Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Isomerisation, Reactivity and Coordination Chemistry of a New Hybrid, Multi-functional Phosphazane

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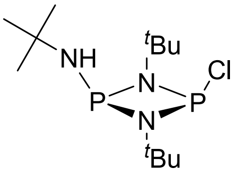
and Dominic S. Wright

1. Synthesis and Supporting Data

All manipulations were carried out under dry, O_2-free nitrogen on a vacuum-line, using standard inert-atmosphere techniques for isolation and characterisation. All spectra were recorded on a Bruker Advanced 400 QNP 500 MHz cryo spectrometer with $SiMe_4$, H_3P0_4 (85%, D_2O), Selenoxanthenone (0.1M, $CDCl_3$) and Dimethyltellurium (0.1 M, $CDCl_3$). Elemental analysis was obtained using a Perkin Elmer 240 Elmer 240 Elemental Analyser. Single-crystal X-ray diffraction was carried out at 220 K on a Bruker D8-QUEST PHOTON-100 diffractometer using an Incoatec IµS Cu microsource (λ = 1.5418 Å). Structures were solved using SHELXT and using SHELXL-2014.[1,2] Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. .

Synthesis of the Chlorodimers $[ClP(\mu\text{-}NR)]_2$, the Sulphurdimer $[S{=}(H)P(\mu\text{-}N^tBu)]_2$ and Benzylsodium were carried out as stated in literature. [4–6]



1

Synthesis of **1**: Distilled PCl_3 (12.5 mL, 143 mmol, 1.00 eq) was added dropwise to a solution of $^tBuNH_2$ (60 mL, 569 mmol, 4.00 eq) in dry THF (300 mL) at -78°C. The reaction mixture was allowed to warm to ambient temperature and was stirred for an hour. The reaction mixture was filtered to remove $^tBuNH_3Cl$ and the solvent as removed under reduced pressure. The residue was distilled at 110°C under high vacuum to give the desired product **1** (9.78 g, 31.4 mmol, 44 %) as white crystals. The spectral data were in agreement with the literature.

^{1}H NMR (500.2 MHz, $CDCl_3$, +25°C): δ [ppm] = 3.75 (1H, bd, $^1J_{P\text{-}H}$ = 8.1 Hz, $^tBuN\mathbf{H}$), 1.38 (18H, s, ^tBu), 1.32 (9H, s, terminal ^tBu).

^{31}P{^{1}H} NMR (161.7 MHz, $CDCl_3$, +25°C): δ [ppm] = 201.2 (d, $^2J_{P\text{-}P}$ = 44.9 Hz, P-Cl), 136.1 (d, $^2J_{P\text{-}P}$ = 44.8 Hz, P-NH^{t}Bu).

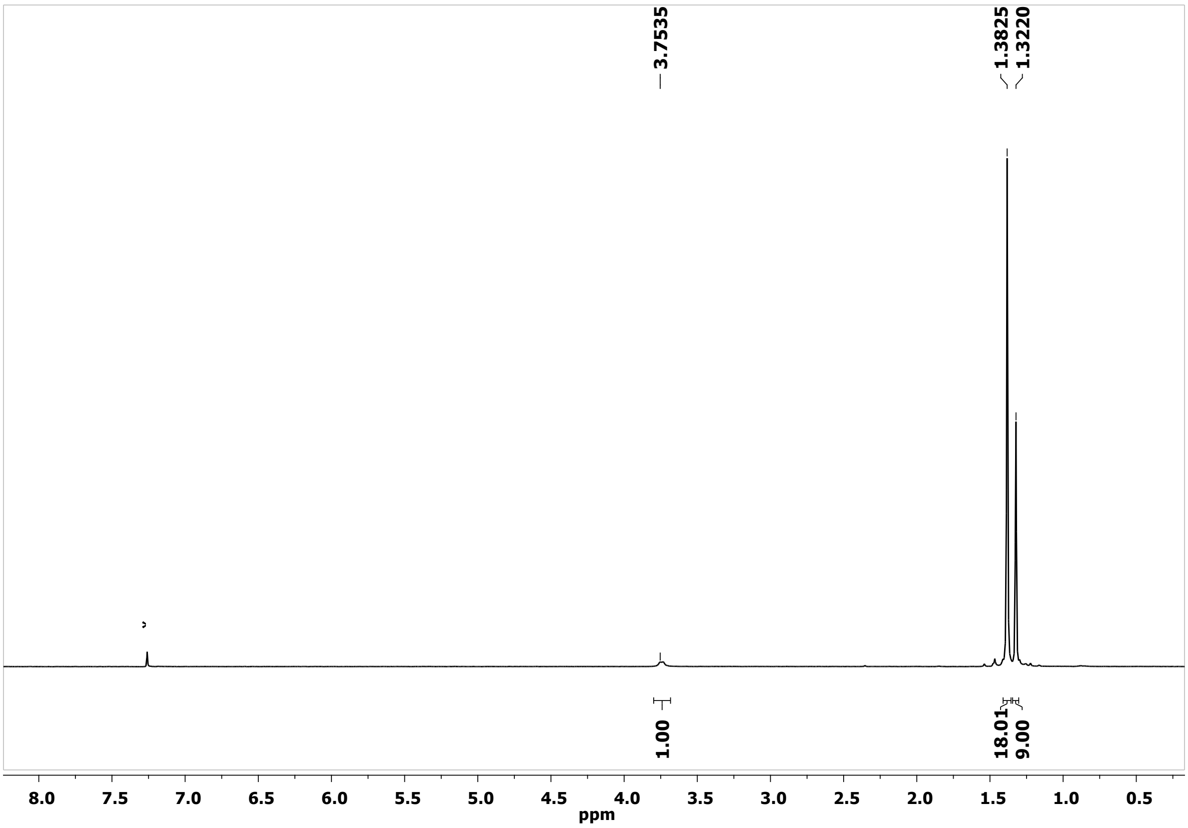


Figure S1 : ^{1}H (25 °C, $CDCl_3$*, 400.12 MHz) of **1**.

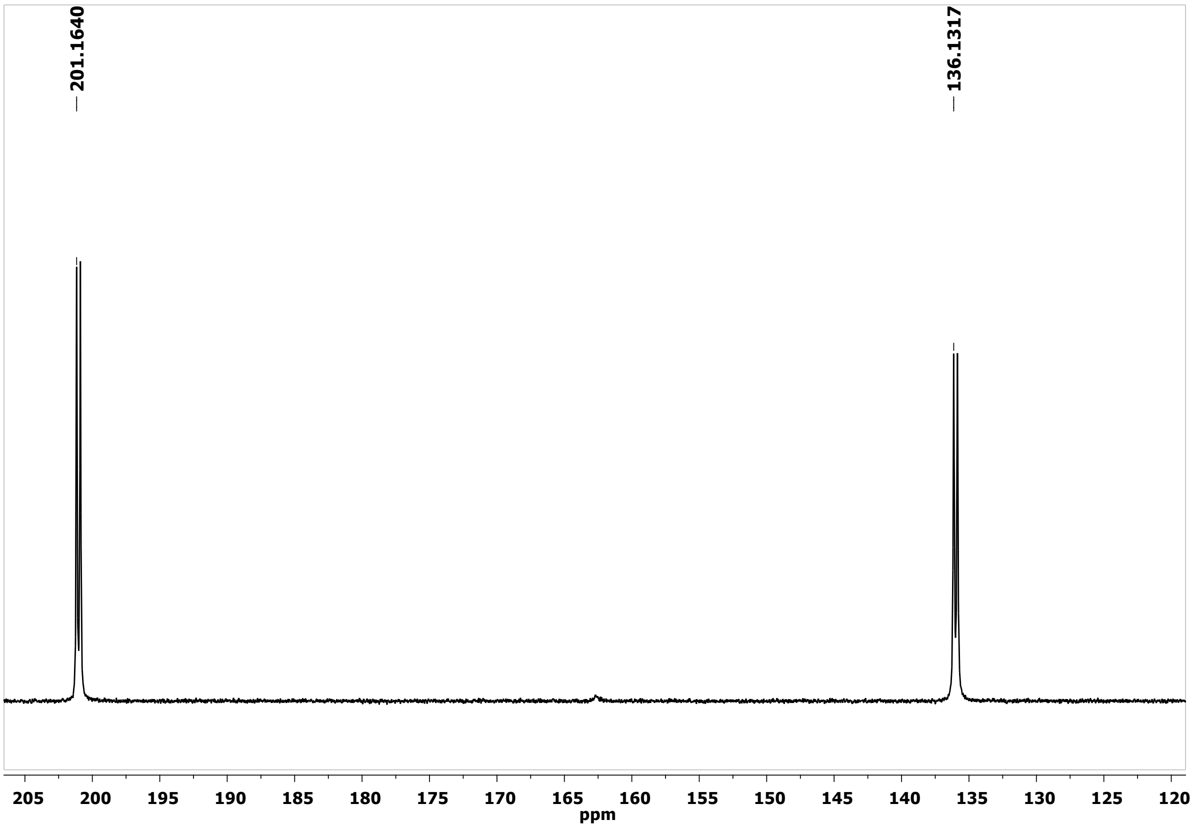
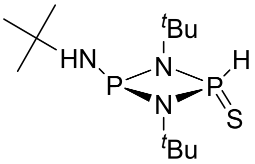


Figure S2 : ^{31}P {^{1}H} (25 °C, $CDCl_3$, 161.7 MHz) NMR of **1**.



2-*trans*

Synthesis of **2**-*trans*: *n*-Butyllithium (1.6 M in hexane, 10.5 mL, 1.0 eq) was dissolved in THF (100 mL) and cooled down to -78°C. H_2S gas was bubbled through the solution for 10 minutes. The solution was allowed to warm up to r.t. and concentrated in vacuo (this step ensures excess H_2S gas is removed from the solution). The reaction mixture was cooled down to -78°C and **1** (5.24 g, 16.8 mmol, 1.0 eq) was added dropwise. The reaction mixture was allowed to warm up to ambient temperature and stirred for 30 minutes. The solvent was removed and the resulting white solid suspended toluene (60 mL). The suspension was filtered and the solvent of the filtrate removed until precipitation of a white solid occurred. The solid was redissolved by gentle heating. Overnight storage at -20°C gave the product **2** (3.28 g, 10.6 mmol, 63 %) as colourless crystals suitable for X-ray analysis.

^{1}H NMR (400.2 MHz, C_6D_6, +25°C): δ [ppm] = 9.68 (1H, dd, $^1J_{P\text{-}H}$ = 531 Hz, $^3J_{P\text{-}H}$ = 9.8 Hz, P-H), 2.56 (1H, bs, NH), 1.39 (s, 18H, ^{t}Bu), 1.01 (9H, d, $^4J_{H\text{-}H}$ = 1.6 Hz, ^{t}Bu).

^{31}P{^{1}H} NMR (161.7 MHz, C_6D_6, +25°C): δ [ppm] = 130.1 (br, P(III)), 51.6 (d, $^2J_{P\text{-}P}$ = 5.45 Hz, P(V), further splitting in the fully ^{1}H-coupled spectrum $^1J_{P\text{-}H}$ = 531.5 Hz).

Elemental analysis (%) calcd for 2: C 46.6, H 9.5, N 13.6; found C 46.4 , H 9.3, N 13.3

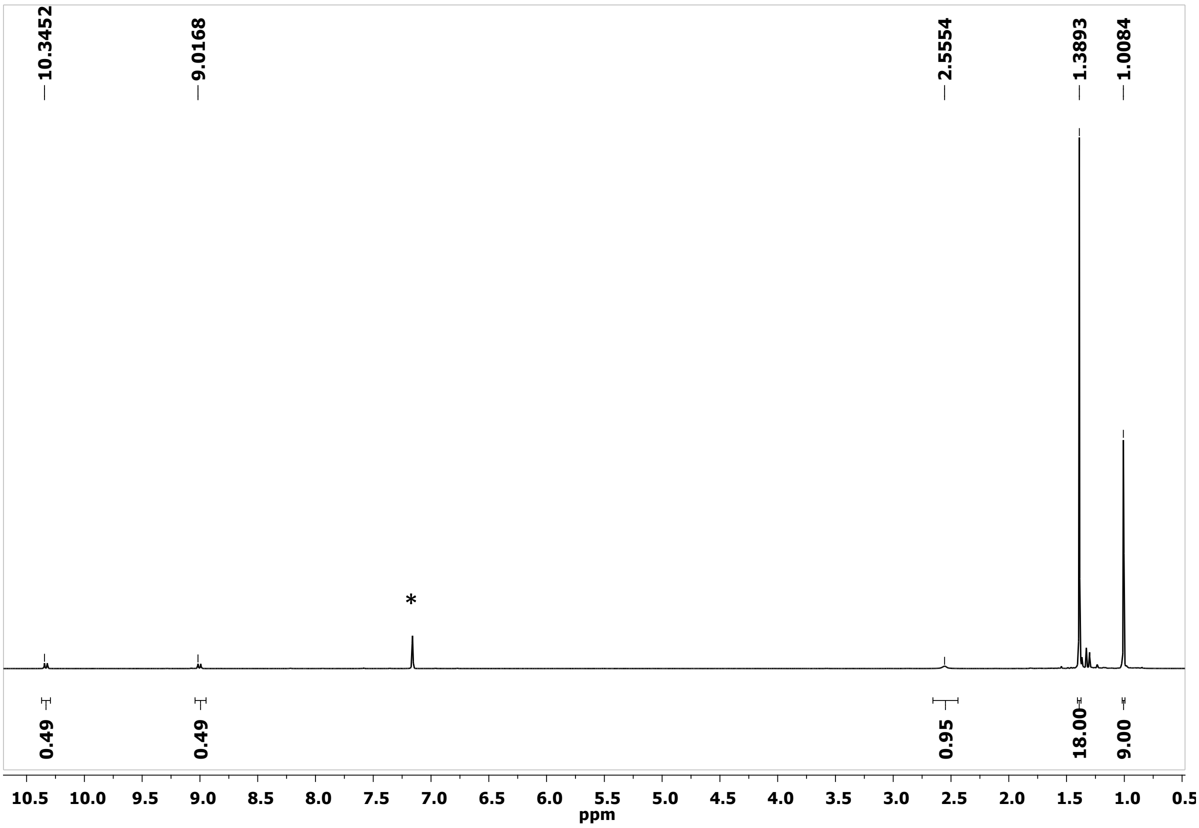


Figure S3: ^{1}H (25 °C, C_6D_6*, 500.12 MHz) NMR of **2**.

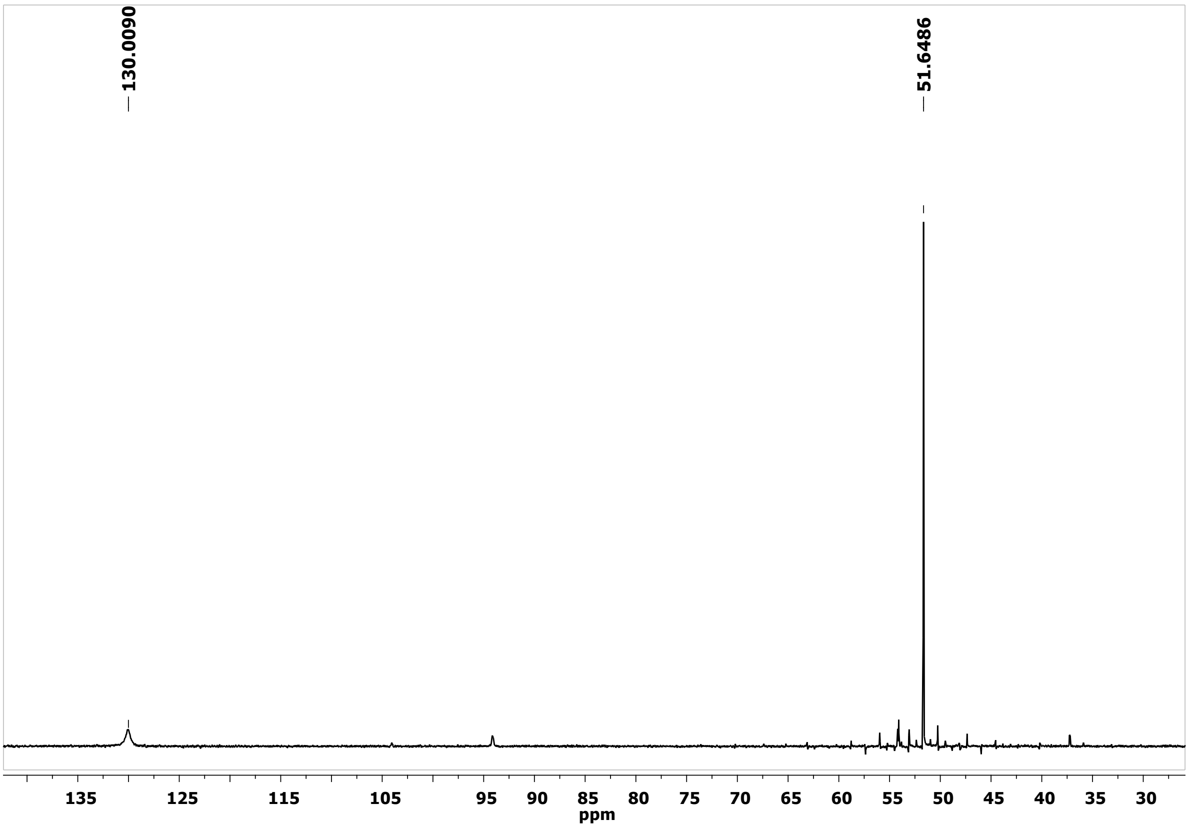
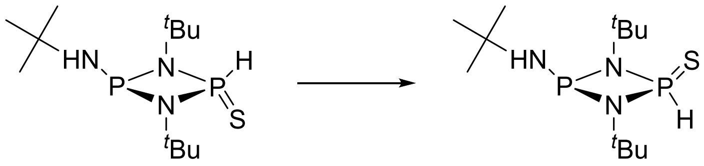


Figure S4: ^{31}P {^{1}H} (25 °C, C_6D_6, 161.7 MHz) NMR of **2**.



2-*trans* **2**-*cis*

Synthesis of **2**-*cis***:** A solution of **2**-*trans* (0.60 g, 1.93 mmol) in THF (20 mL) was stirred overnight at 50 °C. The solution was concentrated under reduced pressure. The solid was suspended in hexane (40 mL). The suspension was filtered and concentrated in vacuo until precipitation of a white solid occurred. The solid was redissolved by gentle heating. Overnight storage at 7 °C and -20 °C gave the product **2**-*cis* (0.51 g, 1.62 mmol, 85 %) as colourless crystals.

^{1}H NMR (400.2 MHz, $CDCl_3$, +25°C): δ [ppm] = 8.47 (dd, $^{1}J_{P\text{-}H}$ = 544.4, 4.4 Hz, 1H), 3.29 (d, $^{4}J_{N\text{-}H}$ = 7.4 Hz, 1H), 1.39 (s, 18H), 1.30 (d, J = 1.4 Hz, 9H).

^{31}P{^{1}H} NMR (161.7 MHz, $CDCl_3$, +25°C): δ [ppm] = 104.03 (d, $^{2}J_{P\text{-}P}$ = 11.1 Hz, P(III)), 37.24 (d, $^{2}J_{P\text{-}P}$ = 11.1 Hz, P(V), further splitting in the fully ^{1}H-coupled spectrum $^{1}J_{P\text{-}H}$ = 588.3 Hz).

Elemental analysis (%) calcd for 2: C 46.6, H 9.5, N 13.6; found C 46.6 , H 9.4, N 13.7

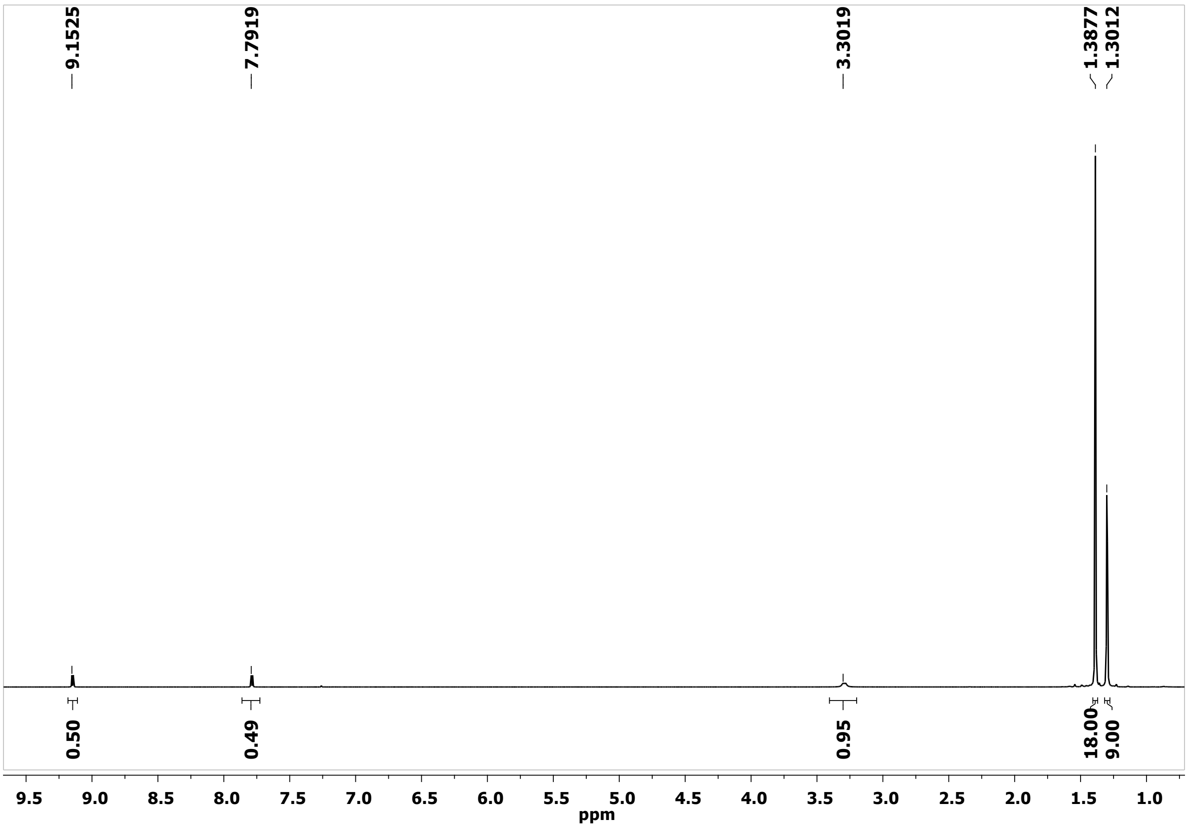


Figure S1 : ^{1}H (25 °C, CDCl$_3$, 400.12 MHz) of **2**-*cis*.

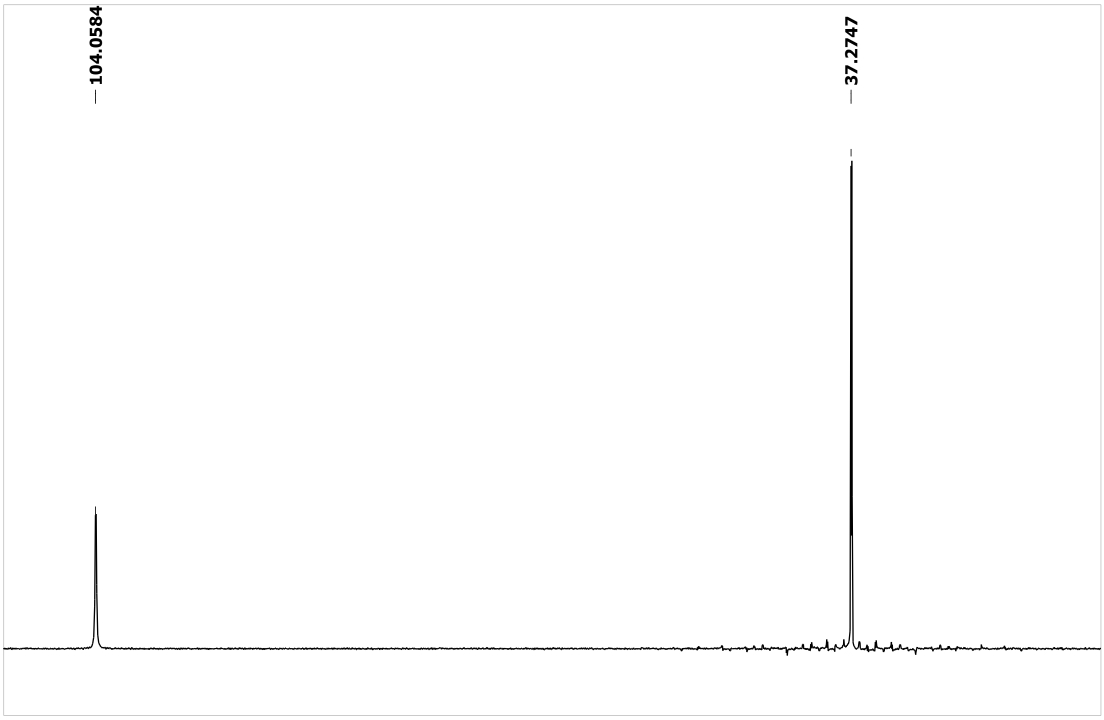
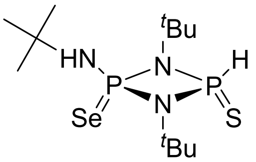


Figure S4: ^{31}P {^{1}H} (25 °C, CDCl$_3$, 161.7 MHz) NMR of **2**-*cis*.



3a

Synthesis of **3a: 2**-*trans* (3.28 g, 10.6 mmol, 1.0 eq) was dissolved in THF (60 mL) and selenium powder (2 g, 25.3 mmol, 2.4 eq) was added. The suspension was stirred overnight at r.t. The reaction mixture was filtered through celite and the solvent was removed to give the title compound **3a** as a yellow powder (3.87 g, 9.97 mmol, 94 %) which was used in the next reaction without further purification.

^{1}H NMR (400.12 MHz, CDCl$_3$, +25°C): δ [ppm] = 9.03 (1H, dd, $^1J_{P-H}$ = 585 Hz, $^3J_{P-H}$ = 10.7 Hz, P-H), 3.49 (d, 1H, $^4J_{N-H}$ = 16.0 Hz, N-H), 1.65 (s, 18H, ^{t}Bu), 0.85 (s, 9H, $^4J_{H-H}$ = 0.4 Hz, ^{t}Bu).

^{31}P{^{1}H} NMR (161.7 MHz, CDCl$_3$, +25°C): δ [ppm] = 36.2 (d, $^2J_{P-P}$ = 14.2 Hz, P(Se), further splitting in the fully ^{1}H-coupled spectrum $^3J_{P-H}$ = 30.1 Hz), 33.5 (d, P(S), $^2J_{P-P}$ = 14.0 Hz, further splitting in the fully ^{1}H-coupled spectrum $^1J_{P-H}$ = 584.6 Hz).

^{77}Se{^{1}H} NMR (95.4 MHz, CDCl$_3$, +25°C): δ [ppm] = 419.8 (d, $^1J_{P-Se}$ = 560.6, 16.6 Hz).

Elemental analysis (%) calcd for 3a: C 37.1, H 7.5, N 10.8; found C 35.8 , H 7.2, N 10.1

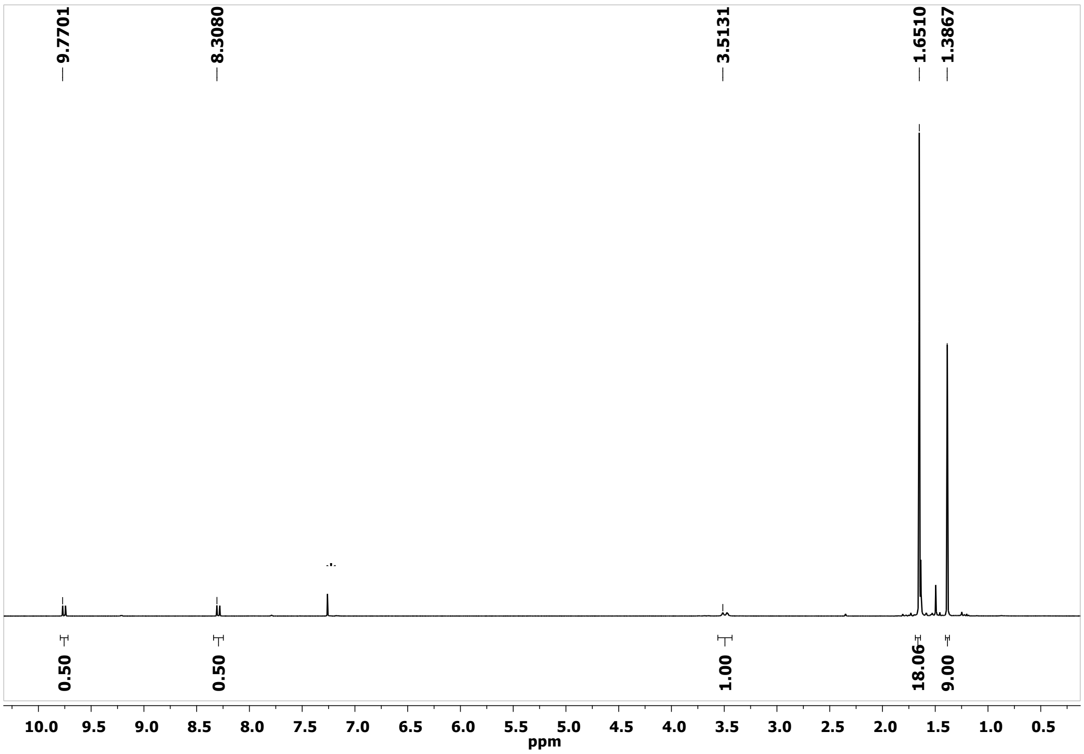


Figure S5: ^{1}H (25 °C, CDCl$_3$*, 400.12 MHz) NMR of **3a**.

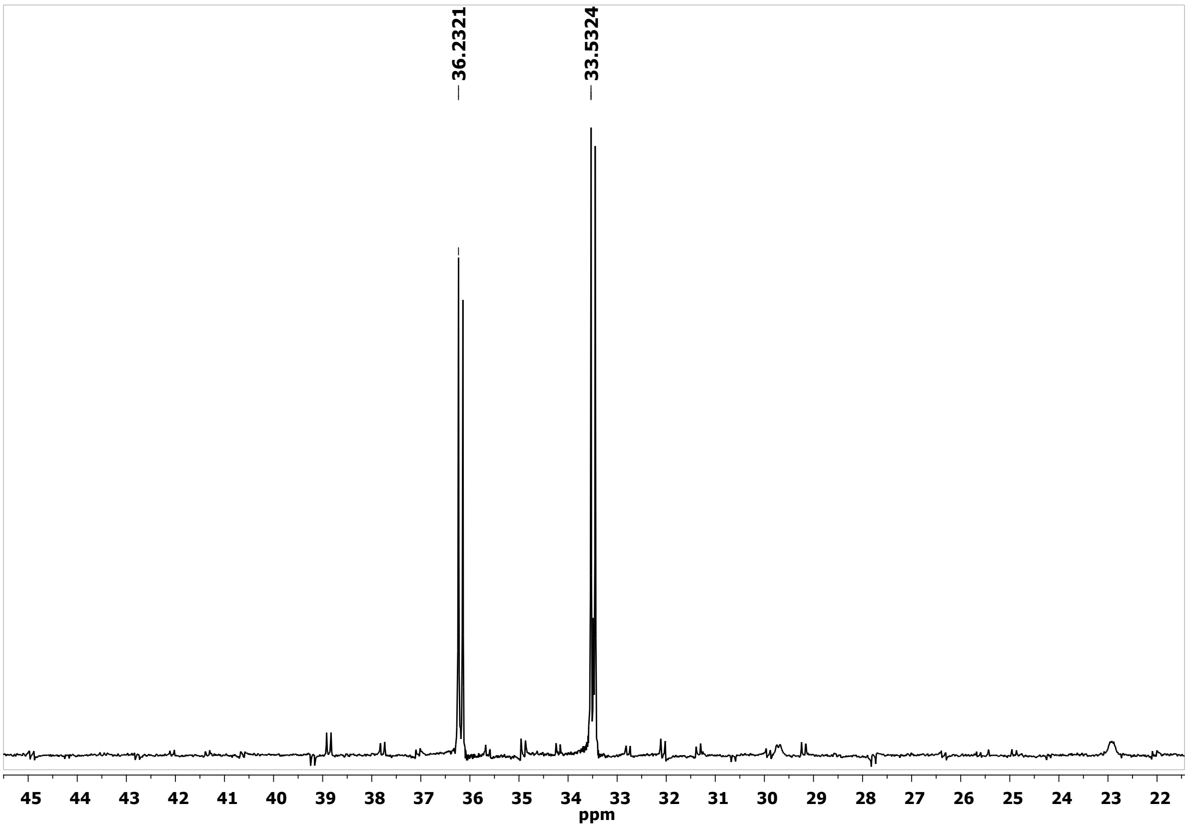


Figure S6: ^{31}P {^{1}H} (25 °C, $CDCl_3$, 161.7 MHz) NMR of **3a**.

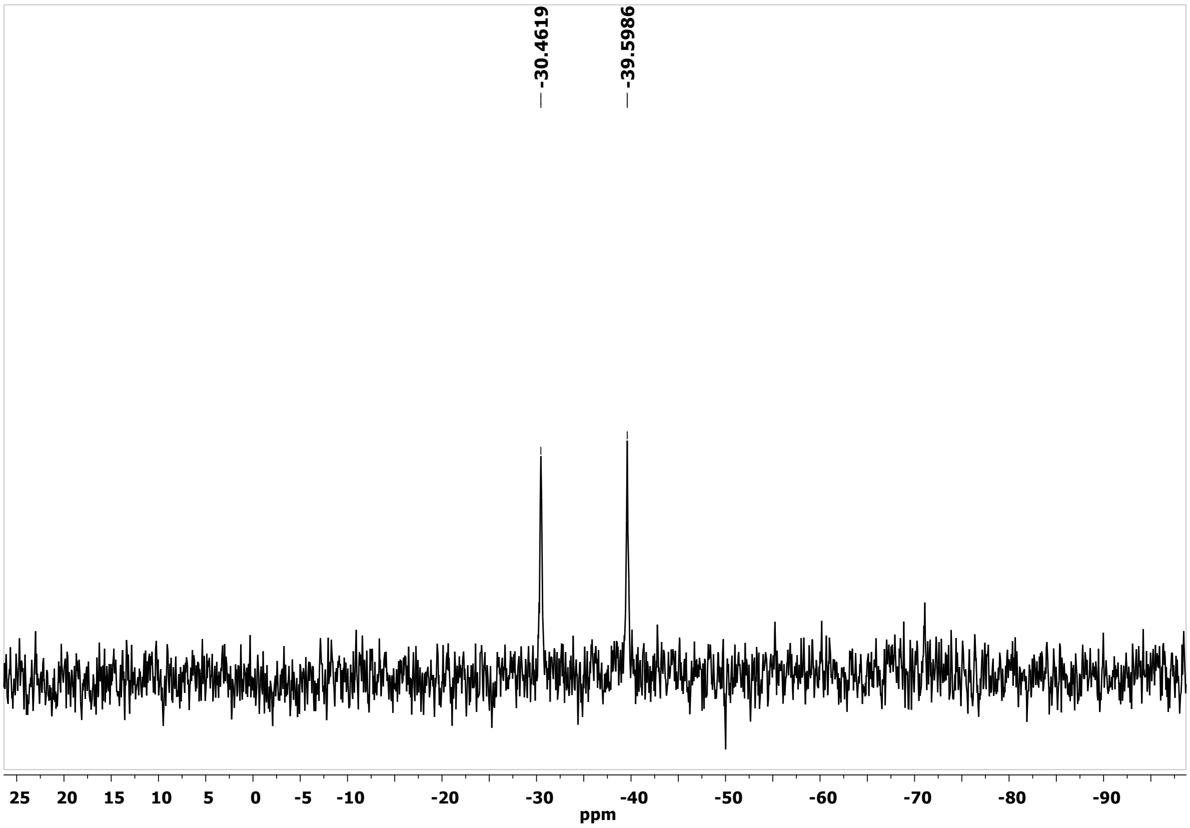
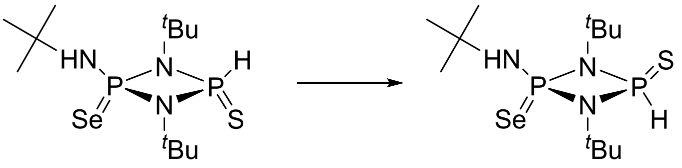


Figure S7: ^{77}Se {^{1}H} (25 °C, $CDCl_3$, 95.4 MHz) NMR of **3a.**



3a **3b**

Isomerisation of **3a:** A solution of **3a** in THF was stirred for 3h at 60 °C. The solvent was removed to afford an isomeric mixture (**3a**/**3b** = 2:1).

^{1}H NMR (400.12 MHz, CDCl$_3$, +25°C): δ [ppm] = 9.04 (dd, $^{1}J_{P\text{-}H}$ = 585.1, $^{3}J_{P\text{-}H}$ =10.7 Hz, 1H(cis)), 8.51 (dd, $^{1}J_{P\text{-}H}$ = 569.3, $^{3}J_{P\text{-}H}$=2.7 Hz, 1H(trans)), 3.68 (d, $^{4}J_{N\text{-}H}$ = 15.8 Hz, 1H(cis)), 3.50 (d, $^{4}J_{N\text{-}H}$ = 16.0 Hz, 1H(trans)), 1.66 (s, 18H(cis)), 1.65 (s, 18H(trans)), 1.51 (s, 9H(cis)), 1.40 (s, 9H(trans)).

^{31}P{^{1}H} NMR (161.7 MHz, CDCl$_3$, +25°C): δ [ppm] = 36.2 (d, J = 14.2 Hz, P(Se, **3a**), 33.5 (d, J = 14.3 Hz P(S, **3a**)), 29.7 (d, J = 9.8 Hz P(Se, **3b**)), 22.9 (d, J = 8.4 Hz P(S, **3b**).

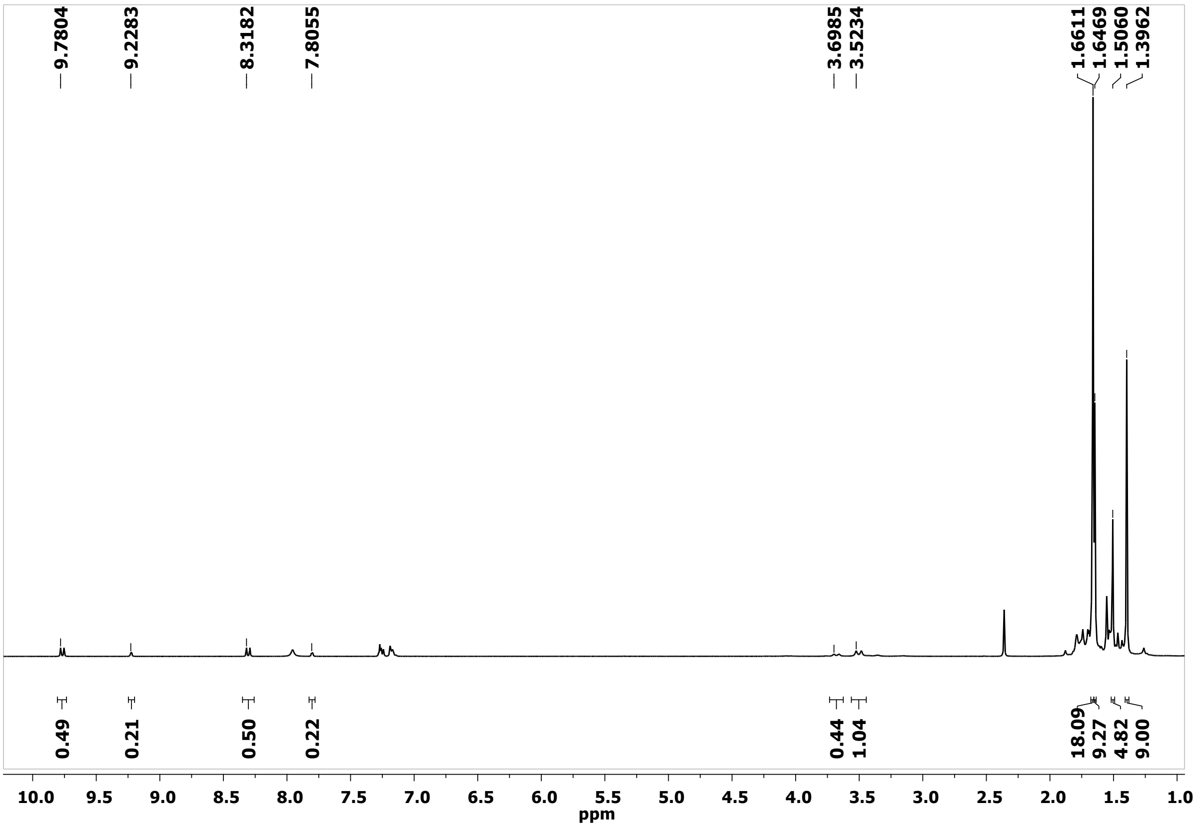


Figure S8: ^{1}H (25 °C, CDCl$_3$, 400.12 MHz) NMR of **3a/3b**, residual toluene at 6.96 ppm and 2.36 ppm.

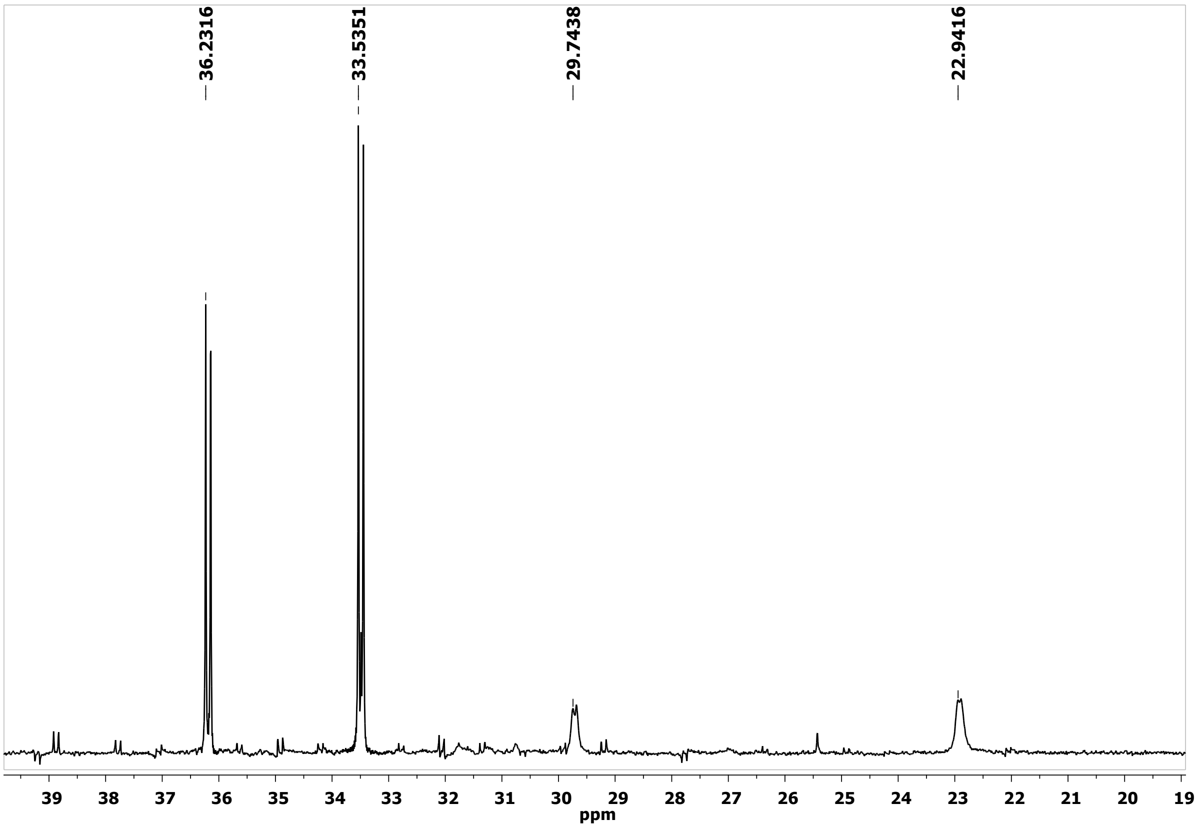
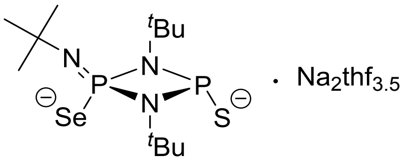


Figure S9: ^{31}P {^{1}H} (25 °C, $CDCl_3$, 161.7 MHz) NMR of **3a/3b**.



6

Synthesis of **4: 3a** (0.10 g, 0.03 mmol, 1.0 eq) dissolved in THF (10 mL) was added to benzylsodium (0.93 g, 0.05 mmol, 3.0 eq). The reaction mixture was stirred for 5 minutes and then layered with n-hexane. After 3 days **6** was yielded as colourless crystals suitable for X-ray diffraction (0.04g, 24%).

^{1}H NMR (500.2 MHz, d_8-THF, +25°C): δ [ppm] = 1.55 (s, 18H), 1.22 (s, 9H).

$^{31}P\{^{1}H\}$ NMR (161.7 MHz, d_8-THF, +25°C): δ [ppm] = 172.9 (d, P(S) $^{2}J_{P\text{-}P}$ = 19.0 Hz), 11.3 (d, P(Se) $^{2}J_{P\text{-}P}$ = 19.7 Hz).

$^{77}Se\{^{1}H\}$ NMR (95.4 MHz, d_8-THF, +25°C):): δ [ppm] = 419.8 (d, $^{1}J_{P\text{-}Se}$ = 560.6, $^{3}J_{P\text{-}Se}$ = 16.6 Hz).

Elemental analysis (%) calcd for 6: C 44.4, H 7.9, N 6.5; found C 43.2 , H 7.2, N 6.0

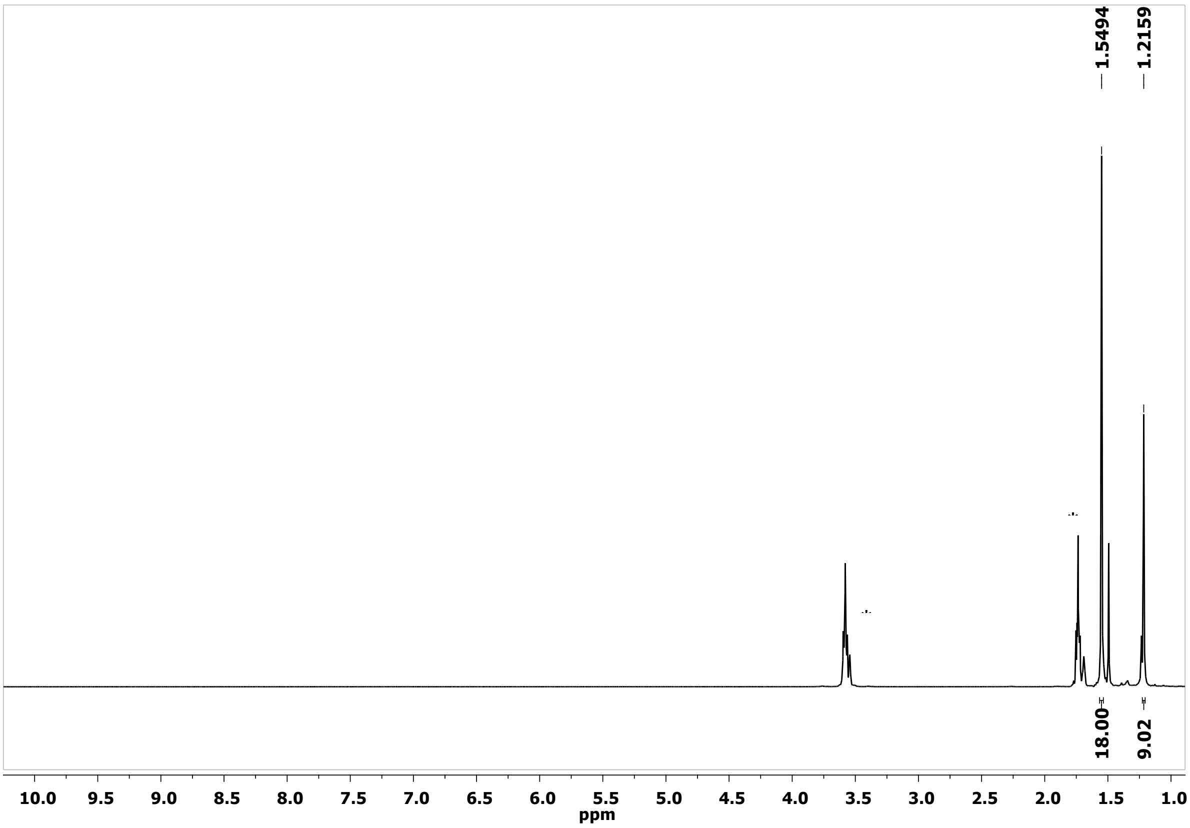


Figure S10: ^{1}H (25 °C, d_8-THF*, 500.12 MHz) NMR of **6**.

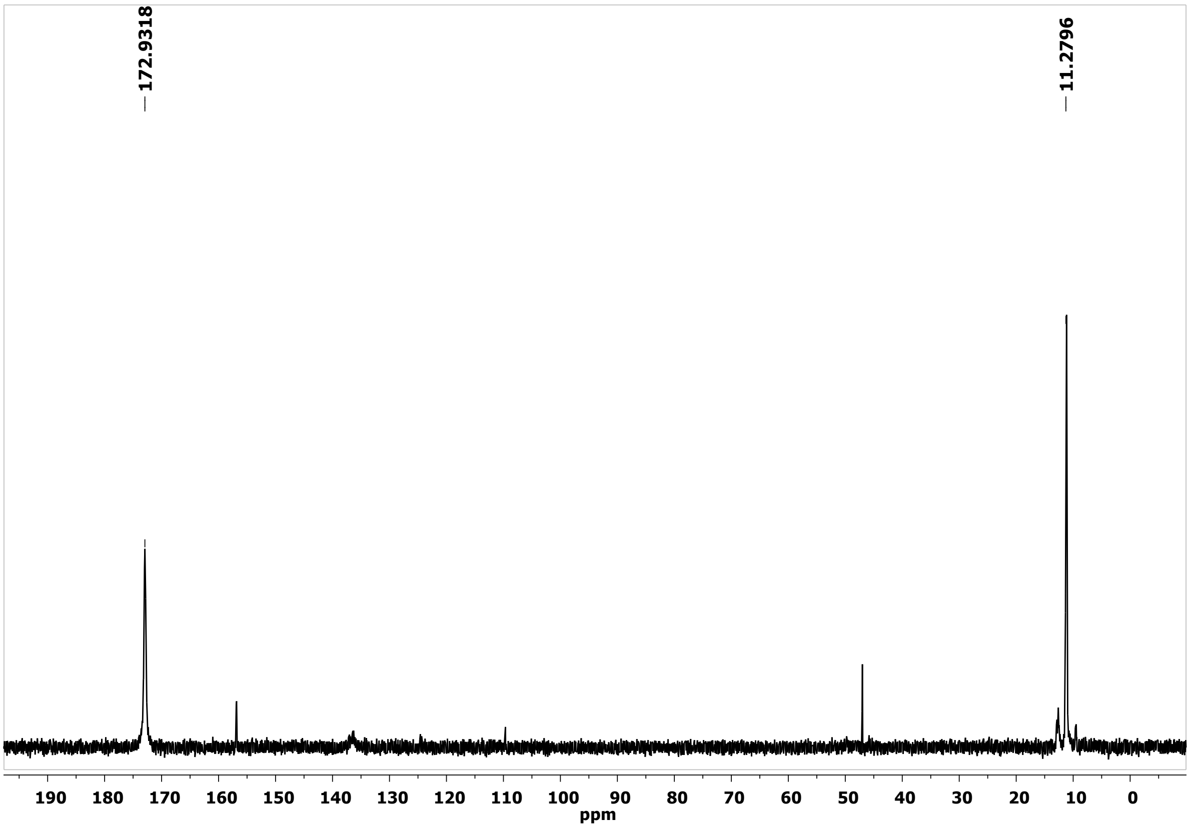


Figure S11: ^{31}P {^{1}H} (25 °C d_8-THF, 161.7 MHz) NMR of **6**.

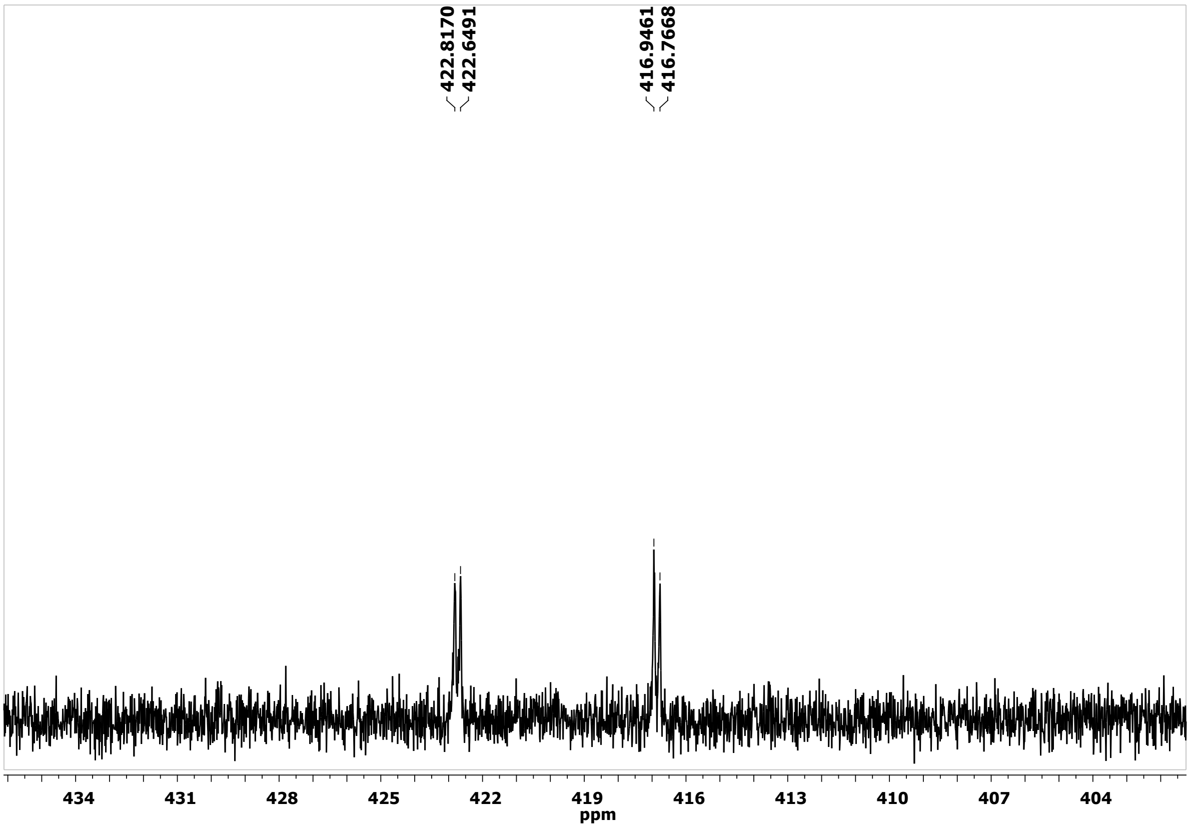


Figure S12: ^{77}Se {^{1}H} (25 °C, C_6D_6, 95.4 MHz) NMR of **6.**

2. Determination of the reaction order

Reaction order of the isomerisation of **3b** to **3b**:
The process was monitored via ^{1}H-NMR at 323.15 K for 588 minutes. The ^{1}H-NMR's were recorded in six minutes time intervals which amounts to 99 experiments in total. The integration of the signal corresponding to the P-H proton of both isomers led to a certain ratio of the species for each interval. This ratio directly correlates to the qualitative concentration $(a-x)$ of the initial isomer at a certain time.

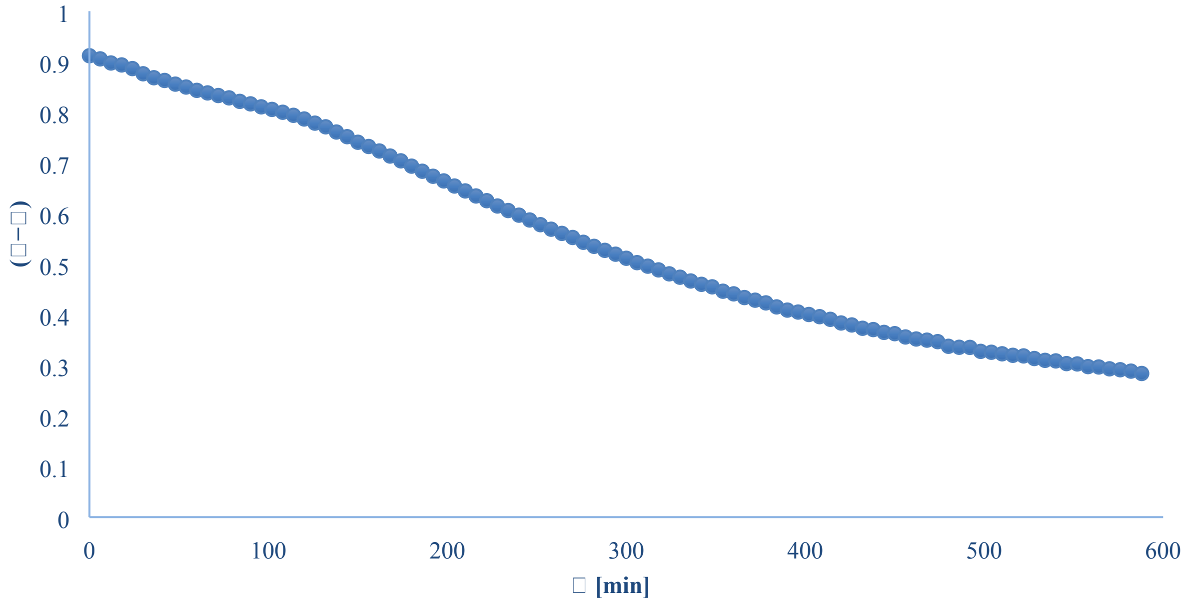


Figure S13: Qualitative concentration of **3b** during the isomerisation.

In order to determine the reaction order the graphical method was used. [1] The following table 1 shows equations which directly correlate to a reaction order:

Table 1: Important equations for the graphical method.*

Order	**Equation**
0	$x = kt$
1	$\log\ (a - x) = -\frac{k}{2.303}t + \log a$
2	$\frac{1}{(a - x)} = kt + \frac{1}{a}$
3	$\frac{1}{(a - x)^2} = 2kt + \frac{1}{a^2}$
…	…
n	$\frac{1}{(a - x)^{n-1}} = (n - 1)kt + \frac{1}{a^{n-1}}$

$*(a - x)$ = concentration of the reactant at time t; k = rate constant; a = initial concentration of the reactant.

Thus, if a plot of the left hand side of the expression against the time is a straight line, the reaction order can be determined. In this case the term $(a - x)$ equals the qualitative concentration of the *trans*-isomer at a certain time t. The following two figures show the plot of $\log\ (a - x)$ and $\frac{1}{(a - x)}$ against the time as well as the correlation coefficient R^2 of the plot:

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[1] S.K. Upadhyay, *Chemical Kinetics and Reaction Dynamics*, Springer, New York, **2006**.

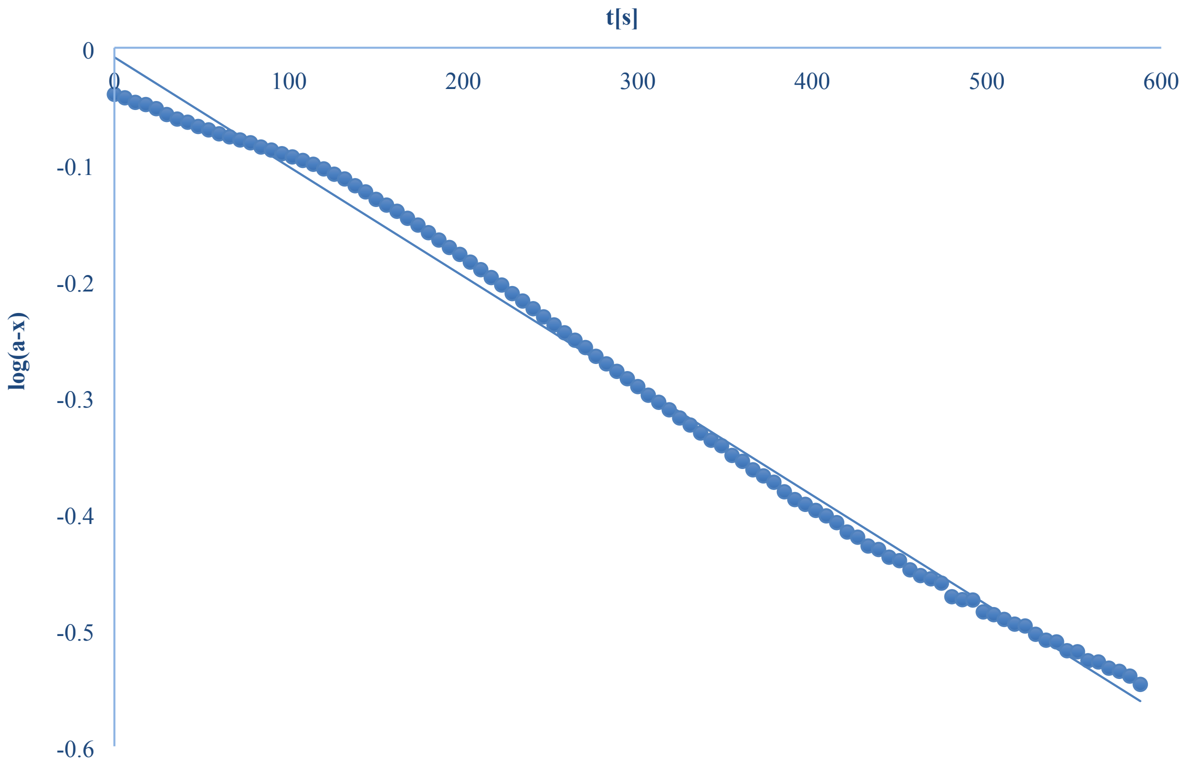

Figure S14: First order plot: The values of $\log\ (a-x)$ were multiplied with (-1) for clarity.

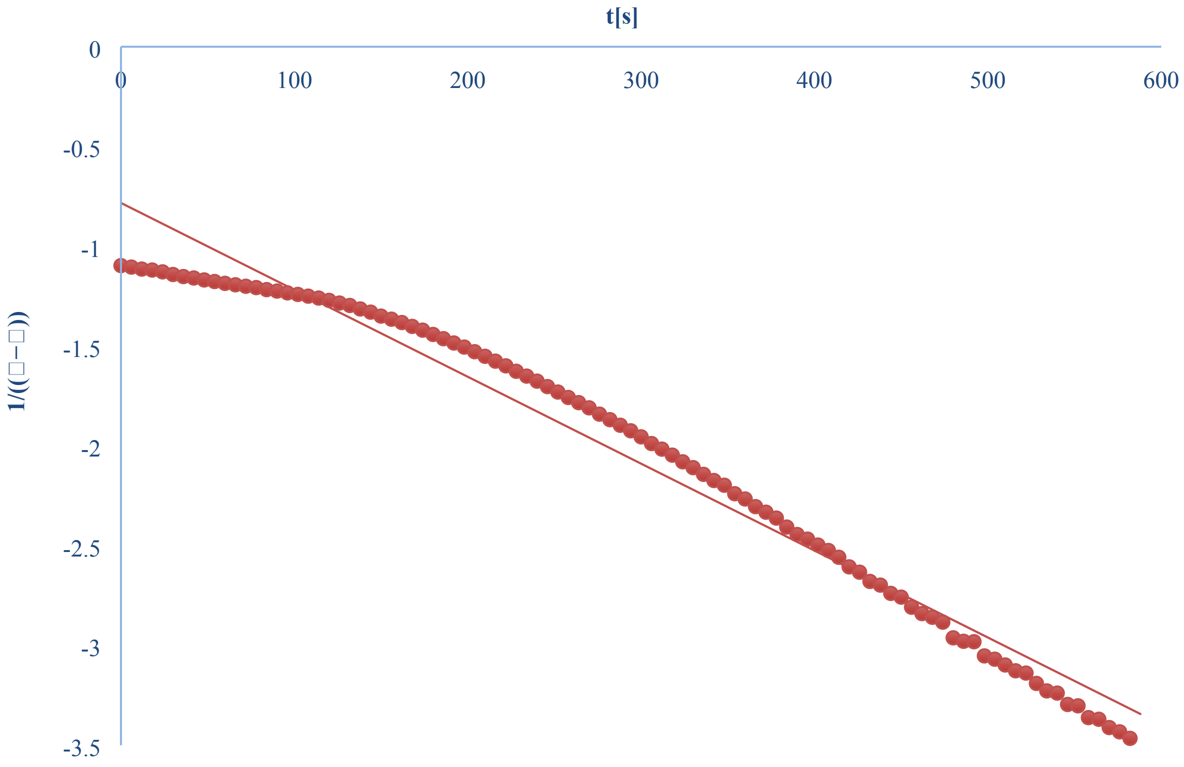

Figure S15: Second order plot.

The comparison of both plots and correlation coefficients led to the assumption that the described isomerisation is a first order reaction.

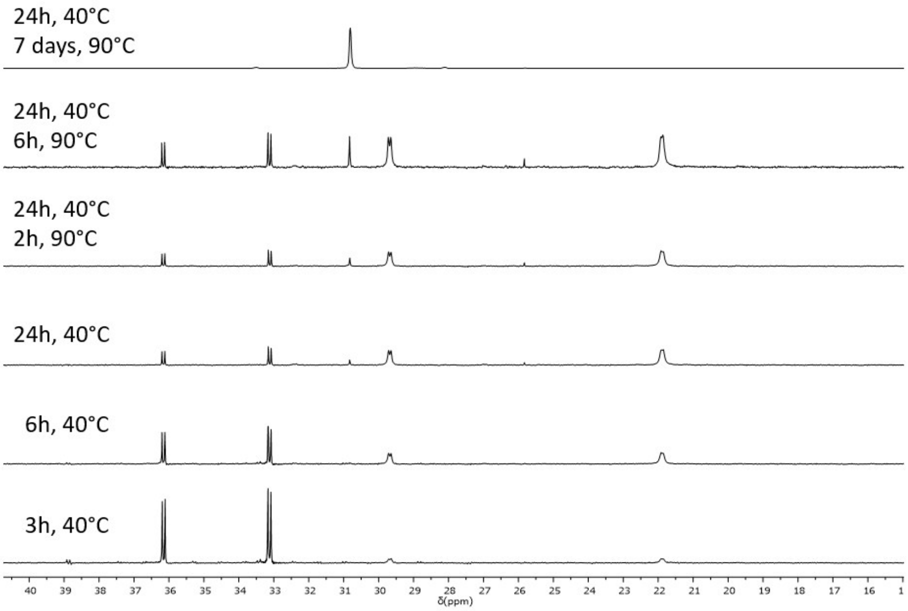

Figure S16: $^{31}P\{^{1}H\}$ (25 °C, d_8-toluene , 161.7 MHz) of different stages of the isomerisation in d_8-toluene

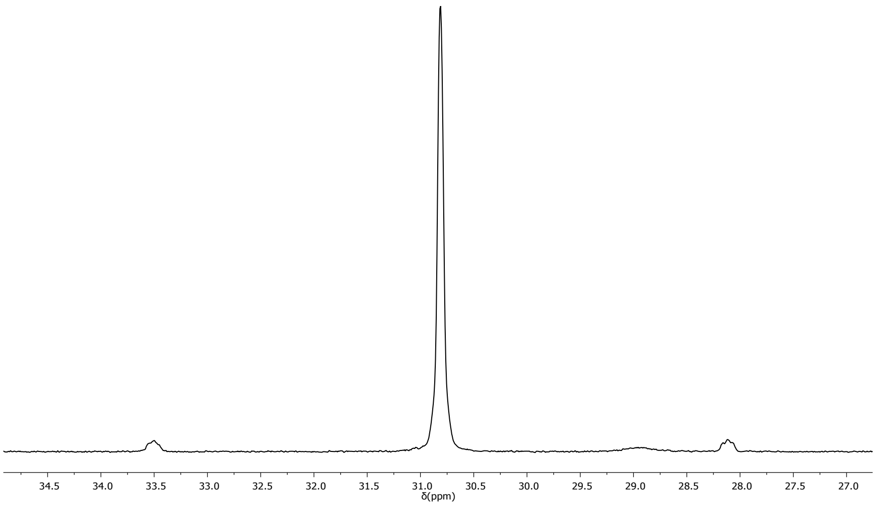

Figure S17: Zoom in into ^{1}H (25 °C, $CDCl_3$, 400.12 MHz) of the resonance for **4**.

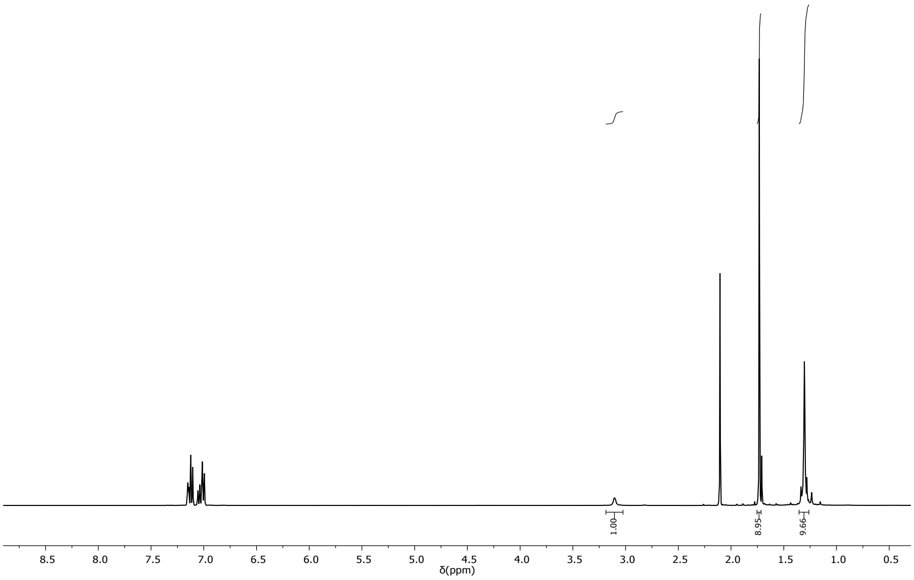

Figure S20: ^{1}H NMR (25 °C, $CDCl_3$, 400.12 MHz) spectrum of **4** crystallised from toluene.

3. X-ray Crystallography

Table 1 Crystal data and structure refinement

	2-*trans*	**2**-*cis*	**3a**	**6**
CCDC Number	1557383	1557386	1557384	1557385
Empirical formula	$C_{12}H_{29}N_3P_2S$	$C_{12}H_{29}N_3P_2S$	$C_{12}H_{29}N_3P_2SSe$	$C_{24}H_{51}N_3Na_2O_3P_2SSe \cdot 0.5THF$
Formula weight	309.38	309.38	388.34	720.72
Temperature/K	180(2)	180(2)	180(2)	180(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a / Å	9.958(2)	20.1254(14)	16.9527(4)	14.6757(4)
b / Å	11.381(2)	9.8130(6)	14.5736(4)	16.6222(5)
c / Å	15.909(3)	20.1672(14)	16.9848(4)	16.4866(5)
α / °	90	90	90	90
β / °	90	115.388(4)	114.4630(10)	1109.2240(10)
γ / °	90	90	90	90
Volume / Å^3	11803.1(6)	3598.2(4)	3819.59(17)	3797.52(10)
Z	4	8	8	4
ρ_{calc} / g cm^{-3}	1.140	1.142	1.489	1.209
μ / mm^{-1}	3.183	3.190	8.366	4.253
$F(000)$	11288	1344	1616	4200
Crystal size / mm^3	0.33×0.21×0.15	0.25×0.18× 0.04	0.34×0.19× 0.16	0.23×0.21× 0.11
Radiation	CuKα (λ = 1.5418)	CuKα (λ = 1.5418)	CuKα (λ = 1.5418)	CuKα (λ = 1.5418)
θ range / °	5.24 to 66.59	4.40 to 66.82	4.17 to 69.79	3.50 to 66.64
Reflections collected	11288	9670	28431	47113
Independent reflections	3164	6102	7208	6707

R_{int}	0.049	0.059	0.049	0.052
Goodness-of-fit on F^2	1.02	1.11	1.06	1.06
Data/restraints/parameters	3164/0/171	6102/302/381	7208/2/360	6707/84/404
$R1$ [$I>2\sigma(I)$]	0.033	0.076	0.044	0.065
w$R2$ [all data]	0.077	0.164	0.103	0.178
Largest diff. peak/hole / e Å^{-3}	0.185/–0.251	0.56/–0.52	0.43/–0.73	1.17/–0.76
Flack Parameter	0.030(14)	-	-	-

Experimental details

Single crystal X-ray diffraction data were collected on a Bruker D8-QUEST PHOTON-100 diffractometer equipped with an Incoatec IµS Cu microsource. Data integration and reduction were undertaken with SAINT in the APEX3 software suite. Multi-scan empirical absorption corrections were applied using SADABS for **2**-*trans*, **3a** and **6**, and using TWINABS for **2**-*cis*. Structures were solved using SHELXT-2014 and refined using full-matrix least squares on F^2 using SHELXL-2014/7.

> G. M. Sheldrick, A. F. H., B. H. M., B. I. J., G. C. R., C. S. C., B. H.-B., D. B., G. S., J. D., et al., *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.
>
> G. M. Sheldrick, B. M. C., Y. H., E. S. H., D. R. T., O. M. J., B. M. C., C. B., C. G. L., G. C., et al., *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8.

Structure refinement details

2-*trans*: PH and NH hydrogens were identified from the electron density map and were allowed to refine freely.

2-*cis*: The crystals were twinned by a two-fold rotation approximately around *c*. The orientation matrices for the two components were identified using CELL_NOW; the two components were then integrated using SAINT and corrected for absorption using TWINABS. The structure was solved using the HKLF 4 type file and then refined using the HKLF 5 type file, resulting in a BASF value of 0.589(2). The crystals contain two isostructural molecules per asymmetric unit. The methyl groups of one *tert*-butyl group were modelled as disordered over two locations with occupancies of 0.7069/0.2932. PH hydrogens were identified from the electron density map and their locations allowed to refine freely. NH hydrogens were also identified from the electron density map but restraints were then applied to the NH distances. The isotropic displacement parameters of the PH and NH hydrogens were constrained to be 1.2 times that of the atom to which they were bonded.

3a: The structure was refined as a 2-component twin [TWIN 0 0 1 0 -1 0 1 0 0, BASF 0.3198]. The crystals contains two isostructural molecules per asymmetric unit. Both PH and NH atoms were identified in the electron density map and both heteroatomic pairs were restrained to be equal between structures using SADI.

6: Multiple THF molecules displayed a significant amount of thermal motion. Atoms with $U_{ij} > 0.4$ were refined to approximate isotropic behaviour (ISOR). One THF molecule was disordered over two sites - one of these was coordinated to a Na^+ ion, the other was not (occupancies of 0.5072/0.4928). On the disordered, coordinated THF molecule very high thermal motion was observed, necessitating EADP restraints.