Supporting Information

Unusual ligand rearrangement: from *N*-phosphinoguanidinato to phosphinimine-amidinato compounds

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General remarks. All manipulations were carried out under dry nitrogen using standard Schlenk and glovebox techniques. Solvents were distilled from appropriate drying agents and stored under N_2 in Schlenk tubes equipped with J. Young-type Teflon stoppers and containing activated molecular sieves (4 Å). Microanalyses were carried out with a LECO CHNS-932 analyser. NMR spectra were recorded on Bruker 400 and 500 spectrometers at 298 K unless otherwise stated, using standard TOPSPIN 4.0 software. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are referenced to residual protons or carbons in deuterated solvent, and ^{31}P{^{1}H} NMR is referenced to external 85% aqueous H_3PO_4. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. The chemical shifts were assigned based on homo- and heteronuclear 2D NMR experiments (COSY, HSQC, HMBC). Guanidines (HN^{i}Pr)$_2$C(NDipp) (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) and (HN^{i}Pr)$_2$C(NMes) (Mes = 2,4,6-Me$_3$C$_6$H$_2$) were obtained in adequate yield by using the method reported in the literature.[1] All reagents were purchased from the usual commercial suppliers.

Preparation of (HN^{i}Pr)(Ph$_2$PN^{i}Pr)C(NDipp) (1a). Method A: A solution of *n*-BuLi (2.69 mL, 4.30 mmol, 1.6 M in hexane) was added slowly to a solution of (HN^{i}Pr)$_2$C(NDipp) (1.30 g, 4.29 mmol) in Et$_2$O (15 mL) in a Schlenk tube at –78 ºC and then the mixture was stirred at room temperature for 5 h. Afterwards, the solution was cooled to −78 °C, a solution of ClPPh$_2$ (0.80 mL, 4.29 mmol) in Et$_2$O (10 mL) was added and the mixture was allowed to stir at room temperature overnight. The resulting yellow solution was dried *in vacuo* and the residue was extracted with *n*-hexane (2 x 25 mL). Finally, the solution was concentrated under vacuum and cooled to –20 ºC to obtain white crystals of compound **1a**. Several crops of crystallisation could be obtained from the mother liquor to increase the overall yield (1.54 g, 78%). Crystals of **1a** suitable for a diffractometric analysis were grown from a saturated hexane solution at room temperature. Method B: A solution of ClPPh$_2$ (0.61 mL, 3.29 mmol) was added dropwise to a solution of (HN^{i}Pr)$_2$C(NDipp) (1.00 g, 3.29 mmol) and NEt$_3$ (0.46 ml, 3.29 mmol) in Et$_2$O (15 mL) at −78 °C. The mixture was stirred at room temperature for 15 h, then the precipitate was filtered off and the solvent was removed under vacuum. The residue obtained was dissolved in pentane, concentrated and kept at –20 °C to afford white crystals that were washed with pentane (2 x 5 mL) and dried under vacuum to yield compound **1a** as a white crystalline powder (1.03 g, 64%). Anal. calcd for $C_{31}H_{42}PN_3$: C, 76.35;H, 8.68; N, 8.62. Found: C, 76.17; H, 8.74; N, 8.50.

^{1}H NMR (500 MHz, C_6D_6): δ 0.59 (d, 6H, J_{HH} = 6.4, HNCH(CH_3)$_2$), 1.32 (d, 6H, J_{HH} = 6.8, CH(CH_3)$_2$-Dipp), 1.40 (d, 6H, J_{HH} = 6.6, CH(CH_3)$_2$-Dipp), 1.40 (d, 6H, J_{HH} = 6.9, PNCH(CH_3)$_2$), 3.43 (sept, 2H, J_{HH} = 6.9, C*H*(CH$_3$)$_2$-Dipp), 3.53 (ddsept, 1H, J_{HH} = 6.4, 9.8, J_{HP} = 1.1, HNC*H*(CH$_3$)$_2$), 4.05 (d, 1H, J_{HH} = 9.8, N*H*), 4.31 (dsept, 1H, J_{HH} = 6.8, J_{HP} = 6.4, PNC*H*(CH$_3$)$_2$), 7.09 (m, 2H, *p*-P*Ph*$_2$), 7.11 (m, 1H, *p*-Dipp), 7.15 (m, 4H, *m*-P*Ph*$_2$), 7.23 (m, 2H, *m*-Dipp), 7.68 (m, 4H, *o*-P*Ph*$_2$). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ 22.9 (s, CH(*C*H$_3$)$_2$-Dipp), 23.3 (d, J_{CP} = 5.1, PNCH(*C*H$_3$)$_2$), 23.8 (s, HNCH(*C*H$_3$)$_2$), 24.7 (s, CH(*C*H$_3$)$_2$-Dipp), 28.8 (s, *C*H(CH$_3$)$_2$-Dipp), 44.8 (d, J_{CP} = 4.6, HN*C*H(CH$_3$)$_2$), 51.9 (d, J_{CP} = 5.0, PN*C*H(CH$_3$)$_2$), 122.6 (s, *p*-Dipp) 123.5 (s, *m*-Dipp), 128.8 (d, J_{CP} = 5.3, *m*-P*Ph*$_2$), 129.1 (s, *p*-P*Ph*$_2$), 132.5 (d, J_{CP} = 20.6, *o*-P*Ph*$_2$), 138.6 (d, J_{CP} = 18.0, *ipso*-P*Ph*$_2$), 139.1 (s, *o*-Dipp), 145.1 (s, *ipso*-Dipp), 150.1 (d, J_{CP} =11.2, *C*N$_3$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 45.2 (br, Δν$_{½}$ = 322 Hz). ^{31}P{^{1}H} NMR (202 MHz, tol-d$_8$, 193 K): 60.3 (s, Δν$_{½}$ = 50 Hz), 51.3 (br, Δν$_{½}$ = 410 Hz), 24.3 (s, Δν$_{½}$ = 50 Hz), ratio 20:1:4.

Preparation of (HN^{i}Pr)(Ph$_2$PN^{i}Pr)C(NMes) (1b). A solution of *n*-BuLi (1.50 mL, 2.40 mmol, 1.6 M in hexane) was added slowly to a solution of (HN^{i}Pr)$_2$C(NMes) (613 mg, 2.34 mmol) in Et$_2$O (10 mL) in a Schlenk tube at –78 ºC and then the mixture was stirred at room temperature for 4.5 h. Afterwards, the solution was cooled to −78 °C, a solution of ClPPh$_2$ (0.45 mL, 2.34 mmol) in Et$_2$O (8 mL) was added and the mixture was allowed to stir at room temperature overnight. The resulting yellow solution was dried *in vacuo* and the residue was extracted with *n*-hexane (3 x 15 mL). Finally, the solution was concentrated under vacuum and cooled to –20 ºC to obtain white crystals of compound **1b** (0.845 g, 81%). Anal. calcd for $C_{28}H_{36}PN_3$: C, 75.48; H, 8.14; N, 9.43. Found: C, 75.33; H, 8.09; N, 9.40.

^{1}H NMR (500 MHz, C_6D_6): δ 0.49 (d, 6H, J_{HH} = 6.4, HNCH(CH_3)$_2$), 1.45 (d, 6H, J_{HH} = 6.7, PNCH(CH_3)$_2$), 2.24 (s, 3H, *p*-CH_3), 2.38 (s, 6H, *o*-CH_3), 3.27 (dsept, 1H, J_{HH} = 6.4, 9.2, HNC*H*(CH$_3$)$_2$), 4.29 (dd, 1H, J_{HH} = 9.2, J_{HP} = 2.7, N*H*), 4.48 (dsept, 1H, J_{HH} = 6.7, J_{HP} = 6.4, PNC*H*(CH$_3$)$_2$), 6.90 (s, 2H, C$_6H_2$Me$_3$), 7.07 (m, 2H, *p*-P*Ph*$_2$), 7.14 (m, 4H, *o*-P*Ph*$_2$), 7.69 (m, 4H, *m*-P*Ph*$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6): δ 19.4 (s, *o*-*C*H$_3$), 21.0 (s, *p*-*C*H$_3$), 23.5 (d, J_{CP} = 6.5, PNCH(*C*H$_3$)$_2$), 23.5 (s, HNCH(*C*H$_3$)$_2$), 44.5 (s, HN*C*H(CH$_3$)$_2$), 51.9 (d, J_{CP} = 10.5, PN*C*H(CH$_3$)$_2$), 128.3, 128.4 (2s, *o*-*C*$_6$H$_2$Me$_3$), 128.8 (d, J_{CP} = 5.2, *o*-P*Ph*$_2$), 129.0 (s, *p*-P*Ph*$_2$), 129.1 (s, *m*-*C*$_6$H$_2$Me$_3$), 129.8 (s, *p*-*C*$_6$H$_2$Me$_3$), 132.2 (d, J_{CP} = 20.4, *m*-P*Ph*$_2$), 138.5 (d, J_{CP} = 17.8, *ipso*-P*Ph*$_2$), 145.2 (s, *ipso*-

$C_6H_2Me_3$), 149.6 (d, J_{CP} = 6.3, CN_3). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 40.7 (br, $\Delta\nu_{½}$ = 217 Hz).

Preparation of [Al{κ²-*N*,*N*'-(N^{i}Pr)(NDipp)C(N^{i}Pr)(PPh$_2$)}Me$_2$] (2a). *NMR scale*: Complex **2a** was obtained on a small scale in an NMR tube fitted with a concentric Teflon valve by adding a solution of compound **1a** (0.081 g, 0.17 mmol) in C_6D_6 (*ca.* 0.8 mL) to a solution of $AlMe_3$ (86 μL, 0.17 mmol, 2.0 M in toluene) at room temperature in a glovebox. Monitoring of the reaction by ^1H and $^{31}P\{^1H\}$ NMR revealed that complex **2a** was obtained after 15 minutes. *Upscale*: In a glovebox, a solution of $AlMe_3$ (313 μL, 0.62 mmol, 2.0 M in toluene) was added slowly to a solution of **1a** (0.300 g, 0.62 mmol) in toluene (15 mL) at room temperature and the mixture was stirred for 15 minutes. The resulting solution was dried *in vacuo* to provide **2a** as a colourless oil (0.320 g, 94%).

^1H NMR (500 MHz, C_6D_6): δ –0.13 (s, 6H, Al*Me*$_2$), 0.91 (d, 6H, J_{HH} = 6.6, CH(C*H*$_3$)$_2$-Dipp), 1.18 (d, 6H, J_{HH} = 6.7, PNCH(C*H*$_3$)$_2$), 1.19 (d, 6H, J_{HH} = 6.1, CH(C*H*$_3$)$_2$-Dipp), 1.20 (d, 6H, J_{HH} = 6.8, NCH(C*H*$_3$)$_2$), 3.60 (dsept, 1H, J_{HH} = 6.7, J_{HP} = 1.8, PNC*H*(CH$_3$)$_2$), 3.70 (m, 3H, NC*H*(CH$_3$)$_2$ + 2 x C*H*(CH$_3$)$_2$-Dipp), 6.97 (m, 6H, *m*,*p*-P*Ph*$_2$), 7.05 (d, 2H, J_{HH} = 6.8, *m*-Dipp), 7.12 (m, 1H, *p*-Dipp), 7.14 (m, 4H, *o*-P*Ph*$_2$). $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6): δ 51.5 (s). ^1H NMR (500 MHz, CD_2Cl_2): δ –0.58 (s, 6H, Al*Me*$_2$), 1.00 (d, 6H, J_{HH} = 6.6, NCH(C*H*$_3$)$_2$), 1.04 (d, 6H, J_{HH} = 6.7, CH(C*H*$_3$)$_2$-Dipp), 1.14 (d, 6H, J_{HH} = 6.8, CH(C*H*$_3$)$_2$-Dipp), 1.22 (d, 6H, J_{HH} = 6.3, PNCH(C*H*$_3$)$_2$), 3.48 (dsept, 2H, J_{HH} = 6.7, J_{HP} = 1.4, C*H*(CH$_3$)$_2$-Dipp), 3.71 (sept, 1H, J_{HH} = 6.6, NC*H*(CH$_3$)$_2$), 3.72 (dsept, 1H, J_{HH} = 6.3, J_{HP} = 6.6, PNC*H*(CH$_3$)$_2$), 7.08 (m, 2H, *m*-Dipp), 7.18 (m, 4H, *o*-P*Ph*$_2$), 7.19 (m, 1H, *p*-Dipp), 7.24 (m, 4H, *m*-P*Ph*$_2$), 7.30 (m, 2H, *p*-P*Ph*$_2$). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ –9.0 (s, Al*Me*$_2$), 22.0 (d, J_{CP} = 2.8, CH(*C*H$_3$)$_2$-Dipp), 23.6 (s, NCH(*C*H$_3$)$_2$), 25.9 (s, PNCH(*C*H$_3$)$_2$), 27.5 (s, CH(*C*H$_3$)$_2$-Dipp), 28.9 (d, J_{CP} = 4.8, *C*H(CH$_3$)$_2$-Dipp), 45.7 (d, J_{CP} = 5.1, PN*C*H(CH$_3$)$_2$), 54.0 (d, J_{CP} = 5.5, N*C*H(CH$_3$)$_2$), 123.5 (s, *m*-Dipp), 125.8 (s, *p*-Dipp), 128.3 (d, J_{CP} = 6.1, *m*-P*Ph*$_2$), 129.2 (s, *p*-P*Ph*$_2$), 133.3 (d, J_{CP} = 21.9, *o*-P*Ph*$_2$), 138.7 (s, *o*-Dipp), 138.9 (s, *ipso*-Dipp), 146.6 (s, *ipso*-P*Ph*$_2$), 166.1 (d, J_{CP} = 23.8, CN_3). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2): δ 50.7 (s).

Preparation of [Al{κ²-*N*,*N*'-(N^{i}Pr)(NMes)C(N^{i}Pr)(PPh$_2$)}Me$_2$] (2b). Complex **2b** was obtained on a small scale in an NMR tube fitted with a concentric Teflon valve by

adding a solution of compound **1b** (0.050 g, 0.112 mmol) in C_6D_6 (*ca*. 0.8 mL) to a solution of $AlMe_3$ (56 µL, 0.112 mmol, 2.0 M in toluene) at room temperature in a glovebox. After 15 minutes complex **2b** was obtained. The resulting solution was dried *in vacuo* to provide **2b** as a white solid (0.054 g, 94%). Crystals of **2b** suitable for an X-ray diffractometric analysis were grown from a concentrated solution in THF/pentane (ca. 1:5) at –20 ºC. Anal. calcd for $C_{30}H_{42}AlN_3P$: C, 71.69; H, 8.42; N, 8.36. Found: C, 71.41; H, 8.37; N, 8.31.

^{1}H NMR (500 MHz, C_6D_6): δ –0.18 (s, 6H, Al*Me*$_2$), 0.76 (d, 6H, J_{HH} = 6.6, CH(C*H*$_3$)$_2$), 1.23 (d, 6H, J_{HH} = 6.3, CH(C*H*$_3$)$_2$), 2.13 (s, 3H, *p*-C*H*$_3$), 2.41 (s, 6H, *o*-C*H*$_3$), 3.77 (dsept, 1H, J_{HH} = 6.6, J_{HP} = 2.1, C*H*(CH$_3$)$_2$), 4.06 (dsept, 1H, J_{HH} = 6.3, J_{HP} = 2.4, C*H*(CH$_3$)$_2$), 6.69 (s, 2H, C$_6$*H*$_2$Me$_3$), 7.04 (m, 6H, *o,p*-P*Ph*$_2$), 7.35 (m, 4H, *m*-P*Ph*$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, C_6D_6): δ –8.7 (s, Al*Me*$_2$), 20.1, 20.2 (2s, *o*-*C*H$_3$), 20.9 (s, *p*-*C*H$_3$), 23.1 (s, CH(*C*H$_3$)$_2$), 25.6 (s, CH(*C*H$_3$)$_2$), 45.6 (d, J_{CP} = 8.3, *C*H(CH$_3$)$_2$), 53.7 (d, J_{CP} = 6.0, *C*H(CH$_3$)$_2$), 128.4 (d, J_{CP} = 6.3, *o*-P*Ph*$_2$), 129.3 (s, *p*-P*Ph*$_2$), 129.6 (s, *m*-Mes), 133.3 (d, J_{CP} = 21.7, *m*-P*Ph*$_2$), 133.3 (s, *p*-Mes), 134.4 (s, *o*-Mes), 139.4 (d, J_{CP} = 18.7, *ipso*-P*Ph*$_2$), 140.3 (s, *ipso*-Mes), 166.7 (d, J_{CP} = 23.3, *C*N$_3$). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 53.3 (s).

Preparation of [Al{κ^2-*N,N'*-(N^{i}Pr)(N^{i}Pr)C(NDipp)(PPh$_2$)}Me$_2$] (3a). In a glovebox, a solution of $AlMe_3$ (313 µL, 0.62 mmol, 2.0 M in toluene) was added slowly at room temperature to a solution of **1a** (0.300 g, 0.62 mmol) in toluene (15 mL). The Schlenk tube was taken outside the glovebox and the mixture was stirred for 4 h at 60 °C. The resulting solution was dried under vacuum to afford compound **3a** as a white solid (0.330 g, 97%). Crystals of **3a** suitable for an X-ray diffractometric analysis were grown from a concentrated solution in pentane at –20 ºC. Anal. calcd. for $C_{33}H_{47}PN_3Al$: C, 72.90; H, 8.71; N, 7.73. Found: C, 72.85; H, 8.54; N, 7.56.

^{1}H NMR (500 MHz, C_6D_6): δ –0.07 (s, 6H, Al*Me*$_2$), 0.73 (d, 6H, J_{HH} = 6.7, CH(C*H*$_3$)$_2$-Dipp), 1.01 (d, 6H, J_{HH} = 6.3, PNCH(C*H*$_3$)$_2$), 1.16 (d, 6H, J_{HH} = 6.7, NCH(C*H*$_3$)$_2$), 1.28 (d, 6H, J_{HH} = 6.7, CH(C*H*$_3$)$_2$-Dipp), 2.89 (sept, 2H, J_{HH} = 6.6, C*H*(CH$_3$)$_2$-Dipp), 3.13 (dsept, 1H, J_{HH} = 6.4, J_{HP} = 16.1, PNC*H*(CH$_3$)$_2$), 3.88 (dsept, 1H, J_{HH} = 6.4, J_{HP} = 1.7, NC*H*(CH$_3$)$_2$), 6.96 (t, J_{HH} = 8.3, 1H, *p*-Dipp), 7.01 – 7.11 (m, 8H, *m,p*-P*Ph*$_2$ + *m*-Dipp), 7.82 (m, 4H, *o*-P*Ph*$_2$). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ –3.2 (s, Al*Me*$_2$), 22.2, 24.3 (2 x s, CH(*C*H$_3$)$_2$-Dipp), 24.7 (s, NCH(*C*H$_3$)$_2$), 25.9 (d, J_{CP} = 6.2, PNCH(*C*H$_3$)$_2$), 29.0

(s, NCH(CH$_3$)$_2$-Dipp), 46.6 (d, J_{CP} = 14.4, NCH(CH$_3$)$_2$), 46.7 (d, J_{CP} = 4.6, PNCH(CH$_3$)$_2$), 122.3 (s, *p*-Dipp), 122.4 (s, *m*-Dipp), 127.2 (s, *ipso*-P*Ph*$_2$), 128.7 (d, J_{CP} = 12.0, *m*-P*Ph*$_2$), 132.7 (d, J_{CP} = 2.7, *p*-P*Ph*$_2$), 133.7 (d, J_{CP} = 9.7, *o*-P*Ph*$_2$), 138.4 (s, *o*-Dipp), 146.8 (d, J_{CP} = 28.6, *ipso*-Dipp), 149.4 (d, J_{CP} = 171.0, N$_2$*C*P). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$): δ 21.3 (s).

Preparation of [Al{κ^2-*N*,*N'*-(N^{i}Pr)(N^{i}Pr)C(NMes)(PPh$_2$)Me$_2$] (3b). Complex **3b** was obtained on a small scale in an NMR tube fitted with a concentric Teflon valve by adding a solution of compound **1b** (0.050 g, 0.112 mmol) in C$_6$D$_6$ (*ca*. 0.6 mL) to a solution of AlMe$_3$ (56 μL, 0.112 mmol, 2.0 M in toluene) at room temperature in a glovebox. Monitoring of the reaction by ^{1}H and ^{31}P{^{1}H} NMR revealed that complex **3b** was obtained after heating at 60 °C for 30 h or at 80 ºC for 6.5 h. The resulting solution was dried *in vacuo* to provide **3b** as a white solid (0.052 g, 92%). Anal. calcd for C$_{30}$H$_{42}$AlN$_3$P: C, 71.69; H, 8.42; N, 8.36. Found: C, 71.59; H, 8.48; N, 8.32.

^{1}H NMR (500 MHz, C$_6$D$_6$): δ –0.05 (s, 6H, Al*Me*$_2$), 1.04 (d, 6H, J_{HH} = 6.5, PNCH(C*H*$_3$)$_2$), 1.16 (d, 6H, J_{HH} = 6.5, NCH(C*H*$_3$)$_2$), 1.97 (s, 6H, *o*-C*H*$_3$), 2.14 (s, 3H, *m*-C*H*$_3$), 3.14 (dsept, 1H, J_{HH} = 6.5, J_{HP} = 12.9, PNC*H*(CH$_3$)$_2$), 3.77 (sept, 1H, J_{HH} = 6.5, NC*H*(CH$_3$)$_2$), 6.73 (s, 2H, C$_6$*H*$_2$Me$_3$), 7.03 (m, 4H, *o*-P*Ph*$_2$), 7.10 (m, 2H, *p*-P*Ph*$_2$), 7.84 (m, 4H, *m*-P*Ph*$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, C$_6$D$_6$): δ –2.9 (s, Al*Me*$_2$), 19.0 (s, *o*-*C*H$_3$), 20.9 (s, *p*-*C*H$_3$), 24.5 (s, NCH(*C*H$_3$)$_2$), 26.0 (d, J_{CP} = 6.0, PNCH(*C*H$_3$)$_2$), 46.8 (d, J_{CP} = 4.9, PNCH(CH$_3$)$_2$), 47.0 (d, J_{CP} = 14.4, NCH(CH$_3$)$_2$), 127.5 (s, *ipso*-P*Ph*$_2$), 127.9 (s, *o*-Mes), 128.4 (s, *m*-Mes), 128.7 (d, J_{CP} = 12.1, *o*-P*Ph*$_2$), 130.04 (s, *p*-Mes), 132.7 (d, J_{CP} = 2.3, *p*-P*Ph*$_2$), 133.9 (d, J_{CP} = 9.8, *m*-P*Ph*$_2$), 146.5 (d, J_{CP} = 28.3, *ipso*-Mes), 169.5 (d, J_{CP} = 169.5, *C*N$_3$). ^{31}P{^{1}H} NMR (202 MHz, C$_6$D$_6$): δ 21.9 (s).

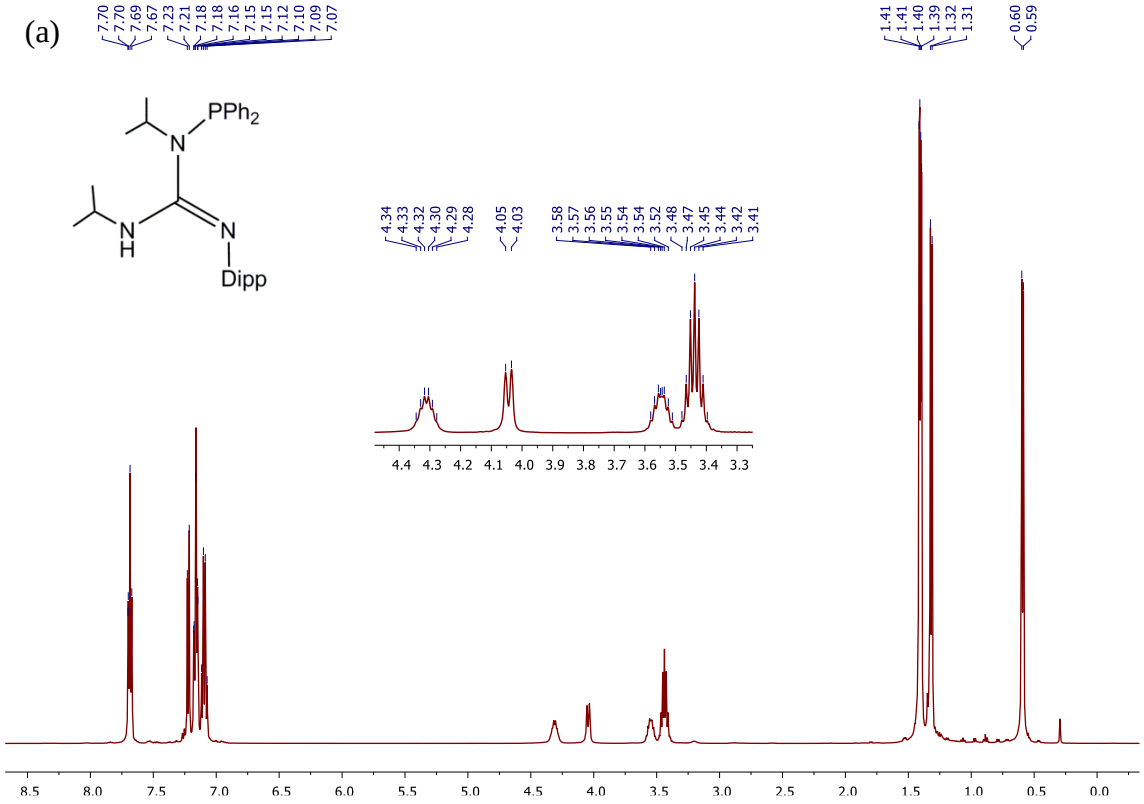
Preparation of solutions containing [Zn{κ^1-*P*-PPh$_2$(N^{i}Pr)C(NDipp)(N^{i}Pr)}Et$_2$] (4). Solutions containing compounds **1a** and **4** in a 1:1 ratio approx. were prepared in an NMR scale in a glovebox by adding a solution of **1a** (0.040 g, 0.08 mmol) in C$_6$D$_6$ (*ca*. 0.8 mL) at room temperature to a solution of ZnEt$_2$ (82 μL, 0.08 mmol, 1.0 M in hexane). After 5 min at 25 ºC the ratio **1a**:**4** was already 1:1 and remained unchanged for a few hours provided that the sample temperature was not increased.

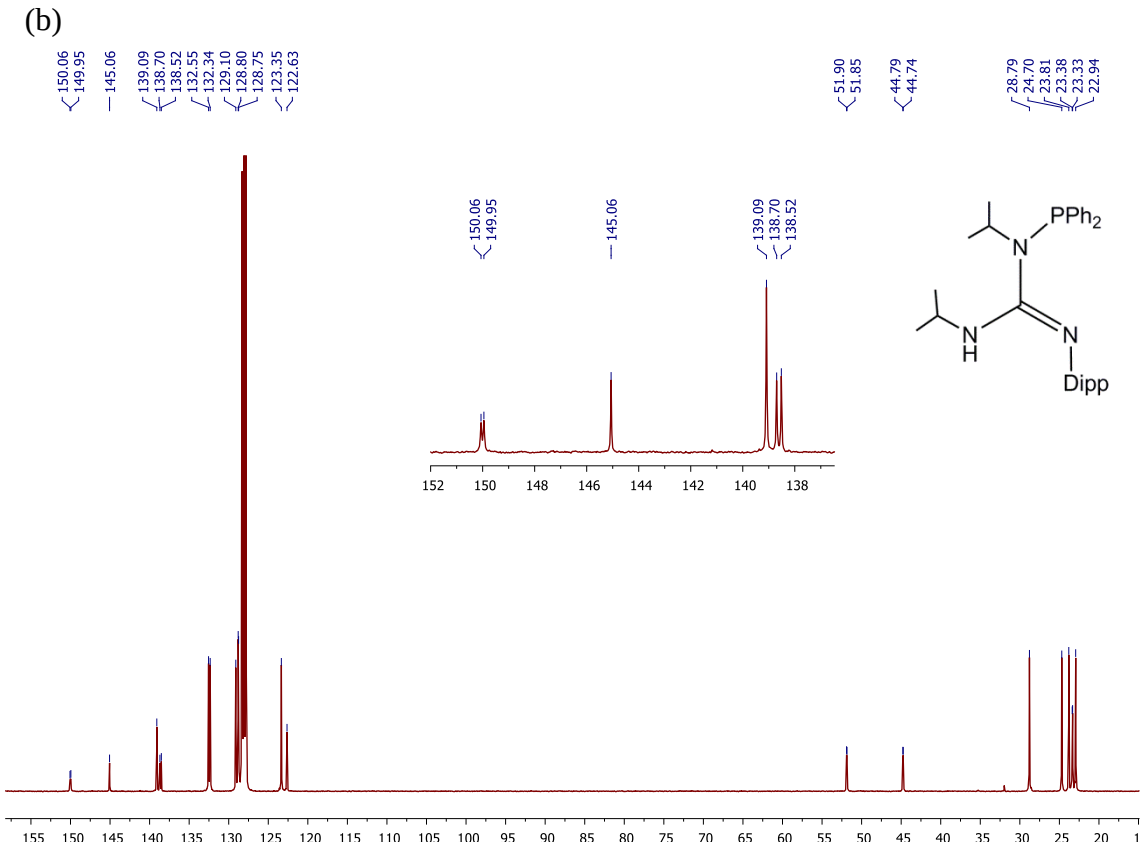
*Partial spectroscopic data for compound **4***: ^{1}H NMR (400 MHz, C_6D_6): δ 3.53 (sept, 2H, J_{HH} = 6.9, C*H*(CH$_3$)$_2$-Dipp), 3.84, 4.09 (2 x br, 2 x 1H, NC*H*(CH$_3$)$_2$), 7.53 (br, 4H, P*Ph*$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 28.2 (br, $\Delta\nu_{½}$ = 150 Hz).

Preparation of [Zn{κ^2-*N,N'*-(N^{i}Pr)(NDipp)C(N^{i}Pr)(PPh$_2$)}Et] (5). *NMR scale:* Complex **5** was obtained on a small scale in an NMR tube fitted with a concentric Teflon valve by adding a solution of **1a** (0.040 g, 0.08 mmol) in C_6D_6 (*ca*. 0.8 mL) to a solution of $ZnEt_2$ (82 μL, 0.08 mmol, 1.0 M in hexane) at room temperature in a glovebox. Monitoring of the reaction by ^{1}H and ^{31}P{^{1}H} NMR revealed that complex **5** was obtained after heating at 45 °C for 20 h. *Upscale:* In a glovebox, $ZnEt_2$ (520 μL, 0.52 mmol, 1.0 M in hexane) was added slowly to a solution of **1a** (0.250 g, 0.52 mmol) in toluene (15 mL) at room temperature. The Schlenk tube was taken outside the glovebox and the mixture was stirred for 20 h at 45 °C. Then, the solvent was removed *in vacuo* and the remaining residue extracted in *n*-hexane (2 x 25 mL), concentrated and cooled to –20 ºC to give a compound **5** as a white precipitate, isolated by filtration (0.280 g, 93%). Crystals of **5** suitable for an X-ray diffractometric analysis were grown from a concentrated solution in *n*-hexane at –20 ºC. Anal. calcd for $C_{33}H_{46}PN_3Zn$: C, 68.21; H, 7.98; N, 7.23. Found: C, 68.34; H, 7.91; N, 7.26.

^{1}H NMR (500 MHz, C_6D_6): δ 0.78 (d, 6H, J_{HH} = 6.4, CH(C*H*$_3$)$_2$-Dipp), 0.87 (d, 2H, J_{HH} = 7.2, ZnC*H*$_2$CH$_3$), 0.98 (d, 6H, J_{HH} = 6.1, PNCH(C*H*$_3$)$_2$), 1.06 (d, 6H, J_{HH} = 6.2, NCH(C*H*$_3$)$_2$), 1.29 (d, 6H, J_{HH} = 6.4, CH(C*H*$_3$)$_2$-Dipp), 1.70 (t, 3H, J_{HH} = 7.2, ZnCH$_2$C*H*$_3$,), 2.93 (sept, 2H, J_{HH} = 6.4, C*H*(CH$_3$)$_2$-Dipp), 3.14 (dsept, 1H, J_{HH} = 6.1, J_{HP} = 16.1, PNC*H*(CH$_3$)$_2$), 3.95 (dsept, 1H, J_{HH} = 6.2, J_{HP} = 1.8, NC*H*(CH$_3$)$_2$), 7.02 (t, 1H, J_{HH} = 8.2, *p*-Dipp), 7.08 (m, 4H, *m*-P*Ph*$_2$), 7.10 (m, 2H, *m*-Dipp), 7.11 (m, 2H, *p*-P*Ph*$_2$), 7.81 (m, 4H, *o*-P*Ph*$_2$). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 4.4 (d, J_{CP} = 4.8, Zn*C*H$_2$CH$_3$), 13.2 (s, ZnCH$_2$*C*H$_3$), 22.5, 24.3 (2s, CH(*C*H$_3$)$_2$-Dipp), 26.7 (s, NCH(*C*H$_3$)$_2$), 27.7 (d, J_{CP} = 6.8, PNCH(*C*H$_3$)$_2$), 28.9 (s, *C*H(CH$_3$)$_2$-Dipp), 46.0 (d, J_{CP} = 5.8, N*C*H(CH$_3$)$_2$), 46.2 (d, J_{CP} = 15.9, PN*C*H(CH$_3$)$_2$), 121.8 (s, *p*-Dipp), 122.4 (s, *m*-Dipp), 127.6 (d, J_{CP} = 88.5, *ipso*-P*Ph*$_2$), 128.4 (d, J_{CP} = 11.9, *m*-P*Ph*$_2$), 132.0 (s, *p*-P*Ph*$_2$), 133.6 (d, J_{CP} = 9.2, *o*-PPh$_2$), 138.4 (s, *o*-Dipp), 148.1 (d, J_{CP} = 30.2, *ipso*-Dipp), 150.2 (d, J_{CP} =181.1, N$_2$*C*P). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ 20.1 (s).

Figure S1. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and $^{31}P\{^{1}H\}$ (c) NMR spectra of compound **1a** in C_6D_6.





(c)

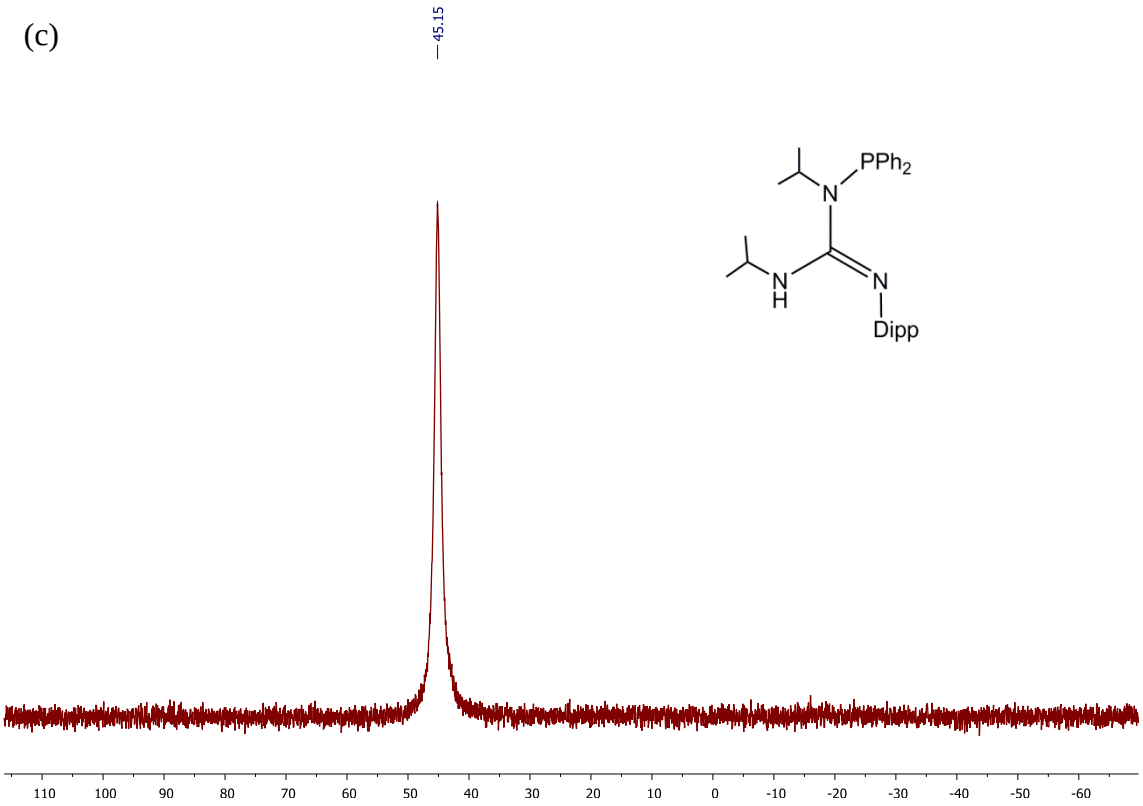


Figure S2. Stacked plot for VT $^{31}P\{^{1}H\}$ NMR spectra of compound **1a** in toluene-d_8.

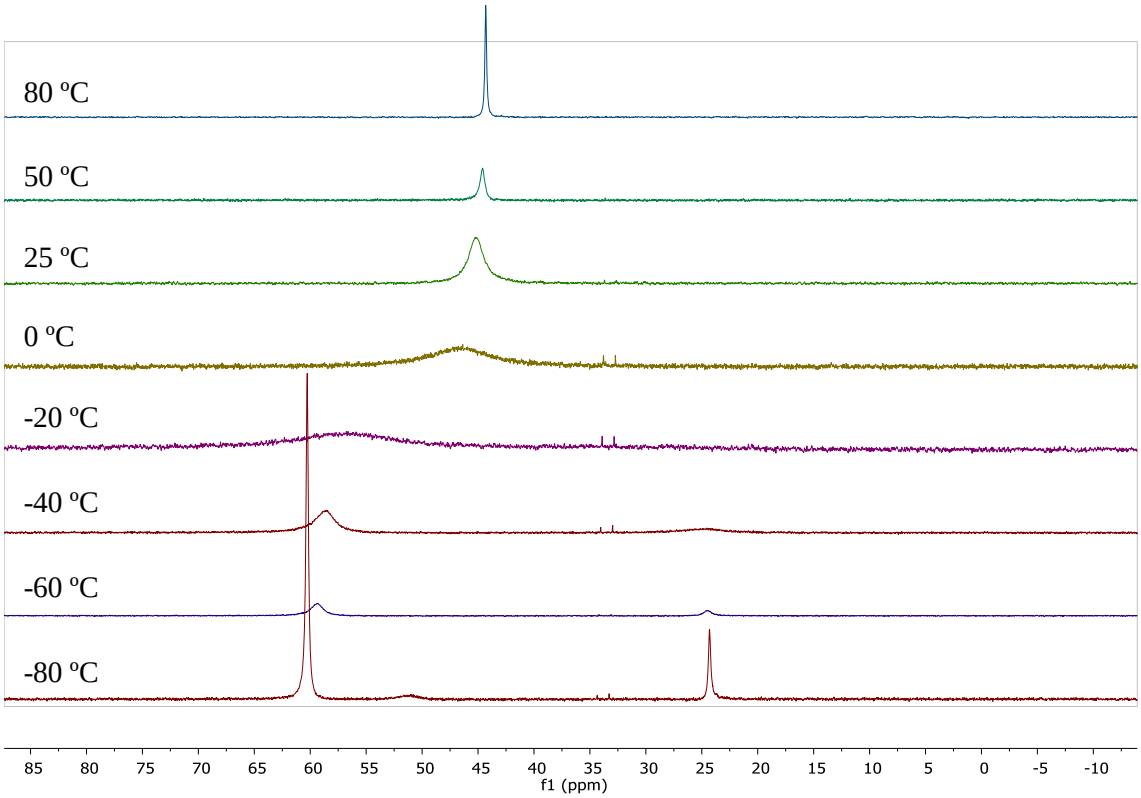
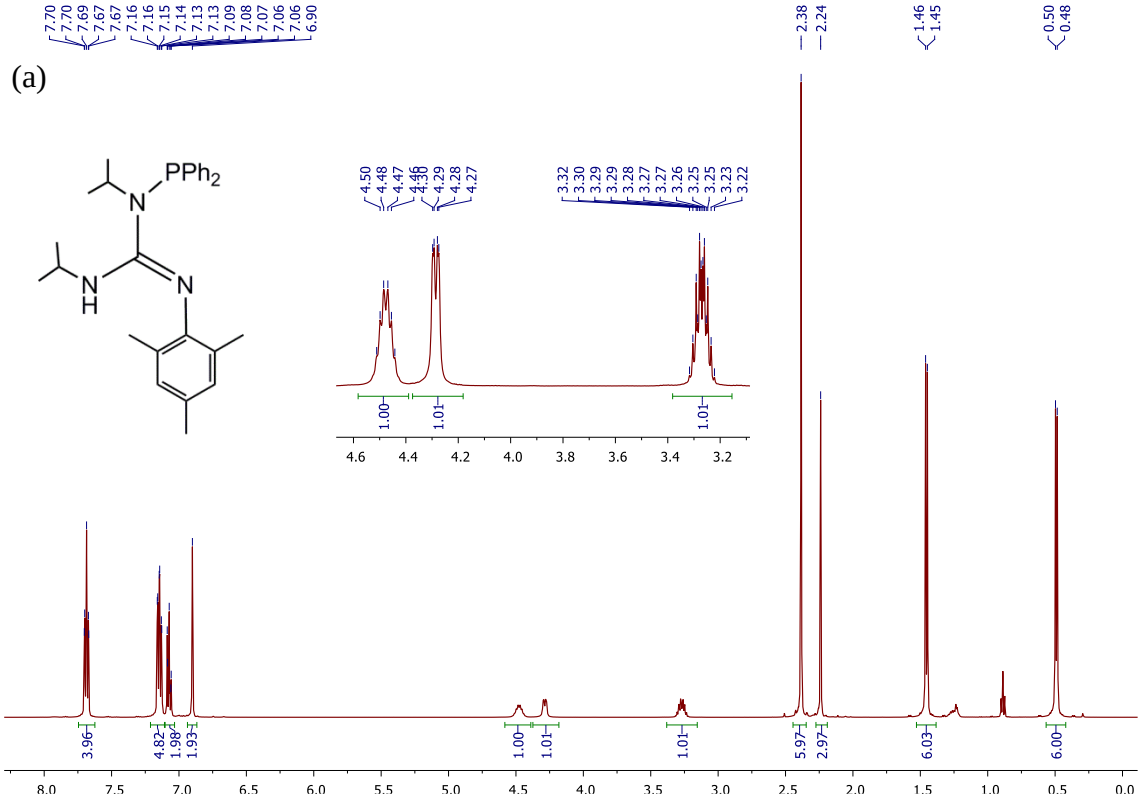
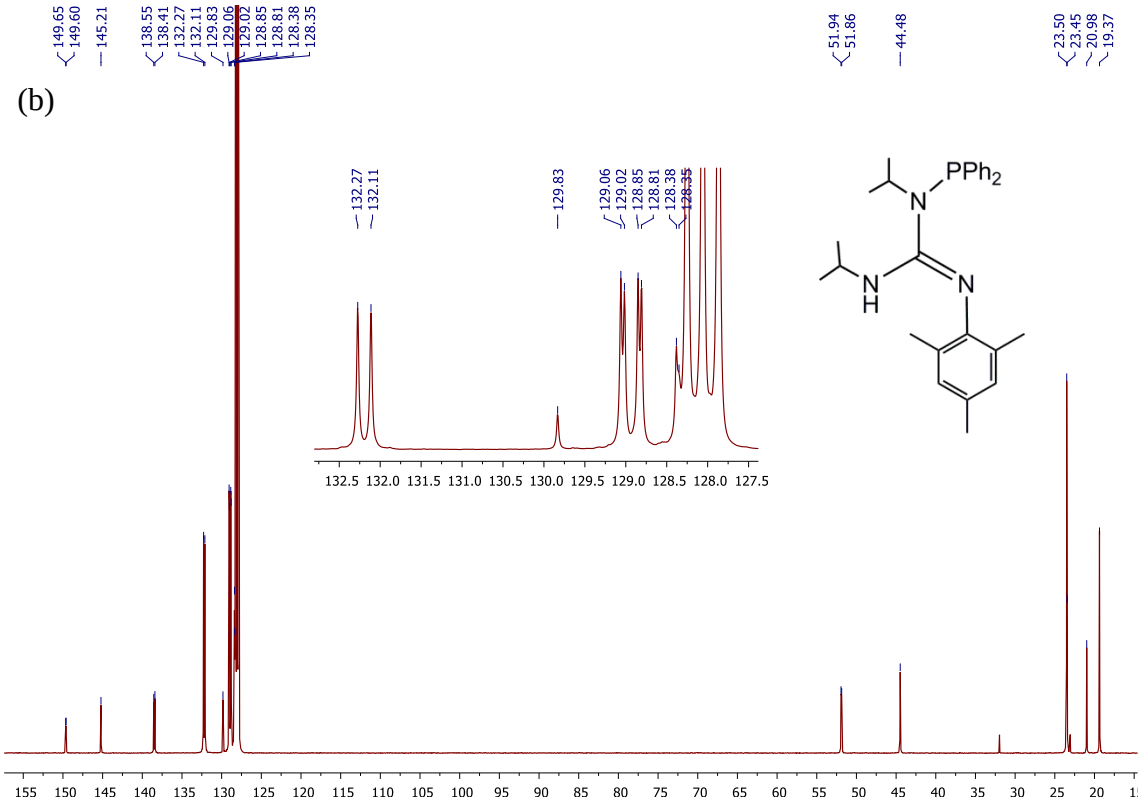


Figure S3. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and $^{31}P\{^{1}H\}$ (c) NMR spectra of compound **1b** in C_6D_6.





(c)

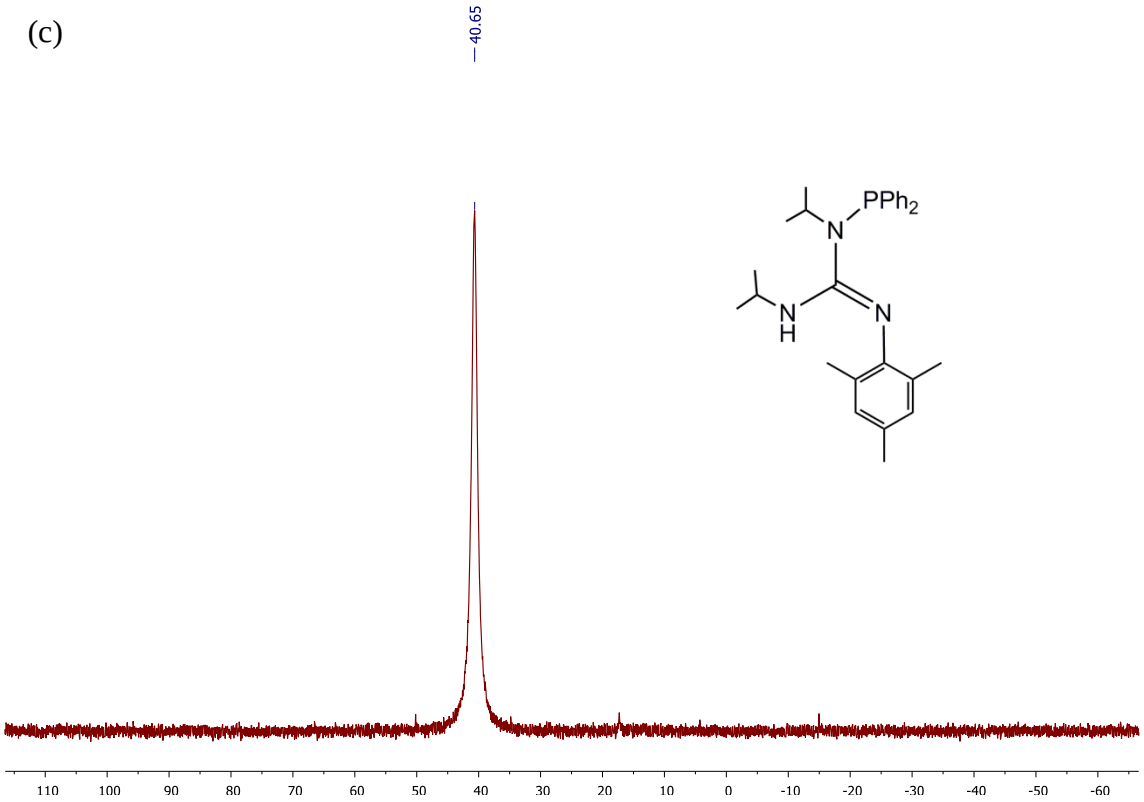
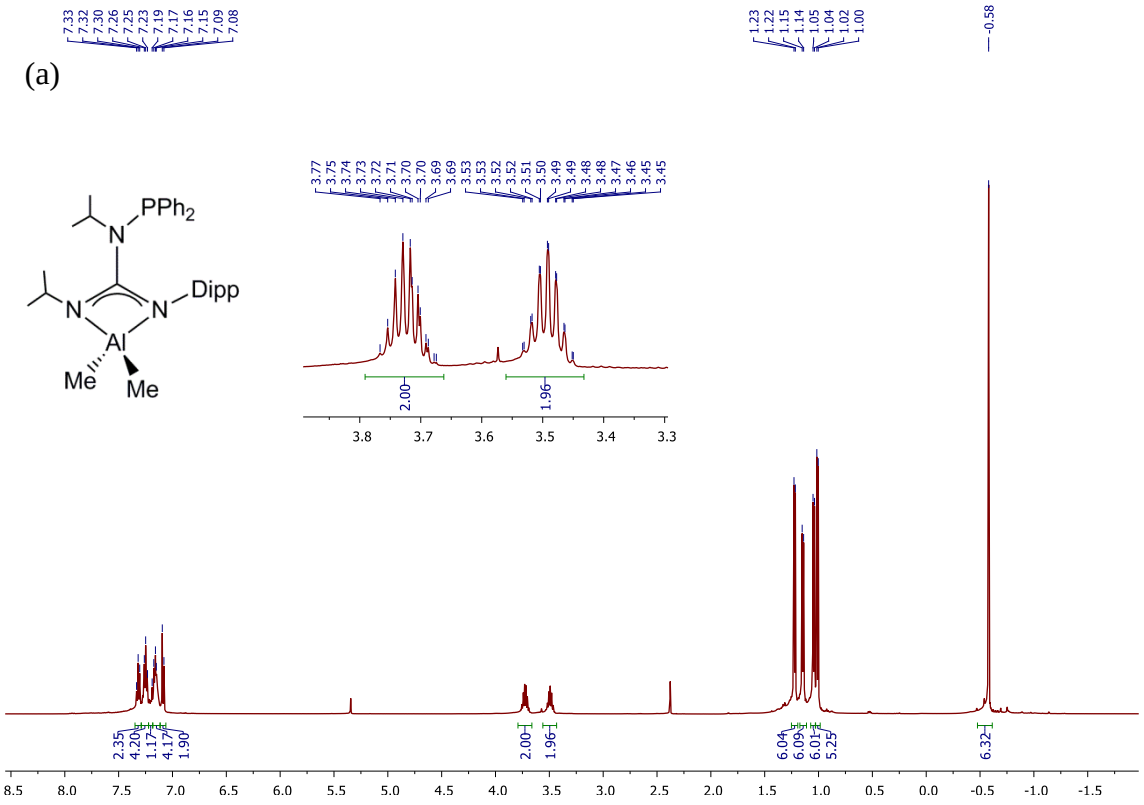
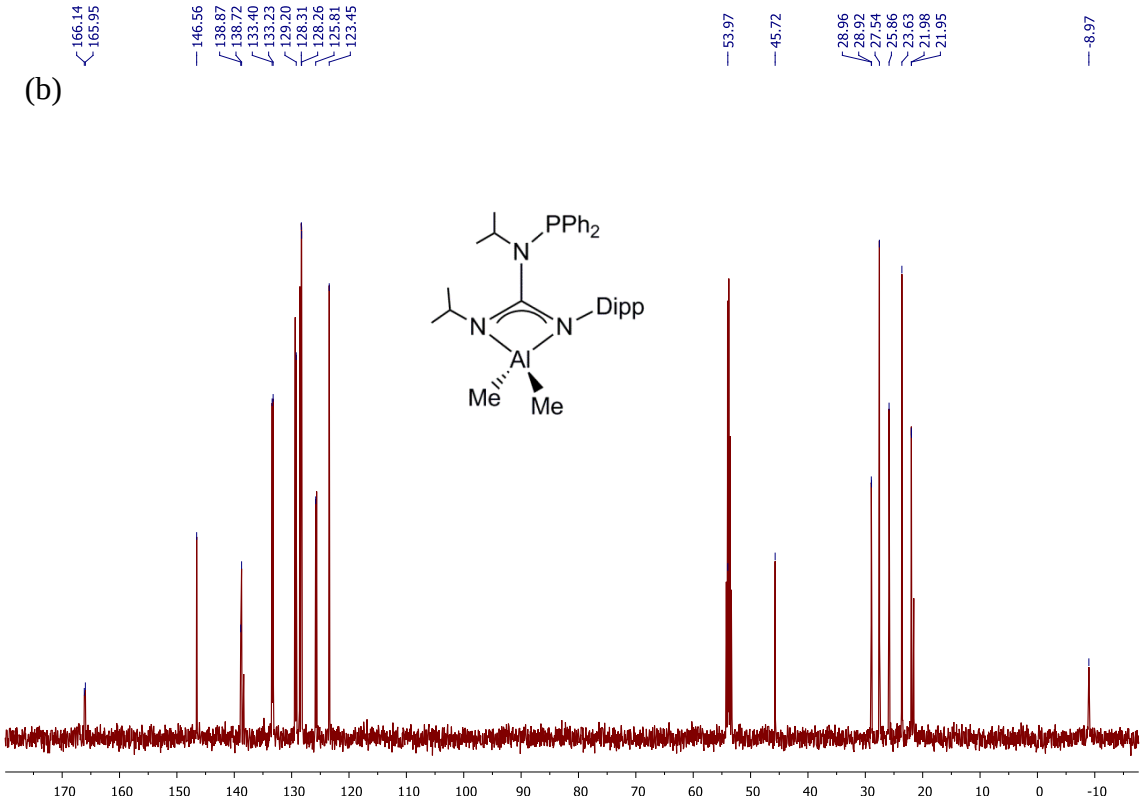


Figure S4. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and $^{31}P\{^{1}H\}$ (c) NMR spectra of compound **2a** in CD_2Cl_2.





(c)

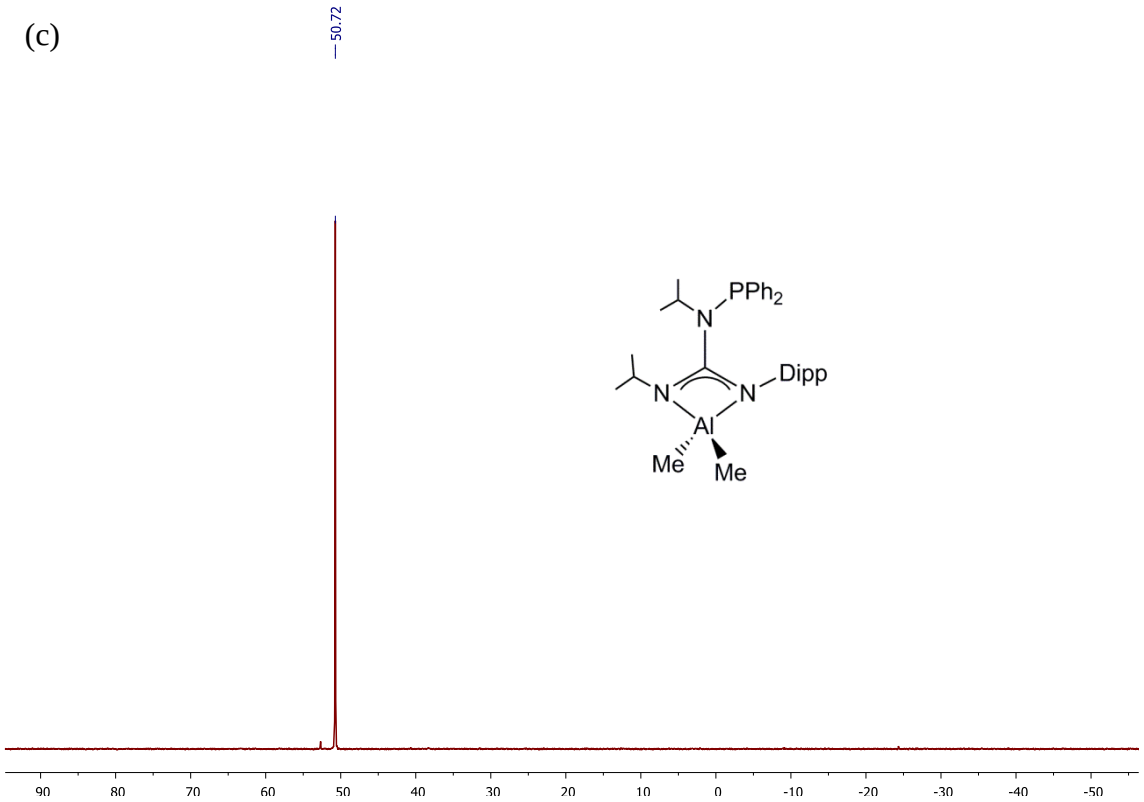
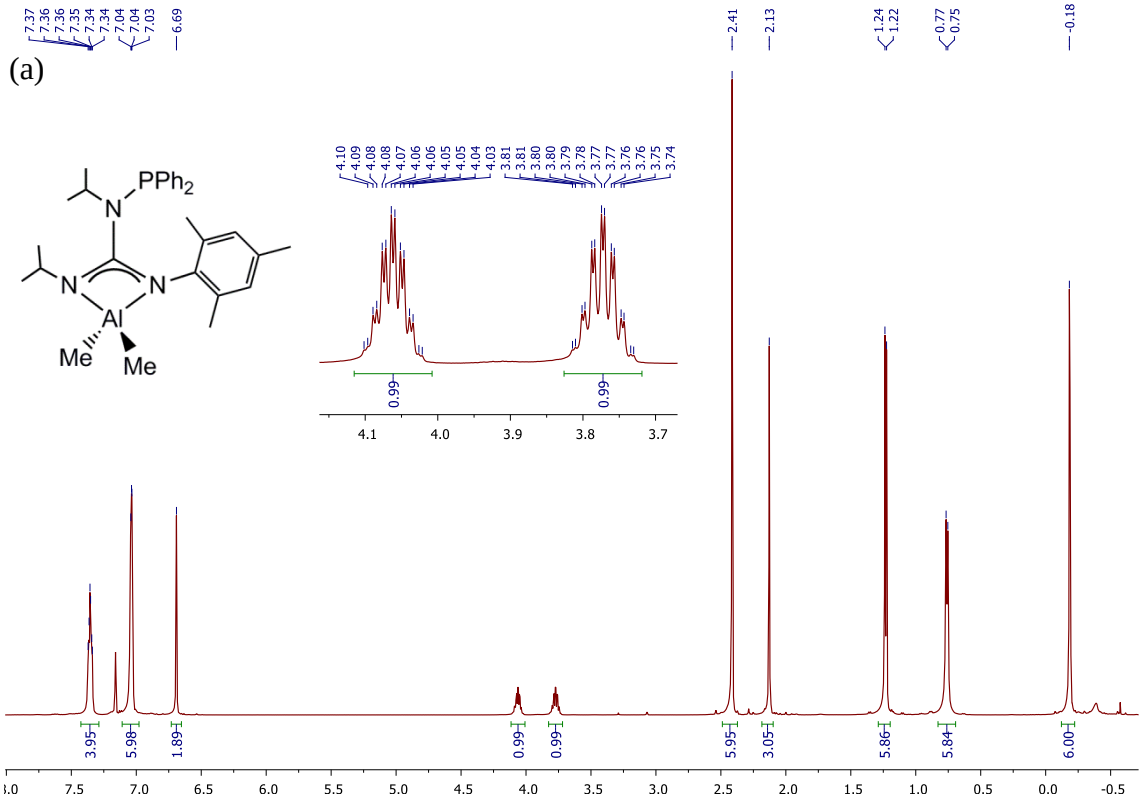
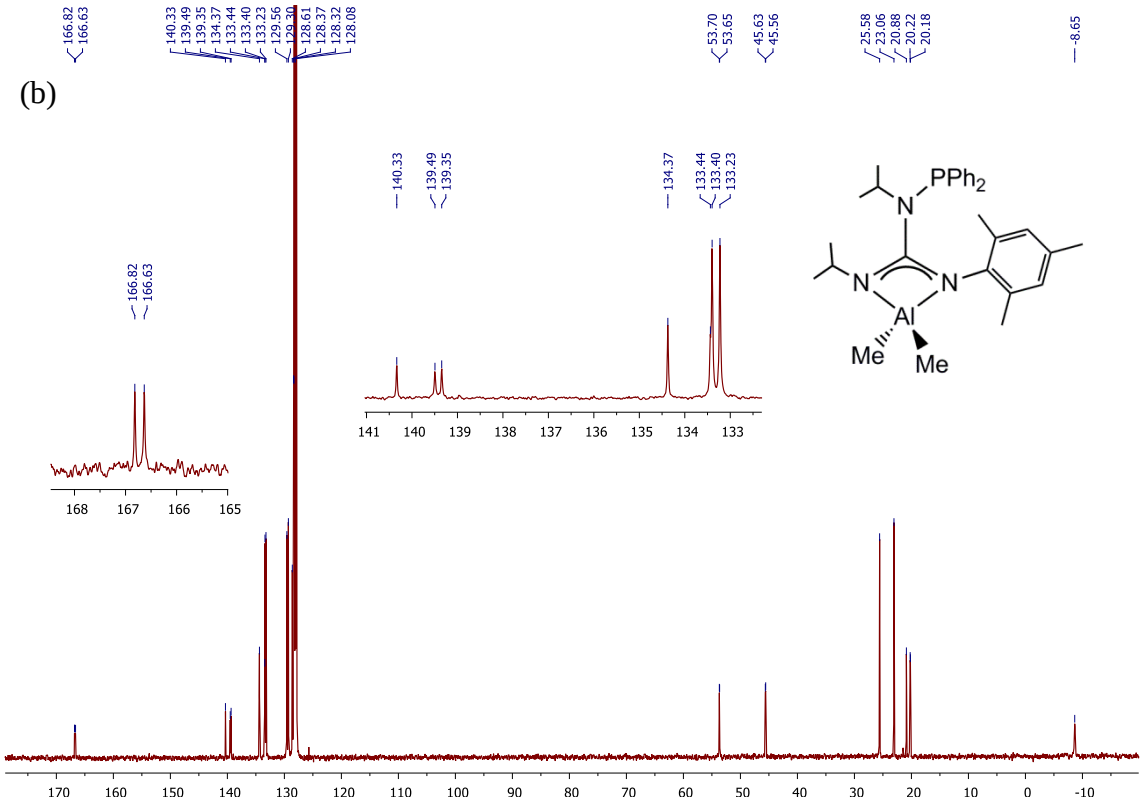

50.72
PPh2
N
N
N
Dipp
Al
Me
Me
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50

Figure S5. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and $^{31}P\{^{1}H\}$ (c) NMR spectra of compound **2b** in C_6D_6.





(c)

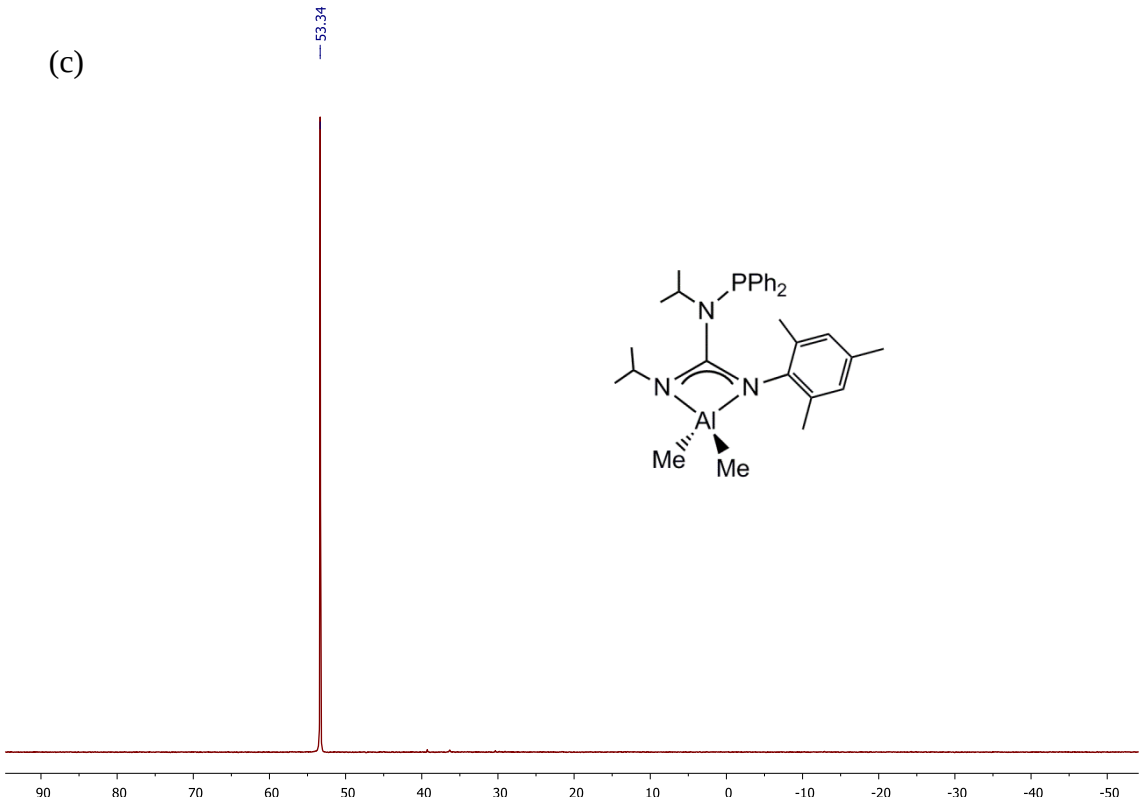
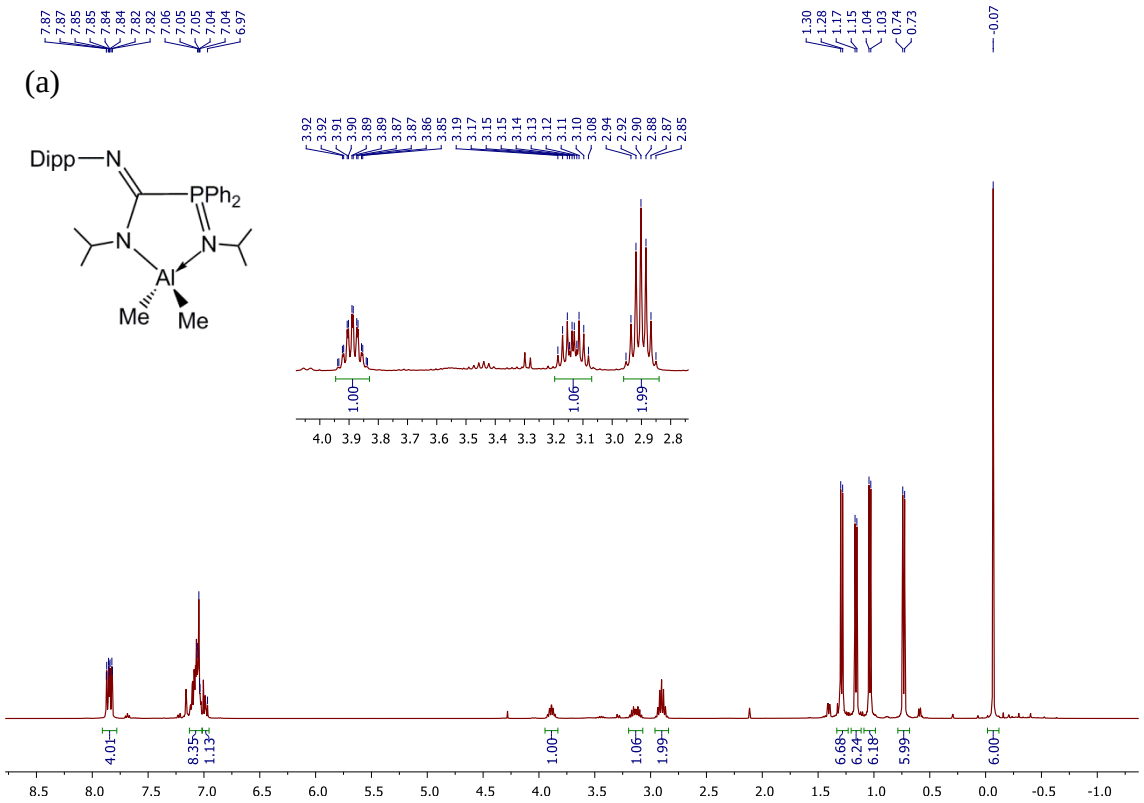
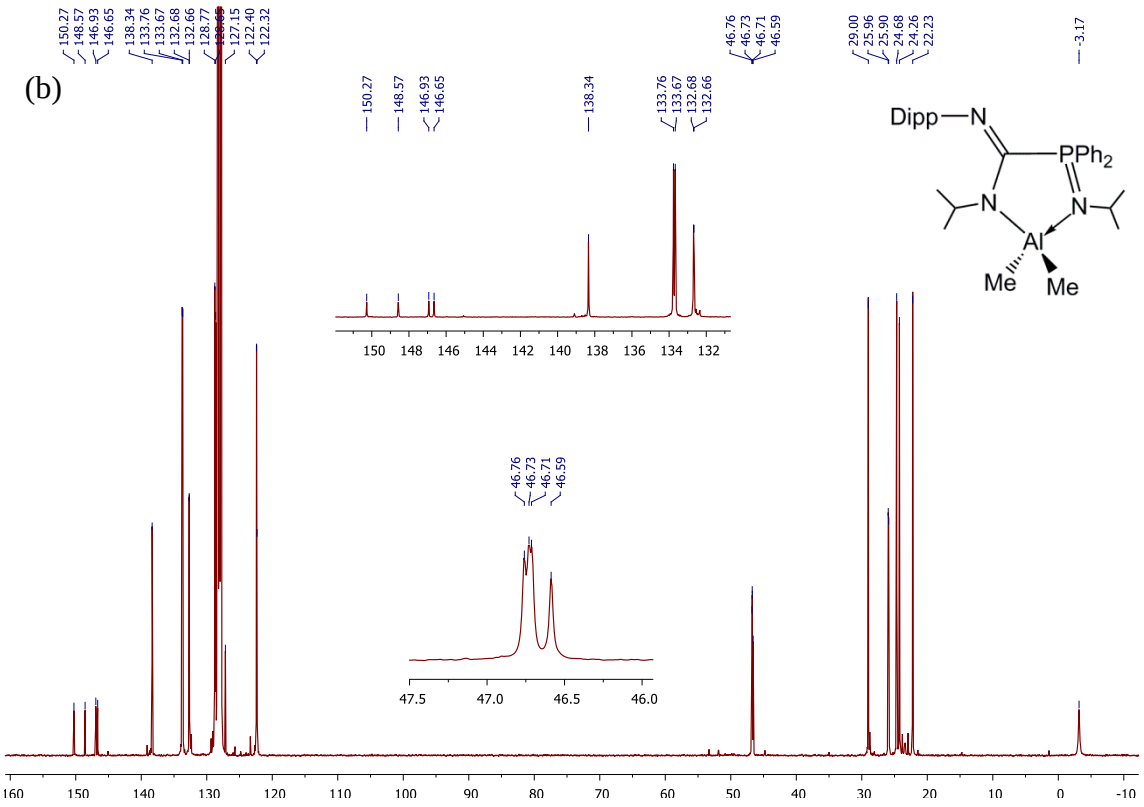


Figure S6. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and $^{31}P\{^{1}H\}$ (c) NMR spectra of compound **3a** in C_6D_6.





(c)

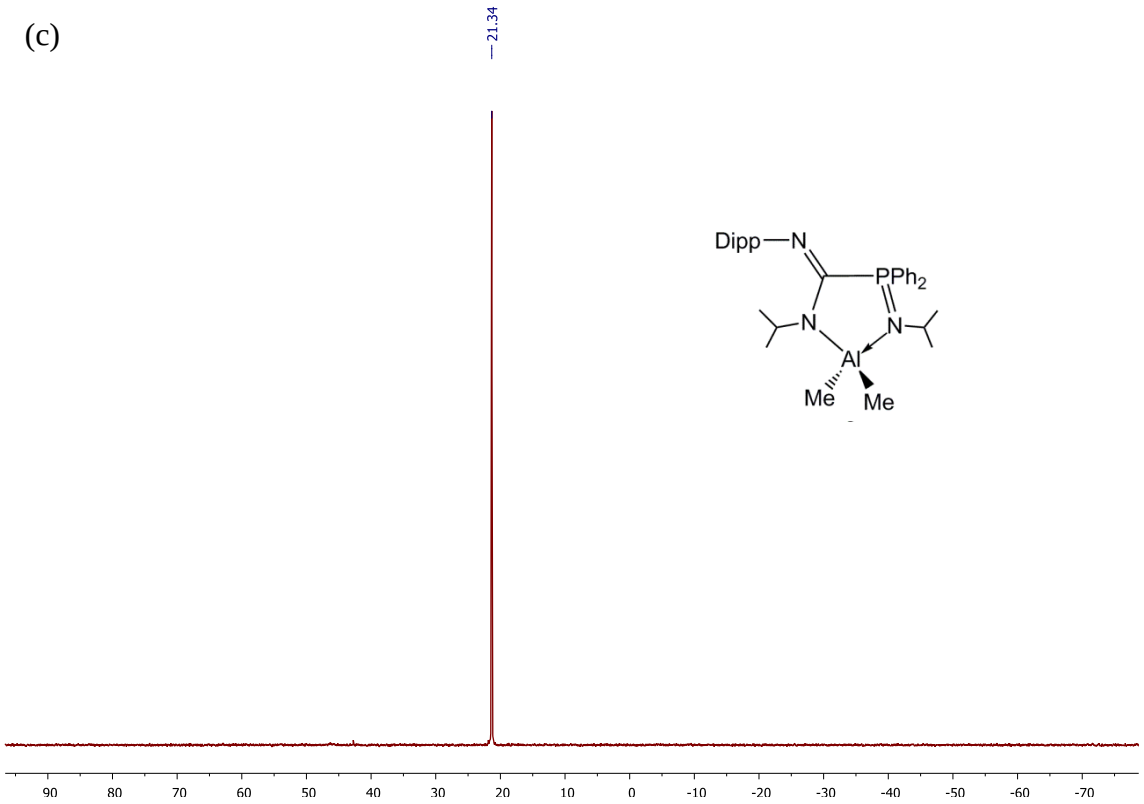
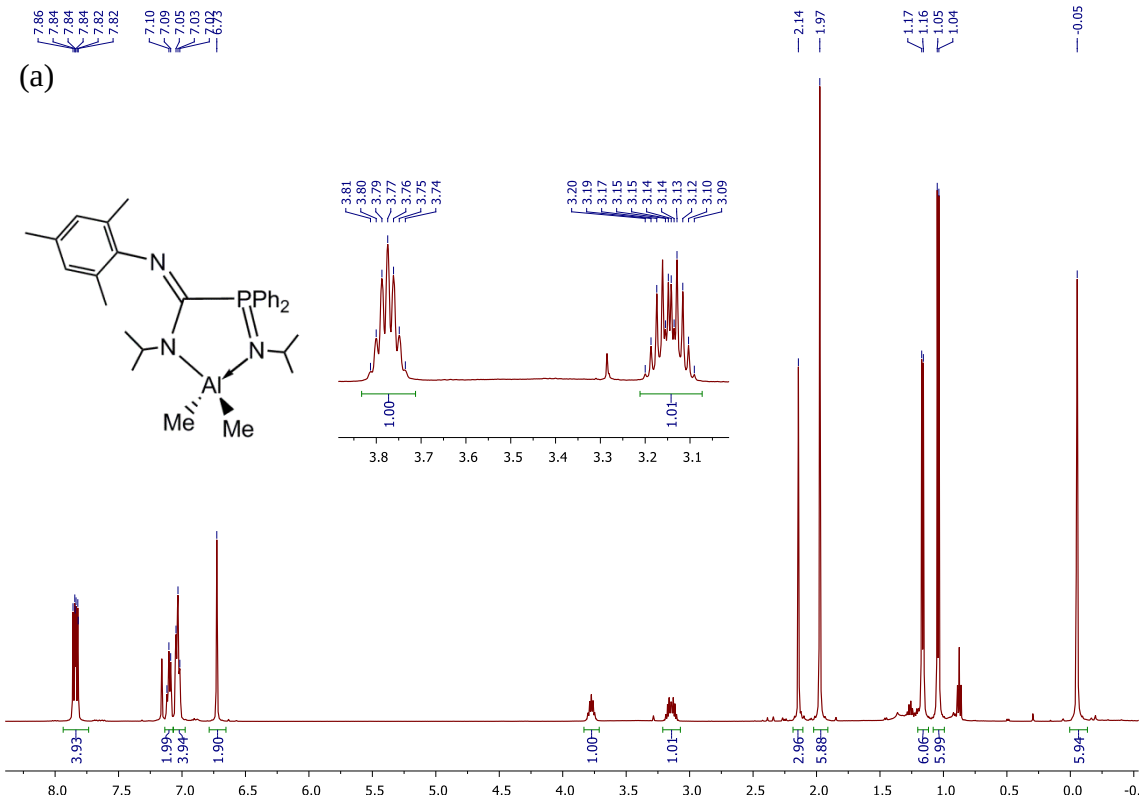
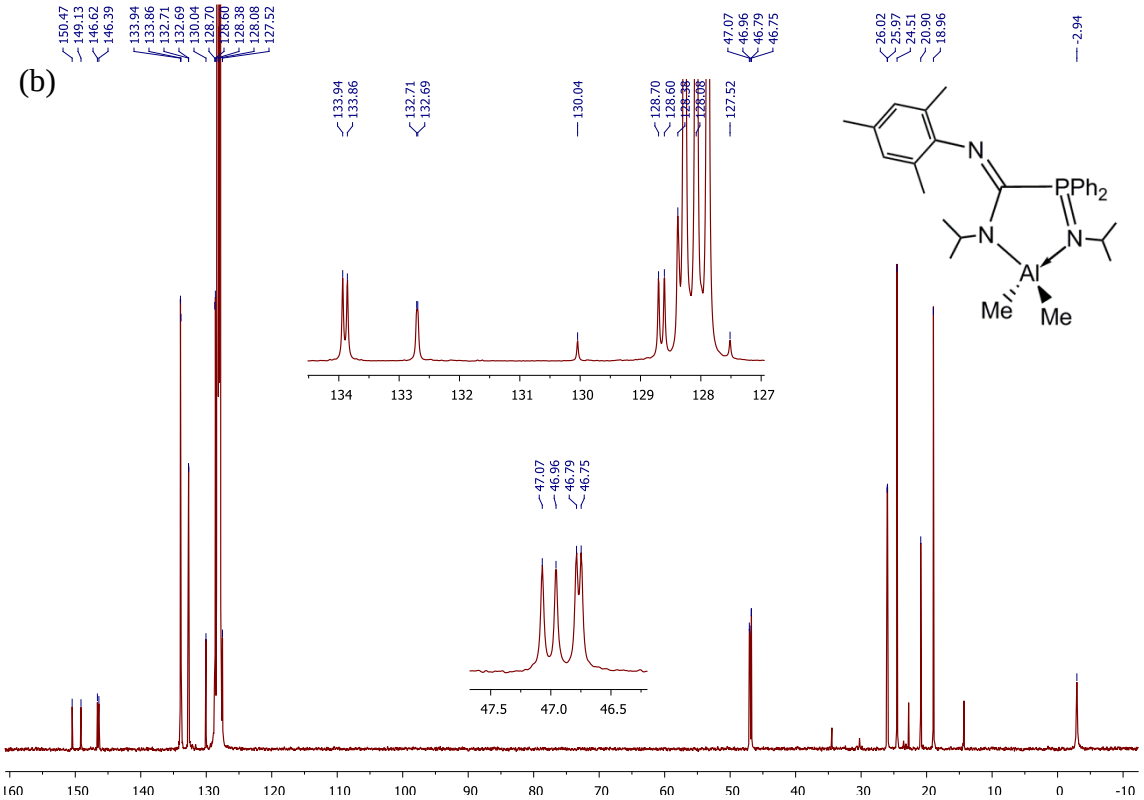

21.34
Dipp
N
PPh2
N
N
Al
Me
Me
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70

Figure S7. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and $^{31}P\{^{1}H\}$ (c) NMR spectra of compound **3b** in C_6D_6.





(c)

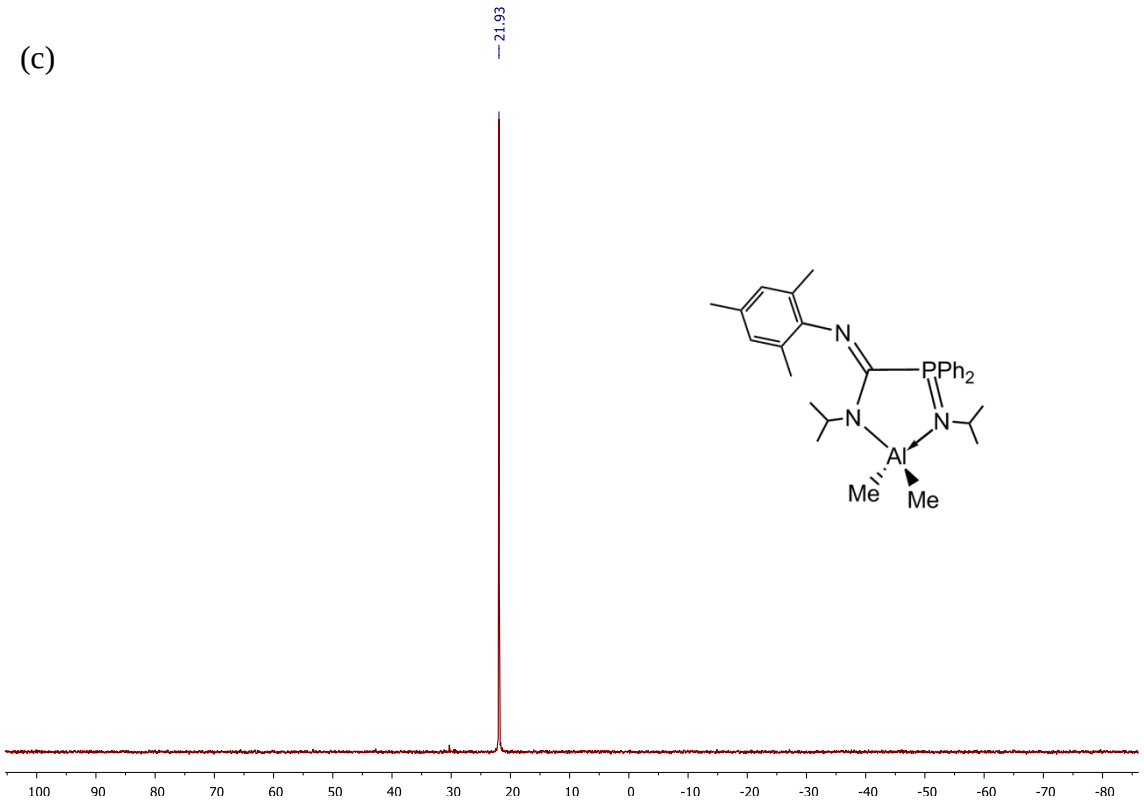
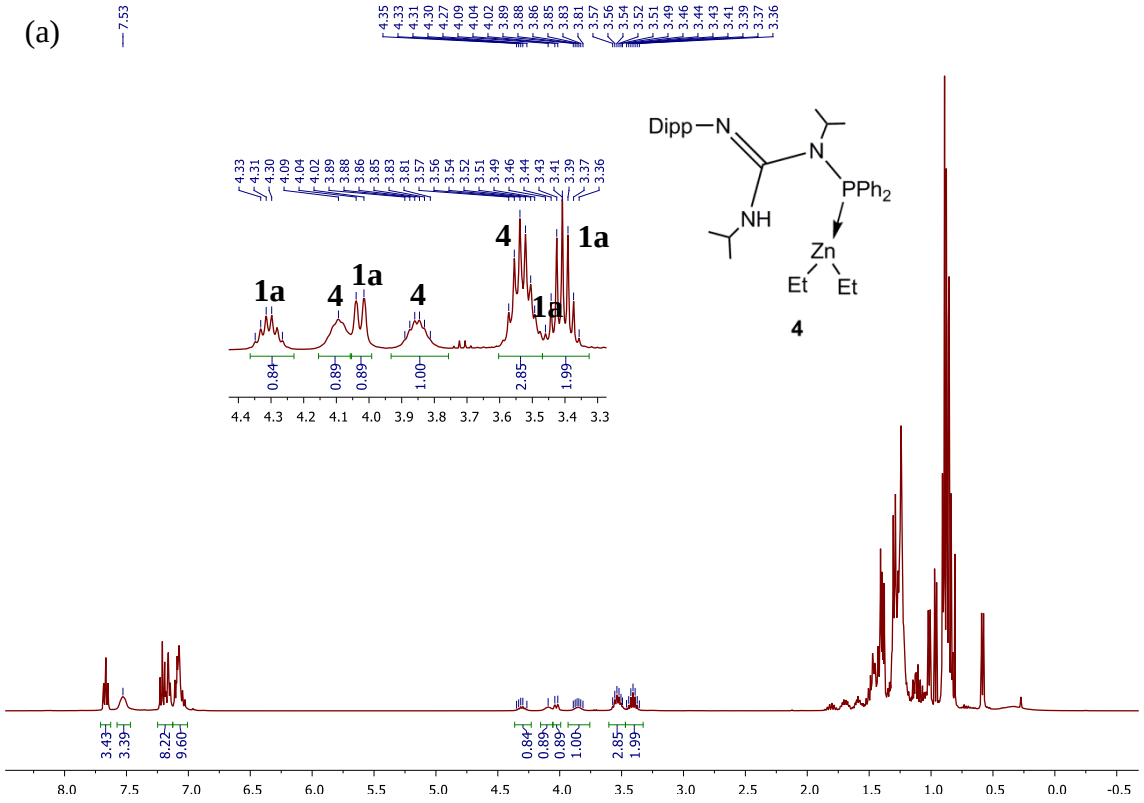

21.93
N
PPh2
N
N
Al
Me
Me
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80

Figure S8. ^{1}H (a) and $^{31}P\{^{1}H\}$ (b) NMR spectra of the equilibrium between compound **1a**, $ZnEt_2$ and compound **4** in C_6D_6.



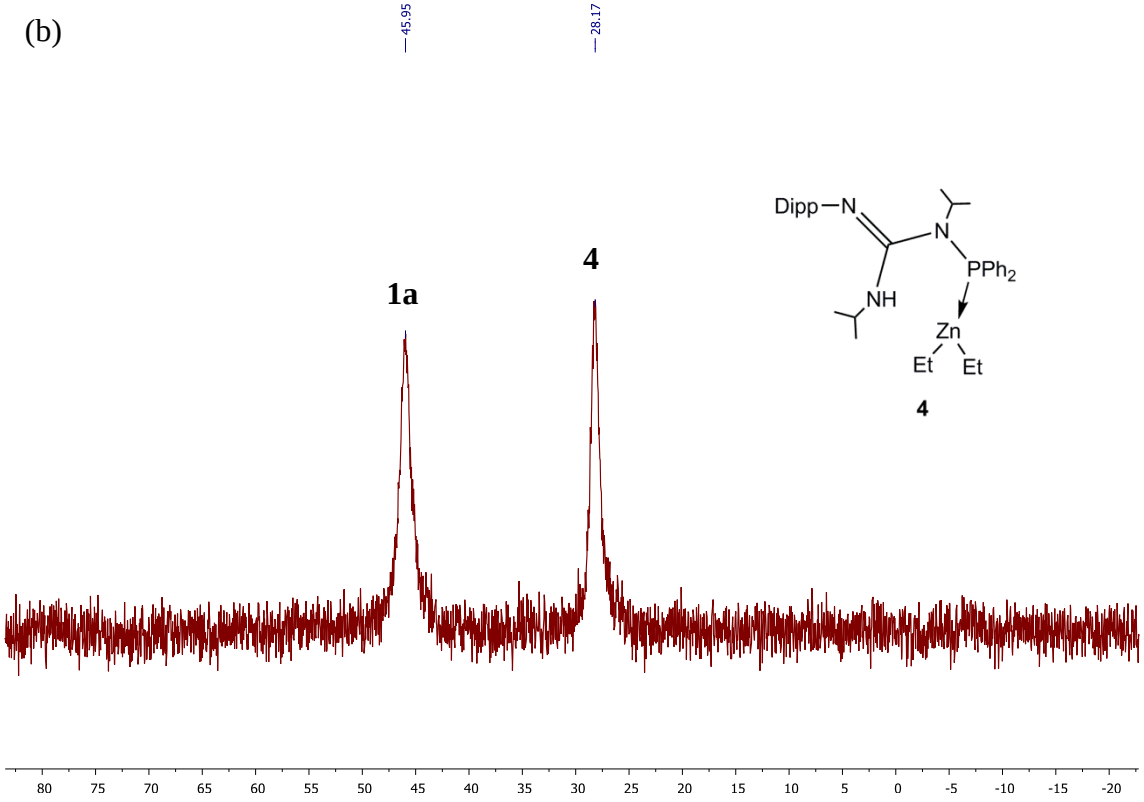
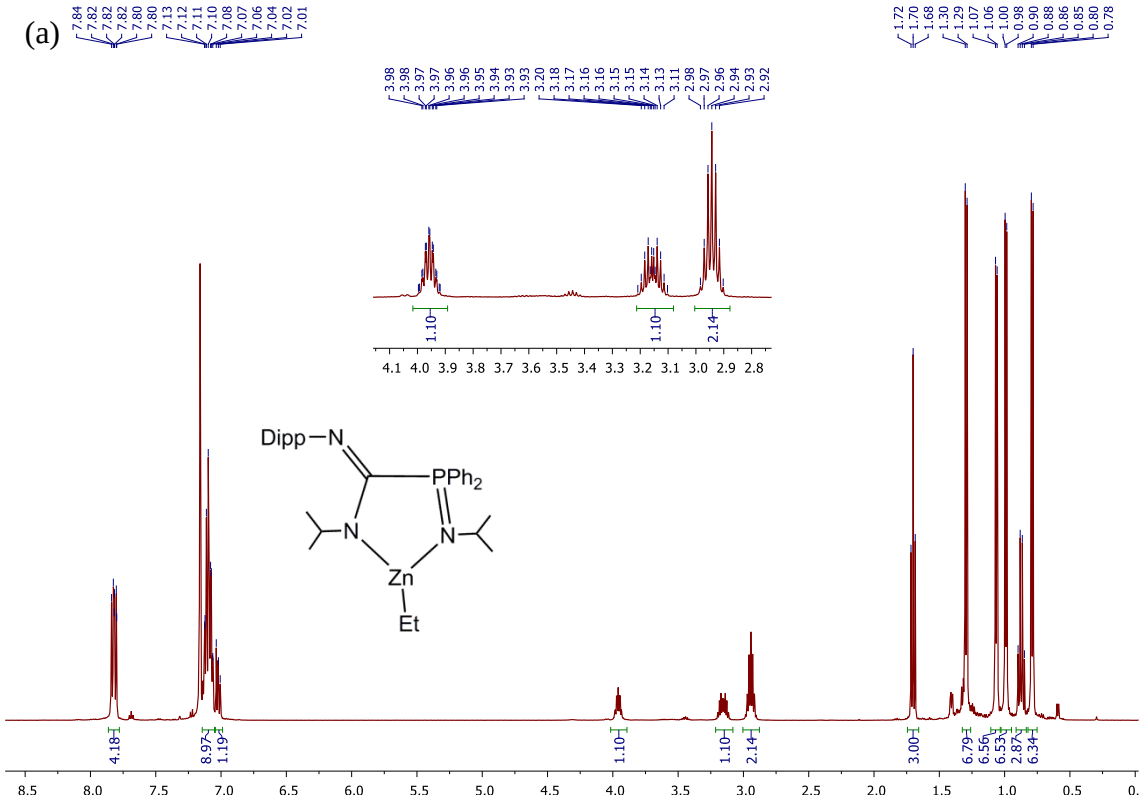
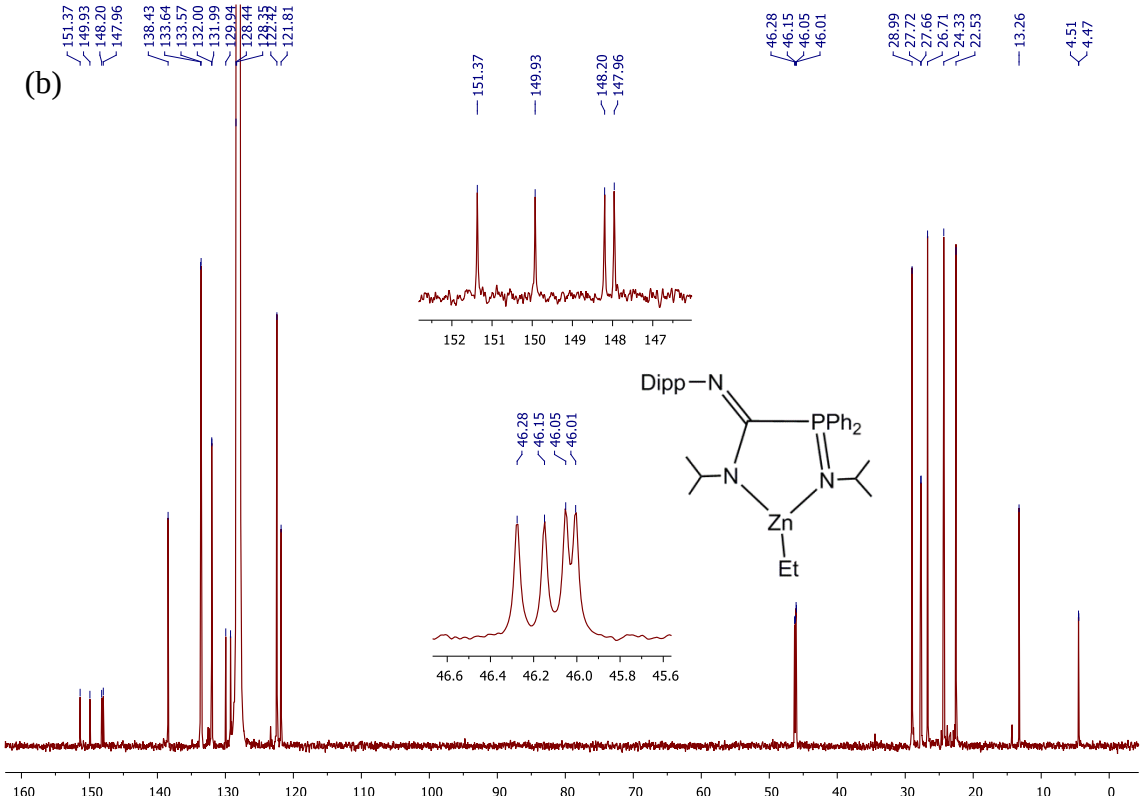
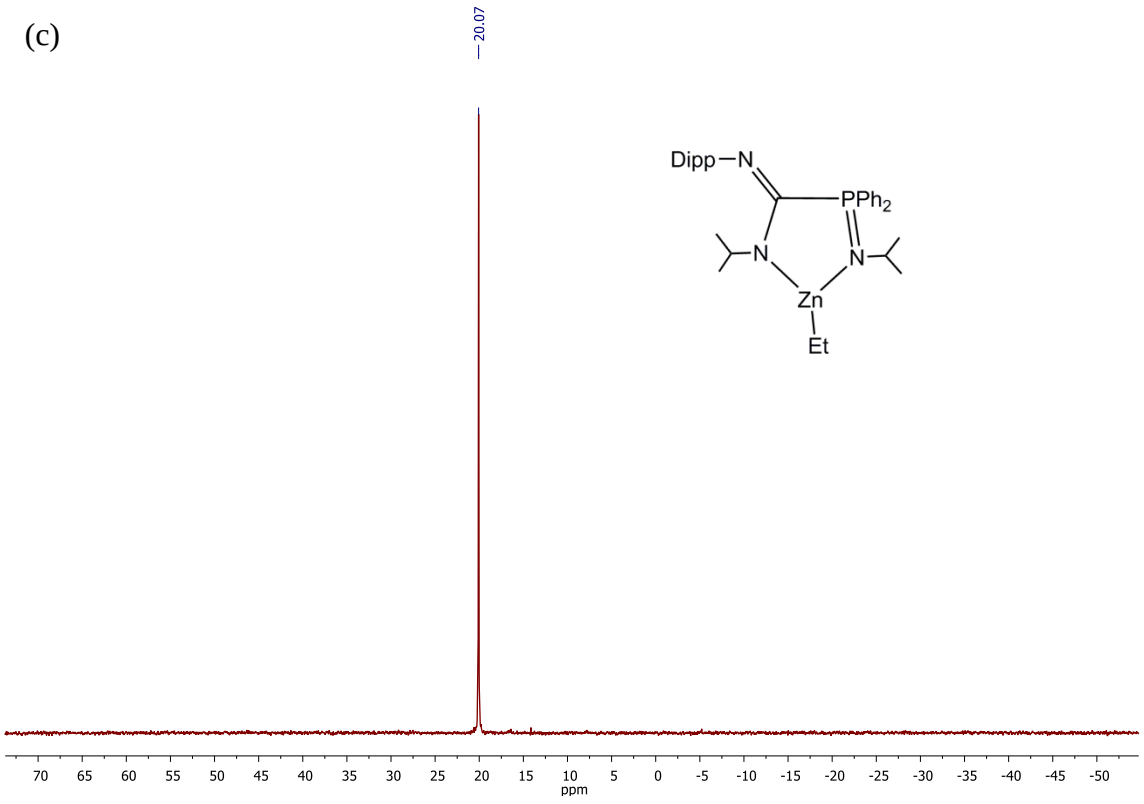


Figure S9. ^{1}H (a), $^{13}C\{^{1}H\}$ (b) and $^{31}P\{^{1}H\}$ (c) NMR spectra of compound **5** in C_6D_6.





(c)


20.07
Dipp—N
PPh2
N
N
Zn
Et
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
ppm

X-ray crystal determination. X-ray data collection of suitable single crystals of compounds **1a**, **2b**, **3a** and **5** were performed at 100(2) K on a Bruker VENTURE area detector equipped with graphite monochromated Mo-K α radiation (λ = 0.71073 Å) by applying the ω-scan method. The data reduction was performed with the APEX2[2] software and corrected for absorption using SADABS.[3] Crystal structures were solved by direct methods using the SIR97 program[4] and refined by full-matrix least-squares on F^2 including all reflections using anisotropic displacement parameters by means of the WINGX crystallographic package.[5] All hydrogen atoms were included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times or 1.5 times those of their parent atoms for the organic ligands. Details of the structure determination and refinement of compounds are summarised in Table S1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1878867, 1878868, 1881080 and 1891458 for compounds **3a, 1a**, **5** and **2b**, respectively. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (Fax: +44-1223-335033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Figure S10. Molecular structure of compound **5**; H atoms omitted for clarity and ellipsoids plotted at 30% probability level. Selected bond lengths (Å) and angles (^{0}): P1-C1 1.832(2), C1-N3 1.302(3), C1-N1 1.332(3), N1-Zn1 1.986(2), Zn1-N2 1.967(2), N2-P1 1.602(2), P1-C1-N1 113.3(1), P1-C1-N3 109.0(1), N3-C1-N1 137.7(2), C1-N1-Zn1 116.5(1), N1-Zn1-N2 91.98(7), Zn1-N2-P1 111.0(1), N2-P1-C1 106.91(7), C2-Zn1-N1 143.0(1), C2-Zn1-N2 125.0(1).

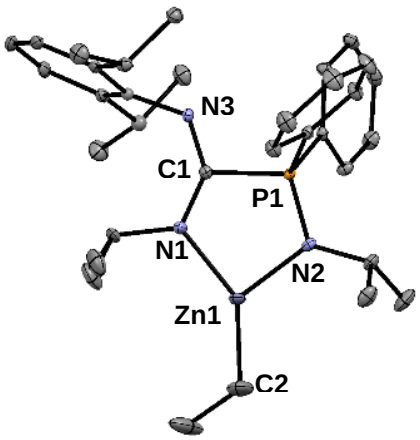


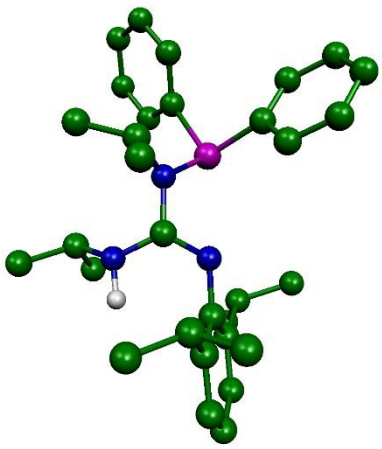
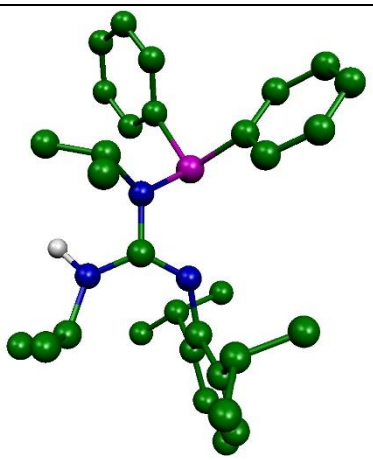
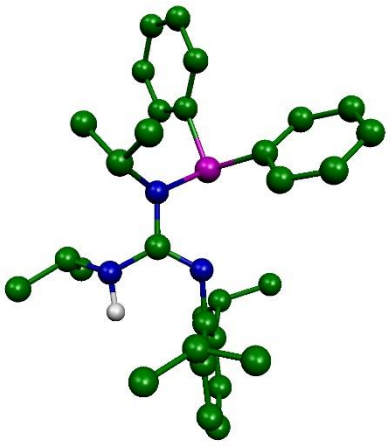
Table S1. Crystallographic data and structure refinement details for all compounds.

Compound	**1a**	**2b**	**3a**	**5a**
Empirical formula	$C_{31}H_{42}PN_3$	$C_{30}H_{42}AlN_3P$	$C_{33}H_{47}PN_3Al$	$C_{31}H_{46}PN_3Zn$
CCDC	1878868	1891458	1878867	1881080
Form. weight	487.64	501.61	543.68	581.07
Cryst. System	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	17.093(3)	12.073(2)	10.081(2)	15.379(3)
b (Å)	15.955(2)	15.298(3)	19.984(3)	12.334(2)
c (Å)	10.358(2)	15.849(3)	16.631(3)	17.878(3)
α (deg)	90	90	90	90
β (deg)	90	99.731(4)	99.198(4)	108.758(5)
γ (deg)	90	90	90	90
Volume (Å^3)	2824.8(8)	2885.1(9)	3307.3(10)	3211.1(10)
Z	4	4	4	4
ρ (g cm^{-3})	1.147	1.155	1.092	1.202
μ (mm^{-1})	0.121	0.148	0.134	0.839
GOF [a]	1.063	1.089	0.996	1.533
R_{int}	0.087	0.108	0.145	0.053
R1 [b] / wR2 [c] [I>2σ(I)]	0.0388/0.0764	0.0527/0.01219	0.0507/0.1093	0.0466/0.1260
R1 [b] / wR2 [c] (all data)	0.0515/0.0805	0.0826/0.1426	0.0932/0.1241	0.0592/0.1364

[a] $S = [\Sigma w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{para}m)]^{1/2}$ [b] $R_1 = \Sigma||F_0|-|F_c|| / \Sigma|F_0|$ [c] $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2 / \Sigma wF_0^2]^{1/2}$
$w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (\max(F_0^2,0) + 2F_c^2)/3$

Theoretical calculations. All the calculations were carried out by using the Gaussian09 suite of programs,[6] using the hybrid functional B3LYP with the Becke three-parameter exchange functional[7] and the Lee-Yang–Parr correlation functional.[8] An accurate numerical integration grid (99,590) was used for all the calculations via the keyword Int = Ultrafine. We have proved recently the accuracy of this methodology for the structural analysis of related complexes.[9] All the elements were described by the 6-31G* basis set.[10] Geometry optimisations were performed under no symmetry restrictions, and frequency analyses were performed for all stationary points to ensure that minimum structures with no imaginary frequencies were achieved. Transition states were optimised through the Synchronous Transit-Guided Quasi-Newton (STQN) Method as implemented in Gaussian09, were characterised by frequency analysis (one imaginary frequency) and their connectivity in general was further corroborated through Intrinsic-Reaction-Coordinate (IRC) calculations. The free energies were calculated within the harmonic approximation for vibrational frequencies. Solvent effects (benzene, ε = 2.2706) were modelled using the polarised-continuum-model (PCM) of Tomasi and coworkers,[11] by using the gas-phase optimised structures.

Figure S11. DFT-computed structures for the different isomers of compound **1a**, with relative Gibbs free energies expressed in kcal mol^{-1}.

		
***E*-1a**, 0.0	***E*-1aA**, 0.3	***E*-1aB** 2.3

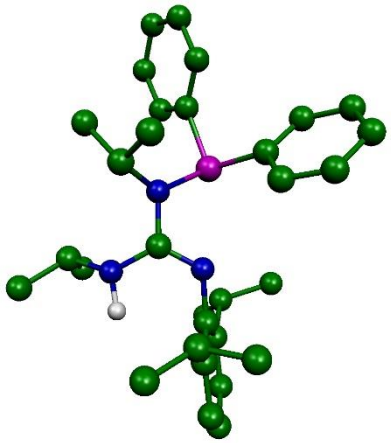
		
***Z*-1**, 8.0		

Figure S12. Computed reaction profile for the formation of complex **3a** from *N*-phosphino-guanidine **1a** and $AlMe_3$, Gibbs free energies expressed in kcal mol^{-1}.

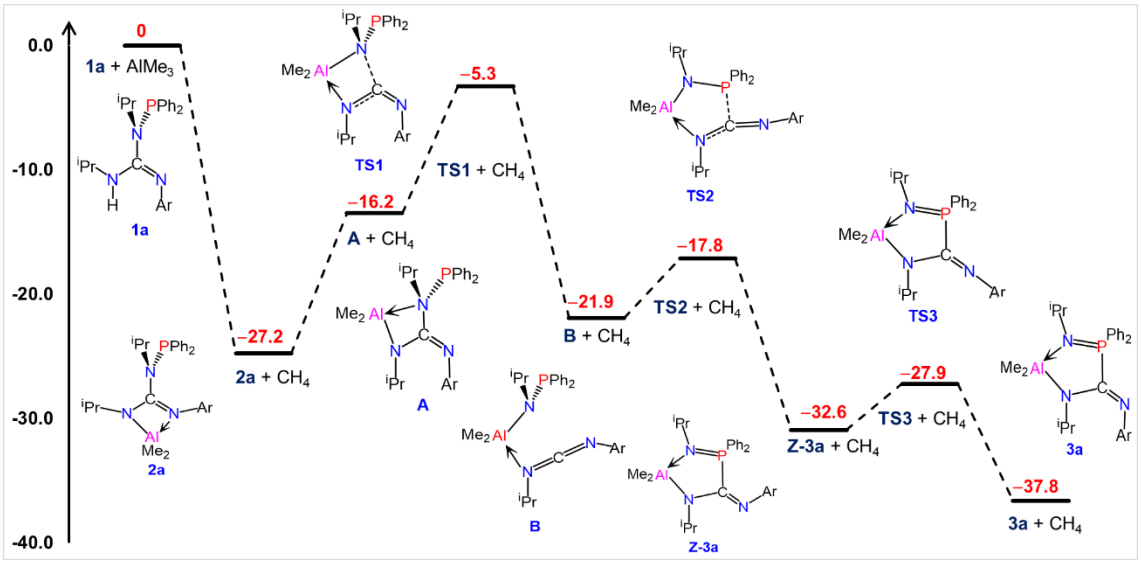


Figure S13. Computed reaction profile for the formation of complex **3a** from *N*-phosphino-guanidine **1a** and $AlMe_3$, Gibbs free energies in C_6H_6 expressed in kcal mol^{-1}.

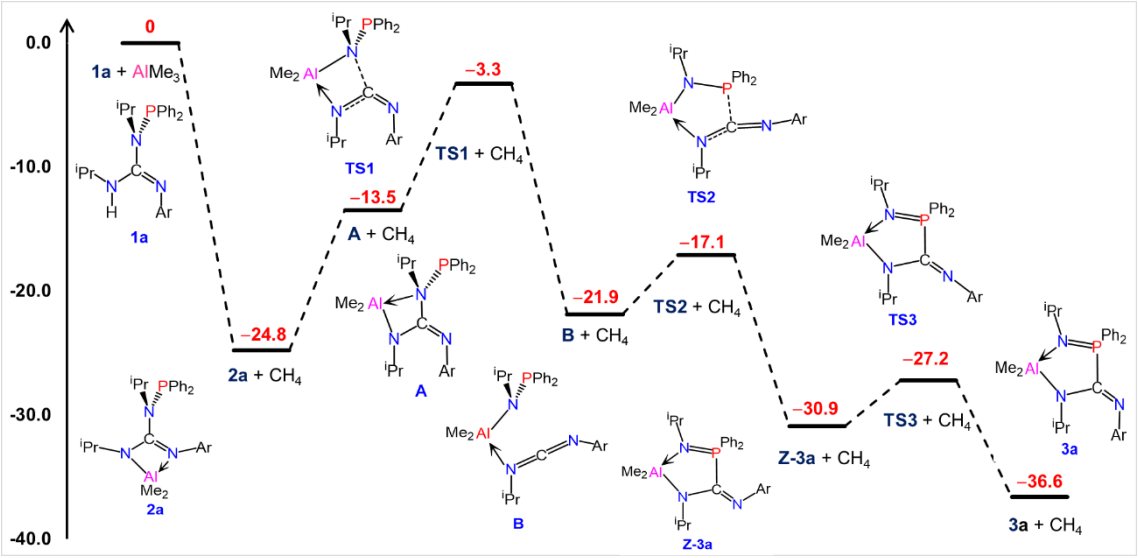
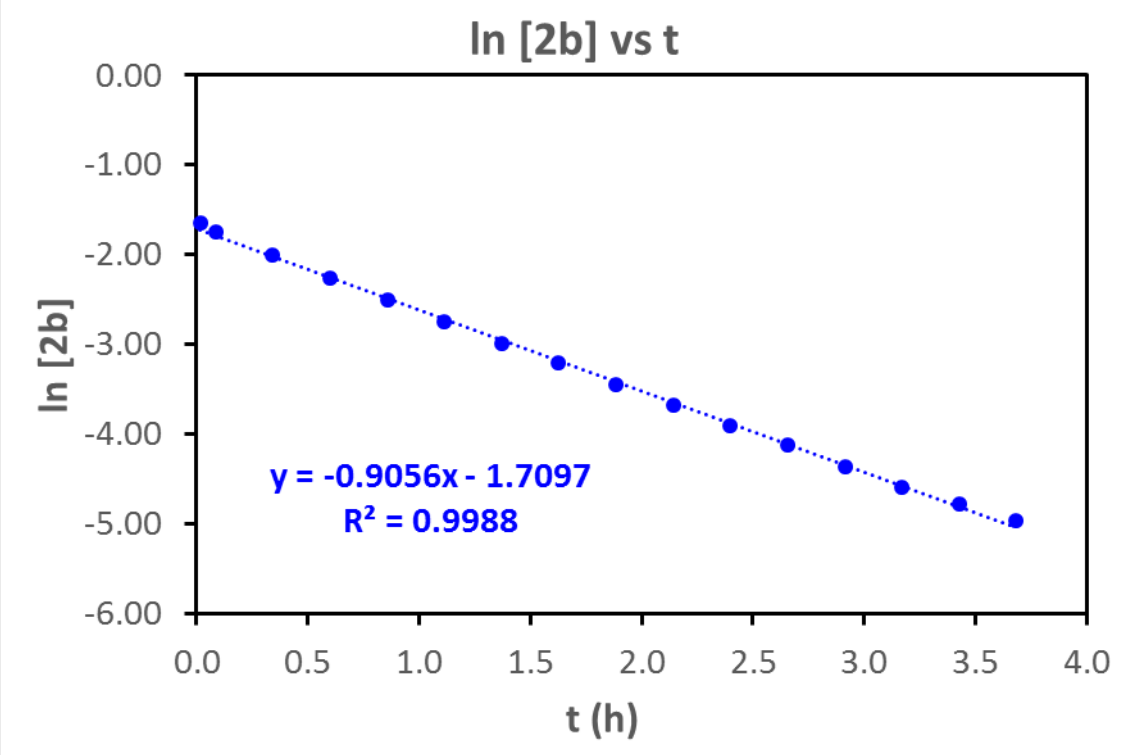


Table S2. Relative gas and solution (benzene) phase Gibbs free energies (kcal·mol^{-1}) for all the computed species in the transformation **2a**→**3a**.

	1a + $AlMe_3$	**2a** + CH_4	**A** + CH_4	**TS1** + CH_4	**B** + CH_4	**TS2** + CH_4	**Z-3a** + CH_4	**TS3** + CH_4	**3a** + CH_4
G_{gas}	-2073.737185	-2073.780552	-2073.762996	-2073.745708	-2073.772146	-2073.765624	-2073.789104	-2073.781708	-2073.797379
ΔG_{gas}	0.0	-27.2	-16.2	-5.3	-21.9	-17.8	-32.6	-27.9	-37.8
$\Delta G_{benzene}$	0.0	-24.8	-13.5	-3.3	-21.9	-17.1	-30.9	-27.2	-36.6

Kinetic studies. Kinetic experiments were carried out for the thermal rearrangement reaction of **2b** into **3b**. In a typical experiment, compound **2b** was *in situ* prepared from **1b** (0.050 g, 0.112 mmol) as described above, dissolved in 400 µL of C_6D_6 and transferred to an NMR tube fitted with a concentric Teflon. Then, tetrakis(trimethylsilyl)silane (TKS, 50 µL of a 0.2 M solution in C_6D_6, 0.01 mmol) was added as internal standard and the final volume was made up to 0.6 mL. The sample was taken out of the glovebox and introduced in the NMR spectrometer, set at 80 ºC. The reaction was followed by ^{1}H NMR, collecting data after fixed intervals of time (900 s) up to more than four half-lives. To determine the order in [**2b**], different plots were made: [**2b**] vs. t, ln [**2b**] vs. t and 1/[**2b**] vs. t, obtaining only a linear plot in the second case, which implies a first-order dependence on [**2b**] (*vide infra*).

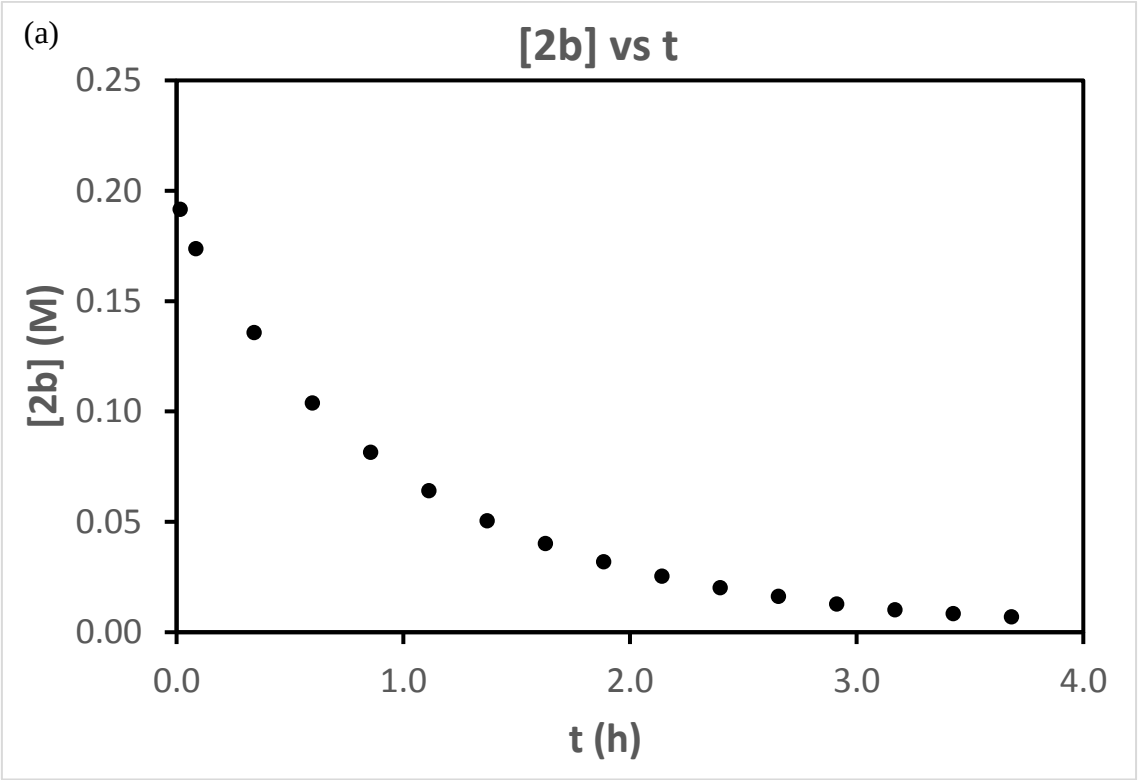
Figure S14. First-order kinetics in [**2b**]: ln [**2b**] vs. t plot

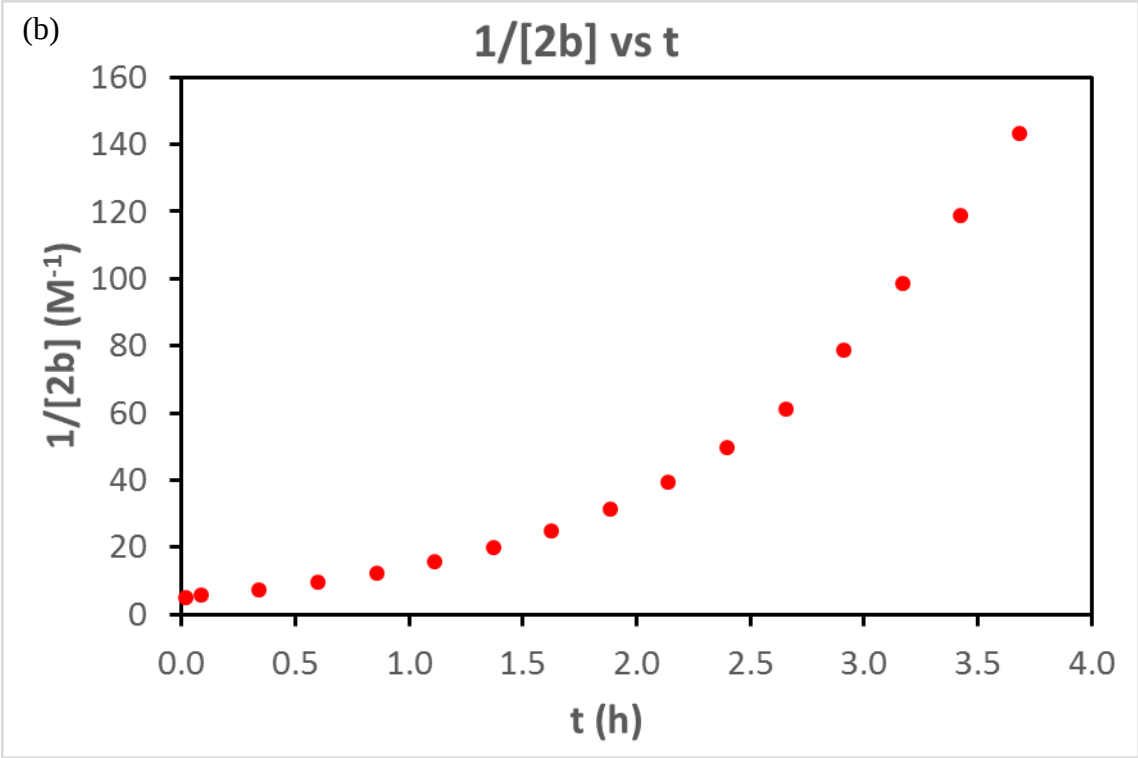


$$\mathbf{2b} \xrightarrow{k_1} \mathbf{3b}$$

$\ln [\mathbf{2b}] = \ln [\mathbf{2b}]_0 - k_1 t$

Figure S15. Non-linear kinetics: (a) [**2b**] vs. t, and (b) 1/[**2b**] vs. t plots.





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