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Supporting information

A new bulky iminophosphonamide as an N,N'-chelating ligand: synthesis and structural characterization of heteroleptic group 13 elements complexes

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(14 Pages)

Contents: 25 Figures: Fig. S1 to Fig. S25 for multinuclear NMR spectrum of compounds **1-8**.

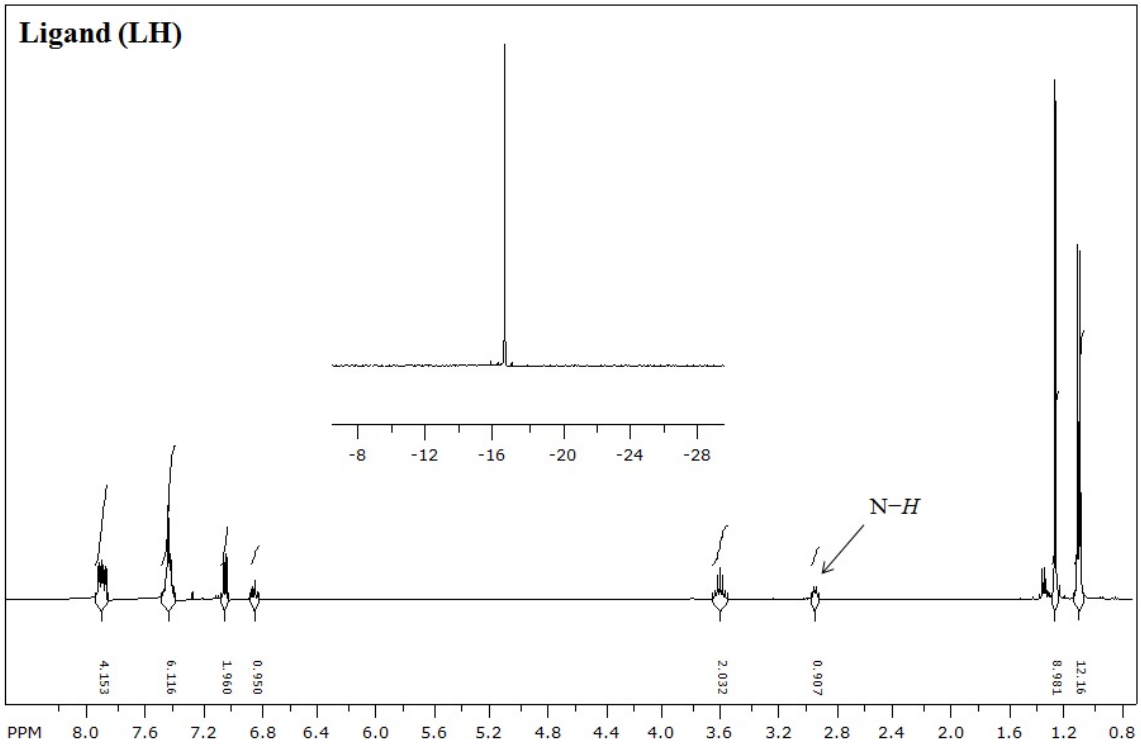

Fig. S1 Room temperature ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [(2,6-*i*$Pr_2C_6H_3N$)P(Ph_2)(N*t*Bu)]H **(LH)**. The Inset shows the $^{31}P\{^{1}H\}$ spectrum.

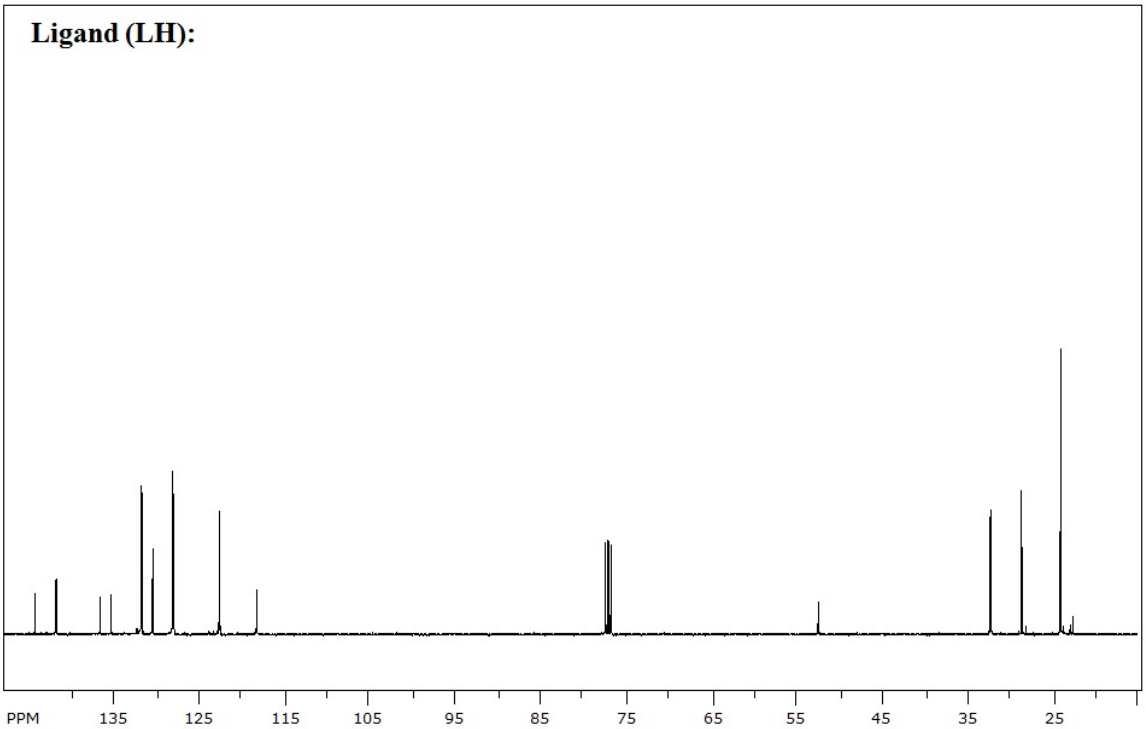

Fig. S2 Room temperature ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of [(2,6-*i*$Pr_2C_6H_3N$)P (Ph_2)(N*t*Bu)]H **(LH)**.

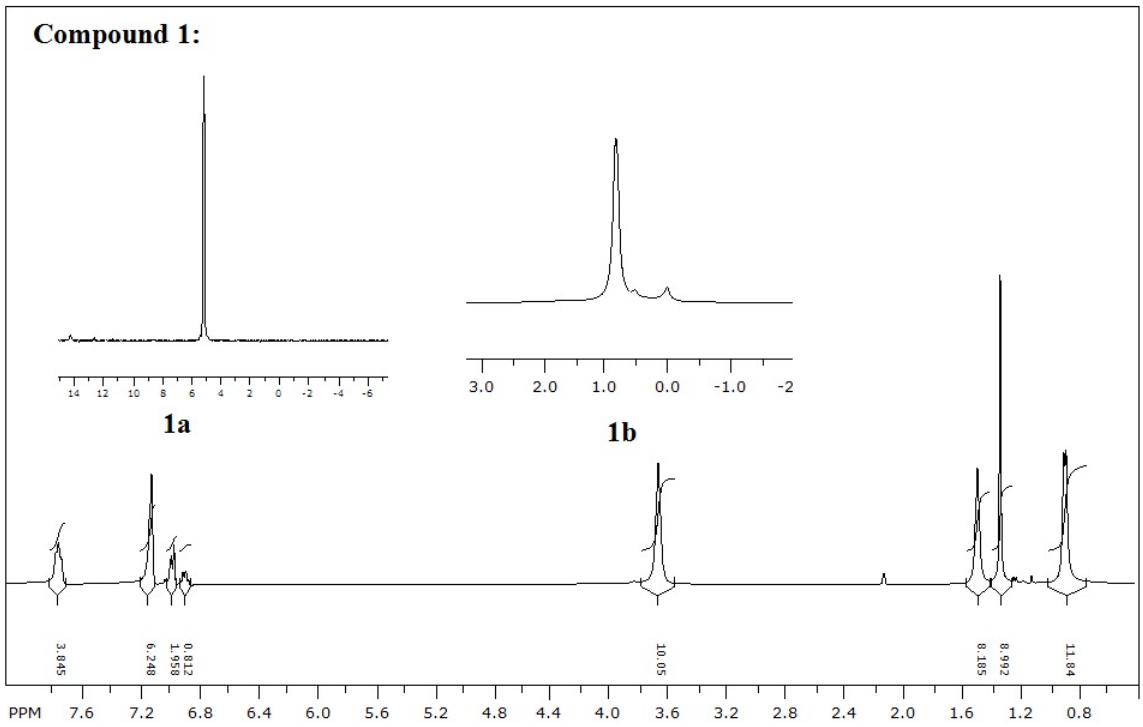

Fig. S3 Room temperature ^{1}H NMR (400 MHz, toluene-d_8) spectrum of [(2,6-*i*$Pr_2C_6H_3N$)$P(Ph_2)$(N*t*Bu)](Li·2THF) **(1)**. Inset **1a** shows the $^{31}P\{^{1}H\}$ NMR (162 MHz, toluene-d_8, –35 °C) spectrum and ^{7}Li NMR (155 MHz, toluene-d_8, –35 °C) spectrum is shown in inset **1b**.

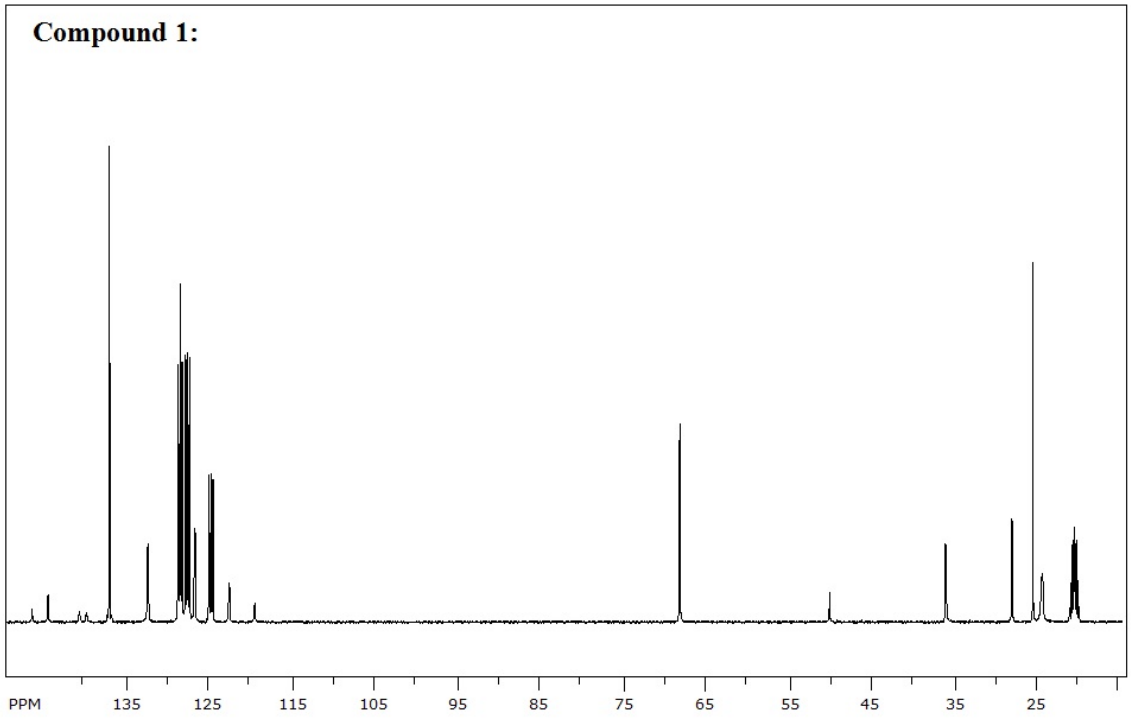

Fig. S4 ^{13}C NMR (100 MHz, toluene-d_8, –35 °C) spectrum of [(2,6-*i*$Pr_2C_6H_3N$)$P(Ph_2)$(N*t*Bu)] (Li·2THF) **(1)**.

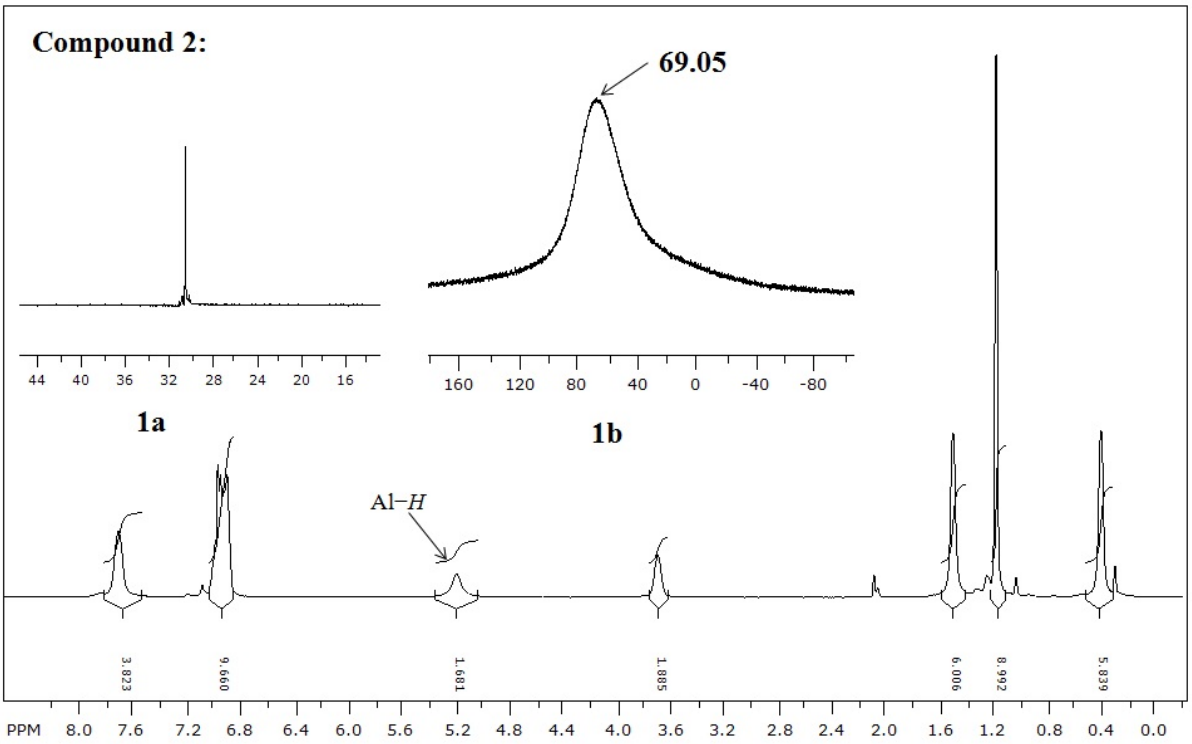

Fig. S5 ^{1}H NMR (400 MHz, toluene-d_8, –35 °C) spectrum of [{(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)}AlH$_2$]$_2$ **(2)**. Inset **1a** shows the ^{31}P{^{1}H} NMR (162 MHz, toluene-d_8, –35 °C) spectrum and ^{27}Al NMR (104 MHz, toluene-d_8, –35 °C) NMR spectrum is shown in inset **1b**.

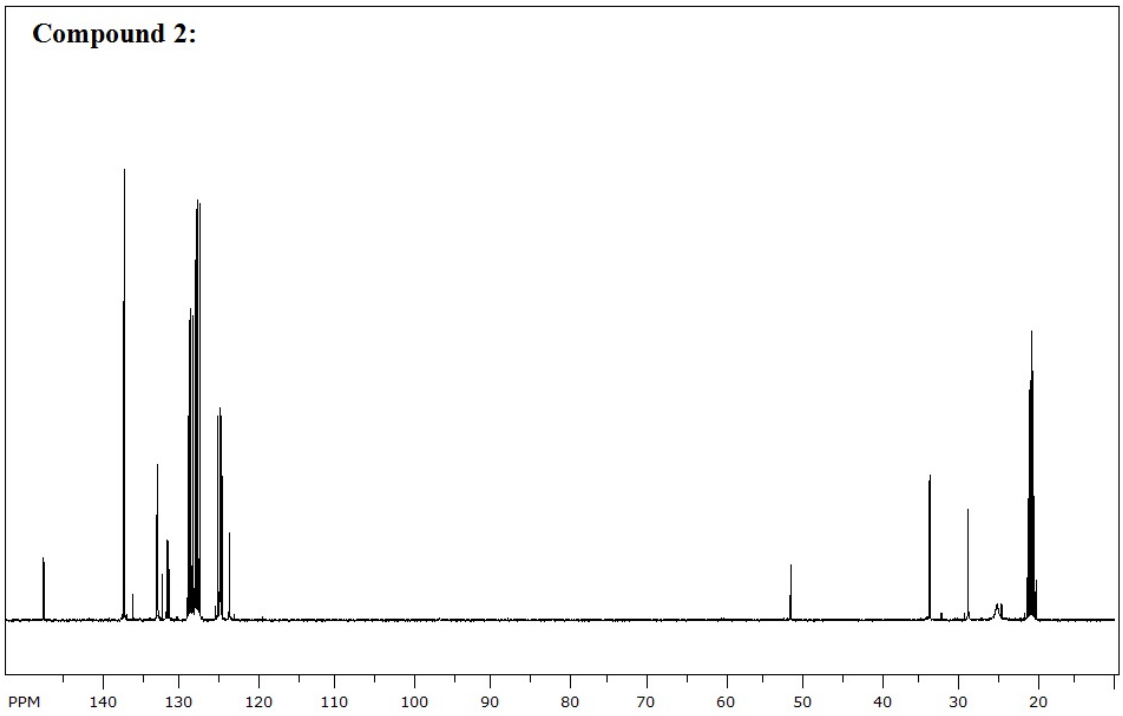

Fig. S6 ^{13}C NMR (100 MHz, toluene-d_8, –35 °C) spectrum of [{(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)}AlH$_2$]$_2$ **(2)**.

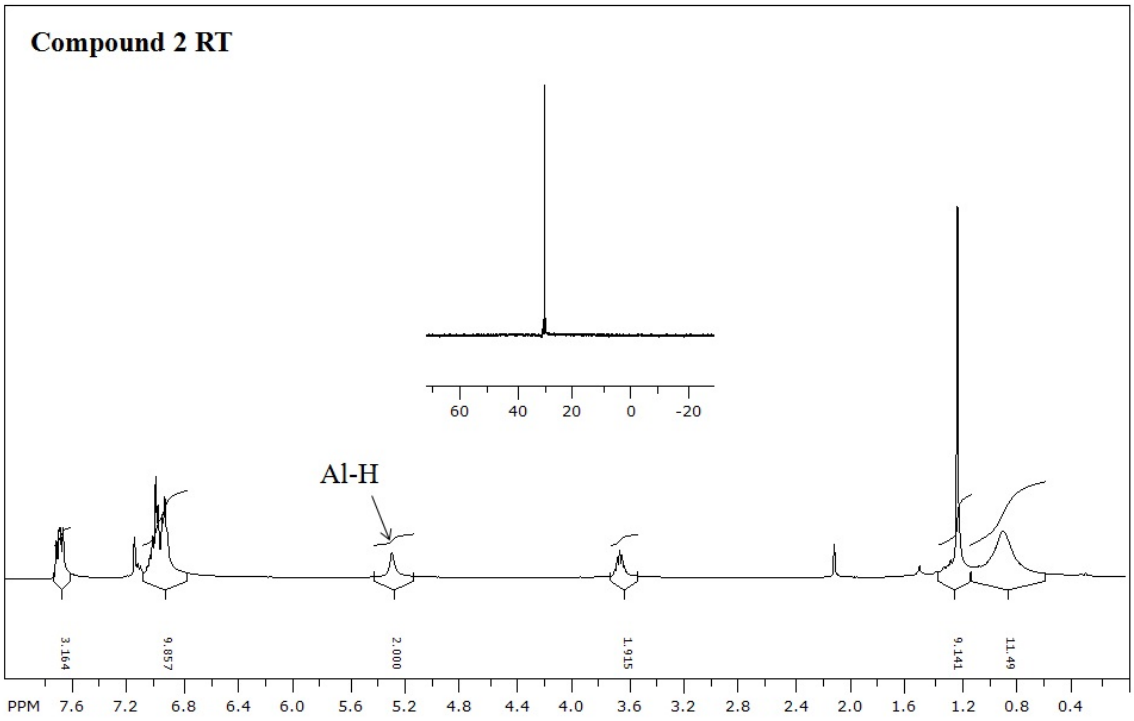

Fig. S7 Room temperature ^{1}H NMR (400 MHz, C_6D_6) spectrum of $[\{(2,6\text{-}i\text{Pr}_2C_6H_3N)P(Ph_2)(N t\text{Bu})\}AlH_2]_2$ **(2)**. Inset **1a** shows the $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) spectrum and ^{27}Al NMR (104 MHz, C_6D_6) NMR spectrum is shown in inset **1b**.

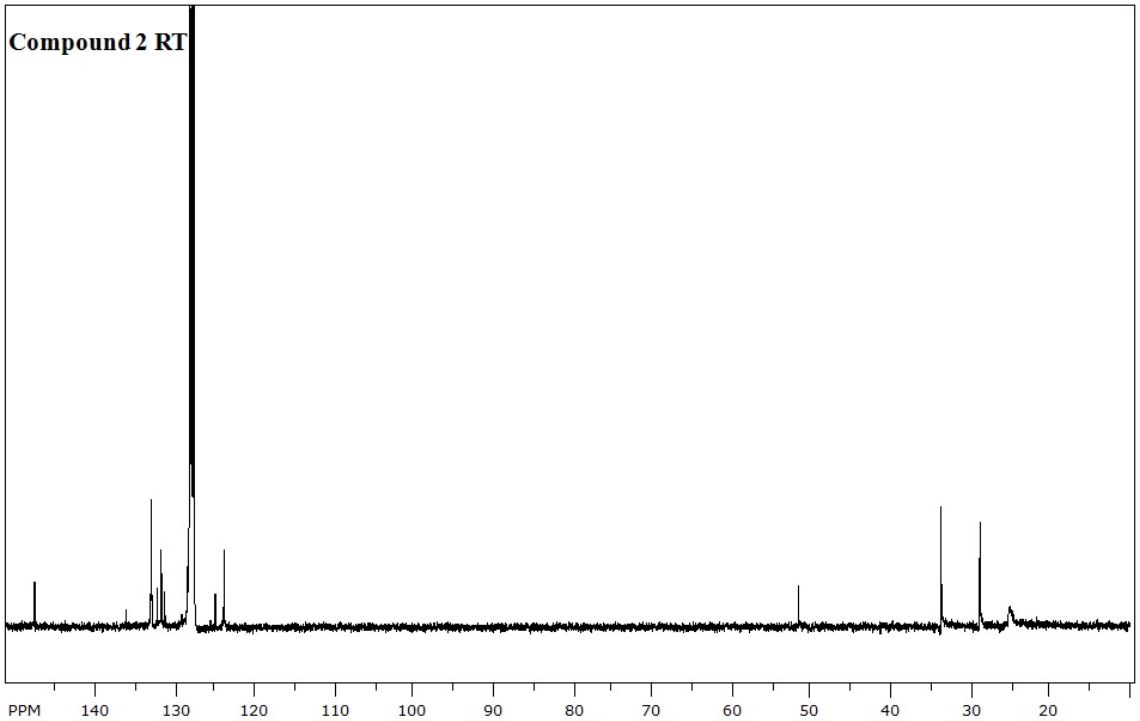

Fig. S8 Room temperature ^{13}C NMR (100 MHz, C_6D_6) spectrum of $[\{(2,6\text{-}i\text{Pr}_2C_6H_3N)P(Ph_2)(N t\text{Bu})\}AlH_2]_2$ **(2)**.

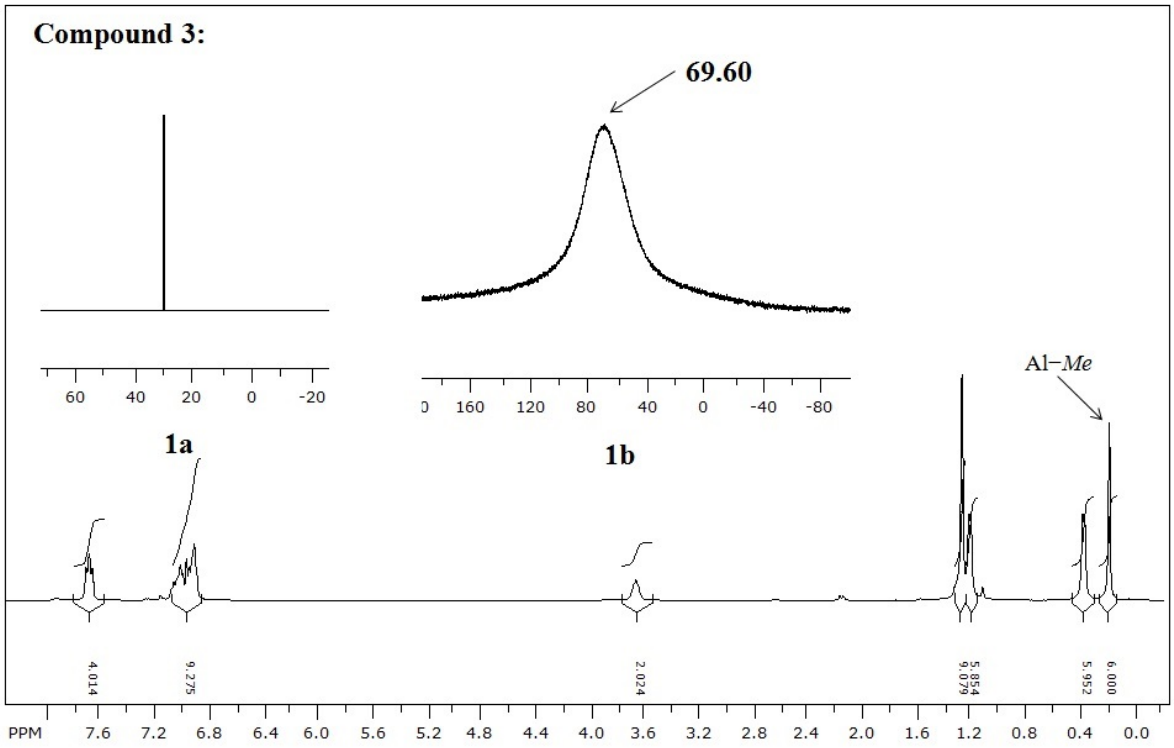

Fig. S9 ^{1}H NMR (400 MHz, toluene-d_8, –35 °C) spectrum of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]AlMe$_2$ **(3)**. Inset **1a** shows the ^{31}P{^{1}H} (162 MHz, toluene-d_8, –35 °C) spectrum and ^{27}Al NMR (104 MHz, toluene-d_8, –35 °C) spectrum is shown in inset **1b**.

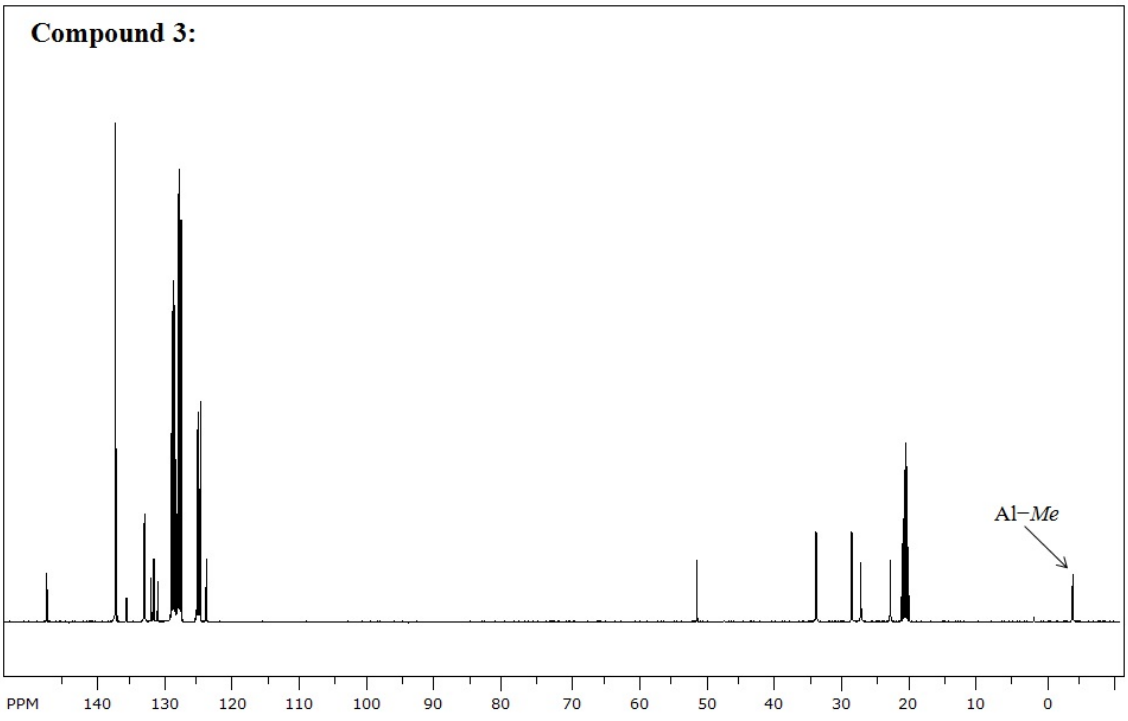

Fig. S10 ^{13}C NMR (100 MHz, toluene-d_8, –35 °C) spectrum of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]AlMe$_2$ **(3)**.

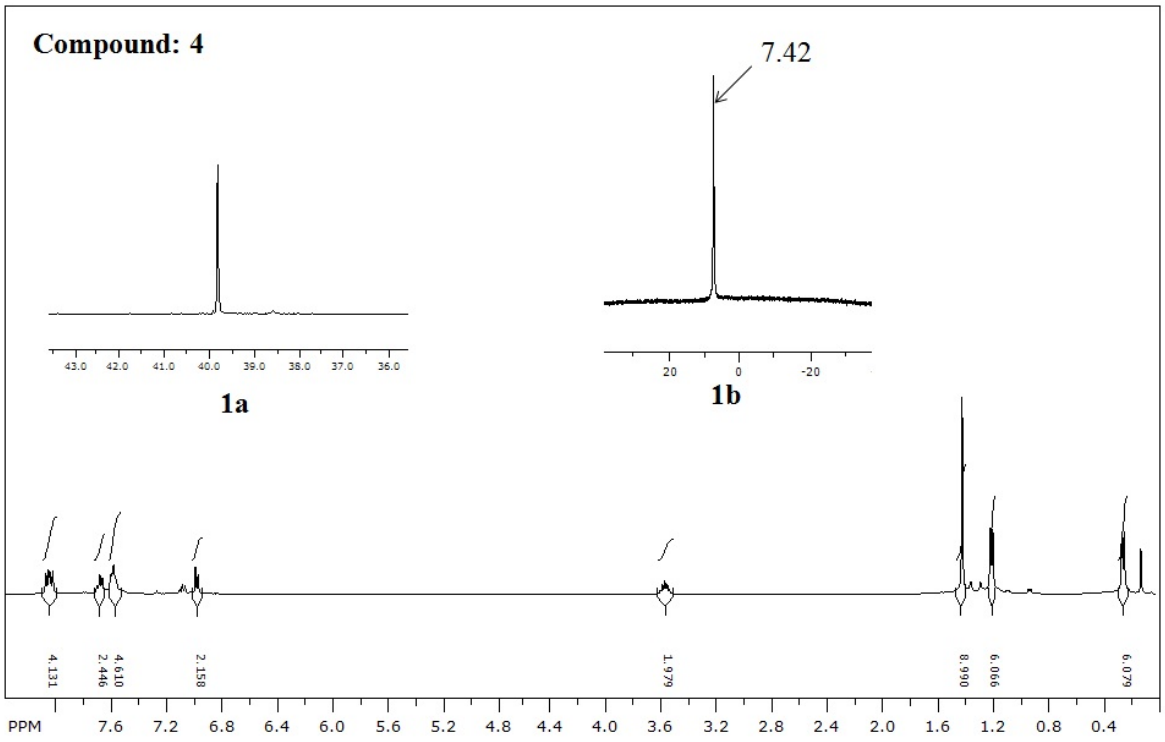

Fig. S11 Room temperature ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $[(2,6\text{-}i\text{Pr}_2C_6H_3N)P(Ph_2)(N\text{t}Bu)]BCl_2$ **(4)**. Inset **1a** shows the $^{31}P\{^{1}H\}$ (162 MHz, $CDCl_3$) spectrum and ^{11}B NMR (128 MHz, $CDCl_3$) spectrum is shown in inset **1b**.

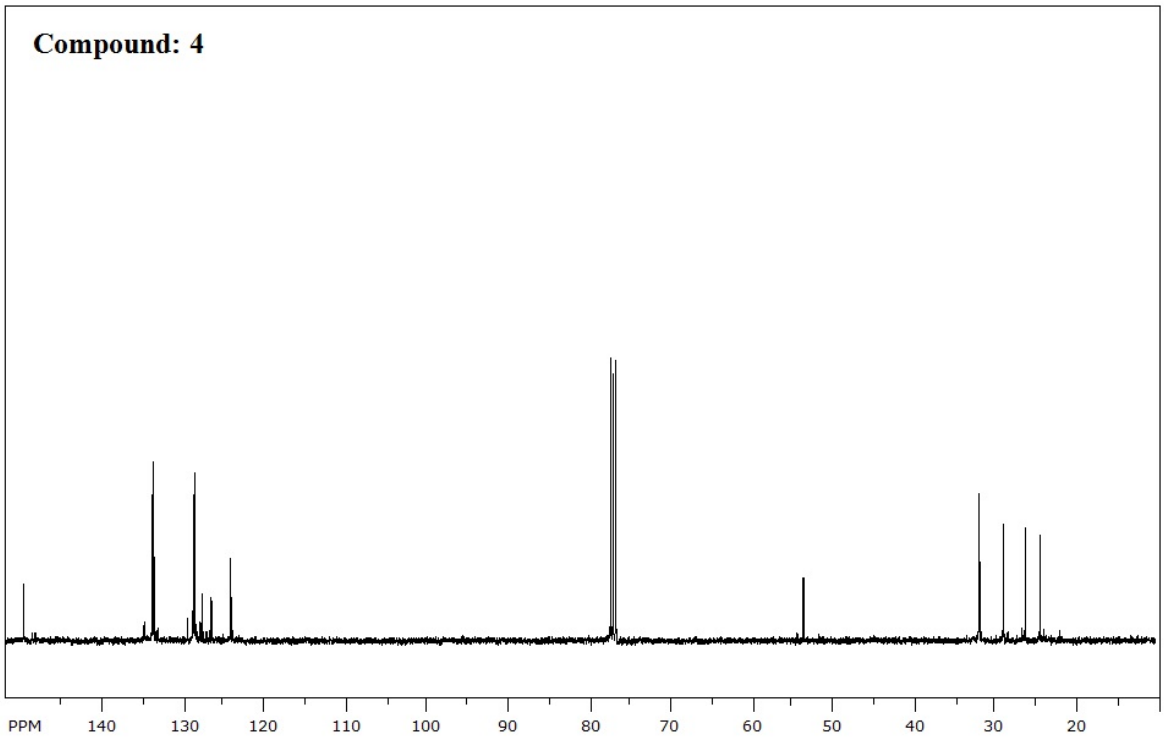

Fig. S12 Room temperature ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of $[(2,6\text{-}i\text{Pr}_2C_6H_3N)P(Ph_2)(N\text{t}Bu)]BCl_2$ **(4)**.

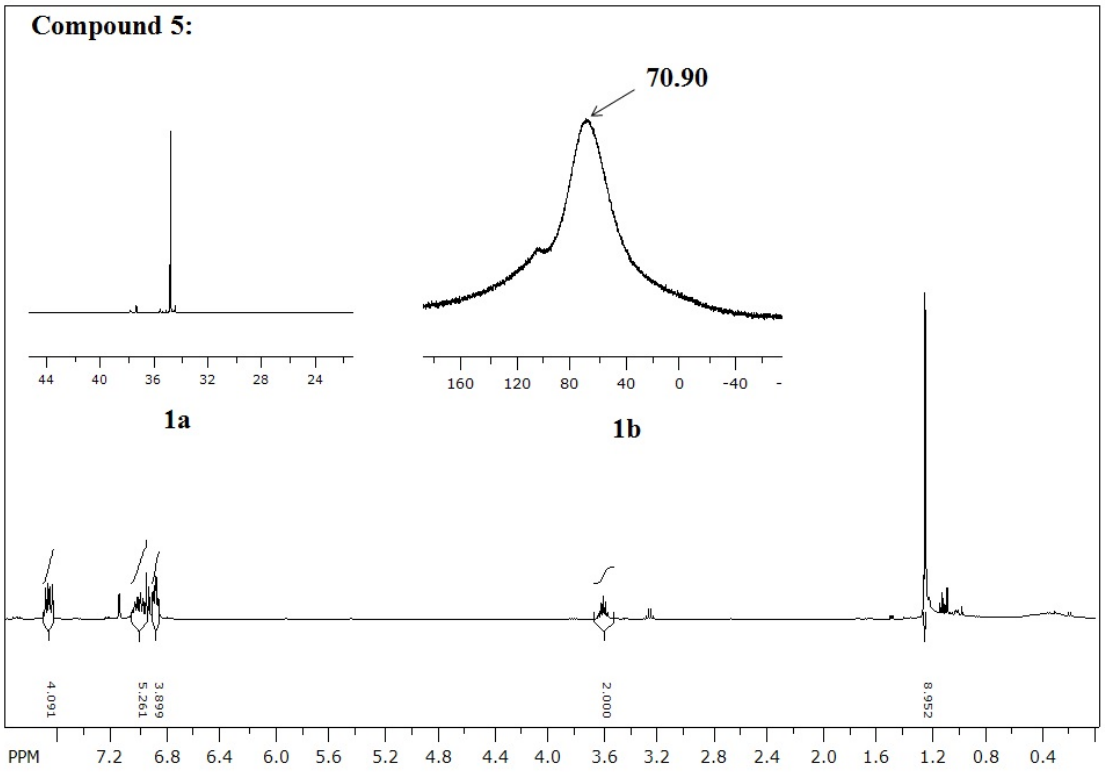

Fig. S13 Room temperature ^{1}H NMR (400 MHz, C_6D_6) spectrum of [(2,6-*i*$Pr_2C_6H_3N$)P(Ph_2)(N*t*Bu)]$AlCl_2$ **(5)**. Inset **1a** shows the $^{31}P\{^{1}H\}$ (162 MHz, C_6D_6) spectrum and ^{27}Al NMR (104 MHz, C_6D_6) spectrum is shown in inset **1b**.

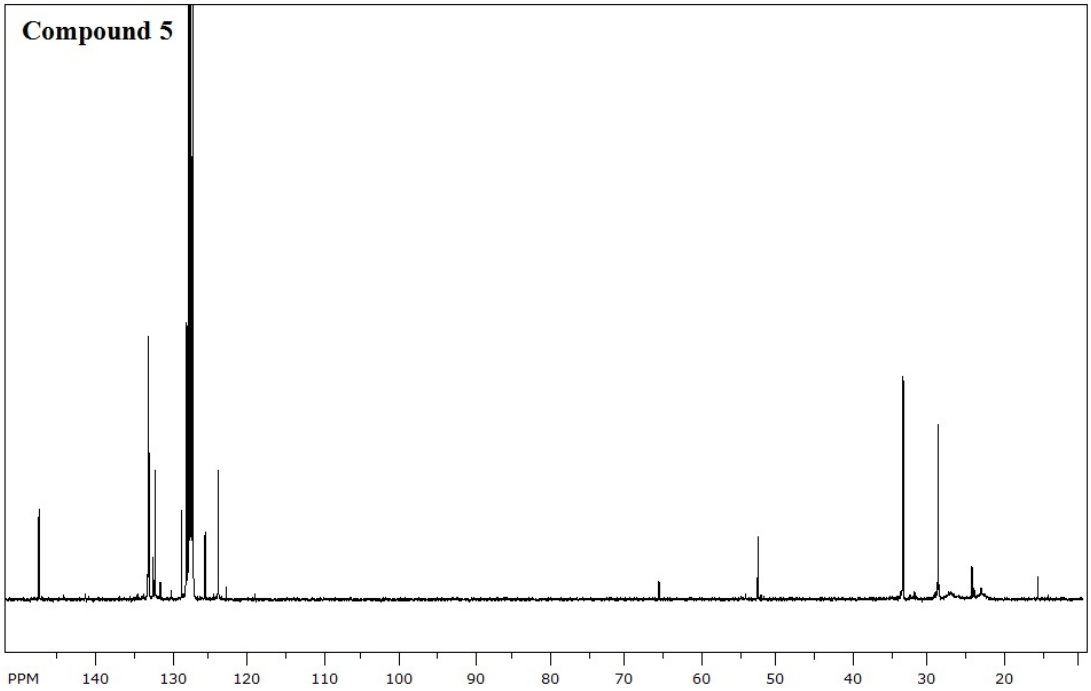

Fig. S14 Room temperature ^{13}C NMR (100 MHz, C_6D_6, 25 °C) spectrum of [(2,6-*i*$Pr_2C_6H_3N$)P(Ph_2)(N*t*Bu)]$AlCl_2$ **(5)**.

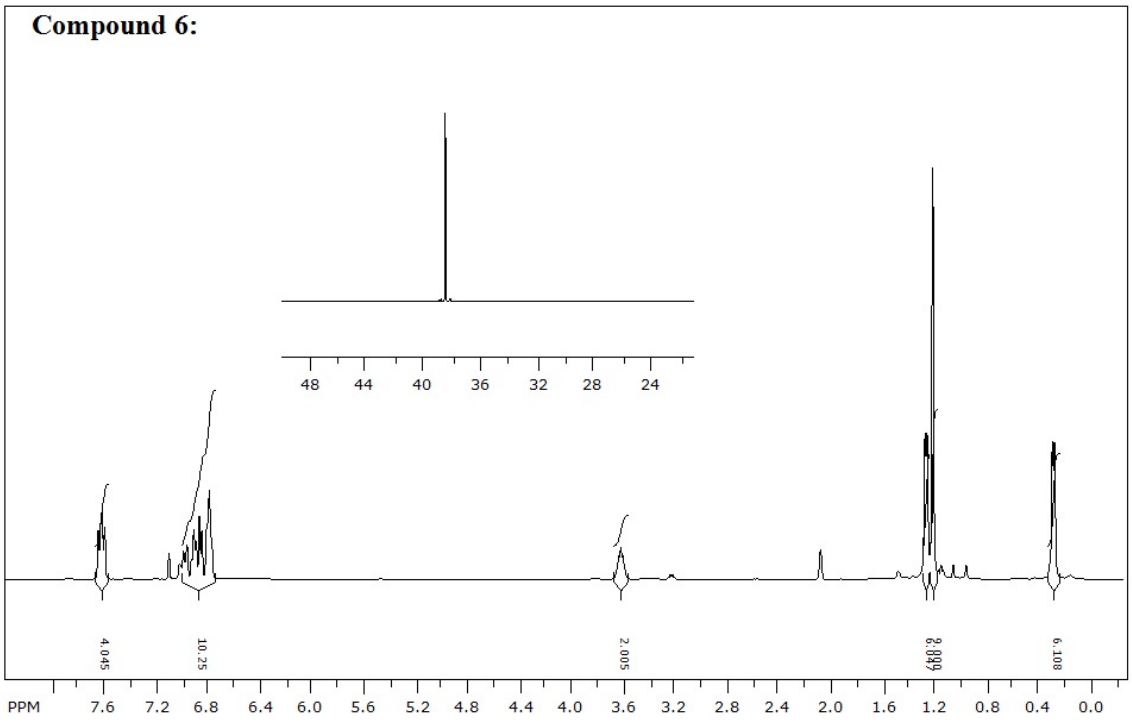

Fig. S15 ^{1}H NMR (400 MHz, toluene-d_8, –35 °C) spectrum of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]GaCl$_2$ **(6)**. Inset shows the ^{31}P{^{1}H} (162 MHz, toluene-d_8, –35 °C) spectrum.

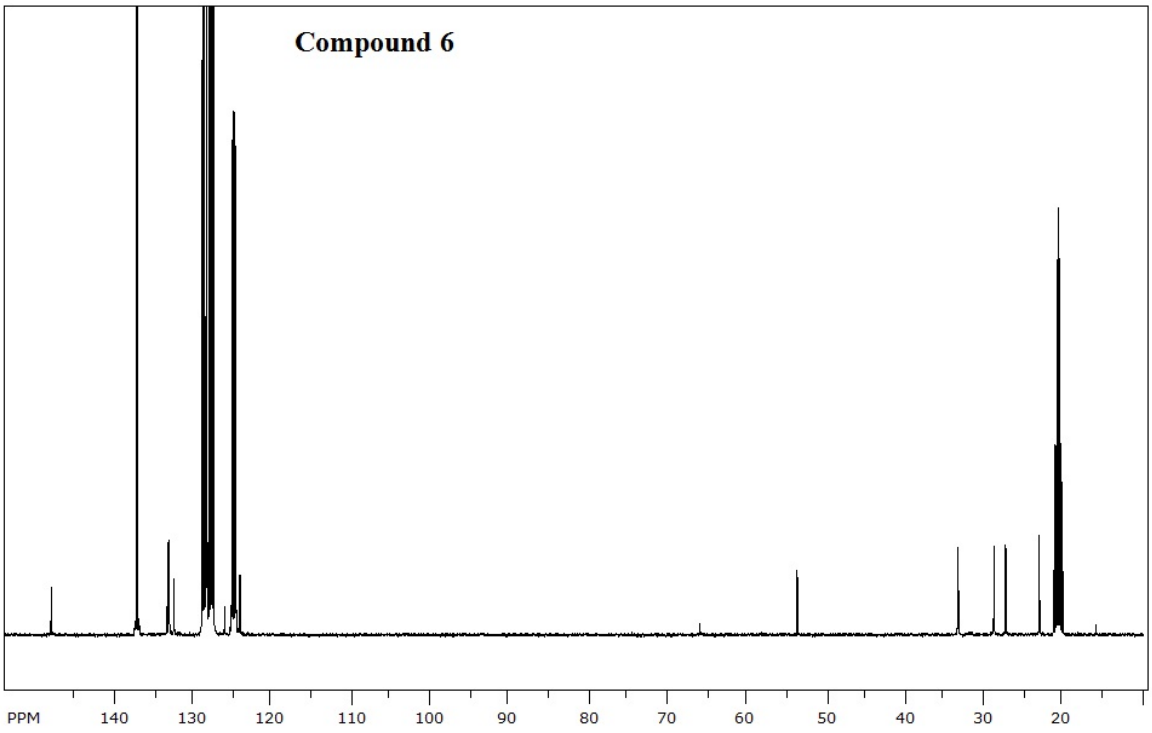

Fig. S16 ^{13}C NMR (100 MHz, toluene-d_8, –35 °C) spectrum of [(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)]GaCl$_2$ **(6)**.

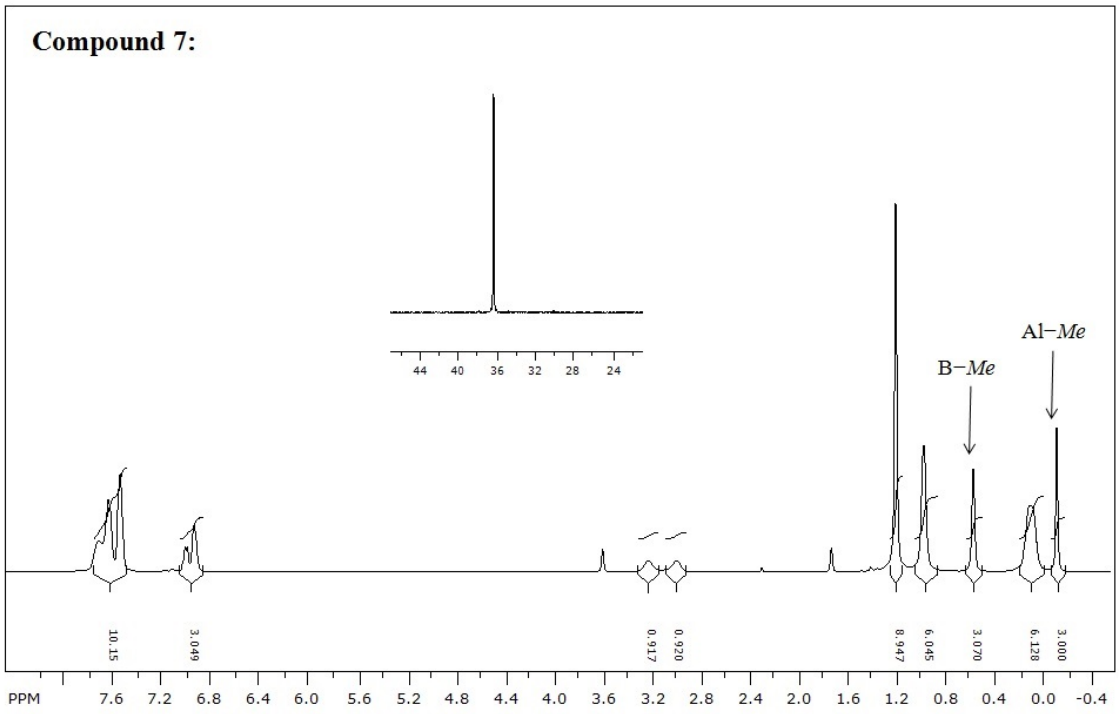

Fig. S17 ^{1}H NMR (400 MHz, THF-d_8, –35 °C) spectrum of [{(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)}AlMe]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ **(7)**. Inset shows the ^{31}P{^{1}H} (162 MHz, THF-d_8, –35 °C) spectrum.

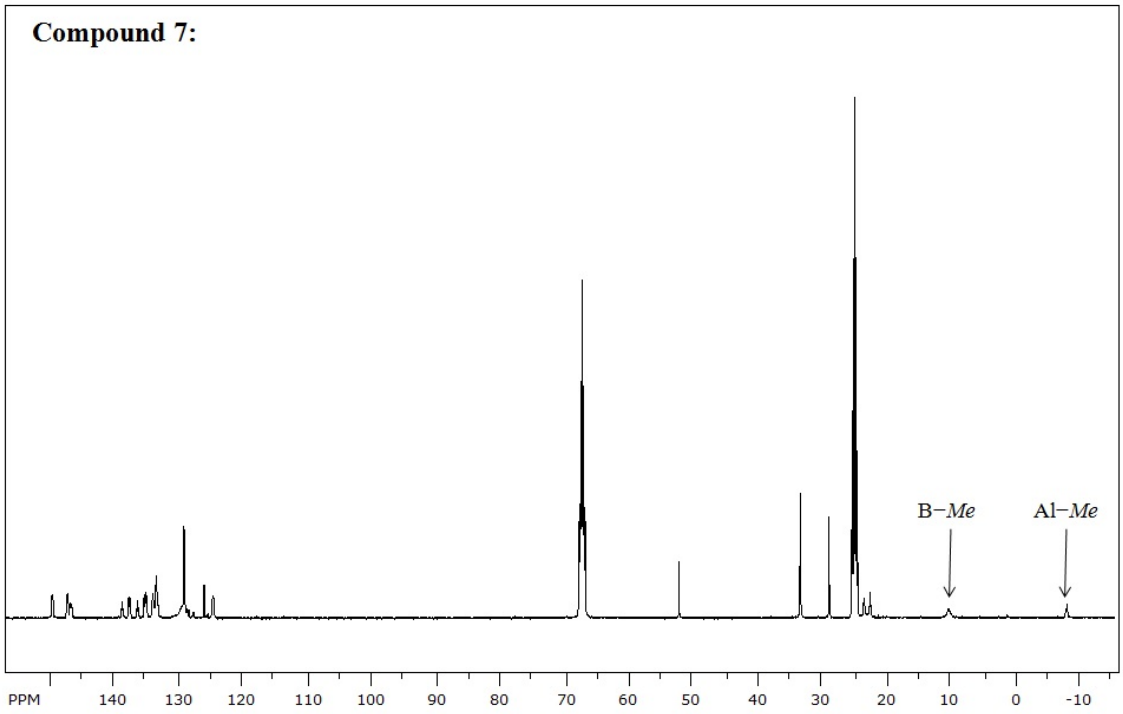

Fig. S18 ^{13}C NMR (100 MHz, THF-d_8, –35 °C) spectrum of [{(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)}AlMe]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ **(7)**.

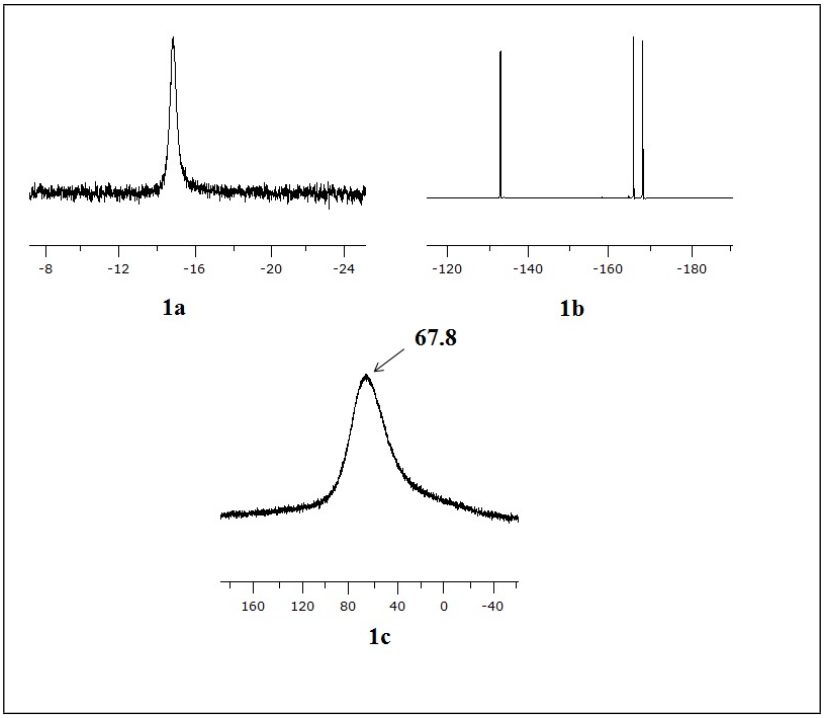

Fig. S19 ^{11}B (128 MHz, THF-d_8, –35 °C), ^{19}F (376 MHz, THF-d_8, –35 °C), and ^{27}Al NMR (104 MHz, THF-d_8, –35 °C) spectrum of [{(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)}AlMe]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ **(7)** is shown in figure **1a**, **1b** and **1c**, respectively.

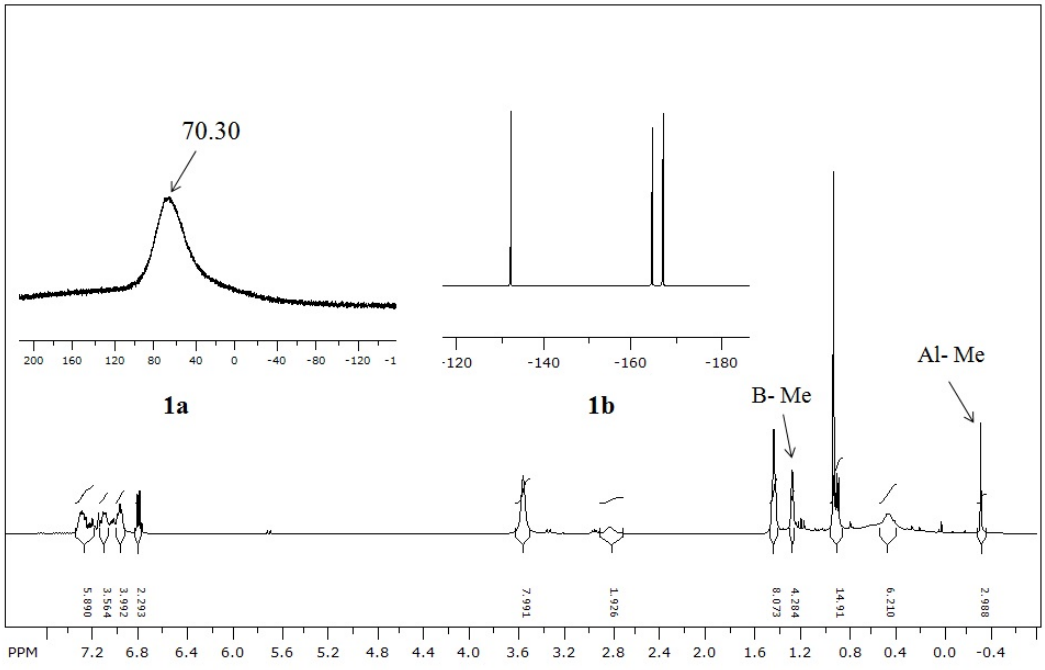

Fig. S20 This sample was prepared in THF at room temperature and NMR recorded in C_6D_6 at room temperature. ^1H NMR (400 MHz, C_6D_6) spectrum of [{(2,6-*i*Pr$_2$C$_6$H$_3$N)P(Ph$_2$)(N*t*Bu)}AlMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ **(7)**. Inset **1a** shows ^{27}Al NMR (104 MHz, C_6D_6) and **1b** shows the ^{19}F NMR (376 MHz, C_6D_6) spectrum.

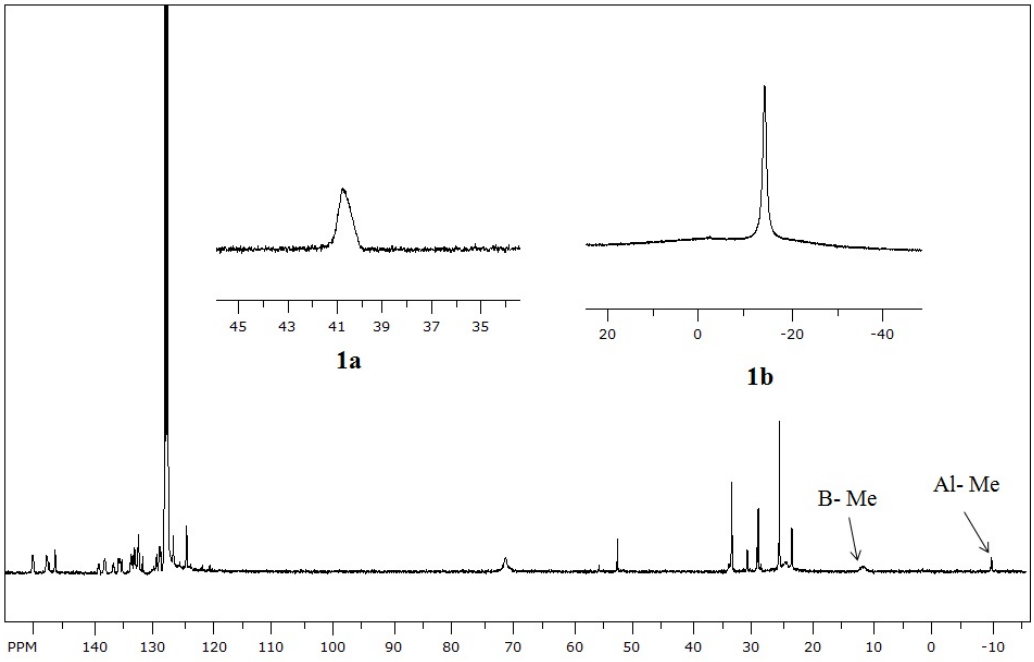

Fig. S21 This sample was prepared in THF at room temperature and NMR recorded in C_6D_6 at room temperature. ^{13}C NMR (100 MHz, C_6D_6) spectrum of [{(2,6-*i*$Pr_2C_6H_3N$)P(Ph_2)(N*t*Bu)}AlMe]$^+$[MeB(C_6F_5)$_3$]$^-$ **(7)**. Inset **1a** shows $^{31}P\{^1H\}$ (162 MHz, C_6D_6) NMR and **1b** shows the ^{11}B (128 MHz, C_6D_6) NMR spectrum.

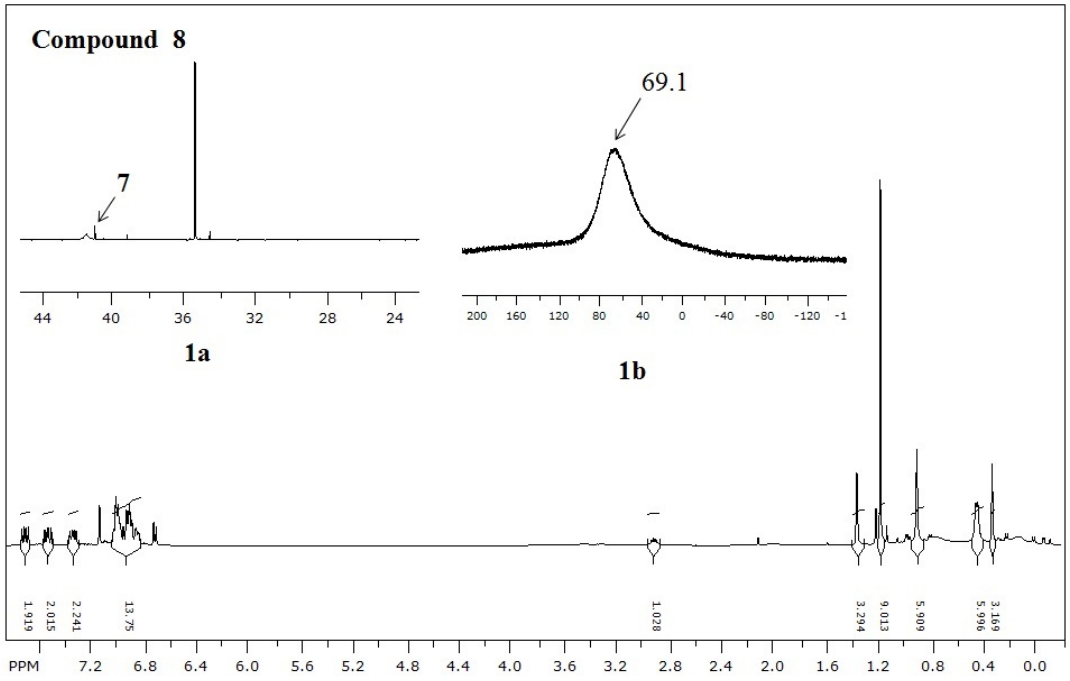

Fig. S22 Room temperature *in-situ* ^1H NMR (400 MHz, C_6D_6) spectrum of [(2,6-*i*$Pr_2C_6H_3N$)P(Ph_2)(N*t*Bu)]AlMe(C_6F_5) **(8)** recorded after 2 days of sample preparation. Inset **1a** shows the $^{31}P\{^1H\}$ (162 MHz, C_6D_6) spectrum and the ^{27}Al NMR (104 MHz, C_6D_6) spectrum is shown in inset **1b**.

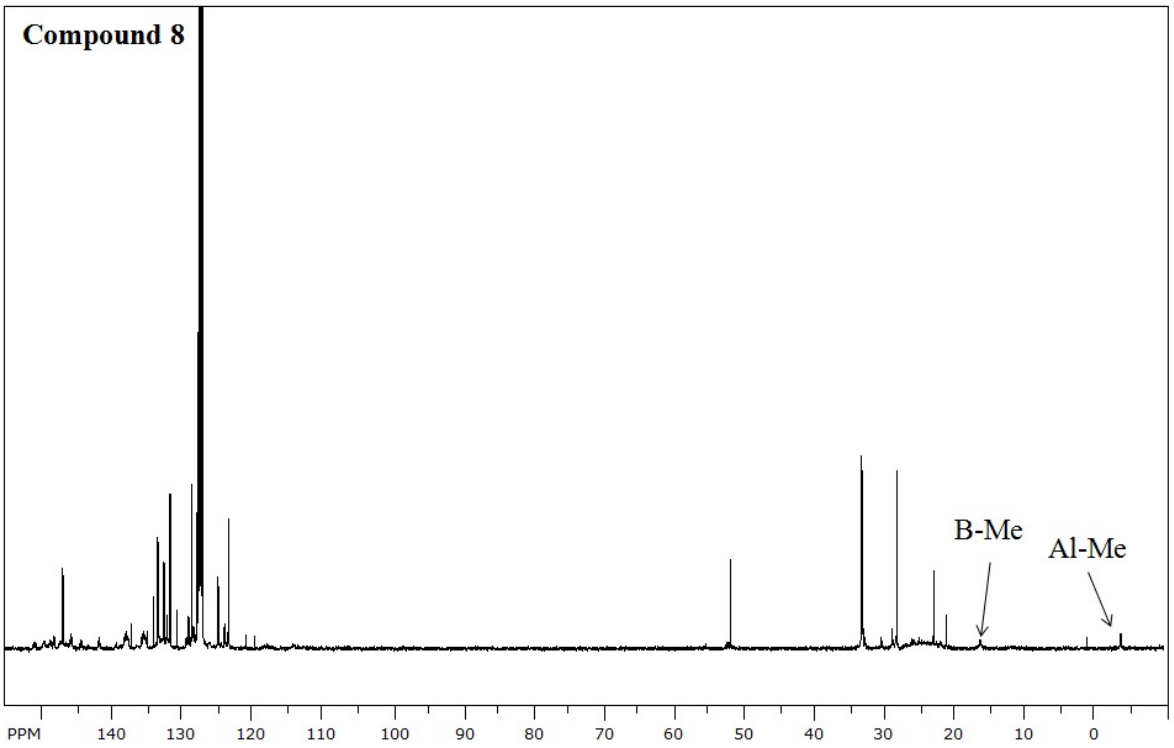

Fig. S23 Room temperature *in-situ* ^{13}C NMR (100 MHz, C_6D_6) spectrum of [(2,6-*i*$Pr_2C_6H_3N$)P(Ph_2)(N*t*Bu)]AlMe(C_6F_5) **(8)** recorded after 2 days of sample preparation.

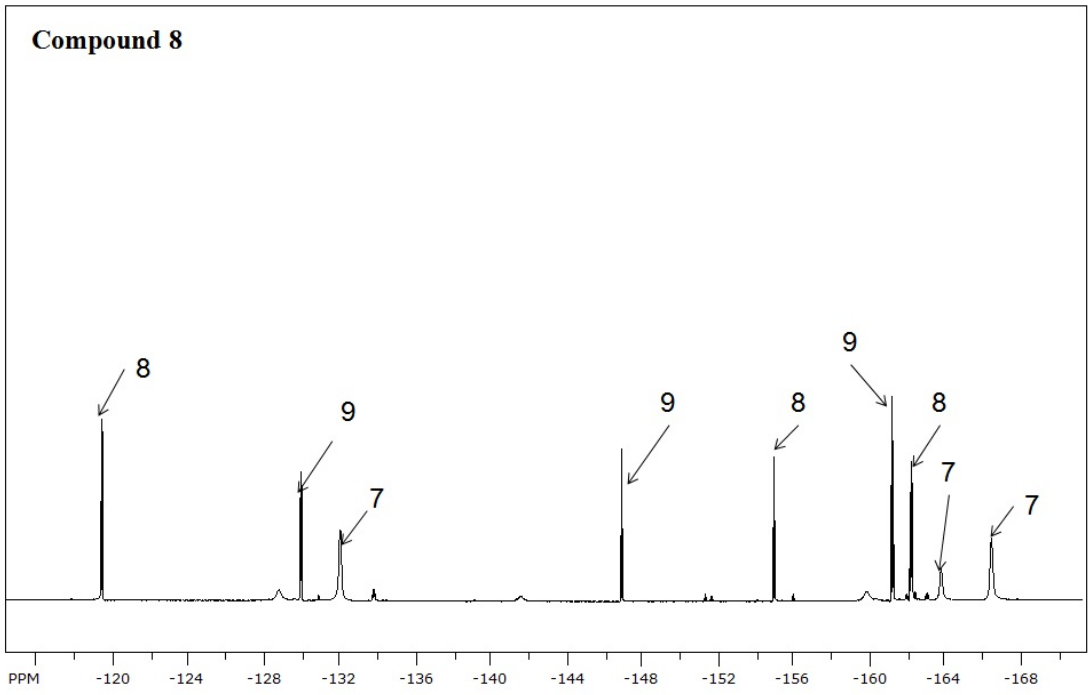

Fig. S24 Room temperature *in-situ* ^{19}F NMR (376 MHz, C_6D_6) spectrum of [(2,6-*i*$Pr_2C_6H_3N$)P(Ph_2)(N*t*Bu)]AlMe(C_6F_5) **(8)** recorded after 2 days of sample preparation. Compound **9** is $MeB(C_6F_5)_2$.

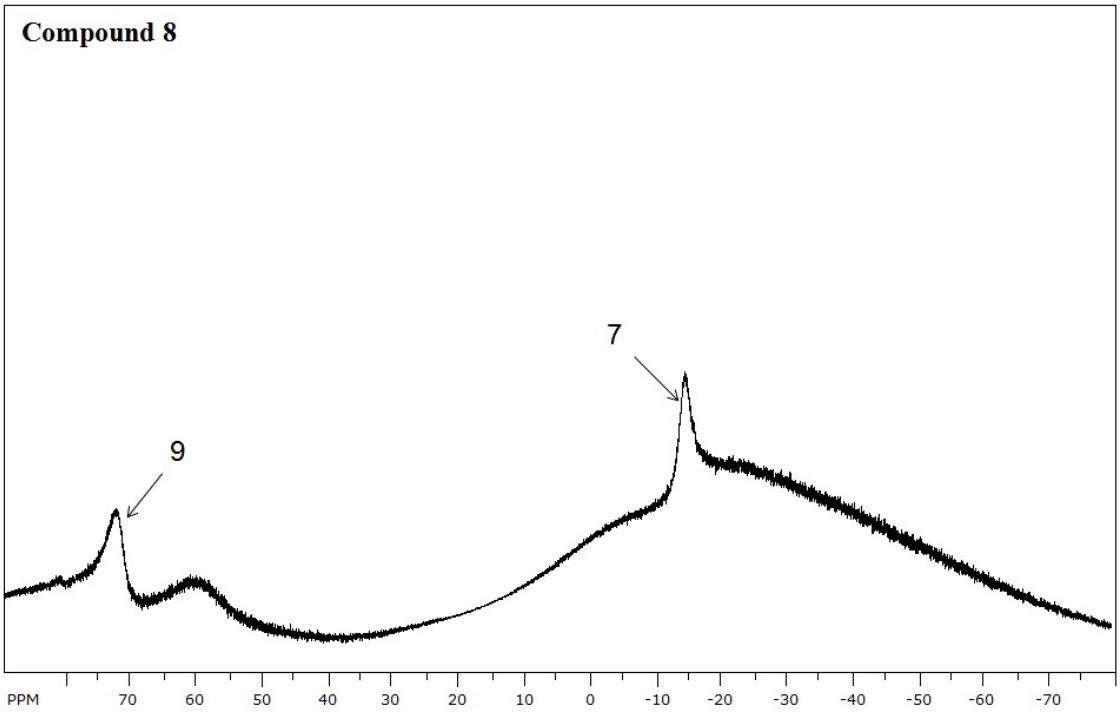

Fig. S25 Room temperature *in-situ* ^{11}B NMR (128 MHz, C_6D_6) spectrum of [(2,6-*i*$Pr_2C_6H_3N$)$P(Ph_2)$(N*t*Bu)]$AlMe(C_6F_5)$ **(8)** recorded after 2 days of sample preparation. Compound **9** is $MeB(C_6F_5)_2$.