**Supporting Information**

# The quest for unligated oxaphosphiranes with phosphorus in different coordination numbers

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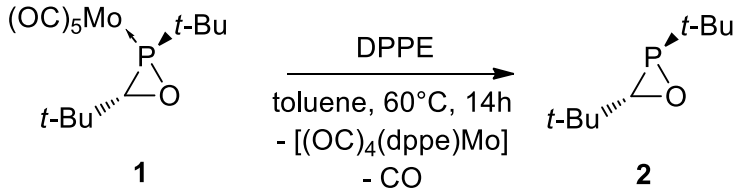
## General working techniques

The syntheses of all compounds were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Toluene, tetrahydrofuran, diethyl ether and *n*-pentane were dried over sodium wire, $CH_2Cl_2$ over $CaH_2$ and further purified by subsequent distillation. All NMR spectra were recorded on a Bruker AVI-300 or a Bruker AV III HD Prodigy 500 spectrometer. The $^{1}H$ and $^{13}C$ NMR spectra were referenced to the residual proton resonances and the $^{13}C$ NMR signals of the deuterated solvents and $^{31}P$ to 85% $H_3PO_4$ as external standards, respectively. Mass spectrometric data were collected either on a MAT 95 XL Finnigan spectrometer using EI, 70 eV, on a Bruker Dalton micrOTOF-Q using ESI(+/-) or on a Orbitrap XL spectrometer for APCI-measurements.

Complex **1** was synthesized according to the literature protocol.[1]

## Synthesis of racemic *trans*-2,3-bis(2,2-dimethylethyl)oxaphosphirane (2)




**Synthesis of 2**: 0.286 g (0.697 mmol) of the oxaphosphirane complex **1** and 0.398 g (0.769 mmol) of DPPE were dissolved in 10 ml of toluene in a 25 ml-Schlenk tube with Teflon valve. The mixture was heated at 60 °C for 14h. After cooling down to room temperature all volatiles were recondensed *in vacuo* ($2 \cdot 10^{-2}$ mbar) in another Schlenk tube with Teflon valve. The obtained solution solely contained the *trans*-isomer of **2** as detected by the $^{1}H$-$^{1}H$-NOESY-NMR spectrum; the displayed stereochemistry is just arbitrary chosen but should not display the absolute stereochemistry!

The concentration of **2** was determined by NMR spectroscopy using an aliquot, to which 0.150 ml (0.697 mmol) of cyclohexane (for $^{1}H$-NMR, reference signal at δ 1.40) and 0.075 ml (0.697 mmol) of diphenyl(ethoxy)phosphane (for $^{31}P$-NMR, reference signal at δ 111.1) was added as references. The NMR measurements were performed using different relaxation times (see figures S1-S6), and the obtained signals were integrated using the reference signal.

**$^{1}H$-NMR** (400 MHz, 298.0 K, toluene): δ /ppm = 0.81 (9H, d, $|^{3}J_{P,H}|$ = 11.79 Hz, P(C(C**H**$_3$)$_3$)), 0.96 (9H, s, C(C(C**H**$_3$)$_3$)), 1.41 (Cyclohexane C**H**$_2$, internal reference) 2.74 (1H, s, P(O)C**H**).

[1] J. Fassbender, G. Schnakenburg, A. Espinosa Ferao and R. Streubel, *Dalton Trans* **2018**, *47*, 9347.

**$^{31}$P-NMR** (400 MHz, 298.0 K, toluene): δ /ppm = -23.7 (m), compound **2**), 111.1 (m), diphenylethoxy-phosphane-internal reference)

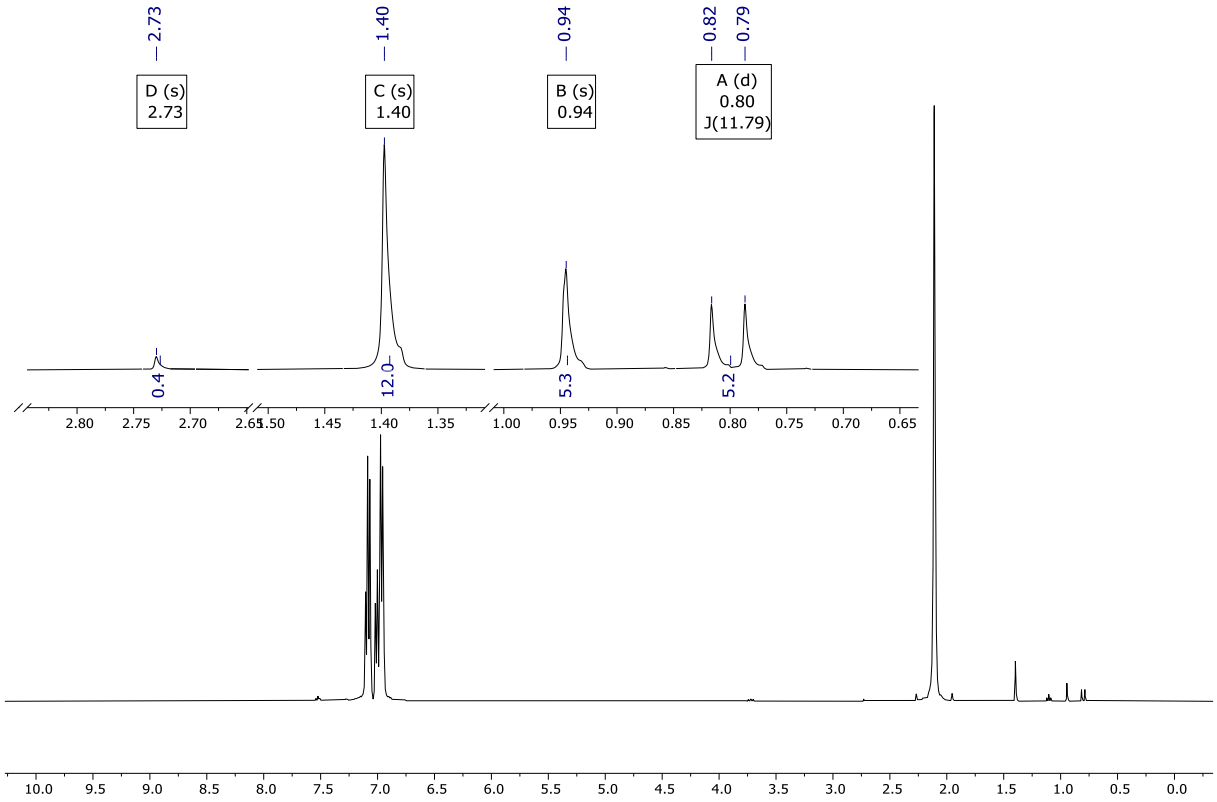



***Figure S1***: $^{1}$H-NMR spectrum of **2** in toluene (Relaxation Delay = 1.000 s)

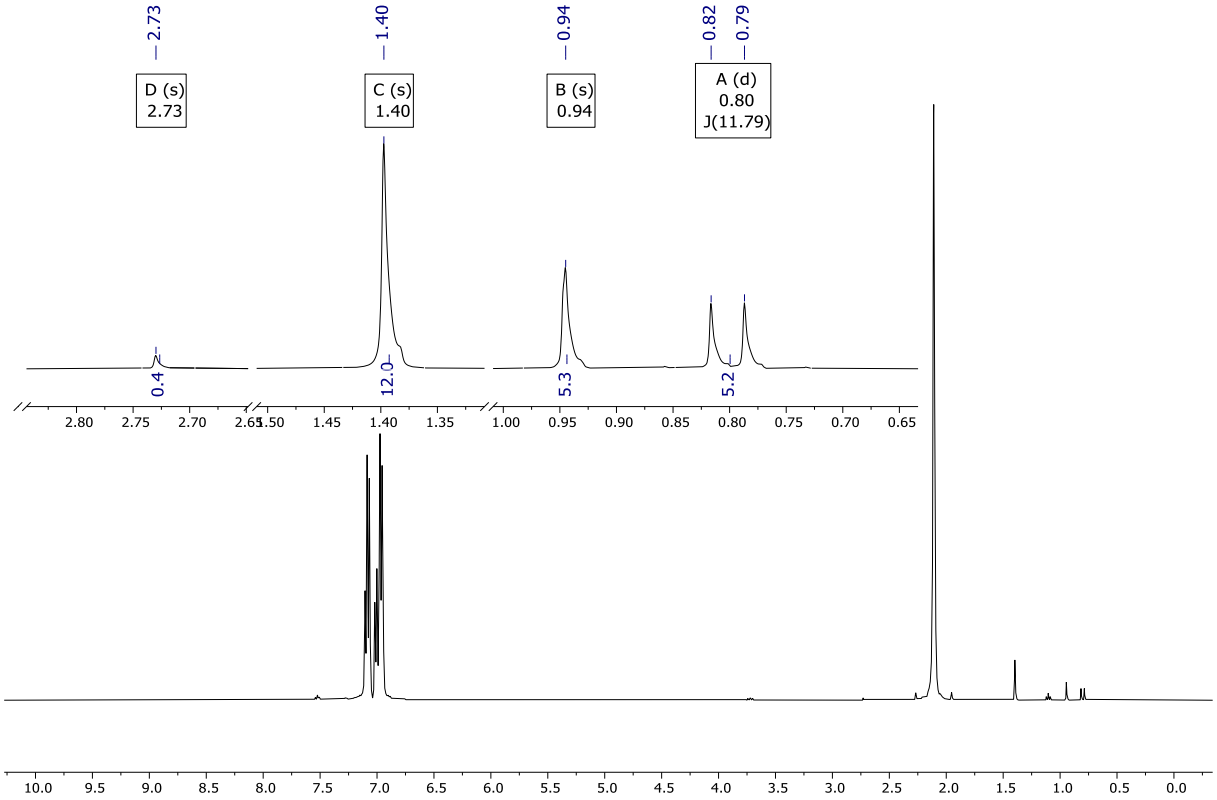



***Figure S2***: $^{1}$H-NMR spectrum of **2** in toluene (Relaxation Delay = 1.500 s)

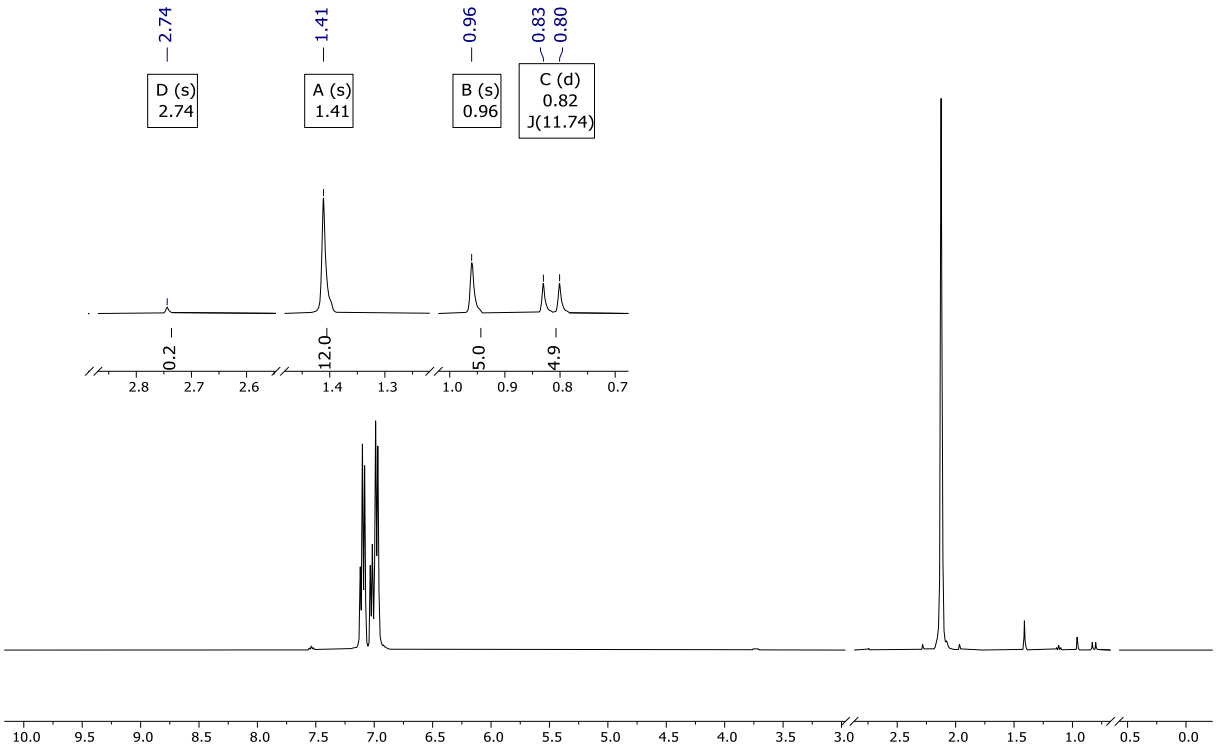



***Figure S3***: $^{1}$H-NMR spectrum of **2** in toluene (Relaxation Delay = 2.000 s)

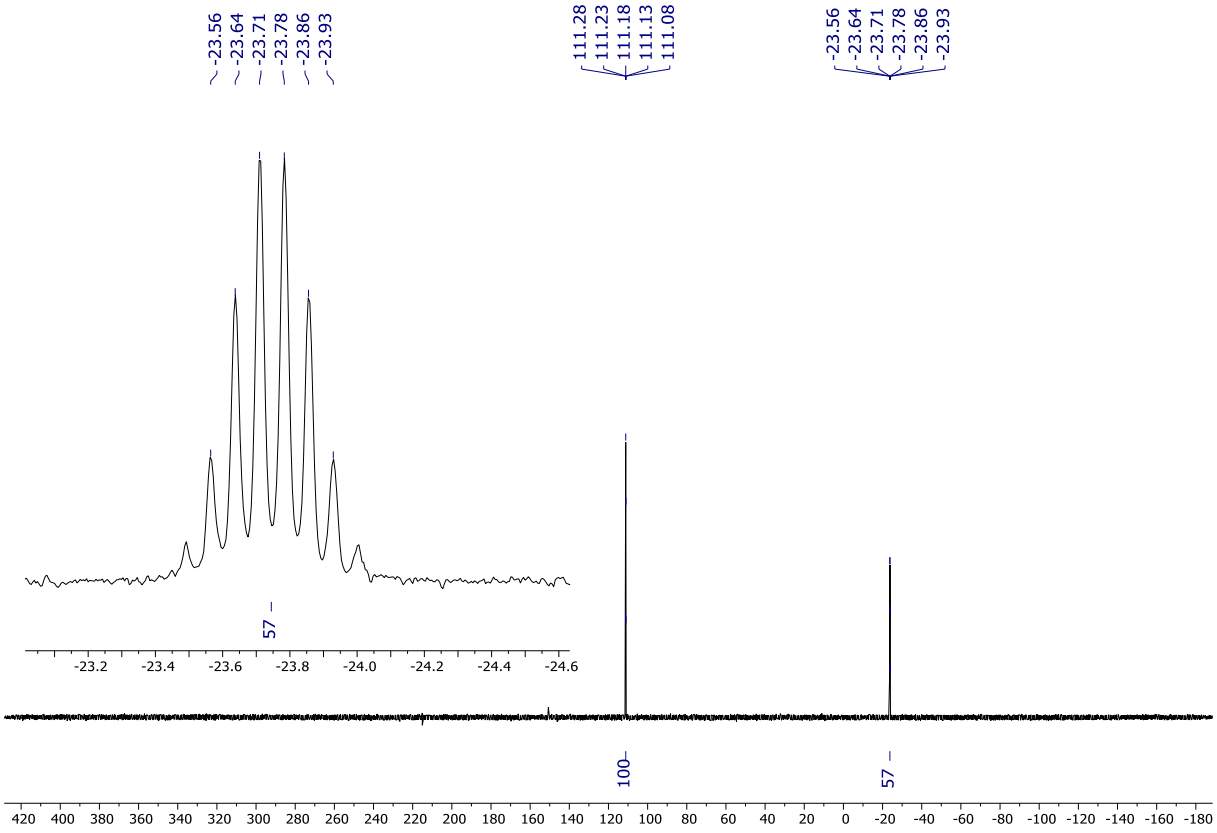



***Figure S4***: $^{31}$P-NMR spectrum of **2** in toluene (Relaxation Delay = 1.000 s)

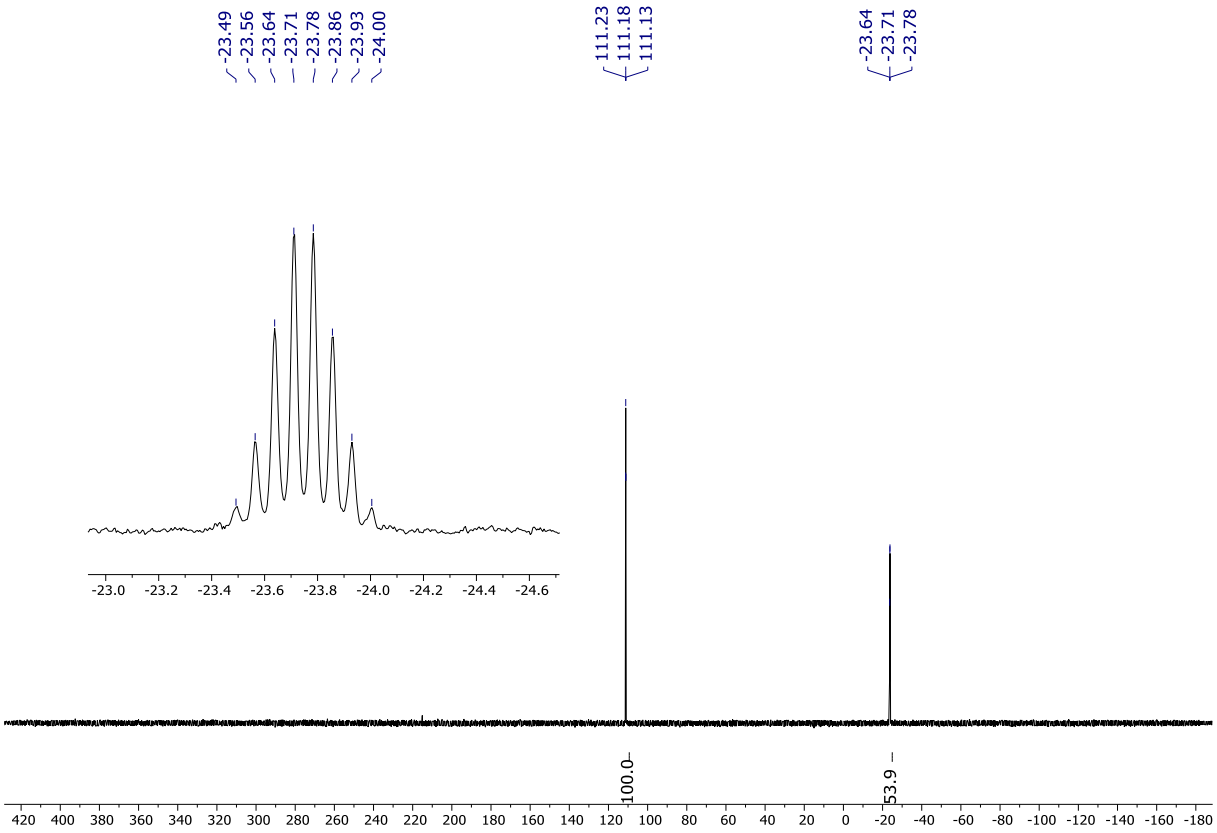



***Figure S5***: $^{31}$P-NMR spectrum of **2** in toluene (Relaxation Delay = 1.500 s)

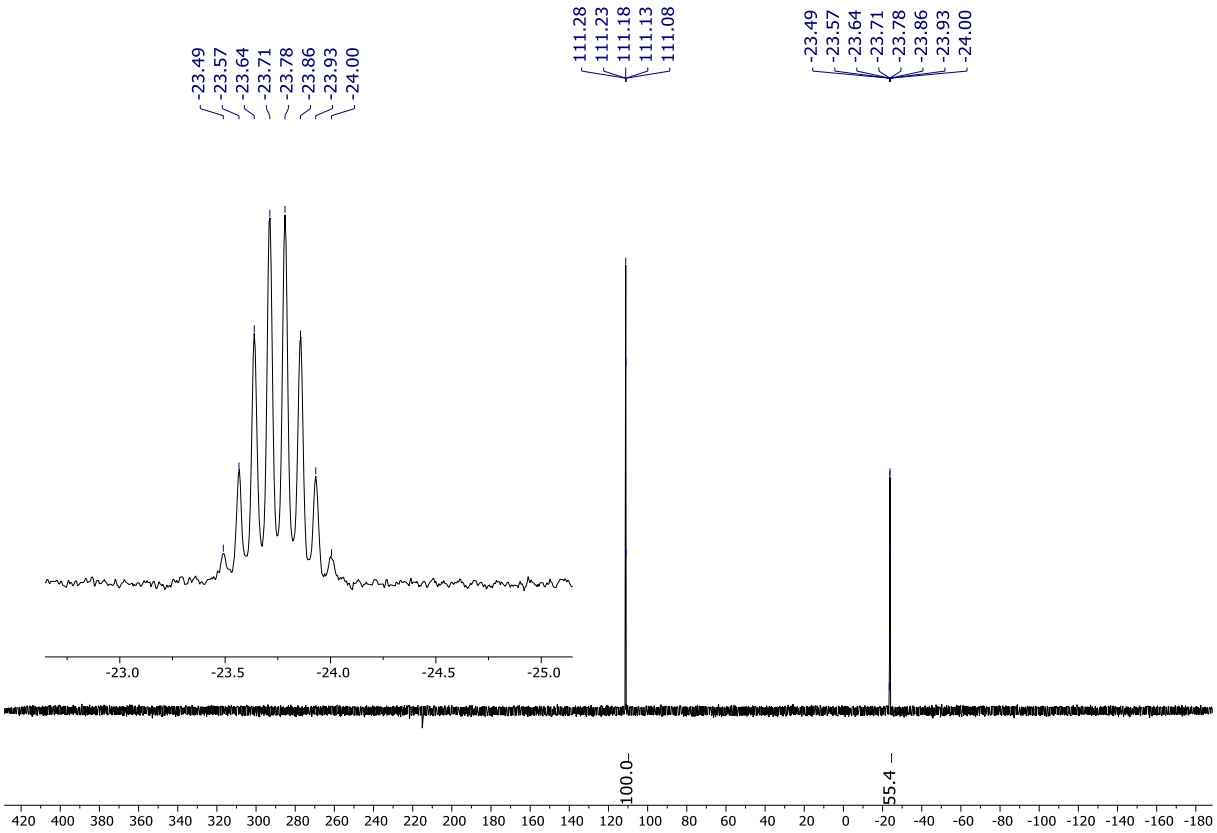



***Figure S6***: $^{31}$P-NMR spectrum of **2** in toluene (Relaxation Delay = 2.000 s)

Content (%) calculated based on the respective NMR spectrum

| Relaxation Delay in sec. | 1.000 | 1.500 | 2.000 |
|---|---|---|---|
| $^{1}$H NMR | 55.55 | 54.55 | 56.94 |
| $^{31}$P NMR | 57.0 | 53.9 | 55.4 |

**MS** (LIFDI): m/z (%): 174.1 (2, $[M]^+$), 92.1 (100, $[toluene]^+$).

**$^{1}$H-NMR** (500.1 MHz, 298.0 K, toluene-$d_8$): δ /ppm = 0.81 (9H, d, $|^{3}J_{P,H}|$ = 11.8 Hz, P(C(C**H**$_3$)$_3$)), 0.96 (9H, d, $|^{4/5}J_{P,H}|$ = 0.9 Hz, C(C(C**H**$_3$)$_3$)), 2.74 (1H, s, P(O)C**H**).

**$^{13}$C{$^{1}$H}-NMR** (125.8 MHz, 298.0 K, toluene-$d_8$): δ /ppm = 25.5 (d, $|^{2}J_{P,C}|$ = 16.8 Hz P(C(**C**H$_3$)$_3$)), 27.0 (d, $|^{3/4}J_{P,C}|$ = 5.0 Hz, C(C(**C**H$_3$)$_3$)), 29.8 (d, $|^{1}J_{P,C}|$ = 44.0 Hz, P(**C**(CH$_3$)$_3$)), 32.3 (d, $|^{2/3}J_{P,C}|$ = 5.8 Hz, C(**C**(CH$_3$)$_3$)), 63.5 (d, $|^{1/2}J_{P,C}|$ = 14.2 Hz, P(O)**C**H).

**$^{31}$P{$^{1}$H}-NMR** (202.5 MHz, 298.0 K, toluene-$d_8$): δ /ppm = -23.7 (s).

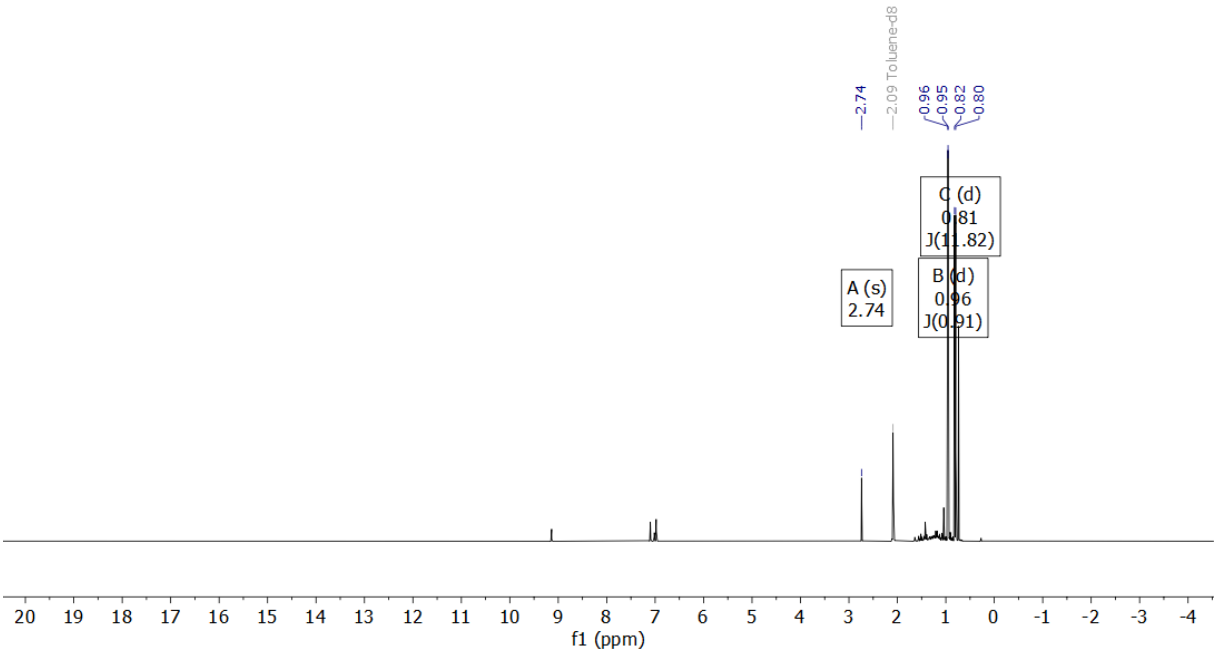



***Figure S7***: $^{1}$H-NMR spectrum of **2** in toluene-$d_8$.

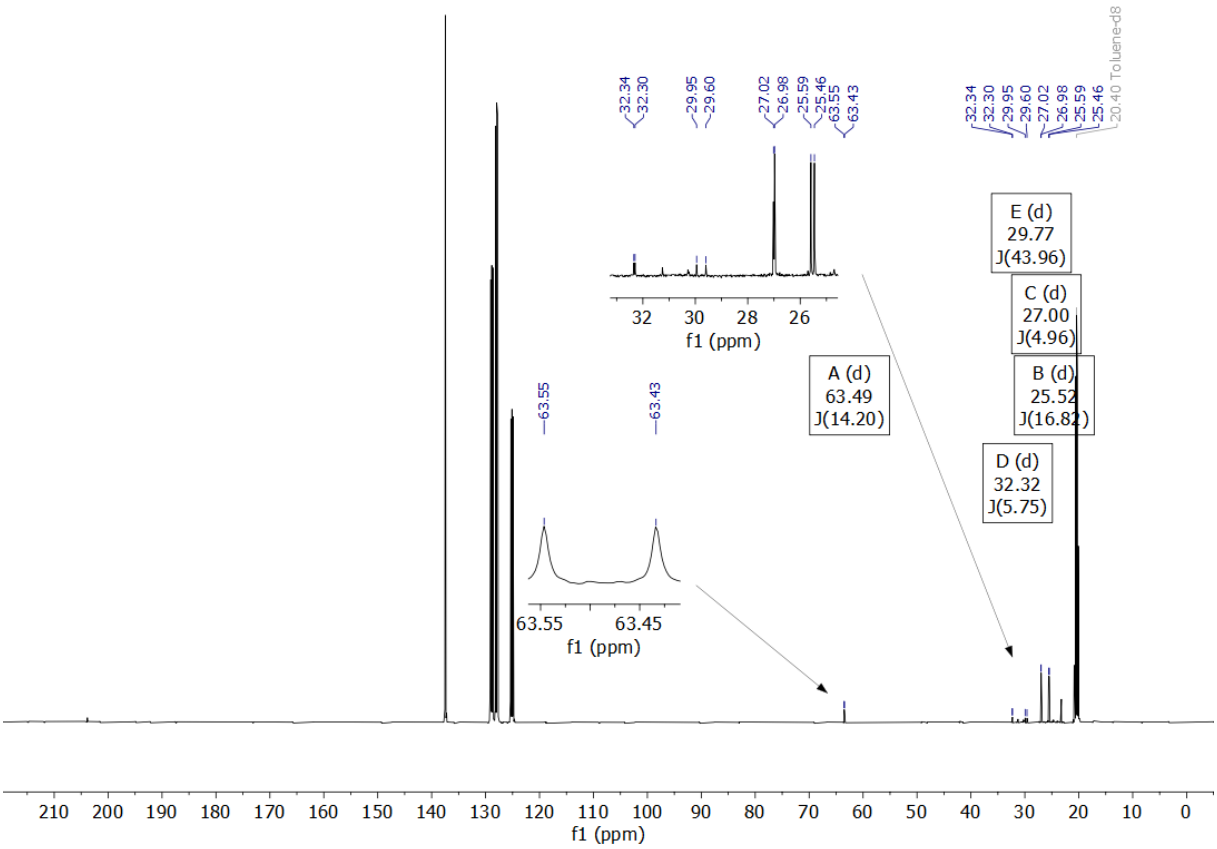



***Figure S8***: $^{13}$C{$^{1}$H}-NMR spectrum of **2** in toluene-$d_8$.

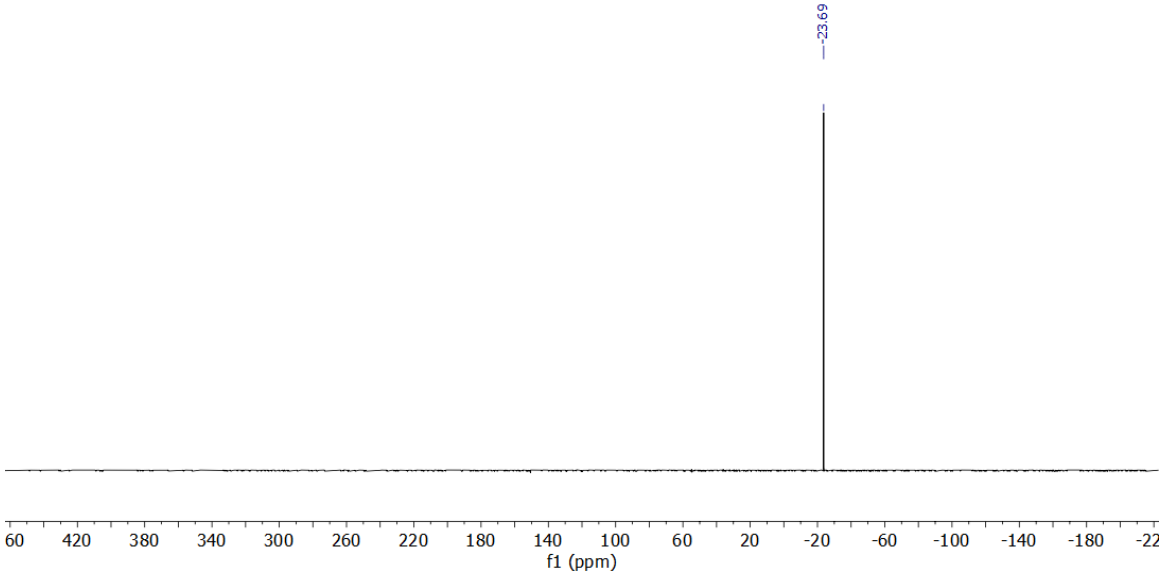
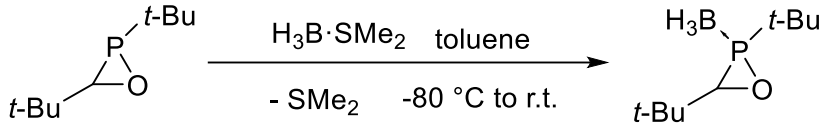



***Figure S9***: $^{31}P\{^{1}H\}$-NMR spectrum of **2** in toluene-$d_8$.

## Generation of [{2,3-Bis-(2,2-dimethylethyl)oxaphosphirane-κP}borane] (3)




**2** **3**

**Synthesis of 2**: To a precooled solution (-80 °C) of the oxaphosphirane **2** (approx. 1.5 ml), 0.01 ml of $H_3B{\cdot}SMe_2$ (10M in $SMe_2$) were added. The solution was warmed to room temperature and was investigated *via* $^{11}B$- and $^{31}P$-NMR spectroscopy.

**$^{11}$B-NMR** (96.29 MHz, 299.0 K, toluene): δ /ppm = -41.1 (qd, $^{1}J_{B,H}$ = 105.3 Hz, $^{2}J_{P,H}$ = 29.6 Hz).

**$^{31}$P{$^{1}$H}-NMR** (121.51 MHz, 299.0 K, toluene): δ /ppm = -23.5 (**2**, 5 %), 38.3 (br m, **3**, 95 %).

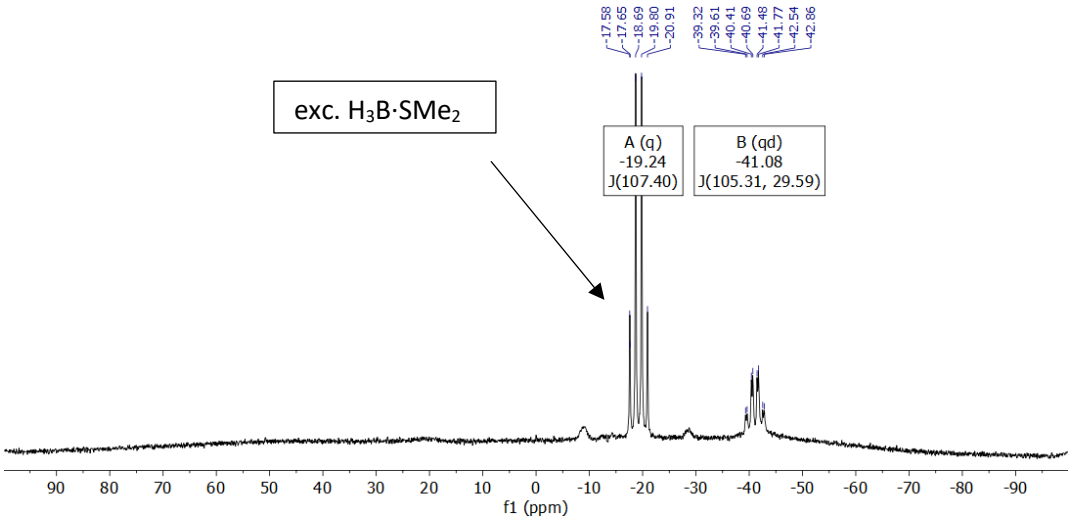



***Figure S10***: $^{11}B$-NMR spectrum of the reaction solution containing **3**.

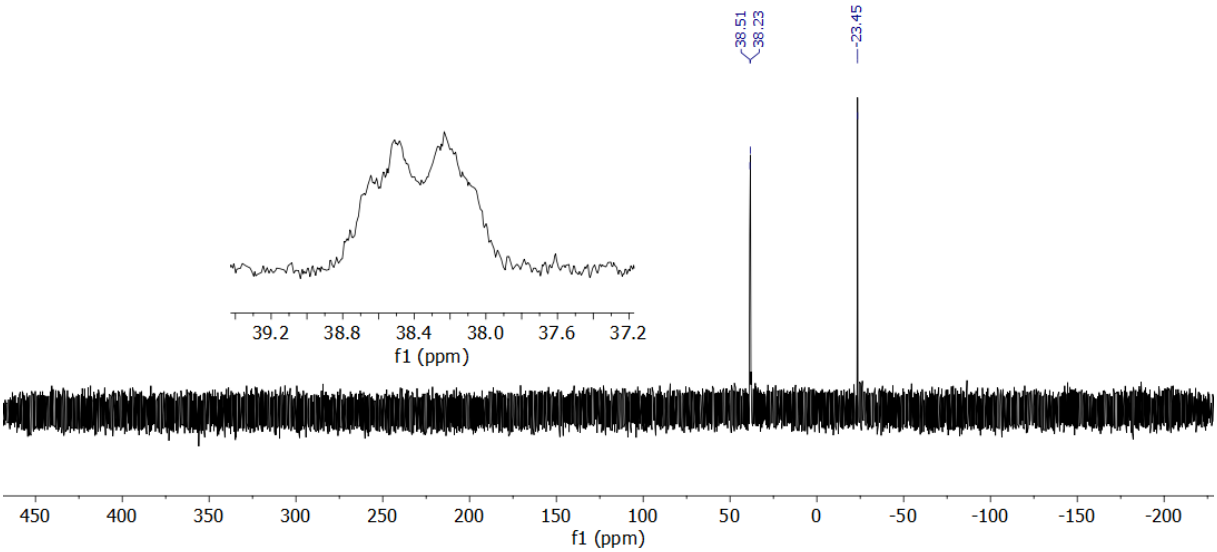
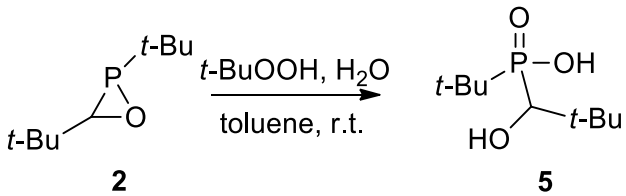



***Figure S11***: $^{31}P\{^{1}H\}$-NMR spectrum of the reaction solution containing **3**.

## Synthesis of (1,1-dimethylethyl)(1-hydroxy-2,2-dimethylpropyl)phosphonic acid (5)




**2** **5**

**Synthesis of 5:** To the solution of the oxaphosphirane **2** (approx. 8 ml), 0.1 ml of *t*-BuOOH (5-6 M in decane) were added. After stirring for 1h at room temperature all volatiles were removed *in vacuo* ($2\cdot10^{-2}$ mbar). and the remaining solid was washed with *n*-pentane (5·1 ml). After drying *in vacuo* ($2\cdot10^{-2}$ mbar) **5** was obtained as a colorless solid.

**$^{1}$H-NMR** (500.1 MHz, 298.0 K, $C_6D_6$): δ /ppm = 1.12 (9H, d, $|^{3}J_{P,H}|$ = 15.1 Hz, P(C(C**H**$_3$)$_3$)), 1.21 (9H, s, C(C(C**H**$_3$)$_3$)), 3.55 (1H, d, $|^{2}J_{P,H}|$ = 0.6 Hz, PC(**H**)OH).

**$^{13}$C{$^{1}$H}-NMR** (125.8 MHz, 298.0 K, $C_6D_6$): δ /ppm = 24.0 (s, P(C(**C**H$_3$)$_3$)), 26.8 (d, $|^{3}J_{P,C}|$ = 4.9 Hz, C(C(**C**H$_3$)$_3$)), 33.1 (d, $|^{1}J_{P,C}|$ = 88.8 Hz, P(**C**(CH$_3$)$_3$)), 36.3 (s, C(**C**(CH$_3$)$_3$)), 73.1 (d, $|^{1}J_{P,C}|$ = 87.6 Hz, P**C**(H)OH).

**$^{31}$P{$^{1}$H}-NMR** (202.5 MHz, 298.0 K, $C_6D_6$): δ /ppm = 62.0 (s).

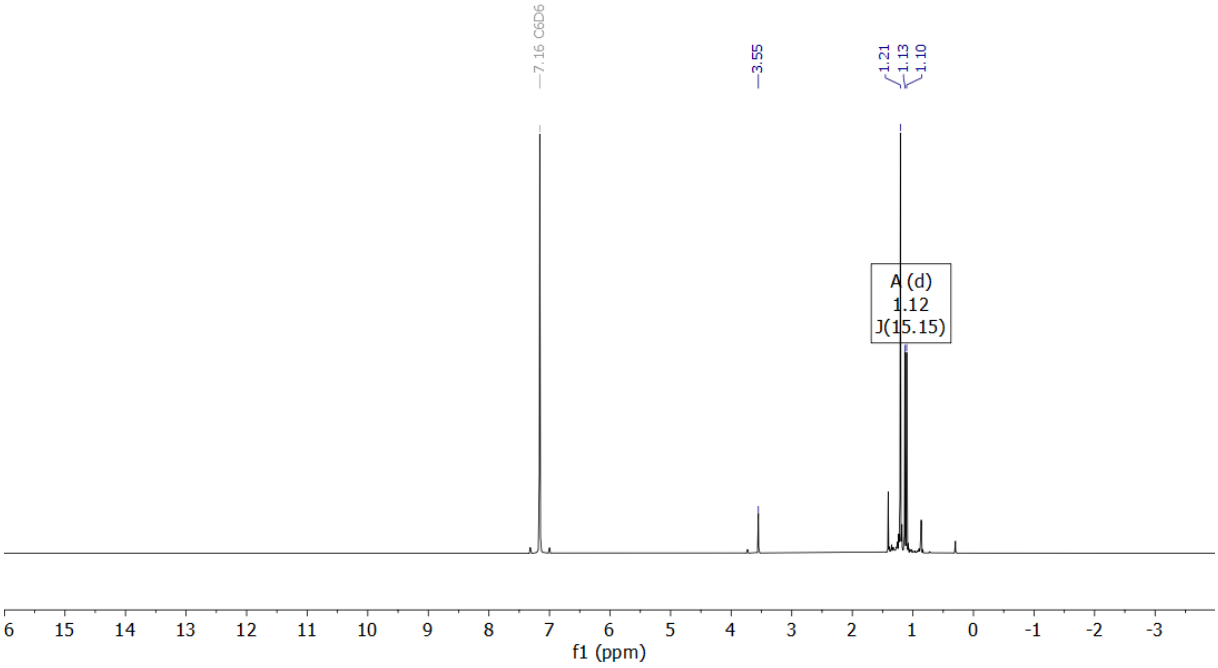



***Figure S12***: $^{1}$H-NMR spectrum of **5** in $C_6D_6$.

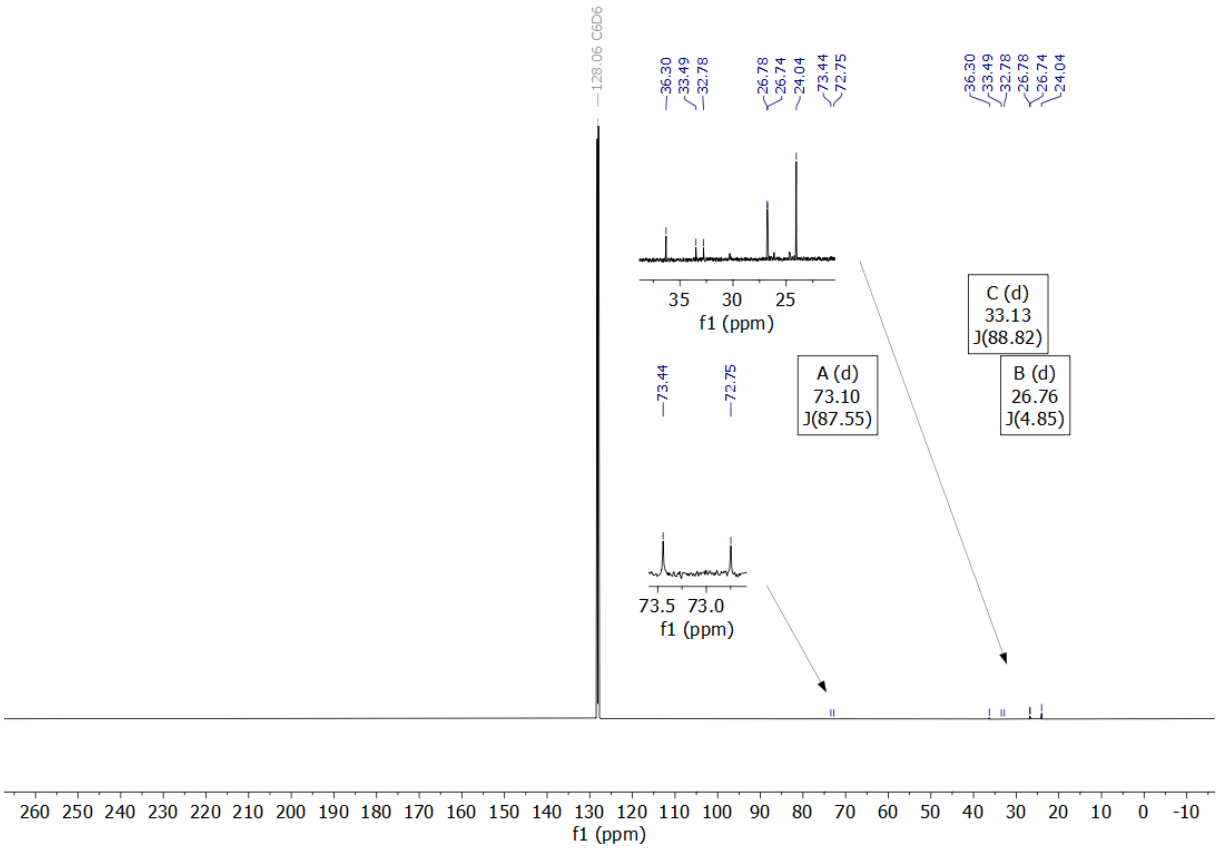



***Figure S13***: $^{13}C\{^{1}H\}$-NMR spectrum of **5** in $C_6D_6$.

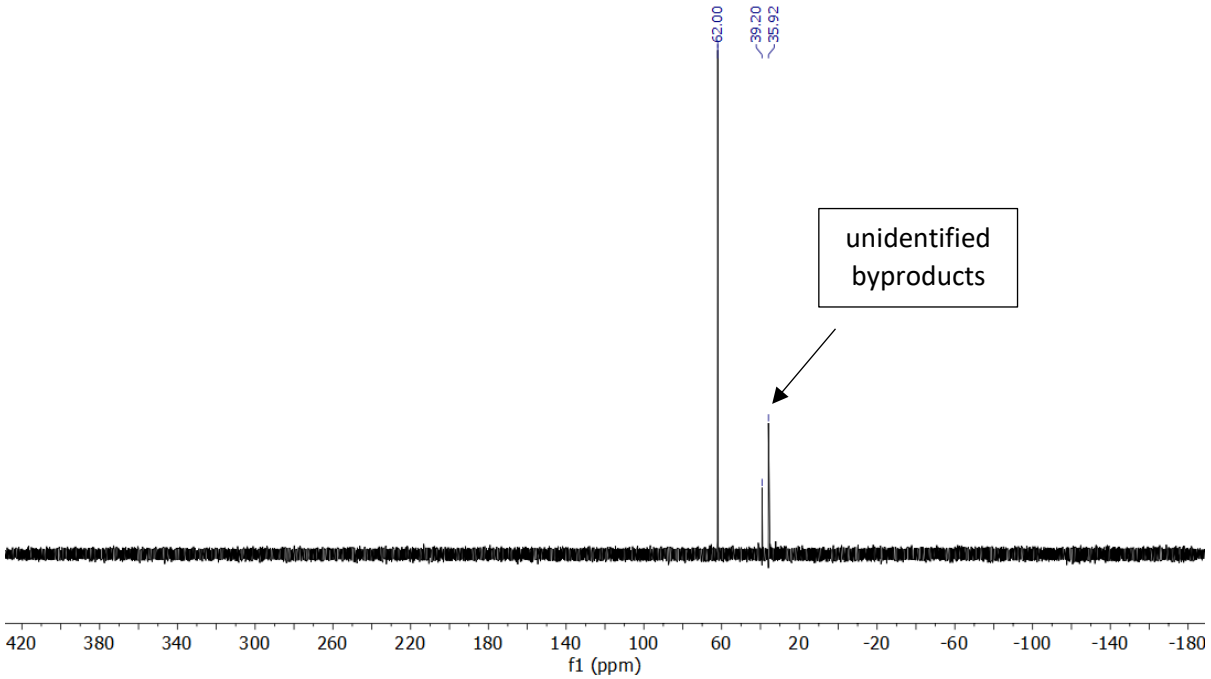
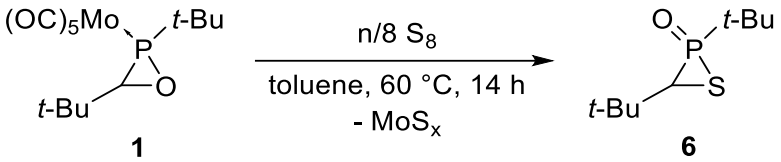
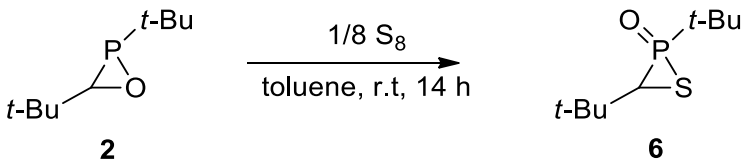



***Figure S14***: $^{31}P\{^{1}H\}$-NMR spectrum of **5** in $C_6D_6$.

## Synthesis of 2,3-bis(2,2-dimethylethyl)thiaphosphirane-*P*-oxide (6)




**Method A**: 180.3 mg of the oxaphosphirane complex **1** (0.44 mmol, 1.00 eq.) and 49.1 mg of sulfur (1.50 mmol, 3.41 eq.) were dissolved in toluene (5 ml) in a Schlenk tube with Teflon valve. The mixture was stirred at 60 °C for 14 h. After cooling down to room temperature all volatiles were removed *in vacuo* ($2 \cdot 10^{-2}$ mbar) and the remaining solid was washed with *n*-pentane (3·4 ml). After drying *in vacuo* **6** was obtained as a yellow solid.




**Method B**: To the solution of the oxaphosphirane **2** (approx. 3 ml), 1 ml THF and one spatula tip of sulfur (exc.) were added. After stirring for 24h at room temperature all volatiles were removed *in vacuo* ($2 \cdot 10^{-2}$ mbar). and the remaining solid was washed with *n*-pentane (3·2 ml). After drying *in vacuo* ($2 \cdot 10^{-2}$ mbar) **6** was obtained as a yellow solid.

**$^{1}$H-NMR** (300.1 MHz, 298.0 K, $C_6D_6$): δ /ppm = 1.06 (9H, d, $|^{3}J_{P,H}|$ = 21.4 Hz, P(C(C**H**$_3$)$_3$)), 1.18 (9H, d, $|^{4/5}J_{P,H}|$ = 0.9 Hz, C(C(C**H**$_3$)$_3$)), 2.67 (1H, d, $|^{2/3}J_{P,H}|$ = 1.8 Hz, P(O)C**H**)).

**$^{13}$C{$^{1}$H}-NMR** (75.5 MHz, 298.0 K, $C_6D_6$): δ /ppm = 26.2 (d, $|^{3/4}J_{P,C}|$ = 2.6 Hz, C(C(**C**H$_3$)$_3$)), 28.9 (d, $|^{2}J_{P,C}|$ = 5.8 Hz P(C(**C**H$_3$)$_3$)), 33.8 (d, $|^{2/3}J_{P,C}|$ = 3.6 Hz, C(**C**(CH$_3$)$_3$)), 40.9 (d, $|^{1}J_{P,C}|$ = 47.5 Hz, P(**C**(CH$_3$)$_3$)), 42.8 (d, $|^{1/2}J_{P,C}|$ = 20.0 Hz, P(O)**C**H).

**$^{31}$P{$^{1}$H}-NMR** (121.5 MHz, 298.0 K, $C_6D_6$): δ /ppm = 21.5 (s).

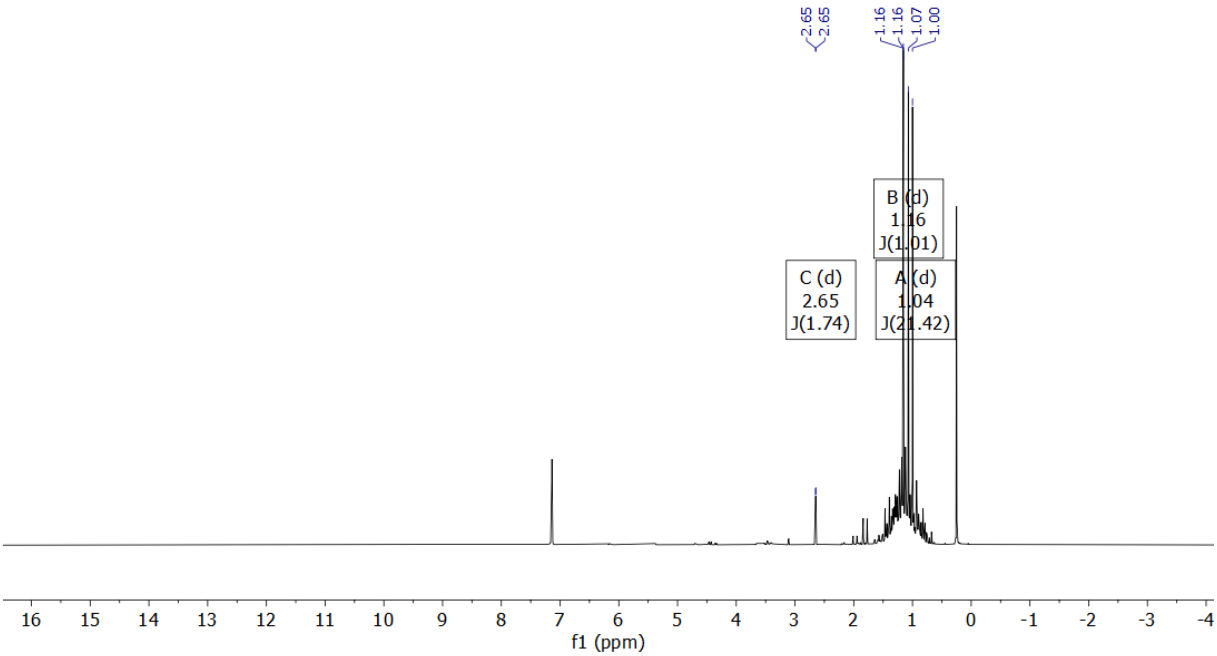



***Figure S15***: $^{1}$H-NMR spectrum of **6** in $C_6D_6$.

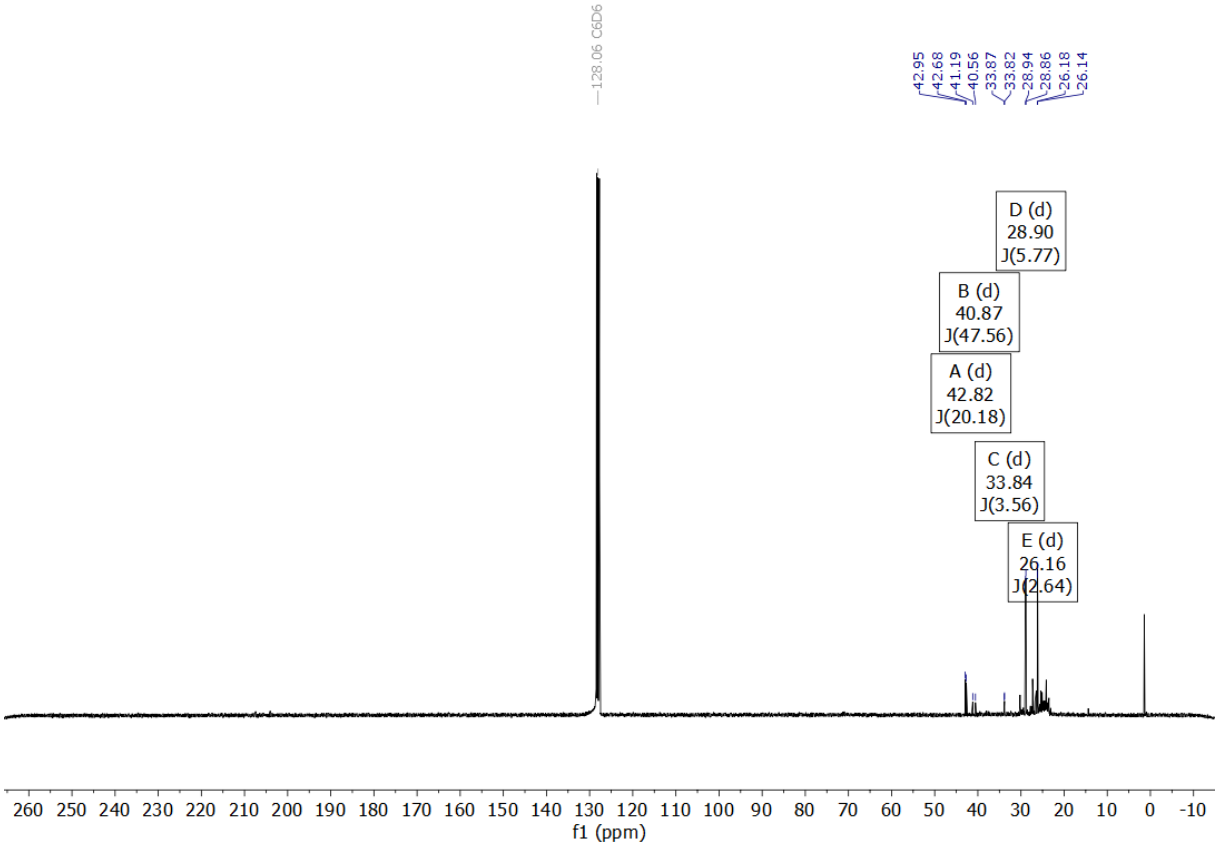



***Figure S16***: $^{13}C\{^{1}H\}$-NMR spectrum of **6** in $C_6D_6$.

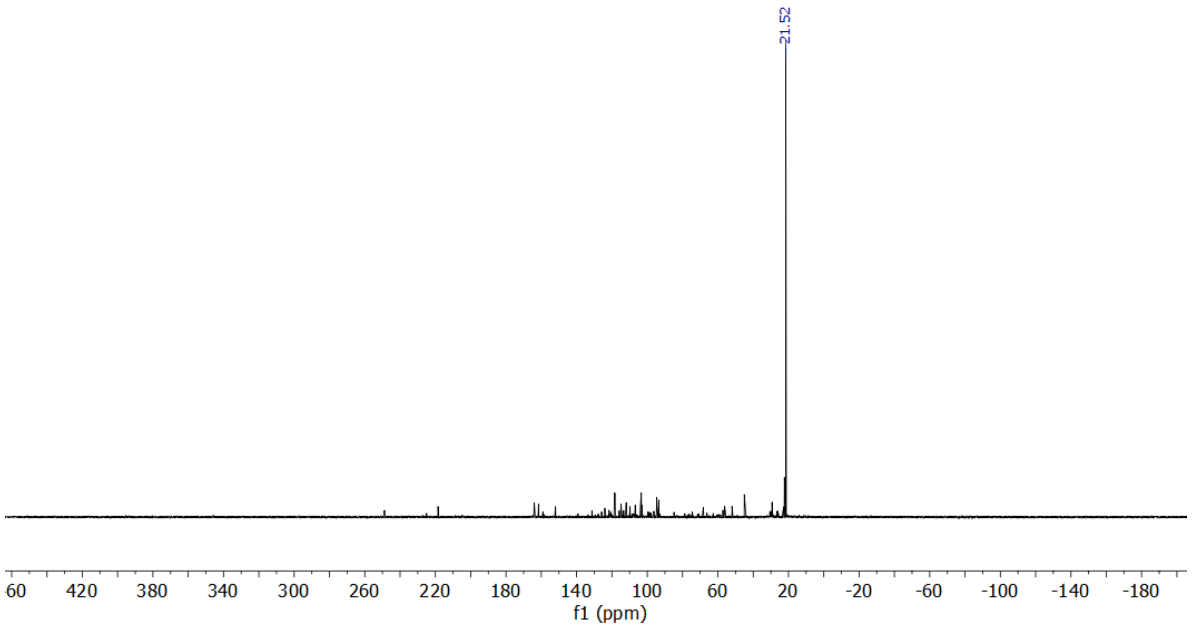
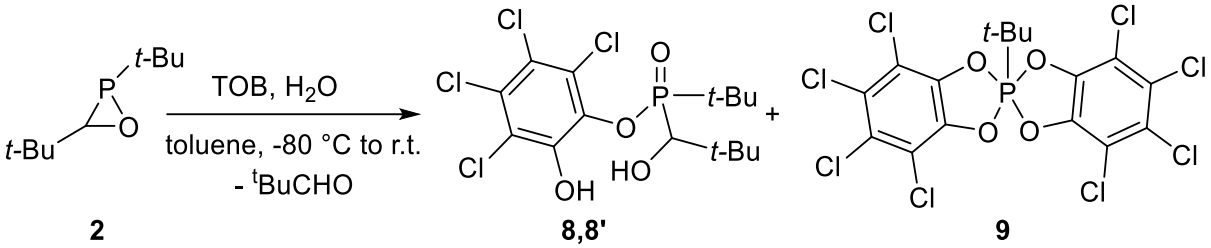



***Figure S17***: $^{31}P\{^{1}H\}$-NMR spectrum of **6** in $C_6D_6$.

## Synthesis of a mixture of (1,1-dimethylethyl)-(1-hydroxy-2,2-dimethylpropyl)-(2,3,4,5-tetrachloro-6-hydroxyphenoxy)phosphaneoxide (8,8') and 4,4',5,5',6,6',7,7'-octachloro-2-(1,1-dimethylethyl)-2,2'-spirobis[1,3,2-benzodioxaphosphole] (9)




**2** **8,8'** **9**

### VT-NMR investigation

6.5 ml of a cooled (-80 °C) oxaphosphirane solution **2** were transferred with a transfer cannula to a -80 °C precooled Schlenk tube containing 49.2 mg of TOB (0.200 mmol). After stirring for 1 minute 0.5 ml of the solution were transferred to a -90 °C precooled Young NMR tube and VT-NMR measurements were conducted from -70 °C to 25 °C.

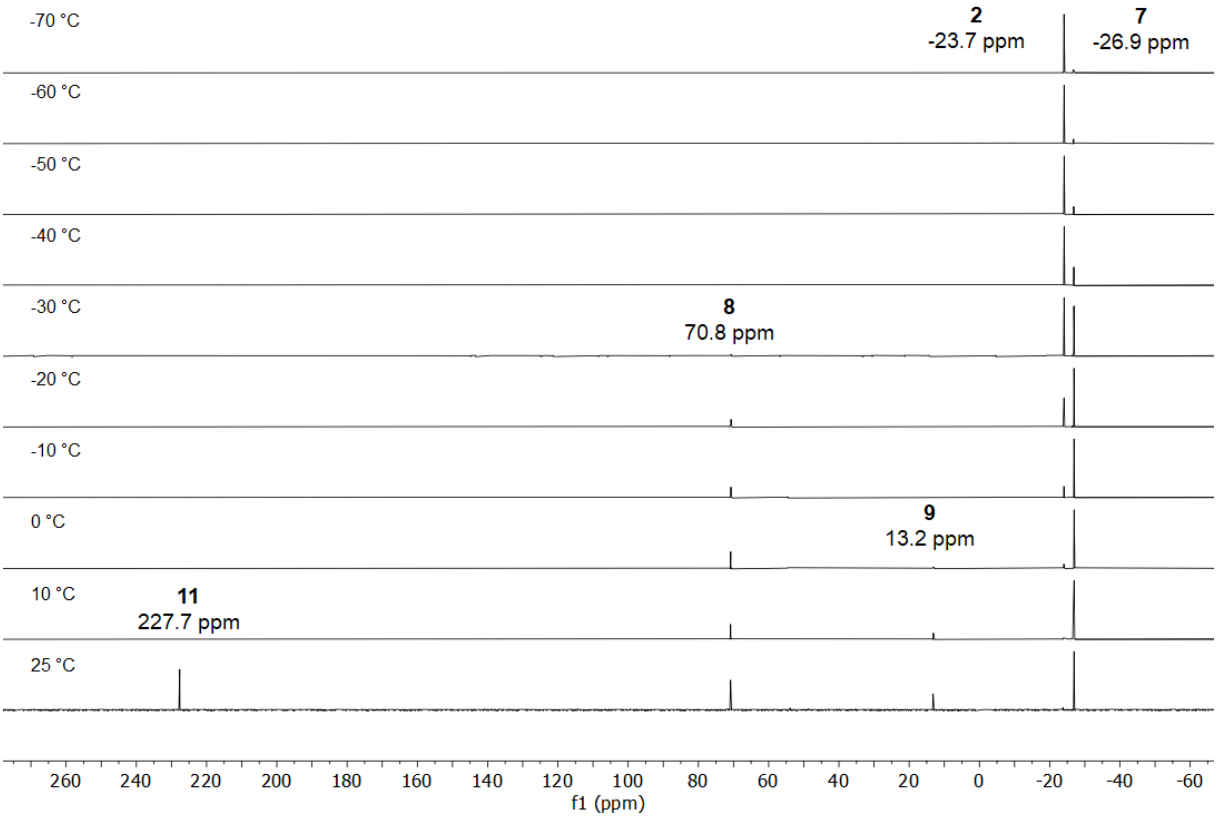



***Figure 18***: $^{31}P\{^{1}H\}$-VT-NMR investigation from -70 °C to 25 °C in toluene.

### Reaction solution

The reaction solution was warmed up to -10 °C and the solvent was removed *in vacuo* ($2 \cdot 10^{-2}$ mbar) at -10 °C. The obtained bright yellow residue was washed with *n*-pentane (3·1.5 ml) at -30 °C and dried *in*

*vacuo* ($2 \cdot 10^{-2}$ mbar). A mixture of **8,8'** and **9** was obtained in a 1:0.05:0.25 ratio as a bright yellow solid. The following data refer to the mixture.

**9**: **MS** (EI) m/z (%): calculated: 575.77 found: 575.7 (10, $[M]^{+\bullet}$), 519.6 (14, $[M\text{-}C_4H_8]^{+\bullet}$), 293.8 (10, $[M\text{-}C_6Cl_4O]^{+\bullet}$), 276.8 (60, $[M\text{-}C_6Cl_4HO_2]^{+\bullet}$), 57.1 (100, $[M\text{-}C_{12}Cl_8O_4P]^{+\bullet}$).

**$^1$H-NMR** (300.13 MHz, 298.0 K, $CDCl_3$): $\delta$ /ppm = 1.27 (d, $|^3J_{P,H}|$= 22.5 Hz, 9H, P(C(C**H**$_3$)$_3$)).

**$^{13}$C{$^1$H}-NMR** (75.48 MHz, 298.0 K, $CDCl_3$): $\delta$ /ppm = 26.9 (d, $|^2J_{P,C}|$= 1.9 Hz, C(C(**C**H$_3$)$_3$), 43.1 (d, $|^1J_{P,C}|$ = 144.6 Hz, C(**C**(CH$_3$)$_3$), 126.2 (s, Ar$^{OP}$), 128.4 (s, Ar$^{Cl}$), 129.2 (s, Ar$^{Cl}$), 141.0 (d, $|^xJ_{P,C}|$= 4.9 Hz, Ar$^{Cl}$), 144.6 (d, $|^xJ_{P,C}|$= 2.3 Hz, Ar$^{Cl}$).

**$^{31}$P-NMR** (121.51 MHz, 298.0 K, $CDCl_3$): $\delta$ /ppm = 14.0 (dez, $|^3J_{P,H}|$= 22.5 Hz).

**8**: **$^1$H-NMR** (300.13 MHz, 298.0 K, $CDCl_3$): $\delta$ /ppm = 1.11 (s, 9H, C(C(C**H**$_3$)$_3$), 1.35 (d, $|^3J_{P,H}|$= 16.4 Hz, 9H, P(C(C**H**$_3$)$_3$)), 3.97 (d, $^2J_{P,H}$ = 5.4 Hz, 1H, PC(**H**)OH), 11.3 (s, 1H, Ar-OH).

**$^{13}$C{$^1$H}-NMR** (75.48 MHz, 298.0 K, $CDCl_3$): $\delta$ /ppm = 24.4 (s, C(**C**H$_3$)$_3$)), 26.5 (d, $|^2J_{P,C}|$= 5.0 Hz, P(C(**C**H$_3$)$_3$)), 35.5 (d, $|^1J_{P,C}|$= 78.1 Hz, P(**C**(CH$_3$)$_3$)), 36.4 (s, C(**C**(CH$_3$)$_3$)), 74.5 (d, $|^1J_{P,C}|$= 81.2 Hz, P**C**(H)OH), 126.2 (s, Ar$^{OP}$/Ar$^{OH}$), 128.4 (s, Ar$^{Cl}$), 129.2 (s, Ar$^{Cl}$), 141.0 (d, $|^xJ_{P,C}|$= 4.9 Hz, Ar$^{Cl}$), 144.6 (d, $|^xJ_{P,C}|$= 2.3 Hz, Ar$^{Cl}$).

**$^{31}$P-NMR** (121.51 MHz, 298.0 K, $CDCl_3$): $\delta$ /ppm = 71.8 ppm (dezd, $|^3J_{P,H}|$= 16.4 Hz, $|^2J_{P,H}|$= 5.4 Hz).

**8'**: **$^{31}$P{$^1$H}-NMR** (121.51 MHz, 298.0 K, $CDCl_3$): $\delta$ /ppm = 72.0 ppm.

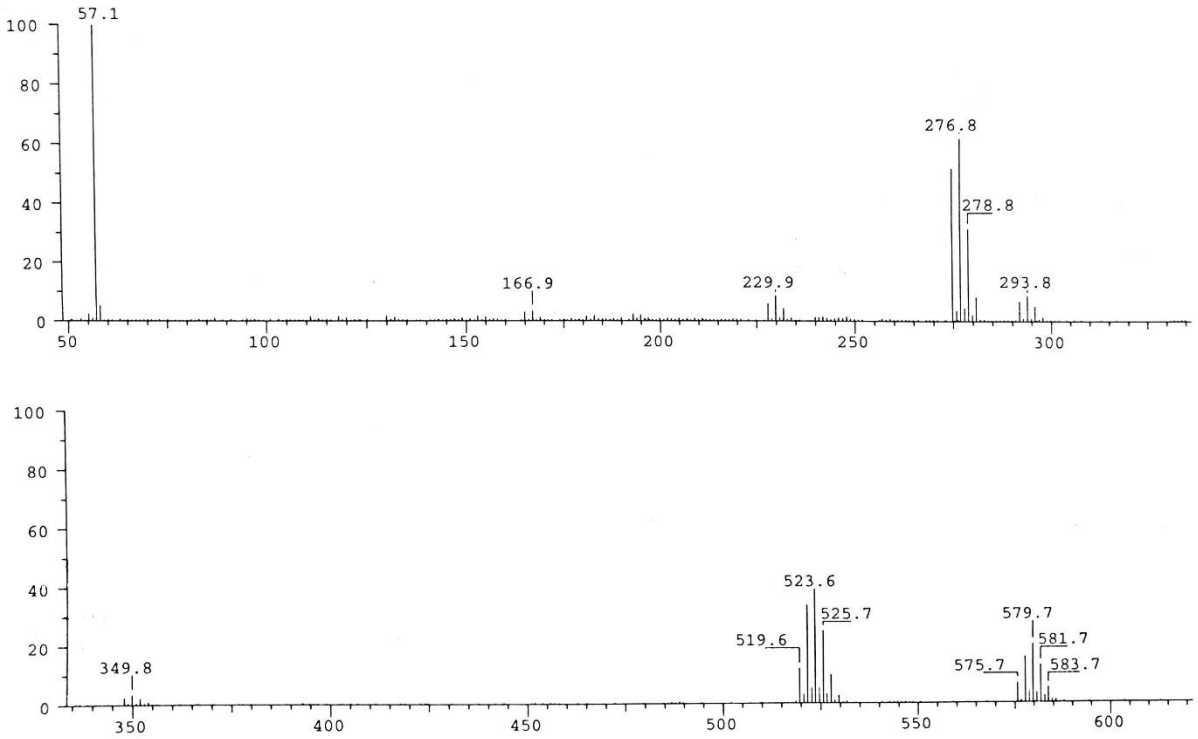



***Figure S19***: MS spectrum (EI) of the product mixture of **8**,**8'** and **9**.

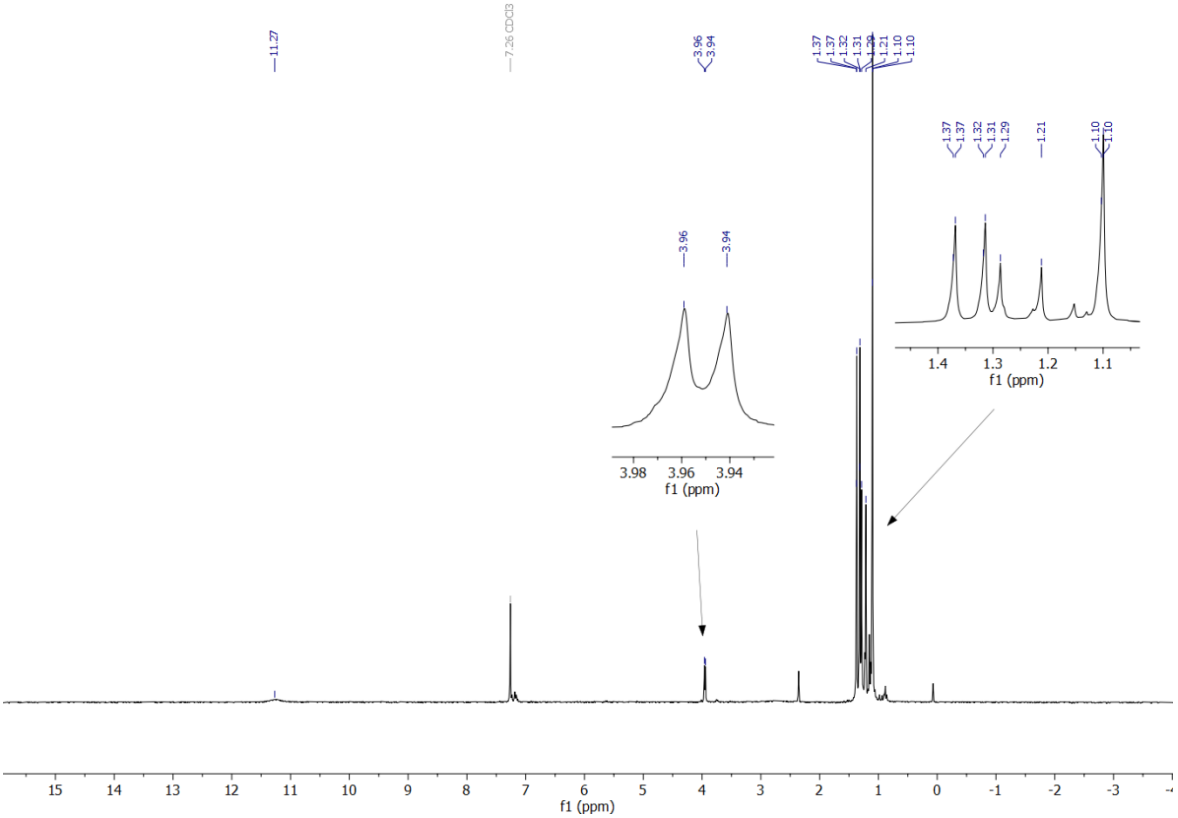



***Figure S20***: $^{1}$H-NMR spectrum of the product mixture **8**,**8'** and **9** in $CDCl_3$.

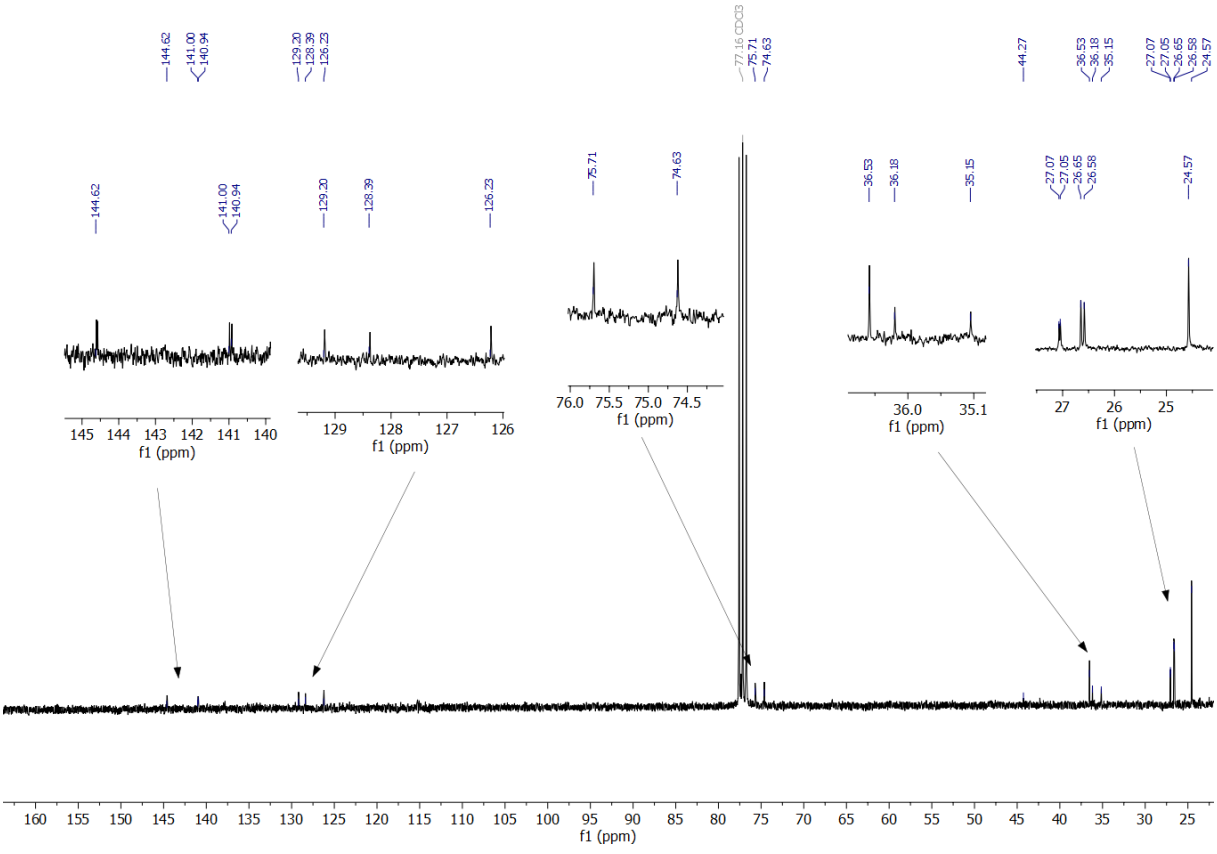



***Figure S21***: $^{13}C\{^{1}H\}$-NMR spectrum of the product mixture **8**,**8'** and **9** in $CDCl_3$.

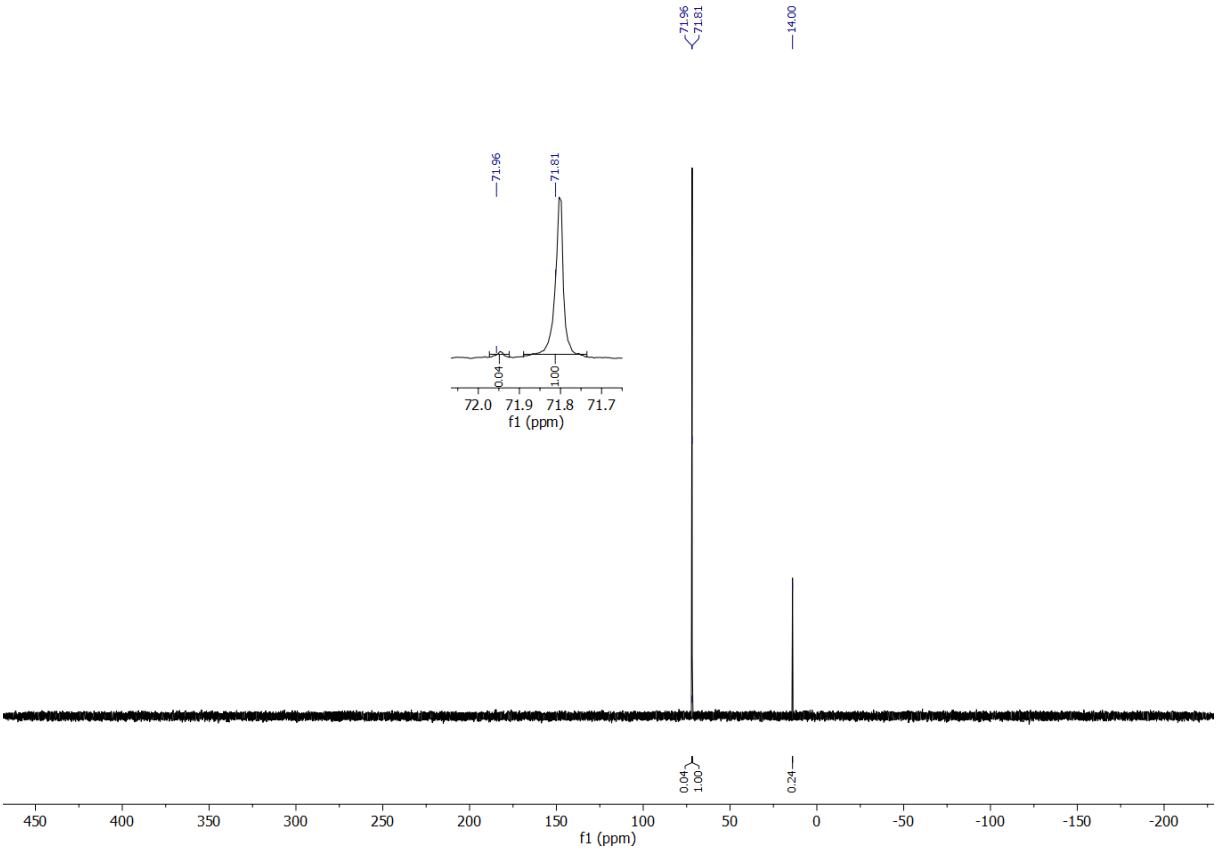
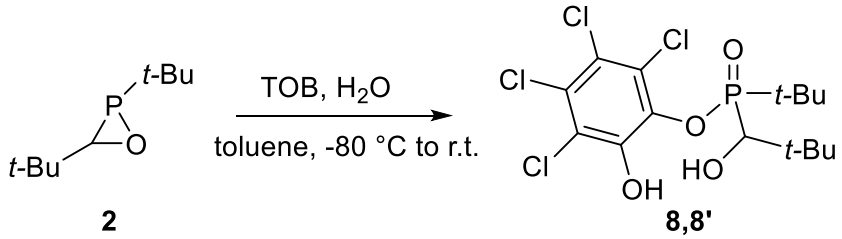



***Figure S22***: $^{31}P\{^{1}H\}$-NMR spectrum of the product mixture **8**,**8'** and **9** in $CDCl_3$.

## Synthesis of (1,1-dimethylethyl)-(1-hydroxy-2,2-dimethylpropyl)-(2,3,4,5-tetrachloro-6-hydroxyphenoxy)phosphaneoxide (8,8')




**2** **8,8'**

To a solution of 23.2 mg TOB in 1 ml toluene, 1 ml of the oxaphosphirane solution **2** was added at -80 °C. The solution was slowly warmed up to room temperature over five hours and stirred at room temperature for 2 days. The solvent was removed *in vacuo* ($2\cdot10^{-2}$ mbar) and a red solid was obtained. The solid was washed with *n*-pentane (4x1 ml) and $Et_2O$ (1x1 ml) at -30 °C and dried *in vacuo* ($2\cdot10^{-2}$ mbar). The product was obtained as a beige solid and as a mixture of both diastereomers **8**,**8'** (1 : 0.02).

**8**: **MS** (APCI) m/z (%): calculated.: 435.99 found: 437.000 (10, $[M+H]^{+\bullet}$), 350.927 (76, $[M-C_5H_9O]^{+\bullet}$).

**$^{1}$H-NMR** (500.04 MHz, 298.0 K, $CD_2Cl_2$): δ /ppm = 1.01 (s, 9H, C(C($CH_3$)$_3$)), 1.25 (d, $|^{3}J_{P,H}|$= 16.4 Hz, 9H, P(C($CH_3$)$_3$)), 2.45 (s, 1H, OH), 3.98 (s, 1H, PC(H)OH), 11.3 (s, 1H, Ar-OH).

**$^{13}$C{$^{1}$H}-NMR** (125.75 MHz, 298.0 K, $CD_2Cl_2$): δ /ppm = 24.5 (s, C(C(**C**$H_3$)$_3$)), 26.6 (d, $|^{2}J_{P,C}|$= 5.0 Hz, P(C(**C**$H_3$)$_3$)), 35.8 (d, $|^{1}J_{P,C}|$= 78.1 Hz, P(**C**($CH_3$)$_3$)), 36.6 (s, C(**C**($CH_3$)$_3$)), 75.3 (d, $|^{1}J_{P,C}|$= 81.8Hz, P**C**(H)OH), 123.3 (s, $Ar^{OP}$/$Ar^{OH}$), 123.4 (s, $Ar^{OP}$/$Ar^{OH}$), 129.5 (s, $Ar^{Cl}$), 138.5 (d, $|^{x}J_{P,C}|$= 12.4 Hz, $Ar^{Cl}$), 145.0 (d, $|^{x}J_{P,C}|$= 2.5 Hz, $Ar^{Cl}$).

**$^{31}$P-NMR** (202.44 MHz, 298.0 K, $CD_2Cl_2$): δ /ppm = 72.1 ppm (dez, $|^{3}J_{P,H}|$= 16.4 Hz).

**8'**: **$^{31}$P{$^{1}$H}-NMR** (202.44 MHz, 298.0 K, $CD_2Cl_2$): δ /ppm = 72.3 ppm.

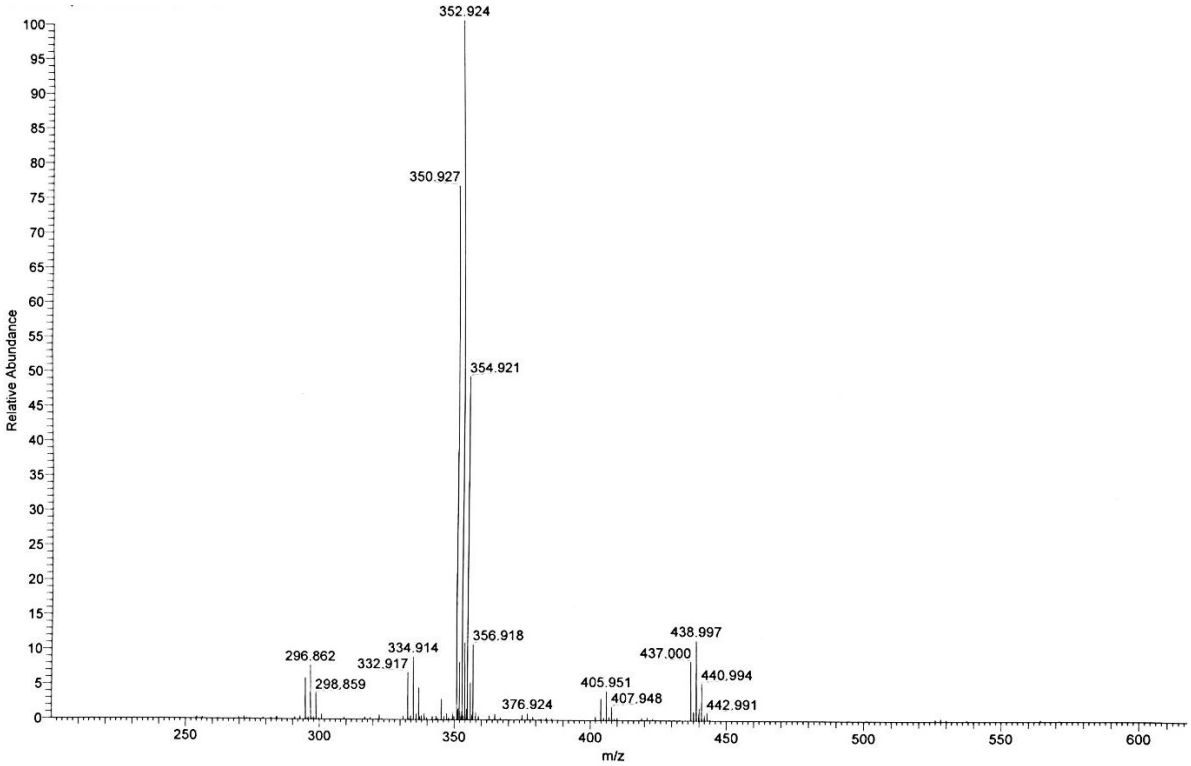



***Figure S23***: MS spectrum (APCI) of **8**,**8'**.

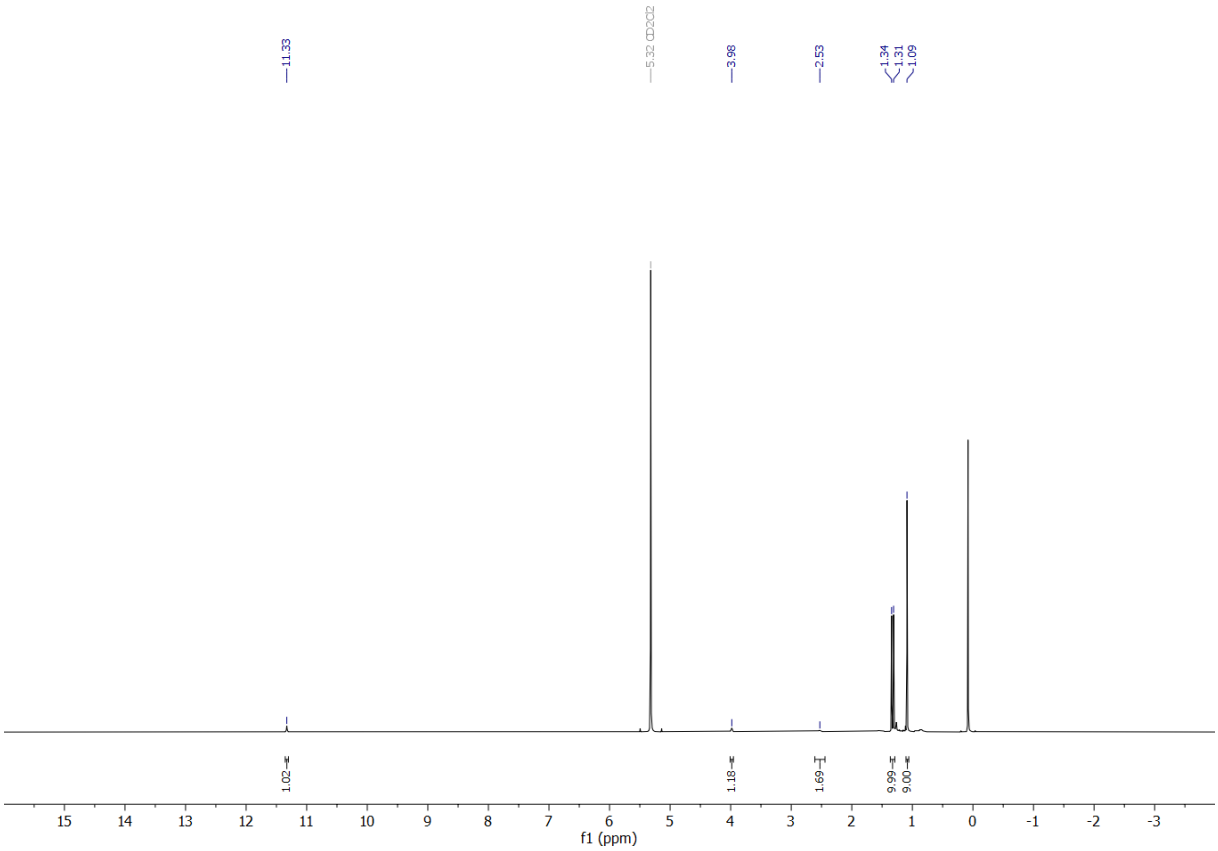



***Figure S24***: $^{1}$H-NMR spectrum of **8**,**8'** in $CD_2Cl_2$.

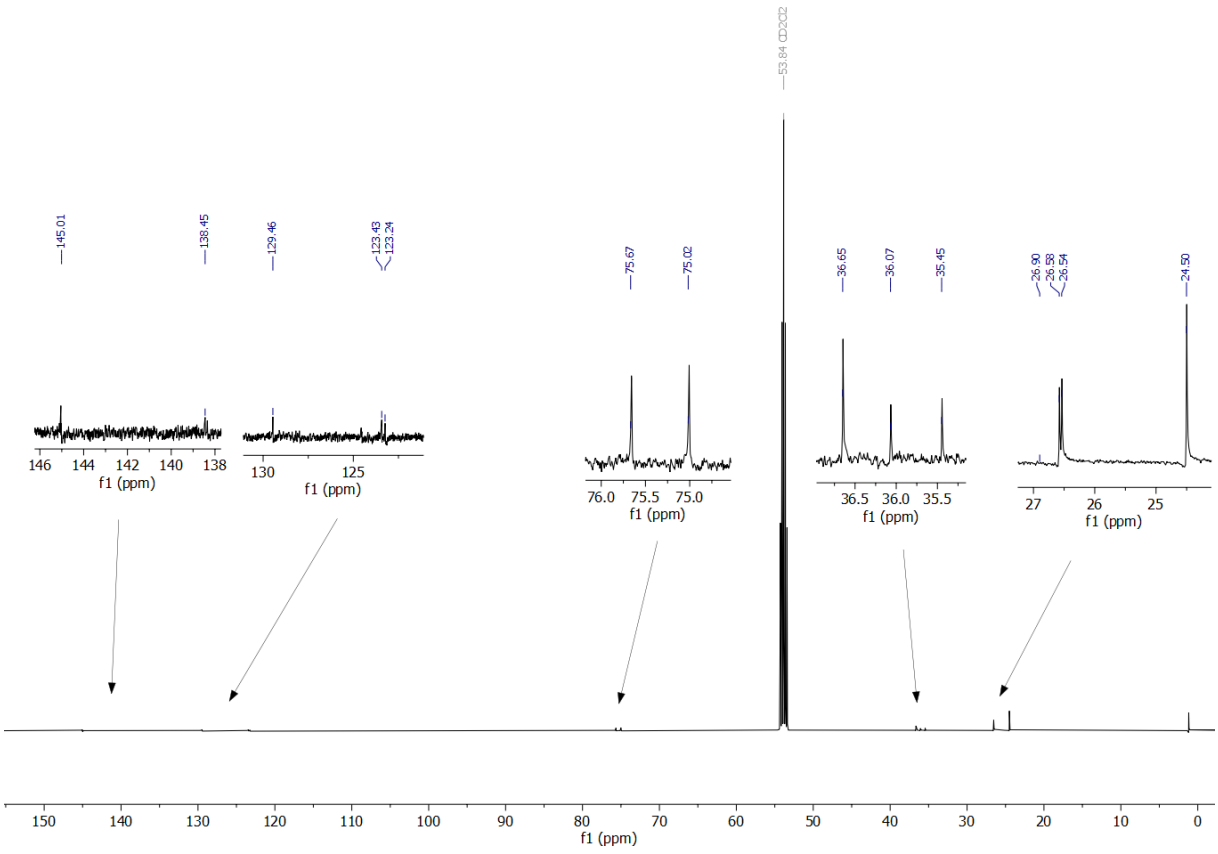



***Figure S25***: $^{13}$C{$^{1}$H}-NMR spectrum of **8**,**8'** in $CD_2Cl_2$.

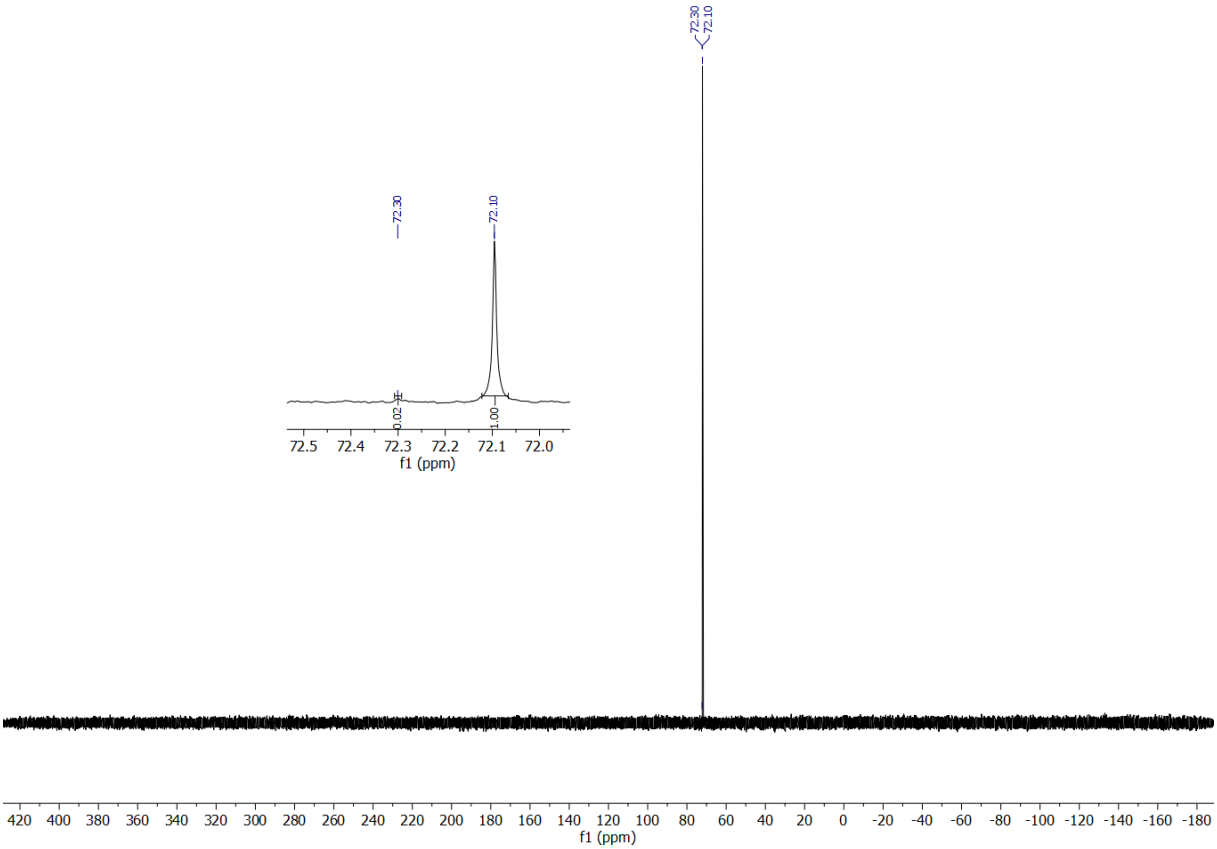



***Figure S26***:$^{31}P\{^{1}H\}$-NMR spectrum of **8**,**8**' in $CD_2Cl_2$.

## Computational details

DFT calculations were performed with the ORCA electronic structure program package (version 4.2.1).[2] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria, in the gas phase and using Grimme's dispersion-corrected composite PBEh-3c level.[3] For the mechanistic study, solvent (toluene) effects were taken into consideration with the CPCM solvation method[4] as implemented in ORCA. Harmonic frequency calculations verified the nature of ground or transition states (TS) having all positive frequencies or only one imaginary frequency, respectively. TS structures were confirmed by following the intrinsic reaction path in both directions of the negative eigenvector. From these optimized geometries, all reported data were obtained by means of single-point (SP) calculations using the higher quality def2-QZVP basis set.[5] Reported energies include the zero point-energy (ZPE) correction term at the optimization level. In case of mechanistic aspects, final energies were obtained by means of double-hybrid-meta-GGA functional PW6B95[6] using the RI-JK[7] approximation for Coulomb and exchange integrals. Additionally, the latest Grimme's semiempirical atom-pair-wise London dispersion correction D4 was included.[8] The *P*-thionation (and isomerization) process **2**→**10**→**6** was re-evaluated by optimization (and frequency calculation) using the B3LYP functional,[9] the D4 correction and the def2-TZVP basis set, and final single-point energy calculation with the double-hybrid-meta-GGA functional PWPB95,[10] the Grimme's semiempirical D3 correction[11] and the def2-QZVPP functional (Figure S22). The RSEs of the parent oxaphosphirane *P*-sulfide and of its thiaphosphirane *P*-oxide isomer were obtained as average of the energies (including zero-point correction) of the three homodesmotic reactions for the cleavage of the three endocyclic calculations, as in previous reports,[12] the final energies being

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[2] F. Neese, The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci,.* 2012, **2**, 73–78.

[3] S. Grimme, J. G. Brandenburg, C. Bannwarth and A. Hansen, Consistent structures and interactions by density functional theory with small atomic orbital basis sets, *J. Chem. Phys.,* 2015, **143**, 54107.

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[5] F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297-3305

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[7] (a) F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, RI-MP2: optimized auxiliary basis sets and demonstration of efficiency, *Chem. Phys. Lett.,* 1998, **294**, 143–152. (b) F. Weigend and M. Häser, RI-MP2: first derivatives and global consistency, *Theor. Chem. Acc.,* 1997, **97**, 331–340. (c) D.E. Bernholdt and R.J. Harrison, Large-scale correlated electronic structure calculations: the RI-MP2 method on parallel computers, *Chem. Phys. Lett.,* 1996, **250**, 477–484.

[8] E. Caldeweyher, C. Bannwarth and S. Grimme, Extension of the D3 dispersion coefficient model. *J. Chem. Phys.,* 2017, **147**, 34112.

[9] (a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648-5652. (b) C. T. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785-789.

[10] (a) L. Goerigk and S. Grimme, Efficient and accurate double-hybrid-meta-GGA density functionals - Evaluation with the extended GMTKN30 database for general main group thermochemistry, kinetics, and noncovalent interactions, *J. Chem. Theory Comput.* 2011, **7**, 291-309. (b) L. Goerigk and S. Grimme, A thorough benchmark of density functional methods for general main group thermochemistry, kinetics, and noncovalent interactions, *Phys. Chem. Chem. Phys.* 2011, **13**, 6670-6688.

[11] (a) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.*, 2010, ***132***, 154104-19. (b) S. Grimme, S. Ehrlich and L. Goerigk, Effect of the damping function in dispersion corrected density functional theory *J. Comput. Chem.*, 2011, **32**, 1456-1465.

[12] A. Espinosa Ferao, A. Rey Planells and R. Streubel, Between oxirane and phosphirane: the spring loaded oxaphosphirane ring, *Eur. J. Inorg. Chem.*, 2021, **4**, 348-353.

computed with the near linear scaling domain-based local pair natural orbital (DLPNO)[13] method to achieve coupled cluster theory with single-double and perturbative triple excitations (CCSD(T))[14] and using the def2-TZVPP basis set.

In case of compounds **2** and **7**, their RSEs were evaluated by means of only one homodesmotic reaction corresponding to the endocyclic C-O bond cleavage (Scheme S1), at the working $CPCM_{tol}$/PW6B95-D4/def2-QZVP//$CPCM_{tol}$/PBEh-3c level.

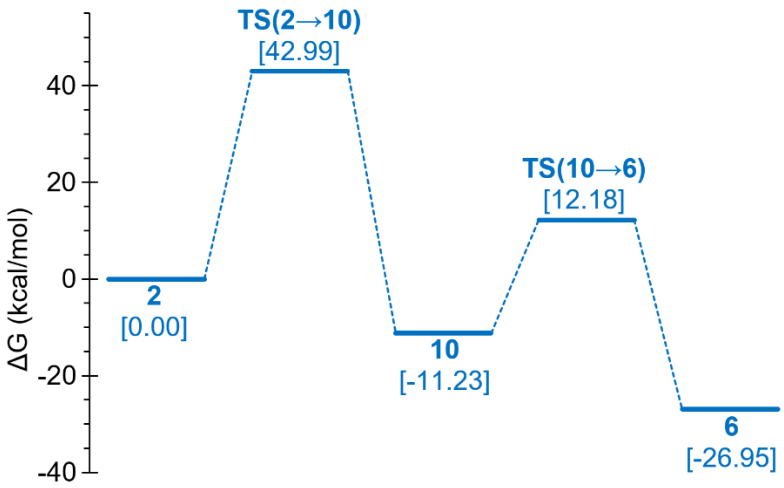
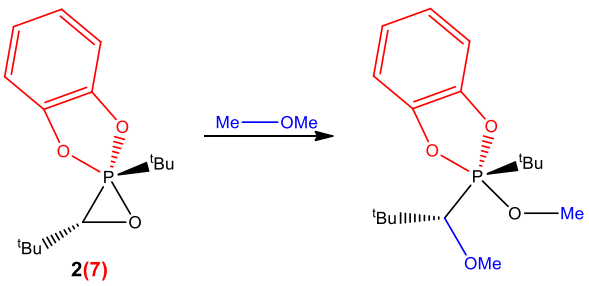



***Figure S27***: Computed (CPCMtol/PWPB95-D3/def2-QZVPP//CPCMtol/B3LYP-D4/def2-TZVP) Gibbs free energy profile for the *P*-thionation of oxaphosphirane **2** followed by isomerization.




***Scheme S1***: Homodesmotic reactions used for RSE evaluation of compounds **2** and **7**.

[13] C. Riplinger, B. Sandhoefer, A. Hansen and F. Neese, Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys.,* 2013, **139**, 134101.

[14] J. A. Pople, M. Head-Gordon and K. Raghavachari, Quadratic configuration interaction. A general technique for determining electron correlation energies, *J. Chem. Phys.,* 1987, **87**, 5968–5975.

## Calculated structures

Cartesian coordinates (in Å), G correction (G-E) and zero-point energy (ZPE) correction (in hartrees) for minima and transition states were computed, unless otherwise stated, at the $CPCM_{tol}$/PBEh-3c whereas electronic energies (in hartrees) were quoted at the $CPCM_{tol}$/PW6B95-D4/def2-QZVP level. Imaginary frequencies were obtained upon frequency calculation at the optimization level.

**$2^{cis}$:** E = -772.025356736206 au

ZPE = 0.27405774 au

$G_{corr}$ = 0.23621866 au

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C | -0.189079 | -0.120914 | 0.016626 | H | -4.197103 | 0.966071 | 2.262392 |
| O | -0.244630 | -0.135579 | 1.430808 | H | -3.184219 | -0.342699 | 1.668046 |
| H | 0.836465 | 0.013150 | -0.349862 | C | -0.841362 | -1.232877 | -0.792599 |
| P | -0.676812 | 1.414528 | 0.853790 | C | -2.155169 | -1.766224 | -0.237639 |
| C | -2.524328 | 1.673319 | 1.112768 | H | -2.961550 | -1.039393 | -0.294025 |
| C | -2.564876 | 3.059065 | 1.779753 | H | -2.468549 | -2.634167 | -0.820540 |
| H | -3.601852 | 3.348317 | 1.965708 | H | -2.054229 | -2.086320 | 0.799263 |
| H | -2.041525 | 3.066619 | 2.737782 | C | 0.165342 | -2.395766 | -0.805912 |
| H | -2.114742 | 3.831529 | 1.152762 | H | -0.216265 | -3.224107 | -1.405822 |
| C | -3.264166 | 1.771707 | -0.220400 | H | 1.123761 | -2.092973 | -1.231991 |
| H | -3.338448 | 0.815031 | -0.732383 | H | 0.350532 | -2.771831 | 0.201661 |
| H | -4.281347 | 2.137045 | -0.055925 | C | -1.029684 | -0.720341 | -2.220627 |
| H | -2.776542 | 2.472452 | -0.902116 | H | -0.092153 | -0.345455 | -2.636822 |
| C | -3.164276 | 0.667910 | 2.063232 | H | -1.381430 | -1.520551 | -2.874296 |
| H | -2.643863 | 0.636802 | 3.021256 | H | -1.757551 | 0.090895 | -2.261789 |

**$2^{cis}$:** E = -769.762141170222 au [$CPCM_{tol}$/DLNPO-CCSD(T)/def2-TZVPP]

ZPE = 0.26467317 au [$CPCM_{tol}$/B3LYP-D4/def2-TZVP]

$G_{corr}$ = 0.22620513 au [$CPCM_{tol}$/B3LYP-D4/def2-TZVP]

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C | 0.278473 | 0.105502 | 0.141911 | H | -0.299747 | -0.052487 | 3.021142 |
| O | 1.702417 | 0.087437 | 0.367696 | H | -0.818780 | -1.725296 | 2.909671 |
| P | 1.147428 | 1.696771 | 0.272500 | C | 1.198277 | 2.470034 | 2.000039 |
| H | 0.051892 | -0.060957 | -0.915194 | C | 2.064652 | 1.685697 | 2.986138 |
| C | -0.631960 | -0.784210 | 0.984947 | H | 1.658246 | 0.706101 | 3.216369 |
| C | -0.607561 | -2.173203 | 0.311430 | H | 3.073420 | 1.544033 | 2.593705 |
| H | 0.403210 | -2.586583 | 0.308494 | H | 2.146999 | 2.249146 | 3.921006 |
| H | -1.257193 | -2.866522 | 0.850104 | C | -0.211008 | 2.739937 | 2.538790 |
| H | -0.955619 | -2.116057 | -0.722146 | H | -0.831151 | 3.246360 | 1.794423 |
| C | -2.055636 | -0.216718 | 0.909203 | H | -0.724702 | 1.829982 | 2.837763 |
| H | -2.370487 | -0.085259 | -0.128981 | H | -0.151529 | 3.394092 | 3.414326 |
| H | -2.761814 | -0.898869 | 1.388218 | C | 1.875822 | 3.829499 | 1.726680 |
| H | -2.124549 | 0.751012 | 1.406714 | H | 2.882919 | 3.703304 | 1.323131 |
| H | 0.842627 | -1.293560 | 2.496704 | H | 1.304481 | 4.431324 | 1.015968 |
| C | -0.194534 | -0.963306 | 2.438310 | H | 1.952309 | 4.392957 | 2.660335 |

**2:** E = -772.043444222908 au

ZPE = 0.27353954 au

$G_{corr}$ = 0.23520200 au

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C | 1.067595 | 0.912873 | 0.183950 | H | -1.645258 | -1.522377 | -2.839707 |
| O | 0.625812 | 2.130624 | -0.392179 | H | -0.831066 | -1.772557 | -1.296772 |
| H | 1.756279 | 0.360807 | -0.457994 | C | 1.516408 | 0.936373 | 1.633914 |
| P | -0.657807 | 1.012041 | -0.325551 | C | 0.539198 | 1.685667 | 2.536617 |
| C | -0.745334 | 0.279020 | -2.045327 | H | -0.443677 | 1.211101 | 2.552572 |
| C | -1.641625 | 1.221783 | -2.855057 | H | 0.913776 | 1.697537 | 3.561629 |
| H | -1.834534 | 0.799974 | -3.844706 | H | 0.408745 | 2.721437 | 2.221761 |
| H | -2.608457 | 1.383207 | -2.373504 | C | 2.888024 | 1.617446 | 1.691631 |
| H | -1.172819 | 2.197009 | -2.997595 | H | 3.271748 | 1.626355 | 2.713735 |
| C | 0.585984 | 0.095413 | -2.761279 | H | 3.618472 | 1.096674 | 1.068792 |
| H | 1.205804 | -0.665938 | -2.286763 | H | 2.831522 | 2.651558 | 1.348539 |
| H | 0.408706 | -0.229452 | -3.789908 | C | 1.638171 | -0.516041 | 2.093433 |
| H | 1.156657 | 1.023857 | -2.806267 | H | 2.329798 | -1.080132 | 1.463666 |
| C | -1.445063 | -1.070891 | -1.865022 | H | 2.011045 | -0.567905 | 3.117787 |
| H | -2.404258 | -0.973101 | -1.350821 | H | 0.670862 | -1.021353 | 2.064082 |

**2:** E = -769.779931293223 au [$CPCM_{tol}$/DLNPO-CCSD(T)/def2-TZVPP]

ZPE = 0.26416819 au [$CPCM_{tol}$/B3LYP-D4/def2-TZVP]

$G_{corr}$ = 0.22536264 au [$CPCM_{tol}$/B3LYP-D4/def2-TZVP]

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C | -0.093847 | 0.115261 | 0.191694 | H | -2.056320 | 1.245704 | -1.350690 |
| O | 1.267786 | -0.336947 | 0.313156 | H | -2.955740 | -0.243659 | -1.661780 |
| P | 1.231807 | 1.281774 | -0.187050 | C | 1.533093 | 2.261394 | 1.394637 |
| H | -0.580115 | 0.204441 | 1.160280 | C | 3.061871 | 2.320786 | 1.546904 |
| C | -0.969458 | -0.573061 | -0.845505 | H | 3.478837 | 1.328382 | 1.731245 |
| C | -1.286657 | -1.984535 | -0.323519 | H | 3.542524 | 2.729198 | 0.654620 |
| H | -1.801558 | -1.942268 | 0.639452 | H | 3.329741 | 2.960686 | 2.392814 |
| H | -1.930781 | -2.518638 | -1.025893 | C | 0.915964 | 1.669793 | 2.659864 |
| H | -0.370196 | -2.562331 | -0.193196 | H | -0.171776 | 1.752156 | 2.658059 |
| C | -0.278902 | -0.678307 | -2.208770 | H | 1.184132 | 0.618580 | 2.778608 |
| H | 0.669900 | -1.209816 | -2.127938 | H | 1.282805 | 2.209436 | 3.538341 |
| H | -0.915817 | -1.224115 | -2.907942 | C | 0.977986 | 3.666395 | 1.122924 |
| H | -0.080768 | 0.307438 | -2.633461 | H | 1.398042 | 4.099060 | 0.210888 |
| H | -2.766584 | 0.340333 | -0.007439 | H | -0.109758 | 3.654448 | 1.021167 |
| C | -2.262091 | 0.242088 | -0.972065 | H | 1.228725 | 4.336862 | 1.949982 |

$S_8$**:** E = -3188.42287609029 au

ZPE = 0.01286354 au

$G_{corr}$ = -0.02474872 au

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| S | 0.096285 | 0.023139 | -0.015430 | S | 3.675032 | -2.523372 | 1.613054 |
| S | -0.024125 | -0.096651 | 2.035593 | S | 2.489958 | -3.696945 | 0.407372 |
| S | 1.896446 | 0.023106 | 2.765254 | S | 1.873990 | -2.524020 | -1.167452 |
| S | 2.507908 | -1.895997 | 3.187733 | S | -0.040023 | -1.895929 | -0.746123 |

TS(**2**+$S_8$→**10**)**:** E = -3960.41964625693 au

ZPE = 0.2873280847 au

$G_{corr}$ = 0.2338461562 au

ν = -228.66 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.930745 | -0.975857 | -0.245944 | H | -1.653643 | -0.869387 | -1.572848 |
| O | 0.458841 | -0.641640 | 1.094126 | H | -1.834504 | -2.615294 | -1.558457 |
| H | 2.005435 | -1.166635 | -0.259315 | H | -1.769018 | -1.728824 | -0.042840 |
| P | 0.497308 | 0.700040 | 0.161418 | C | 0.480739 | -3.361896 | -0.460320 |
| C | 1.858805 | 1.831610 | 0.653409 | H | 0.002315 | -4.144797 | -1.050110 |
| C | 1.391652 | 2.621009 | 1.878562 | H | 1.554532 | -3.559372 | -0.456514 |
| H | 2.188799 | 3.306515 | 2.171826 | H | 0.115165 | -3.448108 | 0.563576 |
| H | 0.506386 | 3.220823 | 1.667504 | C | 0.688981 | -1.899329 | -2.489793 |
| H | 1.178154 | 1.974812 | 2.729988 | H | 1.767535 | -2.064525 | -2.533644 |
| C | 3.118618 | 1.030923 | 0.976070 | H | 0.215288 | -2.658274 | -3.113125 |
| H | 3.506431 | 0.499314 | 0.106996 | H | 0.475536 | -0.925632 | -2.934133 |
| H | 3.894209 | 1.727072 | 1.299126 | S | -1.269797 | 1.596870 | -0.252118 |
| H | 2.960894 | 0.317624 | 1.784624 | S | -2.041349 | 1.529545 | 1.977790 |
| C | 2.095647 | 2.770032 | -0.532713 | S | -2.995670 | -0.124401 | 2.406704 |
| H | 1.205609 | 3.347440 | -0.783769 | S | -5.068504 | 0.227508 | 2.651365 |
| H | 2.882789 | 3.477478 | -0.266618 | S | -5.867976 | -1.174022 | 1.417418 |
| H | 2.421996 | 2.232707 | -1.424368 | S | -6.189823 | -0.186408 | -0.401671 |
| C | 0.153761 | -1.987082 | -1.059509 | S | -4.317346 | 0.518425 | -0.906418 |
| C | -1.356555 | -1.776633 | -1.050645 | S | -4.191986 | 2.378369 | -0.145629 |

**$S_7$:**

E = -2789.86046580544 au

ZPE = 0.0110838 au

$G_{corr}$ = -0.0245969 au

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| S | -0.234923 | -0.336486 | 0.064648 | S | 3.023824 | -2.919252 | 1.531573 |
| S | 0.101038 | 0.328233 | 2.122330 | S | 1.593122 | -3.038949 | 0.064795 |
| S | 2.017874 | -0.029836 | 2.554105 | S | 1.500575 | -1.054077 | -0.615228 |
| S | 2.095484 | -2.045067 | 3.140125 | | | | |

**10:**

E = -1170.62391275481 au

ZPE = 0.2768399 au

$G_{corr}$ = 0.23684445 au

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.094318 | 0.784601 | 0.223760 | H | -1.915975 | -1.359281 | -2.914639 |
| O | 0.800298 | 2.010409 | -0.530474 | H | -1.285696 | -1.689602 | -1.302652 |
| H | 1.744007 | 0.110736 | -0.338268 | C | 1.545480 | 0.916257 | 1.666374 |
| C | -0.787758 | 0.282064 | -2.103796 | C | 0.818578 | 2.008678 | 2.446247 |
| C | -1.447829 | 1.353539 | -2.977098 | H | -0.246209 | 1.806994 | 2.545312 |
| H | -1.659428 | 0.930175 | -3.960995 | H | 1.242048 | 2.073364 | 3.449863 |
| H | -2.389148 | 1.699281 | -2.550856 | H | 0.932997 | 2.985495 | 1.976514 |
| H | -0.798032 | 2.217852 | -3.120847 | C | 3.046091 | 1.231500 | 1.644883 |
| C | 0.533882 | -0.162671 | -2.726410 | H | 3.433812 | 1.299123 | 2.662762 |
| H | 1.004157 | -0.969687 | -2.163873 | H | 3.613452 | 0.456706 | 1.124961 |
| H | 0.336273 | -0.543689 | -3.730121 | H | 3.244540 | 2.183777 | 1.150602 |
| H | 1.244521 | 0.657971 | -2.821526 | C | 1.308091 | -0.445305 | 2.322190 |
| C | -1.723619 | -0.915899 | -1.935666 | H | 1.810085 | -1.249723 | 1.779957 |
| H | -2.680171 | -0.624455 | -1.503877 | H | 1.693302 | -0.448242 | 3.342963 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 0.243204 | -0.680019 | 2.365423 | S | -2.136044 | 1.567993 | 0.480542 |
| P | -0.526172 | 1.037786 | -0.440397 | | | | |

TS(**10**→**6**)**:** E = -1170.58552933398 au

ZPE = 0.27398764 au

$G_{corr}$ = 0.23429785 au

ν = -225.67 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.554873 | -0.059960 | 0.496065 | C | 1.102167 | 0.108867 | 1.833175 |
| O | -1.535762 | -1.340534 | 0.656083 | C | 1.682373 | 1.562390 | 1.673690 |
| H | 1.311648 | -0.286178 | -0.257501 | H | 0.880232 | 2.290302 | 1.577942 |
| C | -1.149400 | -0.203320 | -1.849490 | H | 2.248684 | 1.759352 | 2.585991 |
| C | -2.610831 | -0.214869 | -2.308010 | H | 2.364530 | 1.664411 | 0.829138 |
| H | -2.650588 | -0.337380 | -3.392412 | C | 2.267954 | -0.861463 | 2.065264 |
| H | -3.168233 | -1.038496 | -1.859559 | H | 2.754972 | -0.622866 | 3.010934 |
| H | -3.118056 | 0.716186 | -2.054726 | H | 1.908390 | -1.888503 | 2.120053 |
| C | -0.412598 | 0.969937 | -2.491623 | H | 3.016185 | -0.799495 | 1.274018 |
| H | 0.636686 | 1.022627 | -2.190032 | C | 0.115637 | 0.068072 | 2.991855 |
| H | -0.425654 | 0.859933 | -3.578438 | H | -0.316145 | -0.926060 | 3.091402 |
| H | -0.879926 | 1.921520 | -2.241313 | H | 0.641476 | 0.309934 | 3.915650 |
| C | -0.486200 | -1.528336 | -2.231565 | H | -0.697316 | 0.779186 | 2.862077 |
| H | -0.986008 | -2.379099 | -1.771062 | P | -1.174339 | -0.029311 | -0.009901 |
| H | -0.533351 | -1.657304 | -3.315021 | S | -1.911253 | 1.709109 | 0.522888 |
| H | 0.569854 | -1.568653 | -1.955570 | | | | |

**6:** E = -1170.64885667933 au

ZPE = 0.27643125 au

$G_{corr}$ = 0.23664363 au

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.527669 | 2.161770 | 0.300012 | C | 1.209126 | 1.285668 | 1.506183 |
| O | -1.040793 | 2.104819 | -1.047771 | C | 2.248079 | 1.583998 | 2.588647 |
| H | 2.562322 | 2.041723 | -0.019026 | H | 2.179773 | 2.620325 | 2.924574 |
| C | 1.141912 | 2.770837 | -2.656865 | H | 2.090325 | 0.942689 | 3.457498 |
| C | 0.365030 | 3.881563 | -3.368468 | H | 3.264780 | 1.412928 | 2.228773 |
| H | 0.735470 | 3.983110 | -4.390405 | C | 1.351126 | -0.164592 | 1.032968 |
| H | -0.701648 | 3.664169 | -3.420397 | H | 1.204083 | -0.853210 | 1.866701 |
| H | 0.495361 | 4.843909 | -2.871217 | H | 0.609612 | -0.404695 | 0.268744 |
| C | 2.621887 | 3.127987 | -2.577604 | H | 2.342132 | -0.357889 | 0.616701 |
| H | 3.215499 | 2.334156 | -2.122967 | C | -0.189086 | 1.507239 | 2.076707 |
| H | 3.003342 | 3.273404 | -3.590193 | H | -0.970772 | 1.279367 | 1.354367 |
| H | 2.792369 | 4.049483 | -2.021901 | H | -0.331797 | 0.857918 | 2.941902 |
| C | 0.954774 | 1.436335 | -3.387406 | H | -0.327407 | 2.536583 | 2.408134 |
| H | -0.095319 | 1.159276 | -3.468212 | P | 0.371961 | 2.569261 | -0.997877 |
| H | 1.358587 | 1.521933 | -4.398150 | S | 1.067555 | 3.988153 | 0.339499 |
| H | 1.485397 | 0.622020 | -2.890180 | | | | |

TOB**:** E = -2222.01913774255 au

ZPE = 0.04920142 au

$G_{corr}$ = 0.01163246 au

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O | 0.277907 | -0.929869 | -3.792104 | O | 2.623811 | 0.081715 | -2.875890 |

| | | | | | |
|---|---|---|---|---|---|
| C | 2.418104 | 0.048633 | -4.055498 | C | 1.824567 | -0.069012 | -6.863906 |
| C | 3.383185 | 0.531386 | -5.053241 | Cl | 4.843885 | 1.152056 | -4.450911 |
| C | 1.088273 | -0.522223 | -4.574396 | Cl | 4.218182 | 1.036155 | -7.514079 |
| C | 3.099318 | 0.474727 | -6.367164 | Cl | 1.576198 | -0.089471 | -8.543271 |
| C | 0.878892 | -0.536778 | -6.029011 | Cl | -0.599882 | -1.169487 | -6.571774 |

TS(**2**+TOB→**7**)**:** E = -2994.05722169897 au

ZPE = 0.32406719 au

$G_{corr}$ = 0.27246393 au

ν = -222.28 $cm^{-1}$

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C | -0.194473 | -0.129717 | -0.072095 | H | 3.521967 | -0.641243 | 2.333302 |
| O | 0.253547 | 0.314650 | 1.218856 | C | 3.350020 | -2.212013 | 0.064002 |
| P | 1.565791 | -0.069037 | 0.235930 | H | 3.736422 | -3.129467 | 0.514241 |
| H | -0.707223 | -1.091699 | -0.036145 | H | 3.024074 | -2.453822 | -0.947163 |
| C | -0.892253 | 0.886541 | -0.955889 | H | 4.172943 | -1.503310 | -0.002686 |
| C | -0.918870 | 0.312795 | -2.372658 | C | 1.093707 | -2.733857 | 1.006552 |
| H | 0.089844 | 0.194223 | -2.771405 | H | 0.716431 | -3.004399 | 0.019992 |
| H | -1.409133 | -0.662682 | -2.400917 | H | 1.496343 | -3.641766 | 1.463001 |
| H | -1.467961 | 0.975143 | -3.043851 | H | 0.257151 | -2.405611 | 1.623858 |
| C | -2.321934 | 1.065544 | -0.434134 | O | 2.814042 | 0.186463 | -1.778810 |
| H | -2.872986 | 1.770407 | -1.059363 | O | 3.692988 | 1.217112 | 0.431223 |
| H | -2.868649 | 0.120522 | -0.440453 | C | 3.811071 | 1.899681 | -0.590678 |
| H | -2.327997 | 1.450717 | 0.586625 | C | 4.215622 | 3.281754 | -0.595510 |
| C | -0.183239 | 2.239793 | -0.954173 | C | 3.328638 | 1.308869 | -1.847060 |
| H | -0.120759 | 2.670315 | 0.045098 | C | 4.283009 | 3.973474 | -1.764910 |
| H | 0.829748 | 2.174804 | -1.360277 | C | 3.294724 | 2.132933 | -3.024711 |
| H | -0.726253 | 2.944852 | -1.585233 | C | 3.812549 | 3.391161 | -2.997060 |
| C | 2.205342 | -1.690369 | 0.931788 | Cl | 4.697238 | 3.957991 | 0.891967 |
| C | 2.717130 | -1.375239 | 2.340895 | Cl | 4.899116 | 5.563077 | -1.794469 |
| H | 1.922883 | -1.007686 | 2.990875 | Cl | 3.884976 | 4.323586 | -4.421537 |
| H | 3.110688 | -2.291387 | 2.787366 | Cl | 2.650628 | 1.441084 | -4.443753 |

**7:** E = -2994.1696173707 au

ZPE = 0.3279652 au

$G_{corr}$ = 0.27714634 au

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C | -0.068076 | 0.074076 | 0.055255 | H | -0.559449 | 2.196142 | -2.437836 |
| O | 1.401459 | 0.033129 | 0.077351 | H | 0.798615 | 2.302138 | -3.553105 |
| P | 0.811068 | 1.587156 | 0.093985 | H | 0.457114 | 0.780002 | -2.745411 |
| H | -0.482263 | -0.260983 | -0.900361 | O | -0.342908 | 2.819904 | 0.575017 |
| C | 1.415623 | 2.300796 | -1.494709 | O | 1.822882 | 2.091967 | 1.333162 |
| C | 2.827488 | 1.774244 | -1.767802 | C | 1.373347 | 3.173588 | 1.995845 |
| H | 2.852139 | 0.692828 | -1.883163 | C | 2.028203 | 3.814024 | 3.019003 |
| H | 3.189753 | 2.218009 | -2.696822 | C | 0.127042 | 3.588135 | 1.551919 |
| H | 3.528256 | 2.050751 | -0.979212 | C | 1.407480 | 4.924004 | 3.605277 |
| C | 1.456942 | 3.830671 | -1.429947 | C | -0.494431 | 4.676933 | 2.121910 |
| H | 1.877819 | 4.200330 | -2.366548 | C | 0.159153 | 5.348641 | 3.161083 |
| H | 0.470159 | 4.276861 | -1.320672 | Cl | 3.557997 | 3.252499 | 3.530376 |
| H | 2.099135 | 4.201503 | -0.629575 | Cl | 2.201250 | 5.753923 | 4.874064 |
| C | 0.464208 | 1.861971 | -2.611861 | Cl | -0.592273 | 6.707517 | 3.880022 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Cl | -2.028202 | 5.162100 | 1.544432 | H | -1.162926 | -2.584801 | 1.916238 |
| C | -0.806468 | -0.561256 | 1.221116 | H | -0.967811 | -2.465658 | 0.168681 |
| C | -2.286078 | -0.211621 | 1.053230 | H | 0.441659 | -2.348116 | 1.225503 |
| H | -2.448665 | 0.866291 | 1.099924 | C | -0.313096 | -0.074705 | 2.582892 |
| H | -2.678263 | -0.569960 | 0.099130 | H | 0.753571 | -0.251165 | 2.720902 |
| H | -2.877197 | -0.673740 | 1.845346 | H | -0.514168 | 0.987073 | 2.740979 |
| C | -0.609894 | -2.076836 | 1.124209 | H | -0.837067 | -0.610717 | 3.375441 |

TS(**7**→**11**)**:** E = -2994.12927936905 au

ZPE = 0.32545893 au

$G_{corr}$ = 0.27468801 au

ν = -264.32 $cm^{-1}$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.379720 | -0.171431 | 0.174359 | C | -0.026198 | 3.796592 | 1.467124 |
| O | 1.655856 | -0.230356 | 0.296882 | C | 1.172504 | 4.934333 | 3.672467 |
| P | 0.549704 | 1.798665 | 0.055271 | C | -0.625992 | 4.890556 | 2.047086 |
| H | -0.071163 | -0.415283 | -0.815452 | C | -0.011480 | 5.463246 | 3.166008 |
| C | 1.328111 | 2.337294 | -1.535145 | Cl | 3.213589 | 3.130612 | 3.658921 |
| C | 2.440244 | 1.399778 | -2.005172 | Cl | 1.914940 | 5.640985 | 5.040616 |
| H | 2.091570 | 0.384634 | -2.178361 | Cl | -0.731248 | 6.825485 | 3.906907 |
| H | 2.823522 | 1.789467 | -2.950889 | Cl | -2.077339 | 5.501931 | 1.389303 |
| H | 3.265900 | 1.356551 | -1.298133 | C | -0.570582 | -0.658429 | 1.275088 |
| C | 1.892948 | 3.751023 | -1.368982 | C | -2.004500 | -0.288788 | 0.912413 |
| H | 2.309284 | 4.064912 | -2.327907 | H | -2.157113 | 0.792704 | 0.898825 |
| H | 1.137391 | 4.487228 | -1.096482 | H | -2.283404 | -0.678344 | -0.069311 |
| H | 2.703424 | 3.788551 | -0.641185 | H | -2.704338 | -0.704236 | 1.638752 |
| C | 0.182261 | 2.338492 | -2.557927 | C | -0.413471 | -2.184419 | 1.280238 |
| H | -0.622087 | 3.024015 | -2.290099 | H | -1.091322 | -2.629643 | 2.010436 |
| H | 0.576359 | 2.659458 | -3.523656 | H | -0.649323 | -2.615563 | 0.304816 |
| H | -0.244370 | 1.343699 | -2.697387 | H | 0.603722 | -2.476532 | 1.541224 |
| O | -0.478363 | 3.121000 | 0.395502 | C | -0.199944 | -0.105196 | 2.646783 |
| O | 1.598822 | 2.199915 | 1.285318 | H | 0.860914 | -0.235818 | 2.857681 |
| C | 1.152312 | 3.274331 | 1.970404 | H | -0.441041 | 0.957027 | 2.740545 |
| C | 1.767769 | 3.818746 | 3.072338 | H | -0.764461 | -0.619544 | 3.426046 |

$^{t}$Bu-CHO**:** E = -272.243208915917 au

ZPE = 0.14485613 au

$G_{corr}$ = 0.11447791 au

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.595919 | -0.355377 | 0.735427 | C | -1.291264 | -2.623836 | 0.140745 |
| O | 0.431020 | 0.269134 | 0.733351 | H | -1.518165 | -3.625669 | 0.508348 |
| H | -1.521486 | 0.078903 | 0.301965 | H | -2.204027 | -2.222684 | -0.304549 |
| C | -0.787262 | -1.745292 | 1.292199 | H | -0.544201 | -2.718339 | -0.648789 |
| C | -1.873370 | -1.649736 | 2.370764 | C | 0.506304 | -2.299109 | 1.871995 |
| H | -1.551111 | -1.033195 | 3.211229 | H | 1.290481 | -2.363997 | 1.117310 |
| H | -2.799168 | -1.225704 | 1.976473 | H | 0.880057 | -1.679237 | 2.687304 |
| H | -2.105169 | -2.644274 | 2.754782 | H | 0.341084 | -3.302829 | 2.266532 |

**11:** E = -2721.91069673137 au

ZPE = 0.17842989 au

$G_{corr}$ = 0.13477619 au

| | | | | | |
|---|---|---|---|---|---|
| P | 1.238320 | -0.822633 | -1.143904 | H | 0.050189 | -2.913417 | 0.346687 |
| C | 1.740746 | -2.604152 | -1.018033 | O | 0.322143 | -0.818588 | -2.576987 |
| C | 2.795068 | -2.642347 | 0.094204 | O | 2.582646 | -0.135203 | -1.927078 |
| H | 2.436583 | -2.190548 | 1.022004 | C | 2.392354 | -0.140925 | -3.260667 |
| H | 3.050729 | -3.680152 | 0.317573 | C | 3.332886 | 0.197276 | -4.205076 |
| H | 3.715043 | -2.133182 | -0.196701 | C | 1.112174 | -0.528029 | -3.628732 |
| C | 2.291818 | -3.231479 | -2.293895 | C | 2.965805 | 0.150962 | -5.555344 |
| H | 2.551064 | -4.274269 | -2.094754 | C | 0.738996 | -0.587235 | -4.950896 |
| H | 1.564170 | -3.236057 | -3.105948 | C | 1.682332 | -0.237072 | -5.924357 |
| H | 3.200898 | -2.740744 | -2.642732 | Cl | 4.901541 | 0.651006 | -3.704672 |
| C | 0.476150 | -3.341973 | -0.563398 | Cl | 4.115735 | 0.572549 | -6.749338 |
| H | -0.297632 | -3.340260 | -1.332533 | Cl | 1.241008 | -0.296343 | -7.575850 |
| H | 0.721002 | -4.383769 | -0.346592 | Cl | -0.843238 | -1.086252 | -5.356466 |

TS(**11**→**9**)**:** E = -4943.92502864806 au

ZPE = 0.22885534 au

$G_{corr}$ = 0.17240629 au

ν = -233.14 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | 0.275432 | -0.430784 | -0.737790 | C | -0.809500 | 0.923435 | -3.866261 |
| C | 0.530101 | -1.785507 | 0.612499 | C | -0.109359 | 1.486421 | -4.888546 |
| C | 2.027895 | -1.935623 | 0.906305 | Cl | 3.738800 | 1.062543 | -3.757110 |
| H | 2.353892 | -1.315050 | 1.740099 | Cl | 2.143733 | 2.266872 | -6.174731 |
| H | 2.217388 | -2.974908 | 1.182767 | Cl | -0.927351 | 2.191681 | -6.202076 |
| H | 2.650393 | -1.709684 | 0.043274 | Cl | -2.510975 | 0.918667 | -3.815491 |
| C | 0.123255 | -2.745146 | -0.506301 | P | 0.236940 | 0.014569 | 0.129705 |
| H | 0.325215 | -3.763727 | -0.166930 | O | -1.364187 | 0.294018 | 0.613676 |
| H | -0.938886 | -2.685239 | -0.739755 | O | 0.831424 | 0.775957 | 1.552494 |
| H | 0.691110 | -2.587147 | -1.420251 | C | -0.173386 | 1.199464 | 2.331476 |
| C | -0.267992 | -2.124154 | 1.874685 | C | -1.423062 | 0.911178 | 1.804526 |
| H | -1.344826 | -2.067971 | 1.719902 | C | -1.207215 | 2.221906 | 4.219523 |
| H | -0.037366 | -3.155771 | 2.149957 | C | -2.577190 | 1.259200 | 2.467192 |
| H | -0.001223 | -1.508367 | 2.733699 | C | -2.460933 | 1.925376 | 3.692435 |
| O | -0.682164 | -0.253245 | -1.830572 | C | -0.043149 | 1.858148 | 3.533536 |
| O | 1.914049 | -0.200674 | -1.804111 | Cl | 1.515886 | 2.189982 | 4.145771 |
| C | 1.358613 | 0.277046 | -2.789663 | Cl | -1.074391 | 3.035549 | 5.717991 |
| C | 2.041030 | 0.995010 | -3.839834 | Cl | -3.878461 | 2.371349 | 4.538793 |
| C | -0.112753 | 0.240430 | -2.815972 | Cl | -4.091742 | 0.870931 | 1.781533 |
| C | 1.336386 | 1.522483 | -4.874236 | | | | |

**9:** E = -4944.03937673687 au

ZPE = 0.23334925 au

$G_{corr}$ = 0.17859671 au

C1.774844-2.460749 -0.881760
C3.192810-2.537566 -0.300095
H3.278332-2.045530 0.667531
H3.439315-3.590048 -0.151811
H3.945293-2.117997 -0.966167
C1.727023-3.259805 -2.190075
H2.000122-4.292152 -1.966550
H0.733753-3.278157 -2.636595
H2.440111-2.902825 -2.934074
C0.786658-3.074055 0.115894
H-0.238218-3.073356 -0.252169
H1.074299-4.113245 0.282885
H0.806660-2.581368 1.088784
O0.409593-0.666889 -2.622802
O2.677593-0.164753 -2.133608
C2.437511-0.142770 -3.449686
C3.342609 0.141236 -4.444306
C1.119999-0.435510 -3.735704
C2.886481 0.116768 -5.767443
C0.650804-0.465218 -5.026411
C1.556896-0.182256 -6.055234
Cl4.9624920.494961 -4.041419
Cl3.9848340.454683 -7.033302
Cl1.014199-0.215915 -7.676189
Cl-0.985399-0.843627 -5.327166
P1.348039-0.691007 -1.217992
O-0.151200-0.436233 -0.459805
O2.086315 0.186336 0.023406
C1.264553 0.442471 1.051295
C-0.0366080.081181 0.767953
C0.595993 1.204874 3.197860
C-1.0479740.264741 1.680449
C-0.7175210.838446 2.913656
C1.611234 1.007640 2.254654
Cl3.2357221.432784 2.556738
Cl0.9875511.897863 4.710989
Cl-1.9471461.077795 4.077132
Cl-2.640053-0.206819 1.288096