Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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1. General Experimental

All reactions were carried out under a nitrogen atmosphere in Schlenk-type reaction vessels or NMR tubes. Dry degassed solvents were stored in Young-type flasks over molecular sieves 4Å. Air and moisture sensitive liquids and solutions were transferred *via* syringe. The water content in all solutions as monitored by titration on an Aquamax CouLo instrument was less than 10 ppm v/v.

Reagents and solvents were purchased from commercial suppliers and used as supplied unless otherwise stated. THF, DCM, toluene and diethyl ether were degassed and dried by passing through a Grubbs type Pure Solv-400-3-MD solvent purification system supplied by Innovative Technology Inc.

Oxygen-free nitrogen was obtained from BOC gases and passed over dry molecular sieves 4Å. Flash column chromatography was performed on Davisil particle size 0.040-0.063 mm

Melting points (MP) were determined on a Gallenkamp instrument in atmosphere of dry nitrogen. Mass spectra were run on a Waters LCT-TOF High-Resolution Accurate Mass (HRAM) Mass Spectrometer equipped with Electrospray Ionisation source with LockSpray accessory and Alliance 2795 separations module. NMR spectra were recorded on Agilent VNMRS 300, 400, 500 and 600 MHz spectrometers at 25 °C. Assignments were based on standard ^{1}H-^{1}H and ^{1}H-^{13}C two-dimensional techniques. ^{31}P NMR spectra recorded using a relaxation delay ≥ 3 seconds with suppression of heteronuclear NOE. Peak integrations were determined by using a MestreNova software package. All NMR samples of potentially air-sensitive compounds were made up under a nitrogen atmosphere in dry, degassed deuterated solvents stored over dry molecular sieves 4Å.

Where reactions were conducted at low temperatures, slush baths (liquid N_2 and appropriate solvent) were used:

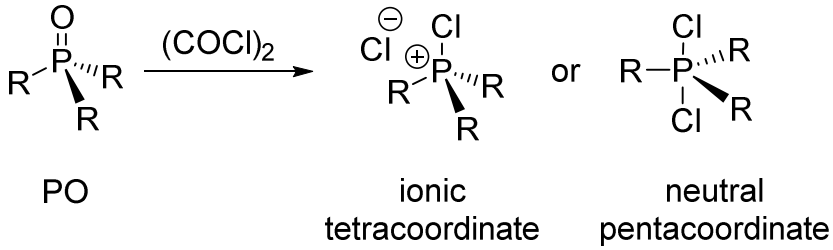
Table S1 Slush bath temperatures and composition for cold bath used to conduct reactions at low temperatures.

Temperature (°C)	Slush baths
-29	o-xylene/liquid N_2
-41	Acetonitrile (MeCN)/liquid N_2
-63	Chloroform/ liquid N_2
-83	Ethyl acetate/ liquid N_2

2. Chlorophosphonium Salts (CPS) & Dichlorophosphoranes

2.1. General procedure A: NMR scale preparation and characterisation of CPS/ dichloro-phosphoranes **3**, **3'**, **4** and **4'**

The CPS and dichlorophosphoranes were prepared by reacting the corresponding phosphine oxide (0.10 mmol, 1.00 equivalent) with oxalyl chloride (0.15 mmol, 1.50 equivalents) in the appropriate deuterated solvent.



Scheme S1 Reaction of phosphine oxide with oxalyl chloride to afford ionic tetracoordinate CPS or neutral pentacoordinate dichlorophosphorane.

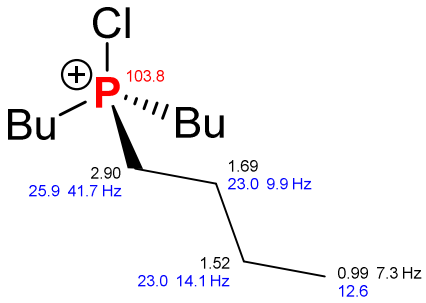
2.2. Characterisation data: Bu_3PCl_2 species

2.2.1. **3** in acetonitrile

^{31}P (162 MHz, CD_3CN) δ 103.8 ppm.

^{1}H (400 MHz, CD_3CN) δ 2.90 (m, 6H), 1.69 (m, 6H), 1.52 (m, 6H), 0.99 (t, *J* = 7.3 Hz, 9H) ppm.

^{13}C (101 MHz, CD_3CN) δ 25.9 (d, *J* = 41.7 Hz), 23.0 (d, *J* = 14.1 Hz), 23.0 (d, *J* = 9.9 Hz), 12.6 ppm.

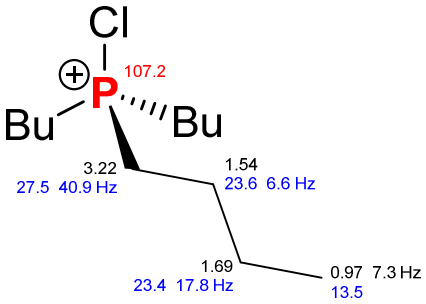


2.2.2. **3** in chloroform

^{31}P (162 MHz, $CDCl_3$) δ 107.2 ppm.

^{1}H (400 MHz, $CDCl_3$) δ 3.22 (m, 6H), 1.69 (m, 6H), 1.54 (m, 6H), 0.97 (t, *J* = 7.3 Hz, 9H) ppm.

^{13}C (101 MHz, $CDCl_3$) δ 27.5 (d, *J* = 40.9 Hz), 23.6 (d, *J* = 6.6 Hz), 23.4 (d, *J* = 17.8 Hz), 13.5 ppm.

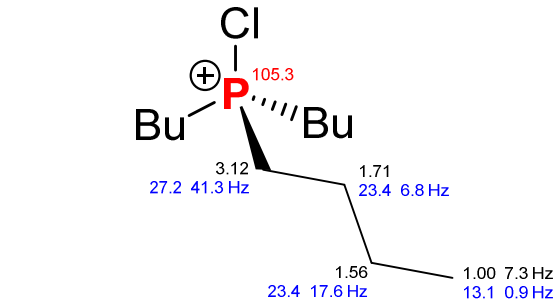


2.2.3. **3** in DCM

^{31}P (162 MHz, CD_2Cl_2) δ 105.3 ppm.

^{1}H (400 MHz, CD_2Cl_2) δ 3.12 (m, 6H), 1.71 (m, 6H), 1.56 (m, 6H), 1.00 (t, *J* = 7.3 Hz, 9H) ppm.

^{13}C (101 MHz, CD_2Cl_2) δ 27.2 (d, *J* = 41.3 Hz), 23.4 (d, *J* = 17.6 Hz), 23.4 (d, *J* = 6.8 Hz), 13.1 (d, *J* = 0.9 Hz) ppm.

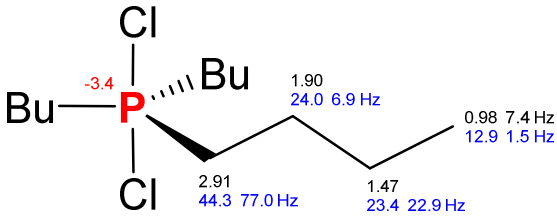


2.2.4. **3'** in THF

^{31}P (121 MHz, C_4D_8O) δ -3.4 ppm.

^{1}H (400 MHz, C_4D_8O) δ 2.91 (m, 6H), 1.90 (m, 6H), 1.47 (m, 6H), 0.98 (t, *J* = 7.4 Hz, 9H) ppm.

^{13}C (101 MHz, C_4D_8O) δ 44.3 (d, *J* = 77.0), 24.0 (d, *J* = 6.9 Hz), 23.4 (d, *J* = 22.9 Hz), 12.9 (d, *J* = 1.5 Hz) ppm.

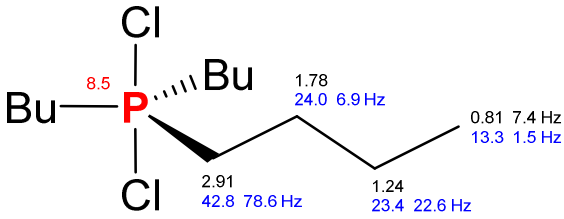


2.2.5. **3'** in benzene

^{31}P (202 MHz, C_6D_6) δ 8.5 ppm.

^{1}H (500 MHz, C_6D_6) δ 2.91 (m, 6H), 1.78 (m, 6H), 1.24 (m, 6H), 0.81 (t, *J* = 7.4 Hz, 9H) ppm.

^{13}C (126 MHz, C_6D_6) δ 42.8 (d, *J* = 78.6 Hz), 24.0 (d, *J* = 6.9 Hz), 23.4 (d, *J* = 22.6 Hz), 13.3 (d, *J* = 1.5 Hz) ppm.

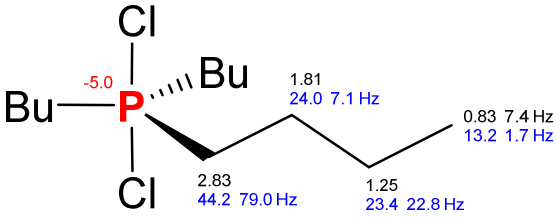


2.2.6. **3'** in toluene

^{31}P (202 MHz, $C_6D_5CD_3$) δ -5.0 ppm.

^{1}H (500 MHz, $C_6D_5CD_3$) δ 2.83 (m, 6H), 1.81 (m, 6H), 1.25 (m, 6H), 0.83 (t, *J* = 7.4 Hz, 9H) ppm.

^{13}C (126 MHz, $C_6D_5CD_3$) δ 44.2 (d, *J* = 79.0 Hz), 24.0 (d, *J* = 7.1 Hz), 23.4 (d, *J* = 22.8 Hz), 13.2 (d, *J* = 1.7 Hz) ppm.



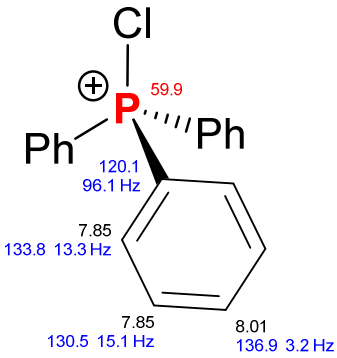
2.3. Characterisation data: Ph_3PCl_2 species

2.3.1. **4** in acetonitrile

^{31}P (162 MHz, CD_3CN) δ 59.9 ppm.

^{1}H (400 MHz, CD_3CN) δ 8.01 (m, 3H), 7.85 (m, 12H) ppm.

^{13}C (101 MHz, CD_3CN) δ 136.9 (d, J = 3.2 Hz), 133.8 (d, J = 13.3 Hz), 130.5 (d, J = 15.1 Hz), 120.1 (d, J = 96.1 Hz) ppm.



2.3.2. **4** in dichloromethane

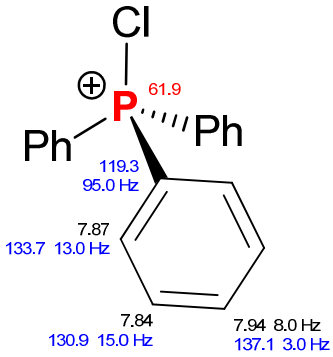
This has been reported elsewhere.[1]

2.3.3. **4** in chloroform

^{31}P (162 MHz, CD_3CN) δ 59.9 ppm.

^{1}H (400 MHz, CD_3CN) δ 8.01 (m, 3H), 7.85 (m, 12H) ppm.

^{13}C (101 MHz, CD_3CN) δ 136.9 (d, J = 3.2 Hz), 133.8 (d, J = 13.3 Hz), 130.5 (d, J = 15.1 Hz), 120.1 (d, J = 96.1 Hz) ppm.

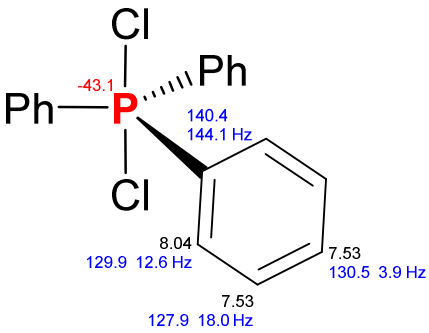


2.3.4. **4'** in THF

^{31}P (162 MHz, C_4D_8O) δ -43.1 ppm.

^{1}H (400 MHz, C_4D_8O) δ 8.04 (m, 6H), 7.53 (m, 9H) ppm.

^{13}C (101 MHz, C_4D_8O) δ 140.4 (d, J = 144.1 Hz), 130.5 (d, J = 3.9 Hz), 129.9 (d, J = 12.6 Hz), 127.9 (d, J = 18.0 Hz) ppm.

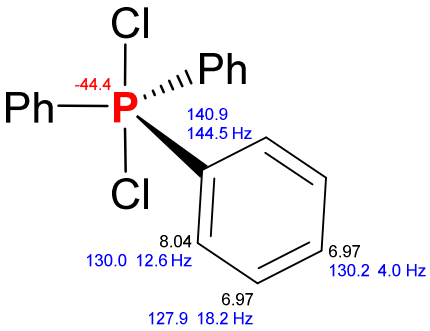


2.3.5. **4'** in benzene

^{31}P (243 MHz, C_6D_6) δ -44.4 ppm.

^{1}H (600 MHz, C_6D_6) δ 8.04 (m, 6H), 6.97 (m, 9H) ppm.

^{13}C (151 MHz, C_6D_6) δ 140.9 (d, *J* = 144.5 Hz), 130.2 (d, *J* = 4.0 Hz), 130.0 (d, *J* = 12.6 Hz), 127.9 (d, *J* = 18.2 Hz) ppm.

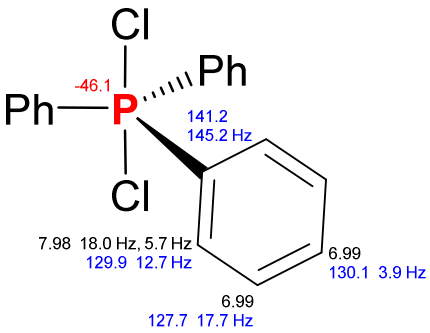


2.3.6. **4'** in toluene

^{31}P (243 MHz, $C_6D_5CD_3$) δ -46.1.

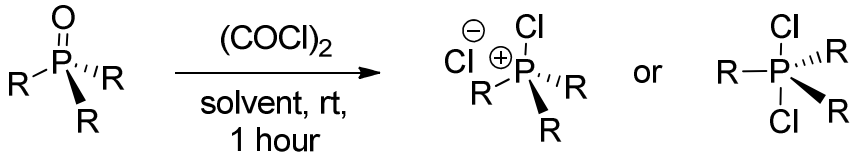
^{1}H (600 MHz, $C_6D_5CD_3$) δ 7.98 (ddt, *J* = 18.0, 5.7, 1.7 Hz, 6H), 6.99 (m, 9H) ppm.

^{13}C (151 MHz, $C_6D_5CD_3$) δ 141.2 (d, *J* = 145.2 Hz), 130.1 (d, *J* = 3.9 Hz), 129.9 (d, *J* = 12.7 Hz), 127.7 (d, *J* = 17.7 Hz) ppm.



3. Screening for reaction conditions

3.1. General procedure B: preparation of dichlorophosphorane/CPS stock solution



1 R = Bu
2 R = Ph

3 R = Bu
4 R = Ph

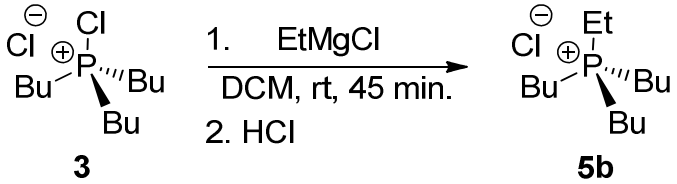
3' R = Bu

Scheme S2 Reaction of phosphine oxide with oxalyl chloride to afford ionic tetracoordinate CPS or neutral pentacoordinate dichlorophosphorane.

A 0.2 M stock solution of dichlorophosphorane/CPS was prepared as follows. A 100 mL Young's flask equipped with a stir bar was charged with phosphine oxide (1 equivalent) under an atmosphere of nitrogen. The oxide was dried gently and the appropriate solvent (a sufficient amount to make a 0.2 M solution of oxide) added. To the solution of oxide, oxalyl chloride (1.02 equivalents) was added slowly by syringe. Effervescence was immediately observed, which ceased within 1 hour. After this time, ^{31}P NMR spectroscopy indicated complete conversion of the oxide to dichlorophosphorane/CPS.

3.2. Solvent screening

3.2.1. Reaction of **3** with ethylmagnesium chloride in DCM



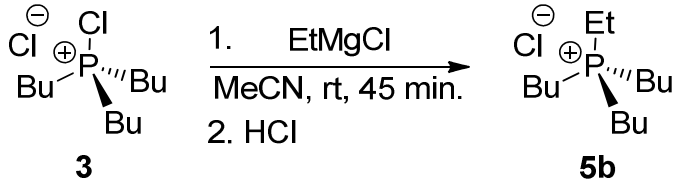
3 **5b**

Scheme S3 Reaction of CPS **3** (1 equivalent) with ethylmagnesium chloride (2 equivalents) in DCM affords QPS **5b**.

A solution of **3** in DCM was prepared according to general procedure B. Then, 0.70 mL of the solution of **3** (0.14 mmol, 1.00 equivalent) was transferred to a dry, N_2-flushed 20 mL flask equipped with a stir bar. To this, ethylmagnesium chloride (2.7 M in THF, 0.10 mL, 0.27 mmol, 1.93 equivalents) was added and the resulting mixture was stirred for 45 minutes. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (0.14 mL, 0.28 mmol, 2.00 equivalents). A small volume of the quenched reaction mixture was withdrawn, and the solvent was removed *in vacuo* and the residue was dissolved in $CDCl_3$ (1.00 mL). Filtration of insoluble inorganic salts gave a transparent solution of the crude product containing **5b** and phosphine oxide hydrochloride **1**•HCl.

^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of two main species: δ 61.8 (**1**•HCl, 3%) and δ 34.7 (QPS **5b**, 96 %).

3.2.2. Reaction of **3** with ethylmagnesium chloride in MeCN



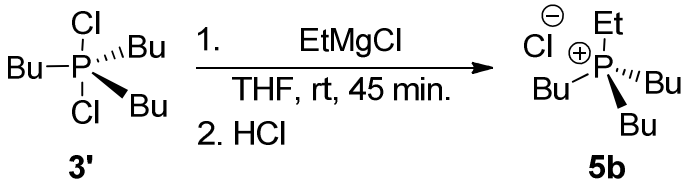
3 **5b**

Scheme S4 Reaction of CPS **3** (1 equivalent) with ethylmagnesium chloride (2 equivalents) in MeCN affords QPS **5b**.

A solution of **3** in MeCN was prepared according to general procedure B. Then, 0.70 mL of the solution of **3** (0.14 mmol, 1.00 equivalent) was transferred to a dry, N_2-flushed 20 mL flask equipped with a stir bar. To this, ethylmagnesium chloride (2.7 M in THF, 0.10 mL, 0.27 mmol, 1.93 equivalents) was added and the resulting mixture was stirred for 45 minutes. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (0.14 mL, 0.28 mmol, 2.00 equivalents). A small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and the residue dissolved in $CDCl_3$ (1.00 mL). Filtration of insoluble inorganic salts gave a transparent solution of the crude product containing **5b** and phosphine oxide hydrochloride **1**•HCl.

^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of two main species: δ 48.7 (**1**•HCl, 73 %) and δ 34.8 (QPS **5b**, 27 %).

3.2.3. Reaction of **3'** with ethylmagnesium chloride in THF



3' **5b**

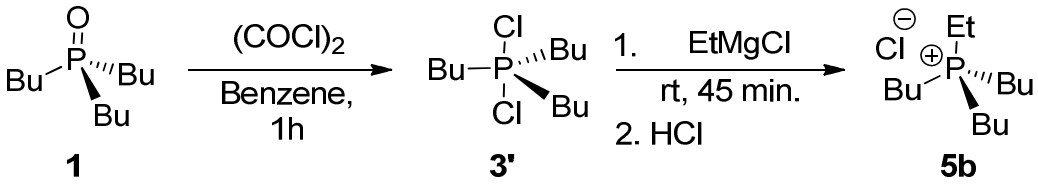
Scheme S5 Reaction of dichlorophosphorane **3'** (1 equivalent) with ethylmagnesium chloride (2 equivalents) in THF affords QPS **5b**.

A solution of **3'** in MeCN was prepared according to general procedure B. Then, 0.70 mL of the solution of **3'** (0.14 mmol, 1.00 equivalent) was transferred to a dry, N_2-flushed 20 mL flask equipped with a stir bar. To this, ethylmagnesium chloride (2.7 M in THF, 0.10 mL, 0.27 mmol, 1.93 equivalents) was added and the resulting mixture was stirred for 45 minutes. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (0.14 mL, 0.28 mmol, 2.00 equivalents). A small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and the residue dissolved in $CDCl_3$ (1.00 mL). Filtration of

insoluble inorganic salts gave a transparent solution of the crude product containing **5b** and phosphine oxide hydrochloride **1**•HCl.

^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis indicated the presence of two main species: δ 60.1 (**1**•HCl, 5 %) and δ 34.7 (QPS **5b**, 95 %).

3.2.4. Reaction of **3'** with ethylmagnesium chloride in benzene

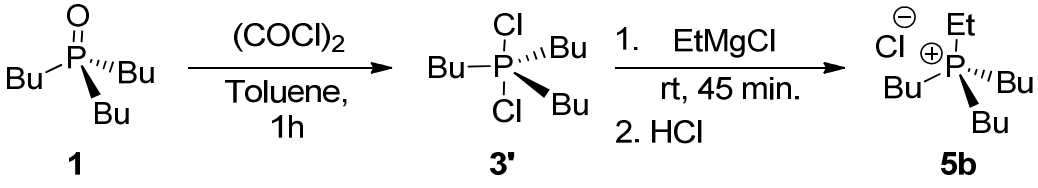


Scheme S6 Reaction of phosphine oxide **1** with oxalyl chloride in benzene affords dichlorophosporane **3'**. Upon reaction of **3'** (1 equivalent) with ethylmagnesium chloride (2 equivalents) QPS **5b** is formed.

A 100 mL flask equipped with a stir bar was charged with tributylphosphine oxide **1** (518 mg, 2.37 mmol,1.00 equivalent). The oxide was dried gently and dry benzene (12.00 mL) added to give a 0.2 M solution of **1**. To the solution of **1**, oxalyl chloride (0.20 mL, 1.02 equivalents) was added slowly by syringe. Effervescence was immediately observed, which ceased within 1 hour. Then, ethylmagnesium chloride (2.7 M in THF, 1.75 mL, 4.74 mmol, 2.00 equivalents) was added and the resulting mixture was stirred for 45 minutes, after which time the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (2.37 mL, 4.74 mmol, 2.00 equivalents). A small volume of the quenched reaction mixture was withdrawn, the solvent was removed *in vacuo* and the residue dissolved in $CDCl_3$ (1.00 mL). Filtration of insoluble inorganic salts gave a transparent solution of the crude product containing **5b** and phosphine oxide hydrochloride **1**•HCl.

^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis indicated the presence of two main species: δ 60.1 (**1**•HCl, 15 %) and δ 34.6 (QPS **5b**, 79 %).

3.2.5. Reaction of **3'** with ethylmagnesium chloride in toluene



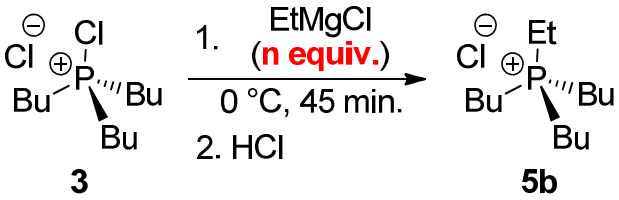
Scheme S7 Reaction of phosphine oxide 1 with oxalyl chloride in toluene affords dichlorophosporane **3'**. Upon reaction of **3'** (1 equivalent) with ethylmagnesium chloride (2 equivalents) QPS **5b** is formed.

A 100 mL flask equipped with a stir bar was charged with tributylphosphine oxide **1** (230 mg, 1.05 mmol,1.00 equivalent). The oxide was dried gently and dry toluene (5.30 mL) added to give a 0.2 M solution of **1**. To the solution of **1**, oxalyl chloride (0.09 mL, 1.02 equivalents) was added slowly by syringe. Effervescence was immediately observed, which ceased within 1 hour. Then, ethylmagnesium chloride (2.7 M in THF, 0.78 mL, 2.10 mmol, 2.00 equivalents) was added and the resulting mixture was stirred for 45 minutes. After this time the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (1.05 mL, 4.74 mmol, 2.00 equivalents). A small volume of the quenched reaction mixture was withdrawn, the solvent was removed *in vacuo* and the residue dissolved in $CDCl_3$ (1.00 mL). Filtration of insoluble inorganic salts gave a transparent solution of the crude product containing **5b** and phosphine oxide hydrochloride **1**•HCl.

^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis indicated the presence of two main species: δ 61.8 (**1**•HCl, 47 %) and δ 34.6 (QPS **5b**, 53 %).

3.3. Grignard reagent equivalent screening

3.3.1. Reaction of **3** with ethylmagnesium chloride



3 **5b**

Scheme S 8 Grignard equivalent screening: reaction of CPS **3** (1 equivalent) with ethylmagnesium chloride (varying equivalents).

To a dry, N_2-flushed 10 mL flask equipped with a stir bar, an appropriate volume of a 0.2 M solution of **3** in DCM (see table S2, prepared according to general procedure B) was added. The flask was cooled to 0 °C. Then, ethylmagnesium chloride (2.7 M in THF, see Table S2) was added and the resulting mixture was stirred for 45 minutes. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (see Table S2).

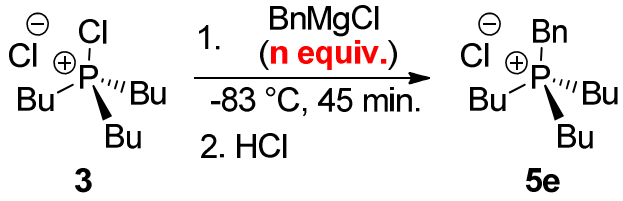
After 10 minutes, the flask was removed from the cold bath and its contents were allowed to warm to room temperature. A small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and the residue dissolved in $CDCl_3$ (1.00 mL). Filtration of the insoluble salts gave a transparent solution containing the crude product **5b** and phosphine oxide hydrochloride **1**•HCl. ^{31}P NMR spectroscopic analysis indicated the yield QPS **5b**, as summarized in Table S2.

Table S2 Grignard equivalent screening for the reaction of chlorotributylphosphonium chloride **3** with ethylmagnesium chloride.

Entry	V, mL **3,** mmol	Eq. **3**	V, mL EtMgCl, mmol	Eq. EtMgCl	V, mL HCl, mmol	Eq. HCl	**5b**[a] %
1	1.20, 0.24	1.00	0.10, 0.27	1.13	0.14, 0.28	1.17	94
2	1.00, 0.20	1.00	0.10, 0.27	1.35	0.14, 0.28	1.40	97
3	0.90, 0.18	1.00	0.10, 0.27	1.50	0.14, 0.28	1.56	97
4	0.70, 0.14	1.00	0.10, 0.27	1.93	0.14, 0.28	2.00	100

[a] determined by ^{31}P NMR of crude reaction mixture.

3.3.2. Reaction of **3** with benzylmagnesium chloride



Scheme S9 Grignard equivalent screening: reaction of CPS **3** (1 equivalent) with benzylmagnesium chloride (varying equivalents).

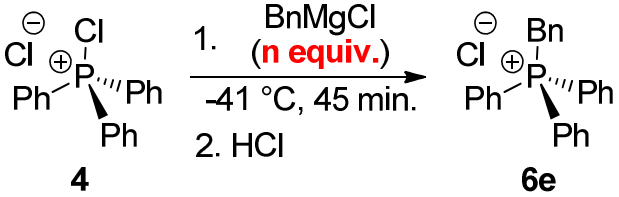
To a dry, N_2-flushed 10 mL flask equipped with a stir bar, an appropriate volume of a 0.2 M solution of **3** in DCM (see table S3, prepared according to general procedure B) was added. The flask was cooled to -83 °C. Then, benzylmagnesium chloride (1.4 M in THF, see Table S3) was added and the resulting mixture was stirred for 45 minutes. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (see Table S3). After 10 minutes, the flask was removed from the cold bath and its contents were allowed to warm to room temperature. A small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and the residue dissolved in $CDCl_3$ (1.00 mL). Filtration of the insoluble salts gave a transparent solution containing the crude product **5e** and phosphine oxide hydrochloride **1**•HCl. ^{31}P NMR spectroscopic analysis indicated the yield QPS **5e**, as summarized in Table S3.

Table S3 Grignard equivalent screening for the reaction of chlorotributylphosphonium chloride **3** with benzylmagnesium chloride

Entry	V, mL **3,** mmol	Eq. **3**	V, mL BnMgCl, mmol	Eq. BnMgCl	V, mL HCl, mmol	Eq. HCl	**5e**[a] %
1	1.00, 0.20	1.00	0.20, 0.28	1.4	0.14, 0.28	1.4	86
2	0.90, 0.18	1.00	0.20, 0.28	1.56	0.14, 0.28	1.56	90
3	0.80, 0.16	1.00	0.20, 0.28	1.75	0.14, 0.28	1.75	92
4	0.70, 0.14	1.00	0.20, 0.28	2.00	0.14, 0.28	2.00	94

[a] determined by ^{31}P NMR of crude reaction mixture.

3.3.3. Reaction of **4** with benzylmagnesium chloride



Scheme S10 Grignard equivalent screening: reaction of CPS **4** (1 equivalent) with benzylmagnesium chloride (varying equivalents).

To a dry, N_2-flushed 10 mL flask equipped with a stir bar, an appropriate volume of a 0.2 M solution of **4** in DCM (see table S4, prepared according to general procedure B) was added. The flask was cooled to -41 °C. Then, benzylmagnesium chloride (1.4 M in THF, see Table S4) was added and the resulting mixture was stirred for 45 minutes. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (see Table S4). After 10 minutes, the flask was removed from the cold bath and its contents were allowed to warm to room temperature. A small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and the residue dissolved in $CDCl_3$ (1.00 mL). Filtration of the insoluble salts gave a transparent solution containing the crude product **6e** and phosphine oxide **2**. ^{31}P NMR spectroscopic analysis indicated the yield QPS **6e**, as summarized in Table S4.

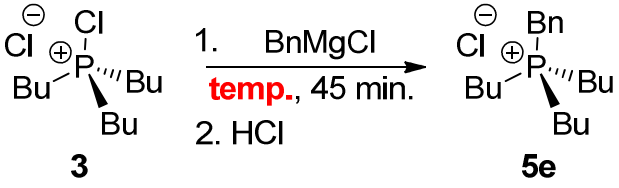
Table S4 Grignard equivalent screening for the reaction of chlorotriphenylphosphonium chloride **4** with benzylmagnesium chloride.

Entry	V, mL **4,** mmol	Eq. **4**	V, mL BnMgCl, mmol	Eq. BnMgCl	V, mL HCl, mmol	Eq. HCl	**6e**[a] %
1	1.20, 0.24	1.00	0.20, 0.28	1.17	0.14, 0.28	1.17	67
2	1.00, 0.20	1.00	0.20, 0.28	1.40	0.14, 0.28	1.40	80
3	0.90, 0.18	1.00	0.20, 0.28	1.56	0.14, 0.28	1.56	87
4	0.70, 0.14	1.00	0.20, 0.28	2.00	0.14, 0.28	2.00	94

[a] determined by ^{31}P NMR of crude reaction mixture.

3.4. Reaction temperature screening

3.4.1. Reaction of **3** with benzylmagnesium chloride



Scheme S11 Reaction temperature screening: reaction of CPS **3** (1 equivalent) with benzylmagnesium chloride (2 equivalents) conducted at different reaction temperatures.

A solution of **3** in DCM was prepared according to general procedure B. Then, 0.70 mL of the solution of **3** (0.14 mmol, 1.00 equivalent) was transferred to a dry, N_2-flushed 20 mL flask equipped with a stir bar. The solution was cooled, where applicable, to the appropriate temperature (see Table S5). Then, benzylmagnesium chloride (1.4 M in THF, 0.20 mL, 0.28 mmol, 2.00 equivalents) was added and the resulting mixture was stirred for 45 minutes. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (0.14 mL, 0.28 mmol, 2.00 equivalents). After 10 minutes, the flask was removed from the cold bath and its contents were allowed to warm to room temperature (where applicable). A small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of the insoluble salts gave a transparent solution containing the crude product **5e** and phosphine oxide hydrochloride **1**•HCl. ^{31}P NMR spectroscopic analysis indicated the yield of the corresponding QPS **5e,** as summarized in Table S5 and illustrated in Figure S1.

Table S5 Temperature screening for the reaction of chlorotributylphosphonium chloride **3** with benzylmagnesium chloride

Entry	T, °C	**5e**[a] %
1	rt	55
2	0	74
4	-41	86
5	-63	87
6	-83	94

[a] determined by ^{31}P NMR of crude reaction mixture.

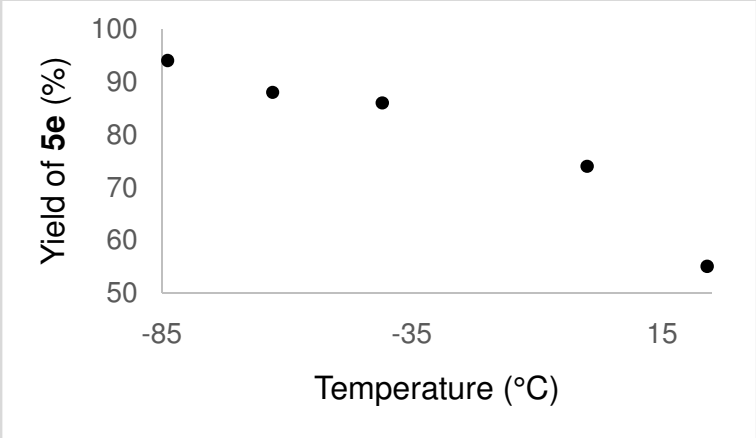
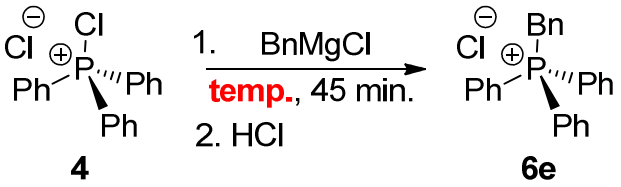


Figure S1 Plot of yield of QPS **5e** as a function of temperature

3.4.2. Reaction of **4** with benzylmagnesium chloride



Scheme S12 Reaction temperature screening: reaction of CPS **4** (1 equivalent) with benzylmagnesium chloride (2 equivalents) conducted at different reaction temperatures.

A solution of **4** in DCM was prepared according to general procedure B. Then, 0.70 mL of the solution of **4** (0.14 mmol, 1.00 equivalent) was transferred to a dry, N_2-flushed 20 mL flask equipped with a stir bar. The solution was cooled, where applicable, to the appropriate temperature (see table S6). Then, benzylmagnesium chloride (1.4 M in THF, 0.20 mL, 0.28 mmol, 2.00 equivalents) was added and the resulting mixture was stirred for 45 minutes. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (0.14 mL, 0.28 mmol, 2.00 equivalents). After 10 minutes, the flask was removed from the cold bath and its contents were allowed to warm to room temperature (where applicable). A small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of insoluble salts gave a transparent solution containing the crude product **6e** and phosphine oxide **2**. ^{31}P NMR spectroscopic analysis indicated the yield of the corresponding QPS **6e,** as summarized in table S6 and illustrated in figure S2.

Table S6 Temperature screening for the reaction of chlorotriphenylphosphonium chloride **4** with benzylmagnesium chloride

Entry	T,°C	**6e**[a] %
1	rt	73
2	0	79
4	-29	92
5	-41	94

[a] determined by ^{31}P NMR of crude reaction mixture.

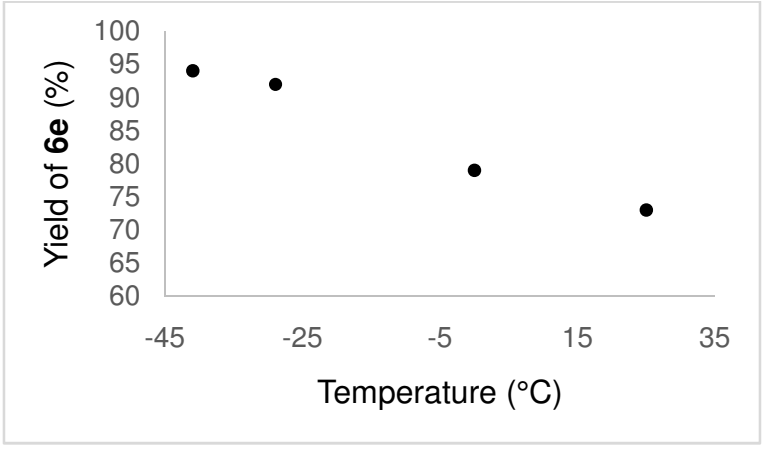
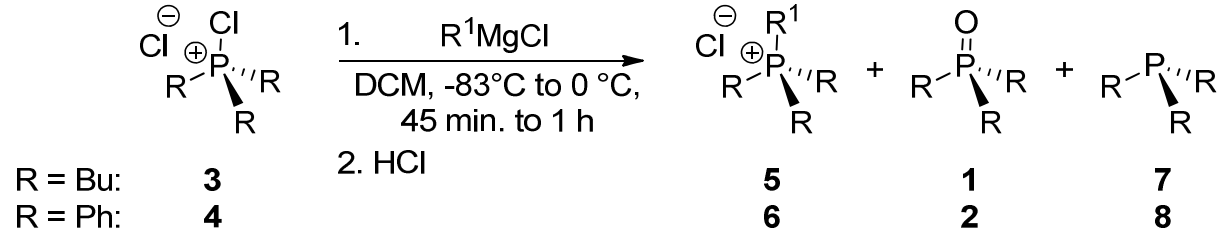


Figure S2 Plot of yield of QPS **6e** as a function of temperature

4. Quaternary phosphonium salts: synthesis & characterisation data.

4.1. General procedure C: Preparation of QPS **3**



R = Bu:	**3**	**5**	**1**	**7**
R = Ph:	**4**	**6**	**2**	**8**

Scheme S13 Preparation of QPS **5**/**6** by reaction of CPS **3**/**4** with organomagnesium chlorides (R^1MgCl).

A 50 mL flask equipped with a stir bar was charged with a DCM solution of CPS and the flask was cooled to the specified reaction temperature. A solution of the appropriate organomagnesium chloride (R^1MgCl, 2.00 equivalents) was added slowly down the side of the flask. The resulting solution was stirred at the specified temperature for 45 minutes to 1 hour. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether. After ten minutes, the flask was removed from the cold bath (where applicable) and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. The filtration of insoluble inorganic salts gave a transparent solution containing the crude QPS product. The bulk of the quenched reaction was concentrated by evaporation to yield, in the majority of cases, an oily residue. The residue was dissolved in DCM (15 mL/1 mmol of CPS used) and the DCM layer was washed with a mixture of equal parts of water and brine (2 x 3 mL for alkyltriphenylphosphonium salts and 2 x 1-2 mL for tetraalkylphosphonium salts). Then, the aqueous phases were combined and washed with an equal volume of DCM. Finally, the organic phases were combined and washed with an equal volume of brine. The organic layer was eluted through sodium sulphate and concentrated *in vacuo* to yield a clear oily residue, which in most cases crystallized on standing to give the QPS.

4.2. Preparation of tetraalkylphosphonium chlorides and phenyltributylphosphonium chloride

4.2.1. Methyltributylphosphonium chloride **5a**

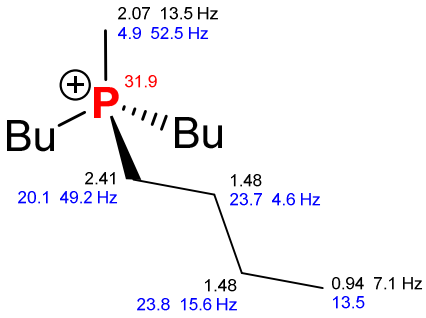
This was prepared from a stock solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and methylmagnesium chloride (3.0 M solution in THF, 0.67 mL, 2.01 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of

5a and **1**•HCl in a 97:3 ratio. The crude product (233 mg) was isolated as transparent oil and characterized without further purification. HRMS (ES^+) m/z: calculated for $C_{13}H_{30}P^+$ 217.2085, found 217.2095.

^{31}P NMR (121 MHz, $CDCl_3$) δ 31.9 ppm.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (m, 6H), 2.07 (d, *J* = 13.5 Hz, 3H), 1.48 (m, 12H), 0.94 (t, *J* = 7.1 Hz, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 23.8 (d, *J* = 15.6 Hz), 23.7 (d, *J* = 4.6 Hz), 20.1 (d, *J* = 49.2 Hz), 13.5, 4.9 (d, *J* = 52.5 Hz) ppm.



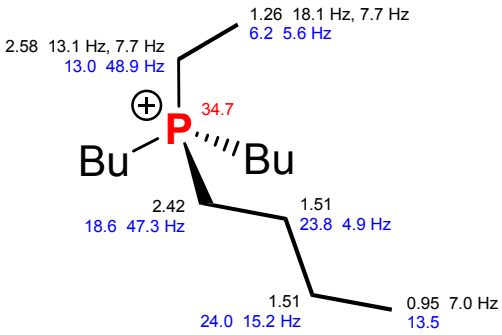
4.2.2. Ethyltributylphosphonium chloride **5b**

This was prepared from a stock solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and ethylmagnesium chloride (2.7 M solution in THF, 0.74 mL, 2.00 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **5b** and **1**•HCl in a 95:5 ratio. The crude product (249 mg) was isolated as a transparent oil that crystallized on standing. Precipitation from ethyl acetate/chloroform using diethyl ether afforded **5b** (226 mg, 85 %) as crystalline sheets: MP 78-80 °C, lit.[7] MP 70.1 °C; HRMS (ES^+) m/z: calculated for $C_{14}H_{32}P^+$ 231.2242, found 231.2248.

^{31}P NMR (121 MHz, $CDCl_3$) δ 34.7 ppm.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.58 (dq, *J* = 13.1, 7.7 Hz, 2H), 2.42 (m, 6H), 1.51 (m, 12H), 1.26 (dt, *J* = 18.1, 7.7 Hz, 3H), 0.95 (t, *J* = 7.0 Hz, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 24.0 (d, *J* = 15.2 Hz), 23.8 (d, *J* = 4.9 Hz), 18.6 (d, *J* = 47.3 Hz), 13.5, 13.0 (d, *J* = 48.9 Hz), 6.2 (d, *J* = 5.6 Hz) ppm.



4.2.3. *n*-Propyltributylphosphonium chloride **5c**

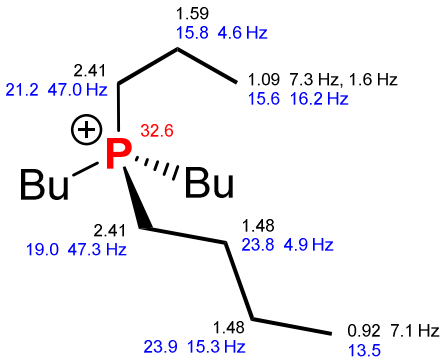
This was prepared from a stock solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and *n*-propylmagnesium chloride (2.0 M solution in diethyl ether, 1.00 mL, 2.00 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **5c** and **1**•HCl in a 97:3 ratio. The crude product (267 mg) was isolated as oil that crystalized on standing. Precipitation from ethyl acetate/chloroform using diethyl ether afforded **5c** (255 mg, 91 %) as transparent crystalline sheets: MP 86-

88 °C, lit.[7] MP 78-80 °C; HRMS (ES$^+$) m/z: calculated for $C_{15}H_{34}P^+$ 245.2398, found 245.2408.

^{31}P NMR (121 MHz, $CDCl_3$) δ 32.6 ppm.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (m, 8H), 1.59 (m, 2H), 1.48 (m, 12H), 1.09 (td, *J* = 7.3, 1.6 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 23.9 (d, *J* = 15.3 Hz), 23.8 (d, *J* = 4.9 Hz), 21.2 (d, *J* = 47.0 Hz), 19.0 (d, *J* = 47.3 Hz), 15.8 (d, *J* = 4.6 Hz), 15.6 (d, *J* = 16.2 Hz), 13.5 ppm.



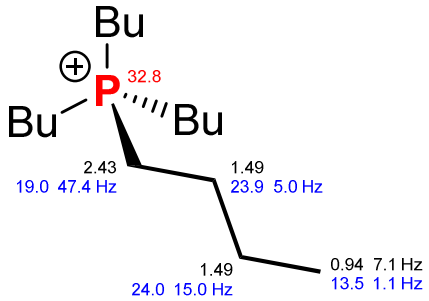
4.2.4. Tetrabutylphosphonium chloride **5d**

This was prepared from a stock solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and *n*-butylmagnesium chloride (2.0 M solution in THF, 1.00 mL, 2.00 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **5d** and **1**•HCl in a 96:4 ratio. The crude product (263 mg) was isolated as yellow oil. Precipitation from ethyl acetate/chloroform using diethyl ether afforded **5d** (236 mg, 80 %) as fine crystals: MP 80-82 °C, lit.[7] MP 78°C; HRMS (ES$^+$) m/z: calculated for $C_{16}H_{36}P^+$ 259.2555, found 259.2557.

^{31}P NMR (121 MHz, $CDCl_3$) δ 32.8 ppm.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (m, 8H), 1.49 (m, 16H), 0.94 (t, *J* = 7.1 Hz,12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 24.0 (d, *J* = 15.0 Hz), 23.9 (d, *J* = 5.0 Hz), 19.0 (d, *J* = 47.4 Hz), 13.5 (d, *J* = 1.1 Hz) ppm.



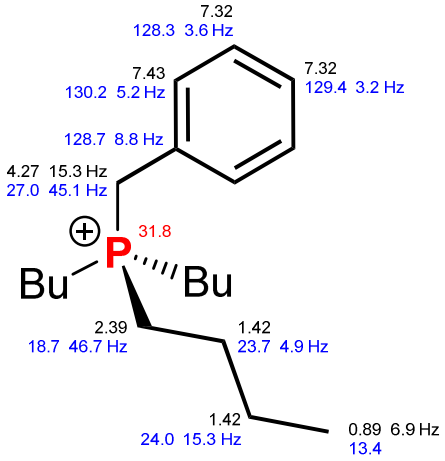
4.2.5. Benzyltributylphosphonium chloride **5e**

This was prepared from stock solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and and benzylmagnesium chloride (1.4 M solution in THF, 1.43 mL, 2.00 mmol) by general method C at -83 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **5e** and **1**•HCl in a 94:6 ratio. Recrystallisation from chloroform/ethyl acetate afforded **5e** (296 mg, 90 %) as fine transparent crystals: MP 164-166 °C, lit.[8] MP 163-164 °C (from xylene/diethyl ether); HRMS (ES$^+$) m/z: calculated for $C_{19}H_{34}P^+$ 293.2398, found 293.2388.

^{31}P NMR (162 MHz, $CDCl_3$) δ 31.8 ppm.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.32 (m, 3H), 4.27 (d, *J* = 15.3 Hz, 2H), 2.39 (m, 6H), 1.42 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.2 (d, *J* = 5.2 Hz), 129.4 (d, *J* = 3.2 Hz), 128.7 (d, *J* = 8.8 Hz), 128.3 (d, *J* = 3.6 Hz), 27.0 (d, *J* = 45.1 Hz), 24.0 (d, *J* = 15.3 Hz), 23.7 (d, *J* = 4.9 Hz), 18.7 (d, *J* = 46.7 Hz), 13.4 ppm.



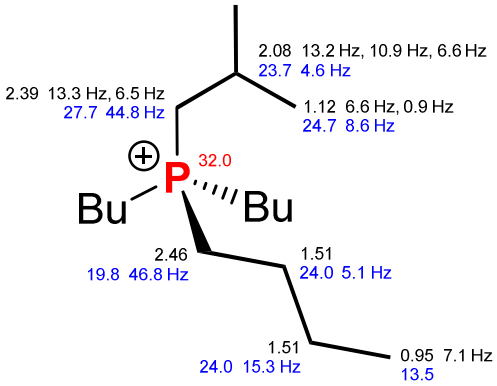
4.2.6. *iso*-Butyltributylphosphonium chloride **5f**

This was prepared from a stock solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and *iso*-butylmagnesium chloride (2.0 M solution in THF, 1.00 mL, 2.00 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **5f** and **1**•HCl in a 95:5 ratio. The crude product (271 mg) was isolated as oily residue and characterized without further purification. HRMS (ES^+) m/z: calculated for $C_{16}H_{36}P^+$ 259.2555, found 259.2565. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **5f** and **1**•HCl in a 95:5 ratio.

^{31}P NMR (121 MHz, $CDCl_3$) δ 32.0 ppm.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.46 (m, 6H), 2.39 (dd, *J* = 13.3, 6.5 Hz, 2H), 2.08 (ddt, *J* = 13.2, 10.9, 6.6 Hz, 1H), 1.51 (m, 12H), 1.12 (dd, *J* = 6.6, 0.9 Hz, 6H), 0.95 (t, *J* = 7.0 Hz, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 27.7 (d, *J* = 44.8 Hz), 24.7 (d, *J* = 8.6 Hz), 24.0 (d, *J* = 15.3 Hz), 24.0 (d, *J* = 5.1 Hz), 23.7 (d, *J* = 4.6 Hz), 19.8 (d, *J* = 46.8 Hz), 13.5 ppm.



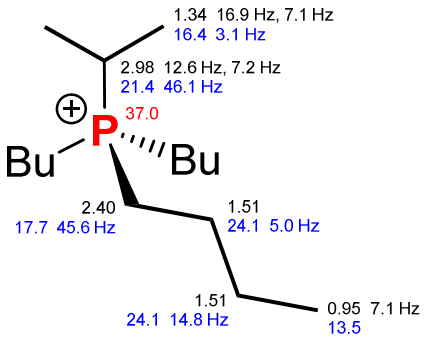
4.2.7. *iso*-Propyltributylphosphonium chloride **5g**

This was prepared from a stock solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and *iso*-propylmagnesium chloride (2.0 M solution in THF, 1.00 mL, 2.00 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **5g**, **1**•HCl and **7**•HCl in a 69:8:23 ratio. The crude product (241 mg) was isolated as oily residue and characterized without further purification. HRMS (ES^+) m/z: calculated for $C_{15}H_{34}P^+$ = 245.2398, found 245.2389.

^{31}P NMR (162 MHz, $CDCl_3$) δ 37.0 ppm.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.98 (dh, *J* = 12.6, 7.2 Hz, 1H), 2.40 (m, 6H), 1.51 (m, 12H), 1.34 (dd, *J* = 16.9, 7.1 Hz, 6H), 0.95 (t, *J* = 7.0 Hz, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 24.1 (d, *J* = 5.0 Hz), 24.1 (d, *J* = 14.8 Hz), 21.4 (d, *J* = 46.1 Hz), 17.7 (d, *J* = 45.6 Hz), 16.4 (d, *J* = 3.1 Hz), 13.5 ppm.



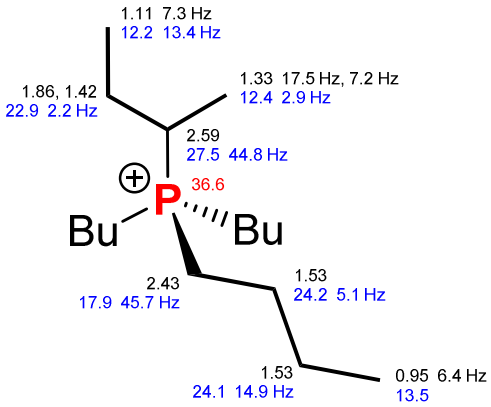
4.2.8. *sec*-Butyltributylphosphonium chloride **5h**

This was prepared from stock solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and *sec*-butylmagnesium chloride (2.0 M solution in THF, 1.00 mL, 2.00 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **5h**, **1**•HCl and **7**•HCl in a 62:8:30 ratio. The crude product (275 mg) was isolated as oily residue and characterized without further purification. HRMS (ES^+) m/z: calculated for $C_{16}H_{36}P^+$ = 259.2555, found 259.2563.

^{31}P NMR (121 MHz, $CDCl_3$) δ 36.6 ppm.

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.59 (m, 1H), 2.43 (m, 6H), 1.86 (m, 1H), 1.42 (m, 1H), 1.53 (m, 12H), 1.33 (dd, *J* = 17.5, 7.2 Hz, 3H), 1.11 (t, *J* = 7.3 Hz, 3H), 0.95 (t, *J* = 6.4 Hz, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 27.5 (d, *J* = 44.8 Hz), 24.2 (d, *J* = 5.1 Hz), 24.1 (d, *J* = 14.9 Hz), 22.9 (d, *J* = 2.2 Hz), 17.9 (d, *J* = 45.7 Hz), 13.5, 12.4 (d, *J* = 2.9 Hz), 12.2 (d, *J* = 13.4 Hz) ppm.



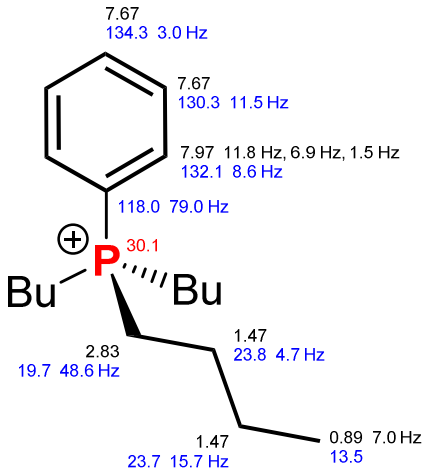
4.2.9. Phenyltributylphosphonium chloride **5i**

This was prepared from a stock solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and phenylmagnesium chloride (2.0 M solution in THF, 1.00 mL, 2.00 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **5i** as a sole product. Recrystallisation from chloroform/ethyl acetate afforded **5i** (299 mg, 95 %) as transparent crystalline sheets: MP 138-140°C; HRMS (ES^+): calculated for $C_{18}H_{32}P^+$ = 279.2242, found 279.2247.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1 ppm.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (ddt, *J* = 11.8, 6.9, 1.5 Hz, 2H), 7.67 (m, 3H), 2.83 (m, 6H), 1.47 (m, 12H), 0.89 (t, *J* = 7.0 Hz, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3 (d, *J* = 3.0 Hz), 132.1 (d, *J* = 8.6 Hz), 130.3 (d, *J* = 11.5 Hz), 118.0 (d, *J* = 79.0 Hz), 23.8 (d, *J* = 4.7 Hz), 23.7 (d, *J* = 15.7 Hz), 19.7 (d, *J* = 48.6 Hz), 13.5 ppm.



4.3. Preparation of alkyltriphenylphosphonium chlorides

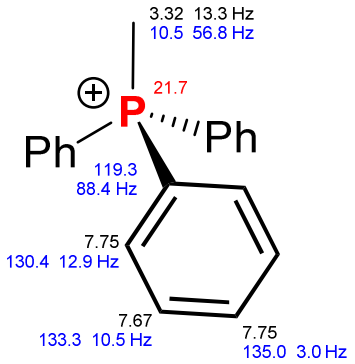
4.3.1. Methyltriphenylphosphonium chloride **6a**

This was prepared from a stock solution of **4** (0.2 M in DCM, 25.00 mL, 5.00 mmol, prepared according to general procedure B) and methylmagnesium chloride (3.0 M solution in THF, 3.35 mL, 10.05 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **6a** as a sole product. Recrystallisation from chloroform/ethyl acetate afforded **6a** (1.53 g, 98 %) as fine white crystals: MP 219-221 °C, lit.[2] MP 217-218.5 °C (from DCM/carbon tetrachloride); HRMS (ES^+) m/z: calculated for $C_{19}H_{18}P^+$ 277.1146, found 277.1135.

^{31}P NMR (162 MHz, $CDCl_3$) δ 21.7 ppm.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (m, 9H), 7.67 (m, 6H), 3.32 (d, *J* = 13.3 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0 (d, *J* = 3.0 Hz), 133.3 (d, *J* = 10.5 Hz), 130.4 (d, *J* = 12.9 Hz), 119.3 (d, *J* = 88.4 Hz), 10.5 (d, *J* = 56.8 Hz) ppm.



4.3.2. Ethyltriphenylphosphonium chloride **6b**

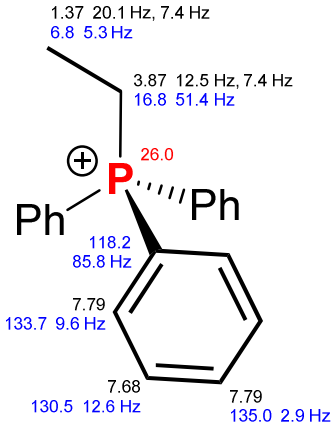
This was prepared from a stock solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and ethylmagnesium chloride (2.7 M solution in THF, 0.74 mL, 2.00 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **6b**, the phosphine oxide hydrochloride **2**•HCl and phosphine **8** in 91:5:4 ratio. Recrystallisation from chloroform/ethyl acetate afforded **6b** (290 mg, 89 %) as fine

white crystals: MP = 234-236 °C, lit.[3] MP 234-236 °C; HRMS (ES$^+$) m/z: calculated for $C_{20}H_{20}P^+$ 291.1303, found 291.1294.

^{31}P NMR (121 MHz, $CDCl_3$) δ 26.0 ppm.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (m, 9H), 7.68 (m, 6H), 3.87 (dq, *J* = 12.5, 7.4 Hz, 2H), 1.37 (dt, *J* = 20.1, 7.4 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0 (d, *J* = 2.9 Hz), 133.7 (d, *J* = 9.6 Hz), 130.5 (d, *J* = 12.6 Hz), 118.2 (d, *J* = 85.8 Hz), 16.8 (d, *J* = 51.4 Hz), 6.8 (d, *J* = 5.3 Hz) ppm.



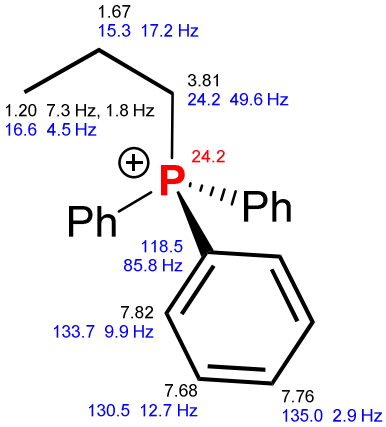
4.3.3. *n*-Propyltriphenylphosphonium chloride **6c**

This was prepared from a stock solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and *n*-propylmagnesium chloride (2.0 M solution in diethyl ether, 1.00 mL, 2.00 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **6c** and **8** in 77:23 ratio. Recrystallisation from chloroform/ DCM/ethyl acetate furnished **6c** (242 mg, 71 %) as fine white crystals: MP 228-230 °C, it.[4] MP 222-230 °C; HRMS (ES$^+$) m/z: calculated for $C_{21}H_{22}P^+$ 305.1459, found 305.1428.

^{31}P NMR (121 MHz, $CDCl_3$) δ 24.2 ppm.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 6H), 7.76 (m, 3H), 7.68 (m, 6H), 3.81 (m, 2H), 1.67 (m, 2H), 1.20 (td, *J* = 7.3, 1.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0 (d, *J* = 2.9 Hz), 133.7 (d, *J* = 9.9 Hz), 130.5 (d, *J* = 12.7 Hz), 118.5 (d, *J* = 85.8 Hz), 24.2 (d, *J* = 49.6 Hz), 16.6 (d, *J* = 4.5 Hz), 15.3 (d, *J* = 17.2 Hz) ppm.



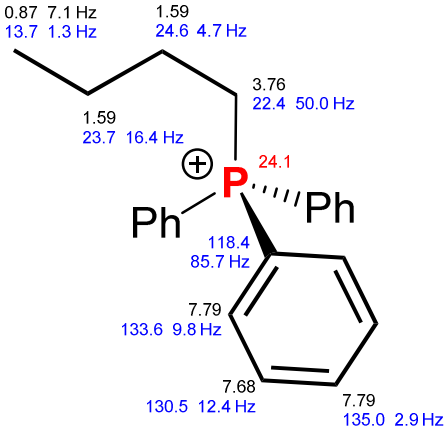
4.3.4. *n*-Butyltriphenylphosphonium chloride **6d**

This was prepared from a stock solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and *n*-butylmagnesium chloride (2.0 M solution in THF, 1.00 mL, 2.00 mmol) by general method C at -41 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **6d, 2**•HCl and **8** in 86:5:9 ratio. Recrystallisation from chloroform/DCM/ethyl acetate furnished **6d** (277 mg, 78 %) as white crystals: MP 228-230 °C, lit.[5] MP 230.2 °C; HRMS (ES$^+$) m/z: calculated for $C_{22}H_{24}P^+$ 319.1616, found 319.1612.

^{31}P NMR (121 MHz, $CDCl_3$) δ 24.1 ppm.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (m, 9H), 7.68 (m, 6H), 3.76 (m, 2H), 1.59 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0 (d, *J* = 2.9 Hz), 133.6 (d, *J* = 9.8 Hz), 130.5 (d, *J* = 12.4 Hz), 118.4 (d, *J* = 85.7 Hz), 24.6 (d, *J* = 4.7 Hz), 23.7 (d, *J* = 16.4 Hz), 22.4 (d, *J* = 50.0 Hz), 13.7 (d, *J* = 1.3 Hz) ppm.



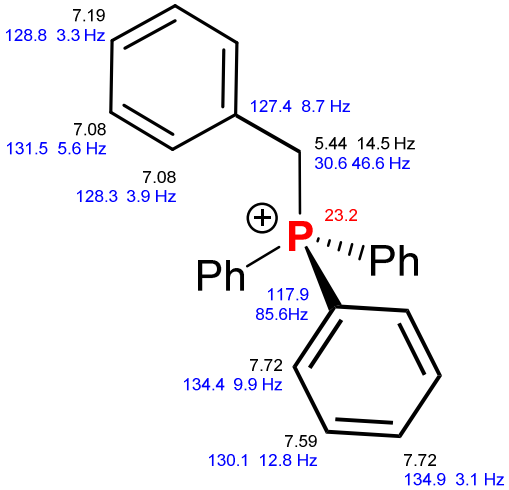
4.3.5. Benzyltriphenylphosphonium chloride **6e**

This was prepared from a stock solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and benzylmagnesium chloride (1.4 M solution in THF, 1.43 mL, 2.00 mmol) by general method C at -41 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **6e, 2** and **8** in a 87:12:1 ratio. Recrystallisation from chloroform/ethyl acetate afforded **6e** (319 mg, 82 %) as white crystals: MP >300 °C, lit.[6] MP 324-326 °C (from chloroform/diethyl ether); HRMS (ES$^+$) m/z: calculated for $C_{25}H_{22}P^+$ 353.1459, found 353.1456.

^{31}P NMR (121 MHz, $CDCl_3$) δ 23.2 ppm.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (m, 9H), 7.59 (m, 6H), 7.19 (m, 1H), 7.08 (m, 4H), 5.44 (d, *J* = 14.5 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.9 (d, *J* = 3.1 Hz), 134.4 (d, *J* = 9.9 Hz), 131.5 (d, *J* = 5.6 Hz), 130.1 (d, *J* = 12.8 Hz), 128.8 (d, *J* = 3.3 Hz), 128.3 (d, *J* = 3.9 Hz), 127.4 (d, *J* = 8.7 Hz), 117.9 (d, *J* = 85.6 Hz), 30.6 (d, *J* = 46.6 Hz) ppm.



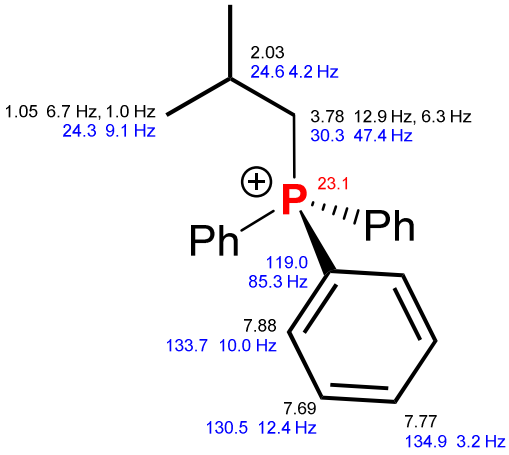
4.3.6. *iso*-Butyltriphenylphosphonium chloride **6f**

This was prepared from a stock solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, prepared according to general procedure B) and *iso*-butylmagnesium chloride (2.0 M solution in THF, 1.00 mL, 2.00 mmol) by general method C at 0 °C. ^{31}P NMR (121 MHz, $CDCl_3$) spectroscopic analysis of the crude product indicated the presence of **6f, 2** and **8** in a 48:6:46 ratio. Recrystallisation from chloroform/ethyl acetate afforded **6f** (135 mg, 38 %) as fine white crystals: MP 197-199°C; HRMS (ES$^+$) m/z: calculated for $C_{22}H_{24}P^+$ 319.1616, found 319.1600.

^{31}P NMR (121 MHz, $CDCl_3$) δ 23.1 ppm.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (m, 6H), 7.77 (m, 3H), 7.69 (m, 6H), 3.78 (dd, *J* = 12.9, 6.3 Hz, 2H), 2.03 (m, 1H), 1.05 (dd, *J* = 6.7, 1.0 Hz, 6H) ppm.

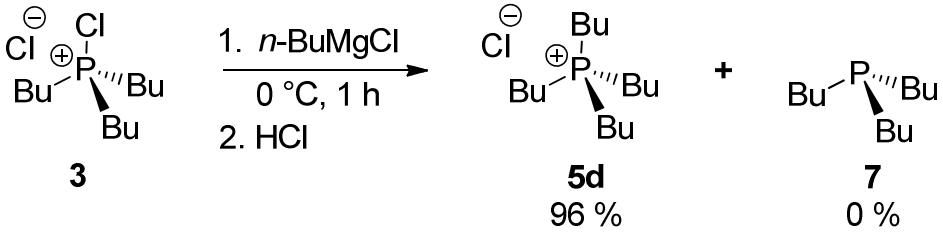
^{13}C NMR (126 MHz, $CDCl_3$) δ 134.9 (d, *J* = 3.2 Hz), 133.7 (d, *J* = 10.0 Hz), 130.5 (d, *J* = 12.4 Hz), 119.0 (d, *J* = 85.3 Hz), 30.3 (d, *J* = 47.4 Hz), 24.6 (d, *J* = 4.2 Hz), 24.3 (d, *J* = 9.1 Hz) ppm.



5. Competing Reaction Pathways: P-attack vs Cl-attack

5.1. Reactions of **3**

5.1.1. Reaction of **3** with *n*-butylmagnesium chloride



3 **5d** 96 % **7** 0 %

Scheme S14 The reaction of **3** with *n*-butylmagnesium chloride affords **5d** only, **7** is not observed.

A 50 mL flask equipped with a stir bar was charged with a solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) and cooled to 0 °C. Then, *n*-butylmagnesium chloride (2.0 M in THF, 1.00 mL, 2.00 mmol, 2.00 equivalents) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 °C by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. A small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **5d** and **1**•HCl:

^{31}P NMR (121 MHz, $CDCl_3$): δ 60.1 (**1**•HCl, 4 %), 32.8 (**5d**, 96 %) ppm.

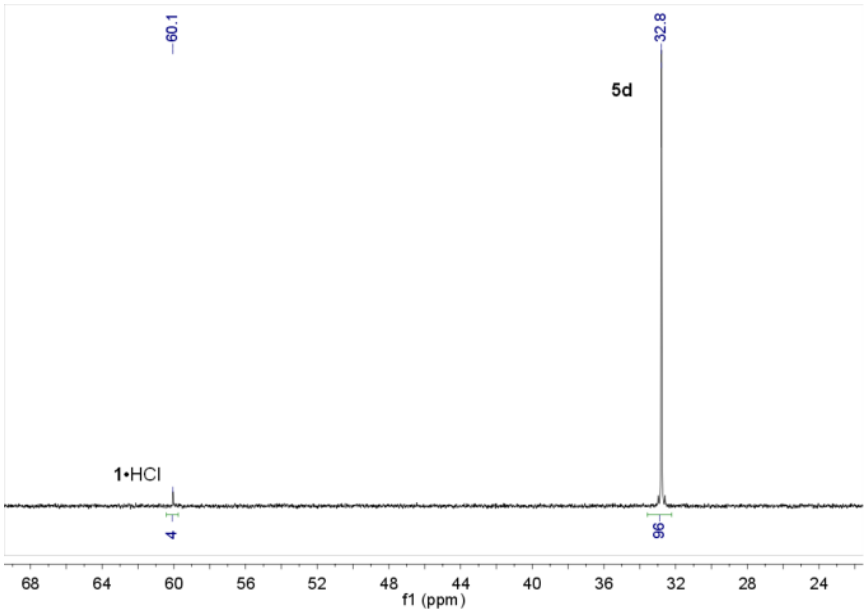
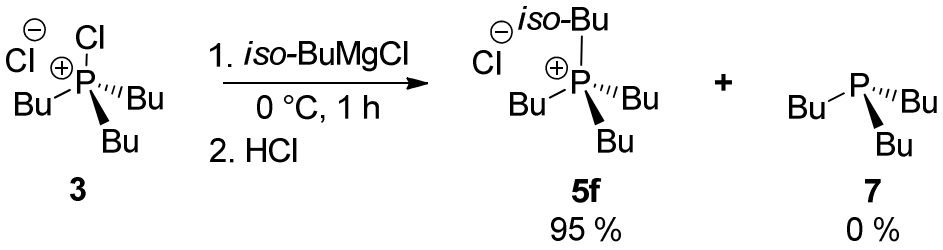


Figure S3 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **1**•HCl (δ 60.1) and **5d** (δ 32.8).

5.1.2. Reaction of **3** with *iso*-butylmagnesium chloride



Scheme S15 The reaction of **3** with *iso*-butylmagnesium chloride affords **5f**, **7** is not observed.

A 50 mL flask equipped with a stir bar was charged with a solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) and cooled to 0 °C. Then, *iso*-butylmagnesium chloride (2.0 M in THF, 1.00 mL, 2.00 mmol, 2.00 equivalents) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 °C by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **5f** and **1**•HCl:

^{31}P NMR (121 MHz, $CDCl_3$): δ 59.9 (**1**•HCl, 5 %), 32.0 (**5f**, 95 %) ppm.

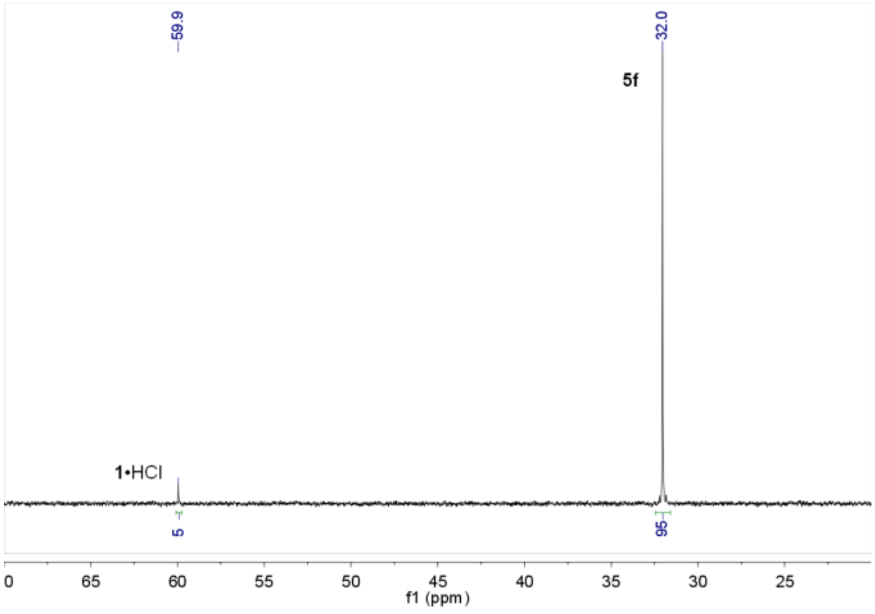
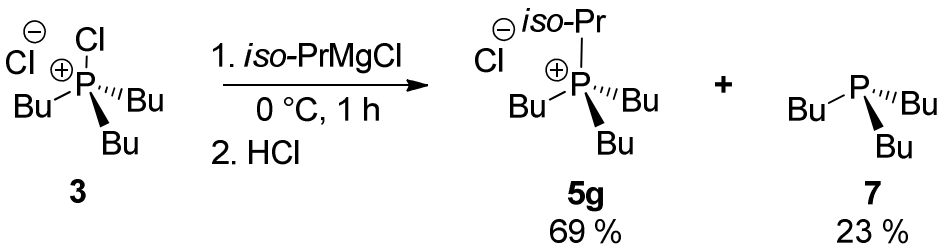


Figure S4 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **1**•HCl (δ 59.9) and **5f** (δ 32.0).

5.1.3. Reaction of **3** with *iso*-propylmagnesium chloride



Scheme S16 The reaction of **3** with *iso*-propylmagnesium chloride affords **5g** and **7**.

A 50 mL flask equipped with a stir bar was charged with a solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) and cooled to 0 °C. Then, *iso*-propylmagnesium chloride (2.0 M in THF, 1 mL, 2.00 mmol, 2.00 equivalents) was slowly added down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 °C by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **5g**, **1**•HCl and **7**•HCl:

^{31}P NMR (121 MHz, $CDCl_3$): δ 60.1 (**1**•HCl, 8 %), 37.0 (**5g**, 69 %), 9.8 (**7**•HCl, 23 %) ppm.

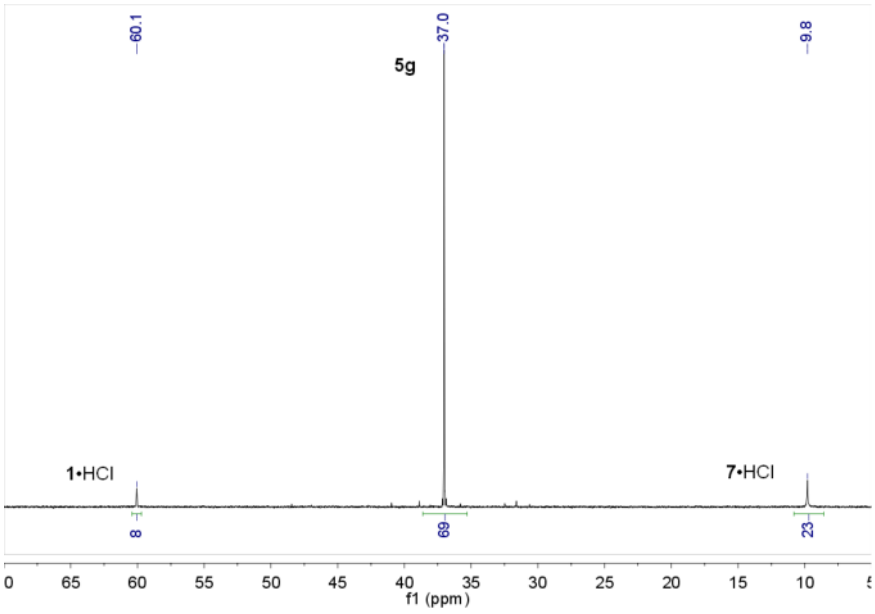
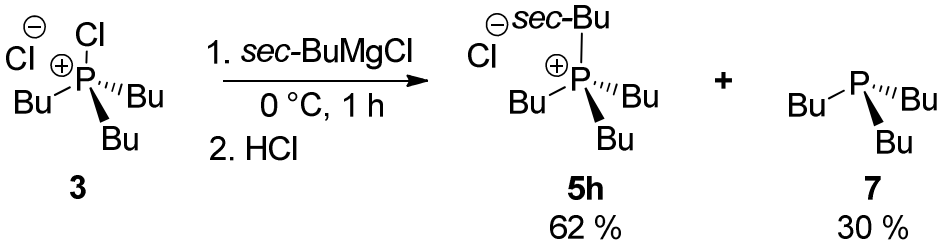


Figure S5 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **1**•HCl (δ 60.1)**, 5g** (δ 37.0) and **7**•HCl (δ 9.8).

5.1.4. Reaction of **3** with *sec*-butylmagnesium chloride



Scheme S17 The reaction of **3** with *sec*-butylmagnesium chloride affords **5h** and **7**.

A 50 mL flask equipped with a stir bar was charged with a solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) and cooled to 0 °C. Then, *sec*-butylmagnesium chloride (2.0 M in THF, 1.00 mL, 2.00 mmol, 2.00 equivalents) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 °C by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **5h**, **1**•HCl and **7**•HCl:

^{31}P NMR (121 MHz, $CDCl_3$): δ 60.4 (**1**•HCl, 8 %), 36.6 (**5h**, 62 %), 9.9 (**7**•HCl, 30 %) ppm.

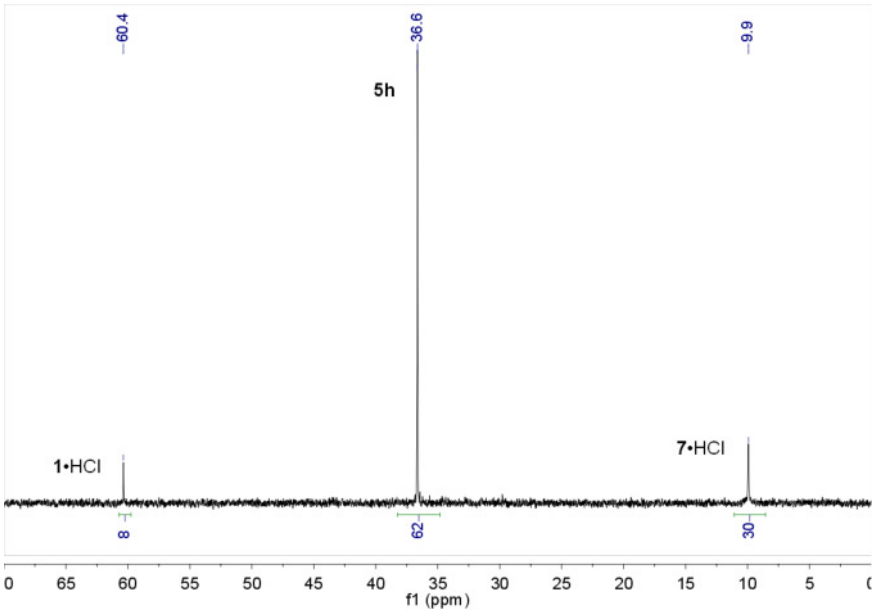
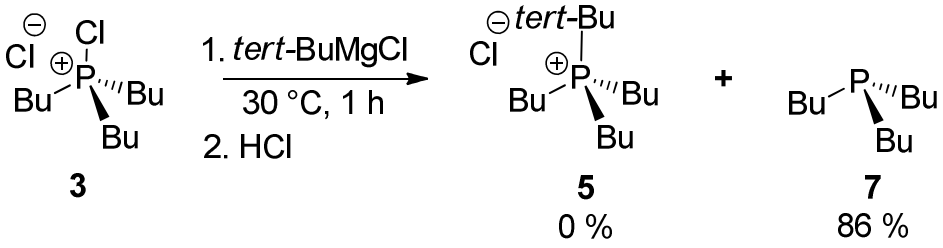


Figure S6 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **1**•HCl (δ 60.4)**, 5h** (δ 36.6) and **7**•HCl (δ 9.9).

5.1.5. Reaction of **3** with *tert*-butylmagnesium chloride



Scheme S18 The reaction of **3** with *tert*-butylmagnesium chloride affords **7**.

A 50 mL flask equipped with a stir bar was charged with a solution of **3** (0.2 M in DCM, 4.00 mL, 0.80 mmol, 1.00 equivalent, prepared according to general procedure B) and warmed to 30 °C. Then, *tert*-butylmagnesium chloride (1.7 M in THF, 0.94 mL, 1.60 mmol, 2.00 equivalents) was slowly added down the side of the flask. The resulting reaction mixture was stirred for 1 hour. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **1**•HCl and **7**•HCl:

^{31}P NMR (121 MHz, $CDCl_3$): δ 61.5 (**1**•HCl, 13 %), 10.8 (**7**•HCl, 86 %) ppm.

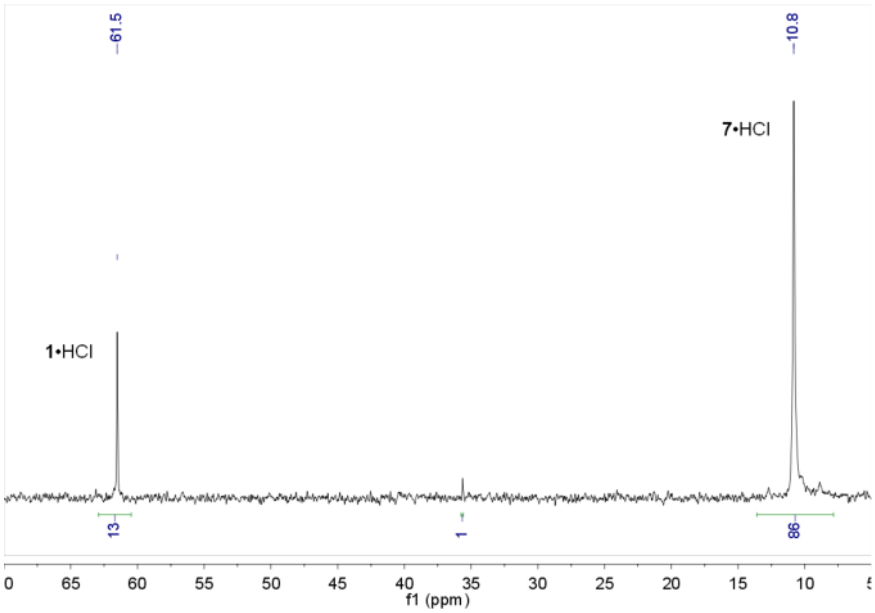
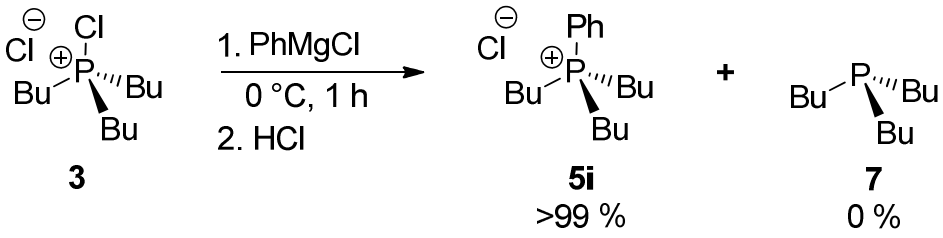


Figure S7 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **1**•HCl (δ 61.5) and **7**•HCl (δ 10.8).

5.1.6. Reaction of **3** with phenylmagnesium chloride



Scheme S19 The reaction of **3** with phenylmagnesium chloride affords **5i**.

A 50 mL flask equipped with a stir bar was charged with a solution of **3** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) and cooled to 0 °C. Then, phenylmagnesium chloride (2.0 M in THF, 1.00 mL, 2.00 mmol, 2.00 equivalents) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 °C by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **5i**.

^{31}P NMR (121 MHz, $CDCl_3$): δ 30.1 (**5i**, >99 %) ppm.

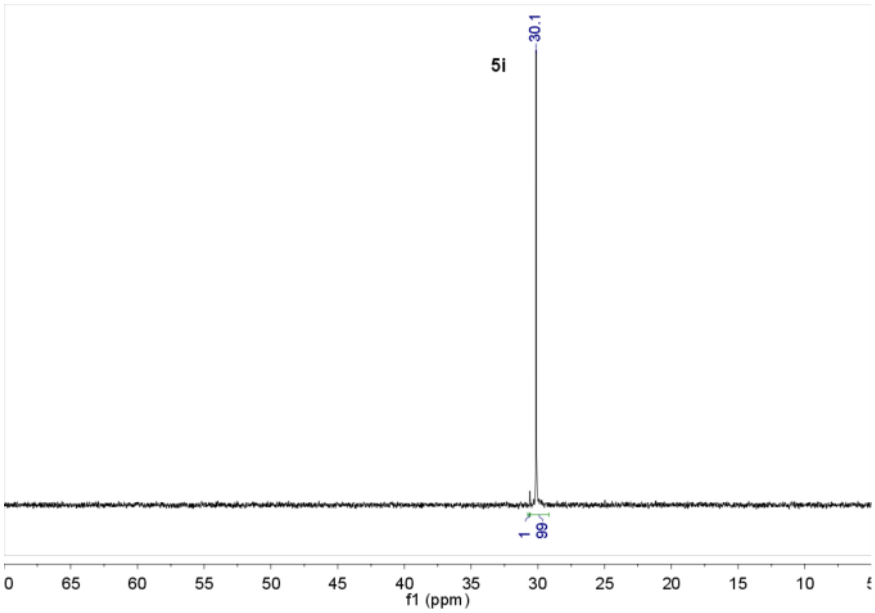
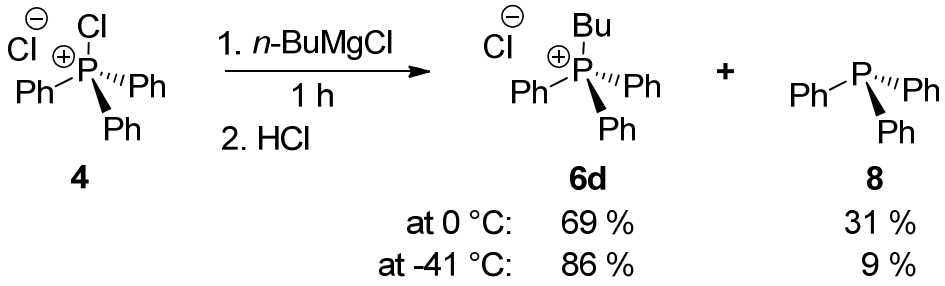


Figure S8 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **5i** (δ 30.1).

5.2. Reactions of **4**

5.2.1. Reaction of **4** with *n*-butylmagnesium chloride at various temperatures



Scheme S20 The reaction of **4** with *n*-butylmagnesium chloride affords **6d** and **8**. By lowering the reaction temperature, the ratio of **6d** to **8** was improved.

A 50 mL flask equipped with a stir bar was charged with a solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) and cooled to 0 °C. Then, *n*-butylmagnesium chloride (2.0 M in THF, 1.00 mL, 2.00 mmol, 2.00 equivalents) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 ° by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **6d** and **8**:

^{31}P NMR (121 MHz, $CDCl_3$): δ 24.1 (**6d**, 69 %), -5.4 (**8**, 31 %) ppm.

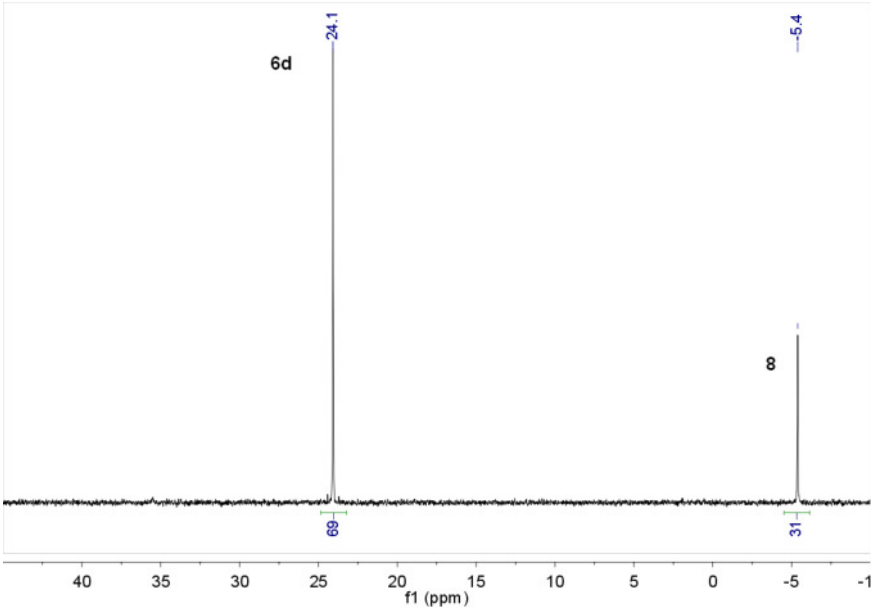


Figure S9 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **6d** (δ 24.1) and **8** (δ -5.4).

The experiment was repeated at -41 °C (see Figure S10):

^{31}P NMR (121 MHz, $CDCl_3$): δ 35.2 (**2**•HCl, 5 %), 24.2 (**6d**, 86 %), -5.4 (**8**, 9 %) ppm.

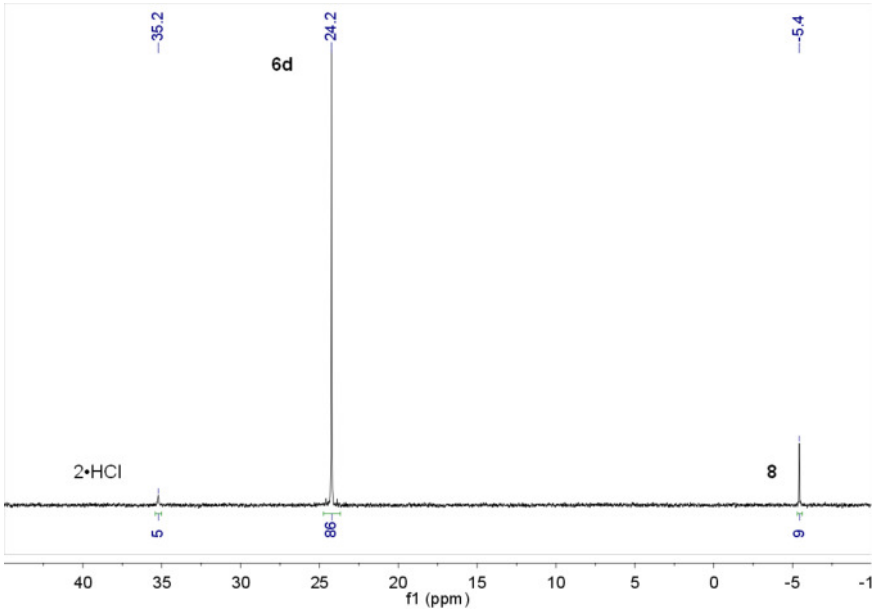
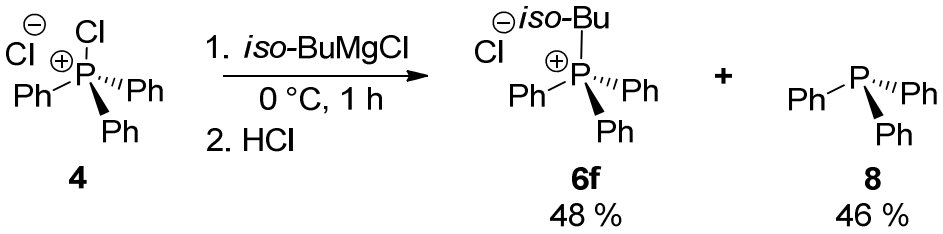


Figure S10 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of**2**•HCl (δ 35.2), **6d** (δ 24.2) and **8** (δ -5.4).

5.2.2. Reaction of **4** with *iso*-butylmagnesium chloride



Scheme S21 The reaction of **4** with *iso*-butylmagnesium chloride affords **6f** and **8**.

A 50 mL flask equipped with a stir bar was charged with a solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure N) and cooled to 0 °C. Then, *iso*-butylmagnesium chloride (2.0 M in THF, 1.00 mL, 2.00 mmol, 2.00 equivalents) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 °C by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **6f**, **2** and **8**:

^{31}P NMR (121 MHz, $CDCl_3$): δ 29.7 (**2**, 6 %), 23.1 (**6f**, 48 %), -5.4 (**8**, 46 %) ppm.

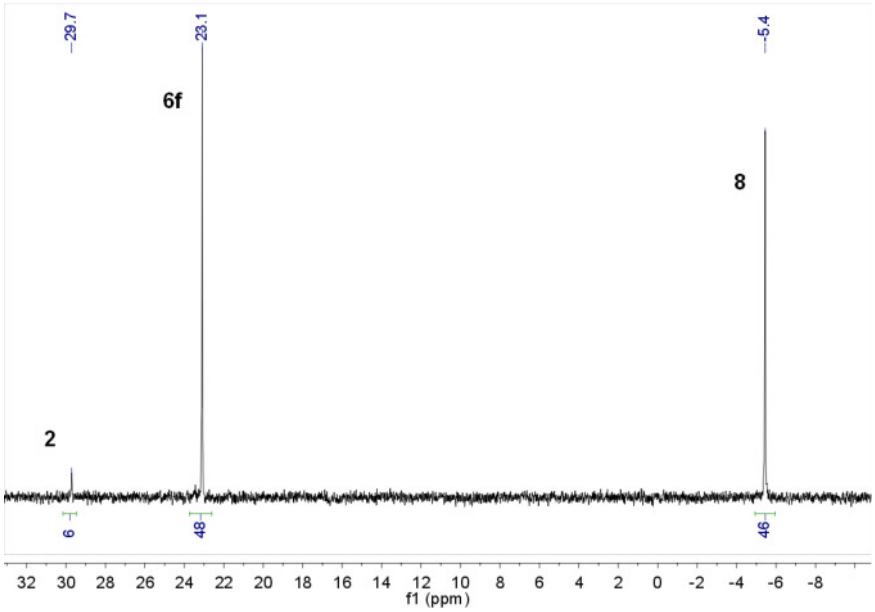
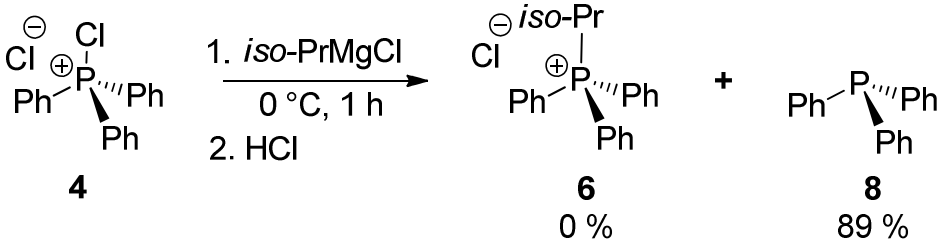


Figure S11 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **2** (δ 29.7), **6f** (δ 23.1) and **8** (δ -5.4).

5.2.3. Reaction of **4** with *iso*-propylmagnesium chloride



4 **6** 0 % **8** 89 %

Scheme S22 The reaction of **4** with *iso*-propylmagnesium chloride affords **8**.

A 50 mL flask equipped with a stir bar was charged with a solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) and cooled to 0 °C. Then, *iso*-propylmagnesium chloride (2.0 M in THF, 1.00 mL, 2.00 mmol, 2.00 equivalents) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 °C by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **2** and **8**:

^{31}P NMR (121 MHz, $CDCl_3$): δ 29.1 (**2**, 11 %), -5.4 (**8**, 89 %) ppm.

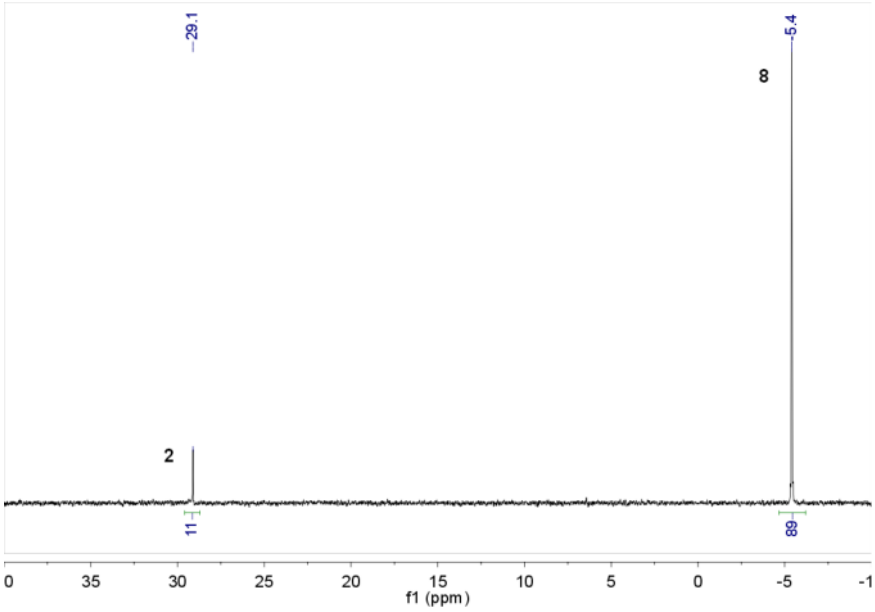
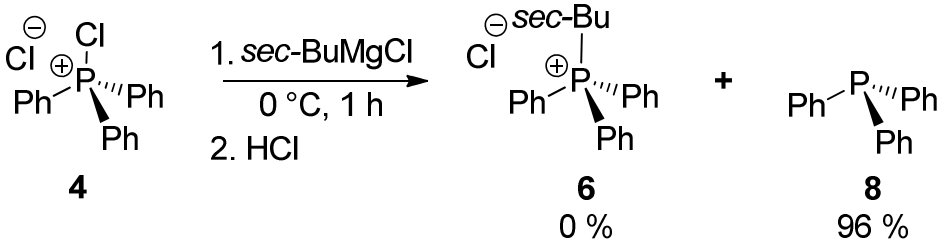


Figure S12 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **2** (δ 29.1) and **8** (δ -5.4).

5.2.4. Reaction of **4** with *sec*-butylmagnesium chloride



4 **6** 0 % **8** 96 %

Scheme S23 The reaction of **4** with *sec*-butylmagnesium chloride affords **8** only.

A 50 mL flask equipped with a stir bar was charged with a solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) and cooled to 0 °C. Then, *sec*-butylmagnesium chloride (2.0 M in THF, 1.00 mL, 2.00 mmol, 2.00 equivalents) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 °C by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **2** and **8**:

^{31}P NMR (121 MHz, $CDCl_3$): δ 29.2 (**2**, 4 %), -5.4 (**8**, 96 %) ppm.

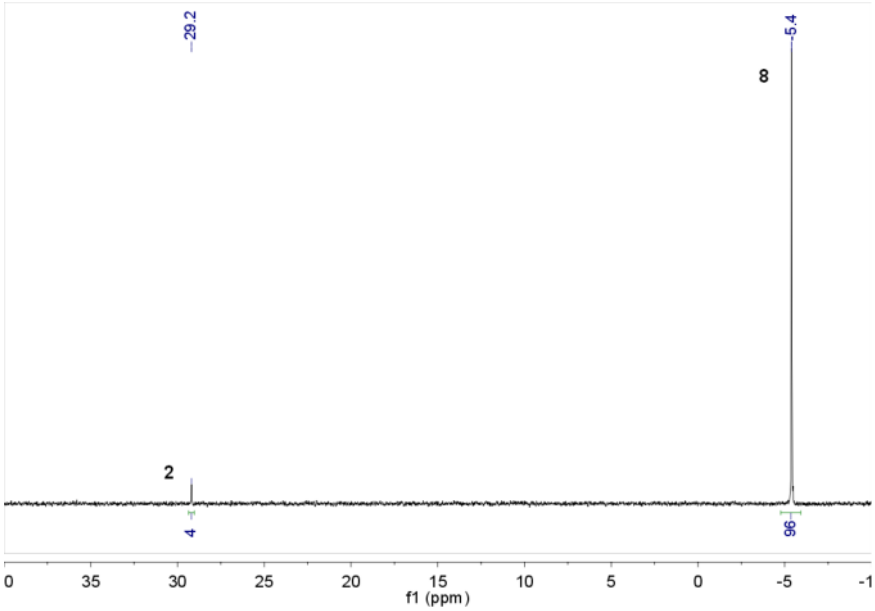
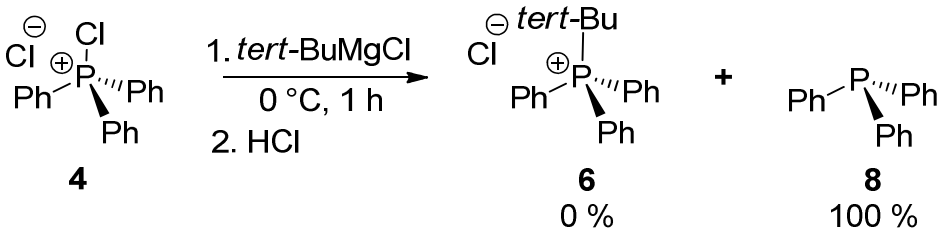


Figure S13 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **2** (δ 29.2) and **8** (δ -5.4).

5.2.5. Reaction of **4** with *tert*-butylmagnesium chloride



Scheme S24 The reaction of **4** with *tert*-butylmagnesium chloride affords **8**.

A 50 mL flask equipped with a stir bar was charged with a solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) and cooled to 0 °C. Then, *tert*-butylmagnesium chloride (1.7 M in THF, 1.18 mL, 2.00 mmol, 2.00 equivalents) was added slowly down the side of the flask. The resulting mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 °C by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **8**:

^{31}P NMR (121 MHz, $CDCl_3$): δ -5.2 (**8**, 100 %) ppm.

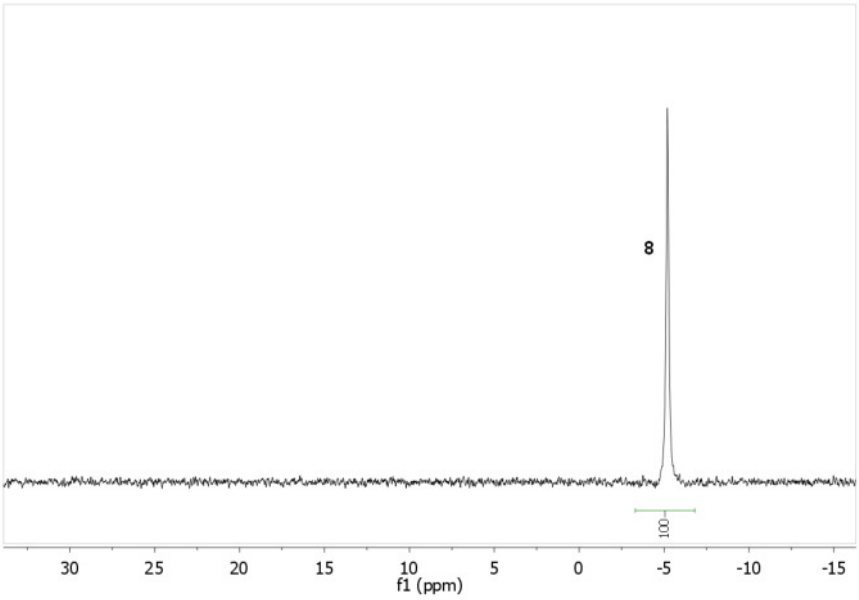
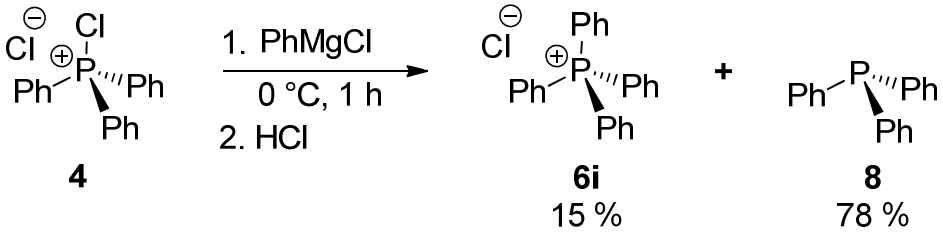


Figure S14 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **8** (δ -5.2).

5.2.6. Reaction of **4** with phenylmagnesium chloride



4 **6i** 15 % **8** 78 %

Scheme S25 The reaction of **4** with phenylmagnesium chloride affords **6i** and **8**.

A 50 mL flask equipped with a stir bar was charged with a solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) under an atmosphere of nitrogen and the flask was cooled to 0 °C. Then, phenylmagnesium chloride (2.0 M in THF, 1.00 mL, 2.00 mmol, 2.00 equivalents) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 ° by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing the crude product **6i**[9], **2** and **8**:

^{31}P NMR (121 MHz, $CDCl_3$): δ 29.3 (**2**, 7%), 23.1 (**6i**, 15 %), -5.4 (**8**, 78 %)

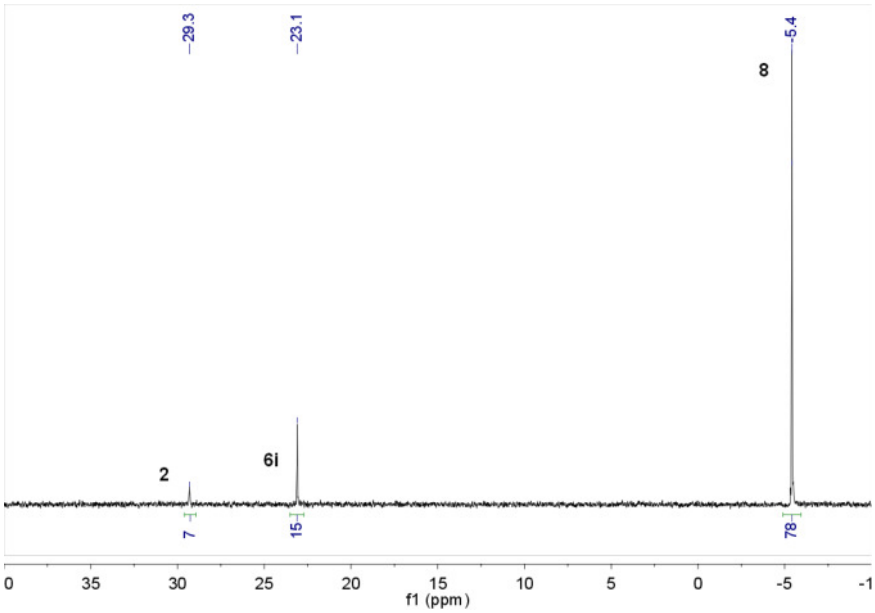
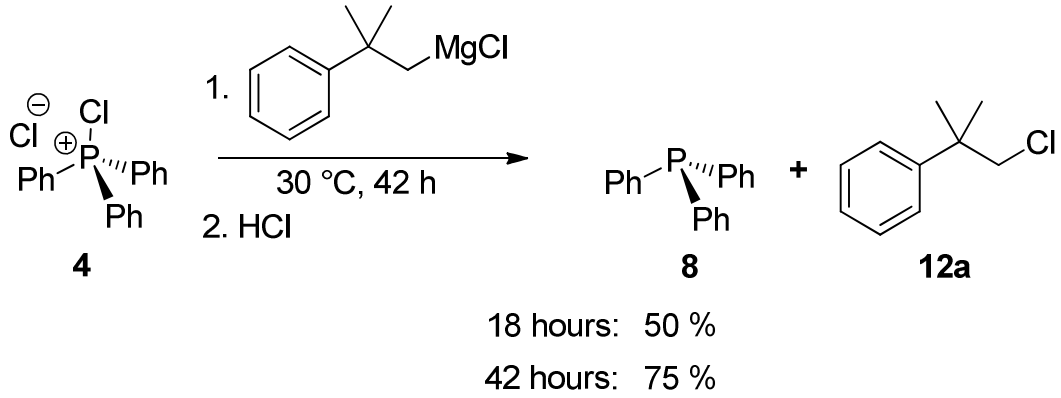


Figure S15 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **2** (δ 29.3), **6i** (δ 23.1) and **8** (δ -5.4).

5.2.7. Reaction of **4** with 2-methyl-2-phenylpropylmagnesium chloride



Scheme S26 The reaction of **4** with 2-methyl-2-phenylpropylmagnesium chloride affords **8** and alkyl chloride **12a**.

A 50 mL flask equipped with a stir bar was charged with a solution of **4** (0.2 M in DCM, 2.50 mL, 0.50 mmol, 1.00 equivalent, prepared according to general procedure B) and warmed to 30 °C. Then, 2-methyl-1-phenylpropylmagnesium chloride (0.5 M in THF, 2.00 mL, 1.00 mmol, 2 equivalents) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 30 °C for 18 hours. After this time, a small volume of the reaction mixture was withdrawn and quenched by addition of a 2.0 M solution of HCl in diethyl ether (approximately 2 equivalents). After ten minutes, the solvent was removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution:

^{31}P NMR (121 MHz, $CDCl_3$) after 18 hours: δ 36.7 (**2**•HCl, 47 %), -5.5 (**8**, 50 %) ppm.

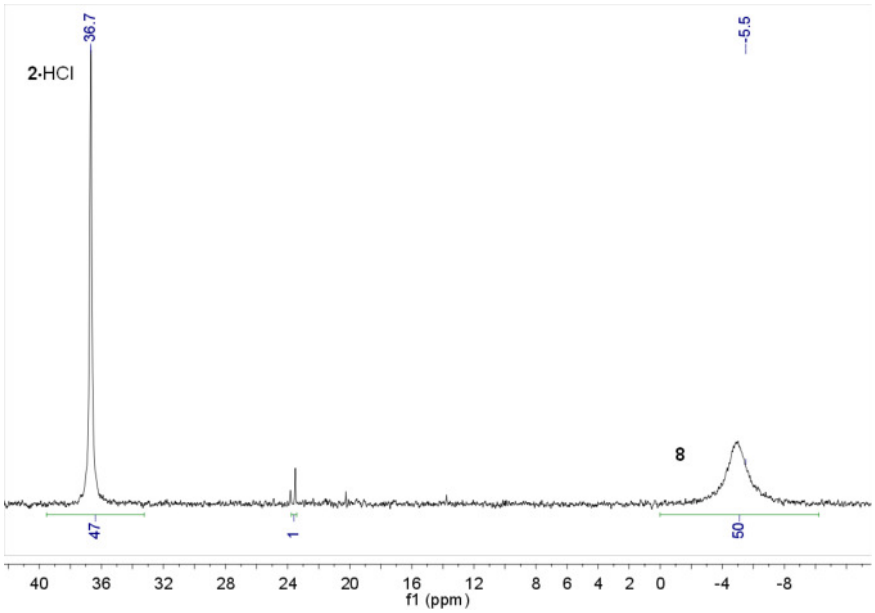


Figure S16 Section of the ^{31}P NMR spectrum of the reaction mixture after 18 h indicating the presence of **2**•HCl (δ 36.7) and **8** (δ -5.5).

The bulk of the reaction mixture was stirred at 30 °C for another 24 hours. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (0.50 mL, 1.00 mmol, just over 2 equivalents). After ten minutes, a small sample was withdrawn from the quenched reaction mixture and the solvent removed *in vacuo.* $CDCl_3$ (1.00 mL) was added and filtration of insoluble salts gave a transparent solution:

^{31}P NMR (121 MHz, $CDCl_3$) after 42 hours: δ 36.2 (**2**•HCl, 25 %), -4.9 (**8**, 75 %)

The bulk of the reaction mixture was concentrated by evaporation to yield an oily residue. The residue was dissolved in DCM (12 mL) and then washed with a mixture of equal parts of water and brine (2 x 3 mL). Finally, the organic phase was washed with an equal volume of brine, eluted through sodium sulphate and concentrated *in vacuo* to yield a clear oily residue. To remove the phosphine oxide, thus residue was eluted through alumina using pentane as eluent. Concertation of the organic layer afforded the purified reaction products as a clear oil (150 mg) containing **12a** and **8**.

The NMR analysis of the purified product indicated the following:

Assigned to 2-methyl-2-phenyl-chloropropane **12a**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 5H), 3.67 (s, 2H), 1.45 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 128.3, 126.5, 125.9, 56.3, 39.8, 26.4 ppm.

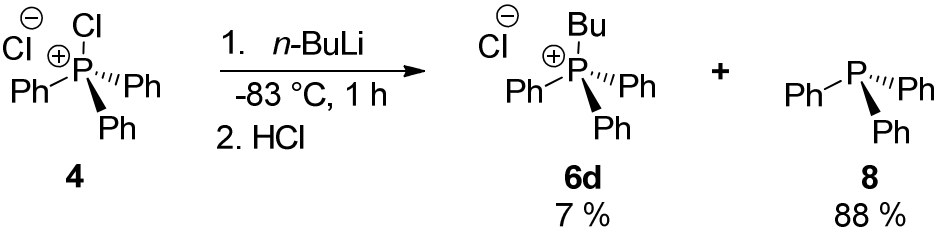
Assigned to triphenylphosphine **8**:

^{31}P NMR (162 MHz, $CDCl_3$) δ -5.4 (**8**, 99 %) ppm.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 15H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2 (d, *J* = 10.7 Hz), 133.7 (d, *J* = 19.5 Hz), 128.6 (d, *J* = 18.3 Hz), 128.5 ppm.

5.2.8. Reaction of **4** with *n*-butyllithium



Scheme S27 The reaction of **4** with *n*-butyllithium affords **6d** and **8**.

A 50 mL flask equipped with a stir bar was charged with a solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) and cooled to -83 °C. Then, *n*-butyllithium (2.5 M in hexanes, 0.80 mL, 2.00 mmol, 2.00 equivalents) was added dropwise. The resulting reaction mixture was stirred at -83 °C for 1 hour. After this time, the reaction mixture was quenched at low temperature C by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the cold bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **6d**, **2**•HCl and **8**:

^{31}P NMR (162 MHz, $CDCl_3$): δ 37.3 (**2**•HCl, 3 %), 23.8 (**6d**, 7 %), -5.4 (**8**, 88 %) ppm.

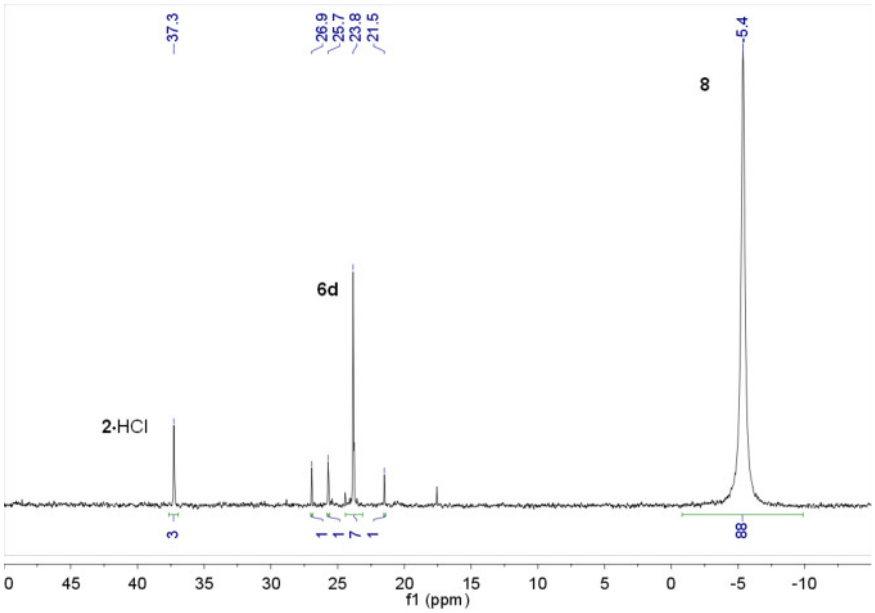
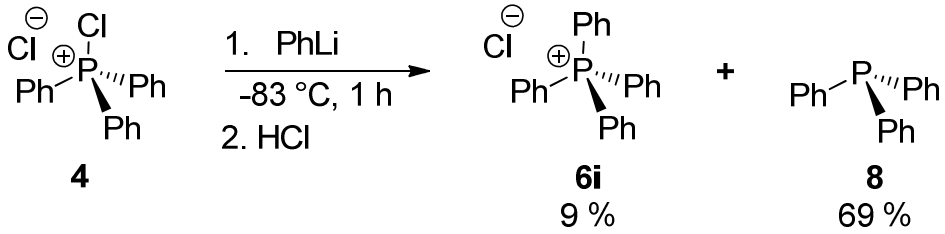


Figure S17 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **2**•HCl (δ 37.3), **6d** (δ 23.8) and **8** (δ -5.4).

5.2.9. Reaction of **4** with phenyllithium



4 **6i** 9 % **8** 69 %

Scheme S28 The reaction of **4** with phenyllithium affords **6i** and **8**.

A 50 mL flask equipped with a stir bar was charged with a solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) under an atmosphere of nitrogen and the flask was cooled to -83 °C. Then, phenyllithium (2.0 M in dibutyl ether, 1.00 mL, 2.00 mmol, 2.00 equivalents) was added dropwise. The resulting reaction mixture was stirred at -83 °C for 1 hour. After this time, the reaction mixture was quenched at low temperature by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the cold bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **6i**[9], **2** and **8**:

^{31}P NMR (121 MHz, $CDCl_3$): δ 29.6 (**2**, 19 %), 24.3 (**6i**, 9 %), -5.4 (**8**, 69 %) ppm.

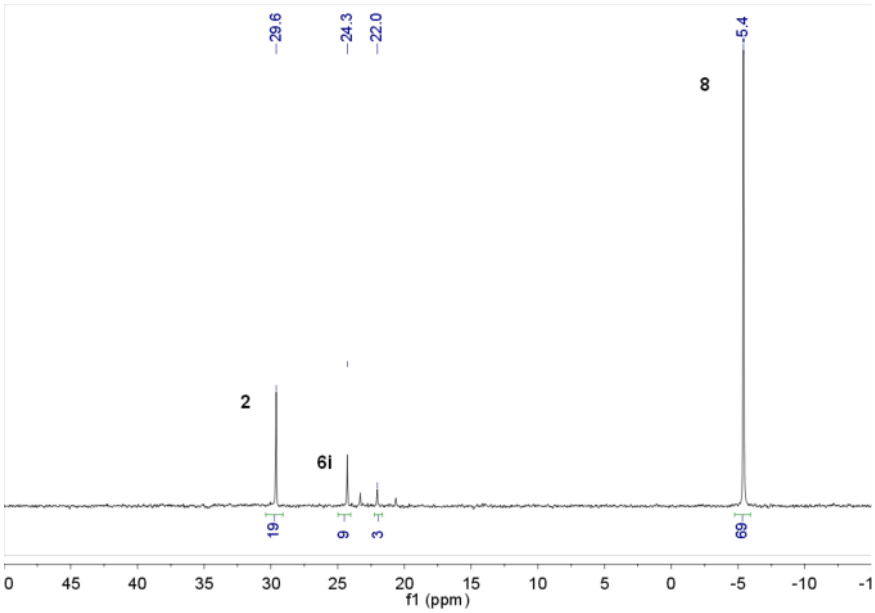
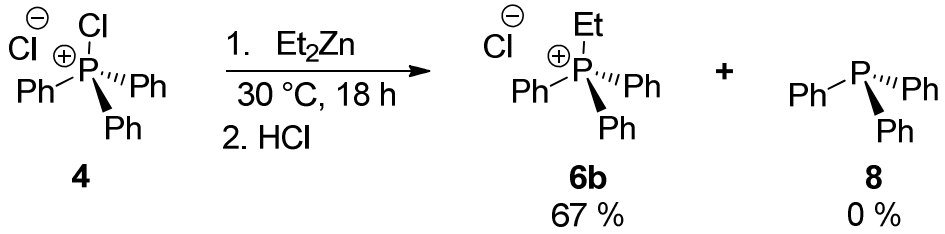


Figure S18 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **2** (δ 29.6), **6i** (δ 24.3) and **8** (δ -5.4).

5.2.10. Reaction of **4** with diethylzinc



Scheme S29 The reaction of **4** with diethylzinc affords **6b** only, **8** is not observed.

A 50 mL flask equipped with a stir bar was charged with a solution of **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure B) under an atmosphere of nitrogen and the flask was warmed to 30 °C. Then, diethyl zinc (1.11 M in hexanes, 0.90 mL, 1.00 mmol, 1 equivalent) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 30 °C for 18 hours. After this time, the reaction mixture was quenched by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **6d** and **2**•HCl:

^{31}P NMR (121 MHz, $CDCl_3$): δ 35.4 (**2**•HCl, 33 %), 26.1 (**6b**, 67 %) ppm.

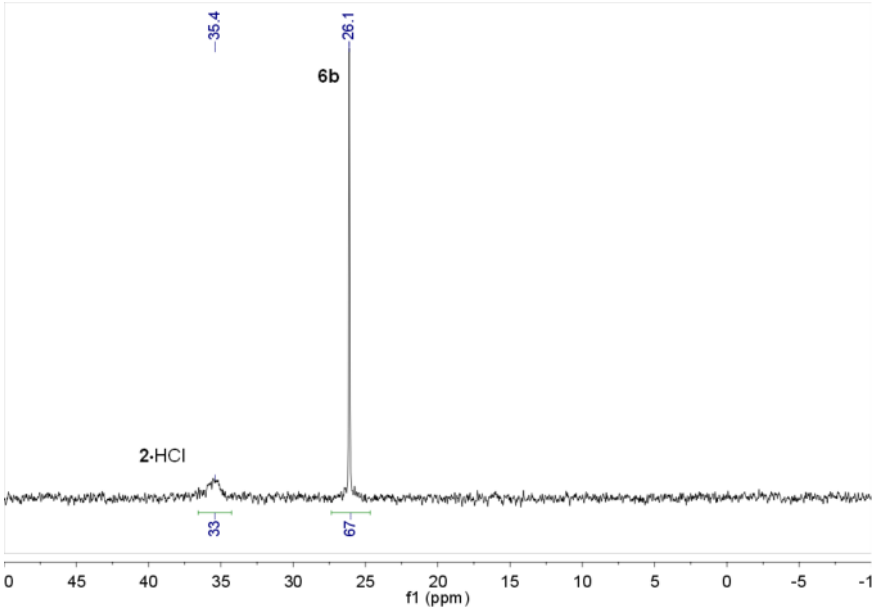
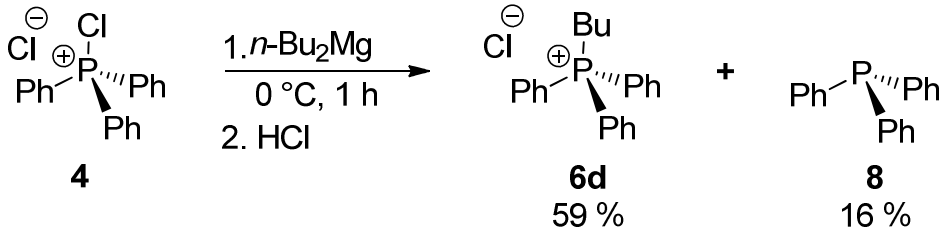


Figure S19 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **2**•HCl (δ 35.4) and **6b** (δ 26.1).

5.2.11. Reaction of **4** with di-*n*-butylmagnesium



4 **6d** 59 % **8** 16 %

Scheme S30 The reaction of **4** with di-*n*-butylmagnesium affords **6d** and **8**.

A 50 mL flask equipped with a stir bar was charged with a solution of CPS **4** (0.2 M in DCM, 5.00 mL, 1.00 mmol, 1.00 equivalent, prepared according to general procedure C) under an atmosphere of nitrogen and the flask was cooled to 0 °C. Then, di-*n*-butylmagnesium (0.5 M in heptane, 2.00 mL, 1.00 mmol, 1.00 equivalent) was added slowly down the side of the flask. The resulting reaction mixture was stirred at 0 °C for 1 hour. After this time, the reaction mixture was quenched at 0 °C temperature by the addition of a 2.0 M solution of HCl in diethyl ether (1.00 mL, 2.00 equivalents). After ten minutes, the flask was removed from the ice bath and its contents were allowed to warm slowly back to room temperature. Then, a small volume of the quenched reaction mixture was withdrawn, the solvent removed *in vacuo* and $CDCl_3$ (1.00 mL) was added. Filtration of this mixture gave a transparent solution containing **6d**, **2**, **8** and an unknown product whose ^{31}P NMR chemical shift suggests a phosphonium salt structure:

^{31}P NMR (121 MHz, $CDCl_3$): δ 35.3 (**2**•HCl, 7 %), 24.1 (**6d**, 59 %), -5.3 (**8**, 16 %) ppm.

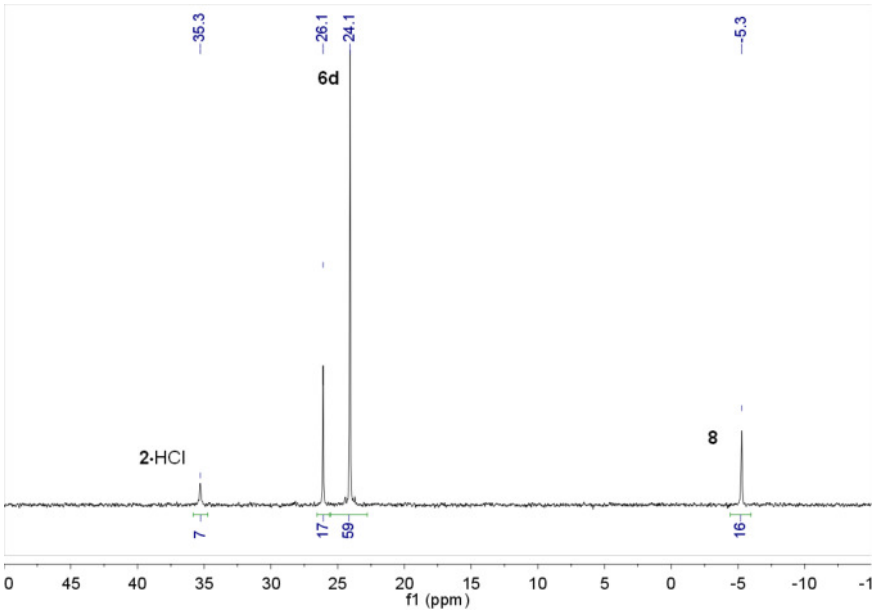
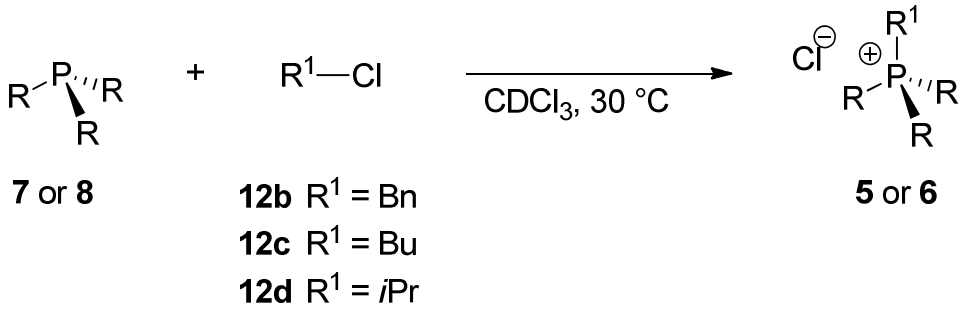


Figure S20 Section of the ^{31}P NMR spectrum of the reaction mixture indicating the presence of **2**•HCl (δ 35.3), unknown phosphonium salt (δ 26.1), **6d** (δ 24.1) and **8** (δ -5.3).

6. Kinetic Investigation of Quaternization Reactions

6.1. General procedure D for kinetic investigations of quaternization reactions

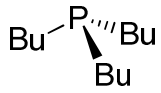
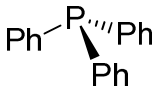
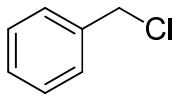
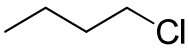
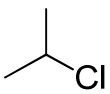


7 or **8** — **12b** R^1 = Bn; **12c** R^1 = Bu; **12d** R^1 = *i*Pr — **5** or **6**

Scheme S31 Quaternization of phosphines **7** and **8** with alkyl halides **12b**-**12d** at NMR scale

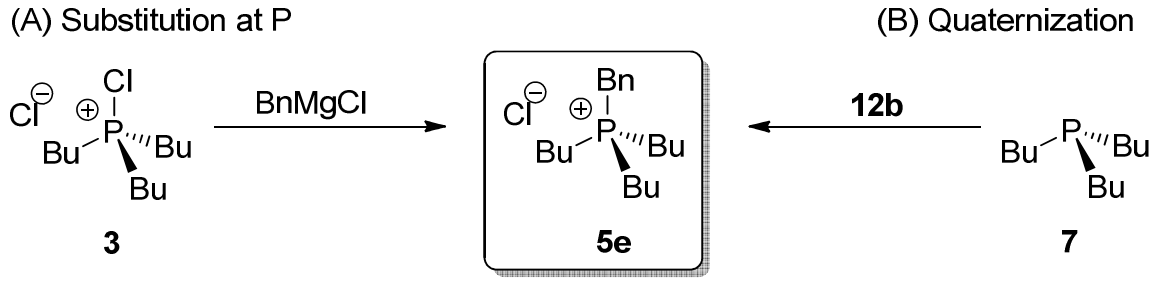
To an NMR tube, an appropriate amount of phosphine **7** or **8** (0.1 mmol, 1.00 equivalent) was dissolved in $CDCl_3$ to give a 0.1 M solution, which was heated to 30 °C. To this, the alkyl halide **12** was added (1 equivalent). The conversion of phosphine to QPS at 30 °C was monitored by ^{31}P NMR. The kinetic rate constants were determined by standard regression analysis and are summarised in Table S7.

Table S7 Second order reaction rate constants k ($M^{-1}s^{-1}$) for the quaternizations of phosphines **7** and **8** with alkyl halides **12b**-**12d**; k_{50} correspond to reactions run at 50 °C. The quaternization reactions were conducted according to general procedure D.

	 **7**	 **8**
 **12b**	$k = 1 \cdot 10^{-3}\ M^{-1}s^{-1}$	$k = 2.6 \cdot 10^{-5}\ M^{-1}s^{-1}$
 **12c**	$k = 3.5 \cdot 10^{-7}\ M^{-1}s^{-1}$ $k_{50} = 1.4 \cdot 10^{-6}\ M^{-1}s^{-1}$	$k_{50} = 1 \cdot 10^{-7}\ M^{-1}s^{-1}$
 **12d**	$k_{50} = 4 \cdot 10^{-7}\ M^{-1}s^{-1}$ (MeCN)	$k < 6 \cdot 10^{-8}\ M^{-1}s^{-1}$ $k_{50} < 1.5 \cdot 10^{-7}\ M^{-1}s^{-1}$

6.2. Discussion of kinetic findings

Let us consider the two pathways to QPS **5e** as shown below in Scheme S32: QPS can be formed by substitution at P (A) or using the traditional quaternization approach (B).



Scheme S32 Two pathways to QPS **3**: (A) Umpolung strategy using electrophilic CPS **3** and benzylmagnesium chloride and (B) traditional quaternization of phosphine **7** with benzyl chloride **12b**.

Rate constant of CPS reaction

To estimate the rate constant of the CPS reaction A (Scheme 32) at -83 °C (conversion of **3** to **5e** was 94 % in 45 minutes, see section 3.3.2), one can use the second order integrated kinetic equation (1):

(1) $$k = \frac{1}{t}\left(\frac{1}{[\mathbf{2a}]_f} - \frac{1}{[\mathbf{2a}]_i}\right) = 2.9 \cdot 10^{-3} M^{-1} s^{-1}$$

Where k is the rate constant in $M^{-1}s^{-1}$, t is the reaction time in seconds, $[\mathbf{3}]_f$ is the final concentration of **3** and $[\mathbf{2}]_i$ is the initial concentration of **3**.

Rate constant of Quaternization reaction

Our conservative estimate for the second order rate constant of quaternization reaction B (Scheme S32), at -83 °C is $k = 3.0 \cdot 10^{-8} M^{-1} s^{-1}$ (using the van't Hoff rule and a temperature quotient of 2.5). The comparison indicates a ca. 10^{-5}-fold difference of reaction rates in favor of the Umpolung process versus much slower quaternization even for the combination of very reactive trialkylphosphine **7** and reactive benzylic chloride **12b**.

7. References

1. K. Nikitin, H. Muller-Bunz, D. Gilheany, *Chemical Communications*, 2013, **49**, 1434.

2. W. J. Considine, *J. Org. Chem.*, 1962, **27**, 647.

3. H.-J. Bestmann, B. Arnason, *Chemische Berichte*, 1962, **95**, 1512.

4. P. Senise, R. M. Luiz, *Anais da Associacao Brasileira de Quimica*, 1961, **20**, 9.

5. K. Takaizumi, T. Wakabayashi, *Journal of Solution Chemistry*, 1980, **9**, 809.

6. N. A. Colabufo, F. Berardi, R. Perrone, S. Rapposelli, M. Digiacomo, A. Balsamo, *Journal of Medicinal Chemistry*, 2006, **49**, 6607.

7. G. Adamova, R. L. Gardas, M. Nieuwenhuyzen, A. V. Puga, L. P. N. Rebelo, A. J. Robertson, K. R. Seddon, *Dalton Transactions*, 2012, **41**, 8316.

8. J. Cvengros, S. Toma, S. Marque, A. Loupy, *Can. J. Chem.-Rev. Can. Chim.*, 2004, **82**, 1365.

9. D. Weber, S. H. Hausner, A. Eisengräber-Pabst, S. Yun, J. A. Krause-Bauer, H. Zimmer, *Inorganica Chimica Acta*, 2004, **357**, 125.