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# Supporting Information



69451 Weinheim, Germany

# Synthesis of P-stereogenic Phosphinates and Phosphine Oxides by Asymmetric Ring Closing Metathesis.

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**Experimental:**

**General experimental procedures**

Reactions requiring anhydrous conditions were conducted in flame-dried apparatus under inert atmosphere (argon or nitrogen) using a Schlenk line. Syringes and needles for the transfer of moisture- or air-sensitive reagents were oven-dried and allowed to cool in a desiccator over self-indicating silica gel. Solvents were purified prior to use by passing through a column of activated alumina under inert atmosphere or by distillation according to standard procedures. Reactions were monitored by $^{1}H$ NMR, $^{31}P$ NMR or thin layer chromatography. TLC was carried out on Merck aluminium-backed silica gel sheets and visualised with a UV lamp (254 nm) or by staining with $KMnO_4$. Flash chromatography was carried out using Merck silica gel (0.040-0.063 mm) and eluents as indicated.

NMR spectra were recorded in deuterated chloroform using Bruker or Varian spectrometers. $^{1}H$ and $^{13}C$ spectra are internally referenced to residual undeuterated solvent and $^{31}P$ spectra are referenced to $H_3PO_4$. $^{13}C$ and $^{31}P$ NMR spectra are proton-decoupled. The following abbreviations are used to indicate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, m = multiplet, br = broad. Structural assignments are supported by phosphorus-decoupled $^{1}H$, $^{13}C$-DEPT and 2D-COSY, HMQC spectra.

Melting points were recorded on a Gallenkamp Griffin apparatus and are uncorrected. IR spectra were recorded as thin films on NaCl plates using a Bruker Tensor 27 FT-IR spectrometer. Mass spectra were recorded on a Fisons Platform, Micromass LC-ToF

or Bruker MicroTof (ESI) or on a Micromass GC-ToF (EI, CI, FI). Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

Reactions using the molybdenum catalysts were carried out under an atmosphere of $N_2$ using a glovebox and all substrates were dried by azeotroping with benzene on a Schlenk line before use. THF and were Benzene distilled over sodium and benzophenone, DCM was dried by passing through a column of activated alumina.

**Synthesis of substrates:**

**General procedure (A) synthesis of acyclic vinyl phosphates/phosphine oxides:**

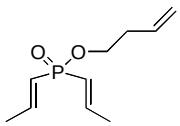
To an 0.25M solution of $POCl_3$ in $Et_2O$ at -78$^oC$ was added dropwise an 0.25M solution of the relevant alcochol and $Et_3N$ in $Et_2O$ (0.25M) over 1h. The reaction mixture was allowed to warm to room temperature overnight. Following this, hexane was added to the reaction mixture and the $NH_4Cl$ removed by filtration through celite. The reaction mix was then dried over sodium sulphate and concentrated *in vacuo*. The crude dichloride was used without further purification. The dichloride was redissolved in DCM (0.1M) and cooled to -78$^oC$. After cooling a solution of vinyl magnesium bromide in THF (0.7M, in hexanes) was added dropwise and the reaction stirred at -78$^oC$ for 4h. The reaction was quenched by pouring the mixture on to water and the resulting emulsion broken by addition of 3N HCl. The aqueous layer was then extracted with DCM, dried over sodium sulphate and concentrated in vacuo to yield a yellow oil which was purified by flash chromatography.

**General procedure (B) synthesis of acyclic allylic phosphates/phosphine oxides:**

A solution of HMDS (2equiv) and ammonium hypophosphate (1 equiv) was heated to 120$^oC$ for 4h. The reaction mixture was allowed to cool to room temperature and a solution of the allylic/homoallylic bromide in toluene (1M) added slowly. The reaction was again heated to 120$^oC$ for 12h, after which it was allowed to cool to room temperature and solution of 1:1 DCM:MeOH added and stirred at 0$^oC$ for 20 min. The mixture was then concentrated *in vacuo* and redissolved in DCM and washed with 3N HCl. The organic layers were combined and dried over sodium

sulphate and concentrated in vacuo to yield the phosphinic acid which was used without purification, (83% yield). This was dissolved in DCM (0.2M) cooled to 0$^{o}$C and solution of oxalyl chloride (3equiv) in DCM added dropwise and a drop of DMF added. The reaction was then stirred at room temperature for 30 min. After this the solvent was removed *in vacuo* and the pale oil placed on the vac pump for 1h to remove any excess oxalyl chloride. The phosphonic acid chloride was then redisolved in DCM (0.2M), cooled to 0$^{o}$C and a solution of the alcohol (3 equiv), $Et_3N$ (3equiv) and DMAP added dropwise. The reaction was then allowed to warm to room temperature and stirred for 4h before being quenched by pouring on to water. The aqueous layer was extracted three times with DCM and the combined organics dried over sodium sulphate and concentrated *in vacuo*.

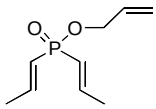
**But-3-en-1-yl (2-methylprop-1-en-1-yl)(1E)-prop-1-en-1ylphosphinate (6)**



(*E*,*E*): Synthesized by general procedure **(A)**: 1.32 g (30%); $R_f$: 0.45 (EtOAc/MeOH 19:1); **$^{1}$H NMR (400 MHz, $CDCl_3$)**: d (**ppm**) 6.45 (2H, ddq, $^{3}J_{(H,P)}$ 45.0, $^{3}J_{(H,H)}$ 13.0, $^{3}J_{(H,H)}$ 7.2 Hz, =C*H*Me), 5.80 (1H, ddt, $^{3}J_{(H,H)}$ 17.1, $^{3}J_{(H,H)}$ 10.3, $^{3}J_{(H,H)}$ 6.7 Hz, C*H*=$CH_2$), 5.67 (2H, ddq, $^{2}J_{(H,P)}$ 20.4, $^{3}J_{(H,H)}$ 13.0, $^{4}J_{(H,H)}$ 1.6 Hz, PCH), 5.06-5.14 (2H, m, =$CH_2$), 3.99 (2H, dt, $^{3}J_{(H,P)}$ 6.9, $^{3}J_{(H,H)}$ 6.9 Hz, $POCH_2$), 2.43 (2H, dddt, $^{3}J_{(H,H)}$ 6.8 x 2, $^{4}J_{(H,H)}$ 1.2 Hz x 2, $POCH_2CH_2$), 2.08 (6H, ddd, $^{3}J_{(H,H)}$ 7.2, $J_{(H,P)}$ 3.1, $^{4}J_{(H,H)}$ 1.6 Hz, $CH_3$); **$^{13}$C NMR (101 MHz, $CDCl_3$)** d (**ppm**) 147.6 (d, $^{2}J_{(C,P)}$ 3.2 Hz, *C*HMe), 133.9 (s, *C*H=$CH_2$), 122.4 (d, $^{1}J_{(C,P)}$ 131.7 Hz, PCH), 117.3 (s, =$CH_2$), 62.9 (d, $^{2}J_{(C,P)}$ 5.7 Hz, $POCH_2$), 35.0 (d, $^{3}J_{(C,P)}$ 6.5 Hz, $POCH_2CH_2$), 16.8 (d, $^{3}J_{(C,P)}$ 8.6 Hz, $CH_3$**); $^{31}$P**

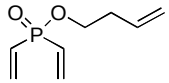
**NMR (162 MHz, $CDCl_3$)**: d 29.1 ppm; **IR (film):** *n* (**$cm^{-1}$**) 1640 (C=C), 1211 (P=O); **HRMS (ES+): *m/z*** calcd for $C_{10}H_{18}O_2P$ $[M+H]^+$: 201.1044; found: 201.1041

**Allyl (2-methylprop-1-en-1-yl)(1E)-prop-1-en-ylphosphinate (8)**



Prepared by method **(A)** as a mixture of isomers (*E*,*E*): 1.11 g (33 %); $R_f$: 0.15 (EtOAc); **$^1$H NMR (400 MHz, $CDCl_3$):** d **(ppm)** 6.72 (2H, ddq, $^3J_{(H,P)}$ 19.9, $^3J_{(H,H)}$ 17.0, $^3J_{(H,H)}$ 6.6 Hz =C*H*Me), 5.78 (1H, ddt, $^3J_{(H,H)}$ 17.1, $^3J_{(H,H)}$ 10.3, $^3J_{(H,H)}$ 6.7 Hz C*H*=$CH_2$), 5.74 (2H, ddq, $^2J_{(H,P)}$ 22.7, $^3J_{(H,H)}$ 17.0, $^4J_{(H,H)}$ 1.7 Hz PCH), 5.11 (1H, ddt, $^3J_{(H,H)}$ 17.1, $^2J_{(H,H)}$ 1.6, $^4J_{(H,H)}$ 1.6 Hz =C$H_{cis}H_{trans}$), 5.08 (1H, ddt, $^3J_{(H,H)}$ 10.3, $^2J_{(H,H)}$ 1.6, $^4J_{(H,H)}$ 1.6 Hz =$CH_{cis}H_{trans}$), 3.89 (2H, m; $POCH_2$), 1.91 ppm (6H, ddd, $^3J_{(H,H)}$ 6.6, $^3J_{(H,P)}$ 1.8, $^4J_{(H,H)}$ 1.7 Hz $CH_3$); **$^{13}$C NMR (101 MHz, $CDCl_3$)** d **(ppm)** 147.9 (d, $^2J_{(C,P)}$ 4.5 Hz, *C*HMe), 133.8 (s, *C*H=$CH_2$), 122.3 (d, $^1J_{(C,P)}$ 136.7 Hz, PCH), 117.3 (s, =$CH_2$), 63.1 (d, $^2J_{(C,P)}$ 5.8 Hz, $POCH_2$), 20.1 ppm (d, $^3J_{(C,P)}$ 20.4 Hz, $CH_3$); **$^{31}$P NMR (162 MHz, $CDCl_3$):** d 29.6 ppm; **IR (film):** *n* **($cm^{-1}$)** 1640 (C=C), 1221 (P=O); **HRMS (ES+): *m/z*** calcd for $C_9H_{16}O_2P$ $[M+H]^+$: 187.0888; found: 187.0898.

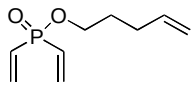
**But-3-enyl divinylphosphinate (9):**



Synthesized following general procedure **(A)** to yield **9** as a pale yellow oil. 1.3 g (86%); $R_f$: 0.3 (EtOAc/MeOH 19:1); **$^1$H NMR (400 MHz, $CDCl_3$): d (ppm)** 6.10-6.36 (6H, m, PC*H*=C$H_2$); 5.79 (1H, ddt, $^3J_{(H,H)}$ 6.8, $^3J_{(H,H)}$ 10.3, $^3J_{(H,H)}$ 17.1 Hz, $PO(CH_2)_2CH$), 5.07-5.16 (2H, m $PO(CH_2)_2CH$=C$H_2$), 4.02 (2H, dt, $^3J_{(H,P)}$ 6.8, $^3J_{(H,H)}$ 6.8 Hz, $POCH_2$), 2.44 (2H, dddt, $^3J_{(H,H)}$ 6.7, $^3J_{(H,H)}$ 6.7, $^4J_{(H,H)}$ 1.3, $^4J_{(H,H)}$ 1.3 Hz,

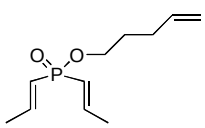
$POCH_2CH_2$); **$^{13}$C NMR (101 MHz, $CDCl_3$): d (ppm)** 135.3 (d, $^2J_{(C,P)}$ 1.5 Hz, $PCH=CH_2$); 133.5 (s, $PO(CH_2)_2CH$), 129.0 (d, $^1J_{(C,P)}$ 131.5 Hz, $PCH=CH_2$), 117.6 (s, $PO(CH_2)_2CH=CH_2$), 63.6 (d, $^2J_{(C,P)}$ 6.2 Hz, $POCH_2$), 34.9 ppm (d, $^3J_{(C,P)}$ 6.5 Hz, $POCH_2CH_2$); **$^{31}$P NMR (162 MHz, $CDCl_3$): d** 28.8 ppm; **IR (film):** *n* (**cm-1)** 1645 and 1600 (C=C), 1214 (P=O); **HRMS (ES+): *m/z*** calcd for $C_8H_{14}O_2P$ $[M+H]^+$: 173.0731; found: 173.0727.

**Pent-4-enyl divinylphosphinate (10):**



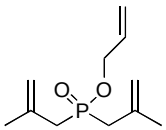
Synthesized following general procedure **(A)** from $POCl_3$ (1 mL, 10.7 mmol) and 5-pentene-1-ol (1.1 mL, 10.7 mmol) to yield **10** as a pale yellow oil. 1.3g (65%); $R_f$: 0.4 (EtOAc), **$^1$H NMR (400MHz, $CDCl_3$)** d **(ppm)** 6.15 (6H, m, $CH_2=CHP$), 5.70 (1H, m, $CH_2=CH$), 4.95 (2H, m, $CH=CH_2$), 3.91 (2H, dt, $^3J_{(H,P)}$ 6.8, $^3J_{(H,H)}$, 6.8Hz, $POCH_2$), 2.11 (2H, m, $POCH_2CH_2CH_2$), 21.7 (2H, m, $POCH_2CH_2$), **$^{13}$C NMR (100MHz, $CDCl_3$)** d **(ppm)** 137.2 (s, $CH_2CH=CH_2$), 135.2 (s, $PCH=CH_2$), 129.0 (d, $^1J_{(C,P)}$ 131Hz, $PCH=CH_2$), 115.3 (s, $CH_2CH=CH_2$), 63.8 (d, $^3J_{(C,P)}$ 6Hz $POCH_2$), 29.6 (2C, m, $POCH_2CH_2CH_2$), **$^{31}$P NMR (161 MHz, $CDCl_3$)** 28.8 ppm, ; **IR (film):** *n* (**$cm^{-1}$)** 1641 and 1607 (C=C), 1220 **(P=O); HRMS (ES+): *m/z*** calcd for $C_9H_{15}O_2PNa$ $[M+Na]^+$: 209.0707; found 209.0702.

**Pent-4-en-1-yl di-(1E)-prop-1-en-1-ylphospinate (11)**



Prepared by method **(A)** as a mixture of isomers (*E*,*E*): 895 mg (35 %) **$^{1}$H NMR (400 MHz, $CDCl_3$):** d **(ppm)** 6.54 (2H, ddq, $^{3}J_{(H,P)}$ 45.0, $^{3}J_{(H,H)}$ 15.0, $^{3}J_{(H,H)}$ 6.4 Hz, =C*H*Me), 5.79 (1H, ddt, $^{3}J_{(H,H)}$ 17.1, $^{3}J_{(H,H)}$ 9.3, $^{3}J_{(H,H)}$ 6.0 Hz, C*H*=$CH_2$), 5.67 (ddq, $^{2}J_{(H,P)}$ 20.0, $^{3}J_{(H,H)}$ 12.0, $^{4}J_{(H,H)}$ 1.2 Hz, PCH), 5.06-5.14 (2H, m, =C*H*$_2$), 3.95 (2H, dt, $^{3}J_{(H,P)}$ 6.9, $^{3}J_{(H,H)}$ 6.9 Hz, POC*H*$_2$), 2.14 (2H, dddt, $^{3}J_{(H,H)}$ 7.2 x 2, $^{4}J_{(H,H)}$ 1.2 Hz x 2, $POCH_2CH_2$), 2.08 ppm (6H, ddd, $^{3}J_{(H,H)}$ 7.2, $^{3}J_{(H,P)}$ 3.1, $^{4}J_{(H,H)}$ 1.8 Hz, C*H*$_3$); 1.77 (2H, tt, $^{3}J_{(H,H)}$ 7Hz x2, $POCH_2CH_2$) **$^{13}$C NMR (101 MHz, $CDCl_3$)** d **(ppm)** 147.6 (d, $^{2}J_{(C,P)}$ 3.2 Hz, *C*HMe), 137.4 (s, *C*H=$CH_2$), 122.9 (d, $^{1}J_{(C,P)}$ 132.1 Hz, PCH), 115.3 (s, =*C*H$_2$), 62.9 (d, $^{2}J_{(C,P)}$ 5.7 Hz, PO*C*H$_2$), 29.0 (s, $POCH_2CH_2$), 29.6 (s, $POCH_2CH_2CH_2$) 16.80 (d, $^{3}J_{(C,P)}$ 8.6 Hz, *C*H$_3$)**; $^{31}$P NMR (162 MHz, $CDCl_3$):** d 29.1 ppm; **IR (film):** *n* (**cm$^{-1}$**)1622 (C=C), 1213 (P=O); **HRMS (ES+): *m/z*** calcd for $C_{11}H_{20}O_2P$ $[M+H]^+$: 215.1201; found: 215.1195

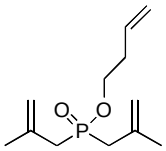
**Allyl bis(2-methylallyl)phosphinate (12):**



Synthesized according to general procedure **(B)** to yield **12** as a pale yellow oil 750mg (88%) $R_f$ = 0.4 (1:1 DCM: EtOAc) **$^{1}$H (400MHz, $CDCl_3$)** d **(ppm)** 5.99 (1H, ddt, $^{3}J_{(H,H)}$ 17.0, 11.0, 5.0 Hz C*H*=$CH_2$), 5.35 (1H, dd, $^{3}J_{(H,Htrans)}$ 17.0 $^{2}J_{(H,H)}$ 1.6 Hz, CH=C*H*$_{2trans}$), 5.22 (1H, dd, $^{3}J_{(H,Hcis)}$ 11.0, $^{2}J_{(H,H)}$ 1.6 Hz, CH=C*H*$_{2cis}$), 4.97 (2H, td, $^{4}J_{(H,H)}$ 3.2, $^{2}J_{(H,H)}$ 1.2 Hz, MeC=C*H*$_{2(trans)}$), 4.89 (2H, br d, $^{4}J_{(H,H)}$ 3.9 Hz, MeC=C*H*$_{2(cis)}$), 4.55 (2H, dd, $^{3}J_{(P,H)}$ 5.7, $^{3}J_{(H,H)}$ 5.0, POC*H*$_2$), 2.63 (4H, d, $^{2}J_{(P,H)}$ 16.8 Hz, P(C*H*$_2$)$_2$), 1.91 (6H, s, P($CH_2C$*Me*)$_2$ **$^{13}$C (100MHz, $CDCl_3$)** d **(ppm)** 136.7 (d, $^{2}J_{(C,P)}$ 10.0 Hz, *C*H$_3$=$CH_2$), 133.4 (d, $^{3}J_{(C,P)}$ 6.2 Hz, *C*H=$CH_2$), 117.5 (s, CH=*C*H$_2$), 115.6 (d, $^{3}J_{(C,P)}$ 10.5 Hz MeC=*C*H$_2$), 65.1 (d, $^{2}J_{(C,P)}$ 6.2 Hz, PO*C*H$_2$), 37.7 (d, $^{2}J_{(P,C)}$

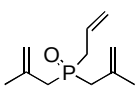
86.2 Hz, P*C*H$_2$), 24.1 (d, $^3J_{(C,P)}$ 2.4 Hz, *C*H$_3$) **$^{31}$P (161 MHz, CDCl$_3$)** d 50.2ppm **IR (film)** n **(cm$^{-1}$)** 1664 (C=C), 1228 (P=O), H**RMS (ES+): *m/z*** calc for $C_{11}H_{19}O_2PNa$ $[M+Na]^+$: 237.1020; found: 237.1016

**But-3-enyl bis(2-methylallyl)phosphinate (13):**



Synthesised according to general procedure **(B)** to yield **13** as a pale yellow oil. 680 mg, (74%) $R_f$=0.4 (1:1 DCM:EtOAc) **$^1$H NMR (400MHz, CDCl$_3$)** d **(ppm)** 5.65 (1H, ddt, $^3J_{(H,H)}$ 16.0, 10.0, 6.0 Hz, CH$_2$=C*H*), 4.96 (2H, m, C*H*$_2$=CH), 4.82 (1H, dt $^2J_{(H,H)}$ 4.9, $^4J_{(H,H)}$ 1.1Hz, Me=C*H*$_{2(trans)}$), 4.74 (1H, d, $^2J_{(H,H)}$ 4.9 Hz, Me=C*H*$_{2(cis)}$), 3.94 (2H, q, $^3J_{(H,H)}$ 7.1Hz POC*H*$_2$), 2.46 (4H, d, $^3J_{(H,P)}$ 17.0Hz, PC*H*$_2$) 2.27( 2H, ddt, $^3J_{(H,H)}$ 6.6, $^3J_{(H,H)}$ 6.6, $^4J_{(H,P)}$ 1.1Hz, POCH$_2$C*H*$_2$), 1.75 (6H, s, *Me*), **$^{13}$C NMR (100MHz, CDCl$_3$)** d **(ppm)** 136.0 (d, $^2J_{(C,P)}$ 8.3Hz, Me*C*=CH$_2$), 133 (s, *C*H=CH$_2$), 117 (s, *C*H=CH$_2$), 115 (d, $^3J_{(C,P)}$, 10.3Hz, *C*H$_2$=CMe), 63 (d, $^2J_{(C,P)}$ 7.3Hz, PO*C*H$_2$), 38 (d, $^1J_{(C,P)}$, 84Hz, P*C*H$_2$), 35 (d, $^3J_{(C,P)}$ 5.9Hz, POCH$_2$*C*H$_2$), 24 (s, *Me*), **$^{31}$P NMR (162MHz, CDCl$_3$)** d **(ppm)** 49.1ppm, **IR (film) (cm$^{-1}$)** n 1643 (C=C), 1228 (P=O), HRMS (ES): *m/z* calc for $C_{12}H_{22}O_2P$ $[M+H]^+$: 229.1357; found: 229.1352.

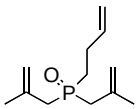
**Allylbis(2-methylallyl)phosphine oxide (22):**



Synthesized according to general procedure **(B)**, to yield **22** as a white solid. 480 mg (61%); *R*$_f$: 0.2 (EtOAc); m.p. 58-59 °C; **$^1$H NMR (400 MHz, CDCl$_3$):** d **(ppm)** 5.83

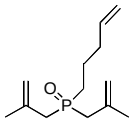
(1H, m, C*H*=$CH_2$), 5.20-5.27 (2H, m, CH=C$H_2$), 5.00 (2H, m, CMe=C$H_A$$H_B$), 4.84 (2H, m, CMe=C$H_A$$H_B$), 2.69 (2H dd, $^2J_{(H,P)}$ 15.6, $^3J_{(H,H)}$ 7.6 Hz; PC$H_2$CH), 2.60 ( 2H dd, $^2J_{(H,P)}$ 14.8, $^2J_{(H,H)}$ 13.7 Hz; PC$H_A$$H_B$CMe), 2.54 (2H, dd, $^2J_{(H,P)}$ 14.4, $^2J_{(H,H)}$ 13.7 Hz; PC$H_A$$H_B$CMe), 1.94 ppm (6H, s, $CH_3$), **$^{13}$C NMR (101 MHz, $CDCl_3$):** d **(ppm)** 137.3 (d, $^2J_{(C,P)}$ 9.3 Hz, PC$H_2$*C*Me), 128.2 (d, $^2J_{(C,P)}$ 8.0 Hz, PC$H_2$*C*H), 120.6 (d, $^3J_{(C,P)}$ 11.5 Hz, CH=*C*$H_2$), 115.5 (d, $^3J_{(C,P)}$ 9.6 Hz, CMe=*C*$H_2$), 37.3 (d, $^1J_{(C,P)}$ 61.7 Hz, P*C*$H_2$CMe), 33.8 (d, $^1J_{(C,P)}$ 63.0 Hz, P*C*$H_2$CH), 24.5 ppm (d, $^3J_{(C,P)}$ 1.8 Hz, $CH_3$), **$^{31}$P NMR (162 MHz, $CDCl_3$): d** 41.5 ppm; **IR (flim):** *n* (**cm$^{-1}$**) 1640 (C=C), 1176 (P=O); H**RMS (ES+): *m/z*** calc for $C_{11}H_{20}OP$ $[M+H]^+$: 199.1252; found: 199.1254.

**Allyl bis(2-methylallyl)phosphine oxide (23):**



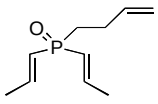

Synthesised according to general procedure **(B)** to yield **23** as a colourless oil. 895 mg, (53%), $R_f$=0.3 (9:1 EtOAc:MeOH) **$^1$H NMR (400MHz, $CDCl_3$)** d **(ppm)** 5.80 (1H, ddt, $^3J_{(H,H)}$ 16.6, 9.4, 6.1 Hz C*H*=$CH_2$) 4.88 (2H, dq, $^2J_{(H,H)}$ 17.6, $^3J_{(H,H)}$ 1.4 Hz, CH=C$H_{2trans}$), 4.82 (2H, dq, $^3J_{(H,H)}$ 10.8, $^2J_{(H,H)}$ 1.4 Hz, CH=C$H_{2cis}$), 4.78 (2H, dt, $^2J_{(H,H)}$ 4.0, $^3J_{(H,H)}$ 1.4 Hz, MeC=C$H_{2a}$), 4.64 (2H, d, $^2J_{(H,H)}$ 4.0 Hz MeC=C$H_{2b}$), 2.42 (2H, dd, $^2J_{(H,P)}$ 14.1, $^2J_{(H,H)}$ 14.1 Hz, PC$H_{2a}$C=CMe), 2.35 (2H, dd, $^2J_{(H,P)}$ 13.7, $^2J_{(H,H)}$ 13.7 Hz, PC$H_{2b}$C=CMe), 2.17 (2H, m, PC$H_2$$CH_2$), 1.75 (6H, s, C$H_3$), 1.64 (2H, m, $PCH_2$C$H_2$) **$^{13}$C NMR (100 MHz, $CDCl_3$)** d **(ppm)** 174 (s, *C*=CMe), 137 (s, *C*H=$CH_2$), 115 (d, $^3J_{(C,P)}$ 11 Hz MeC=*C*$H_2$), 114 (s, CH=*C*$H_2$) 38 (d, $^1J_{(C,P)}$ 56 Hz, P*C*$H_2$C=CMe), 26 (d, $^1J_{(C,P)}$ 63 Hz, P*C*$H_2$$CH_2$), 25 (d, $^3J_{(C,P)}$ 16 Hz, $PCH_2$*C*$H_2$), 24 (s, *C*$H_3$), **$^{31}$P NMR (161MHz, $CDCl_3$)** d 47.0 ppm, **IR (film)** n **(cm$^{-1}$)** 1641 (C=C), 1191 (P=O), H**RMS (ES+): *m/z*** calc for $C_{12}H_{21}OPNa$ $[M+H]^+$: 235.1228; found: 235.1222

**Bis(2-methylprop-2-en-1yl)(pent-4-en-1-yl) phosphine oxide (24)**



Synthesised according to general procedure **(B)** to yield **24** as a colourless oil. 485 mg, (37%), $R_f$=0.1 (EtOAc) **$^{1}$H (400MHz, CDCl$_3$)** d **(ppm)** 5.70 (1H, ddt, $^{3}J_{(H,H)}$ 16.1, 10.3, 4.2 Hz, C*H*=$CH_2$), 4.85-5.00 (4H, m, C=C$H_{2a}$, CH=C$H_2$), 4.74 (2H, d $^{2}J_{(H,H)}$ 4.02Hz, C=C$H_{2b}$), 2.41 (2H, dd, $^{2}J_{(H,P)}$ 14.1, $^{2}J_{(H,H)}$ 14.1 Hz, PC$H_2$C=CMe), 2.34 (2H, dd, $^{3}J_{(H,H)}$ 14.1, 14.1 Hz), 1.96 (2H, dd, $^{2}J_{(H,P)}$ 6.5, $^{2}J_{(H,H)}$ 6.5 Hz, PC$H_2$$CH_2$), 1.81 (7H, m, PCH2C=C*Me*, $PCH_2CH_{2a}$), 1.61 (3H, m, $PCH_2CH_{2b}$). **$^{13}$C (100Mhz, CDCl$_3$)** d **(ppm)** 158.9 (s, *C*=CMe), 137.1 (s, *C*H=$CH_2$), 115.7 (s, CH=*C*$H_2$), 115.1 (d, $^{3}J_{(C,P)}$ 9 Hz, $PCH_2C$=*C*$H_2$), 38.1 (d, $^{2}J_{(P,C)}$ 60 Hz, P*C*$H_2C$=$CH_2$), 34.8 (d, $^{3}J_{(P,C)}$ 15 Hz, $PCH_2$*C*$H_2$), 26.8 (d, $^{2}J_{(C,P)}$ 67 Hz, P*C*$H_2CH_2$), 24.3 (d, $^{3}J_{(P,C)}$ 2hz, *C*$H_3$) 21.0 (d, $^{3}J_{(P,C)}$ 3hz, $PCH_2CH_2$*C*$H_2$) ), **$^{31}$P (161MHz, CDCl$_3$)** d 43.6 ppm **IR** *n* **(cm$^{-1}$)** 1641 (C=C), 1193 (P=O), H**RMS (ES+): *m/z*** calc for $C_{13}H_{23}OPNa$ $[M+Na]^+$: 249.1384; found: 249.1379.

**But-3-en-1-yl[di-(1E)-prop-1-en-1-yl]phosphine oxide (29)**



Prepared by method **(A)** 800 mg (50 %); $R_f$: 0.37 (EtOAc:MeOH 9:1); **$^1$H NMR (400 MHz, $CDCl_3$):** d (**ppm)** 6.26 (m, =C*H*Me), 5.46 (2H, m, PC*H*=CHMe, $PCH_2CH_2CH$), 4.66 (1H, dq, $^3J_{(H,H)}$ 16.7, $^4J_{(H,H)}$ 1.5 Hz, =C$H_{2(trans)}$), 4.60 (1H, dm, $^3J_{(H,H)}$ 9.7 Hz =C$H_{2(cis)}$) 1.92 (2H, m, PC$H_2$), 1.55 (3H, dd, $^3J_{(H,H)}$ 2.0, $^4J_{(H,P)}$ 2.0 Hz, C$H_3$) 1.53 (3H, dd, $^3J_{(H,H)}$ 2.0, $^4J_{(P,H)}$ 2.0 Hz; C$H_3$), 1.12 (2H, m, $PCH_2CH_2$) **$^{13}$C NMR (101 MHz, $CDCl_3$)** d (**ppm)** 145.7 (d, $^2J_{(C,P)}$ 1.7 Hz, *C*HMe), 137.2 (d, $^2J_{(P,C)}$ 15.2 Hz, *C*H=$CH_2$), 123.2 (d, $^1J_{(C,P)}$ 98.7 Hz, P*C*H), 114.6 (s, =$CH_2$), 29.4 (d, $^1J_{(C,P)}$ 73.6 Hz, P*C*$H_2$), 25.1 (d, $^2J_{(C,P)}$ 3.4 Hz, $PCH_2CH_2$), 19.9 (d, $^3J_{(P,C)}$ 17.5 Hz, *C*$H_3$); **$^{31}$P NMR (162 MHz, $CDCl_3$):** d 25.4 ppm**; IR (film):** *n* (**$cm^{-1}$)** 1634 (C=C), 1164 $cm^{-1}$ (P=O); **HRMS (ES+):** ***m/z*** calcd for $C_9H_{16}O_2PNa$ $[M+H]^+$: 207.0915; found: 207.0909

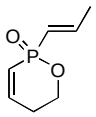
**General procedure for RCM with achiral catalysts (C):**

To an 0.02M solution of phosphate in DCM was added 2mol% Grubbs II and the reaction heated to reflux for 2h. The reaction mix was then concentrated in vacuo to yield a dark drown oil which was purified by flash chromatography to yield the desired product.

**General procedure for ARCM with chiral molybdenum catalysts (D):**

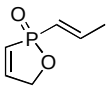
A one-dram vial containing a stirrer bar was charged with the 10mol% catalyst and diluted with benzene (0.2ml) in an $N_2$-filled glove box. To this, a solution of substrate (10mg) in benzene (0.2ml) was added dropwise. The vial was sealed with Teflon-lined cap and reaction stirred at 60$^o$C for 12h. The vessel was then removed from the glove-box and quenched by exposure to air. The solution was concentrated in vacuo to yield a green oil which was purified by flash chromatography (EtOAc).

**2-(*E*)-Propenyl-5,6-dihydro-1,2-oxaphosphorin 2-oxide (7)**



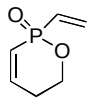
Synthesised according to general procedure **C** from **6** (40mg, 0.20mmol) and Grubbs II (4mg, 0.0045mmol). Purification by flash chromatography (EtOAc:MeOH 9:1) to yield **7** as a dark brown oil (25mg) Yield (80%) **$^{1}$H NMR (400MHz, $CDCl_3$)** d (**ppm)** 6.70 (2H, m, CH=C*H*Me, CH=C*H*$CH_2$), 5.90 (1H, dddd, $^{2}J_{(P,H)}$ 23.0, $^{3}J_{(H,H)}$ 11.5, 1.4, 2.3 Hz, PC*H*=CH), 5.62 (1H, ddq, $^{2}J_{(P,H)}$ 23.3, $^{3}J_{(H,H)}$ 17.0, 1.5 Hz, PC*H*=CHMe), 4.38 (1H, m, POC$H_{2a}$), 4.14 (1H, m, POC$H_{2b}$), 2.40 (1H, m, $POCH_2CH_{2a}$), 2.20 (1H, m, $POCH_2CH_{2b}$), 1.83 (3H, dt, $^{3}J_{(P,H)}$ 6.5, $^{3}J_{(H,H)}$ 2 Hz, PCH=C*H*Me) **$^{13}$C (100MHz, $CDCl_3$)** d **(ppm)** 150.0 (d, $^{2}J_{(P,C)}$ 5 Hz, PCH, =*C*H), 145.9 (d, $^{2}J_{(P,C)}$ 2 Hz, PCH=C*H*Me), 122.2 (d, $^{1}J_{(C,P)}$ 48 Hz, P*C*H=CH), 120.1 (d, $^{1}J_{(C,P)}$ 18.0 Hz, PCH=*C*HMe), 62.6 (d, $^{2}J_{(C,P)}$ 7.0 Hz, PO*C*$H_2$), 27.2 (d, $^{3}J_{(C,P)}$ 11 Hz, $POCH_2CH_2$), 20.1 (d, $^{3}J_{(C,P)}$ 22 Hz, PCH=C*Me*) **$^{31}$P NMR (161Mhz, $CDCl_3$)** d 21.0 ppm. **IR (film): *?* ($cm^{-1}$)** 1607 (C=C), 1218 (P=O) H**RMS (ES+): *m/z*** calc for $C_7H_{11}O_2PNa$ $[M+Na]^+$: 181.0394; found: 181.0393. Enatiomers separated by chiral GC using a CDGTA column at 130$^{o}$C and 20psi. Retention times: 143.8mins and 160.3mins 60%ee.

**2-[(1*E*)-prop-1-en-1-yl]-2,5-dihydro-1,2-oxaphosphole 2-oxide (14)**



Synthesised according to general proceedure **C** from **8** (400 mg, 2.15 mmol) and Grubbs II (37 mg, 0.04 mmol) Purification by flash chromatography (EtOAc/MeOH 9:1) afforded **14** as a brown oil. Yield: 252 mg (82%); $R_f$ :0.2 (EtOAc/MeOH 9:1); **$^1$H NMR (400 MHz, $CDCl_3$):** d (**ppm)** 8.86 (1H, dddd, $^3J_{(H,P)}$ 38.2, $^3J_{(H,H)}$ 8.1, $^3J_{(H,H)}$ 2.3 Hz × 2, PCH=C*H*), 6.12-6.38 (4H m, PC*H*=C$H_2$ and PC*H*=CH), 5.03 (ddd, $^2J_{(H,H)}$ 16.2, $^3J_{(H,H)}$ 1.6, $^3J_{(H,P)}$ 1.6 Hz, 1H; POC$H_A$H$_B$), 4.83 (4H, dddd, $^2J_{(H,H)}$ 16.2, $^3J_{(H,P)}$ 10.8, $^3J_{(H,H)}$ 1.6, $^4J_{(H,P)}$ 1.6 Hz, POCH$_A$$H_B$); **$^{13}$C NMR (101 MHz, $CDCl_3$):** d (**ppm)** 149.6 (d, $^2J_{(C,P)}$ 4.1 Hz, PCH=*C*HMe), 147.5 (d, $^2J_{(C,P)}$ 13.3 Hz, PC=*C*H), 122.0 (d, $^1J_{(C,P)}$ 75.5 Hz, P*C*H=CHMe), 120.7 (d, $^1J_{(C,P)}$ 50.3 Hz, P*C*H=CH), 73.5 ppm (d, $^2J_{(C,P)}$ 5.8 Hz, POCH$_2$) 19.9 (d, $^3J_{(C,P)}$ 21.5Hz); **$^{31}$P NMR (162 MHz, $CDCl_3$):** d 53.7 ppm; **IR (film):** *n* (**cm$^{-1}$)**1645 (C=C), 1217 (P=O); **HRMS (ES+): *m/z*** calcd for $C_5H_8O_2PNa$ $[M+Na]^+$: 167.0238; found: 167.0232.

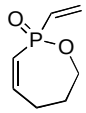
**2-vinyl-5,6-dihydro-2H-1,2-oxaphosphine 2-oxide (15):**



Syntheised according to general procedure **C** from **9** (104mg, 0.60 mmol) and Grubbs II (10 mg, 0.012 mmol). Purification by flash chromatography (EtOAc/MeOH 19:1) afforded **15** as a brown oil. Yield: 73 mg (85%); $R_f$ 0.1 (EtOAc/MeOH 19:1); **$^1$H NMR (400 MHz, $CDCl_3$): d (ppm)** 6.84 (1H, ddddd, $^3J_{(H,P)}$ 37.8, $^3J_{(H,H)}$ 12.6, $^3J_{(H,H)}$ 5.4, $^3J_{(H,H)}$ 2.8 Hz, $^4J_{(H,H)}$ 1.0 Hz, PCH=C*H*), 6.04-6.38 (3H, m, PC*H*=C$H_2$), 6.02 (1H, dddd, $^2J_{(H,P)}$ 22.9, $^3J_{(H,H)}$ 12.6, $^4J_{(H,H)}$ 2.7, $^4J_{(H,H)}$ 1.4 Hz, PC*H*=CH), 4.47 (1H, dddd, $^3J_{(H,H)}$ 11.5, $^3J_{(H,H)}$ 10.0, $^3J_{(H,P)}$ 8.6, $^2J_{(H,H)}$ 3.5 Hz, POC$H_A$H$_B$), 4.26 (1H, ddddd, $^3J_{(H,P)}$ 16.7, $^3J_{(H,H)}$ 11.5, $^3J_{(H,H)}$ 5.2, $^2J_{(H,H)}$ 3.2, $^4J_{(H,H)}$ 1.0, POCH$_A$$H_B$), 2.45-2.56 (1H, m, POCH$_2$C$H_A$$H_B$), 2.28-2.37 ppm (1H, m, POCH$_2$CH$_A$$H_B$); **$^{13}$C NMR (100 MHz,**

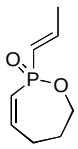
**$CDCl_3$): d (ppm)** 146.7 (d, $^2J_{(C,P)}$ 1.2 Hz, PCH=*C*H), 136.0 (d, $^2J_{(C,P)}$ 2.4 Hz, PCH=*C*$H_2$), 129.0 (d, $^1J_{(C,P)}$ 138.1 Hz, P*C*H=$CH_2$), 120.6 (d, $^1J_{(C,P)}$ 119.4 Hz, P*C*H=$CH_2$), 62.8 (d, $^2J_{(C,P)}$ 6.4 Hz, PO*C*$H_2$), 27.2 (d, $^3J_{(C,P)}$ 10.8 Hz, $POCH_2CH_2$); **$^{31}$P NMR (162 MHz, $CDCl_3$): d** 21.7 ppm; **IR (film):** *n* **(cm$^{-1}$)** 1614 (C=C), 1221 (P=O); **HRMS (ES+):** ***m/z*** calcd for $C_6H_{10}O_2P$ $[M+H]^+$: 145.0418; found: 145.0418. Enatiomers separated by chiral GC using a β-dex column at 140$^o$C and 15psi. Retention times: 38.2mins and 39.1mins 86%ee.

**2-vinyl-2,5,6,7-tetrahydro-1,2-oxaphosphine 2-oxide (16)**



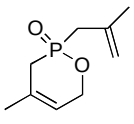
Synthesised according to general procedure **C** to yield **16** as a dark brown oil. Yield 366mg (86%) **$^1$H NMR (400MHz, $CDCl_3$)** d **(ppm)** 6.61 (1H, m, PCH=C*H*), 6.10 (3H, m, PC*H*=C$H_2$), 5.85 (1H, m, PC*H*=CH), 4.40 (1H, m, $POCH_{2a}$), 4.05 (1H, m, $POCH_{2b}$), 2.41 (2H, m, $PCH=CHCH_2CH_2$), 2.21 (1H, m, $POCH_2CH_{2a}$), 1.95 (1H, m, $POCH_2CH_{2b}$), **$^{13}$C NMR (100MHz, $CDCl_3$)** d **(ppm)** 148.1 (s, PCH=*C*$H_2$), 134.1 (d, $^2J_{(C,P)}$ 2.1 Hz, PCH=*C*H), 130.0 (d, $^1J_{(C,P)}$ 130 Hz, P*C*H=$CH_2$), 123.2 (d, $^1J_{(C,P)}$ 120 Hz, P*C*H=CH), 66.0 (d, $^2J_{(C,P)}$ 6 Hz, PO*C*$H_2$), 28.8 (m, $POCH_2CH_2CH_2$), **$^{31}$P NMR(161Mhz, $CDCl_3$)** d 31.5ppm, **IR (film):** *n* (**cm**$^{-1}$)1640 (C=C), 1211 (P=O) H**RMS (ES+):** ***m/z*** calc for $C_7H_{11}O_2PNa$ $[M+Na]^+$: 181.0394; found: 181.0389 . Enantiomers separated by chiral GC using a β–dex column at 140$^o$C and 15psi. Retention times: 39.8mins and 40.9mins 73% ee.

**2-[(1E)-prop-1-en-1-yl]-2,5,6,7-tetrahydro-1,2-oxaphosphepine 2-oxide (17)**



Synthesised according to general procedure **C** from **20** (100 mg, 0.46 mmol) and Grubbs II (8 mg, 0.009 mmol). Purification by flash chromatography (EtOAc:MeOH 9:1) to yield **17** as a dark brown oil (64 mg) Yield (81%) **$^{1}$H NMR (400MHz, $CDCl_3$)** d **(ppm)** 6.70 (2H, m, CH=C*H*Me, CH=C*H*$CH_2$), 5.90 (2H, m, PC*H*=CHMe, PC*H*=CH), 4.41 (1H, m, POC$H_{2a}$), 4.05 (1H, m, POC$H_{2b}$), 2.50 (2H, m, $POCH_2CH_2$), 2.23 (1H, m, $POCH_2CH_2CH_{2a}$), 1.97 (1H, m, $POCH_2CH_2CH_{2b}$) 1.87 (3H, dt, $^{3}J_{(P,H)}$ 6.5, $^{3}J_{(H,H)}$ 2 Hz, PCH=C*H*Me), **$^{13}$C (100MHz, $CDCl_3$)** d **(ppm)** 147.6 (d, $^{2}J_{(P,C)}$ 6 Hz, PCH=*C*$HCH_2$), 147.2 (s, PCH=C*H*Me), 124.5 (d, $^{1}J_{(C,P)}$ 120 Hz, P*C*H=CH), 122.1 (d, $^{1}J_{(C,P)}$ 142 Hz, PCH=*C*HMe), 65.7 (d, $^{2}J_{(C,P)}$ 6 Hz, PO*C*$H_2$), 28.5 (d, $^{3}J_{(C,P)}$ 6 Hz, $POCH_2CH_2$), 28.4 (d, $^{3}J_{(C,P)}$ 6 Hz, PCH=CH*C*$H_2$), 20.1 (d, $^{3}J_{(P,C)}$, 20 Hz, PCH=CH*Me*) **$^{31}$P NMR (161MHz, $CDCl_3$)** d 31.4ppm. H**RMS (ES+): *m/z*** calc for $C_8H_{13}O_2PNa$ $[M+Na]^+$: 195.0551; found: 195.0555. Enatiomers separated by chiral GC using a β-dex column at 140$^{o}$C and 15psi. Retention times: 85.7mins and 88.2mins 27%ee.

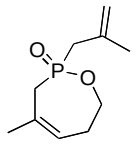
**4-methyl-2-(2-methylprop-2-en-1-yl)-3,6-dihydro-2*H*-1,2-oxaphosphine 2-oxide (18):**



Synthesised according to general procedure **C** from **12** (100 mg, 0.47 mmol) and Grubbs II (6 mg, 2 mol%). Purification by flash chromatography: EtOAc to EtOAc : MeOH (9:1) to yield **18** as a dark brown oil (77 mg, 88%) $R_f$: 0.16 (EtOAc) **$^{1}$H**

**(400MHz, $CDCl_3$)** d **(ppm)** 5.51 (1H, br, MeC=C*H*R), 4.97 (1H, dt, $^4J_{(H,H)}$ 4.8, $^2J_{(H,H)}$ 1.5 $CH_2C=CH_{2(trans)}$), 4.85 (1H, t, br, $^4J_{(H,H)}$ 4.6, $CH_2C=CH_{2(cis)}$), 4.82 (1H, m, $POCH_{2\alpha}$), 4.58 (1H, m, $POCH_{2\beta}$), 2.65 (2H, d, $^3J_{(P,H)}$ 17.6 Hz, $P(CH_2C=CH2)$), 2.46 (1H, dd, $^2J_{(H,H)}$ 17.0, $^2J_{(H,P)}$ 9.4 Hz, $PCH_{2\alpha}C=CR$), 2.24 (1H, dd, $^2J_{(H,H)}$ 16.9, $^2J_{(P,H)}$ 16.9 Hz, $PCH_{2\beta}C=CR$), 1.91 (3H, s, $CH_3$), 1.81 (3H, s, $CH_3$), **$^{13}$C (100MHz, $CDCl_3$)** d **(ppm)** 136.5 (s, Me*C*=CHR), 129.5 (s, $MeC=CH_2$), 119.5 (s, $C=CH_2$), 115.5 (s, C=*C*HR), 65.5 (s, $POCH_2$), 38.0 (d, $PCH_2C(Me)C=CH_2$), 37.7 (d, PCH2C(Me)=CH), 25.8, 23.8 (both s, both $CH_3$) **IR (flim)** n **($cm^{-1}$)** 1641 (C=C), 1170 (P=O**).** H**RMS (ES+): *m/z*** calc for $C_9H_{15}O_2PNa$ $[M+Na]^+$: 209.0707; found: 209.0702

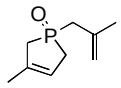
**4-methyl-2-(2-methylprop-2-en-1-yl)-2,3,6,7-tetrahydro-1,2-oxaphosphine oxide (19):**



Synthesised according to general procedure **C** from **13** (350 mg, 1.53 mmol) and Grubbs II (26 mg, 0.03 mmol) to yield **19** as a colourless oil. 266 mg (87%) $R_f$=0.2 (EtOAc:MeOH 9:1) $^1$H NMR (400MHz, $CDCl_3$) δ 5.60 (1H, m, C=C*H*), 4.95 (1H, m, $C=CH_{2trans}$), 4.82 (1H, d, $^2J_{(H,H)}$ 5.9 Hz, $C=CH_{2cis}$), 4.38 (1H, m, $POCH_{2a}$), 4.00 (1H, m, $POCH_{2b}$), 2.80(1H, t, dd $^3J_{(H,H)}$ 13.4 $^3J_{(H,H)}$ 13.1 Hz, $POCH_2CH_{2a}$), 2.56 (4H, m, $PCH_{2a}$=CH, $POCH_2C=CH_2$, $POCH_2CH_{2b}$), 2.32 (1H, m, $PCH_{2b}C=CH$), 1.88 (3H, s, *Me*C=$CH_2$), 1.82 (3H, s, *Me*C=CH), **$^{13}$C NMR (100MHz, $CDCl_3$)** d **(ppm)** 136.8 (d, $^3J_{(C,P)}$ 9 Hz, CH=*C*Me), 131.1 (d, $^3J_{(C,P)}$ 10 Hz, $CH_2$=*C*Me), 124.3 ( d, $^4J_{(C,P)}$ 7 Hz, C=*C*H), 115.4 (d, $^4J_{(C,P)}$ 11 Hz, C=*C*$H_2$) , 65 (d, $^2J_{(C,P)}$ 6 Hz, POCH2), 39.7 (d, $^1J_{(C,P)}$ 91 Hz, $PCH_2C=CH$), 33.0 (d, $^1J_{(C,P)}$ 81 Hz, $PCH_2C=CH_2$), 30.3 (s, $POCH_2CH_2$), 27.6

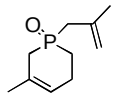
(d, $^{3}J_{(C,P)}$ 7 Hz, $CH_3C$=CH), 23.9 (s, $CH_3C$=$CH_2$), **$^{31}$P NMR (161, $CDCl_3$)** d 44.4 ppm, , **IR (film):** *n* (**cm$^{-1}$**) 1645 (C=C), 1223 cm$^{-1}$ (P=O) H**RMS (ES+):** ***m/z*** calc for $C_{10}H_{18}O_2P$ $[M+H]^+$: 201.1044; found: 201.1040. Enantiomers separated by chiral GC using a β–dex column at 120$^{o}$C and 20psi. Retention times: 170. 8mins and 172.9mins 96% ee. $[\alpha_D]^{22.5}$ = -47.467$^{o}$, $Ci_{22.5}$ = 0.75g/100ml

**4-methyl-2-(2-methylprop-2-en-1-yl)-2,3-dihydro-1,2-oxaphosphole 2-oxide (25):**



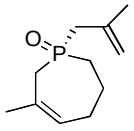
Synthesised according to gerneral procedure **C** from **22** (450 mg, 2.27 mmol) and Grubbs II (39 mg, 0.05 mmol. Purification by flash chromatography (EtOAc) afforded **26** as a brown oil. Yield: 300mg (78%); $R_f$ 0.2 (EtOAc/MeOH 19:1); **$^{1}$H NMR (400 MHz, $CDCl_3$):** d (**ppm)** 5.42 (1H, d, $^{3}J_{(H,P)}$ 29.9 Hz, $PCH_2CH$), 4.92 ( 1H, m, C=C$H_A$$CH_B$), 4.76 (1H m, C=$CH_A$$H_B$), 2.62 (2H, d, $^{2}J_{(H,P)}$ 14.2 Hz, $PCH_2$CMe=$CH_2$), 2.49-2.52 (2H, m, $PCH_2$CH), 2.40-2.44 (2H, m, $PCH_2$CMe=CH), 1.88 (3H, s, C($CH_3$)=$CH_2$), 1.73 (3H, s, C($CH_3$)=CH); **$^{13}$C NMR (101 MHz, $CDCl_3$)** d **(ppm)** δ 137.4 (d, $^{2}J_{(C,P)}$ 9.5 Hz, $PCH_2C$Me=$CH_2$), 136.7 (d, $^{2}J_{(C,P)}$ 12.9 Hz, $C$Me=CH), 120.6 (d, $^{2}J_{(C,P)}$ 8.3 Hz, $PCH_2CH$), 115.0 (d, $^{3}J_{(C,P)}$ 9.6 Hz, =$CH_2$), 39.3 (d, $^{1}J_{(C,P)}$ 58.0 Hz, $PCH_2$CMe=$CH_2$), 34.7 (d, $^{1}J_{(C,P)}$ 66.5 Hz, $PCH_2$CMe=CH), 31.8 (d, $^{1}J_{(C,P)}$ 63.5 Hz, $PCH_2$CH), 24.1 (d, $^{3}J_{(C,P)}$ 2.1 Hz, C($CH_3$)=$CH_2$), 20.2 ppm (d, $^{3}J_{(C,P)}$ 10.5 Hz, C($CH_3$)=CH); **$^{31}$P NMR (162 MHz, $CDCl_3$)** d δ 67.3 ppm; **IR (film): *?* (cm$^{-1}$)** 1644 (C=C), 1174 (P=O); HRMS (ES): *m/z* calcd for $C_9H_{16}OP$ $[M+H]^+$: 171.0939; found: 171.0935. Enantiomers separated by chiral GC using a β-dex column at 15psi and 140$^{o}$C. Retention times: 44.8min and 47.7.0 min 74%ee.

**5-methyl-1-(2-methylprop-2-en-1-yl)-1,2,3,6-tetrahydrophosphine oxide (26):**



Synthesised according to general procedure **C** from **23** (100 mg, 0.47 mmol) and Grubbs II (8 mg, 0.009 mmol). Purification by flash chromatography (EtOAc:MeOH 9:1) to yield **27** as a dark brown oil (70 mg) Yield (81%) **$^{1}$H NMR (400MHz, $CDCl_3$)** d **(ppm)** 5.42 (1H, s, C=C*H*), 4.97 (1H, m, C=C$H_{2trans}$), 4.76 (1H, d, $^{2}J_{(H,H)}$ 4.2 Hz, C=C$H_{2cis}$), 2.59 (3H, m, PC$H_2$C=$CH_2$, PC$H_{2a}CH_2$), 2.41 (3H, m, PC$H_2$C=CH, PC$H_{2b}CH_2$), 1.92 (5H, m, $PCH_2CH_2$, $PCH_2C$*Me*=$CH_2$), 1.75 (3H, s, $PCH_2C$*Me*=CH) **$^{13}$C (100MHz, $CDCl_3$)** d **(ppm)** 136.5 (s, Me*C*=CHR), 129.5 (s, Me*C*=$CH_2$), 121.7 (d, $^{3}J_{(C,P)}$ 14 Hz, $PCH_2C$=*C*$H_2$), 115.1 (d, $^{3}J_{(C,P)}$ 10 Hz, $PCH_2C$=*C*$H_2$), 36.9 (d, $^{1}J_{(C,P)}$ 63 Hz, P*C*$H_2C$=$CH_2$), 29.9 (d, $^{1}J_{(C,P)}$ 63 Hz, P*C*$H_2C$=CH), 26.0 (d, $^{3}J_{(C,P)}$ 10 Hz, $PCH_2C$*Me*=CH) 24.4 (s, PCH2C*Me*=$CH_2$), 23.4 (d, $^{2}J_{(C,P)}$ 5 Hz, $PCH_2$*C*$H_2$), 21.3 (d, $^{1}J_{(C,P)}$ 63 Hz, P*C*$H_2CH_2$) **$^{31}$P NMR (161MHz, $CDCl_3$)** d 38.5 ppm. **IR (film): *?* ($cm^{-1}$)** 1644 (C=C), 1186 (P=O) H**RMS (ES+): *m/z*** calc for $C_{10}H_{18}OP$ $[M+H]^+$: 185.1095; found: 185.1093 Enatiomers separated by chiral GC using a β-dex column at 120$^{o}$C and 20psi. Retention times: 194.9mins and 216.2mins 74%ee.

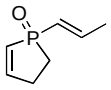
**6-methyl-(1,2-methylprop-2-en-1-yl)-2,3,4,7-tetrahydro-1Hphosphepine 1-oxide (27)**



Synthesised according to general procedure **C** from **24** (175 mg, 0.77 mmol) and Grubbs II (15 mg, 0.015 mmol). Purification by flash chromatography (EtOAc:MeOH 9:1) to yield **28** as a dark brown solid mpt: 68-70$^{o}$C (137 mg, 80%) **$^{1}$H NMR**

**(400Mhz, $CDCl_3$)** d (**ppm)** 5.66 (1H, dd, $^3J_{(H,H)}$ 6.5, 6.5 Hz, C=C*H*), 4.94 (1H, m, C=C$H_{2a}$), 4.76 (1H, d, $^2J_{(H,H)}$ 4.5 Hz, C=C$H_{2b}$), 2.84 (1H, dd, $^3J_{(H,H)}$ 19, 15 Hz, PC$H_2$C=CHC$H_{2a}$), 2.62 (1H, dd, $^3J_{(H,H)}$ 14, 11 Hz, PC$H_2$C=CHC$H_{2b}$), 2.50 (2H, m, PC$H_2$C=C$H_2$), 2.10 (4H, m, PC$H_2$CMe=CH, PC$H_2$C$H_2$), 1.90 (4H, m, PC$H_2$C*Me*=CH2, PC$H_{2a}$C$H_2$), 1.77 (3H, s, PC$H_2$C*Me*=CH), 1.64 (1H, m, PC$H_{2a}$C$H_{2b}$) **$^{13}$C (100MHz, $CDCl_3$)** d **(ppm)** 137.5 (d, $^2J_{(P,C)}$ 10 Hz, Me*C*=CHR), 130.0 (d, $^2J_{(P,C)}$ 7 Hz, Me*C*=C$H_2$), 121.7 (d, $^3J_{(C,P)}$ 14 Hz, PC$H_2$C=*C*$H_2$), 127.9 (d, $^3J_{(C,P)}$ 7 Hz, PC$H_2$C=*C*HR), 115.9 (d, $^3J_{(C,P)}$ 10 Hz, PC$H_2$C=*C*$H_2$), 37.2 (d, $^1J_{(C,P)}$ 65 Hz, P*C*$H_2$C=CH), 35.0 (d, $^1J_{(C,P)}$ 58 Hz, P*C*$H_2$C$H_2$) 32.2 (d, $^1J_{(C,P)}$ 65 Hz P*C*$H_2$CMe=C$H_2$), 27.4 (s, PC$H_2$C$H_2$*C*$H_2$), 26.3 (d, $^2J_{(C,P)}$ 14 Hz, PC$H_2$*C*$H_2$), 24.5 (d, $^3J_{(C,P)}$ 3 Hz), 22.4 (d, $^3J_{(P,C)}$ 4 Hz) **$^{31}$P NMR (161MHz, $CDCl_3$)** d 35.8ppm. **IR (film): *?* ($cm^{-1}$)** 1644 (C=C), 1174 (P=O) H**RMS (ES+): *m/z*** calc for $C_{11}H_{20}OP$ $[M+H]^+$: 199.1252; found: 199.1247 Enatiomers separated by chiral GC using a β-dex column at 140$^o$C and 15psi. Retention times: 143.6mins and 148.7mins 98%ee. $[\alpha_D]_{25}$= -3.857o, $ci_{25}$ = 0.7g / 100 ml

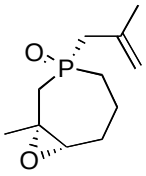
**2-[(1*E*)-prop-1-en-1-yl]-2,3-dihydro-1*H*-1,2-oxaphosphole 1-oxide (30)**



Synthesised according to general proceedure **C** from **29** (260 mg, 1.41 mmol) and Grubbs II (24 mg, 0.028 mmol) Purification by flash chromatography (EtOAc/MeOH 9:1) afforded **29** as a brown oil. Yield: 190 mg (94%); $R_f$ 0.1 (EtOAc/MeOH 9:1); **$^1$H NMR (400 MHz, $CDCl_3$):** d (**ppm)** 6.82 (1H, dddd, $^3J_{(H,P)}$ 44.5, $^3J_{(H,H)}$ 9.3, $^3J_{(H,H)}$ 2.3 Hz × 2, PCH=C*H*C$H_2$), 6.56 (1H, m, PC*H*=C*H*Me), 6.08 (ddt, $^2J_{(P,H)}$ 25.5, $^3J_{(H,H)}$ 6.8, $^3J_{(H,P)}$ 2.1 Hz; PC*H*=CHC$H_2$), 5.69 (1H, ddq, $^2J_{(P,H)}$ 27.6, $^3J_{(H,P)}$ 18.2, $^4J_{(H,H)}$ 1.6 Hz,

PC*H*=HMe), 2.70 (1H, m, $PCH_2CH_{2a}$), 2.51 (1H, m, PCH2C$H_{2b}$), 1.85 (5H, m, C$H_3$, PC$H_2$); **$^{13}$C NMR (101 MHz, $CDCl_3$):** d **(ppm)** 151.5 (d, $^2J_{(C,P)}$ 23.6 Hz, PCH=*C*HCH$_2$), 146.3 (d, $^2J_{(C,P)}$ 2.3 Hz, PC=*C*HMe), 126.1 (d, $^1J_{(C,P)}$ 95.4 Hz, P*C*H=CHCH$_2$), 124.2 (d, $^1J_{(C,P)}$ 95.3 Hz, P*C*H=CHMe), 29.5 ppm (d, $^2J_{(C,P)}$ 9.8 Hz, $PCH_2CH_2$) 124.1 (d, $^1J_{(C,P)}$ 73.2Hz), 20.1 (d, $^3J_{(C,P)}$ 18.3 Hz); **$^{31}$P NMR (162 MHz, $CDCl_3$):** d 57.6 ppm; **IR (neat):** *n* (**cm$^{-1}$**)1633 (C=C), 1165 (P=O); **HRMS (ES+):** ***m/z*** calcd for $C_7H_{11}OPNa$ $[M+H]^+$: 165.0445; found: 165.0440.

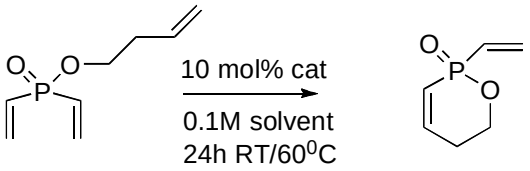
**(1S,3R,7S)-1-methyl-3-(2-methylprop-2-en-1-yl)-8-oxa-3-phosphabicyclo [5.1.0] octane 3-oxide (28)**




An 0.1M solution of **27** (100 mg, 0.5 mmol) in DCM (5 mL) was cooled to 0$^o$C and *m*CPBA (174 mg, 0.5 mmol) added and reaction allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 2h after which TLC analysis showed almost complete consumption of starting material. The mixture was then quenched with $NaHSO_4$ (1M, 10ml), extracted with DCM and washed with $NaHCO_3$ and dried over NaSO4 and concentrated *in vacuo*. $^{31}$P NMR analysis of the curde mixture showed an 6:1 dr. The mixture was purified by chromatography (9:1, EtOAc:MeOH) to yield **30** a white solid, mpt: 72-74$^o$C Yield 70 mg (66%) $^1$H NMR assignment for the major *trans* diastereomer: **$^1$H NMR (400MHz, $CDCl_3$)** d **(ppm)** 4.95 (1H, ddd, $^3J_{(H,H)}$ 4, $^4J_{(H,H)}$ 2, $^4J_{(P,H)}$ 2 Hz C=C$H_{2trans}$), 4.77 (2H, m, C=C$H_{2cis}$), 2.96 (1H, dd, $^3J_{(H,H)}$ 8, 6 Hz, MeCOC*H*), 2.45 (2H, m, PC$H_{2a}$C=$CH_2$ ,

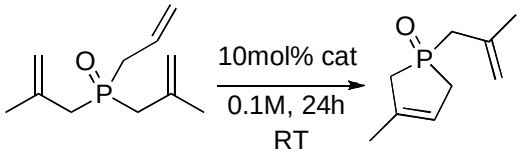
$PCH_2CH_2CH_{2b}$) 2.14 (1H, m, $PCH_2aCH_2$), 1.96 (2H, m, $PCH_2CH_{2a}$, $PCH_{2a}COC$) 1.88 (3H, m, $PCH_2CMe{=}CH_2$), 1.80 (1H, m, $PCH_{2b}COC$), 1.47 (4H, m, $PCH_2CMeOCH$, $PCH_{2b}CH_2$), 1.20 (1H, m, $PCH_2CH_2CH_{2b}$) **$^{13}$C (100MHz, $CDCl_3$)** d **(ppm)** 138.4 (d, $^2J_{(P,C)}$ 10 Hz, $PCH_2C{=}CMe$), 114.4 (d, $^3J_{(P,C)}$ 10 Hz, $MeC{=}CH_2$), 62.2 (s, $PCH_2COCH$), 56.6 (d, $^3J_{(C,P)}$ 2 Hz, $PCH_2COMe$), 40.6 (d, $^1J_{(C,P)}$ 61 Hz, $PCH_2C{=}CH_2$), 34.9 (d, $^1J_{(C,P)}$ 58 Hz, $PCH_2COCH$), 31.9 (d, $^1J_{(C,P)}$ 65 Hz, $PCH_2CH_2$) 31.4 (s, $PCH_2CH_2CH_2$), 25.6 (s, $PCH_2CCH_3O$), 24.7 (s, $=CMe$), 17.1 (d, $^2J_{(C,P)}$ 7 Hz $PCH_2CH_2$), 22.4 (d, $^3J_{(P,C)}$ 4 Hz) **$^{31}$P NMR (161MHz, $CDCl_3$)** d 41.7ppm. **IR (film): ? (cm$^{-1}$)** 1644 (C=C), 1183 (P=O) H**RMS (ES+): *m/z*** calc for $C_{11}H_{20}O_2P$ $[M+H]^+$: 215.1201; found: 215.1195 Characteristic data for the minor diastereomer: $^{31}$P NMR (161Mhz $CDCl_3$) 43.6ppm

**Substrate Screening:**




**9** **15**

| Entry | Cat | Solvent | % conv[a] | ee[b] (%) |
|---|---|---|---|---|
| 1 | **1a** | **Benzene** | **60** | **86** |
| 2 | 1a | DCM | 90 | 70 |
| 3 | 3b | Benzene | <2 | - |
| 4 | 3b | DCM | <2 | - |
| 5 | 4a | Benzene | 15 | 51 |
| 6 | 4a | DCM | 19 | 46 |
| 7 | 4b | Benezene | | |
| 8 | 4b | DCM | | |
| 9 | 1b | Benzene | 23 | 68 |
| 10 | 1b | DCM | 54 | 61 |
| 11 | 2 | Benzene | <2 | - |
| 12 | 2 | DCM | <2 | - |

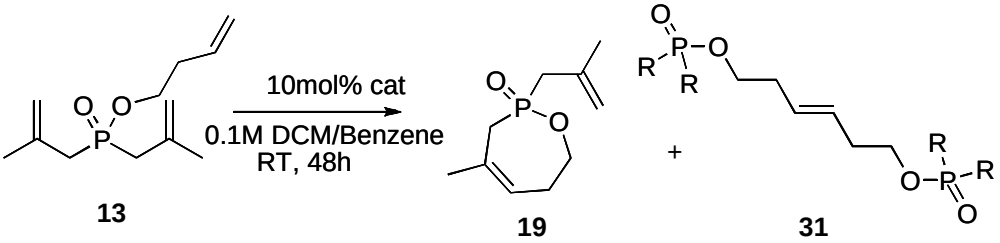



**22** **25**

| Entry | Catalyst | Solvent | Conversion[a] % | % ee[b] |
|---|---|---|---|---|
| 1 | 1a | DCM | 40 | 28 |
| 2 | 1b | DCM | 82 | 38 |
| 3 | 2 | DCM | 49 | 44 |
| 4 | 4b | DCM | 42 | 12 |
| **5** | **4a** | **DCM** | **68** | **70** |
| 6 | 3a | DCM | 28 | 42 |

| Entry | Catalyst | Solvent | Temperature | Conv % | Ee % |
|---|---|---|---|---|---|
| 1 | 4a | DCM | RT | 68 | 75 |
| 2 | 4a | Benzene | RT | 64 | 24 |

| | | | | | |
|---|---|---|---|---|---|
| 3 | 4a | THF | RT | <2% | - |
| 4 | 4a | Benzene | 60 | 70 | 27 |
| **5** | **4a** | **DCM** | **60** | **>96** | **71** |
| 6 | 4a | THF | 60 | <2% | - |



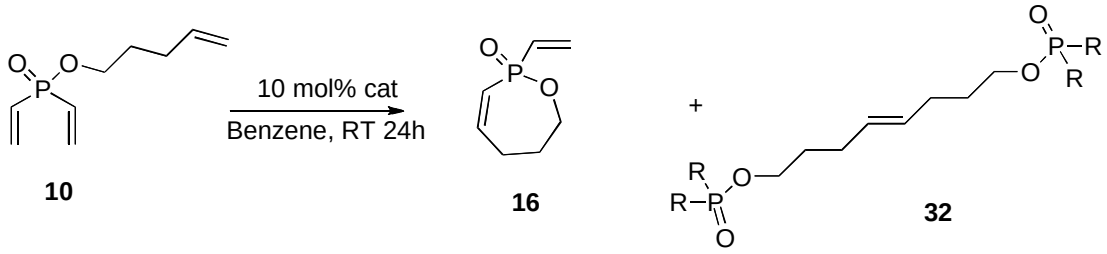

| Entry | Cat | Solvent | % conv[a] (**19**) | % conv[a] (**31**) | ee[b] (%) |
|---|---|---|---|---|---|
| 1 | 1a | **Benzene** | **33** | **26** | **83** |
| 2 | | DCM | 60 | 29 | 82 |
| 3 | 3b | Benzene | 64 | 22 | -90 |
| 4 | | **DCM** | **86** | **8** | **-93** |
| 5 | 4a | **Benzene** | **41** | **27** | **96** |
| 6 | | DCM | 32 | 29 | 91 |
| 7 | 4b | Benezene | 15 | 44 | 41 |
| 8 | | DCM | 37 | 33 | 12 |
| 9 | 1b | Benzene | 33 | 32 | 73 |
| 10 | | DCM | 54 | 23 | 73 |
| 11 | 2 | **Benzene** | **30** | **36** | **-91** |
| 12 | | DCM | 17 | 25 | -50 |

| Entry | Catalyst | Solvent | T/oC | % Conv[a](**P**) | % ee[b] |
|---|---|---|---|---|---|
| 1a | 1a | Benzene | RT | 35 | 83 |
| 2a | 1a | DCM | RT | 65 | 82 |
| 3a | 1a | THF | RT | 35 | 68 |
| 4a | 1a | Benzene | 60 | 57 | 78 |
| **5a** | **1a** | **DCM** | **60** | **70** | **82** |
| 6a | 1a | THF | 60 | 30 | 68 |

| | | | | | |
|---|---|---|---|---|---|
| 1b | 4a | Benzene | RT | 51 | 95 |
| 2b | 4a | DCM | RT | 36 | 91 |
| 3b | 4a | THF | RT | 19 | 95 |
| **4b** | **4a** | **Benzene** | **60** | **81** | **96** |
| 5b | 4a | DCM | 60 | 67 | 79 |
| 6b | 4a | THF | 60 | 48 | 90 |

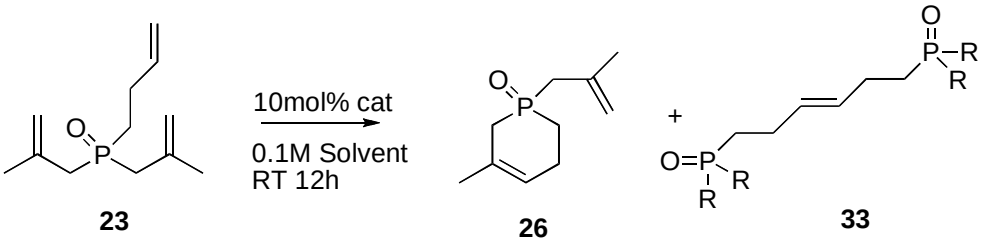
| | | | | | |
|---|---|---|---|---|---|
| **1c** | **2** | **Benzene** | **RT** | **43** | **-93** |

| | | | | | |
|---|---|---|---|---|---|
| 2c | 2 | DCM | RT | 25 | -78 |
| 3c | 2 | THF | RT | 17 | -17 |
| **4c** | **2** | **Benzene** | **60** | **70** | **-81** |
| 5c | 2 | DCM | 60 | 38 | -39 |
| 6c | 2 | THF | 60 | 25 | -9 |



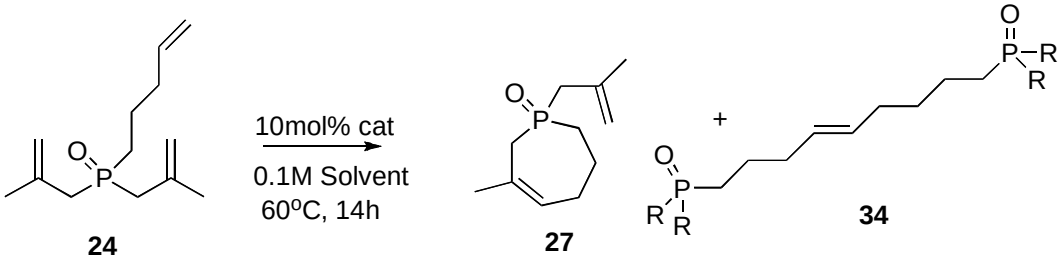

**10** **16** **32**

| Entry | Catalyst | Temperature | Conv. (**16**) % | % Conv. (**32**) | Ee % |
|---|---|---|---|---|---|
| **1** | **4a** | **RT** | **48** | **22** | **73** |
| 2 | 4a | 60 | 49 | 24 | 63 |
| 3 | 2 | RT | <2% | <2 | - |
| 4 | 2 | 60 | <2% | 8 | - |
| 5 | 1a | RT | 23% | 18 | 43 |
| 6 | 1a | 60 | 25% | 23 | 41 |

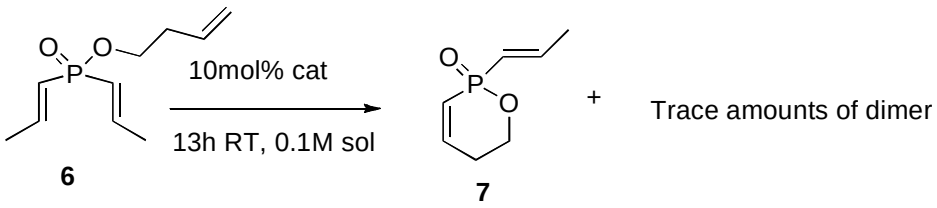



**23** **26** **33**

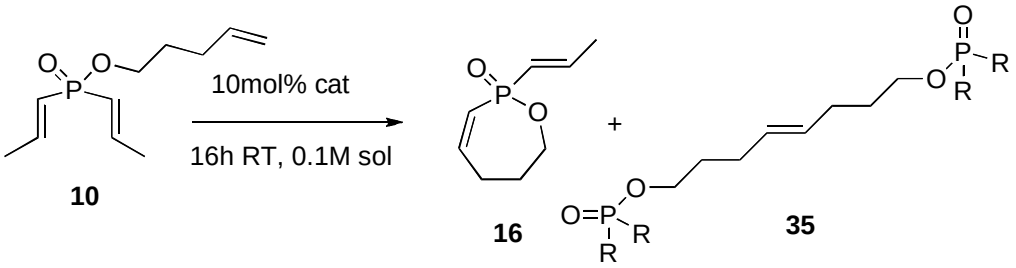
| Entry | Catalyst | Solvent | % Conv (**26**). | % Conv. (**33**) | % ee |
|---|---|---|---|---|---|
| 1 | 1a | Benzene | 52 | 26 | -20 |
| 2 | 1a | DCM | 84 | 11 | -65 |
| 3 | 4a | Benzene | 53 | 23 | 73 |
| 4 | 4a | DCM | 88 | - | 69 |
| 5 | 2 | Benzene | 67 | 22 | 73 |
| 6 | 2 | DCM | >95 | - | 69 |
| 7 | 3b | Benzene | 48 | 20 | 38 |
| **8** | **3b** | **DCM** | **84** | **12** | **74** |
| 9 | 3a | Benzene | 86 | 13 | 4 |
| 10 | 3a | DCM | 91 | 5 | 43 |



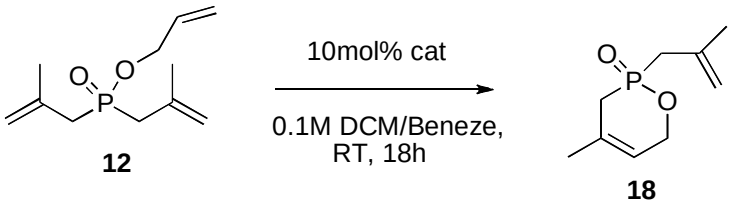

| Entry | Catalyst | Solvent | %Conv (**27**). | %Conv. (**34**) | % ee |
|---|---|---|---|---|---|
| 1 | 1a | Benzene | 45 | 36 | 91 |
| 2 | 1a | DCM | 61 | 22 | 88 |
| **3** | **4a** | **Benzene** | **49** | **34** | **98** |
| 4 | 4a | DCM | 32 | 47 | 97 |
| 5 | (*R*)-2 | Benzene | 50 | 42 | 73 |
| 6 | (*R*)-2 | DCM | 55 | 31 | 39 |
| 7 | 3b | Benzene | 43 | 41 | -89 |
| **8** | **3b** | **DCM** | **81** | **10** | **-91** |
| 9 | 3a | Benzene | 82 | 16 | -23 |
| 10 | 3a | DCM | 86 | 12 | -73 |



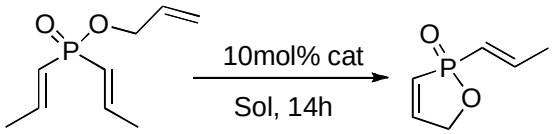

| Entry | Catalyst | Solvent | % Conv(**7**). | % ee |
|---|---|---|---|---|
| 1 | 1a | Benzene | <2 | - |
| 2 | 1a | DCM | <2 | - |
| 3 | 1b | Benzene | 45 | 51 |
| **4** | **1b** | **DCM** | **63** | **60** |
| 5 | 4a | Benzene | 51 | 16 |
| 6 | 4a | DCM | 65 | 11 |
| 7 | 2 | Benzene | 15 | 22 |
| 8 | 2 | DCM | 49 | 11 |
| 9 | 3b | Benzene | <2 | - |
| 10 | 3b | DCM | <2 | - |
| 11 | 3a | Benzene | 38 | 60 |
| 12 | 3a | DCM | 32 | 53 |




| Entry | Catalyst | Solvent | % Conv. (**16**) | % Conv. (**35**) | % ee |
|---|---|---|---|---|---|
| 1 | 1a | Benzene | <2 | <2 | - |
| 2 | 1a | DCM | <2 | 18 | - |
| **3** | **1b** | **Benzene** | **32** | **17** | **27** |
| 4 | 1b | DCM | 40 | 19 | 12 |
| 5 | 4a | Benzene | <2 | 19 | - |
| 6 | 4a | DCM | <2 | 26 | - |
| 7 | 2 | Benzene | <2 | 10 | - |
| 8 | 2 | DCM | <2 | 23 | - |
| 9 | 3b | Benzene | <2 | <2 | - |
| 10 | 3b | DCM | <2 | 11 | - |
| 11 | 3b | Benzene | <2 | 9 | - |
| 12 | 3b | DCM | 12 | 9 | - |

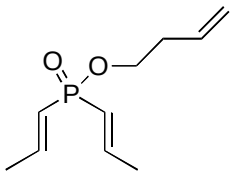



| Catalyst | Solvent | Conversion (%) |
|---|---|---|
| 1a | Benzene | <2% |
| | DCM | <2% |
| 3a | Benzene | <2% |
| | DCM | <2% |
| 4a | Benzene | <2% |
| | DCM | <2% |
| 4b | Benzene | <2% |
| | DCM | <2% |
| 1b | Benzene | <2% |
| | DCM | <2% |
| 2 | Benzene | <2% |
| 2 | THF | <2% |



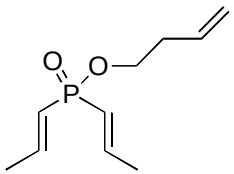

**8** **14**

| Catalyst | Solvent | Conversion (%) |
|---|---|---|
| 1b | Benzene | <2% |
| | DCM | <2% |
| 3a | Benzene | <2% |
| | DCM | <2% |
| 4a | Benzene | <2% |
| | DCM | <2% |
| 4b | Benzene | <2% |
| | DCM | <2% |
| 1b | Benzene | <2% |
| | DCM | <2% |
| 2 | Benzene | <2% |
| 2 | DCM | <2% |



**6**

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.



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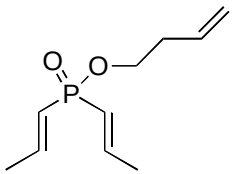

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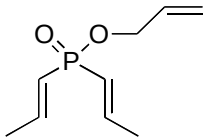

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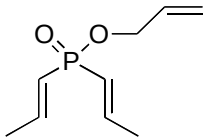

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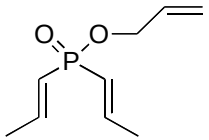

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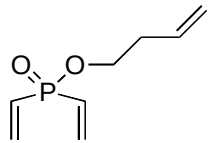

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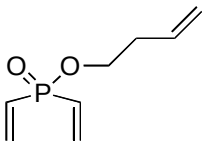

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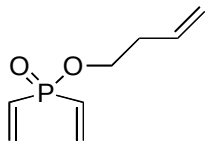

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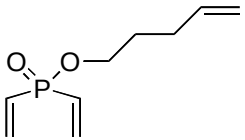

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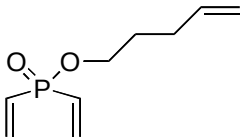

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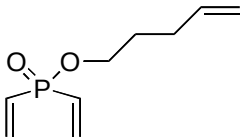

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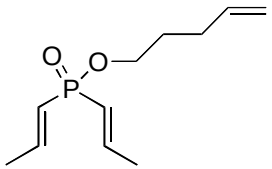

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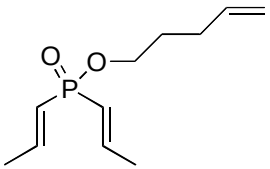

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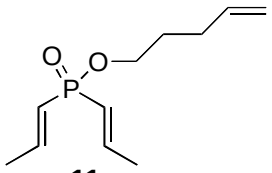

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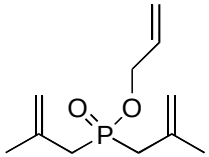


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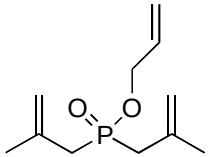

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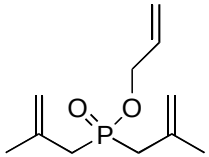

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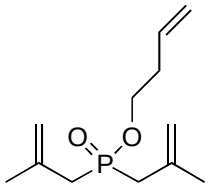

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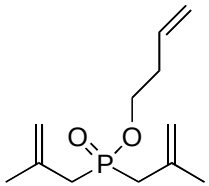


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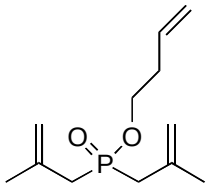

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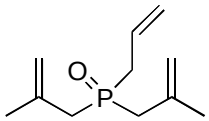


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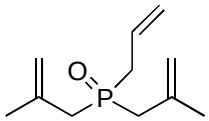


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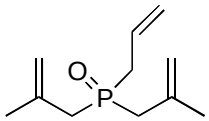


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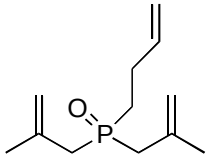


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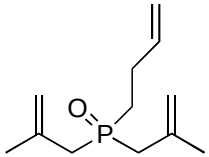


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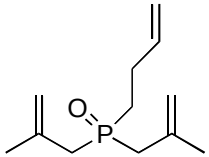


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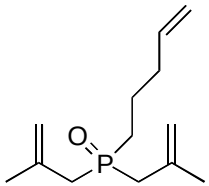


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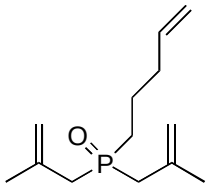


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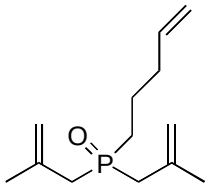


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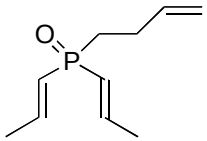

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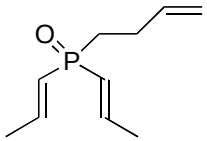

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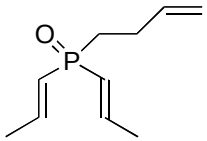

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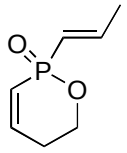


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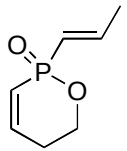


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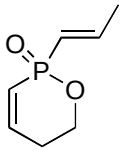


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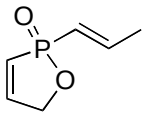

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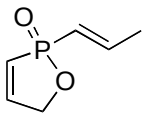


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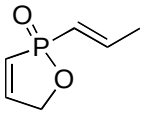


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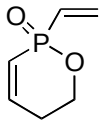
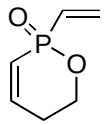
TIFF (Uncompressed) decompressor
are needed to see this picture.



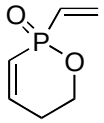

**15**

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.



**15**

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.




**15**

QuickTime™ and a
TIFF (Uncompressed) decompressor
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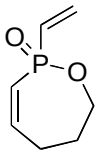


**16**

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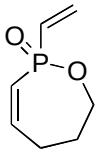


**16**

QuickTime™ and a
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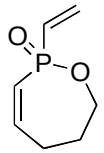


**16**

QuickTime™ and a
TIFF (Uncompressed) decompressor
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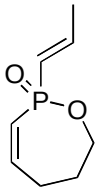


**17**

QuickTime™ and a
TIFF (Uncompressed) decompressor
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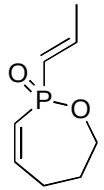


**17**

QuickTime™ and a
TIFF (Uncompressed) decompressor
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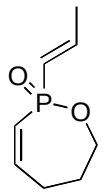


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TIFF (Uncompressed) decompressor
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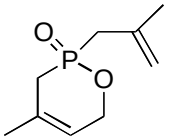


**18**

QuickTime™ and a
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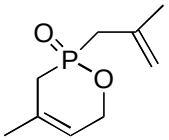


**18**

QuickTime™ and a
TIFF (Uncompressed) decompressor
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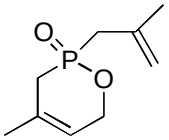


**18**

QuickTime™ and a
TIFF (Uncompressed) decompressor
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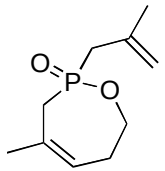


**19**

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TIFF (Uncompressed) decompressor
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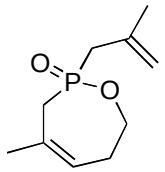

**19**

QuickTime™ and a
TIFF (Uncompressed) decompressor
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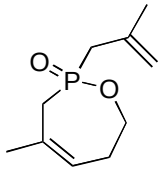


**19**

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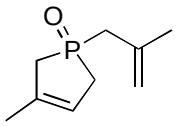


**25**

QuickTime™ and a
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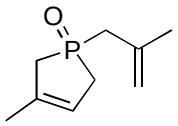


**25**

QuickTime™ and a
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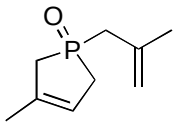

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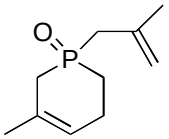


**26**

QuickTime™ and a
TIFF (Uncompressed) decompressor
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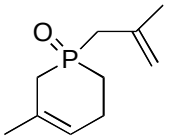
=



**26**

QuickTime™ and a
TIFF (Uncompressed) decompressor
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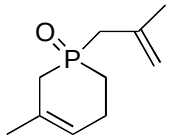

**26**

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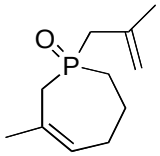


**27**

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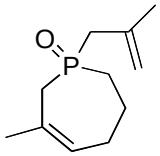
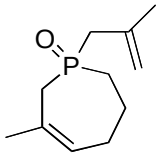



**27**

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.




**27**

QuickTime™ and a
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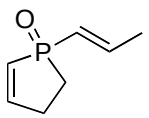

**30**

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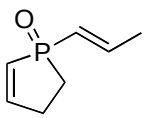


**30**

QuickTime™ and a
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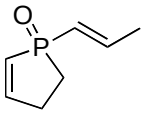


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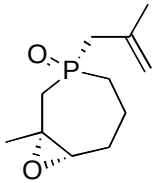


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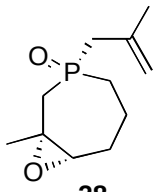

**28**

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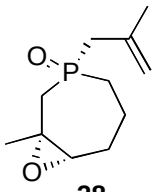


**28**

QuickTime™ and a
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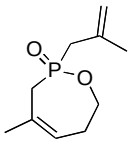
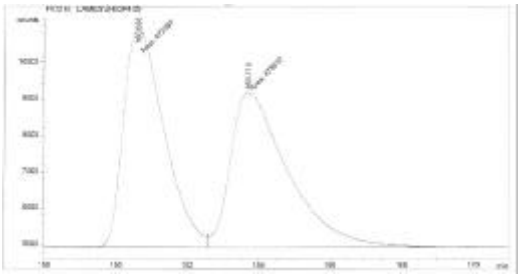
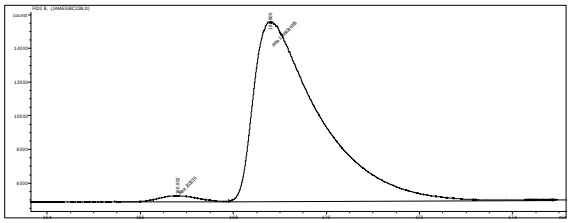
Chiral GC traces:

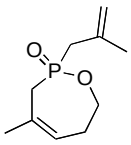


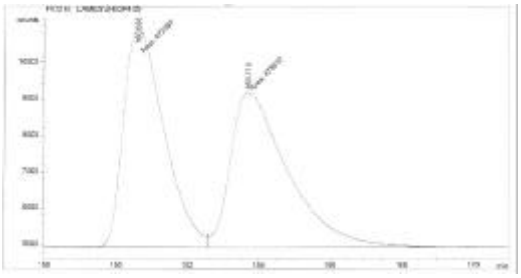


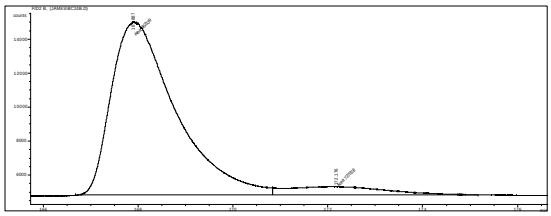


| Peak | Time/min | %Area |
|---|---|---|
| 1 | 160.635 | 49.67 |
| 2 | 163.710 | 50.32 |

| Peak | Time/min | %Area |
|---|---|---|
| 1 | 166.753 | 2.34 |
| 2 | 168.806 | 97.65 |

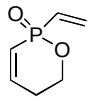


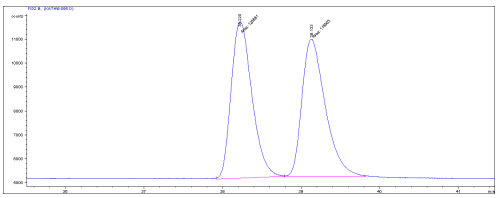


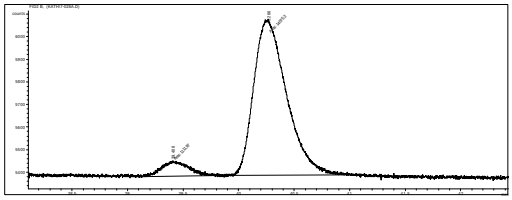


| Peak | Time/min | %Area |
|---|---|---|
| 1 | 160.635 | 49.67 |
| 2 | 163.710 | 50.32 |

| Peak | Time/min | %Area |
|---|---|---|
| 1 | 167.887 | 96.27 |
| 2 | 172.287 | 3.73 |

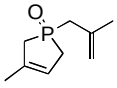


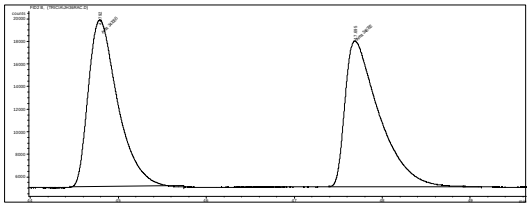


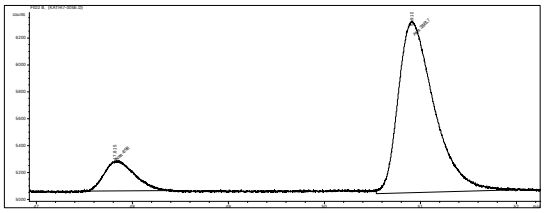


| Peak | Time/min | %Area |
|---|---|---|
| 1 | 38.22 | 50.41 |
| 2 | 39.133 | 49.59 |

| Peak | Time/min | %Area |
|---|---|---|
| 1 | 39.408 | 7.32 |
| 2 | 40.266 | 92.68 |

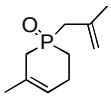


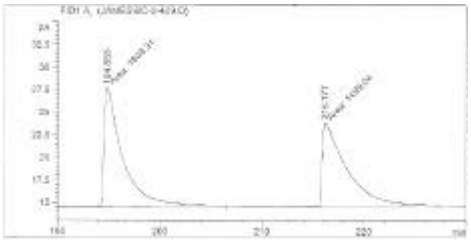


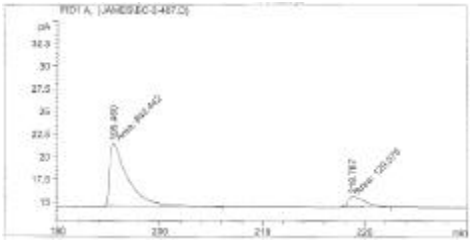


| Peak | Time/min | %Area |
|---|---|---|
| 1 | 44.792 | 49.58 |
| 2 | 47.695 | 50.52 |

| Peak | Time/min | %Area |
|---|---|---|
| 1 | 47.815 | 12.69 |
| 2 | 50.91 | 87.30 |

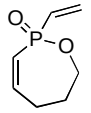


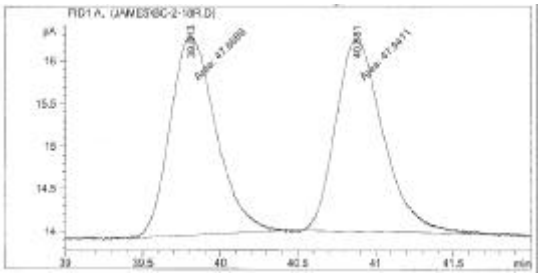


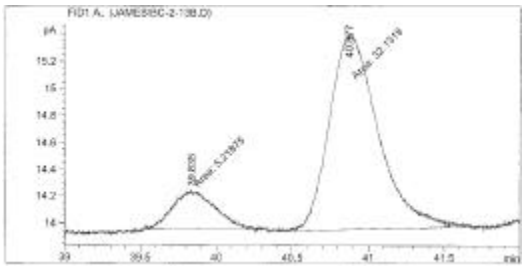


| Peak | Time/min | %Area |
|---|---|---|
| 1 | 194.856 | 52.38 |
| 2 | 216.177 | 47.61 |

| Peak | Time/min | %Area |
|---|---|---|
| 1 | 195.460 | 86.67 |
| 2 | 218.787 | 13.33 |

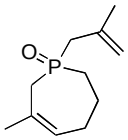


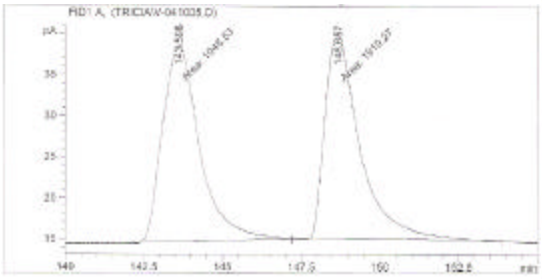


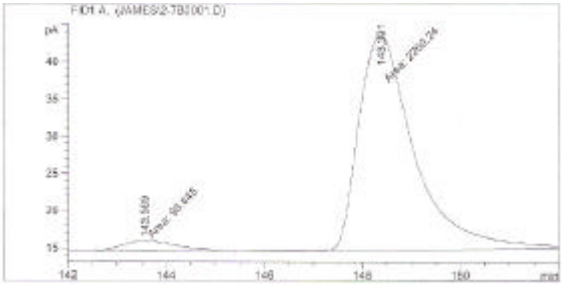


| Peak | Time/min | %Area |
|---|---|---|
| 1 | 39.813 | 49.96 |
| 2 | 40.881 | 50.03 |

| Peak | Time/min | %Area |
|---|---|---|
| 1 | 39.835 | 13.97 |
| 2 | 40.877 | 86.03 |

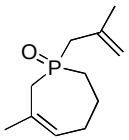


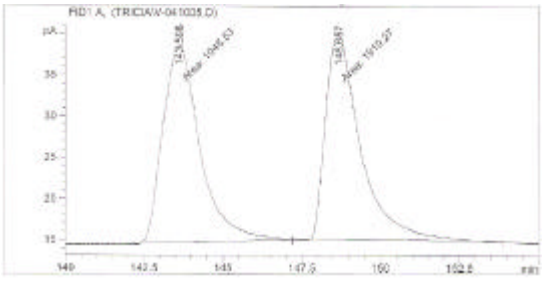


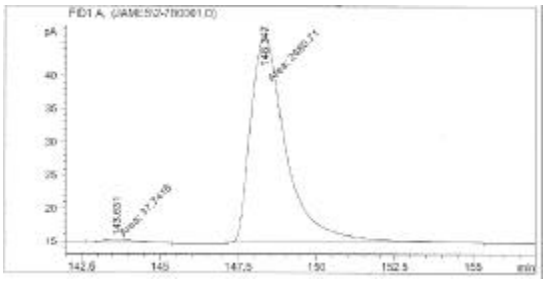


| Peak | Time/min | %Area |
|---|---|---|
| 1 | 143.598 | 50.37 |
| 2 | 148.657 | 49.62 |

| Peak | Time/min | %Area |
|---|---|---|
| 1 | 143.569 | 4.18 |
| 2 | 148.391 | 95.81 |







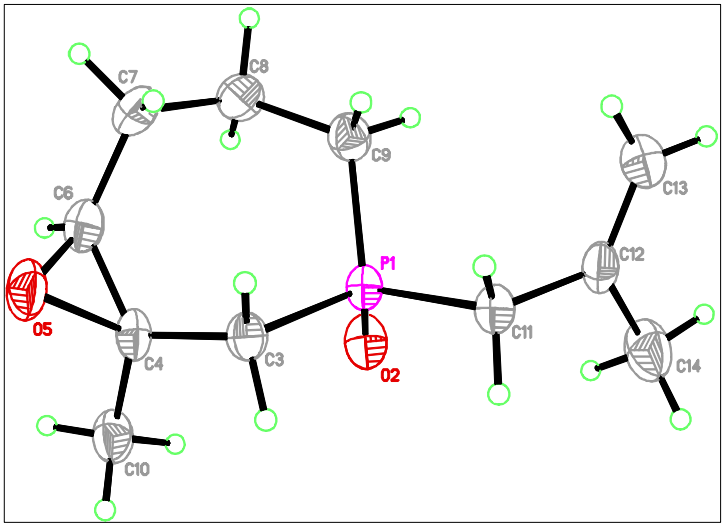
| Peak | Time/min | %Area |
|---|---|---|
| 1 | 143.598 | 50.37 |
| 2 | 148.657 | 49.62 |

| Peak | Time/min | %Area |
|---|---|---|
| 1 | 143.631 | 1.49 |
| 2 | 148.347 | 98.51 |

X-ray Single Crystal Diffraction Data:

Crystals of **28** were grown by slow evaporation of diethyl ether at room temperature. The crystals were generally hexagonal plates and split on cutting along the 010 face causing severe damage and loss of crystallinity. So, plate was chosen and cut to give a large needle shaped sample and changes in illuminated volume were taken into account[1] by the multi-scan inter-frame scaling.[2] Single crystal X-ray diffraction data were collected using graphite monochromated Mo Ka radiation (? = 0.71073 Å) on an Enraf-Nonius KappaCCD diffractometer. The diffractometer was equipped with a Cryostream N2 open-flow cooling device,[3] and the data were collected at 200(2) K. Series of ? -scans were performed in such a way as to cover a sphere of data to a maximum resolution of 0.77 Å. Cell parameters and intensity data were processed using the DENZO-SMN package.[2] The structures were solved by direct methods[4] and refined by full-matrix least squares on F using the CRYSTALS suite.[5] Intensities were corrected for absorption effects by the multi-scan method, based on multiple scans of identical and Laue equivalent reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. In general, the hydrogen atoms were visible in a difference map. However, they were repositioned geometrically, then refined with soft restraints on the bond lengths and angles to regularise their geometry after which the positions were refined with riding constraints. The Flack *x* parameter[6] was refined to a value of -0.08(6) and examination of the Bijvoet pairs gave the Hooft *y* parameter[7] as -0.06(3) with G=1.12(6) (giving a probability that the absolute configuration is correct as 100%).

Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge from http://www.ccdc.cam.ac.uk/products/csd/request/ (CCDC ??????).

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[2] Otwinowski, Z; Minor W. Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol. **1997**, 276, Eds C. W. Carter, R. M. Sweet, Academic Press.
[3] Cosier, J; Glazer, A. M. *J. Appl. Cryst.*, **1986**, *19*, 105.
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[5] Betteridge, P.W.; Carruthers, J.R.;Cooper, R.I.; Prout, K; Watkin, D.J; J. Appl. Cryst., **2003**, *36*, 1487.
[6] Flack, H. D., *Acta Cryst.* **1983**, *A39*, 876-881; Flack, H. D. & Bernardinelli, G., *J. Appl. Cryst.*, **2000**, *33*, 1143-1148.
[7] R. W. W. Hooft, L. H. Straver, & A. L. Spek, *J. Appl. Cryst.*, **2008**, *41*, 96-103.

Table 1. Crystal data and structure refinement for **28**.

| | | |
|---|---|---|
| Identification code | 5969 | |
| Empirical formula | C11 H19 O2 P1 | |
| Formula weight | 214.24 | |
| Temperature | 150 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P 1 21 1 | |
| Unit cell dimensions | a = 10.4548(2) Å | α= 90°. |
| | b = 5.39910(10) Å | β= 109.8377(9)°. |
| | c = 10.8511(3) Å | γ = 90°. |
| Volume | 576.16(2) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.235 $Mg/m^3$ | |
| Absorption coefficient | 0.213 $mm^{-1}$ | |
| F(000) | 232 | |
| Crystal size | 0.80 x 0.29 x 0.24 $mm^3$ | |
| Theta range for data collection | 5.177 to 27.479°. | |
| Index ranges | -13<=h<=13, -6<=k<=7, -14<=l<=13 | |
| Reflections collected | 7557 | |
| Independent reflections | 2523 [R(int) = 0.026] | |
| Completeness to theta = 27.479° | 98.8 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.95 and 0.71 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2440 / 1 / 128 | |
| Goodness-of-fit on $F^2$ | 1.1118 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0260, wR2 = 0.0269 | |
| R indices (all data) | R1 = 0.0274, wR2 = 0.0288 | |
| Absolute structure parameter | -0.08(6) | |
| Largest diff. peak and hole | 0.20 and -0.15 $e.Å^{-3}$ | |