SUPPORTING INFORMATION

Phosphine-catalyzed reductive coupling of Dihalophosphines

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This file includes:

1 Experimental

General Information. If not stated otherwise, all manipulations were carried out under oxygen- and moisture-free conditions under an inert atmosphere of argon using standard Schlenk or Drybox techniques. All glassware was heated three times *in vacuo* using a heat gun and cooled under argon atmosphere. Solvents were transferred using syringes, which were purged three times with argon prior to use. Solvents and reactants were either obtained from commercial sources or synthesized as detailed in Table S1.

Table S1: Origin and purification of solvents and reactants.

Substance	Origin	Purification
THF, *n*-hexane, toluene	local trade	solvent purification system, stored under argon
PEt_3, PMe_3	Sigma Aldrich	used as received
CD_2Cl_2	euriso-top	dried over P_4O_{10} and CaH_2 freshly distilled prior to use
C_6D_6	euriso-top	dried over Na freshly distilled prior to use
Mes-Br	TCI Chemicals, 99%	used as received
Tip-Br	Sigma Aldrich, 95%	used as received
Dip-NH_2	abcr, technical grade 90%	used as received
PBr_3	Sigma Aldrich, for synthesis	used as received
Mg	abcr, 99.8%, for Grignards	used as received
$[BrPEt_3]Br$	Synthesized[1]	
Cl_2PMe_3	Synthesized[2]	

NMR spectra were recorded on Bruker spectrometers (AVANCE 300, AVANCE 400 or Fourier 300) and were referenced internally to the deuterated solvent (^{13}C: C_6D_6 δ_{ref} = 128.06 ppm) or to protic impurities in the deuterated solvent[3] (^1H: C_6HD_5 δ_{ref} = 7.16 ppm) or externally (^{31}P: 85% H_3PO_4 δ_{ref} = 0 ppm). All measurements were carried out at ambient temperature unless denoted otherwise. NMR signals were assigned using experimental data (e.g. chemical shifts, coupling constants, integrals where applicable).

IR spectra of crystalline samples were recorded on a Bruker Alpha II FT-IR spectrometer equipped with an ATR unit at ambient temperature under argon atmosphere. Relative intensities are reported according to the following intervals: weak (w, 0–33%), medium (m, 33–66%), strong (s, 66–100%).

Elemental analyses were obtained using a Leco Tru Spec elemental analyzer.

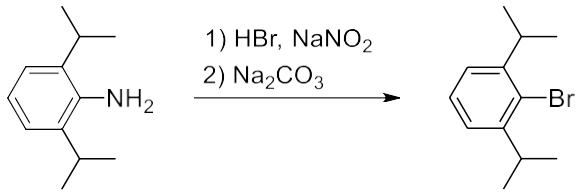
Mass spectra were performed by the LIKAT analytic department. Electron Impact (EI^+) spectra were performed at 70 eV using methane as the carrier gas, with time-of-flight (TOF) mass analyzer. Electrospray ionization (ESI^+) spectra were performed using a time-of-flight (TOF) mass analyzer. Data are reported in the form of m/z. High-resolution mass was obtained by using Waters Q-TOF Ultima ESI and Agilent 6230 ESI TOF LC/MS spectrometers.

UV-Vis spectra were acquired on a Mettler Toledo UV5iso spectrometer.

Cyclic Voltammetry (CV) were recorded using a Methrom Autolab PGSTAT204 potentiostat at 23 °C in THF containing 0.1 M $[N^nBu_4][PF_6]$ at scan rates of 100 $mV \cdot s^{-1}$. A standard three-electrode cell configuration was employed using a glassy carbon working electrode, a platinum wire counter electrode, and a silver wire serving as the reference electrode. Formal redox potentials are referenced to the $[FeCp_2]/[FeCp_2]^+$ redox couple.

2 Syntheses of starting materials

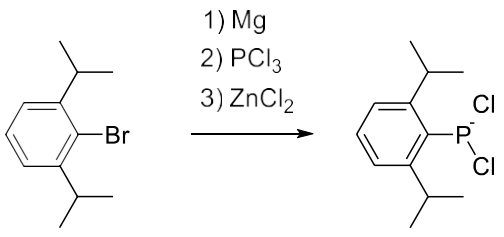
2.1 2,6-Diisopropylphenylbromine DipBr



DipBr is prepared according to a slightly modified literature procedure.[4] 2,6-Diisopropylaniline (30.2 g, 0.170 mmol) is added dropwise to concentrated hydrobromic acid (48%, 150 mL) with vigorous stirring. The pink suspension was cooled to −78 °C, and sodium nitrite (20.0 g, 289 mmol), dissolved in H_2O (90 mL) was added dropwise. The brownish suspension was stirred overnight at room temperature and neutralized with Na_2CO_3. The aqueous phase was extracted with Et_2O (3x 150 mL). The combined organic layers were washed with a saturated aqueous $Na_2S_2O_3$ solution. The organic layer was then dried with Na_2SO_4 and after filtration the solvent was removed *in vacuo*. Fractional distillation of the remaining reddish oil at 0.01 mbar yielded the product as a light yellow liquid (boiling temperature: 65 °C). Yield: 25.5 g (0.106 mol, 62%).

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.10 – 6.90 (m, 3H, $C_{Ar}H$), 3.59 (hept, $^3J_{HH}$ = 6.9, 2H, $CH(CH_3)_2$), 1.14 (d, $^3J_{HH}$ = 6.9 Hz, 12H, $CH(CH_3)_2$) ppm.

2.2 2,6-Diisopropylphenyldibromophosphine $DipPCl_2$



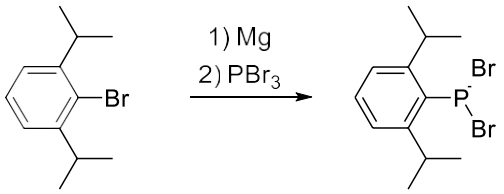
$DipPCl_2$ was prepared according to a slightly modified literature procedure.[5]

Magnesium turnings (1.46 g, 60 mmol) were suspended in THF (80 mL) and 2,6-diisopropyl-1-bromobenzene (9.85 g, 40.84 mmol) was added slowly at room

temperature and stirring was continued for 1 h. Afterwards the mixture was heated to reflux for an additional 2 h resulting in a brownish solution. To a solution of PCl_3 (10.5 mL, 120 mmol) in toluene (50 mL) the Grignard reagent was added dropwise *via* a filter cannula at −78 °C and the mixture was allowed to warm to room temperature overnight. Afterwards the solvent was removed from the reaction mixture *in vacuo* and the yellowish, sticky residue ($DipPX_2$) was extracted with *n*-hexane and subsequently the *n*-hexane was distilled off from the filtrate. The remaining yellow solid was dissolved in THF (80 mL). Anhydrous $ZnCl_2$ (27.25 g, 200 mmol) was added to this solution and stirring at room temperature was continued overnight. Subsequently, thereaction was filtered over a celite-padded frit (G3), the filtrate was evaporated and extracted with fresh *n*-hexane (50 mL), resulting in a clear pale yellow solution. From this solution *n*-hexane was distilled off, affording $DipPCl_2$ (3.82 g, 14.5 mmol, 36 %) as pale yellow oil.

^{1}H NMR (C_6D_6, 300 MHz): δ = 7.10 (m, 1H), 6.93-6.97 (m, 2H), 4.14 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, C*H*$(CH_3)_2$), 1.14 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3)_2$). **^{31}P NMR** (C_6D_6, 121.51 MHz): δ = 164.2 ppm.

2.3 2,6-Diisopropylphenyldibromophosphine $DipPBr_2$

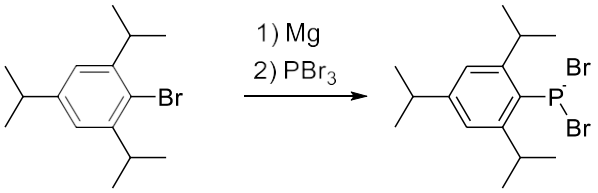


$DipPBr_2$ was prepared according to a slightly modified literature procedure.[5]

Magnesium turnings (1.46 g, 60 mmol) were suspended in THF (80 mL) and 2,6-diisopropyl-1-bromobenzene (9.85 g, 40.84 mmol) was added slowly at room temperature and stirring was continued for 1 h. Afterwards the mixture was heated to reflux for additional 4 h resulting in a brownish solution. To a solution of PBr_3 (3.9 mL, 41 mmol) in THF (50 mL) the Grignard reagent was added dropwise *via* a filter cannula at −78°C and the mixture was allowed to warm to room temperature overnight. Afterwards, the solvent was removed from the reaction mixture *in vacuo* and the yellowish, sticky residue was extracted with *n*-hexane and subsequently the solvent was distilled off from the filtrate. $DipPBr_2$ (9.25 g, 26 mmol, 63 %) is obtained as a yellow oil.

^{1}H NMR (C_6D_6, 300 MHz) δ = 7.13 – 6.91 (m, 3H, C_{Ar}*H*), 4.25 – 4.08 (m, 2H, C*H*$(CH_3)_2$), 1.17 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3)_2$) ppm. **^{31}P NMR** (C_6D_6, 122 MHz) δ = 151.01 ppm.

2.4 2,4,6-Triisopropylphenyldibromophosphine TipPBr$_2$

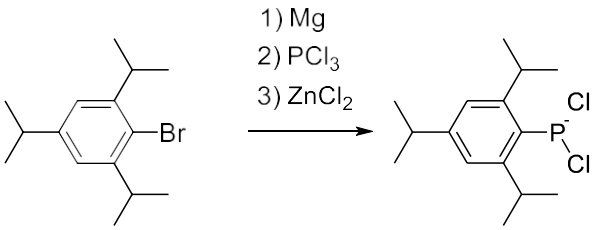


TipPBr$_2$ was prepared according to the literature procedure.[5]

Magnesium turnings (0.27 g, 11 mmol) were suspended in THF (50 mL) and 2,4,6-triisopropyl-1-bromobenzene (TipBr) (2.83 g, 10 mmol) was added slowly at room temperature and stirring was continued for 1 h. Afterwards, the mixture was heated to reflux for 1 h, resulting in a brownish solution. To a solution of PBr_3 (1.42 mL, 15 mmol) in THF (15 mL) the Grignard reagent was added dropwise *via* a filter cannula at −78 °C and the mixture was allowed to warm to room temperature overnight. Afterwards, the solvent was removed from the reaction mixture *in vacuo* and the yellowish residue was extracted with *n*-hexane, resulting in a clear yellow solution, which was concentrated to incipient crystallization and allowed to stand at 5 °C for a period of 24 h, resulting in the deposition of yellow needles of TipPBr$_2$ (2.01 g, 5.1 mmol, 51%).

^{1}H NMR (C_6D_6, 300.13 MHz): δ = 7.03 (d, J_{PH} = 3.6 Hz, 2H, $C_{Ar}H$), 4.23 (m, 2H, *o*-C*H*$(CH_3)_2$), 2.61 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-C*H*$(CH_3)_2$), 1.24 (d, $^3J_{HH}$ = 6.4 Hz, 12H, o-CH(C*H*$_3)_2$), 1.08 (d, $^3J_{HH}$ = 6.9 Hz, 6H, p-CH(C*H*$_3)_2$) ppm. **^{31}P NMR** (C_6D_6, 121.51 MHz,): δ = 151.8 ppm.

2.5 2,4,6-Triisopropylphenyldichlorophosphine TipPCl$_2$



TipPCl$_2$ was prepared according to a modified the literature procedure.[5]

Magnesium turnings (0.81 g, 33 mmol) were suspended in THF (80 mL) and 2,6-triisopropyl-1-bromobenzene (TipBr) (8.49 g, 30 mmol) was added slowly at room temperature and stirring was continued for 1 h. Afterwards the mixture was heated to reflux for additional 4 h resulting in a brownish solution. To a solution of PCl_3 (5.25 mL, 60 mmol) in THF (100 mL) the Grignard reagent was added dropwise *via* a filter cannula

at −78°C and the mixture was allowed to warm to room temperature overnight. Afterwards, the solvent was removed from the reaction mixture *in vacuo* and the yellowish, sticky residue ($TipPX_2$) was extracted with *n*-hexane and subsequently the *n*-hexane was distilled off from the filtrate. The remaining yellow solid was dissolved in THF (100 mL). Anhydrous $ZnCl_2$ (13.625 g, 100 mmol) was added to this solution and stirring at room temperature was continued overnight. Subsequently, the reaction was filtered over a celite-padded frit (G3), the volatiles were evaporated from the filtrate and the residue was extracted with fresh *n*-hexane (75 mL), resulting in a clear pale yellow solution. From this solution, *n*-hexane was distilled off, affording $TipPCl_2$ (4.522g, 14.82 mmol, 49%) as an off-white crystalline solid.

^{1}H NMR (C_6D_6, 400 MHz) δ = 7.06 (d, $^4J_{PH}$ = 3.5 Hz, 2H, $C_{Ar}H$), 4.21 (hd, $^3J_{HH}$ = 6.7 Hz, J_{PH} 4.7 Hz, 2H, o-C*H*$(C_3)_2$), 2.65 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, p-C*H*$(CH_3)_2$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 12H, o-CH(C*H*$_3)_2$), 1.10 (d, $^3J_{HH}$ = 7.0 Hz, 6H, p-CH(C*H*$_3)_2$) ppm. **^{31}P NMR** (C_6D_6, 162 MHz) δ = 164.84 ppm.

2.6 Bis-(2,4,6-trimethylphenyl)halophosphane (Mes_2PX)

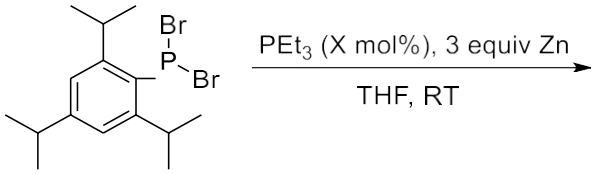
MesBr (10.0 g, 50.2 mmol) in THF (100 mL) was added dropwise to a suspension of magnesium turnings (1.34 g, 55 mmol) in THF (100 mL) at room temperature. The Grignard reaction started after ca. 30 minutes and was cooled to 0 °C. Once the vigorous reaction ceased the mixture was refluxed for 4 h and the mixture was subsequently cooled to room temperature. The brownish clear solution was filtered through a canula fitted with a glass microfiber filter. Afterwards the filtrate solution was cooled to −78 °C and PCl_3 (6.9 g, 50.2 mmol) was added dropwise. The mixture was allowed to warm to room temperature overnight and the volatiles were evaporated *in vacuo*. The remaining solid mixture was extracted with *n*-hexane (100 mL) and the filtrate was then concentrated to incipient crystallization. Storage at −30 °C for 24 h afforded Mes_2PX as a pale yellow crystalline solid (3.8 g, $M_{avg.}$ = 324.56 g/mol; X = Cl 55.3%, Br 44.7%, 11.71 mmol, 46.6 % based on MesBr).

^{1}H NMR (C_6D_6, 400 MHz) δ = 6.60 (m, 2H, $C_{Ar}H$), 2.4-2.35 (m, 6H, o-C_3), 2.01 (3H, p-C*H*$_3$) ppm. **^{31}P NMR** (C_6D_6, 162 MHz) δ = 85.4 (Mes_2PCl), 74.9 (Mes_2PBr) ppm.

3 Catalytic Trial Reactions

3.1 Catalysis with PEt_3

3.1.1 Optimisation of the PEt_3 catalysed reductive coupling of $TipPBr_2$

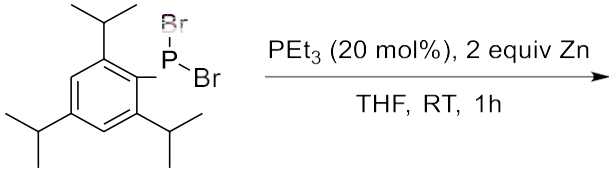


For each run, a suspension of 100 mg (0.25 mmol) $TipPBr_2$ and 49 mg (0.75 mmol) zinc powder in THF (5 mL) was prepared. This suspension was cooled to −78 °C and 70 µL (0.05 mmol, 20 mol%), 35 µL (0.025 mmol, 10 mol%) or 18 µL (0.0125 mmol, 5 mol%) of a 0.71 M stock solution of PEt_3 in THF were added, respectively. The reaction mixture was stirred at −78 °C or at room temperature. For the NMR studies, 0.5 mL aliquots of each reaction were taken. The solvent was evaporated *in vacuo* and the solid residue was taken up in C_6D_6 (0.5 mL). From the obtained $^{31}P\{1H\}$ NMR spectra the proportions of remaining $TipPBr_2$ (A) and the products (B, C, D, E) formed are obtained by integrating the signals and normalization.

Table S2. Catalytic trials using x mol% of PEt_3 as a catalyst in the reductive coupling of $TipPBr_2$ in THF at room temperature using Zn dust as sacrificial reductant (best entries highlighted in yellow). All runs have been duplicated.

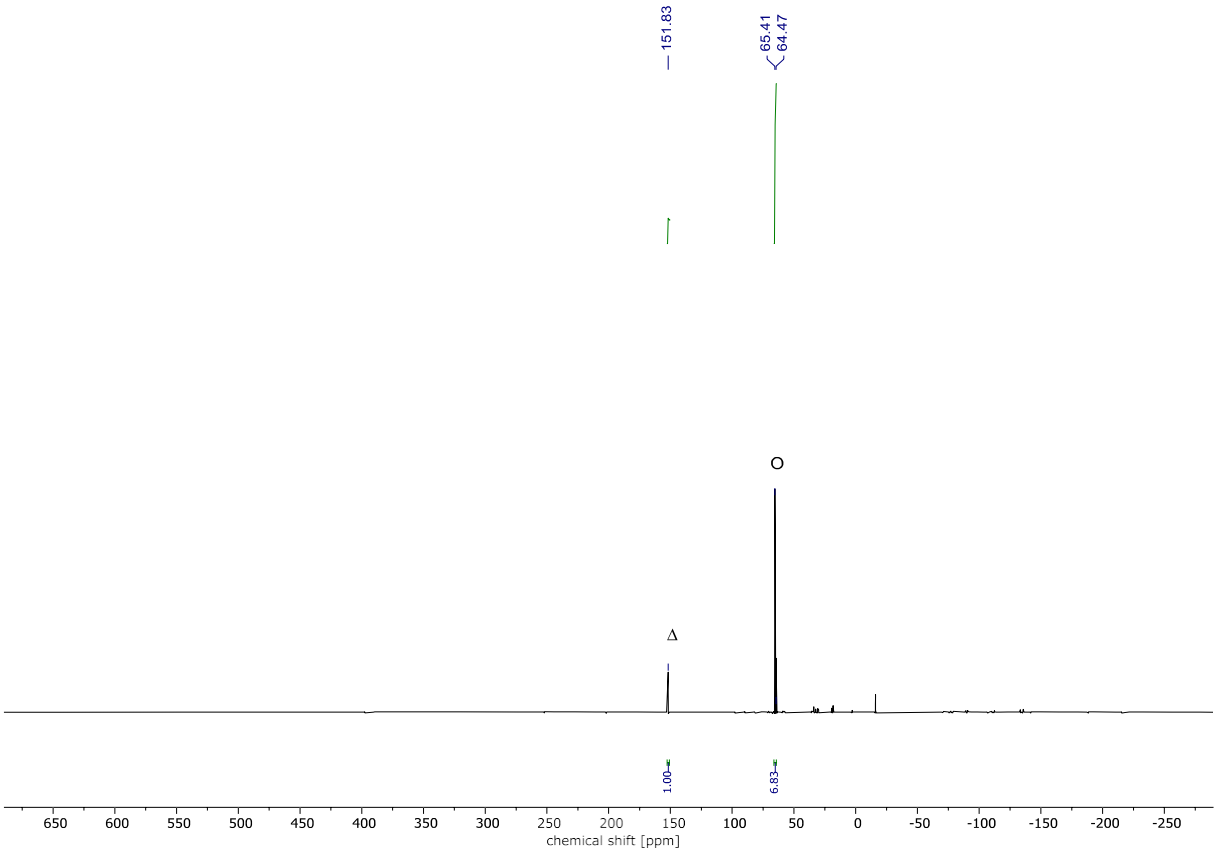
PEt_3 [mol%]	**T [°C]**	**T [h]**	**$TipPBr_2$ [%]**	**$(TipPBr)_2$ [%]**	**$(PTip)_2$ [%]**	**$(PTip)_3$ [%]**	**$(PTip)_4$ [%]**
20	-78 °C	1	64	36	0	0	0
20	r.t.	1	23	77	0	0	0
20	r.t.	16	0	0	36	41	23
10	r.t.	1	54	46	0	0	0
10	r.t.	3	31	69	0	0	0
5	r.t.	1	100	0	0	0	0
5	r.t.	16	42	58	0	0	0

3.1.2 $TipPBr_2$ + PEt_3 (20 mol%)

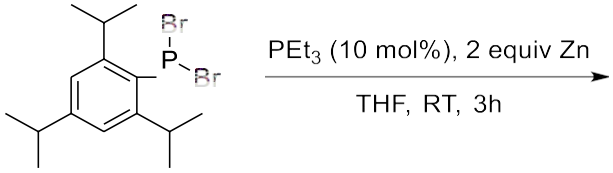


$TipPBr_2$ (0.100 g, 0.26 mmol) and zinc (0.049 g, 0.75 mmol) were dissolved in THF (2.5 mL). PEt_3 (0.5 ml, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 1 h at room temperature. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S1: ^{31}P NMR spectrum of the reaction of $TipPBr_2$ with PEt_3 (20 mol%, 3 eq. Zn, 1 h). Δ $TipPBr_2$, O $(TipPBr)_2$.

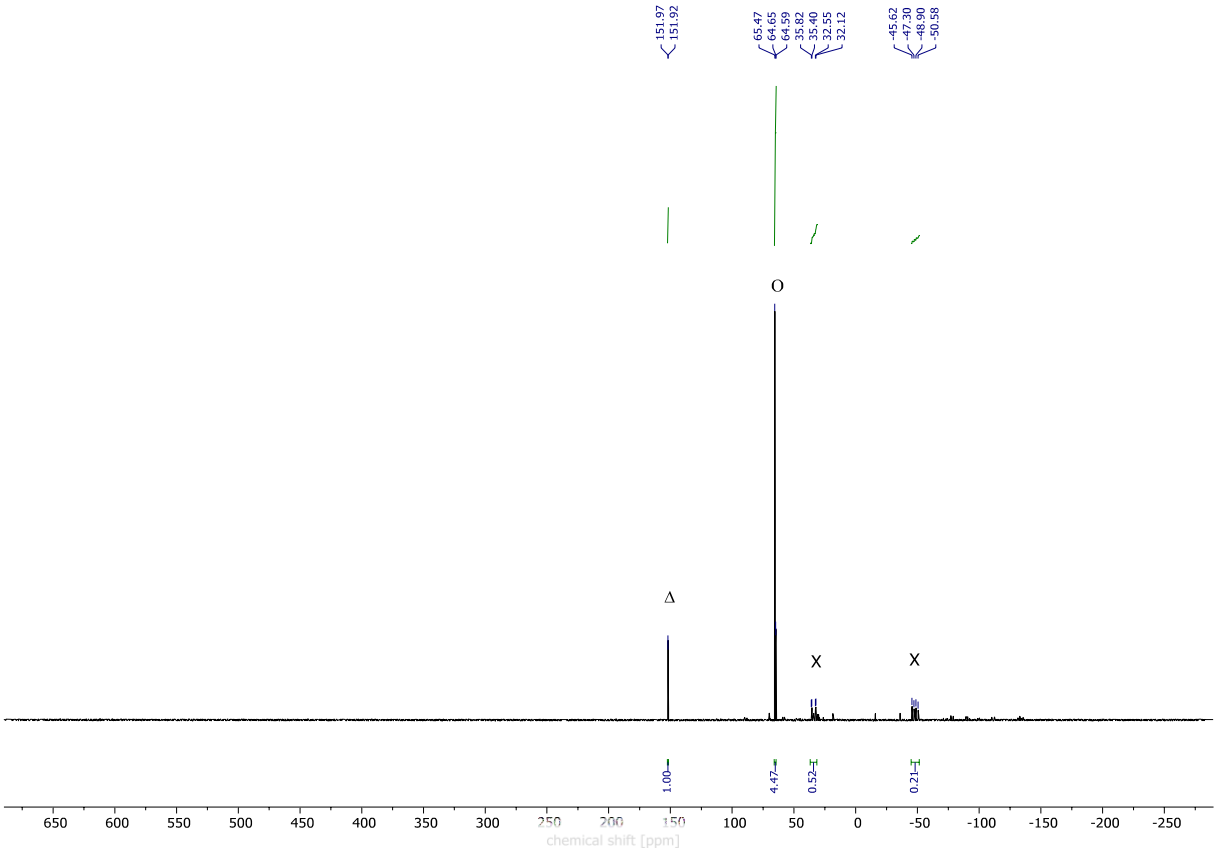


3.1.3 $TipPBr_2$ + PEt_3 (10 mol%)

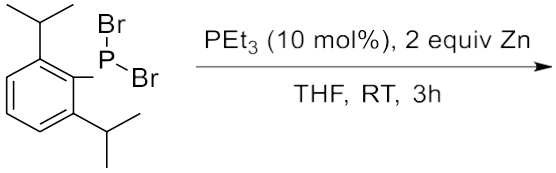


$TipPBr_2$ (197 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). PEt_3 (0.5 ml, 0.1 M in THF) is slowly added to the stirring solution at room temperature. The mixture is allowed to stir under the exclusion of light for 3 hrs. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured without delay.

Figure S2: ^{31}P NMR spectrum of the reaction of $TipPBr_2$ with PEt_3. Δ $TipPBr_2$, O $(TipPBr)_2$, X unidentified side products.

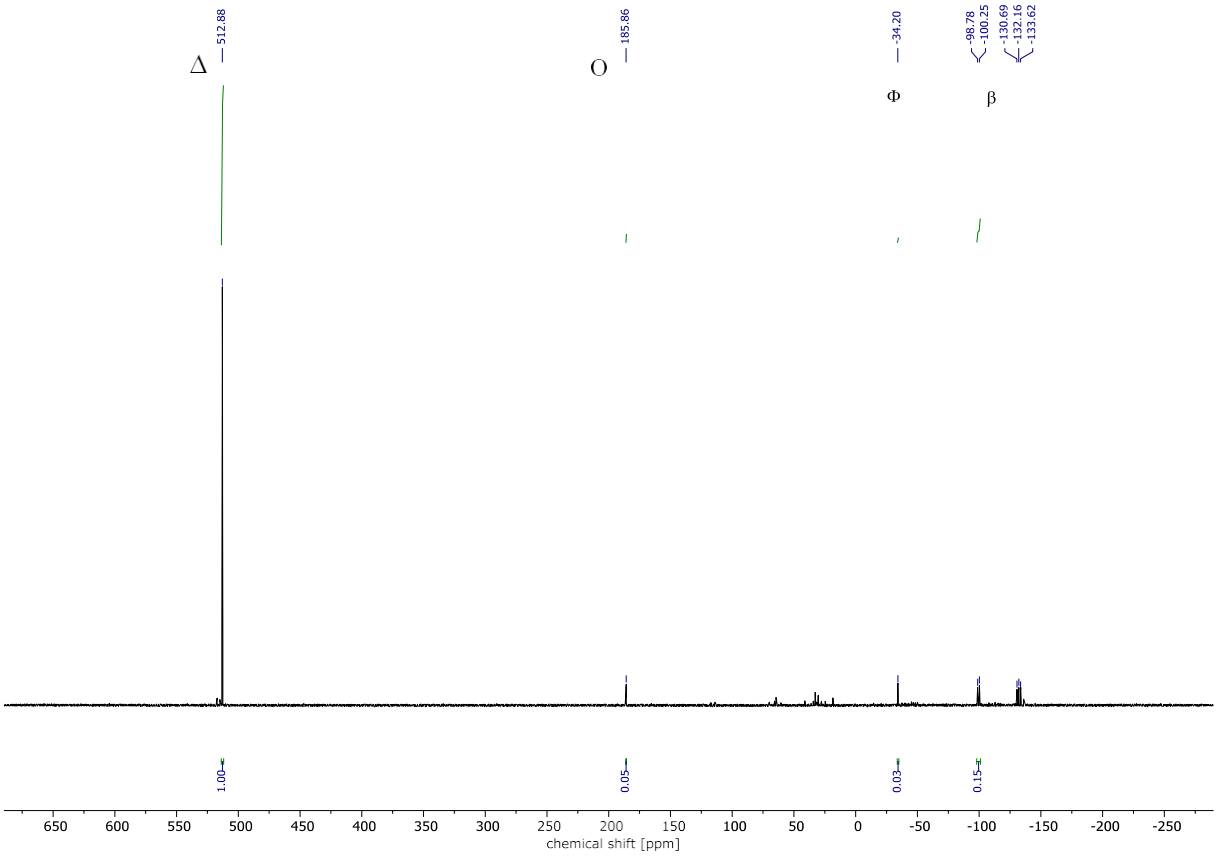


3.1.4 $DipPBr_2$ + PEt_3 (10 mol%)

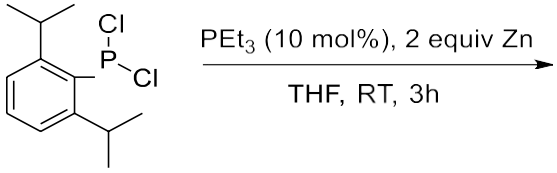


To $DipPBr_2$ (176 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) THF (2 mL) was added. PEt_3 (0.5 ml, 0.1 M in THF, 0.05 mmol) is slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S3: ^{31}P NMR spectrum of the reaction of $DipPBr_2$ with PEt_3 (10 mol%, 2 eq. Zn, 3 h). Δ Dip_2P_2, O unidentified side product, Φ Dip_4P_4, β Dip_3P_3.

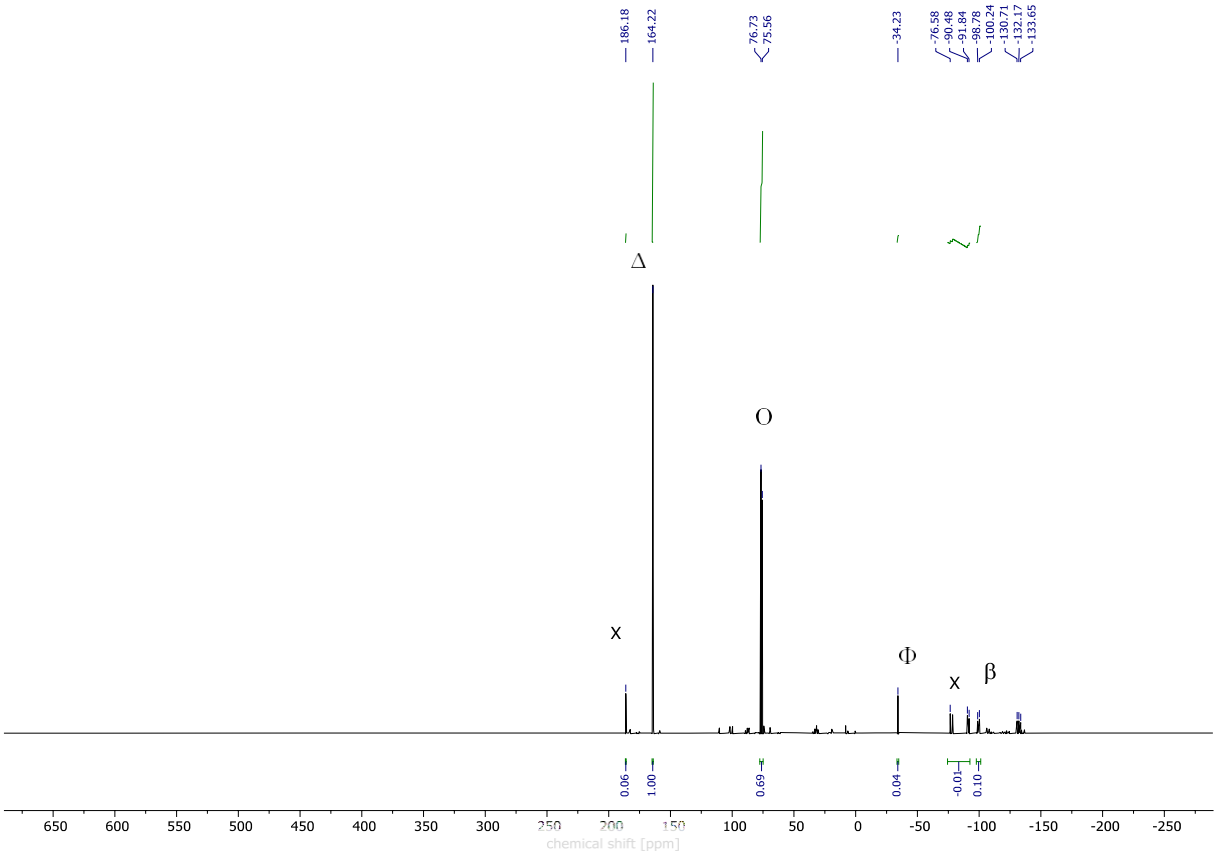


3.1.5 $DipPCl_2$ + PEt_3 (10 mol%)

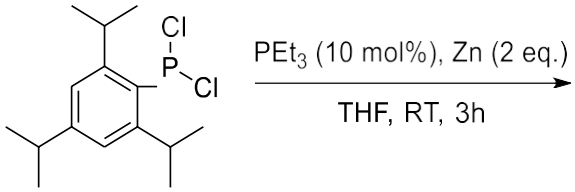


To $DipPCl_2$ (132 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) THF (2 mL) was added. PEt_3 (0.5 ml, 0.1 M in THF, 0.05 mmol) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S4: ^{31}P NMR spectrum of the reaction of $DipCl_2$ with PEt_3. Δ $DipPCl_2$, O $(DipPCl)_2$, Φ Dip_4P_4, β Dip_3P_3, X unidentified side products.

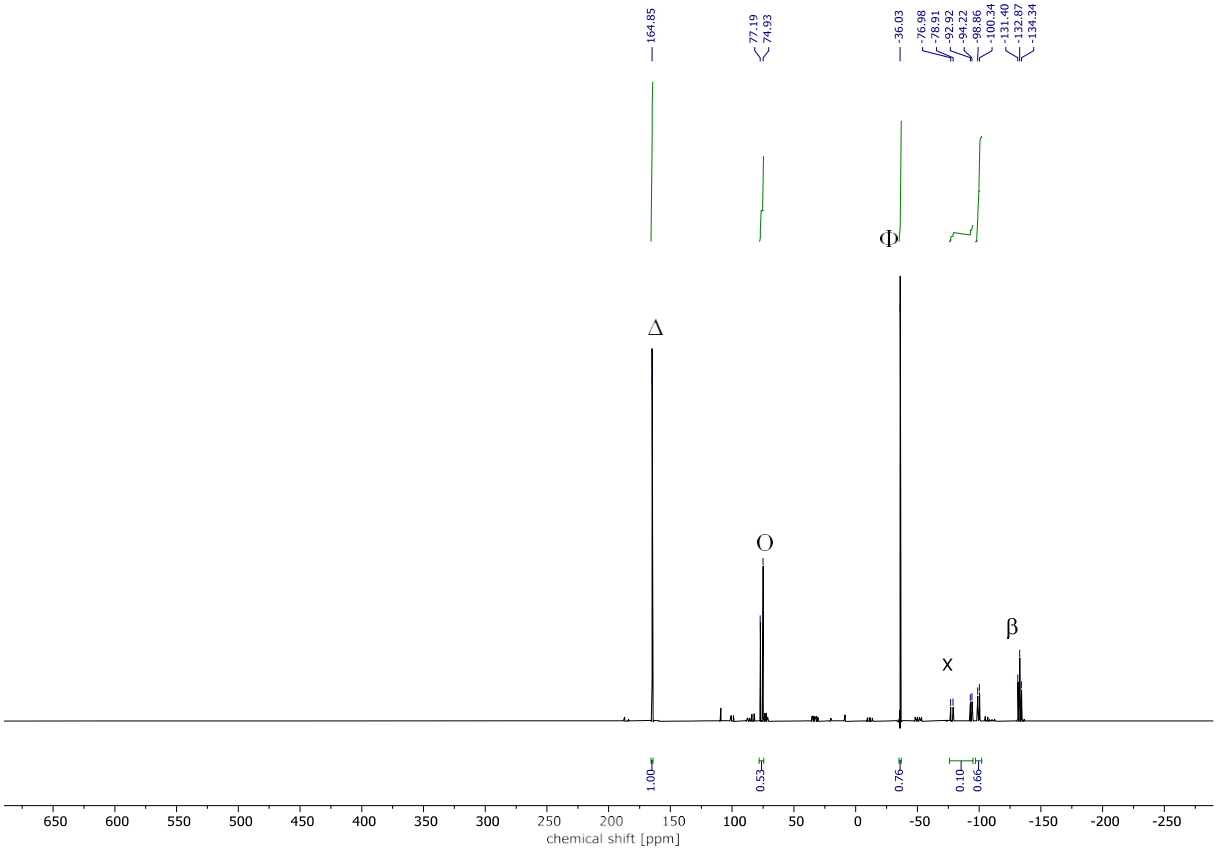


3.1.6 $TipPCl_2$ + PEt_3 (10 mol%)

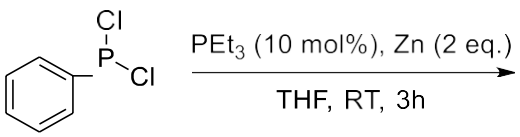


To $TipPCl_2$ (153 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) THF (2 mL) was added. PEt_3 (0.5 mL, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S5: ^{31}P NMR spectrum of the reaction of $TipCl_2$ with PEt_3. Δ $TipPCl_2$, O $(TipPCl)_2$, Φ Tip_4P_4, β Tip_3P_3, X unidentified side products.



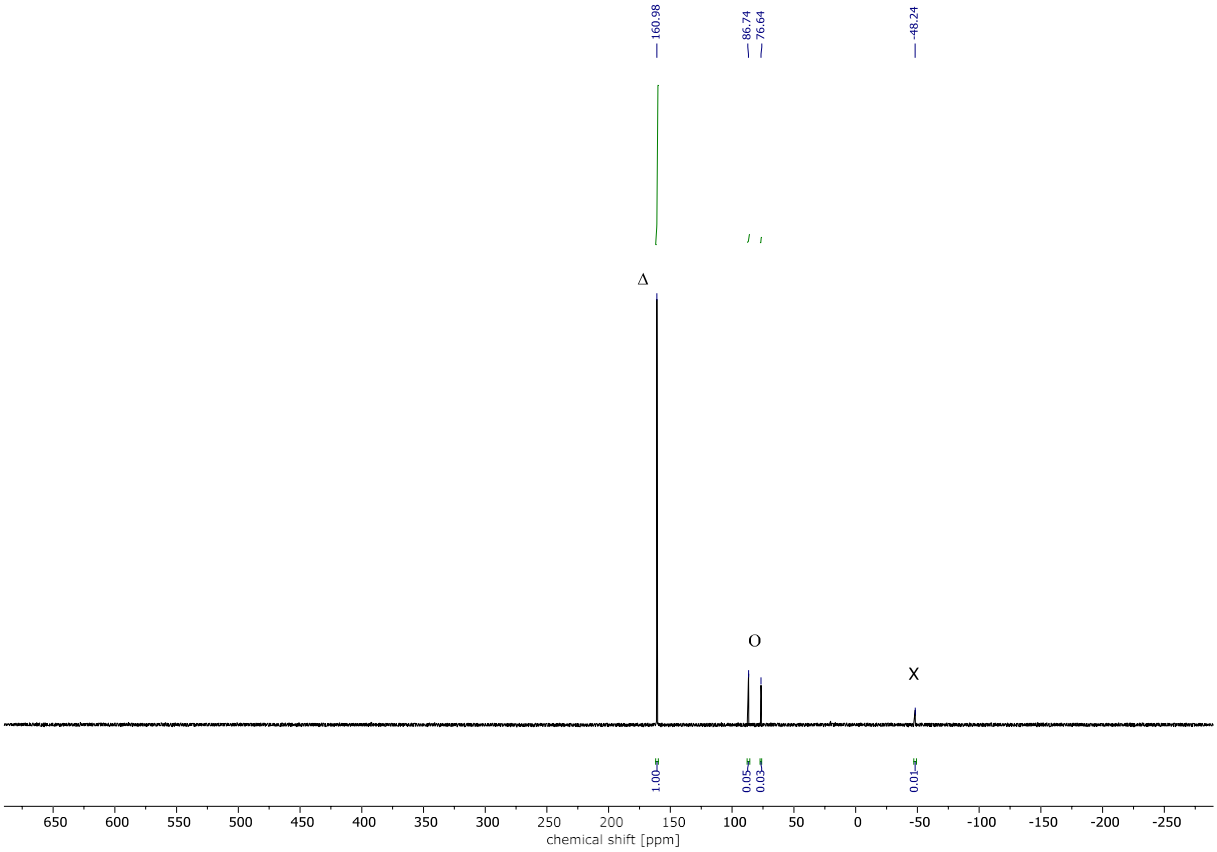
3.1.7 $PhPCl_2$ + PEt_3 (10 mol%)



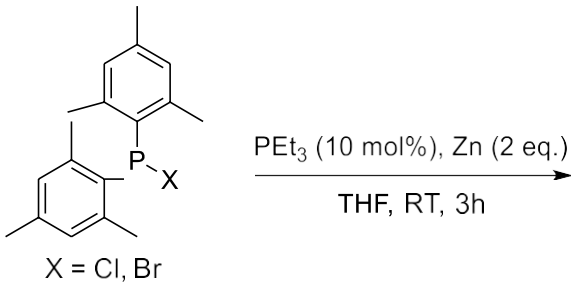
To $PhPCl_2$ (84 mg, 0.47 mmol) and zinc (65.0 mg, 1 mmol) THF (2.5 mL) was added. PEt_3 (0.47 mL, 0.1 M in THF) was slowly added to the stirring solution at room temperature.

The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S6: ^{31}P NMR spectrum of the reaction of $PhPCl_2$ with PEt_3. Δ $PhPCl_2$, O $(PhPCl)_2$, X unidentified side products.

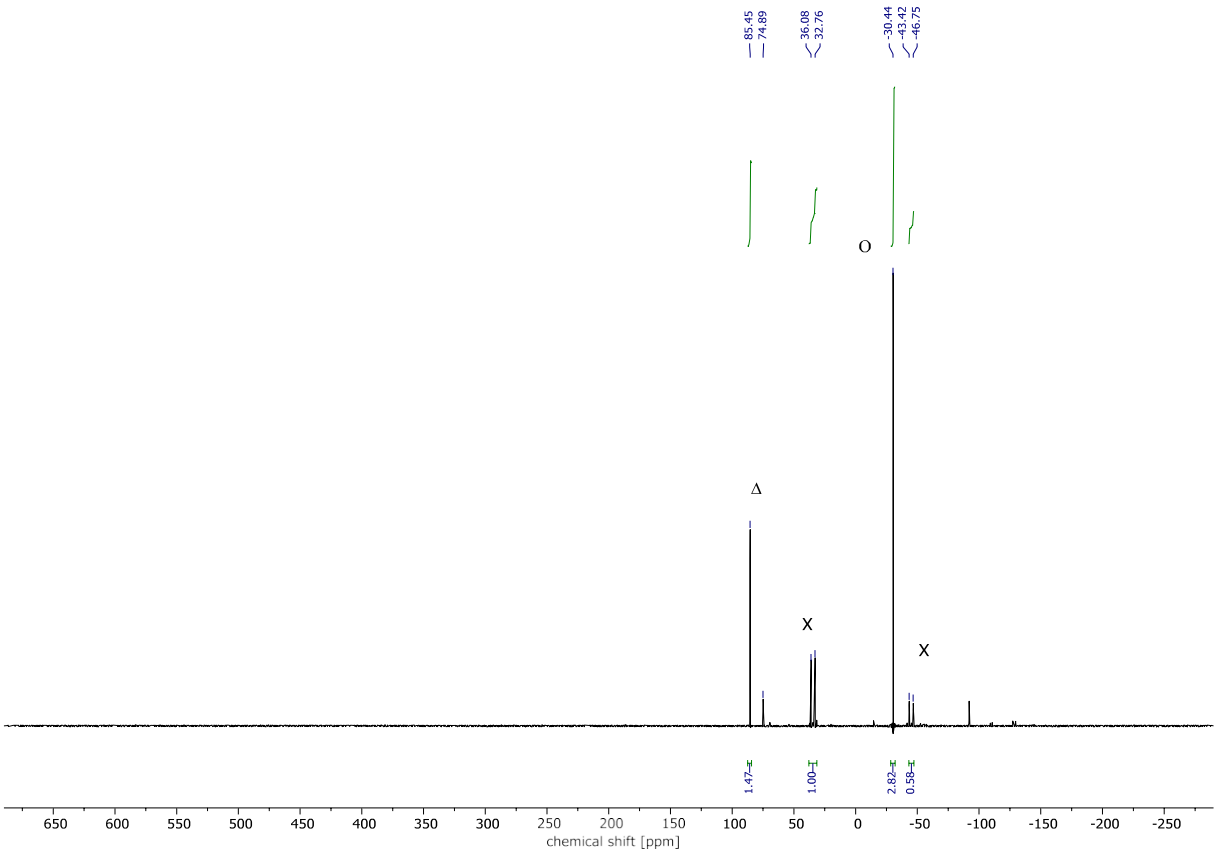


3.1.8 Mes_2PX (X = Cl, Br) + PEt_3 (10 mol%)



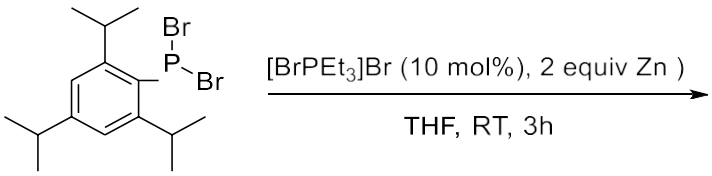
To Mes_2PX (X = Cl, Br) (119 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) THF (2 mL) was added. PEt_3 (0.5 mL, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S7: ^{31}P NMR spectrum of the reaction of Mes_2PX with PEt_3. Δ Mes_2PX, O $(Mes_2P)_2$, X unidentified side products.



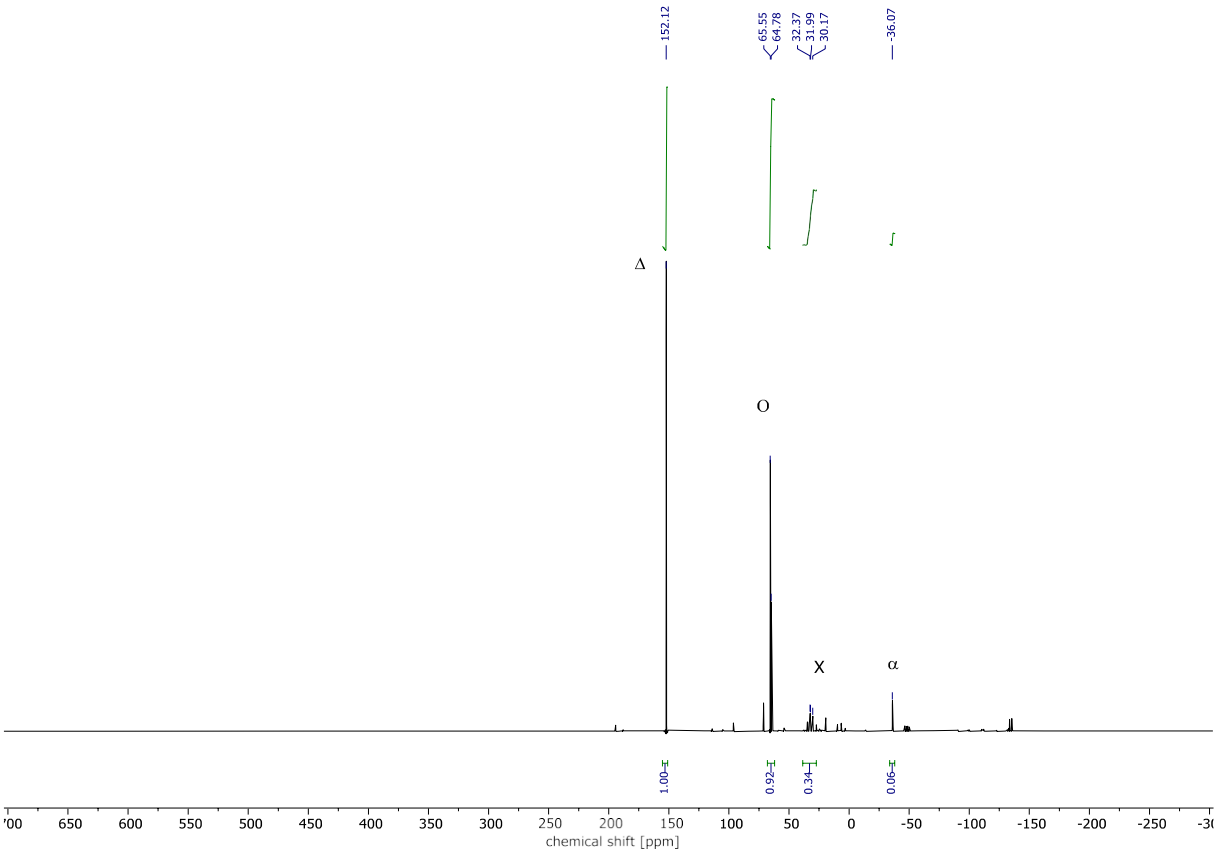
3.2 Catalysis with $[BrPEt_3]Br$

3.2.1 $TipPBr_2$ + $[BrPEt_3]Br$ (10 mol%)

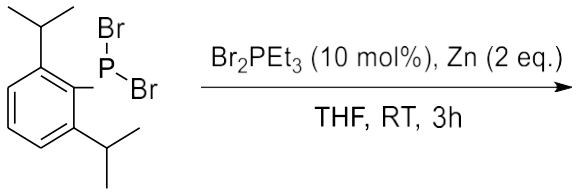


$TipPBr_2$ (0.197 g, 0.5 mmol), $[BrPEt_3]Br$ (0.014 mg, 0.05 mmol) and zinc (0.064 mg, 1 mmol) were dissolved in THF (2.5 mL). The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S8: ^{31}P NMR spectrum of the reaction of $TipPBr_2$ with Br_2PEt_3. Δ $TipPBr_2$, O $(TipPBr)_2$, α Tip_4P_4, X unidentified side products.

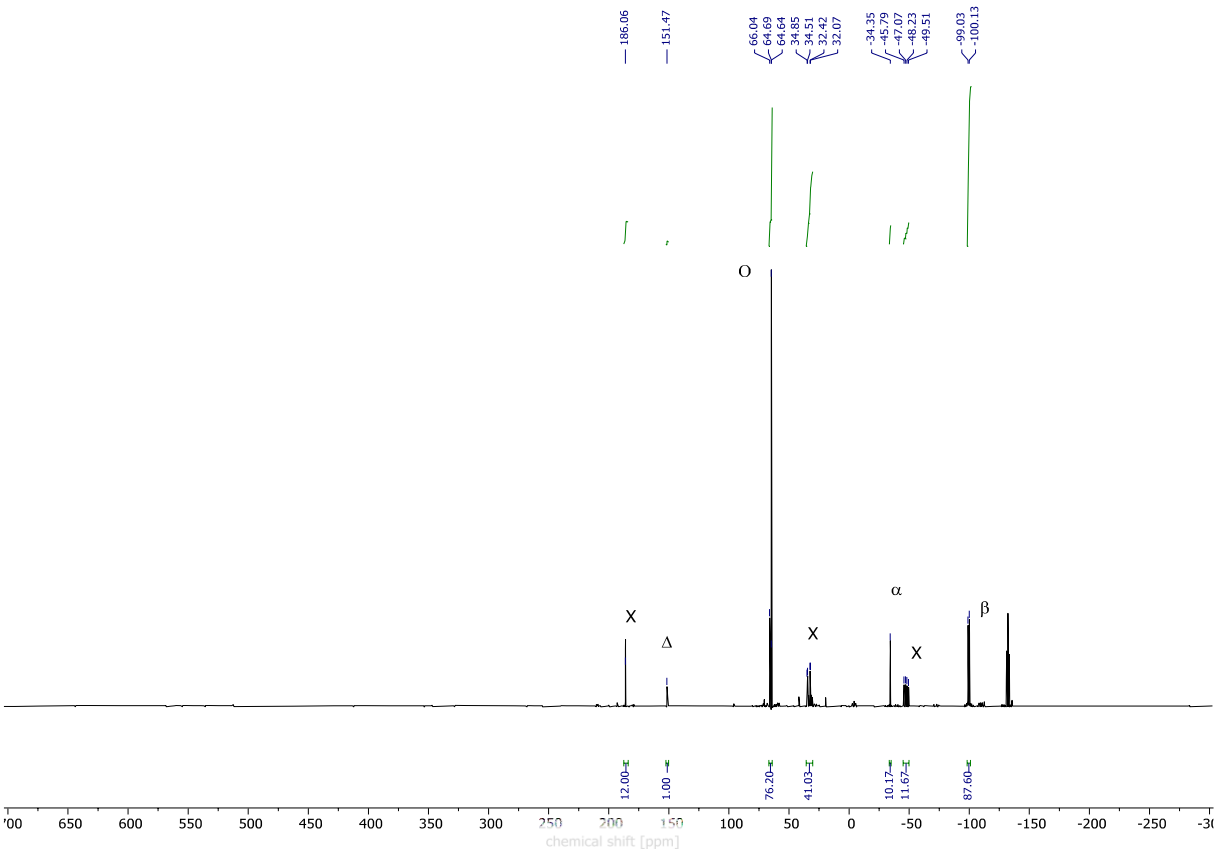


3.2.2 $DipPBr_2$ + $[BrPEt_3]Br$ (10 mol%)

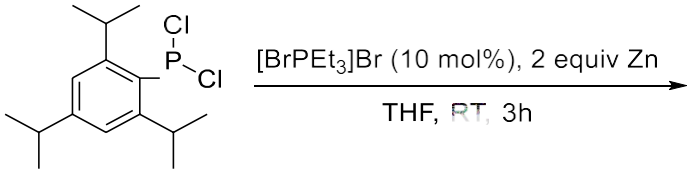


$DipPBr_2$ (198 mg, 0.56 mmol), $[BrPEt_3]Br$ (15.5 mg, 0.056 mmol) and zinc (70 mg, 1.1 mmol) were dissolved in THF (2.5 mL). The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S9: ^{31}P NMR spectrum of the reaction of $DipPBr_2$ with Br_2PEt_3. Δ $DipPBr_2$, O $(DipPBr)_2$, α Dip_4P_4, β Dip_3P_3, X unidentified side products.

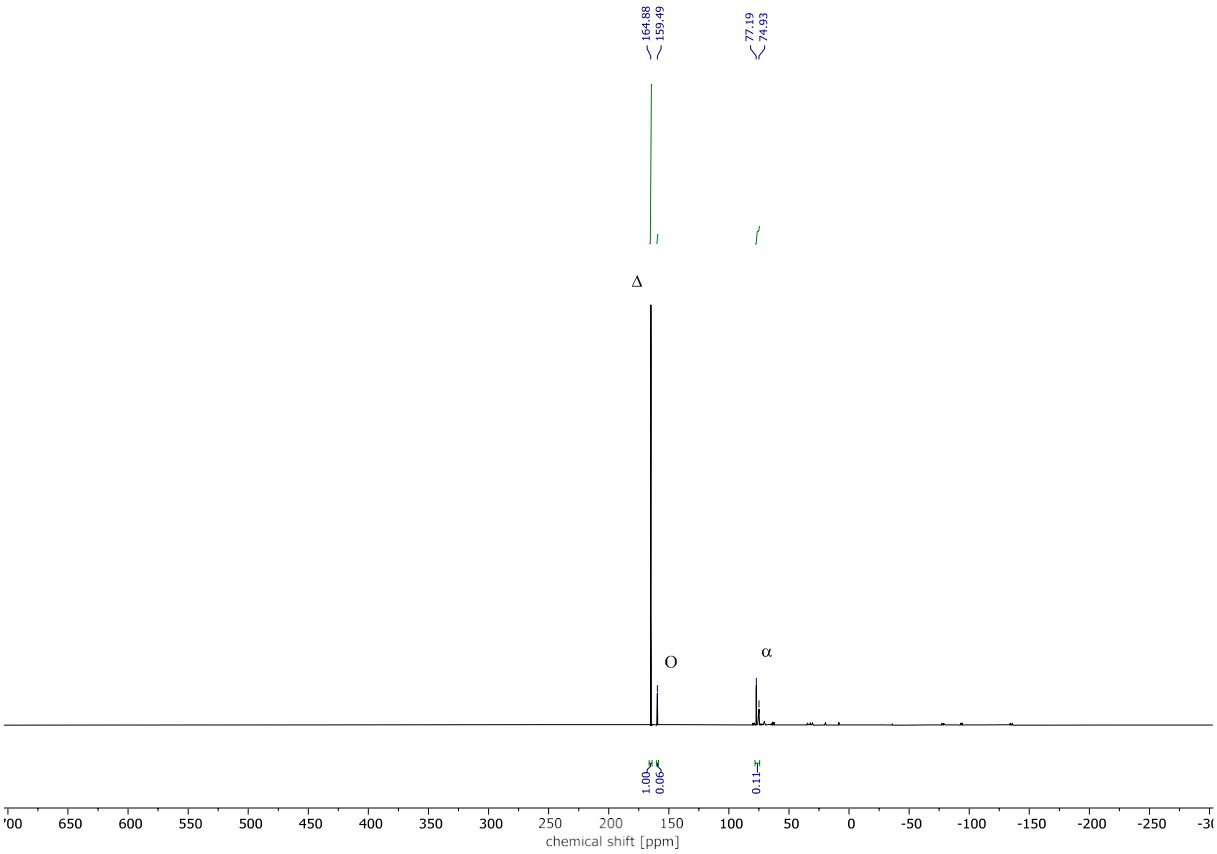


3.2.3 $TipPCl_2$ + $[BrPEt_3]Br$ (10 mol%)

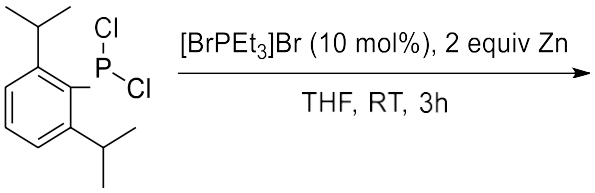


$TipPCl_2$ (176 mg, 0.5 mmol), $[BrPEt_3]Br$ (13.9 mg, 0.05 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S10: ^{31}P NMR spectrum of the reaction of $TipPCl_2$ with $[BrPEt_3]Br$. Δ $TipPCl_2$, O TipPBrCl, α $(TipPCl)_2$.

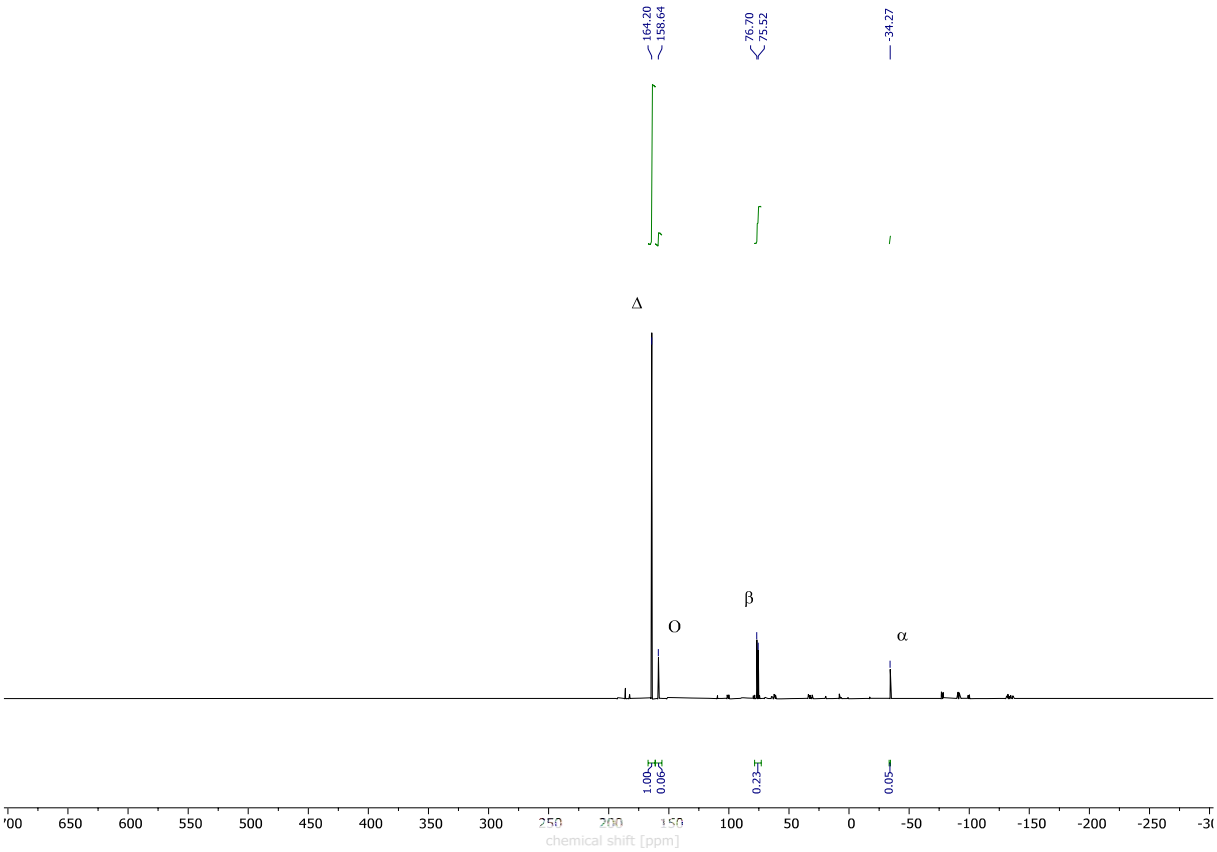


3.2.4 $DipPCl_2$ + $[BrPEt_3]Br$ (10 mol%)



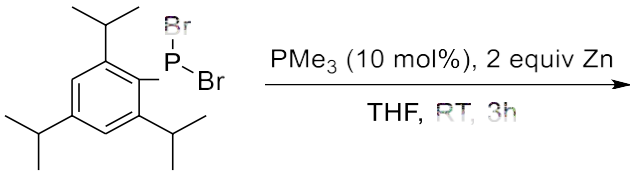
$DipPCl_2$ (0.126 g, 0.48 mmol), $[BrPEt_3]Br$ (0.013 mg, 0.048 mmol) and zinc (0.064 g, 1 mmol) were dissolved in THF (2.5 mL). The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S11: ^{31}P NMR spectrum of the reaction of $DipPCl_2$ with $[BrPEt_3]Br$. Δ $DipPCl_2$, O DipPBrCl, β $(DipPCl)_2$ and α Dip_4P_4.



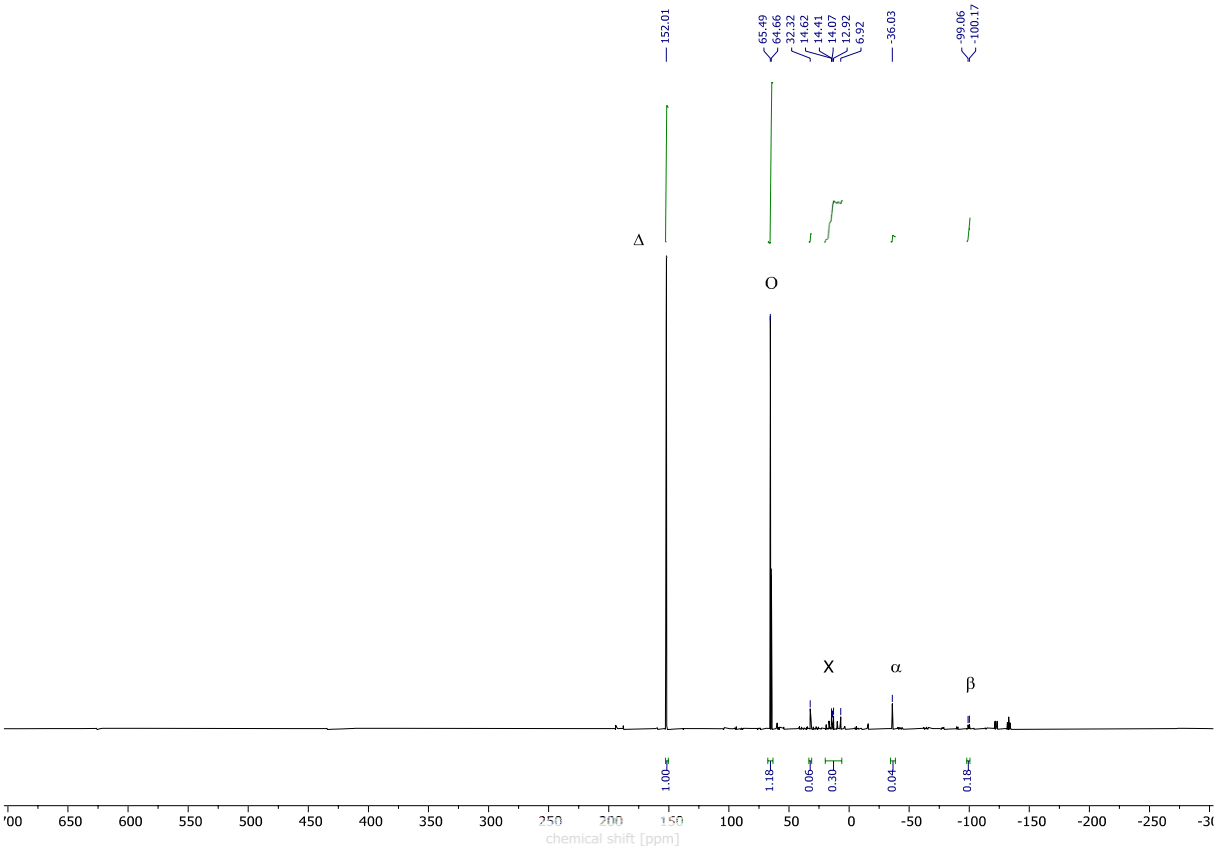
3.3 Catalysis with PMe_3

3.3.1 $TipPBr_2$ + PMe_3 (10 mol%)

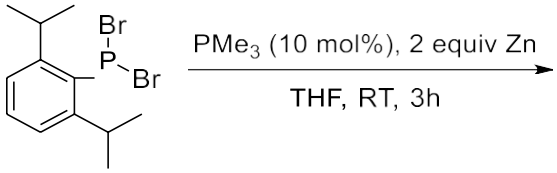


$TipPBr_2$ (197 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). PMe_3 (0.5 ml, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S12: ^{31}P NMR spectrum of the reaction of $TipPBr_2$ with PMe_3. Δ $TipPBr_2$, O $(TipPBr)_2$, α Tip_4P_4, β Tip_3P_3, X unidentified side products.

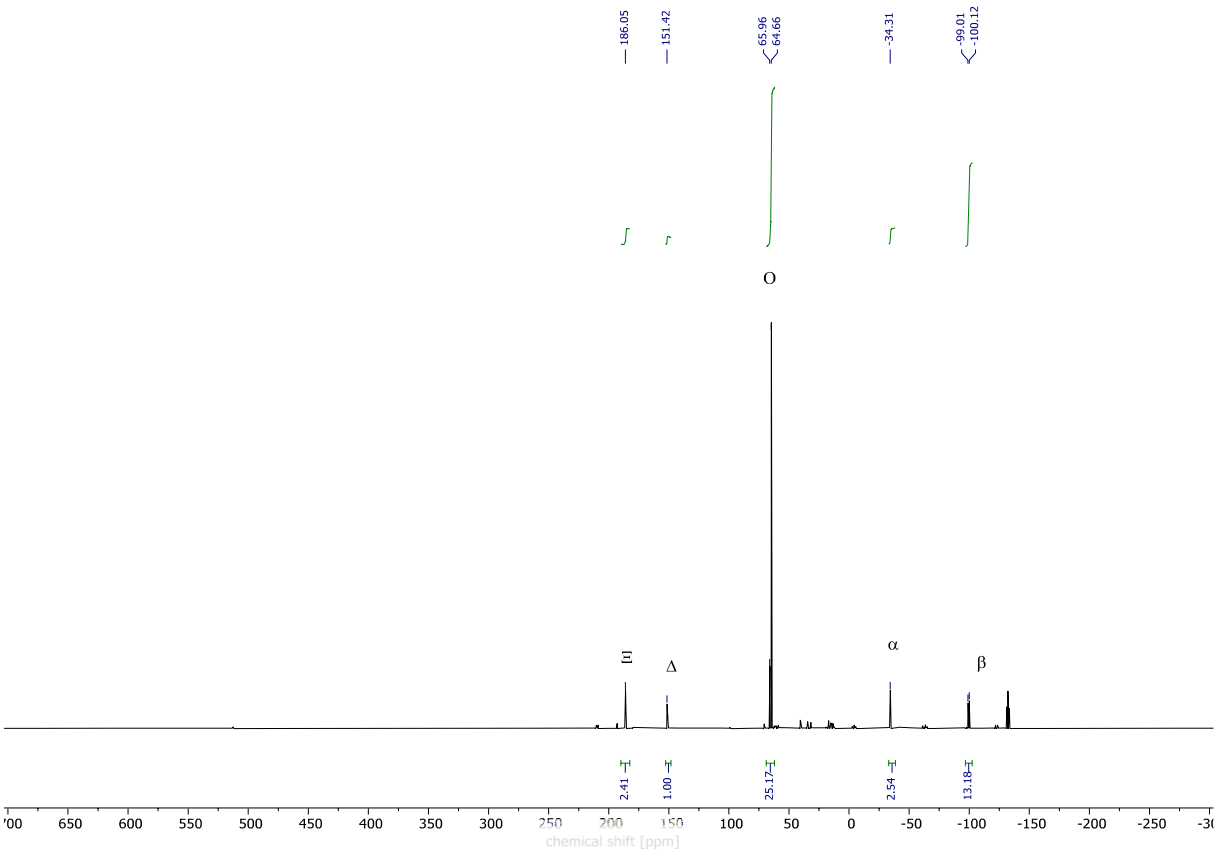


3.3.2 $DipPBr_2$ + PMe_3 (10 mol%)

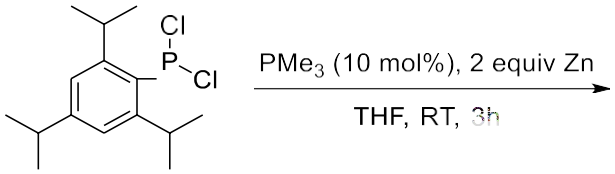


$DipPBr_2$ (204 mg, 0.58 mmol) and zinc (73.6 mg, 1.16 mmol) were dissolved in THF (2.5 mL). PMe_3 (0.58 ml, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S13: ^{31}P NMR spectrum of the reaction of $DipPBr_2$ with PMe_3. Δ $DipPBr_2$, O $(DipPBr)_2$, α Dip_4P_4, β Dip_3P_3, X unidentified side products.

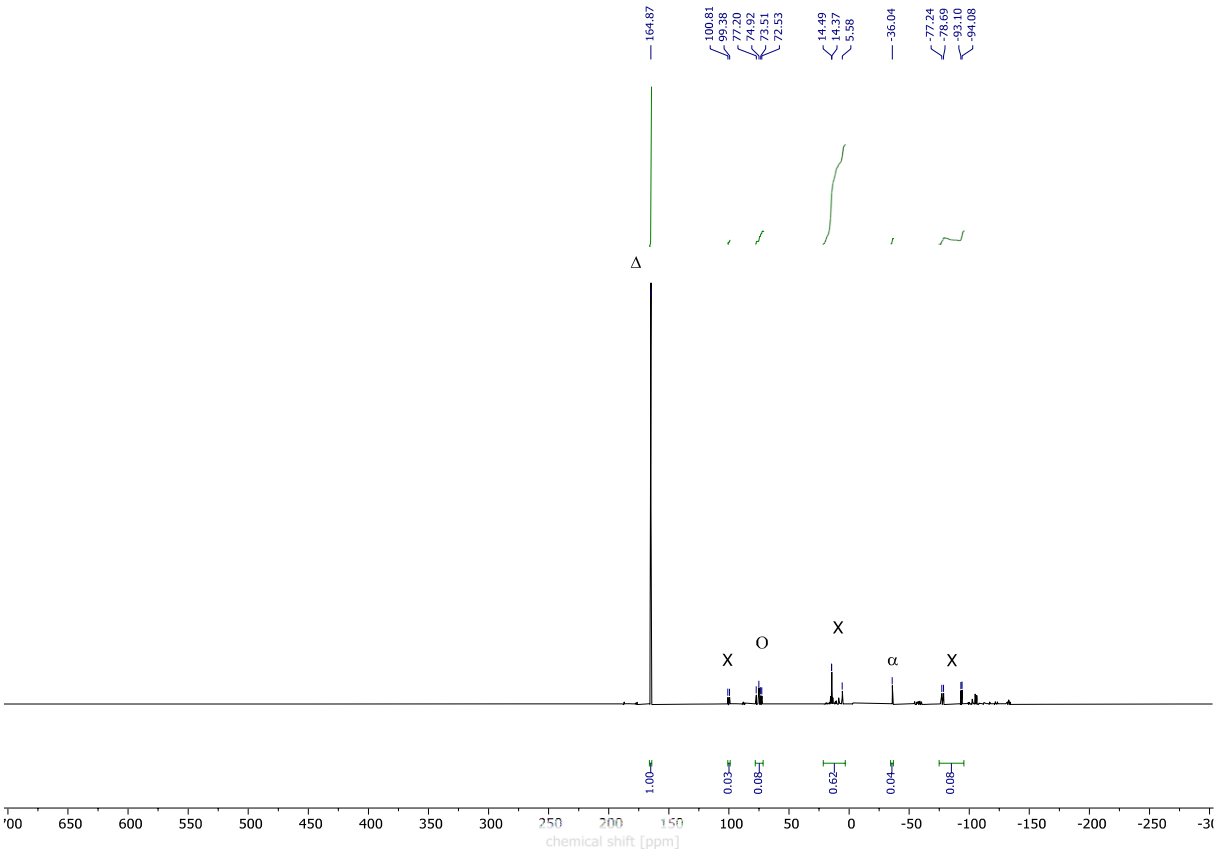


3.3.3 $TipPCl_2$ + PMe_3 (10 mol%)

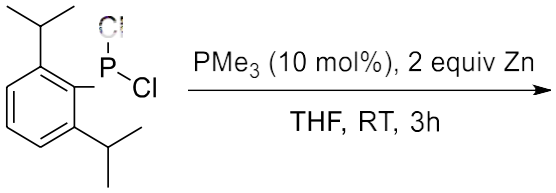


$TipPCl_2$ (153 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). PMe_3 (0.5 ml, 0.1 M in THF) is slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S14: ^{31}P NMR spectrum of the reaction of $TipPCl_2$ with PMe_3. Δ $TipPCl_2$, O $(TipPCl)_2$, α Tip_4P_4, X unidentified side products.

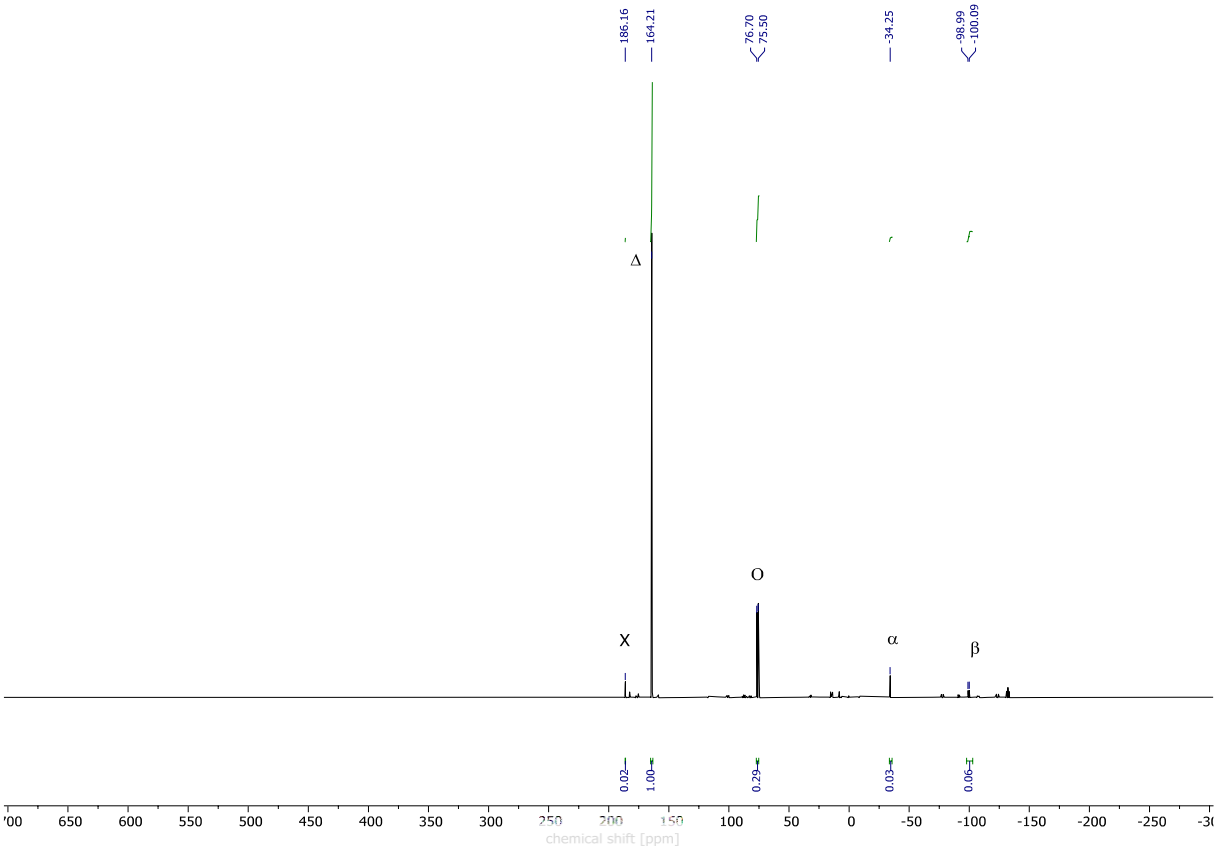


3.3.4 $DipPCl_2$ + PMe_3 (10 mol%)



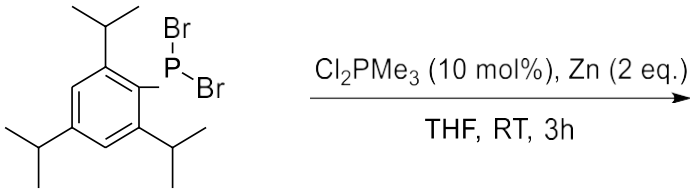
$DipPCl_2$ (0.132 g, 0.5 mmol) and zinc (0.064 mg, 1 mmol) were dissolved in THF (2.5 mL). PMe_3 (0.5 ml, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S15: ^{31}P NMR spectrum of the reaction of $DipPCl_2$ with PMe_3. Δ $DipPCl_2$, O $(DipPCl)_2$, α Dip_4P_4, β Dip_3P_3, X unidentified side products.



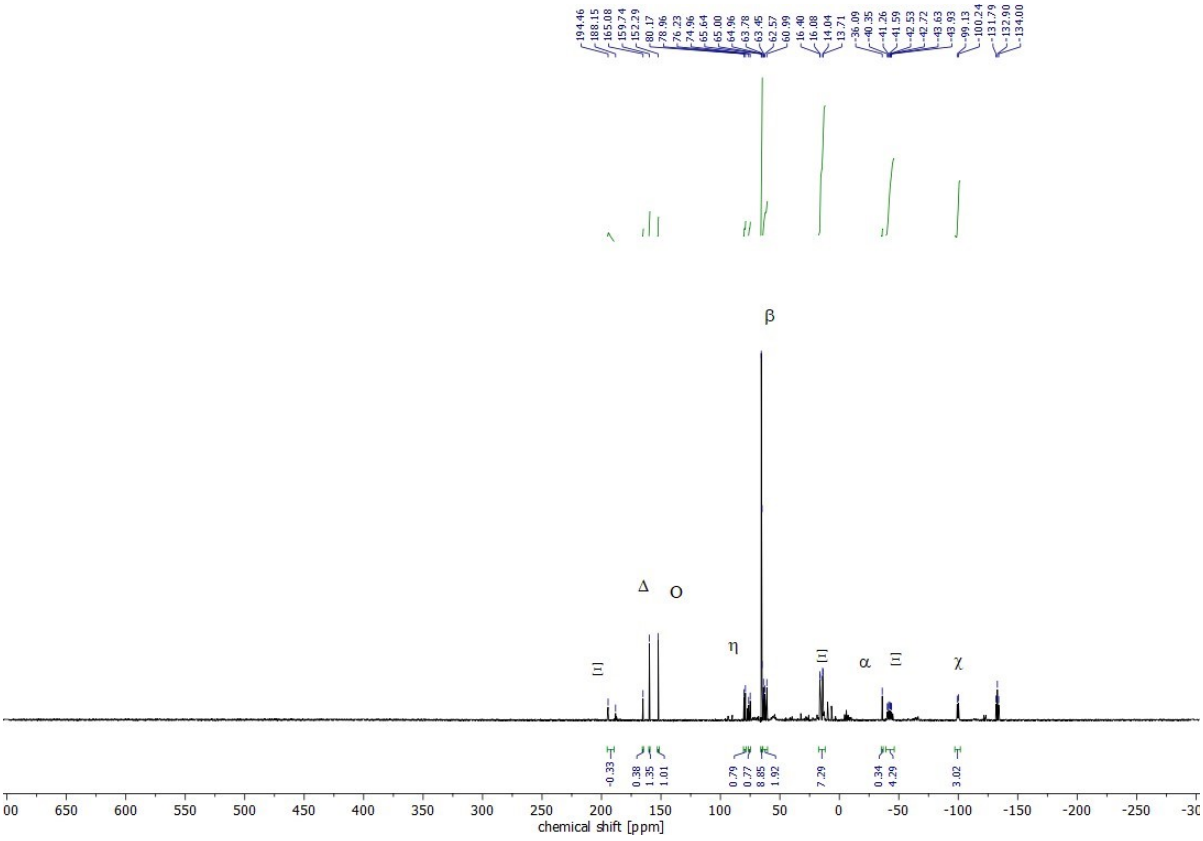
3.4 Catalysis with Cl_2PMe_3

3.4.1 $TipPBr_2$ + Cl_2PMe_3 (10 mol%)

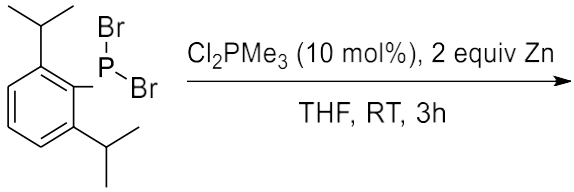


$TipPBr_2$ (197 mg, 0.5 mmol), Cl_2PMe_3 (7.6 mg, 0.05 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). The mixture was allowed to stir under the exclusion of light for 3 hrs. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S16: ^{31}P NMR spectrum of the reaction of $TipPBr_2$ with Cl_2PMe_3. Δ TipPBrCl, O $TipPBr_2$, η $(TipPCl)_2$, β $(TipPBr)_2$, α Tip_4P_4, χ Tip_3P_3, X unidentified side products.

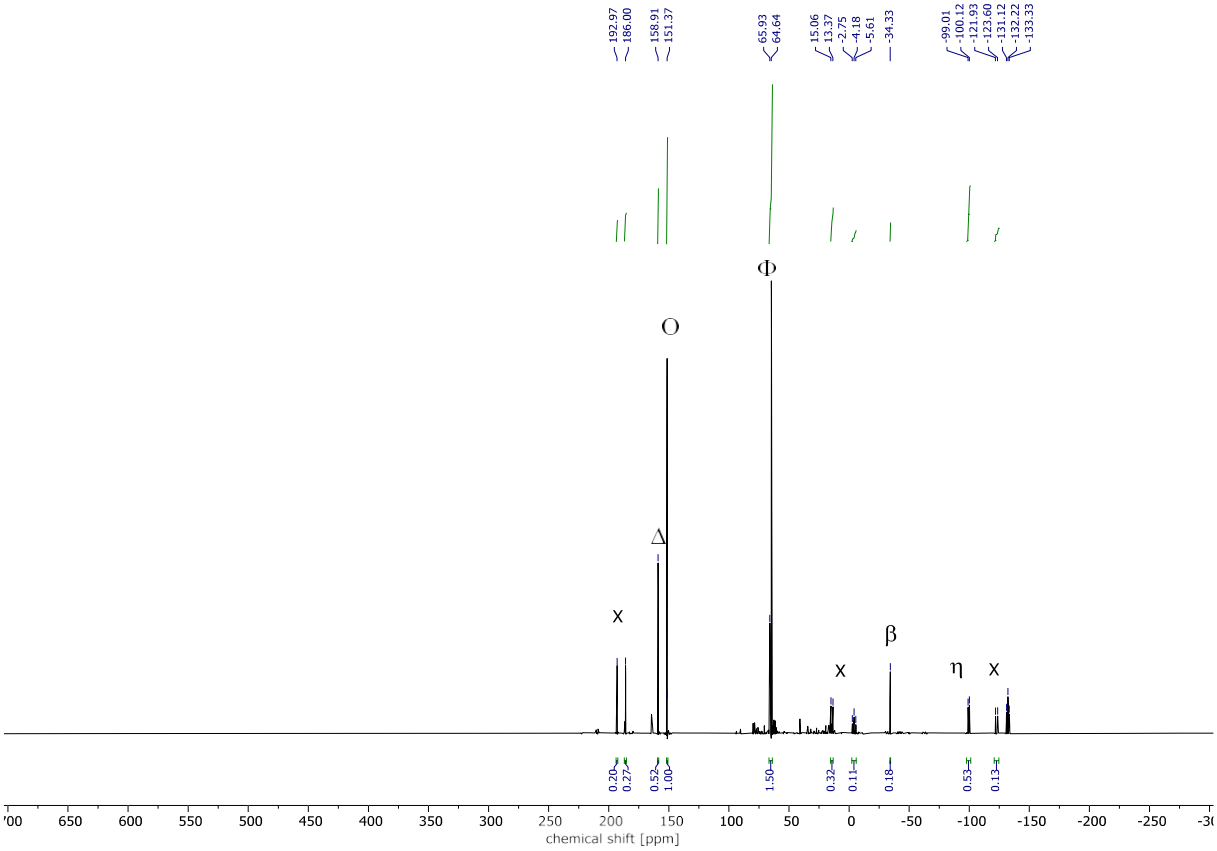


3.4.2 $DipPBr_2$ + Cl_2PMe_3 (10 mol%)

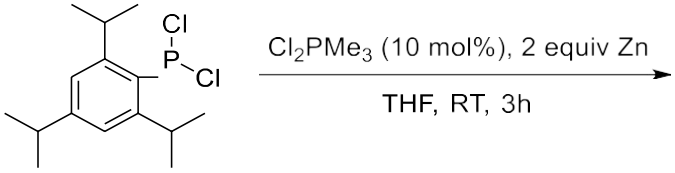


$DipPBr_2$ (176 mg, 0.5 mmol), Cl_2PMe_3 (7.6 mg, 0.05 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S17: ^{31}P NMR spectrum of the reaction of $DipPBr_2$ with Cl_2PMe_3. Δ DipPBrCl, O $DipPBr_2$, F $(DipPBr)_2$, β Dip_4P_4, η Dip_3P_3, X unidentified side products.

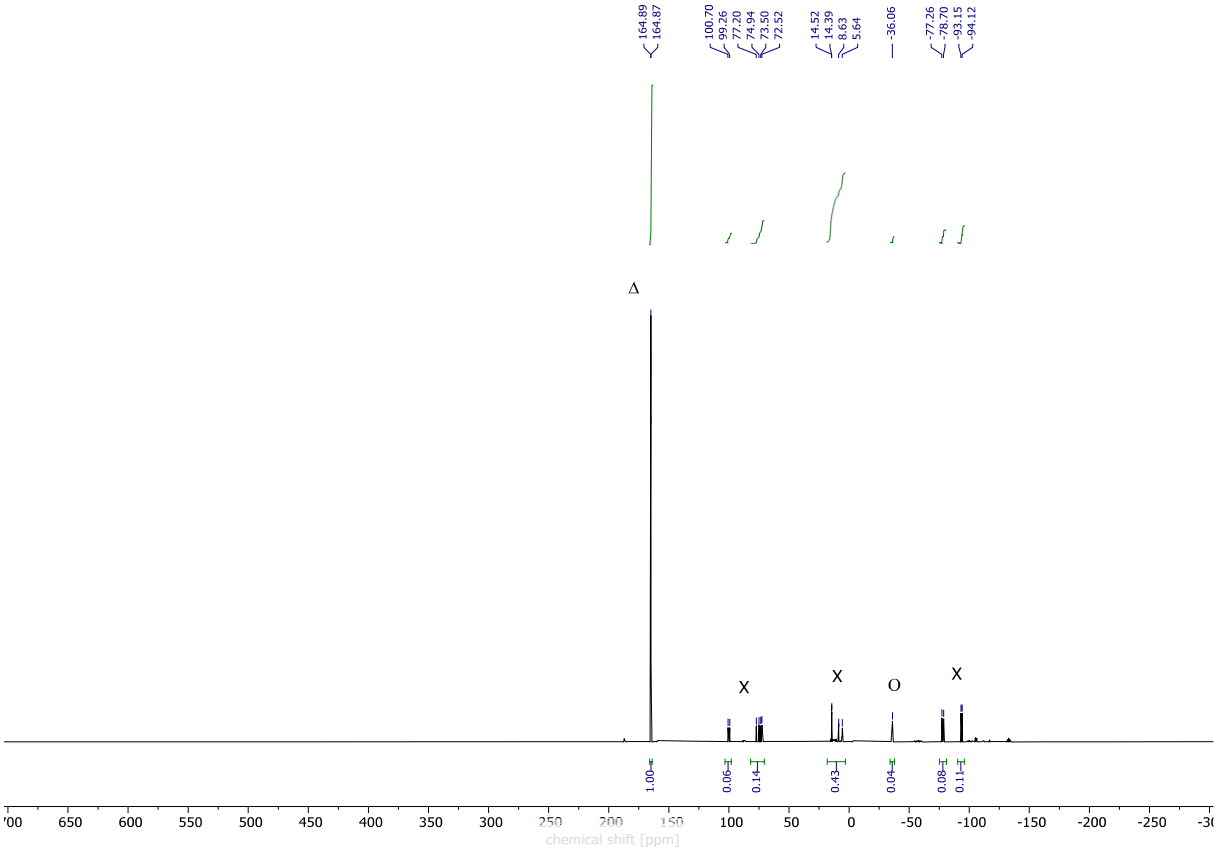


3.4.3 $TipPCl_2$ + Cl_2PMe_3 (10 mol%)

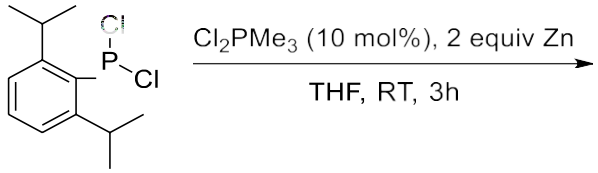


$TipPCl_2$ (153 mg, 0.5 mmol), Cl_2PMe_3 (7.6 mg, 0.05 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S18: ^{31}P NMR spectrum of the reaction of $TipPCl_2$ with Cl_2PMe_3. Δ $TipPCl_2$, O Tip_4P_4, X unidentified side products.

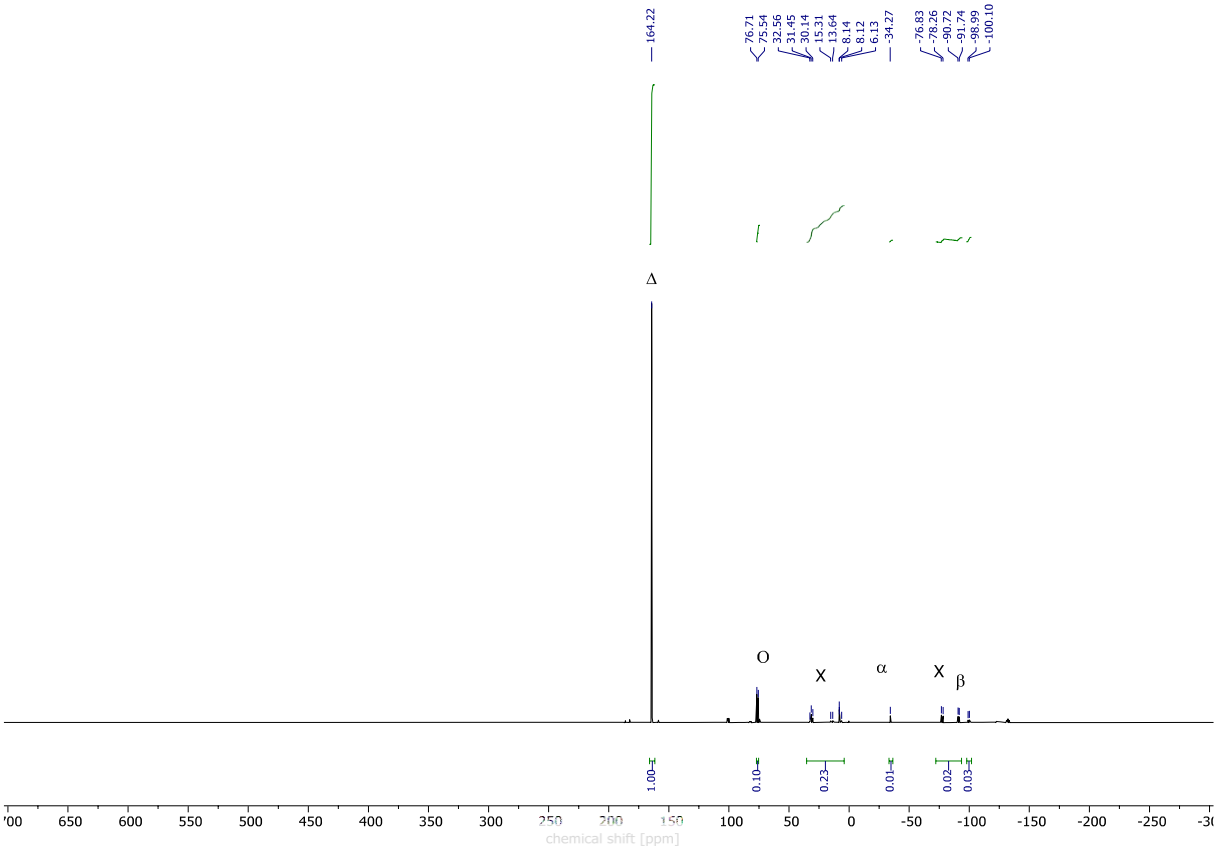


3.4.4 $DipPCl_2$ + Cl_2PMe_3 (10 mol%)



$DipPCl_2$ (176 mg, 0.5 mmol), Cl_2PMe_3 (7.6 mg, 0.05 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). The mixture was allowed to stir under the exclusion of light for 3 hrs. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S19: ^{31}P NMR spectrum of the reaction of $DipPCl_2$ with Cl_2PMe_3. Δ $DipPCl_2$, O $(DipPCl)_2$, a Dip_4P_4, β Dip_3P_3, X unidentified side products.



3.5 Catalysis with P*n*Bu$_3$

3.5.1 DipPBr$_2$ + P*n*Bu$_3$ (10 mol%)

DipPBr$_2$ (176 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). P*n*Bu$_3$ (0.5 ml, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

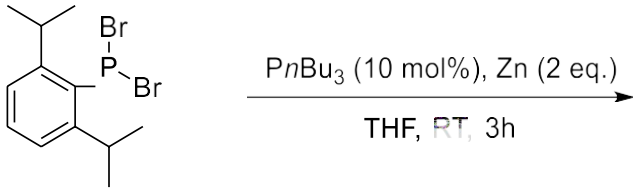
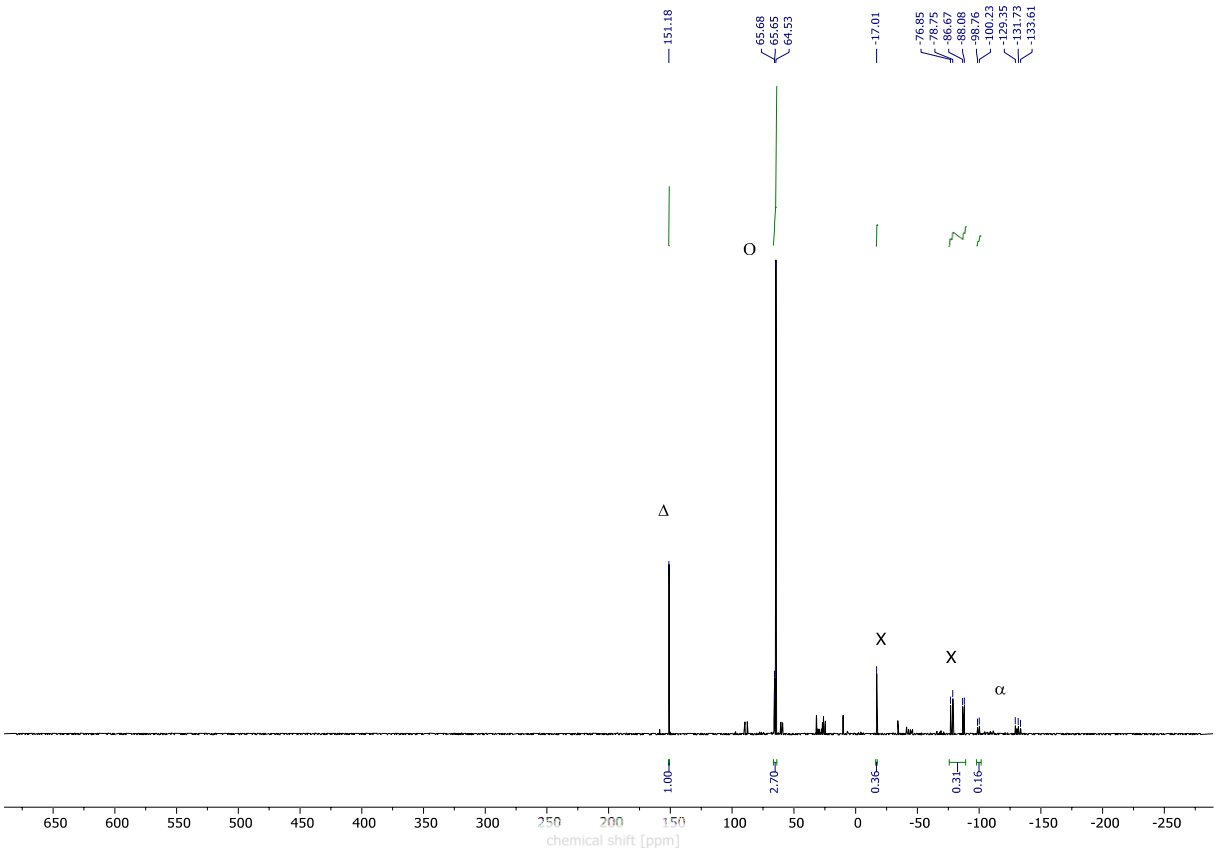


Figure S20: ^{31}P NMR spectrum of the reaction of DipPBr$_2$ with P*n*Bu$_3$. Δ DipPBr$_2$, O (DipPBr)$_2$, a Dip$_3$P$_3$, X unidentified side products.



3.5.2 TipPBr$_2$ + P*n*Bu$_3$ (10 mol%)

TipPBr$_2$ (197 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). P*n*Bu$_3$ (0.5 ml, 0.1 M in THF) was slowly added to the stirring solution at room

temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

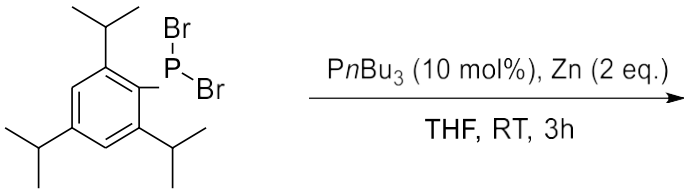
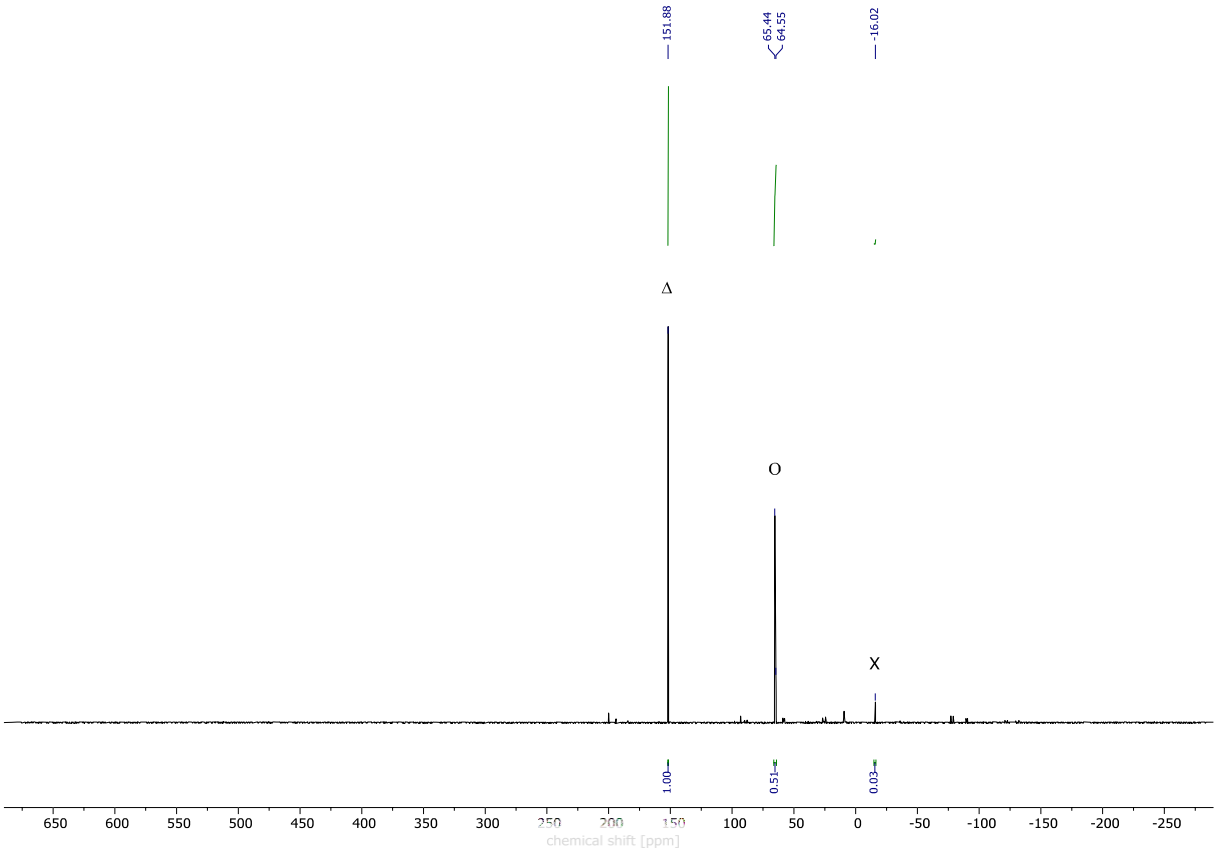


Figure S21: ^{31}P NMR spectrum of the reaction of $TipPBr_2$ with P*n*Bu_3. Δ $TipPBr_2$, O $(TipPBr)_2$, X unidentified side products.



3.5.3 $TipPCl_2$ + P*n*Bu_3 (10 mol%)

$TipPBr_2$ (197 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). P^nBu_3 (0.5 ml, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 hrs.

Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

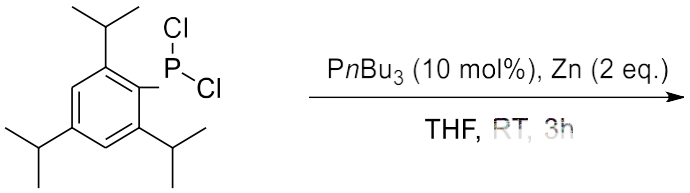
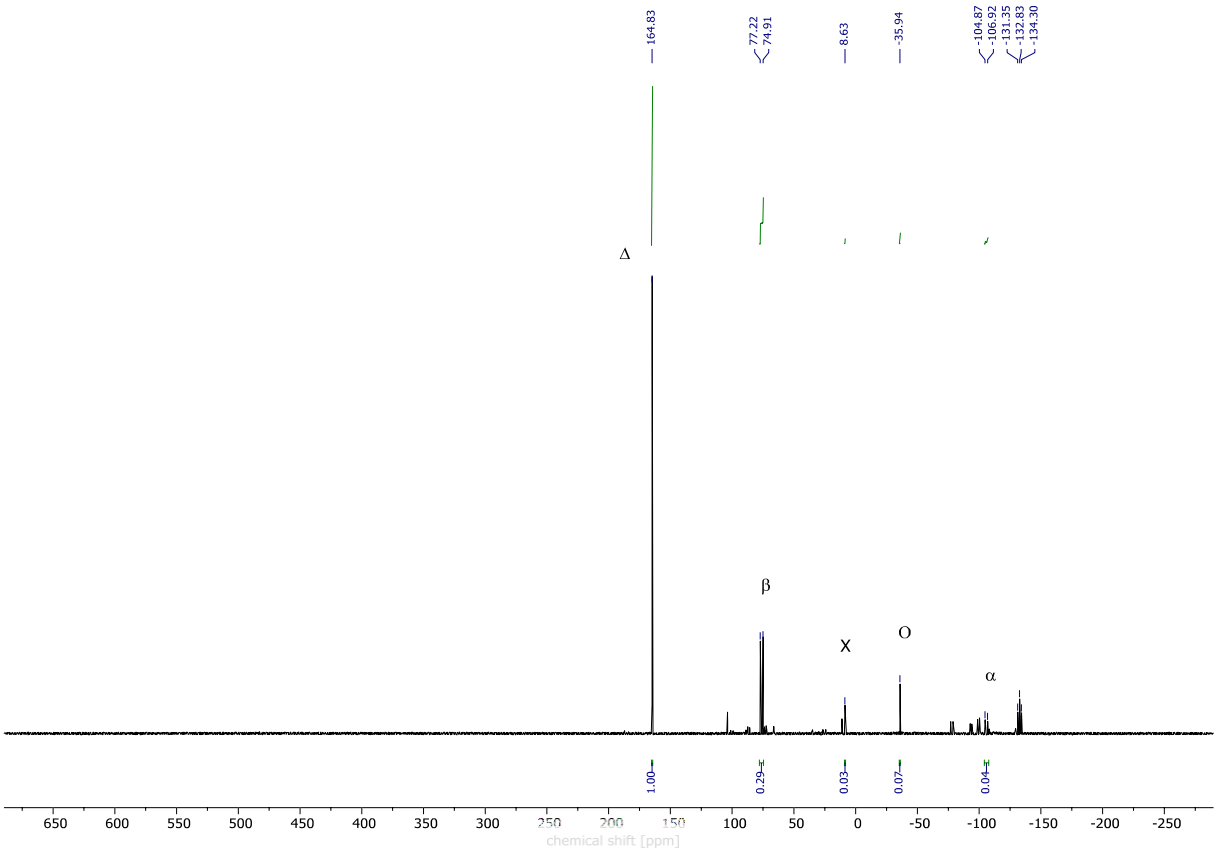


Figure S22: ^{31}P NMR spectrum of the reaction of $TipPCl_2$ with P*n*Bu_3. Δ $TipPCl_2$, β $(TipPCl)_2$, O Tip_4P_4, a Tip_3P_3, X unidentified side products.



3.5.4 $DipPCl_2$ + P*n*Bu_3 (10 mol%)

$DipPCl_2$ (85 mg, 0.323 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). P*n*Bu_3 (0.32 ml, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

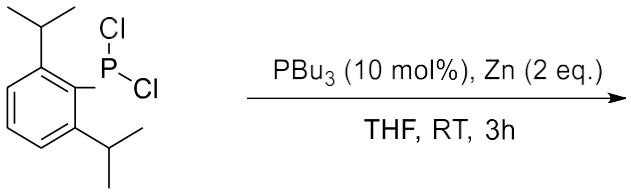
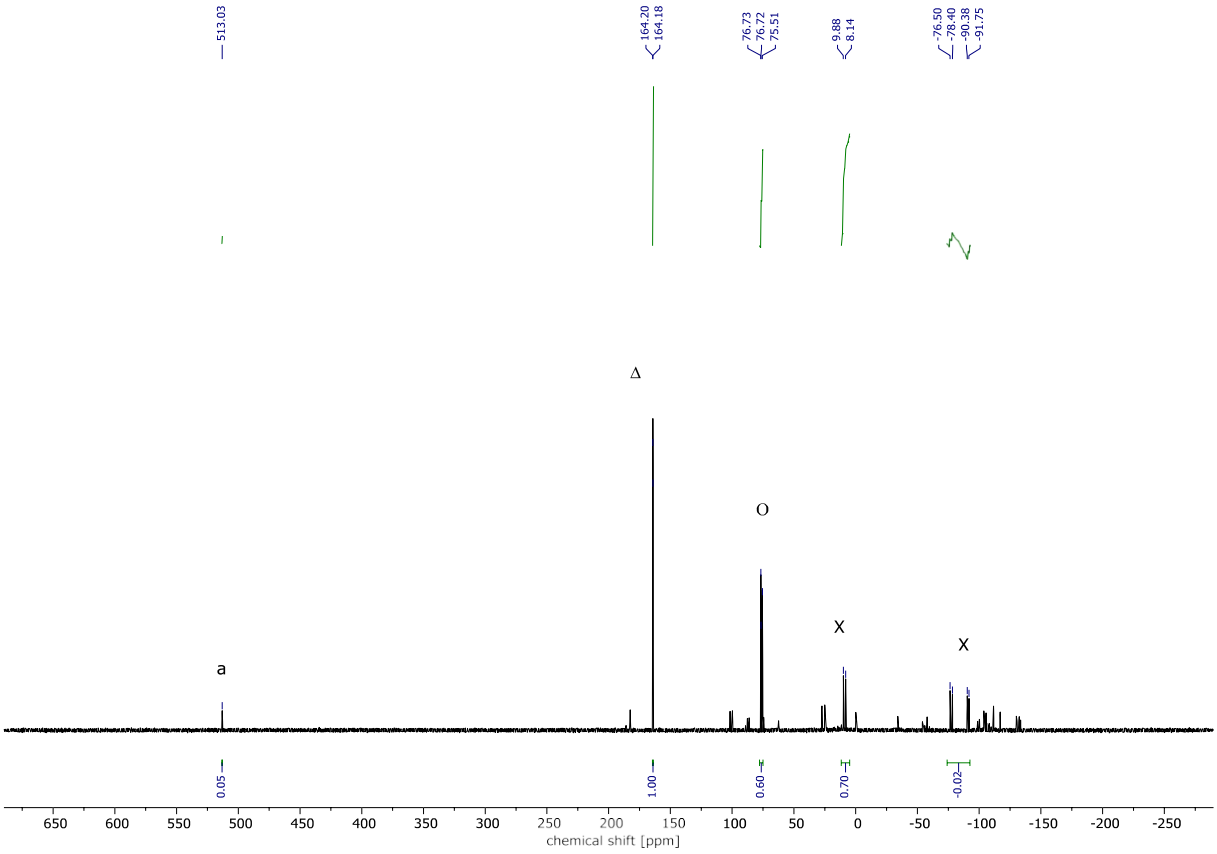


Figure S23: ^{31}P NMR spectrum of the reaction of $DipPCl_2$ with P*n*Bu_3. Δ $DipPCl_2$, O $(DipPCl)_2$, a Dip_2P_2, X unidentified side products.



3.5.5 $PhPCl_2$ + P^nBu_3 (10 mol%)

$PhPCl_2$ (94.2 mg, 0.53 mmol) and zinc (65.0 mg, 1 mmol) were dissolved in THF (2.5 mL). P^nBu_3 (0.53 ml, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 hrs. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

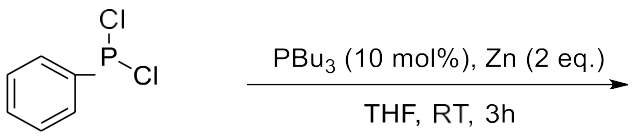
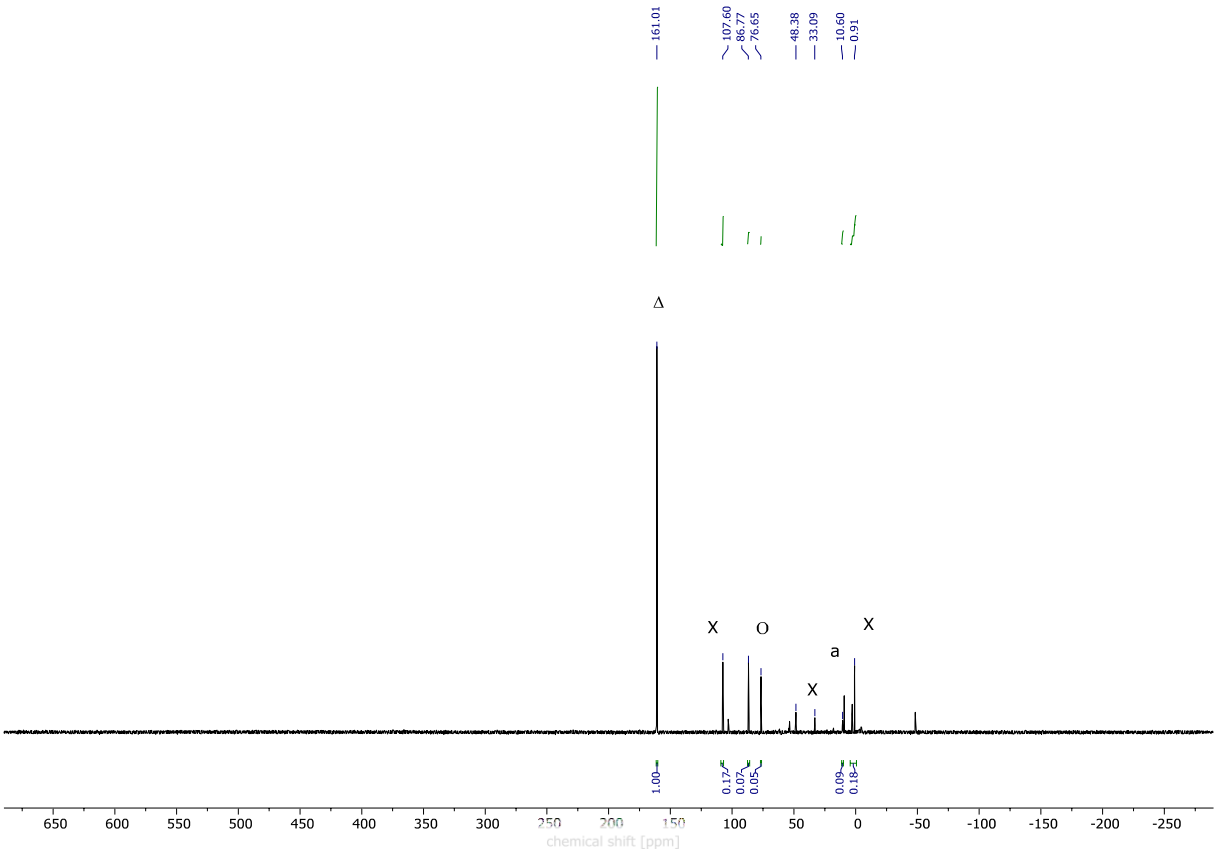
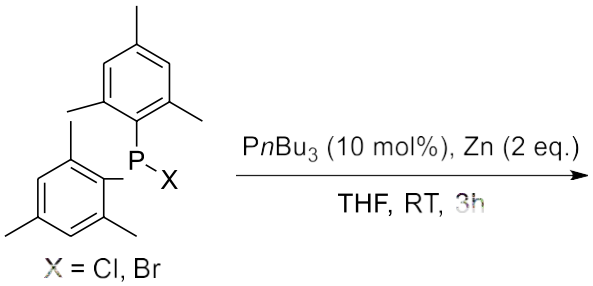


Figure S24: ^{31}P NMR spectrum of the reaction of $PhPCl_2$ with P*n*Bu$_3$. Δ $PhPCl_2$, O $(PhPCl)_2$, a Ph_5P_5, X unidentified side products.

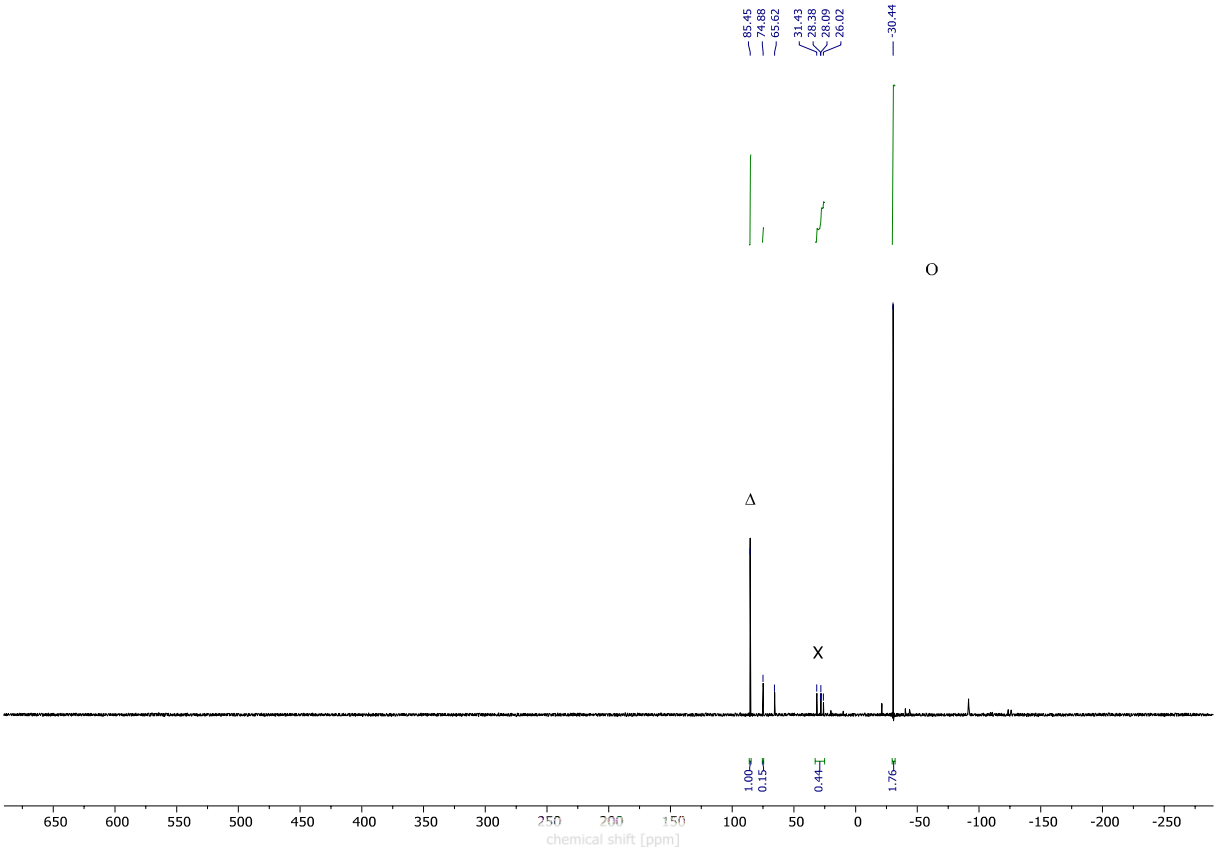


3.5.6 Mes_2PX (X = Cl, Br) + P*n*Bu$_3$ (10 mol%)



To Mes_2PX (X = Cl, Br) (119 mg, 0.5 mmol) and zinc (65.0 mg, 1 mmol) THF (2 mL) was added. P*n*Bu$_3$ (0.5 mL, 0.1 M in THF) was slowly added to the stirring solution at room temperature. The mixture was allowed to stir under the exclusion of light for 3 h. Afterwards the volatiles were evaporated. The ^{31}P NMR spectrum was measured immediately.

Figure S25: ^{31}P NMR spectrum of the reaction of Mes_2PX with P*n*Bu_3. Δ Mes_2PX, O $(Mes_2P)_2$, X unidentified side products.



3.6 Control experiments

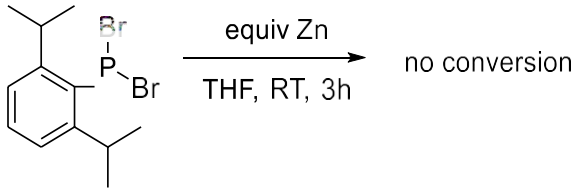
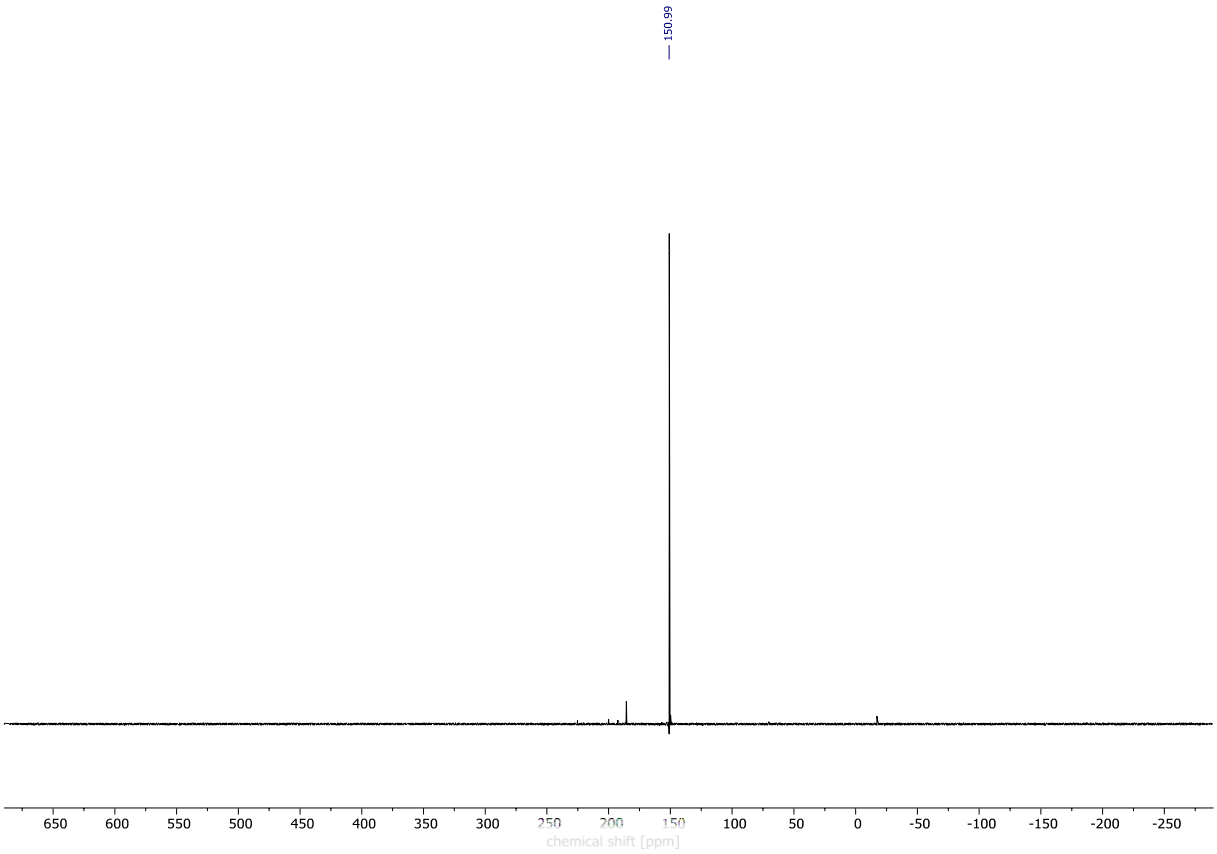


Figure S26: ^{31}P-NMR spectra of reaction of $DipPBr_2$ and zinc. No conversion occurs without the addition of PEt_3.



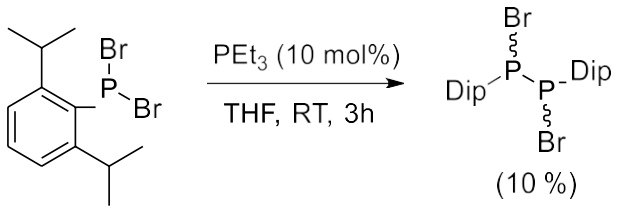
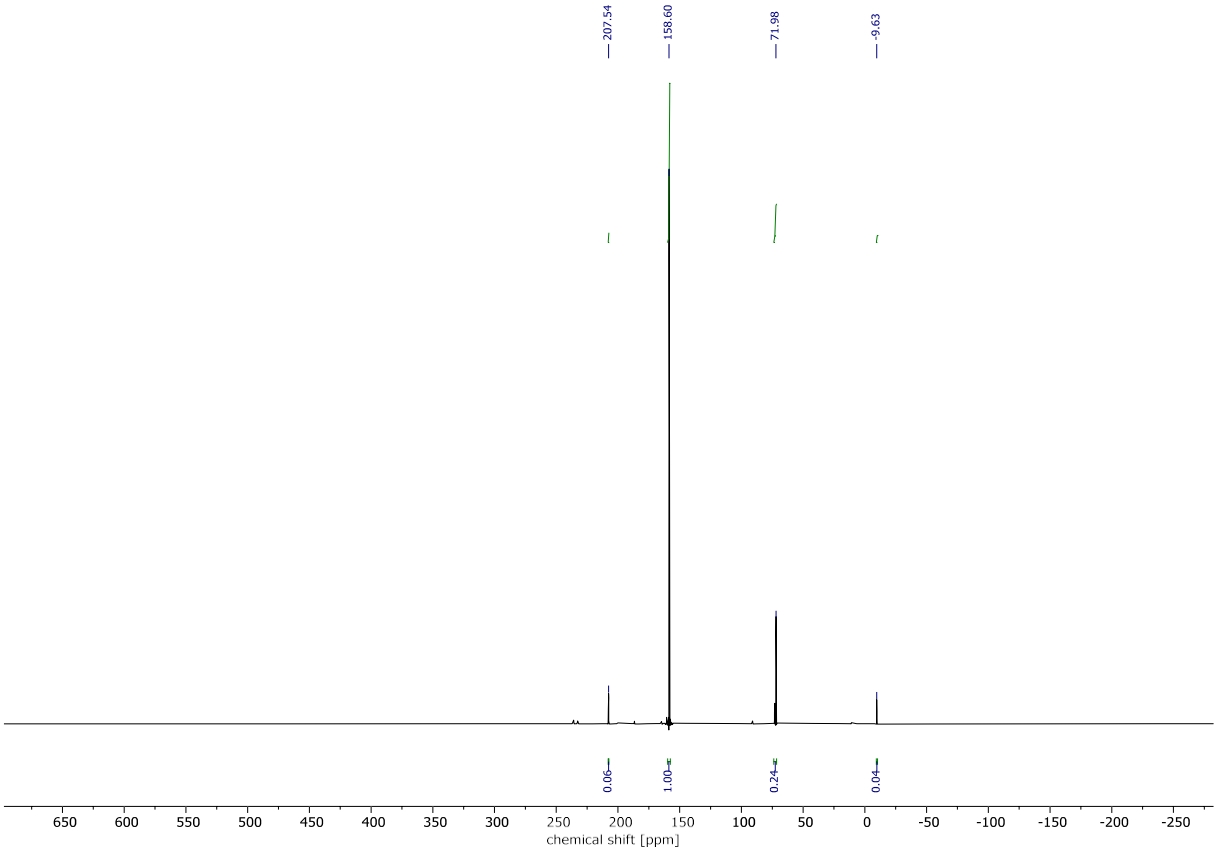


Figure S27: ^{31}P-NMR spectra of reaction of $DipPBr_2$ and PEt_3 (10 mol%). Ca. 10% of $(DipPBr)_2$ are formed.



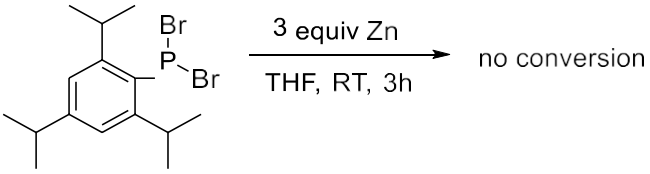
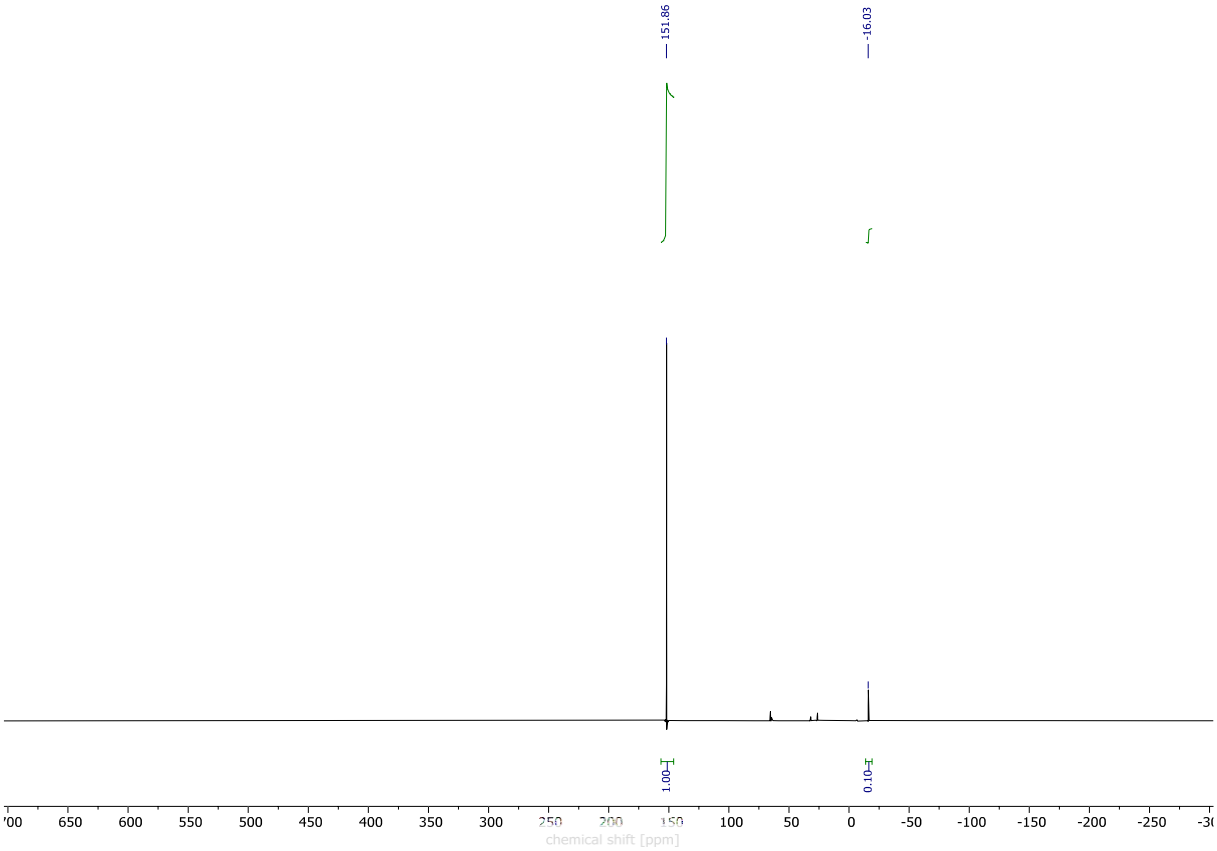


Figure S28: ^{31}P-NMR spectrum of the reaction of $TipPBr_2$ and zinc. No conversion occurs without the addition of PEt_3.



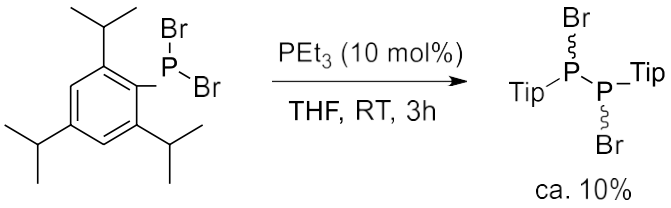
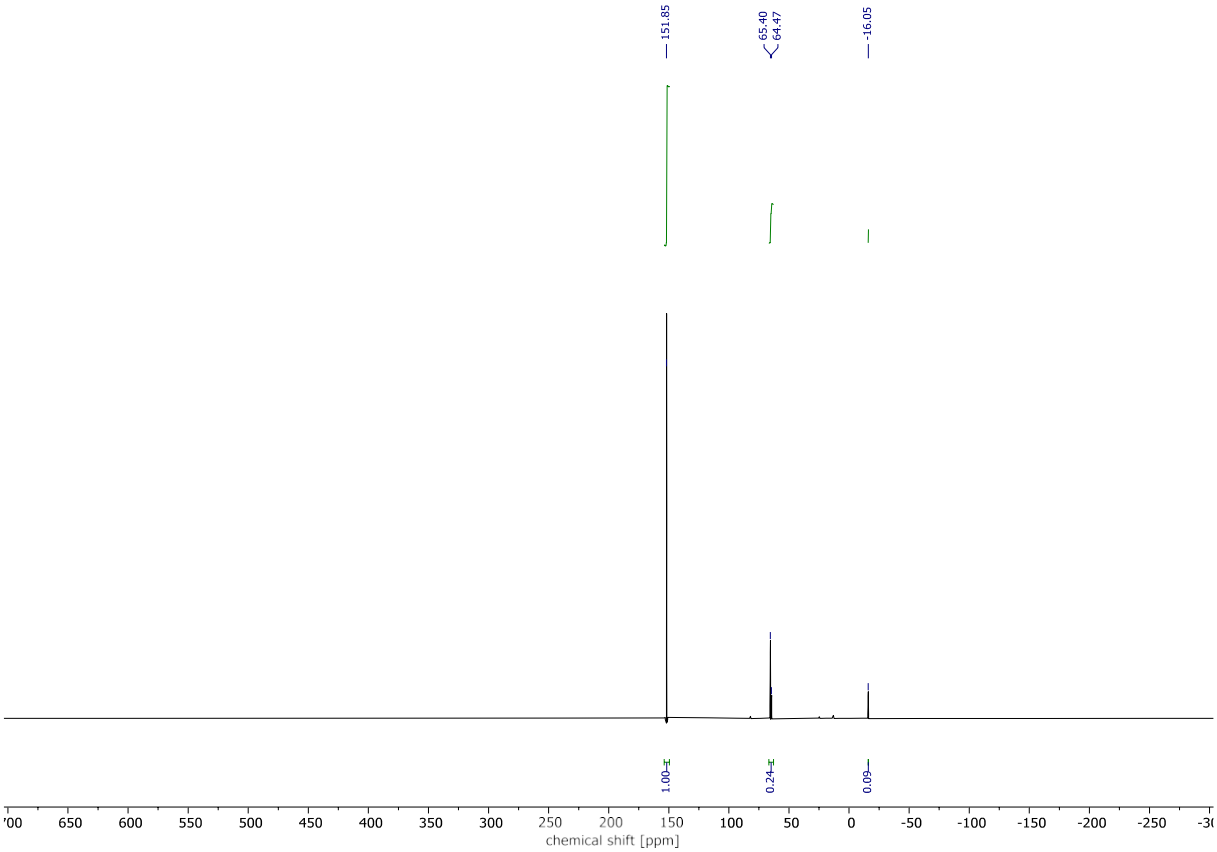


Figure S29: ^{31}P-NMR spectra of reaction of $TipPBr_2$ and PEt_3 (10 mol%). Small amounts of $(TipPBr)_2$ are formed.



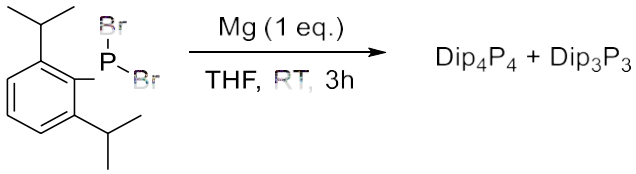
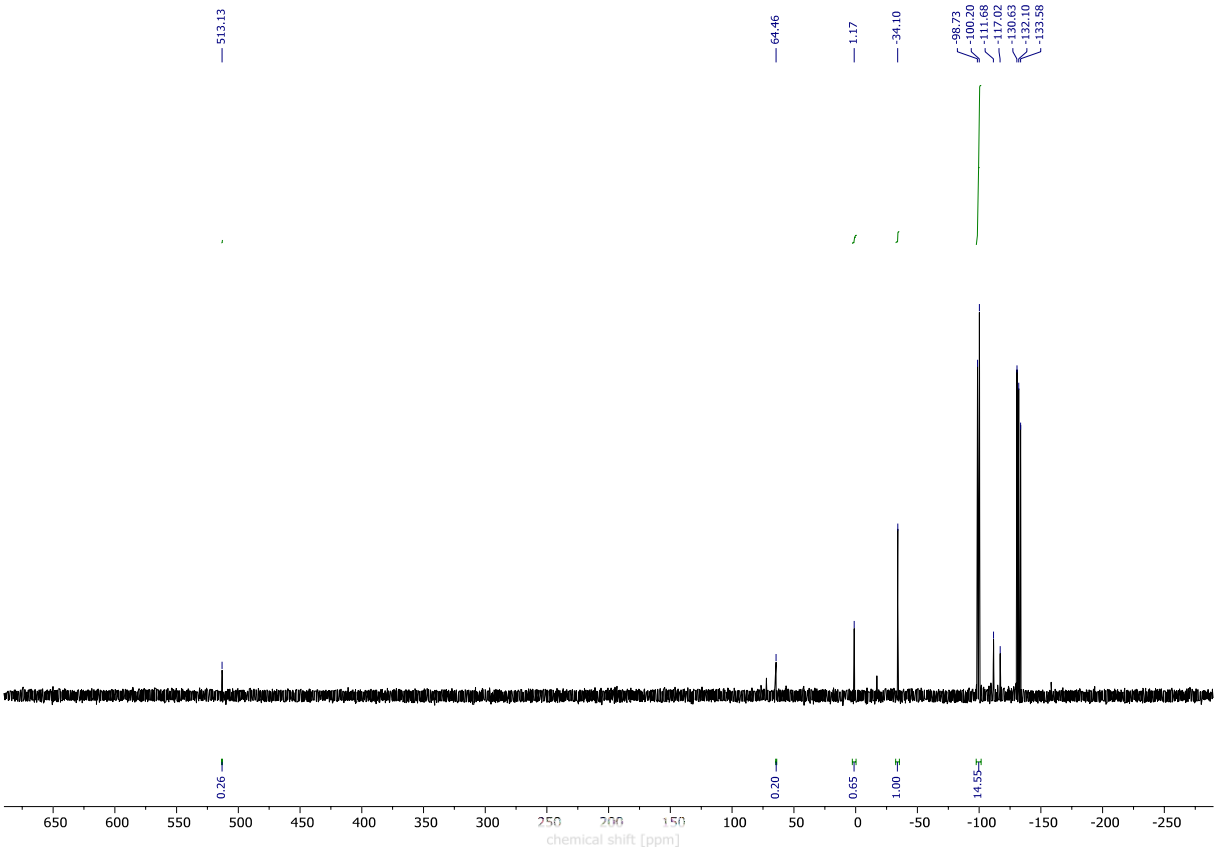


Figure S30: ^{31}P-NMR spectrum of the reaction of $DipPBr_2$ and Mg (1 eq.) after 3 hrs.



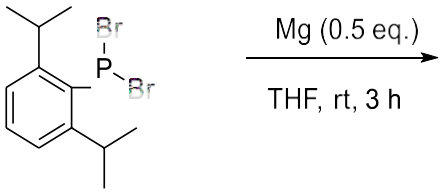
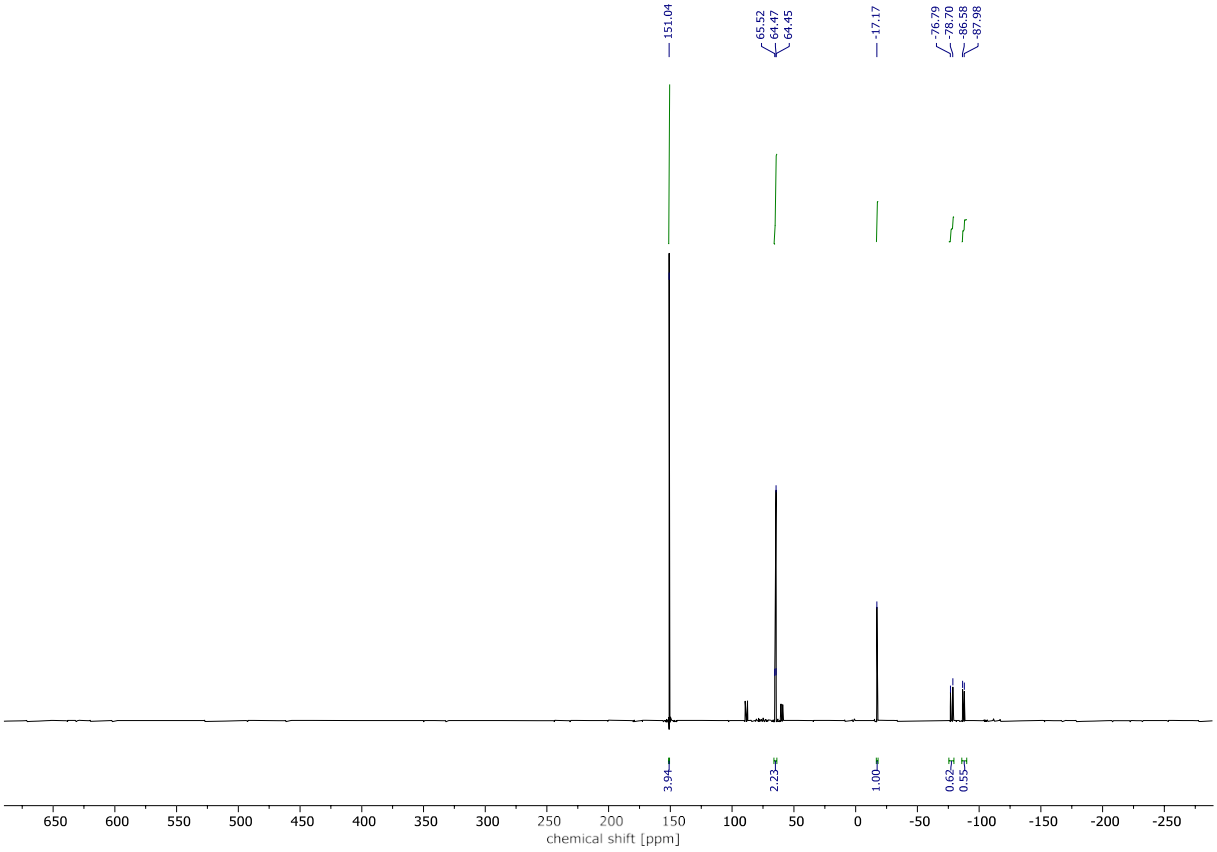


Figure S31: ^{31}P-NMR spectrum of the reaction of $DipPBr_2$ and Mg (0.5 eq.) after 3 h.



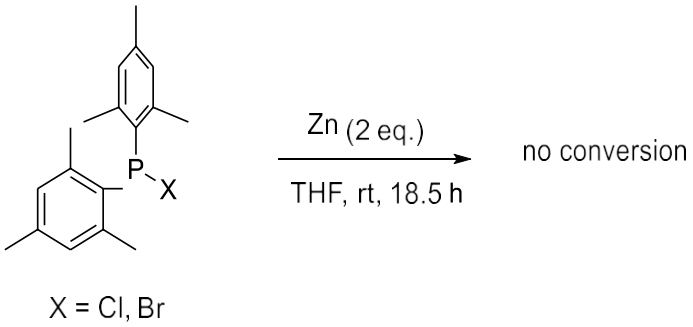
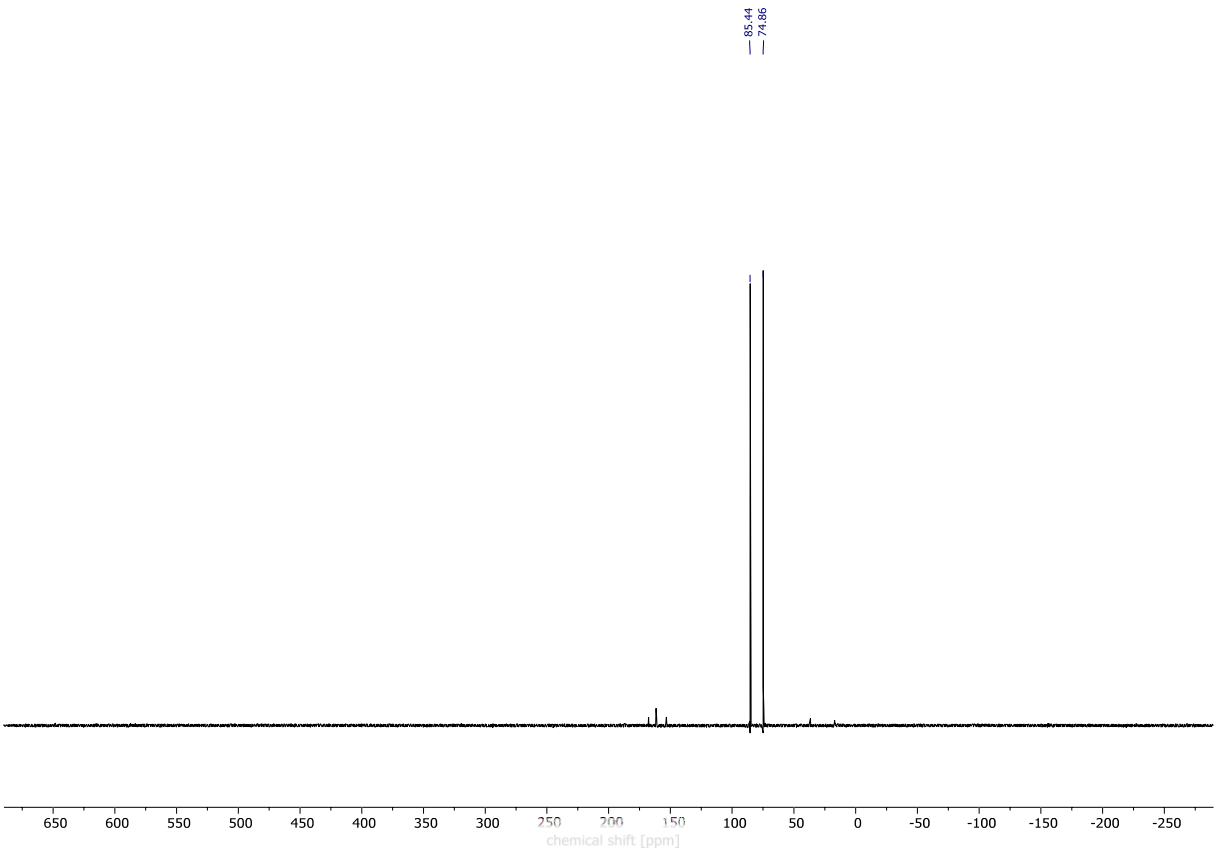


Figure S32: ^{31}P-NMR spectrum of the reaction of Mes_2PX and Zn (2 eq.) after 18.5 h.



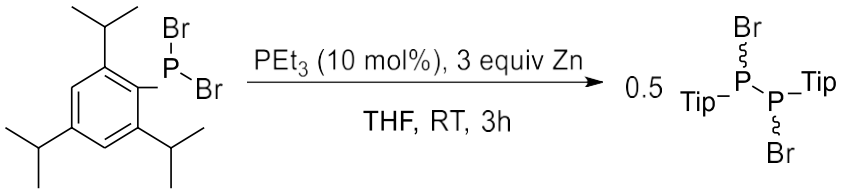
3.7 Conclusion

Table S3. Main products of the catalytic reactions with the respective trialkylphosphanes or trialkyl phosphane precursors.

	PEt_3 (10 mol%)	Br_2PEt_3 (10 mol%)	PMe_3 (10 mol%)	Cl_2PMe_3 (10 mol%)
$DipPBr_2$	P_2Dip_2	$(DipPBr)_2$	$(DipPBr)_2$	$DipPBr_2$, $(DipPBr)_2$
$TipPBr_2$	$(TipPBr)_2$	$TipPBr_2$, $(TipPBr)_2$	$TipPBr_2$, $(TipPBr)_2$	$(TipPBr)_2$
$DipPCl_2$	$DipPCl_2$, $(DipPCl)_2$	$DipPCl_2$	$DipPCl_2$	$DipPCl_2$
$TipPCl_2$	$TipPCl_2$, Tip_4P_4	$TipPCl_2$	$TipPCl_2$	$TipPCl_2$

4 Syntheses of compounds

4.1 Synthesis of $(TipPBr)_2$ (**1**)



A PEt_3 solution (0.5 mL, 0.1 M in THF, 0.05 mmol) was added dropwise to a stirred solution of $TipPBr_2$ (197 mg, 0.5 mmol) and zinc (100 mg, 1.575 mmol) in THF (2 mL) at ambient temperature. The mixture was stirred under the exclusion of light for 3 h. After removing the solvent *in vacuo*, extraction with toluene (10 mL) yielded a yellow solution. The filtrate was concentrated to incipient crystallization and was stored at −78 °C for 48 h, yielding $(TipPBr)_2$ as yellow crystalline solid (53 mg, 0.084 mmol, 34 %).

X-Ray quality crystals of *R*,*S*-**1** and *S*,*S*-**1** were grown from saturated *n*-hexane solutions at 5 °C.

CHN calc. (found) in %: C 57.34 (57.47), H 7.38 (7.60). **^{31}P NMR** (122 MHz, C_6D_6) δ = 65.38, 64.43. **IR** (ATR, 32 scans, cm^{-1}): *ν*= 2954.9 (s), 2925.4 (m), 2865.5 (m), 1597.8 (s), 1544.4 (w), 1459.8 (m), 1418.7 (m), 1380.3 (m), 1361.2 (m), 131.8 (w),1263.3 (w), 1191.3 (w), 1131.1 (w), 1103.2 (m), 1068.8 (w), 1051.2 (w), 1033.2 (w), 934.8 (m), 880.6 (s), 841.0 (w), 752.5 (w), 727.5 (w), 652.2 (m), 567.3 (m), 516.0 (w), 478.5 (m) cm^{-1}. **MS** (EI) expected 626.14360, observed 626.14351.

Figure S33: ^{1}H NMR spectrum of $(TipPBr)_2$ in C_6D_6 at r.t.

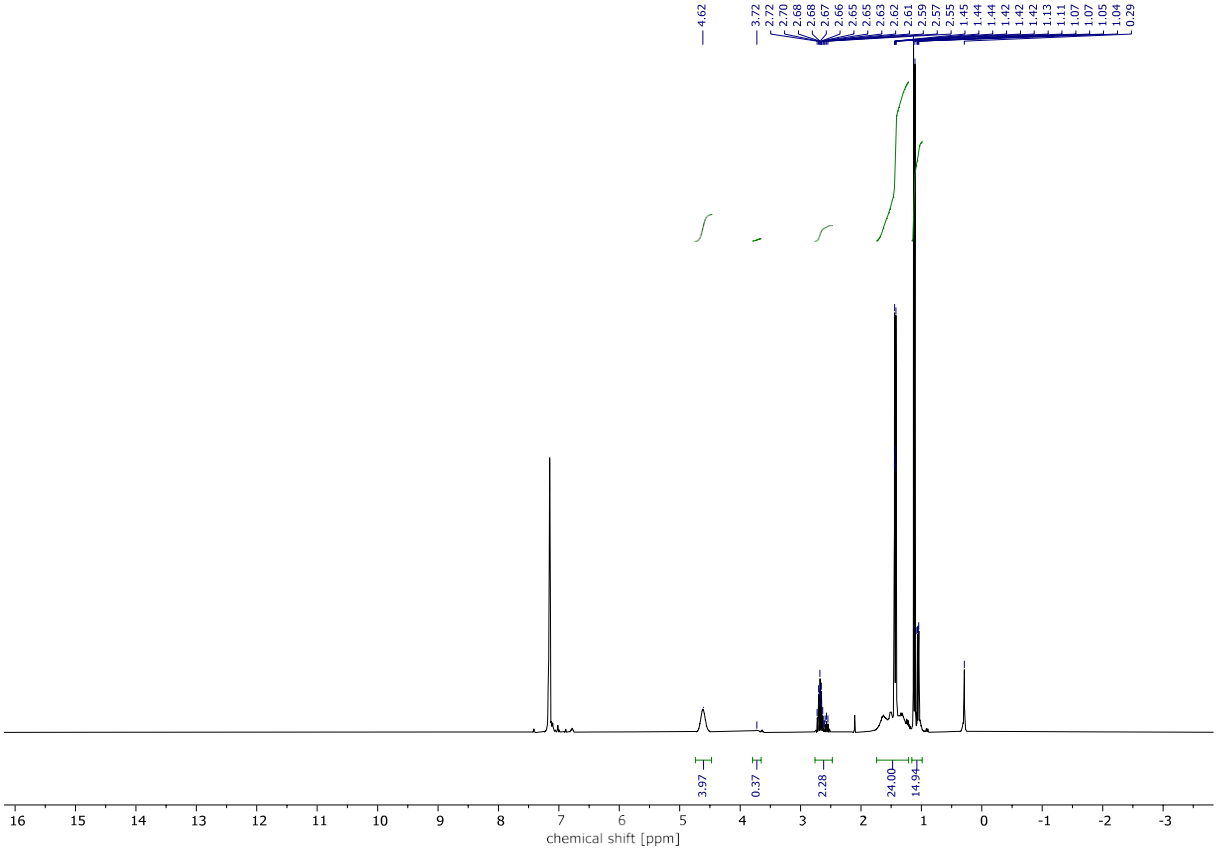


Figure S34: $^{31}P\{^{1}H\}$ NMR spectrum of $(TipPBr)_2$ in C_6D_6 at r.t.

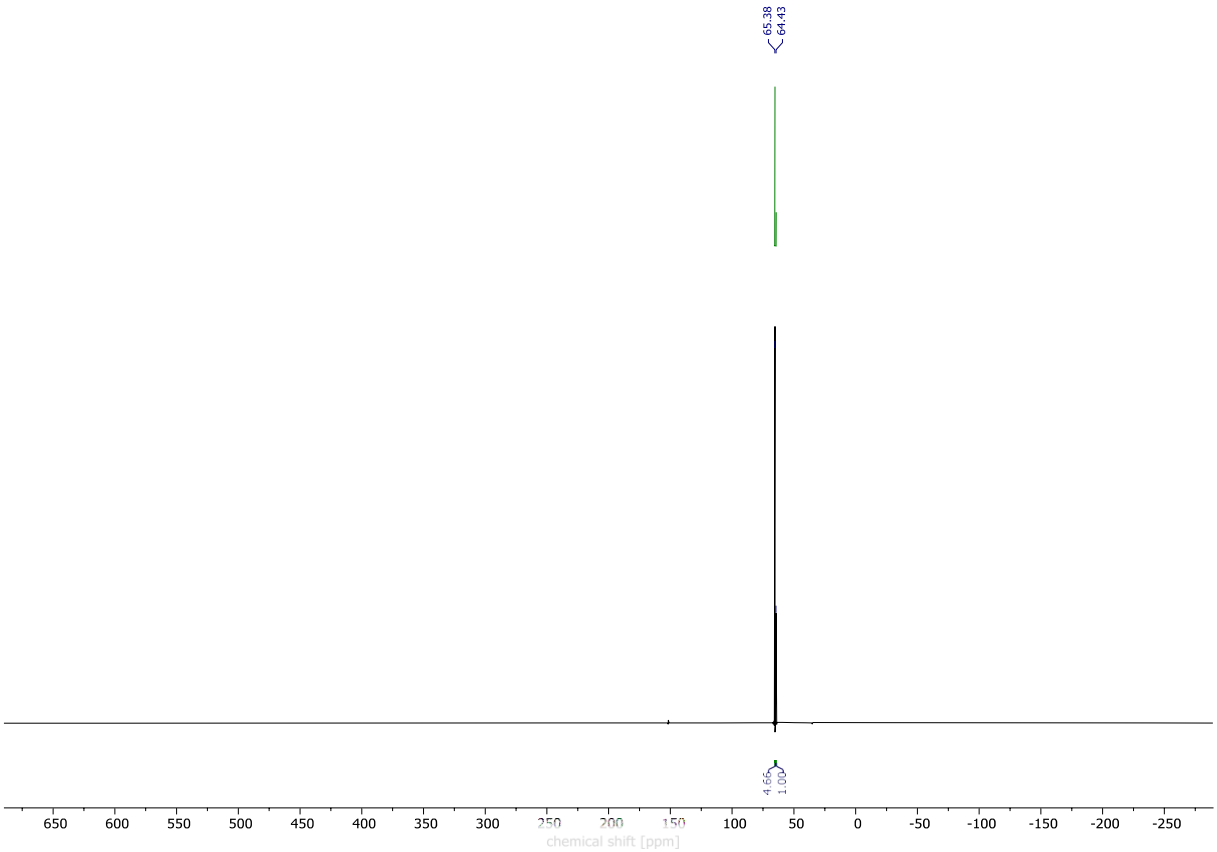
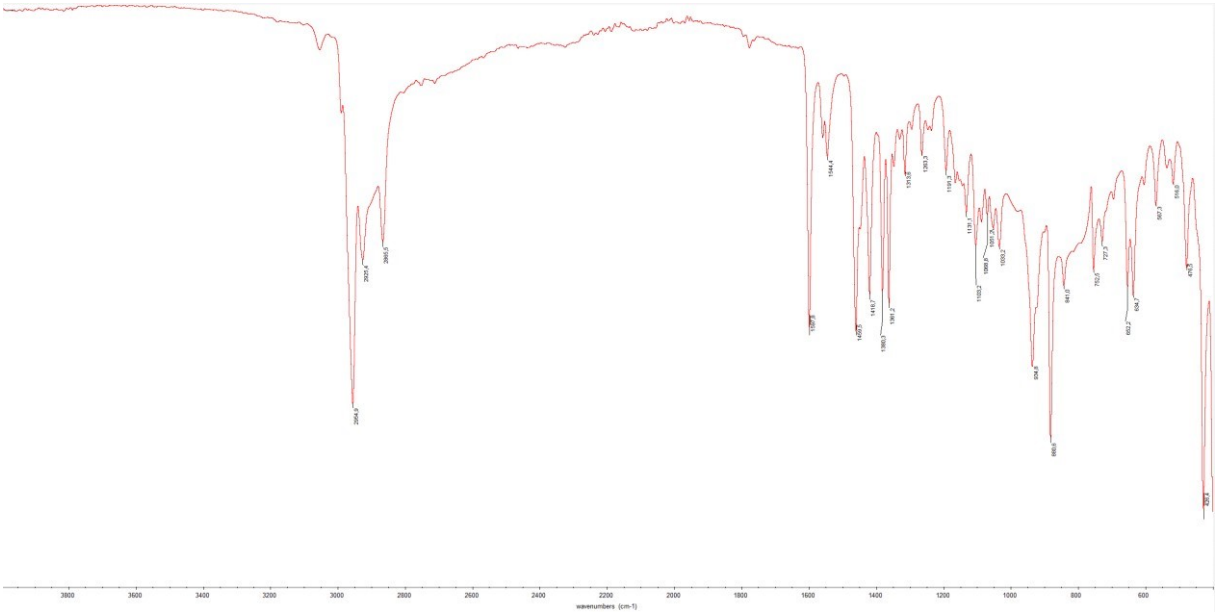


Figure S35: IR spectrum of crystalline $(TipPBr)_2$.



4.1.1 Thermal stability of $(TipPBr)_2$

$(TipPBr)_2$ (21 mg, 0.03 mmol) was dissolved in C_6D_6 and monitored via ^{31}P-NMR in a Y-Jung NMR tube. The conversion was determined via ^{31}P NMR integrals.

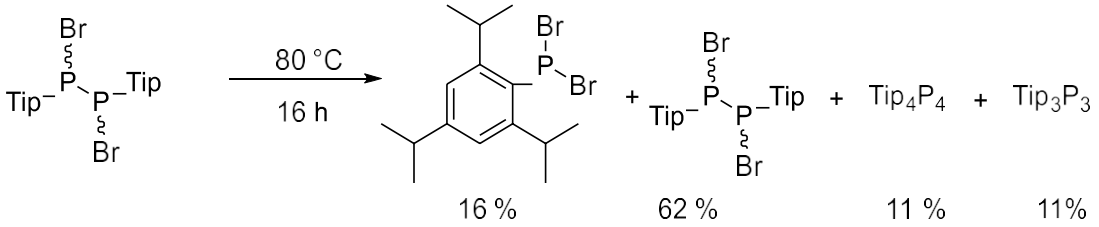
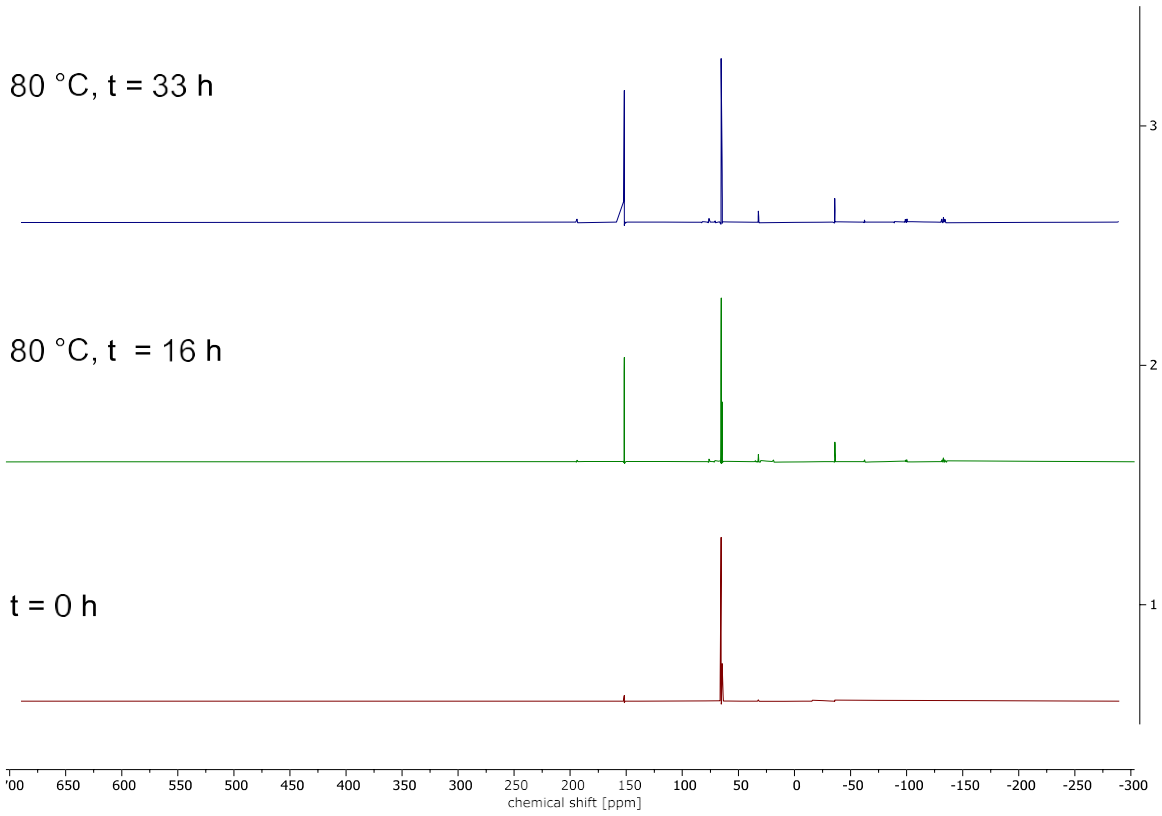


Figure S36: $^{31}P\{^{1}H\}$ NMR spectrum of $(TipPBr)_2$ in C_6D_6 at r.t. (bottom), after 80 °C for 16 h (middle), after 80 °C for 33 h (top).



$TipPBr_2$ (10 mg, 0.016 mmol) and $(TipPBr)_2$ (6.3 mg, 0.016 mmol) were dissolved in C_6D_6 and monitored via ^{31}P-NMR in a Y-Jung NMR tube.

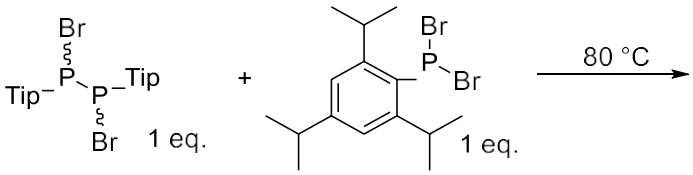
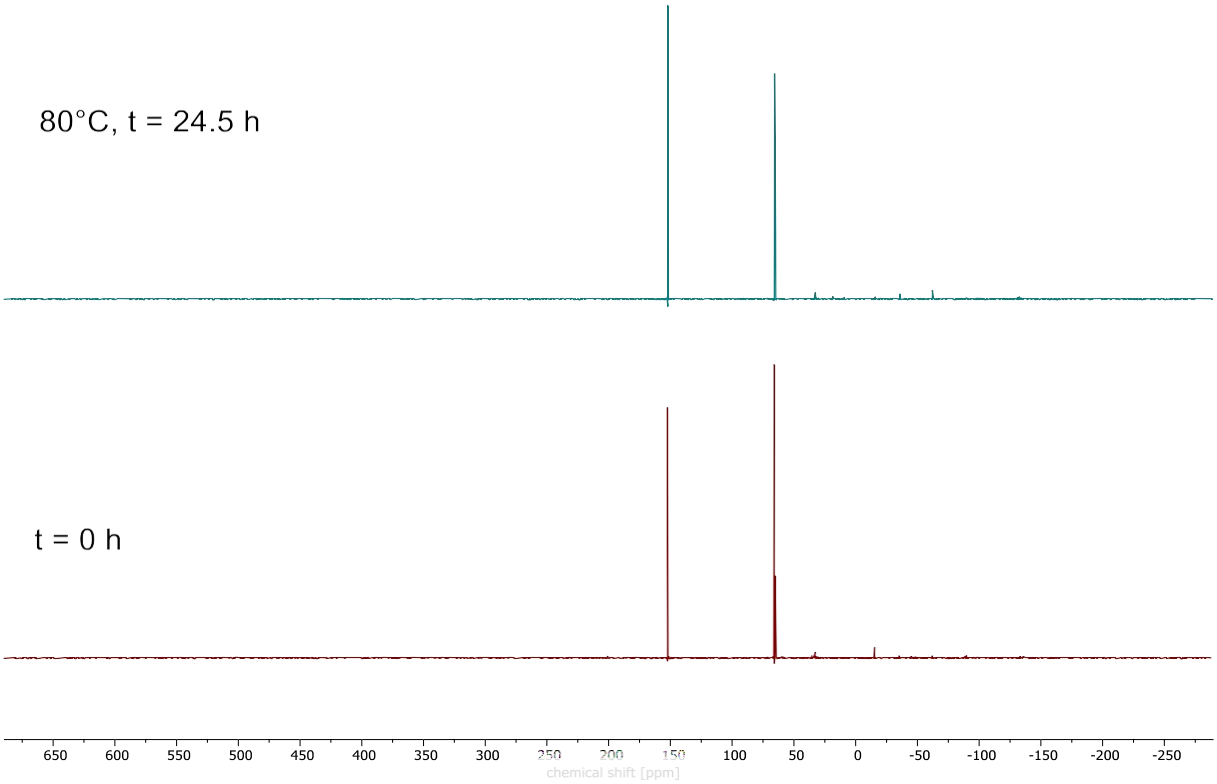
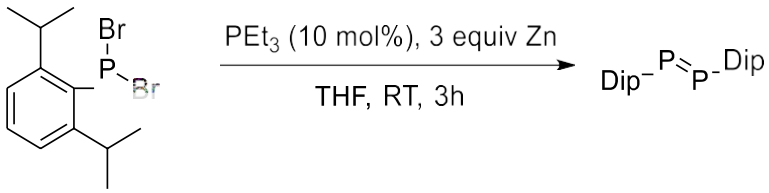


Figure S37: $^{31}P\{^{1}H\}$ NMR spectrum of $(TipPBr)_2$ and $TipPBr_2$ in C_6D_6 at r.t. (bottom), after 80 °C for 24.5 h (top).



4.2 Synthesis of (PDip)(**2**)



To $DipPBr_2$ (0.672 g, 1.9 mmol) and zinc (0.189 g, 3 eq.) THF (10 mL) was added. PEt_3 (1.9 ml, 0.1 M in THF, 0.19 mmol) was added dropwise to the stirring mixture. The solution turned bright yellow immediately and was stirred under the exclusion of light for 3 h. The solvent was removed *in vacuo* and the resulting yellow/green residue was thoroughly dried (3 freeze-pump-thaw cycles). The residue was then extracted with *n*-hexane (3 x 10 mL) and filtered over an G4 frit. The filtrate was then concentrated to incipient crystallization (under the exclusion of light) and was stored at −30 °C for 24 h. $(PDip)_2$ was afforded as yellow crystalline solid (0.135 g, 0.35 mmol, 37 %).

X-Ray quality crystal were grown from saturated a *n*-hexane solution at 5 °C.

CHN calc. (found) in %: C 74.97 (74.67), H 8.91 (9.03). **^{1}H NMR** (C_6D_6, 300 MHz): δ = 7.35-7.22 (m, 2H, *p*-$C_{Ar}H$), 7.14 (m, 4H, m-$C_{Ar}H$), 3.45 – 3.30 (hept, $^{3}J_{HH}$ = 6.7 Hz, 4H, $CH(CH_3)_2$), 1.26 (d, $^{3}J_{HH}$ = 6.7 Hz, 24H, $CH(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz): δ = 150.6, 141.1, 130.2, 123.7, 33.8, 23.5 ppm. **^{31}P{^{1}H} NMR** (C_6D_6, 121.5 MHz): δ = 513.0 ppm. **IR** (ATR, 32 scans, cm^{-1}): ν= 3050.2 (w), 2952.5 (s), 2928.0 (m), 2861.3 (m), 1583.3 (w), 1569.7 (w), 1457.4 (s), 1380.0 (m), 1357.5 (m) 1340.2 (w), 1301.3 (w), 1233.6 (m), 1177.2 (w), 1158.4 (w), 1101.4 (w), 1051.2 (w), 1034.2 (m), 930.4 (m), 795.0 (s), 732.4 (s), 505.9 (w) cm^{-1}. **MS** (ESI-TOF): expected 385.2214, observed 385.2211.

Figure S38: ^{1}H NMR spectrum of $(PDip)_2$ (**2**) in C_6D_6 at r.t.

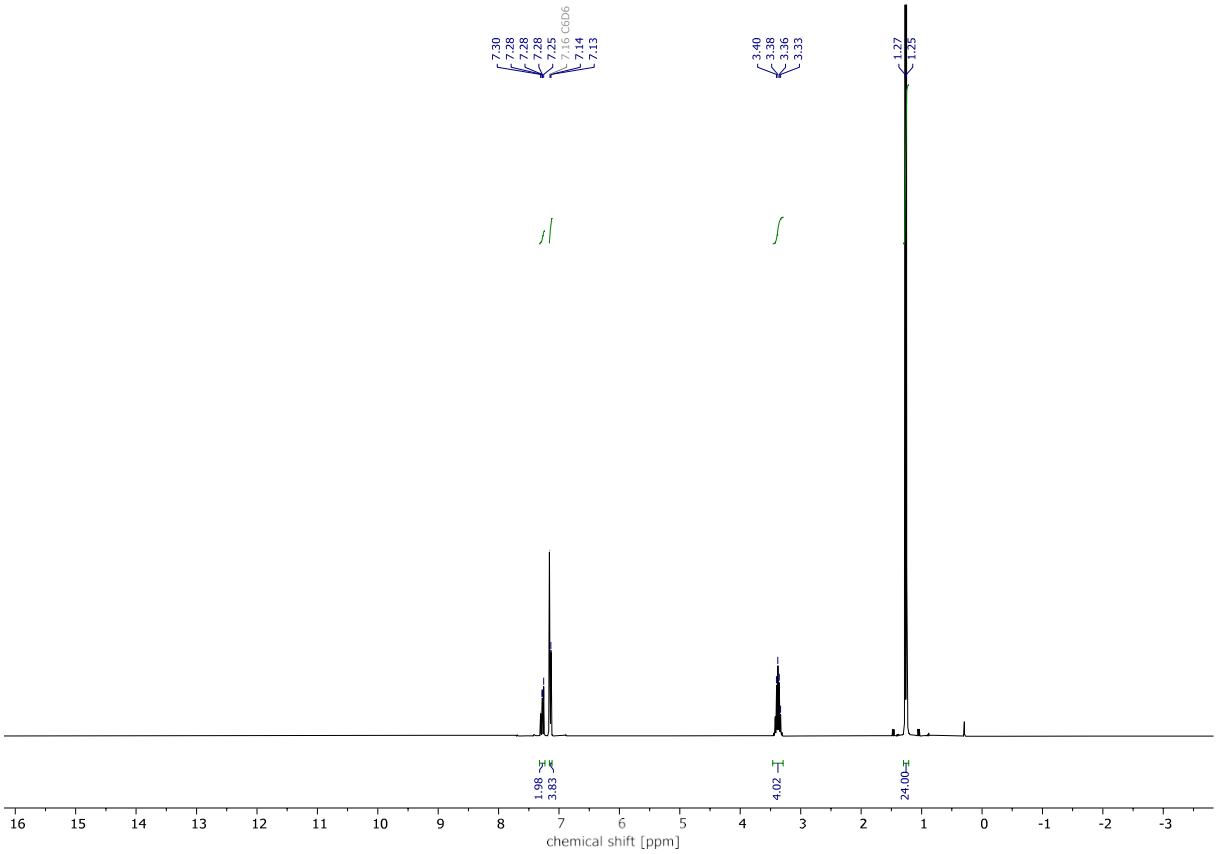


Figure S39: ^{13}C NMR spectrum of $(PDip)_2$ (**2**) in C_6D_6 at r.t.

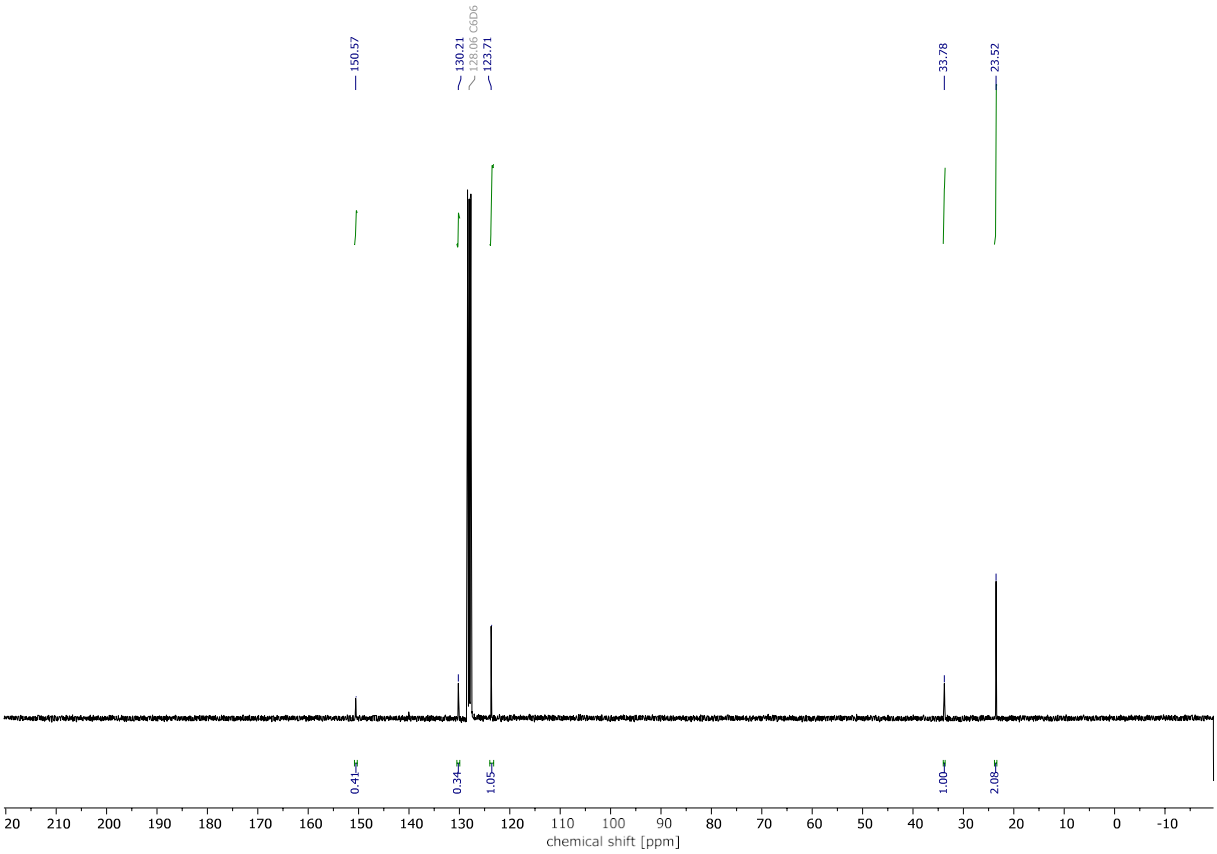


Figure S40: $^{31}P\{^1H\}$ NMR spectrum of $(PDip)_2$ in C_6D_6 at r.t.

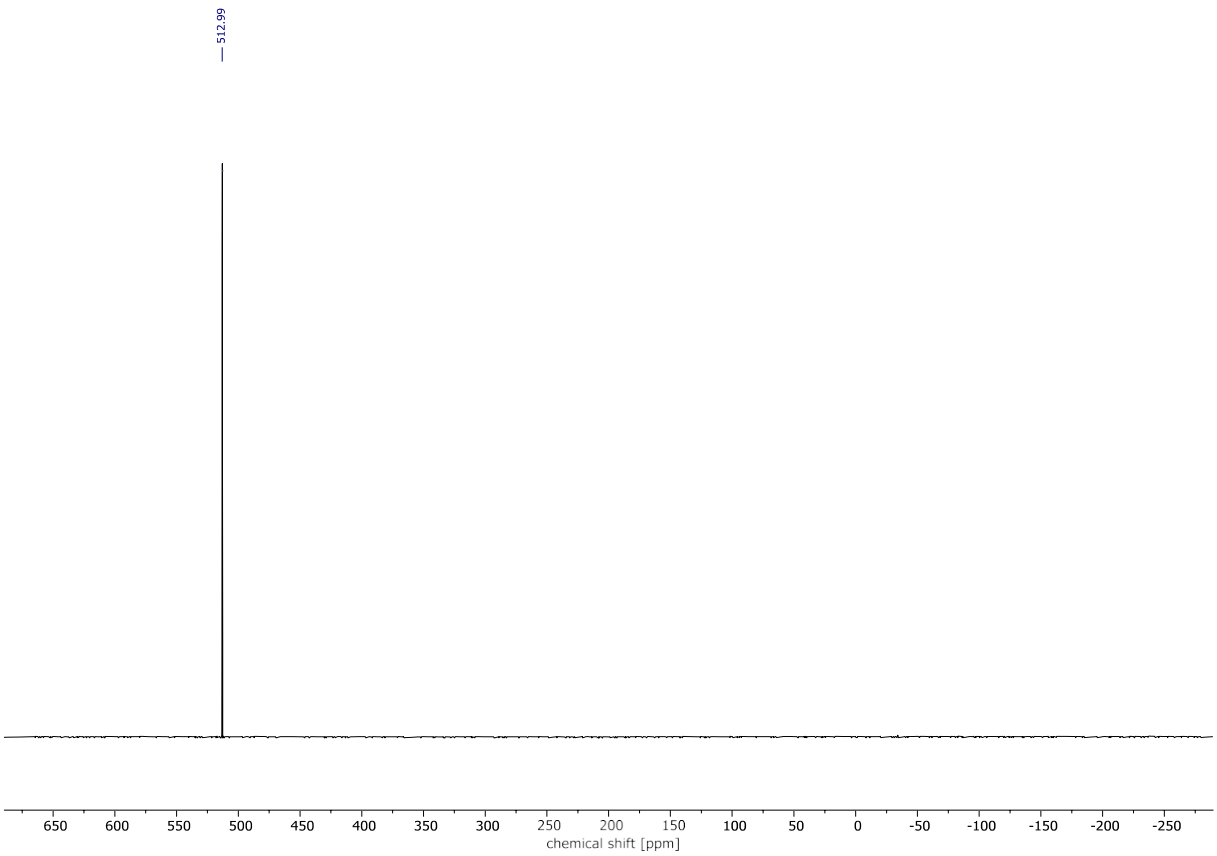
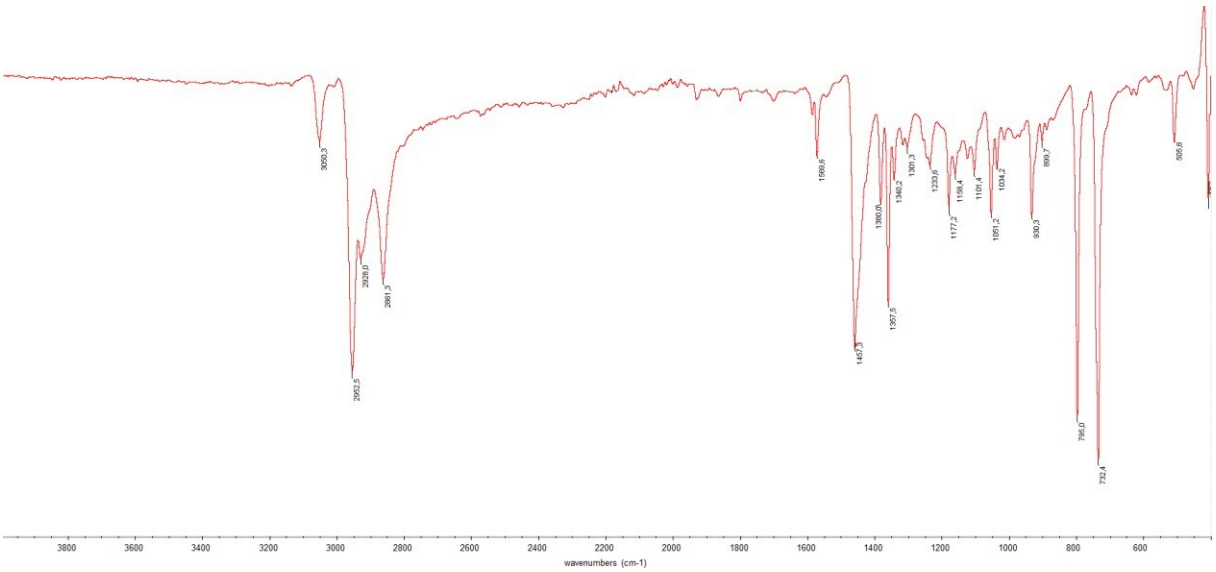
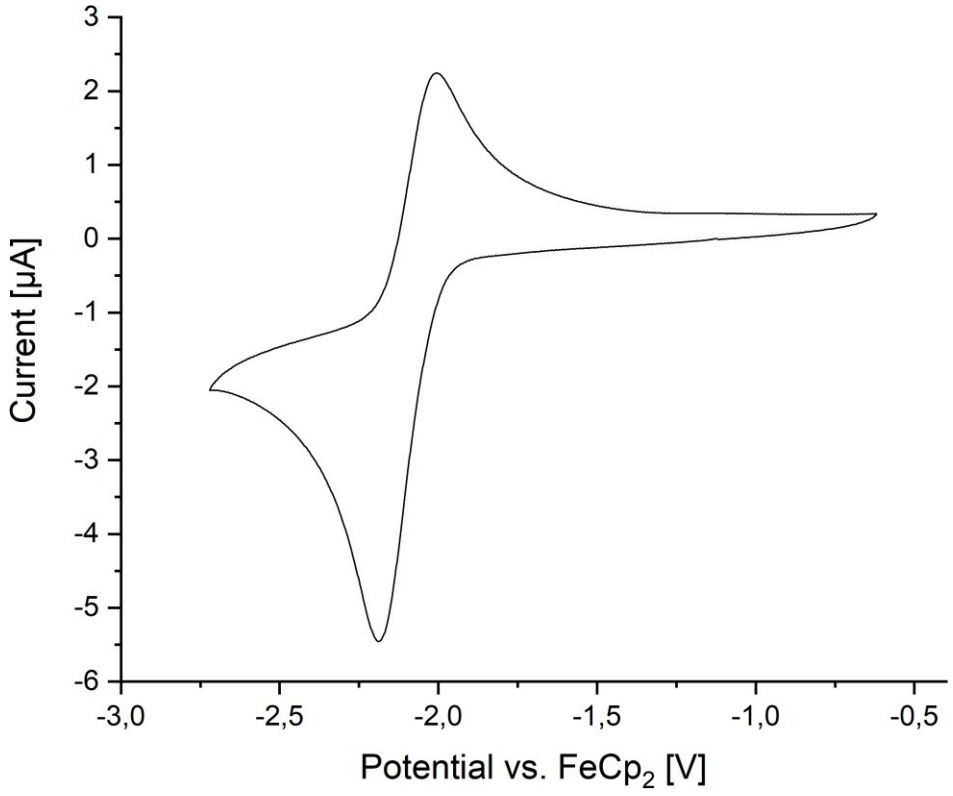


Figure S41: IR spectrum of crystalline $(PDip)_2$.



4.2.1 Cyclic Voltammetry Studies of **2**

Figure S42: Cyclic voltammogram of $(PDip)_2$ (**2**) in THF, 0.1 M $[N^nBu_4]PF_6$, obtained at 23 °C at a scan rate of 100 mV s^{-1}. $E_{1/2red}$ = −2.10 V (vs. $FeCp_2/[FeCp_2]^+$ redox couple)



4.2.2 Thermal stability of **2**

A sample of $(PDip)_2$ (20 mg) was dissolved in C_6D_6 in a J-Young NMR tube and was kept in the dark at room temperature. The sample was monitored via ^{31}P NMR spectroscopy over a period of 71 days. The conversion was determined via ^{31}P NMR integrals.

Figure S43: ^{31}P NMR spectra of Dip_2P_2 in C_6D_6 over a period of 71 days.

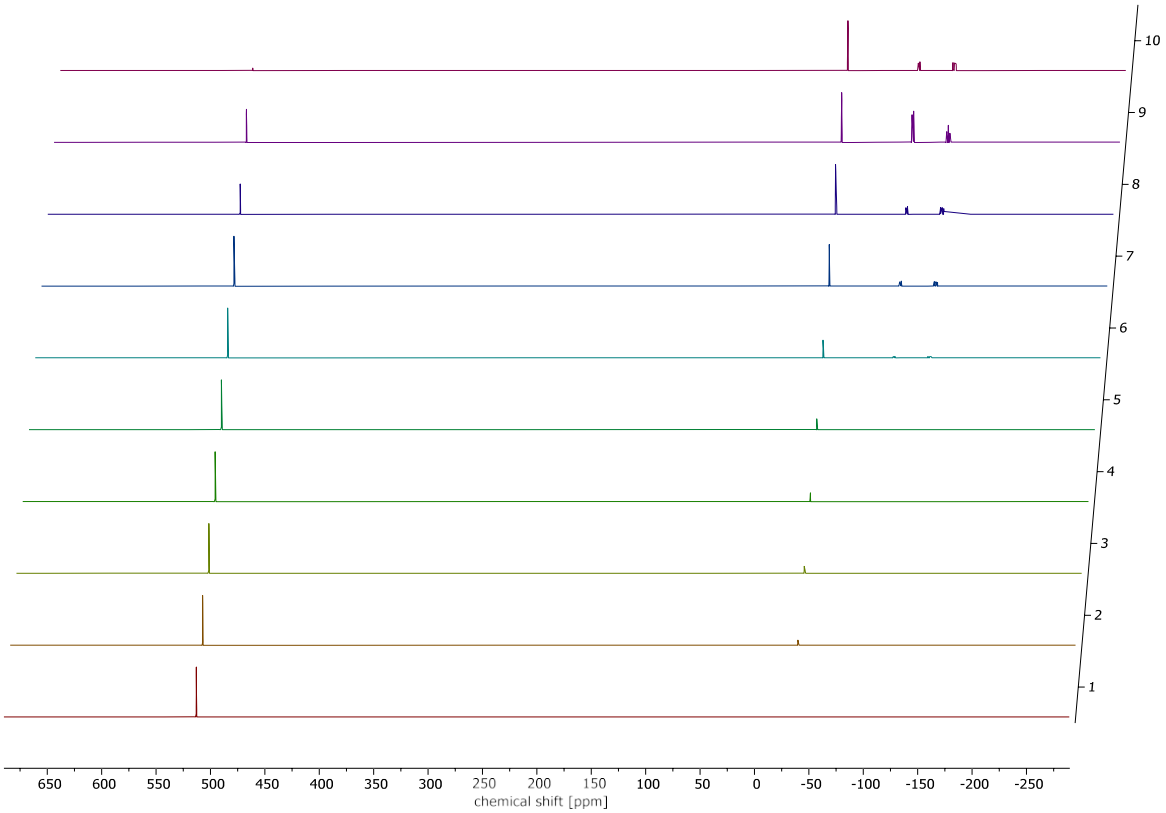
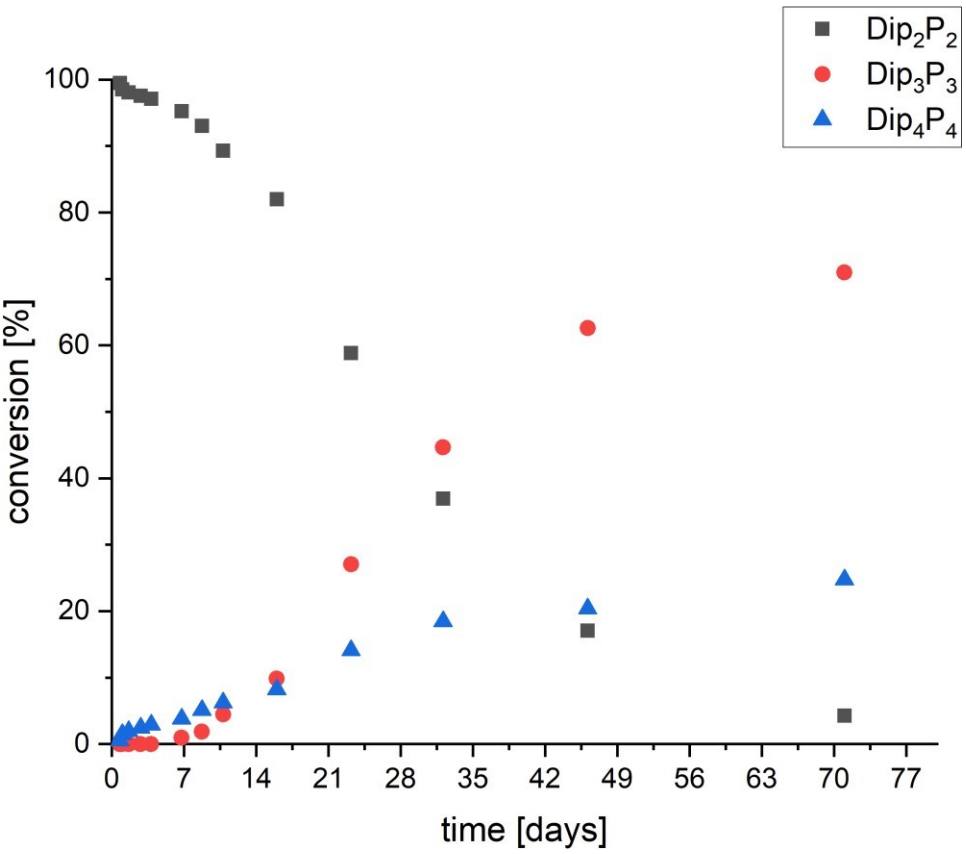


Table S4. Decay of $(PDip)_2$ monitored in a J-Young NMR tube. Ratios determined via ^{31}P NMR spectroscopy.

	Integrals determined via ^{31}P NMR spectra			Conversion		
Time [d]	$(PDip)_2$ (int)	$(PDip)_3$ (int)	P_4Dip_4 (int)	P_2Dip_2 [%]	P_3Dip_3 [%]	P_4Dip_4 [%]
0	1	0	0	100	0	0
0.80	1	0	0.01	99.5	0.0	0.5
1.03	1	0	0.03	98.5	0.0	1.5
1.67	1	0	0.04	98.0	0.0	2.0
2.82	1	0	0.05	97.6	0.0	2.4
3.83	1	0	0.06	97.1	0.0	2.9
6.78	1	0.01	0.08	95.2	1.0	3.8
8.74	1	0.02	0.11	93.0	1.9	5.1
10.80	1	0.05	0.14	89.3	4.5	6.3
16.01	1	0.12	0.2	82.0	9.8	8.2

23.20	1	0.46	0.48	58.8	27.1	14.1
32.11	1	1.21	1	36.9	44.6	18.5
46.14	1	3.67	2.39	17.1	62.6	20.4
71.02	1	16.66	11.62	4.3	71.0	24.8

Figure S44: Decay of $(PDip)_2$ in C_6D_6 to Dip_3P_3 and Dip_4P_4, giving a half-life time of ca. 28 days for **2**.



Based on this monitoring we can estimate a half life time of $(PDip)_2$, which is ca. 27 days.

4.2.3 Thermal stability of $(PDip)_2$ (2).

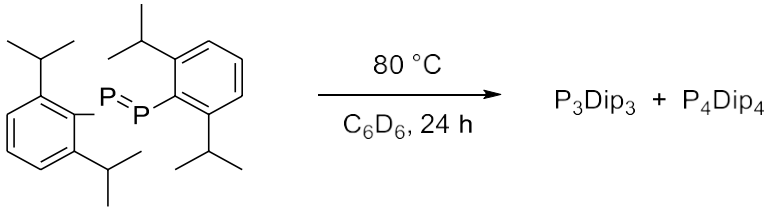
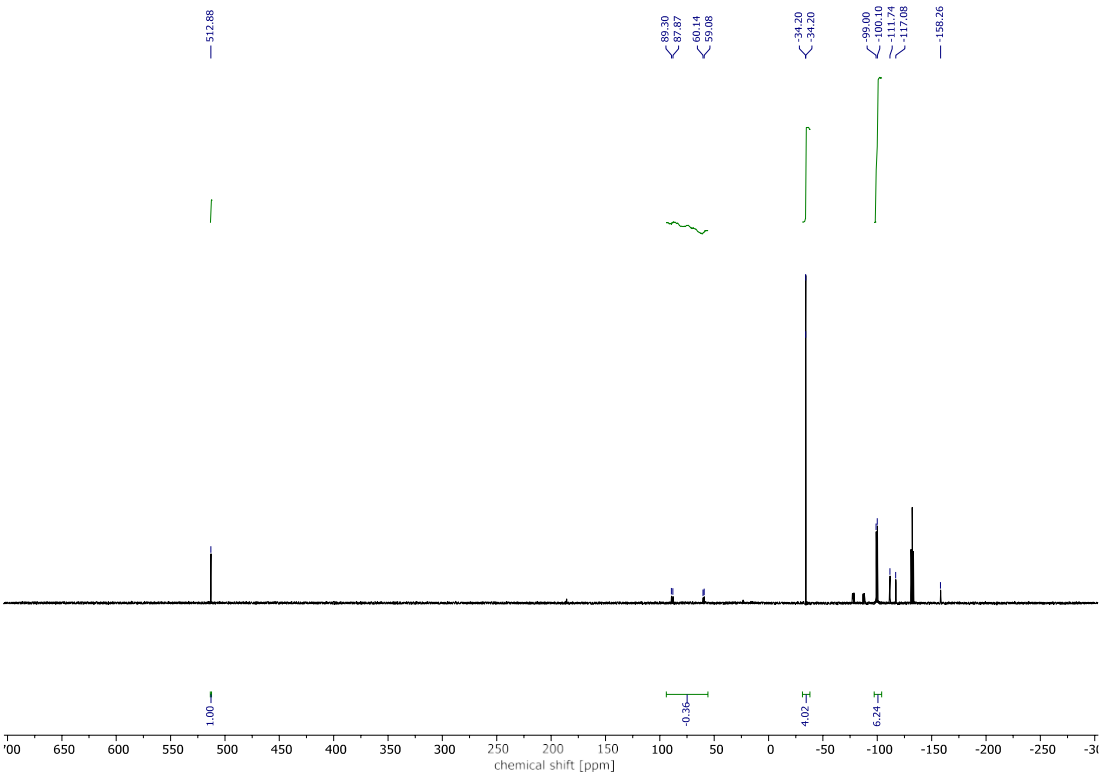


Figure S45: Decay of $(PDip)_2$ (**2**) in C_6D_6 at 80 °C to Dip_3P_3 and Dip_4P_4.



4.2.4 Photochemical decay of $(PDip)_2$ (**2**) and UV-Vis data

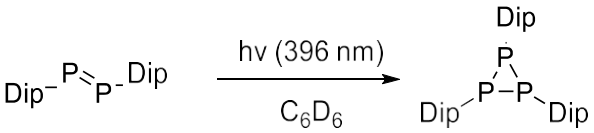


Figure S46: UV-Vis spectrum of Dip_2P_2 in MeCN.

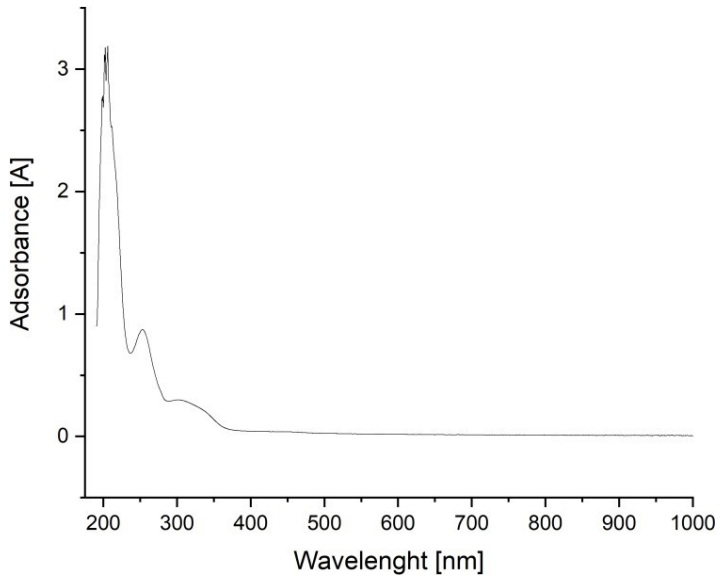


Figure S47: After irradiation with 396 nm light, the solution turned clear. The respective UV-Vis spectra show a shift in absorption maxima of Dip_2P_2. Spectra were recorded in MeCN.

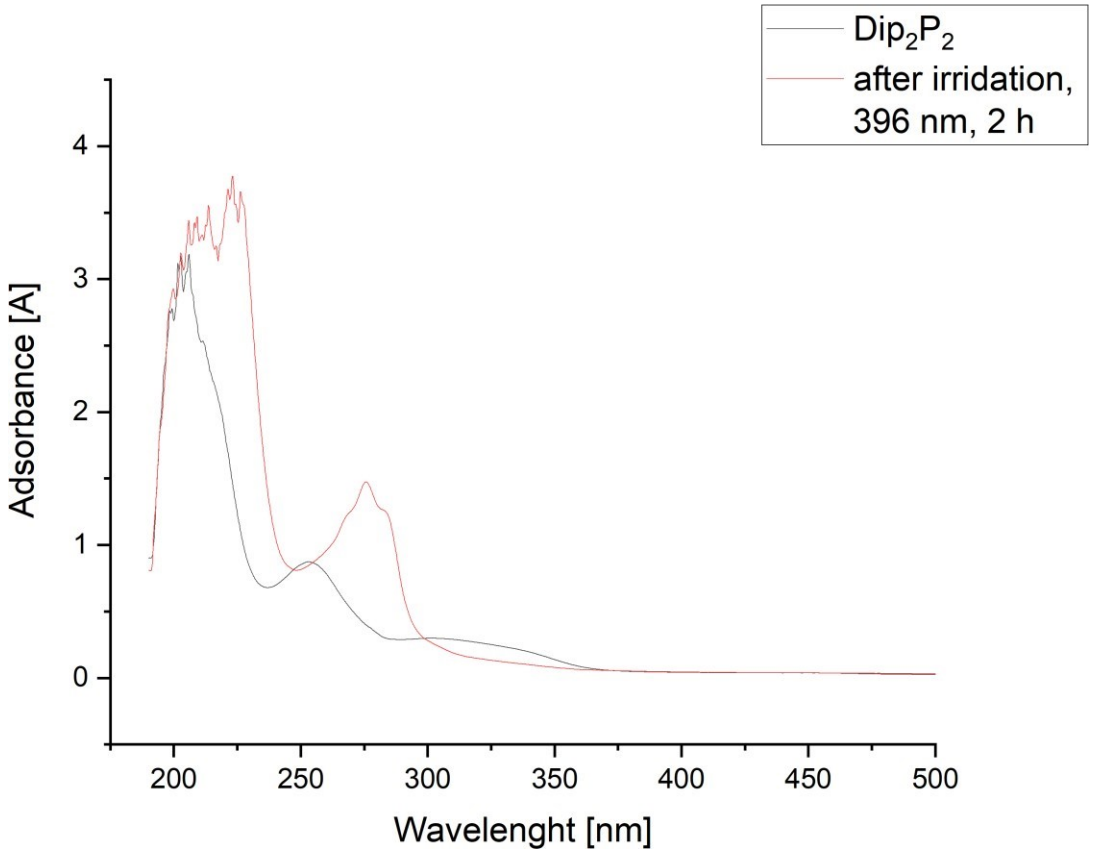
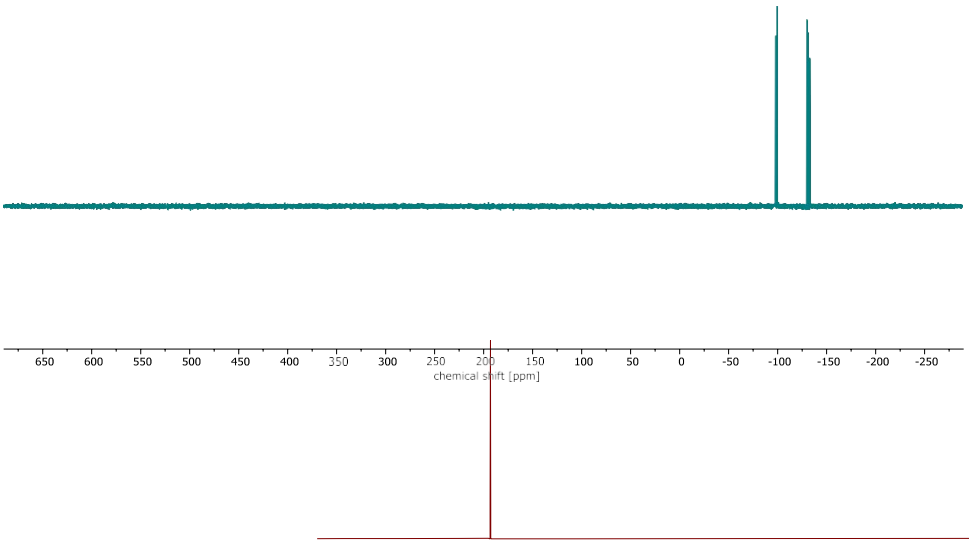


Figure S48: Light induced reaction monitored by ^{31}P NMR. Bottom Dip_2P_2, top after irradiation Dip_3P_3 the main product.



4.2.5 Reaction of $(PDip)_2$ with Pd(II) salts

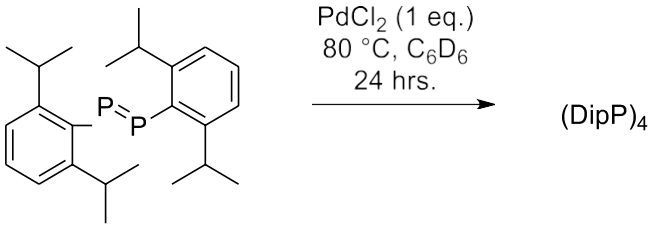


Figure S49: ^{31}P NMR of the reaction of Dip_2P_2 with $PdCl_2$ (1 equiv) after 24 h.

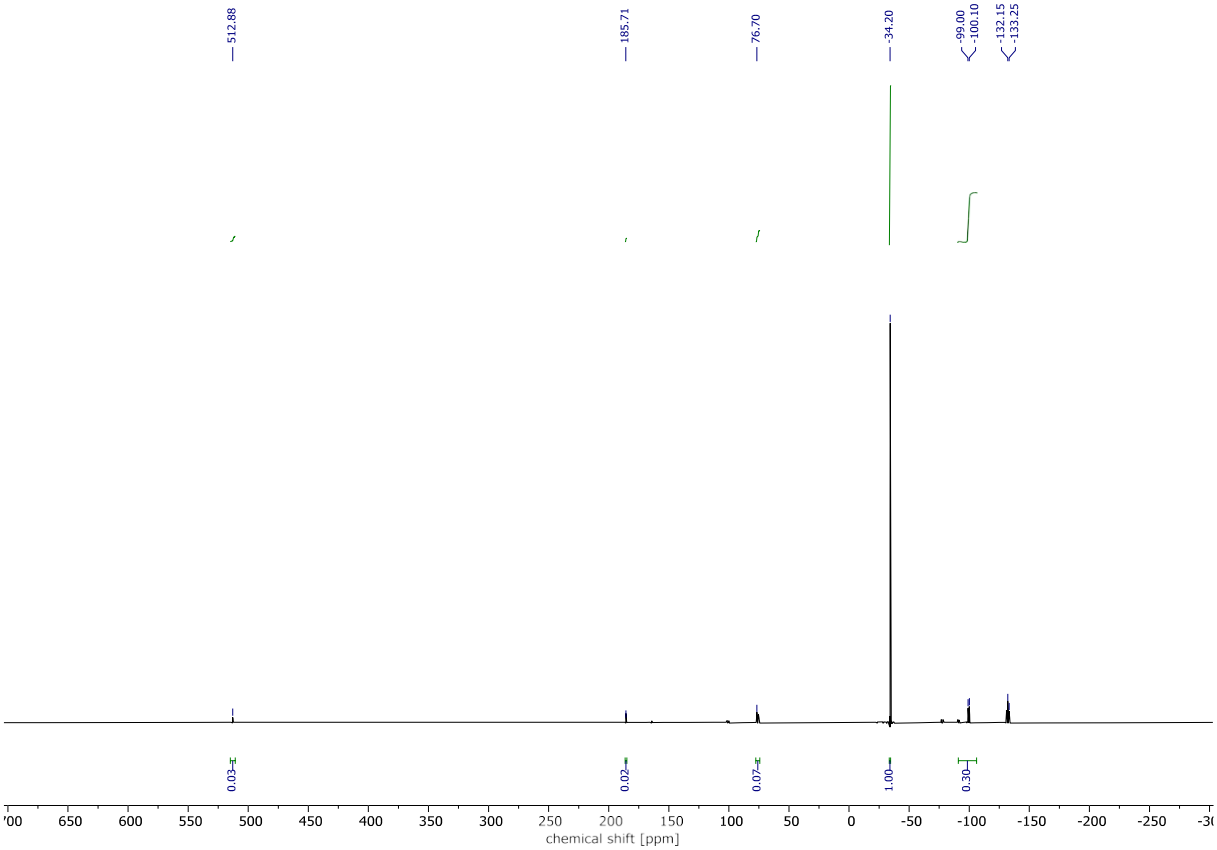
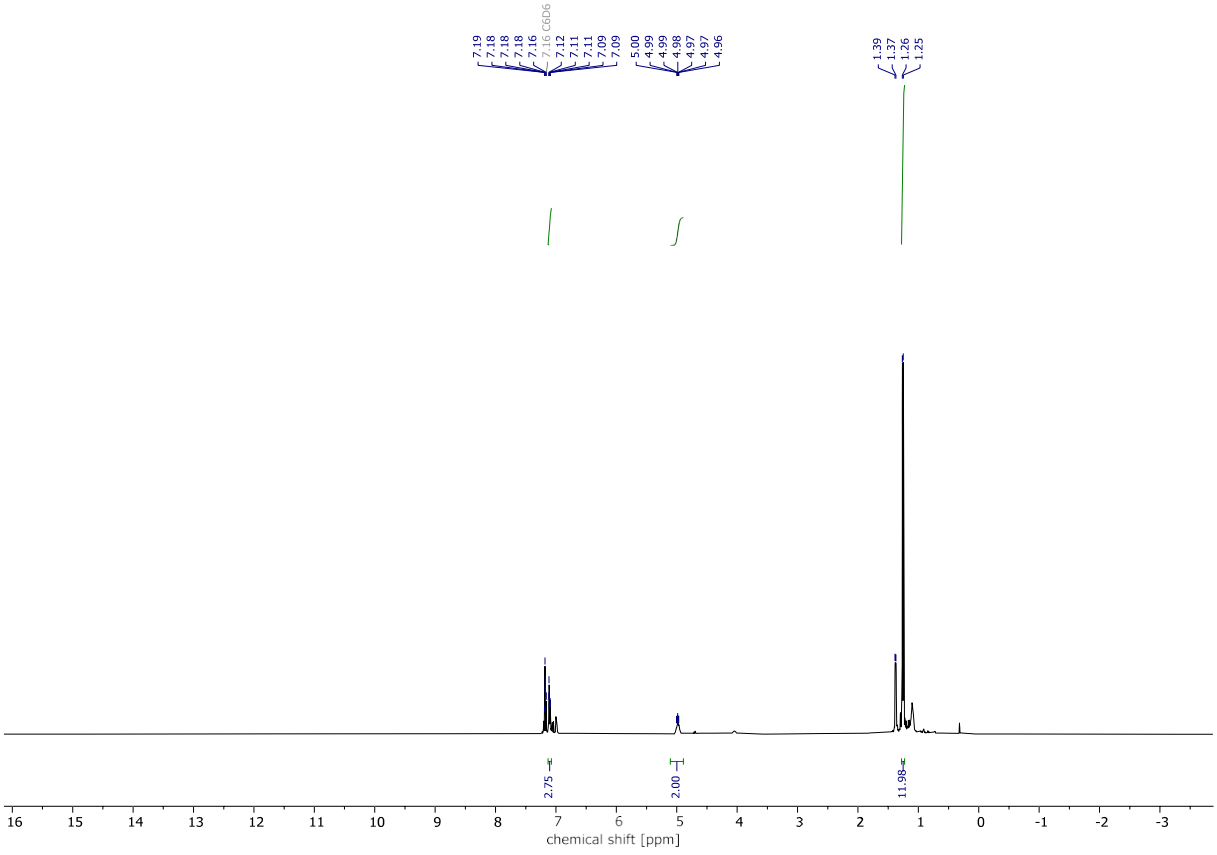
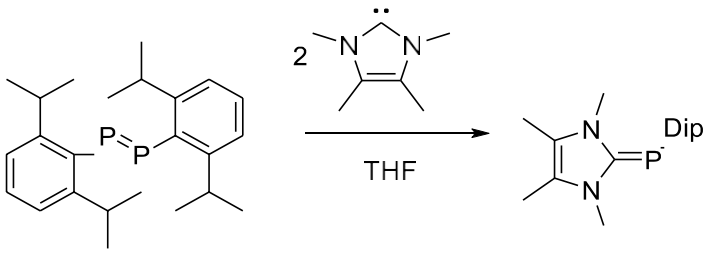


Figure S50: ^{1}H NMR of the reaction of $(PDip)_2$ (**2**) with $PdCl_2$ (1 equiv) after 24 hrs.



4.3 Synthesis of DipP=IMe$_4$ (5).



IMe$_4$ (11.6 mg, 0.0938 mmol) was dissolved in THF (5 mL) and cooled to −78 °C. P_2Dip_2 (18 mg, 0.0469 mmol) was dissolved in THF (2 mL) and was added dropwise to the stirred solution of IMe$_4$. The solution was allowed to warm to room temperature over a period of two days. Afterwards the solvent was removed *in vacuo*. The resulting yellow oil was extracted with *n*-hexane and was concentrated to incipient crystallization. Standing at −30 °C afforded DipP=IMe$_4$ (**5**) as yellow crystalline solid (14.7 mg, 0.046 mmol, 50 %).

X-ray quality crystals of **5** were grown from a saturated n-hexane solution at −30 °C.

^{1}H NMR (300 MHz, C_6D_6) δ = 7.38 – 7.21 (m, 3H), 4.75 (hd, $^3J_{HH}$ = 6.9 Hz, J_{PH} = 5.0 Hz, 2H, C*H*$(CH_3)_2$), 2.79 (d, J_{PH} = 1.2 Hz, 6H, NC*H*$_3$), 1.36 (d, $^3J_{HH}$ = 6.9 Hz, 12H), 1.26 (s, 6H) ppm. **^{31}P NMR** (122 MHz, C_6D_6) δ = -86.34 ppm. **^{13}C NMR** (101 MHz, C_6D_6) δ = 169.20 (d, $^1J_{PC}$ = 103.0 Hz), 154.42 (d, J_{PC} = 8.4 Hz), 140.79 (d, J_{PC} = 48.4 Hz), 127.12, 122.76, 120.70 (d, J_{PC} = 3.6 Hz), 33.92 (d, J_{PC} = 11.8 Hz), 32.17 (d, J_{PC} = 12.8 Hz), 24.38, 8.40. **IR** (ATR, 32 scans, cm^{-1}): *ν*= 2948.8 (s), 2915.5 (m), 2857.6 (m), 1670.6 (w), 1459.8 (s), 1435.8 (m), 1413.4 (w), 1369.0 (s), 1351.2 (s), 1336.2 (s), 1303.9 (s), 1245.6 (w), 1222.0 (w), 1162.8 (m), 1125.6 (w), 1094.3 (s), 1051.7 (m), 1026.6 (m), 925.5 (w), 851.8 (m), 801.1 (s), 749.6 (s), 643.4 (w), 585.7 (w), 562.1 (w), 520.4 (w), 499.6 (w), 431.5 (w) cm^{-1}. **EA** calc. C 72.12% H 9.24% N 8.85%, obs. C 72.34%, H 9.47%, N 8.51%.

Figure S51: ^{1}H NMR spectrum of DipP=IMe$_4$ (5) in C_6D_6 at r.t.

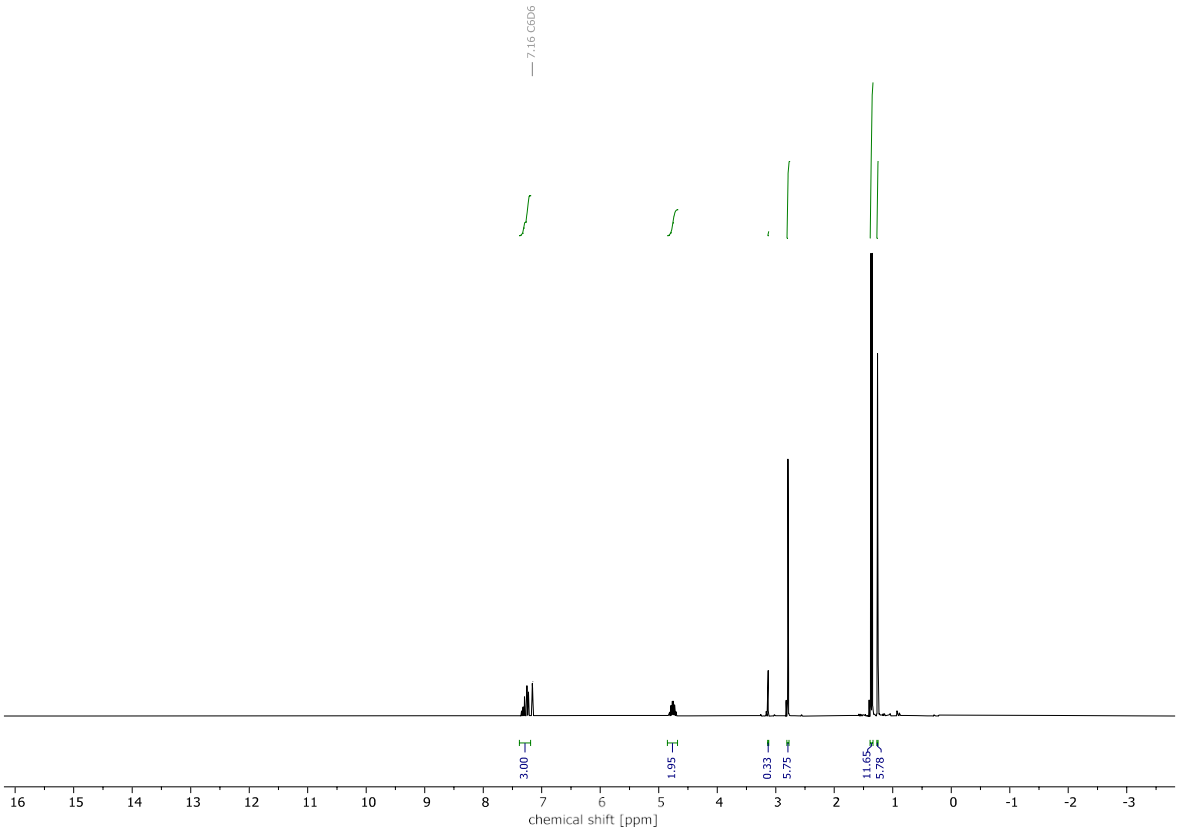


Figure S52: ^{13}C NMR spectrum of DipP=IMe$_4$ (5) in C_6D_6 at r.t.

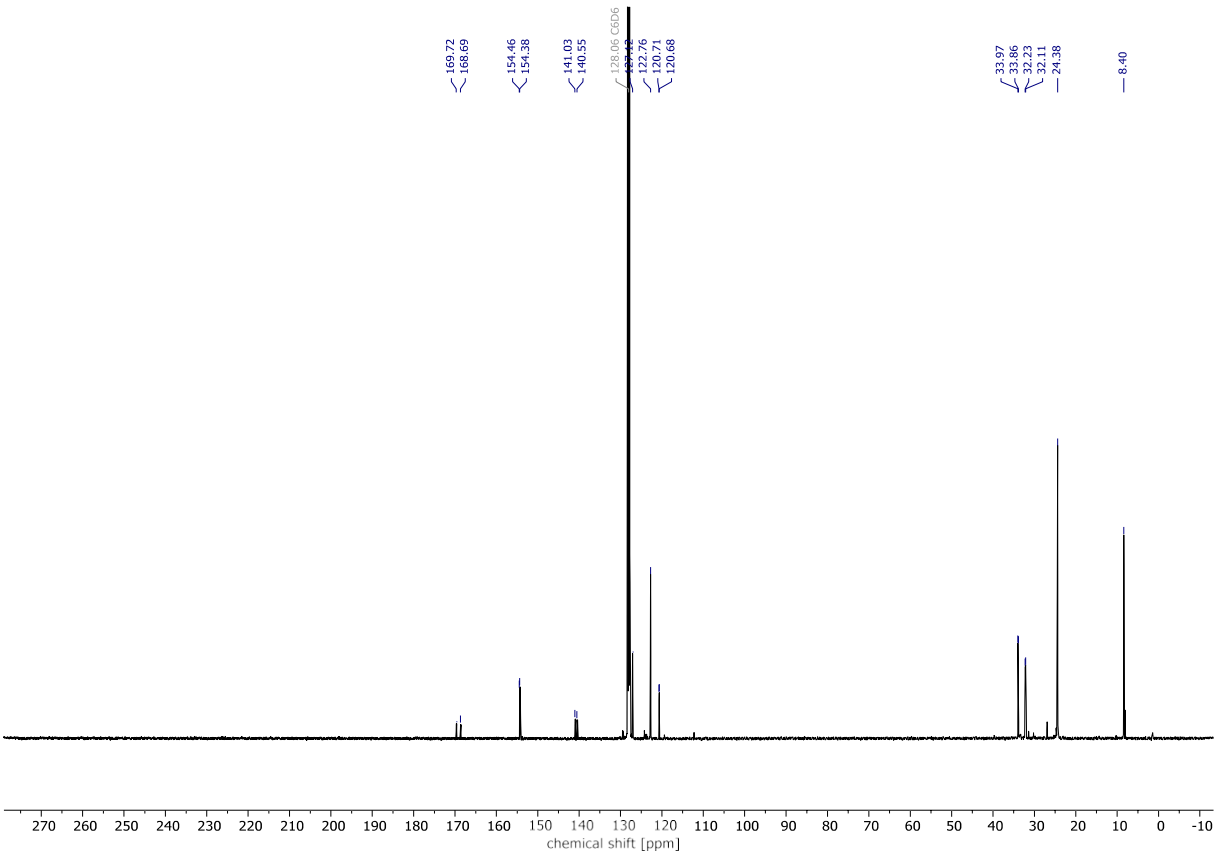


Figure S53: $^{31}P\{^{1}H\}$ NMR spectrum of DipP=IMe$_4$ (**5**) in C_6D_6 at r.t.

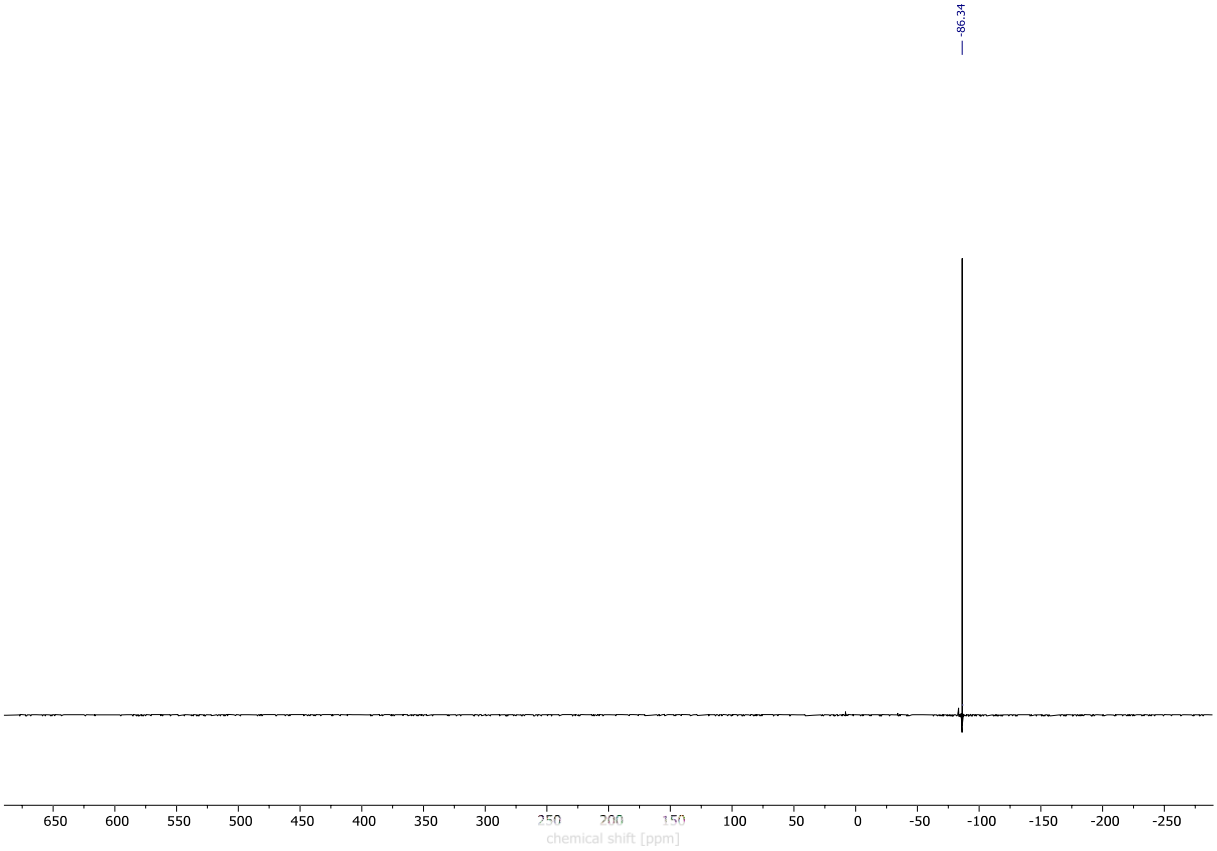
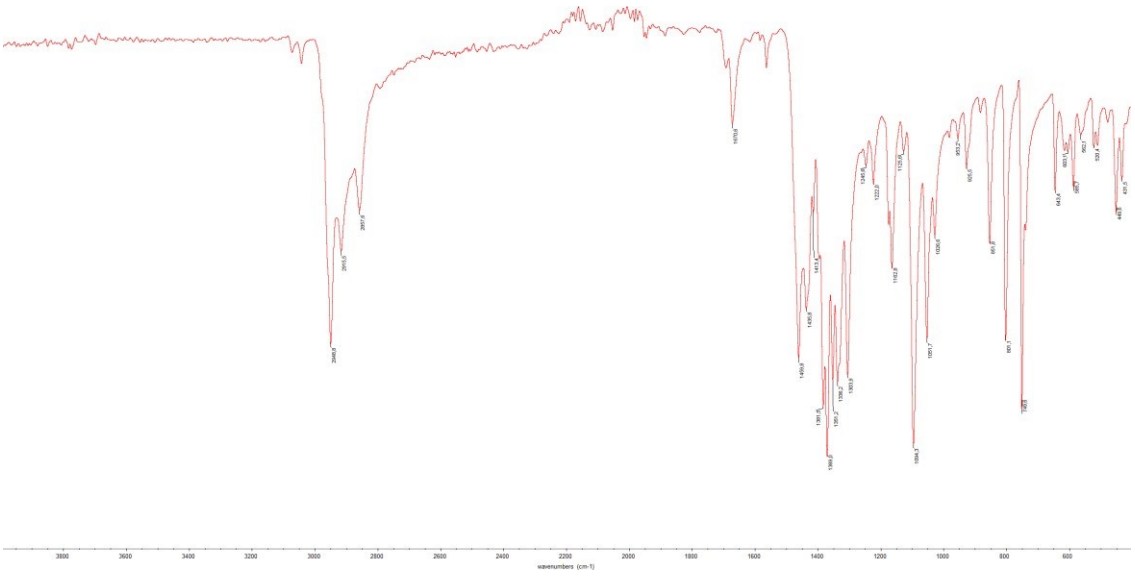
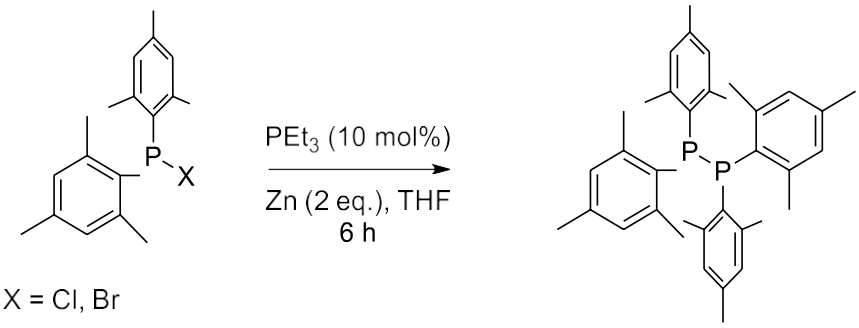


Figure S54: IR spectrum of crystalline DipP=IMe$_4$.



4.4 Synthesis of $(Mes_2P)_2$ (6).



To Mes_2PX (0.475 g, 1.46 mmol) and zinc (0.186 g, 2 eq.) THF (20 mL) was added. PEt_3 (1.46 ml, 0.1 M in THF, 0.2 mmol) was added dropwise to the stirring mixture. After 6 h all volatiles were removed in vacuo and the white residue was extracted with benzene (20 mL). The solvent was removed in vacuo and the white crystalline solid was washed with pentane (2x 2 mL) yielding $(Mes_2P)_2$ (**6**) (0.338 g, 0.63 mmol, 86 %).

^{1}H NMR (300 MHz, C_6D_6) δ = 6.61 (s, 2H), 2.81 – 2.17 (m, 6H), 2.02 (s, 3H) ppm.
^{31}P NMR (300 MHz, C_6D_6) δ = −30.4 ppm.

Figure S55: ^{1}H NMR spectrum of $(Mes_2P)_2$ in C_6D_6 at r.t.

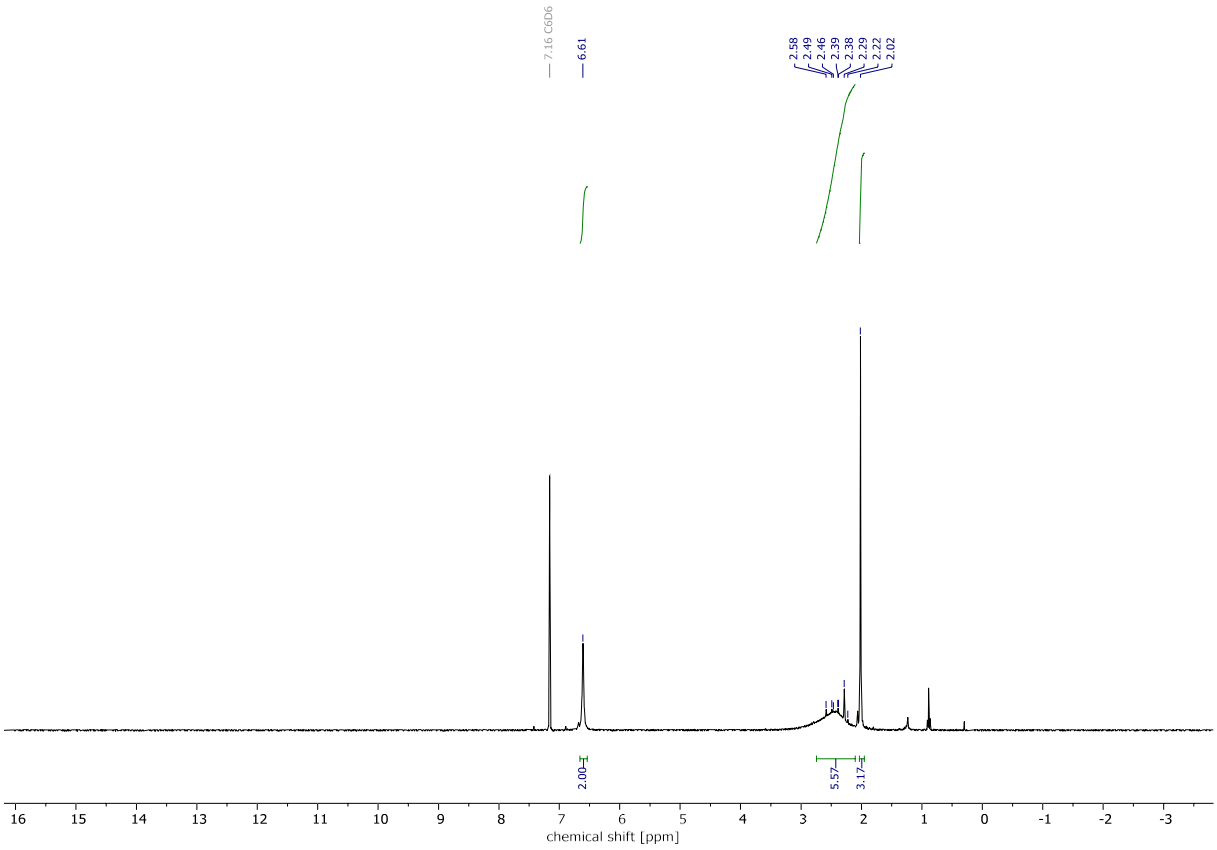
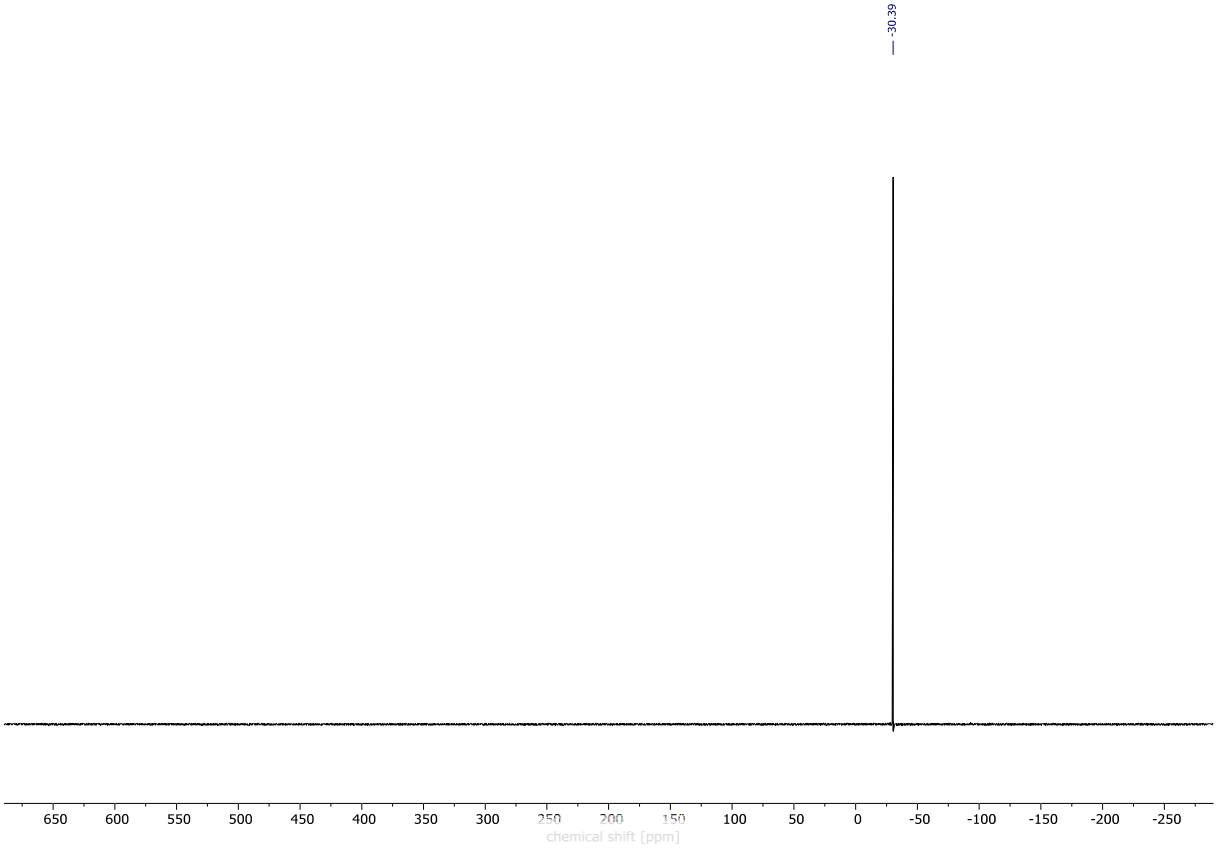
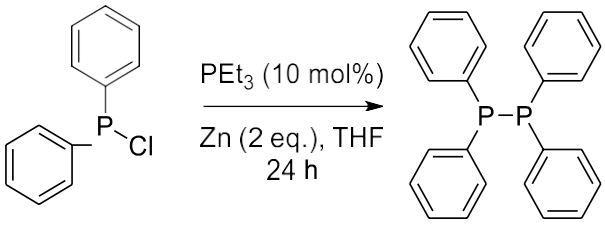


Figure S56: ^{31}P NMR spectrum of $(Mes_2P)_2$ in C_6D_6 at r.t.



4.5 Synthesis of $(Ph_2P)_2$ (7).



To Ph_2PCl (0.244 g, 1.1 mmol) and zinc (0.140 g, 2.2 eq.) THF (10 mL) was added. PEt_3 (1.1 ml, 0.1 M in THF, 0.11 mmol) was added dropwise to the stirring mixture. After 24 h all volatiles were removed in vacuo and the white residue was extracted with benzene (20 mL). The solvent was removed in vacuo and the white crystalline solid was washed with *n*-pentane (2x 2 mL) at −30 °C yielding $(Ph_2P)_2$ (**6**) (0.117 g, 0.32 mmol, 58 %).

^{1}H NMR (300 MHz, C_6D_6) δ 7.64 – 7.55 (m, 2H), 7.02 – 6.93 (m, 3H) ppm. **^{31}P NMR** (122 MHz, C_6D_6) δ −14.30 ppm.[6]

^{1}H NMR (300 MHz, THF-d_8) δ 7.41 – 7.31 (m, 2H), 7.27 – 7.06 (m, 3H). **^{31}P NMR** (122 MHz, THF-d_8) δ −15.62.

5 Structure elucidation

X-ray Structure Determination: X-ray quality crystals of all compounds were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature or in Fomblin© Y perfluoroether (Sigma Aldrich) at −30 °C under a constant stream of nitrogen. The samples were cooled to 150(2) K during measurement. The data were collected on a Bruker Kappa Apex II diffractometer using Mo K_α radiation (λ = 0.71073 Å) or Cu K_α radiation (λ = 1.54178 Å), or on a STOE-IPDS II diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 150(2) K. The structures were solved by iterative methods (SHELXT)[7] and refined by full matrix least squares procedures (SHELXL).[8] Semi-empirical absorption corrections were applied (SADABS[9] or LANA). All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

In *S*,*S*-**1** the second Tip-group was found to be disordered and was split into two parts. The occupancy of each part was allowed to refine freely.

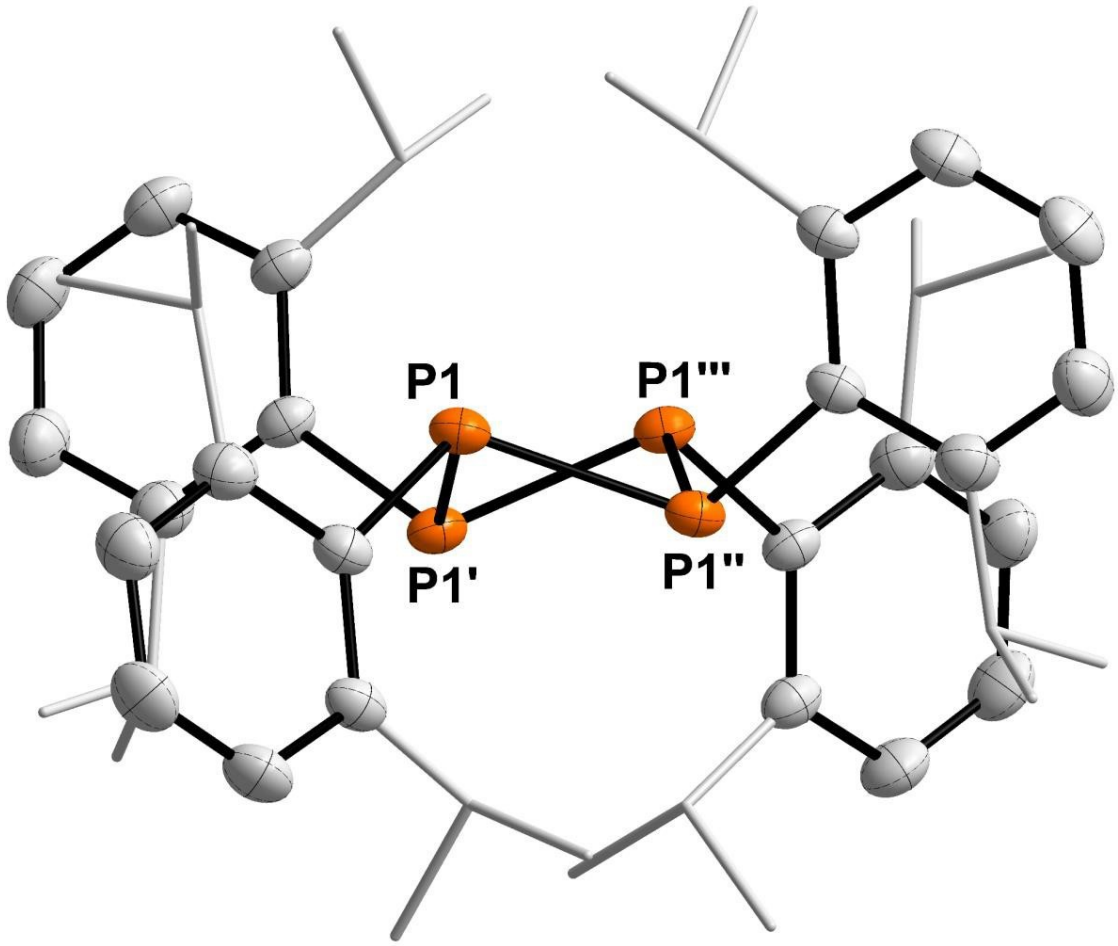
Table S5: Crystallographic details of *R*,*S*-**1**, *S*,*S*-**1** and **2**.

Compound	*R*,*S*-**1**	*S*,*S*-**1**	**2**
Chem. Formula	$C_{30}H_{46}P_2Br_2$	$C_{30}H_{46}P_2Br_2$	$C_{24}H_{34}P_2$
Formula weight [g/mol]	628.43	628.43	384.45
Colour	yellow	yellow	yellow
Crystal system	orthorhombic	triclinic	monoclinic
Space group	*Pbca*	*P*1	$P2_1/n$
a [Å]	9.0324(4)	9.7477(16)	6.1450(12)
b [Å]	16.1088(8)	12.232(2)	8.4640(17)
c [Å]	21.3757(11)	13.591(2)	21.620(4)
α [°]	90	90.634(4)	90
β [°]	90	102.776(3)	92.81(3)
γ [°]	90	96.594(3)	90
V [Å^3]	3110.2(3)	1568.8(4)	1123.1(4)
Z	4	2	2
$\rho_{calcd.}$ [g/cm^3]	1.342	1.330	1.137
μ [mm^{-1}]	2.726	2.702	0.199
T [K]	150(2)	150(2)	150(2)
Measured reflections	39293	76651	21095
Independent reflections	4538	9672	3038
Reflections with $I > 2\sigma(I)$	3482	8242	2480
R_{int}	0.0404	0.0276	0.0276
F(000)	1304	652	416
$R_1(R[F^2>2\sigma(F^2)])$	0.0293	0.0261	0.0305
$wR_2(F^2)$	0.0757	0.0713	0.0865
GooF	1.020	1.026	1.028
No. of Parameters	160	443	122
CCDC #	2098825	2098826	2098827

Table S6: Crystallographic details of **4** and **5**.

Compound	**4**	**5**
Chem. Formula	$C_{19}H_{29}N_2P$	$C_{48}H_{68}P_4$ 2 C_6H_6
Formula weight [g/mol]	316.41	925.12
Colour	yellow	colourless
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/n$	$P4n2$
a [Å]	14.2549(15)	11.9767(2)
b [Å]	9.7910(10)	11.9767(2)
c [Å]	14.6252(15)	19.3408(4)
α [°]	90	90
β [°]	115.911(2)	90
γ [°]	90	90
V [Å^3]	1836.0(3)	2774.27(11)
Z	4	2
$\rho_{calcd.}$ [g/cm^3]	1.145	1.147
μ [mm^{-1}]	0.149	0.242
T [K]	150(2)	150(2)
Measured reflections	21175	24887
Independent reflections	4961	4057
Reflections with $I > 2\sigma(I)$	4003	3689
R_{int}	0.0296	0.0316
$F(000)$	688	1000
$R_1(R[F^2>2\sigma(F^2)])$	0.0407	0.0357
w$R_2(F^2)$	0.1118	0.0951
GooF	1.014	1.048
No. of Parameters	207	151
CCDC #	2098828	2098829

Figure S57: Molecular structure of **4**. Hydrogen atoms have been omitted and *i*Pr-groups rendered as wireframe for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): P1–C1 1.8562(18), P1–P′ 2.2231(9), P1–P1′ 2.2563(9); C1–P1–P1′ 104.45(6), C1–P1–P1′′ 113.64(6); P1′–P1–P1′′ 82.158(14); P1′′′–P1′–P1–P1′′ -40.181(19).



6 Computational details

6.1 General remarks

Computations were carried out using Gaussian09[10] and the standalone version of NBO 6.0.[11]

Structure optimizations employed the hybrid DFT functional PBE0[12] in conjunction with Grimme's dispersion correction D3(BJ)[13] and the def2-TZVP basis set[14] (notation PBE0-D3/def2-TZVP). All structures were fully optimized and confirmed as minima by frequency analyses. Partial charges were determined by Natural Population analysis using the NBO program. Chemical shifts were derived by the GIAO method at the PBE0-D3/def2-TZVP level of theory.[15] The calculated absolute shifts ($\sigma_{calc,X}$) were referenced to the experimental absolute shift of 85% H_3PO_4 in the gas phase ($\sigma_{ref,1}$ = 328.35 ppm),[16] using PH_3 ($\sigma_{ref,2}$ = 594.45 ppm) as a secondary standard:[17]

$$\begin{aligned}\delta_{calc,X} &= (\sigma_{ref,1} - \sigma_{ref,2}) - (\sigma_{calc,X} - \sigma_{calc,PH_3}) \\ &= \sigma_{calc,PH_3} - \sigma_{calc,X} - 266.1 \text{ ppm}\end{aligned}$$

At the PBE0-D3/def2-TZVP level of theory, $\sigma_{calc,PH3}$ amounts to +571.6 ppm.

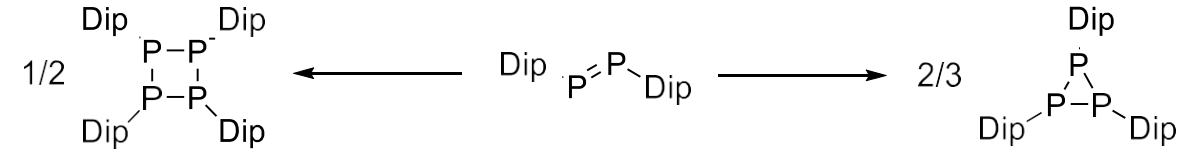
Please note that all computations were carried out for single, isolated molecules in the gas phase (ideal gas approximation). There may well be significant differences between the gas phase structures and those in the condensed phase.

6.2 Thermodynamic observations

6.2.1 Relative stability of Dip_2P_2 (**2**)

We observed the decomposition of Dip_2P_2 (**2**) into Dip_3P_3 (**3**) and Dip_4P_4 (**4**) over several weeks at room temperature under the exclusion of light. Therefore, we calculated the relative stability of diphosphene 2 with respect to the 3- and 4-membered cyclo-oligophosphanes **3** and **4**. These results indicate that 2 is thermodynamically unstable with respect to **3** and **4**, with Dip_3P_3 (**3**) being thermodynamically more stable than Dip_4P_4 (**4**). This is in line with **3** being the predominant product after 71 d.

Figure S58: Calculated enthalpy and Gibbs free energy at the PBE0-D3/DEF2-TZVP level of theory.



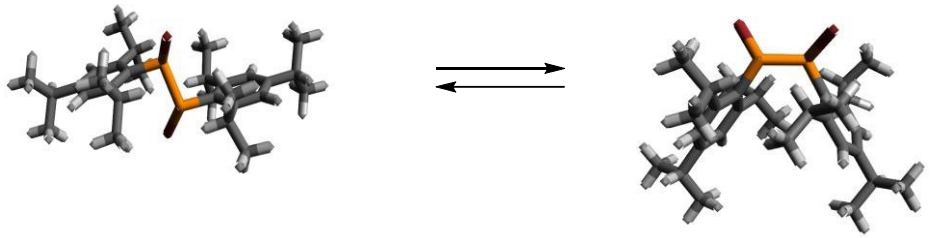
ΔH = -14.07 kcal/mol
ΔG = -4.50 kcal/mol

ΔH = -14.14 kcal/mol
ΔG = -8.54 kcal/mol

6.2.2 Relative stability of $(TipPBr)_2$ (**1**)

Compound **1** forms as a mixture of both *meso*-**1** and *rac*-**1** and the relative stability of both forms was determined based on the molecular structures of both forms obtained by single crystal X-Ray crystallography. This shows that *meso*-**1** in which both bromine atoms are in *trans* position is more stable than *rac*-**1**.

Figure S59: Calculated enthalpy and total Gibbs free energy at the PBE0-D3/DEF2-TZVP level of theory.

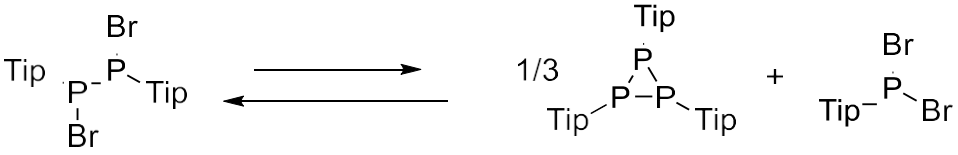


$(TipPBr)_2$ meso
P(R)-**P**(S)
ΔH = 0 kcal/mol
ΔG = 0 kcal/mol

$(TipPBr)_2$ rac
P(S)-**P**(S)
ΔH = 1.78 kcal/mol
ΔG = 4.15 kcal/mol

6.2.3 Disproportionation of $(TipPBr)_2$ (**1**)

Figure S60: Calculated enthalpy and total Gibbs free energy at the PBE0-D3/DEF2-TZVP level of theory for the disproportionation of $(TipPBr)_2$.



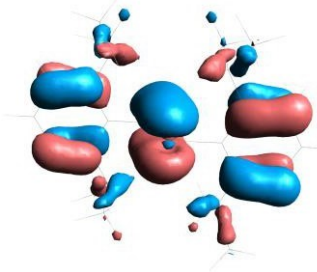
ΔH = 4.8 kcal/mol
ΔG = 0.8 kcal/mol

6.2.4 Calculated UV-Vis spectra

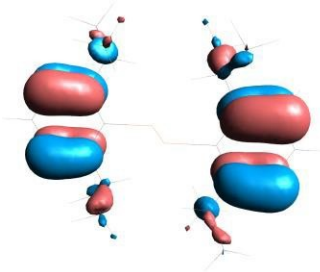
Table S7. Calculated electronic excitations of $(PDip)_2$ (**2**) (PBE0-D3/def2-TZVP).

State	Symmetry	λ [nm]	Oscillator strength	Main excitation
S1	^1BG	459	0.0000	HOMO→LUMO
S2	^1BG	343	0.0067	HOMO-3→LUMO HOMO-1→LUMO
S3	^1AG	341	0.0000	HOMO-2→LUMO+2

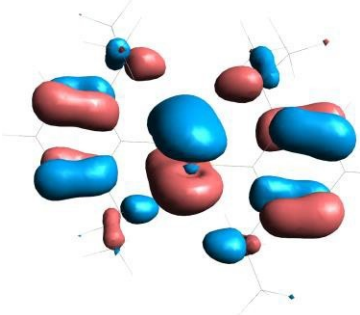
Figure S61. Relevant Kohn-Sham orbitals of $(PDip)_2$ (**2**) (PBE0-D3/def2-TZVP).



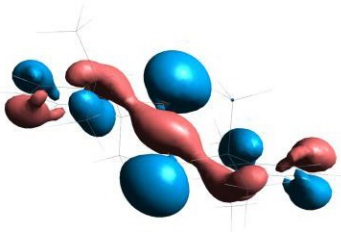
HOMO−3
−7.01 eV
a



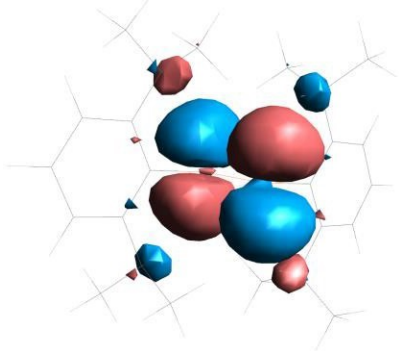
HOMO-2
−6.88 eV
a



HOMO-1
−6.75 eV
a



HOMO
−6.30 eV
a

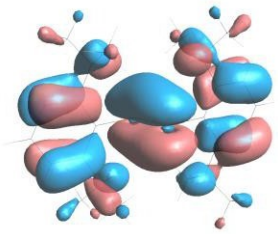


LUMO
−2.35 eV
a

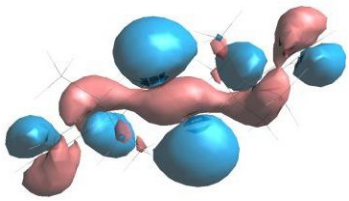
6.3 Bonding analysis of $(PDip)_2$ (**2**)

The HOMO of P_2Dip_2 shows the σ-type lone pairs located at the P-atoms. The HOMO-1 resembles the P π-bond. The LUMO exhibts π* antibonding character. Furthermore, the NBO analysis confirms the double bonded character and the respective P−P σ and π bonds are depicted in Figure S45 (NLMOs) along with the s-type LP on phosphorus.The Wiberg bond index (WBI) of the P=P bond is 1.83 in line with a double bond.

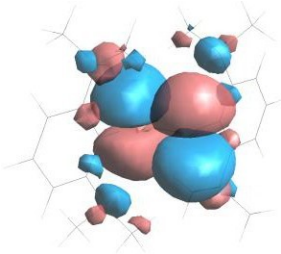
Figure S62: Relevant Kohn-Sham orbitals of Dip_2P_2 (point group C_{2h}, PBE0-D3/def2-TZVP).



HOMO−1
−6.75 eV
a

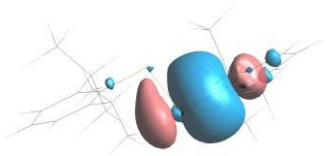


HOMO
−6.30 eV
a

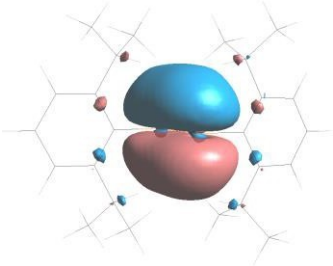


LUMO
−2.35 eV
a

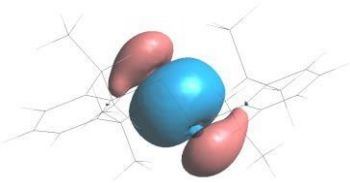
Figure S63: Selected NLMOs of Dip_2P_2 (point group C_{2h}, PBE0-D3/def2-TZVP).



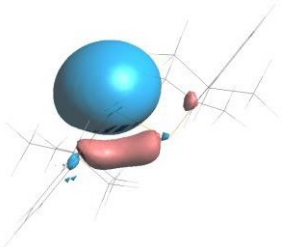
(P-C_{Aryl})
−15.8 eV
37 % P
61 % C



π (P-P)
−7.6 eV
49 % P
49 % P



S (P-P)
49 % P
49 % P



LP P
98 % P

6.4 Calculated ^{31}P-NMR shifts

Table S8.: Calculated ^{31}P-NMR shifts at PBE0-D3/def2-TZVP using PH_3 as internal standard.

Structure	**δ exp. [ppm]**	**δ calc [ppm]**
P_2Dip_2	512.99	587.11
P_3Dip_3	-99.51, -132.13	-85.50, -122.01
P_4Dip_4	-34.14	-8.57
$TipPBr_2$	151.95	202.41
$TipPCl_2$	164.84	189.40
$(TipPBr)_2$ meso	64.62	81.46
$(TipPBr)_2$ rac	65.47	124.69
$(TipPCl)_2$ meso	74.93	87.49
$(TipPCl)_2$ rac	77.19	131.35

6.5 Summary of calculated data

Table S9. Summary of calculated data, including electronic energies. Total SCF energy in a.u.

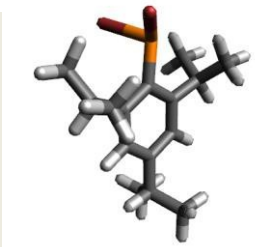
Structure	PG	NIMAG	E_{tot}	U_{298}	H_{298}	$G°_{298}$
$TipPBr_2$	C_1	0	-6073.62168	-6073.59954	-6073.5986	-6073.67463
$(TipPBr)_2$ rac	C_1	0	-6999.53693	-6999.49462	-6999.49367	-6999.61580
$(TipPBr)_2$ meso	C_1	0	-6999.53331	-6999.49178	-6999.49084	-6999.60919
Tip_3P_3	C_1	0	-2777.71665	-2777.65873	-2777.65779	-2777.80997
$TipPCl_2$	C_1	0	-1846.03016	-1846.00854	-1846.00759	-1846.08124
$(TipPCl)_2$ rac	C_1	0	-2771.94018	-2771.89850	-2771.89755	-2772.01622
$(TipPCl)_2$ meso	C_1	0	-2771.93732	-2771.896350	-2771.89541	-2772.01045
Dip_2P_2	C_{2h}	0	-1616.22384	-1616.19441	-1616.19346	-1616.28326
Dip_3P_3	C_1	0	-2424.36918	-2424.32493	-2424.32399	-2424.44531
Dip_4P_4	S_4	0	-3232.49184	-3232.43271	-3232.43176	-3232.58087

6.6 Optimized structures (.xyz-files)

6.6.1 PH_3

```
4
PH3 @ PBE0-D3/def2-TZVP
 P       0.000000000      0.0000000556      0.1248839635
 H      -0.0000074925      1.1905919728     -0.6488470574
 H      -1.0310790996     -0.5953023918     -0.6488470574
 H       1.0310865921     -0.5952894143     -0.6488470574
```

6.6.2 $TipPBr_2$



```
41
TipPBr2 @ PBE0-D3/def2-TZVP
 C        -0.8808398902      0.4991743295      0.0403738047
 C        -2.2508325189      0.1246810811      0.1781138993
 C        -3.2364413253      1.0661874662     -0.0929642063
 C        -2.9458207288      2.3597669568     -0.4870262107
 C        -1.6115007203      2.7072064095     -0.5812573112
 C        -0.5572238653      1.832055237      -0.323632817
 H        -4.2734577564      0.7644594353      0.0104621637
 H        -1.367998925       3.7264800089     -0.8663865312
 C        -2.8048689513     -1.2352447667      0.6137968657
 H        -3.8852588819     -1.0647339578      0.6412368351
 C        -2.4358734184     -1.6479194138      2.0389665413
 H        -3.0583236621     -2.4929648079      2.3458016169
 H        -1.3940741669     -1.9591412295      2.1285970863
 H        -2.6086553701     -0.8279323165      2.7395718627
 C        -2.6116657452     -2.3651317758     -0.3986764087
 H        -3.2413365097     -3.2146845401     -0.1201112007
 H        -2.8995068166     -2.0439284969     -1.4021434803
 H        -1.5812033866     -2.7214555302     -0.4410396887
 C         0.7959647414      2.5376383663     -0.3843763811
 H         0.5824471779      3.4349373302     -0.9737880309
 C         1.180303473       3.0520277788      1.0062214398
 H         1.3712489222      2.2378222078      1.7030175448
 H         2.0856953774      3.661346397       0.94014955
 H         0.3820617783      3.6715710728      1.4217901358
 C         1.9634614635      1.8848583742     -1.1088810726
 H         1.6780577134      1.5660415948     -2.1117166761
 H         2.7609244008      2.6267988699     -1.2068085957
 H         2.3830848978      1.0301047873     -0.5857850771
 P         0.1699495121     -0.9779081204      0.2939083237
 Br        1.0874224789     -1.3127539056     -1.7290332095
 Br        1.9008713185     -0.4156822674      1.6063841482
 C        -4.035320075       3.3570095563     -0.789813477
 C        -4.8888137888      3.6410522066      0.4437314815
 C        -4.8994979636      2.8989468005     -1.9619542452
 H        -3.5431493487      4.2919466358     -1.0802168927
 H        -4.2768044559      3.9903406165      1.2780015751
```

```
H       -5.6377023282    4.4059909756    0.2236607813
H       -5.4178152441    2.7418213341    0.770435394
H       -4.2949444791    2.7155612065    -2.8526265184
H       -5.4290822067    1.9734331659    -1.7208502617
H       -5.6482323959    3.6570191476    -2.2050574268
```

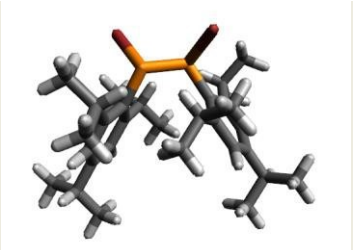
6.6.3 $(TipPBr)_2$ rac

```
80
(TipPBr)2 rac @ PBE0-D3/def2-TZVP
P     -0.5155761463  0.9327520523    -0.7126074483
P     0.4491721887   -0.0410882481   1.061319249
Br     0.0530155224  1.6754180453    2.474832075
Br     0.2902919506 -0.3928454651     -2.3527247169
C     -2.2467539236  0.3968965371    -0.4566631261
C     -3.1889575129  1.4497565083    -0.4921149057
C     -2.6872837711  -0.9208968157    -0.1836061313
C     -4.5237814056 1.1702036693     -0.2167493498
C     -4.0331806158  -1.1340380054    0.0683056316
C     -4.968668029 -0.107365316   0.0681318081
H     -5.2442055089   1.9818177549   -0.2272739167
H     -4.3666016618   -2.1460280461   0.2719323912
C     2.2233610603   0.0250464197   0.62483464
C     2.8707531013   -1.2299378703   0.7000463964
C     2.9523448086   1.158505324 0.1981839613
C     4.2116756806   -1.3182519539   0.340440712
C     4.2912099429   1.0071810825   -0.1249611784
C     4.9420028422   -0.2183257394   -0.070900211
H     4.7051712349   -2.2841244788   0.3811463543
H     4.8456809505   1.8821270643   -0.4474133164
C     -1.7941134744   -2.1441226025   -0.1902710535
H     -0.7631701204   -1.8215325168   -0.3267318805
C     -1.8468583489   -2.9068563349   1.1298987961
H     -2.8407227889   -3.3176514068   1.3240808055
H     -1.1445847275   -3.7445006909   1.1046646823
H     -1.5769700054   -2.2596707073   1.9667925591
C     -2.1327181676   -3.0540237198   -1.3691620012
H     -2.0544456173   -2.5145691481   -2.314633299
H     -1.4439790612   -3.9024830225   -1.4019280639
H     -3.1491232997   -3.4477933081   -1.2849448846
C     -2.8353205254   2.8934329915    -0.7981992256
H     -2.68115947    4.794972328    0.2263761351
C     -3.6605531254   3.4487182238    -1.9557448271
H     -3.3213856173   4.4569229007    -2.2066963766
H     -3.5623557198  2.824204976    -2.8464083778
H     -4.7226874506   3.5128093314    -1.7063828654
C     -6.4221963307   -0.3761535349    0.3679649859
H     -6.9522145197   0.5779535935    0.2696761579
```

```
C     -6.6077029844   -0.8691725485    1.80105294
H     -6.1046362027   -1.8279972489    1.9532576513
H     -6.1949258565   -0.1588962325    2.5205204867
H     -7.6682318113   -1.0095344744    2.0254177236
C     -7.0317574455   -1.3545521747    -0.6324940921
H     -8.0982295808   -1.4899904856    -0.4353976955
H     -6.9142851416   -0.9973705519    -1.6577540329
H     -6.5546861637   -2.3358884229    -0.5638188326
C     2.3693704106   2.5487386605    0.063073253
```

6.6.4 $(TipPBr)_2$ meso

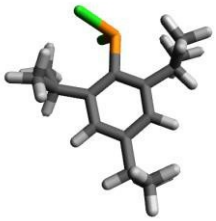
```
80
(TipPBr)2 meso @ PBE0-D3/def2-TZVP
P      0.9945191482  -1.7186797789   0.5272317607
P      -0.9955817509  -1.7181590792   -0.5269624577
Br      -1.9681042615   -3.1269542931    0.9528680845
Br      1.9661683065   -3.1283468107    -0.9523488595
C      1.8976485659   -0.1531002313    0.2150979164
C      2.706432766  0.2717533589   1.2989577771
C      1.8776817125   0.6042685889    -0.9727312124
C      3.4281192329   1.4515174825    1.1727176893
C      2.6234860449   1.7735666057    -1.0374015756
```



C	3.3964702676	2.2222354147	0.0212589467
H	4.0403978178	1.7883545852	2.0007078723
H	2.6030997271	2.3501396948	-1.9555155095
C	-1.8979448592	-0.1520920087	-0.2150440935
C	-2.7066240026	0.2729089133	-1.2989191121
C	-1.8778327779	0.6052850576	0.9727734589
C	-3.4281734234	1.4527541164	-1.172657942
C	-2.6235574871	1.7746286647	1.0374889214
C	-3.3965230728	2.2233922306	-0.0211451312
H	-4.0403833377	1.7896827176	-2.0006616216
H	-2.6030878482	2.3511735906	1.955618939
C	1.1413745838	0.1961070312	-2.2270226483
H	0.511488965	-0.6711592642	-1.99676269
C	0.2369252721	1.3026981727	-2.758456284
H	0.8196877259	2.1581289734	-3.108712328
H	-0.3386183912	0.9345779003	-3.6103737863
H	-0.460786121	1.6545781412	-1.9974195863
C	2.1288408909	-0.2505665987	-3.3050360401
H	2.7681638715	-1.0572260039	-2.9461139297
H	1.5907484959	-0.6055127412	-4.1877305761
H	2.7672668165	0.5832623326	-3.6103175759
C	2.8677504557	-0.542560583	2.5712570141
H	1.9063441277	-1.0166068628	2.7889584648
C	3.2561106108	0.278141479	3.7952209045
H	4.2909317976	0.6269077888	3.7416274099
H	4.80286579	3.2868301949	-2.1501531809
C	-1.1412681744	0.1972366466	2.226959058
H	-0.5117258501	-0.6702900153	1.9967329149
C	-2.8680506713	-0.5413337551	-2.571255487
H	-1.9068204318	-1.0158141775	-2.7887734412
C	-4.1889590401	3.5030811505	0.0767943626
H	-4.69820546	3.6398720136	-0.8837775348
C	-3.2784833591	4.707843795	0.2995892567
H	-2.5271796418	4.7876060436	-0.4890485664
H	-3.8609637824	5.6325562542	0.3142227009
H	-2.7522266769	4.6307358312	1.2547809496
C	-5.2571515203	3.4135644325	1.1639766918
H	-5.8584694318	4.3259833117	1.1881945658

```
H    -5.9249825413   2.5663116063   0.9945681449
H    -4.8026850271   3.2880300214   2.1504007214
C    -2.1284321295  -0.2488345442   3.3054869778
H    -2.7664522291   0.5852631863   3.6108844515
H    -2.7681763338  -1.0553570291   2.9470053352
H    -1.5900934361  -0.6037779769   4.1880317224
C    -0.2363039621   1.3037639414   2.757655865
H     0.4612727235   1.6551128433   1.9962575624
H    -0.818711451    2.1595156375   3.1077226615
H     0.3394129018   0.9358323198   3.609540925
C    -3.8898558493  -1.6581294696  -2.3494313276
H    -3.6028487754  -2.3175341321  -1.5280759852
H    -4.8682038561  -1.2319392318  -2.1096891435
H    -3.9930602518  -2.2664289807  -3.2517348899
C    -3.2557967017   0.2795771925  -3.7952794729
H    -4.2905051533   0.6287154159  -3.741936401
H    -2.6110795667   1.1508283794  -3.9258927939
H    -3.1751468068  -0.3417120233  -4.6900367151
```

6.6.5 $TipPCl_2$



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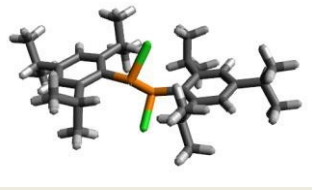
41
TipPCl2 @ PBE0-D3/def2-TZVP
C    -0.8839618759   0.4922501601   0.053752693
C    -2.2539190096   0.1127800043   0.1611495754
C    -3.2379018964   1.0583862391  -0.0999874439
C    -2.9438712682   2.3624278332  -0.4565418261
C    -1.6092359951   2.7056059418  -0.5540584648
C    -0.556649099    1.8223655342  -0.3142474483
H    -4.2759326003   0.7536734183  -0.0174515215
H    -1.3628282001   3.7264711455  -0.8316386404
C    -2.8089615249  -1.2608088704   0.548021814
H    -3.8914865316  -1.120547564    0.4726296368
C    -2.562152912   -1.6544597563   2.0050675147
H    -3.1770448198  -2.5226527632   2.2580249006
H    -1.5213703789  -1.9212882759   2.1932896232
H    -2.8338886732  -0.8392284039   2.67944639
C    -2.4924241063  -2.3932544913  -0.4298318404
H    -3.1541813792  -3.2404821342  -0.2293662146
H    -2.6511365287  -2.0762003077  -1.4628392186
H    -1.467087833   -2.7553145871  -0.340481906
C     0.8004584526   2.5157428916  -0.4314128895
H     0.5790915067   3.3770369408  -1.0699750696
C     1.2183212585   3.1124189211   0.9156815542
H     1.4281883026   2.341733303    1.6550106459
H     2.1207038987   3.7168556351   0.7896836543
H     0.4304897797   3.756399104    1.3135049615
C     1.9513711737   1.8147660209  -1.1387622612
H     1.635193052    1.399543145   -2.0961160678
H     2.7309935576   2.5559665083  -1.335562136
H     2.4049397285   1.0185445886  -0.5554504235
P     0.1892699504  -0.9434666324   0.4224482995
```

```
Cl      1.1094401396 -1.3232843792   -1.3938658806
Cl      1.7416675845 -0.2344596994    1.5866299765
C      -4.0313918465  3.3704561424   -0.7299581715
C      -4.8849570243  3.6172452176    0.5115517192
C      -4.8957895327  2.9506474749   -1.9162100217
H      -3.5372074735  4.3129630347   -0.9910756028
H      -4.2725223025  3.9401736766    1.3560549235
H      -5.6333776222  4.3890152954    0.3149376202
H      -5.4141807044  2.7085276277    0.8105104198
H      -4.2911211087  2.7946776511   -2.8120625887
H      -5.4267657029  2.0186883773   -1.7047025088
H      -5.6435321052  3.7168842525   -2.135722446
```

6.6.6 $(TipPCl)_2$ rac



```
80
(TipPCl)2 rac @ PBE-D3/def2-TZVP
P      -0.5691041791   -0.7802030392 0.8020033357
P       0.4126379575    0.0834694499 -1.0281479953
C      -2.2919227262    -0.2412236698 0.5022143501
C      -3.2471437465    -1.2815972022 0.5373243687
C      -2.7092014444    1.07666668    0.199080514
C      -4.5726351277    -0.9897790271 0.2310188788
C      -4.0487977037    1.3057006125  -0.071960218
C      -4.9965419801    0.2903642281  -0.0758133453
H      -5.3035800009    -1.7915907953 0.2369297465
H      -4.3657878664    2.3197509011  -0.2910731618
C       2.1755977322    0.0992067772  -0.5391769736
C       2.7891314844    1.3679696914  -0.6407953902
C       2.9368410009    -1.0068361648 -0.098610599
C       4.1395994096    1.4914097292  -0.3318505487
C       4.2837666029    -0.8227608512 0.1725025421
C       4.909365921     0.4121394486  0.0627173367
H       4.6087705446    2.46788852    -0.4001347848
H       4.8660855264    -1.6789786371 0.4963708416
C      -1.7922059422    2.282857048   0.188579181
H      -0.7663864778    1.94045753    0.3171501453
C      -1.843247977     3.0375225257  -1.1358708001
H      -2.8319006696    3.4613735977  -1.3269750962
H      -1.129732972     3.8658644503  -1.119651296
H      -1.5875492772    2.3808657342  -1.9699436404
C      -2.1013976196    3.2063601778  1.3649435578
H      -2.0185920585    2.6728538699  2.313321953
H      -1.4007919459    4.0453278851  1.3813681899
H      -3.1135983657    3.6130657369  1.2908735902
C      -2.9066116053    -2.7241717365 0.8624811156
H      -1.9012781695    -2.7438012914 1.2910293147
C      -2.8740350195    -3.5693805976 -0.4082758472
H      -3.8494390578    -3.5648046982 -0.9030669078
H      -2.136862888     -3.186868717  -1.1175990351
H      -2.6182884873    -4.6060345665 -0.1732855799
C      -3.844662349     -3.325808659  1.9048205714
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H       -3.8965569213   -2.7017356684 2.799605189
H       -4.86051258   -3.4509623896    1.5217899592
C       -6.4428261144   0.5739261973   -0.3975450949
H       -6.9774381208   -0.3808832231    -0.3396711196
C       -6.6018346575   1.1144138428   -1.8163267598
H       -6.0963152548   2.0772841086   -1.9279536597
H       -6.1764335935   0.4279385214   -2.5513471466
H       -7.6580319385   1.2631973846   -2.0549926062
C       -7.0663826511   1.5211460108   0.6244199778
H       -8.1270804109   1.6744548601   0.4096502447
H       -6.9747264682   1.1255988084   1.6381856478
H       -6.5779494259   2.4989947872   0.6023556177
C       2.3780457367   -2.3969455435   0.1226617423
H       1.3083791319   -2.3810850975   -0.0739078725
C       2.0470960452   2.6353432762   -1.0218955573
H       1.0364156379   2.3582137711   -1.3323808095
C       6.3751125824   0.5753073462   0.379293578
H       6.6258689516   1.6280626446   0.2064407375
C       7.2443696396   -0.2702313866   -0.5477612195
H       7.0533810064   -0.0319017727   -1.5962307945
H       8.3043039553   -0.0985039047   -0.3433101249
H       7.0470590998   -1.3362310579   -0.4066425671
C       6.6664465317   0.2594989419   1.8442881998
H       7.7215481161   0.4309737901   2.0725848799
H       6.0648997526   0.8813637558   2.5105906787
H       6.4419047759   -0.7860266315   2.0716529755
C       2.5445795745   -2.8335887356   1.5765786326
H       3.5971563489   -2.9398841648   1.8516112315
H       2.0896041862   -2.1111976266   2.2576725492
H       2.0607306968   -3.8011826029   1.7332522718
C       2.9989873374   -3.4072417375   -0.8378244306
H       2.8342802855   -3.1120183381   -1.8757007783
H       4.0768006609   -3.498718611   -0.6781778695
H       2.5538709469   -4.3944426019   -0.6890172307
C       1.9104184093   3.5615079914   0.1844683328
H       1.4123367151   3.0566830444   1.0153980187
H       2.8892885386   3.8966733475   0.5378675408
H       1.3276865237   4.4483037863   -0.0797958195
C       2.6885614741   3.3517046411   -2.2058705155
H       3.6924386332   3.7127726115   -1.9686290697
H       2.7656341182   2.6906020684   -3.0718020941
H       2.0866222739   4.2184309891   -2.4908806632
Cl      0.15865276   0.5322090078    2.2460871155
Cl      0.1735793355    -1.6137409475 -2.2127384279
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6.6.7 $(TipPCl)_2$ meso

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80
(TipPCl)2 meso @ PBE-D3/def2-TZVP
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P         1.0534608527     -1.7677914184     0.3994761005
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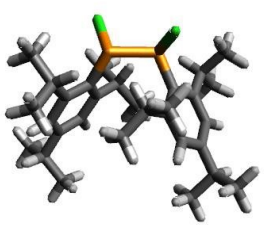

C	-1.8935806793	-0.1731507467	-0.072649464
C	-2.7881982992	0.240327285	-1.0896788856
C	-1.7488770158	0.6116563887	1.0876230619
C	-3.4686232491	1.4412941398	-0.9334452956
C	-2.4568467875	1.8021626087	1.1850314759
C	-3.3087918838	2.2436491802	0.1854861611
H	-4.1451011017	1.7741303419	-1.711621994
H	-2.3403657658	2.4043332876	2.0791659832
C	1.8944978722	-0.1723670126	0.0718321556
C	2.7889941587	0.2406772515	1.0891386514
C	1.749352898	0.6133371646	-1.0877812582
C	3.468845444	1.4420953969	0.9338582426
C	2.4567737889	1.8042436865	-1.184257859
C	3.3085739539	2.2453009879	-0.1844004821
H	4.1452327146	1.7745985688	1.7122530438
H	2.339928735	2.4071125057	-2.0778767417
C	-0.9141490001	0.211535834	2.2815427308
H	-0.305205553	-0.6581478139	2.0075850459
C	0.0290860516	1.3207621329	2.7332512834
H	-0.5230017569	2.1685376368	3.1458216361
H	0.685261301	0.9501012338	3.5234373704
H	0.6489081259	1.6834101211	1.9126826514
C	-1.8140313407	-0.2257817959	3.4376694379
H	-2.4792030092	-1.0356018276	3.1380579685
H	-1.2083300565	-0.5708593432	4.2795109664
H	-2.4269366815	0.6118438194	3.7826238062
C	-3.0755589203	-0.6063329893	-2.317670528
H	-2.1399652346	-1.0887002702	-2.6162465752
C	-3.5822562042	0.1813565741	-3.5198423348
H	-4.6039933896	0.5406492994	-3.370648805
H	-2.9506699726	1.0429573117	-3.74514622
H	-3.5980347717	-0.4673731842	-4.3985384023
C	-4.0712371611	-1.7132817785	-1.9672277496
H	-4.2643457435	-2.3439435379	-2.83887397
H	-3.7029875748	-2.3519112565	-1.1619392006
H	-5.0203825488	-1.2781342969	-1.6417730402
C	-4.0349039388	3.5605991128	0.304068506
H	-4.6700054894	3.6592565014	-0.5834618475
C	-3.0503590841	4.7281022452	0.3073460446
H	-2.3953864843	4.6825598087	1.18162005
H	-2.4179958364	4.7144261849	-0.5830619075
H	-3.5827962155	5.6822453652	0.3370194045
C	3.0768212408	-0.6069071669	2.3163918796
H	2.1415242294	-1.0901785459	2.6144420284
C	4.0340685239	3.5626856042	-0.3019377499
H	4.6691842658	3.660896226	0.5856321786
C	3.0489797284	4.7297337347	-0.3041749181

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H        2.4166779133    4.7150163361    0.5862599312
H        3.5809676964    5.684151145    -0.3330817474
H        2.3939740193    4.6846168889    -1.178445844
C        4.9387087433    3.6053371026    -1.5302744461
H        5.4965041222    4.5446615163    -1.5629640105
H        5.6548025679    2.7809224711    -1.5236584717
H        4.355917528    3.5342723443    -2.4524753516
C        1.8145419114    -0.2223529012    -3.4384301438
H        2.4272565893    0.6156537466    -3.782798586
H        2.4798963236    -1.0322561977    -3.1394515119
H        1.2088680878    -0.5669362286    -4.2804938908
C        -0.0288075654    1.3233214646    -2.7327757601
H        -0.6486584019    1.6852534375    -1.9119142164
H        0.5231257937    2.1714996735    -3.1447288373
H        -0.6849477759    0.9531420049    -3.5232159384
C        4.0732868288    -1.7128648456    1.9650522091
H        3.7055566333    -2.3510232581    1.1591562694
H        5.0221674051    -1.2767783651    1.6400828215
H        4.266738078    -2.3441783222    2.8361504864
C        3.5828624486    0.1800090267    3.5193430904
H        4.6043718818    0.5401269422    3.3705844908
H        2.9506695442    1.0409722795    3.7453830029
H        3.5989899438    -0.4695242468    4.3974391115
Cl       1.8244632847    -2.9642378371    -1.129804212
Cl       -1.8222936441    -2.965774417    1.1270263142
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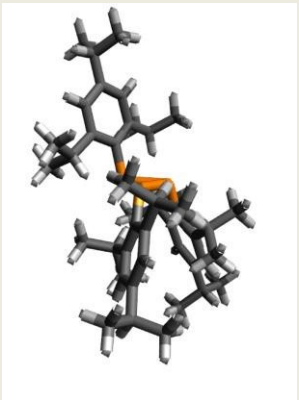
6.6.8 Tip_3P_3



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 C      3.62679 -3.04758 -0.62531
 C     -0.27791 -4.43905 1.20729
 C      2.79382 -3.48947 0.39213
 C      1.52207 -4.10233 2.91597
 C     -2.96808 -1.60097 -3.25157
 C      3.2133 -1.95591 -1.36723
 C      0.72961 -3.45045 1.7898
 C      1.58894 -2.86905 0.68046
 C     -2.86741 -2.0722 -1.80042
 C      0.87588 -0.70107 -3.2559
 C      2.01374 -1.29241 -1.12618
 C      1.18297 -1.7448 -0.08494
 C     -4.97263 -1.43525 -0.61483
 C     -3.64944 -1.13369 -0.90651
 C      1.63656 -0.1614 -2.04915
 C      2.81671 0.69424 -2.48754
 C     -5.7922 -0.57321  0.09832
 C      3.55361 -0.56795 2.49996
 C     -3.10472 0.08135 -0.43464
 C     -5.2593    0.64226 0.49256
 C      2.27823 0.25748  2.42504
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C	-3.94138	0.99671	0.22845
C	2.31198	1.34571	1.3745
C	1.94285	0.86905	3.78539
C	1.14583	1.79054	0.7173
C	3.51447	1.99804	1.12867
C	-3.50826	2.39277	0.61428
C	0.08544	3.62173	-2.24858
C	3.60784	3.09393	0.28603
C	-4.22356	3.43226	-0.24473
C	1.21197	2.93943	-0.09655
C	2.44046	3.55323	-0.3017
C	0.00213	3.59308	-0.727
C	-3.68742	2.67391	2.10078
C	-0.22753	4.98758	-0.15203
H	0.24254	-5.26971	0.72268
H	-2.55887	-4.15833	-2.22864
H	1.98864	-5.03968	2.60244
H	3.10005	-4.33876	0.9905
H	-4.25794	-3.72675	-2.10338
H	-3.27491	-3.86354	-0.63813
H	-2.37295	-2.24133	-3.90814
H	-0.91901	-4.84627	1.99347
H	-0.91601	-3.9584	0.46349
H	0.85052	-4.34144	3.74358
H	-4.00691	-1.63245	-3.59129
H	3.85547	-1.6038	-2.16665
H	2.30615	-3.44381	3.29445
H	1.51777	-1.35692	-3.85108
H	-5.38923	-2.37526	-0.95869
H	-1.81481	-2.01178	-1.51169
H	-0.00125	-1.27302	-2.94904
H	-2.60902	-0.57529	-3.36181
H	0.16023	-2.6307	2.23956
H	0.53678	0.11903	-3.89463
H	3.46863	0.17048	-3.19122
H	3.82758	-0.96364	1.5208
H	3.40611	-1.41265	3.17599
H	0.9662	0.49895	-1.49994
H	3.41004	1.0113	-1.62922
H	2.45346	1.59168	-2.99252
H	4.39453	0.0095	2.89233
H	1.46908	-0.42899	2.16825
H	1.87139	0.09008	4.54914
H	-5.8903	1.35164	1.01849
H	0.18053	2.61157	-2.65118
H	4.41499	1.6467	1.61921
H	-4.04996	3.24889	-1.30762
H	2.71929	1.57646	4.08933
H	0.99118	1.40441	3.75601
H	-5.30333	3.41181	-0.07558
H	-2.44453	2.48263	0.40311
H	-0.87125	2.99532	-0.47331
H	0.94046	4.20885	-2.59391

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H     -0.81842   4.06907 -2.67002
H      2.47962   4.42862 -0.94191
H     -3.1357    1.94767 2.70035
H     -3.86441   4.43697 -0.00604
H     -4.73909   2.63238 2.39517
H     -3.31421   3.67179 2.3454
H     -1.14567   5.41942 -0.55914
H     -0.31846   4.95254 0.93592
H      0.59661   5.66269 -0.39619
P     -0.46433  -1.1124  0.44292
P     -1.33483   0.44806 -0.82822
P     -0.45873   0.98414 1.14445
C     -7.21909  -0.94579 0.41399
C     -8.20977   0.03015 -0.2131
C     -7.44081  -1.05999 1.91918
H     -7.39613  -1.93306 -0.02742
H     -8.06875   0.09606 -1.29392
H     -9.23819  -0.28507 -0.0186
H     -8.08627   1.03438 0.20093
H     -6.75153  -1.77947 2.36584
H     -7.28047  -0.09664 2.41071
H     -8.46288  -1.38072 2.13699
C      4.93262   3.76878  0.03433
C      4.92459   5.2168   0.5147
C      5.33204   3.68222 -1.43574
H      5.68356   3.22549  0.61883
H      4.6596    5.28067 1.57213
H      5.90733   5.67547  0.37814
H      4.19932   5.81157 -0.04696
H      5.37224   2.64522 -1.7752
H      4.61298   4.21028 -2.06772
H      6.31387   4.13476 -1.5972
C      4.95532  -3.70779 -0.89282
C      4.80649  -5.19501 -1.19447
C      5.91961  -3.47651 0.26779
H      5.37855  -3.22577 -1.7812
H      4.12599  -5.36253 -2.03183
H      5.77506  -5.6346 -1.44549
H      4.41242  -5.73579 -0.33015
H      6.05429  -2.41027 0.46171
H      5.54196  -3.93614 1.1851
H      6.89807  -3.91331 0.05158
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6.6.9 Dip_2P_2

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Dip2P2 @ PBE-D3/def2-TZVP
P        3.3167993861    4.673508082    11.2731673116
C        3.0692915899    4.0225625421   12.9769962096
C        3.7161789801    2.8391211467   13.3673539172
C        3.5427518914    2.3813765398   14.6686617182
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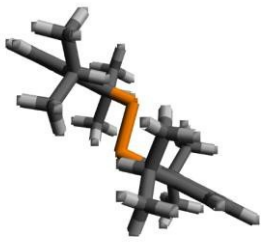

H	4.0246546649	1.4621158355	14.9826109881
C	2.7607062416	3.0821259802	15.5703572441
H	2.6321130586	2.7095894931	16.5805682964
C	2.1513200719	4.2638253094	15.1857336928
H	1.5492305958	4.8111278243	15.902519234
C	2.2993215348	4.7559576189	13.8938715469
C	4.5618386479	2.0486902528	12.3931642638
H	4.772362743	2.704131015	11.5373739895
C	3.7896866056	0.8462528309	11.8598759624
H	3.5292541852	0.1655811704	12.6751640313
H	4.3880800939	0.2925609547	11.1309747379
H	2.8592484238	1.1587647462	11.3797137945
C	5.9076385432	1.6301193627	12.9738006292
H	6.4530660748	2.4888987933	13.370602106
H	6.5215945369	1.1617726126	12.2003595344
H	5.7912107666	0.9026278106	13.7810403695
C	1.610785958	6.0411008598	13.4897894181
H	2.0627227022	6.3700920747	12.5443730909
C	0.1293367331	5.7982598488	13.2199440588

```
H       3.7705769317    1.5051991113    6.1495104826
H       3.6919042835    0.3644491773    7.4880463425
H       2.2115061488    1.1326878456    6.8933514329
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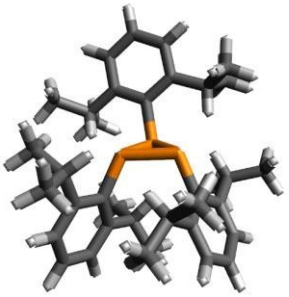
6.6.10 Dip_3P_3



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Dip2P2 @ PBE-D3/def2-TZVP
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C       -4.2149501688   -2.2802313504    1.3160130658
C       -1.1594444225   -4.380374688     -1.223436774
C       -3.7116809348   -2.842244113     0.1587756573
C       -3.0748037481   -3.5229925336    -2.596655208
C       2.8019458234    -2.3787045566    2.7531680729
C       -3.4855079846   -1.3113409762    1.9752255402
C       -1.9769363153   -3.1483009725    -1.6075245701
C       -2.4820783093   -2.450701895     -0.3551215562
C       2.3644953354    -2.7298950862    1.3299327736
C       -0.6811060633   -0.5917123855    3.4166018579
C       -2.2460893888   -0.8836265566    1.5067318463
C       -1.7305221402   -1.4579702652    0.3265396077
C       4.3680892085    -2.5168461315    -0.1482961181
C       3.1966535917    -1.9476593452    0.3339073488
C       -1.4912134909   0.1240419339    2.339255051
C       -2.375015289    1.204538071     2.9504061316
C       5.2314487624    -1.8067522029    -0.9640798052
C       -4.1740357766   0.331544345     -1.747950824
C       2.8719890432    -0.6238658881    -0.0491069763
C       4.9430117616    -0.4955623522    -1.2795219951
C       -2.7649947263   0.8737625302    -1.9456659174
C       3.7802311855    0.1212131436    -0.823468987
C       -2.3607921962   1.9122998645    -0.9205014184
C       -2.5926091222   1.4473966778    -3.3529514145
C       -1.0280609178   2.0587581815    -0.4728490198
C       -3.3197923643   2.819869756     -0.4847883709
C       3.6061245322    1.5916603533    -1.1344911675
C       0.9142142239    3.490933839     2.2614830191
C       -2.9904327189   3.8732575558    0.3477630029
C       4.6278776813    2.4266112197    -0.3651668696
C       -0.6792608204   3.1629590597    0.3318581617
C       -1.6777376847   4.0434992182    0.7374933943
H       -4.29053116     -3.5970494677   -0.358345896
H       3.3524804126    -4.6770235357   1.374051521
H       2.1572020689    -4.498997812    0.0810572303
H       2.1830334713    -2.9014260935   3.48757298
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H       -0.7686545838   -4.8788015074   -2.1145246368
H       -0.3145611311   -4.1117819308   -0.5857666774
H       -2.6230631391   -3.8677635086   -3.5296663749
H       3.8437480284    -2.6695177023   2.9137698785
H       -3.8859832409   -0.8743297813   2.8815829754
H       -3.7200870463   -2.6727652685   -2.8258242017
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H       -1.3054310933   -2.4611216937   -2.1314613516
H       -0.0770832191   0.1229951838    3.9823845207
H       -3.005606675    0.8181360056    3.7551551556
H       -4.3208514913   -0.0319797816   -0.7292388312
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H       -2.8378372858   0.6944120681    -4.1068899736
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H       2.6204834952    1.8941136729    -0.7860313593
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6.6.11 Dip_4P_4

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120
Dip4P4 @ PBE-D3/def2-TZVP
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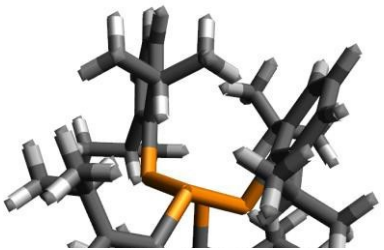

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P	-1.581292459	-0.0011352224	-0.0411386556
P	0.0011352224	-1.581292459	0.0411386556
P	1.581292459	0.0011352224	-0.0411386556
C	0.3595196891	-2.1367641775	1.782700238
C	1.6303031269	-2.7477761535	1.9320487318
C	-0.5160692416	-2.1065039671	2.886909985
C	2.026283395	-3.2106541854	3.1788357588
C	-0.0638730845	-2.578518921	4.1188581502
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C	2.7477761535	1.6303031269	-1.9320487318
C	2.1065039671	-0.5160692416	-2.886909985
C	3.2106541854	2.026283395	-3.1788357588
C	2.578518921	-0.0638730845	-4.1188581502
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C	0.0638730845	2.578518921	4.1188581502
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H	3.1710015086	4.4743505128	-1.8176490887
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C	1.9612659228	1.6637327917	2.8352900958
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