

Supplementary information for ja507433g

Degenerate Nucleophilic Substitution in Phosphonium Salts

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1. Synthesis and characterisation of phosphine oxides **1a**, **2a**, **3a**, **4a**, **5a**, **6a**, **7a**
2. Synthesis and characterisation of halophosphonium halides **1b**, **1c**, **2b**, **2c**, **3b**, **3c**, **4b**, **4c**, **5b**, **5c**, **6b**, **6c**
3. Variable temperature NMR experiments
4. Exchange spectroscopy (EXSY) experiments to determine epimerisation rate of **4b**
5. EXSY to determine order of epimerisation
6. Reaction profiles of $\text{P}^t\text{BuMe}_2\text{Cl}_2$ and $\text{PEtMe}_2\text{Cl}_2$
7. Eyring and lineshape analysis of **3c**
8. Comparison of computational and experimental barriers
9. DFT Calculated Total Energies

1. Synthesis and characterisation of phosphine oxides **1a**, **2a**, **3a**, **4a**, **5a**, **6a**, **7a**

All chemicals supplied by Aldrich with the exception of Merck silica 9385 (partical size 0.040-0.063 mm). All chemicals were used without further purification except diethyl ether and THF, which were dried in Grubbs solvent press and stored in Strauss flasks, and CDCl_3 which was dried over molecular sieves.

NMR chemical shifts are reported in parts per million (ppm). NMR samples were made up using CDCl_3 as solvent. ^1H , ^{13}C and ^{31}P $\{^1\text{H}\}$ NMR spectra were obtained on Varian 400 and Varian 500 MHz machines. Double decoupled ^{13}C $\{^1\text{H}\}$ $\{^{31}\text{P}\}$ NMR spectra were obtained on Varian 600 MHz machine. ^1H and ^{13}C NMR chemical shifts were measured relative to tetramethylsilane. ^{31}P NMR chemical shifts were measured relative to an external orthophosphoric acid standard.

All products are pure by NMR unless otherwise stated.

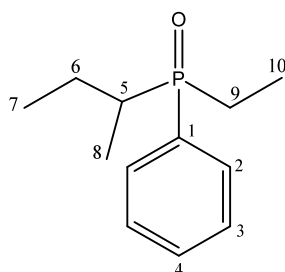
Diastereomeric phosphine oxides were characterised as mixtures by HSQC, NOESY, COSY, TOCSY and phosphorus-proton HSQC. Due to signal overlap, many multiplet shifts are quoted as the centre of the peak determined by correlation spectroscopy rather than as a range.

High resolution mass spectra were obtained in electrospray mode. Samples were dissolved in methanol.

TLC was performed on Merck pre-coated alumina 90 F-254 plates with realisation by UV irradiation and iodination.

1.4.1 General procedure for phosphine oxides

Sec-butylethylphenylphosphine oxide **2a**



To a flame dried 250 mL Schlenk-adapted round-bottomed flask under nitrogen was added PPhCl_2 (1.30 g, 7.3 mmol) and dry diethyl ether (20 mL). The flask was cooled to -78°C and sec-butylmagnesium chloride (2M in diethylether, 3.65 mL, 7.3 mmol) was added dropwise over ten minutes. The flask was allowed to warm to room temperature and stirred for two hours. The flask was cooled over ice and ethylmagnesium bromide (3M in diethylether, 3 mL, 9 mmol) was added. This was stirred for three hours at rt. Degassed aqueous NH_4Cl (2M, 20 mL) was added via syringe. The mixture was stirred for ten minutes and then the aqueous layer was removed via syringe. The reaction mixture was cooled over ice. Hydrogen peroxide (30 % wt in water, 2 mL) was added to a beaker with 20 mL water and this was slowly poured into the reaction vessel. The reaction was stirred for 30 min and the solvent was removed under reduced pressure. The product was extracted from the aqueous layer

with DCM (5 x 20 mL). The combined extracts were washed with brine (20 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure to give **2a** as a yellow oil. Crude yield 1.27g, 84%. The product was purified by column chromatography using cyclohexane : ethyl acetate : methanol (6:2:1) to give a colourless oil (1.02 g, 67% yield) which was a mixture of two racemic pairs of diastereomers in 1:1 ratio. (m/z): $[M + H]^+ = 211.1257$ (Calculated 211.1252), 2.5 PPM; IR (NaCl) $\nu = 1168.4 \text{ cm}^{-1}$ (PO).

NMR Signals assigned to diastereomer A:

^{31}P NMR (243 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 47.05 ppm;

^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3 , numbering in accord with the chart above) δ ppm 7.72- 7.66 (m, 1H, H-4), 7.54- 7.46 (m, 4H, H-3, H-2) 1.90-2.08 (m, 2H, H-9), 1.81 (m, 1H, H-5), 1.64 (m, 1H, H-6), 1.31 (m, 1H, H-6), 1.22 (dd, $J = 7.3, 16.1$, 3H, H-8), 1.07-1.14 (m, 3H, H-10) 0.91 (t, $J = 7.4 \text{ Hz}$, 3H, H-7)

^{13}C NMR (126 MHz, CDCl_3) δ ppm 131.6 (C-1, 90Hz) 131.3 (C-4), 131.0 (C-2), 128.4 (C-3), 22.5 (C-6), 20.0 (C-9), 14.2 (C-5), 12.3 (C-7), 11.5 (C-8), 5.5 (C-10),

NMR signals attributed to diastereomer B

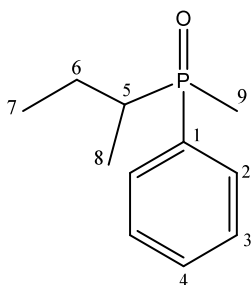
^{31}P NMR (243 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 47.00

^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 7.72- 7.66 (m, 1H, H-4), 7.54- 7.46 (m, 4H, H-3, H-2), 1.90- 2.08 (m, 2H, H-9), 1.92 (m, 1H, H-6), 1.81 (m, 1H, H-5), 1.31 (m, 1H, H-6), 1.07-1.14 (m, 3H, H-10), 1.05 (m, 3H, H-8), 1.01 (t, $J = 7.3 \text{ Hz}$, 3H, H-7)

^{13}C NMR (126 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 131.6 (C-1, 90Hz) 131.3 (C-4), 131.0 (C-2), 128.4 (C-3), 35.3 (C-5) 22.0 (C-6), 19.4 (C-9), 12.2 (C-7), 12.0 (C-8), 5.5 (C-10)

Sec-butylmethylphenylphosphine oxide 1a

0.94g, 66% yield from PPhCl_2 (1.30 g, 7.3 mmol)



HRMS (m/z): $[M + H]^+ = 197.1103$ (Calculated for $\text{C}_{11}\text{H}_{18}\text{PO}$ 197.1095), 3.9 PPM; IR (NaCl) $\nu = 1166, 1149$

NMR signals attributed to diastereomer A

^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 1.76 (m, 1H, H-5), 1.69 (m, 1H, H-6), 1.29 (m, 1H, H-6), 1.20 (dd, $J = 6.9, 14.2$, 3H, H-8), 0.92 (t, $J = 7.0 \text{ Hz}$, 3H, H-7)

^{13}C NMR (126 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 36.5 (C-5), 22.2 (C-6), 12.2 (C-7), 11.6 (C-8)

NMR signals attributed to diastereomer B

^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 1.88 (m, 1H, H-6), 1.79 (m, 1H, H-5), 1.35 (m, 1H, H-6), 1.06 (dd, $J = 7.0, 12.6$, 3H, H-8), 1.01 (t, $J = 7.3 \text{ Hz}$, 3H, H-7)

^{13}C NMR (126 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 36.0 (C-5), 22.1 (C-6), 12.1 (C-7), 11.7 (C-8)

NMR signals not yet assigned to A or B

^{31}P NMR (121 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 42.9, 43.0

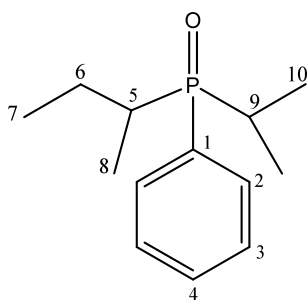
^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 7.70 (m, 4H, Ar-H), 7.49 (m, 6H, Ar-H), 1.70 (m, 6H, H-9)

^{13}C NMR (126 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 133.1, 132.4, 131.5, 131.4, 130.4, 130.3, 128.5, 128.4, 13.4 (C-9), 12.8 (C-9)

Sec-butylphenyl iso-propylphosphine oxide 3a

0.77 g, 3.43 mmol, 47% yield from PPhCl_2 (1.30 g, 7.3 mmol)

HRMS (m/z): $[M + H]^+ = 225.1399$ (Calculated for $\text{C}_{13}\text{H}_{22}\text{PO}$ 225.1408), -4.1 PPM; IR (NaCl) $\nu = 1173, 1148$



NMR signals attributed to diastereomer A

^{31}P NMR (243 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 50.65

^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 2.06 (m, 1H, H-9), 2.06 (m, 1H, H-5), 1.96 (m, 1H, H-6), 1.19 (m, 1H, H-6), 1.05 (m, 6H, H-10), 1.05 (m, 3H, H-8), 1.01 (t, $J = 7.4$ Hz, 3H, H-7),

NMR signals attributed to diastereomer B

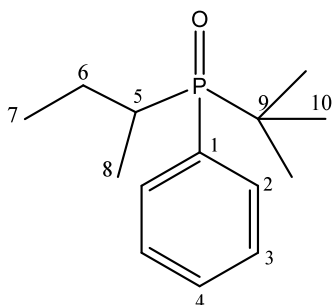
^{31}P NMR (243 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 50.85

^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 2.33 (m, 1H, H-9), 2.04 (m, 1H, H-5), 1.62 (m, 1H, H-6), 1.26 (m, 1H, H-6), 1.23 (m, 3H, H-8), 1.21 (m, 3H, H-10), 1.17 (m, 3H, H-10), 0.94 (t, $J = 7$ Hz, 3H, H-7)

NMR signals not yet assigned to A or B

^{13}C NMR (126 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 131.5, 131.4, 131.4, 131.3, 129.7, 129.7, 128.3, 128.2, 32.3, 31.8, 25.2, 24.7, 21.7, 21.7, 15.9, 15.8, 14.9, 14.8, 12.2, 12.1, 12.0, 11.0

Sec-butyl tert-butyl phenylphosphine oxide 4a



Tert-butylethylphenylphosphine oxide (**7a**) was synthesised by the above method, but with the addition of *tert*-butylmagnesium chloride first. The product was purified by column chromatography 5 : 4 : 1 cyclohexane : ethyl acetate : ethanol. 0.87 g, 4.2 mmol, 57% yield from PPhCl_2 (1.30 g, 7.3 mmol).

^{31}P NMR (202 MHz, CDCl_3) δ 51.65.

^1H NMR (500 MHz, CDCl_3) δ 7.70 (ddd, $J = 9.8, 8.2, 1.5$ Hz, 2H), 7.55 – 7.45 (m, 3H), 2.11 – 2.00 (m, 2H), 1.13 (d, $J = 14.3$ Hz, 9H), 1.15-1.08 (m, 3H)

Tert-butylethylphenylphosphine oxide (**7a**) (0.54 g, 2.6 mmol) was dried by azeotrope with 3 mL dry toluene three times and dissolved in dry diethylether (5 mL) and cooled to 0 $^{\circ}\text{C}$. Freshly prepared LDA (1M in diethylether, 2.6 mL, 2.6 mmol) was added dropwise and stirred for 2 h. Ethyl bromide (0.2 mL, 2.7 mmol) was added and stirred overnight. Water (5 mL) was added and the diethylether was removed under reduced pressure. The product was extracted with DCM (3 x 25 mL) and the combined extracts were washed with brine (25 mL) and dried over magnesium sulfate. Crude yield: 0.68 g, 110%. The product was purified by column chromatography ethyl acetate : cyclohexane : ethanol. (6:3:1) 0.44 g 1.85 mmol, 71% yield

HRMS (m/z): $[\text{M} + \text{H}]^+ = 238.1492$ (Calculated for $\text{C}_{14}\text{H}_{24}\text{PO}$ 238.1487), 2.1 PPM; IR (NaCl) $\nu = 1146, 1162$

NMR signals attributed to diastereomer A

^{31}P NMR, (243 Hz, 30 $^{\circ}\text{C}$, CDCl_3) δ 52.75

^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 7.72 (m, 2H, H-3), 7.49 (m, 1H, H-4), 7.46 (m, 2H, H-2), 2.09 (m, 1H, H-5), 1.46 (m, 1H, H-6), 1.39-1.42 (dd, $J = 7.06, 14.9$, 3H, H-8), 1.36 (m, 1H, H-6), 1.16 (d, 9H, H-10), 0.88 (t, $J = 7.4$ Hz, 3H, H-7),

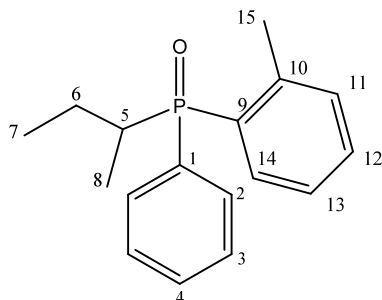
^{13}C NMR (126 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 131.4 (C-3), 131.0 (C-4), 128.1 (C-2), 31.8 (C-5), 31.3 (C-9), 25.9 (C-10), 23.6 (C-6), 12.4 (C-8), 12.0 (C-7)

NMR signals attributed to diastereomer B

³¹P NMR, (243 MHz, 30 °C, CDCl₃) δ 52.15

¹H NMR (500 MHz, 30 °C, CDCl₃) δ 7.72 (m, 2H, H-3), 7.49 (m, 1H, H-4), 7.46 (m, 2H, H-2), 2.17 (m, 1H, H-6), 2.06 (m, 1H, H-6), 1.65 (m, 1H, H-6), 1.18 (d, 9H, H-10), 1.06 (t, *J* = 7.3 Hz, 3H, H-8), 1.01-1.06 (dd, *J* = 7.3, 15.7, 3H, H-8).

¹³C NMR (126 MHz, 30 °C, CDCl₃) δ 131.5 (C-3), 130.9 (C-4), 128.1 (C-2), 33.5 (C-9), 31.7 (C-5), 26.0 (C-10), 22.8 (C-6), 12.4 (C-8), 12.0 (C-7)

Sec-butylphenyl(ortho-tolyl)phosphine oxide 5a

76% yield from 1.30 g (7.3 mmol) PPhCl₂

HRMS (m/z): [M+H]⁺ = 273.1407 (Calculated for C₂₇H₂₂PO 273.1330), -0.5 PPM; IR (NaCl) ν = 1179.5

NMR signals attributed to diastereomer A

³¹P NMR (243 MHz, 30 °C, CDCl₃) δ 39.424

¹H NMR (500 MHz, 30 °C, CDCl₃) δ 2.38 (s, 3H, H-15) 2.16 (m, 1H, H-5), 1.65 (m, 1H, H-6), 1.42 (m, 1H, H-6), 1.31 (dd, *J* = 7.1, 16.9, 9H, H-8), 0.98 (t, *J* = 7.4 Hz, 3H, H-7),

¹³C NMR (126 MHz, 30 °C, CDCl₃) δ 30.8 (C-5), 22.5 (C-6), 21.4 (C-15), 12.2 (C-7), 11.9 (C-8)

NMR signals attributed to diastereomer B

³¹P NMR (243 MHz, 30 °C, CDCl₃) δ 39.418

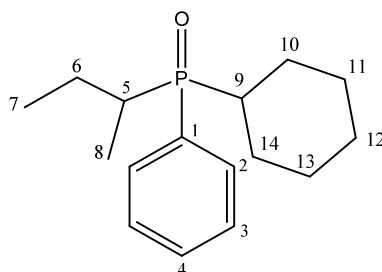
¹H NMR (500 MHz, 30 °C, CDCl₃) δ 2.38 (s, 3H, H-15), 2.16 (m, 1H, H-5), 1.98 (m, 1H, H-6), 1.49 (m, 1H, H-6), 1.12 (dd, *J* = 7.1, 16.9 Hz, 3H, H-8), 1.06 (t, *J* = 7.4 Hz, 3H, H-7),

¹³C NMR (126 MHz, 30 °C, CDCl₃) δ 30.8 (C-5), 22.6 (C-6), 21.4 (C-15), 12.3 (C-7), 12.1 (C-8),

NMR signals not yet assigned to A or B

¹H NMR (500 MHz, CDCl₃) δ 7.17-7.74 (m, 9H, H-2, H-3, H-4, H-11, H-12, H-13, H-14)

¹³C NMR (126 MHz, CDCl₃) δ 132.3, 132.2, 131.5, 131.5, 131.3, 131.2, 131.1, 131.1, 128.4, 128.3, 125.3, 125.2,

Sec-butyl cyclo-hexylphenylphosphine oxide 6a

68% yield from 1.30 g (7.3 mmol) PPhCl₂

HRMS (m/z): [M + H]⁺ = 265.1731 (Calculated for C₁₆H₂₆PO 265.1721), 3.7 PPM; IR (NaCl) ν = 1166.2

NMR signals attributed to diastereomer A

³¹P NMR (243 MHz, 30 °C, CDCl₃) δ 47.65

^1H NMR (500 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 7.61 (m, 2H, H-2), 7.45 (m, 1H, H-4), 7.40 (m, 2H, H-3), 2.02 (m, 1H, H-9), 1.98 (m, 1H, H-14), 1.94 (m, 1H, H-5), 1.76 (m, 1H, H-11), 1.68 (m, 1H, H-13), 1.55 (m, 2H, H-12), 1.52 (m, 1H, H-6), 1.25 (m, 1H, H-11), 1.20 (m, 1H, H-10), 1.18 (m, 1H, H-13), 1.18 (m, 1H, H-6), 1.15 (m, 1H, H-14), 1.14 (m, 1H, H-8), 0.86 (m, 3H, H-7)
 ^{13}C NMR (126 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 131.36 (d, J = 8 Hz, C-2), 131.16 (d, J = 3 Hz, C-4), 130.06 (d, J = 85 Hz, C-1), 128.15 (d, J = 11 Hz, C-3), 35.60 (d, J = 69 Hz, C-9), 31.60 (d, J = 66 Hz, C-5), 26.4 (d, J = 13 Hz, C-13), 26.2 (d, J = 13 Hz, C-11), 25.8 (C-10), 25.61 (d, J = 2 Hz, C-12), 24.56 (d, J = 3 Hz, C-14), 22.6 (C-6), 12.22 (d, J = 13 Hz, C-7), 10.95 (d, J = 3 Hz, C-8)

NMR signals attributed to diastereomer B

^{31}P NMR (243 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 47.52

^1H NMR (500 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 7.61 (m, 2H, H-2), 7.45 (m, 1H, H-4), 7.40 (m, 2H, H-3), 1.99 (m, 1H, H-9), 1.98 (m, 1H, H-14), 1.97 (m, 3H, H-8), 1.89 (m, 1H, H-6), 1.76 (m, 1H, H-11), 1.68 (m, 1H, H-13), 1.60 (m, 2H, H-12), 1.26 (m, 1H, H-14), 1.25 (m, 1H, H-11), 1.20 (m, 1H, H-10), 1.18 (m, 1H, H-13), 1.12 (m, 1H, H-6), 1.09 (m, 1H, H-10), 0.97 (m, 3H, H-8), 0.93 (m, 3H, H-7)

^{13}C NMR (126 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 131.39 (d, J = 8 Hz, C-3), 131.34 (d, J = 3 Hz, C-4), 129.94 (d, J = 85 Hz, C-1), 128.15 (d, J = 11 Hz, C-3), 35.15 (d, J = 67 Hz, C-9), 31.58 (d, J = 66 Hz, C-5), 26.4 (d, J = 13 Hz, C-13), 26.2 (d, J = 13 Hz, C-11), 25.8 (C-10), 25.35 (d, J = 2 Hz, C-12), 24.55 (d, J = 3 Hz, C-14), 21.5 (d, J = 2 Hz, C-6), 12.05 (d, J = 12 Hz, C-7), 12.04 (d, J = 2 Hz, C-8)

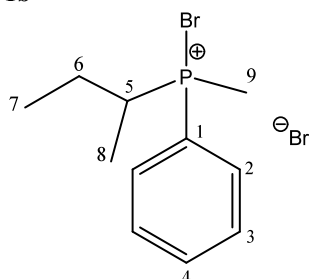
2. Synthesis and characterisation of halophosphonium halides 1b, 1c, 2b, 2c, 3b, 3c, 4b, 4c, 5b, 5c, 6b, 6c

Preparation of NMR samples

CDCl_3 was dried and stored over molecular sieves in a Schlenk tube. Oxalyl chloride and oxalyl bromide were stored over molecular sieves in Young's flasks. Phosphine oxides were stored in a vacuum dessicator over phosphorus pentoxide for at least one week prior to use.

Phosphine oxide (0.032 mmol, 1 eq) was transferred to a dry 5 mL pear shaped flask fitted with a nitrogen inlet and subsequently placed under vacuum for one hour, then refilled with nitrogen and re-evacuated three times. Oxalyl chloride or oxalyl bromide (0.064 mmol, 2 eq) was added neat via oven-dried glass microsyringe. CDCl_3 (0.65 mL) was added via 1mL syringe to give a 0.05M solution of halophosphonium salt.

1b

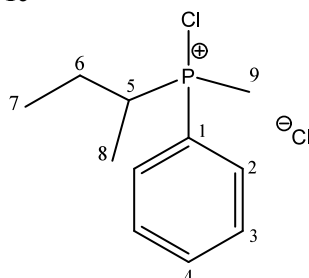


^1H NMR (400 MHz, 30 $^\circ\text{C}$, CDCl_3 , 30 $^\circ\text{C}$) δ 8.18 – 8.11 (m, 2H, H-2), 7.70 – 7.62 (m, 1H, H-4), 7.62 – 7.54 (m, 2H, H-3), 3.88 – 3.59 (m, 1H, H-5), 3.11 (d, J = 12.3 Hz, 3H, H-9), 1.87 – 1.64 (m, 1H, H-6), 1.40 – 1.25 (m, 1H, H-6), 1.18 (dd, J = 24.6, 6.8 Hz, 3H, H-8), 0.95 (t, J = 7.3 Hz, 3H, H-7).

^{13}C NMR (101 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 135.7 (d, J = 3.4 Hz, C-4), 132.5 (d, J = 12.1 Hz, C-2), 130.3 (d, J = 13.9 Hz, C-3), 118.6 (d, J = 75.4 Hz, C-1), 36.3 (d, J = 35.7 Hz, C-5), 22.7 (d, J = 2.4 Hz, C-6), 15.9 (d, J = 42.8 Hz, C-9), 12.1 (d, J = 3.0 Hz, C-8), 11.17 (d, J = 17.3 Hz, C-7).

^{31}P NMR (162 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 82.4

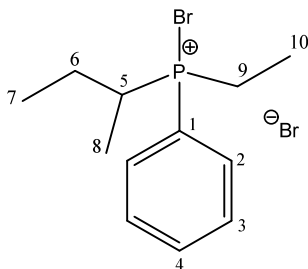
1c



^1H NMR (400 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 8.40 – 8.24 (m, 2H, H-2), 7.92 – 7.83 (m, 1H, H-4), 7.83 – 7.71 (m, 2H, H-3), 4.03 – 3.84 (m, 1H, H-5), 3.17 (dd, J = 12.3, 1.0 Hz, 3H, H-9), 2.05 – 1.88 (m, 1H, H-6), 1.61 – 1.48 (m, 1H, H-6), 1.41 (dd, J = 23.9, 6.9 Hz, 3H, H-8), 1.13 (t, J = 7.3 Hz, 3H, H-7).

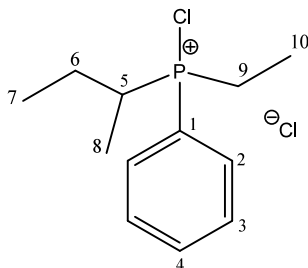
^{13}C NMR (101 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 135.9 (d, $J = 3.4$ Hz, C-4), 132.0 (d, $J = 12.4$ Hz, C-2), 130.4 (d, $J = 14.1$ Hz, C-3), 118.7 (d, $J = 81.7$ Hz, C-1), 35.9 (d, $J = 40.4$ Hz, C-5), 22.1 (d, $J = 2.7$ Hz, C-6), 15.0 (d, $J = 46.9$ Hz, C-9), 11.3 (d, $J = 3.3$ Hz, C-8), 11.2 (d, $J = 16.9$ Hz, C-7).
 ^{31}P NMR (202 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 95.6

2b



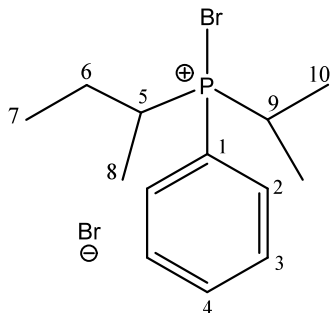
^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 8.41 – 8.31 (m, 2H), 7.86 – 7.79 (m, 1H), 7.80 – 7.71 (m, 2H), 4.30 – 4.19 (m, 1H, H-5), 4.02– 3.40 (bs, 2H, H-9), 2.09–1.72 (m, 1H, H-6) 1.53 – 1.42 (m, 1H, H-6), 1.41 – 1.27 (m, 3H, H-8, C-8), 1.21 (dt, $J = 23.5$, 7.3 Hz, 4H, H-10), 1.13 (t, $J = 7.8$ Hz, 3H, H-7).
 ^{13}C NMR (126 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 135.6 (d, $J = 3.4$ Hz, C-4), 133.0 (d, $J = 11.6$ Hz, C-2), 130.5 (d, $J = 13.6$ Hz, C-3), 116.3 (d, $J = 71.9$ Hz, C-1), 36.2 (d, $J = 32.3$ Hz, C-5), 23.1 (d, $J = 3.1$ Hz, C-6), 22.6 (d, $J = 36.0$ Hz, C-9), 12.5 (s, C-8), 11.1 (d, $J = 16.6$, Hz, C-7), 6.6 (d, $J = 7.4$ Hz, C-10).
 ^{31}P NMR (121 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 97.2

2c



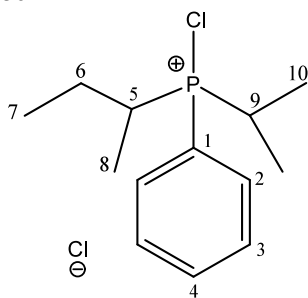
^1H NMR (400 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 8.23 – 8.13 (m, 2H, H-2), 7.85 – 7.78 (m, 1H, H-4), 7.75 (dd, $J = 7.7$, 4.3 Hz, 2H, H-3), 3.80 (m, 1H, H-5), 3.45 (m, 2H, H-9), 1.95 – 1.79 (m, 1H, H-6), 1.53 – 1.39 (m, 1H, H-6), 1.33 (dd, $J = 23.0$, 6.6 Hz, 3H, H-8), 1.20 (dt, $J = 22.8$, 7.2 Hz, 3H, H-10), 1.05 (t, $J = 7.2$ Hz, 3H, H-7).
 ^{13}C NMR (101 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 135.9 (d, $J = 3.4$ Hz, C-4), 132.2 (d, $J = 11.8$ Hz, C-2), 130.6 (d, $J = 13.7$ Hz, C-3), 116.18 (d, $J = 78.1$ Hz, C-1), 35.68 (d, $J = 37.7$ Hz, C-5), 22.32 (d, $J = 3.2$ Hz, C-6), 21.23 (d, $J = 40.8$ Hz, C-9), 11.6 (d, $J = 3.8$ Hz, C-8), 11.2 (d, $J = 16.3$ Hz, C-7), 5.7 (d, $J = 7.3$ Hz, C-10).
 ^{31}P NMR (162 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 103.5

3b



Partially decoalesced

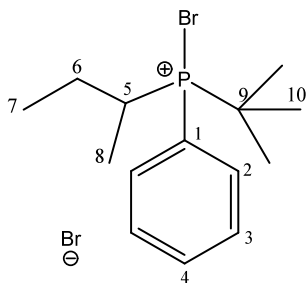
^1H NMR (400 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 8.19 (dd, $J = 13.2$, 7.5 Hz, 6H), 7.77 (ddd, $J = 15.0$, 7.2, 3.4 Hz, 4H), 4.19 (s, 2H, H-5), 3.80 (s, 2H, H-9), 2.10 (s, 1H, H-6), 1.82 (s, 1H, H-6), 1.51 – 1.20 (m, 20H, H-6, H-8, H-10), 1.15–1.01 (m, 6H, H-7)
 ^{13}C NMR (101 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 135.8 (d, $J = 3.4$ Hz, C-4), 133.3 (d, $J = 10.6$ Hz, C-2), 130.6 (d, $J = 13.0$ Hz, C-3), 115.3 (d, $J = 68.1$ Hz, C-1), 34.7 (d, $J = 29.9$ Hz, C-5), 29.0 (s, C-9), 23.7 (s, C-6), 23.3 (s, C-6), 16.9 (s, C-10), 13.0 (d, $J = 3.2$ Hz, C-8), 11.4 (d, $J = 17.0$ Hz, C-7).
 ^{31}P NMR (162 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 102.0, 101.6.

3c

^1H NMR (300 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 8.27 – 8.11 (m, 2H, H-2), 7.89 – 7.72 (m, 3H, H-3, H-4), 4.14 (hept, J = 6.8 Hz, 1H, H-9), 3.84 – 3.68 (m, 1H, H-5), 2.11 – 1.88 (m, 1H, H-6), 1.52 – 1.26 (m, 10H, H-6, H-8, H-10), 1.11 (t, J = 7.3 Hz, 3H, H-7).

^{13}C NMR (75 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 135.9 (d, J = 3.3 Hz, C-4), 132.6 (d, J = 10.9 Hz, C-2), 130.6 (d, J = 13.2 Hz, C-3), 115.3 (d, J = 74.3 Hz, C-1), 33.9 (d, J = 34.7 Hz, P-C), 28.2 (d, J = 35.8 Hz, P-C), 22.7 (s, C-6), 15.9 (bs, C-10), 12.1 (d, J = 3.2 Hz, C-8), 11.3 (d, J = 15.9 Hz, C-7).

^{31}P NMR (121 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 106.3

4b

Major diastereomer

^1H NMR (400 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 8.22 – 8.13 (m, 2H, H-2), 7.82 – 7.70 (m, 3H, H-3, H-4), 1.61- 1.51 (m, 1H, H-6) 1.60- 1.51 (m, 1H, H-6), 1.58 (dd, J = 21.8, 6.4 Hz, 3H, H-8), 1.46 (d, J = 20.2 Hz, 9H, H-10), 1.11 (t, J = 7.3 Hz, 3H, H-7).

^{13}C NMR (101 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 135.6 (d, J = 3.3 Hz, C-4), 133.5 (d, J = 9.9 Hz, C-2), 130.6 (d, J = 12.6 Hz, C-3), 116.2 (d, J = 66.5 Hz, C-1), 39.9 (d, J = 25.8 Hz, C-9), 32.8 (d, J = 24.3 Hz, C-5), 26.1 (d, J = 2.0 Hz, C-10), 25.4 (d, J = 4.1 Hz, C-6), 14.0 (d, J = 3.5 Hz, C-8), 10.9 (d, J = 15.1 Hz, C-7).

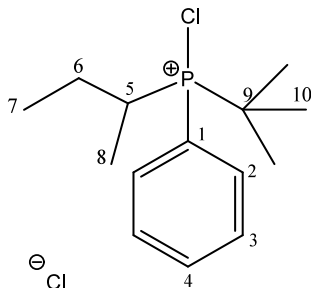
^{31}P NMR (162 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 106.7

Minor diastereomer

^1H NMR (400 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 8.24 – 8.13 (m, 1H), 7.81 – 7.71 (m, 2H), 2.28-2.14 (m, 1H, H-6) 1.73-1.60, m, 1H, H-6), 1.47 (d, J = 20.2 Hz, 9H), 1.27 (t, J = 7.3 Hz, 3H, H-7), 1.20 (dd, J = 22.5, 6.6 Hz, 3H, H-8).

^{13}C NMR (101 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 135.5 (d, J = 3.2 Hz, C-4), 133.5 (d, J = 9.9 Hz, C-2), 130.5 (d, J = 12.6 Hz, C-3), 116.3 (d, J = 66.1 Hz, C-1), 39.9 (d, J = 25.8 Hz, C-9), 33.1 (d, J = 23.6 Hz, C-5), 26.3 (d, J = 2.0 Hz, C-10), 24.1 (d, J = 3.1 Hz, C-6), 14.3 (d, J = 4.4 Hz, C-8), 11.2 (d, J = 15.4 Hz, C-7).

^{31}P NMR (162 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 106.6

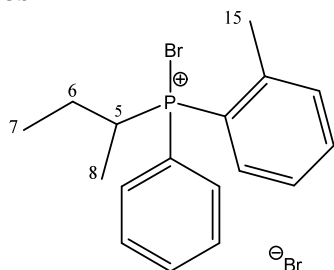
4c

Partially decoalesced

^1H NMR (300 MHz, 30 $^\circ\text{C}$, CDCl_3) δ 8.35 (dd, J = 12.7, 7.2 Hz, 4H), 7.90 – 7.58 (m, 6H), 5.47 – 5.19 (m, 2H, H-5), 2.33 – 2.11 (m, 1H, H-6), 1.77 – 1.62 (m, 1H, H-6), 1.64- 1.53 (m, 1H, H-6) 1.57 (dd, J = 21.3, 6.4 Hz, 3H, H-8), 1.46 (d, J = 19.8

Hz, 18H, H-10), 1.39 – 1.30 (m, 1H, H-6), 1.24 (t, $J = 7.7$ Hz, 3H, H-7), 1.21 – 1.11 (m, 3H, H-8), 1.07 (t, $J = 7.3$ Hz, 3H, H-7).
 ^{31}P NMR (121 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 110.08 (s).
 ^{13}C NMR (75 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 135.5 (d, $J = 3.2$ Hz, C-4), 133.0 (d, $J = 10.7$ Hz, C-2), 130.3 (d, $J = 13.0$ Hz, C-3), 116.4 (d, $J = 72.3$ Hz, C-1), 39.3 (bs, C-9), 32.2 (bs, C-5), 25.7 (bs, C-10), 24.1 (bs, C-6), 13.2 (bs, C-8), 10.7 (bs, C-7).
 bs = broad singlet

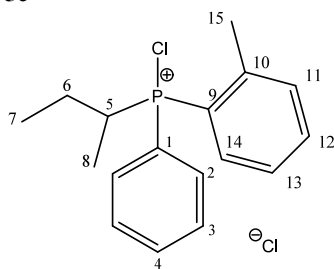
5b



Signals very broad due to exchange. No carbon signals.

^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 8.40 (dd, $J = 15.1$, 7.5 Hz, 1H), 8.33 – 8.24 (m, 0H), 7.90 (dd, $J = 14.9$, 7.8 Hz, 2H), 7.76 – 7.70 (m, 1H), 7.69 – 7.60 (m, 4H), 7.40 – 7.31 (m, 1H), 4.67 (ddt, $J = 12.5$, 9.0, 4.4 Hz, 1H, H-5), 2.20 (s, 3H, H-15), 2.13 – 1.59 (m, 3H, H-8), 1.55 – 1.25 (m, 2H, H-6), 1.25 – 1.10 (m, 3H, H-7).
 ^{31}P NMR (121 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 70.1

5c

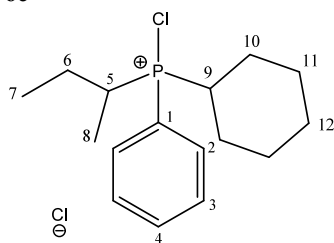


^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 8.62 (ddd, $J = 14.9$, 7.2, 2.0 Hz, 1H, ArH), 8.10 – 8.00 (m, 2H, PhH), 7.86 – 7.79 (m, 1H, ArH), 7.79 – 7.70 (m, 4H, 2 ArH, 2 PhH), 7.46 – 7.41 (m, 1H, ArH), 5.20 – 5.11 (m, 1H, H-5), 2.31 (s, 3H, H-15), 2.00 – 1.87 (m, 1H, H-6), 1.58 – 1.54 (m, 3H, H-6), 1.50 (dd, $J = 23.4$, 6.6 Hz, 3H, H-8), 1.25 (t, $J = 7.3$ Hz, 3H, H-7).
 ^{13}C NMR (126 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 136.9 (d, $J = 2.9$ Hz, Ar), 135.9 (d, $J = 3.4$ Hz, Ar), 135.6 (d, $J = 14.7$ Hz, 135.6), 133.9 (d, $J = 11.8$ Hz), 132.5 (d, $J = 12.6$ Hz, Ph), 130.6 (d, $J = 14.2$ Hz, Ph), 128.1 (d, $J = 14.2$ Hz, Ar), 119.5 (d, $J = 82.1$ Hz, Ar), 116.5 (d, $J = 78.8$ Hz, Ph), 33.2 (d, $J = 38.6$ Hz, C-5), 23.5 (d, $J = 2.7$ Hz, C-6), 22.1 (d, $J = 5.4$ Hz, C-15), 13.1 (d, $J = 3.5$ Hz, C-7), 11.2 (d, $J = 17.0$ Hz, C-8).
 ^{31}P NMR (121 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 83.3

6b was exchanging at such a rate that proton and carbon signals were obscured at 30 $^{\circ}\text{C}$.

^{31}P NMR (202 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 98.2

6c



^1H NMR (500 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 8.25 (dd, $J = 13.1$, 7.6 Hz, 2H, H-2), 7.88- 7.79 (m, 4H, H-3, H-4), 4.03- 3.98 (m, 1H, H-9), 3.98- 3.92 (m, 1H, H-5), 2.17- 2.06 (m, 1H, H-10) 2.05- 1.96 (m, 1H, H-6), 1.93- 1.85 (m, 1H, H-12), 1.83- 1.76 (m, 2H, H-11), 1.72- 1.62 (m, 1H, H-12), 1.46-1.37 (m, 1H, H-6), 1.45 (m, 3H, H-8), 1.41- 1.28 (m, 1H, H-10) 1.23- 1.12 (m, 2H, H-11), 1.15 (t, 3H, $J = 7.7$ Hz, H-7)
 ^{13}C NMR (126 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 135.7 (d, $J = 3.4$ Hz, C-4), 132.6 (d, $J = 11.1$ Hz, C-2), 130.5 (d, $J = 13.3$ Hz, C-3), 115.6 (d, $J = 73.9$ Hz, C-1), 36.8 (d, $J = 33.5$ Hz, C-5), 33.5 (d, $J = 33.8$ Hz, C-9), 31.0 , 25.69(d, $J = 3.6$ Hz, C-10), 25.1 (d, $J = 1.4$ Hz, C-12), 25.0 (d, $J = 1.5$ Hz, C-11), 22.9 (s, C-6), 12.1 (d, $J = 3.7$ Hz, C-8), 11.1 (d, $J = 15.8$ Hz, C-7).
 ^{31}P NMR (202 MHz, 30 $^{\circ}\text{C}$, CDCl_3) δ 103.4

3. Variable temperature NMR experiments

All experiments were run on a Varian 500. The temperature increments were decreased when decoalescence approached.

The appearance of rotamers in compound **4c** is expected in accordance with literature:

Hagele, G.; Kuckelhaus, W.; Tossing, G.; Seega, J.; Harris, R. K.; Creswell, C. J.; Jageland, P. T.

J. Chem. Soc., Dalton Trans., **1987**, 795-805

The spectra are arrayed in such a way that temperature increases from top to bottom. The temperatures given in degrees Celcius are those at which the spectra shown are run.

During the course of the VT-NMR experiments the lock was not maintained. Therefore random drift of chemical shift is apparent in the VT-NMR experiments and may not agree with the characterisation data given above, in which the spectrometer was locked to deuterium in CDCl₃.

Compound **1c** epimerised too rapidly to be measured by this method. The ³¹P NMR spectra of compound **5c** were not obtained

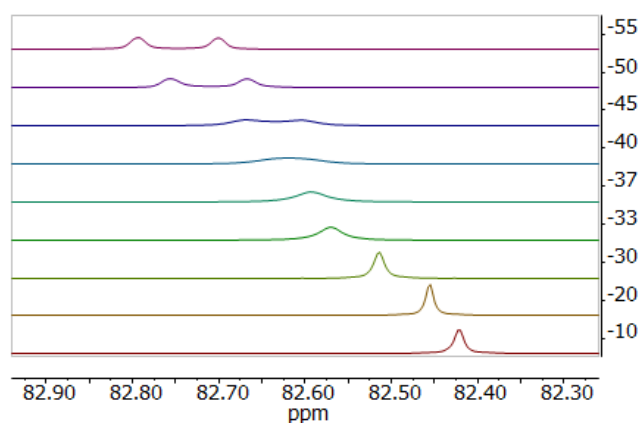


Figure 1: ³¹P VT-NMR spectra of **1b**

Tc = -40 °C, Final separation = 19 Hz

82.79 ppm, 82.80 ppm

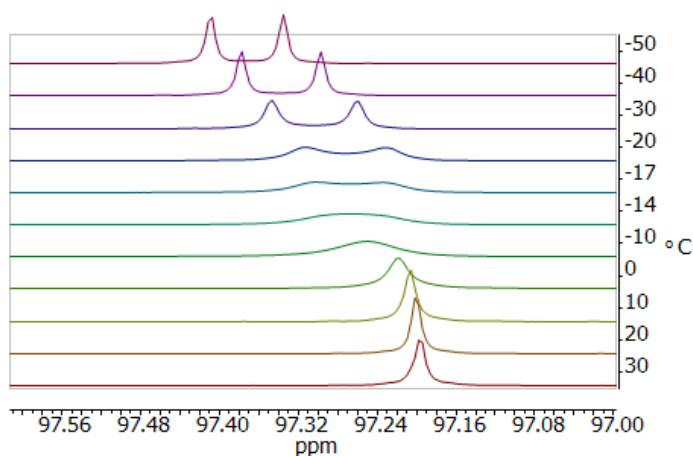


Figure 2: ³¹P VT-NMR spectra of **2b**

Tc = -14 °C, Final separation = 15 Hz

97.41 ppm, 97.31 ppm

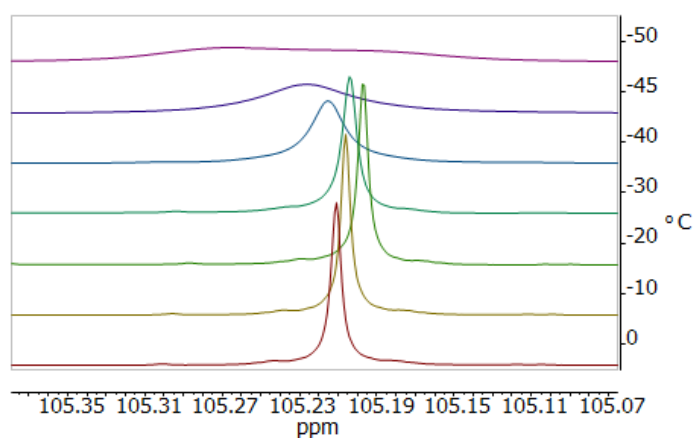


Figure 3: ^{31}P VT-NMR spectra of **2c**
 $T_c = -45\text{ }^{\circ}\text{C}$, Final separation = 27 Hz
 105.31 ppm, 105.17 ppm

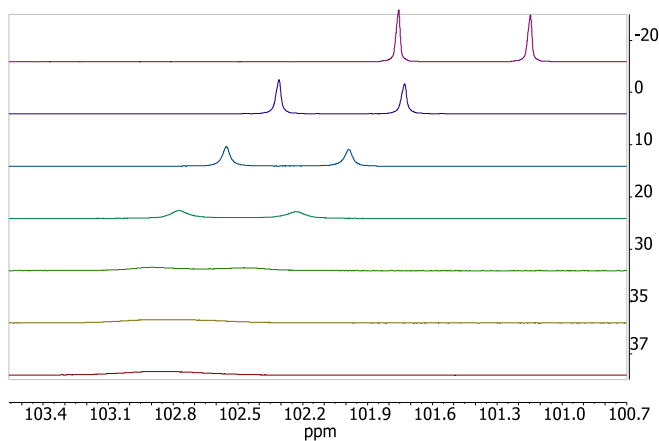


Figure 4: ^{31}P VT-NMR spectra of **3b**
 $T_c = 35\text{ }^{\circ}\text{C}$, Final separation = 122 Hz
 101.76 ppm, 101.15 ppm

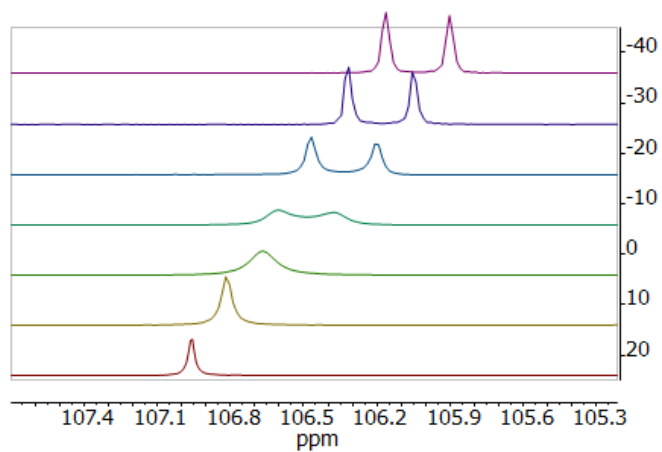


Figure 5: ^{31}P VT-NMR spectra of **3c**
 $T_c = 0\text{ }^{\circ}\text{C}$, Final separation = 52.6 Hz
 106.16 ppm and 105.90 ppm

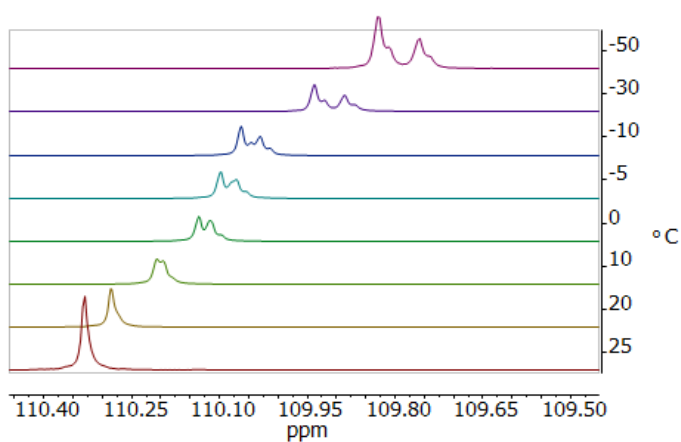


Figure 6: ^{31}P VT-NMR spectra of **4c**
 $T_c = 17\text{ }^\circ\text{C}$, Final separation = 14 Hz,
 109.83 ppm, 109.76 ppm

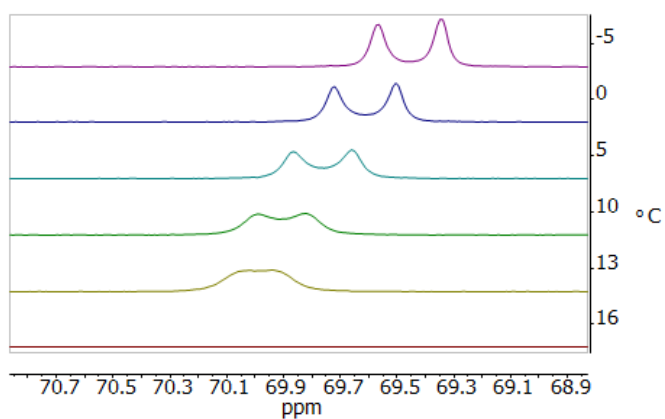


Figure 7: ^{31}P VT-NMR spectra of **5b**
 $T_c = 16\text{ }^\circ\text{C}$, Final separation = 45 Hz
 69.57 ppm 69.35 ppm

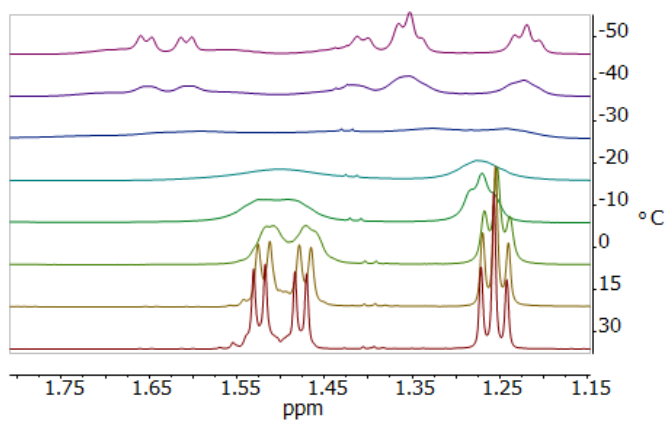


Figure 8: ^1H VT-NMR spectra of **5c** decoalescence of triplet at 1.26 ppm
 $T_c = -20\text{ }^\circ\text{C}$, Final separation = 67 Hz, 1.35 ppm, 1.22 ppm

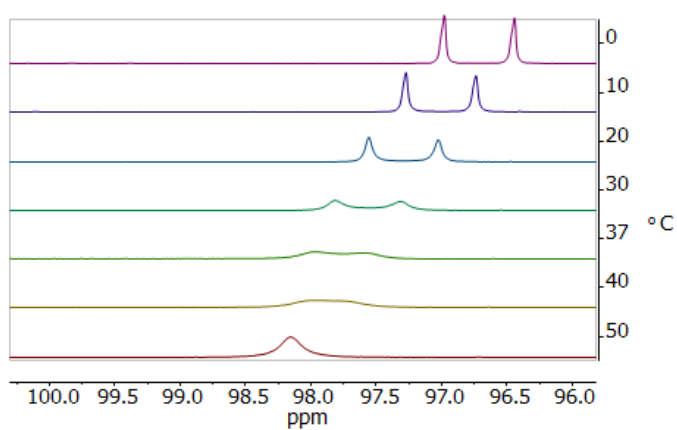


Figure 9: ^{31}P VT-NMR spectra of **6b**
 $T_c = 40\text{ }^\circ\text{C}$, Final separation = 109 Hz
 96.97 ppm, 96.44 ppm

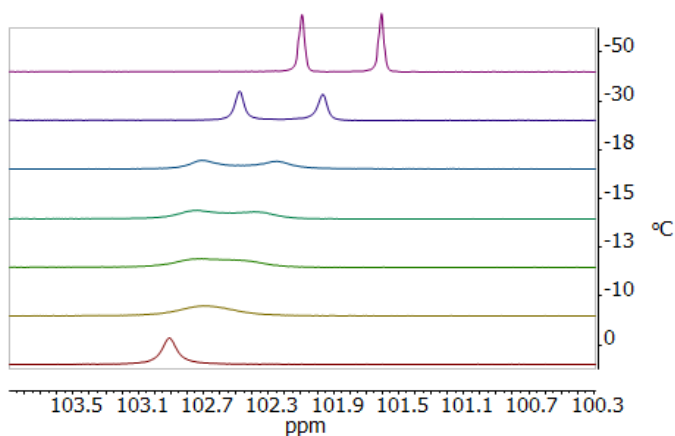


Figure 10: ^{31}P VT-NMR spectra of **6c**
 $T_c = -10\text{ }^\circ\text{C}$, Final separation = 99 Hz
 102.09ppm, 101.60 ppm

4. EXSY to determine epimerisation rate of 4b

EXSY performed at 50 °C. Green ovals denote volume integrations. Mixing times are in top left corner of each spectrum. The rate of epimerisation can be calculated from the volume integrals of the diagonal peaks versus the volume integrals of the cross peaks over time. Mixing times were from 100 ms to 1000 ms.

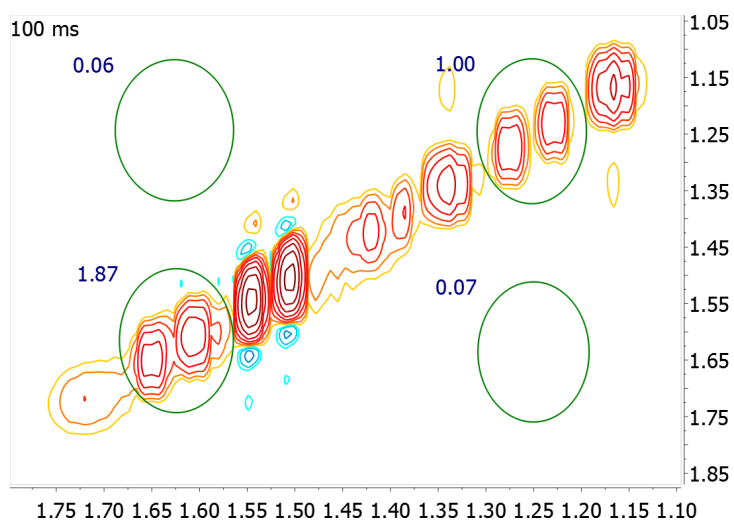


Figure 11: EXSY 4b, 0.05M, 50 °C, 100 ms

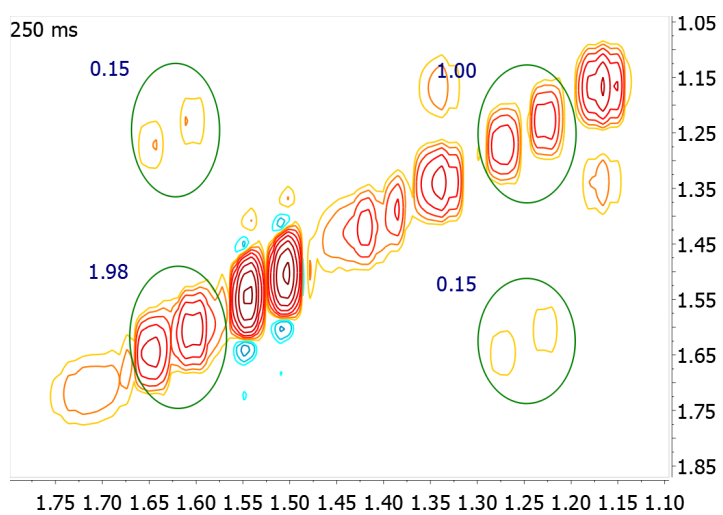


Figure 12: EXSY 4b, 0.05M, 50 °C, 250 ms

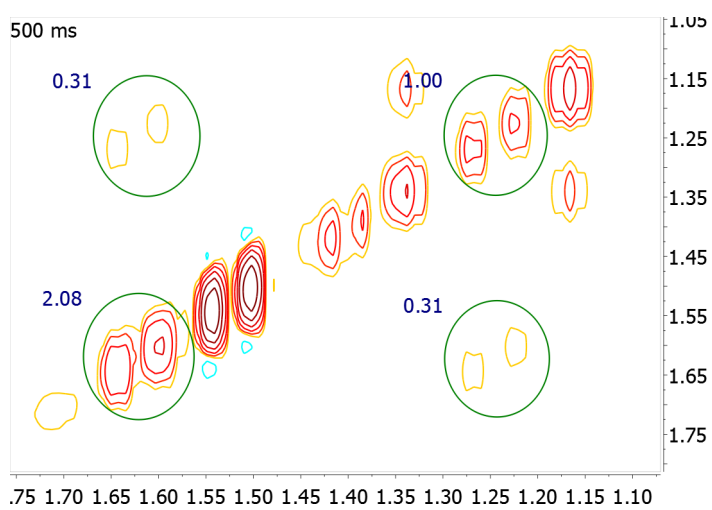


Figure 13: EXSY 4b, 0.05M, 50 °C,

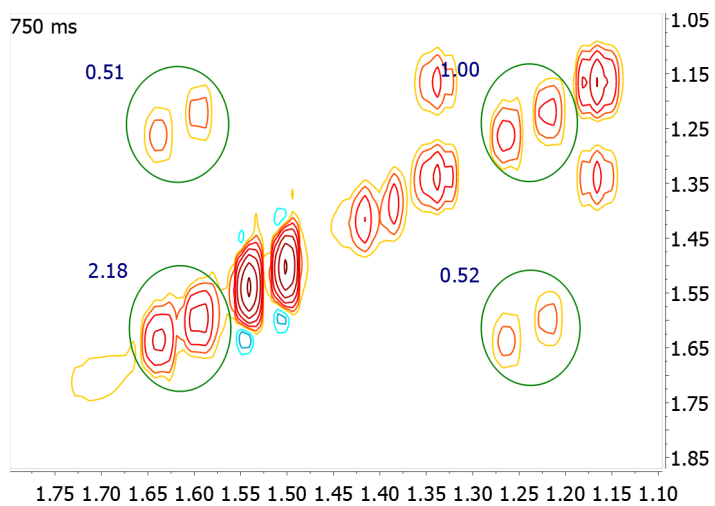


Figure 14: EXSY **4b**, 0.05M, 50 °C, 750 ms

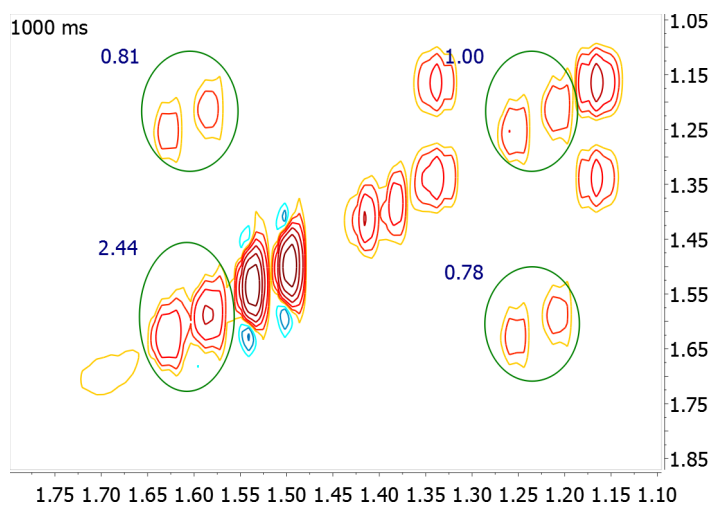


Figure 15: EXSY **4b**, 0.05M, 50 °C, 1000 ms

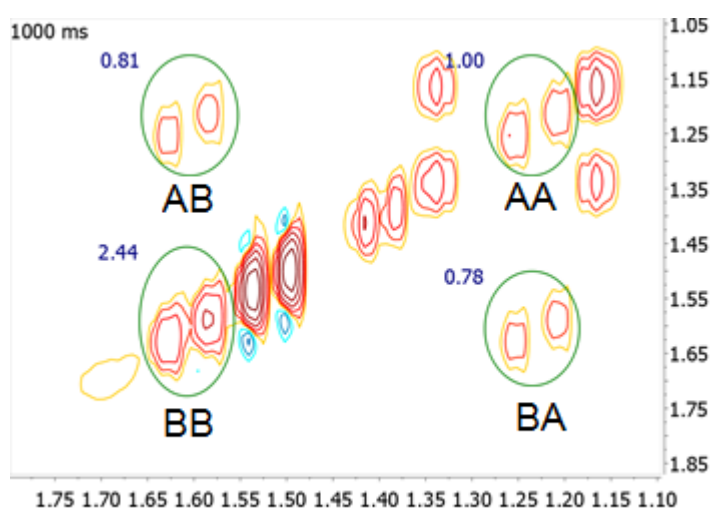


Figure 15b: EXSY **4b**, 0.05M, 50 °C, 1000 ms with peaks labelled

Table 1: EXSY data giving calculated activation energy of 1.92×10^4 cal/mol, 19.2 kcal/mol.

K_{eq} is the ratio of the two isomers, as determined by proton NMR. This is **not** the same as the ratio of the integrations of the diagonal peaks. r is the average integration of the cross peaks.

	biggest	smallest	cross	cross						Keq
Tm	BB	AA	AB	BA	r	(kc+kb) t	kb (s ⁻¹)	Barrier (kcal/mol)	T, C	
100	1.87	1	0.06	0.07	0.065	0.11	0.64	1.92E+04	50	0.73
250	1.98	1	0.15	0.15	0.15	0.26	0.59	1.93E+04	50	0.73
500	2.08	1	0.32	0.31	0.315	0.54	0.62	1.92E+04	50	0.73
750	2.18	1	0.51	0.52	0.515	0.89	0.68	1.92E+04	50	0.73
1000	2.44	1	0.81	0.78	0.795	1.45	0.84	1.90E+04	50	0.73

5. EXSY to determine order of epimerisation of 4c

In main paper

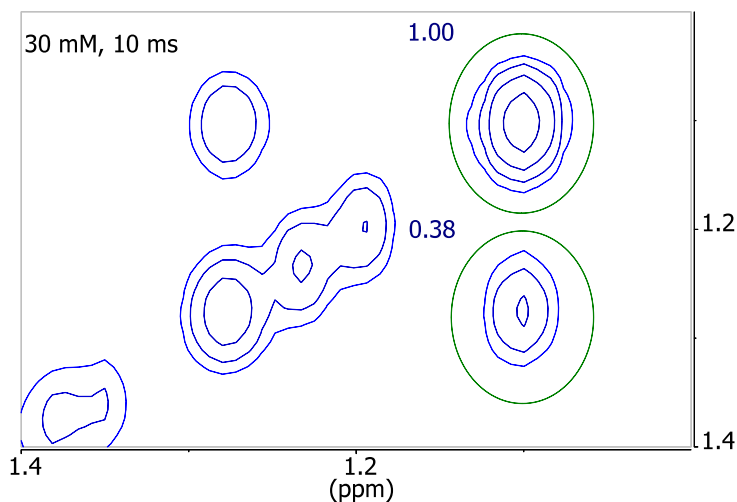


Figure 16: EXSY 4c, 0.03 M, 30 °C, 10 ms

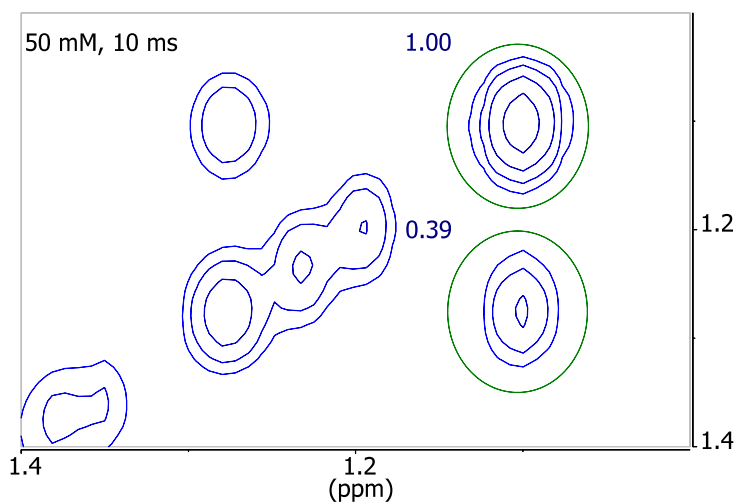


Figure 17: EXSY 4c 0.05 M, 30 °C, 10 ms

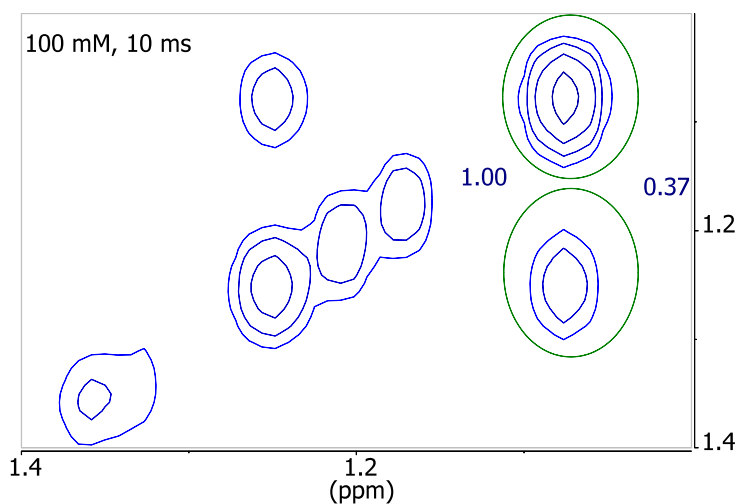


Figure 18: EXSY 4c, 0.1 M, 30 °C, 10 ms

EXSY spectra of **4c** show no change in rate constant with varying concentration (from 100 mM to 30 mM) and constant mixing time (10 ms). The rate of epimerisation can be calculated from the volume of the diagonal peaks and the volume of the cross peaks. The volumes integrated are denoted by the green ovals.

Ratio of diastereomers

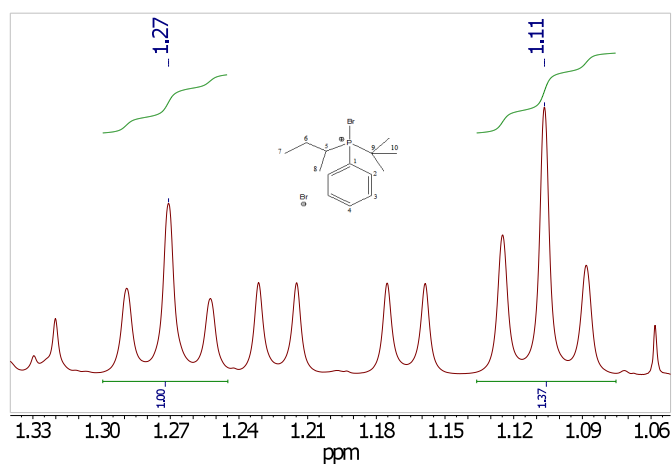


Figure 19: proton spectrum of **4b** at 303 K showing ratio of diastereomers 1: 1.37, the inverse of which, 0.73, is used in the EXSY calculations. Triplets at 1.11 and 1.27 ppm correspond to H-7. The ratio 1:1.37 at 303 K found in **4b** indicates a difference in stability of 0.19 kcal mol⁻¹ between the two diastereomers.

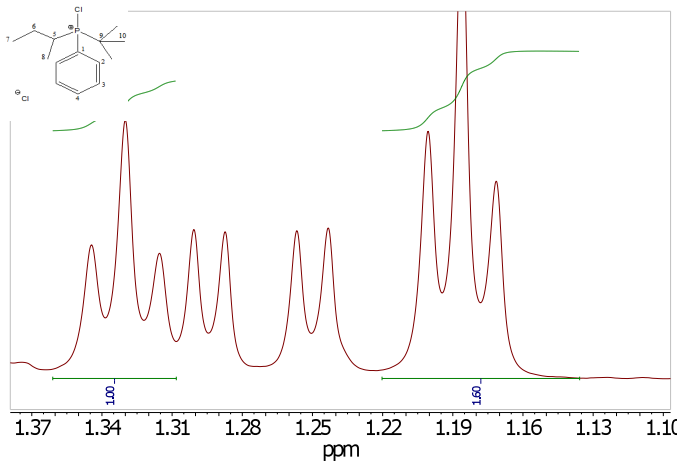


Figure 20: proton spectrum of 4c at 223 K showing ratio of diastereomers 1:1.6. The ratio of diastereomers of 4c at 223 K is 1:1.6, giving a difference in energy of 0.21 kcal/mol.

6. Reaction profiles

The model systems RMe_2PCl_2 , where $\text{R} = \text{Me}, \text{Et}, \text{tBu}$ were employed to examine the effect of sterics on the transition state. Indeed, the reaction profile for the trimethyl species had a pronounced double crested reaction profile denoting a true, stabilised, pentacoordinate intermediate; the ethyldimethyl species had a slight depression at the maximum, whereas the tert-butyldimethyl species had a single crest and the pentacoordinate form was merely a transition state. Interestingly, the bulkier the system the wider reaction energy profiles owing to their slightly elongated and weakened phosphorus-halogen bonds. Since the chlorine atoms are diastereotopic, both were separately constrained to give slightly different reaction profiles.

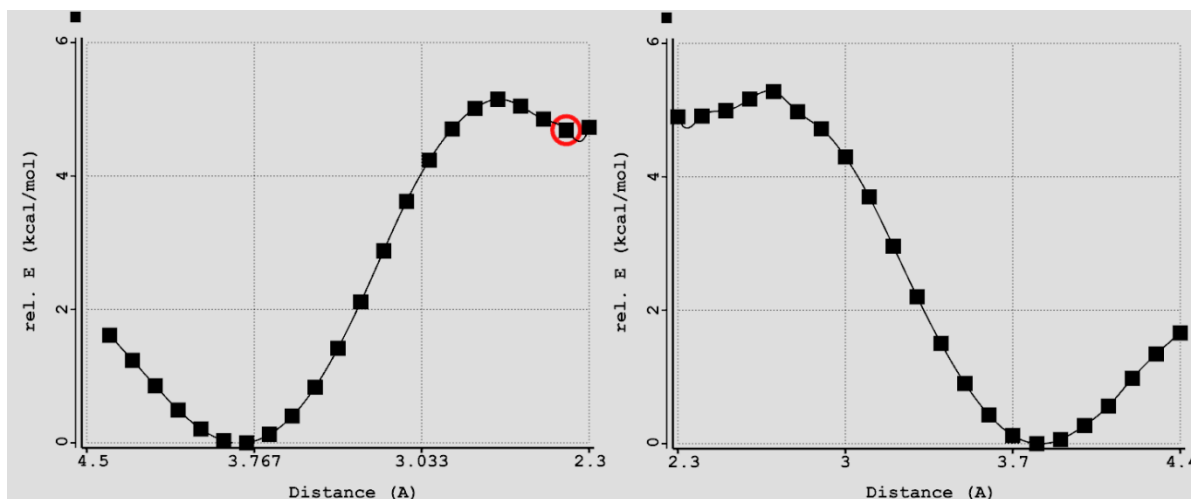


Figure 21 a: $\text{EtMe}_2\text{PCl}_2$ reaction profiles showing both possible reaction trajectories giving a barrier to the same local minimum where the P-Cl bonds are between 2.3 Å and 2.4 Å

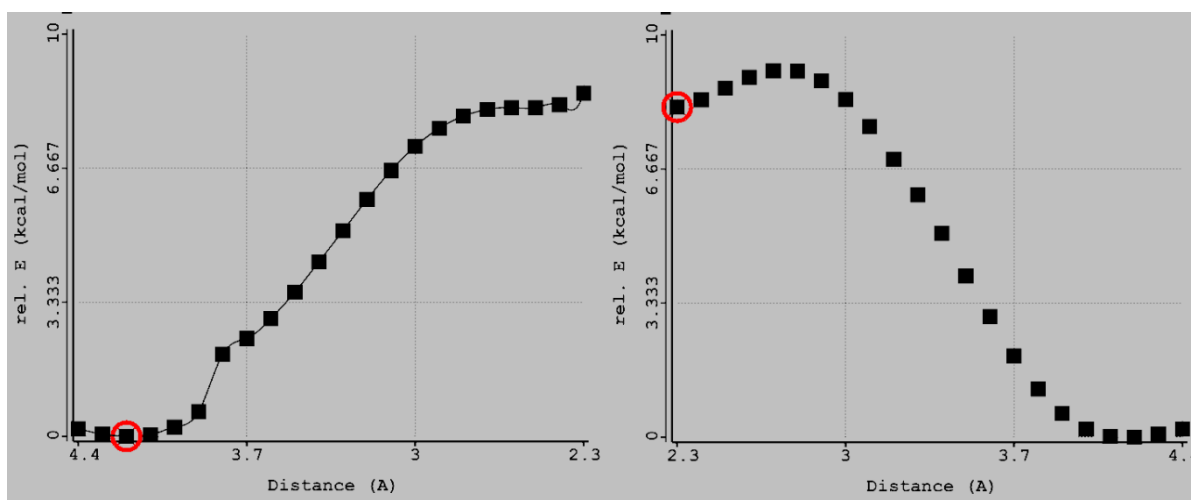


Figure 21 b: $\text{tBuMe}_2\text{PCl}_2$ reaction profiles plotting P-Cl distance showing a single maximum from one trajectory (shown right) and no local maximum from the other (shown left: the apparent maximum is not local. As the distance decreases the energy continues to increase). This combines to give a single-crested reaction profile, denoting a transition state.

7. Eyring and lineshape analysis of 3c

Table 2. Spinworks lineshape analysis results k given final separation of peaks and T at which they match experimentally obtained spectra.

k	T	k/T	ln(k/T)	1/T
1400	303	4.62	1.53	0.0033
660	293	2.25	0.81	0.003413
420	283	1.48	0.39	0.003534
190	273	0.70	-0.36	0.003663
52	263	0.20	-1.62	0.003802
15	253	0.06	-2.83	0.003953

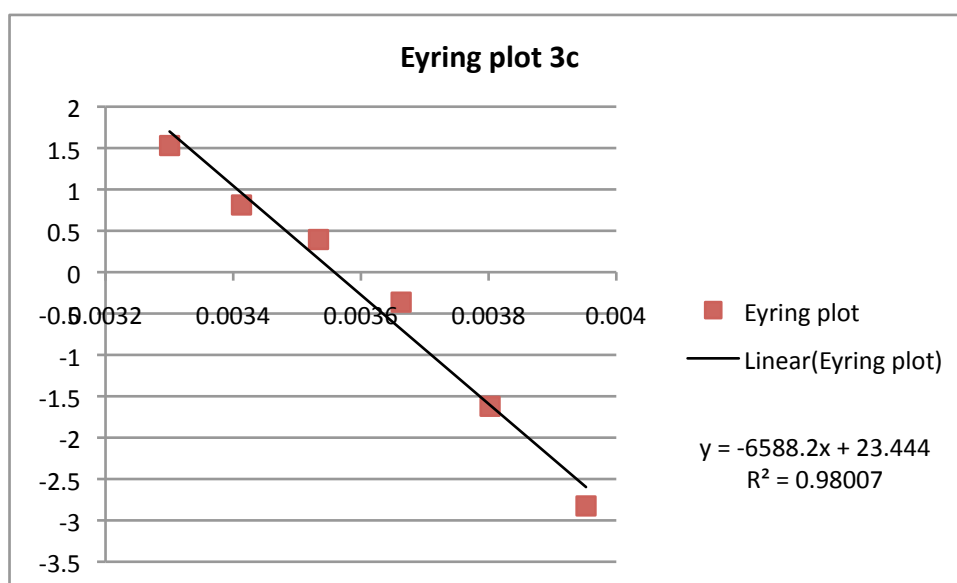


Figure 22. Eyring plot for 3c. Rates from Spinworks lineshape analysis.

Slope = -6588 ± 470

$6588.2 \times 1.987 \text{ cal.mol}^{-1}.\text{K}^{-1} = 13084.2 \text{ cal/mol} \pm 933 = \Delta H^\ddagger$

Intercept = 23.434 ± 1.7

$\Delta S^\ddagger = -0.65 \pm 3.4 \text{ cal.mol}^{-1}.\text{K}^{-1}$

The larger slope, the larger the intercept. So the largest value for entropy is subtracted from largest value for enthalpy (Highest) and the lowest value for entropy is subtracted from the smallest value for enthalpy (Lowest).

Highest ΔG at 273 K = $13084 + 933 - (273)(2.75) = 13266 = 13.3 \text{ kcal/mol}$

No error ΔG at 273 K = $13084 - (273)(-0.65) = 13261 = 13.3 \text{ kcal/mol}$

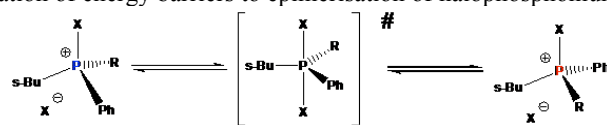
Lowest ΔG at 273 K = $13084 - 933 - (273)(-4.05) = 13256 = 13.3 \text{ kcal/mol}$

ΔG at 273 K = $13.3 \text{ kcal/mol} \pm 0.05 \text{ kcal/mol}$

(This can be compared with VT-NMR decoalescence which gives $13.2 \pm 0.1 \text{ kcal/mol}$. The larger error for the VT-NMR measurement results from imprecision in the T_c varying from 268 to 273 K)

8. Comparison of computational and experimental barriers

Table 3. Computational estimation of energy barriers to epimerisation of halophosphonium salts



Parent system	Exp ΔG^\ddagger , kcal mol ⁻¹		Calculated ^a ΔH^\ddagger , kcal mol ⁻¹	
	X = Cl	X = Br	X = Cl	X = Br
1	<9	11.7	7.1	9.2
2	11.3	13.2	7.75	10.7
3	13.1	14.6	8.9	12.3
4	15.1	19.2	13.5	18.4
5	11.7	14.1	8.75	11.6
6	12.5	14.9	9.5	12.4

^a a relative energy of pentacoordinate intermediate referenced to ion pair

9. DFT Calculated Total Energies

Table 4. Data supporting figure 9b in main text

Species	Medium	E, Ha	Geometry at P
Me ₃ PCl ₂	Vacuum	-1381.528648	trigonal bipyramid
Me ₃ PBr ₂	Vacuum	-5608.902157	trigonal bipyramid
Me ₃ PCl ₂	DCM	-1381.538761	trigonal bipyramid
Me ₃ PBr ₂	DCM	-5608.916699	trigonal bipyramid
Me ₃ PCl ₂	Vacuum	-1381.502481	Ion pair
Me ₃ PBr ₂	Vacuum	-5608.881054	Ion pair
Me ₃ PCl ₂	DCM	-1381.547707	Ion pair
Me ₃ PBr ₂	DCM	-5608.929662	Ion pair

Table 5. Data supporting figure 10a in main text

Species	Medium	E, Ha	d(P-Cl), Å
Me ₃ PCl ₂	vacuum	-1381.50313	3.9
		-1381.50444	3.85
		-1381.50566	3.8
		-1381.50675	3.75
		-1381.50773	3.7
		-1381.50859	3.65
		-1381.50934	3.6
		-1381.50999	3.55
		-1381.51057	3.5
		-1381.5111	3.45
		-1381.5116	3.4
		-1381.51207	3.35
		-1381.51255	3.3
		-1381.51303	3.25
		-1381.51354	3.2
		-1381.51411	3.15
		-1381.51474	3.1

		-1381.51546	3.05
		-1381.51627	3
		-1381.51716	2.95
		-1381.51812	2.9
		-1381.51912	2.85
		-1381.52016	2.8
		-1381.52122	2.75
		-1381.52228	2.7
		-1381.52337	2.65
		-1381.52443	2.6
		-1381.52594	2.55
		-1381.5269	2.5
		-1381.52774	2.45
		-1381.52841	2.4
		-1381.52884	2.35

Table 6. Data supporting figure 10b in main text

Species	Medium	E, Ha	d _(PCI) , Å
Me ₃ PCl ₂	toluene	-1381.53	3.9
		-1381.53	3.85
		-1381.53	3.8
		-1381.53	3.75
		-1381.53	3.7
		-1381.53	3.65
		-1381.53	3.6
		-1381.53	3.55
		-1381.53	3.5
		-1381.53	3.45
		-1381.53	3.4
		-1381.53	3.35
		-1381.53	3.3
		-1381.53	3.25
		-1381.53	3.2
		-1381.53	3.15
		-1381.53	3.1
		-1381.53	3.05
		-1381.53	3
		-1381.53	2.95
		-1381.53	2.9
		-1381.53	2.85
		-1381.53	2.8
		-1381.53	2.75
		-1381.53	2.7
		-1381.53	2.65
		-1381.53	2.6
		-1381.53	2.55
		-1381.53	2.5
		-1381.54	2.45
		-1381.54	2.4
		-1381.54	2.35
		-1381.54	2.3

Table 7. Data supporting figure 10c in main text

Species	Medium	E, Ha	d _(PCI) , Å
Me ₃ PCl ₂	DCM	-1381.55	3.9
		-1381.55	3.85
		-1381.55	3.8
		-1381.55	3.75
		-1381.55	3.7
		-1381.55	3.65
		-1381.55	3.6
		-1381.55	3.55

		-1381.55	3.5
		-1381.55	3.45
		-1381.55	3.4
		-1381.54	3.35
		-1381.54	3.3
		-1381.54	3.25
		-1381.54	3.2
		-1381.54	3.15
		-1381.54	3.1
		-1381.54	3.05
		-1381.54	3
		-1381.54	2.95
		-1381.54	2.9
		-1381.54	2.85
		-1381.54	2.8
		-1381.54	2.75
		-1381.54	2.7
		-1381.54	2.65
		-1381.54	2.6
		-1381.54	2.55
		-1381.54	2.5
		-1381.54	2.45
		-1381.54	2.4
		-1381.54	2.35
		-1381.54	2.3

Table 8. Data supporting figure 10d in main text

Species	Medium	<i>E</i> , Ha	<i>d</i> (PCl), Å
Me ₃ PCl ₂	chloroform	-1381.54	3.9
		-1381.54	3.85
		-1381.54	3.8
		-1381.54	3.75
		-1381.54	3.7
		-1381.54	3.65
		-1381.54	3.6
		-1381.54	3.55
		-1381.54	3.5
		-1381.54	3.45
		-1381.54	3.4
		-1381.54	3.35
		-1381.54	3.3
		-1381.54	3.25
		-1381.54	3.2
		-1381.54	3.15
		-1381.54	3.1
		-1381.54	3.05
		-1381.54	3
		-1381.54	2.95
		-1381.54	2.9
		-1381.54	2.85
		-1381.54	2.8
		-1381.54	2.75
		-1381.54	2.7
		-1381.54	2.65
		-1381.54	2.6
		-1381.54	2.55
		-1381.54	2.5
		-1381.54	2.45
		-1381.54	2.4
		-1381.54	2.35
		-1381.54	2.3

Table 9 Data supporting **figure 13** in main text. (configuration of *s*-Bu is *S* in all cases)

Species	Medium	<i>E</i> , Ha	<i>E</i> _(rel) , kcal/mol	Geometry and configuration at P
1b	DCM	-5918.58532	9.20	trigonal bipyramid
1b	DCM	-5918.59999		<i>R_P</i> ion pair
5b	DCM	-6149.62454	11.6	trigonal bipyramid
5b	DCM	-6149.64303		<i>R_P</i> ion pair
2b	DCM	-5957.89661	10.7	trigonal bipyramid
2b	DCM	-5957.91360		<i>R_P</i> ion pair
3b	DCM	-5997.20385	12.3	trigonal bipyramid
3b	DCM	-5997.22343		<i>R_P</i> ion pair
4b	DCM	-6036.50129	18.4	trigonal bipyramid
4b	DCM	-6036.53062		<i>R_P</i> ion pair
6b	DCM	-6113.94363	12.4	trigonal bipyramid
6b	DCM	-6113.96342		<i>R_P</i> ion pair
1c	DCM	-1691.20842	7.1	trigonal bipyramid
1c	DCM	-1691.21971		<i>R_P</i> ion pair
5c	DCM	-1922.24970	8.75	trigonal bipyramid
5c	DCM	-1922.26365		<i>R_P</i> ion pair
2c	DCM	-1730.52072	7.75	trigonal bipyramid
2c	DCM	-1730.53308		<i>R_P</i> ion pair
3c	DCM	-1769.82798	8.9	trigonal bipyramid
3c	DCM	-1769.8422		<i>R_P</i> ion pair
4c	DCM	-1809.12846	13.5	trigonal bipyramid
4c	DCM	-1809.1497		<i>R_P</i> ion pair
6c	DCM	-1886.56742	9.5	trigonal bipyramid
6c	DCM	-1886.58253		<i>R_P</i> ion pair

10.

Table 10 Data supporting Figure 12 in main text. $d_{(P-Cl)}$ in Å; E in kcal/mol

$d_1 \backslash d_2$	2	2.05	2.1	2.15	2.2	2.25	2.3	2.35	2.4	2.45	
2	-866898.11	-866903.25	-866907.38	-866910.72	-866913.42	-866916.06	-866917.9	-866919.38	-866920.6	-866921.6	
2.05	-866903.3	-866908.22	-866912.13	-866915.23	-866917.71	-866920.01	-866921.6	-866922.91	-866923.92	-866924.7	
2.1	-866907.49	-866912.18	-866915.85	-866918.74	-866920.99	-866922.97	-866924.4	-866925.45	-866926.26	-866926.9	
2.15	-866910.87	-866915.33	-866918.79	-866921.44	-866923.48	-866925.15	-866926.4	-866927.22	-866927.84	-866928.3	
2.2	-866913.62	-866917.85	-866921.09	-866923.53	-866925.35	-866926.73	-866927.7	-866928.4	-866928.82	-866929.1	
2.25	-866915.86	-866919.88	-866922.89	-866925.12	-866926.73	-866927.83	-866928.6	-866929.12	-866929.36	-866929.4	
2.3	-866917.7	-866921.5	-866924.3	-866926.32	-866927.72	-866928.58	-866929.2	-866929.48	-866929.54	-866929.4	
2.35	-866919.21	-866922.8	-866925.4	-866927.21	-866928.41	-866929.04	-866929.5	-866929.57	-866929.45	-866929.2	
2.4	-866920.46	-866923.85	-866926.24	-866927.86	-866928.86	-866929.35	-866929.5	-866929.46	-866929.17	-866928.7	
2.45	-866921.49	-866924.69	-866926.89	-866928.31	-866929.13	-866929.45	-866929.5	-866929.21	-866928.75	-866928.1	
2.5	-866922.37	-866925.36	-866927.38	-866928.62	-866929.28	-866929.43	-866929.3	-866928.85	-866928.23	-866927.5	
2.55	-866923.1	-866925.91	-866927.75	-866928.81	-866929.29	-866929.32	-866929	-866928.42	-866927.65	-866926.7	
2.6	-866923.73	-866926.36	-866928.02	-866928.93	-866929.24	-866929.15	-866928.7	-866927.95	-866927.04	-866926	
2.65	-866924.27	-866926.74	-866928.24	-866928.98	-866929.19	-866928.96	-866928.4	-866927.46	-866926.4	-866925.2	
2.7	-866924.78	-866927.09	-866928.49	-866929.09	-866929.11	-866928.76	-866928	-866926.97	-866925.77	-866924.4	
2.75	-866925.34	-866927.51	-866928.71	-866929.16	-866929.02	-866928.56	-866927.7	-866926.48	-866925.15	-866923.7	
2.8	-866925.85	-866927.87	-866928.91	-866929.21	-866928.93	-866928.37	-866927.3	-866926.02	-866924.55	-866923	
2.85	-866926.34	-866928.2	-866929.1	-866929.26	-866929.05	-866928.21	-866927	-866925.58	-866923.99	-866922.3	
2.9	-866926.8	-866928.9	-866929.63	-866929.63	-866929.06	-866928.07	-866926.8	-866925.19	-866923.48	-866921.7	
2.95	-866927.76	-866929.31	-866929.93	-866929.79	-866929.1	-866927.97	-866926.5	-866924.84	-866923.01	-866921.1	
3	-866928.28	-866929.74	-866930.22	-866929.97	-866929.15	-866927.9	-866926.3	-866924.54	-866922.6	-866920.6	
	2.5	2.55	2.6	2.65	2.7	2.75	2.8	2.85	2.9	2.95	3
2	-866922	-866923	-866923.65	-866924.3	-866924.88	-866925.42	-866925.93	-866926.42	-866926.88	-866927.33	-866927.76
2.05	-866925	-866926	-866926.31	-866926.78	-866927.2	-866927.57	-866927.92	-866928.26	-866928.59	-866928.9	-866929.2
2.1	-866927	-866928	-866927.99	-866928.28	-866928.53	-866928.75	-866928.94	-866929.14	-866929.32	-866929.51	-866929.69
2.15	-866929	-866929	-866928.91	-866929.03	-866929.11	-866929.17	-866929.21	-866929.27	-866929.32	-866929.37	-866929.44
2.2	-866929	-866929	-866929.24	-866929.2	-866929.12	-866929.02	-866928.92	-866928.83	-866928.75	-866928.68	-866928.63
2.25	-866929	-866929	-866929.13	-866928.92	-866928.69	-866928.44	-866928.2	-866927.98	-866927.76	-866927.57	-866927.4
2.3	-866929	-866929	-866928.68	-866928.32	-866927.93	-866927.54	-866927.16	-866926.8	-866926.46	-866926.15	-866925.87
2.35	-866929	-866928	-866927.97	-866927.46	-866926.93	-866926.4	-866925.88	-866925.4	-866924.93	-866924.51	-866924.12
2.4	-866928	-866927	-866927.07	-866926.41	-866925.75	-866925.08	-866924.44	-866923.83	-866923.25	-866922.71	-866922.22
2.45	-866927	-866927	-866926.04	-866925.24	-866924.44	-866923.65	-866922.88	-866922.15	-866921.46	-866920.81	-866920.22
2.5	-866927	-866926	-866924.92	-866923.99	-866923.06	-866922.15	-866921.26	-866920.41	-866919.61	-866918.86	-866918.17
2.55	-866926	-866925	-866923.74	-866922.68	-866921.63	-866920.6	-866919.61	-866918.65	-866917.74	-866916.89	-866916.11

2.6	-866925	-866924	-866922.52	-866921.35	-866920.19	-866919.05	-866917.94	-866916.88	-866915.87	-866914.93	-866914.05
2.65	-866924	-866923	-866921.3	-866920.01	-866918.74	-866917.49	-866916.29	-866915.12	-866914.02	-866912.98	-866912.01
2.7	-866923	-866922	-866920.08	-866918.68	-866917.31	-866915.96	-866914.65	-866913.39	-866912.2	-866911.07	-866910.02
2.75	-866922	-866921	-866918.88	-866917.38	-866915.9	-866914.46	-866913.06	-866911.7	-866910.42	-866909.2	-866908.07
2.8	-866921	-866920	-866917.71	-866916.11	-866914.54	-866913	-866911.51	-866910.06	-866908.69	-866907.39	-866906.18
2.85	-866921	-866919	-866916.59	-866914.89	-866913.23	-866911.6	-866910.02	-866908.48	-866907.03	-866905.65	-866904.36
2.9	-866920	-866918	-866915.51	-866913.73	-866911.98	-866910.26	-866908.6	-866906.97	-866905.44	-866903.99	-866902.62
2.95	-866919	-866917	-866914.5	-866912.63	-866910.79	-866909	-866907.24	-866905.54	-866903.93	-866902.49	-866900.96
3	-866918	-866916	-866913.54	-866911.59	-866909.68	-866907.88	-866905.97	-866904.18	-866902.49	-866900.96	-866899.47

11.