Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:
9-BBN and Chloride Catalyzed Reduction of Chlorophosphines to Phosphines and Diphosphines

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1. General

Unless otherwise stated, all catalytic reactions were conducted under an inert atmosphere of dry nitrogen, using Schlenk technique or a MBraun LABmaster SP glovebox, equipped with closed loop circulation and a -35 °C freezer. Toluene, *n*-pentane, and diethyl ether were collected from a Grubbs-type column system manufactured by Innovative Technology, subsequently degassed under negative pressure, and stored over 3 Å molecular sieves. Dichloromethane (DCM), *ortho*-difluorobenzene (*o*DFB) and acetonitrile (CH_3CN) were dried over CaH_2, followed by distillation, and degassing. Molecular sieves (3 Å, pellets, 3.2 mm diameter) were purchased from Sigma Aldrich and activated prior to use by heating at 250 °C under dynamic vacuum for 48 hours. Deuterated solvents were distilled from CaH_2 and stored over 3 Å molecular sieves. Reactions were performed using glassware that was flame or oven dried (180°C) and subsequently cooled under negative pressure. Chlorophosphines were purchased from commercial providers and used as received, unless stated otherwise. The chlorophosphines (*o*-$NMe_2C_6H_4)_2PCl$[1], (*m*-$MeC_6H_4)_2PCl$[2], (*p*-Cl-$C_6H_4)_2PCl$[3] and (2,4,6-$(CF_3)_3C_6H_2)PCl_2$[4, 5] were synthesized

according to literature procedures. Cl-9-BBN was synthesized from 9-BBN and HCl according to a literature procedure[6] and purified by distillation.

NMR spectra were measured on a Bruker Avance III 400 MHZ spectrometer. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent peaks.[7] Chemical shifts (δ) are reported in ppm and the absolute values of the coupling constants (*J*) are in Hz, while the multiplicity of the signals is indicated as "s", "d", "t", or "m" for singlet, doublet, triplet, or multiplet, respectively. Conversions in ^{31}P NMR spectra were determined from relative integrals. No decoupling was used for ^{31}P NMR spectra that were used for conversion determination to avoid complicating NOEs. All ^{31}P NMR spectra were measured with a standard 30 degree pulse. The number of scans was at least 128 and was increased if unfavorable signal to noise ratios were obtained. D1 was set to 2 seconds. If precipitates were observed in the reaction mixture the solvent was removed and a more suitable solvent was used to ensure full solubility of all compounds. ***Since T1 of different phosphorus species differ no true quantitation was possible.*** For example for the system Ph_2PH (T1 = 6.7 s) and Ph_2PCl (T1 = 5 s) with a large difference in T1 at a d1 of 2 seconds the amount of Ph_2PCl in the reaction mixture will be overestimated (A 1:1 mixture of Ph_2PCl:Ph_2PH would show a ratio of ~1.28: 1).[8] An increase of D1 would have resulted in long measurement times and was not deemed practicable given the number of experiments run in this study. Nevertheless relative integrals in ^{31}P NMR spectra are good approximations for the actual amount of phosphorus species in solution and within one $R_2PCl/R_2PH/P_2R_4$ system comparison of different catalytic systems seems reasonable.

2. Catalysis

2.1 9-BBN catalyzed reactions

2.1.1 Initial screening reactions

General procedure: Ph_2PCl (19.9 mg, 0.09 mmol, 1 equiv), silane (1 equiv) and 9-BBN (0.05 equiv or 0.1 equiv) were dissolved in solvent (0.6 ml) and kept at the indicated temperature in a J-Young tube. The reaction progress was monitored by ^{31}P NMR spectroscopy. Reactions under static vacuum were frozen directly after mixing of the reagents and the headspace of the J-Young tube was evacuated, after which the mixture was kept at the indicated temperature.

Table S 1: Conversion of Ph_2PCl to Ph_2PH and P_2Ph_4 with 9-BBN and silanes.

Silane	Solvent	Temperature [°C]	Time [h]	Conv. [%]	Ph_2PH (%),P_2Ph_4 (%)
Et_3SiH	1,2-DCE	60	18	35	PH (43%), PP (57%)
Et_3SiH	*o*DFB	60	72	55	PH (35%), PP (65%)
Et_3SiH[a]	*o*DFB	60	7	<1	PH (-), PP (99%)
Et_3SiH	*o*DFB	rt	7	2	PH (-), PP (99%)
Et_3SiH	*o*DCB	100	18	93	PH (62%), PP (38%)
Et_3SiH	*o*DCB	80	96	95	PH (47%), PP (53%)
$PhSiH_3$	1,2-DCE	70	30	>99	PH (84%), PP (16%)
Et_3SiH[b]	1,2-DCE	70	54	83	PH (55%), PP (45%)
Et_3SiH[b]	1,2-DCE	60	8	20	PH (-), PP (>99%)
$PhSiH_3$	1,2-DCE	60	30	>99	PH (75%), PP (25%)
Ph_2ClSiH	1,2-DCE	60	48	23	PH (72%), PP (28%)
$PhSiH_3$	1,2-DCE	30	24	>99	PH (49%), PP (51%)
Et_3SiH[b],[c]	1,2-DCE	60	30	66	PH (40%), PP (60%)
$PhSiH_3$[d]	1,2-DCE	30	10	58	PH (41%), PP (59%)
$PhSiH_3$[e]	1,2-DCE	30	10	58	PH (33%), PP (67%)

$PhSiH_3$[f]	1,2-DCE	30	10	63	PH (38%), PP (62%)
$PhSiH_3$	MeCN	30	20	>99	PH (-), PP (>99%)
$PhSiH_3$	*o*DFB	30	10	>99	PH (36%), PP (64%)
$PhSiH_3$[a]	MeCN	30	24	46	PH (-), PP (>99%)
$PhSiH_3$	MeCN	50	8	>99	PH (21%), PP (79%)
Et_3SiH[b]	MeCN	60	32	92	PH (-), PP (>99%)
$PhSiH_3$[a]	1,2-DCE	30	32	1	PH (-), PP (>99%)
$PhSiH_3$	oDFB/MeCN[g]	30	20	99	PH (-), PP (>99%)

Reaction conditions unless stated otherwise: 0.5 mol% 9-BBN, 1 equiv silane, 0.15 M in solvent. [a] No 9-BBN used. [b] 10 mol% 9-BBN used. [c] Reaction was kept under static vacuum. [d] 1.2 equiv $PhSiH_3$ were used. [e] 1.4 equiv $PhSiH_3$ were used. [f] 1.6 equiv $PhSiH_3$ were used. [g] *o*DFB/MeCN, 2/1, V/V.

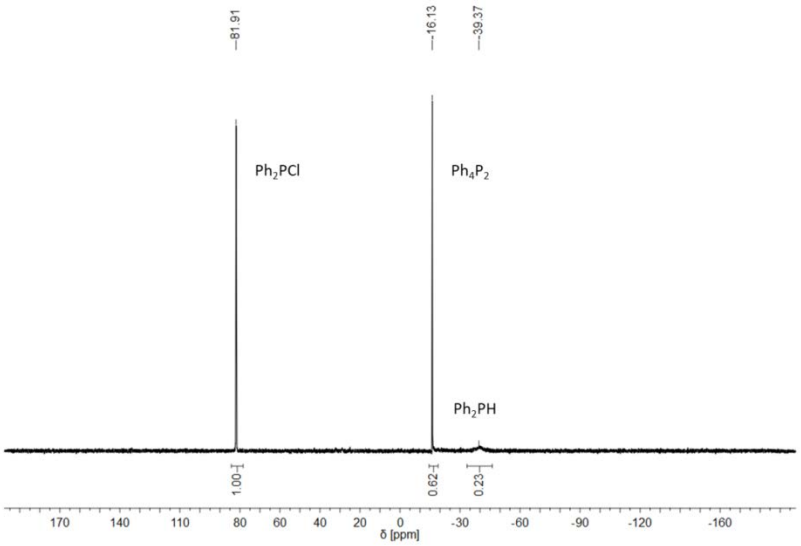

Figure S 1: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with Et_3SiH (60°C, 1,2-DCE, after 18 hours).

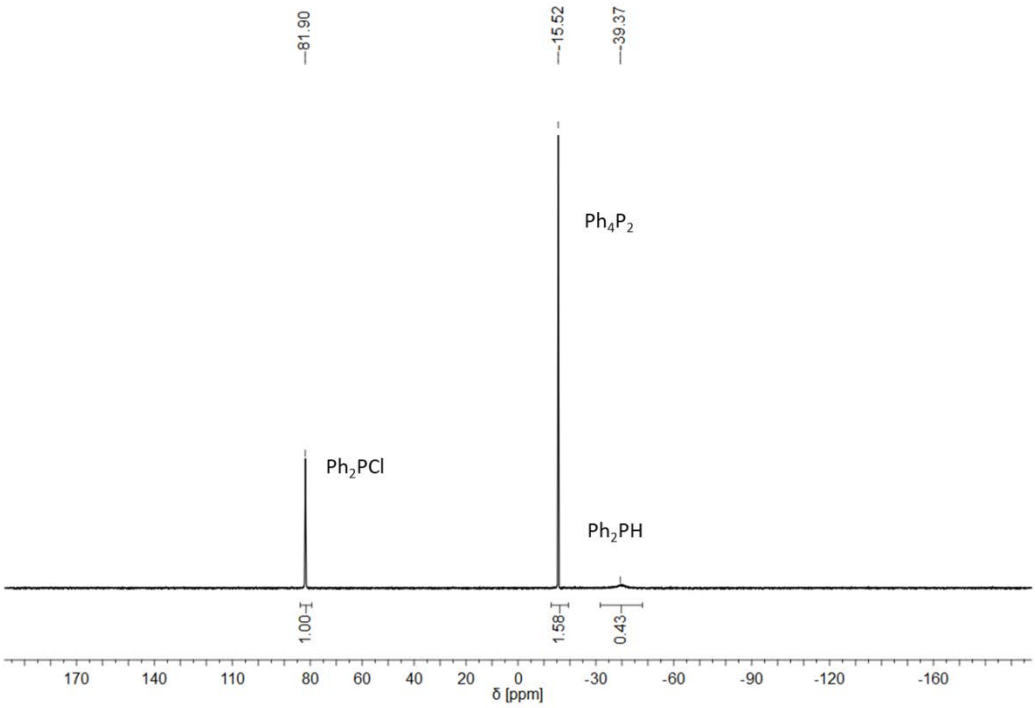

Figure S 2: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with Et_3SiH (60°C, *o*DFB, after 72 hours).

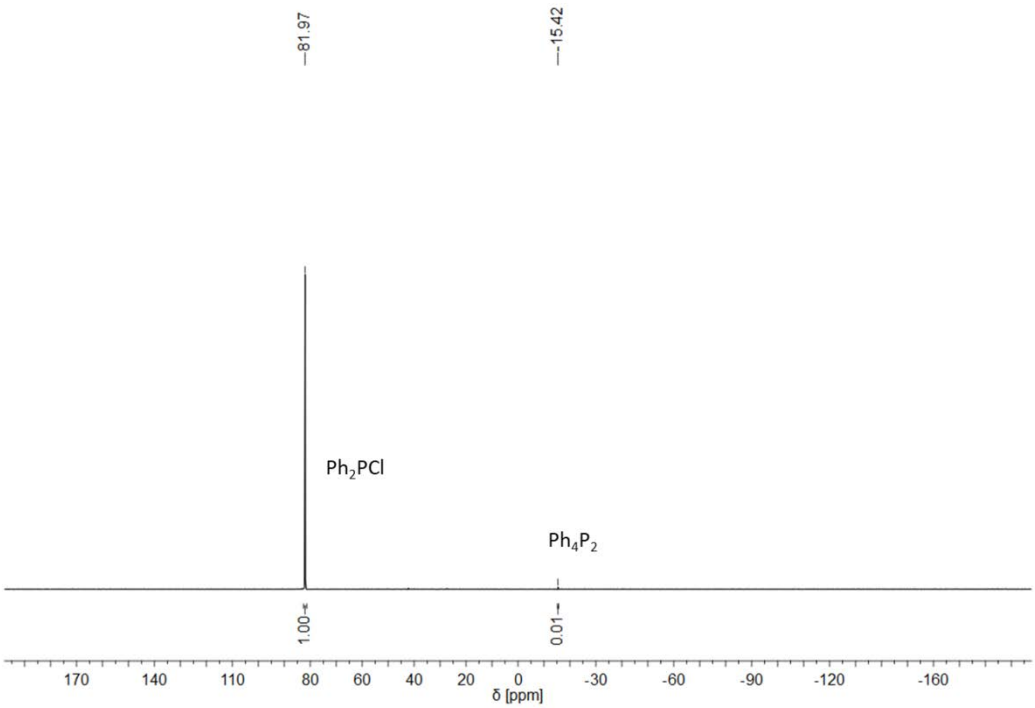

Figure S 3: ^{31}P NMR spectrum of reaction of Ph_2PCl with Et_3SiH (60°C, *o*DFB, after 7 hours). No 9-BBN was added.

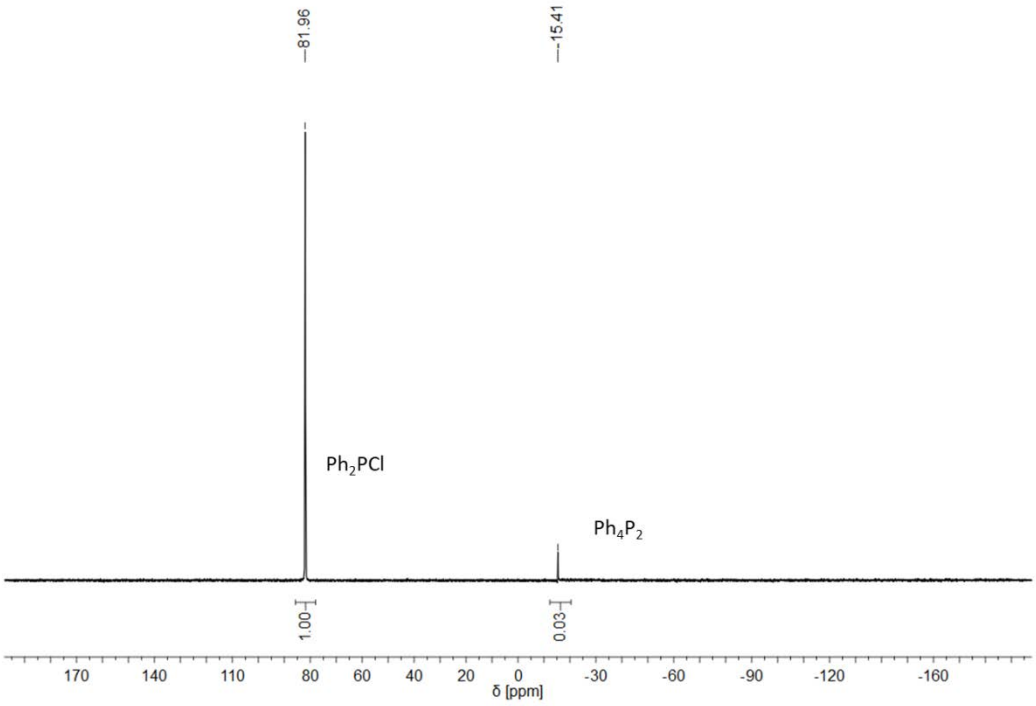

Figure S 4: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with Et_3SiH (rt, *o*DFB, after 7 hours).

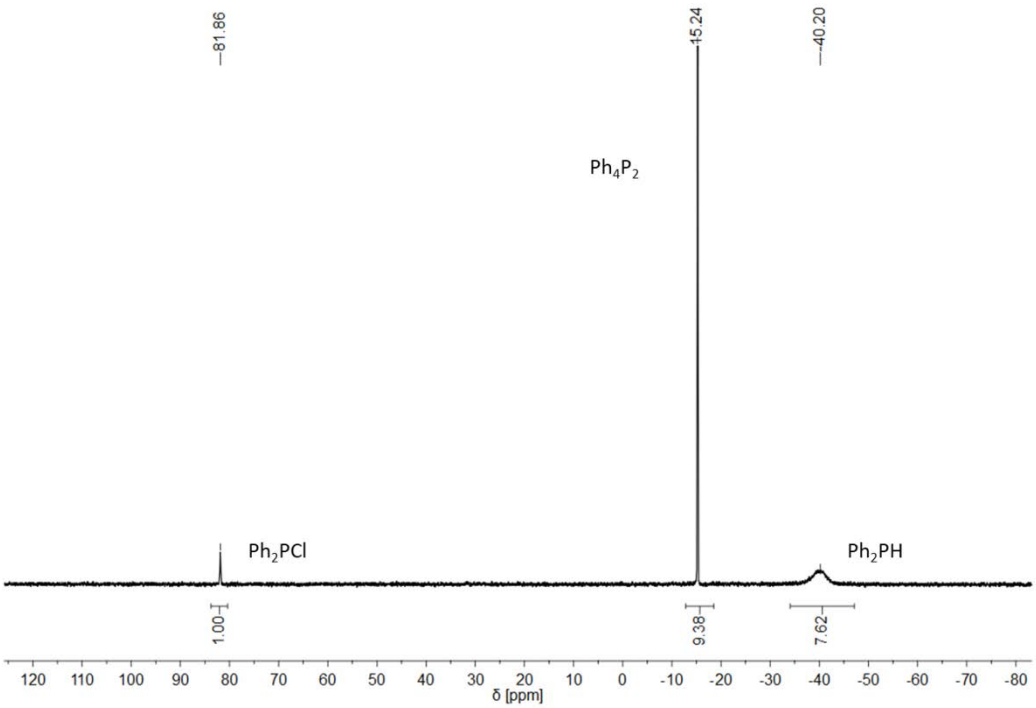

Figure S 5: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with Et_3SiH (100°C, *o*DCB, after 18 hours).

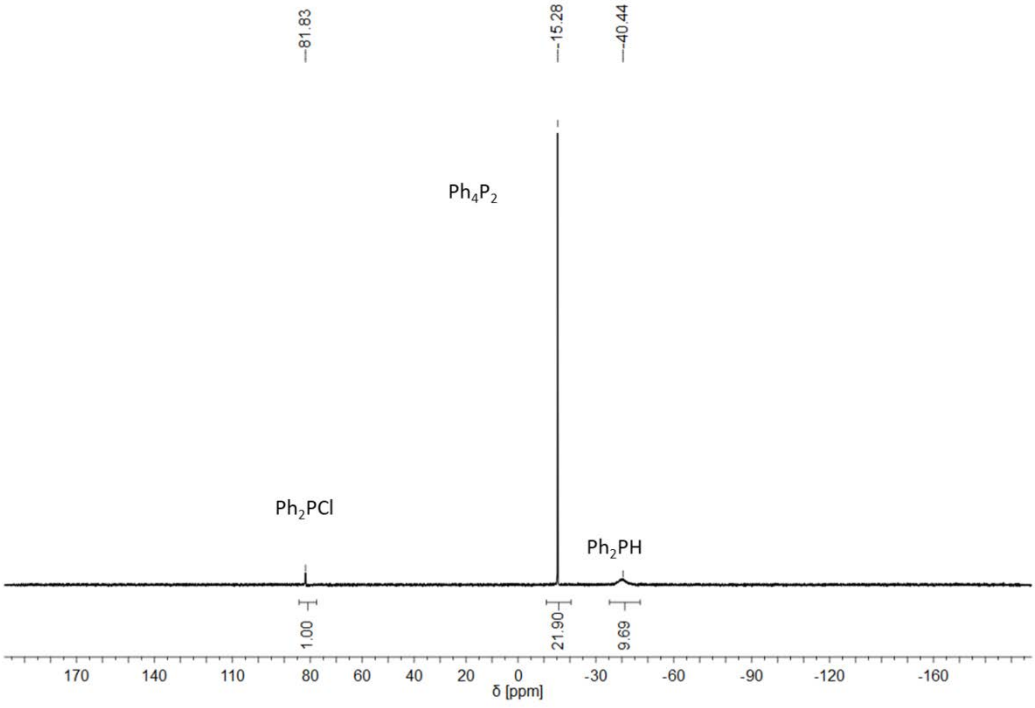

Figure S 6: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with Et_3SiH (80°C, *o*DCB, after 96 hours).

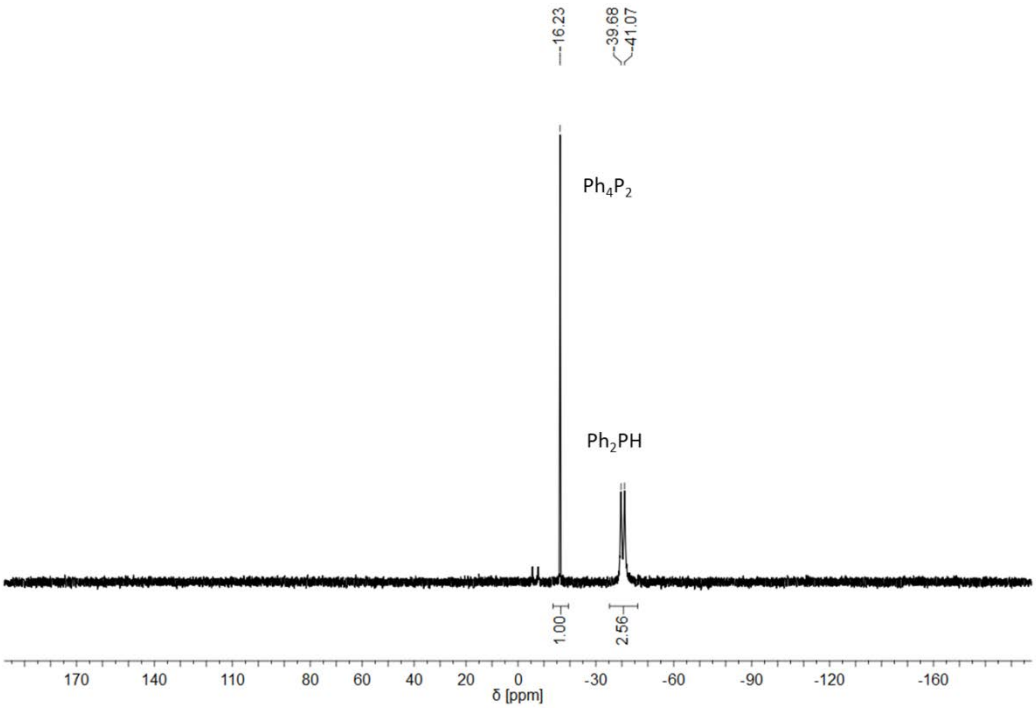

Figure S 7: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (70°C, 1,2-DCE, after 30 hours).

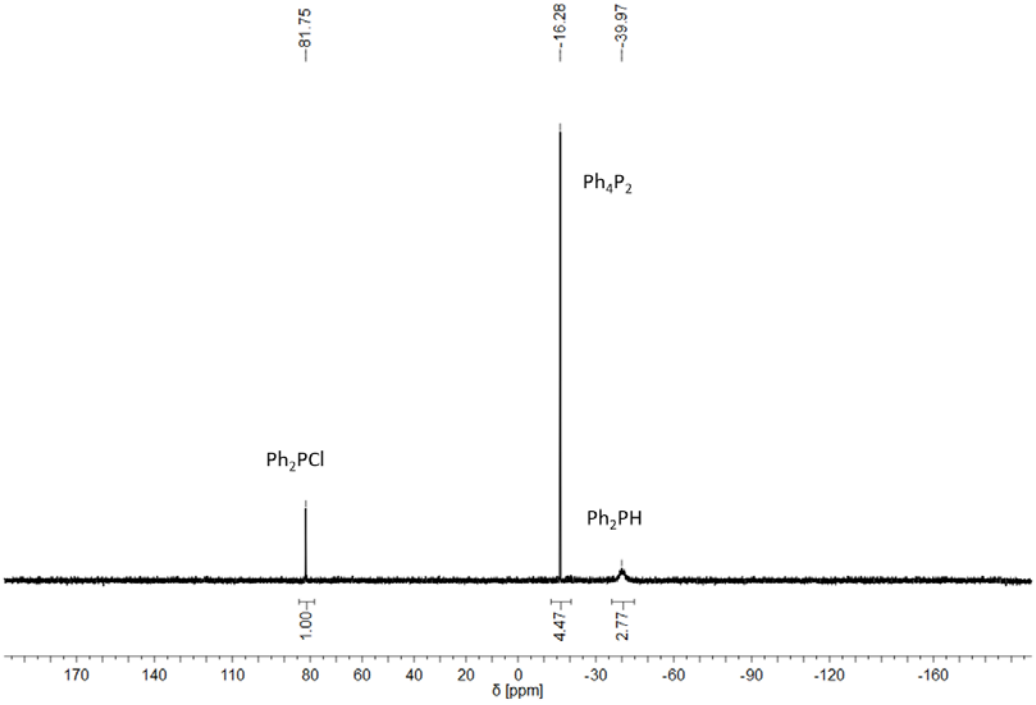

Figure S 8: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with Et_3SiH (70°C, 1,2-DCE, after 54 hours). 10 mol% 9-BBN used.

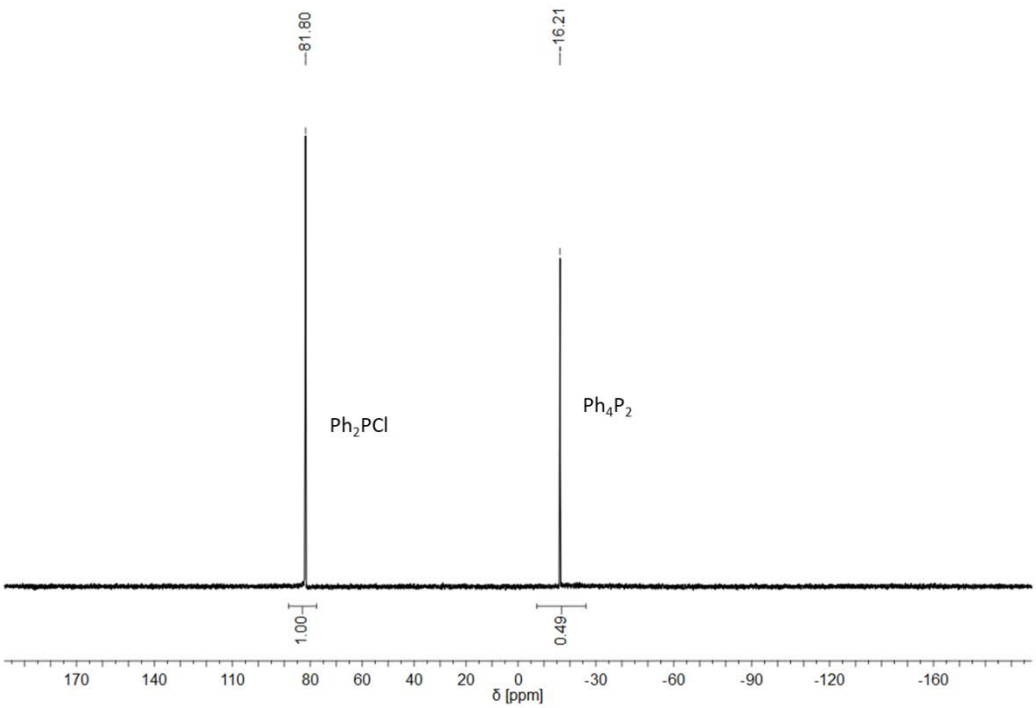

Figure S 9: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with Et_3SiH (60°C, 1,2-DCE, after 8 hours). 10 mol% 9-BBN used.

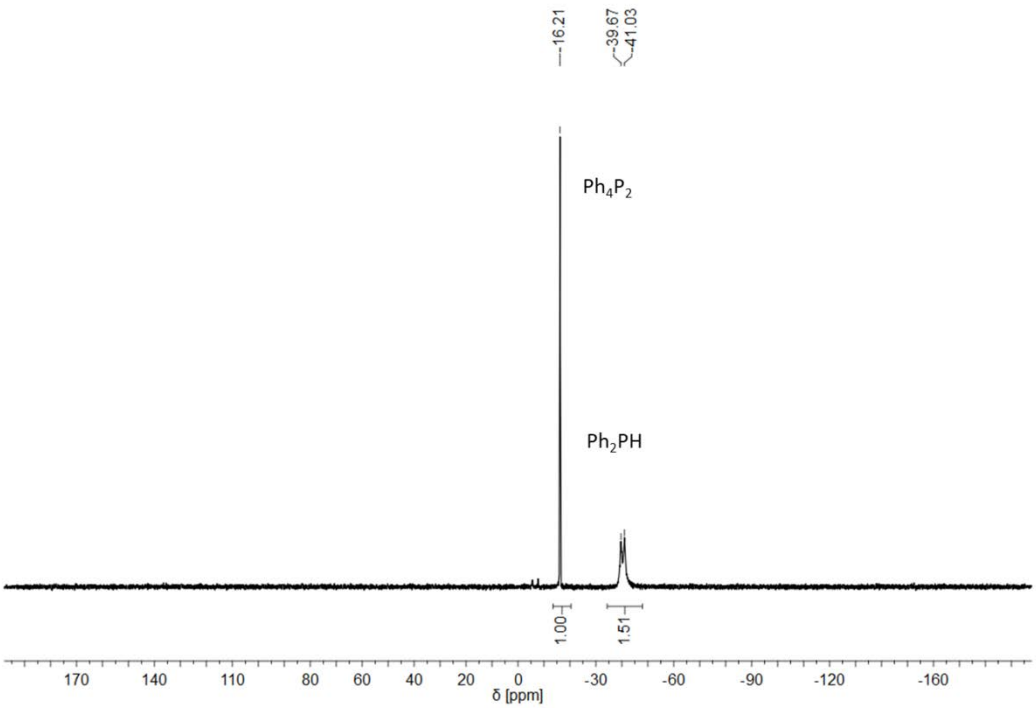

Figure S 10: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (60°C, 1,2-DCE, after 30 hours).

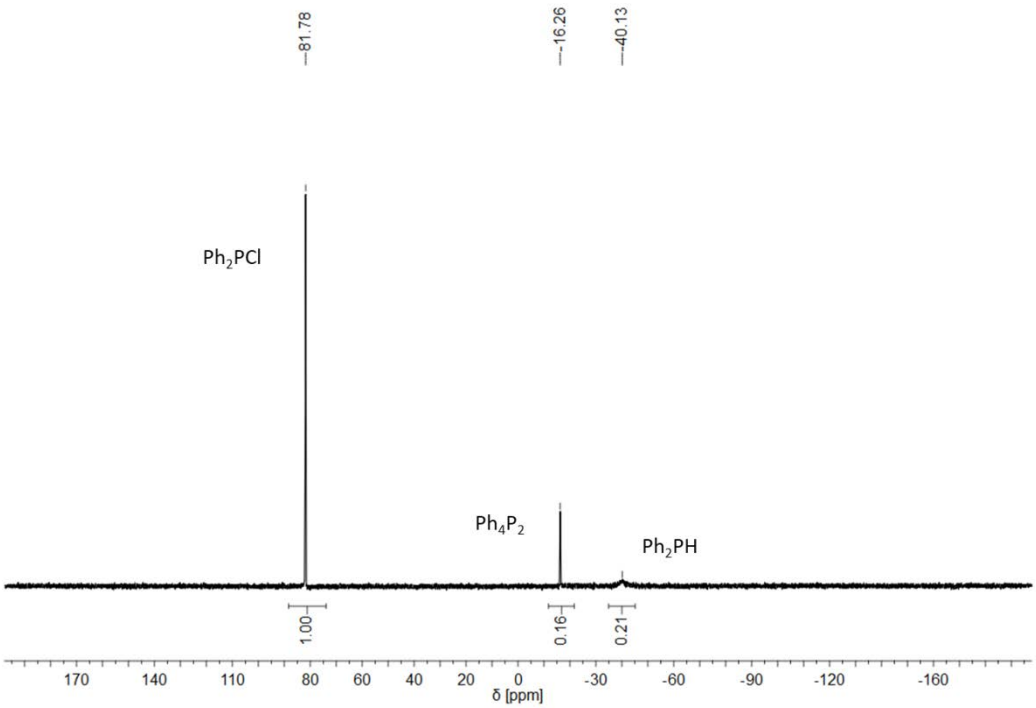

Figure S 11: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with Ph_2ClSiH (60°C, 1,2-DCE, after 48 hours).

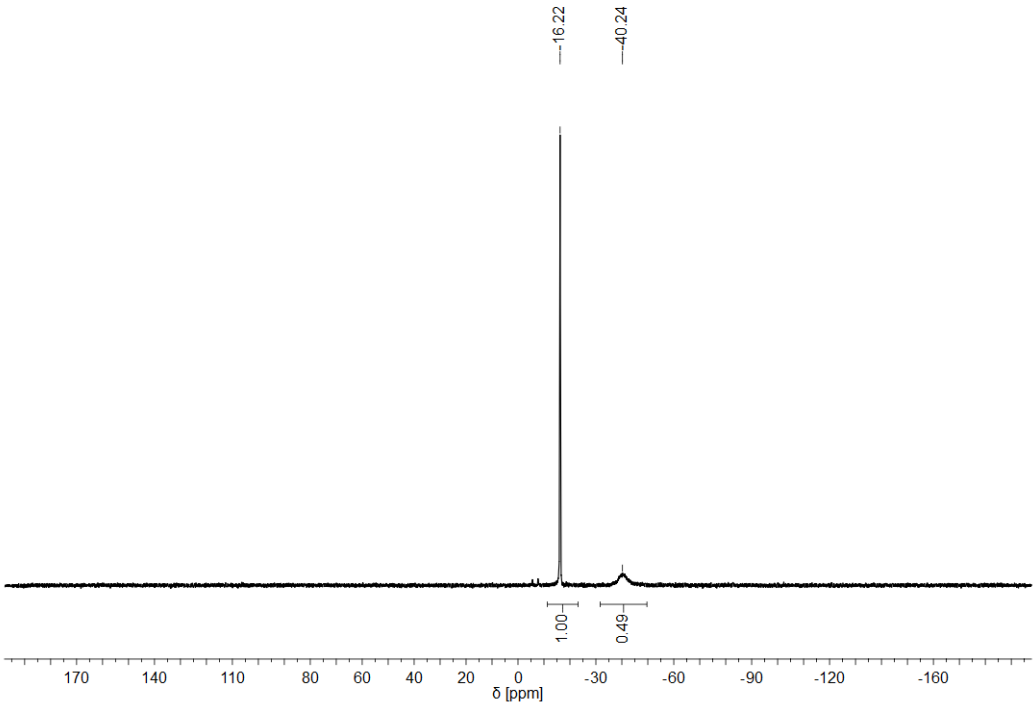

Figure S 12: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, 1,2-DCE, after 24 hours).

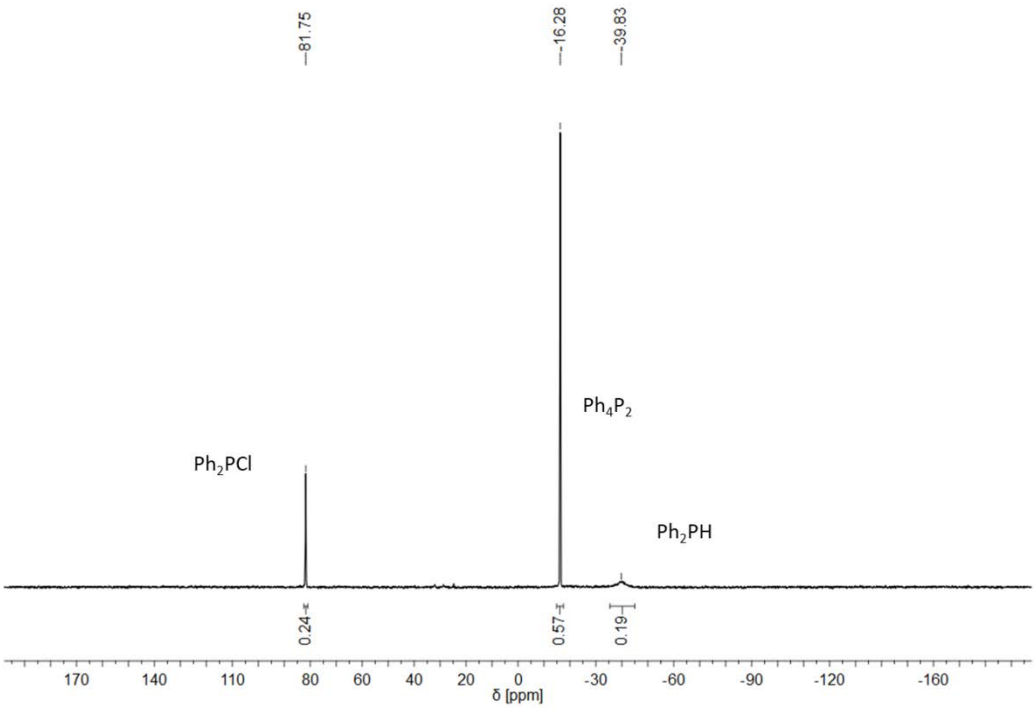

Figure S 13: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with Et_3SiH (60°C, 1,2-DCE, after 30 hours). Reaction was kept under static vacuum (freeze pump thaw).

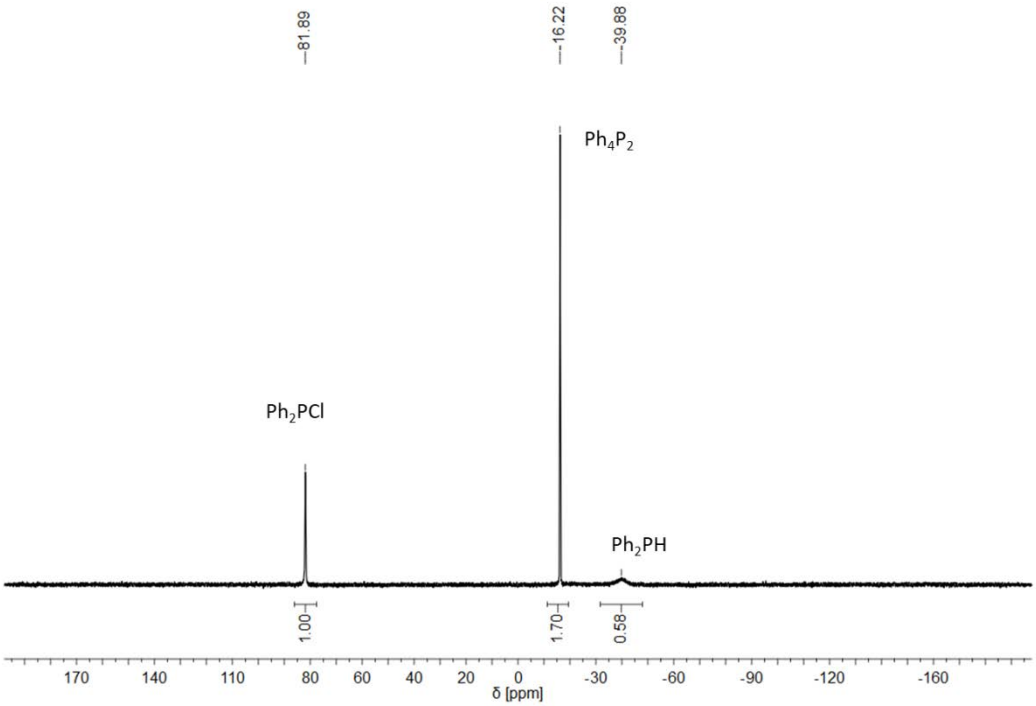

Figure S 14: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, 1,2-DCE, after 10 hours). 1.2 equiv of $PhSiH_3$ were used.

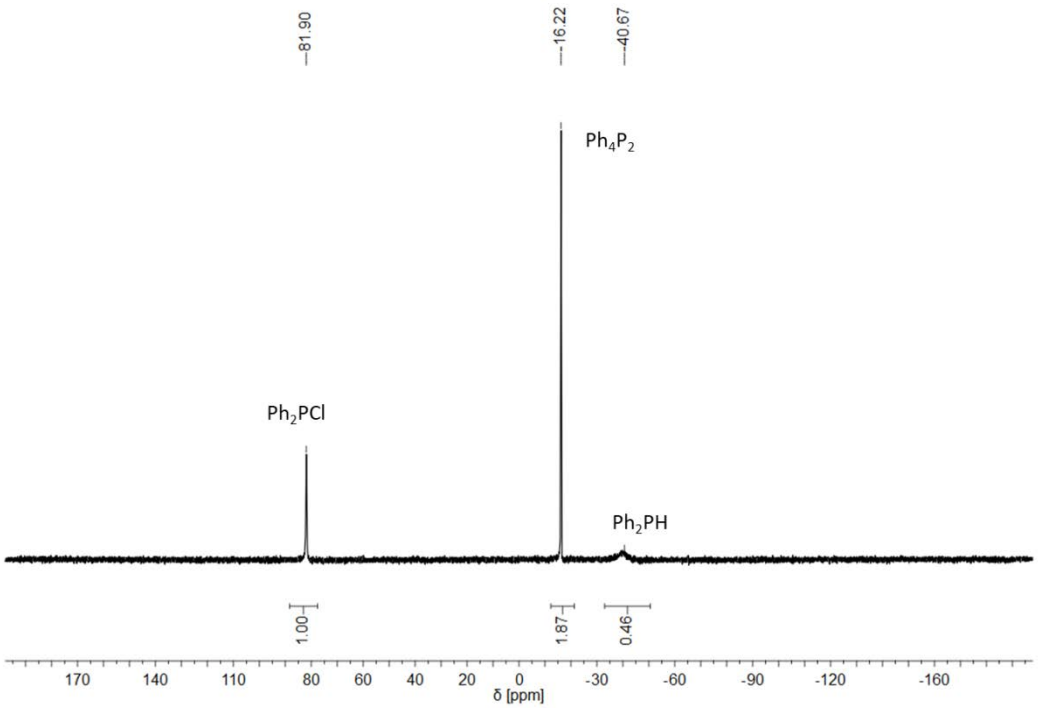

Figure S 15: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, 1,2-DCE, after 10 hours). 1.4 equiv of $PhSiH_3$ were used.

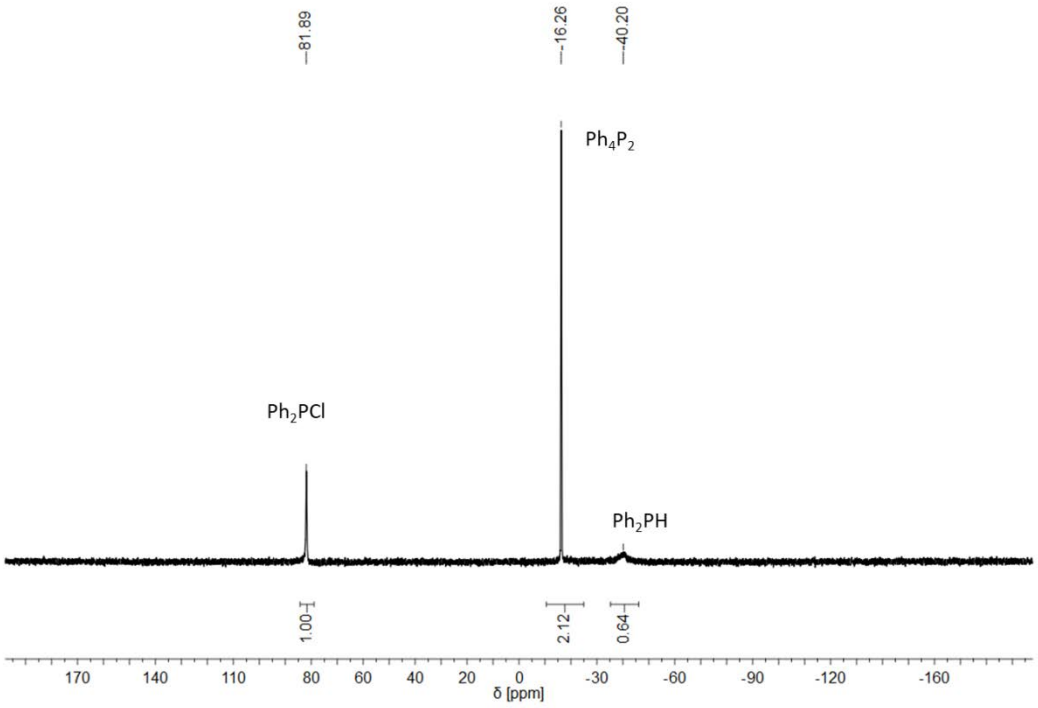

Figure S 16: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, 1,2-DCE, after 10 hours). 1.6 equiv of $PhSiH_3$ were used.

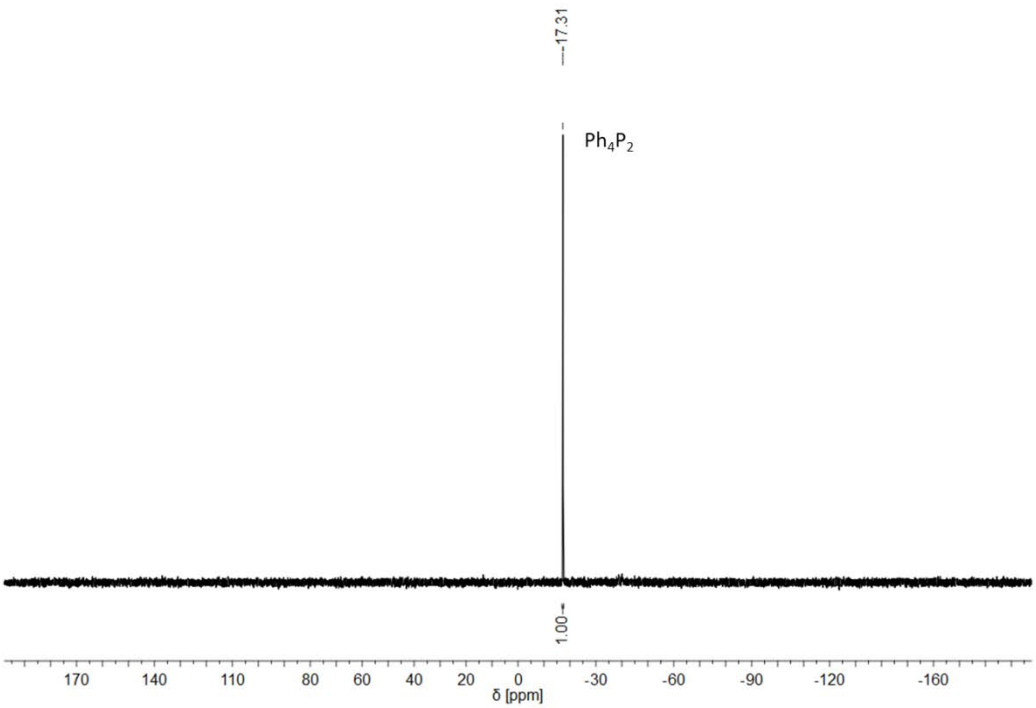

Figure S 17: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, MeCN, after 20 hours).

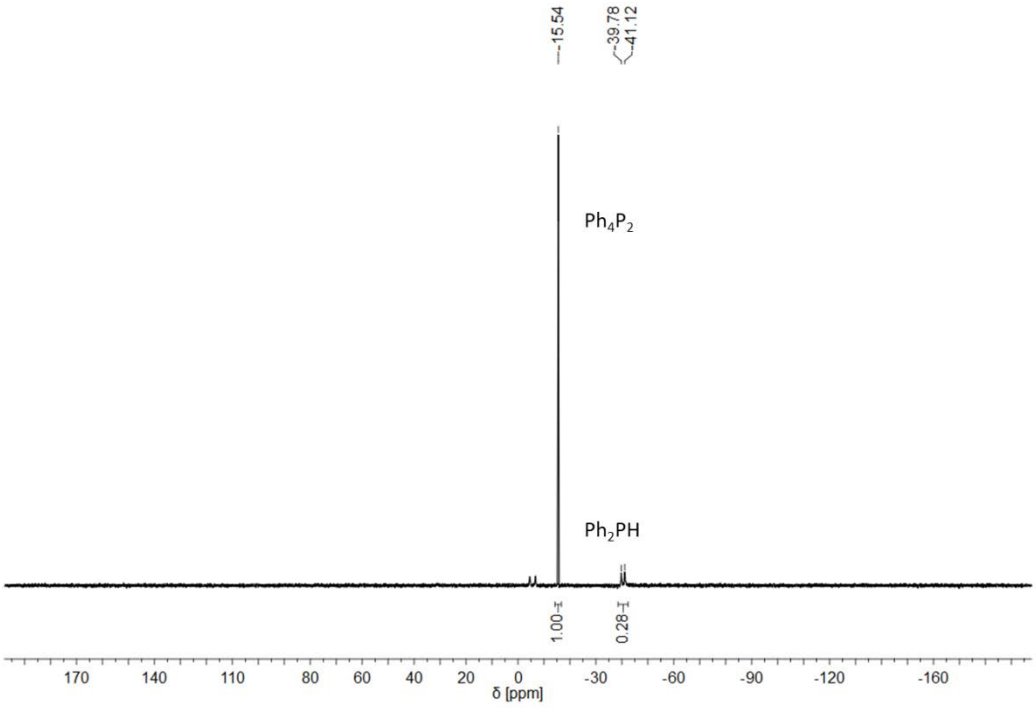

Figure S 18: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, *o*DFB, after 10 hours).

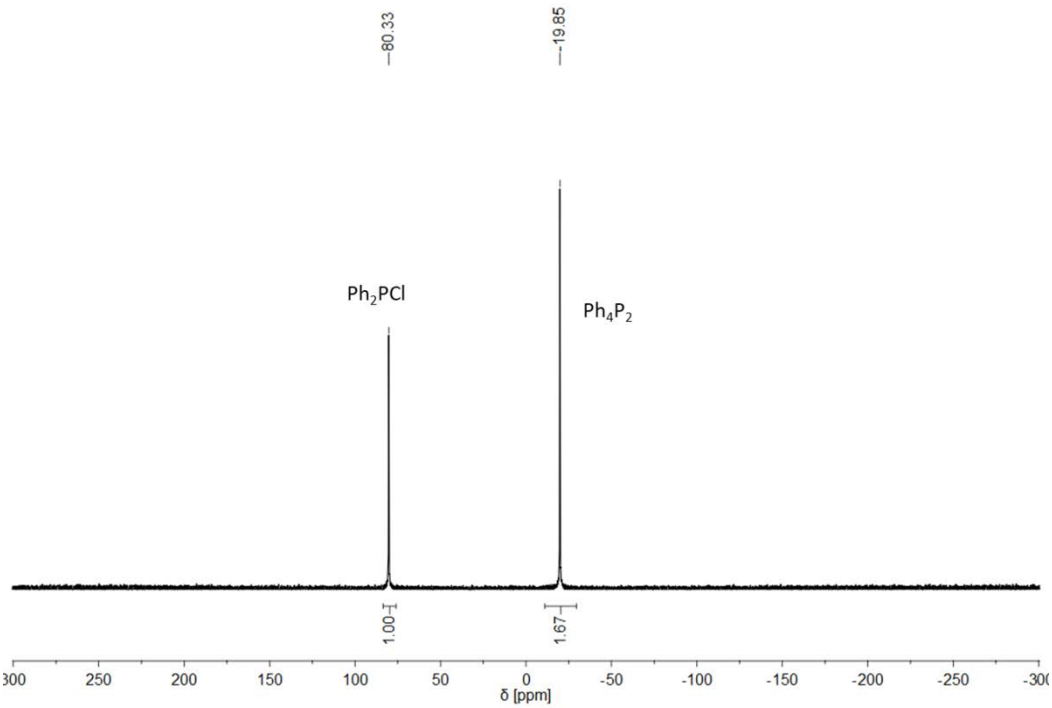

Figure S 19: ^{31}P NMR spectrum of reaction of Ph_2PCl with $PhSiH_3$ (30°C, MeCN, after 24 hours). No 9-BBN used.

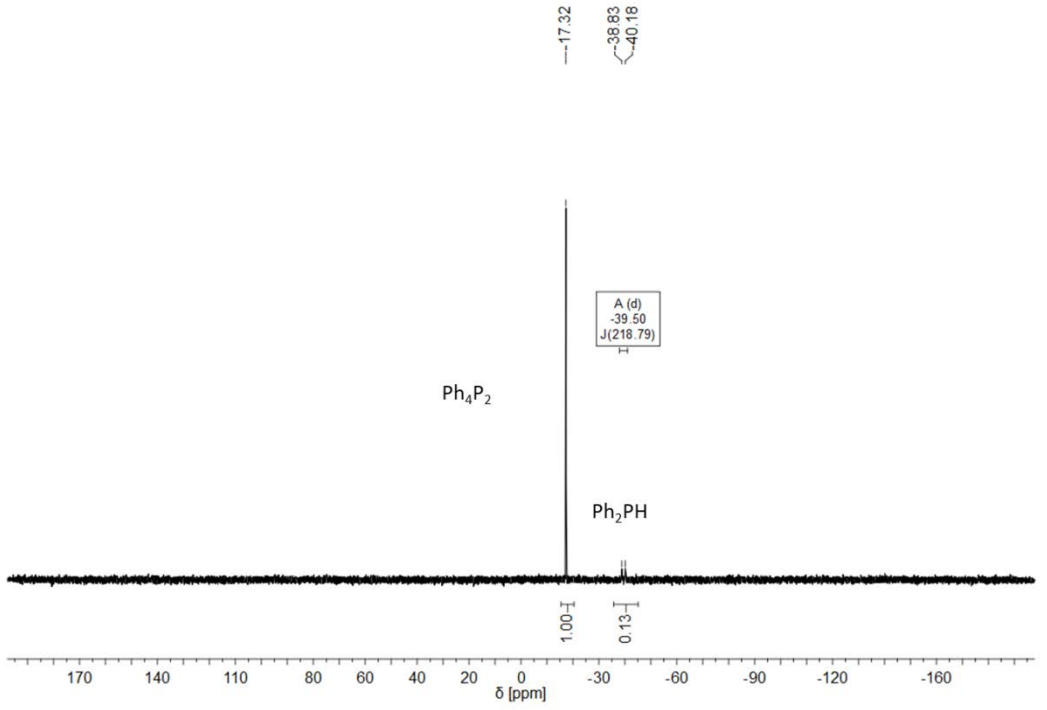

Figure S 20: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (50°C, MeCN, after 8 hours).

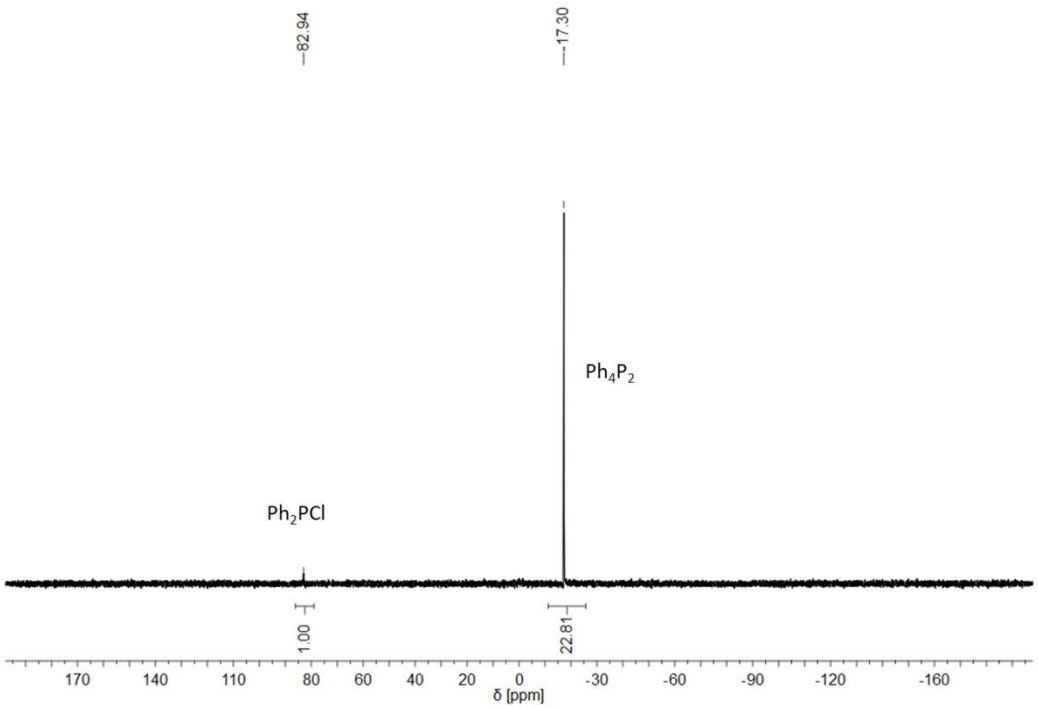

Figure S 21: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with Et_3SiH (60°C, MeCN, after 32 hours).

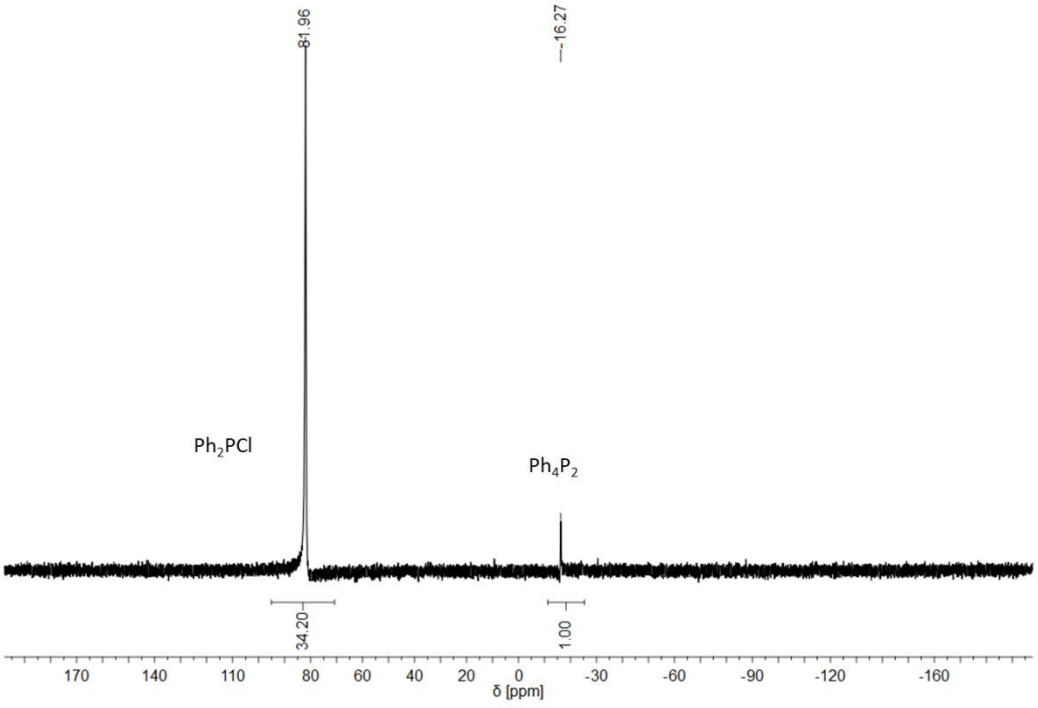

Figure S 22: ^{31}P NMR spectrum of reaction of Ph_2PCl with $PhSiH_3$ (60°C, 1,2-DCE, after 32 hours). No 9-BBN used.

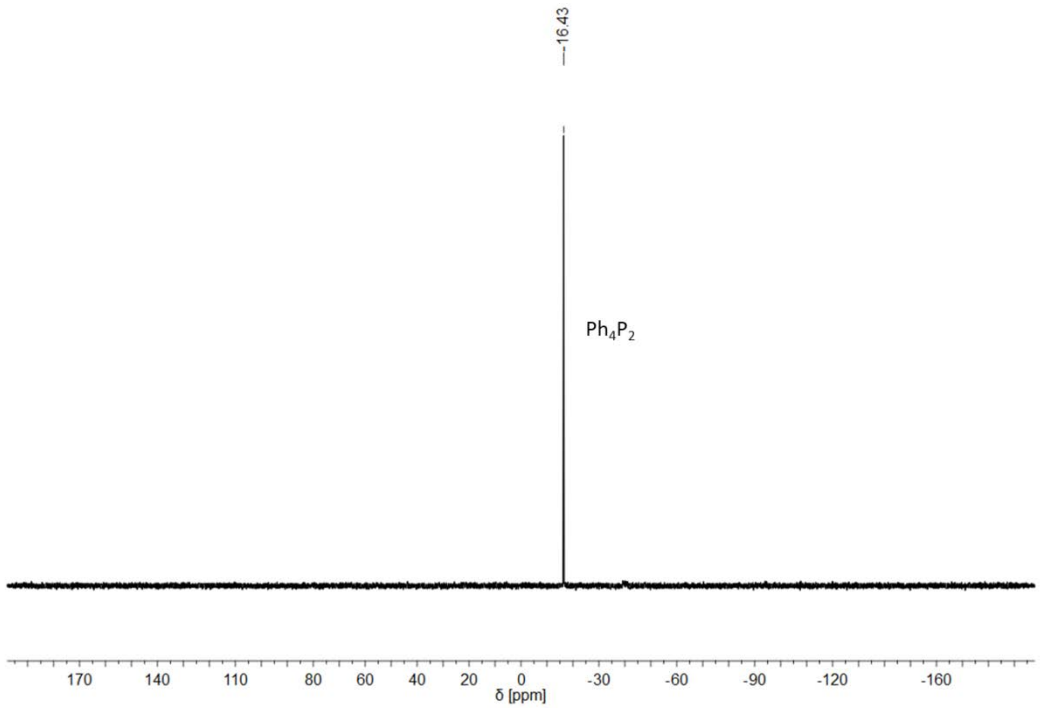

Figure S 23: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, MeCN/*o*DFB, after 20 hours).

2.1.2 Catalysis with 9-BBN and phenylsilane: Phosphine scope

General procedure: R_2PCl (0.09 mmol, 1 equiv), silane (1 equiv) and 9-BBN (0.05 equiv or 0.1 equiv) were dissolved in solvent (0.6 ml) and kept at the indicated temperature in a J-Young tube. The reaction progress was monitored by ^{31}P NMR spectroscopy.

Table S 2: Synthesis of R_2PH and R_2PPR_2 from R_2PCl with 9-BBN and $PhSiH_3$.

Phosphine	Temp. [°C]	Time [h]	solvent	Conv [%]	Product	δ(^{31}P)[ppm]	Literature δ(^{31}P) [ppm]
Ph_2PCl	30	20	MeCN/oDFB	>99	Ph_2PPPh_2	-16.4 (s)	-16.7 (CH_2Cl_2)[8]
iPr_2PCl	30	20	MeCN	45	*i*Pr_2PH	-16.2 (d, $^1J_{PH}$ = 199 Hz)	-16.49 (^{31}P[9], C_6D_6) [10]
iPr_2PCl	30	42	MeCN/oDFB	92	*i*Pr_2PH		
iPr_2PCl	60	8	MeCN/oDFB	>99	*i*Pr_2PH		
iPr_2PCl[a]	60	12	MeCN/oDFB	-			
Cy_2PCl	30	38				-27.9 (d, $^1J_{PH}$ = 195 Hz)	-28.1 (d, $^1J_{PH}$ = 198 Hz, CD_3CN)[11]
Cy_2PCl	60	8	MeCN/oDFB	>99	Cy_2PH		
tBu_2PCl	30	8 d	MeCN/oDFB	75	*t*Bu_2PH	19.7 (d, $^1J_{PH}$ = 201 Hz)	19.5 (d, $^1J_{PH}$ = 203 Hz)[8]
tBu_2PCl	60	48	MeCN/oDFB	65	*t*Bu_2PH		
tBu_2PCl	80	5 d	MeCN/oDFB	96	*t*Bu_2PH		
*t*BuPhPCl	30	42	MeCN/oDFB	85	*t*BuPhPH (77%) ; *t*BuPhPP*t*BuPh (23%)	-6.1 (d, $^1J_{PH}$ = 212 Hz); 2.4 (s), -4.6 (s)	-5.7 (d, $^1J_{PH}$ = 210 Hz)[8]; 1.9[8], -4.7[8]
*t*BuPhPCl	60	48	MeCN/oDFB	49	*t*BuPhPH (56%) ; *t*BuPhPP*t*BuPh (44%)		
*t*BuPhPCl	80	24	MeCN/oDFB	>99	*t*BuPhPH (92%)		

					; *t*BuPhPP*t*BuPh (8%)		
(*o*-$OMeC_6H_4)_2PCl$	30	10	MeCN/oDFB	95	(*o*-$OMePh)_2PP(o$-$OMePh)_2$ (88%); (*o*-$OMePh)_2PH$ (12%)	-46.4 (s); -73.8 (d, $^1J_{PH}$ = 226 Hz)	-46.18 (CD_2Cl_2)[12]; -73.2 (d, $^1J_{PH}$ = 226 Hz)[11]
(o-tol)$_2$PCl	30	7	MeCN/oDFB	>99	(*o*-tol)$_2$PP(o-tol)$_2$ (>99%); (*o*-tol)$_2$PH (-)	-37.8 (s); -56.0 (d, $^1J_{PH}$ = 223 Hz)	-37.2 (s)[12]; -59.1 (d, $^1J_{PH}$ = 222 Hz, THF-d8)[13]
Mes_2PCl	30	24	MeCN/oDFB	>99	Mes_2PPMes_2 (3%); Mes_2PH (97%)	-30.3 (s); -94.1 (d, $^1J_{PH}$ = 231 Hz)	-30.3 (CD_2Cl_2)[12]; -92.9 (d, $^1J_{PH}$ = 229 Hz, C_6D_6)[14]
(*p*-$FC_6H_4)_2PCl$	30	20	MeCN/oDFB	>99	(*p*-$FC_6H_4)_2PP(p$-$FC_6H_4)_2$ (70%); (*p*-$FC_6H_4)_2PH$ (30%)	-18.77 (s); -43.9 (d, $^1J_{PH}$ = 221 Hz)	-16.8 (C_6D_6)[15]; -44.2 ($^1J_{PH}$ = 221 Hz, CD_3CN)[11]
(*p*-$CF_3C_6H_4)_2PCl$	30	20	MeCN/oDFB	>99	(*p*-$CF_3C_6H_4)_2PP(p$-$CF_3C_6H_4)_2$ (48%); (*p*-$CF_3C_6H_4)_2PH$ (52%)	-14.5 (s), -41.3 (d, $^1J_{PH}$ = 222 Hz)	-13.2 (C_6D_6)[15]; -42.7 ($^{31}P\{^1H\}$)[16]
(3,5-$(CF_3)_2$-$C_6H_3)_2PCl$	30	6	MeCN/*o*DFB		(3,5-$(CF_3)_2$-$C_6H_3)_2PP(3,5$-$(CF_3)_2$-$C_6H_3)_2$ (19%); (3,5-$(CF_3)_2$-$C_6H_3)_2PH$ (81%)	-12.91 (s), -41.51 (m)	-12.5 (THF)[17], -41.7 (CD_3CN)[11]
$PhPCl_2$	30	48	MeCN/oDFB	>99	PP (>99) Ph_5P_5 (93%) Ph_4P_4 (5%) Ph_6P_6 (2%)	Ph_5P_5 -4 (m) Ph_4P_4 -48.8; Ph_6P_6 -22.4	Ph_5P_5 -3 (m);[18] Ph_4P_4 -48 (CH_2Cl_2)[18]; Ph_6P_6 -21.2 (C_6D_6)[9]

Reaction conditions: 5 mol% 9-BBN, 0.15 M (R_2PCl), 1 equiv $PhSiH_3$, *o*DFB/MeCN, 2/1, V/V. [a] No 9-BBN used.

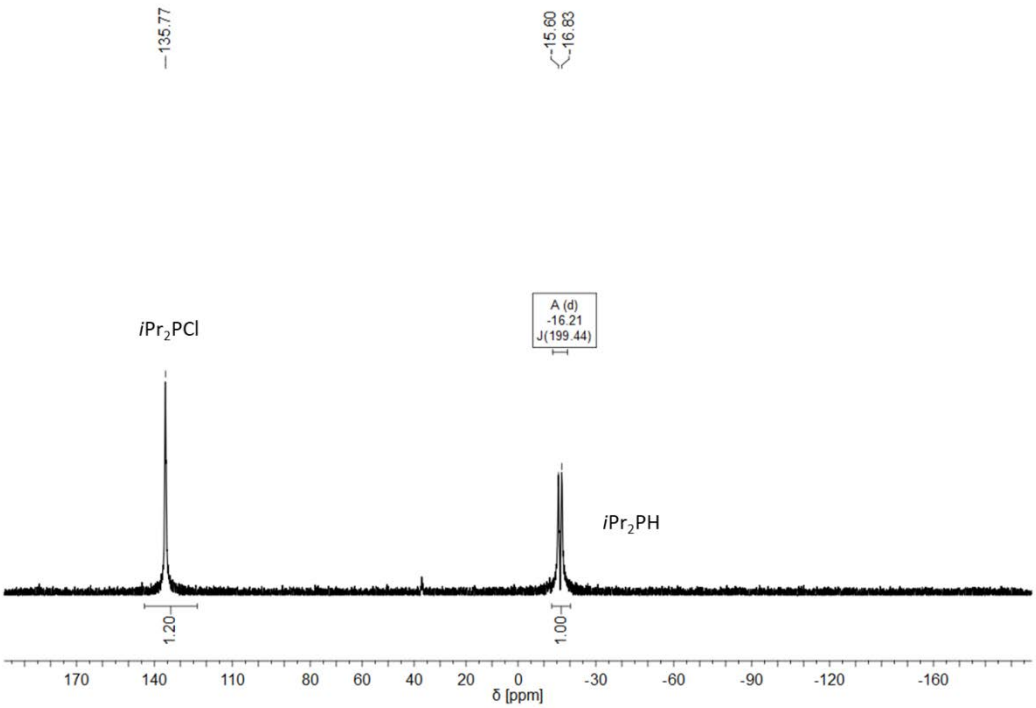

Figure S 24: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of *i*Pr$_2$PCl with PhSiH$_3$ (30°C, MeCN, after 20 hours).

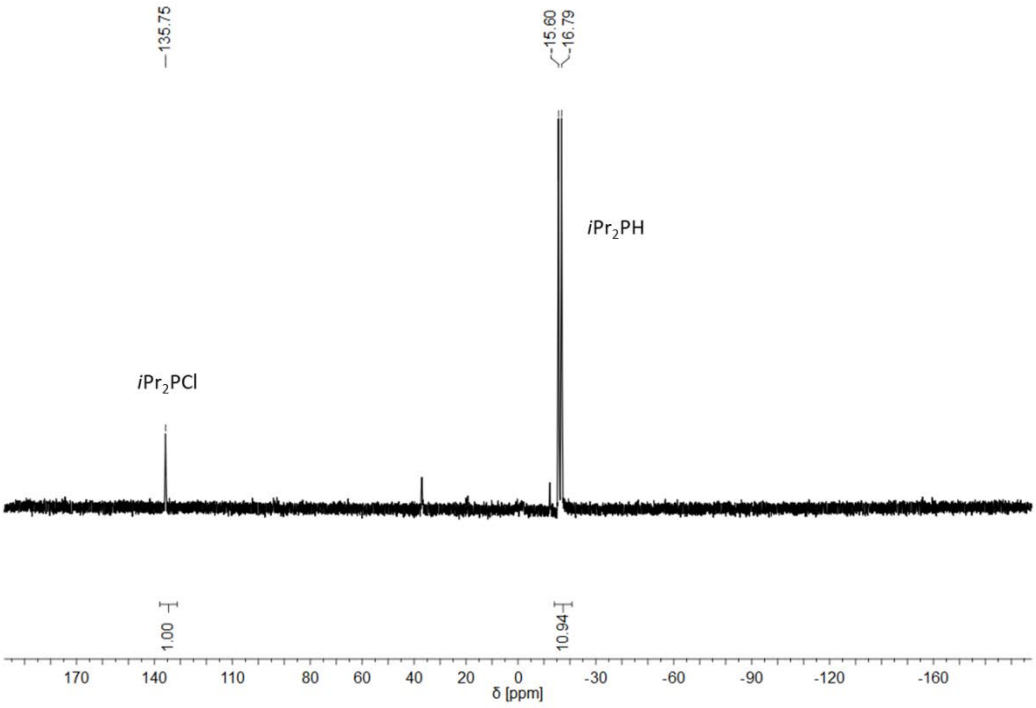

Figure S 25: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of *i*Pr$_2$PCl with PhSiH$_3$ (30°C, oDFB/MeCN, after 42 hours).

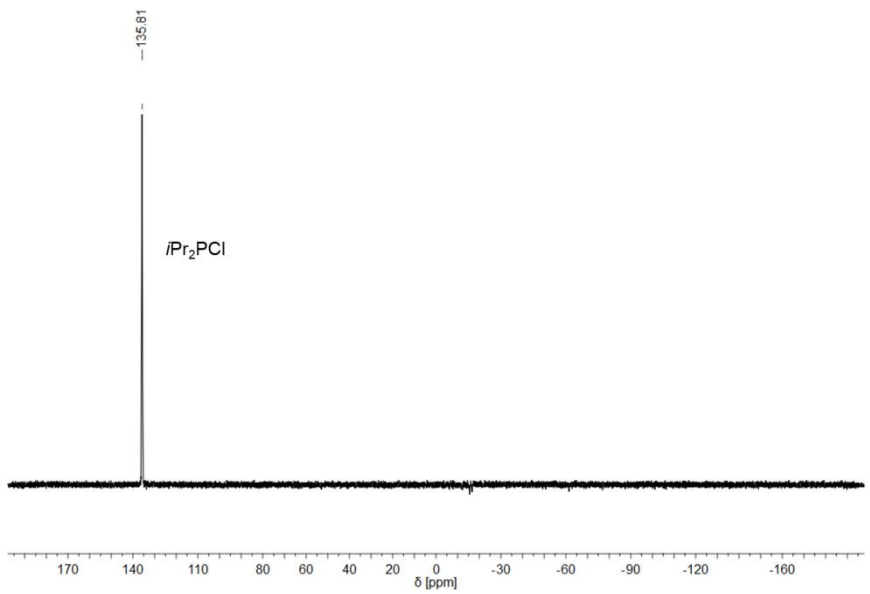

Figure S 26: ^{31}P NMR spectrum of reaction of *i*Pr$_2$PCl with PhSiH$_3$ (60°C, oDFB/MeCN, after 12 hours). No 9-BBN used.

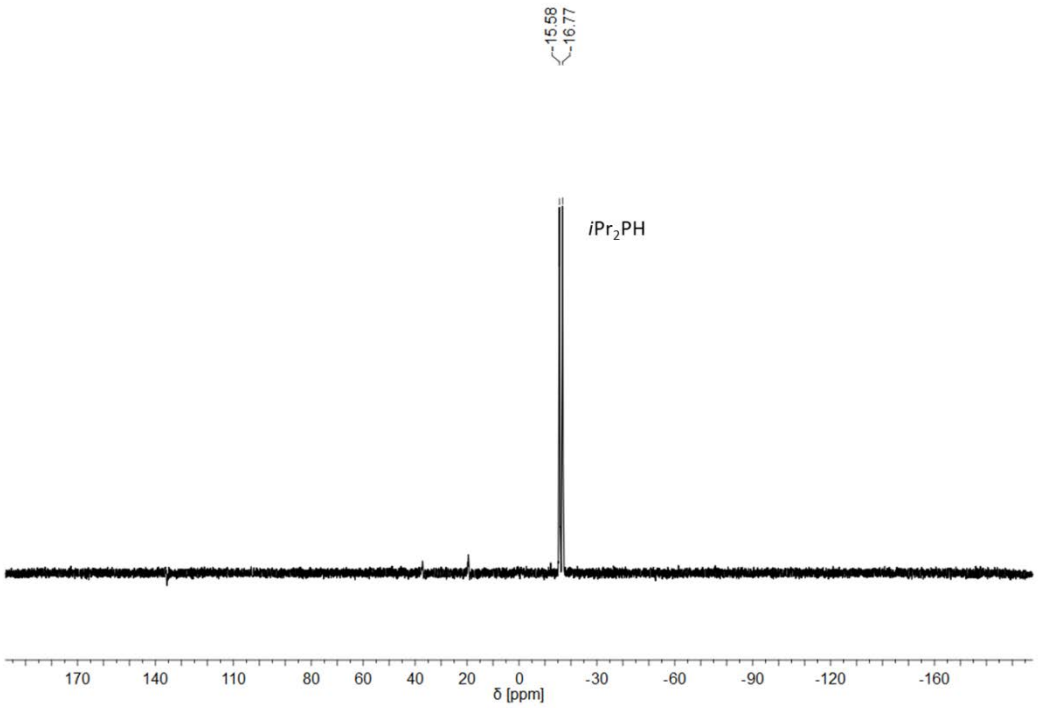

Figure S 27: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of *i*Pr$_2$PCl with PhSiH$_3$ (60°C, oDFB/MeCN, after 8 hours).

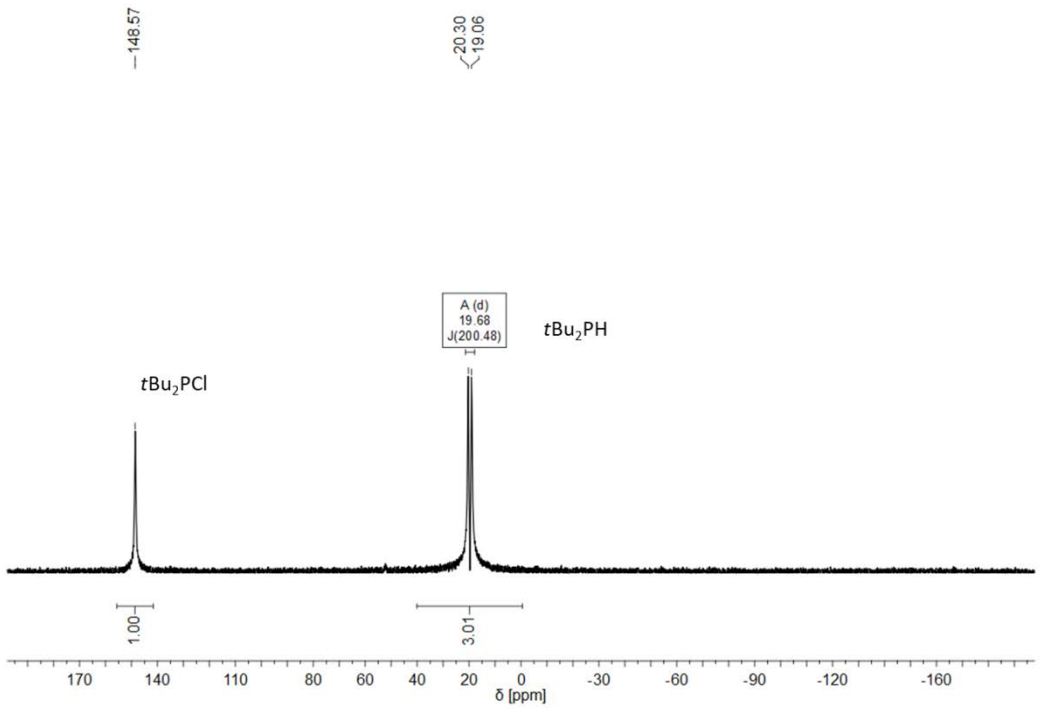

Figure S 28: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of *t*Bu$_2$PCl with PhSiH$_3$ (30°C, oDFB/MeCN, after 8 days).

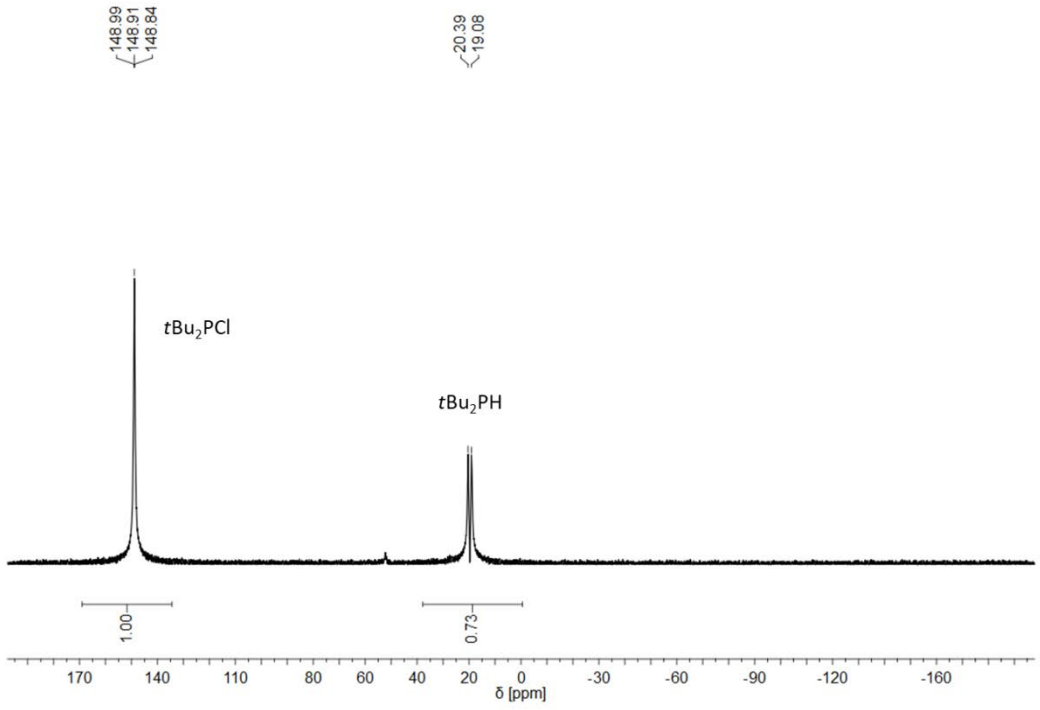

Figure S 29: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of *t*Bu$_2$PCl with PhSiH$_3$ (60°C, oDFB/MeCN, after 48 hours).

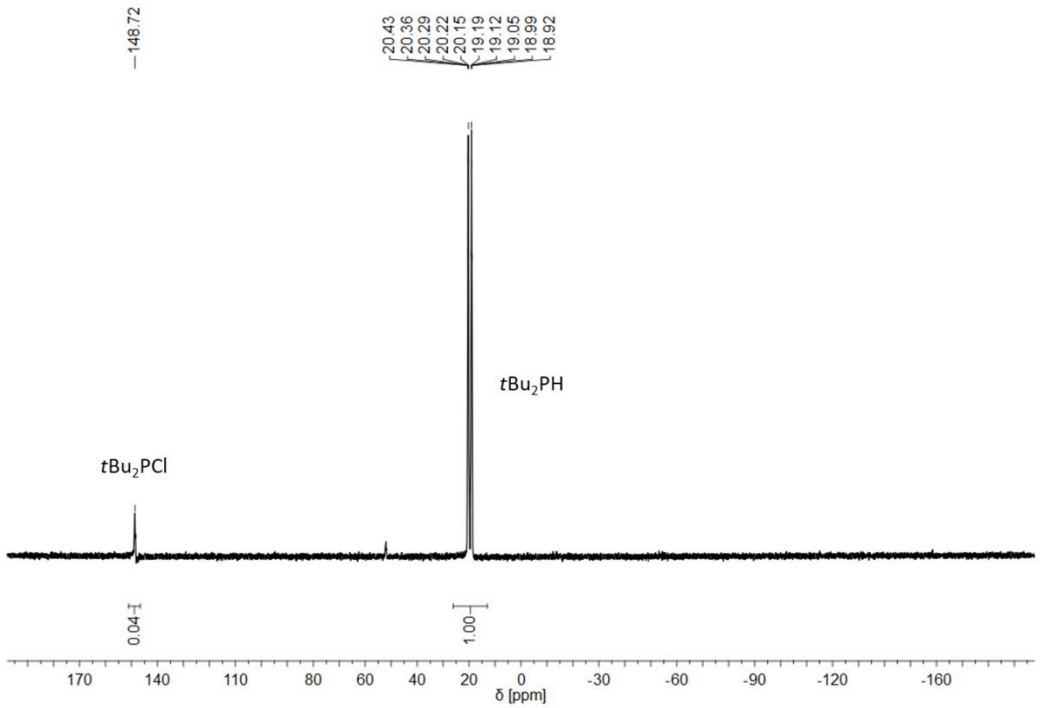

Figure S 30: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of *t*Bu$_2$PCl with PhSiH$_3$ (80°C, oDFB/MeCN, after 5 days).

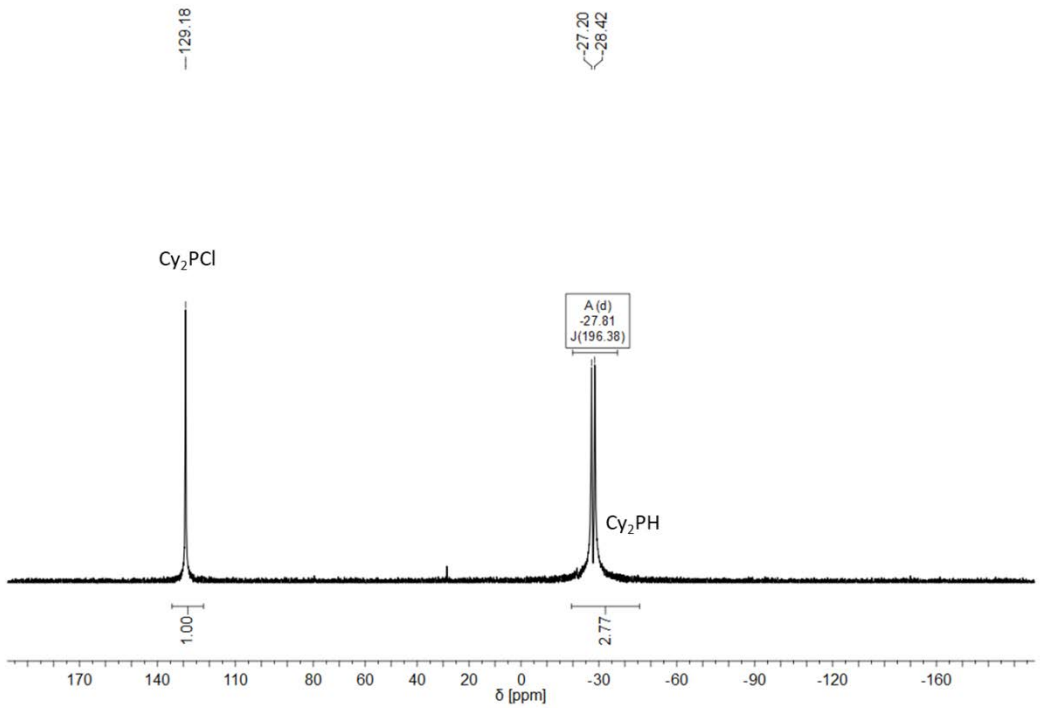

Figure S 31: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Cy$_2$PCl with PhSiH$_3$ (30°C, MeCN/oDFB, after 38 hours).

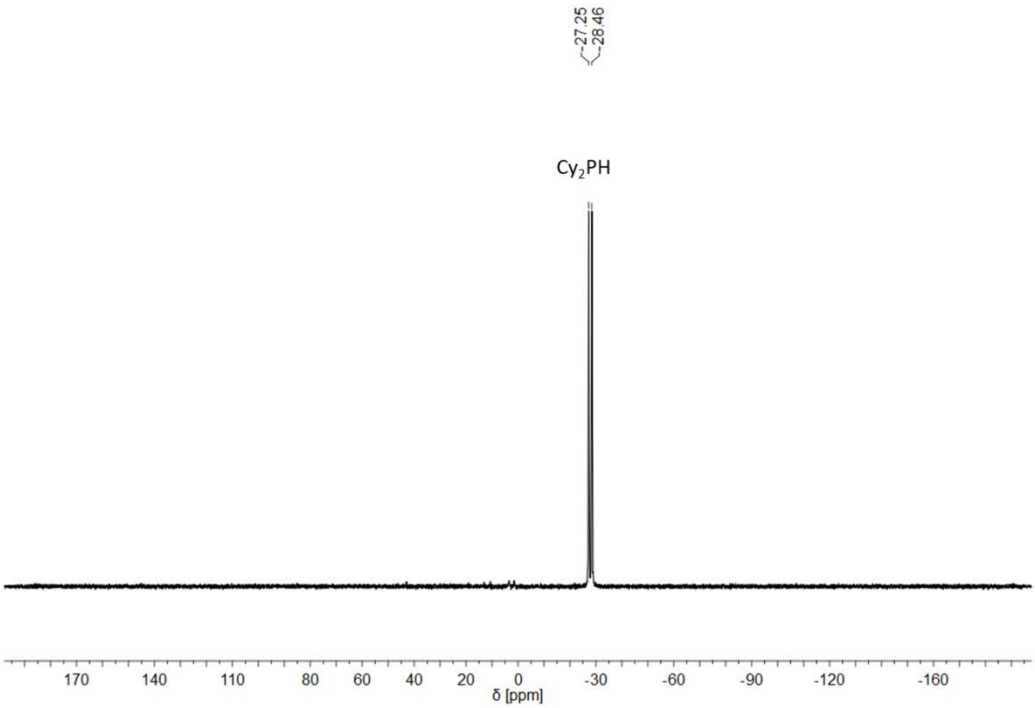

Figure S 32: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Cy_2PCl with $PhSiH_3$ (60°C, MeCN/oDFB, after 8 hours).

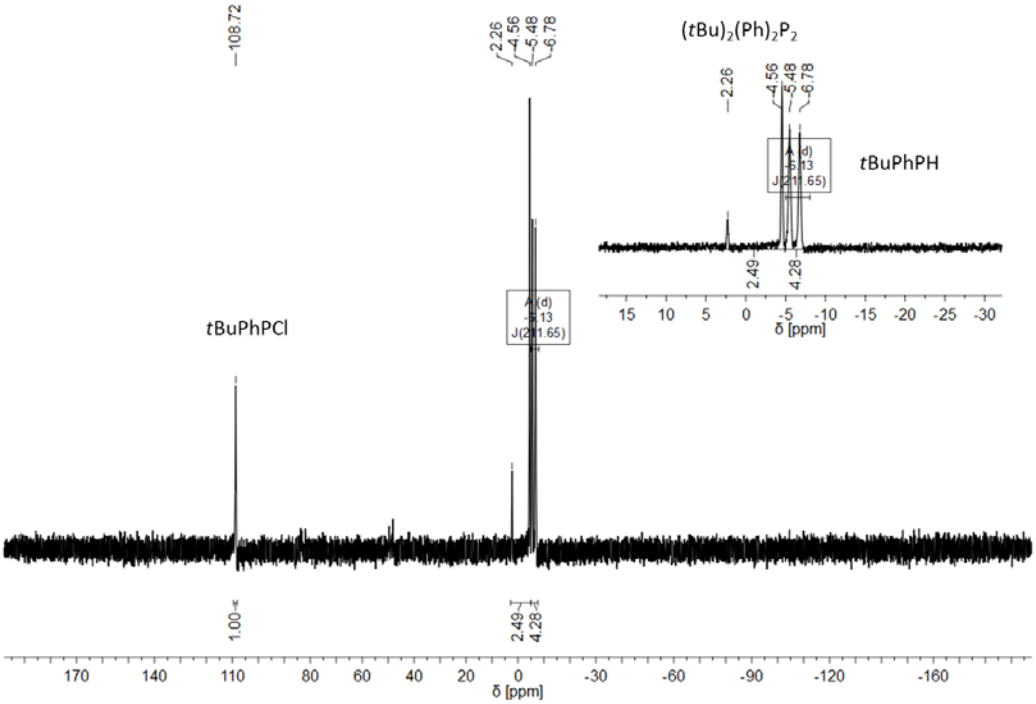

Figure S 33: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of *t*BuPhPCl with $PhSiH_3$ (30°C, MeCN/oDFB, after 42 hours).

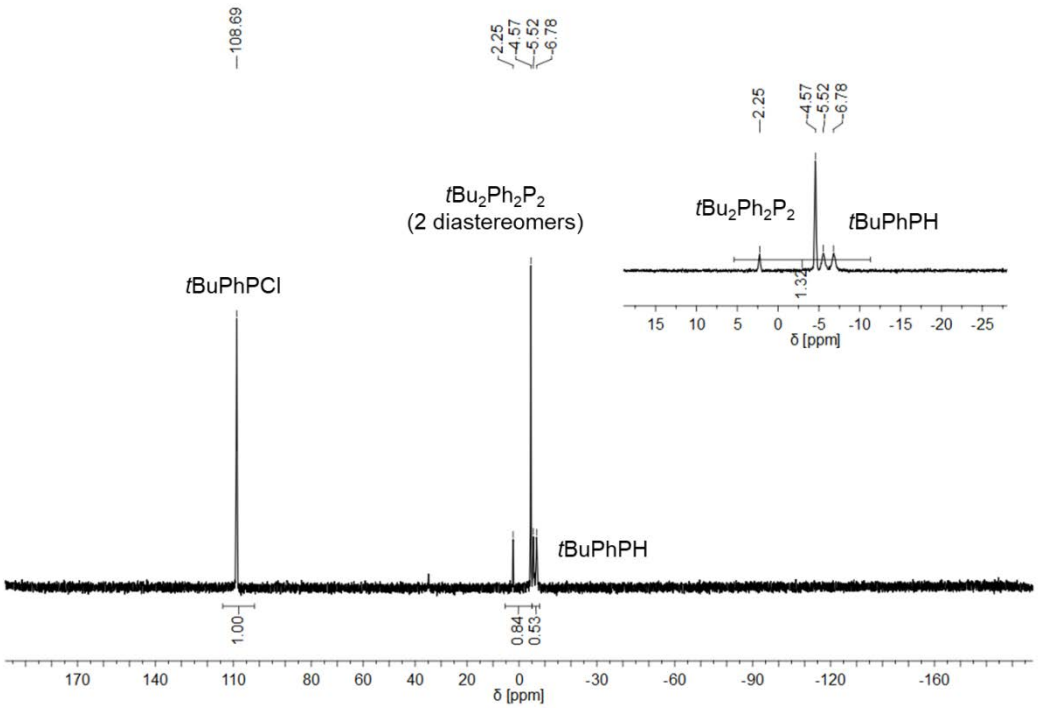

Figure S 34: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of *t*BuPhPCl with $PhSiH_3$ (60°C, MeCN/oDFB, after 48 hours).

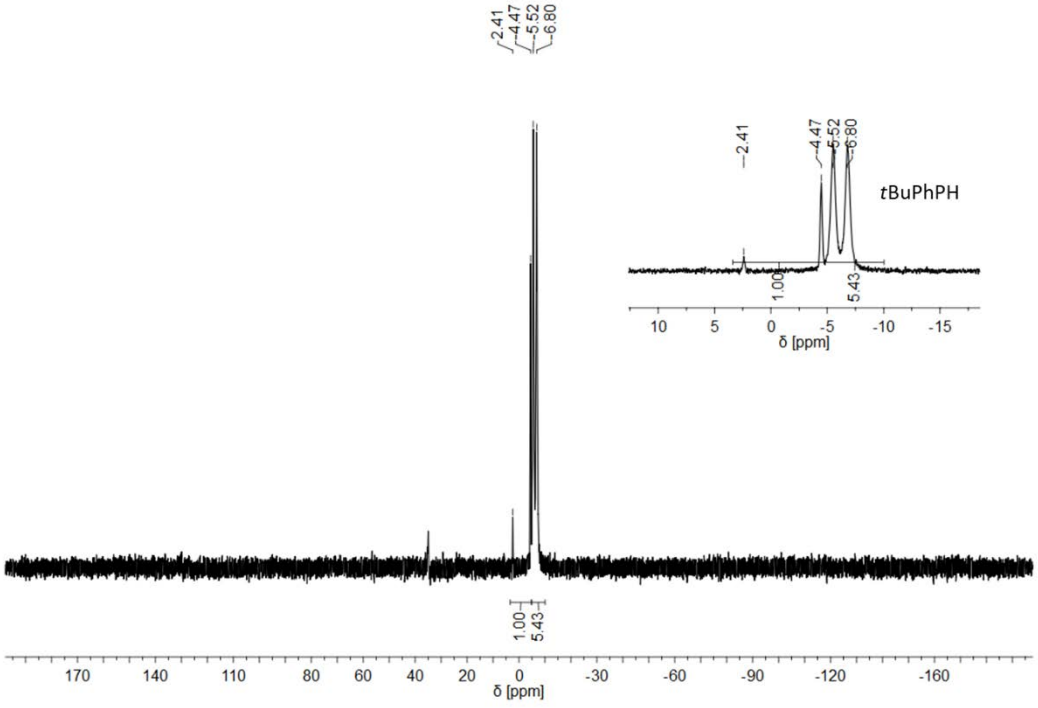

Figure S 35: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of *t*BuPhPCl with $PhSiH_3$ (80°C, MeCN/oDFB, after 24 hours).

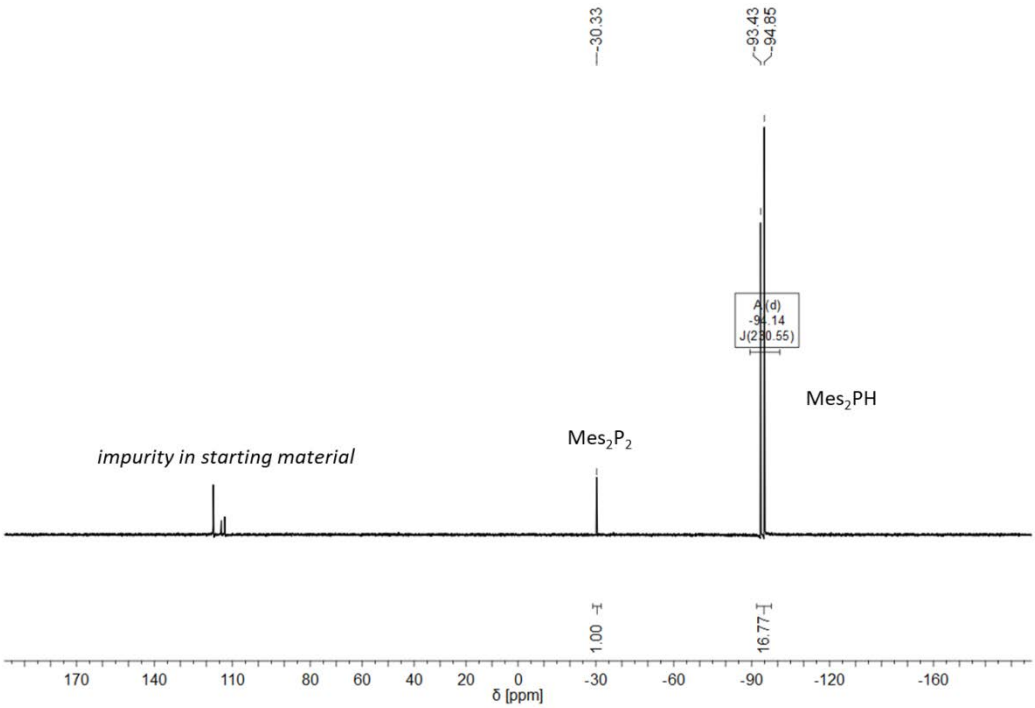

Figure S 36: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of Mes_2PCl with $PhSiH_3$ (30°C, MeCN/oDFB, after 24 hours).

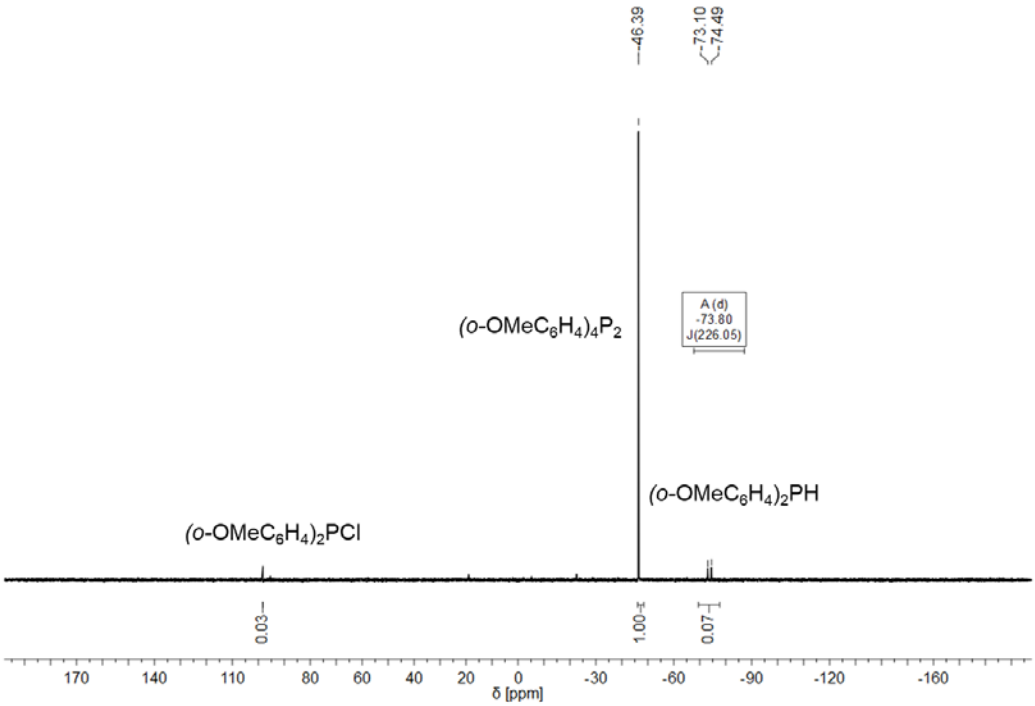

Figure S 37: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of (o-$OMeC_6H_4)_2PCl$ with $PhSiH_3$ (30°C, MeCN/oDFB, after 10 hours).

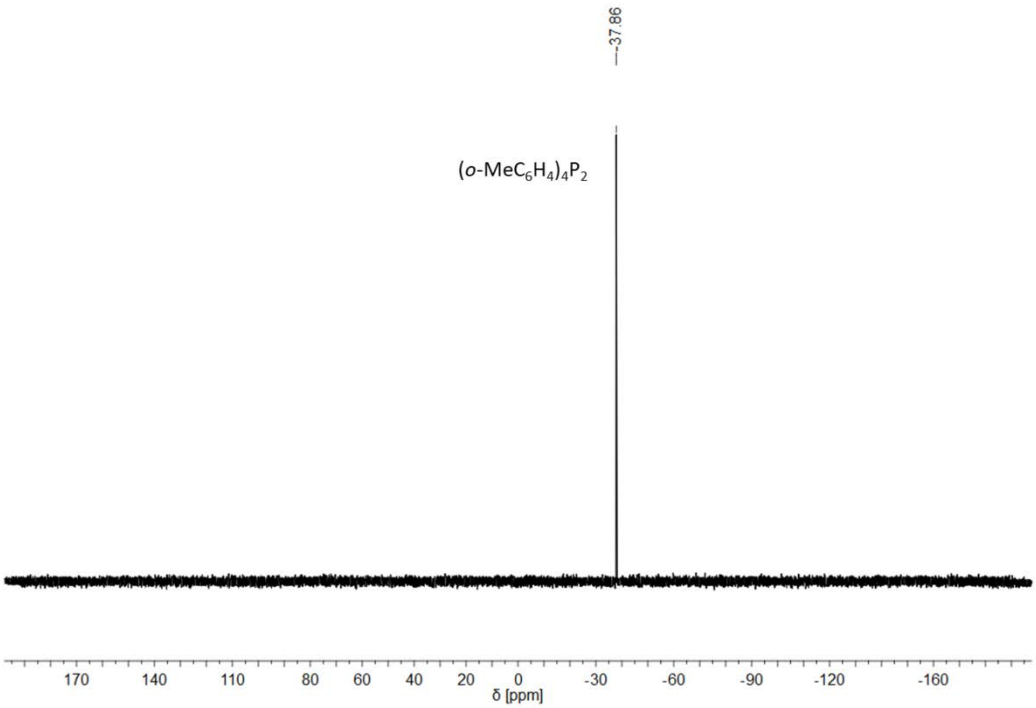

Figure S 38: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of $(MeC_6H_4)_2PCl$ with $PhSiH_3$ (30°C, MeCN/*o*DFB, after 7 hours).

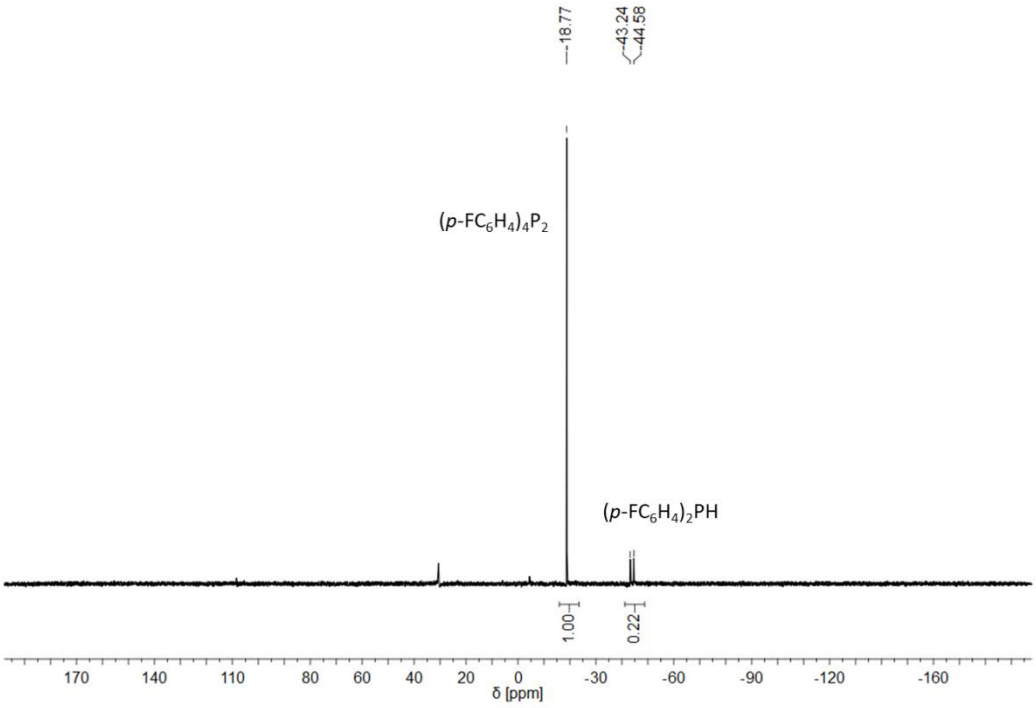

Figure S 39: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of $(p\text{-}FC_6H_4)_2PCl$ with $PhSiH_3$ (30°C, MeCN/*o*DFB, after 20 hours).

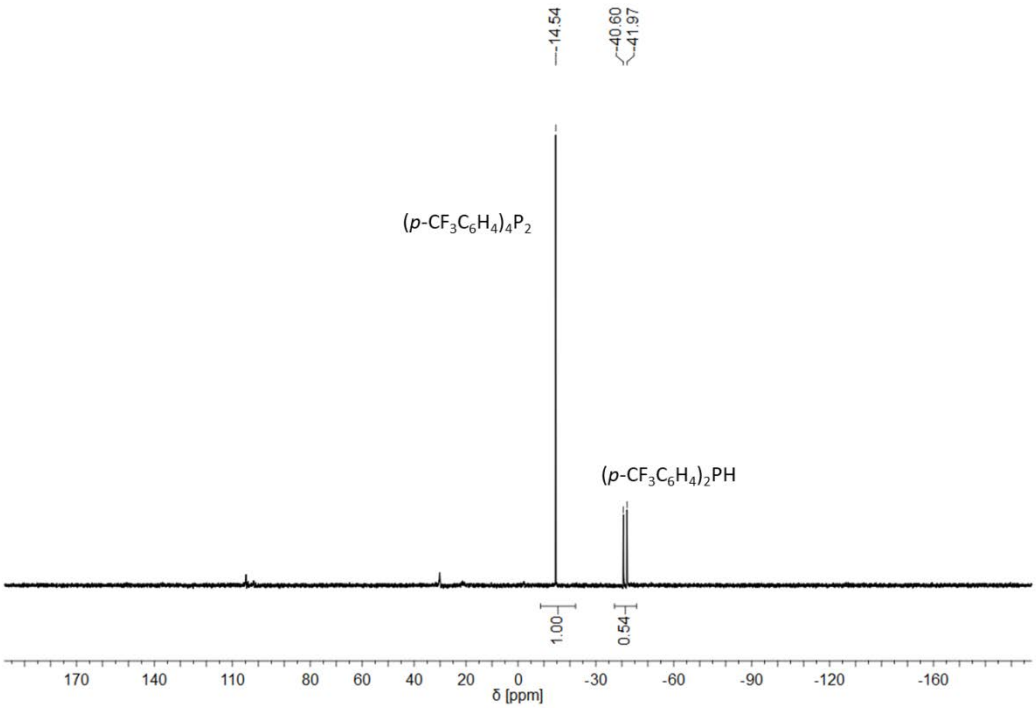

Figure S 40: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of (p-$CF_3C_6H_4)_2PCl$ with $PhSiH_3$ (30°C, MeCN/*o*DFB, after 20 hours).

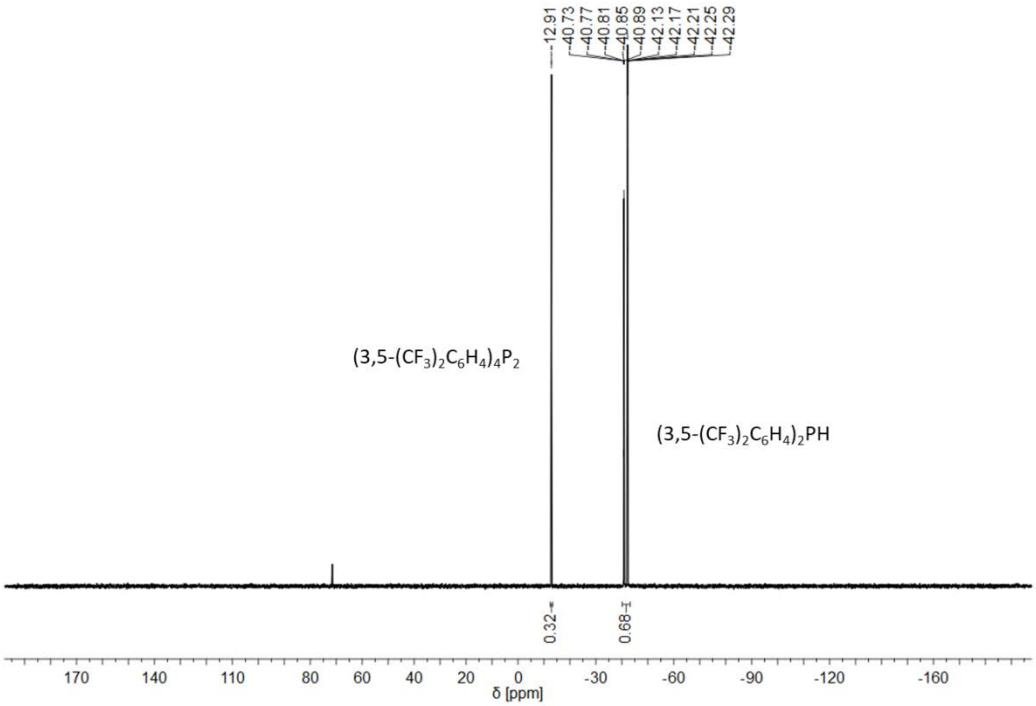

Figure S 41: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of ($3,5$-$(CF_3)_2C_6H_3)_2PCl$ with $PhSiH_3$ (30°C, MeCN/*o*DFB, after 6 hours).

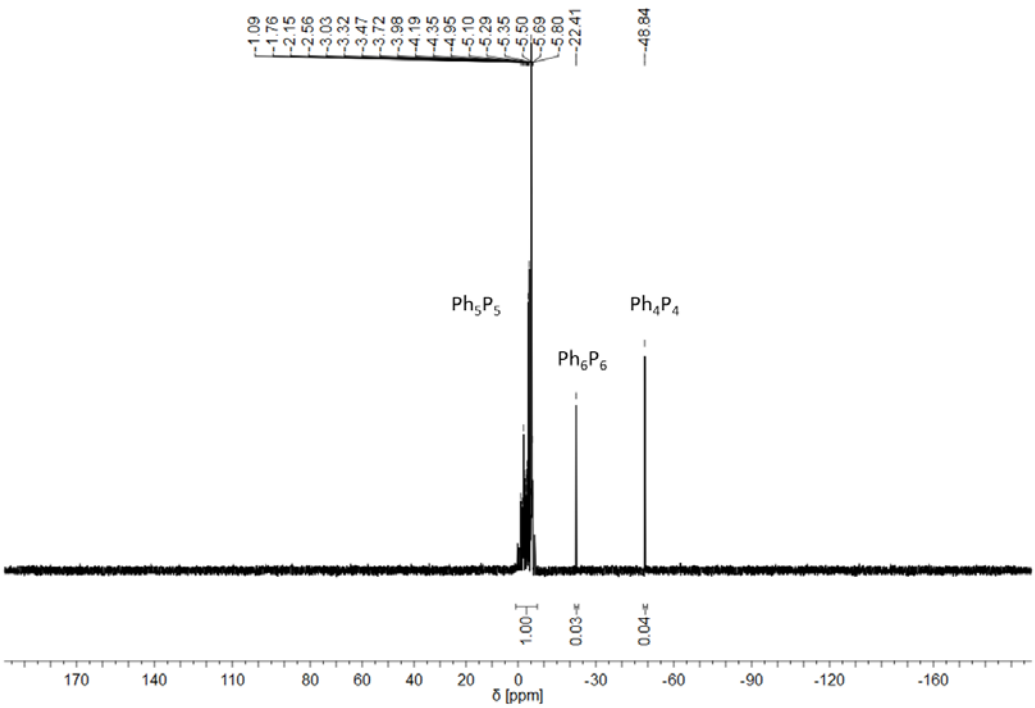

Figure S 42: ^{31}P NMR spectrum of 9-BBN catalyzed reaction of $PhPCl_2$ with $PhSiH_3$ (30°C, MeCN/*o*DFB, after 48 hours).

2.2 Lewis base ([Et_4N]Cl) catalyzed reactions

2.2.1 Lewis base screening

Several Lewis bases were tested for their ability to catalyze reduction of Ph_2PCl to P_2Ph_4 with $PhSiH_3$.

General procedure: Ph_2PCl (19.9 mg, 0.09 mmol, 1 equiv), $PhSiH_3$ (9.7 mg, 0.09 mmol, 1 equiv) and Lewis base (0.05 equiv) were dissolved in a mixture of *o*DFB/MeCN (0.6 ml, 2/1; V/V) and heated to 30 °C. The reaction progress was monitored by ^{31}P NMR spectroscopy.

Table S 3: Catalyst screening. Conversion of Ph_2PCl to Ph_4P_2.

Lewis base	time [h]	conversion [%][a]
[*n*Bu_4N]Cl	3	>99
[Et_4N]Cl	2	>99
LiCl	24	9
LiCl/12-crown-4[c]	24	84
KCl	24	5
$CaCl_2$	24	4
[*n*Bu_4N][Br]	16	83[b]
[*n*Bu_4N][F_2Ph_3Si]	2	>99
DBU	2	25
	16	>99

Reaction conditions: 0.5 mol% catalyst, 30°C, *o*DFB/MeCN (2/1, V/V), J-Young NMR tube, 0.15 M in Ph_2PCl. [a] Determined by ^{31}P NMR spectroscopy. [b] 20% P_2Ph_4 and 80% unidentified product. [c] 0.1 equiv 12-crown-4 was added to the reaction mixture.

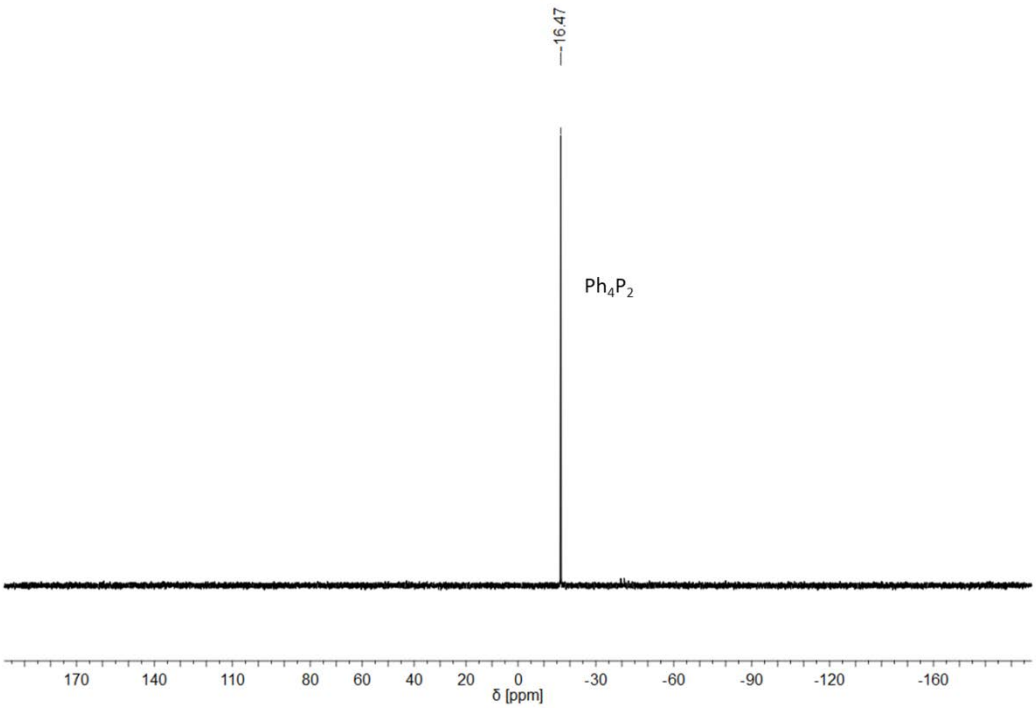

Figure S 43: ^{31}P NMR spectrum of [*n*Bu$_4$N][Cl] catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 3 hours).

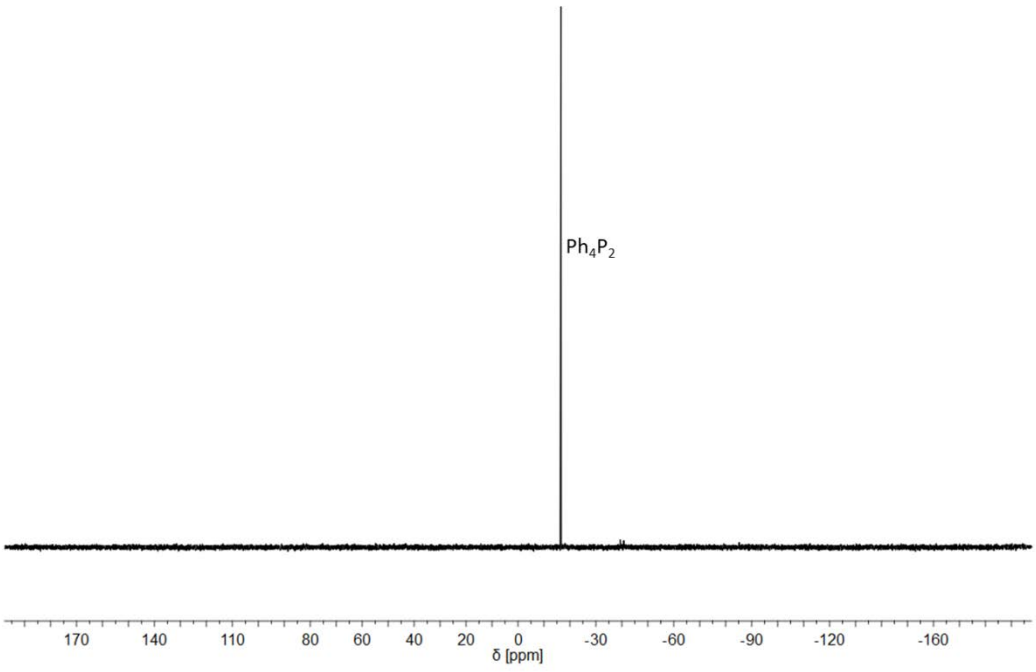

Figure S 44: ^{31}P NMR spectrum of [Et$_4$N]Cl catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 2 hours).

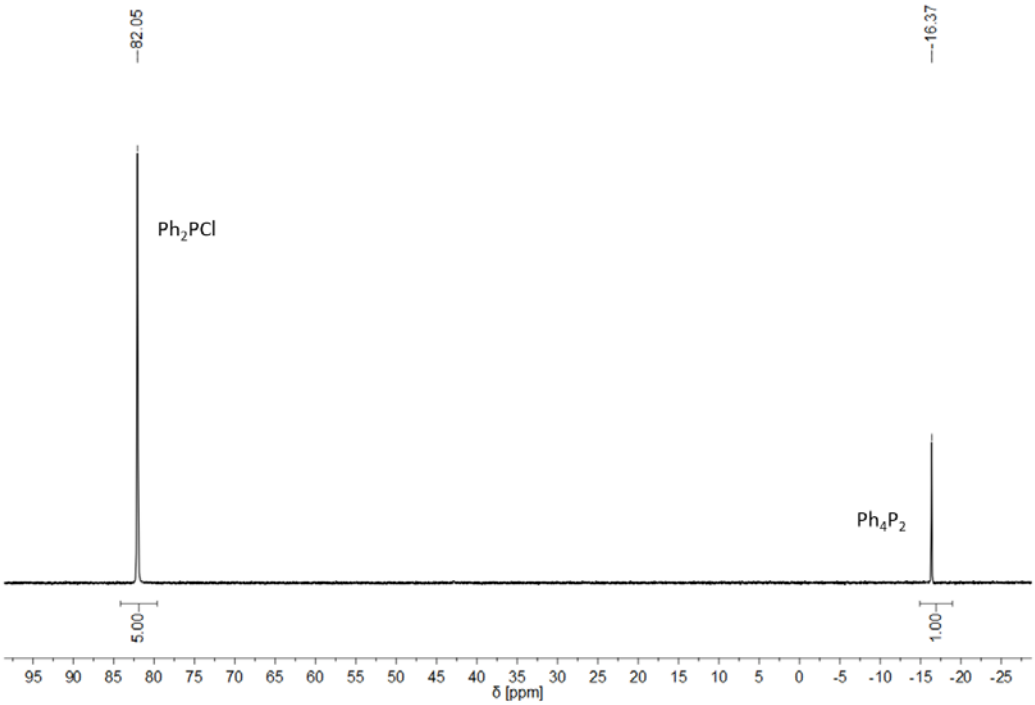

Figure S 45: ^{31}P NMR spectrum of LiCl catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 24 hours).

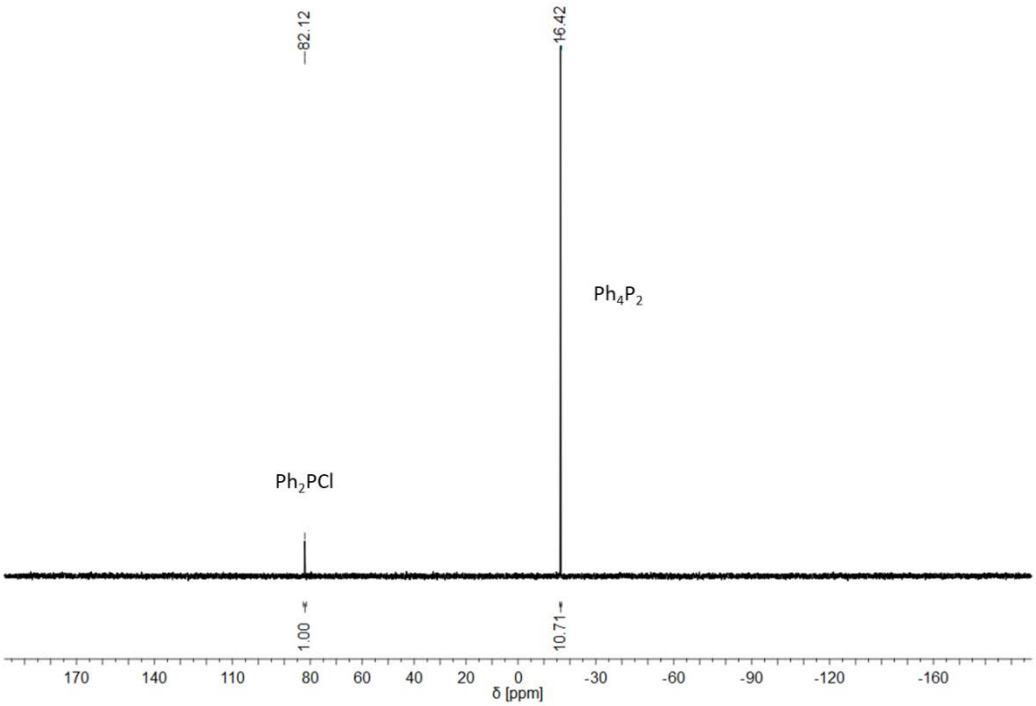

Figure S 46: ^{31}P NMR spectrum of LiCl catalyzed reaction of Ph_2PCl with $PhSiH_3$ and 12-crown-4 (30°C, *o*DFB/MeCN, after 24 hours).

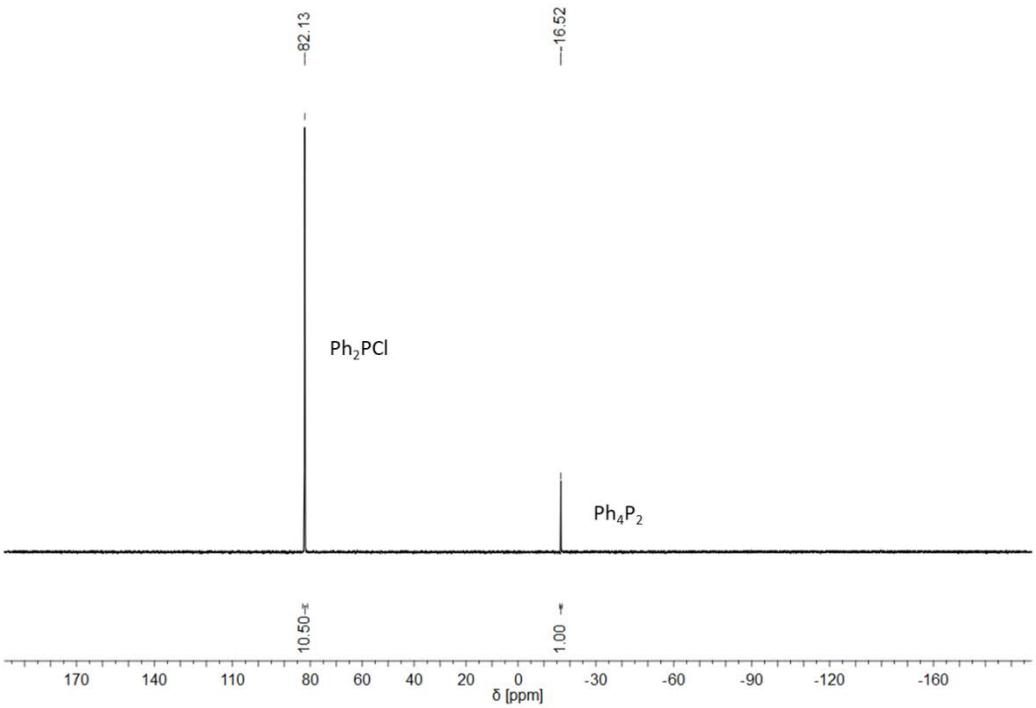

Figure S 47: ^{31}P NMR spectrum of KCl catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 24 hours).

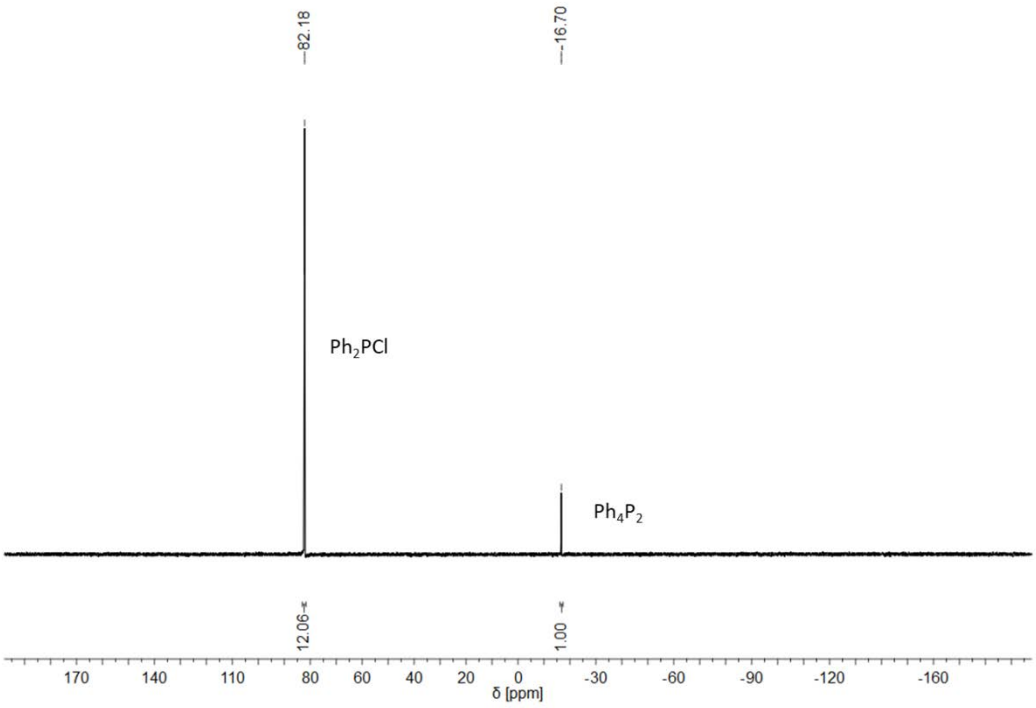

Figure S 48: ^{31}P NMR spectrum of $CaCl_2$ catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 24 hours).

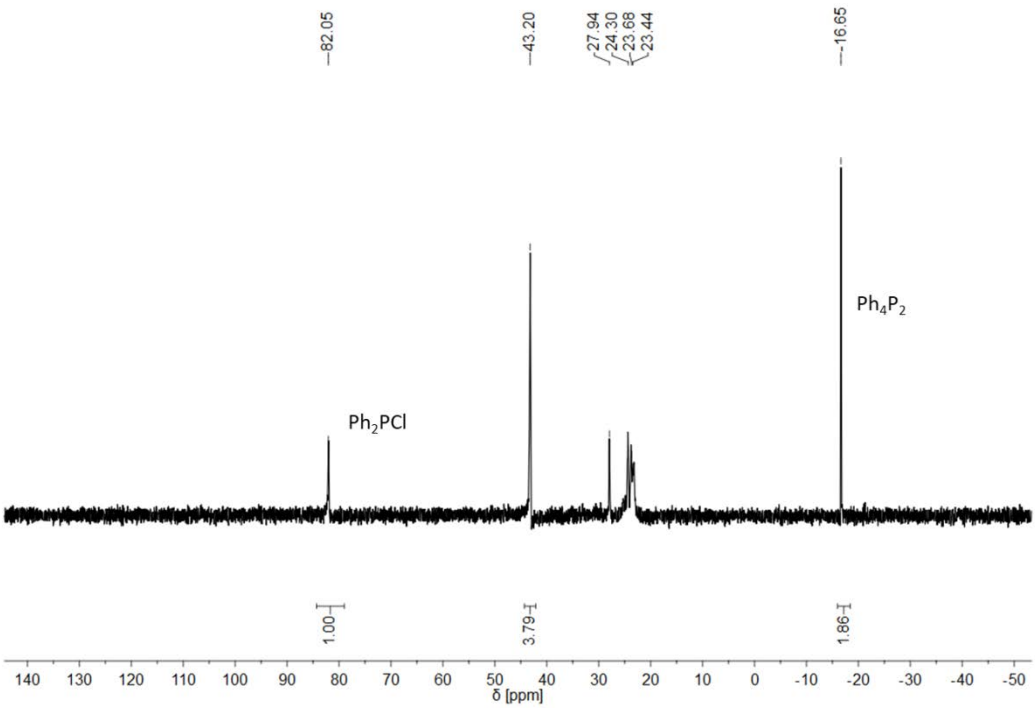

Figure S 49: ^{31}P NMR spectrum of [*n*Bu$_4$N][Br] catalyzed reaction of Ph$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 16 hours).

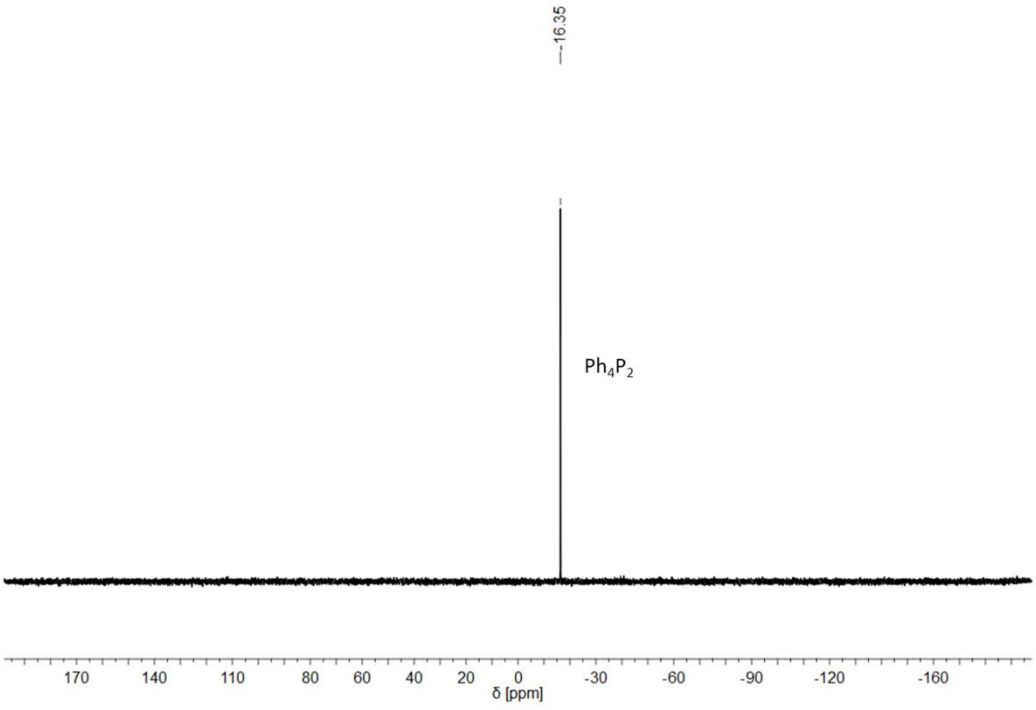

Figure S 50: ^{31}P NMR spectrum of [*n*Bu$_4$N][SiF$_2$Ph$_3$] catalyzed reaction of Ph$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

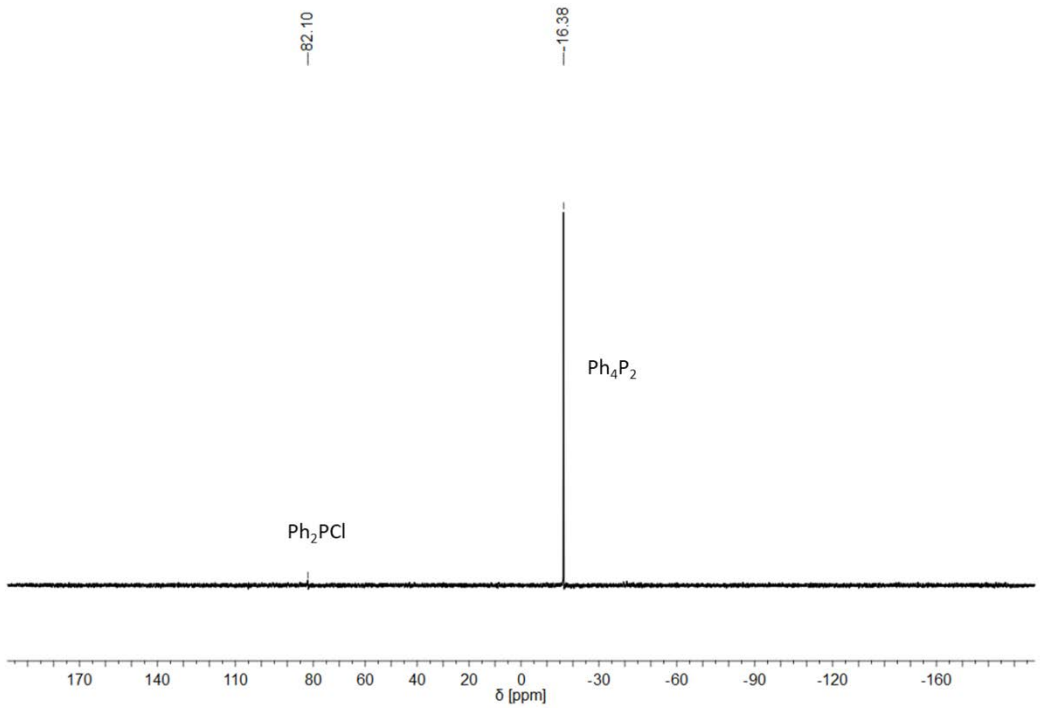

Figure S 51: ^{31}P NMR spectrum of DBU catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 16 hours).

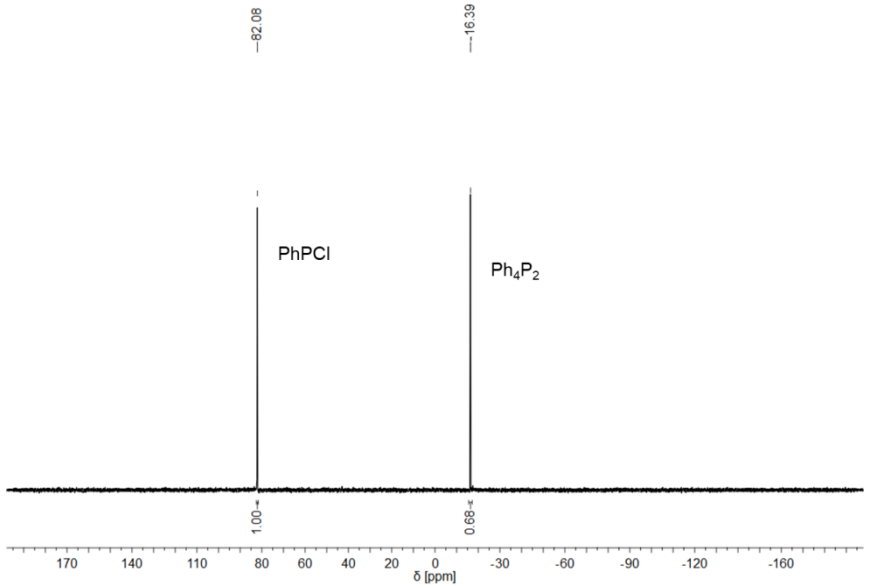

Figure S 52: ^{31}P NMR spectrum of DBU catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 2 hours).

2.2.2 Silane screening

Several silanes were screened for their ability to act as reductant in the [Et_4N]Cl catalyzed reduction of Ph_2PCl to P_2Ph_4.

General procedure: Ph_2PCl (19.9 mg, 0.09 mmol, 1 equiv), silane (1 equiv) and [*n*Bu_4N][Cl] (1.3 mg, 0.0045 mmol, 0.05 equiv) were dissolved in a mixture of *o*DFB/MeCN (0.6 ml, 2/1; V/V) and heated to 30 °C. The reaction progress was monitored by ^{31}P NMR spectroscopy.

Table S 4: Silane screening. Conversion of Ph_2PCl to Ph_4P_2.

Silane	Time [h]	Conversion [%][a]

$PhSiH_3$	3	>99
Ph_3SiH	24	<1
$Me_2HSiOSiHMe_2$	16	37 [b]
Et_3SiH	24	0
iPr_3SiH	16	0

Reaction conditions: 0.5 mol% [*n*Bu_4N][Cl], 30°C, J-Young NMR tube, 0.15 M in Ph_2PCl, *o*DFB/MeCN, V/V, 2/1. [a] Determined by ^{31}P NMR spectroscopy. [b] No conversion to Ph_4P_2, conversion to two unidentified products.

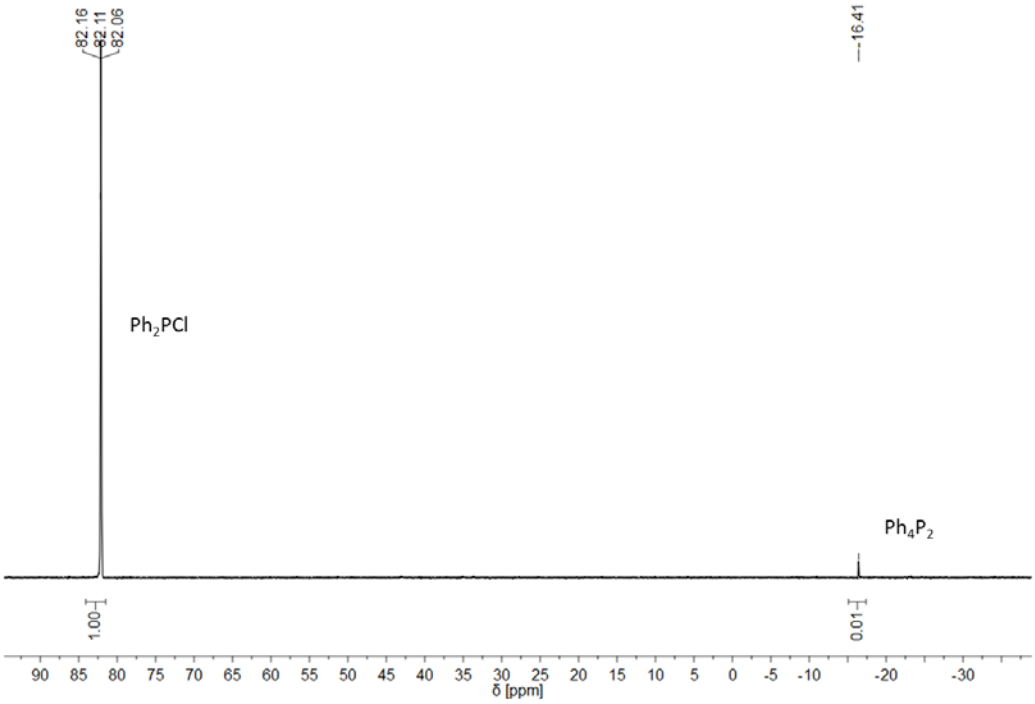

Figure S 53: ^{31}P NMR spectrum of [*n*Bu_4N][Cl] catalyzed reaction of Ph_2PCl with Ph_3SiH (30°C, *o*DFB/MeCN, after 24 hours).

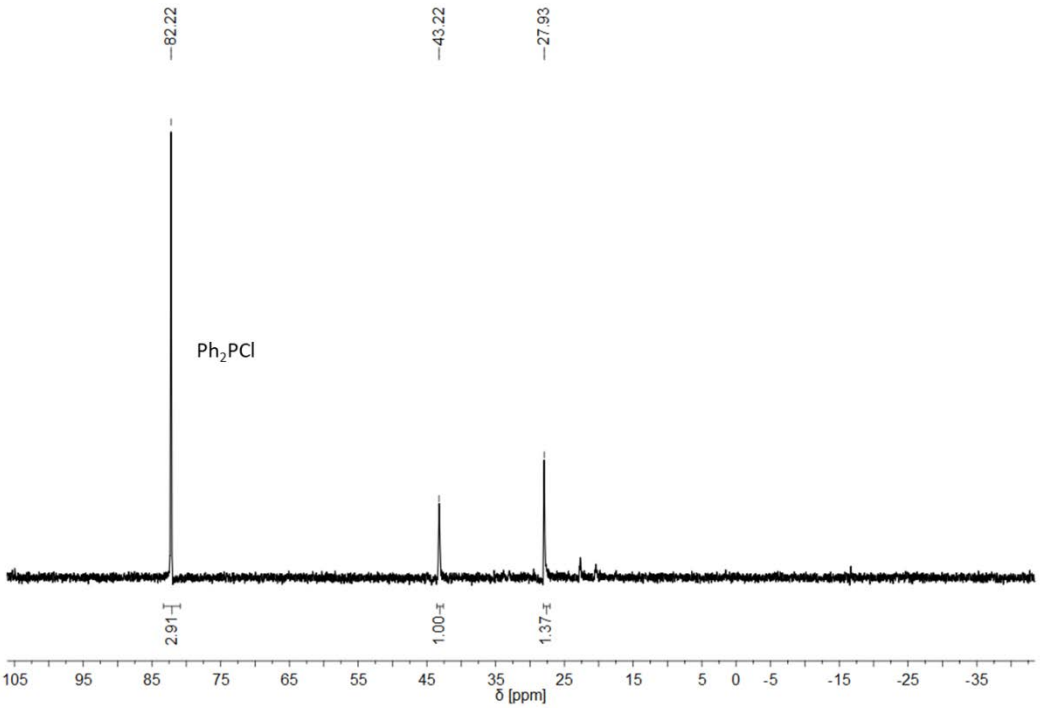

Figure S 54: ^{31}P NMR spectrum of [*n*Bu$_4$N][Cl] catalyzed reaction of Ph$_2$PCl with HMe$_2$SiOSiMe$_2$H (30°C, *o*DFB/MeCN, after 16 hours).

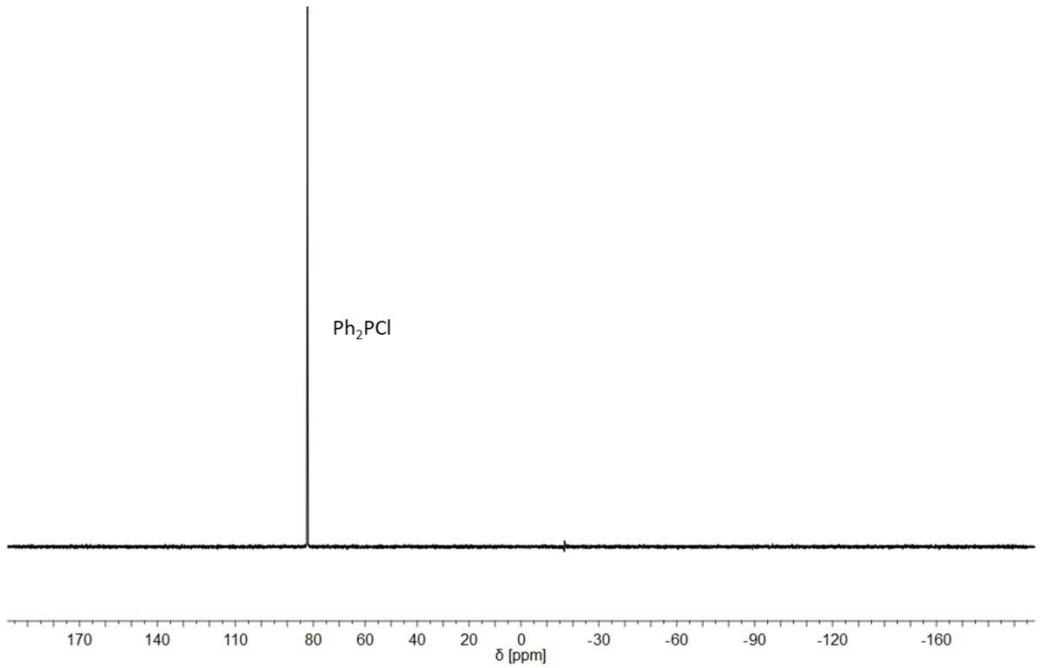

Figure S 55: ^{31}P NMR spectrum of [*n*Bu$_4$N][Cl] catalyzed reaction of Ph$_2$PCl with Et$_3$SiH (30°C, *o*DFB/MeCN, after 24 hours).

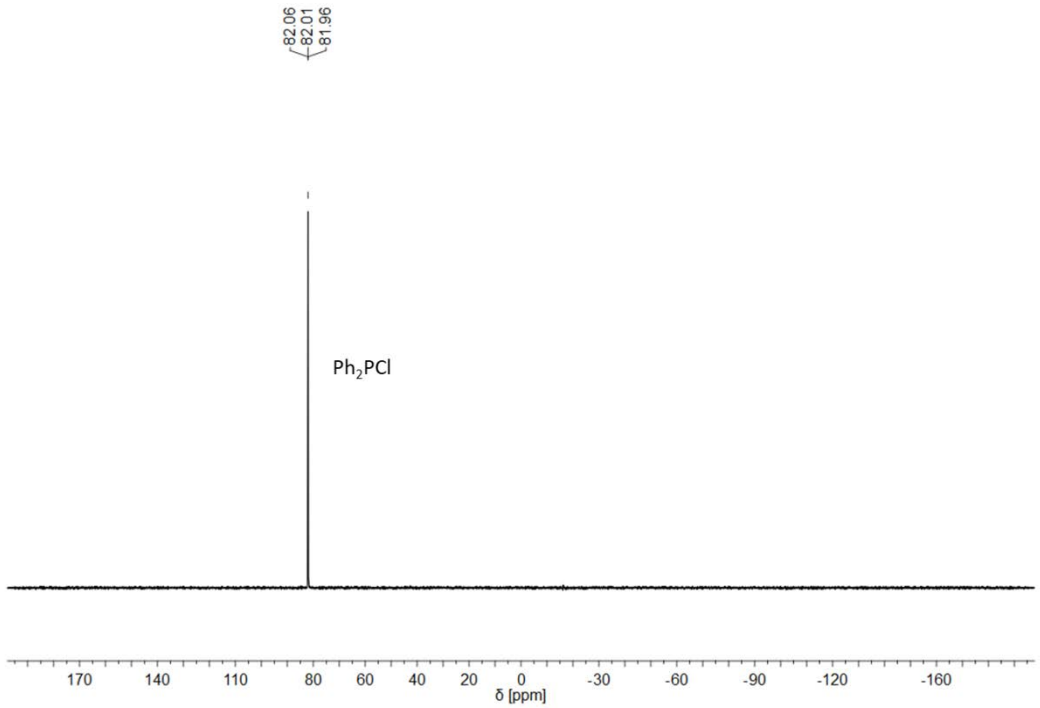

Figure S 56: ^{31}P NMR spectrum of [*n*Bu$_4$N][Cl] catalyzed reaction of Ph$_2$PCl with *i*Pr$_3$SiH (30°C, *o*DFB/MeCN, after 16 hours).

2.2.3 Solvent screening

Table S 5: Solvent screening. Conversion of Ph$_2$PCl to Ph$_4$P$_2$.

Solvent	Time [h]	Conversion [%][a]
oDFB	2	18
MeCN	2	>99
toluene	2	0[b]
oDFB/MeCN	2	>99

Reaction conditions: 0.5 mol% [Et$_4$N]Cl, 30°C, J-Young NMR tube, 0.15 M in Ph$_2$PCl, *o*DFB/MeCN, V/V, 2/1. [a] Determined by ^{31}P NMR spectroscopy. [b] [Et$_4$N]Cl shows low solubility in toluene.

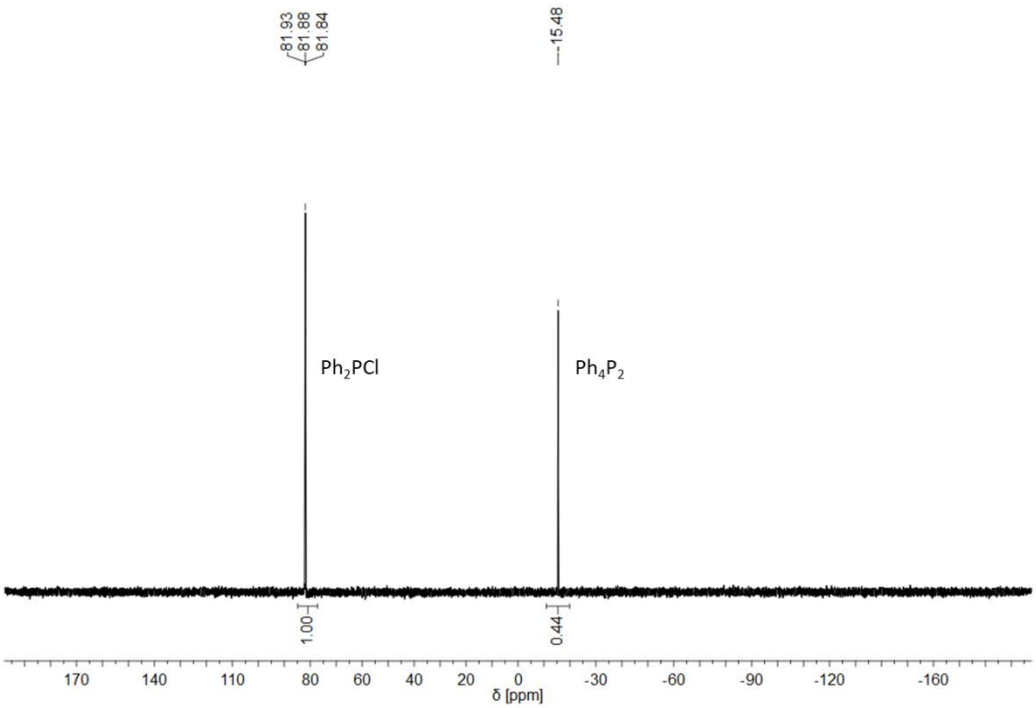

Figure S 57: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, *o*DFB, after 2 hours).

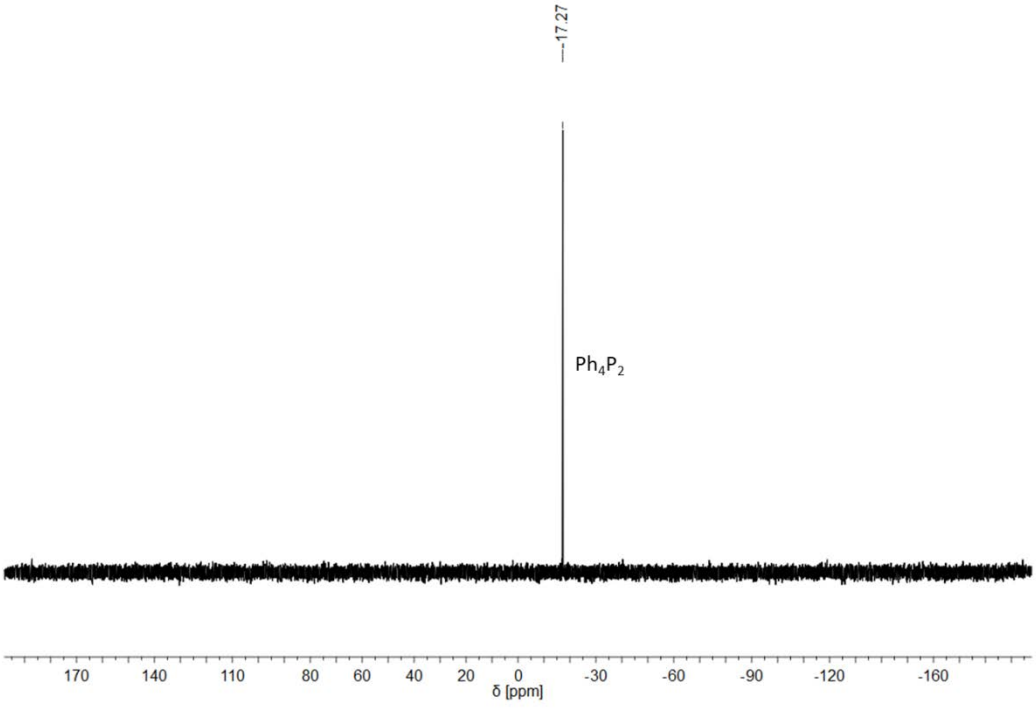

Figure S 58: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, MeCN, after 2 hours).

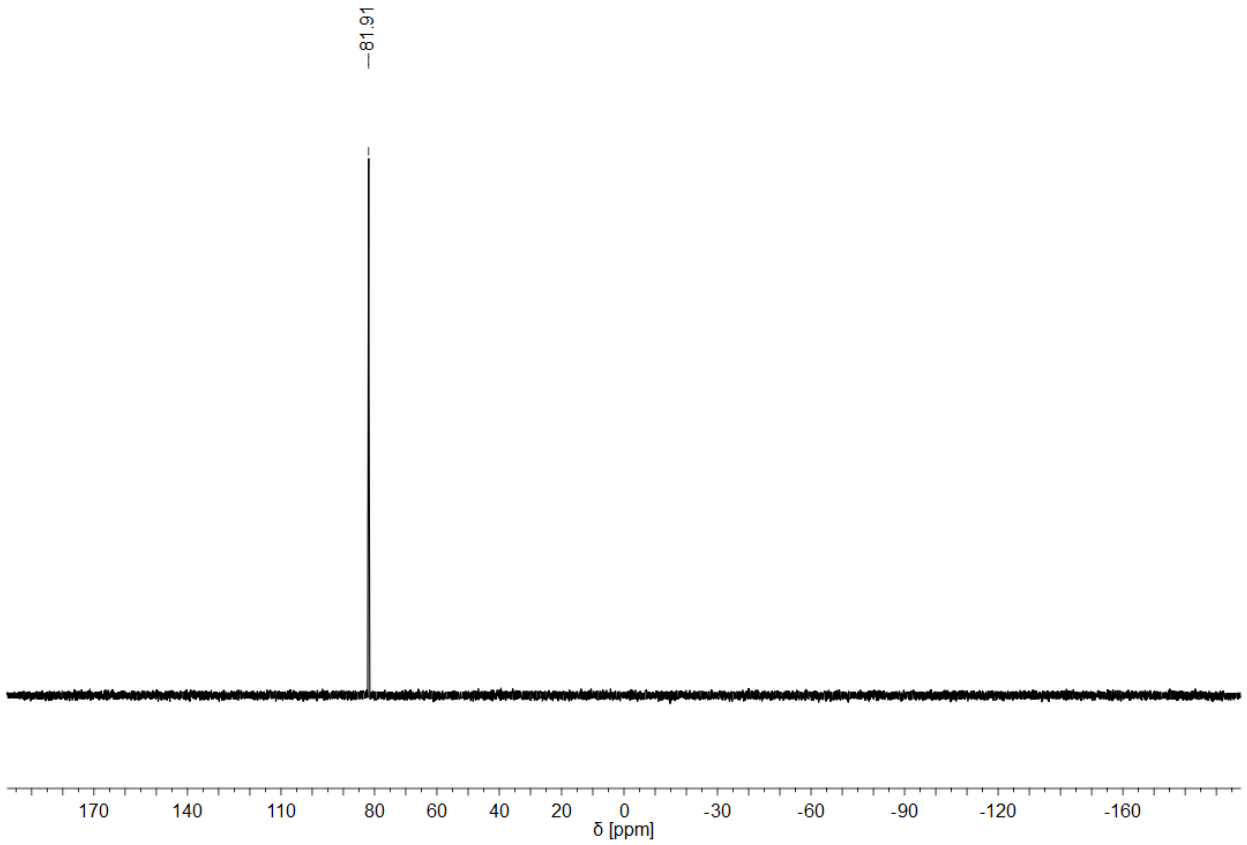

Figure S 59: ^{31}P NMR spectrum of [Et$_4$N]Cl catalyzed reaction of Ph$_2$PCl with PhSiH$_3$ (30°C, toluene, after 2 hours).

2.2.4 Phosphine scope

General procedure: R$_2$PCl (0.09 mmol, 1 equiv), silane (1 equiv) and [Et$_4$N]Cl (0.05 equiv) were dissolved in solvent (0.6 ml) and kept at the indicated temperature in a J-Young tube. The reaction progress was monitored by ^{31}P NMR spectroscopy.

Table S 6: Synthesis of R$_2$PPR$_2$ from R$_2$PCl with [Et$_4$N]Cl and PhSiH$_3$.

phosphine	temp. [°C]	time [h]	conv. [%]	product	δ(^{31}P) [ppm] (m)	literature δ(^{31}P) [ppm]
Ph$_2$PCl	30	3	>99	Ph$_2$PPPh$_2$	-16.4 (s)	-16.7 (CH$_2$Cl$_2$)[8]
*i*Pr$_2$PCl	60	12	0	-	-16.2 (d, $^1J_{PH}$ = 199 Hz)	-16.5 (^{31}P{^{1}H}, C$_6$D$_6$) [10]
Cy$_2$PCl	60	13	7	Cy$_2$PH	-28.5 (d, $^1J_{PH}$ = 195 Hz)	-28.1 (d, $^1J_{PH}$ = 198 Hz, CD$_3$CN)[11]
*t*Bu$_2$PCl	80	15	0	-	19.7 (d, $^1J_{PH}$ = 201 Hz)	19.5 (d, $^1J_{PH}$ = 203 Hz)[8]
*t*BuPhPCl	80	15	0	-	-6.1 (d, $^1J_{PH}$ = 212 Hz); 2.4 (s), -4.6 (s)	-5.7 (d, $^1J_{PH}$ = 210 Hz)[8]; 1.9[8], -4.7[8]
(*o*-OMeC$_6$H$_4$)$_2$PCl	30 21 23	2 46 76	13	(*o*-OMePh)$_2$PP(*o*-OMePh)$_2$ (>99 %)[a]; (*o*-OMePh)$_2$PH	-46.4 (s); -73.8 (d, $^1J_{PH}$ = 226 Hz)	-46.18 (CD$_2$Cl$_2$)[12]; -73.2 (d, $^1J_{PH}$ = 226 Hz)[11]

				(0 %)[a]		
(*o*-$OMeC_6H_4)_2PCl$	60	3 15 19	42 92 >99	(*o*-$OMePh)_2PP$(*o*-$OMePh)_2$ (>99 %)[b]; (*o*-$OMePh)_2PH$ (0 %)[b]		
(o-$MeC_6H_4)_2PCl$	30	23	76	(*o*-$tol)_2PP$(o-$tol)_2$ (>99 %)[b]; (*o*-$tol)_2PH$ (0 %)[b]	-37.8 (s); -56.0 (d, $^1J_{PH}$ = 223 Hz)	-37.2 (s)[12]; -59.1 (d, $^1J_{PH}$ = 222 Hz, THF-d8)[13]
(o-$MeC_6H_4)_2PCl$	60	3 15	73 >99	(*o*-$tol)_2PP$(o-$tol)_2$ (>99 %)[c]; (*o*-$tol)_2PH$ (0 %)[c]		
(2,4,6-$Me_3C_6H_2)_2PCl$	60	15 18 23	63 69 87	Mes_2PPMes_2 (1 %)[b]; Mes_2PH (99 %)[b]	-30.3 (s); -94.1 (d, $^1J_{PH}$ = 231 Hz)	-30.3 (CD_2Cl_2)[12]; -92.9 (d, $^1J_{PH}$ = 229 Hz, C_6D_6)[14]
(*p*-$FC_6H_4)_2PCl$	60	3	>99	(*p*-$FC_6H_4)_2PP$(*p*-$FC_6H_4)_2$ (91 %); (*p*-$FC_6H_4)_2PH$ (9 %)	-18.77 (s); -43.9 (d, $^1J_{PH}$ = 221 Hz)	-16.8 (C_6D_6)[15]; -44.2 ($^1J_{PH}$ = 221 Hz, CD_3CN)[11]
(*p*-$FC_6H_4)_2PCl$	30	2	>99	(*p*-$FC_6H_4)_2PP$(*p*-$FC_6H_4)_2$ (>99); (*p*-$FC_6H_4)_2PH$ (-)		
(*p*-$CF_3C_6H_4)_2PCl$	60	3	>99	(*p*-$CF_3C_6H_4)_2PP$(*p*-$CF_3C_6H_4)_2$ (77%); (*p*-$CF_3C_6H_4)_2PH$ (23%)	-14.5 (s), -41.3 (d, $^1J_{PH}$ = 222 Hz)	-13.2 (C_6D_6)[15]; -42.7 ($^{31}P\{^1H\}$)[16]
(*p*-$CF_3C_6H_4)_2PCl$	30	2	>99	(*p*-$CF_3C_6H_4)_2PP$(*p*-$CF_3C_6H_4)_2$ (76 %); (*p*-$CF_3C_6H_4)_2PH$ (24 %)		
(3,5-$(CF_3)_2C_6H_4)_2PCl$	60	2	>99	(3,5-$(CF_3)_2C_6H_4)_2PP$(3,5-$(CF_3)_2C_6H_4)_2$ (21%); (3,5-$(CF_3)_2C_6H_4)_2PH$ (79%)	-12.9 (s), -41.5 (d, $^1J_{PH}$ = 227 Hz)	-12.6 (THF-d8)[19], -40.4 (d, $^1J_{PH}$ = 229 Hz, $CDCl_3$)[13]
(3,5-$(CF_3)_2C_6H_4)_2PCl$	30	2	>99	(3,5-$(CF_3)_2C_6H_4)_2PP$(3,5-$(CF_3)_2C_6H_4)_2$ (23%); (3,5-$(CF_3)_2C_6H_4)_2PH$ (77%)	-14.5 (s), -41.3 (d, $^1J_{PH}$ = 222 Hz)	-13.2 (C_6D_6)[15]; -42.7 ($^{31}P\{^1H\}$)[16]
$PhPCl_2$	30	2	>99	Ph_5P_5 (83%) Ph_4P_4 (15%) Ph_6P_6 (2%)	Ph_5P_5 -4 (m) Ph_4P_4 -48.8; Ph_6P_6 -22.4	Ph_5P_5 -3 (m);[18] Ph_4P_4 -48 (CH_2Cl_2)[18]; Ph_6P_6 -21.2

	$(C_6D_6)^9$

Reaction conditions: 5 mol% $[Et_4N]Cl$, 1 equiv $PhSiH_3$, 0.15 M (R_2PCl) in oDFB/MeCN (2/1;V/V).[a] Values after 21 hours. [b] Values after 19 hours. [c] Values after 15 hours.

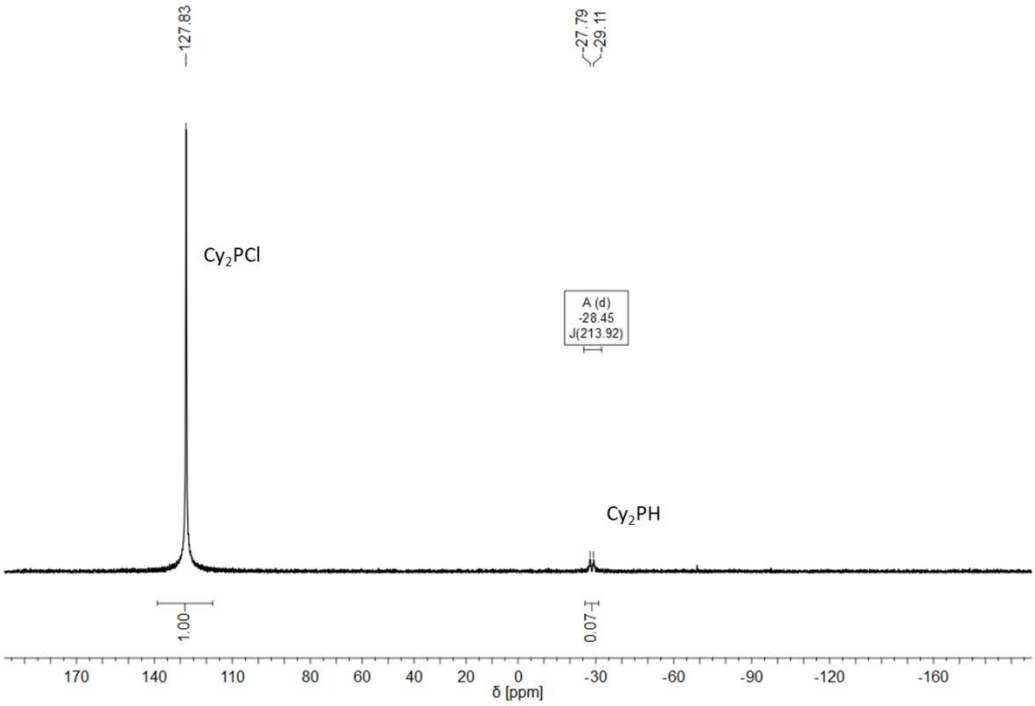

Figure S 60: ^{31}P NMR spectrum of $[Et_4N]Cl$ catalyzed reaction of Cy_2PCl with $PhSiH_3$ (60°C, *o*DFB/MeCN, after 13 hours).

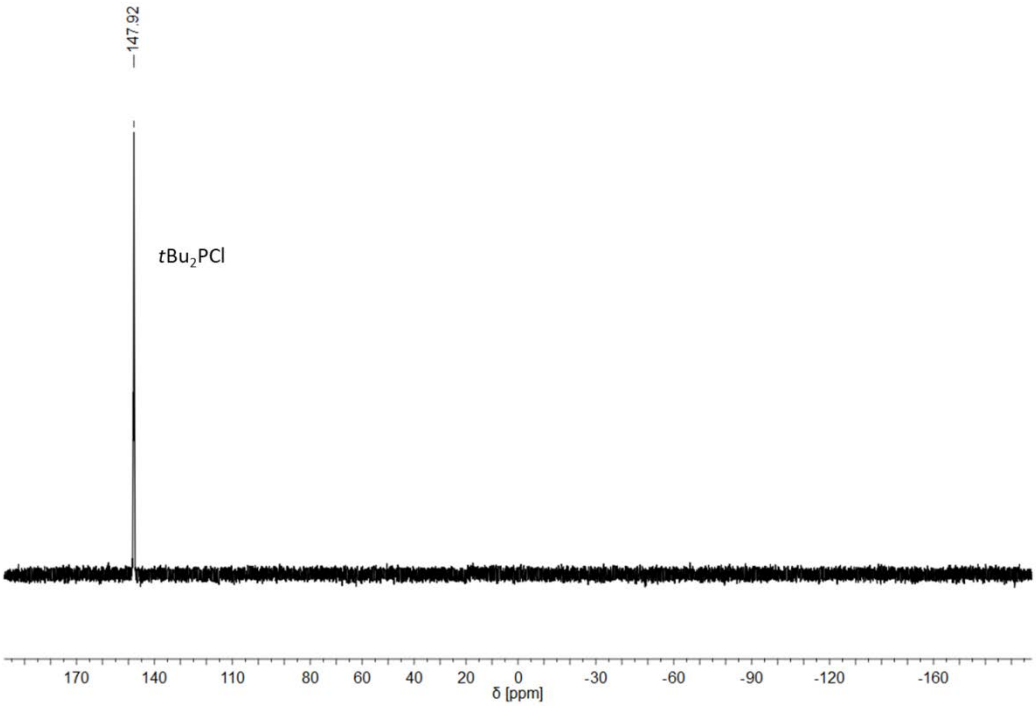

Figure S 61: ^{31}P NMR spectrum of $[Et_4N]Cl$ catalyzed reaction of *t*Bu_2PCl with $PhSiH_3$ (80°C, *o*DFB/MeCN, after 15 hours).

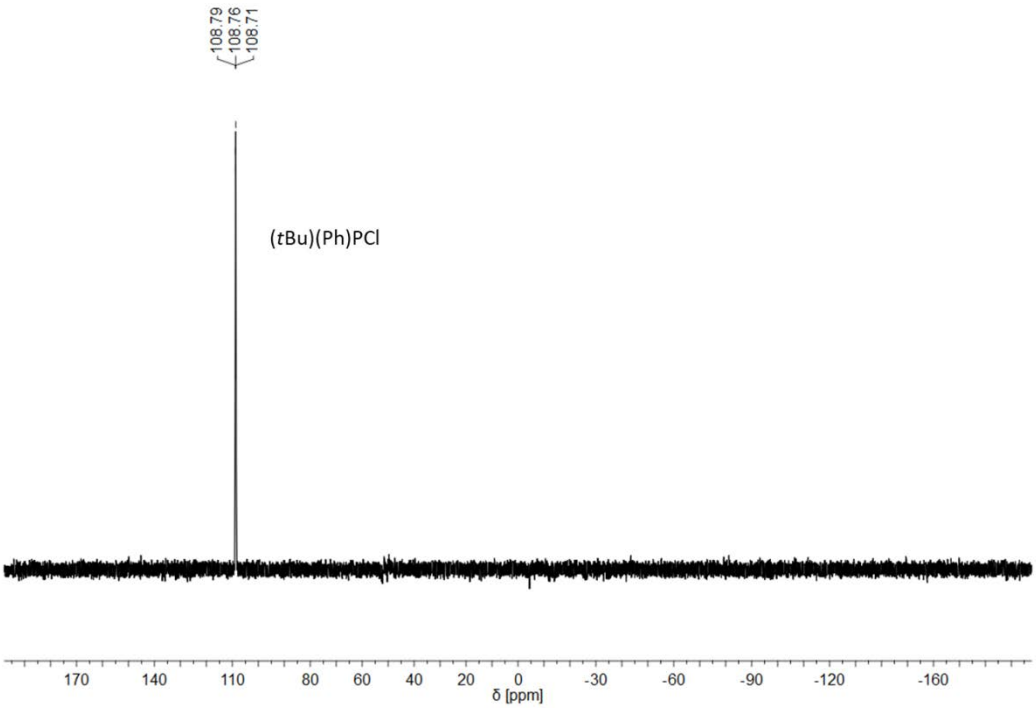

Figure S 62: ^{31}P NMR spectrum of [Et$_4$N]Cl catalyzed reaction of (Ph)(*t*Bu)PCl with PhSiH$_3$ (80°C, *o*DFB/MeCN, after 15 hours).

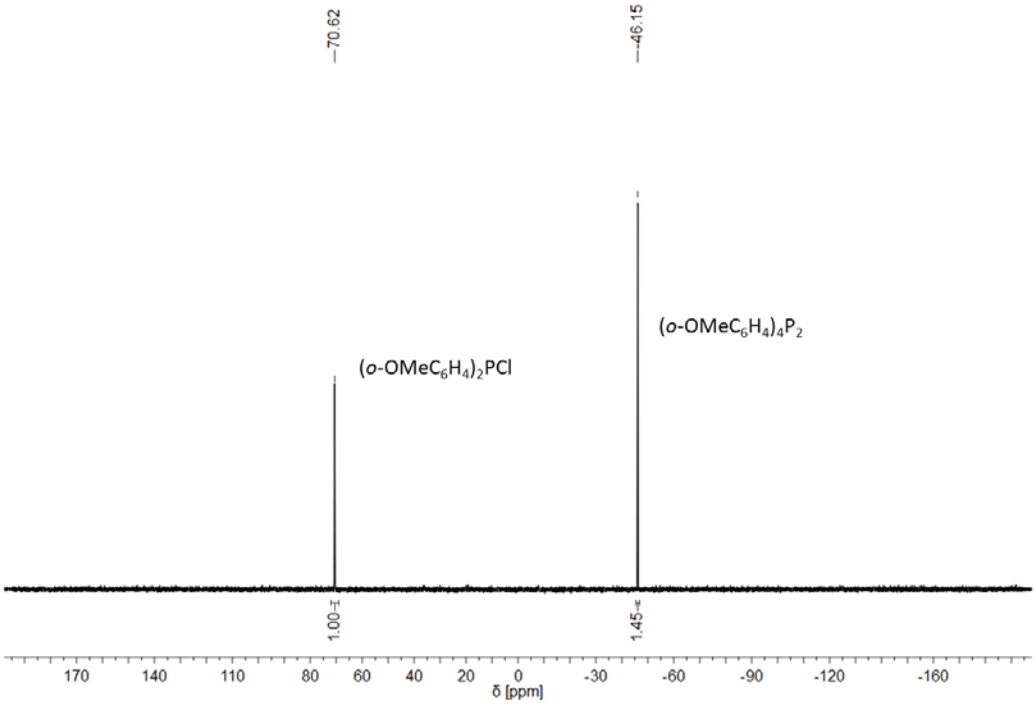

Figure S 63: ^{31}P NMR spectrum of [Et$_4$N]Cl catalyzed reaction of (*o*-OMeC$_6$H$_4$)$_2$PCl with PhSiH$_3$ (60°C, *o*DFB/MeCN, after 3 hours).

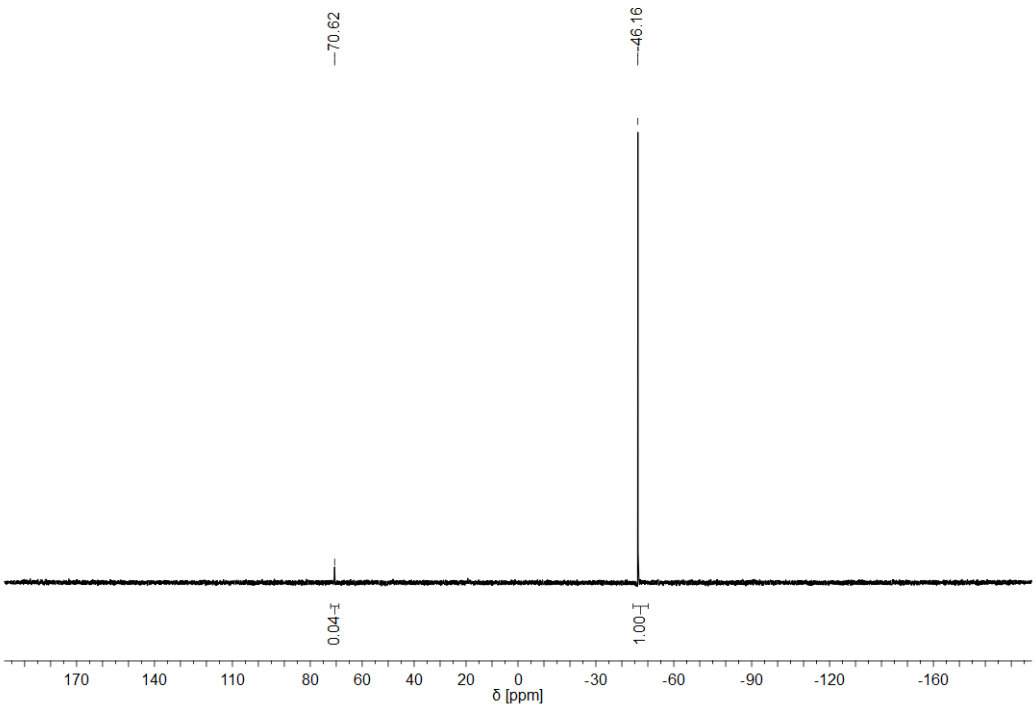

Figure S 64: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of (*o*-$OMeC_6H_4)_2PCl$ with $PhSiH_3$ (60°C, *o*DFB/MeCN, after 15 hours).

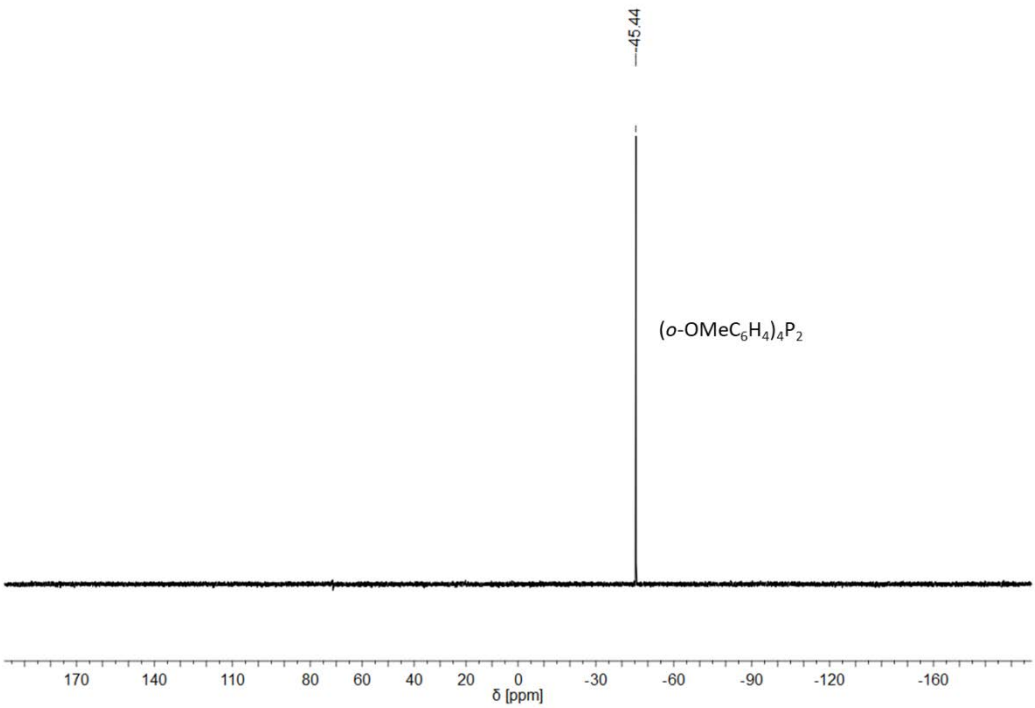

Figure S 65: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of (*o*-$OMeC_6H_4)_2PCl$ with $PhSiH_3$ (60°C, *o*DFB/MeCN, after 19 hours).

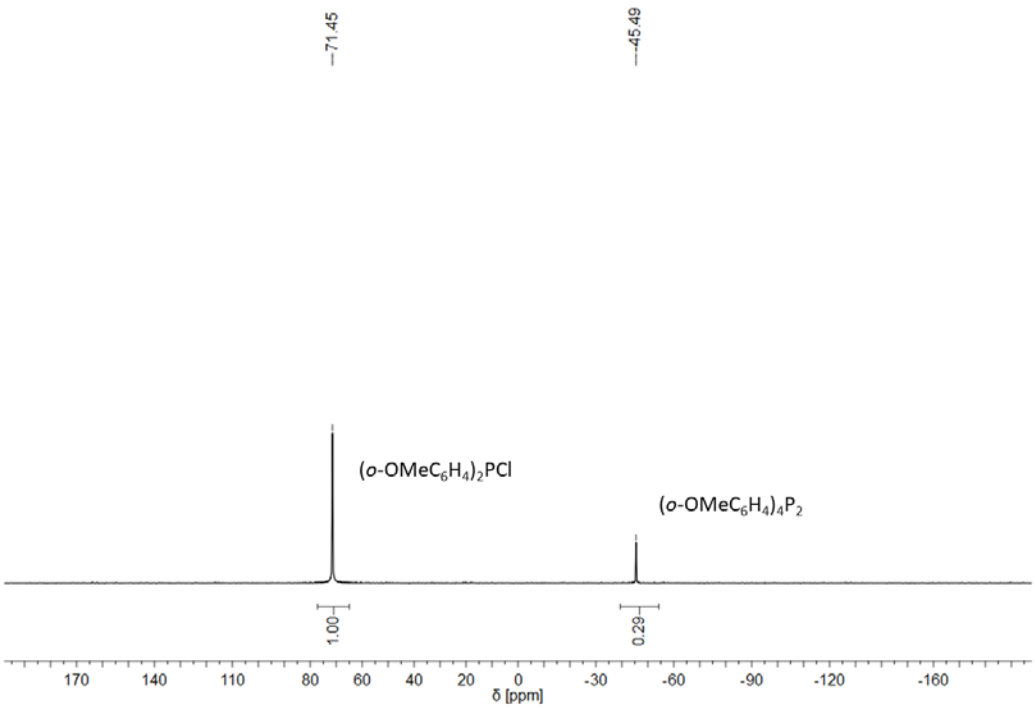

Figure S 66: ^{31}P NMR spectrum of [Et$_4$N]Cl catalyzed reaction of (*o*-OMeC$_6$H$_4$)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

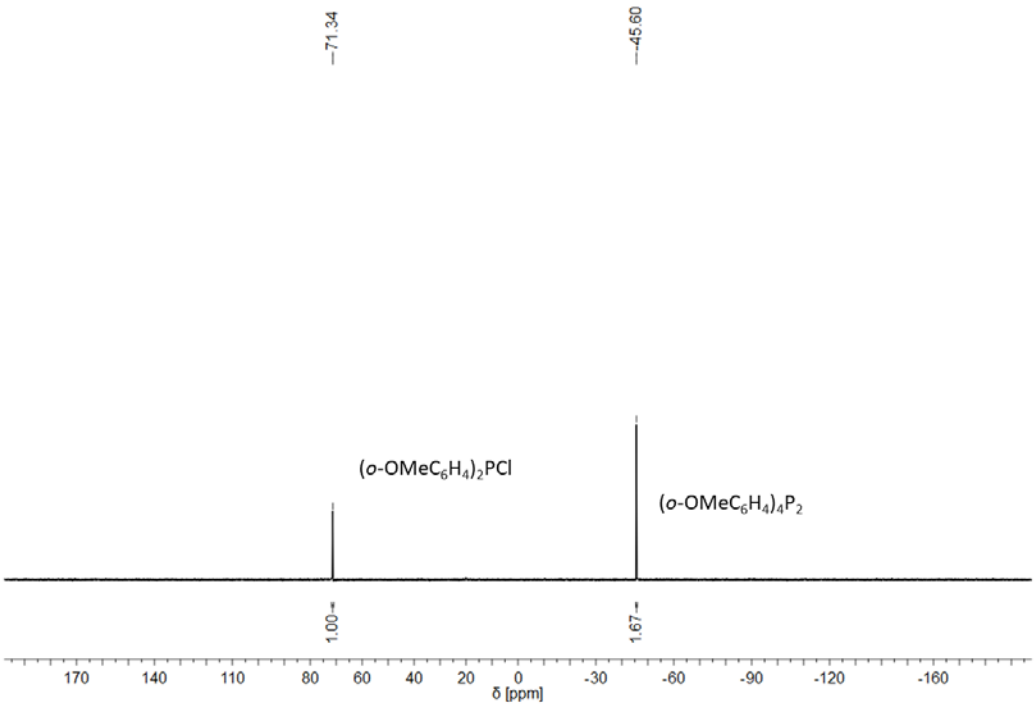

Figure S 67: ^{31}P NMR spectrum of [Et$_4$N]Cl catalyzed reaction of (*o*-OMeC$_6$H$_4$)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 21 hours).

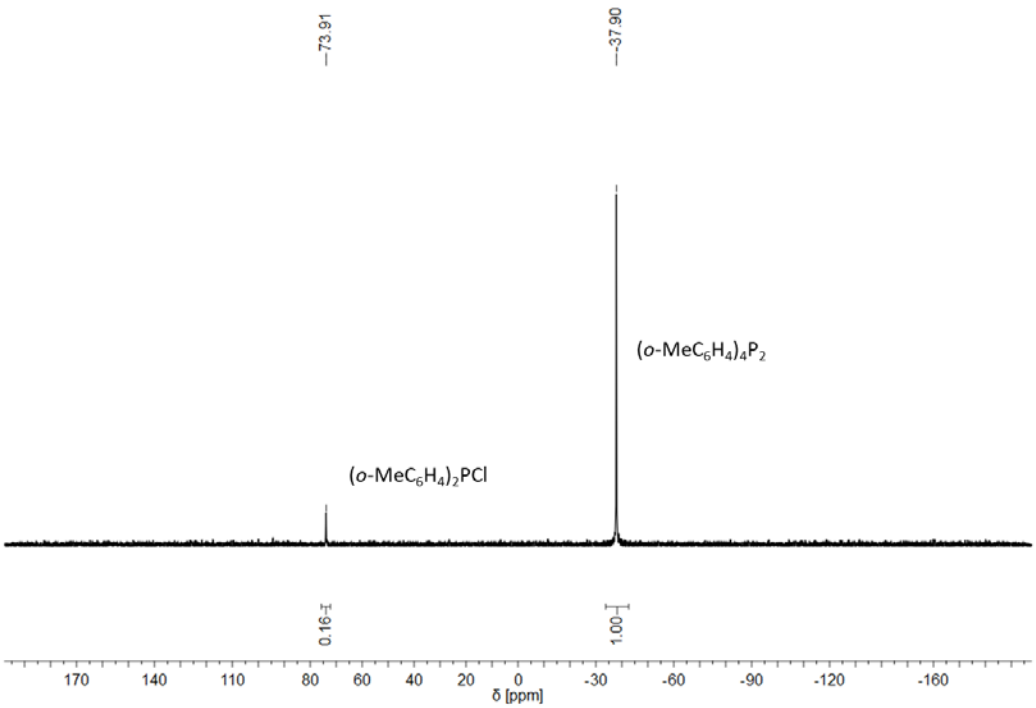

Figure S 68: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of (o-MeC_6H_4)$_2$PCl with $PhSiH_3$ (30°C, oDFB/MeCN, after 23 hours).

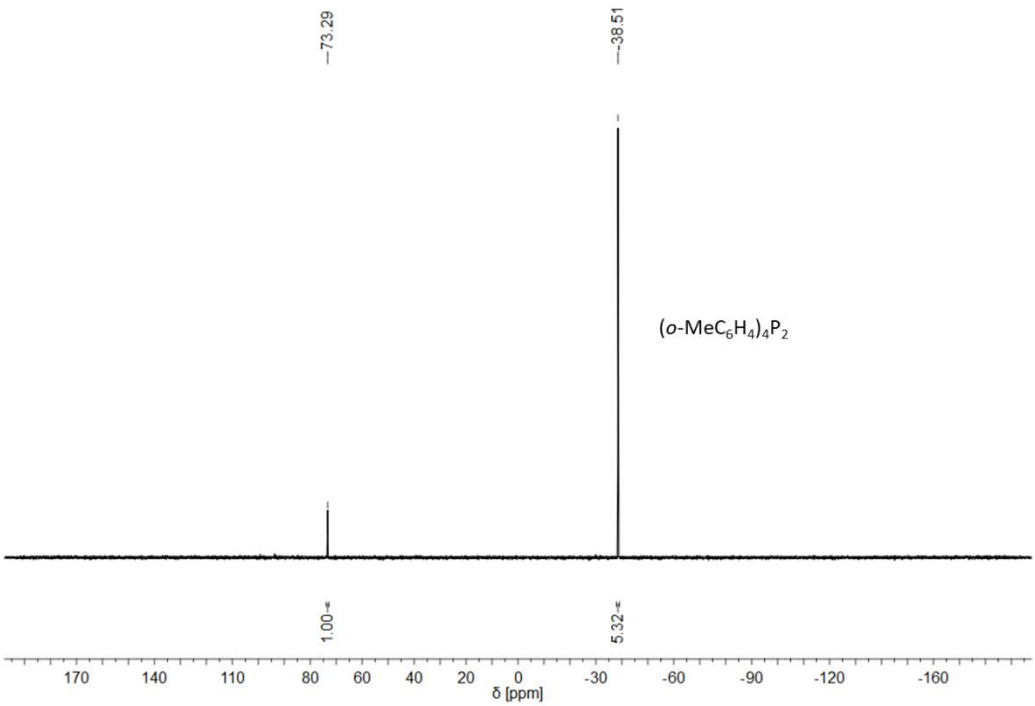

Figure S 69: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of (o-MeC_6H_4)$_2$PCl with $PhSiH_3$ (60°C, oDFB/MeCN, after 3 hours).

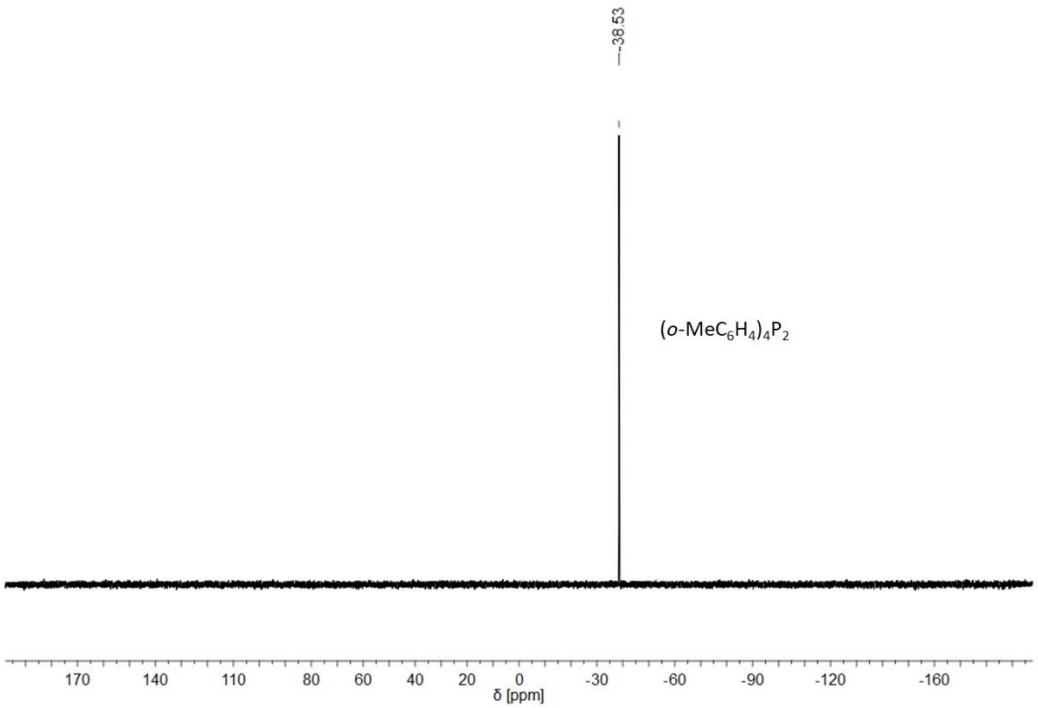

Figure S 70: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of (o-MeC_6H_4)$_2$PCl with $PhSiH_3$ (60°C, oDFB/MeCN, after 15 hours).

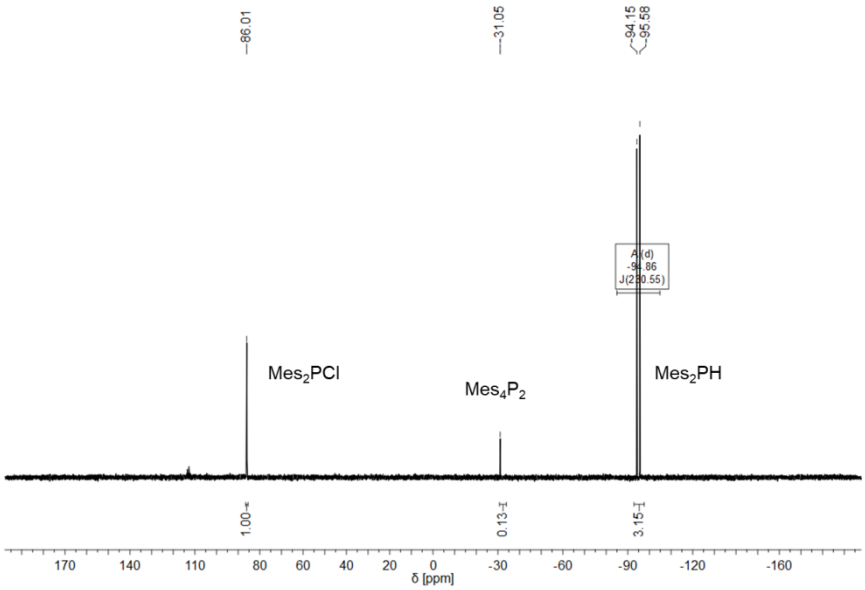

Figure S 71: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of $(Mes)_2PCl$ with PhSiH3 (60°C, oDFB/MeCN, after 15 hours).

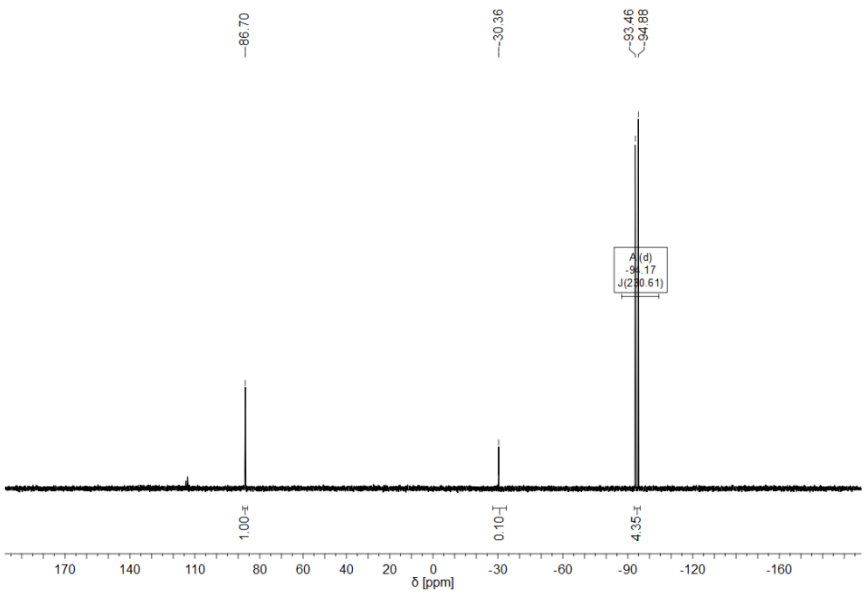

Figure S 72: ^{31}P NMR spectrum of $[Et_4N]Cl$ catalyzed reaction of $(Mes)_2PCl$ with $PhSiH_3$ (60°C, *o*DFB/MeCN, after 18 hours).

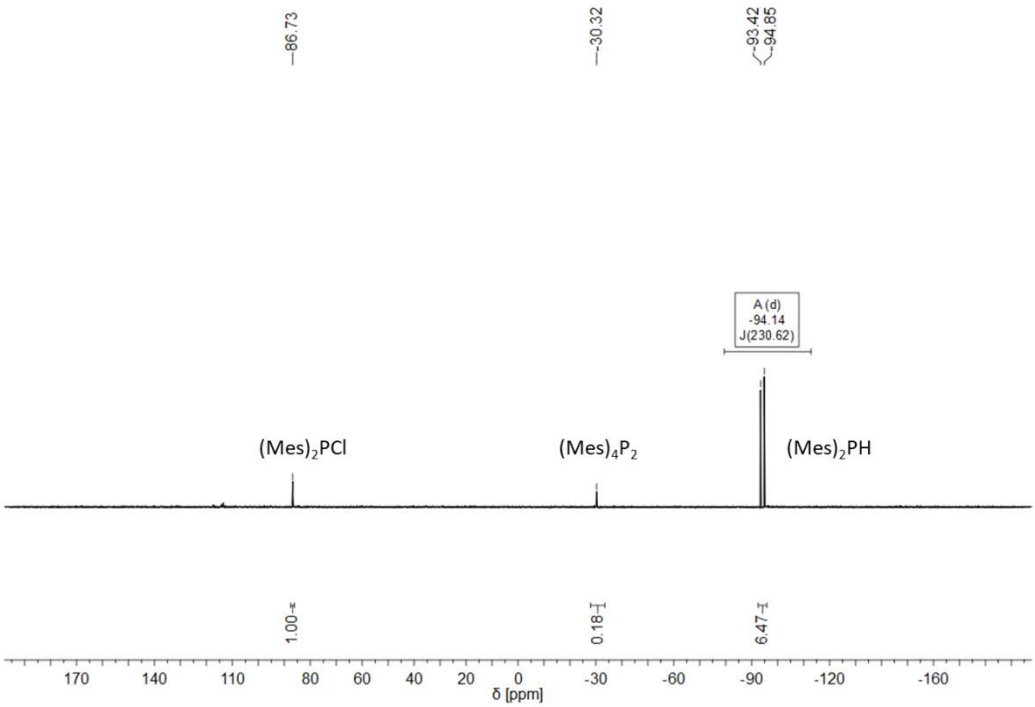

Figure S 73: ^{31}P NMR spectrum of $[Et_4N]Cl$ catalyzed reaction of $(Mes)_2PCl$ with $PhSiH_3$ (60°C, *o*DFB/MeCN, after 23 hours).

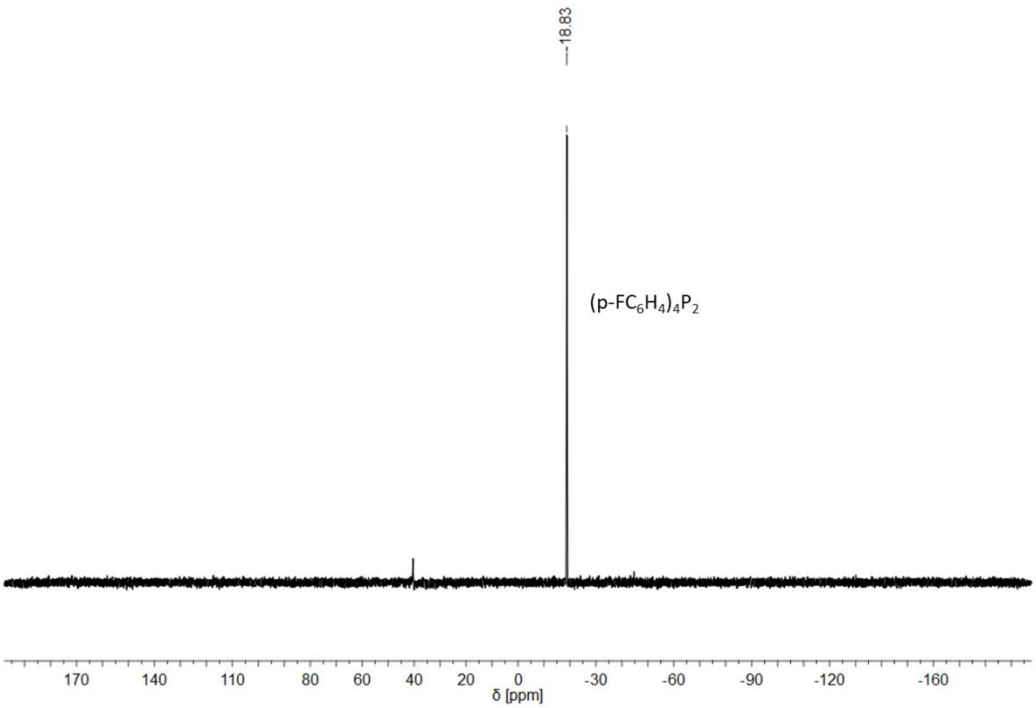

Figure S 74: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of (*p*-FC_6H_4)$_2$PCl with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 2 hours).

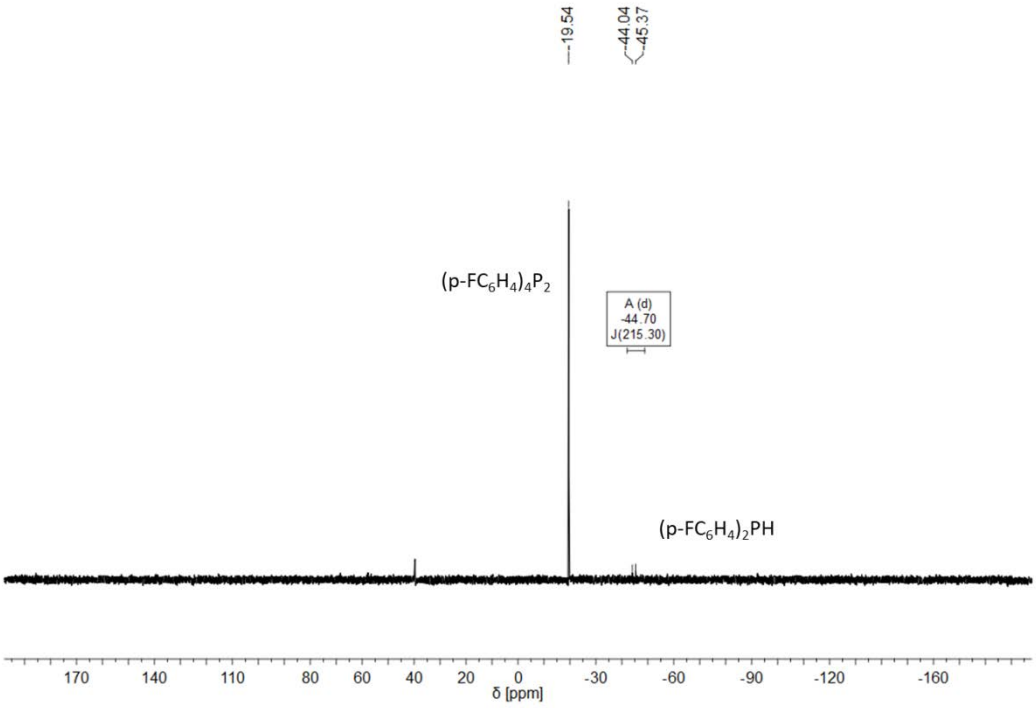

Figure S 75: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of (*p*-FC_6H_4)$_2$PCl with $PhSiH_3$ (60°C, *o*DFB/MeCN, after 3 hours).

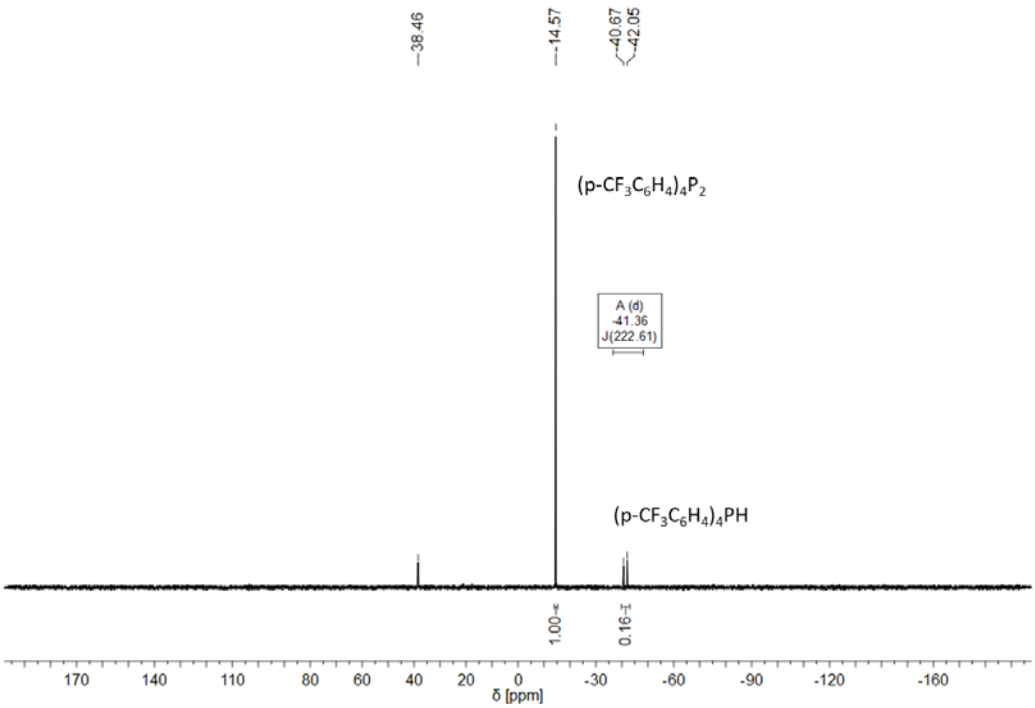

Figure S 76: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of (*p*-$CF_3C_6H_4)_2PCl$ with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 2 hours).

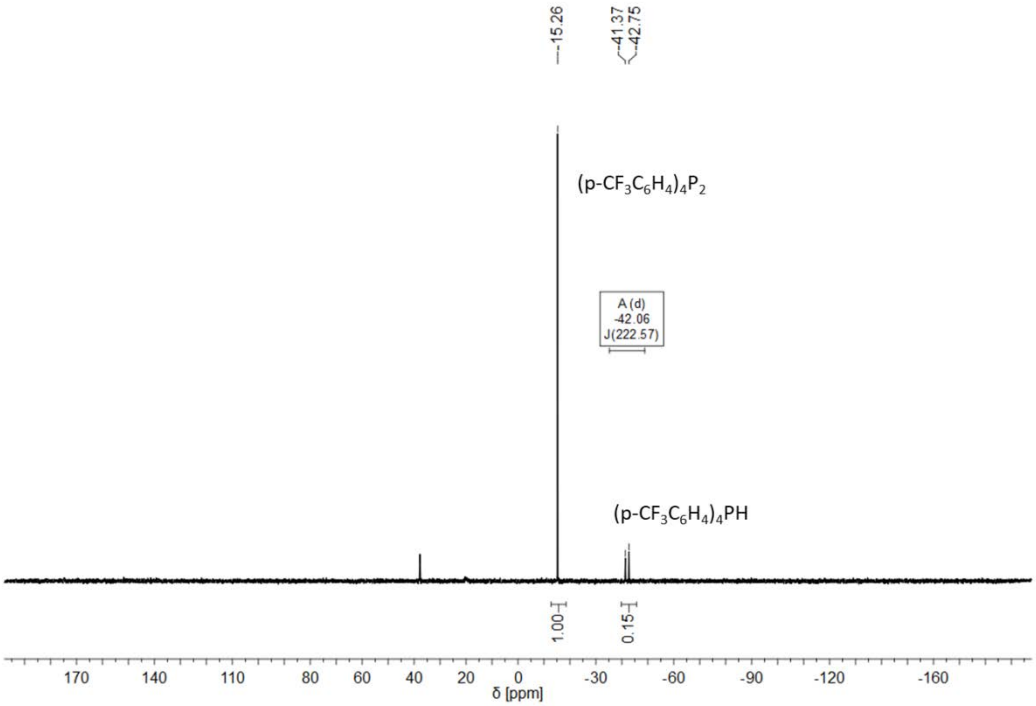

Figure S 77: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of (*p*-$CF_3C_6H_4)_2PCl$ with $PhSiH_3$ (60°C, *o*DFB/MeCN, after 3 hours).

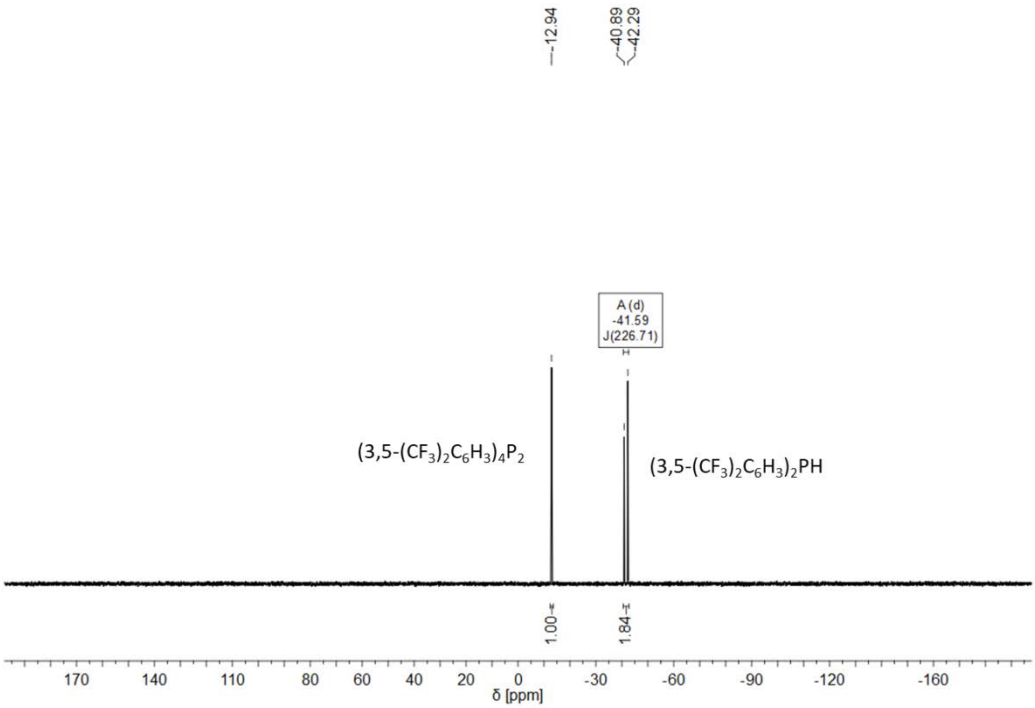

Figure S 78: ^{31}P NMR spectrum of [Et$_4$N]Cl catalyzed reaction of (3,5-(CF$_3$)$_2$C$_6$H$_3$)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

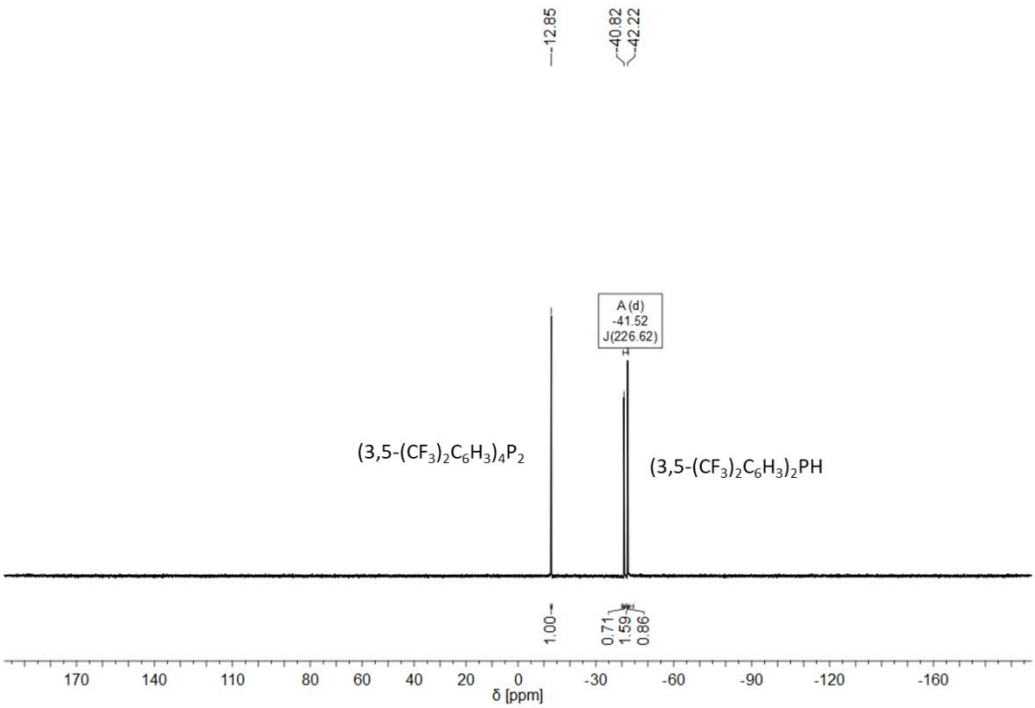

Figure S 79: ^{31}P NMR spectrum of [Et$_4$N]Cl catalyzed reaction of (3,5-(CF$_3$)$_2$C$_6$H$_3$)$_2$PCl with PhSiH$_3$ (60°C, *o*DFB/MeCN, after 2 hours).

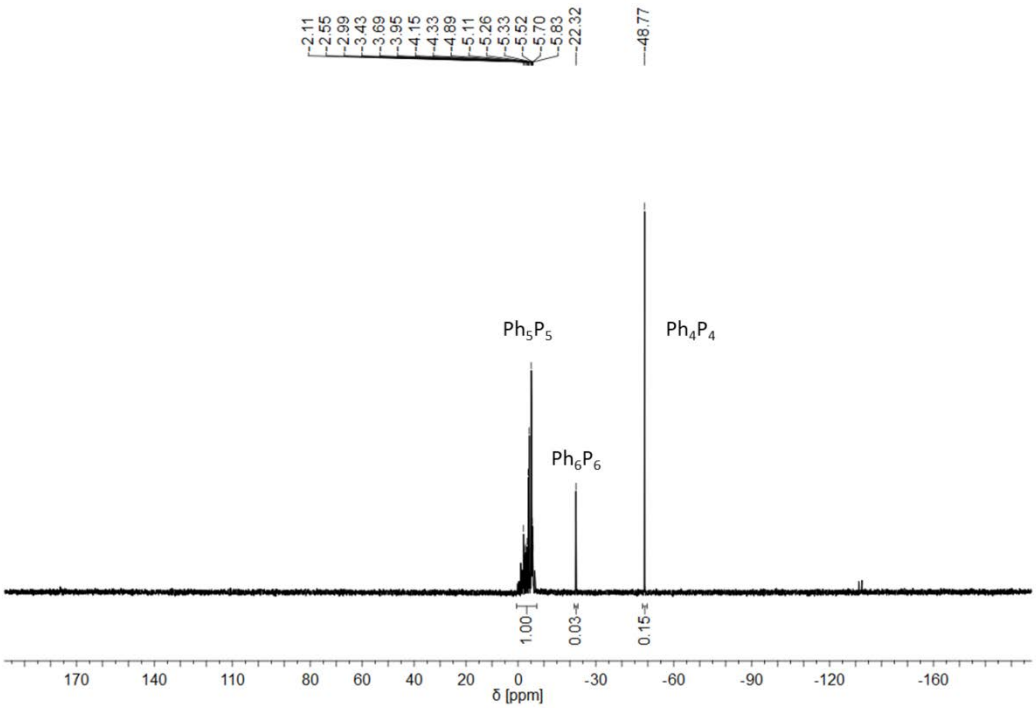

Figure S 80: ^{31}P NMR spectrum of [Et_4N]Cl catalyzed reaction of $PhPCl_2$ with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 2 hours).

2.3 Two-component catalysis with 9-BBN and [Et_4N]Cl

General procedure: R_2PCl (0.09 mmol, 1 equiv), silane (1 equiv), [Et_4N]Cl (0.7 mg, 0.0045 mmol, 0.05 equiv) and 9-BBN (0.5 mg, 0.0045 mmol, 0.05 equiv) were dissolved in a mixture of *o*DFB/MeCN (0.6 ml, 2/1; V/V) and heated to the indicated temperature. The reaction progress was monitored by ^{31}P NMR spectroscopy.

Table S 7: Synthesis of R_4P_2 and R_2PH from R_2PCl with [Et_4N]Cl /9-BBN and $PhSiH_3$.

R_2PCl	T [°C]	t [h]	conv. [%]	product
Ph_2PCl	30	2	>99	PP (89 %) PH (11 %)
iPr_2PCl	30	2	0	-
	60	2	>99	PP (2 %) PH (98 %)
tBu_2PCl	80	5 d	97	PH (>99 %)
*t*BuPhPCl	30	72	98	PP (89 %) PH (11 %)
*t*BuPhPCl	60	8	>99	PP (78 %) PH (22 %)
(*o*-$OMeC_6H_4)_2PCl$	30	2	>99	PP (>99) PH (-)
(o-$MeC_6H_4)_2PCl$	30	2	>99	PP (89 %) PH (11 %)
(2,4,6-$Me_3C_6H_2)_2PCl$	30	2	>99	PP (<1%) PH (>99%)
(*p*-$FC_6H_4)_2PCl$	30	2	>99	PP (85 %) PH (15 %)
(*p*-$CF_3C_6H_4)_2PCl$	30	2	99	PP (66 %) PH (33 %)

(3,5-$(CF_3)_2C_6H_3)_2PCl$	30	2	>99	PP (17 %) PH (83 %)
(*o*-$NMe_2C_6H_4)_2PCl$	30	4	>99	PP (98%), PH (2%)
(*p*-Cl-$C_6H_4)_2PCl$	30	2	>99	PP (55%) ($\delta(^{31}P)$ = -18.1 ppm; lit[20]: $\delta(^{31}P, CD_2Cl_2)$ = -17.7 ppm (d, $^1J_{PH}$ = 219 Hz), PH (45%) ($\delta(^{31}P)$ = -43.4 ppm (d, $^1J_{PH}$ = 214 Hz); lit[13]: $\delta(^{31}P, THF\text{-}d8)$ = -45.6 ppm (d, $^1J_{PH}$ = 219 Hz)
(*m*-Me-C6H4)2PCl	30	2	>99	PP (98%), PH (2%) ($\delta(^{31}P)$ = -39.7 ppm (d, $^1J_{PH}$ = 215 Hz); lit[21]: $\delta(^{31}P, C_6D_6)$ = -40.3 ppm (d, $^1J_{PH}$ = 215 Hz)
(2,4,6-$(CF_3)_2C_6H_2)PCl_2$	30	4	>99	(2,4,6-$(CF_3)_2C_6H_2)PH_2$ (99 %) ($\delta(^{31}P\{^1H\})$ = -139.4 ppm (sept, $^4J_{PF}$ = 29 Hz); lit[5]: $\delta(^{31}P\{^1H\}, C_6D_6)$ = -139.1 ppm (sept q, $^4J_{PF}$ = 29 ; $^6J_{PF}$ = 2.3 Hz))
$PhPCl_2$[a]	30	2	>99	PP (>99) Ph_5P_5 (64 %) Ph_4P_4 (35 %) Ph_6P_6 (1 %)

Reaction conditions: 5 mol% $[Et_4N]Cl$ and 9-BBN, 1 equiv $PhSiH_3$, 0.15 M (R_2PCl) in *o*DFB/MeCN (2/1;V/V). [a] 2 equiv of $PhSiH_3$ were used.

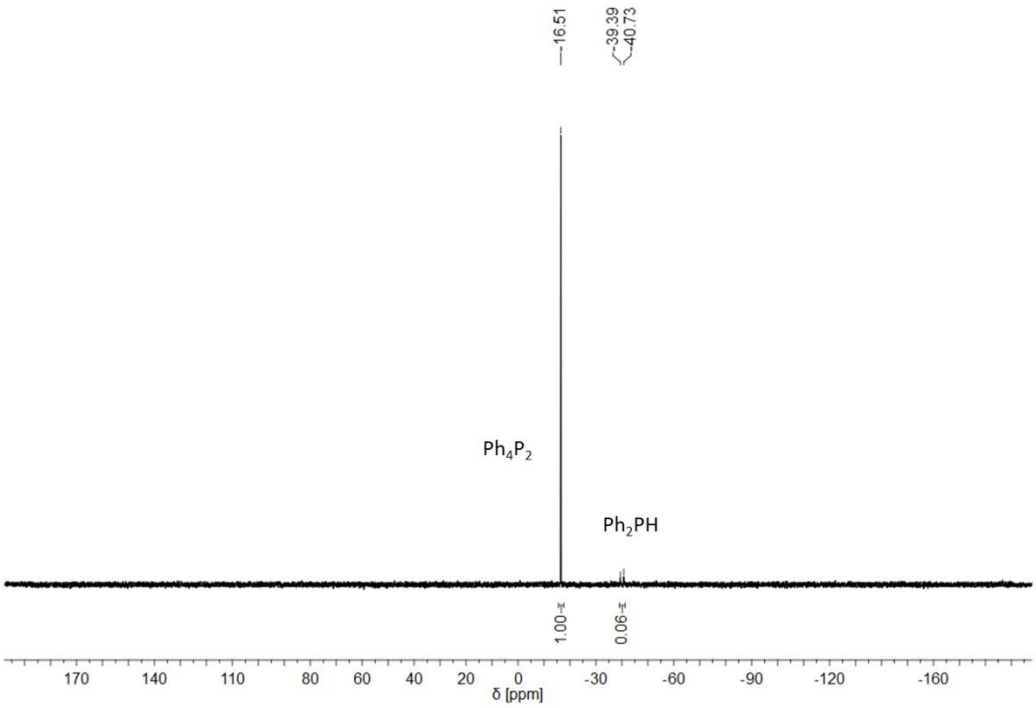

Figure S 81: ^{31}P NMR spectrum of $[Et_4N]Cl$ /9-BBN catalyzed reaction of Ph_2PCl with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 2 hours).

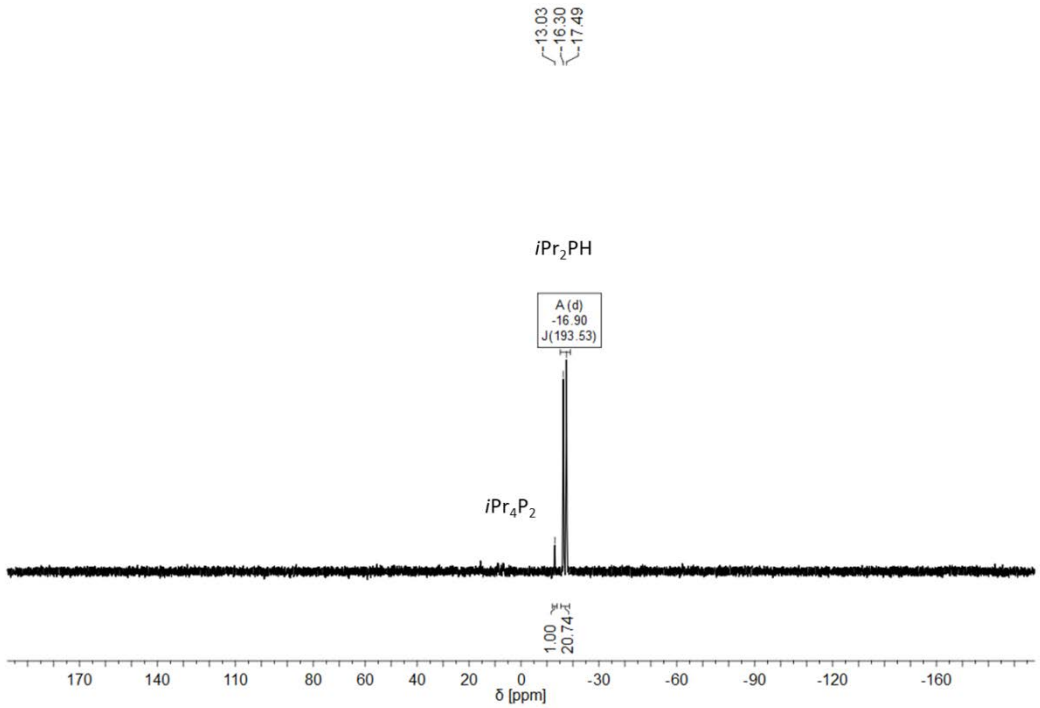

Figure S 82: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of *i*Pr$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

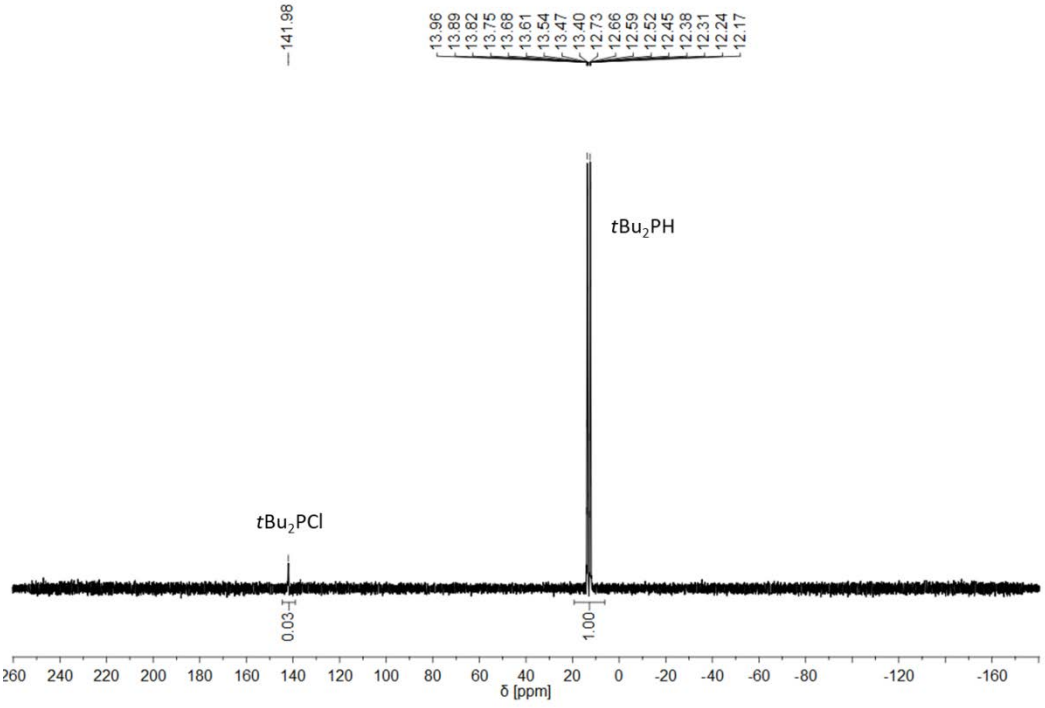

Figure S 83: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of *t*Bu$_2$PCl with PhSiH$_3$ (80°C, *o*DFB/MeCN, after 5 days).

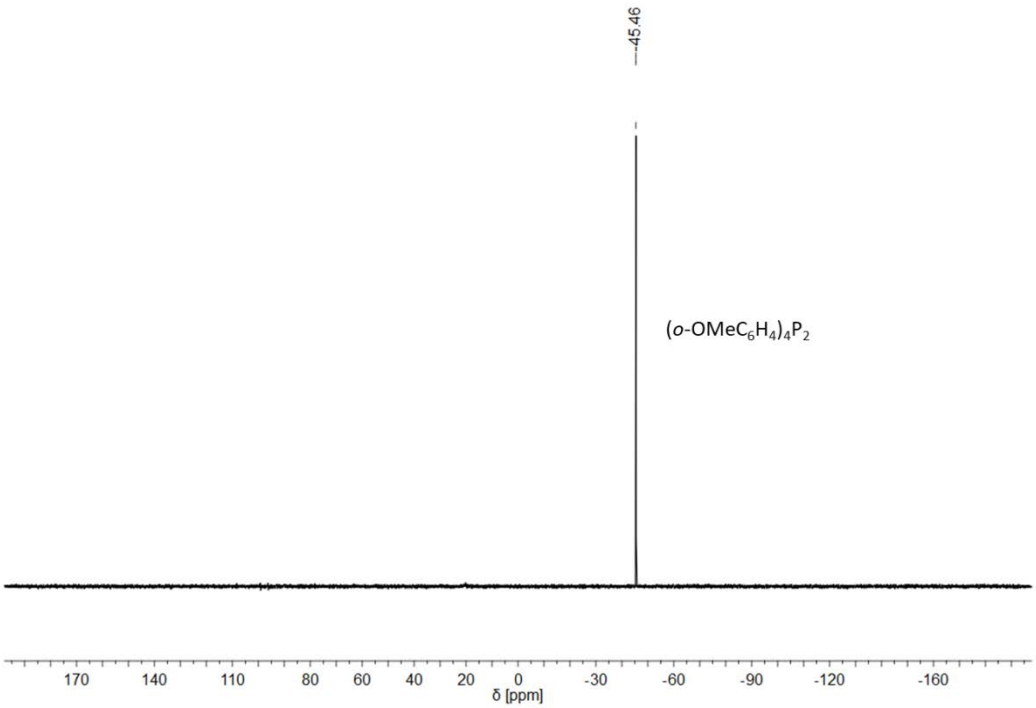

Figure S 84: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (*o*-OMeC$_6$H$_4$)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

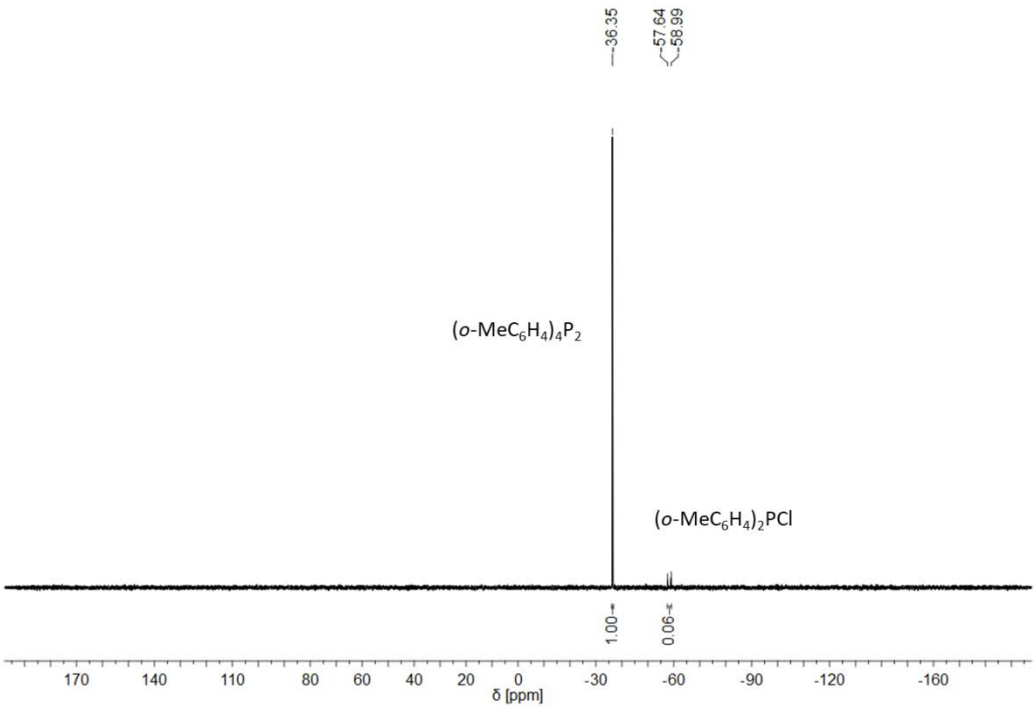

Figure S 85: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (*o*-MeC$_6$H$_4$)$_2$PCl with PhSiH$_3$ (30°C, reaction run in *o*DFB/MeCN, NMR measured in C$_6$D$_6$, after 2 hours).

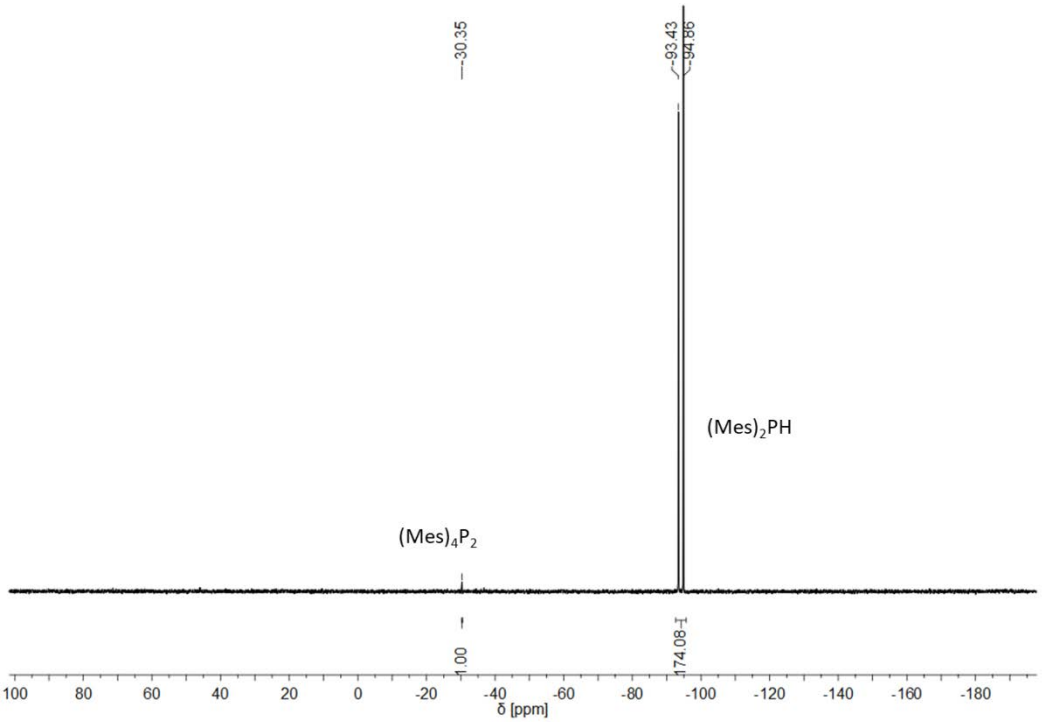

Figure S 86: ^{31}P NMR spectrum of [Et$_4$N]Cl 9-BBN catalyzed reaction of (Mes)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

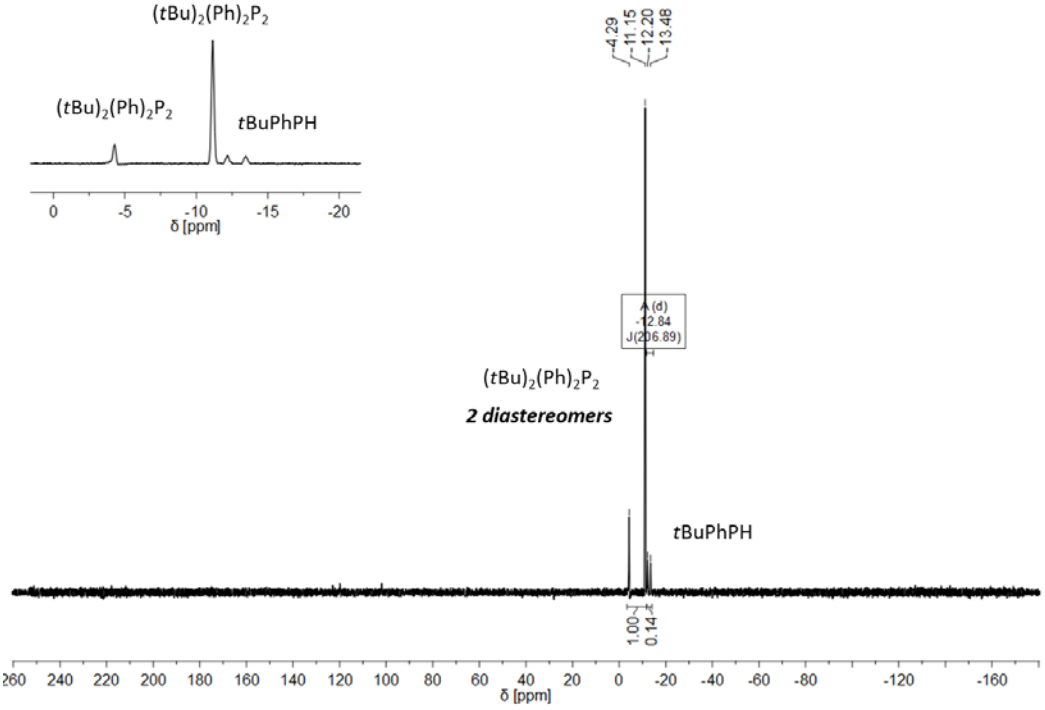

Figure S 87: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (*t*Bu)(Ph)PCl with PhSiH$_3$ (60°C, *o*DFB/MeCN, after 8 hours).

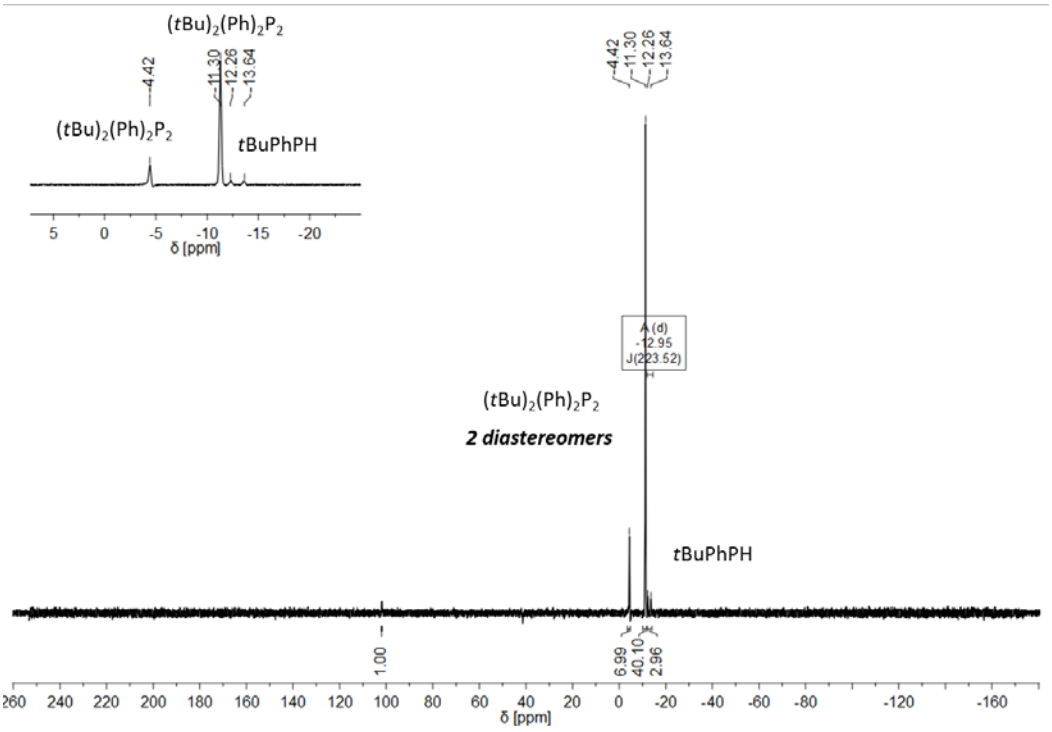

Figure S 88: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (*t*Bu)(Ph)PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 72 hours).

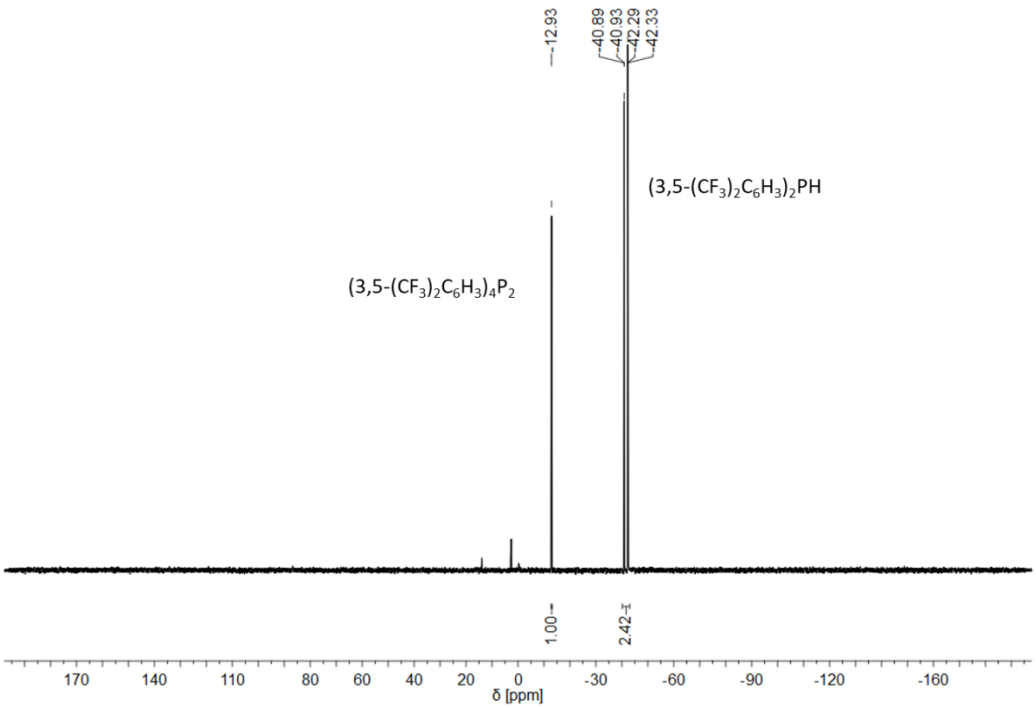

Figure S 89: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (3,5-(CF$_3$)$_2$C$_6$H$_3$)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

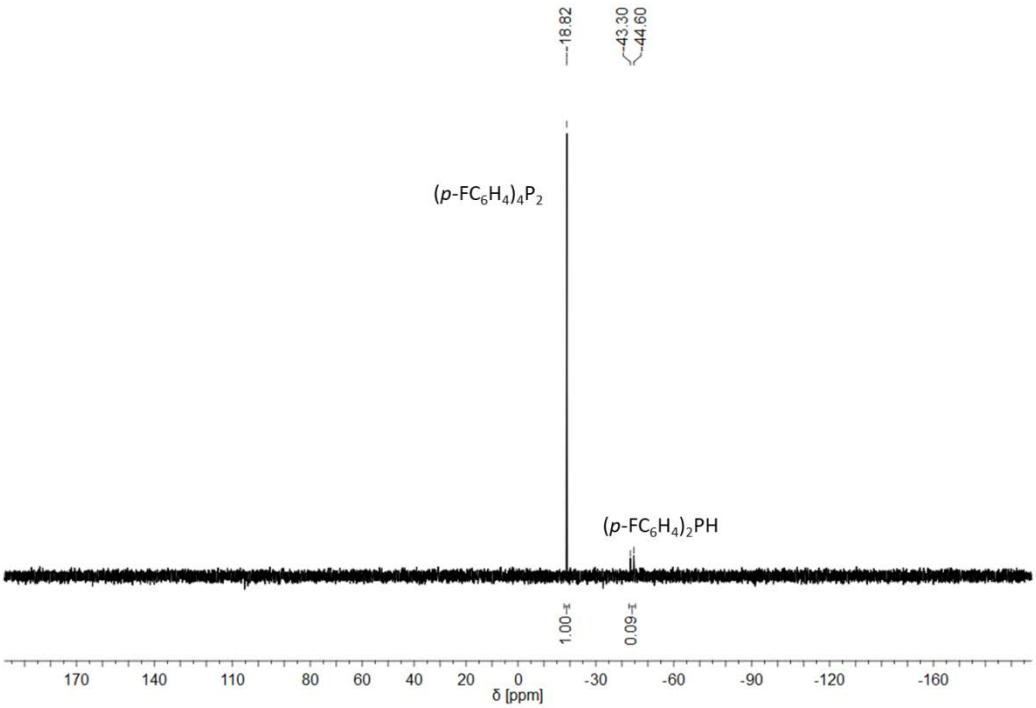

Figure S 90: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (*p*-FC$_6$H$_4$)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

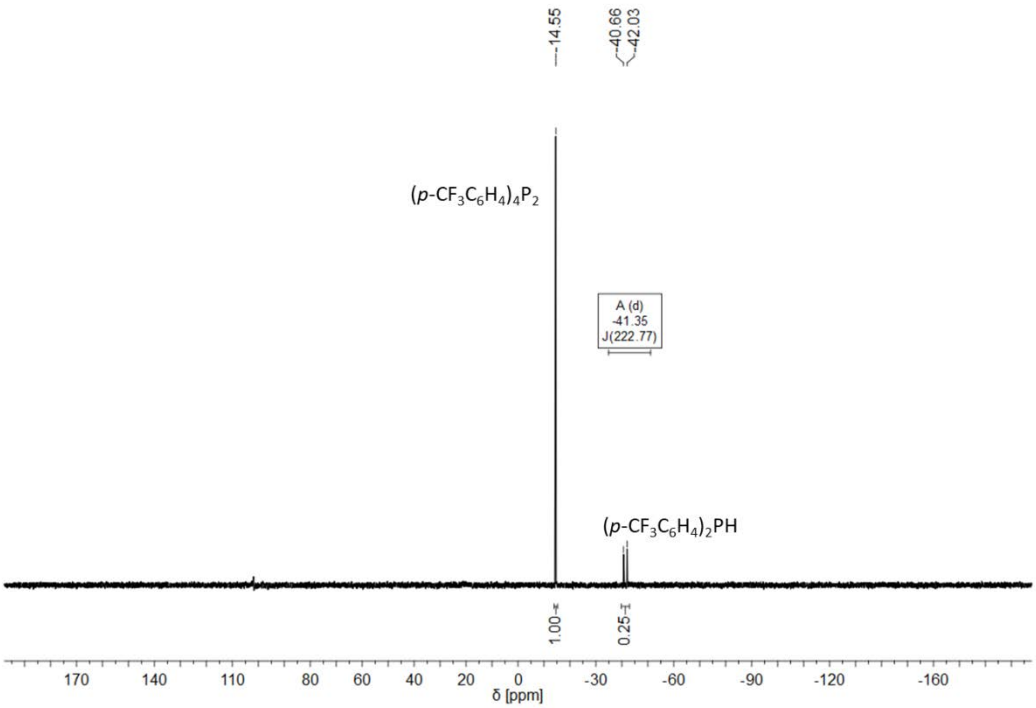

Figure S 91: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (*p*-CF$_3$C$_6$H$_4$)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

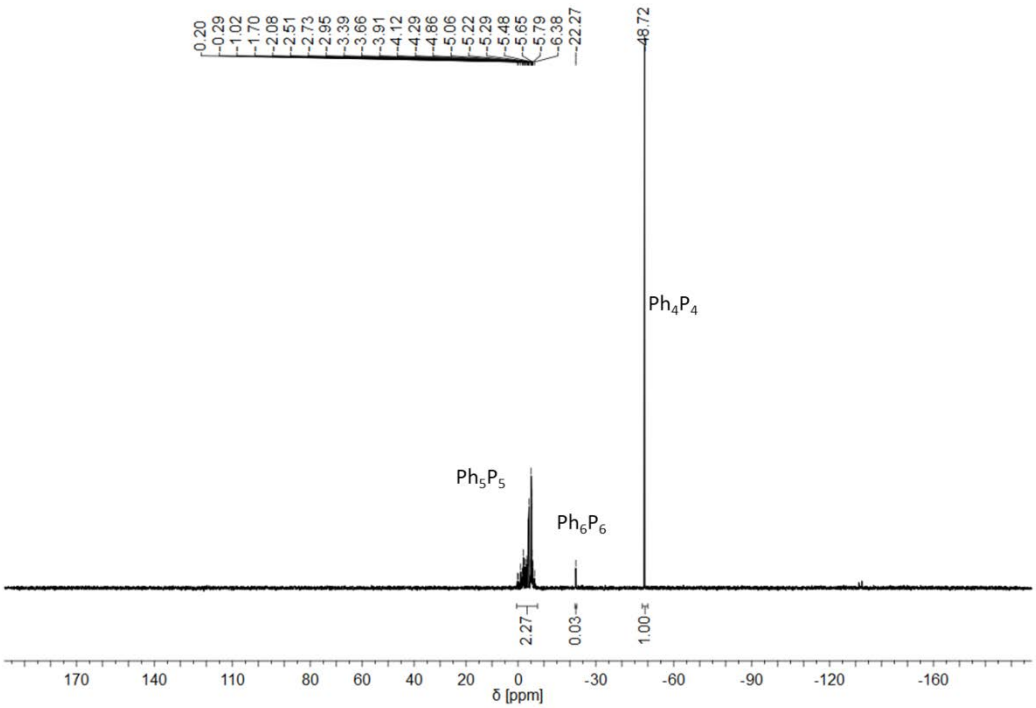

Figure S 92: ^{31}P NMR spectrum of [Et_4N]Cl /9-BBN catalyzed reaction of $PhPCl_2$ with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 2 hours).

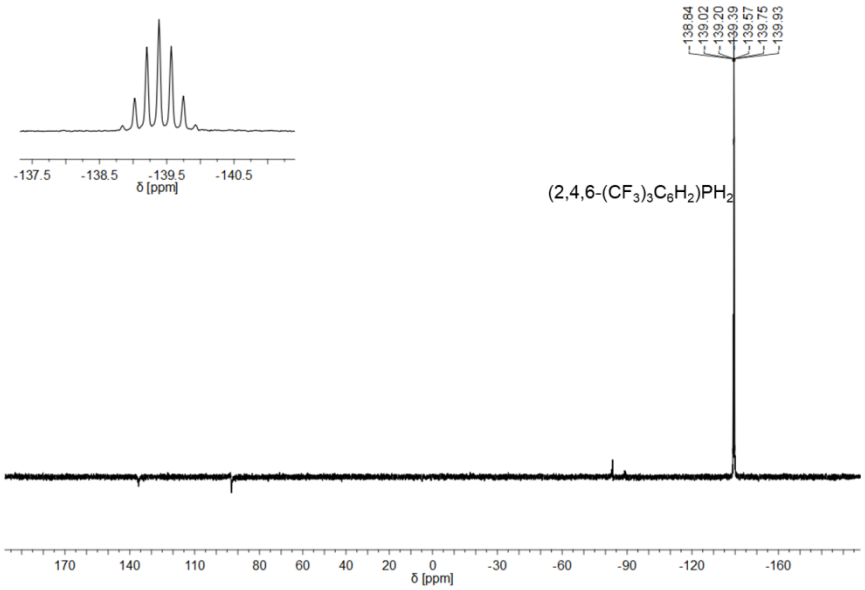

Figure S 93: $^{31}P\{^1H\}$ NMR spectrum of [Et_4N]Cl /9-BBN catalyzed reaction of $(2,4,6\text{-}(CF_3)_3C_6H_4)PCl_2$ with $PhSiH_3$ (30°C, *o*DFB/MeCN, after 4 hours).

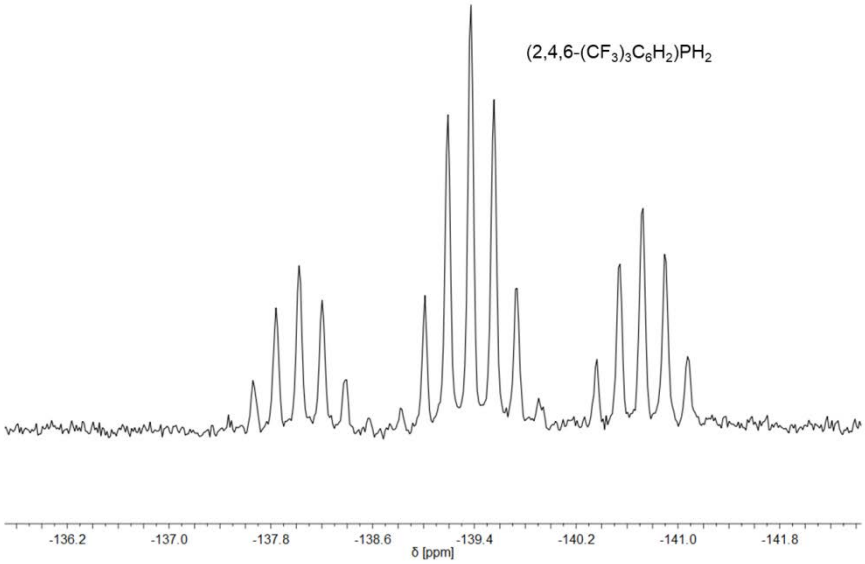

Figure S 94: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (2,4,6-(CF$_3$)$_3$C$_6$H$_4$)PCl$_2$ with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 4 hours).

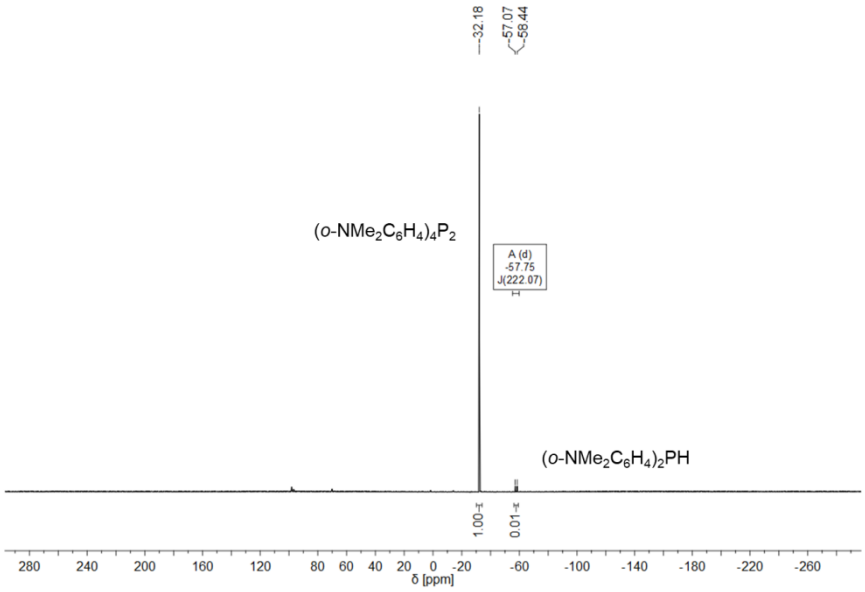

Figure S 95: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (*o*-NMe$_2$C$_6$H$_4$)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 4 hours).

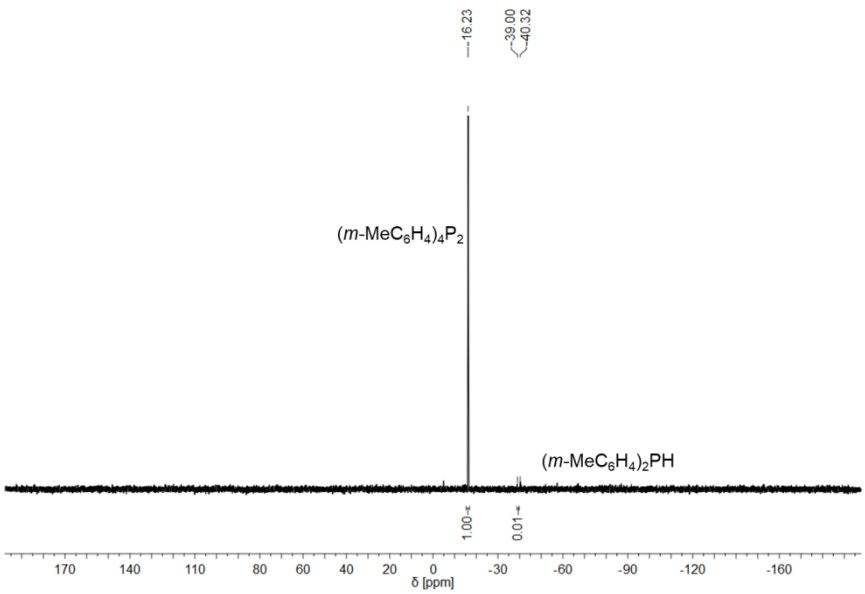

Figure S 96: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (*m*-MeC$_6$H$_4$)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

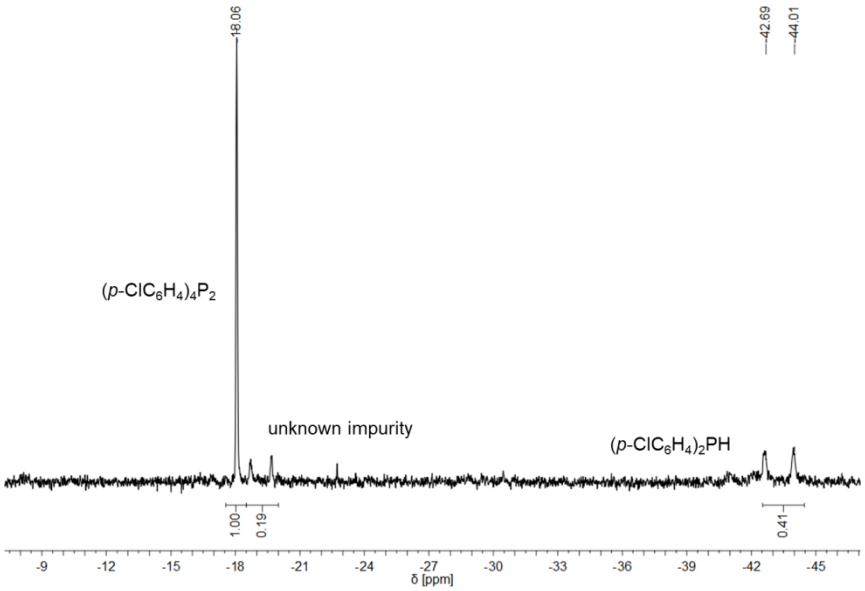

Figure S 97: ^{31}P NMR spectrum of [Et$_4$N]Cl /9-BBN catalyzed reaction of (*p*-ClC$_6$H$_4$)$_2$PCl with PhSiH$_3$ (30°C, *o*DFB/MeCN, after 2 hours).

3. Mechanistic investigations

To investigate the mechanism of PH and PP bond formation with 9-BBN several reactions were performed. Reaction of equimolar amounts of 9-BBN with Ph_2PCl/iPr_2PCl and regeneration of 9-BBN from Cl-9-BBN and $PhSiH_3$ were independently performed to demonstrate feasibility of the proposed catalytic cycle for formation of R_2PH from R_2PCl. The influence of [Et_4N][Cl] on regeneration of 9-BBN from Cl-9-BBN and $PhSiH_3$ was investigated. Furthermore dehydrogenative coupling of Ph_2PH by 9-BBN and Cl-9-BBN was investigated to probe the mechanism for PP bond formation. Reaction of Ph_2PCl with Ph_2PH was performed in different solvents to demonstrate that P_2Ph_4 can be formed under such circumstances.

3.1 Reaction of 9-BBN with Ph_2PCl

9-BBN (11 mg, 0.45 mmol, 1 equiv) and Ph_2PCl (19.9 mg, 0.45 mmol, 1 equiv) were dissolved in 1,2-dichloroethane (0.6 mL) and stirred at room temperature for 18 hours. The volatiles were removed and the resulting residue washed with *n*-pentane (2x2 mL). The resulting colourless solid was dried under vacuum to afford the Ph_2PCl Cl-9-BBN adduct in 94% yield (145 mg, 0.042 mmol). NMR data show broad signals, indicating a dynamic adduct. ^1H NMR ($CDCl_3$) δ = 7.82-7-76 (m, 4H, Ph_2PH), 7-56-7.52 (m, 2H, Ph_2PH), 7.49-7.44 (m, 4H, Ph_2PH), 6.66 (d, $^1J_{HP}$ = 358 Hz, 1H, PH), 1.99-1.87 (m, 6H, Cl-9-BBN), 1.77 (br s, Cl-9-BBN), 1.64-1.59 (m, 2H, Cl-9-BBN), 1.06 (br s, 2H, Cl-9-BBN) ppm. ^{31}P NMR ($CDCl_3$) δ = -18.9 (d, $^1J_{HP}$ = 358 Hz, 1H, PH) ppm. ^{11}B NMR ($CDCl_3$) δ = 4.8 (br s) ppm.^{13}C NMR ($CDCl_3$) δ = 134.3 (d, J_{CP} = 8.2 Hz), 132.0 (d, J_{CP} = 2.5 Hz), 129.3 (d, J_{CP} = 10 Hz), 122.7 (d, J_{CP} = 54.8 Hz), 31.4 (br s), 24.6-24.7 (br s), 24.8 ppm.

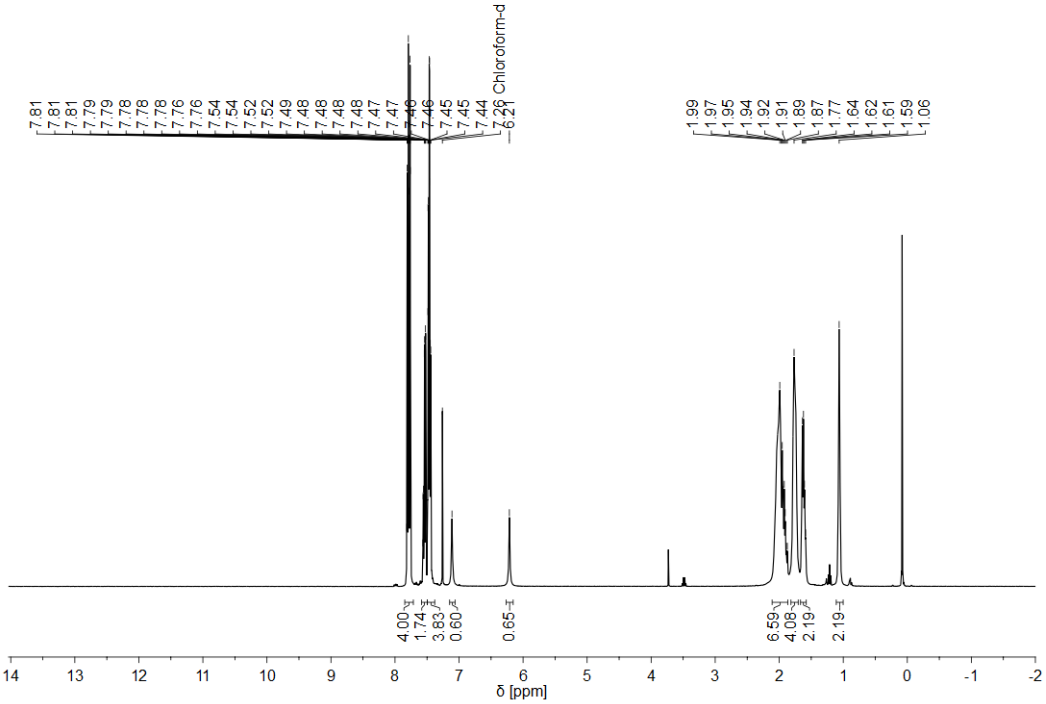

Figure S 98: ^1H NMR spectrum of dynamic adduct of Ph_2PH and Cl-9-BBN ($CDCl_3$).

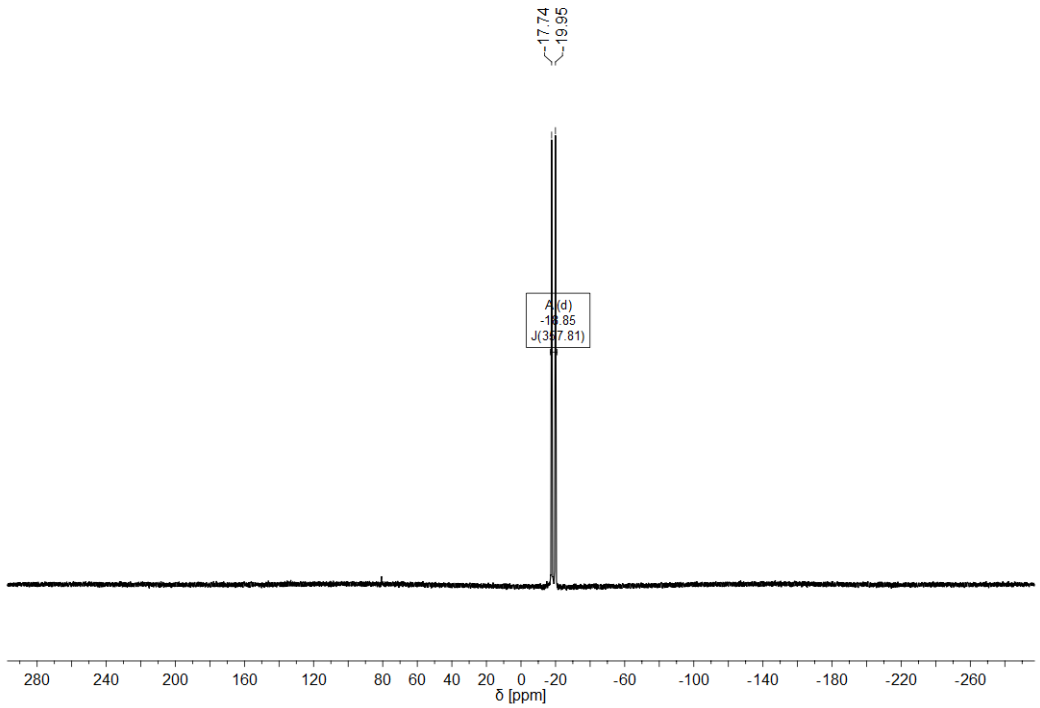

Figure S 99: ^{31}P NMR spectrum of dynamic adduct of Ph_2PH and Cl-9-BBN ($CDCl_3$).

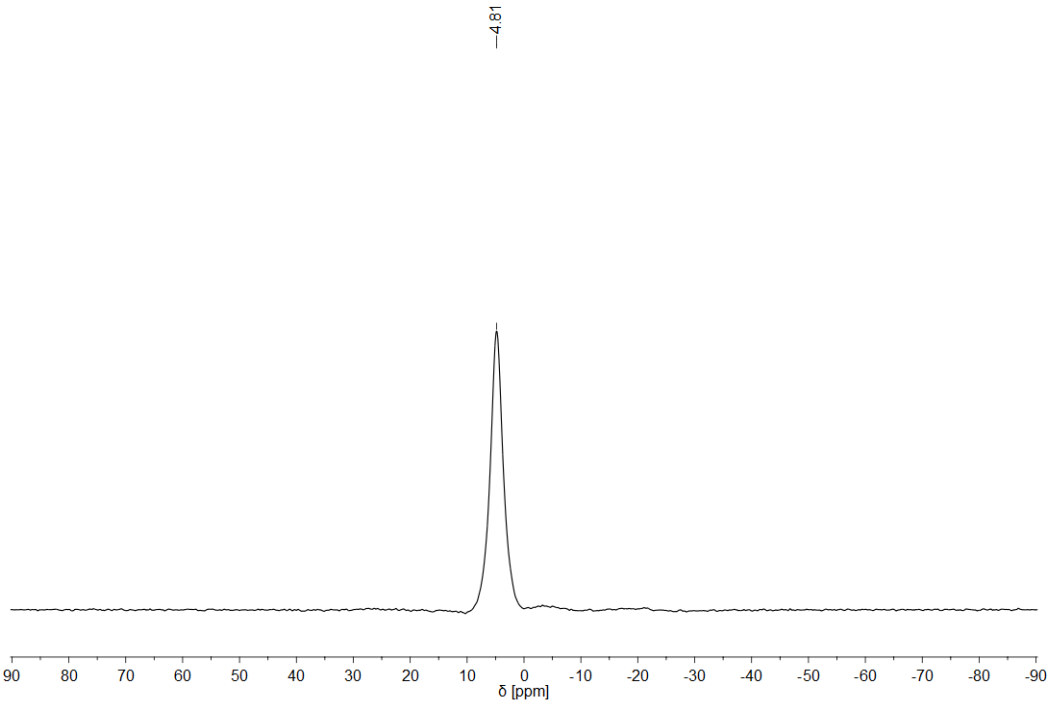

Figure S 100: ^{11}B NMR spectrum of dynamic adduct of Ph_2PH and Cl-9-BBN ($CDCl_3$).

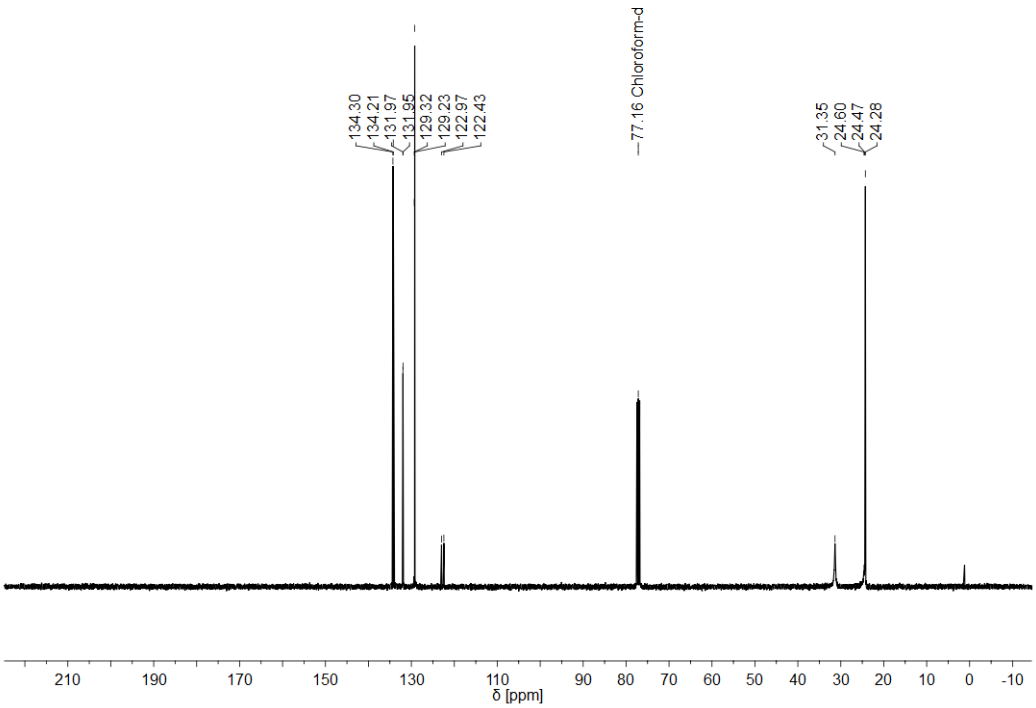

Figure S 101: ^{13}C NMR spectrum of dynamic adduct of Ph_2PH and Cl-9-BBN ($CDCl_3$).

3.2 Reaction of Cl-9-BBN with $PhSiH_3$

3.2.1 Without catalyst

Cl-9-BBN (14.1 mg, 0.09 mmol, 1 equiv) and $PhSiH_3$ (10.5 mg, 0.09 mmol, 1 equiv) were dissolved in *o*DFB (0.6 mL) and heated at 30°C in a J-Young NMR tube. The reaction was monitored by ^{11}B NMR spectroscopy for 14 h. After 30 minutes mainly Cl-9-BBN starting material and hydrolysis-derived 9-OH-9-BBN were observed in the ^{11}B NMR spectrum. After 14 hours 9-BBN product and hydrolysis-derived 9-OH-9-BBN were observed in the ^{11}B NMR spectrum. 9-OH-9-BBN resonance was assigned in accordance with literature.[22]

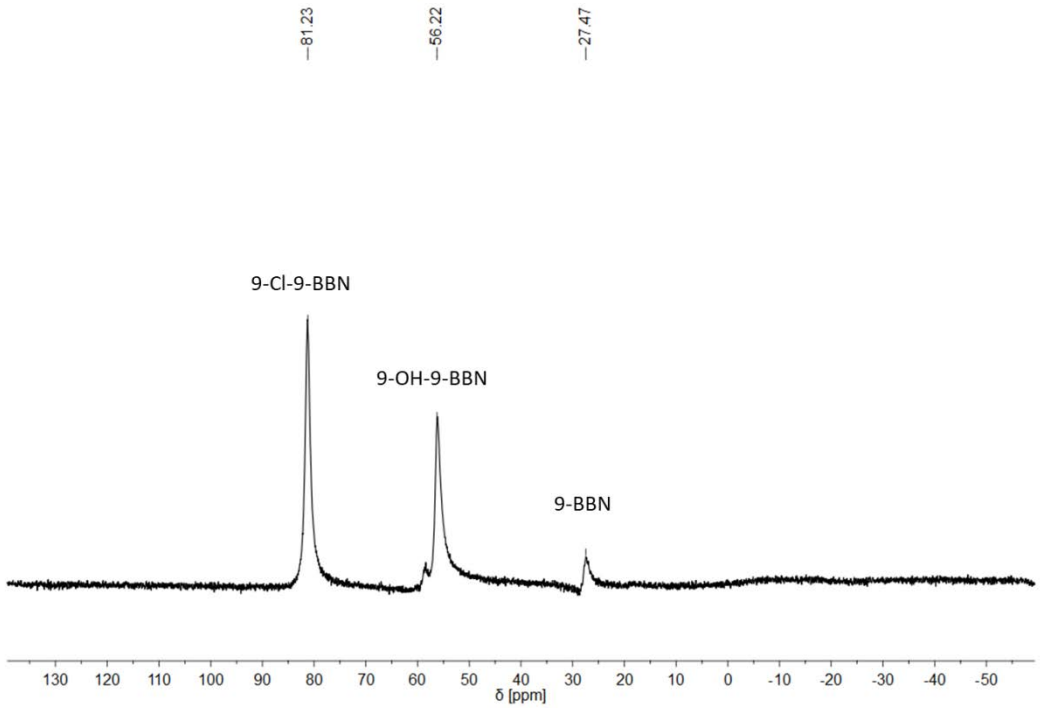

Figure S 102: ^{11}B NMR spectrum of reaction of Cl-9-BBN with $PhSiH_3$ in *o*DFB after 30 minutes at 30°C. 9-OH-9-BBN stems from glove box atmosphere-related hydrolysis of Cl-9-BBN.

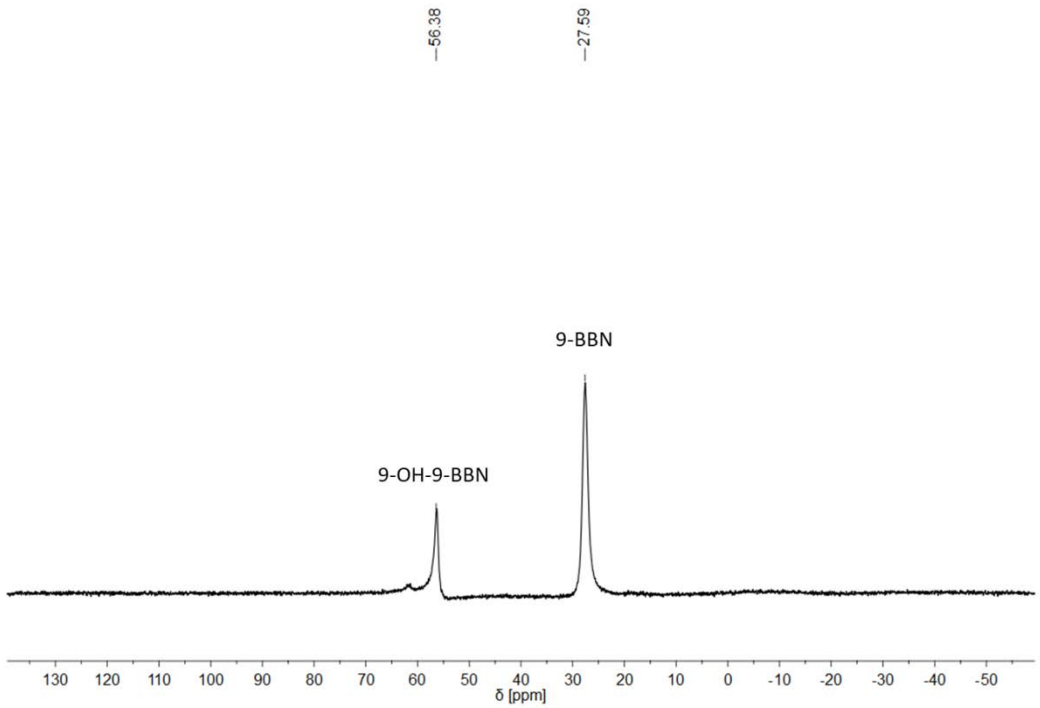

Figure S 103: ^{11}B NMR spectrum of reaction of Cl-9-BBN with $PhSiH_3$ in *o*DFB after 14 hours at 30°C. 9-OH-9-BBN stems from glove box atmosphere-related hydrolysis of Cl-9-BBN.

3.2.2 With [Et$_4$N]Cl catalyst

Cl-9-BBN (14.1 mg, 0.09 mmol, 1 equiv), $PhSiH_3$ (9.7 mg, 0.09 mmol, 1 equiv) and [Et_4N]Cl (0.7 mg, 0.005 mmol, 0.05 equiv) were dissolved in *o*DFB (0.6 mL) and placed in a J-Young NMR tube. The reaction was monitored by ^{11}B NMR spectroscopy. After 10 minutes at room temperature only 9-BBN and

hydrolysis-derived 9-OH-9-BBN were observed in the ^{11}B NMR spectrum. 9-OH-9-BBN resonance was assigned in accordance with literature.[22] This accounts for a substantial acceleration compared to the reaction without $[Et_4N]Cl$.

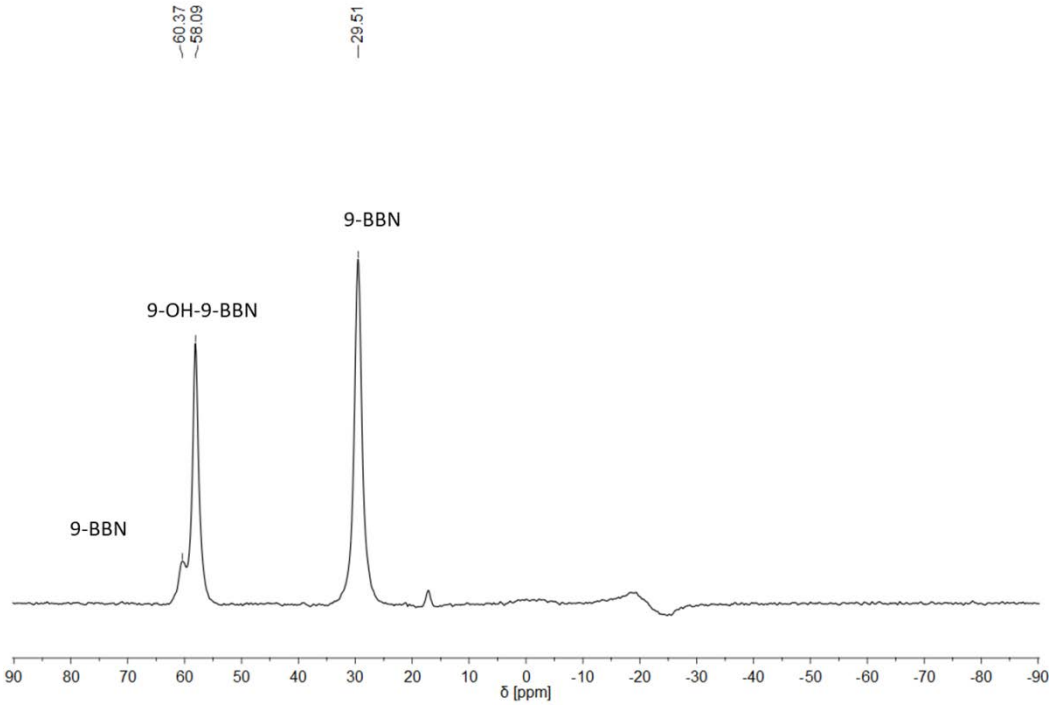

Figure S 104: ^{11}B NMR spectrum of reaction of Cl-9-BBN with $PhSiH_3$ with $[Et_4N]Cl$ catalyst in *o*DFB after 10 minutes. 9-OH-9-BBN stems from glove box atmosphere-related hydrolysis of Cl-9-BBN.

3.3 Attempted dehydrogenative coupling of R_2PH with 9-BBN and Cl-9-BBN

General procedure: Ph_2PH (16.8 mg, 0.09 mmol) and the respective boron compound (0.005 mmol, 0.5 equiv) were dissolved in MeCN/oDFB (0.6 mL, 1/2, V/V) and heated to 30 °C in a J-Young tube. The reaction progress was monitored via ^{31}P NMR spectroscopy.

In case of Cl-9-BBN: After 20 hours of reaction time Ph_2PCl (19.9 mg, 0.09 mmol, 1 equiv compared to Ph_2PH) was added to the reaction mixture and the reaction progress was monitored by ^{31}P NMR spectroscopy.

3.3.1 With Cl-9-BBN

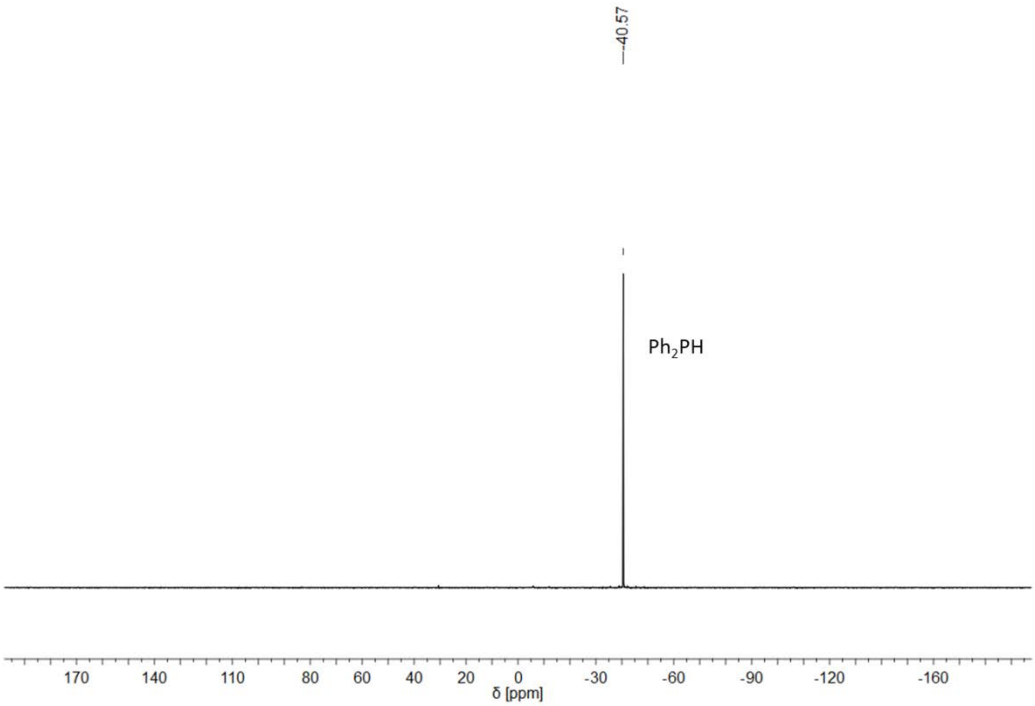

Figure S 105: $^{31}P\{^{1}H\}$ NMR spectrum of the attempted dehydrogenative coupling of Ph_2PH with catalytic amounts of Cl-9-BBN in oDFB/MeCN at 30 °C after 16 hours.

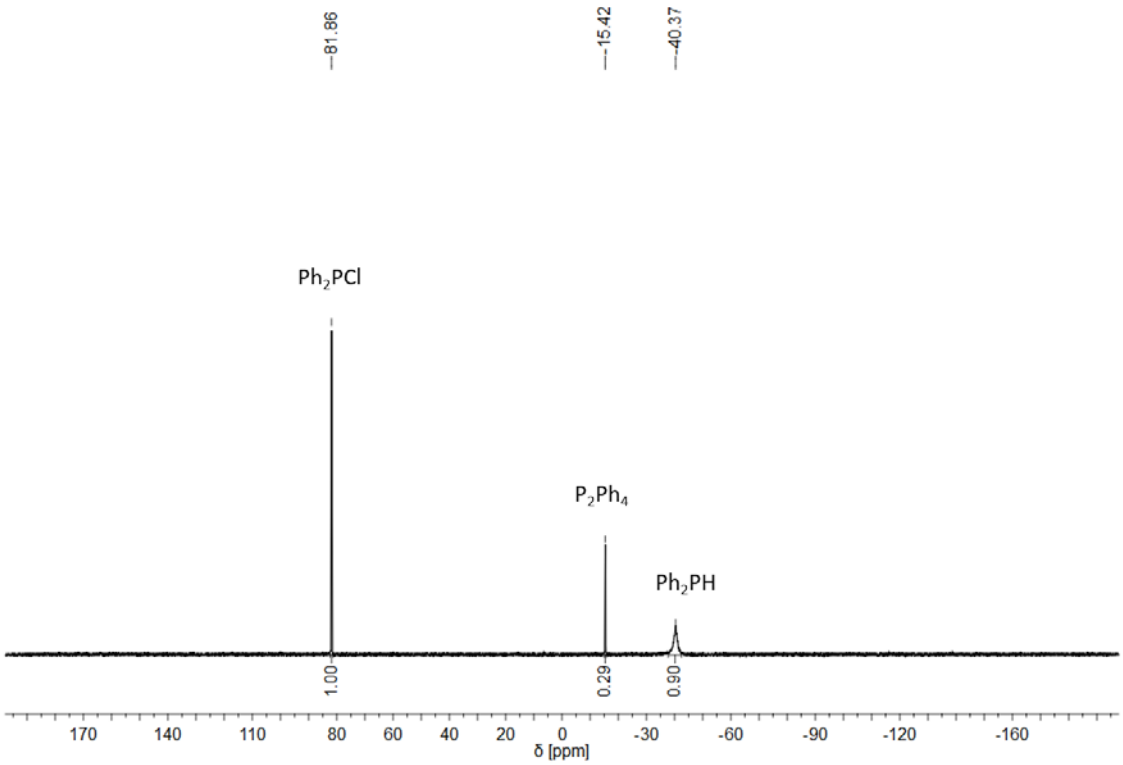

Figure S 106: $^{31}P\{^{1}H\}$ NMR spectrum of the addition of Ph_2PCl to the reaction mixture of the attempted dehydrogenative coupling of Ph_2PH with catalytic amounts of Cl-9-BBN in oDFB/MeCN at 30 °C; 30 min after the addition of Ph_2PCl.

3.3.2 With 9-BBN

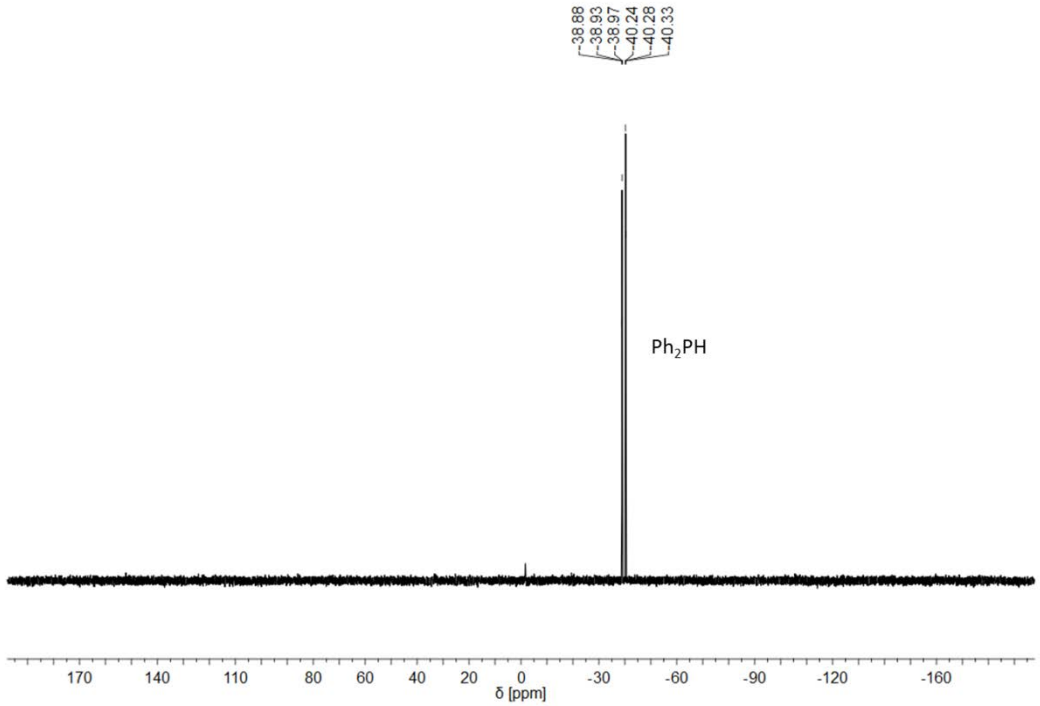

Figure S 107: ^{31}P NMR spectrum of attempted dehydrogenative coupling of Ph_2PH with catalytic amounts of 9-BBN in oDFB/MeCN at 30 °C after 20 hours.

3.4 Reaction of Ph_2PH with Ph_2PCl

Ph_2PCl (19.9 mg, 0.09 mmol, 1 equiv) and Ph_2PH (16.8 mg, 0.09 mmol, 1 equiv) were dissolved in the respective solvent (0.6 mL) and heated to 30 °C in a J-Young tube. After 3 hours a ^{31}P NMR spectrum was recorded.

3.4.1 In toluene

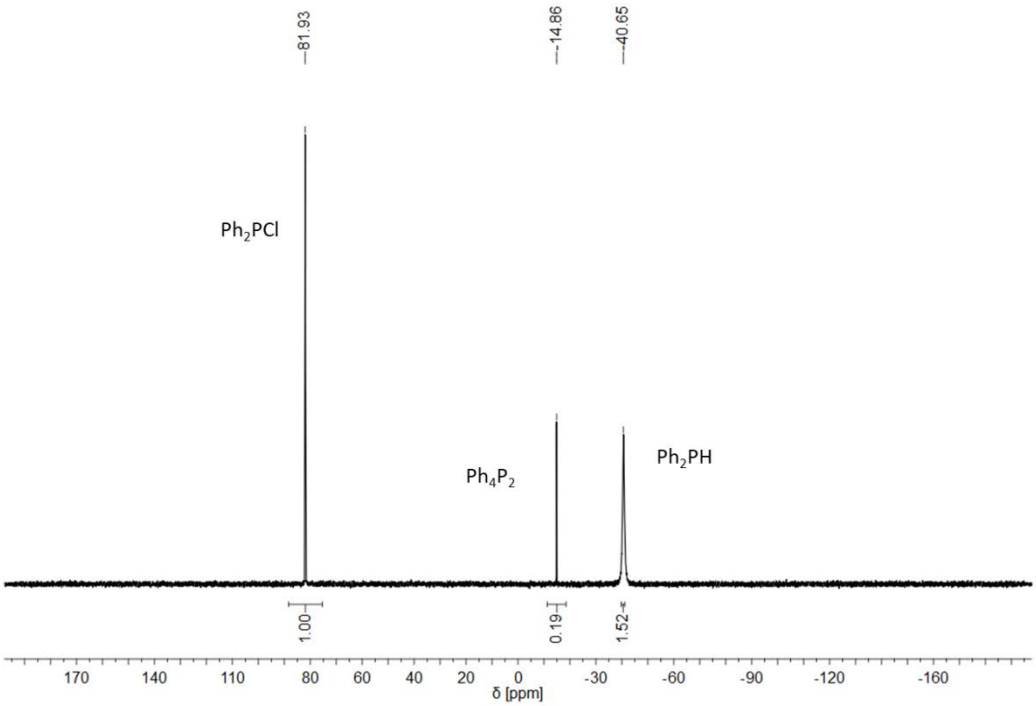

Figure S 108: ^{31}P NMR spectrum of the reaction of Ph_2PCl with Ph_2PH at 30 °C in toluene after 3 hours.

3.4.2 In oDCB

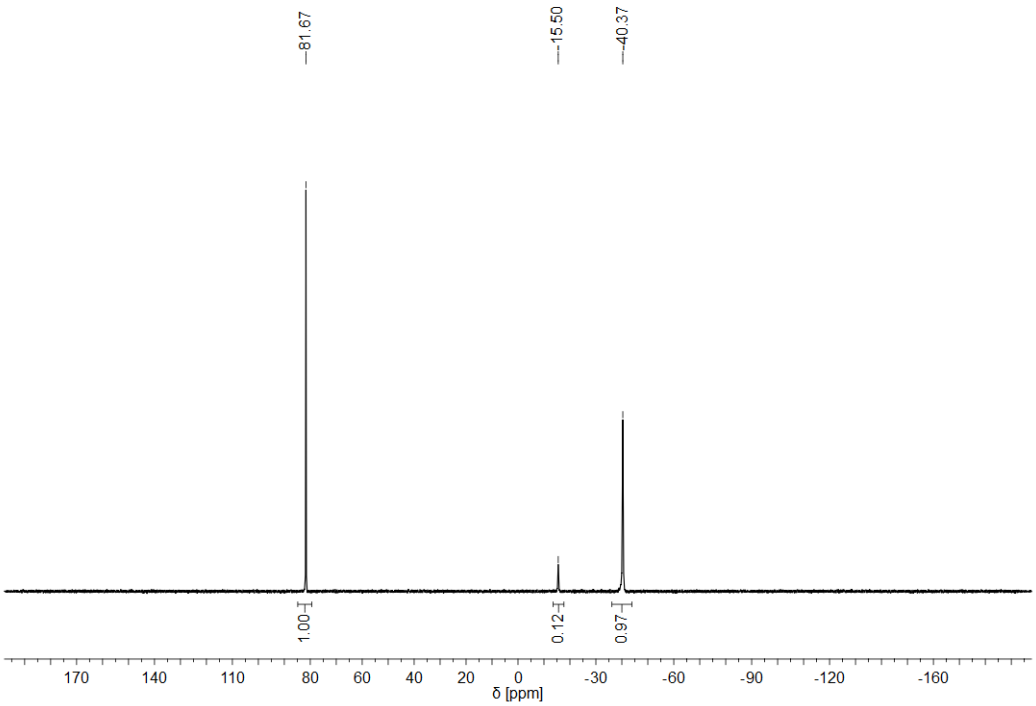

Figure S 109: ^{31}P NMR spectrum of the reaction of Ph_2PCl with Ph_2PH at 30 °C in *o*DCB after 3 hours.

3.4.3 In oDFB

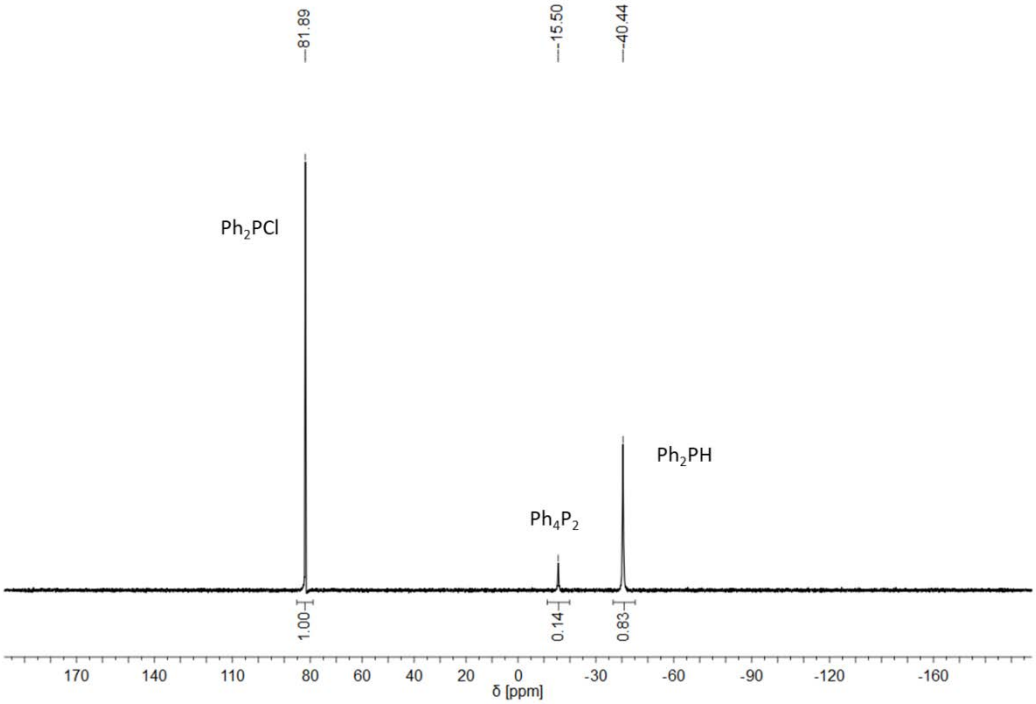

Figure S 110: ^{31}P NMR spectrum of the reaction of Ph_2PCl with Ph_2PH at 30 °C in *o*DFB after 3 hours.

3.4.4 In oDFB/MeCN

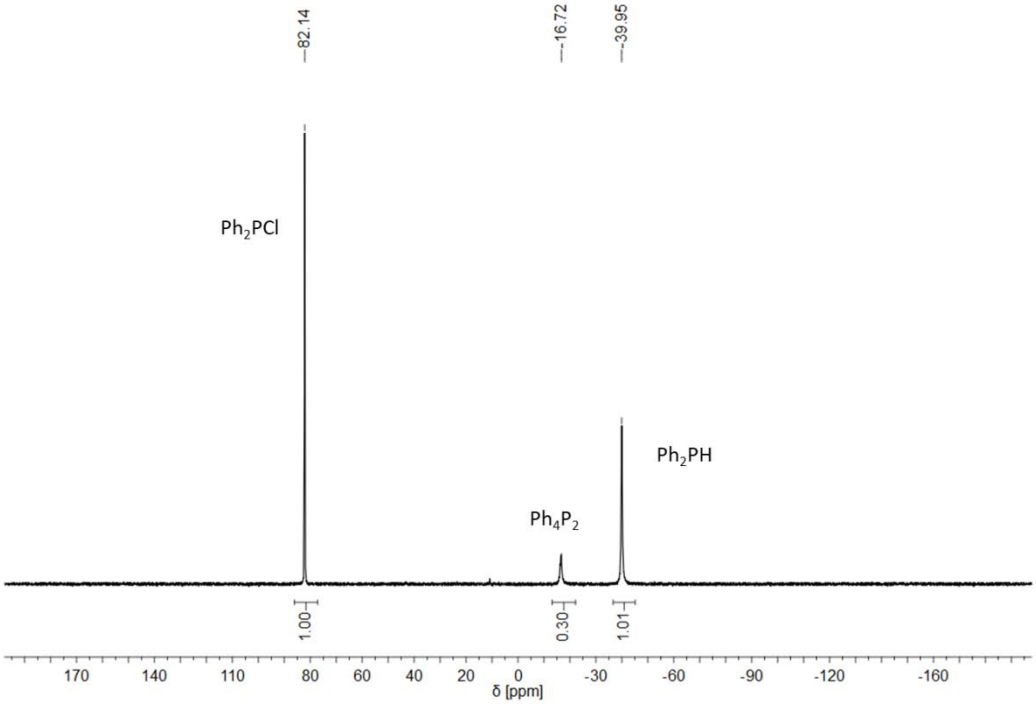

Figure S 111: ^{31}P NMR spectrum of the reaction of Ph_2PCl with Ph_2PH at 30 °C in *o*DFB/MeCN after 3 hours.

3.5 Reaction of *t*Bu_2PH with *t*Bu_2PCl

tBu_2PCl (16.3 mg, 0.09 mmol) and *t*Bu_2PH (13.2 mg, 0.09 mmol) were dissolved in *o*DFB/MeCN (0.6 mL, 2/1, V/V) and heated to 80 °C for 24 h. The reaction progress was monitored via ^{31}P NMR spectroscopy.

After 24 h $PhSiH_3$ (4.9 mg, 0.05 mmol) was added and the mixture heated to 80 °C. The reaction progress was monitored by ^{31}P NMR spectroscopy.

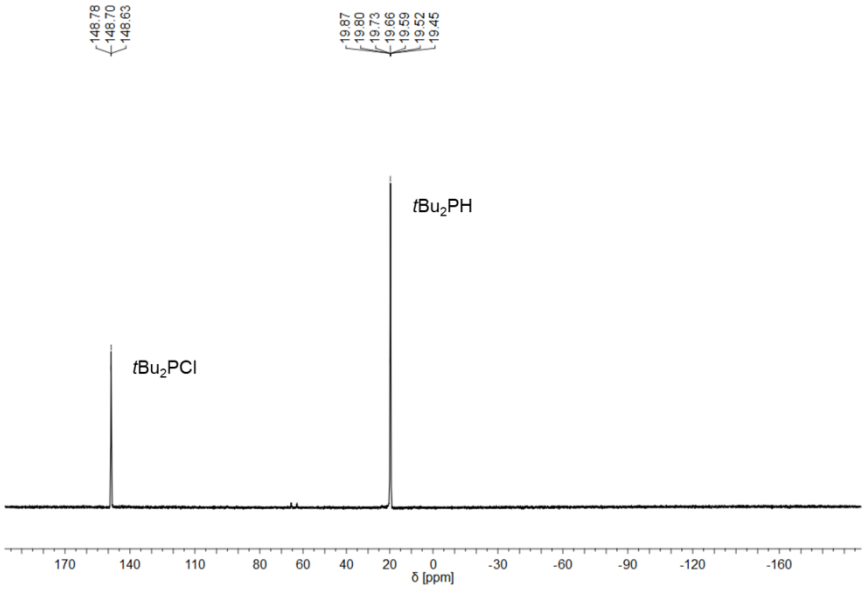

Figure S 112: ^{31}P NMR spectrum of reaction of *t*Bu_2PCl with *t*Bu_2PH in oDFB/MeCN after 24 h at 80 °C.

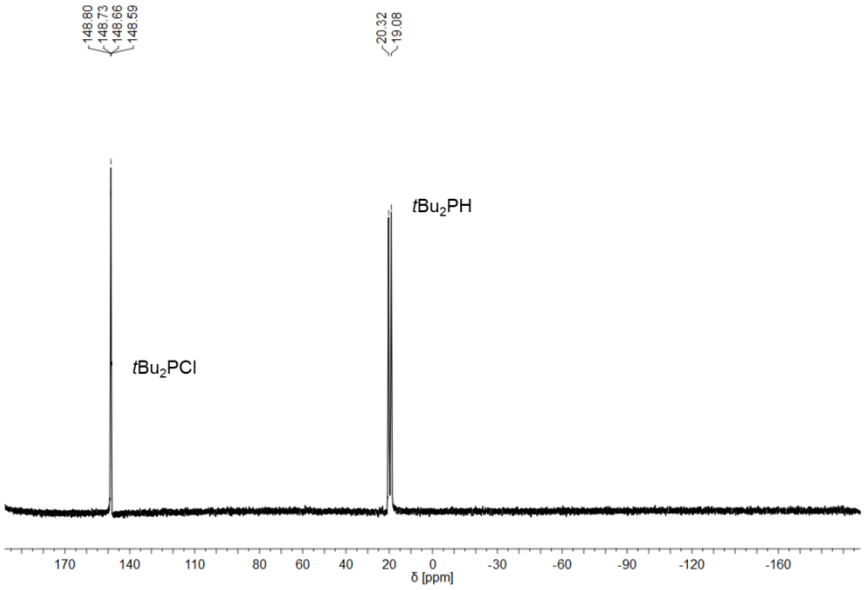

Figure S 113: ^{31}P NMR spectrum of reaction of *t*Bu_2PCl with *t*Bu_2PH and $PhSiH_3$ in oDFB/MeCN after 48 h at 80 °C.

3.6 Chlorination of $PhSiH_3$ with HCl

Chlorination of $PhSiH_3$ with HCl as a critical step in PP bond formation from R_2PH and R_2PCl was investigated and the influence of catalytic amounts of $[Et_4N]Cl$ was demonstrated. Addition of 9-BBN did not have an impact on chlorination of $PhSiH_3$ with HCl.

3.6.1 Without catalyst

$PhSiH_3$ (9.7 mg, 0.09 mmol, 1 equiv) was dissolved in MeCN-d3 (0.3 mL) and 1,2-dichloroethane (2 drops, internal standard for ^1H NMR spectroscopy) was added. A reference ^1H NMR spectrum was measured.

HCl in diethyl ether (1 M, 0.36 mL, 0.36 mmol, 4 equiv) was added, the mixture was kept at 30°C in a J-Young NMR tube and the reaction progress was monitored via ^{1}H NMR spectroscopy.

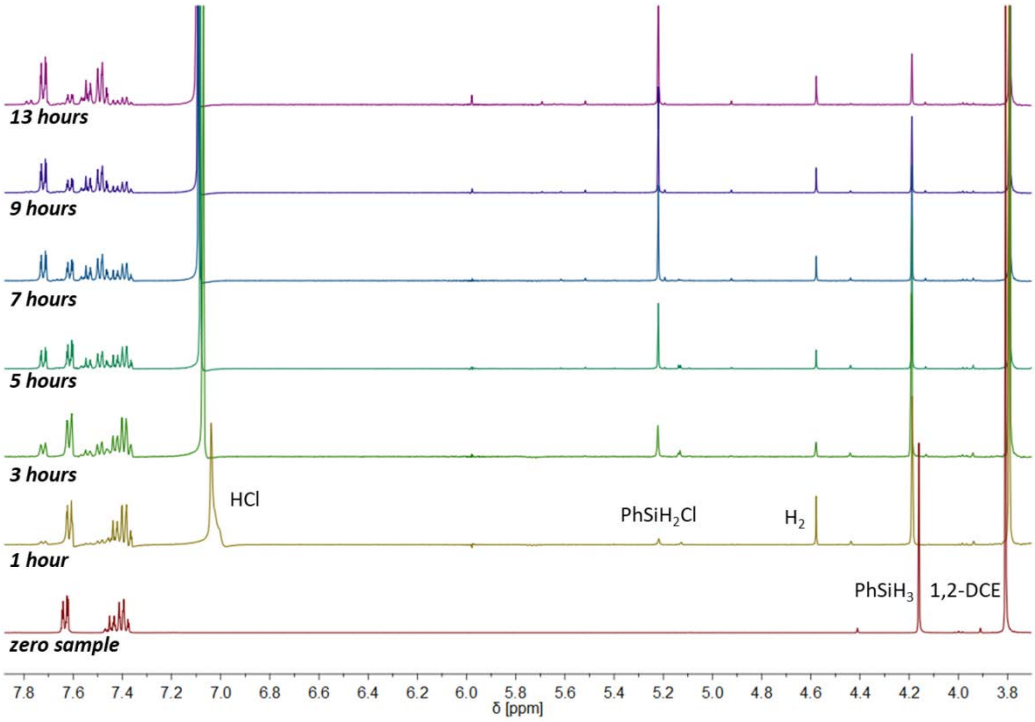

Figure S 114: ^{1}H NMR spectrum of reaction of $PhSiH_3$ with HCl at 30 °C in MeCN-d3 after indicated time intervals. Zero sample: before addition of HCl. Spectrum is magnified to facilitate recognition of important resonances.

3.6.2 With 9-BBN

$PhSiH_3$ (9.7 mg, 0.18 mmol, 1 equiv) and 9-BBN (0.5 mg, 0.005 mmol, 0.05 equiv) were dissolved in MeCN-d3 (0.3 mL) and 1,2-dichloroethane (2 drops, internal standard for ^{1}H NMR spectroscopy) was added. A reference ^{1}H NMR spectrum was measured. HCl in diethyl ether (1 M, 0.36 mL, 0.36 mmol, 4 equiv) was added, the mixture was kept at 30°C in a J-Young NMR tube and the reaction progress was monitored via ^{1}H NMR spectroscopy.

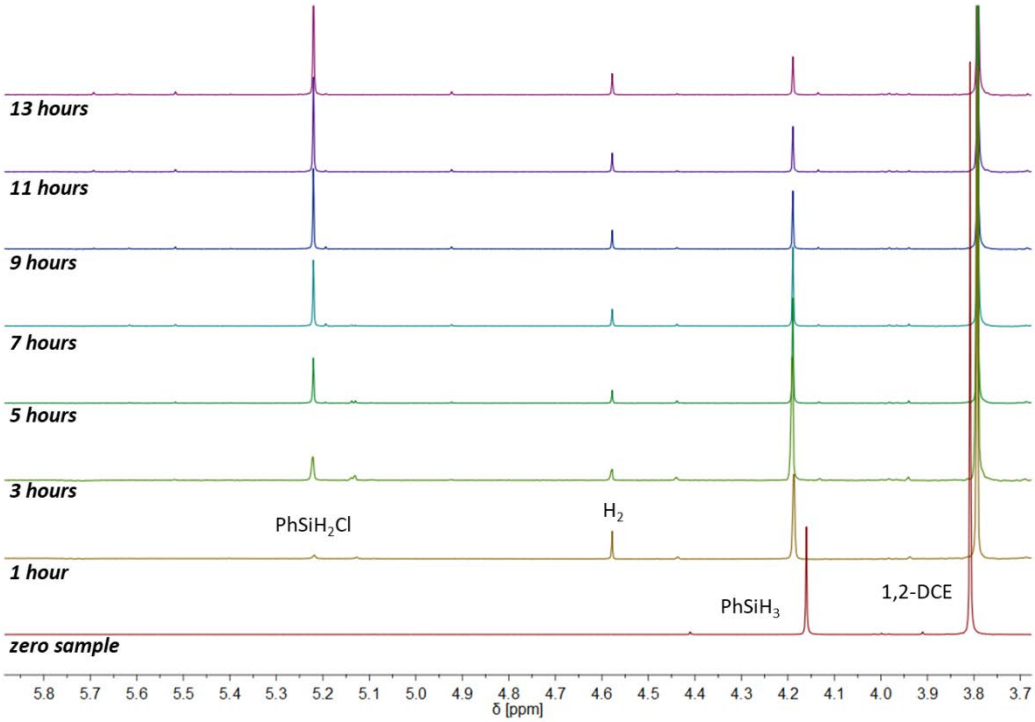

Figure S 115: ^{1}H NMR spectrum of reaction of $PhSiH_3$ with HCl and 9-BBN at 30 °C in MeCN-d3 after indicated time intervals. Zero sample: before addition of HCl. Spectrum is magnified to facilitate recognition of important resonances.

3.6.3 With [Et$_4$N]Cl

$PhSiH_3$ (19.5 mg, 0.18 mmol, 1 equiv) and [Et_4N]Cl (1.5 mg, 0.01 mmol, 0.05 equiv) were dissolved in MeCN-d3 (0.3 mL) and 1,2-dichloroethane (2 drops, internal standard for ^{1}H NMR spectroscopy) was added. A reference ^{1}H NMR spectrum was measured. HCl in diethyl ether (1 M, 0.36 mL, 0.36 mmol, 2 equiv) was added, the mixture was kept at 30°C in a J-Young NMR tube and the reaction progress was monitored via ^{1}H NMR spectroscopy. After 2 hours full consumption of $PhSiH_3$ is observed. Resonances for the silanes[23] $PhSiH_3$ (δ=4.16 ppm), $PhSiH_2Cl$ (δ=5.22 ppm), $PhSiHCl_2$ (δ=5.98 ppm) and for H_2 (δ=4.58 ppm)[7] were assigned by comparison with literature.

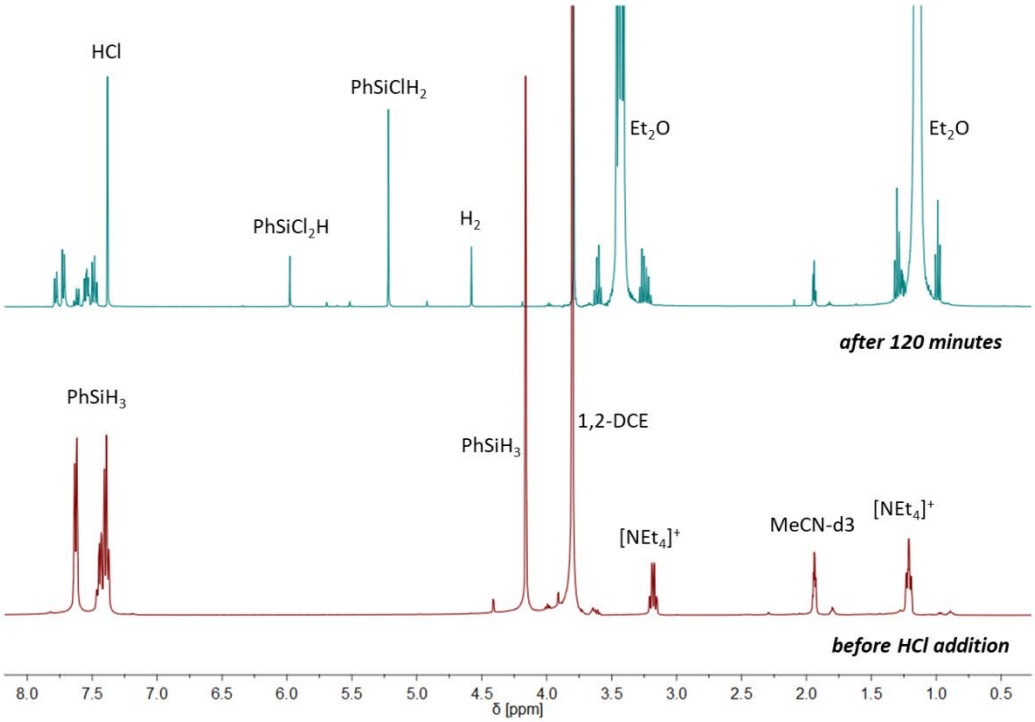

Figure S 116: ^{1}H NMR spectra of [Et_4N]Cl catalyzed chlorination of $PhSiH_3$ with HCl in MeCN-d3. *Bottom*: Before addition of HCl. *Top*: Reaction mixture after 120 minutes at 30 °C.

3.7 Test for radical mechanism

To rule out a radical mechanism for PP bond formation we performed the reaction of Ph_2PCl with $PhSiH_3$ under [Et_4N]Cl *catalysis in the presence of radical scavengers. The two investigated radical scavengers (2,2,6,6-Tetramethylpiperidinyloxyl (TEMPO), 9,10-dihydroanthracene) did not slow down the reaction, thereby indicating that no radicals are involved in PP bond formation.*

Ph_2PCl (19.9 mg, 0.09 mmol, 1 equiv), $PhSiH_3$ (9.7 mg, 0.09 mmol, 1 equiv), [Et_4N]Cl (0.7 mg, 0.005 mmol, 0.5 equiv) and the appropriate radical scavenger (0.09 mmol, 1 equiv) were dissolved in a mixture of *o*DFB/MeCN (0.6 mL, 2/1, V/V) in a J-Young tube and heated to 30°C. The reaction progress was followed by ^{31}P NMR spectroscopy. A reference reaction without radical scavenger was run at the same time.

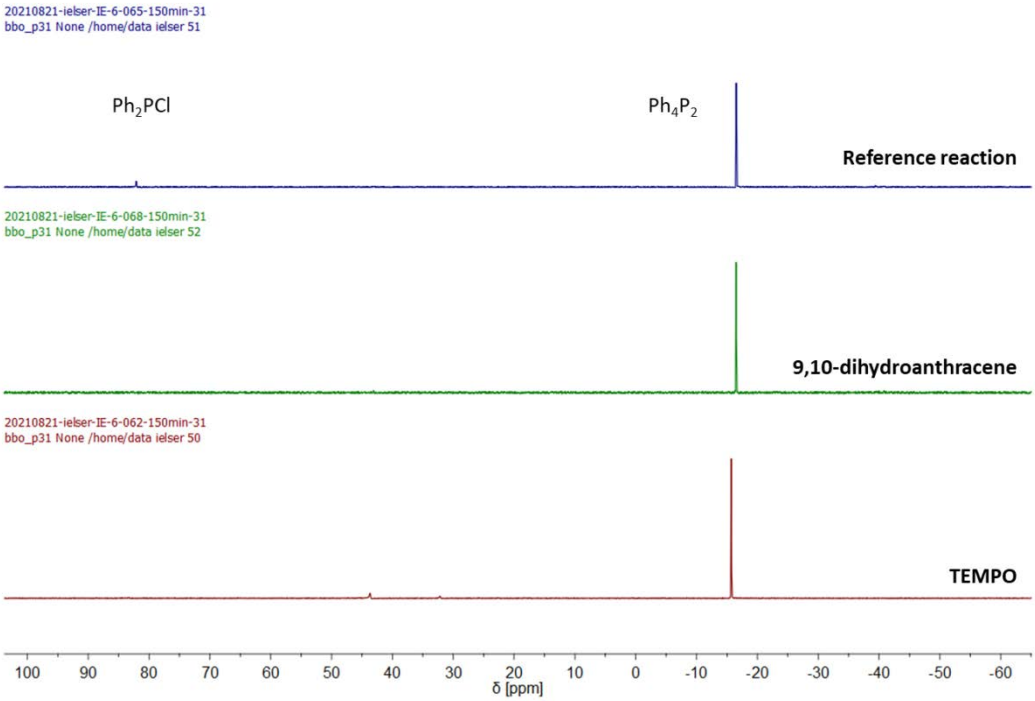

Figure S 117: Stack of ^{31}P NMR spectra of the reaction of Ph_2PCl with $PhSiH_3$ catalyzed by $[Et_4N]Cl$ in the presence of radical scavengers after 150 min.

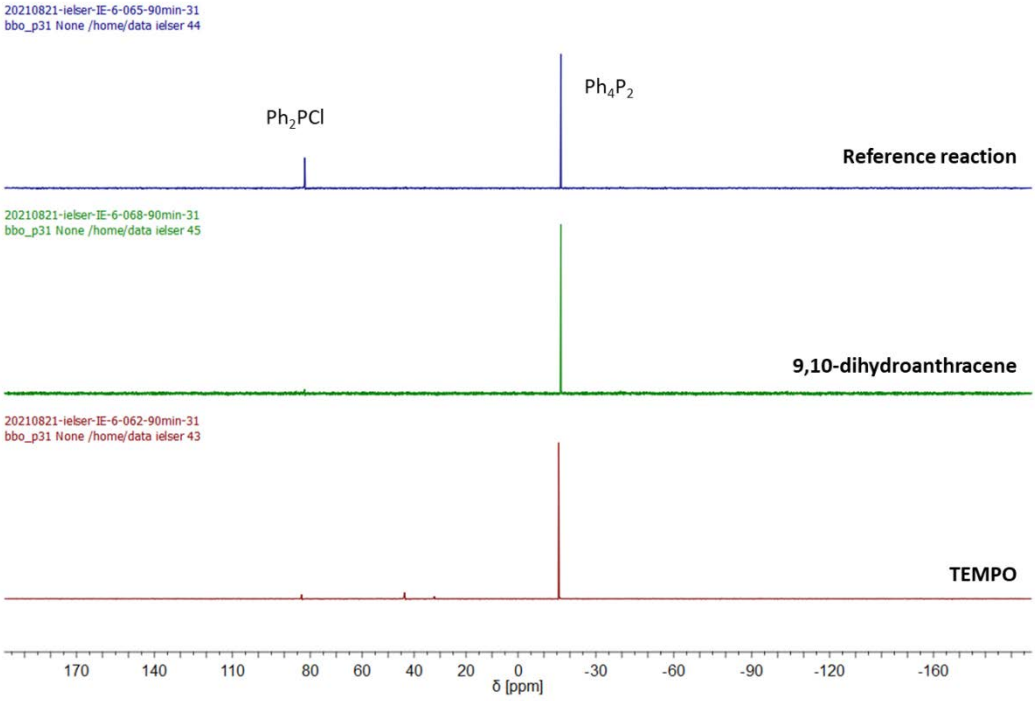

Figure S 118: Stack of ^{31}P NMR spectra of the reaction of Ph_2PCl with $PhSiH_3$ catalyzed by $[Et_4N]Cl$ in the presence of radical scavengers after 90 min.

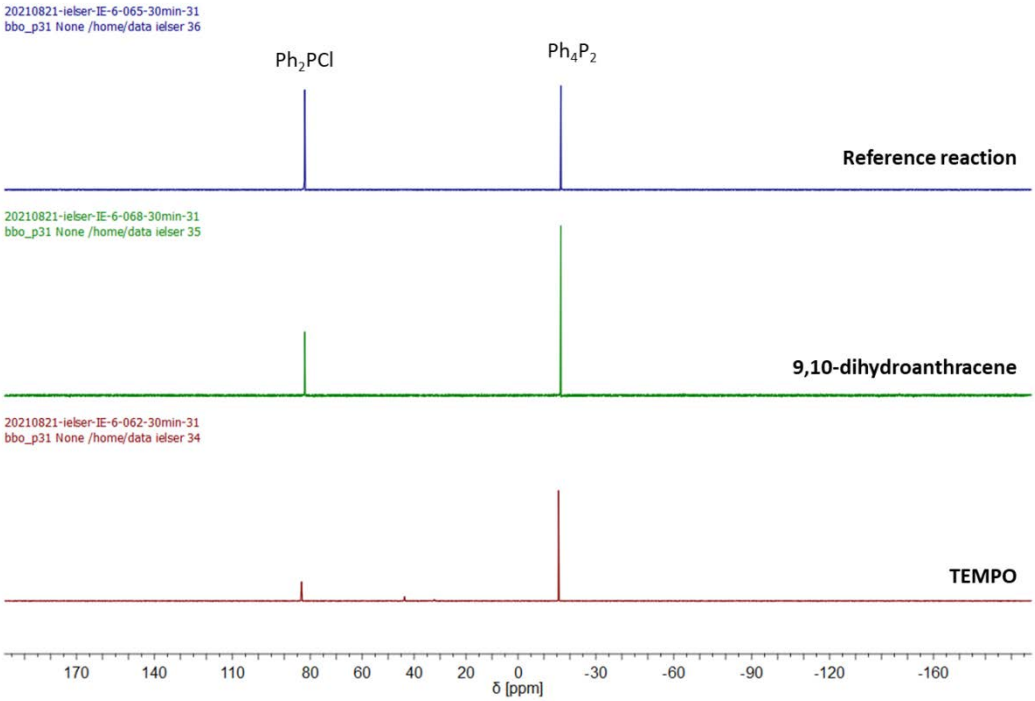

Figure S 119: Stack of ^{31}P NMR spectra of the reaction of Ph_2PCl with $PhSiH_3$ catalyzed by $[Et_4N]Cl$ in the presence of radical scavengers after 30 min.

3.8 Test for silylium catalysis

To rule out silylium-based catalysis,[24-27] by silane activation with 9-BBN or 9-Cl-BBN we performed the reaction of Ph_2PCl with $PhSiH_3$ or Et_3SiH with $[CPh_3][B(C_6F_5)_4]$ instead of 9-BBN. $[CPh_3][B(C_6F_5)_4]$ has been shown to generate catalytically active silylium by hydride abstraction.[26] In our hands, under the optimized reaction conditions (0.5 mol% $[CPh_3][B(C_6F_5)_4]$, 30 °C, 1 equiv silane, solvent) usage of $[CPh_3][B(C_6F_5)_4]$ did not lead to any conversion, thereby ruling out a silylium-based mechanism.

3.8.1 With $PhSiH_3$

Ph_2PCl (19.9 mg, 0.09 mmol, 1 equiv), $PhSiH_3$ (9.7 mg, 0.09 mmol, 1 equiv) and $[CPh_3][B(C_6F_5)_4]$ (4.2 mg, 0.005 mmol, 0.5 equiv) were dissolved in a mixture of *o*DFB/MeCN (0.6 mL, 2/1, V/V) in a J-Young tube and heated to 30°C. The reaction progress was followed by ^{31}P NMR spectroscopy. After 17 hours no conversion of Ph_2PCl was observed.

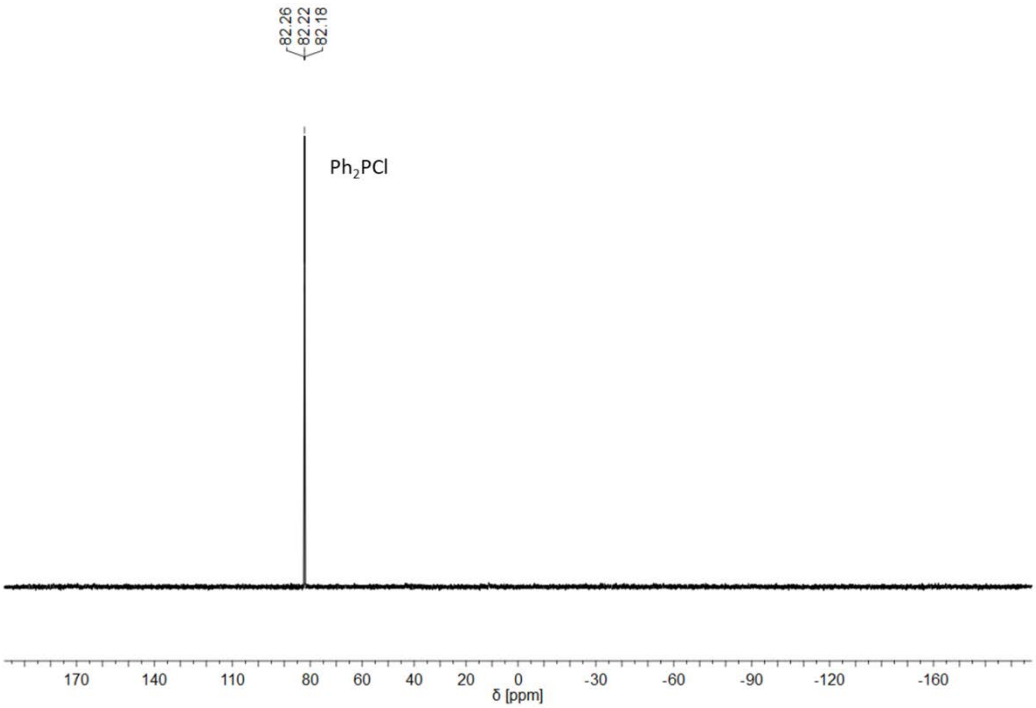

Figure S 120: ^{31}P NMR spectrum of the reaction of Ph_2PCl with $PhSiH_3$ in the presence of $[CPh_3][B(C_6F_5)_4]$ (30 °C, *o*DFB/MeCN, 17 h).

Ph_2PCl (19.9 mg, 0.09 mmol, 1 equiv), $PhSiH_3$ (9.7 mg, 0.09 mmol, 1 equiv) and $[CPh_3][B(C_6F_5)_4]$ (4.2 mg, 0.005 mmol, 0.5 equiv) were dissolved in *o*DFB (0.6 mL) in a J-Young tube and heated to 30°C. The reaction progress was followed by ^{31}P NMR spectroscopy. After 17 hours no conversion of Ph_2PCl was observed.

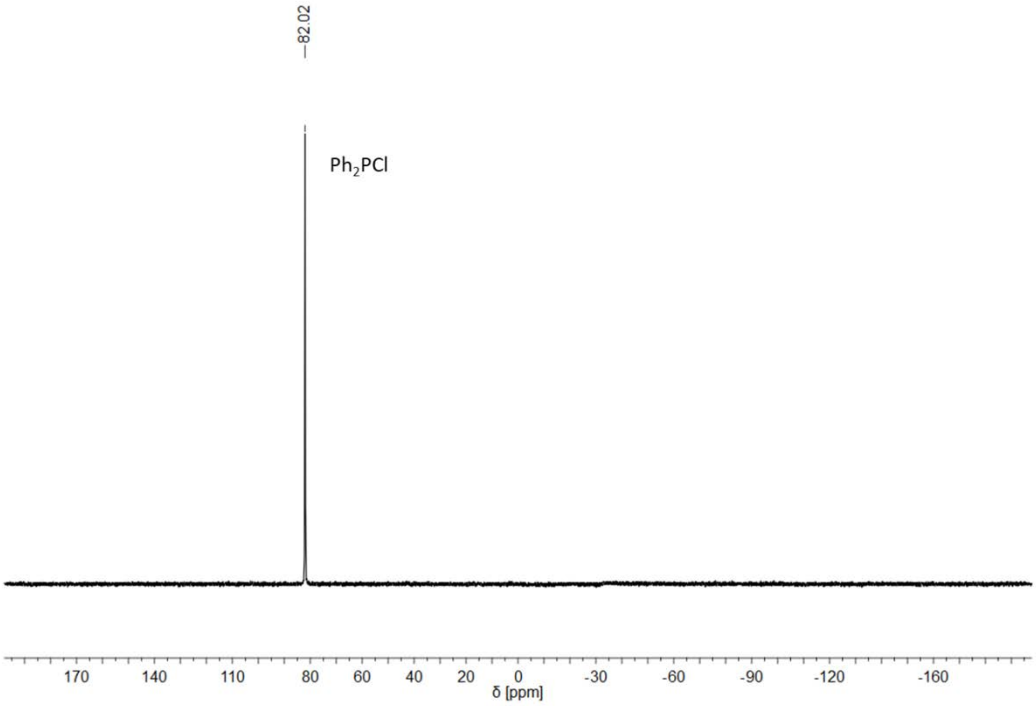

Figure S 121: ^{31}P NMR spectrum of the reaction of Ph_2PCl with $PhSiH_3$ in the presence of $[CPh_3][B(C_6F_5)_4]$ (30 °C, *o*DFB, 17 h).

3.8.2 With Et_3SiH

Ph_2PCl (17.7 mg, 0.08 mmol, 1 equiv), Et_3SiH (9.3 mg, 0.08 mmol, 1 equiv) and $[CPh_3][B(C_6F_5)_4]$ (3.7 mg, 0.004 mmol, 0.5 equiv) were dissolved in 1,2-dichloroethane (0.6 mL) in a J-Young tube and heated to 30°C. The reaction progress was followed by ^{31}P NMR spectroscopy. After 3 hours no conversion of Ph_2PCl was observed.

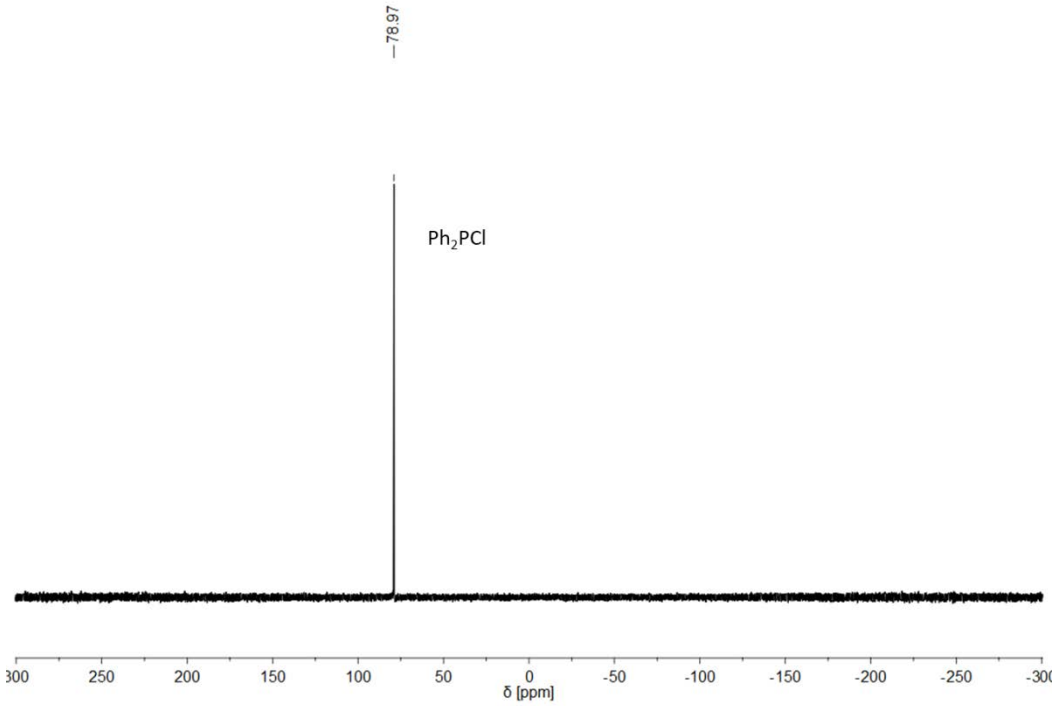

Figure S 122: ^{31}P NMR spectrum of the reaction of Ph_2PCl with Et_3SiH in the presence of $[CPh_3][B(C_6F_5)_4]$ (30 °C, 1,2-dichloroethane, 3 h).

4. Larger scale reactions

4.1 Synthesis of Ph_4P_2 by 9-BBN catalysis

Ph_2PCl (551.6 mg, 2.5 mmol, 1 equiv) and $PhSiH_3$ (270.6 mg, 2.5 mmol, 1 equiv) were dissolved in MeCN/*o*DFB (16 mL, 2/1, VV) and added to 9-BBN (15.3 mg, 0.13 mmol, 0.05 equiv) and the mixture was placed in a Schlenk tube. The mixture was heated to 30°C for 24 hours (open to the Schlenk line for pressure release, H_2 formation). After 24 hours all volatiles were removed and the mixture was washed with pentane (2 x 2 mL). The remaining colourless powder was dried under vacuum to afford 81% (375 mg, 1 mmol) of Ph_4P_2. ^1H NMR (C_6D_6) δ = 7.57-7.51 (m, 8H), 6.97-6.94 (m, 12H) ppm. ^{31}P NMR (C_6D_6) δ = -14.9 (s) ppm. ^{13}C NMR (C_6D_6) δ = 136.6 (m), 134.8 (t, J_{CP} = 12.9 Hz), 128.9, 128.6 (t, J_{CP} = 3.33 Hz) ppm.

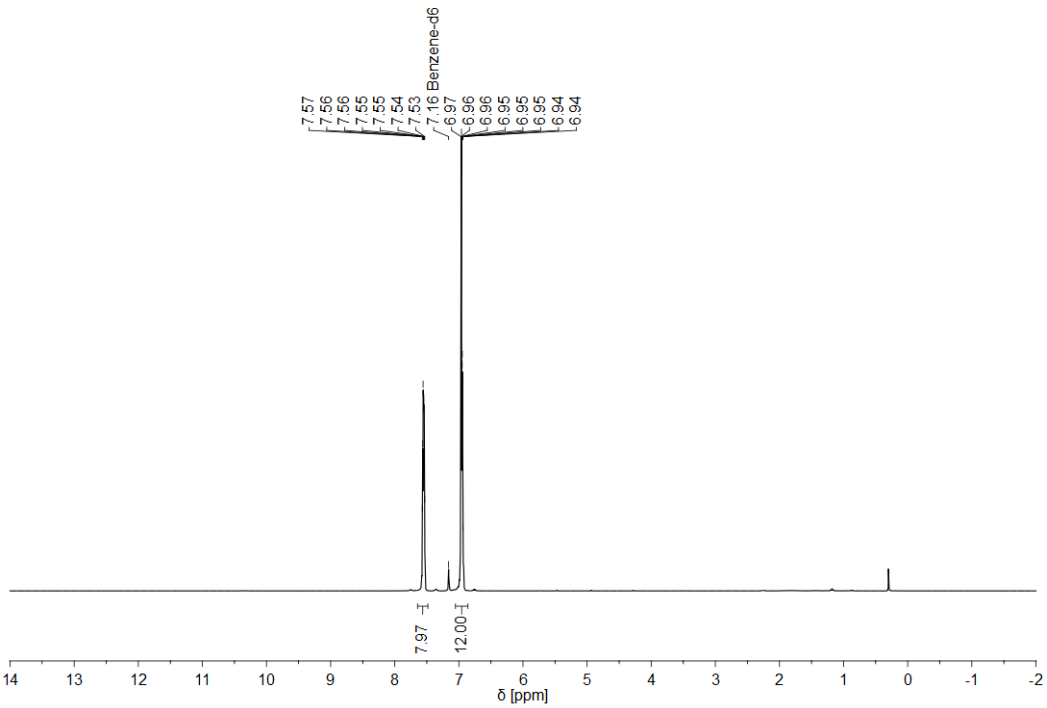

Figure S 123: ^{1}H NMR spectrum of Ph_4P_2 synthesized from Ph_2PCl and $PhSiH_3$ by 9-BBN catalysis (C_6D_6).

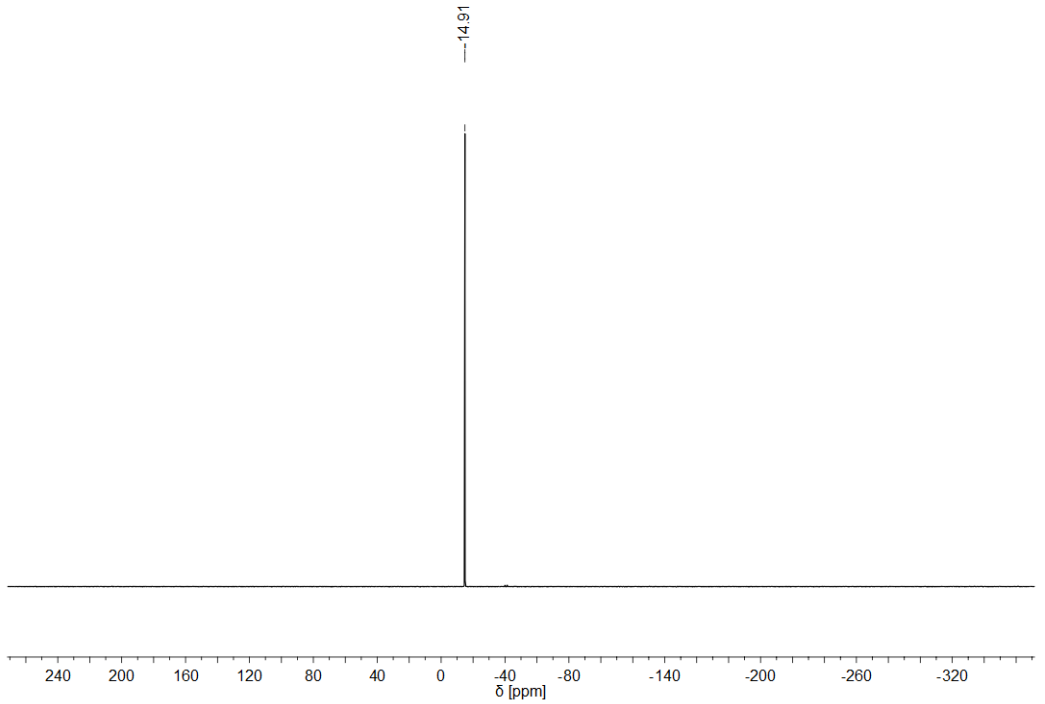

Figure S 124: ^{31}P NMR spectrum of Ph_4P_2 synthesized from Ph_2PCl and $PhSiH_3$ by 9-BBN catalysis (C_6D_6).

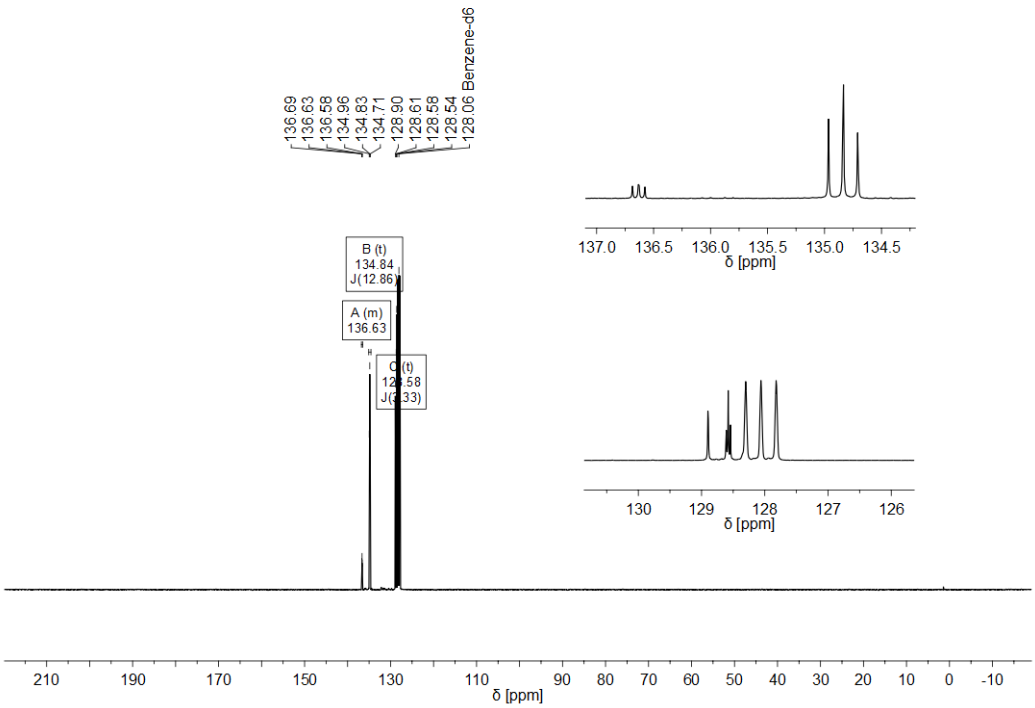

Figure S 125: ^{13}C NMR spectrum of Ph_4P_2 synthesized from Ph_2PCl and $PhSiH_3$ by 9-BBN catalysis (C_6D_6).

4.2 Synthesis of (*o*-$MeC_6H_4)_4P_2$ by 9-BBN/$[Et_4N]Cl$ catalysis

(o-$MeC_6H_4)_2PCl$ (174.1 mg, 0.7 mmol, 1 equiv) and $PhSiH_3$ (75.8 mg, 0.7 mmol, 1 equiv) were dissolved in MeCN/oDFB (4.5 mL, 1/2, V/V) and added to 9-BBN (4.3 mg, 0.04 mmol, 0.05 equiv) and $[Et_4N]Cl$ (5.8 mg, 0.04 mmol, 0.05 equiv). The mixture was placed in a Schlenk tube and stirred at room temperature for two hours (open to the Schlenk line for pressure release, H_2 formation). After two hours all volatiles were removed. The residue was washed with *n*-pentane (2x2 mL), then with toluene (2 mL) and the washings discarded. The remaining colorless solid was dried under vacuum to afford (*o*-$MeC_6H_4)_4P_2$ in 74 % yield (110 mg, 0.26 mmol). ^{1}H NMR ($CDCl_3$) δ =7.41 (d, $^3J_{HH}$ = 7.46 Hz, 4H), 7.07 (t, $^3J_{HH}$ = 7.46 Hz, 4H), 6.96 (t, $^3J_{HH}$ = 7.47 Hz, 4H), 6.92-6.90 (m, 4H), 1.83 (s, 12H) ppm. ^{31}P NMR ($CDCl_3$) δ = -35.8 ppm. ^{13}C NMR ($CDCl_3$) δ = 143.2 (t, J_{PC} = 13.44), 135.3 (J_{PC} = 5.1 Hz), 129.9 (t, J_{PC} = 2.5 Hz), 128.7, 125.8, 20.9 (t, J_{CP} = 9.4 Hz) ppm.

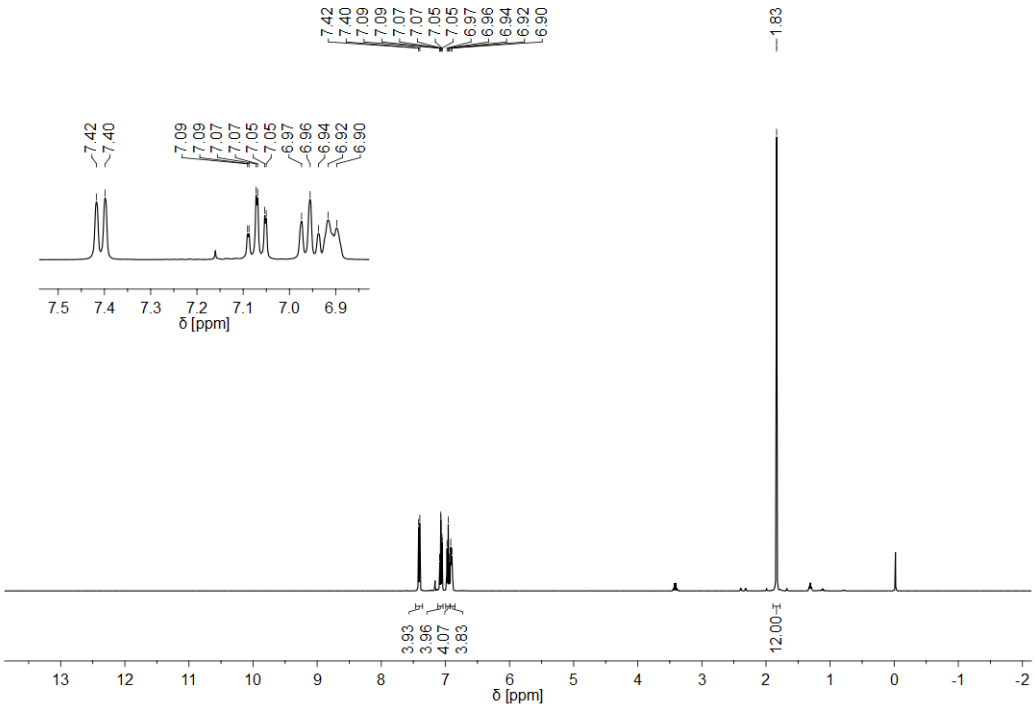

Figure S 126: ^{1}H NMR spectrum of (*o*-MeC_6H_4) $_4P_2$ synthesized from (*o*-MeC_6H_4)$_2$PCl and $PhSiH_3$ by 9-BBN/[Et_4N]Cl catalysis ($CDCl_3$).

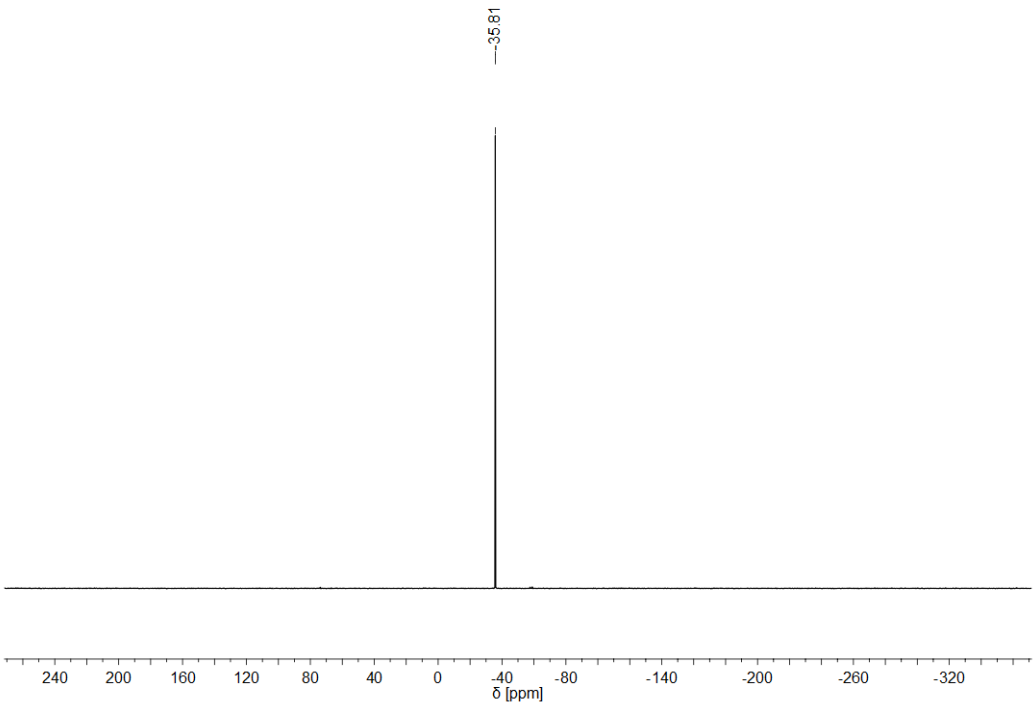

Figure S 127: ^{31}P NMR spectrum of (*o*-MeC_6H_4) $_4P_2$ synthesized from (*o*-MeC_6H_4)$_2$PCl and $PhSiH_3$ by 9-BBN/[Et_4N]Cl catalysis ($CDCl_3$).

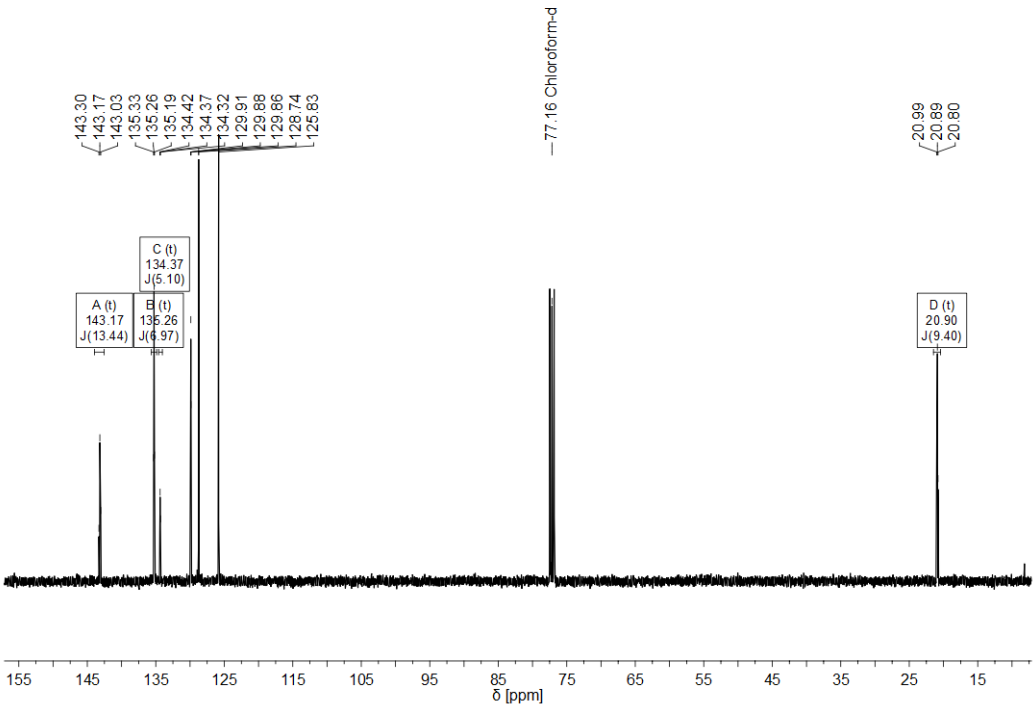

Figure S 128: ^{13}C NMR spectrum of (*o*-MeC$_6$H$_4$) $_4$P$_2$ synthesized from (*o*-MeC$_6$H$_4$)$_2$PCl and PhSiH$_3$ by 9-BBN/[Et$_4$N]Cl catalysis (CDCl$_3$).

4.3 Synthesis of (*o*-NMe$_2$C$_6$H$_4$)$_4$P$_2$ by 9-BBN/[Et$_4$N]Cl catalysis

(o-NMe$_2$C$_6$H$_4$)$_2$PCl (55.2 mg, 0.18 mmol, 1 equiv) and PhSiH$_3$ (19.5 mg, 0.0.18 mmol, 1 equiv) were dissolved in MeCN/oDFB (4.5 mL, 1/2, V/V) and added to 9-BBN (1.1 mg, 0.01 mmol, 0.05 equiv) and [Et$_4$N]Cl (1.5 mg, 0.01 mmol, 0.05 equiv). The mixture was placed in a Schlenk tube and stirred at room temperature for four hours (open to the Schlenk line for pressure release, H_2 formation). After four hours all volatiles were removed. The residue was washed with *n*-pentane (2x2 mL) and the washings discarded. The remaining colorless solid was dried under vacuum to afford (*o*-NMe$_2$C$_6$H$_4$)$_4$P$_2$ in 77 % yield (38 mg, 0.07 mmol). ^{1}H NMR (CDCl$_3$) δ = 7.56 (dd, $^3J_{HH}$ = 7.6; $^4J_{HH}$ = 1.5 Hz, H$_{ar}$, 4H), 7.12 (ddd, $^3J_{HH}$ = 7.8; 7.8; $^4J_{HH}$ = 1.54 Hz, H$_{ar}$, 4H), 6.95 (m, H$_{ar}$, 4H), 6.88 (m, H$_{ar}$, 4H), 2.38 (s, 12H, NMe$_2$) ppm. ^{31}P NMR (CDCl$_3$) δ = -34.1 (s) ppm. ^{13}C NMR (CDCl$_3$) δ = 157.9 (m, C$_{ar}$), 136.5 (t, JCP = 7.33 Hz, C$_{ar}$), 136.1 (m, C$_{ar}$), 128.8 (s, C$_{ar}$), 124.0 (s, C$_{ar}$), 120.3 (m, C$_{ar}$), 45.2 (t, $^4J_{CP}$ = 1.2 Hz) ppm.

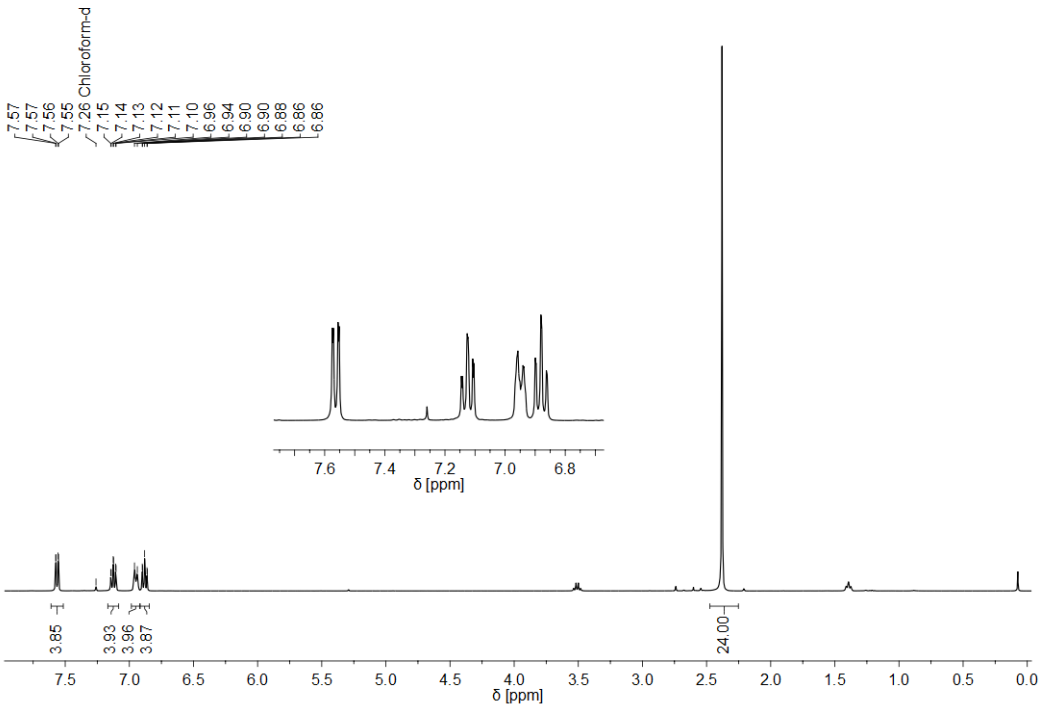

Figure S 129: ^{1}H NMR spectrum of (*o*-$NMe_2C_6H_4$)$_4P_2$ synthesized from (*o*-$OMeC_6H_4$)$_2$PCl and $PhSiH_3$ by 9-BBN/[Et_4N]Cl catalysis ($CDCl_3$).

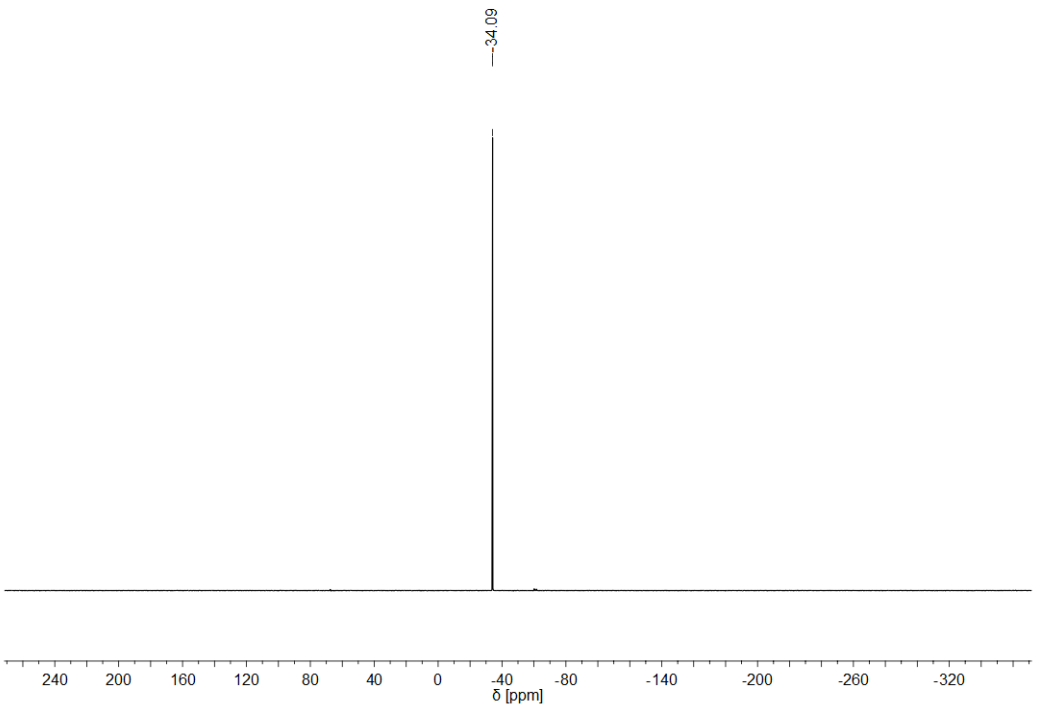

Figure S 130: ^{31}P NMR spectrum of (*o*-$NMe_2C_6H_4$)$_4P_2$ synthesized from (*o*-$OMeC_6H_4$)$_2$PCl and $PhSiH_3$ by 9-BBN/[Et_4N]Cl catalysis ($CDCl_3$).

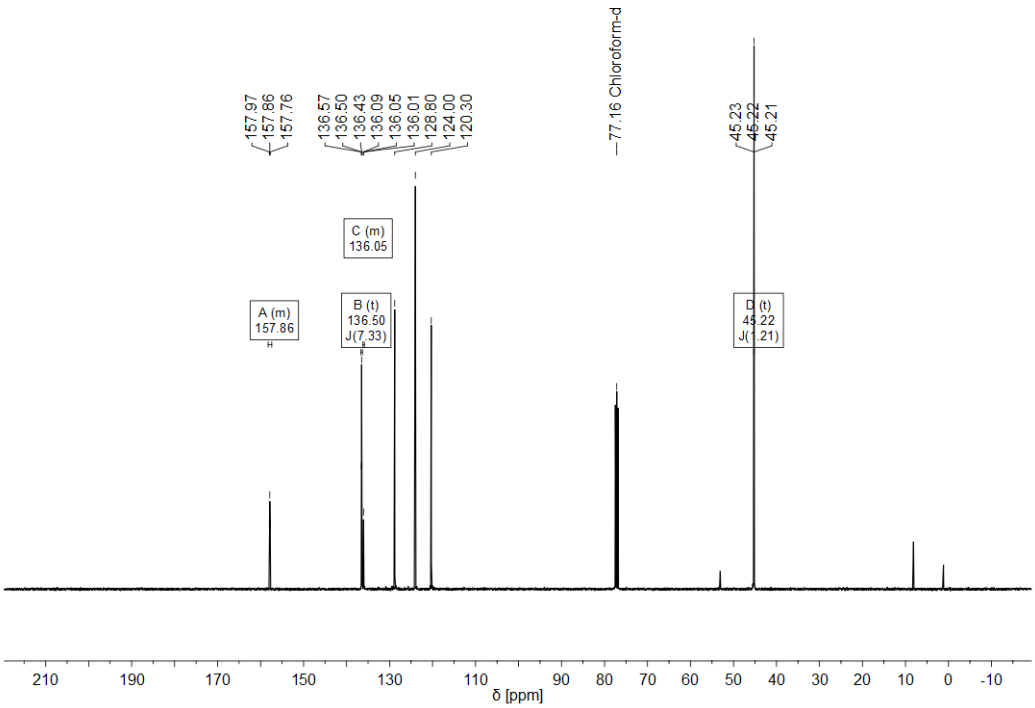

Figure S 131: ^{13}C NMR spectrum of (*o*-NMe$_2$C$_6$H$_4$) $_4$P$_2$ synthesized from (*o*-OMeC$_6$H$_4$)$_2$PCl and PhSiH$_3$ by 9-BBN/[Et$_4$N]Cl catalysis (CDCl$_3$).

4.4 Synthesis of (*o*-OMeC$_6$H$_4$)$_4$P$_2$ by 9-BBN/[Et$_4$N]Cl catalysis

(*o*-OMeC$_6$H$_4$)$_2$PCl (50.5 mg, 0.18 mmol, 1 equiv) and PhSiH$_3$ (19.7 mg, 0.18 mmol, 1 equiv) were dissolved in MeCN/oDFB (1.5 mL, 1/2, V/V) and added to 9-BBN (1.2 mg, 0.01 mmol, 0.05 equiv) and [Et$_4$N]Cl (1.5 mg, 0.01 mmol, 0.05 equiv). The mixture was placed in a Schlenk tube and stirred at room temperature for two hours (open to the Schlenk line for pressure release, H_2 formation). After two hours all volatiles were removed. The residue was washed with *n*-pentane (2x2 mL), filtered over a filter pipet and the washings discarded. The filter cake was dissolved in dichloromethane (2 mL) and again filtered. The filtrate was evaporated to dryness and the remaining colorless solid was dried under vacuum to afford (*o*-OMeC$_6$H$_4$)$_4$P$_2$ in quantitative yield (44 mg, 0.09 mmol). ^{1}H NMR (CDCl$_3$) δ = 7.60 (dd, $^3J_{HH}$ = 7.51, $^3J_{HP}$ = 1.62 Hz, 4H), 7.15 (m, 4H), 6.81 (t, $^3J_{HH}$ = 7.3 Hz, 4H), 6.55 (m, 4H), 3.47 (s, OMe, 12H) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$) δ = -46.8 ppm. ^{13}C NMR (CDCl$_3$) δ = 161.1 (t, J_{CP} = 9.18 Hz), 135.4 (t, J_{CP} = 8.44 Hz), 129.4, 123.8 (t, J_{CP} = 5.0 Hz), 120.3, 109.4, 55.2 ppm.

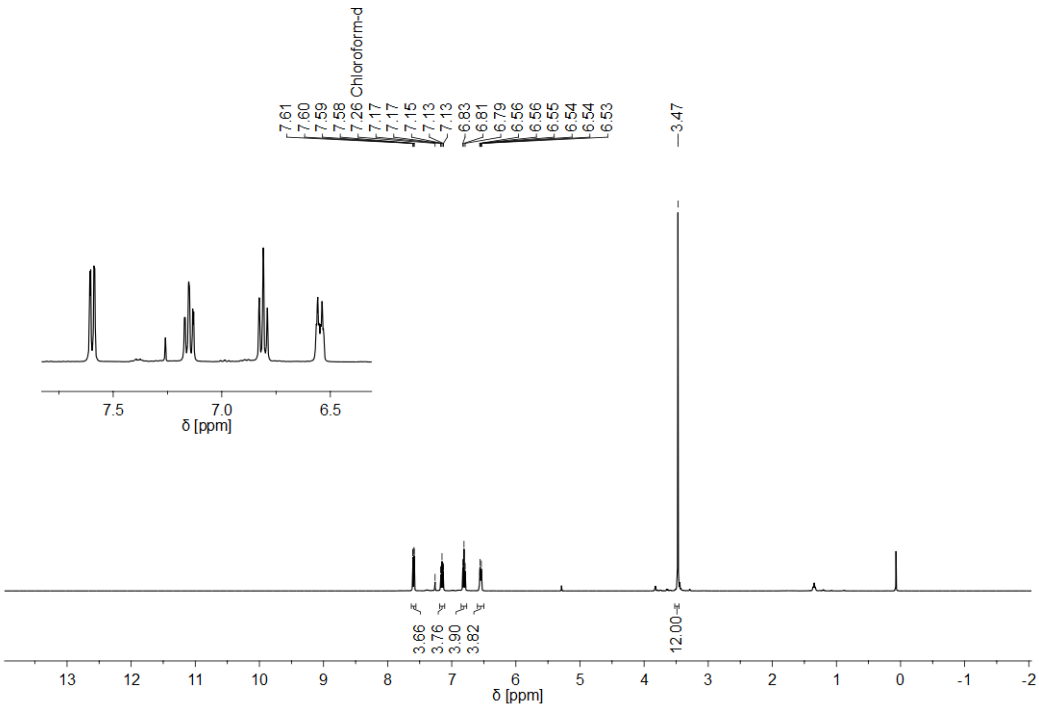

Figure S 132: ^{1}H NMR spectrum of (*o*-OMeC$_6$H$_4$)$_4$P$_2$ synthesized from (*o*-OMeC$_6$H$_4$)$_2$PCl and PhSiH$_3$ by 9-BBN/[Et$_4$N]Cl catalysis (CDCl$_3$).

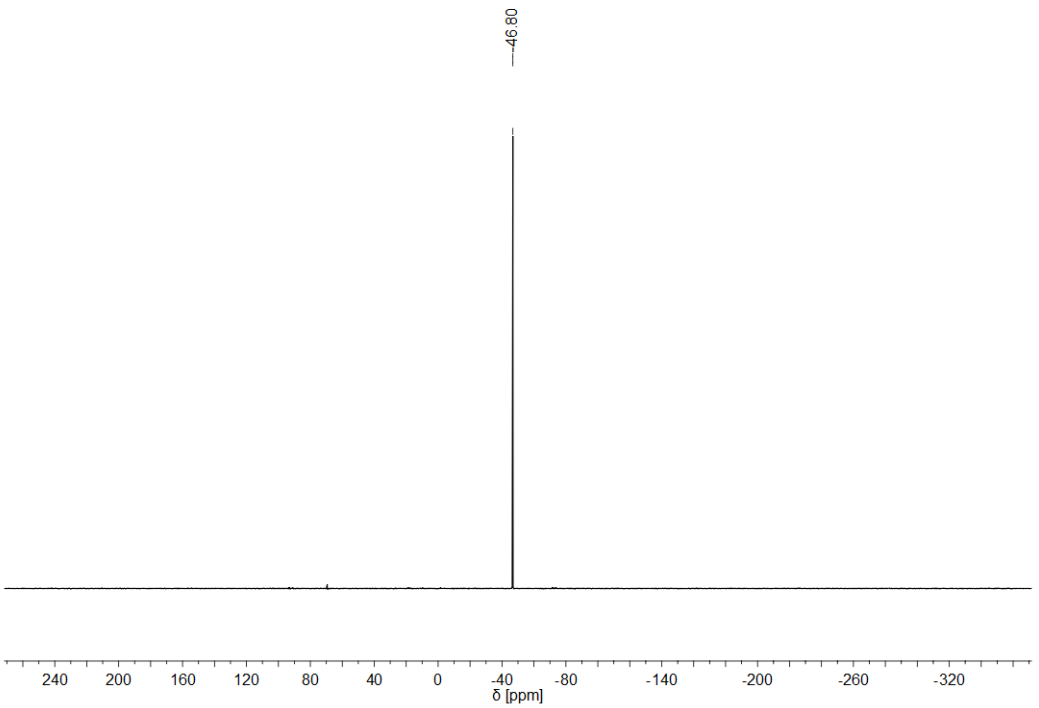

Figure S 133: ^{31}P{^{1}H} NMR spectrum of (*o*-OMeC$_6$H$_4$)$_4$P$_2$ synthesized from (*o*-OMeC$_6$H$_4$)$_2$PCl and PhSiH$_3$ by 9-BBN/[Et$_4$N]Cl catalysis (CDCl$_3$).

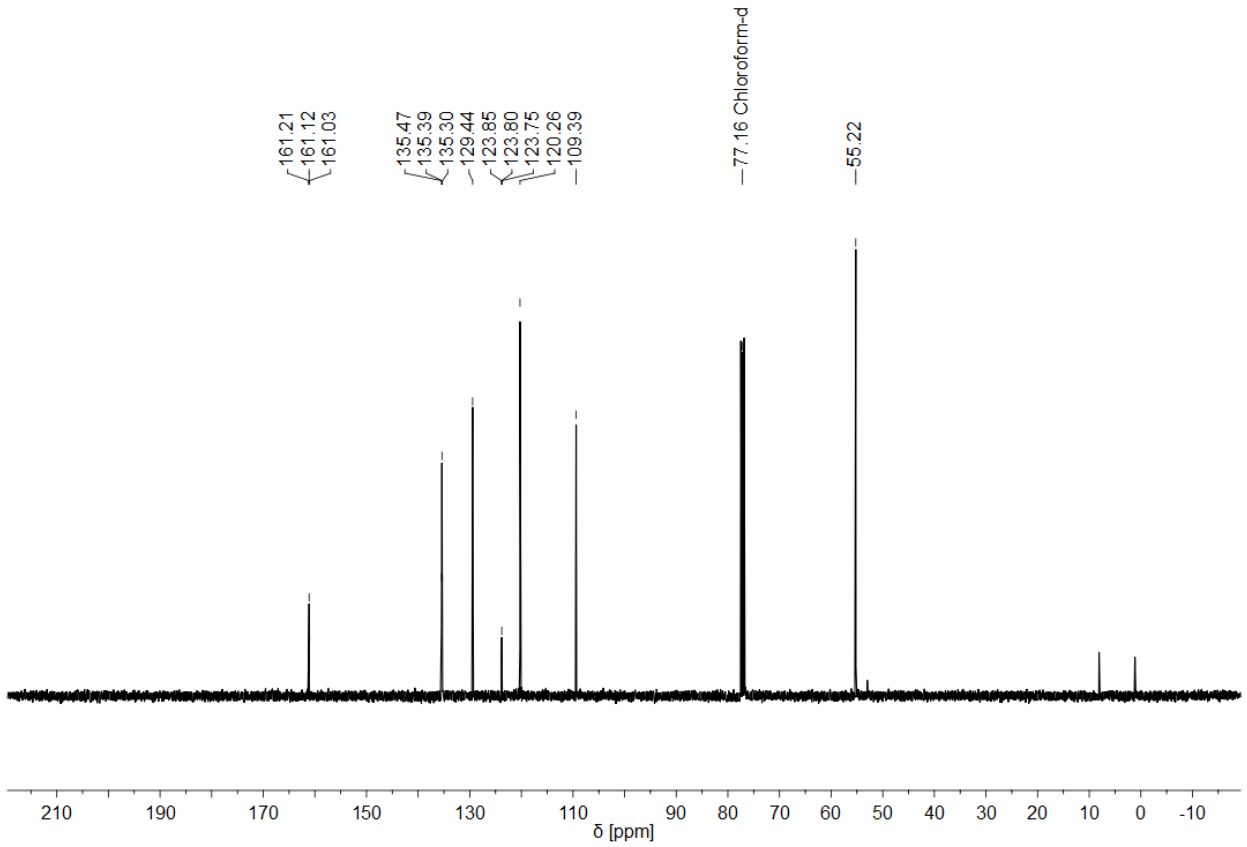

Figure S 134: ^{13}C NMR spectrum of (o-$OMeC_6H_4)_4P_2$ synthesized from (o-$OMeC_6H_4)_2PCl$ and $PhSiH_3$ by 9-BBN/$[Et_4N]Cl$ catalysis ($CDCl_3$).

4.5 Synthesis of (2,4,6-Me_3-$C_6H_2)_2PH$ by 9-BBN/$[Et_4N]Cl$ catalysis

(2,4,6-Me_3-$C_6H_2)_2PCl$ (54.9 mg, 0.18 mmol, 1 equiv), $PhSiH_3$ (19.5 mg, 0.18 mmol, 1 equiv), 9-BBN (1.1 mg, 0.01 mmol, 0.05 equiv) and $[Et_4N]Cl$ (1.5 mg, 0.01 mmol, 0.05 equiv) were dissolved in a mixture of MeCN/*o*DFB (1.5 mL, 1/2, V/V) and heated to 30 °C in a Schlenk tube. After 2 hours the volatiles were removed under vacuum. The remaining residue was dissolved in toluene and filtered over glass fiber filter paper. The filtrate was evaporated to dryness to afford (2,4,6-Me_3-$C_6H_2)_2PH$ in 76 % yield (37 mg, 0.14 mmol) ^1H NMR (C_6D_6) δ = 6.70 (s, 4H, $C_6Me_3H_2$), 5.32 (d, $^1J_{PH}$ = 229.5 Hz, PH), 2.27 (*o*-CH_3, Mes), 2.08, (s, *p*-CH_3, Mes) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6) δ = -93.2 (d, $^1J_{PH}$ = 229.5 Hz) ppm. ^{13}C NMR (C_6D_6) δ = 142.4 (d, J_{CP} = 12.35 Hz), 137.8, 130.0 (d, J_{CP} = 16.6 Hz), 129.6 (d, J_{CP} = 29 Hz), 23.0 (d, J_{CP} = 11.0 Hz), 21.0 ppm.

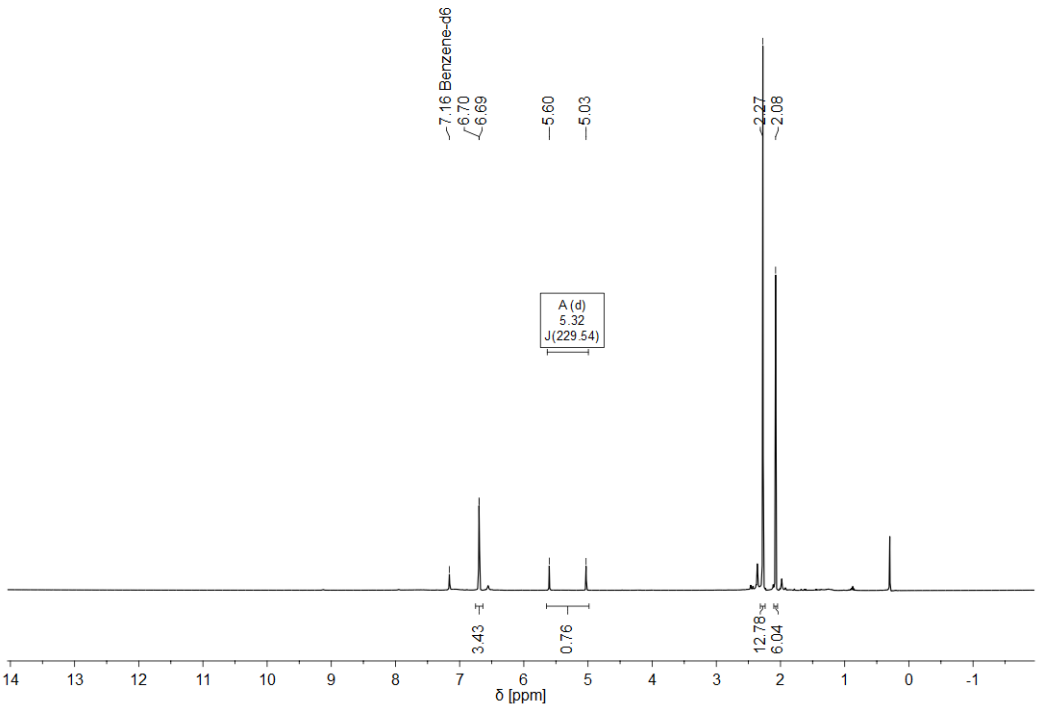

Figure S 135: ^{1}H NMR spectrum of Mes_2PH synthesized from Mes_2PCl and $PhSiH_3$ by 9-BBN/$[Et_4N]Cl$ catalysis (C_6D_6).

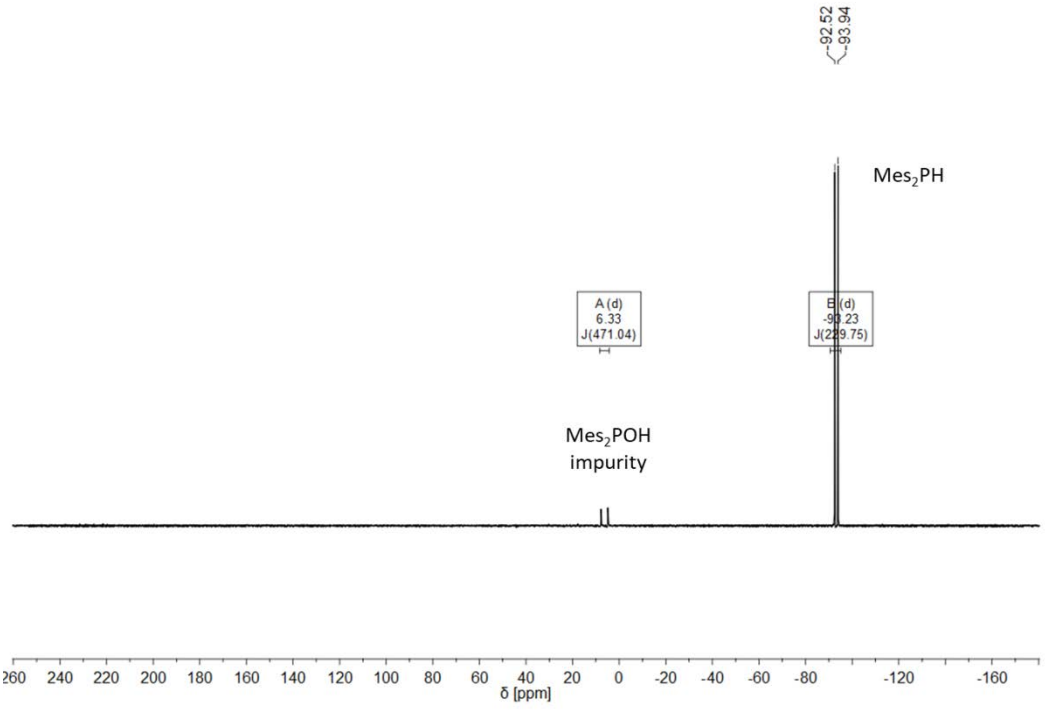

Figure S 136: ^{31}P NMR spectrum of Mes_2PH synthesized from Mes_2PCl and $PhSiH_3$ by 9-BBN/$[Et_4N]Cl$ catalysis (C_6D_6).

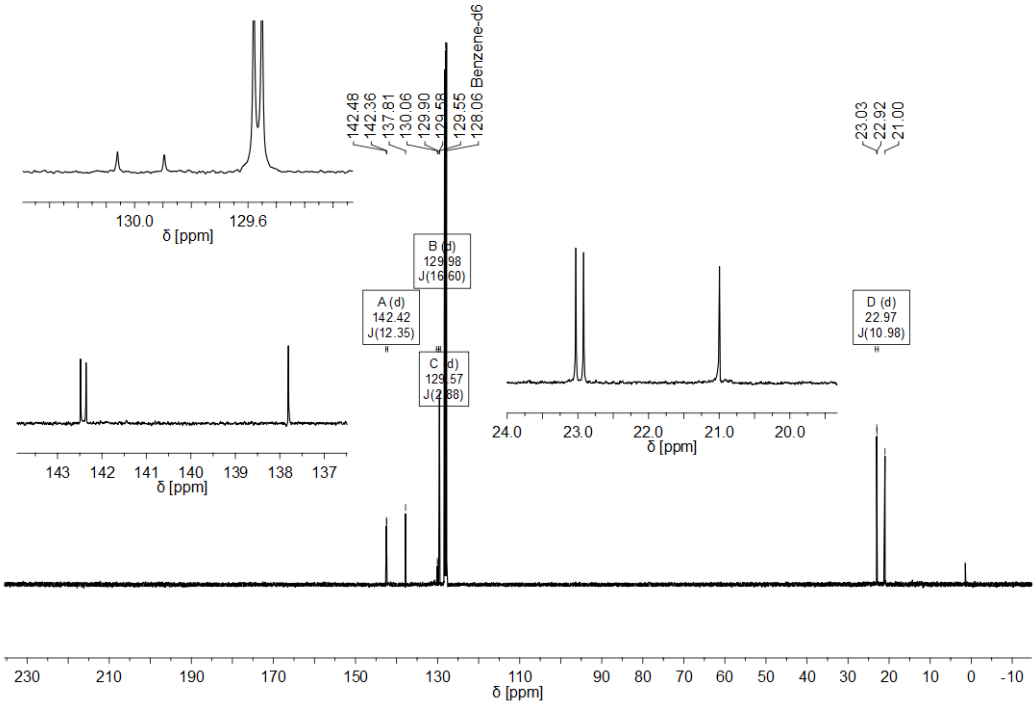

Figure S 137: ^{13}C NMR spectrum of Mes_2PH synthesized from Mes_2PCl and $PhSiH_3$ by 9-BBN/$[NEt_4][Cl]$ catalysis (C_6D_6).

4.6 Synthesis of $Ph_2tBu_2P_2$ by 9-BBN/$[Et_4N]Cl$ catalysis

Ph*t*BuPCl (180.6 mg, 0.9 mmol, 1 equiv), $PhSiH_3$ (97.4 mg, 0.9 mmol, 1 equiv), 9-BBN (5.5 mg, 0.05 mmol, 0.05 equiv) and $[Et_4N]Cl$ (7.5 mg, 0.05 mmol, 0.05 equiv) were dissolved in oDFB/MeCN (6 mL, 2/1, V/V) and heated to 60 °C for 8 hours. After 8 hours the volatiles were removed and the resulting residue was taken up in *n*-pentane and the solution was filtered. The filtrate was evaporated to dryness to afford $Ph_2tBu_2P_2$ in 73% yield (108 mg, 0.33 mmol). $Ph_2tBu_2P_2$ was isolated as a mixture of distereomers: 85% major isomer, 15% minor isomer. ^{1}H NMR (C_6D_6) δ = 8.05-6.84 (m, 10 H, Ph), 1.30 (pseudo triplet, tBu, minor diastereomer, 15%), 0.96 (pseudo triplet, *t*Bu, major isomer, 85%) ppm. ^{31}P NMR (C_6D_6) δ =-2.16 (s, minor isomer, 15%), -4.16 (s, major isomer, 85%) ppm. ^{13}C NMR (C_6D_6) δ = 29.97 (pseudo triplet, C(*C*H$_3$)$_3$, minor isomer), 30.04 (pseudo triplet, C(*C*H$_3$)$_3$, major isomer), 30.9 (m, *C*(CH$_3$)$_3$, minor isomer), 31.8 (pseudo triplet, *C*(CH$_3$)$_3$, major isomer), 127.6 (pseudo triplet, C_{ar}, minor isomer), 128.2 (pseudo triplet, C_{ar}, major isomer), 128.8 (s, C_{ar}, minor isomer), 129.8 (s, C_{ar}, major isomer), 133.7 (m, C_{ar}, minor isomer), 137.1 (m, C_{ar}, minor isomer), 137.6 (pseudo triplet, C_{ar}, major isomer), 137.9 (pseudo triplet, C_{ar}, major isomer) ppm. Data are similar to data reported in $CDCl_3$ from literature.[28]

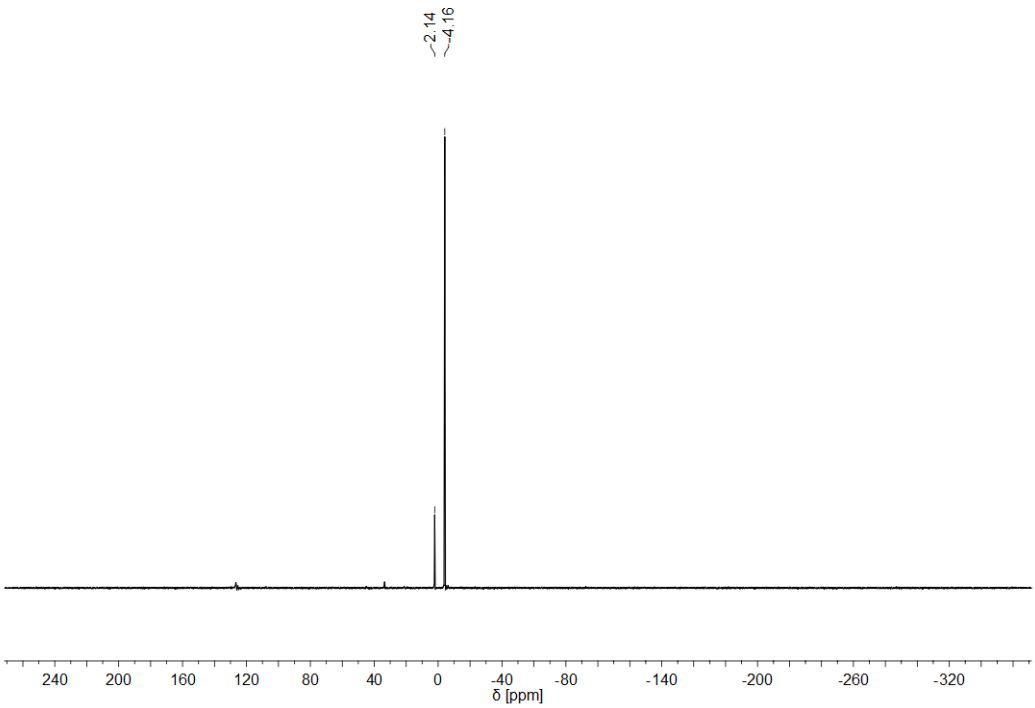

Figure S 138: ^{31}P NMR spectrum of $P_2Ph_2tBu_2$ synthesized from *t*BuPhPCl and $PhSiH_3$ by 9-BBN/$[Et_4N]Cl$ catalysis (C_6D_6).

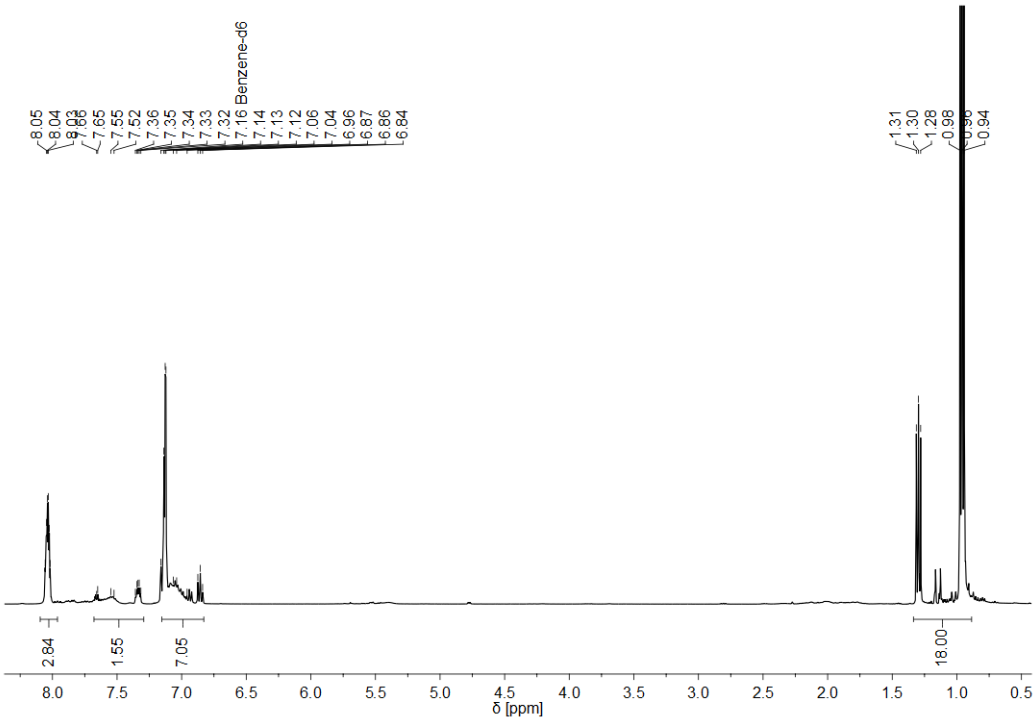

Figure S 139: ^{1}H NMR spectrum of $P_2Ph_2tBu_2$ synthesized from *t*BuPhPCl and $PhSiH_3$ by 9-BBN/$[Et_4N]Cl$ catalysis (C_6D_6).

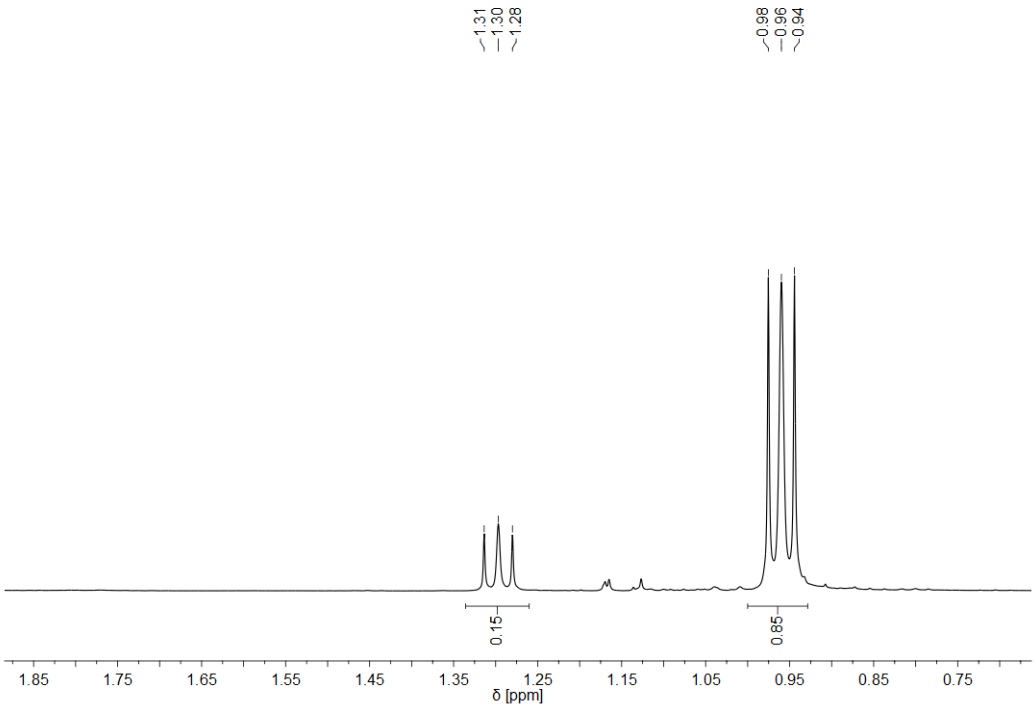

Figure S 140: Detail of ^{1}H NMR spectrum of $P_2Ph_2tBu_2$ synthesized from *t*BuPhPCl and $PhSiH_3$ by 9-BBN/$[Et_4N]Cl$ catalysis (C_6D_6).

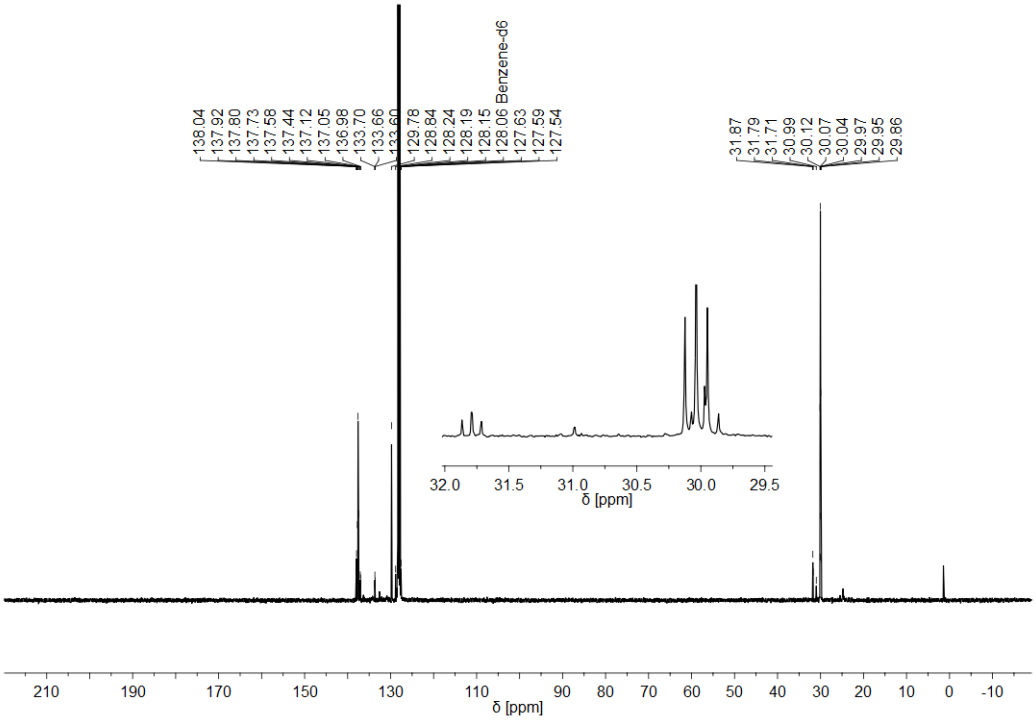

Figure S 141: ^{13}C NMR spectrum of $P_2Ph_2tBu_2$ synthesized from *t*BuPhPCl and $PhSiH_3$ by 9-BBN/$[Et_4N]Cl$ catalysis (C_6D_6).

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