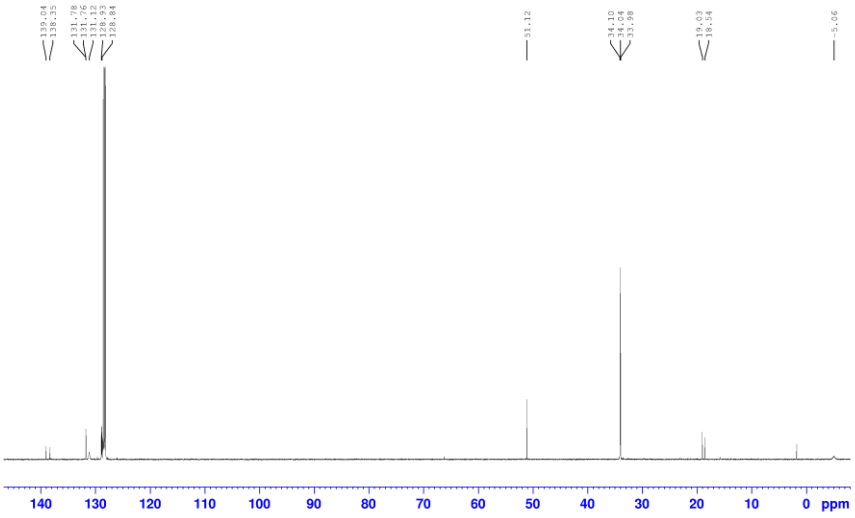


Fig. S39. $^{13}C\{^{1}H\}$ NMR spectrum of **10**.

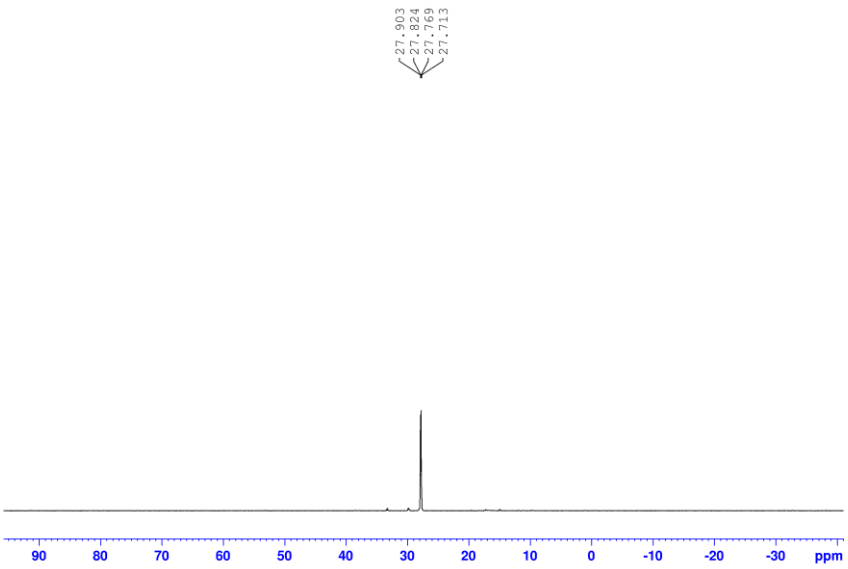


Fig. S40. ^{31}P NMR spectrum of **10**.

Spectroscopic characterization of [Ph(Me$_3$Si)P(N*t*Bu)$_2$]AlMe$_2$ (11).

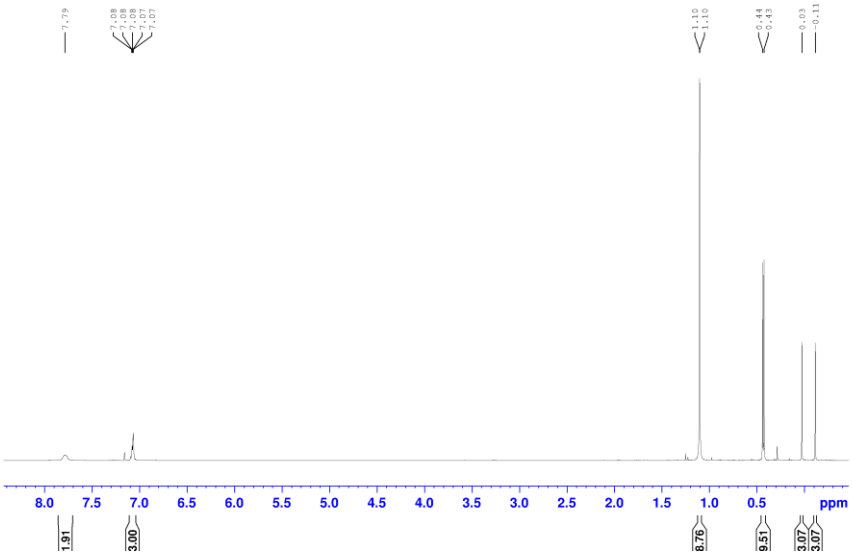


Fig. S41. ^{1}H NMR spectrum of **11**.

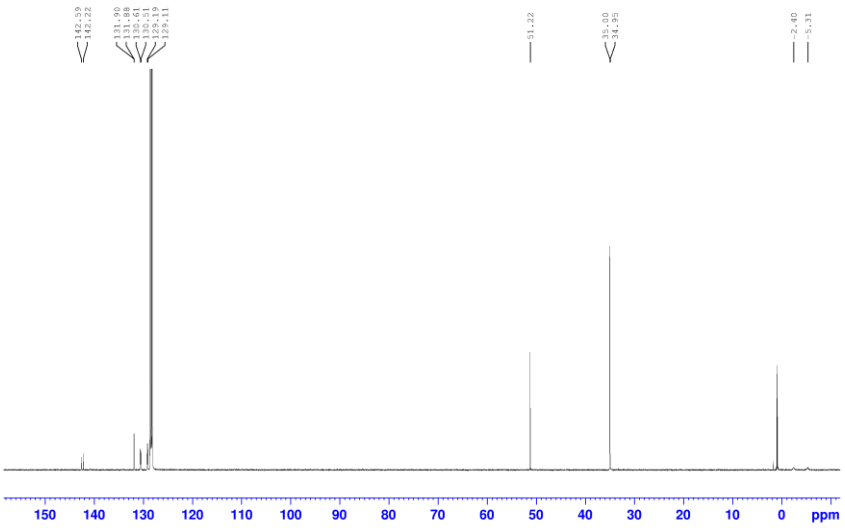


Fig. S42. ^{13}C{^{1}H} NMR spectrum of **11**.

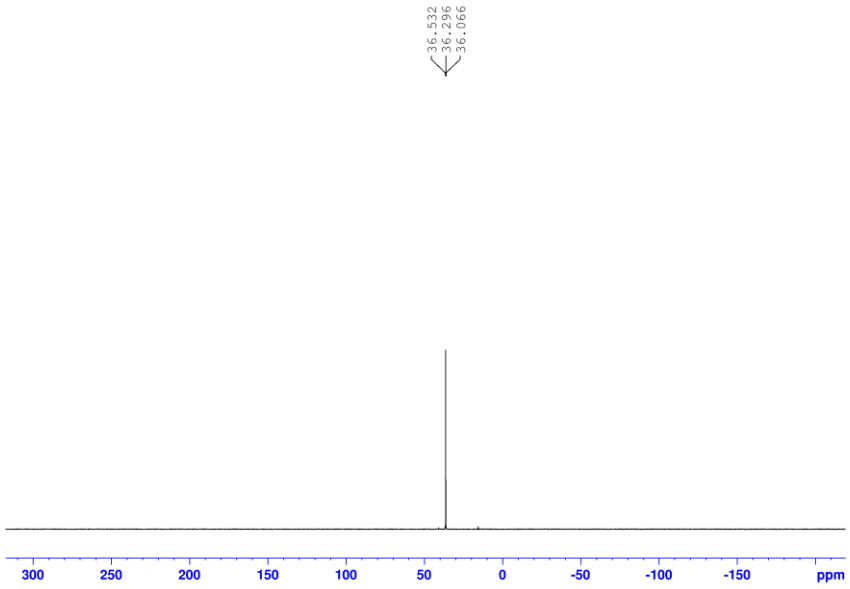


Fig. S43. ^{31}P NMR spectrum of **11**.

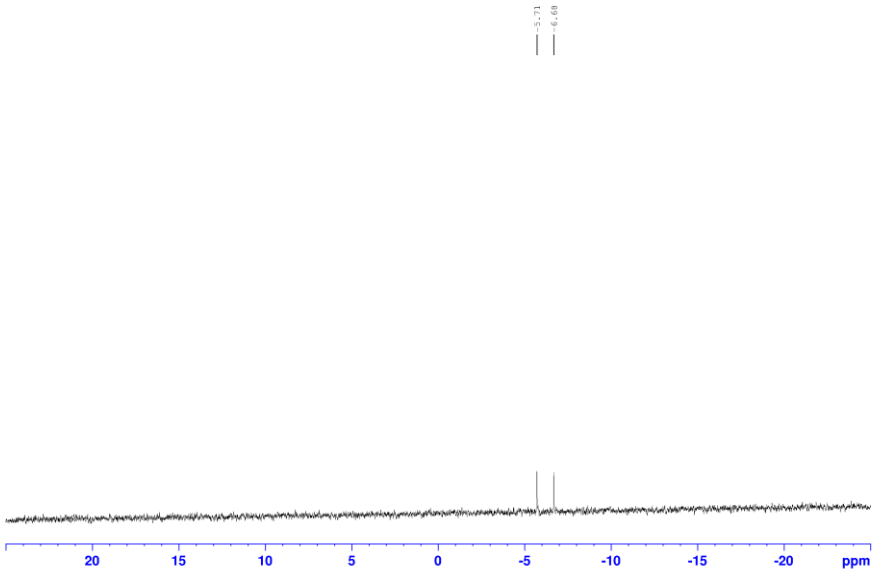


Fig. S44. ^{29}Si NMR spectrum of **11**.

Spectroscopic characterization of [Ph(Ph$_3$Sn)P(N*t*Bu)$_2$]AlMe$_2$ (12).

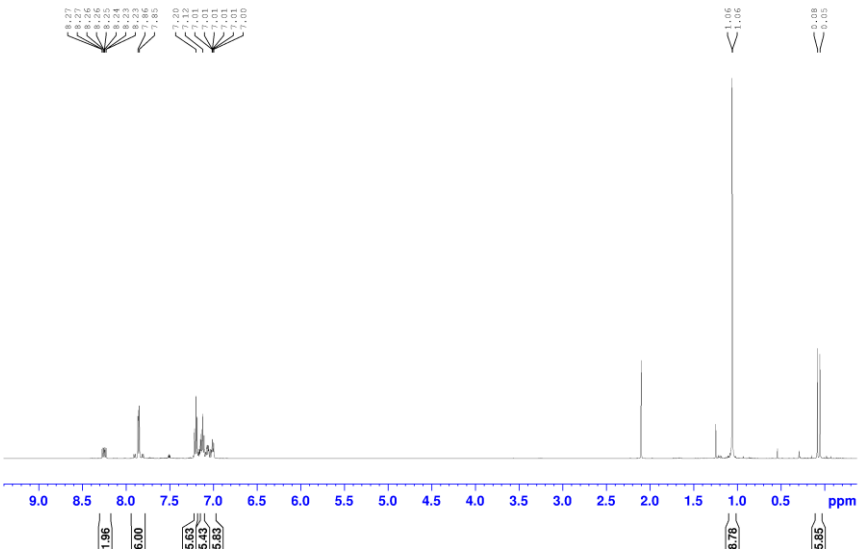


Fig. S45. ^{1}H NMR spectrum of **12**.

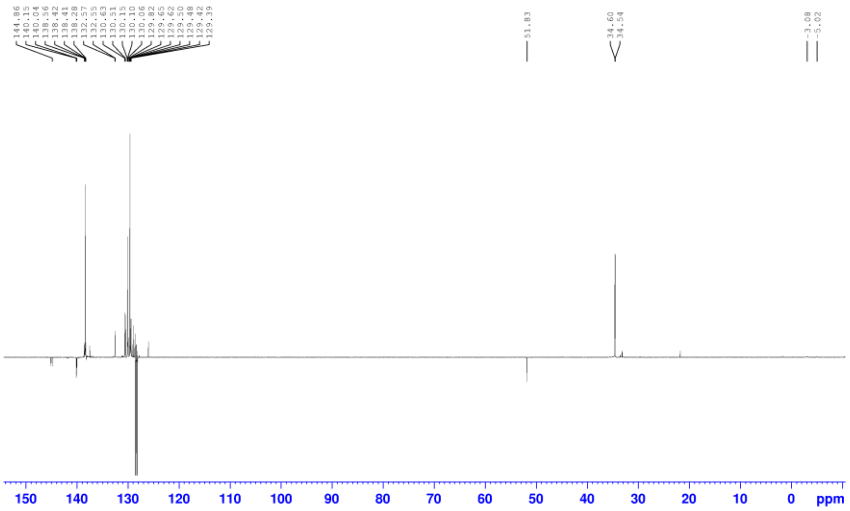


Fig. S46. ^{13}C{^{1}H} APT NMR spectrum of **12**.

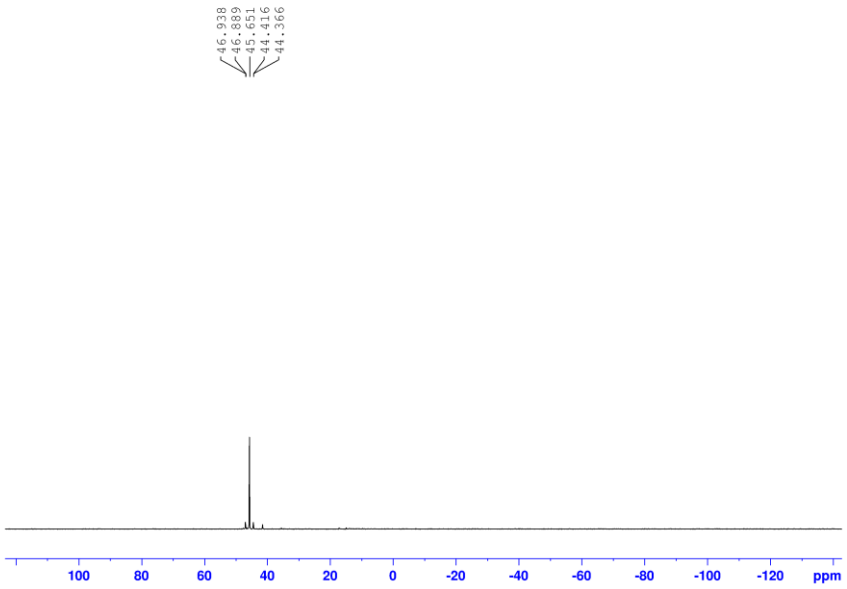


Fig. S47. ^{31}P NMR spectrum of **12**

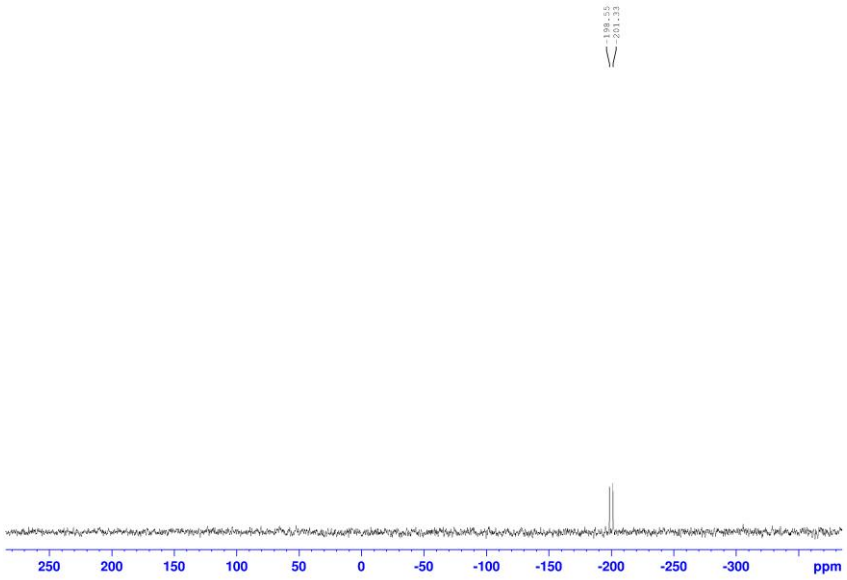


Fig. S48. ^{119}Sn NMR spectrum of **12**

Spectroscopic characterization of [Ph(Me$_3$Pb)P(N*t*Bu)$_2$]AlMe$_2$ (13).

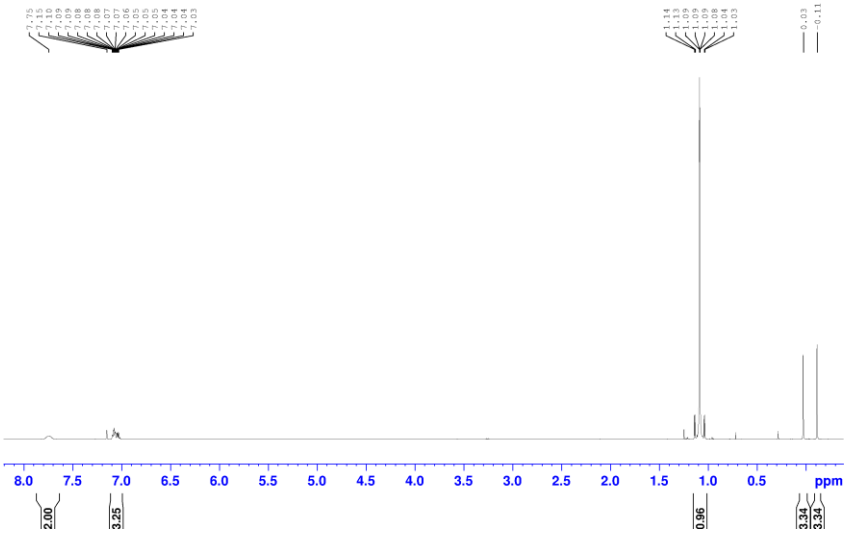


Fig. S49. ^{1}H NMR spectrum of **13**.

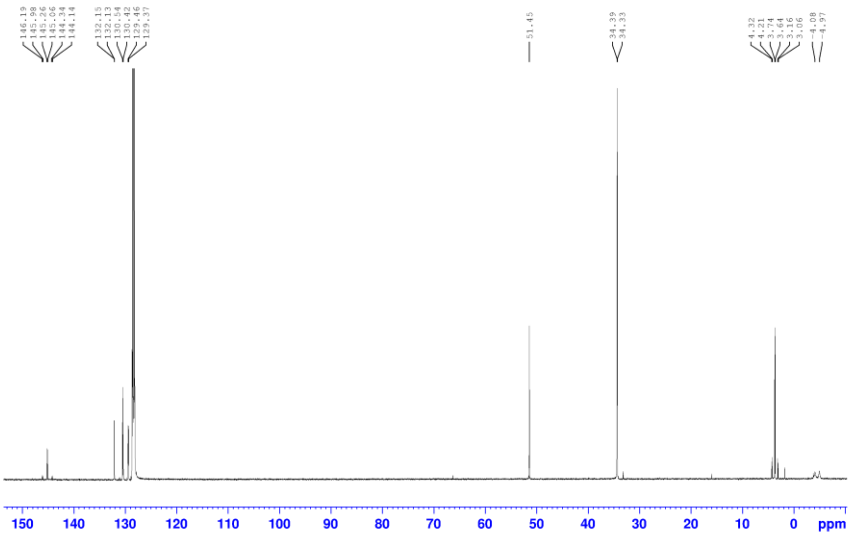


Fig. S50. ^{13}C{^{1}H} NMR spectrum of **13**.

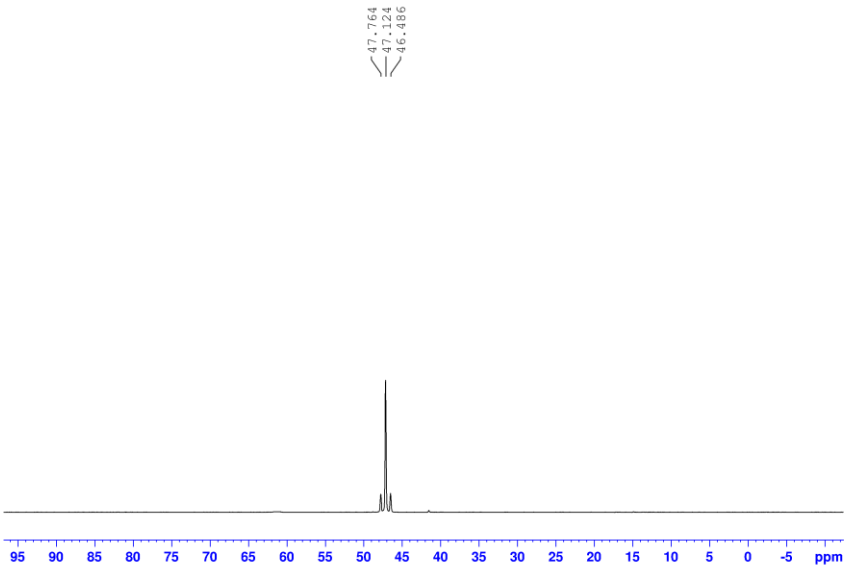


Fig. S51. ^{31}P NMR spectrum of **13**.

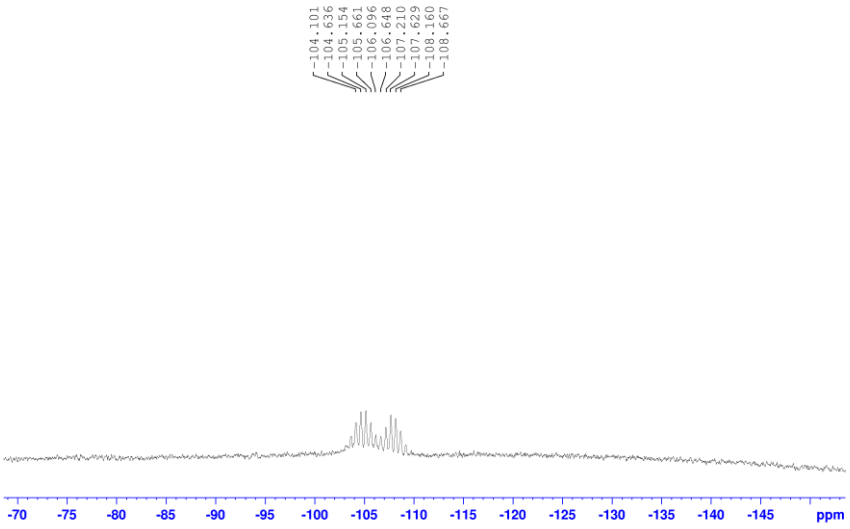


Fig. S52. ^{207}Pb NMR spectrum of **13**.

Spectroscopic characterization of {Ph[2,6-*i*Pr$_2$-C$_6$H$_3$(H)N(Ph)P]P(N*t*Bu)$_2$}AlMe$_2$ (14).

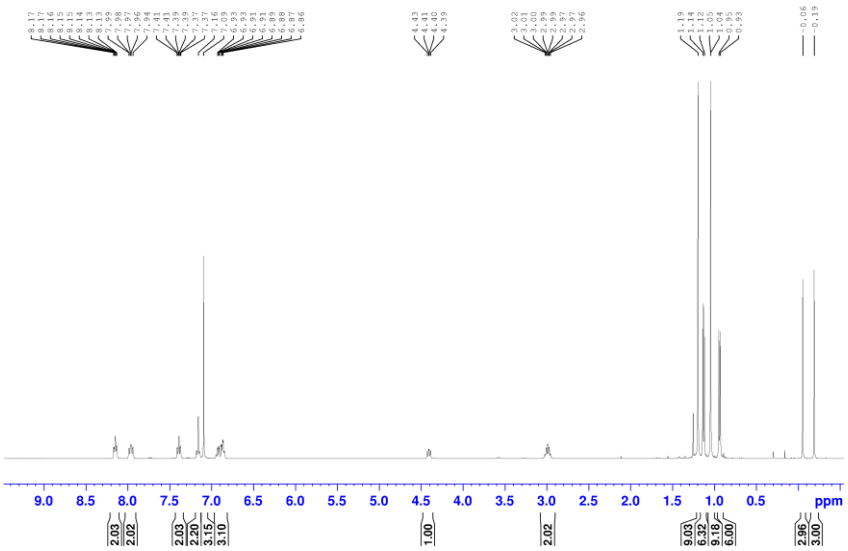


Fig. S53. ^{1}H NMR spectrum of **14**.

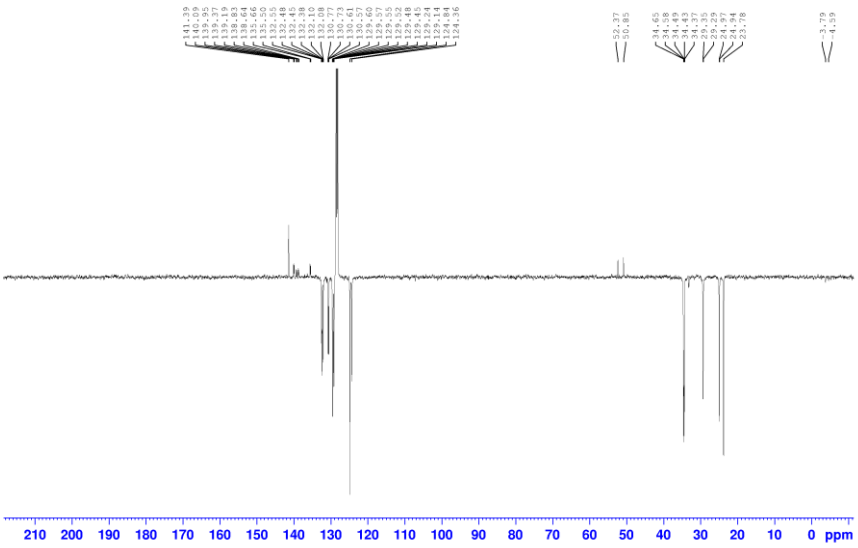


Fig. S54. ^{13}C{^{1}H} APT NMR spectrum of **14**.

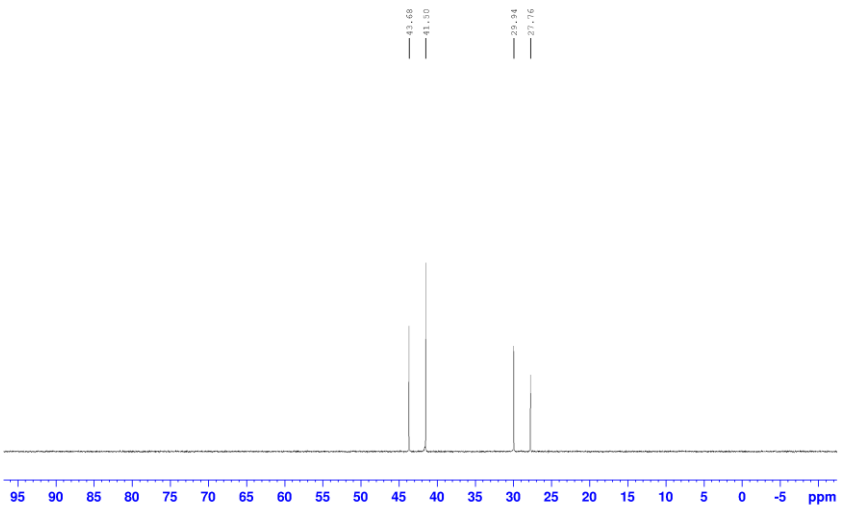


Fig. S55. ^{31}P NMR spectrum of **14**.

Spectroscopic characterization of [Ph(Ph$_2$P)P(N*t*Bu)$_2$]AlMe$_2$ (15).

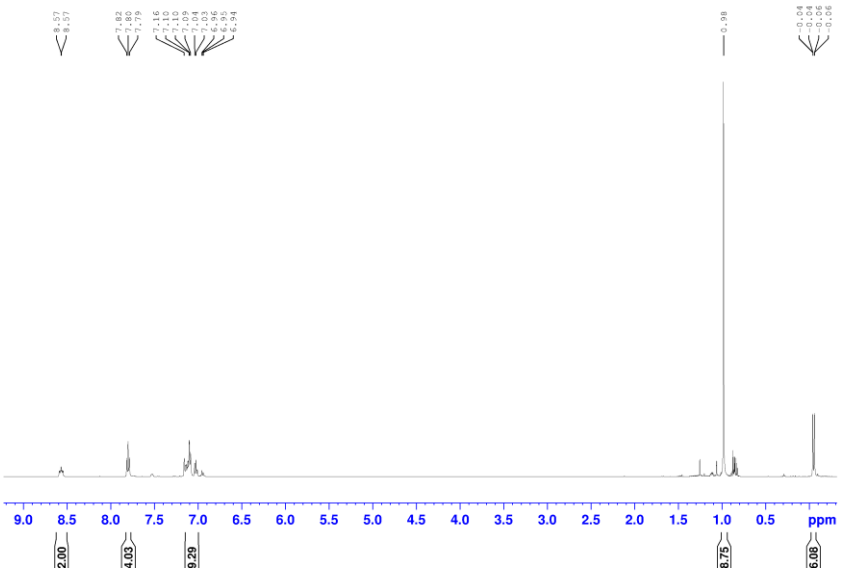


Fig. S56. ^{1}H NMR spectrum of **15**.

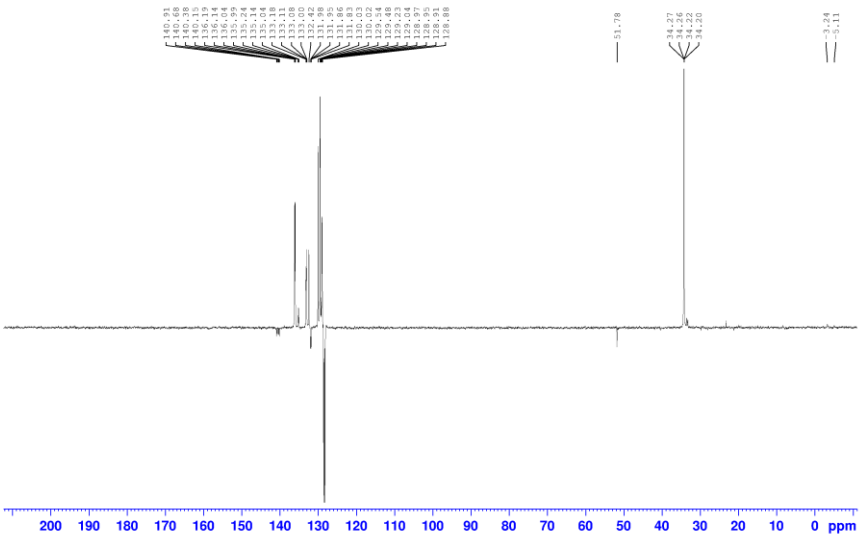


Fig. S57. $^{13}C\{^{1}H\}$ APT NMR spectrum of **15**.

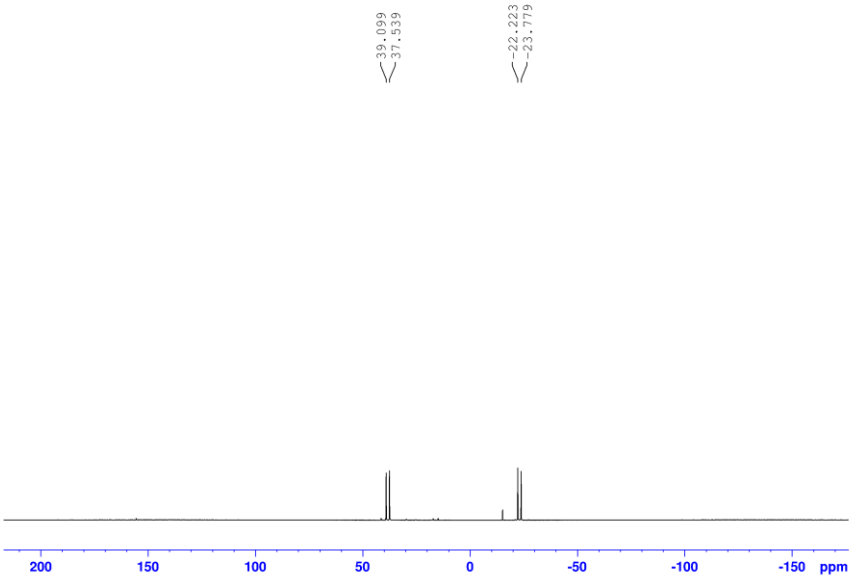


Fig. S58. ^{31}P NMR spectrum of **15**.

Spectroscopic characterization of {Ph[Ph(Cl)P]P(N*t*Bu)$_2$}AlMe$_2$ (16).

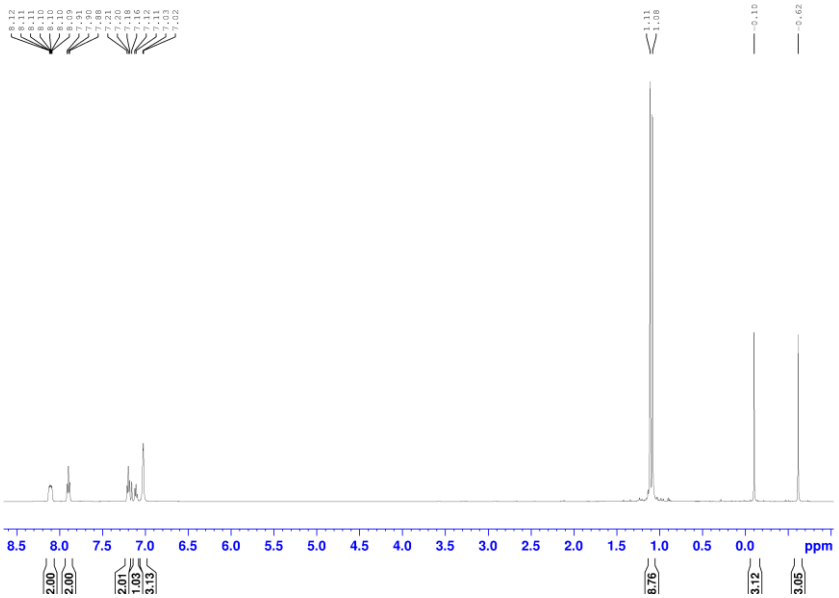


Fig. S59. ^{1}H NMR spectrum of **16**.

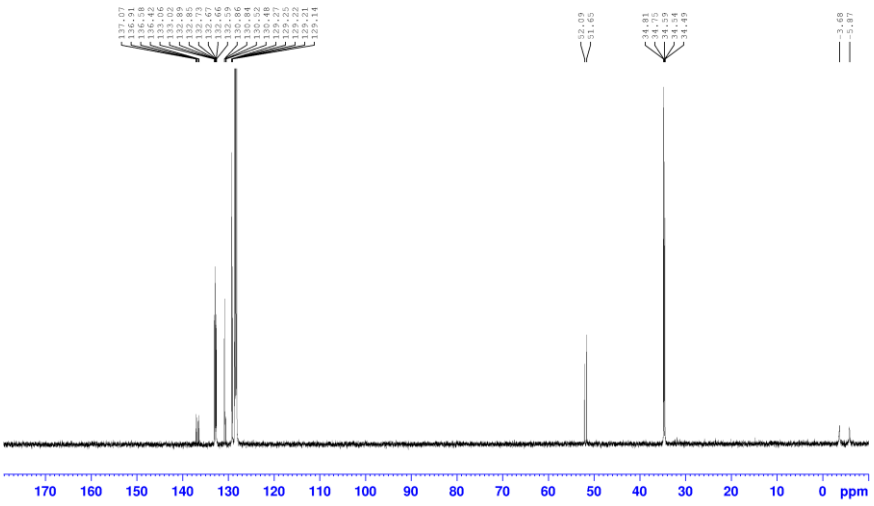


Fig. S60. ^{13}C{^{1}H} APT NMR spectrum of **16**.

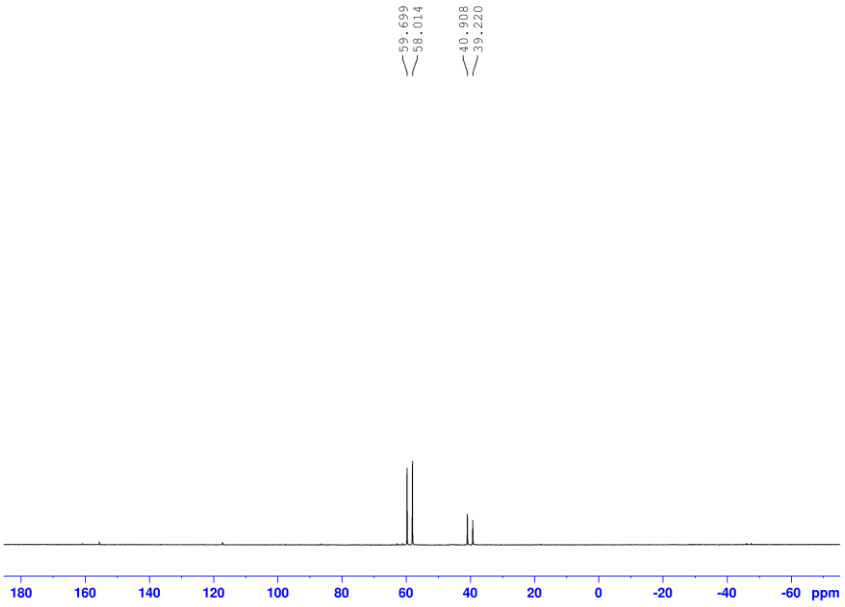


Fig. S61. ^{31}P NMR spectrum of **16**.

Spectroscopic characterization of {Ph[*t*Bu(Cl)P]P(N*t*Bu)$_2$}AlMe$_2$ (17).

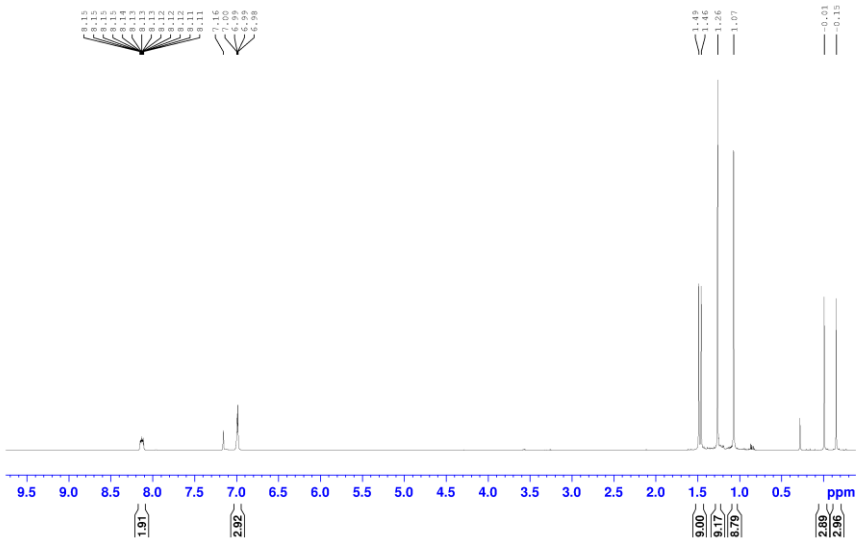


Fig. S62. ^{1}H NMR spectrum of **17**.

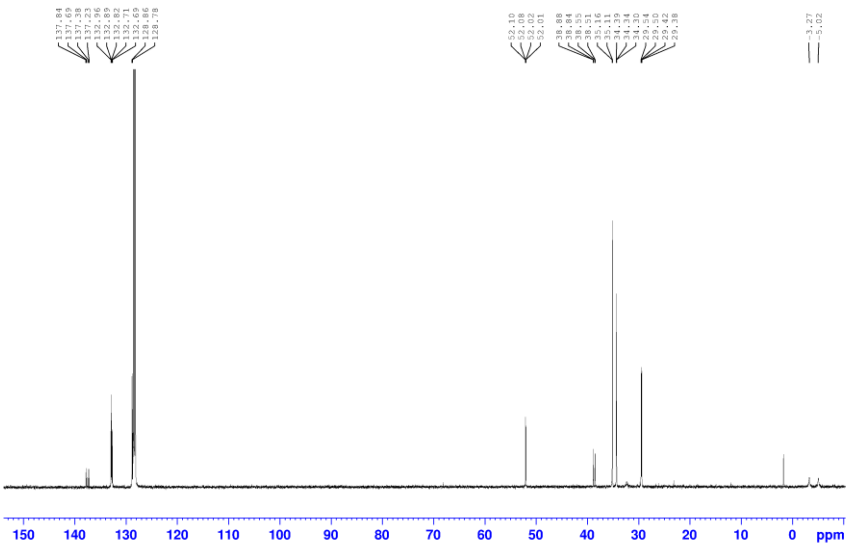


Fig. S63. $^{13}C\{^{1}H\}$ NMR spectrum of **17**.

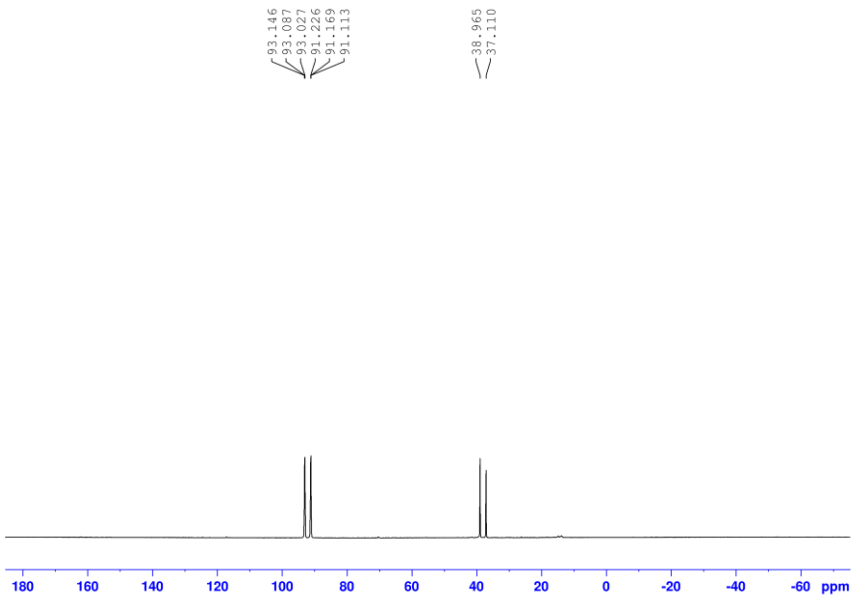


Fig. S64. ^{31}P NMR spectrum of **17**.

Spectroscopic characterization of {Ph[Me$_2$(Cl)Si]P(N*t*Bu)$_2$}AlMe$_2$ (18).

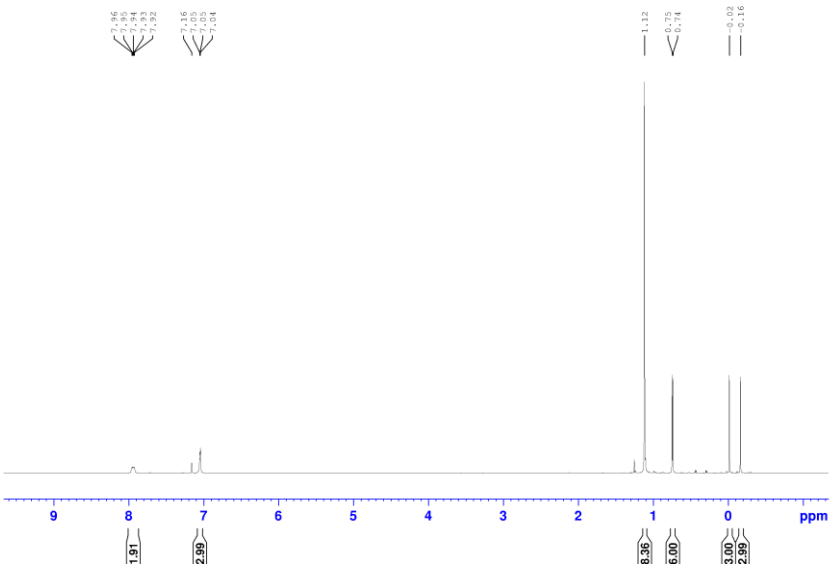


Fig. S65. ^{1}H NMR spectrum of **18**.

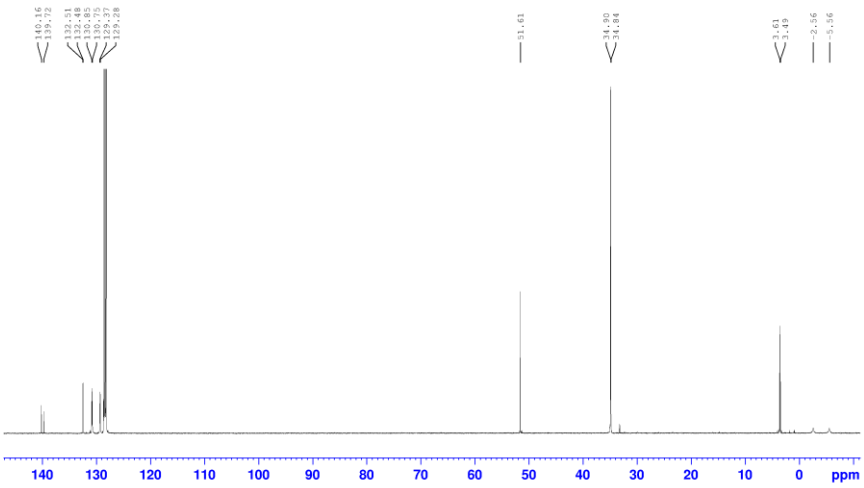


Fig. S66. ^{13}C{^{1}H} APT NMR spectrum of **18**.

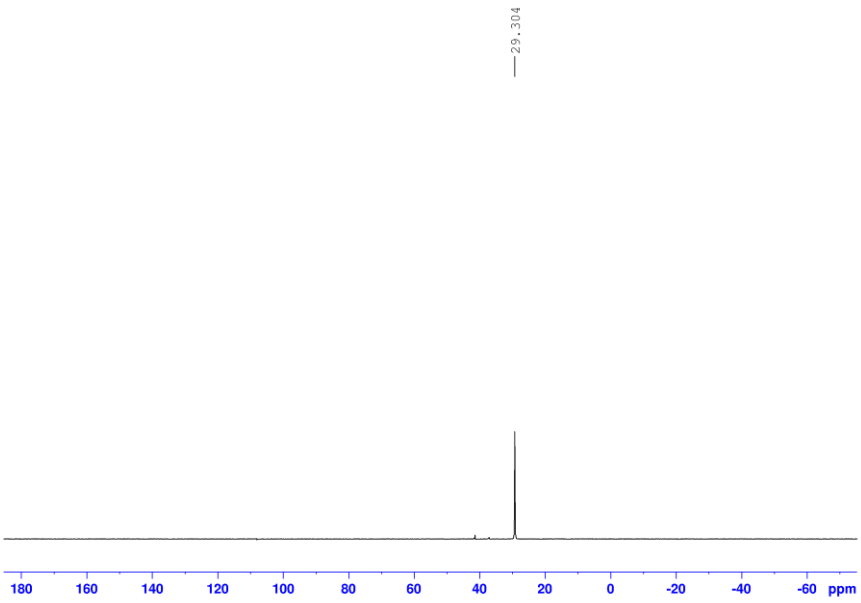


Fig. S67. ^{31}P NMR spectrum of **18**.

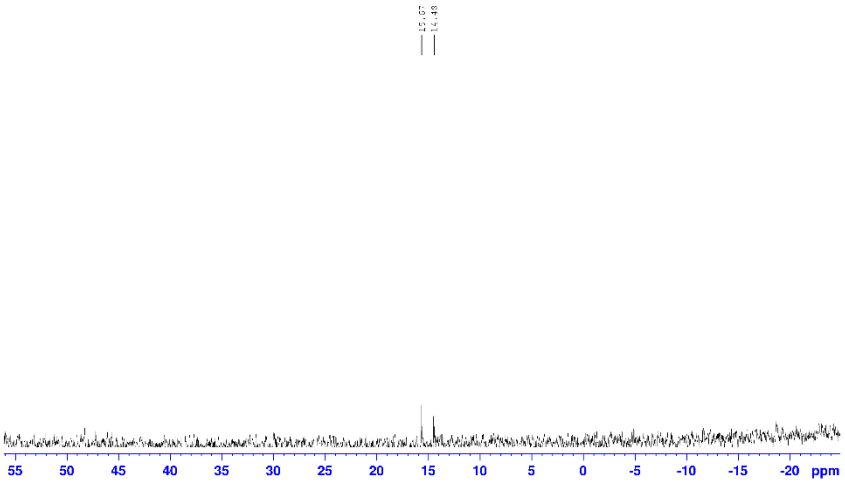


Fig. S68. ^{29}Si NMR spectrum of **18**.

Spectroscopic characterization of {Ph[Me$_2$(Cl)Ge]P(N*t*Bu)$_2$}AlMe$_2$ (19).

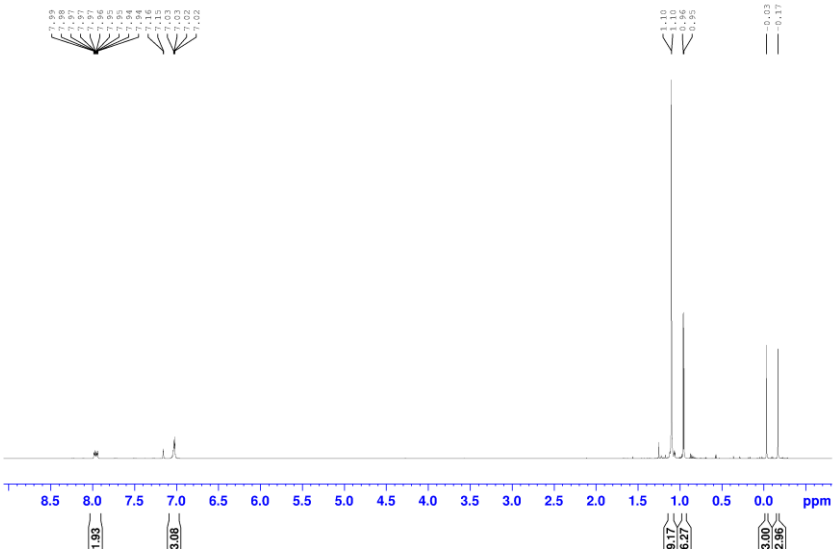


Fig. S69. ^{1}H NMR spectrum of **19**.

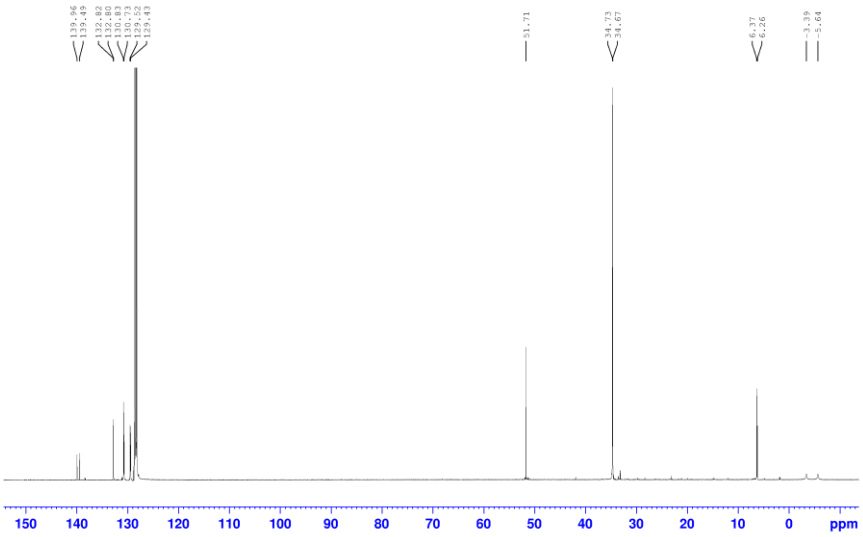


Fig. S70. ^{13}C{^{1}H} NMR spectrum of **19**.

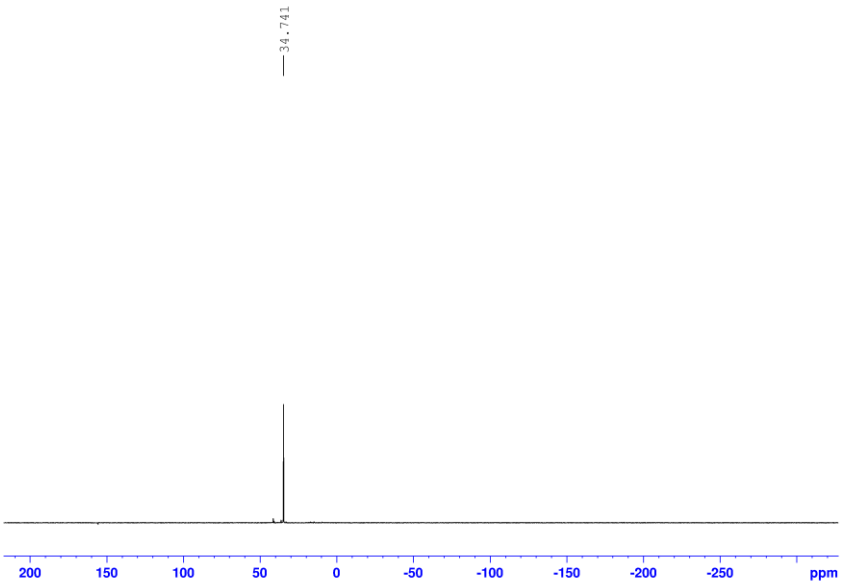


Fig. S71. ^{31}P NMR spectrum of **19**.

Spectroscopic characterization of {[PhP(N*t*Bu)$_2$]AlMe$_2$}$_2$SnMe$_2$ (20).

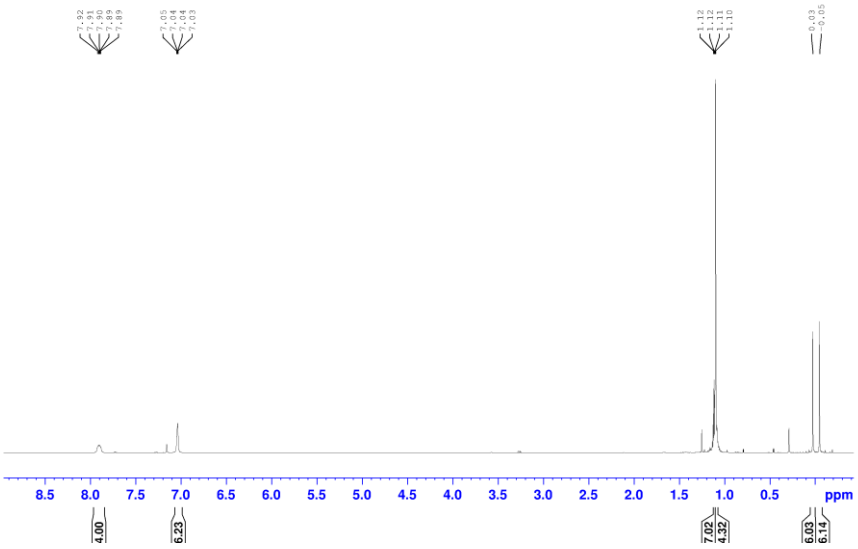


Fig. S72. ^{1}H NMR spectrum of **20**.

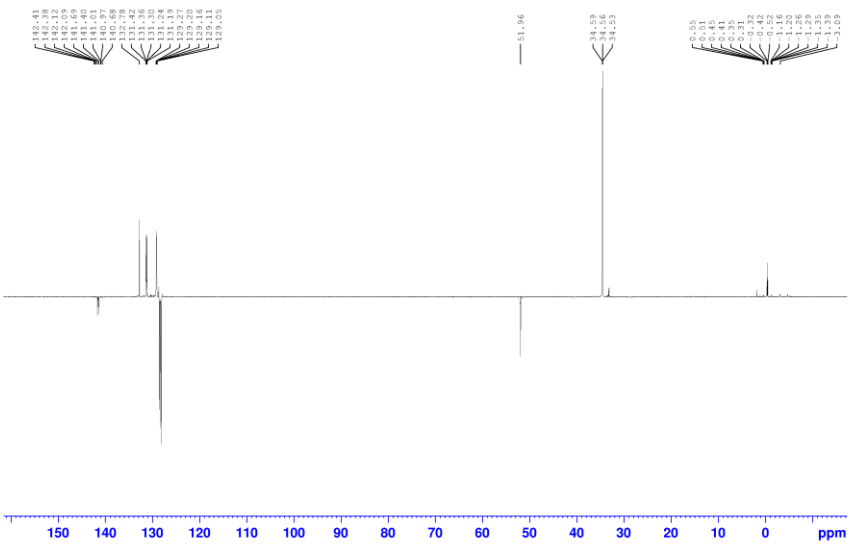


Fig. S73. $^{13}C\{^{1}H\}$ APT NMR spectrum of **20**.

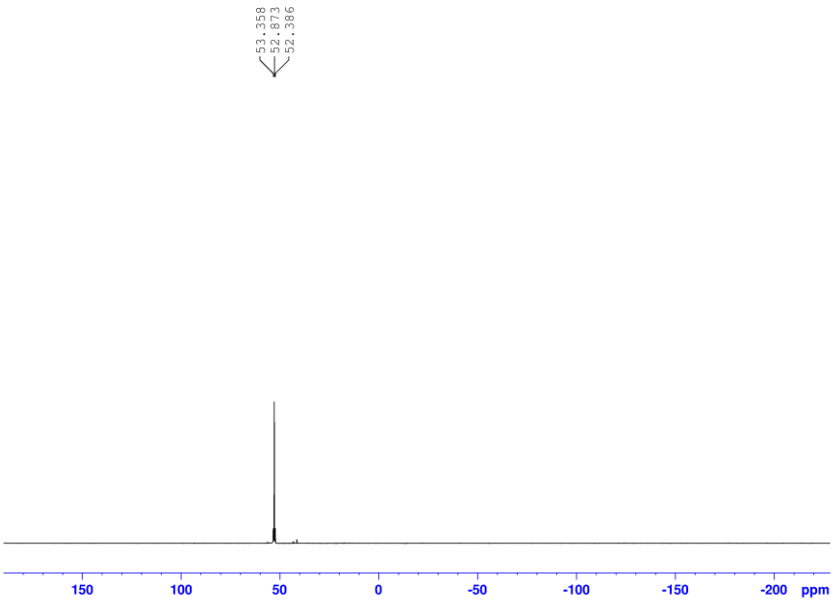


Fig. S74. ^{31}P NMR spectrum of **20**.

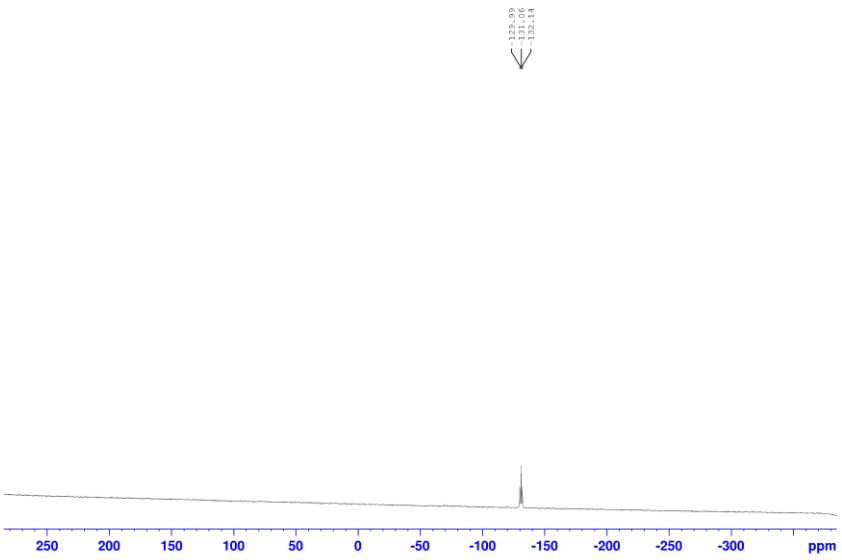


Fig. S75. ^{119}Sn NMR spectrum of **20**.

3. Crystallographic data of prepared compounds

Table S1. Crystal data and structure refinement for [PhP(N*t*Bu)$_2$AlMe$_2$]Li.OEt$_2$ (**1**).

Crystal data	
Chemical formula	$C_{20}H_{39}AlLiN_2OP$
M_r	388.42
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	10.7730(12), 17.3471(17), 13.7090(12)
β (°)	108.295(8)
V (Å^3)	2432.4(4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.16
Crystal size (mm)	0.50 × 0.43 × 0.23
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.945, 0.970
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14651, 5484, 4457
R_{int}	0.026
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.104, 1.14
No. of reflections	5484
No. of parameters	236
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.25

Table S2. Crystal data and structure refinement for [PhP(N*t*Bu)$_2$AlMe$_2$]K (**2**).

Crystal data	
Chemical formula	$C_{16}H_{29}AlKN_2P$
M_r	346.46
Crystal system, space group	Tetragonal, $I4_1cd$
Temperature (K)	150
a, c (Å)	24.3190(3), 14.0521(4)
V (Å^3)	8310.6(3)
Z	16
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.37
Crystal size (mm)	0.59 × 0.51 × 0.47
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.837, 0.864
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11764, 4146, 3707
R_{int}	0.040
(sin θ/λ)$_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.116, 1.09
No. of reflections	4146
No. of parameters	215
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 14.1943P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.25
Absolute structure	Flack x determined using 1522 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	1.02 (4)

Table S3. Crystal data and structure refinement for [PhP(N*t*Bu)$_2$AlH$_2$]Li.THF (**3**).

Crystal data	
Chemical formula	$C_{36}H_{66}Al_2Li_2N_4O_2P_2$
M_r	716.70
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	10.3410(3), 10.4791(4), 11.8430(5)
α, β, γ (°)	105.389(4), 104.811(3), 110.097(3)
V (Å^3)	1073.39(9)
Z	1
Radiation type	Mo *K*α
μ (mm^{-1})	0.18
Crystal size (mm)	0.52 × 0.36 × 0.23
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.935, 0.970
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22689, 4901, 4275
R_{int}	0.025
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.079, 1.08
No. of reflections	4901
No. of parameters	217
H-atom treatment	H-atom parameters mixed
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.24

Table S4. Crystal data and structure refinement for [*t*BuP(N-2,6-*i*Pr$_2$C$_6$H$_3$)$_2$AlMe$_2$]Li.(OEt$_2$)$_2$ (**4**).

Crystal data	
Chemical formula	$C_{38}H_{69}AlLiN_2O_2P$
M_r	650.84
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	12.824(1), 17.7230(18), 19.1321(18)
β (°)	109.123(8)
V (Å^3)	4108.4(7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.12
Crystal size (mm)	0.43 × 0.33 × 0.29
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.967, 0.980
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28594, 9084, 6901
R_{int}	0.033
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.127, 1.01
No. of reflections	9084
No. of parameters	410
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, −0.31

Table S5. Crystal data and structure refinement for [Ph(O)P(N*t*Bu)$_2$AlMe$_2$]Li.OEt$_2$ (**5**).

Crystal data	
Chemical formula	$C_{40}H_{78}Al_2Li_2N_4O_4P_2$
M_r	808.84
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	12.9400(13), 22.914(2), 17.3140(15)
β (°)	104.565(7)
V (Å^3)	4968.7(8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.16
Crystal size (mm)	0.50 × 0.46 × 0.31
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.939, 0.960
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34289, 11222, 9020
R_{int}	0.033
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.109, 1.17
No. of reflections	11222
No. of parameters	493
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.31

Table S6. Crystal data and structure refinement for [Ph(Se)P(N*t*Bu)$_2$AlMe$_2$]Li (**7**).

Crystal data	
Chemical formula	$C_{32}H_{58}Al_2Li_2N_4P_2Se_2 \cdot 2(C_7H_8)$
M_r	970.79
Crystal system, space group	Orthorhombic, *Pna*2$_1$
Temperature (K)	150
a, *b*, *c* (Å)	18.9620(17), 14.0040(8), 19.703(2)
V (Å^3)	5232.0(8)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	1.54
Crystal size (mm)	0.36 × 0.34 × 0.17
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.692, 0.805
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22864, 9633, 6821
R_{int}	0.067
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.055, 0.129, 1.15
No. of reflections	9633
No. of parameters	513
No. of restraints	44
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0151P)^2 + 18.4682P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.83, −0.49
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.35 (3)

Table S7. Crystal data and structure refinement for Bu_4N^+ $[Ph(Te)P(N\textit{t}Bu)_2AlMe_2]^-$ (**9**).

Crystal data	
Chemical formula	$C_{32}H_{65}AlN_3PTe$
M_r	677.42
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	12.9731(13), 16.3990(8), 21.5490(12)
β (°)	125.056(6)
V (Å^3)	3752.8(5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.88
Crystal size (mm)	0.44 × 0.37 × 0.12
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.785, 0.934
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26646, 8521, 6192
R_{int}	0.040
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.081, 1.19
No. of reflections	8521
No. of parameters	343
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.69, −0.56

Table S8. Crystal data and structure refinement for $Ph(Ph_3Sn)P(NtBu)_2AlMe_2$ (**12**).

Crystal data	
Chemical formula	$C_{34}H_{44}AlN_2PSn$
M_r	657.35
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	8.6830(5), 21.2480(12), 19.063(2)
β (°)	112.827(6)
V (Å^3)	3241.6(5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.89
Crystal size (mm)	× ×
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.815, 0.869
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	50129, 7308, 6181
R_{int}	0.045
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.022, 0.058, 1.15
No. of reflections	7308
No. of parameters	352
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.70, −0.53

Table S9. Crystal data and structure refinement for $Ph(Me_3Pb)P(NtBu)_2AlMe_2$ (**13**).

Crystal data	
Chemical formula	$C_{19}H_{38}AlN_2PPb$
M_r	559.65
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	9.4990(8), 12.1891(13), 20.8711(17)
β (°)	91.820(7)
V (Å^3)	2415.3(4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	7.09
Crystal size (mm)	0.55 × 0.37 × 0.25
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.135, 0.297
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19655, 5503, 4084
R_{int}	0.073
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.117, 1.28
No. of reflections	5503
No. of parameters	217
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 10.9742P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.73, −3.09

Table S10. Crystal data and structure refinement for Ph[2,6-*i*Pr$_2$-C$_6$H$_3$(H)N(Ph)P]P(N*t*Bu)$_2$AlMe$_2$ (**14**).

Crystal data	
Chemical formula	$C_{34}H_{52}AlN_3P_2$
M_r	591.70
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	11.2329(10), 18.4331(17), 18.3680(9)
β (°)	115.710(5)
V (Å^3)	3426.7(5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.18
Crystal size (mm)	0.59 × 0.34 × 0.14
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.937, 0.975
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30571, 7695, 6191
R_{int}	0.030
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.101, 1.15
No. of reflections	7695
No. of parameters	361
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.34

Table S11. Crystal data and structure refinement for $Ph(Ph_2P)P(NtBu)_2AlMe_2$ (**15**).

Crystal data	
Chemical formula	$C_{28}H_{39}AlN_2P_2$
M_r	492.53
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	16.4341(13), 10.063(1), 18.193(1)
β (°)	109.016(5)
V (Å^3)	2844.5(4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.20
Crystal size (mm)	0.59 × 0.55 × 0.16
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.909, 0.977
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25036, 6414, 4416
R_{int}	0.062
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.132, 1.19
No. of reflections	6414
No. of parameters	298
No. of restraints	6
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.46

Table S12. Crystal data and structure refinement for Ph[Ph(Cl)P]P(N*t*Bu)$_2$AlMe$_2$ (**16**).

Crystal data	
Chemical formula	$C_{22}H_{34}AlClN_2P_2$
M_r	450.88
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	9.1990(11), 17.8961(19), 15.6220(4)
β (°)	107.492(6)
V (Å^3)	2452.9(4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.33
Crystal size (mm)	0.59 × 0.59 × 0.37
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.858, 0.925
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21225, 5311, 4520
R_{int}	0.063
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.091, 1.16
No. of reflections	5311
No. of parameters	253
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.37

Table S13. Crystal data and structure refinement for Ph[*t*Bu(Cl)P]P(N*t*Bu)$_2$AlMe$_2$ (**17**).

Crystal data	
Chemical formula	$C_{20}H_{38}AlClN_2P_2$
M_r	430.89
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	10.7201(5), 15.4029(14), 17.697(1)
β (°)	122.919(5)
V (Å^3)	2453.0(3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.33
Crystal size (mm)	0.55 × 0.41 × 0.33
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.869, 0.926
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	38806, 5596, 4698
R_{int}	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.087, 1.18
No. of reflections	5596
No. of parameters	235
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, −0.33

Table S14. Crystal data and structure refinement for Ph[Me_2(Cl)Si]P(N*t*Bu)$_2$AlMe_2 (**18**).

Crystal data	
Chemical formula	$C_{18}H_{35}AlClN_2PSi$
M_r	400.97
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	18.4470(11), 12.0000(17), 27.7450(8)
β (°)	131.264(7)
V (Å^3)	4616.6(8)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.33
Crystal size (mm)	0.59 × 0.28 × 0.27
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.869, 0.940
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	80243, 10545, 8587
R_{int}	0.038
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.101, 1.12
No. of reflections	10545
No. of parameters	442
No. of restraints	4
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, −0.44

Table S15. Crystal data and structure refinement for Ph[Me_2(Cl)Ge]P(N*t*Bu)$_2$AlMe_2 (**19**).

Crystal data	
Chemical formula	$C_{18}H_{35}AlClGeN_2P$
M_r	445.47
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	18.5602(3), 12.0744(4), 27.8681(3)
β (°)	131.731(2)
V (Å^3)	4660.8(2)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.54
Crystal size (mm)	0.57 × 0.45 × 0.41
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.521, 0.691
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	56816, 10045, 7474
R_{int}	0.058
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.118, 1.23
No. of reflections	10045
No. of parameters	433
H-atom treatment	H-atom parameters constrained
	$w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 10.1905P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.93, −0.56

Table S16. Crystal data and structure refinement for $[PhP(NtBu)_2AlMe_2]_2SnMe_2$ (**20**).

Crystal data	
Chemical formula	$C_{34}H_{64}Al_2N_4P_2Sn$
M_r	763.48
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	15.2710(17), 10.3050(8), 27.009(5)
β (°)	104.275(11)
V (Å^3)	4119.1(10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.77
Crystal size (mm)	0.59 × 0.30 × 0.18
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Integration Gaussian integration (Coppens, 1970)
T_{min}, T_{max}	0.790, 0.914
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26412, 8854, 7541
R_{int}	0.029
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.067, 1.14
No. of reflections	8854
No. of parameters	388
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.42, −0.54

4. Molecular structures of prepared compounds

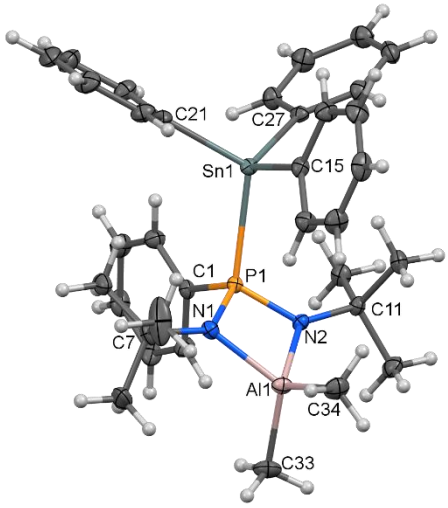


Figure S76. The molecular structure of **12**. ORTEP-type plots, 40% probability level. Selected structural parameters [Å, °]: P1-N1 1.6248(16), P1-N2 1.6233(15), Al1-N1 1.9286(17), Al1-N2 1.9106(16), Al1-C33 1.970(3), Al1-C34 1.970(2), P1-Sn1 2.5894(5), N1-P1-N2 94.21(10), N1-Al1-N2 76.55(7), C33-Al1-C34 112.62(10), C1-P1-Sn1 107.91(6), N1-P1-Sn1 116.55(6).

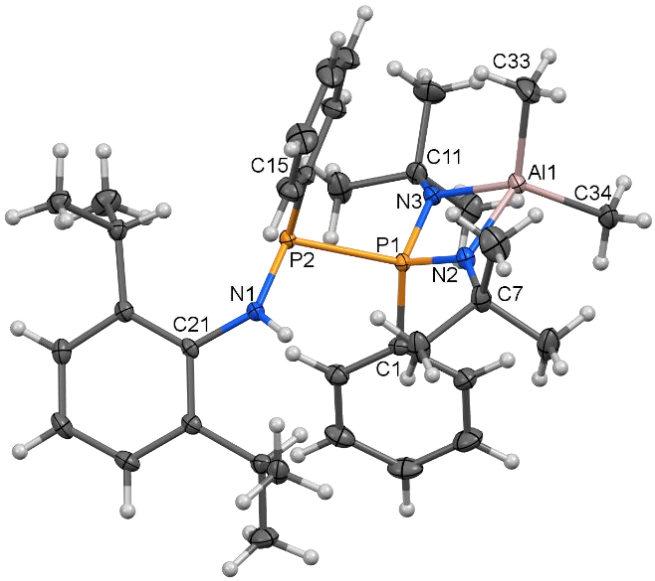


Figure S77. The molecular structure of **14**. ORTEP-type plots, 40% probability level. Selected structural parameters [Å, °]: P1-N2 1.6167(15), P1-N3 1.6237(14), Al1-N2 1.9245(15), Al1-N3 1.9291(15), Al1-C33 1.963(2), Al1-C34 1.9752(19), P1-P2 2.2505(6), N2-P1-N3 94.96(7), N2-Al1-N3 76.60(6), C33-Al1-C34 112.18(9), C1-P1-P2 104.76(6).

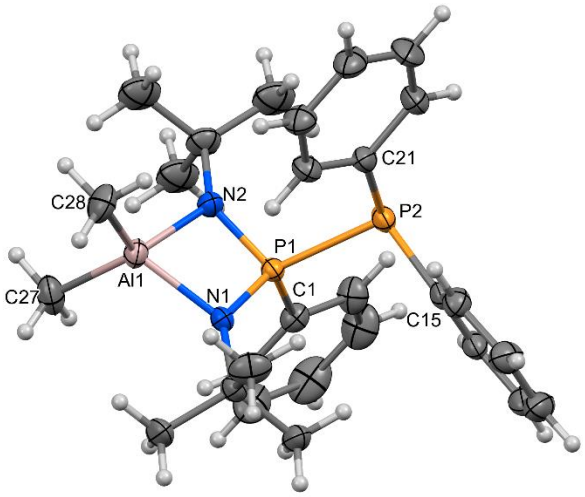


Figure S78. The molecular structure of **15**. ORTEP-type plots, 40% probability level. Selected structural parameters [Å, °]: P1-N1 1.615(2), P1-N2 1.619(2), Al1-N1 1.933(2), Al1-N2 1.913(2), Al1-C27 1.965(3), Al1-C28 1.978(3), P1-P2 2.2306(10), N1-P1-N2 95.05(11), N1-Al1-N2 76.66(9), C27-Al1-C28 111.60(15), C1-P1-P2 101.72(9).

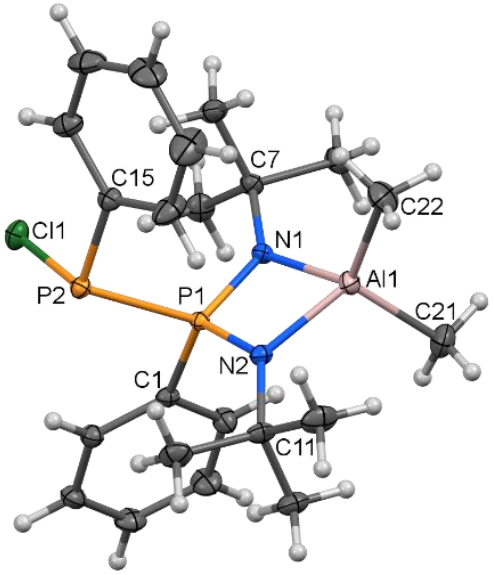


Figure S79. The molecular structure of **16**. ORTEP-type plots, 40% probability level. Selected structural parameters [Å, °]: P1-N1 1.6110(15), P1-N2 1.6184(14), Al1-N1 1.9241(15), Al1-N2 1.9321(16), Al1-C21 1.978(2), Al1-C22 1.956(2), P1-P2 2.2497(6), N1-P1-N2 95.63(7), N1-Al1-N2 76.71(6), C21-Al1-C22 113.69(10), C1-P1-P2 102.42(6).

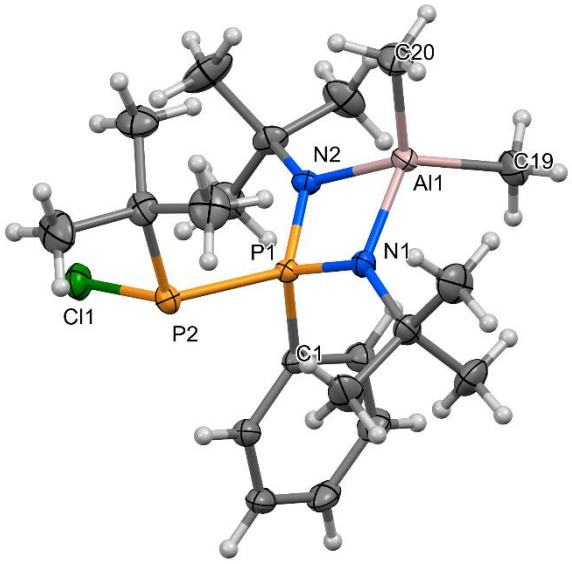


Figure S80. The molecular structure of **17**. ORTEP-type plots, 40% probability level. Selected structural parameters [Å, °]: P1-N1 1.6195(13), P1-N2 1.6118(12), Al1-N1 1.9248(13), Al1-N2 1.9346(13), Al1-C19 1.9677(18), Al1-C20 1.9562(18), P1-P2 2.2517(5), N1-P1-N2 95.89(6), N1-Al1-N2 76.87(5), C19-Al1-C20 113.76(8), C1-P1-P2 102.65(5).

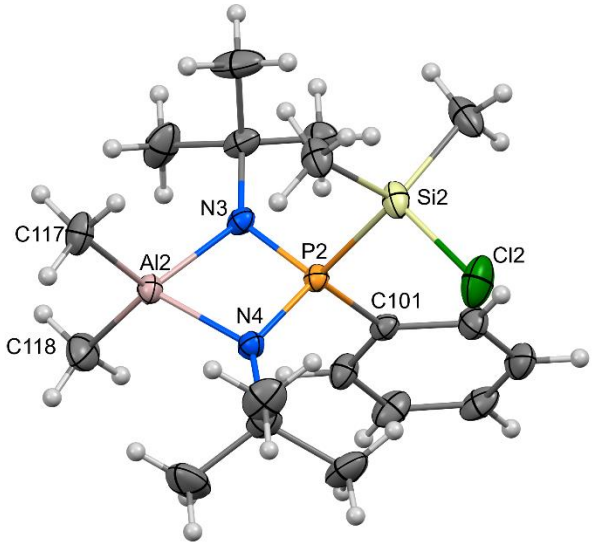


Figure S81. The molecular structure of **18**. ORTEP-type plots, 40% probability level. Selected structural parameters [Å, °]: P2-N3 1.6223(14), P2-N4 1.6211(14), Al2-N3 1.9151(15), Al2-N4 1.9204(15), Al2-C117 1.961(2), Al2-C118 1.968(2), P2-Si2 2.2928(6), N3-P2-N4 94.29(7), N3-Al2-N4 76.61(6), C117-Al2-C118 113.66(9), C101-P2-Si2 110.71(6).

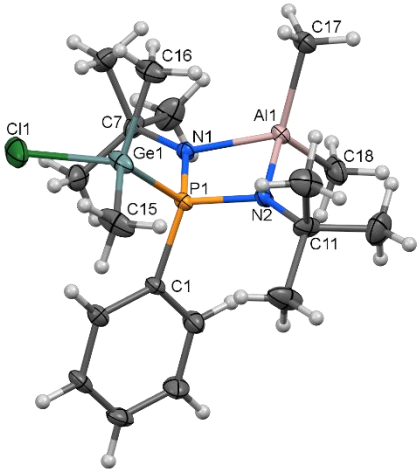


Figure S82. The molecular structure of **19**. ORTEP-type plots, 40% probability level. Selected structural parameters [Å, °]: P1-N1 1.611(3), P1-N2 1.622(3), Al1-N1 1.917(3), Al1-N2 1.920(3), Al1-C17 1.962(4), Al1-C18 1.970(4), P1-Ge1 2.3503(9), N1-P1-N2 94.76(14), N1-Al1-N2 76.62(12), C17-Al1-C18 114.57(17), C1-P1-Ge1 108.51(11).

5. Computational data

All the calculations were performed with the Gaussian 16 program.[S1] The geometries of the compounds **1**, **3** and **4** were fully optimized at B3LYP/6-311+G(d,p), PBE1PBE/6-311+G(d,p) and M06-2X/6-311+G(d,p) levels of theory[S2] without any simplifications. The structures of complexes obtained by X-ray diffraction were used as the initial data. The polarizable continuum model (CPCM)[S3] was employed for the solvation effects (benzene). All the structures are minima on the potential energy surface, as confirmed by the frequency calculations at the same level of theory and transition states by only one imaginary frequency. Taking into the account the initial coordinates and optimized ones differ only slightly and the complex **2** and the comparative complex $[(N,N'\text{-}t\text{Bu}_2\text{-}C_3N_2H)AlMe_2(\mu\text{-}Me)Li(THF)]_n$ [S4] are of polymeric nature, which need to be simplified, thus the single point energies for crystallographically determined atom coordinates (simplified polymeric structure of **2** and $[(N,N'\text{-}t\text{Bu}_2\text{-}C_3N_2H)AlMe_2(\mu\text{-}Me)Li(THF)]_n$ [S4]) were calculated at M06-2X/6-311+G(d,p) level of theory, which is suggested to be the most appropriate for systems containing an agostic interaction[S5] without solvent corrections and dispersion correction. The orbitals were visualized by NBO7 program.[S6] The topological analysis of the theoretical function ρ(*r*) was performed using the AIMALL program package.[S7] Within the framework of Atoms in Molecules theory, the atomic charges in all compounds together with bond, ring and cluster critical points were calculated, the interaction energies within the critical points were calculated according to Espinosa's equation.[S8]

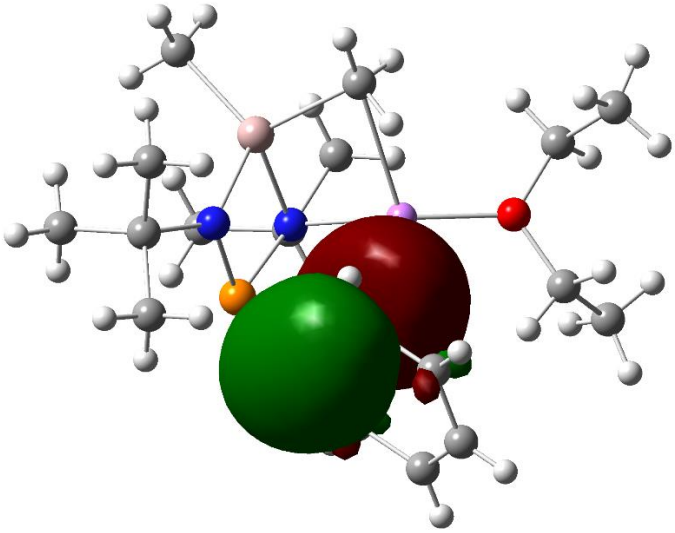


Figure S83. The HOMO-2 molecular orbital of **1** at -8.51eV responsible for the π-electron cloud to lithium atom interaction (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

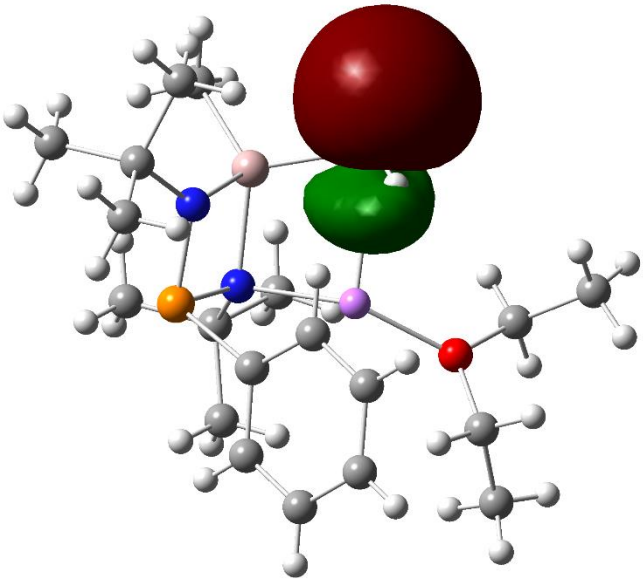


Figure S84. The HOMO-18 molecular orbital of **1** at -14.21eV partially responsible for the agostic interaction of methyl group and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

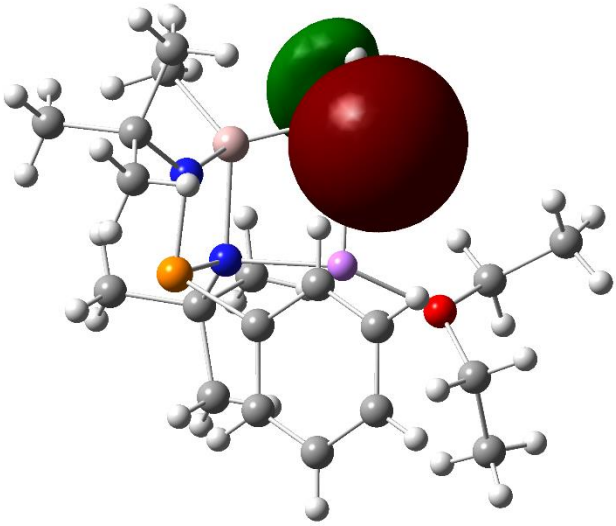


Figure S85. The HOMO-31 molecular orbital of **1** at -14.73eV partially responsible for the agostic interaction of methyl group and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

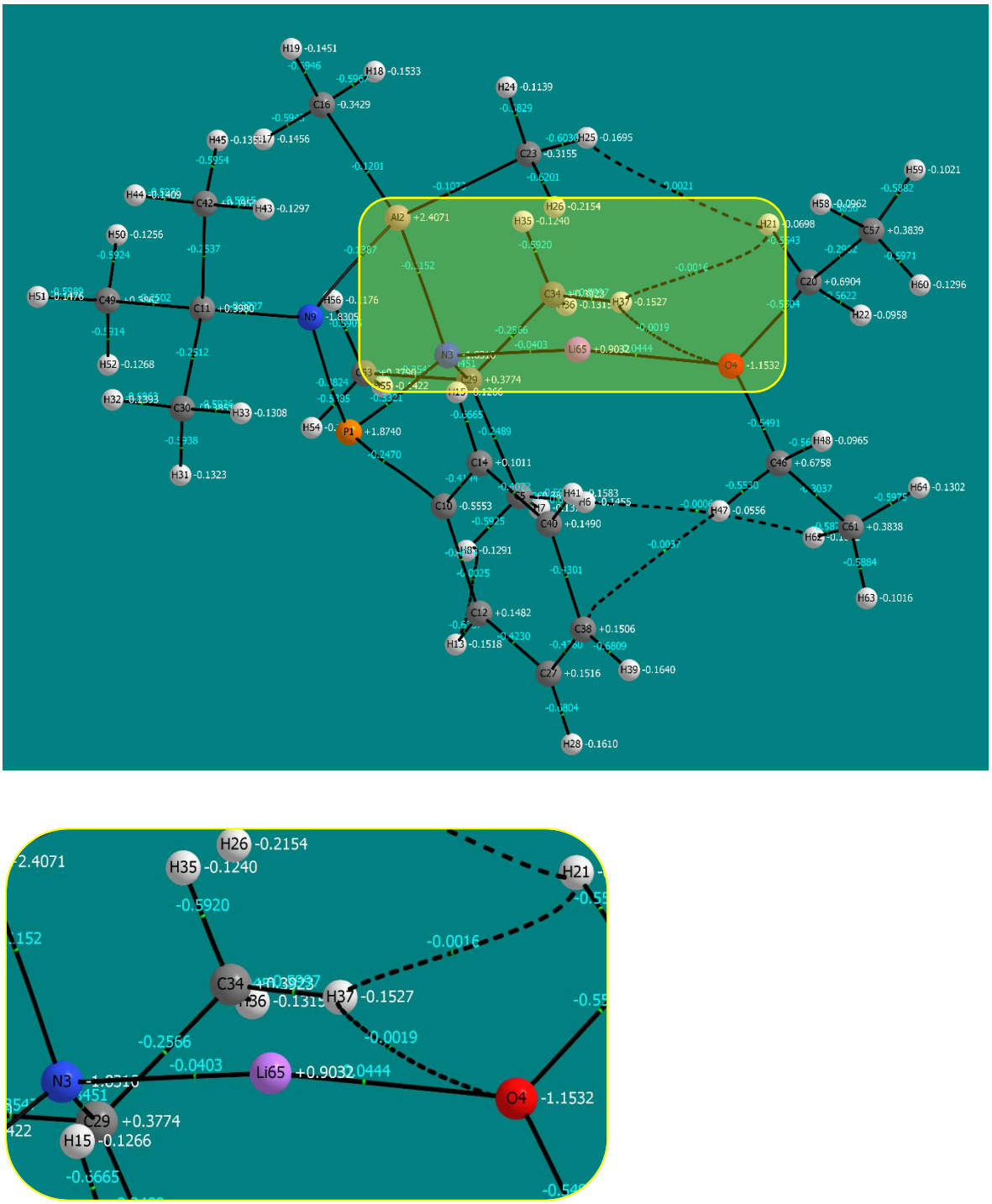


Figure S86. The representation of AIM charges (white values) and bond critical points (light green dots with light blue values) of **1** with magnified detail of area of interest. Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

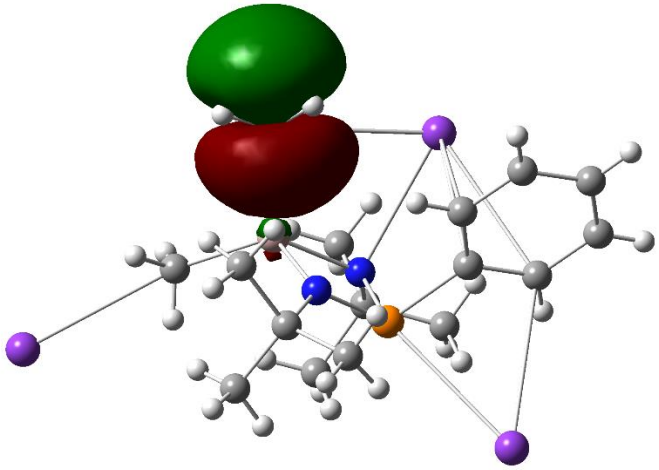


Figure S87. The HOMO-1 molecular orbital of **2** at -6.43 eV responsible for the interaction of methyl group and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates – simplified polymeric structure). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

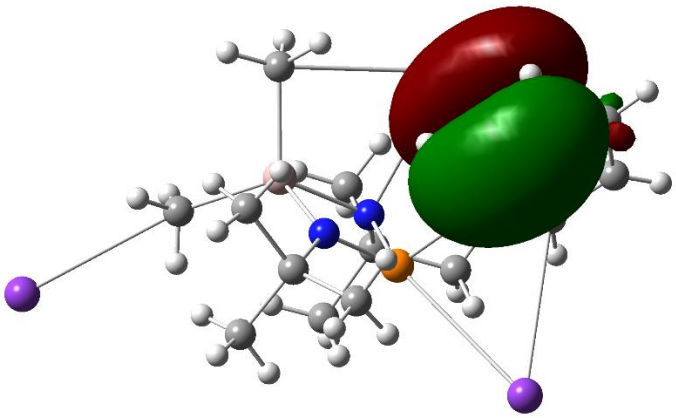


Figure S88. The HOMO-5 molecular orbital of **2** at -8.77 eV responsible for the interaction of π-electron cloud and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates – simplified polymeric structure). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

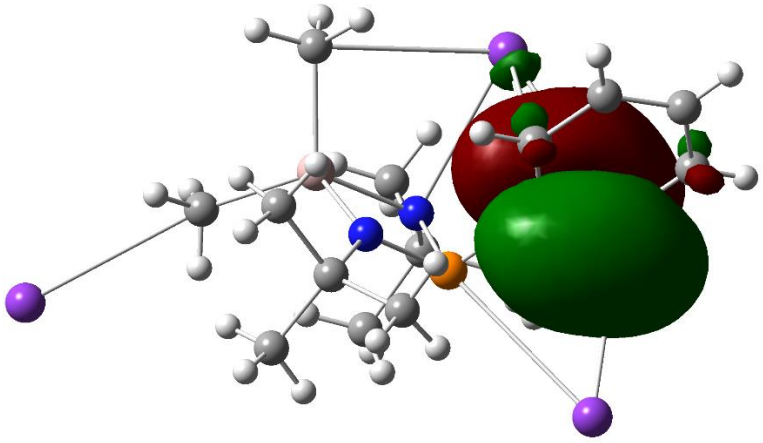


Figure S89. The HOMO-6 molecular orbital of **2** at -8.87 eV responsible for the interaction of π-electron cloud and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates – simplified polymeric structure). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

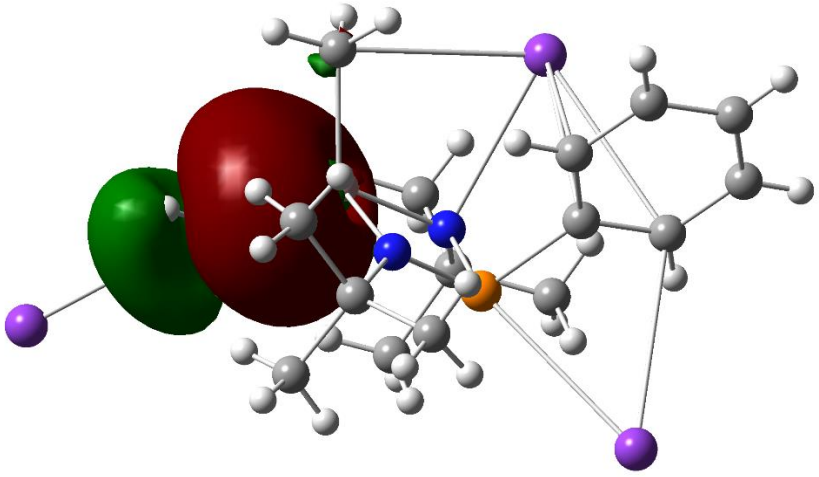


Figure S90. The HOMO-8 molecular orbital of **2** at -10.31 eV responsible for the interaction of methyl group and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates – simplified polymeric structure). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

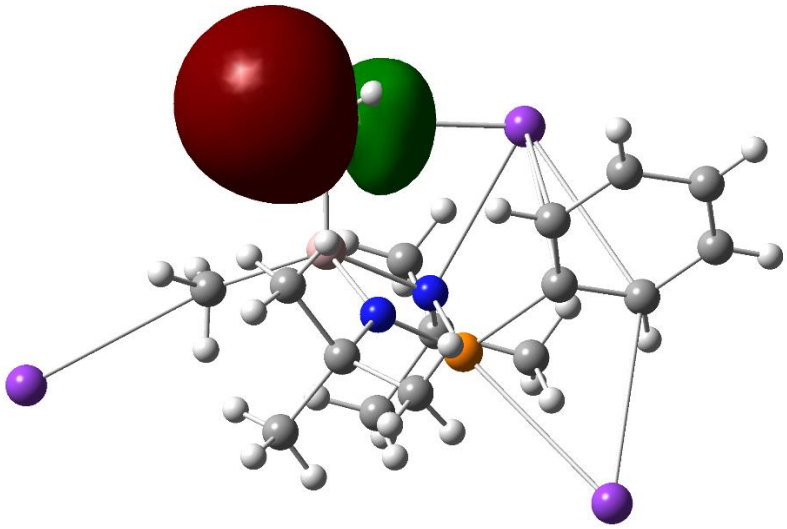
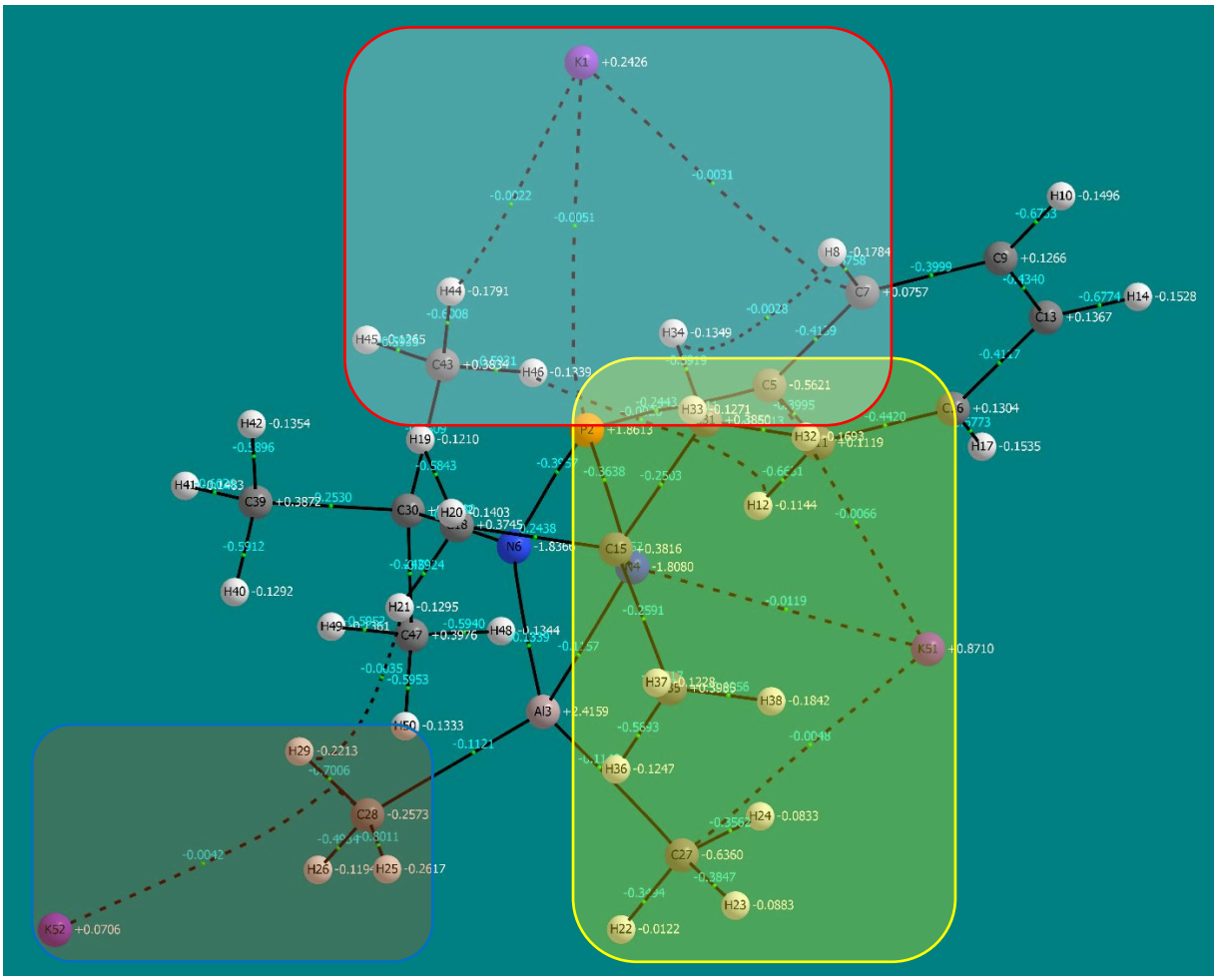


Figure S91. The HOMO-12 molecular orbital of **2** at -14.35 eV responsible for the interaction of methyl group and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates – simplified polymeric structure). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.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H10 -0.1496
H8 -0.1784
C9 +0.1266
H44 -0.1791
C7 +0.0757
H14 -0.1528
C13 +0.1367
H34 -0.1349
H45
C43 +0.3834
H46 -0.1339
C5 -0.5621
H33 -0.1271
C16 +0.1304
H42 -0.1354
H19 -0.1210
P2 +1.8613
H32 -0.1693
H17 -0.1535
H41
C39 +0.3872
C30
H20 -0.1403
H12 -0.1144
N6
C15 +0.3816
H40 -0.1292
H21 -0.1295
H49
C47 +0.3976
H48 -0.1344
K51 +0.8710
H37
H38 -0.1842
Al3 +2.4159
H50 -0.1333
H29 -0.2213
H36 -0.1247
C28 -0.2573
H24 -0.0833
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H26 -0.1194
H25 -0.2617
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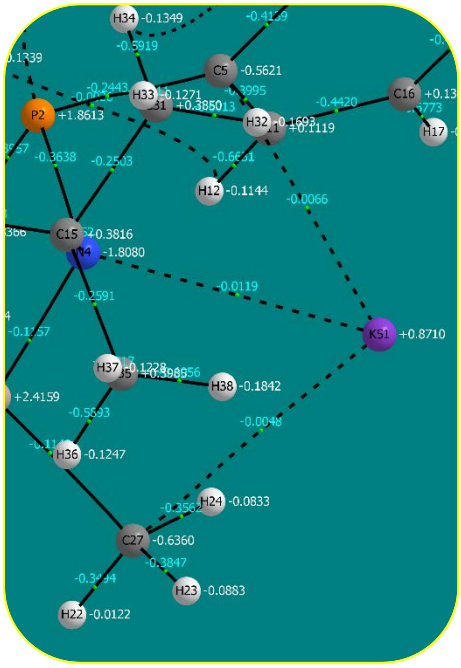
H22 -0.0122
K52 +0.0706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C5 -0.5621
H33
C16
P2 +1.8613
H32
H17
H12 -0.1144
C15 +0.3816
K51 +0.8710
H37
H38 -0.1842
H36 -0.1247
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C27 -0.6360
H23 -0.0883
H22 -0.0122

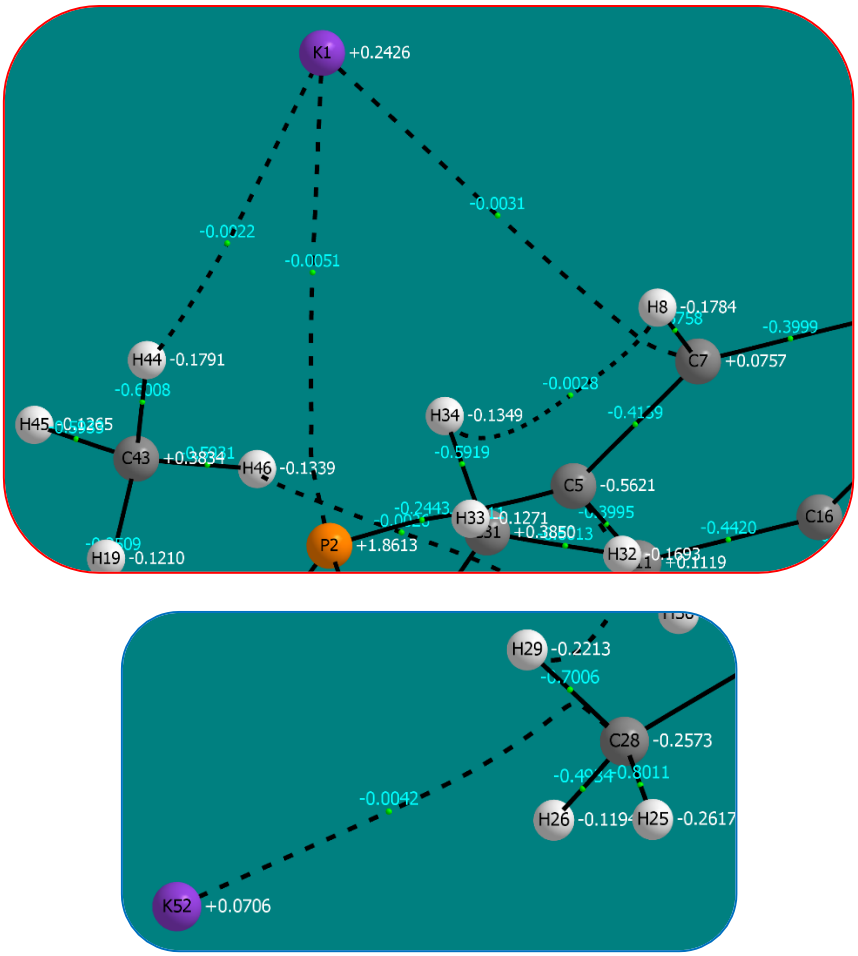

Figure S92. The representation of AIM charges (white values) and bond critical points (light green dots with light blue values) of **2** with magnified details of areas of interest - simplified polymeric structure. Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

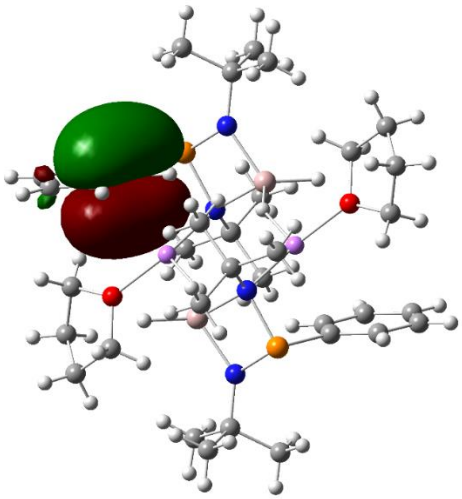

Figure S93. The HOMO-1 molecular orbital of **3** at -7.90 eV responsible for the interaction of π-electron cloud and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

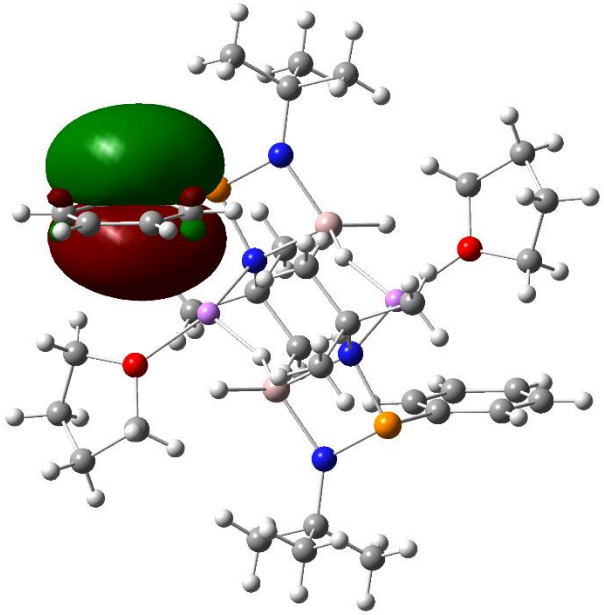

Figure S94. The HOMO-2 molecular orbital of **3** at -7.91 eV responsible for the interaction of π-electron cloud and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

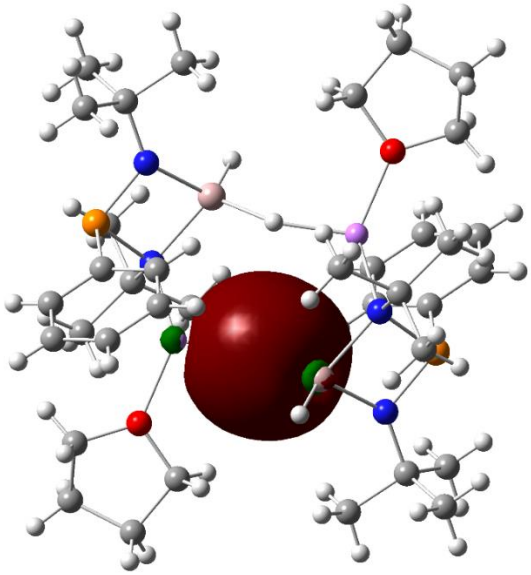

Figure S95. The HOMO-9 molecular orbital of **3** at -9.50 eV responsible for the interaction of hydride and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

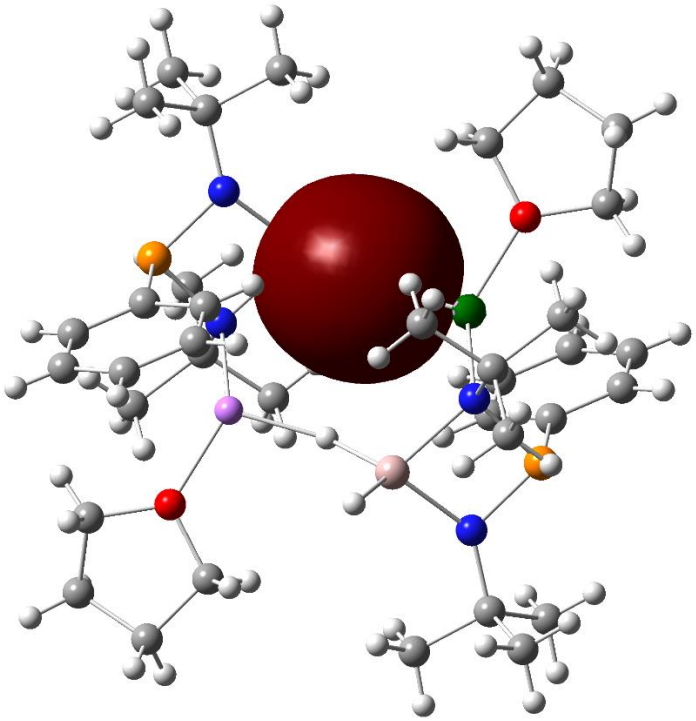

Figure S96. The HOMO-10 molecular orbital of **3** at -9.51 eV responsible for the interaction of hydride and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

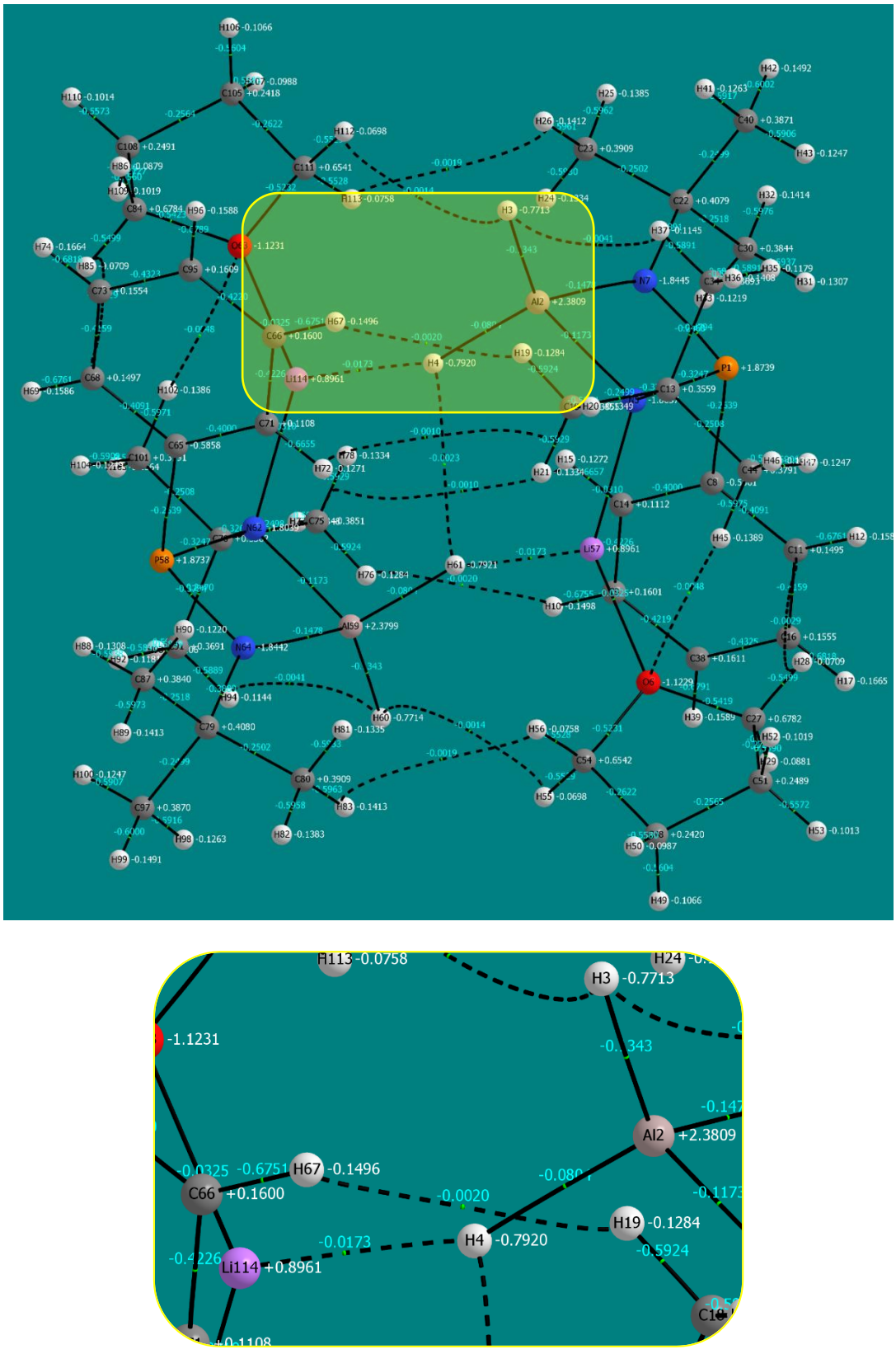

Figure S97. The representation of AIM charges (white values) and bond critical points (light green dots with light blue values) of **3** with magnified detail of area of interest. Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

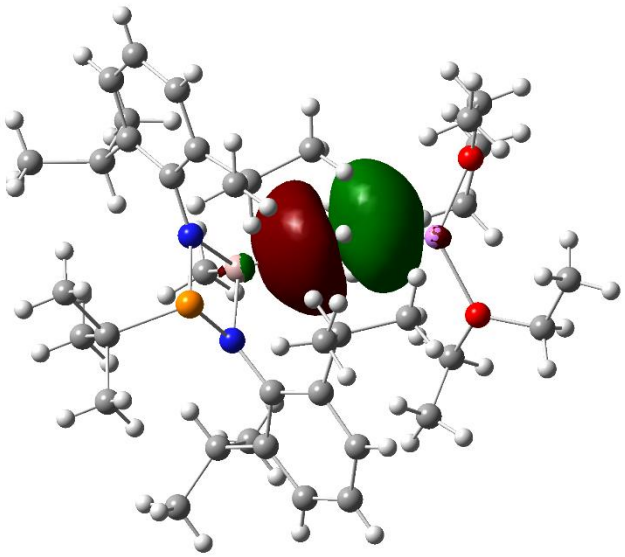

Figure S98. The HOMO molecular orbital of **4** at -6.19 eV responsible for the agostic interaction of methyl group and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

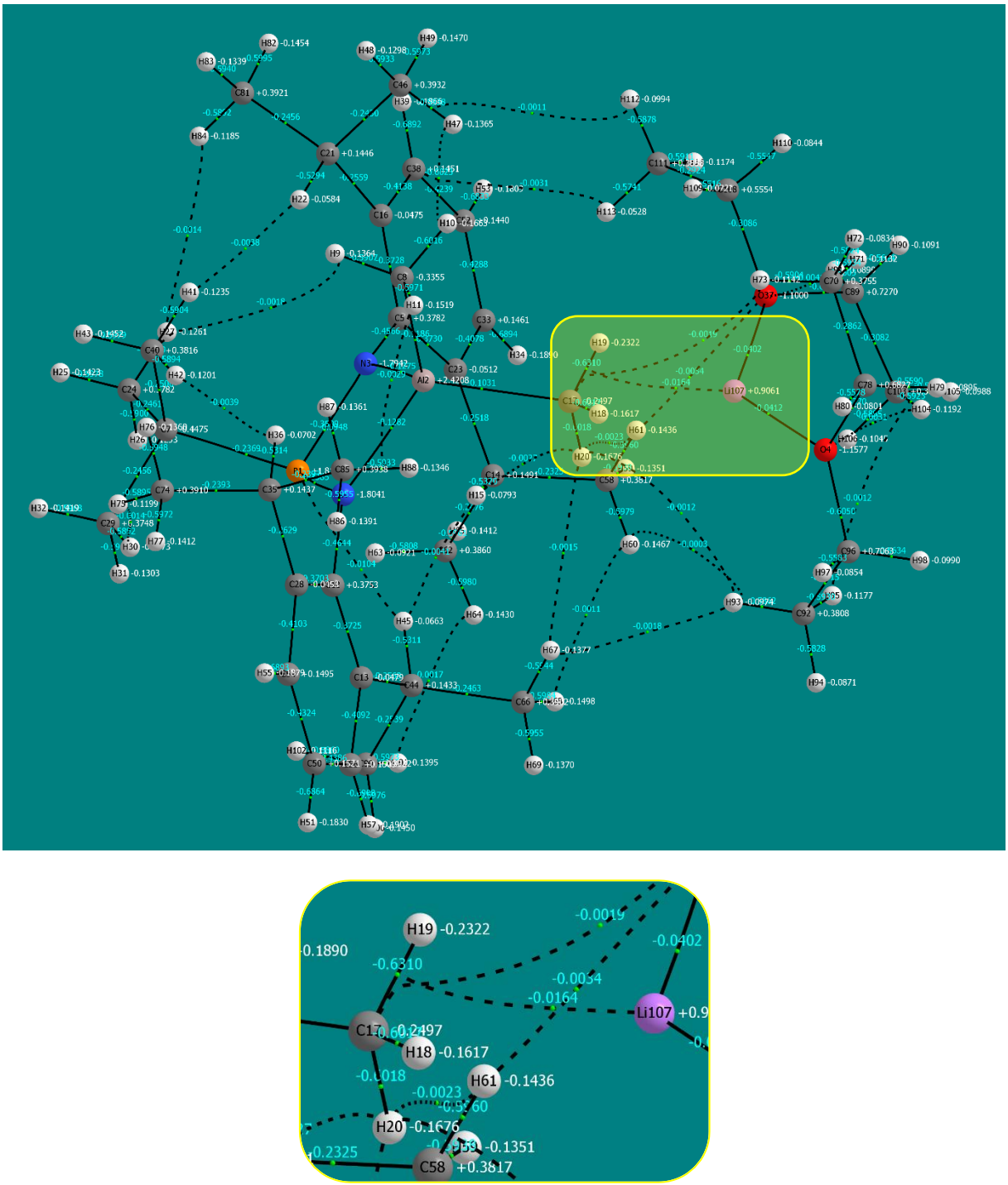

Figure S99. The representation of AIM charges (white values) and bond critical points (light green dots with light blue values) of **4** with magnified detail of area of interest. Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

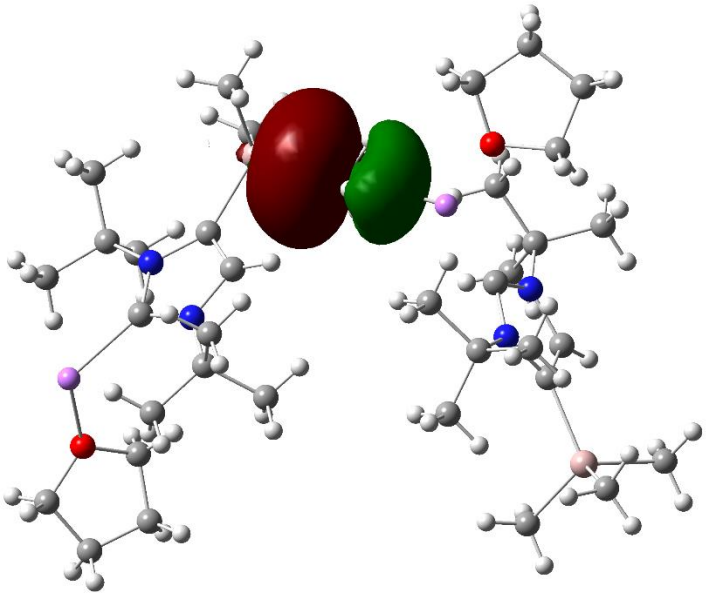

Figure S100. The HOMO-10 molecular orbital of the comparative compound [(N,N'-*t*Bu$_2$-C$_3$N$_2$H)AlMe$_2$(μ-Me)Li(THF)]$_n$ [S4] at -9.33 eV responsible for the interaction of methyl group and lithium atom (M06-2X/6-311+G(d,p), single point energy from crystallographically determined atom coordinates – simplified polymeric structure). Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

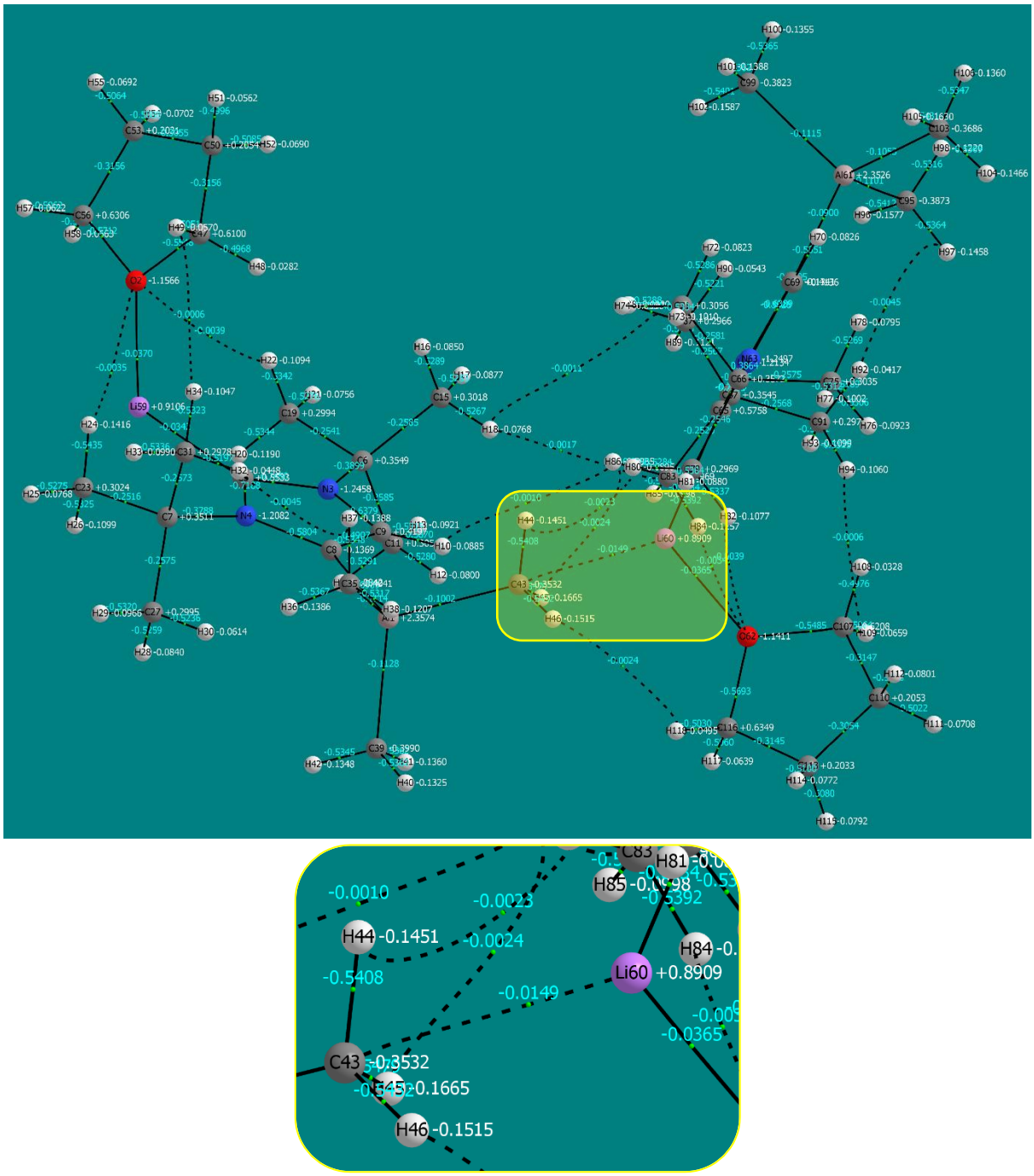

Figure S101. The representation of AIM charges (white values) and bond critical points (light green dots with light blue values) with magnified detail of area of interest - simplified polymeric structure of the comparative compound $[(N,N'\text{-}t\text{Bu}_2\text{-}C_3N_2H)AlMe_2(\mu\text{-}Me)Li(THF)]_n$ [S4]. Color codes: Al - pink, Li - violet, N - blue, P - orange, O - red, C -gray, H - white.

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