Electronic Supplementary Material (ESI) for Dalton Transactions.

Insertion of ^{t}BuNC into Thorium-Phosphorus and Thorium-Arsenic Bonds: Phosphaazaallene and Arsaazaallene Moieties in *f* Element Chemistry

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Supporting Information

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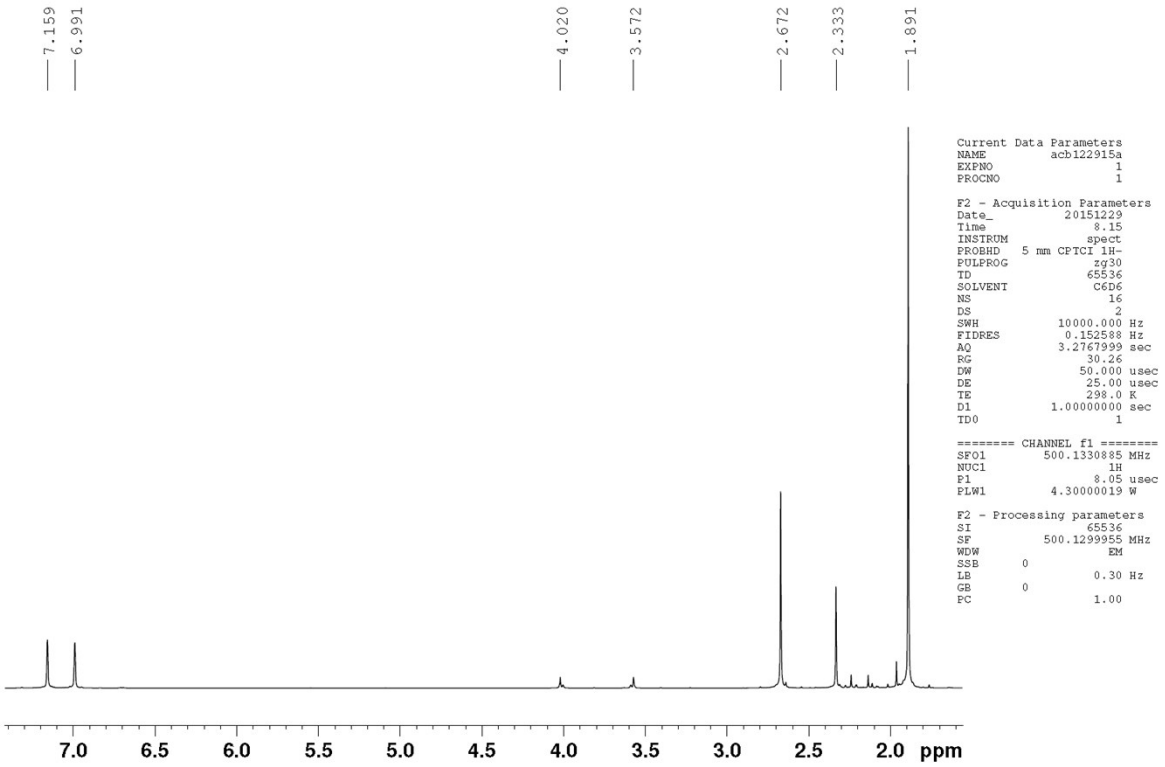

Figure S1. ^{1}H NMR spectrum (C_6D_6) of $(C_5Me_5)_2Th[P(H)Mes]_2$, **1** (Mes = 2,4,6−$Me_3C_6H_2$).

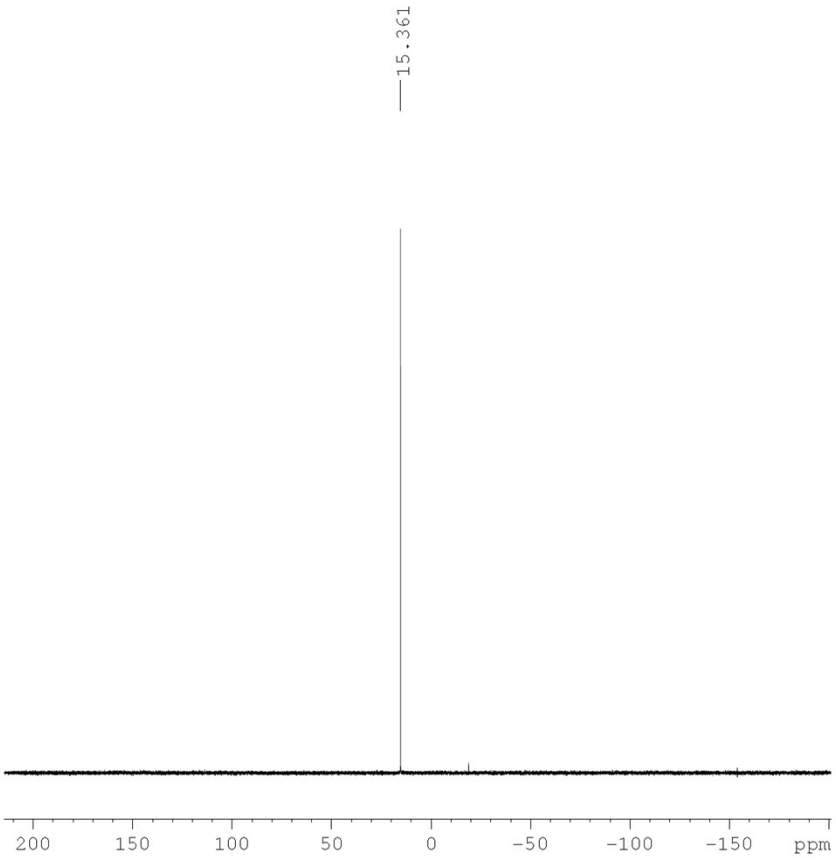


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Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6) of $(C_5Me_5)_2Th[P(H)Mes]_2$, **1.**

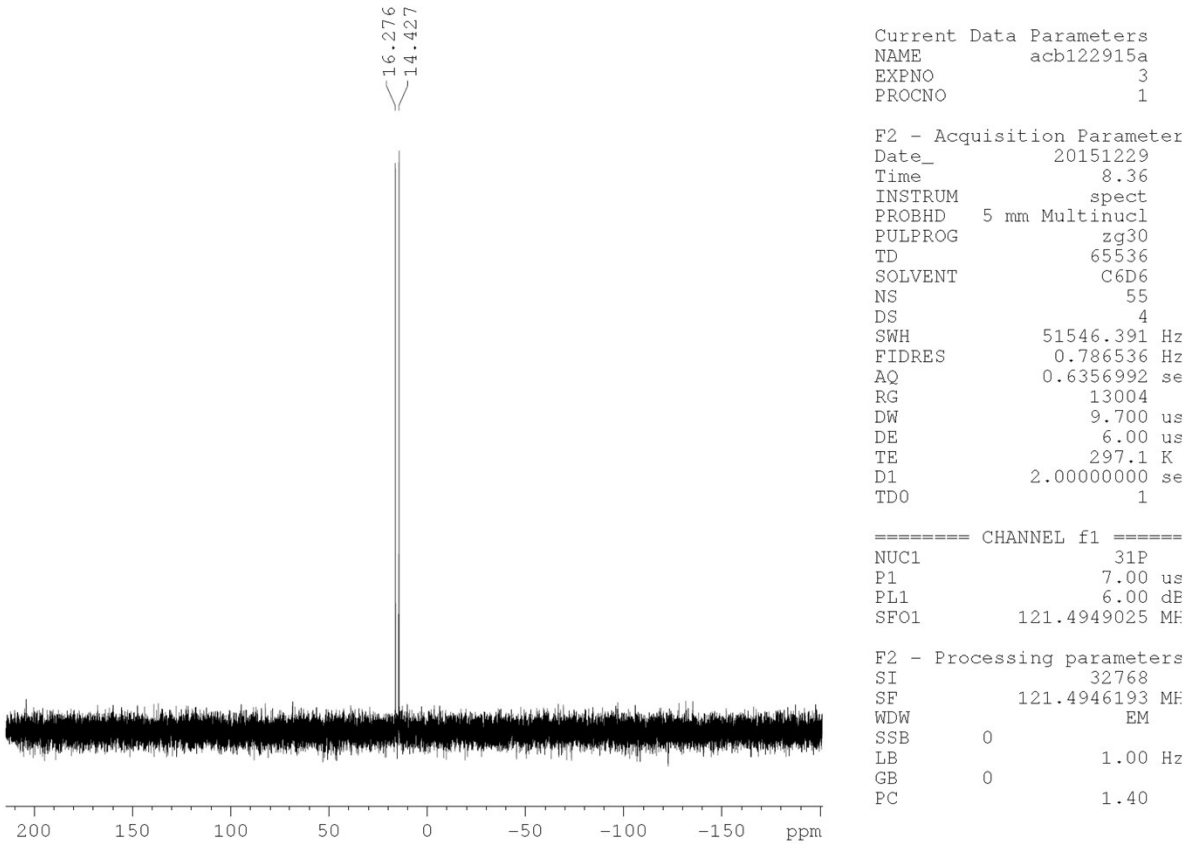


Figure S3. ^{31}P NMR spectrum (C_6D_6) of $(C_5Me_5)_2Th[P(H)Mes]_2$, **1.**

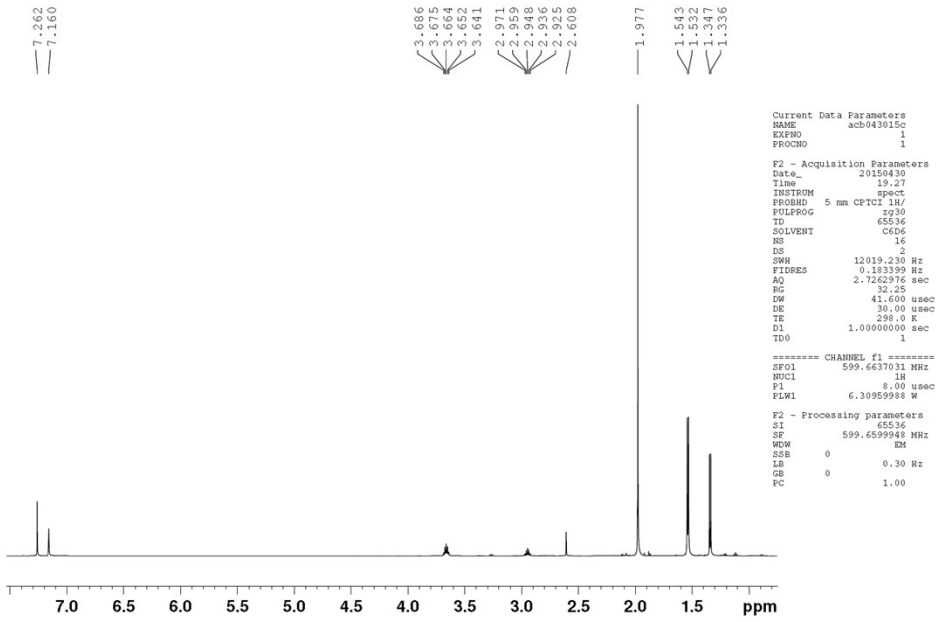


Figure S4. ^{1}H NMR spectrum (C_6D_6) of $(C_5Me_5)_2Th[As(H)Tipp]_2$, **2**, (Tipp = 2,4,6−$^{i}Pr_3C_6H_2$)**.**

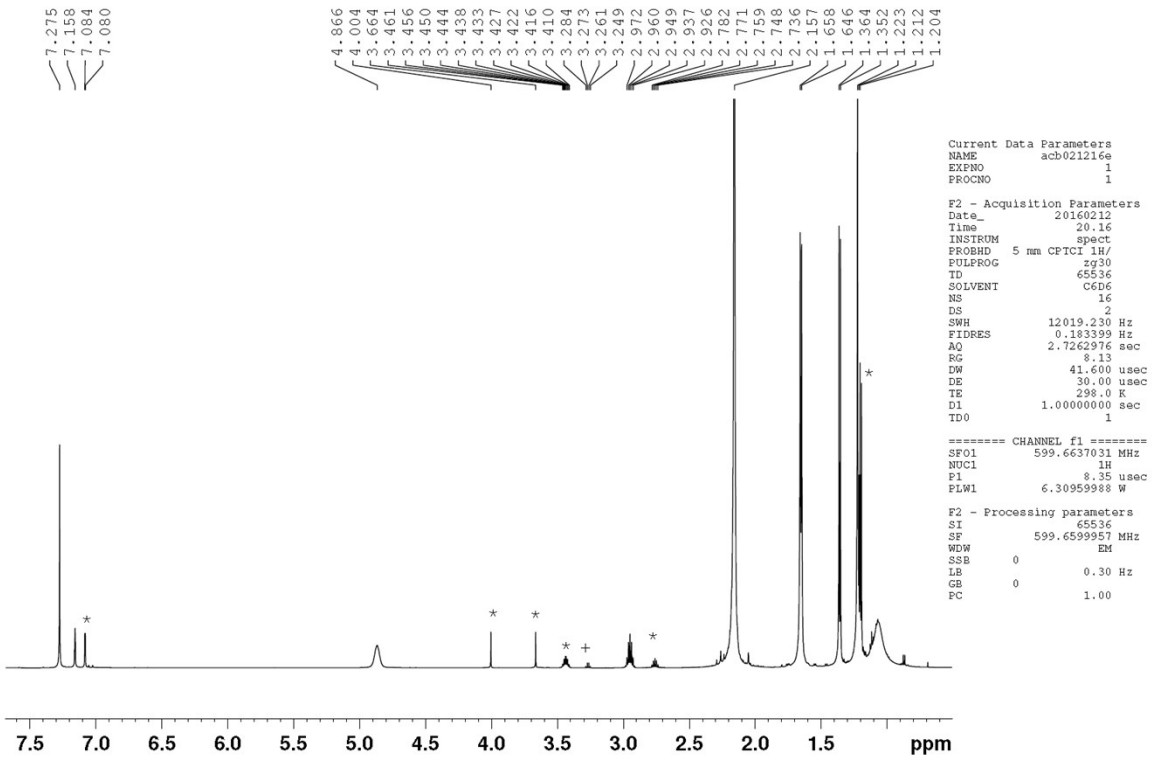
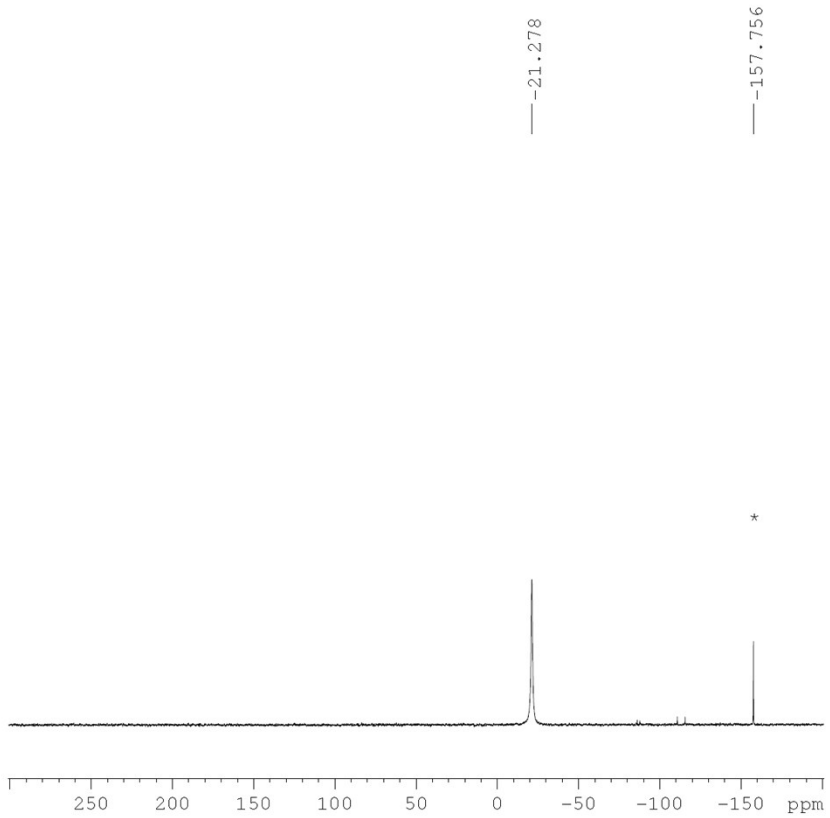


Figure S5. ^{1}H NMR spectrum (C_6D_6) of $(C_5Me_5)_2Th(CN^tBu)(\eta^2\text{-}(N,C)\text{-}(^t\text{BuNCPTipp})$, **3**. (*) represents presence of H_2PTipp; (+) represents presence of diethyl ether.

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F2 - Processing parameters
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Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6) of $(C_5Me_5)_2Th(CN^tBu)(\eta^2\text{-}(N,C)\text{-}(^t\text{BuNCPTipp})$, **3.** (*) represents presence of H_2PTipp.

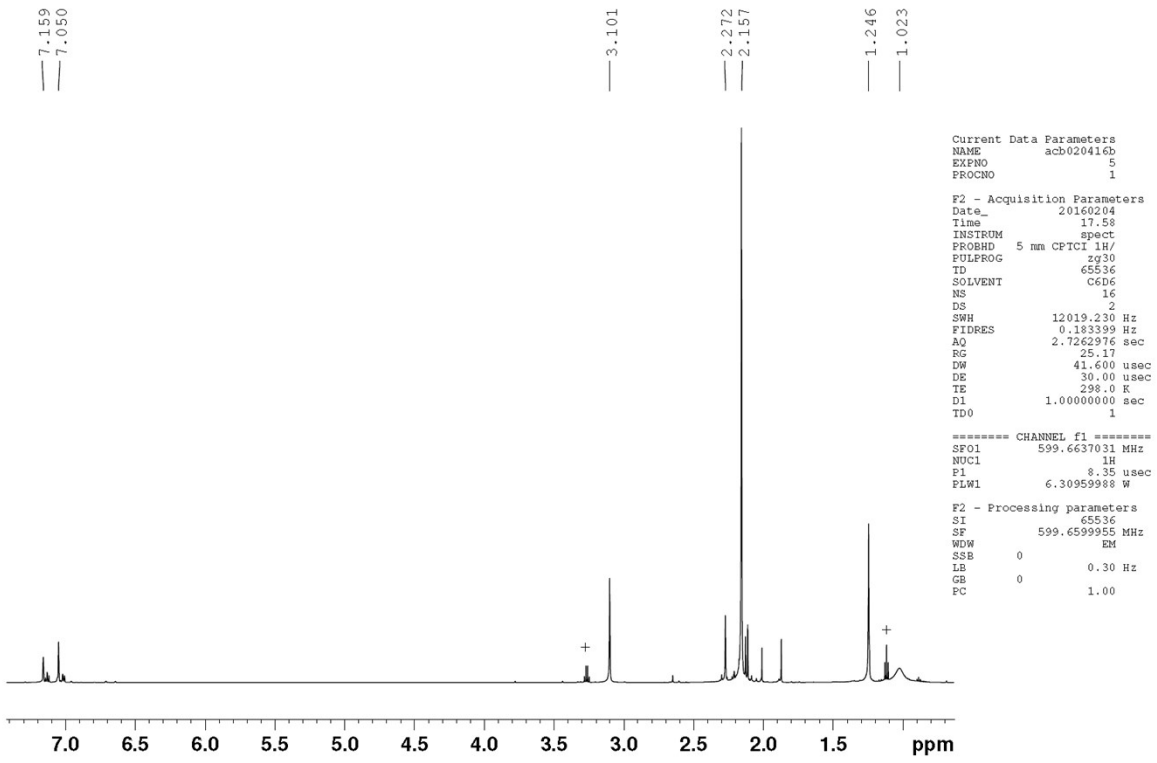

Figure S7. ^{1}H NMR spectrum (C_6D_6) of $(C_5Me_5)_2Th(CN^tBu)(\eta^2\text{-}(N,C)\text{-}(^t\text{BuNCPMes})$, **4.** (+) represents presence of diethyl ether.

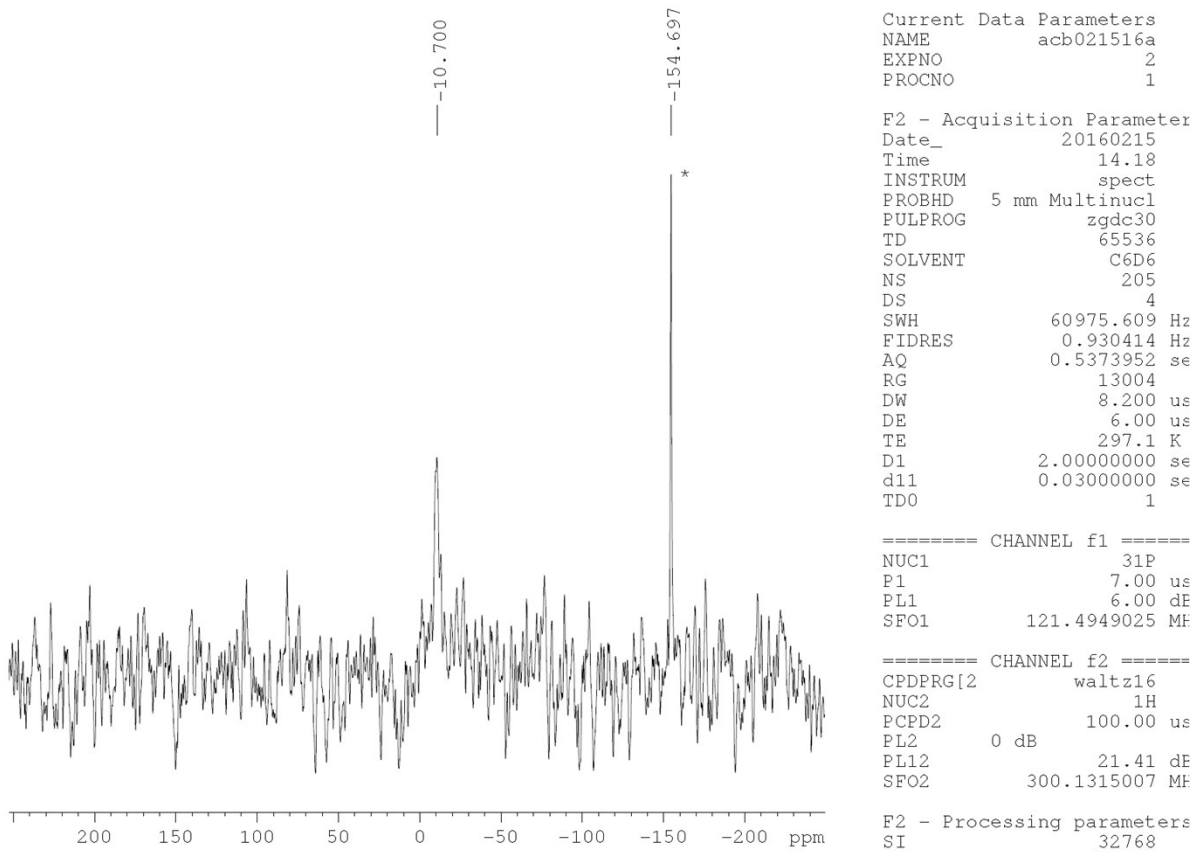

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6) of $(C_5Me_5)_2Th(CN^tBu)(\eta^2\text{-}(N,C)\text{-}(^t\text{BuNCPMes})$, **4.** (*****) represents presence of H_2PMes.

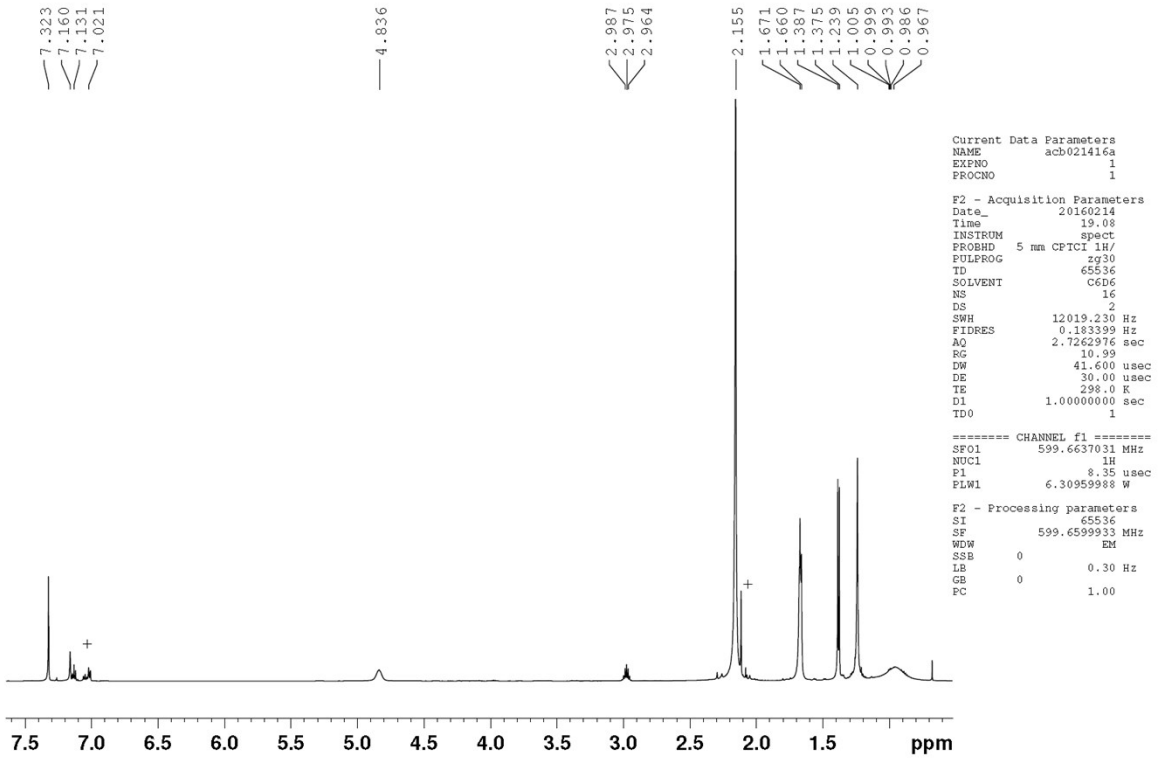

Figure S9. ^{1}H NMR spectrum (C_6D_6) of $(C_5Me_5)_2Th(CN^tBu)(\eta^2\text{-}(N,C)\text{-}(^t\text{BuNCAsTipp})$, **5.** **(+)** represents presence of toluene.

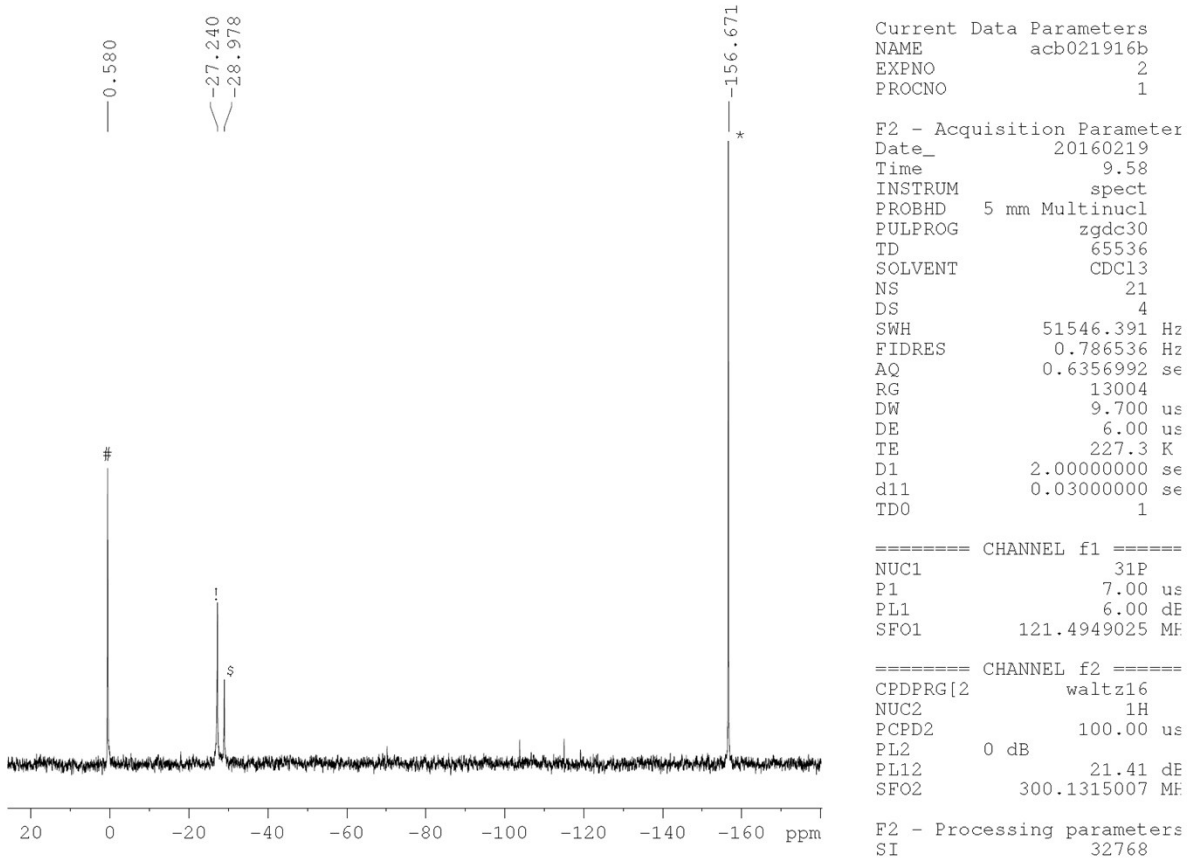

Figure S10. −80 °C $^{31}P\{^{1}H\}$ NMR spectrum (C_7D_8) of $(C_5Me_5)_2Th[P(H)Tipp]_2$ and two equivalents of ^{t}BuNC. (#) represents $(C_5Me_5)_2Th[P(H)Tipp]_2$; (!) represents unidentified intermediate; ($) represents 1,1−insertion product (**3**); (*) represents H_2PTipp.

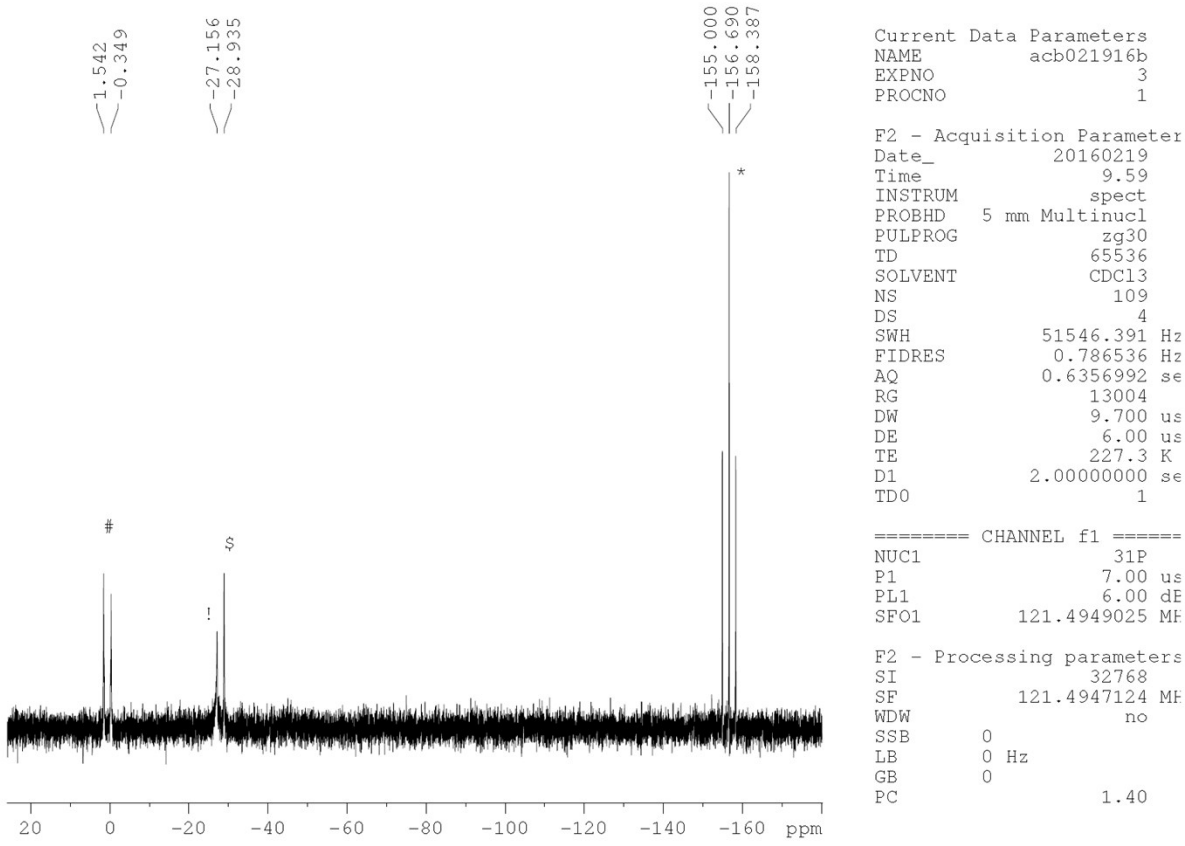

Figure S11. −80 °C ^{31}P NMR spectrum (C_7D_8) of $(C_5Me_5)_2Th[P(H)Tipp]_2$ and two equivalents of ^{t}BuNC. (#) represents $(C_5Me_5)_2Th[P(H)Tipp]_2$; (!) represents unidentified intermediate; ($) represents 1,1−insertion product (**3**); (*) represents H_2PTipp.

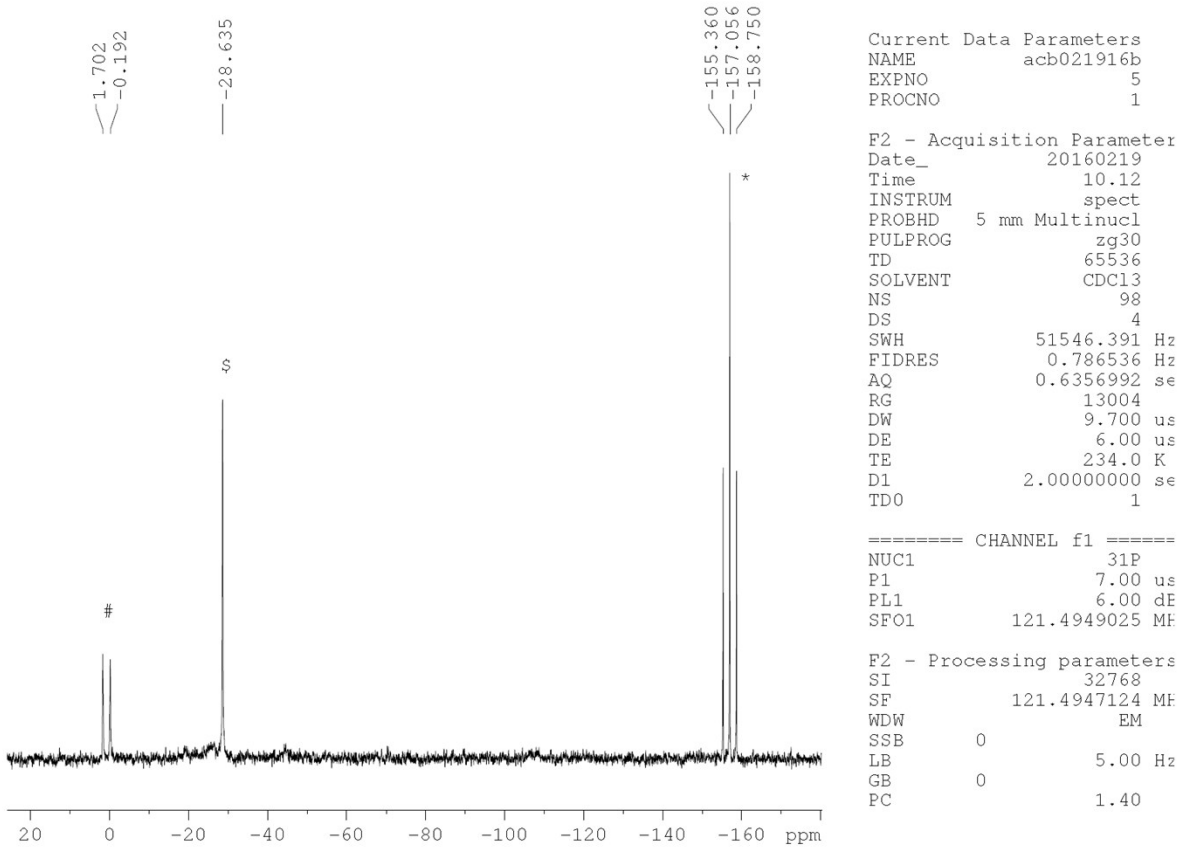

Figure S12. −70 °C ^{31}P NMR spectrum (C_7D_8) of $(C_5Me_5)_2Th[P(H)Tipp]_2$ and two equivalents of ^{t}BuNC. (#) represents $(C_5Me_5)_2Th[P(H)Tipp]_2$; ($) represents 1,1−insertion product (**3**); (*) represents H_2PTipp.

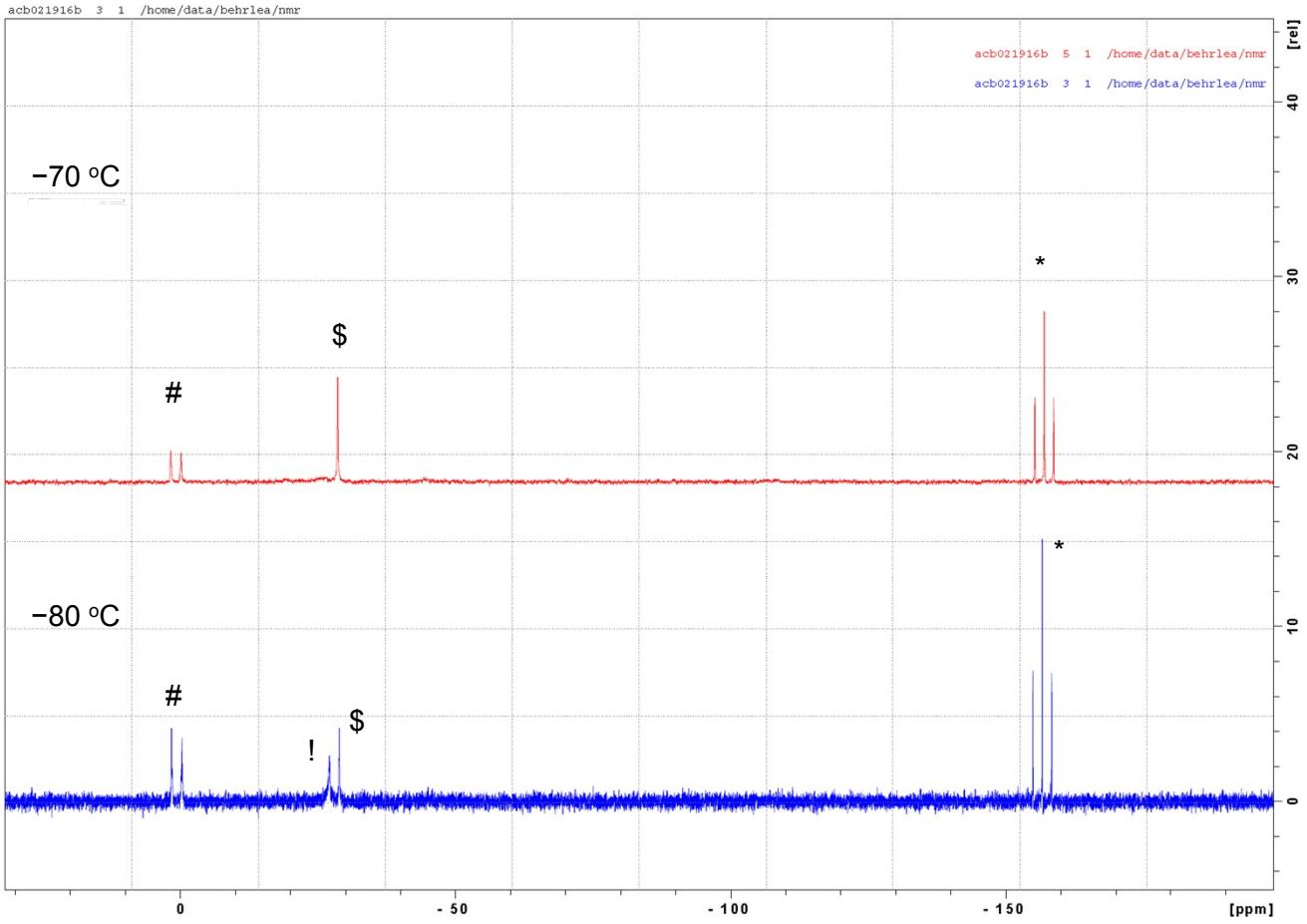

Figure S13. Stacked VT ^{31}P NMR spectra (C_7D_8) of $(C_5Me_5)_2Th[P(H)Tipp]_2$ and two equivalents of ^{t}BuNC. Bottom spectrum is −80 °C displaying unidentified intermediate resonance at −27.16 ppm (!). (#) represents $(C_5Me_5)_2Th[P(H)Tipp]_2$; ($) represents 1,1−insertion product (**3**); (*) represents H_2PTipp.