Supporting Information

A route to asymmetrically substituted secondary phosphines

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1. Experimental Details:

1.1 General remarks:

All experiments were performed under an atmosphere of dry argon using standard glovebox and Schlenk techniques. All glassware were dried with a heat gun at 630 °C for 15 min prior to use. THF-d_8 was distilled from NaK, 2,5,8,11,14-pentaoxapentadecane (tetraglyme) was dried and deoxygenated by distillation under argon atmosphere from calcium hydride. All other solvents were taken from a solvent purification system of the type MB-SPS-800 from the company MBRAUN (Garching, Germany), degassed at room temperature, and stored over molecular sieves. ^{1}H, ^{13}C{^{1}H} and ^{31}P NMR spectra were recorded at room temperature on a Bruker Avance400 spectrometer (Brucker Instruments, Ettlingen, Germany) (^{1}H: 400.130 MHz, ^{13}C: 100.613 MHz, ^{31}P: 161.976 MHz). Chemical shifts (δ) are reported in parts per million (ppm) relative to the external standard $(CH_3)_4Si$ (^{1}H, ^{13}C) or 85% phosphoric acid (^{31}P), respectively and coupling constants (*J*) are provided in Hertz (Hz). Signal multiplicities are described using common abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet) and br (broad). Mass spectra were recorded on a Jeol AccuTOF GCX at the mass spectrometry department of the central analytic services of the university of Regensburg. The compounds [Cp*Fe(η^5-P_5)],[1] [Cp*Fe(η^4-P_5Me_2)],[2] [Cp*Fe(η^4-P_5Me*i*Pr)],[2] [Cp*Fe(η^4-P_5*t*BuMe)],[2] and [Cp*Fe(η^4-P_5PhMe)][2] were prepared according to literature procedures. $LiAlH_4$ was purified by extraction with Et_2O and filtration over diatomaceous earth.

1.2 Synthesis and characterization of *tert*-butylmethylphosphine (2a, $C_5H_{13}P$):

Method A:

A mixture of [Cp*Fe(η^4-P_5*t*BuMe)] (**1a**, 125 mg, 0.30 mmol, 1 eq) and $LiAlH_4$ (14 mg, 0.36 mmol, 1.2 eq) was dissolved in THF-d_8 (2 mL) and stirred at room temperature overnight. The reaction vessel was connected to a second Schlenk flask via a condensation bridge. The solvent and the formed *tert*-butylmethylphosphine (**2a**) were distilled off under reduced pressure ($1\cdot10^{-3}$ mbar, 95°C, 30 min). The receiving flask was cooled in liquid nitrogen to collect the condensate.

Yield:	0.223 mmol, 71% (according to ^{31}P NMR via internal standard of PPh_3 (13.4 mg, 0.05 mmol)).
^{1}H NMR (THF-d_8):	*δ* [ppm] = 2.95 (dq, 1H, P<u>H</u>, $^{1}J_{P\text{-}H}$ = 191.9 Hz, $^{3}J_{H\text{-}H}$ = 7.7 Hz), 1.12 (d, 9H, C(C<u>H</u>$_3$)$_3$, $^{3}J_{P\text{-}H}$ = 11.7 Hz), 1.03 (dd, 3H, C<u>H</u>$_3$, $^{3}J_{H\text{-}H}$ = 7.7 Hz, $^{2}J_{P\text{-}H}$ = 2.9 Hz).
^{13}C{^{1}H} NMR (THF-d_8):	*δ* [ppm] = 29.8 (d, <u>C</u>(CH$_3$)$_3$, $^{1}J_{P\text{-}C}$ = 13.0 Hz), 26.5 (d, C(<u>C</u>H$_3$)$_3$, $^{2}J_{P\text{-}C}$ = 6.7 Hz), 0.8 (d, <u>C</u>H$_3$, $^{1}J_{P\text{-}C}$ = 17.3 Hz).
^{31}P NMR (THF-d_8):	*δ* [ppm] = -39.5 (d, $^{1}J_{P\text{-}H}$ = 191.3 Hz).
^{31}P{^{1}H} NMR (THF-d_8):	*δ* [ppm] = -39.5 (s).

Method B:

[Cp*Fe(η⁴-P₅^{t}BuMe)] (**1a**, 209 mg, 0.50 mmol, 1 eq) and $LiAlH_4$ (23 mg, 0.60 mmol, 1.2 eq) were weighed into a Schlenk flask to which tetraglyme (4 mL) was added. The suspension was stirred at room temperature overnight resulting in a reddish-brown solution. The *tert*-butylmethylphosphine (**2a**) was distilled off under reduced pressure ($1 \cdot 10^{-3}$ mbar, 70°C, 45 min).

Yield:	0.31 mmol, 62%
^{1}H NMR (THF-d_8):	δ [ppm] = 3.02 (dq, 1H, PH, $^1J_{P\text{-}H}$ = 192.5 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz), 1.01 (d, 9H, C(CH$_3$)$_3$, $^3J_{P\text{-}H}$ = 11.8 Hz), 0.84 (dd, 3H, CH$_3$, $^3J_{H\text{-}H}$ = 7.5 Hz, $^2J_{P\text{-}H}$ = 3.4 Hz).
^{31}P NMR (THF-d_8):	δ [ppm] = -39.7 (d, $^1J_{P\text{-}H}$ = 192.8 Hz).
^{31}P{^{1}H} NMR (THF-d_8):	δ [ppm] = -39.7 (s).

Method C:

[Cp*Fe(η⁴-P₅^{t}BuMe)] (**1a**, 125 mg, 0.30 mmol, 1 eq), KH (14 mg, 0.36 mmol, 1.2 eq) were weighed into a Schlenk flask to which THF-d_8 (2 mL) was added. The mixture was stirred overnight at room temperature. The solvent and the formed *tert*-butylmethylphosphine (**2a**) were distilled off under reduced pressure ($1 \cdot 10^{-3}$ mbar, 85°C, 30 min).

Yield:	0.075 mmol, 25% (according to ^{31}P NMR via internal standard of PPh_3 (13.6 mg, 0.05 mmol)).
^{1}H NMR (THF-d_8):	δ [ppm] = 2.95 (dq, 1H, PH, $^1J_{P\text{-}H}$ = 191.5 Hz, $^3J_{H\text{-}H}$ = 7.7 Hz), 1.12 (d, 9H, C(CH$_3$)$_3$, $^3J_{P\text{-}H}$ = 11.9 Hz), 1.03 (dd, 3H, CH$_3$, $^3J_{H\text{-}H}$ = 7.7 Hz, $^2J_{P\text{-}H}$ = 3.3 Hz).
^{31}P NMR (THF-d_8):	δ [ppm] = -39.6 (d, $^1J_{P\text{-}H}$ = 191.2 Hz).
^{31}P{^{1}H} NMR (THF-d_8):	δ [ppm] = -39.6 (s).

Method D:

[Cp*Fe(η⁴-P₅^{t}BuMe)] (**1a**, 125 mg, 0.30 mmol, 1 eq), NaH (8.6 mg, 0.36 mmol, 1.2 eq) were weighed into a Schlenk flask to which THF-d_8 (2 mL) was added. The mixture was stirred for several days at room temperature. The solvent and the formed *tert*-butylmethylphosphine (**2a**) were distilled off under reduced pressure ($1 \cdot 10^{-3}$ mbar, 90°C, 30 min).

Yield:	0.038 mmol, 13% (according to ^{31}P NMR via internal standard of PPh_3 (13.6 mg, 0.05 mmol)).
^{1}H NMR (THF-d_8):	δ [ppm] = 2.95 (dq, 1H, PH, $^1J_{P\text{-}H}$ = 191.5 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz), 1.12 (d, 9H, C(CH$_3$)$_3$, $^3J_{P\text{-}H}$ = 11.8 Hz), 1.03 (dd, 3H, CH$_3$, $^3J_{H\text{-}H}$ = 7.6 Hz, $^2J_{P\text{-}H}$ = 3.4

Hz).

^{31}P NMR (THF-d_8): δ [ppm] = -39.6 (d, $^1J_{P-H}$ = 192.0 Hz).

^{31}P{^{1}H} NMR (THF-d_8): δ [ppm] = -39.6 (s).

Method E:

To a solution of [Cp*Fe(η^4-P_5*t*BuMe)] (**1a**, 125 mg, 0.30 mmol, 1 eq) in THF (2 mL), a solution of [Li][$HBEt_3$] in THF (V = 0.36 mL, c = 1 M, n = 0.36 mmol, 1.2 eq) was added and stirred overnight at room temperature. The performed $^{31}P\{^1H\}$ NMR of the reaction in THF with tol-d_8 capillary in the presence of PPh_3 (c = 0.2 mol/L) as internal standard showed a conversion to about 1% *tert*-butylmethylphosphine (**2a**) with most of the starting material [Cp*Fe(η^4-P_5*t*BuMe)] unreacted.

^{31}P{^{1}H} NMR (THF-d_8): δ [ppm] = -39.0 (s).

Method F:

To a solution of [Cp*Fe(η^4-P_5*t*BuMe)] (**1a**, 125 mg, 0.30 mmol, 1 eq) in THF (2 mL), a solution of [Li][$HBEt_3$] in THF (V = 0.36 mL, c = 1 M, n = 0.36 mmol, 1.2 eq) was added and stirred overnight at room temperature. The performed $^{31}P\{^1H\}$ NMR of the reaction in THF with tol-d_8 capillary in the presence of PPh_3 (c = 0.2 mol/L) as internal standard showed a conversion to about 1% *tert*-butylmethylphosphine (**2a**) with most of the starting material [Cp*Fe(η^4-P_5*t*BuMe)] unreacted.

^{31}P{^{1}H} NMR (Tol-d_8): δ [ppm] = -39.0 (s).

Method G: A suspension of $NaBH_4$ (13.6 mg, 0.36 mmol, 1.2 eq) in THF-d_8 (1 mL) was added to a solution of [Cp*Fe(η^4-P_5*t*BuMe)] (**1a**, 125 mg, 0.30 mmol, 1 eq) in THF-d_8 (1 mL) and stirred overnight at room temperature. However, no reaction was detected by NMR spectroscopic methods.

1.3 Synthesis and characterization of isopropylmethylphosphine (2b, $C_4H_{11}P$):

2-Iodopropane (0.05 mL, 0.5 mmol, 1 eq) was added to a solution of [$Li(DME)_3$][Cp*Fe(η^4-P_5Me)] (319 mg, 0.5 mmol, 1 eq) in DME and stirred for 30 min. All volatiles were removed in vacuo and the residue was extracted with *n*-hexane (3 x 5 mL) and filtrated over diatomaceous earth. The filtrate was dried in vacuo to give [Cp*Fe(η^4-P_5Me*i*Pr)] (**1b**) as a brown oil. $LiAlH_4$ (13.7 mg, 0.36 mmol, 0.72 eq) in THF-d_8 (2 mL) was added, and the mixture was stirred overnight at room temperature. The formed isopropylmethylphosphine (**2b**) and the solvent were distilled off under reduced pressure ($1 \cdot 10^{-3}$ mbar, 90°C, 30 min).

Yield: 0.33 mmol, 66% (according to ^{31}P NMR via internal standard of PPh_3 (15.0mg, 0.06 mmol)).

^{1}H NMR (THF-d_8): δ [ppm] = 2.99 (m, 1H, P<u>H</u>), 1.83 (m, 1H, C<u>H</u>(CH_3)$_2$), 1.10 (d, 4H, CH(C<u>H</u>$_3$)$_2$, $^{3}J_{H-H}$ = 7.0 Hz)$^{\#}$, 1.05 (dd, 4H, C<u>H</u>$_3$, $^{3}J_{H-H}$ = 7.6 Hz, $^{2}J_{P-H}$ = 3.1 Hz)$^{\#}$.

^{13}C{^{1}H} NMR (THF-d_8): δ [ppm] = 26.5 (s, <u>C</u>H(CH_3)$_2$, $^{1}J_{P-C}$ = 13.0 Hz), 20.8 (d, CH(<u>C</u>H$_3$)$_2$, $^{2}J_{P-C}$ = 9.3 Hz), 1.0 (d, <u>C</u>H$_3$, $^{1}J_{P-C}$ = 14.8 Hz).

^{31}P NMR (THF-d_8): δ [ppm] = -58.8 (d, $^{1}J_{P-H}$ = 191.3 Hz).

^{31}P{^{1}H} NMR (THF-d_8): δ [ppm] = -58.8 (s).

#: overlap of product-signal and signals for ^{i}PrPH_2 and MePH_2 causes wrong integrals.

1.4 Synthesis and characterization of methylphenylphosphine (2c, C_7H_9P):

To a Schlenk flask [Cp*Fe(η^4-P_5PhMe)] (**1c**, 131 mg, 0.3 mmol, 1 eq), $LiAlH_4$ (13.7 mg, 0.36 mmol, 1.2 eq) and THF-d_8 (2 mL) were added. Upon stirring overnight at room temperature, the greenish brown suspension turned brown. The formed methylphenylphosphine (**2c**) and THF-d_8 were distilled off under reduced pressure ($1\cdot10^{-3}$ mbar, 95°C, 30 min).

Yield: 0.134 mmol, 45% (according to ^{31}P NMR via internal standard of PPh_3 (14.3 mg, 0.05 mmol)).

^{1}H NMR (THF-d_8): δ [ppm] = 7.48 (m, 2H, C_6<u>H</u>$_5$), 7.27 (m, 3H, C_6<u>H</u>$_5$), 4.14 (dq, 1H, P<u>H</u>, $^{1}J_{P-H}$ = 203.4 Hz, $^{3}J_{H-H}$ = 7.7 Hz), 1.36 (dd, 3H, C<u>H</u>$_3$, $^{3}J_{H-H}$ = 7.7 Hz, $^{2}J_{P-H}$ = 3.4 Hz).

^{13}C{^{1}H} NMR (THF-d_8): δ [ppm] = 132.5 (d, <u>C</u>$_6$H$_5$, $^{1}J_{P-C}$ = 16.3 Hz), 128.2 (d, <u>C</u>$_6$H$_5$, $^{1}J_{P-C}$ = 5.8 Hz), 127.7 (s, <u>C</u>$_6$H$_5$) 5.3 (d, <u>C</u>H$_3$, $^{1}J_{P-C}$ = 12.7 Hz).

^{31}P NMR (THF-d_8): δ [ppm] = -70.1 (d, $^{1}J_{P-H}$ = 203.8 Hz).

^{31}P{^{1}H} NMR (THF-d_8): δ [ppm] = -70.1 (s).

1.5 Synthesis and characterization of dimethylphosphine (2d, C_2H_7P):

In a Schlenk flask, [Cp*Fe(η^4-P_5Me_2)] (**1d**, 82 mg, 0.21 mmol, 1 eq) and $LiAlH_4$ (9.5 mg, 0.25 mmol, 1.2 eq) were dissolved in THF-d_8 (2 mL). The solution was stirred at room temperature overnight, resulting in a color change from greenish brown to reddish brown. The formed dimethylphosphine (**2d**) and the solvent were distilled off under reduced pressure ($1\cdot10^{-3}$ mbar, 90°C, 30 min).

Yield: 0.147 mmol, 70% (according to ^{31}P NMR via internal standard of PPh_3 (13.2 mg, 0.05 mmol)).

^{1}H NMR (THF-d_8): δ [ppm] = 3.10 (dsept, 1H, P<u>H</u>, $^{1}J_{P-H}$ = 191.9 Hz, $^{3}J_{H-H}$ = 7.4 Hz), 1.10 (dd, 6H, C<u>H</u>$_3$, $^{3}J_{H-H}$ = 7.7 Hz, $^{2}J_{P-H}$ = 3.3 Hz).

^{13}C{^{1}H} NMR (THF-d_8): δ [ppm] = 5.6 (d, CH_3, $^{1}J_{P-C}$ = 11.0 Hz).

^{31}P NMR (THF-d_8): δ [ppm] = -98.3 (d, $^{1}J_{P-H}$ = 192.0 Hz).

$^{31}P\{^{1}H\}$ NMR ($THF\text{-}d_8$): δ [ppm] = -98.3 (s).

1.6 Synthesis and characterization of [Cp*Fe(η⁴-$P_5{}^tBuH$)] (5, $C_{14}H_{25}FeP_5$):

$[Li(THF)_4]$ [Cp*Fe(η⁴-$P_5{}^tBu$)] (**4**, 308 mg, 0.44 mmol, 1 eq) was dissolved in THF (10 mL) and cooled to -30°C. A solution of HCl in Et_2O (V = 1 mL, c = 0.525 M, n = 0.53 mmol, 1.2 eq) was added and the reaction mixture was further stirred at -30°C for 45 min before being allowed to reach room temperature. During the reaction, the color changed from reddish brown to brown. After then, the solvent was removed, and the brown residue was extracted with *n*-hexane (15 mL) and filtered over diatomaceous earth. Crystals of [Cp*Fe(η⁴-$P_5{}^tBuH$)] (**5**) suitable for single crystal X-ray structure analysis were obtained by storing a concentrated solution of **5** at -30°C.

Yield:	0.37 mmol, 84%
^{1}H NMR (C_6D_6):	δ [ppm] = 1.56 (s, 15H, $C_5(C\underline{H}_3)_5$), 6.78 (dt, 1H, $^{1}J_{P\text{-}H}$ = 363.1 Hz, $2J_{P\text{-}H}$ = 32.3 Hz, P<u>H</u>), 0.13 (d, 9H, $C(C\underline{H}_3)_3$, $^{3}J_{P\text{-}H}$ = 15.6 Hz).
^{31}P NMR (C_6D_6):	δ [ppm] = 111.1 (m, 1P, P_A), 34.9 (m, 2P, $P_{M,M'}$), -122.6 (m, 2P, $P_{X,X'}$).
$^{31}P\{^{1}H\}$ NMR (C_6D_6):	δ [ppm] = 111.1 (m, 1P, P_A), 34.9 (m, 2P, $P_{M,M'}$), -122.6 (m, 2P, $P_{X,X'}$).
FD-MS (toluene):	404.0 100%, $[M]^+$)

1.7 Reactivity of [Cp*Fe(η⁴-$P_5{}^tBuH$)] (5) towards MeLi:

[Cp*Fe(η⁴-$P_5{}^tBuH$)] (83 mg, 0.2 mmol, 1 eq) was dissolved in THF (2 mL) and cooled to -80°C. A solution of MeLi in Et_2O (V = 0.34 mL, c = 0.597 M, n = 0.2 mmol, 1 eq) was added via syringe and stirred at -80°C for one hour. The color changed from brown to red brown. The ^{31}P NMR spectrum shows a quantitative formation of $[Li(THF)_4]$[Cp*Fe(η⁴-$P_5{}^tBu$)] (**4**).

$^{31}P\{^{1}H\}$ NMR (THF/C_6D_6-capillary): δ [ppm] = 105.6 (m, 1P, P_A), 20.3 (m, 2P, $P_{M,M'}$), -70.2 (m, 2P, $P_{X,X'}$).

^{31}P NMR (THF/C_6D_6-capillary): δ [ppm] = 105.6 (m, 1P, P_A), 20.3 (m, 2P, $P_{M,M'}$), -70.2 (m, 2P, $P_{X,X'}$).

1.8 Reactivity of [Cp*Fe(η⁴-P₅ᵗBuH)] (5) towards $LiAlH_4$:

THF-d_8 (2 mL) was added to a mixture of [Cp*Fe(η⁴-P₅ᵗBuH)] (121 mg, 0.3 mmol, 1 eq) and $LiAlH_4$ (14 mg, 0.36 mmol, 1.2 eq), which resulted in a rapid color change to red brown. After stirring overnight, the formed *tert*-butylphosphine ($C_4H_{11}P$) and THF-d_8 were distilled off under reduced pressure ($1 \cdot 10^{-3}$ mbar, 90°C, 30 min).

Yield: 0.003 mmol, 1% (according to ^{31}P NMR via internal standard of PPh_3 (13.2 mg, 0.05 mmol)).

^{1}H NMR (THF-d_8, 293 K): δ [ppm] = 2.84 (d, 2H, P$\underline{H}_2$, $^1J_{P\text{-}H}$ = 186.2 Hz), 1.23 (d, 9H, C(C$\underline{H}_3$)$_3$, $^3J_{P\text{-}H}$ = 11.9 Hz).

^{31}P{^{1}H} NMR (THF-d_8, 293 K): δ [ppm] = -80.7 (s).

^{31}P NMR (THF-d_8, 293 K): δ [ppm] = -80.7 (m).

2. Crystallographic data

Crystals suitable for single X-ray diffraction analysis were obtained as described above. The crystallographic data was collected on a GV50 diffractometer (Rigaku) equipped with an Titan CCD detector using Cu-K_α radiation. Data collection and reduction were performed with CrysAlisPro software package.[3] The structure was solved with Olex2 (1.5-alpha)[4] using ShelXT[5] and a least-square refinement on F^2 was carried out with ShelXL.[6] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms at the carbon atoms were refined with isotropic displacement parameters according to the riding model. The H atom at P1 in [Cp*Fe(η^4-$P_5{}^t$BuH)] can be located in the difference density map and was refined freely (isotropic displacement). Pictures of the crystal structures were made with Olex2 (1.5-alpha).

CCDC reference number 2528045 contains supplementary crystallographic data and is deposited in Cambridge Crystallographic Data Centre.

*Table S1: Selected parameters for the single crystal X-ray diffraction experiment of [Cp*Fe(η^4-$P_5{}^t$BuH)].*

Compound	SK190
Formula	$C_{14}H_{25}FeP_5$
CCDC number	2528045
$D_{calc.}$/ g cm^{-3}	1.364
μ/mm^{-1}	9.893
Formula weight	404.04
Colour	brown
Shape	needle
Size/mm^3	0.36 × 0.07 × 0.05
T/K	123.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.00330(10)
b/Å	15.17660(10)
c/Å	12.33030(10)
α/°	90
β/°	107.1030(10)
γ/°	90
V/Å^3	1968.01(3)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_α
F(000)	840
θ_{min}/°	4.204

θ_{max}/°	66.634
Measured Refl's	31700
Ind't Refl's	3488
Refl's with I≥σ(I)	3488
R_{int}	0.1043
Parameters	193
Restraints	0
Largest Peak	0.70
Deepest Hole	-0.67
GooF	1.020
wR_2 (all data)	0.1306
wR_2	0.1273
R_1 (all data)	0.0496
R_1	0.0476

[Cp*Fe(η^4-$P_5{}^t$BuH)] crystalizes in the monoclinic space group $P2_1/c$ in form of brown needles from a concentrated *n*-hexane solution at -30°C. The asymmetric unit contains one molecule of [Cp*Fe(η^4-$P_5{}^t$BuH)].

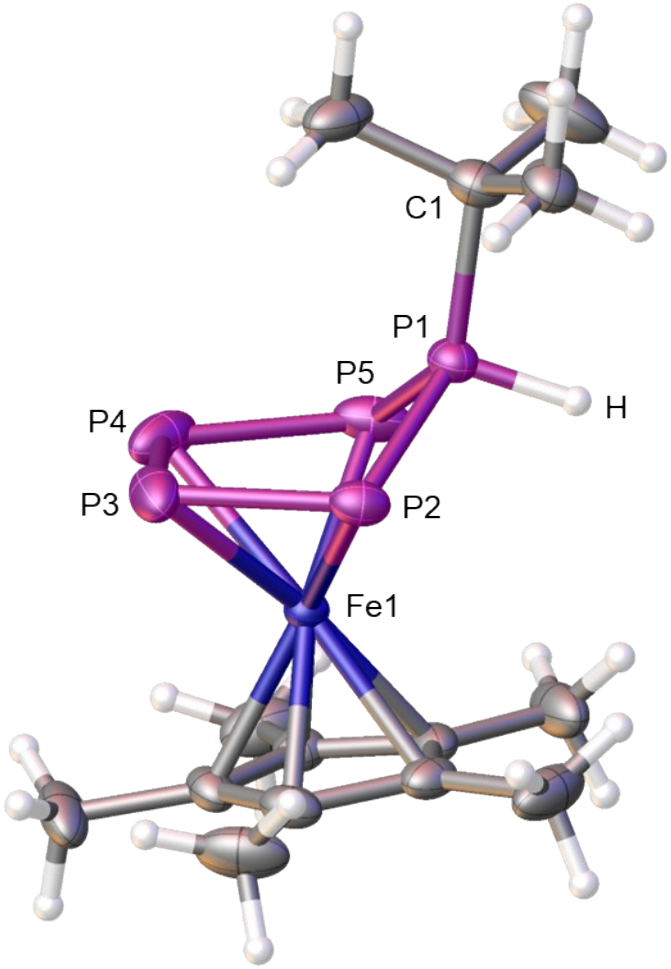

*Figure S1: Molecular structure of [Cp*Fe(η⁴-P₅ᵗBuH)] (**5**) in the solid state. Thermal ellipsoids are depicted at 50% probability level.*

*Table S2: Selected bond lengths of [Cp*Fe(η⁴-P₅ᵗBuH)] (**5**).*

Atom-Atom	Bond-Length [Å]
P1-P2	2.1292(10)
P2-P3	2.1357(12)
P3-P4	2.1384(15)
P4-P5	2.1458(14)
P1-P5	2.1363(11)

Atom-Atom	Bond-Length [Å]
Fe1-P2	2.3248(8)
Fe1-P3	2.3336(8)
Fe1-P4	2.3379(9)
Fe1-P5	2.3275(9)
P1-C1	1.847(3)

*Table S3: Selected angles of [Cp*Fe(η⁴-P₅ᵗBuH)] (**5**).*

Atom-Atom-Atom	Angle [°]
P1-P2-P3	101.61(5)
P2-P3-P4	105.58(5)

Atom-Atom-Atom	Angle [°]
P5-P1-P2	101.22(4)
C1-P1-P2	121.15(10)

P3-P4-P5	105.80(5)
P4-P5-P1	100.91(5)

C1-P1-P5	123.82(11)

3. NMR Spectra

3.1 NMR spectra of HP^{t}BuMe:

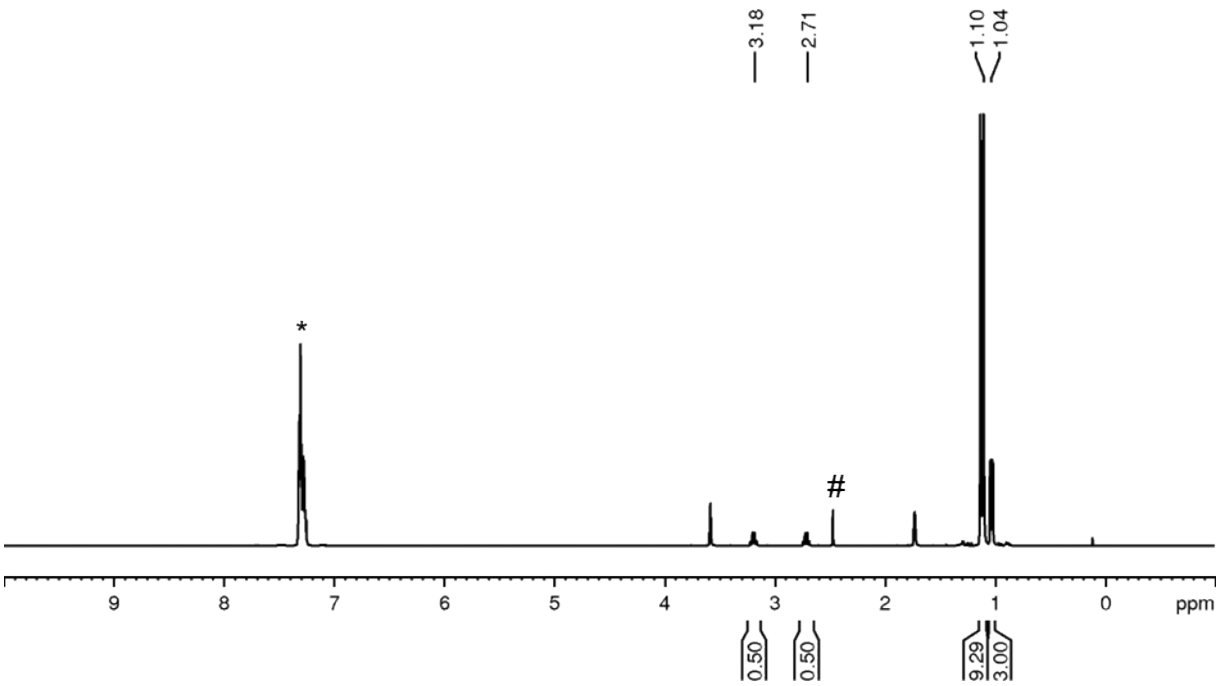

Figure S2: ^{1}H NMR spectrum of HP^{t}BuMe prepared via method A, in THF-d8 with PPh_3 as internal reference recorded at room temperature (= PPh_3, # = H_2O).*

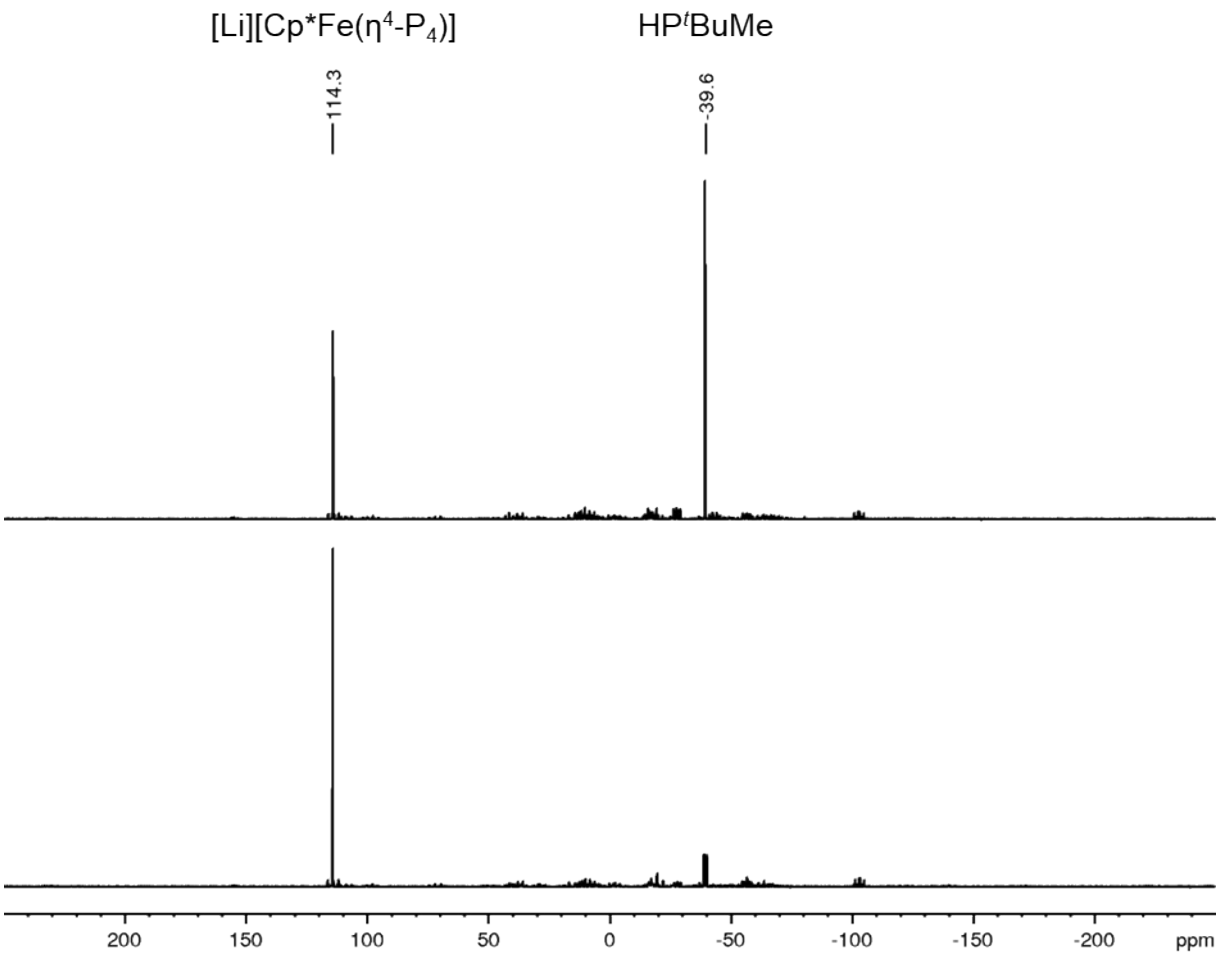

*Figure S3: Experimental $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of the reaction of [Cp*Fe(η^4-$P_5{}^t$BuMe)] with $LiAlH_4$ in THF-d_8 recorded at room temperature.*

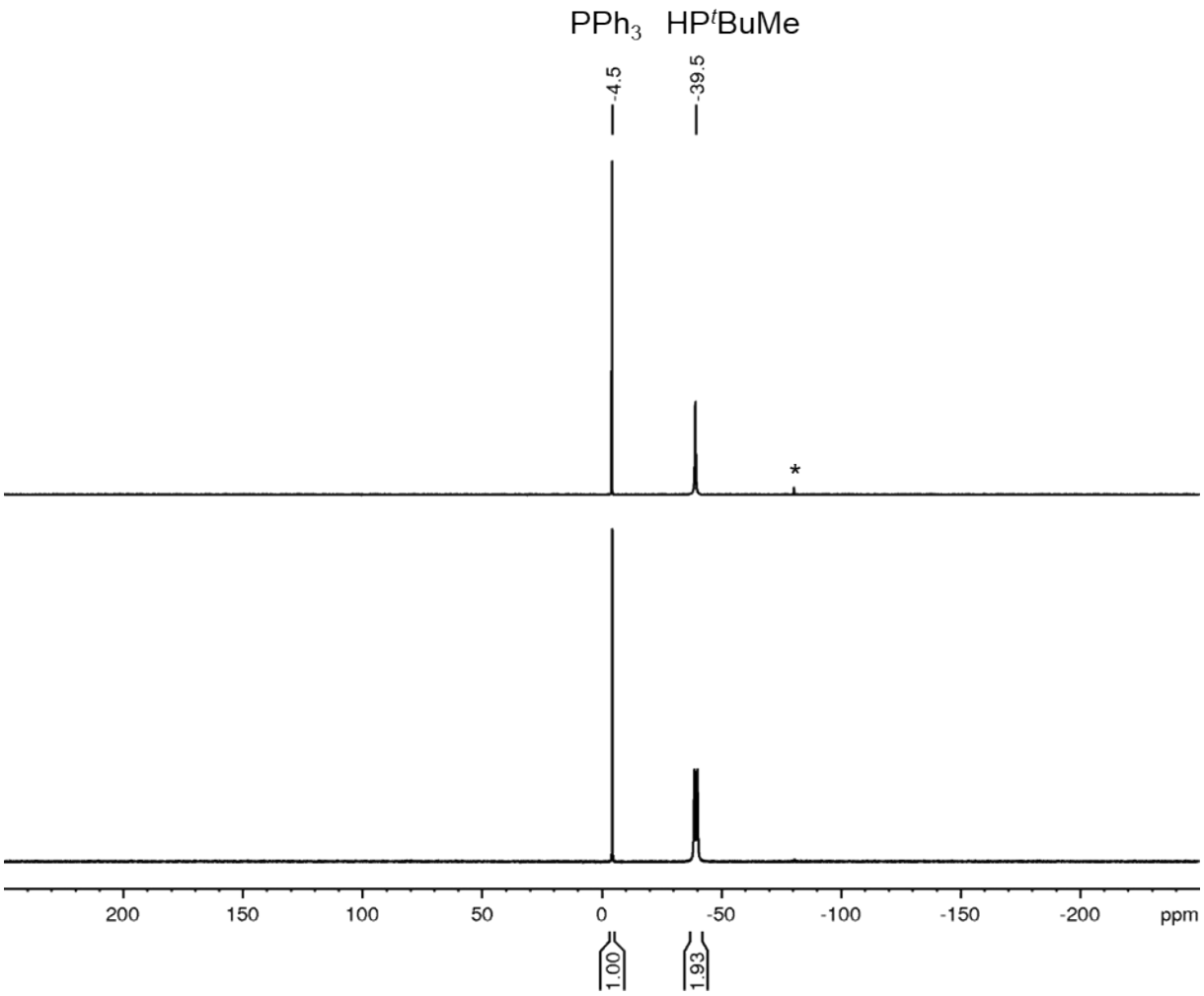

Figure S4: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of HPtBuMe prepared via method A, in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= H_2P^tBu).*

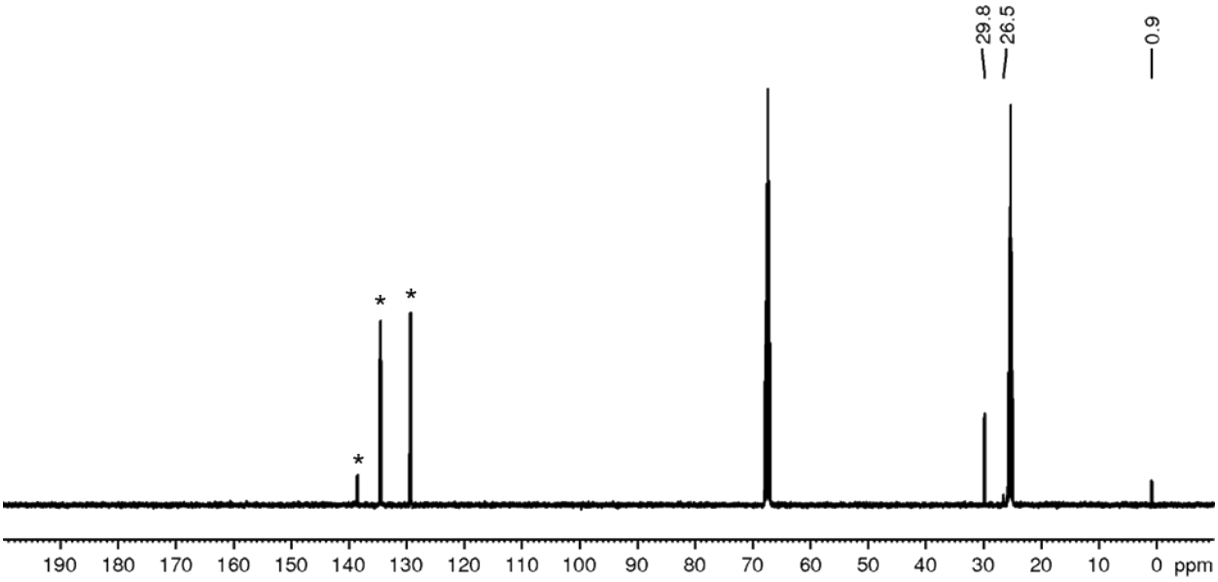

Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of HP^{t}BuMe prepared via method A, in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= PPh_3).*

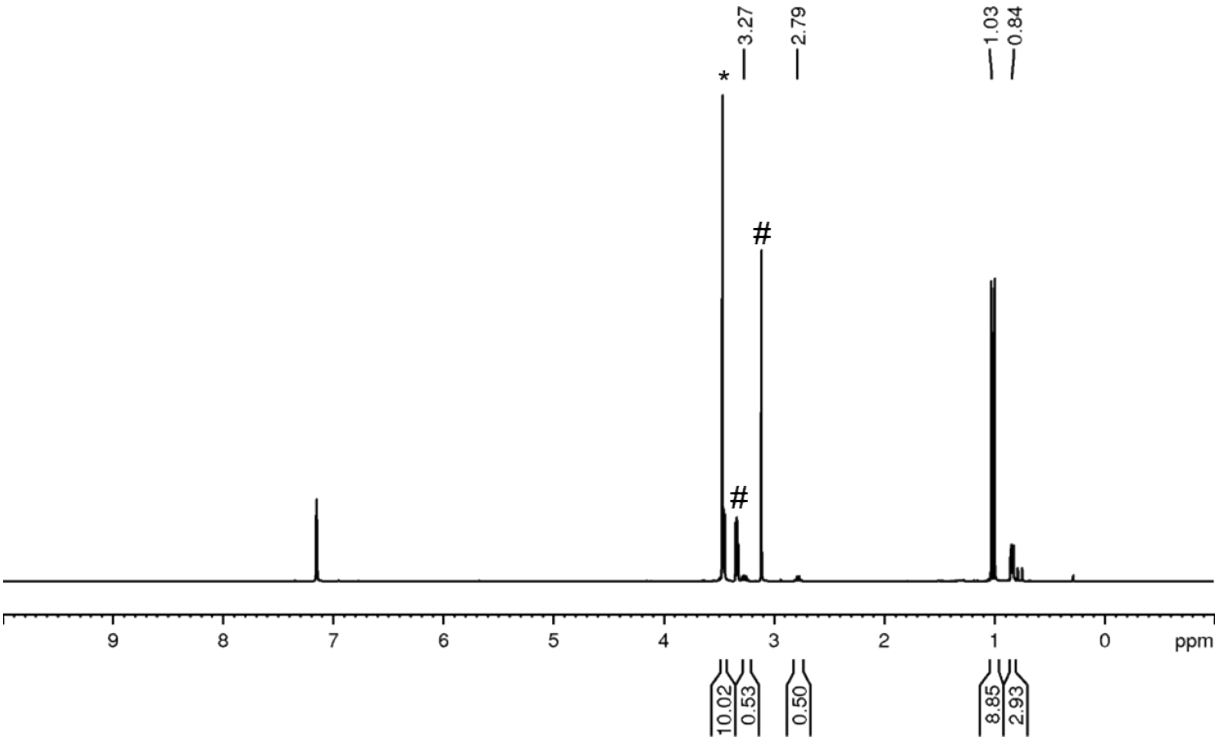

Figure S6: ^{1}H NMR spectrum of HP^{t}BuMe prepared via method B, in C_6D_6 recorded at room temperature (= Tetraglyme, # = Diglyme).*

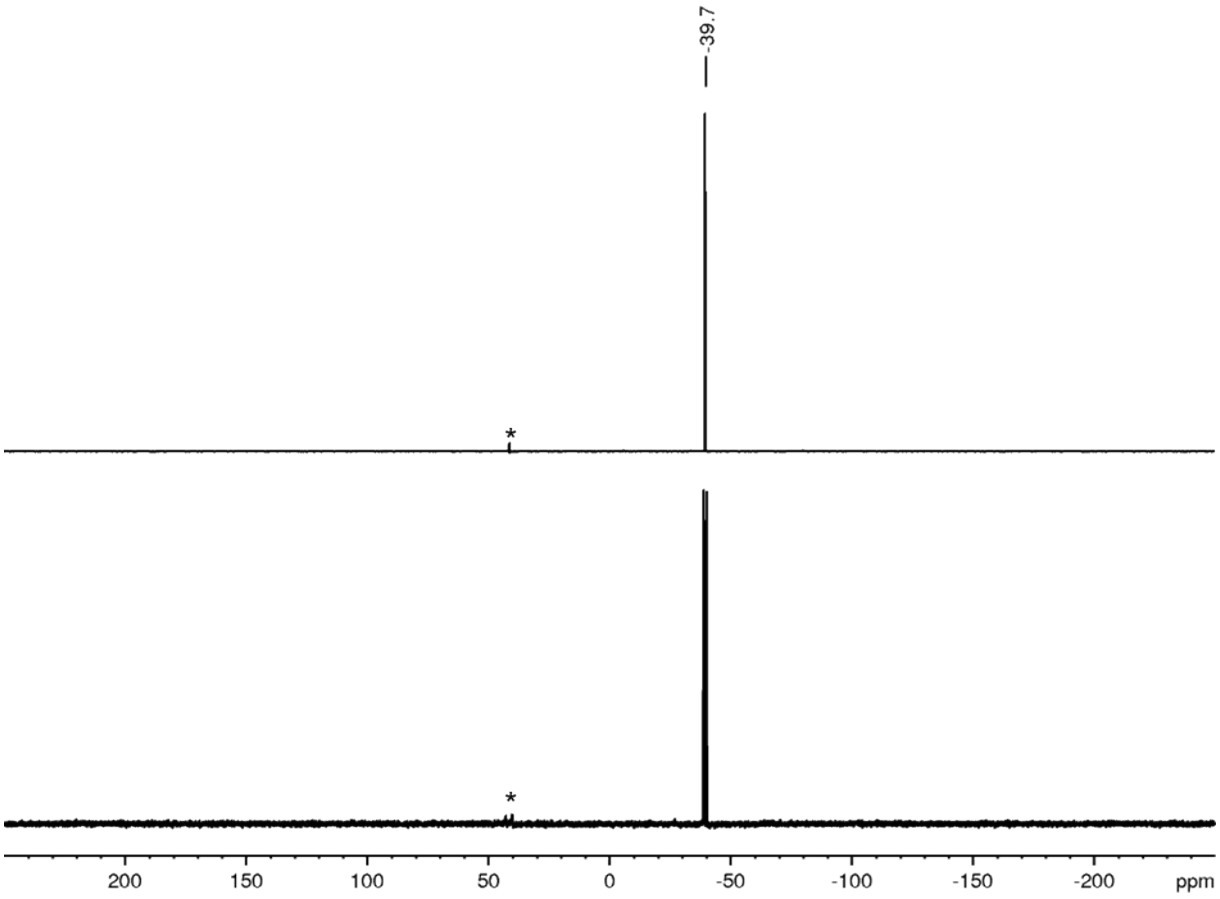

Figure S7: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of HP^{t}BuMe prepared via method B, in C_6D_6 recorded at room temperature (= OPH^{t}BuMe).*

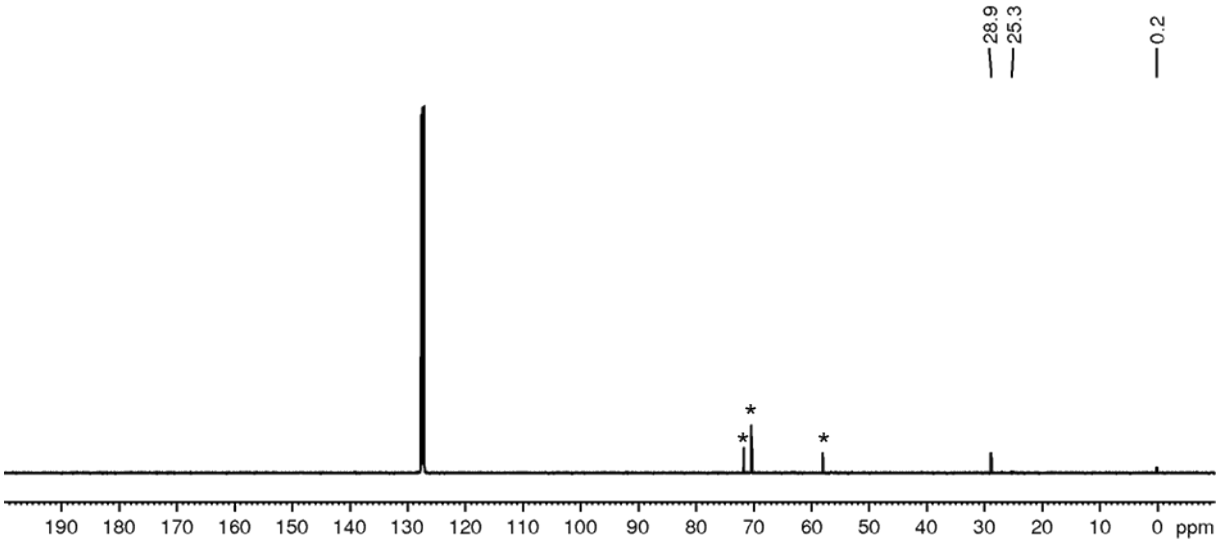

Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum of HP^{t}BuMe prepared via method B, in C_6D_6 recorded at room temperature (= Tetraglyme).*

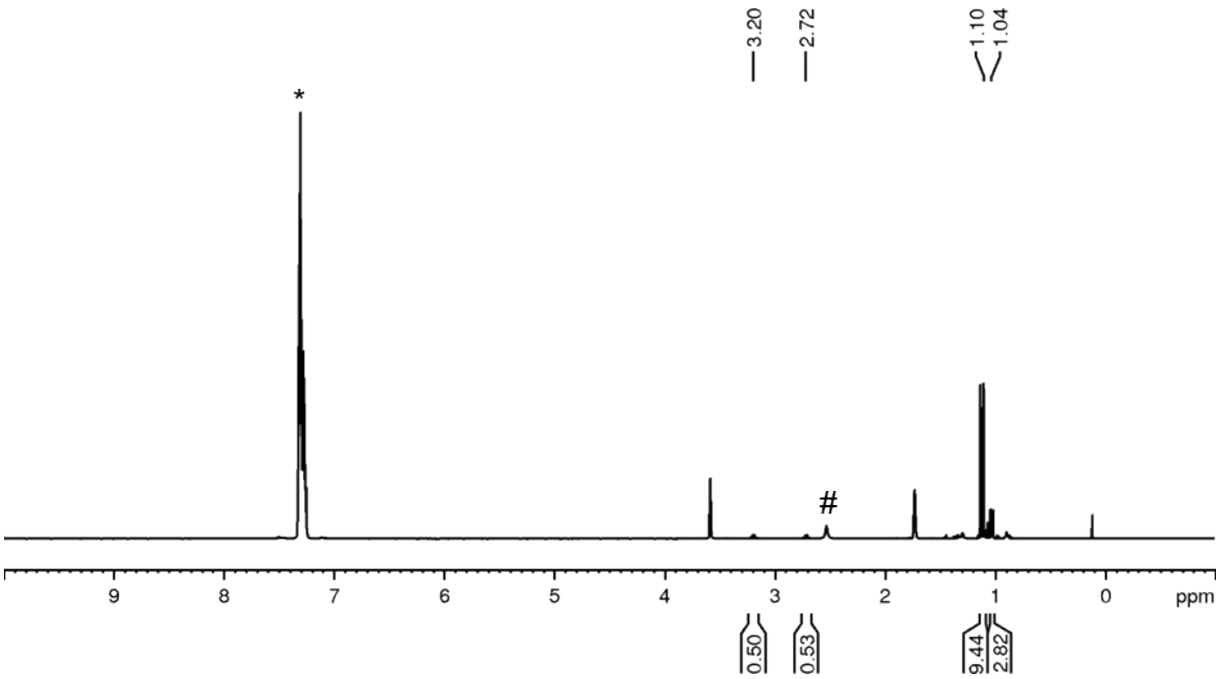

Figure S9: ^{1}H NMR spectrum of HP^{t}BuMe prepared via method C in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= PPh_3, # = H_2O).*

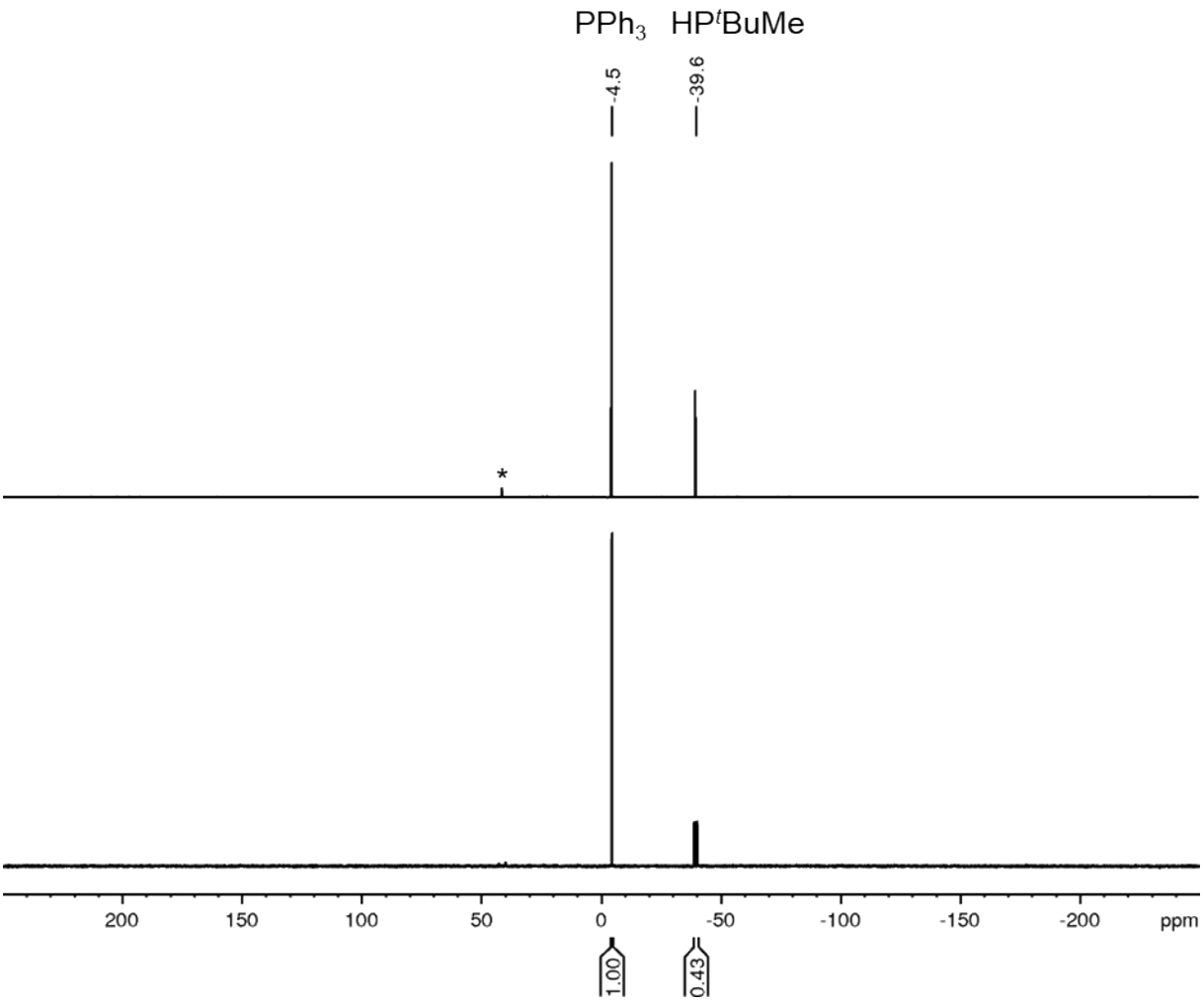

Figure S10: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of HP^{t}BuMe prepared via method C, in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= OPH^{t}BuMe).*

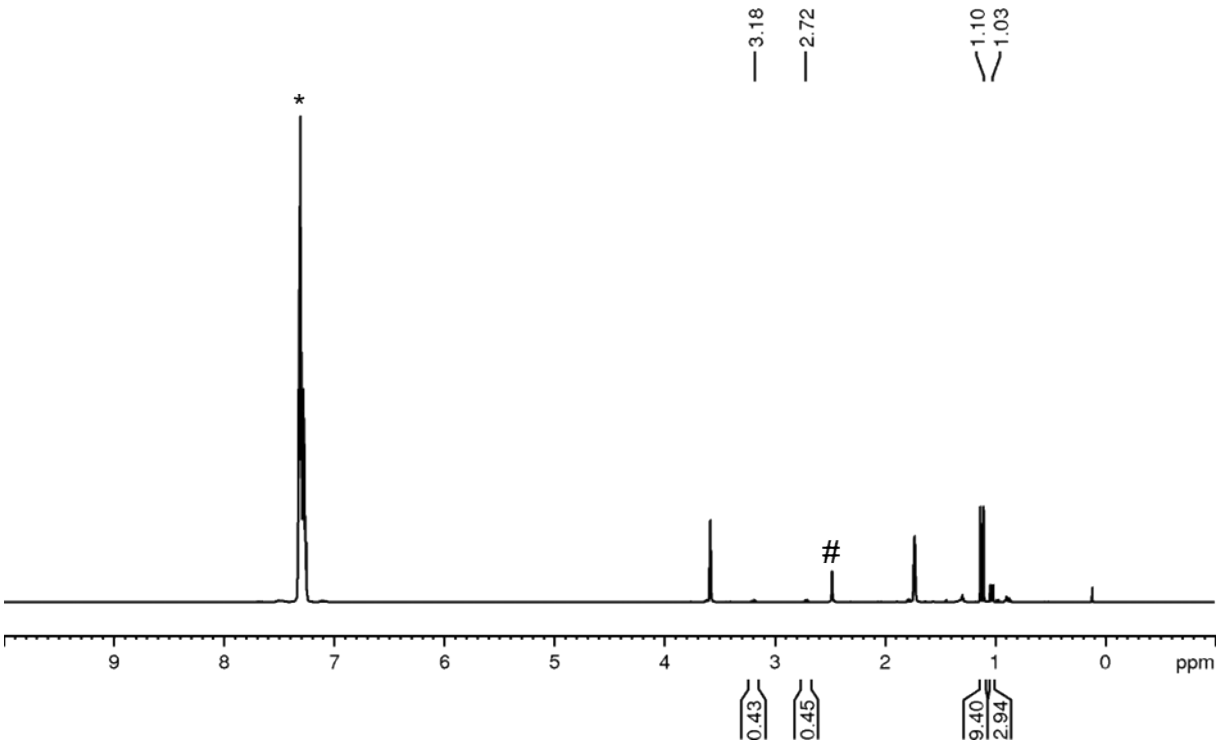

Figure S11: ^{1}H NMR spectrum of HP^{t}BuMe prepared via method D in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= PPh_3, # = H_2O).*

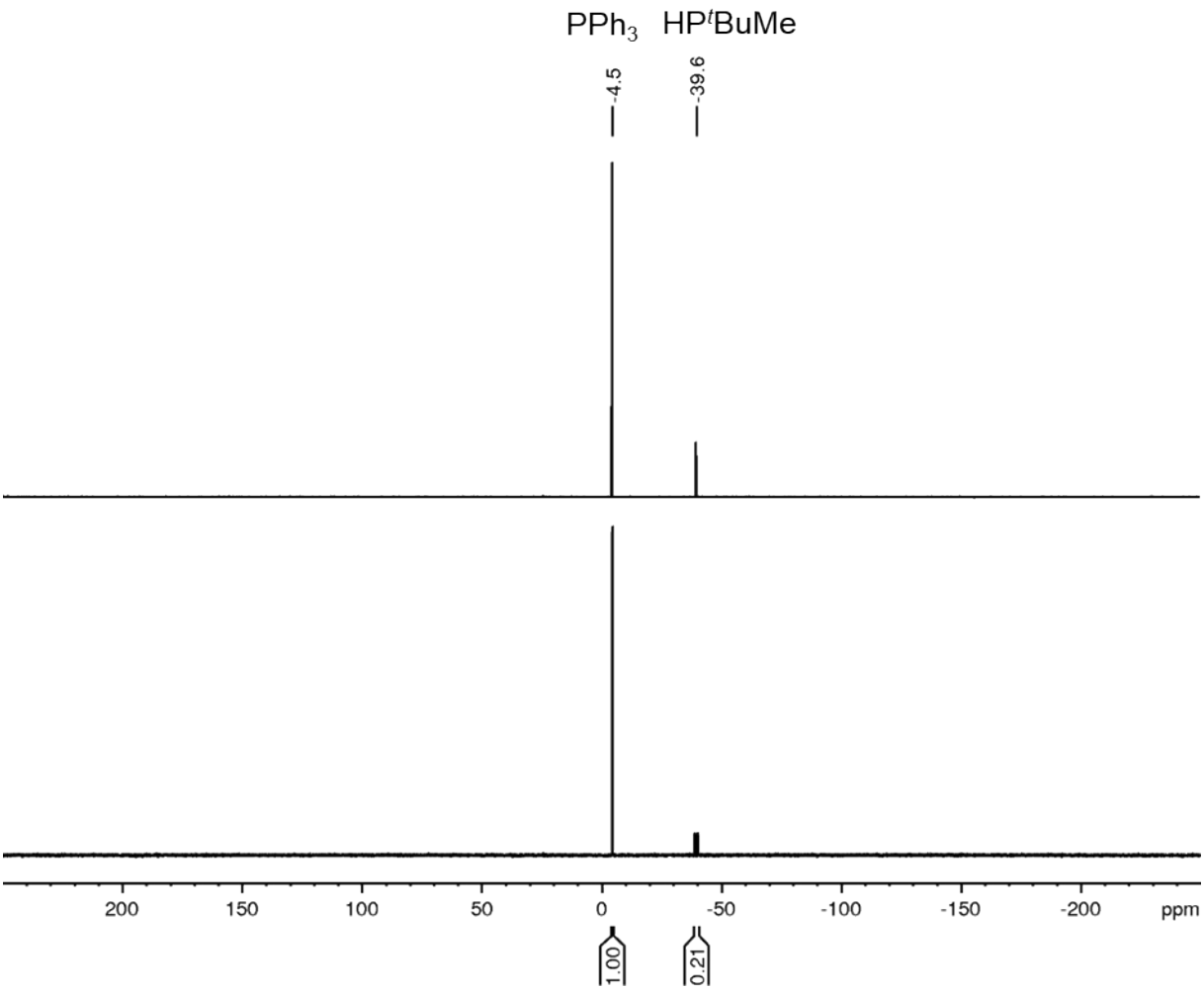

Figure S12: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of HP^{t}BuMe prepared via method D, in THF-d_8 with PPh_3 as internal reference recorded at room temperature.

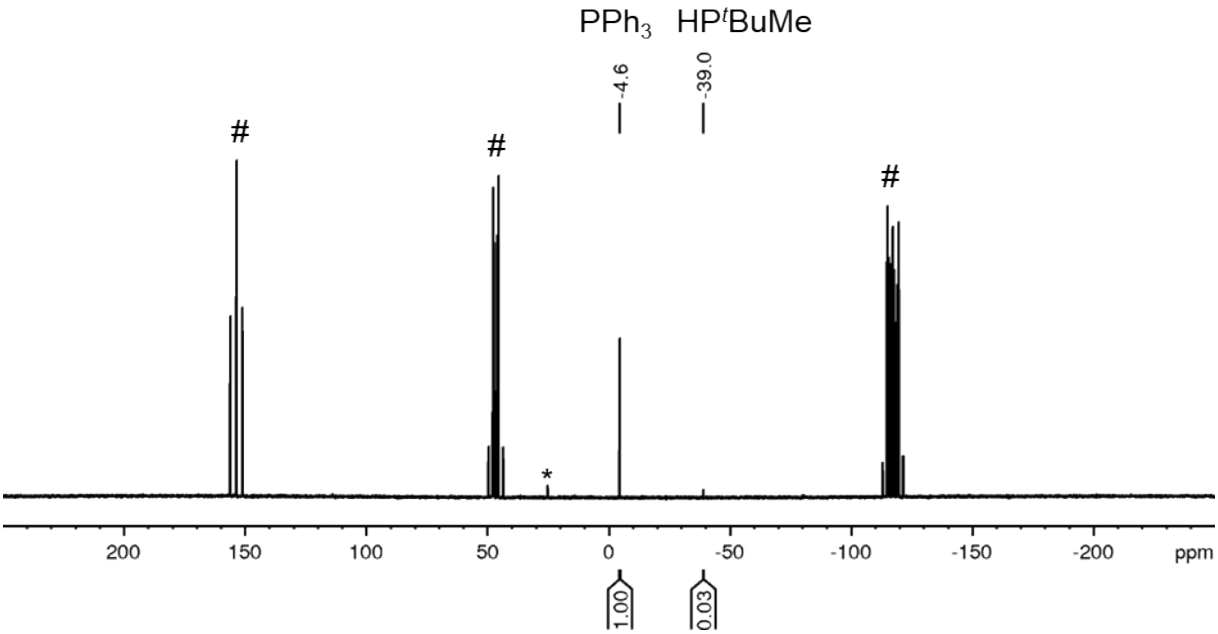

*Figure S13: Experimental $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [Cp*Fe(η^4-$P_5{}^t$BuMe)] with [Li][HBEt$_3$] in THF with tol-d8 capillary with PPh_3 (c = 0.2 mol/L) as internal standard recorded at room temperature (* = OPH^{t}BuMe, # = [Cp*Fe(η^4-$P_5{}^t$BuMe)]).*

3.2 NMR spectra of HPiPrMe:

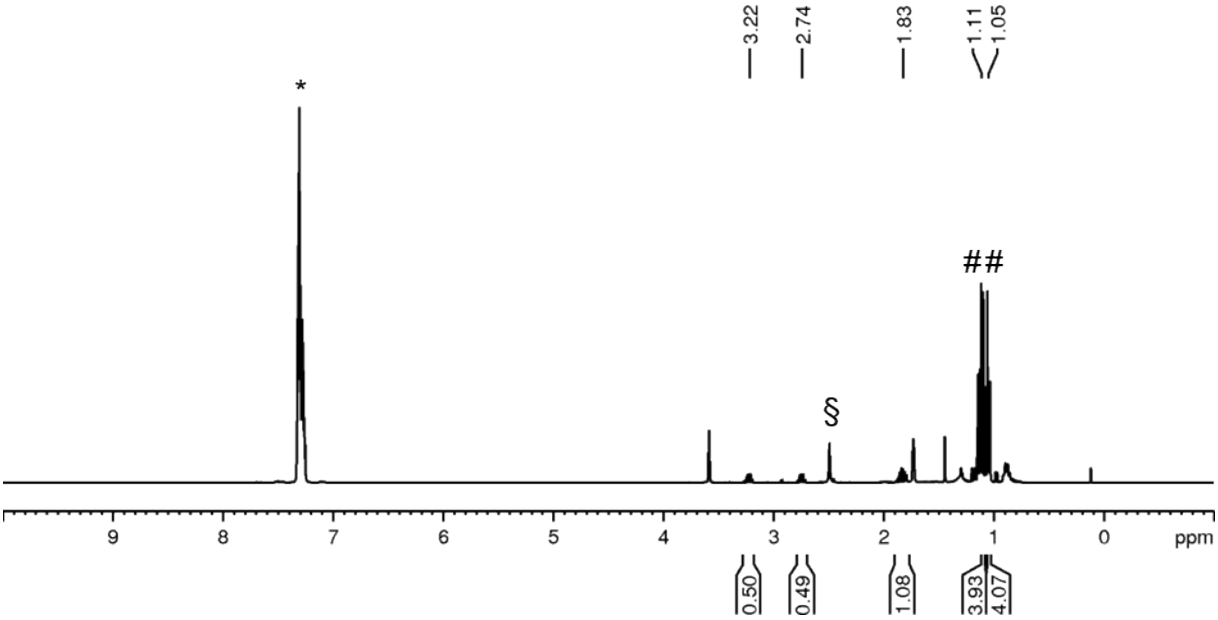

Figure S14: ^{1}H NMR spectrum of HP^{i}PrMe in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= PPh_3, § = H_2O, # = wrong integrals due to overlap of product-signal and signals for $^i PrPH_2$ and $MePH_2$).*

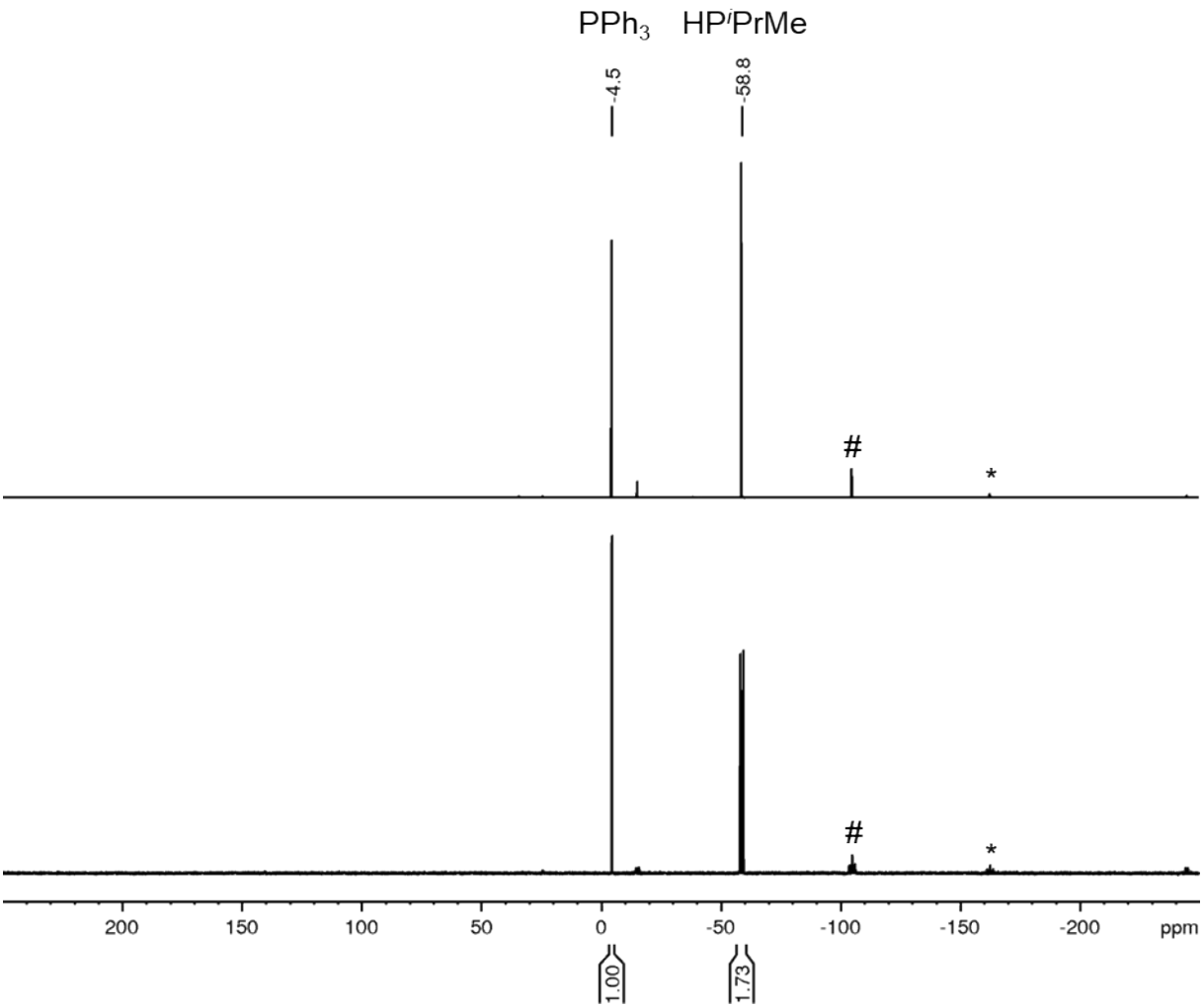

Figure S15: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of $HP^{i}PrMe$ in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= H_2PCH3, # = $H_2P^{i}Pr$).*

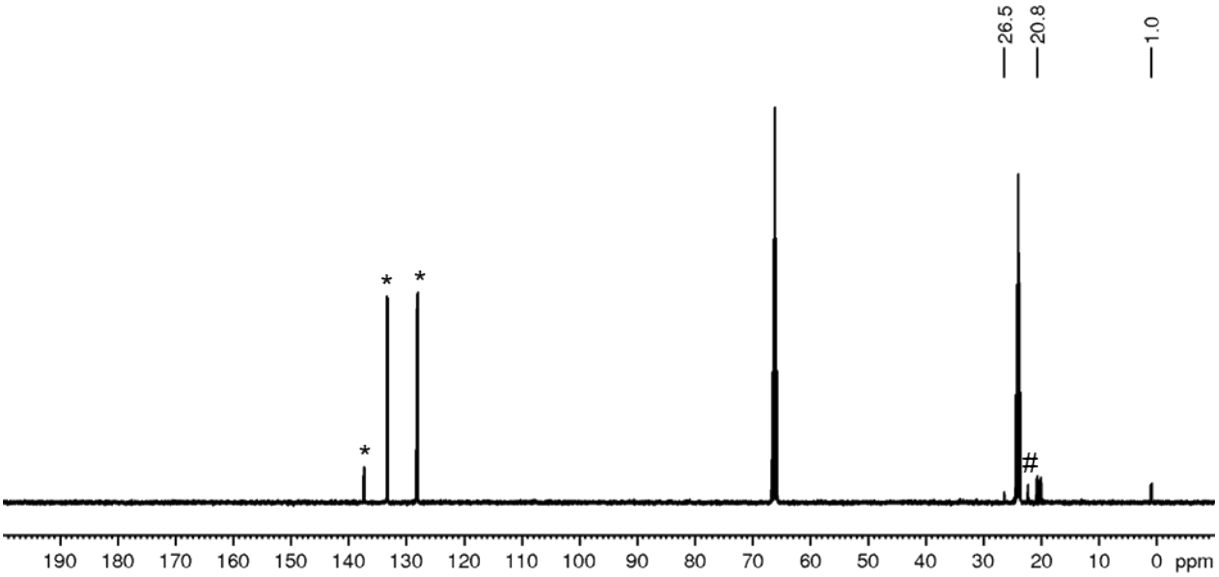

Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum of HP^{i}PrMe in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= PPh_3, # = $H_2P^{i}Pr$).*

3.3 NMR spectra of HPPhMe:

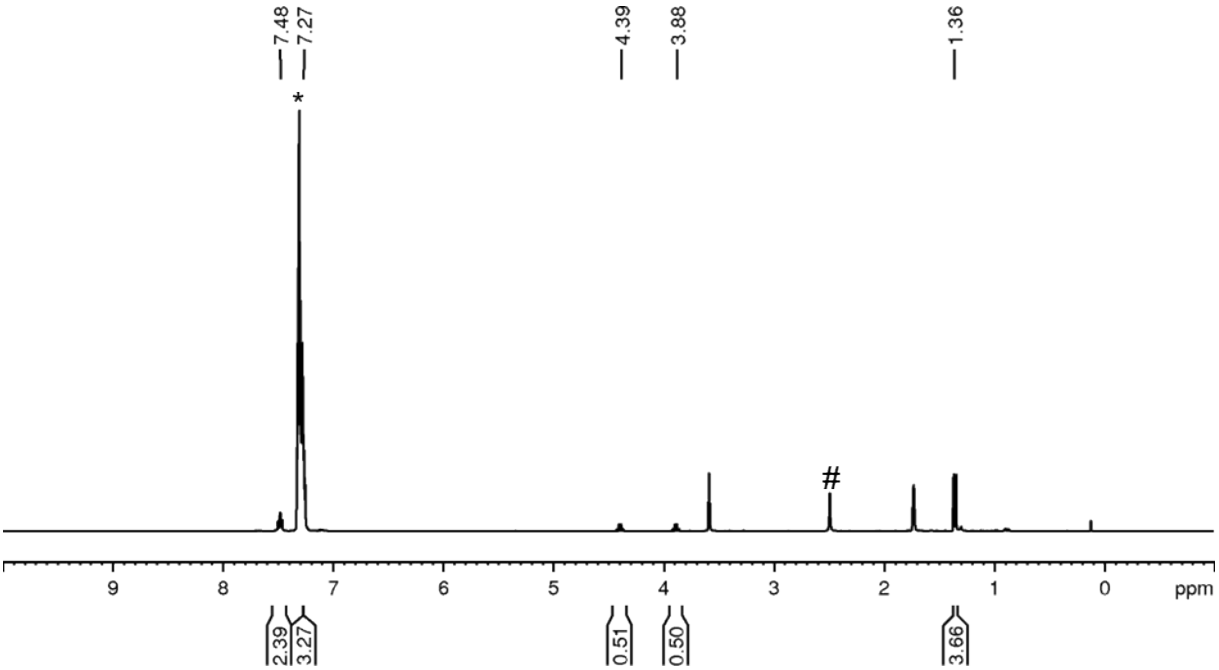

Figure S17: ^{1}H NMR spectrum of HPPhMe in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= PPh_3, # = H_2O).*

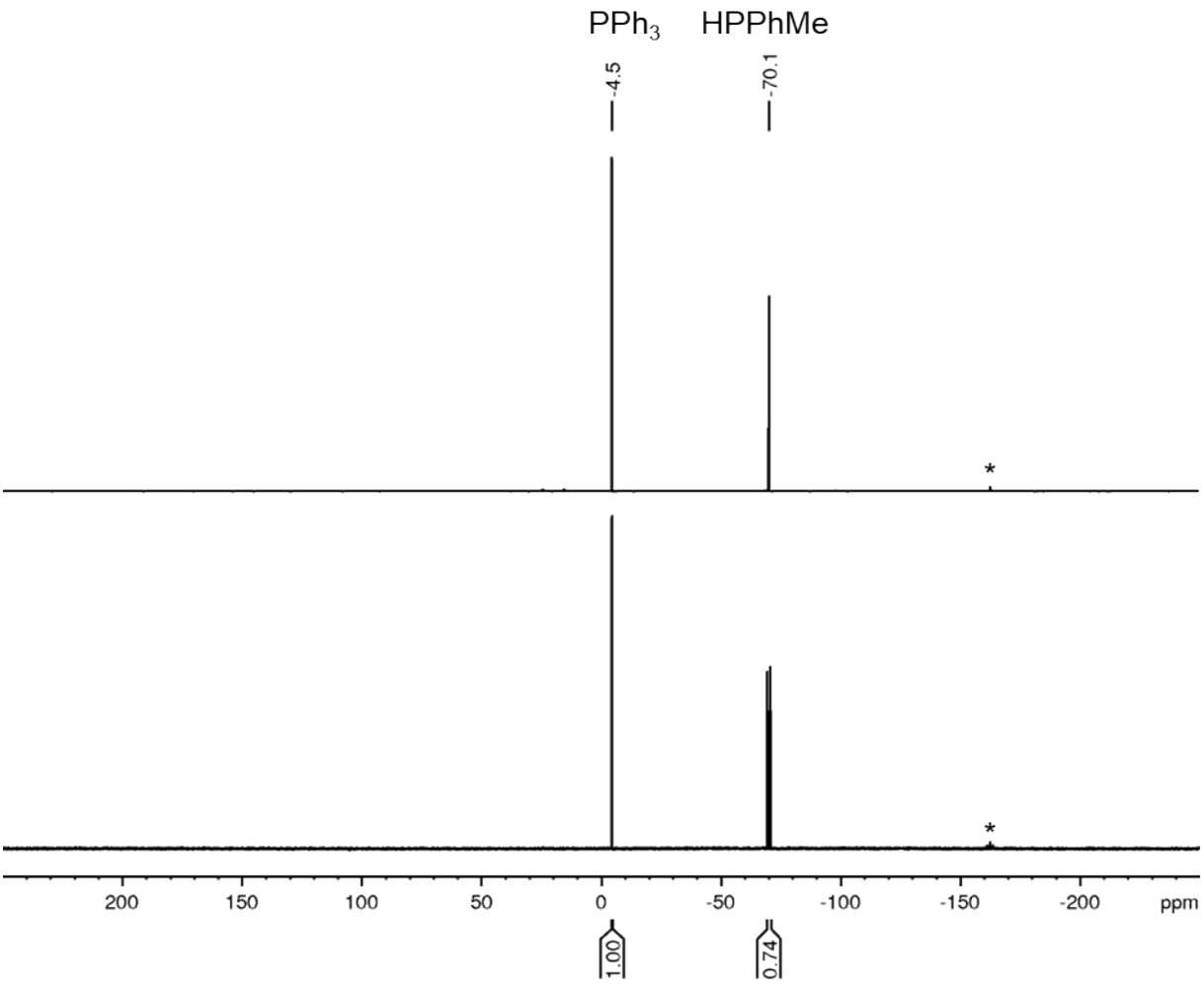

Figure S18: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of HPPhMe in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= H_2PCH_3).*

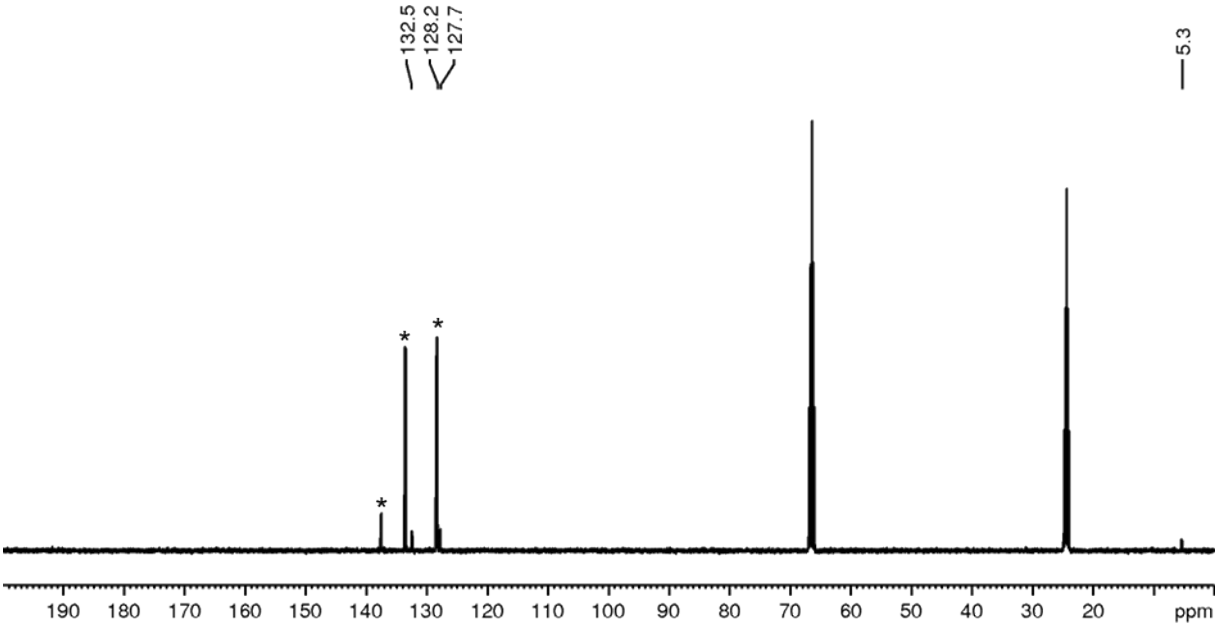

Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of HPPhMe in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= PPh_3).*

3.4 NMR spectra of $HPMe_2$:

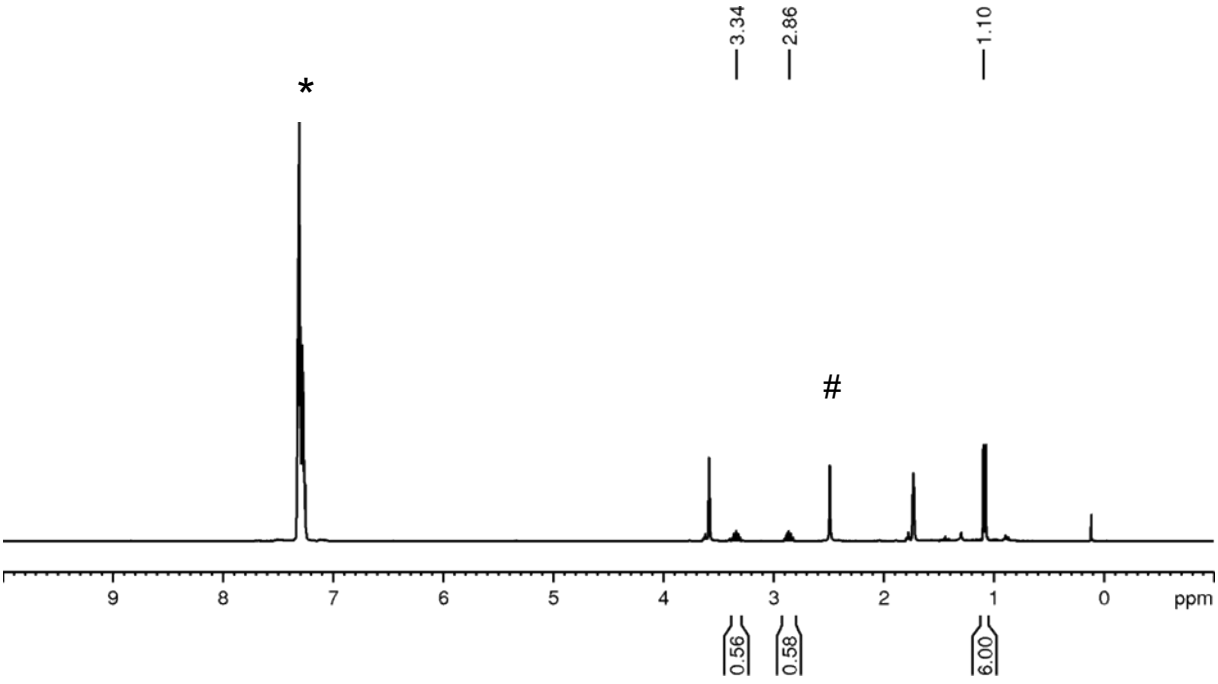

Figure S20: ^{1}H NMR spectrum of $HPMe_2$ in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= PPh_3, # = H_2O).*

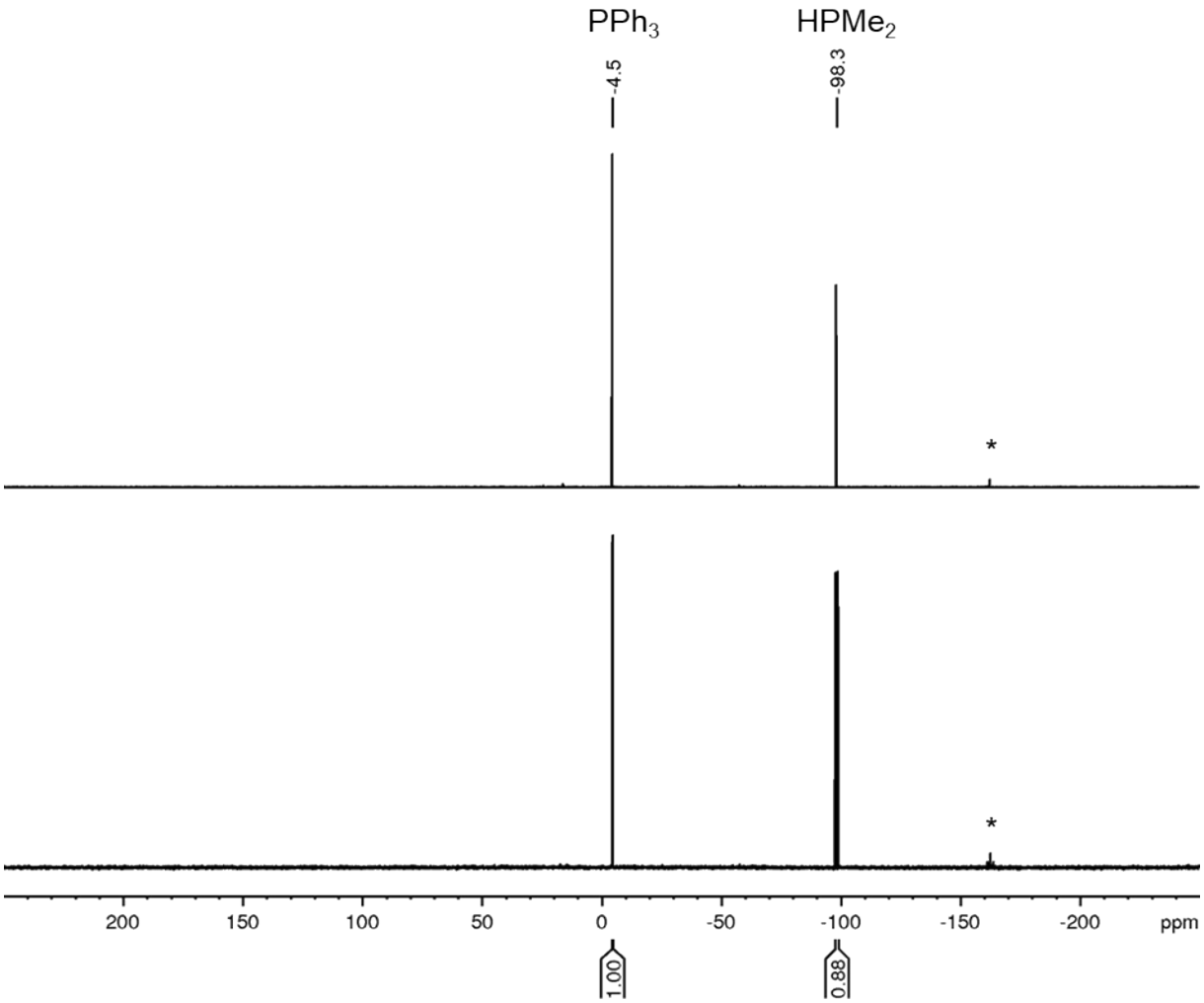

Figure S21: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of $HPMe_2$ in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= H_2PCH_3).*

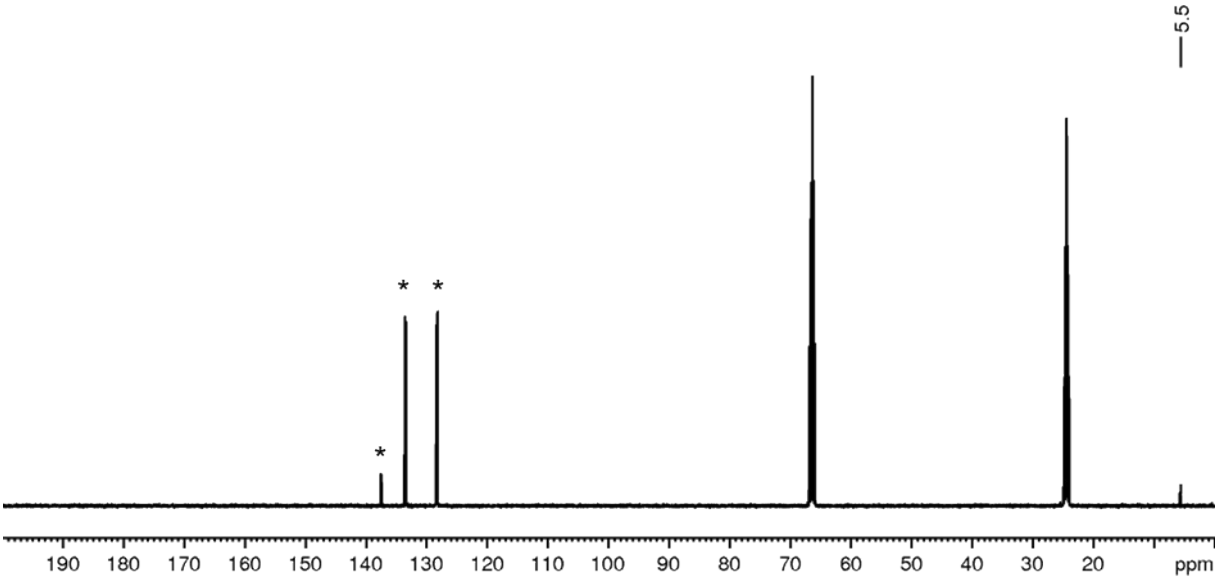

Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum of $HPMe_2$ in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= PPh_3).*

3.5 NMR spectra of $HPMe_2[Cp^*Fe(\eta^4\text{-}P_5{}^t\text{BuH})]$:

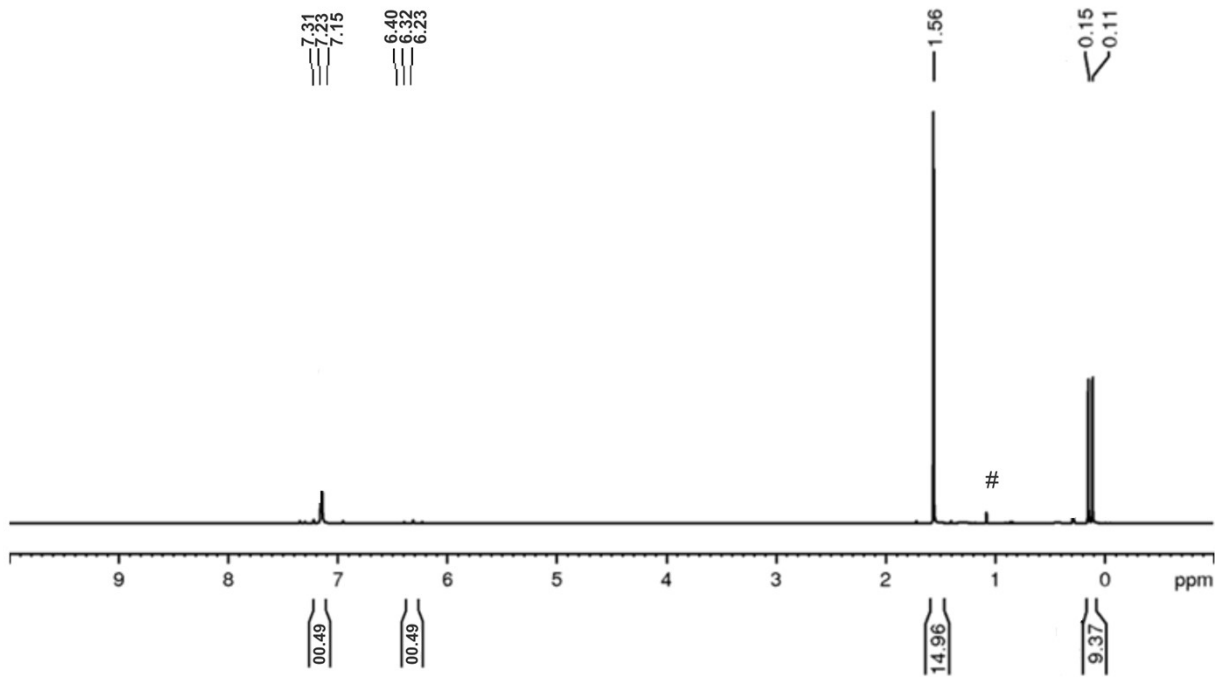

Figure S23: ^{1}H NMR spectrum of $[Cp^*Fe(\eta^4\text{-}P_5{}^t\text{BuH})]$ in C_6D_6 recorded at room temperature (# = $[Cp^*Fe(\eta^5\text{-}P_5)]$).

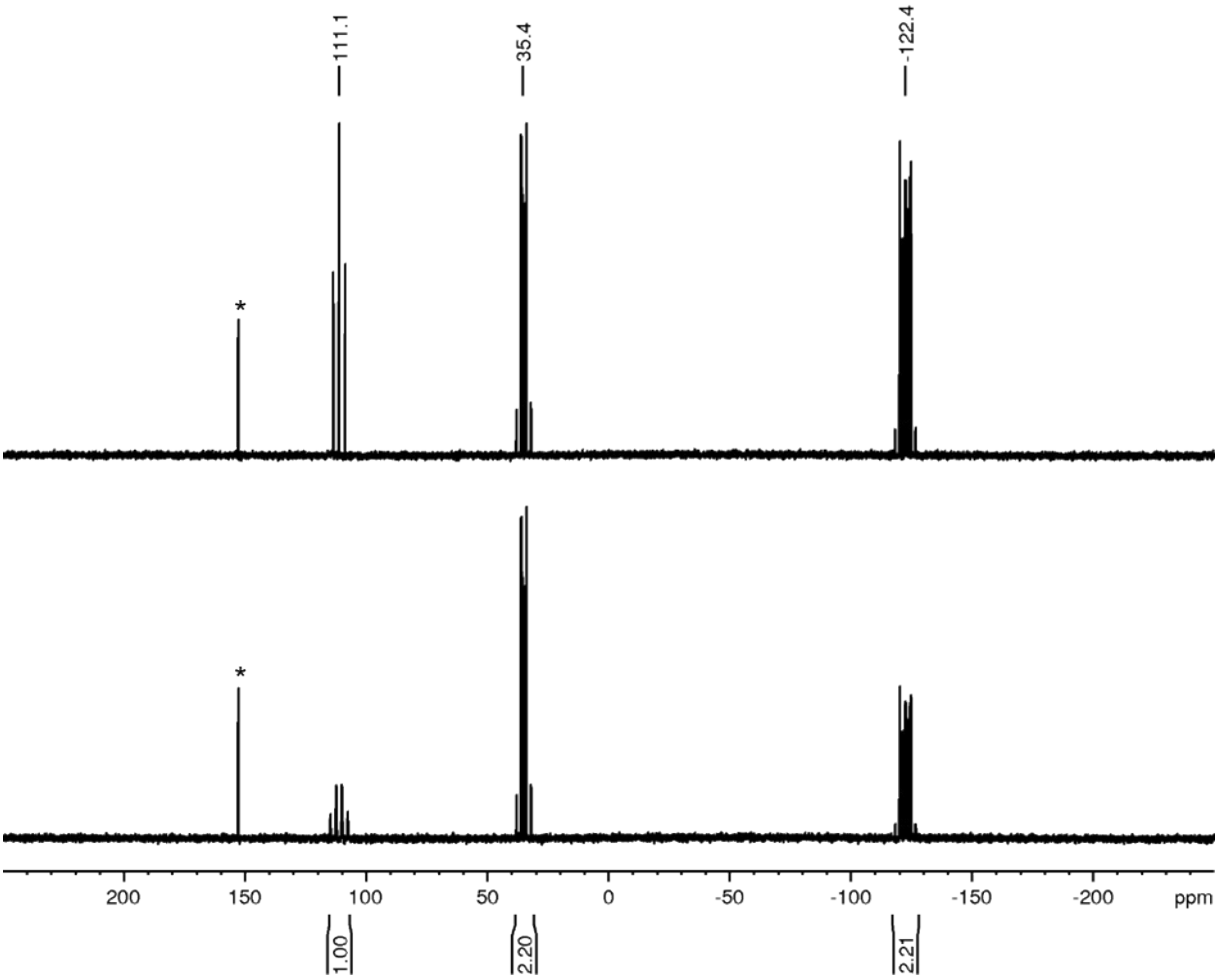

*Figure S24: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of [Cp*Fe(η^4-$P_5{}^tBuH$)] in C_6D_6 recorded at room temperature (* = [Cp*Fe(η^5-P_5)]).*

3.6 Reactivity of [Cp*Fe(η⁴-P₅ᵗBuH)] towards MeLi

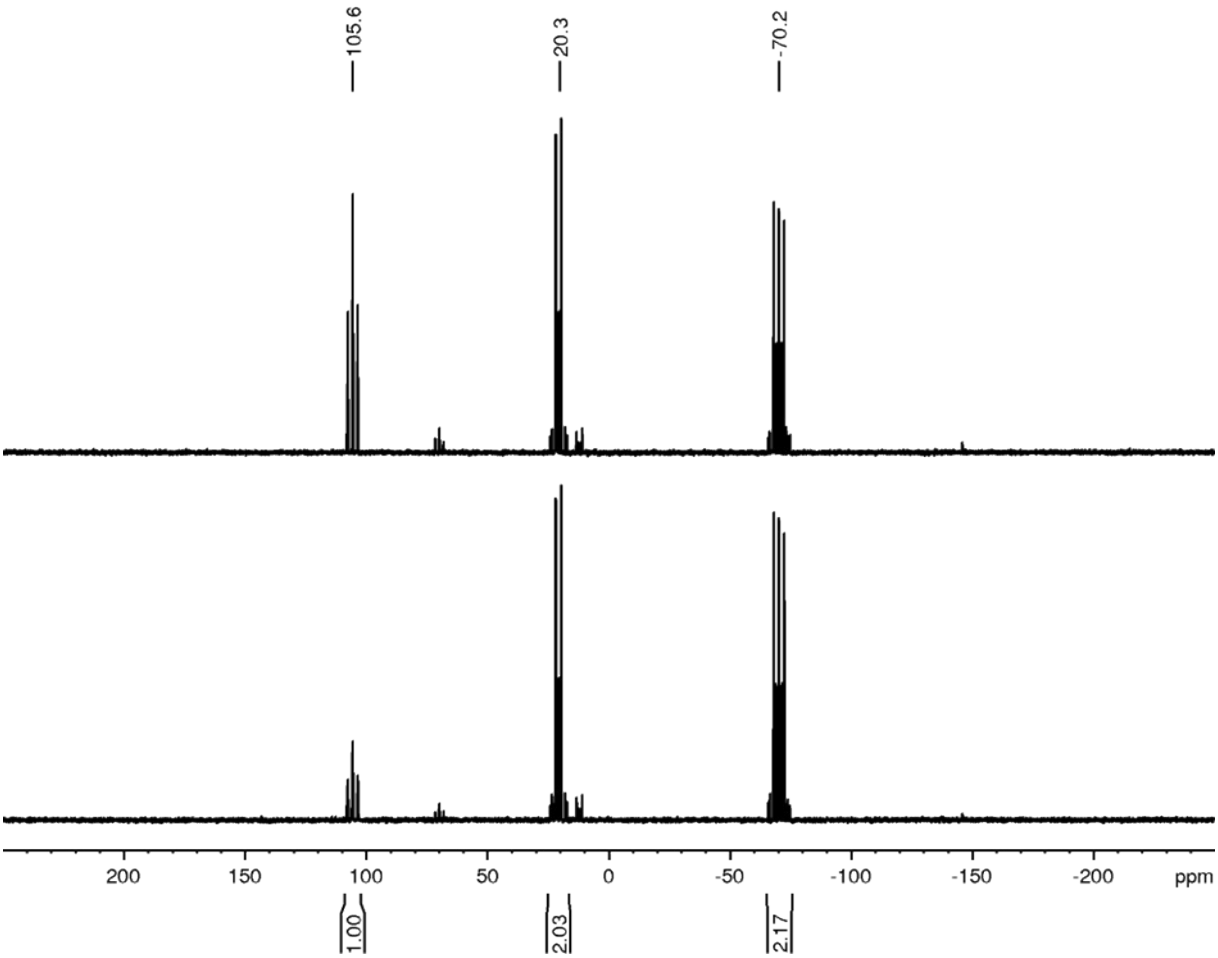

*Figure S25: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) NMR spectra of the reaction of [Cp*Fe(η⁴-P₅ᵗBuH)] with MeLi in THF and C_6D_6-capillary recorded at room temperature.*

3.7 Reactivity of [Cp*Fe(η⁴-P₅ᵗBuH)] towards $LiAlH_4$

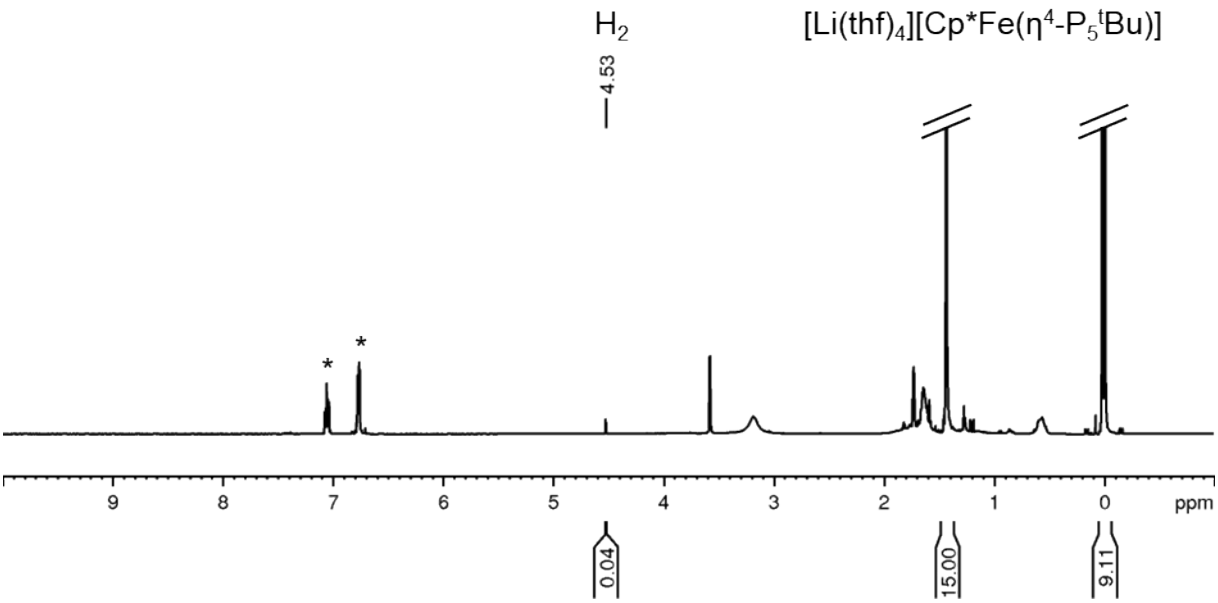

*Figure S26: Experimental ^1H NMR spectrum of the reaction of [Cp*Fe(η⁴-P₅ᵗBuH)] with $LiAlH_4$ in THF-d_8 recorded at room temperature (* = PPh_3-capillary).*

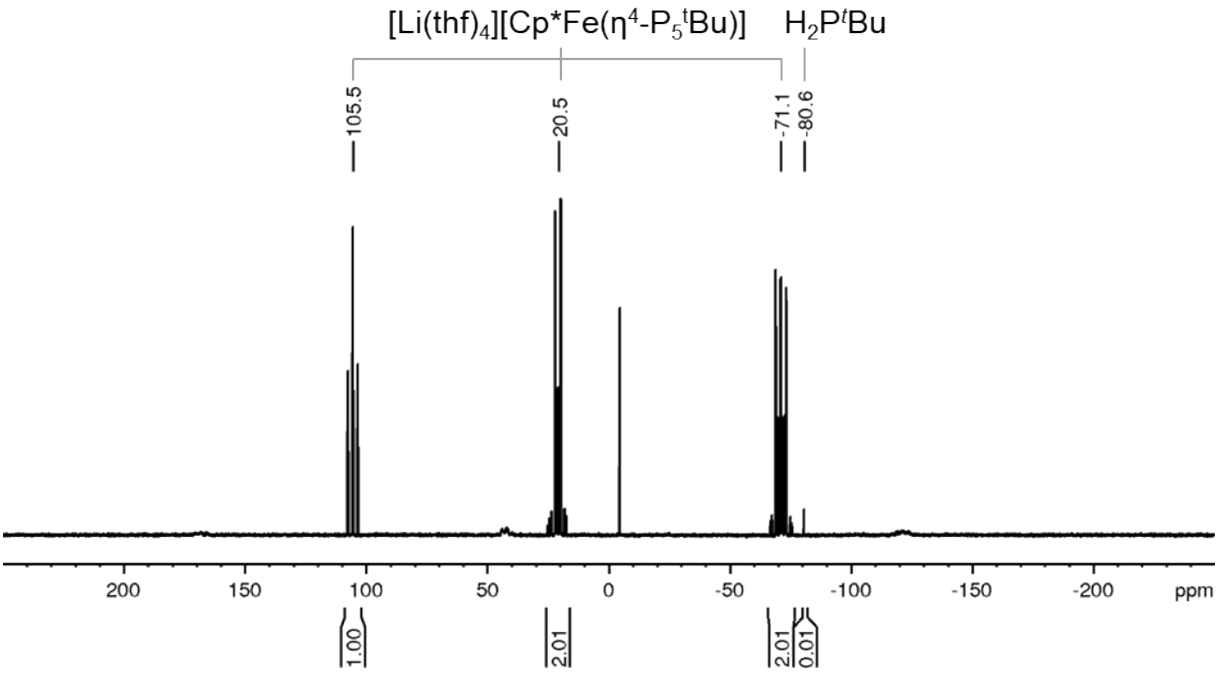

*Figure S27: Experimental $^{31}P\{^1H\}$ NMR spectrum of the reaction of [Cp*Fe(η⁴-P₅ᵗBuH)] with $LiAlH_4$ in THF-d_8 recorded at room temperature (* = PPh_3-capillary).*

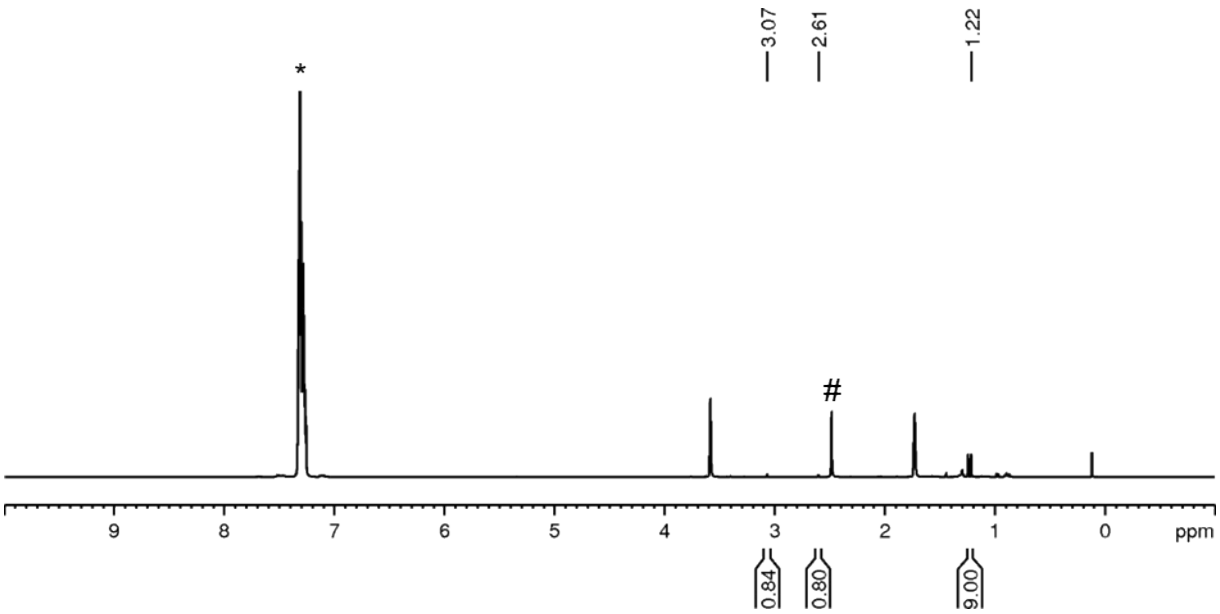

Figure S28: ^1H NMR spectrum of H_2P^tBu in THF-d_8 with PPh_3 as internal reference recorded at room temperature (= PPh_3, # = H_2O).*

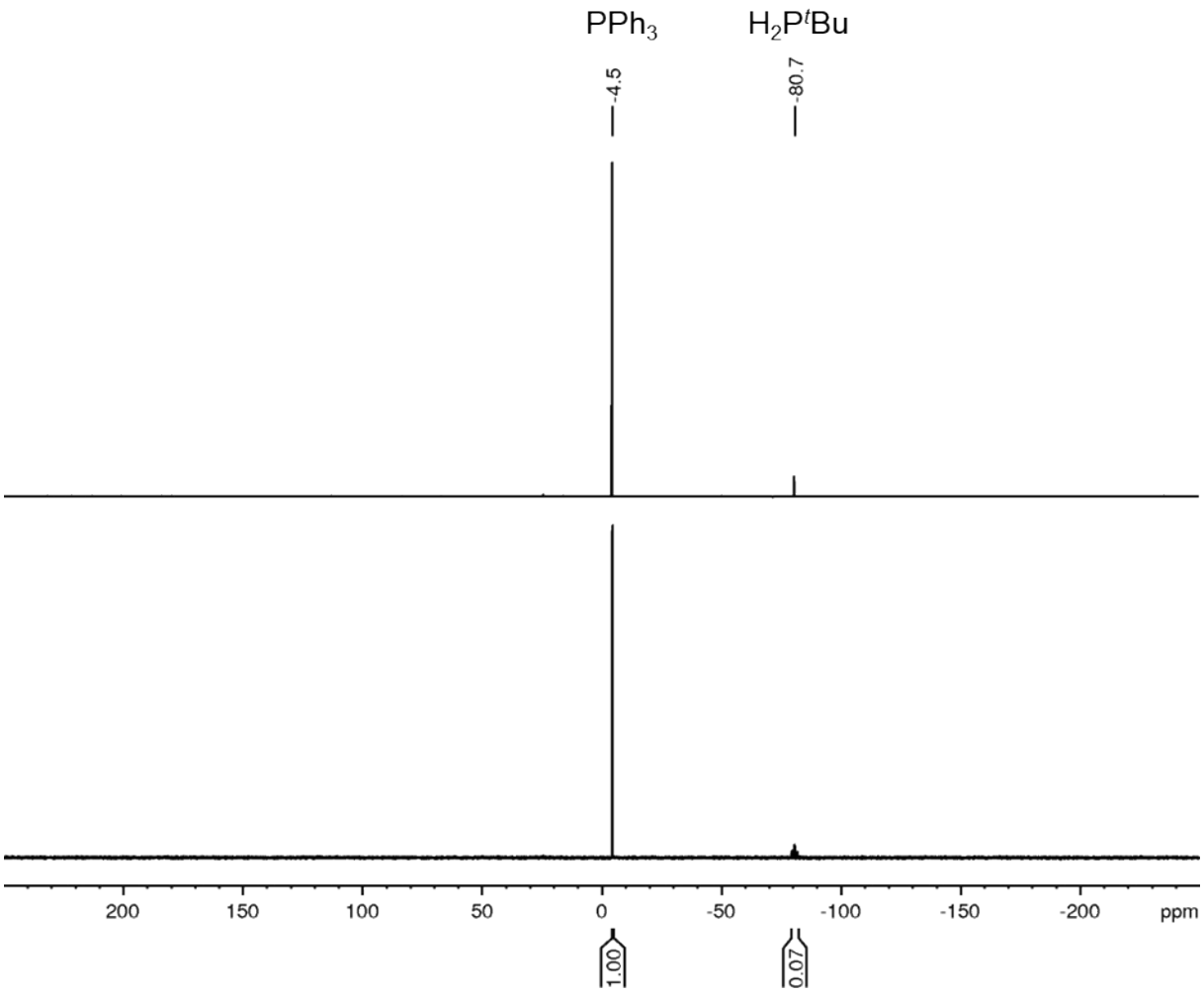

Figure S29: $^{31}P\{^{1}H\}$ (top) and ^{31}P (bottom) spectra of H_2P^tBu in THF-d_8 with PPh_3 as internal reference recorded at room temperature.

4. References:

1. O. J. Scherer and T. Brück, *Angew. Chem. Int. Ed. Engl.*, 1987, **26**, 59.
2. S. Reichl, E. Mädl, F. Riedlberger, M. Piesch, G. Balázs, M. Seidl and M. Scheer, *Nature communications*, 2021, **12**, 5774.
3. Aglient Technologies Ltd, *CrysAlis PRO*, Yarnton, Oxfordshire, England, 2014.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl Crystallogr*, 2009, **42**, 339-341.
5. G. M. Sheldrick, *Acta crystallographica. Section A, Foundations and advances*, 2015, **71**, 3-8.
6. G. M. Sheldrick, *Acta crystallographica. Section C, Structural chemistry*, 2015, **71**, 3-8.