Desymmetrization of *Meso*-Bisphosphates Using Copper Catalysis and Alkylzirconocene Nucleophiles

Reece Jacques, Robert D. C. Pullin and Stephen P. Fletcher*

*Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, OX1 3TA, UK.*
Supplementary Information

Contents

Supplementary Table 1 - Dialkylphosphate Optimisation Table S1

General Information S2

Chemicals S3

Supplementary Methods S4

General procedure 1a: Racemic allylic alkylation products S4

General procedure 1b: Asymmetric allylic alkylation products S5

General procedure 1c: Asymmetric allylic alkylation products with quaternary centers S6

General procedure 2: Phosphate reduction and esterification for HPLC analysis S7

General procedure 3: Oxidation of diones S8

General procedure 4: Luche reduction of dienones S8

General procedure 5: Phosphorylation of diols via anion approach S9

Experimental Procedures and Characterisation of Compounds S10

Starting Materials S10

Cis-4-cyclopentene-1,3-diol S10

Cis-5-cyclopentene-1,4-diol S11

Cis-6-cyclopentene-1,5-diol S12

Meso-4-cyclopentene-1,3-bisdimethylphosphate S13

Meso-4-Cyclopentene-1,3-bisdiethylphosphate (1a) S13
Meso-4-Cyclopentene-1,3-bisdiisopropylphosphate S14
Meso-4-Cyclopentene-1,3-bisdiphenylphosphate S15
Meso-5-Cyclohexene-1,4-bisdiethylphosphate (2a) S16
Meso-6-Cycloheptene-1,5-bisdiethylphosphate (3a) S17
(1S,3S)-Cyclopent-4-ene-1,3-diy1 tetraethyl bis(phosphate) (13) S18
2,2-Dimethylcyclopentane-1,3-dione S21
2- Allyl-2-methylcyclopentane-1,3-dione S22
2- Benzyl-2-methylcyclopentane-1,3-dione S19
2- (2-Chlorobenzyl)-2-methylcyclopentane-1,3-dione S23
2-((Benzyloxy)methyl)-2-methylcyclopentane-1,3-dione S23
2',3'-Dihydrospiro[cyclopentane-1,1'-indene]-2,5-dione S24
Spiro[chromane-4,1'-cyclopentane]-2',5'-dione S25
2,2-Dimethylcyclopent-4-ene-1,3-dione S25
2- Allyl-2-methylcyclopent-4-ene-1,3-dione S26
2- Benzyl-2-methylcyclopent-4-ene-1,3-dione S26
2- (2-Chlorobenzyl)-2-methylcyclopent-4-ene-1,3-dione S27
2-((Benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-dione S27
2',3'-Dihydrospiro[cyclopent-4-ene-1,1'-indene]-2,5-dione S28
Spiro[chromane-4,1’-cyclopent-4-ene]-2’,5’-dione S28
(1R,2S,3S)-2-Benzyl-2-methylcyclopent-4-ene-1,3-diol S29
Cis-2,2-dimethylcyclopent-4-ene-1,3-diol S30

Siii
(1R,2S,3S)-2-Allyl-2-methylcyclopent-4-ene-1,3-diol

(1R,2S,3S)-2-(2-Chlorobenzyl)-2-methylcyclopent-4-ene-1,3-diol

(1R,2S,3S)-2-((Benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-diol

(1S,2R,5S)-2',3'-Dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-diol

(2'R,4S,5'S)-Spiro[chromane-4,1'-cyclopentan]-3'-ene-2',5'-diol

(1R,2S,3S)-2-Benzyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (4a)

Cis-2,2-dimethylcyclopent-4-ene-1,3-bis(diethyl phosphate) (5a)

(1R,2S,3S)-2-Allyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (6a)

(1R,2S,3S)-2-(2-Chlorobenzyl)-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (7a)

(1R,2S,3S)-2-((Benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (8a)

(1S,2R,5S)-2',3'-Dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-bis(diethyl phosphate) (9a)

(2'R,4S,5'S)-Spiro[chromane-4,1'-cyclopentan]-3'-ene-2',5'-bis(diethyl phosphate) (10a)

1,1'-Oxybis(but-3-en-2-ol)

Cis-2,3,6,7-tetrahydrooxepine-3,6-diol

Tetraethyl ((3R,6S)-2,3,6,7-tetrahydrooxepine-3,6-diyl) bis(phosphate) (11a)

 tert-Butyl (3R,4S)-3,4-dihydroxypyrrolidine-1-carboxylate

 tert-Butyl bis(2-hydroxybut-3-en-1-yl) carbamate

 tert-Butyl (3R,6S)-3,6-dihydroxy-2,3,6,7-tetrahydro-1H-azepine-1-carboxylate

 tert-Butyl (3R,6S)-3,6-bis((diethoxyphosphoryl)oxy)-2,3,6,7-tetrahydro-1H-azepine-1-carboxylate (12a)

Desymmetrization Products
Dimethyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate

Diethyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate (1b)

Diisopropyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate

Diphenyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate

Diethyl ((1R,2R)-2-(4-phenylbutyl)cyclohex-3-en-1-yl) phosphate (2b)

Diethyl ((1R,2R)-2-(4-phenylbutyl)cyclohept-3-en-1-yl) phosphate (3b)

Diethyl ((1R,2R)-2-ethylcyclopent-3-en-1-yl) phosphate (1c)

Diethyl ((1R,2R)-2-ethylcyclohex-3-en-1-yl) phosphate (2c)

Diethyl ((1R,2R)-2-hexylcyclopent-3-en-1-yl) phosphate (1d)

Diethyl ((1R,2R)-2-hexylcyclohex-3-en-1-yl) phosphate (2d)

Diethyl ((1R,2R)-2-tetradecylcyclopent-3-en-1-yl) phosphate (1e)

Diethyl ((1R,2R)-2-tetradecylcyclohex-3-en-1-yl) phosphate (2e)

Diethyl ((1R,2R)-2-isopentylcyclopent-3-en-1-yl) phosphate (1f)

Diethyl ((1R,2R)-2-isopentylcyclohex-3-en-1-yl) phosphate (2f)

Diethyl (1R,2R)-2-(3,3-dimethylbutyl)cyclopent-3-en-1-yl) phosphate (1g)

Diethyl (1R,2R)-2-(3,3-dimethylbutyl)cyclohex-3-en-1-yl) phosphate (2g)

Diethyl (1R,2R)-2-(2-cyclohexylethyl)cyclopent-3-en-1-yl phosphate (1h)

Diethyl (1R,2R)-2-(2-cyclohexylethyl)cyclohex-3-en-1-yl phosphate (2h)

(1R,2R)-2-(6-chlorohexyl)cyclopent-3-en-1-yl diethyl phosphate (1i)

(1R,2R)-2-(6-chlorohexyl)cyclohex-3-en-1-yl diethyl phosphate (2i)

(1R,2R)-2-(4-((tert-butyldiphenylsilyl)oxy)butyl)cyclopent-3-en-1-yl diethyl phosphate (1j)
(1R,2R)-2-(4-((tert-butylidiphenylsilyl)oxy)butyl)cyclohex-3-en-1-yl diethyl phosphate (2j) S73
(1R,2R)-2-(4-((tert-butylidiphenylsilyl)oxy)butyl)cyclohept-3-en-1-yl diethyl phosphate (3j) S74
Diethyl ((1R,2R)-2-(4-methoxyphenethyl)cyclopent-3-en-1-yl) phosphate (1k) S76
Diethyl ((1R,2R)-2-(4-methoxyphenethyl)cyclohex-3-en-1-yl) phosphate (2k) S77
Diethyl ((1R,2R)-2-(4-methoxyphenethyl)cyclohept-3-en-1-yl) phosphate (3k) S78
(1R,2R)-2-(2-bromophenethyl)cyclopent-3-en-1-yl diethyl phosphate (1l) S79
(1R,2R)-2-(2-bromophenethyl)cyclohex-3-en-1-yl diethyl phosphate (2l) S81
(1S,2R,5R)-2-benzyl-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (4b) S83
(1S,2R,5R)-2-Benzyl-5-(3-(benzyloxy)propyl)-2-methylcyclopent-3-en-1-yl diethyl phosphate (4c) S84
(1S,2R,5R)-2-Benzyl-5-(4-bromobutyl)-2-methylcyclopent-3-en-1-yl diethyl phosphate (4d) S85
1S,2R,5R)-2-Benzyl-5-(2-bromo-5-fluorophenethyl)-2-methylcyclopent-3-en-1-yl diethyl phosphate (4e) S87
(1S,2R,5R)-2-Benzyl-5-(4-(dibenzylamino)butyl)-2-methylcyclopent-3-en-1-yl diethyl phosphate (4f) S88
(1S,5R)-2,2-Dimethyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (5b) S90
(1S,2R,5R)-2-Allyl-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (6b) S91
(1S,2R,5R)-2-(2-chlorobenzyl)-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (7b) S93
(1S,2S,5R)-2-(((benzyloxy)methyl)-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (8b) S94
Diethyl ((1S,4R,5S)-4-(4-phenylbutyl)-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-en-5-yl) phosphate (9b) S96
Diethyl ((4S,4'R,5'S)-4'-(4-phenylbutyl)spiro[chromane-4,1'-cyclopentan]-2'-en-5'-yl) phosphate (10b) S97
Diethyl ((3S,4R)-4-(4-phenylbutyl)-2,3,4,7-tetrahydrooxepin-3-yl) phosphate (11b) S99
tert-Butyl (3S,4R)-3-((diethoxyphosphoryl)oxy)-4-(4-phenylbutyl)-2,3,4,7-tetrahydro-1H-azepine-1-carboxylate (12b) S100
Diethyl ((1S,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate (14) S102
Derivatization Products

(1R,2R)-2-ethylcyclopent-3-en-1-ol (15)

Diethyl ((1R,4aR,10aR)-1,4,4a,9,10,10a-hexahydrophenanthren-1-yl) phosphate (16)

(1S,2R,3R,4S,5R)-2-benzyl-3,4-dihydroxy-2-methyl-5-(4-phenylbutyl) cyclopentyl diethyl phosphate (17)

Supplementary Figures 2 – 67

Supplementary References
Supplementary Table 1 - Dialkylphosphate Optimisation Table

\[
\begin{array}{ccc}
\text{R} & \text{Yield (\%)} & \text{ee (\%)} \\
\text{Me} & 55 & 86 \\
\text{iPr} & 45 & 84 \\
\text{Ph} & 20 & 70 \\
\text{Et} & 70 & 86 \\
\end{array}
\]
General Information

Procedures using oxygen and/or moisture-sensitive materials were performed with anhydrous solvents under an atmosphere of anhydrous argon in flame-dried flasks, using standard Schlenk techniques. Analytical thin-layer chromatography was performed on precoated glass-backed plates (Silica Gel 60 F254; Merck), and visualized using a combination of UV light (254 nm) and anisaldehyde solution or aqueous basic potassium permanganate stain. Flash column chromatography was carried out using Apollo Scientific silica gel 60 (0.040 – 0.063 nm), Merck 60 Å silica gel, VWR (40-63 μm) silica gel and Sigma Aldrich silica gel. Pressure was applied at the column head via hand bellows or a flow of nitrogen with the solvent system used in parentheses.

Reactions at 0 °C were performed using an ice-water bath, covered with cotton wool and aluminium foil if overnight stirring is needed. Other temperatures were obtained using a Julabo FT902 immersion cooler or the heating plate of the stirrer.

Unless stated otherwise, solution NMR spectra were recorded at room temperature; $^1$H, $^{31}$P and $^{13}$C NMR experiments were carried out using Bruker AVIII HD 400 (400/101/162 MHz) or AVIII HD 500 (500/126/202 MHz) spectrometers. Chemical shifts are reported in ppm from the residual solvent peak. Chemical shifts (δ) are given in ppm and coupling constants (J) are quoted in hertz (Hz). Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Assignments were made with the assistance of COSY, HSQC, HMBC or NOESY NMR spectra.

Chiral HPLC separations were achieved using an Agilent 1230 Infinity series normal phase HPLC unit and HP Chemstation software. Chiral SFC separations were achieved using a Waters Acquity UPC²™ unit. Chiralpak® columns (250 × 4.6 mm), fitted with matching Chiralpak® Guard Cartridges (10 × 4 mm), were used as specified in the text. Solvents used were of HPLC grade (Fisher Scientific, Sigma Aldrich or Rathburn); all eluent systems were isocratic.
Chiral SFC (supercritical fluid chromatography) separations were conducted on a Waters Acquity UPC2 system using Waters Empower software. Chiralpak® columns (150 × 3 mm, particle size 3 μm) were used as specified in the text. Solvents used were of HPLC grade (Fisher Scientific, Sigma Aldrich or Rathburn). Compounds 14e, 14f and 22 used specific instruments and conditions detailed later in the text.

Chiral GC measurements were conducted on an Agilent 7820A GC (He as a vector gas) with the stated column in the characterisation. Temperature programs are described as follows: initial temperature (°C) – initial time (min) – temperature gradient (°C/min) – final temperature (°C) – holding time (min). Flow rate is given in mL/min. Retention times (RT) are given in min.

Low-resolution mass spectra were recorded using a Walters LCT premier XE. High-resolution mass spectra (EI and ESI) were recorded using a Bruker MicroTOF spectrometer by the internal service at the University of Oxford. Infrared measurements (neat, thin film) were carried out using a Bruker Tensor 27 FT-IR with internal calibration in the range 600-4000 cm⁻¹. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 25°C in a 10 cm cell in the stated solvent; [α]₀ values are given in 10⁻¹ deg.cm² g⁻¹ (concentration c given as g/100 mL).

**Chemicals**

Dry THF and CH₂Cl₂ were collected fresh from an mBraun SPS-5 solvent purification system having been passed through anhydrous alumina columns. All other dry solvents used were dried over 3 Å molecular sieves and stored under argon. All other solvents were used as purchased from Sigma Aldrich, Honeywell or Fisher Scientific. Unless stated otherwise, commercially available reagents were purchased from Sigma-Aldrich, Fisher Scientific, Apollo Scientific, Acros Organics, Strem Chemicals, Alfa Aesar or TCI UK and were used without purification. Petroleum ether refers to light petroleum boiling in the range 40-60 °C. Deuterated solvents were purchased from Sigma-Aldrich (CDCl₃). PPL refers to Lipase from porcine pancreas, Type II, 100-500 units/mg of protein, purchased from Sigma-Aldrich (Cat no. L3126). Schwartz reagent was prepared according to the literature procedure from Cp₂ZrCl₂ purchased from Acros or Strem Chemicals.
Supplementary Methods

General procedure 1a: Racemic allylic alkylation products

Note: All manipulations are carried out under an Ar atmosphere and in the absence of light where possible. Additional details on the procedure are described here: *Nature Protoc.*, 2014, 9, 104-111. Procedures can be carried out without flame drying, instead using oven dried glassware and N$_2$ purging without detriment to yield or ee.

Flask A: A flame-dried 5 mL round bottomed flask was charged with CuCl (4 mg, 0.04 mmol, 0.1 eq) and racemic (3,5-dioxo-4-phosphacyclohepta[2,1-a:3,4-a’]dinaphthalen-4-yl)dimethylamine (MonoPhos®) (17.2 mg, 0.048 mmol, 0.12 eq). Dry CH$_2$Cl$_2$ (1.5 mL) was added to the mixture which was left to stir at room temperature for 1 hour. AgNTf$_2$ (23 mg, 0.06 mmol, 0.15 eq) was then added to the flask and left to stir at room temperature for 15 mins. A pale brown suspension was formed.

Flask B: Meanwhile a separate flame-dried round bottomed flask was charged with Cp$_2$ZrHCl (206 mg, 0.8 mmol, 2.0 eq) and suspended in dry CH$_2$Cl$_2$ (0.8 mL). Alkene (1.0 mmol, 2.5 eq) was added to the mixture which was left to stir at room temperature in the absence of light, until the mixture became a homogenous yellow solution (approx. 30 mins, varies with alkene). Note: The alkylzirconium species can be left for up to 2-3 hours without issue.

The contents of flask A were transferred into flask B using a syringe equipped with a Camlab PTFE syringe filter (13 mm size, pore diameter 0.22 μm) to remove excess AgCl. The combined flask contents formed a black mixture which was left to stir at room temperature in the absence of light for 10 mins. Meso-cyclic bisphosphate (2a-
c) (0.4 mmol) was added to the mixture which was left to stir at room temperature in the absence of light for 16 hours.

The mixture was quenched with 1M aq. NH₄Cl (1 mL) and left to stir for 10 mins. The organic layer was separated, filtered through a plug of Celite and evaporated in vacuo to give an off-white mixture of solid and oil. The crude product was purified on silica (eluent specified below) to give a yellow oil.

**General procedure 1b: 5 and 7-membered asymmetric allylic alkylation products**

![Diagram]

Note: All manipulations are carried out under an Ar atmosphere and in the absence of light where possible. Additional details on the procedure are described here: Nature Protoc., 2014, 9, 104-111. Procedures can be carried out without flame drying, instead using oven dried glassware and N₂ purging without detriment to yield or ee.

**Flask A:** A flame-dried 5 mL round bottomed flask was charged with CuCl (4 mg, 0.04 mmol, 0.1 eq) and phosphoramidite ligand F (28 mg, 0.048 mmol, 0.12 eq). Dry CH₂Cl₂ (1.5 mL) was added to the mixture which was left to stir at room temperature for 1 hour. AgNTf₂ (23 mg, 0.06 mmol, 0.15 eq) was then added to the flask and left to stir at room temperature for 15 mins. A pale brown suspension was formed.

**Flask B:** Meanwhile a separate flame-dried round bottomed flask was charged with Cp₂ZrHCl (206 mg, 0.8 mmol, 2.0 eq) and suspended in dry CH₂Cl₂ (0.8 mL). Alkene (1.0 mmol, 2.5 eq) was added to the mixture which was left to stir at room temperature in the absence of light, until the mixture became a homogenous yellow solution (approx. 30 mins, varies with alkene). Note: The alkylzirconium species can be left for up to 2-3 hours without issue.
The contents of flask A were transferred into flask B using a syringe equipped with a Camlab PTFE syringe filter (13 mm size, pore diameter 0.22 µm) to remove excess AgCl. The combined flask contents formed a black mixture which was left to stir at 0 °C in the absence of light for 10 mins. *Meso*-cyclic bisphosphate (2a-c) (0.4 mmol) was added to the mixture which was left to stir at 0 °C in the absence of light for 16 hours.

The mixture was quenched with 1M aq. NH₄Cl (1 mL) and left to stir for 10 mins. The organic layer was separated, filtered through a plug of Celite and evaporated *in vacuo* to give an off-white mixture of solid and oil. The crude product was purified on silica (eluent specified below) to give a yellow oil.

**General procedure 1c: Asymmetric allylic alkylation products with quaternary centers, 6-membered rings and heterocycles**

![Chemical Reaction Diagram]

| 4-Phenyl-1-butene | CuCl, E, AgNTf₂, Cp₂ZrHCl | CH₂Cl₂, rt |
|-------------------|--------------------------|-----------|
| OP(OEt)₂          | OP(OEt)₂                 |
| Ph                | Ph                       |
| R, R'             | R, R'                    |
| E (S,S)           |                           |

Note: All manipulations are carried out under an Ar atmosphere and in the absence of light where possible. Additional details on the procedure are described here: *Nature Protoc.*, 2014, 9, 104-111.

**Flask A:** A flame-dried 5 mL round bottomed flask was charged with CuCl (4 mg, 0.04 mmol, 0.1 eq) and phosphoramidite ligand E (24.7 mg, 0.048 mmol, 0.12 eq). Dry CH₂Cl₂ (1.3 mL) was added to the mixture which was left to stir at room temperature for 1 hour. AgNTf₂ (23 mg, 0.06 mmol, 0.15 eq) was then added to the flask and left to stir at room temperature for 15 mins. A pale brown suspension was formed.

**Flask B:** Meanwhile a separate flame-dried round bottomed flask was charged with Cp₂ZrHCl (206 mg, 0.8 mmol, 2.0 eq) and suspended in dry CH₂Cl₂ (0.8 mL). Alkene
(1.0 mmol, 2.5 eq) was added to the mixture which was left to stir at room temperature in the absence of light, until the mixture became a homogenous yellow solution (approx. 30 mins, varies with alkene). Note: The alkylzirconium species can be left for up to 2-3 hours without issue.

The contents of flask A were transferred into flask B using a syringe equipped with a Camlab PTFE syringe filter (13 mm size, pore diameter 0.22 µm) to remove excess AgCl. The combined flask contents formed a black mixture which was left to stir at room temperature in the absence of light for 10 mins. *Meso*-cyclic bisphosphate (4a-12a) (0.4 mmol) in CH₂Cl₂ (0.2 mL) was added to the mixture which was left to stir at room temperature in the absence of light for 16 hours.

The mixture was quenched with 1M aq. NH₄Cl (1 mL) and left to stir for 10 mins. The organic layer was separated, filtered through a plug of Celite and evaporated *in vacuo* to give an off-white mixture of solid and oil. The crude product was purified on silica (eluent specified below) to give a yellow oil.

**General procedure 2: Phosphate reduction and esterification for HPLC analysis**

Phosphate (0.1 mmol, 1.0 eq) was dissolved in Et₂O (1.0 mL) and cooled to 0 °C before adding LiAlH₄ (1.0 M in Et₂O, 0.6 mL, 0.6 mmol, 6 eq) dropwise. The solution was warmed to room temperature and left to stir for 30 mins. The reaction mixture was quenched with H₂O dropwise until effervescence stopped. The residue was suspended in CH₂Cl₂ and filtered through celite, washing with CH₂Cl₂. The filtrate was evaporated *in vacuo* to give the crude alcohol.

The alcohol (0.1 mmol) was dissolved in CH₂Cl₂ (2.0 mL) before adding NEt₃ (28 µL, 0.2 mmol, 2.0 eq), DMAP (5 mg, 0.04 mmol, 0.4 eq) and *p*-nitrobenzoyl chloride (37 mg, 0.2 mmol, 2.0 eq). The mixture was left to stir for 1 hour, and was then
evaporated in vacuo to give a yellow residue. The residue was purified on silica (5\% EtOAc in petroleum ether) to give a colourless oil.

**General procedure 3: Oxidation of diones**

Under Ar dione (15 mmol, 1.0 eq) was dissolved in anhydrous MeOH (100 mL) before addition of CuBr$_2$ (7.37 g, 33.0 mmol, 2.2 eq). The mixture was heated to reflux and stirred for 1 hour. The resulting black mixture was cooled, quenched with dropwise addition of H$_2$O (25 ml) and 1M HCl (50 mL). The mixture was concentrated in vacuo to remove MeOH. The resulting mixture was extracted with EtOAc (3 x 75 mL) and the organic extracts were combined, washed with brine (2 x 50 mL), dried (MgSO$_4$) and concentrated in vacuo. The crude material was purified on silica (eluent specified below) to give the dienone product. **NOTE:** All examples presented give bright yellow products.

**General procedure 4: Luche reduction of dienones**

Dienone (5.00 mmol, 1.0 eq) was dissolved in MeOH (60 mL, not dry) and stirred until dissolution. CeCl$_3$·7H$_2$O (4.66 g, 12.50 mmol, 2.5 eq) was added and stirred until dissolution. The resulting solution was cooled to 0 °C before portionwise addition of NaBH$_4$ (416 mg, 11 mmol, 2.2 eq) over 10 minutes. The resulting suspension was left to stir at 0 °C for 2 hours before slow quenching with H$_2$O (5 mL) and 1M HCl (10 mL). The mixture was concentrated in vacuo to remove MeOH. The resulting mixture was extracted with EtOAc (3 x 30 mL) and the organic extracts were combined, washed with brine (2 x 30 mL), dried (MgSO$_4$) and concentrated in vacuo. The crude material was purified on silica (eluent specified below) to give the
dial product. NOTE: The examples presented gave separable 1:1 cis/trans mixtures unless stated otherwise. The cis isomer was isolated and characterised in all cases.

General procedure 5: Phosphorylation of diols via a dianion approach

A solution of dial (10.0 mmol, 1.0 eq.) in THF (60 mL) and TMEDA (15 mL) was cooled to -40 °C using a MeCN/CO₂ bath before nBuLi (2.5 M in hexane, 8.80 mL, 22.0 mmol, 2.2 eq.) was added dropwise. The resulting solution was left to stir for 10 minutes at -40 °C before dialkyl chlorophosphate (25.0 mmol, 2.5 eq.) was added dropwise. The resulting mixture was left to stir at -40 °C for 2 hours and then warmed to 0 °C. Brine (10 mL) was added slowly to the mixture which was then poured over H₂O (80 mL) and extracted with CH₂Cl₂ (3 x 80 mL). The organic extracts were combined, washed with brine (100 mL), dried (MgSO₄) and evaporated in vacuo. The crude material was purified on silica (eluent specified below) to give the diphosphate product.
Experimental Procedures and Characterisation of Compounds

Starting Materials

Unsubstituted Diphosphates

*Cis*-4-cyclopentene-1,3-diol

\[
\text{Chemical Formula: C}_6\text{H}_8\text{O}_2 \\
\text{Molecular Weight: 100.1170}
\]

Cyclopentadiene (2.00 mL, 24.3 mmol, 1.0 eq.), thiourea (1.84g, 24.3 mmol, 1.0 eq.) and Rose Bengal (50 mg, 0.048 mmol, 0.002 eq.) were added to a round-bottomed flask containing methanol (400 mL). O\textsubscript{2} gas was bubbled through the resulting pink solution for 15 mins before being maintained under an atmosphere of O\textsubscript{2}. The flask was partially submersed in an ice bath and irradiated with a 500 W halogen lamp with stirring for 8 hours (*Supplementary Figure 1*). The lamp was turned off and the mixture was left to stir in the dark at room temperature for 16 hours. The mixture was evaporated *in vacuo* to give a viscous pink residue. The residue was dissolved in water (250 mL) and extracted with Et\textsubscript{2}O (3 x 200 mL). The aqueous layer was evaporated *in vacuo* to give a pink residue, which was dissolved in methanol (50 mL) and loaded onto Chem Tube-Hydromatrix for purification on silica (1% MeOH in EtOAc) to give *cis*-4-cyclopentene-1,3-diol as a white solid (1.72 g, 71% yield).

\[^1\text{H} \text{NMR (400 MHz, DMSO-}d_6\text{)} \delta_{\text{H/}}/\text{ppm: 5.75 (s, 2H), 4.84 (dd, 2H, } J = 7.8, 2.0 \text{ Hz), 2.96-2.85 (m, 2H), 1.28-1.21 (m, 2H); } ^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} \delta_{\text{C/}}/\text{ppm: 137.0, 75.7, 44.2. Consistent with data in the literature.}^2\]
Supplementary Figure 1. Setup of photo-oxidation, illustrating partial submersion of flask in an ice bath.

**Cis-5-cyclohexene-1,4-diol**

![Chemical structure of Cis-5-cyclohexene-1,4-diol]

1,3-Cyclohexadiene (2.50 mL, 26.2 mmol, 1.0 eq.) was dissolved in CH₂Cl₂ (105 mL) before adding meso-tetraphenylporphyrin (56 mg, 0.09 mmol, 0.0035 eq.). O₂ gas was bubbled through the resulting purple solution for 15 mins before being maintained under an atmosphere of O₂. The flask was partially submersed in an ice bath and irradiated with a 500 W halogen lamp with stirring for 8 hours (Supplementary Figure 1). The reaction mixture was then evaporated in vacuo to give a purple residue which was then dissolved in MeOH (105 mL) and thiourea (2.01 g, 26.5 mmol, 1.01 eq.) was added. The mixture was left to stir in the dark at room temperature for 16 hours. The mixture was then evaporated in vacuo to give a viscous, dark brown residue which was dissolved in methanol (50 mL) and loaded onto Chem Tube-Hydromatrix for purification on silica (2% MeOH in Et₂O), to give cis-5-cyclohexene-1,4-diol as a white solid (2.28 g, 76% yield).
1H NMR (400 MHz, DMSO-d$_6$) $\delta$/ppm: 5.75 (s, 2H), 4.07 (br. s, 2H), 3.90 (br. s, 2H), 1.78-1.71 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta/$ppm: 132.6, 64.1, 28.6. Consistent with data in the literature.$^3$

**Cis-6-cycloheptene-1,5-diol**

![Chemical Structure](image)

Chemical Formula: C$_{12}$H$_{16}$O$_2$
Molecular Weight: 128.1716

1,3-Cycloheptadiene (1.00 g, 210.6 mmol, 1.0 eq.) was dissolved in CH$_2$Cl$_2$ (80 mL) before adding meso-tetraphenylporphyrin (23 mg, 0.04 mmol, 0.0035 eq.). O$_2$ gas was bubbled through the resulting purple solution for 15 mins before being maintained under an atmosphere of O$_2$. The flask was partially submersed in an ice bath and irradiated with a 500 W halogen lamp with stirring for 8 hours (Supplementary Figure 1). The reaction mixture was then evaporated in vacuo to give a purple residue which was then dissolved in MeOH (80 mL) and thiourea (816 mg, 10.7 mmol, 1.01 eq.) was added. The mixture was left to stir in the dark at room temperature for 16 hours. The mixture was then evaporated in vacuo to give a viscous, dark brown residue which was dissolved in methanol (50 mL) and loaded onto Chem Tube-Hydromatrix for purification on silica (2-3% MeOH in CH$_2$Cl$_2$), to give cis-6-cycloheptene-1,5-diol as a white solid (576 mg, 42% yield).

1H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 5.76 (s, 2H), 4.30 (d, 2H, $J$ = 8.0 Hz), 2.10-2.00 (m, 1H) 1.78-1.73 (m, 2H), 1.75 (br. s, 1H), 1.72-1.56 (m, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ppm: 135.8, 71.4, 36.0, 23.1. Consistent with data in the literature.$^4$
**Meso-4-cyclopentene-1,3-bisdimethylphosphate**

Synthesised according to general procedure 5 using cis-4-cyclopentene-1,3-diol on 1.0 mmol scale. Purified by flash chromatography (4% MeOH in CH₂Cl₂) to give meso-4-cyclopentene-1,3-bisdimethylphosphate as a pale yellow oil (207 mg, 65% yield).

![Chemical Structure](attachment:image.png)

$^1$H NMR (400 MHz, CDCl₃) $\delta$/ppm: 6.15 (s, 2H, 2CH-(3)), 5.27 – 5.18 (m, 2H, 2CH-(2)), 3.77 (d, $J = 11.1$ Hz, 12H, 4CH₂-(4)), 2.98 – 2.85 (m, 1H, $CHH^\prime$-(1)), 2.10 – 1.99 (m, 1H, $CHH^\prime$-(1)); $^13$C NMR (101 MHz, CDCl₃) $\delta$/ppm: 135.1 (C(3)), 79.4 (C(2)), 54.3 (C(4)), 39.5 (C1)); $^{31}$P NMR (162 MHz, CDCl₃) $\delta$/ppm: 0.29; HRMS (ESI) $m/z$ calcd for C₁₀H₁₈O₈P₂Na$[M+Na]^+$: 339.0369, found: 339.0365; IR (ATR) ν (cm⁻¹) thin film, CHCl₃: 2980.7 (w), 1461.7 (w), 1377.8 (w), 1266.4 (m), 1185.8 (w), 1037.9 (s), 991.8 (s), 934.3 (w), 849.5 (m), 751.8 (w).

**Meso-4-Cyclopentene-1,3-bisdiethylphosphate (1a)**

![Chemical Structure](attachment:image.png)

To a solution of cis-4-cyclopentene-1,3-diol (3.15 g, 31.5 mmol, 1.0 eq) in CH₂Cl₂ (142 mL) was added NEt₃ (13.2 mL, 94.4 mmol, 3.0 eq) and DMAP (1.92 g, 15.8 mmol, 0.5 eq). The resulting solution was cooled to 0 °C before dropwise addition of
diethylchlorophosphate (13.7 mL, 94.4 mmol, 3.0 eq). The resulting mixture was left to stir at room temperature for 16 hours. The mixture was then quenched with H₂O (100 mL) and extracted with CH₂Cl₂ (3 x 100 mL). The organic extracts were combined, washed with brine (100 mL), dried (MgSO₄) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (3% MeOH in EtOAc) to give meso-4-cyclopentene-1,3-bisdiethylphosphate (1a) as a pale yellow oil (11.23g, 96% yield).

\[
\text{\text{H NMR (400 MHz, CDCl}_3\text{) } \delta_{\text{H}}/\text{ppm: 6.12 (d, } J = 0.8 \text{ Hz, 2H, CH}_2-(3), 5.21 (d, } J = 4.4 \text{ Hz, 2H, CH}_2-(2)), 4.10 (m, } J = 8.3, 7.1, 1.3 \text{ Hz, 8H, CH}_2-(4), 2.91 (dt, } J = 14.6, 7.3 \text{ Hz, 1H, CHH'}-(1), 2.03 (dt, } J = 14.6, 4.3 \text{ Hz, 1H, CHH'}-(1), 1.33 (t, } J = 7.1 \text{ Hz, 12H, CH}_3-(5)); \text{ C NMR (101 MHz, CDCl}_3\text{) } \delta_{\text{C}}/\text{ppm: 135.2 (C(3)), 79.3 (C(2)), 64.0 (C(4)), 39.7 (C(1)), 16.3 (C(5)); \text{ P NMR (162 MHz, CDCl}_3\text{) } \delta_{\text{P}}/\text{ppm: -1.91; HRMS (ESI) m/z calcd for C}_{13}\text{H}_{26}\text{O}_8\text{P}_2\text{Na}[M+Na]^+: 395.0995, found: 395.0993; IR (ATR) v (cm}^{-1}\text{) thin film, CHCl}_3: 2982.8 (w), 1373.3 (w), 1261.4 (m), 1165.5 (w), 1024.0 (s), 980.7 (s), 802.9 (w), 749.9 (w). Consistent with data in the literature.}^5
\]

**Meso-4-Cyclopentene-1,3-bisdiisopropylphosphate**

\[
\text{Synthesised according to general procedure 5 using cis-4-cyclopentene-1,3-diol on 1.50 mmol scale. Purified by flash chromatography (3% MeOH in CH}_2\text{Cl}_2\text{) to give meso-4-cyclopentene-1,3-bisdiisopropylphosphate as a pale yellow oil (456 mg, 71% yield).}^5
\]
'\text{H NMR (400 MHz, CDCl}_3^3) \delta \text{u/ppm: } 6.09 (s, 2H, 2\text{CH-(3)}), 5.16 (q, J = 6.4 \text{ Hz, 2H, 2CH-(2)}), 4.61 (m, J = 12.3, 6.7, 6.2 \text{ Hz, 4H, 4CH-(4)}), 2.88 (dt, J = 14.6, 7.3 \text{ Hz, 1H, CHH}^\prime-(1)), 2.00 (dt, J = 14.5, 4.6 \text{ Hz, 1H, CHH}^\prime-(1)), 1.31 (d, J = 6.2 \text{ Hz, 24H, 8CH}_3-(5)); \text{^13C NMR (101 MHz, CDCl}_3^3 \delta \text{c/ppm: } 135.4 \text{ (C(3))}, 79.5 \text{ (C(2))}, 73.0 \text{ (C(4))}, 40.2 \text{ (C(1))}, 24.2 \text{ (C(5))}; \text{^31P NMR (162 MHz, CDCl}_3^3 \delta \text{v/ppm: } -3.50; \text{HRMS (ESI) } m/z \text{ calcld for C}_17\text{H}_{34}\text{O}_8\text{P}_2\text{Na}[M+Na]^+: 451.1621, \text{ found: } 451.1618; \text{IR (ATR) } \nu (\text{cm}^{-1}) \text{ thin film, CHCl}_3: 2981.0 \text{ (w), 1467.8 } \text{ (w), 1376.3 } \text{ (w), 1259.8 } \text{ (m), 1179.3 } \text{ (w), 1142.8 } \text{ (w), 1108.6 } \text{ (w), 979.5 } \text{ (s), 928.5 } \text{ (m), 779.3 } \text{ (w), 729.3 } \text{ (w).}

\text{Meso-4-Cyclopentene-1,3-bisdiphenylphosphate}

Synthesised according to general procedure 5 using cis-4-cyclopentene-1,3-diol on 1.0 mmol scale. Purified by flash chromatography (EtOAc:Petroleum Ether, 1:1, using silica which was pre-washed with 2\% NEt}_3 in petroleum ether) to give meso-4-cyclopentene-1,3-bisdiphenylphosphate as a yellow oil (462 mg, 82\% yield).

\text{H NMR (400 MHz, CDCl}_3^3 \delta \text{u/ppm: } 7.36 - 7.31 \text{ (m, 8H, ArH-(5))}, 7.23 - 7.16 \text{ (m, 12H, ArH-(6,7))}, 6.11 \text{ (s, 2H, 2CH-(3))}, 5.46 - 5.42 \text{ (m, 2H, 2CH-(2))}, 2.89 \text{ (dt, J = }
14.7, 7.2 Hz, 1H, CHH\textsuperscript{\textprime}-(1)), 2.08 (dt, J = 14.9, 3.9 Hz, 1H, CHH\textsuperscript{\textprime}-(1)); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ/ppm: 150.5 (C(4)), 135.3 (C(3)), 129.9 (C(6)), 125.6 (C(5)), 120.2 (C(7)), 80.9 (C(2)), 39.3 (C(1)); \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}) δ/ppm: -12.74; HRMS (ESI) m/z calcd for C\textsubscript{29}H\textsubscript{26}O\textsubscript{8}P\textsubscript{2}Na [M+Na]\textsuperscript{+}: 587.0995, found: 587.0988; IR (ATR) ν (cm\textsuperscript{-1}) thin film, CHCl\textsubscript{3}: 2980.6 (w), 1589.6 (w), 1486.9 (m), 1573.2 (w), 1284.1 (m), 1218.5 (w), 1186.1 (s), 1161.8 (m), 1071.3 (w), 990.1 (m), 942.4 (s), 754.8 (s), 687.8 (m), 616.7 (w).

\textit{Meso-5-Cyclohexene-1,4-bisdiethylphosphatate (2a)}

\begin{align*}
\text{O} & \quad \text{O} \\
\text{(EtO)}_2\text{PO} & \quad \cdots \quad \text{OP(OEt)}_2 \\
\text{2a} \\
\end{align*}

Chemical Formula: C\textsubscript{14}H\textsubscript{28}O\textsubscript{8}P\textsubscript{2}  
Molecular Weight: 386.3175

To a solution of cis-5-cyclohexene-1,4-diol (2.20 g, 19.3 mmol, 1.0 eq) in CH\textsubscript{2}Cl\textsubscript{2} (87 mL) was added NEt\textsubscript{3} (8.06 mL, 57.8 mmol, 3.0 eq) and DMAP (1.18 g, 9.64 mmol, 0.5 eq). The resulting solution was cooled to 0 °C before dropwise addition of diethylchlorophosphate (8.36 mL, 57.8 mmol, 3.0 eq). The resulting mixture was left to stir at room temperature for 16 hours. The mixture was then quenched with H\textsubscript{2}O (100 mL) and extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 x 100 mL). The organic extracts were combined, washed with brine (100 mL), dried (MgSO\textsubscript{4}) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (3% MeOH in EtOAc) to give \textit{meso}-5-cyclohexene-1,4-bisdiethylphosphatate (2a) as a yellow oil (6.56 g, 88% yield).

\begin{align*}
\begin{array}{c}
\text{O} \\
\text{H} \quad \text{H} \\
\text{P} \quad \text{O} \\
\text{2a} \\
\end{array}
\end{align*}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ/ppm: 5.97 (d, J = 1.4 Hz, 2H, 2CH-(3)), 4.92 – 4.70 (m, 2H, 2CH-(2)), 4.10 (dq, J = 7.9, 7.0 Hz, 8H, 4CH\textsubscript{2}-(4)), 2.07 – 1.99 (m, 2H, 2CH\textsubscript{H}-(1)), 1.98 – 1.89 (m, 2H, 2CH\textsubscript{H}-(1)), 1.34 (td, J = 7.0, 1.0 Hz, 12H, 4CH\textsubscript{3}-}
(5); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$C/ppm: 130.7 (C(3)), 70.9 (C(2)), 63.8 (C(4)), 26.1 (C(1)), 16.2 (C(5)); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$P/ppm: -1.38; HRMS (ESI) $m/z$ calcd for C$_{14}$H$_{28}$O$_8$P$_2$ [M+H]$^+$: 387.1338, found: 387.1379; IR (ATR) v (cm$^{-1}$) thin film, CHCl$_3$: 2985.2 (w), 1644.4 (w), 1396.8 (w), 1261.4 (m), 1164.2 (w), 1027.0 (s), 989.3 (s), 817.6 (w). Consistent with data in the literature.$^5$

**Meso-6-Cycloheptene-1,5-bisdiethylphosphate (3a)**

![Chemical Structure](image)

Chemical Formula: C$_{14}$H$_{28}$O$_8$P$_2$
Molecular Weight: 400.3445

To a solution of cis-6-cycloheptene-1,5-diol (400 mg, 3.12 mmol, 1.0 eq) in CH$_2$Cl$_2$ (14 mL) was added NEt$_3$ (1.30 mL, 9.36 mmol, 3.0 eq) and DMAP (191 mg, 1.56 mmol, 0.5 eq). The resulting solution was cooled to 0 °C before dropwise addition of diethylchlorophosphate (1.35 mL, 9.36 mmol, 3.0 eq). The resulting mixture was left to stir at room temperature for 16 hours. The mixture was then quenched with H$_2$O (50 mL) and extracted with CH$_2$Cl$_2$ (3 x 50 mL). The organic extracts were combined, washed with brine (50 mL), dried (MgSO$_4$) and evaporated *in vacuo* to give a yellow oil. The yellow oil was purified by flash chromatography (2% MeOH in CH$_2$Cl$_2$) to give *meso*-6-cycloheptene-1,5-bisdiethylphosphate (3a) as a yellow oil (1.10 g, 88% yield).

![Meso-6-Cycloheptene-1,5-bisdiethylphosphate (3a)](image)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$H/ppm: 5.79 (s, 2H, 2CH-(4)), 5.06 – 4.71 (m, 2H, 2CH-(3)), 4.34 – 3.92 (m, 8H, 4CH$_2$-(5)), 2.12 – 1.94 (m, 3H, 3CHH’-(1, 2)), 1.74 – 1.59 (m, 3H, 3CHH’-(1, 2)), 1.31 (tq, J = 7.1, 1.1 Hz, 12H, 2CH$_3$-(6)); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$c/ppm: 133.07 (C(4)), 77.57 (C(3)), 63.86 (C(5)), 34.01 (C(2)), 22.64...
(C(1)), 16.24 (C(6)); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta_{ppm}$: -1.68; HRMS (ESI) m/z calcd for C$_{15}$H$_{30}$O$_8$P$_2$ [M+H]$^+$: 400.1316, found: 400.1441; IR (ATR) $\nu$ (cm$^{-1}$) thin film, CHCl$_3$: 2985.4 (w), 1646.2 (w), 1396.3 (w), 1263.5 (m), 1164.6 (w), 1027.5 (s), 988.9 (s), 804.1 (w) Consistent with data in the literature.$^5$

**Trans-Bisphosphate**

![Scheme S1. Synthesis of 13](image)

(1S,3S)-Cyclopent-4-ene-1,3-diyl tetraethyl bis(phosphate) (13)

(1S,4R)-4-hydroxycyclopent-2-en-1-yl acetate

To a solution of cis-4-cyclopentene-1,3-diol (200 mg, 2.00 mmol, 1.0 eq) in THF (5.33 mL) was added NEt$_3$ (0.195 mL, 1.40 mmol, 0.7 eq) and vinyl acetate (1.29 mL, 14.0 mmol, 7.0 eq). PPL lipase (400 mg) was then added, and the resulting beige suspension was left to stir at room temperature for 22 hours. The reaction mixture was filtered through Celite and evaporated in vacuo to give a yellow oil. The oil was purified on silica (30-40-50% EtOAc in petroleum ether) to give a white solid. The white solid was recrystallised using a 3:1 mixture of pentane : Et$_2$O to give (1S,4R)-4-hydroxycyclopent-2-en-1-yl acetate as colourless needles (126 mg, 44%). **NOTE:** Diacetate by-product (135 mg, 37%) obtained from column and recycled.
GC analysis indicated an enantiomeric excess of >99% [Beta DEX 325 (Supelco) column; initial temperature 80 °C, initial hold time 5 min, progress rate 5 °C/min, final temperature 160 °C, final hold time 10 min; Flow rate 2 mL/min; minor enantiomer, \( t_R = 14.789 \) min; major enantiomer, \( t_R = 15.175 \) min].

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \text{)} \quad \delta_{H/\text{ppm}}: \quad 6.10 (d, \ J = 5.5 \text{ Hz, 1H}), \quad 5.97 (d, \ J = 5.5 \text{ Hz, 1H}), \quad 5.61 – 5.19 (m, 1H), \quad 4.71 (s, 1H), \quad 2.79 (dt, \ J = 14.6, 7.3 \text{ Hz, 1H}), \quad 2.04 (s, 3H), \quad 1.64 (dt, \ J = 14.6, 3.9 \text{ Hz, 1H}); \]

\[ ^{13}C \text{NMR (101 MHz, CDCl}_3 \text{)} \quad \delta_{C/\text{ppm}}: \quad 170.9, \quad 138.6, \quad 132.7, \quad 77.2, \quad 74.9, \quad 40.6, \quad 21.3. \]

Consistent with data found in the literature.\(^6\)

\((1S,3S)-\text{Cyclopent-4-ene-1,3-diyl tetraethyl bis(phosphate)} \) (13)

\((1S,4R)-\text{4-hydroxycyclopent-2-en-1-yl acetate} \) (529 mg, 3.72 mmol, 1.0 eq) and \( \text{PPh}_3 \) (1.95 g, 7.44 mmol, 2.0 eq) were dissolved in toluene (10.5 mL) before addition of \( \text{HCO}_2\text{H} \) (288 \( \mu \)L, 7.63 mmol, 2.05 eq). The resulting solution was cooled to 0 °C before dropwise addition of \( \text{DIAD} \) (1.46 mL, 7.44 mmol, 2.00 eq). The resulting solution was left to stir at 0 °C for 4 hours 40 mins, before being poured over sat. aq. \( \text{NaHCO}_3 \) (50 mL). The aqueous layer was extracted with EtOAc (3 x 50 mL). The organic extracts were combined, washed with brine (30 mL), dried (\( \text{MgSO}_4 \)) and evaporated in vacuo to give a yellow oil. The oil was filtered through a short plug of silica, washing with CH\(_2\)Cl\(_2\). The filtrate was evaporated in vacuo to give the crude diester (518 mg) which was used immediately in the next step.

The diester was dissolved in MeOH (21 mL) before addition of \( \text{H}_2\text{O} \) (323 \( \mu \)L, 18.27 mmol, 6.0 eq) and \( \text{LiOH} \) (437 mg, 18.27 mmol, 6.0 eq). The resulting mixture was left to stir at room temperature for 13 hours. The mixture was evaporated in vacuo and the resulting residue was filtered through a short plug of silica, rinsing with 5% MeOH in CH\(_2\)Cl\(_2\). The filtrate was evaporated in vacuo to give the crude alcohol (290 mg) that was used immediately in the next step.
To a solution of the alcohol in CH₂Cl₂ (13 mL) was added NEt₃ (1.21 mL, 8.69 mmol, 3.0 eq) and DMAP (172 mg, 1.45 mmol, 0.5 eq). The resulting solution was cooled to 0 °C before dropwise addition of diethylchlorophosphate (1.26 mL, 8.69 mmol, 3.0 eq). The resulting mixture was left to stir at room temperature for 16 hours. The mixture was then quenched with H₂O (30 mL) and extracted with CH₂Cl₂ (3 x 30 mL). The organic extracts were combined, washed with brine (20 mL), dried (MgSO₄) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (2-3% MeOH in EtOAc) to give (1S,3S)-cyclopent-4-ene-1,3-diyl tetraethyl bis(phosphate) (13) as colourless oil (948 mg, 68% yield over 3 steps).

**NOTE:** Procedure used to produce racemic ±13 from racemic 4-hydroxycyclopent-2-en-1-yl acetate.

Enantiomeric excess of 13 determined by use in General Procedure 1a.

\[^{1}H \text{NMR} (400 \text{ MHz, CDCl}_3) \delta_H/\text{ppm}: 6.16 (d, J = 1.0 \text{ Hz, } 2\text{H, }2\text{CH-(3)}), 5.54 (m, J = 5.2 \text{ Hz, } 2\text{H, }2\text{CH-(2)}), 4.08 (m, J = 7.9, 7.1, 5.1 \text{ Hz, } 8\text{H, }4\text{CH}_2-(4)), 2.36 (t, J = 4.9 \text{ Hz, } 2\text{H, }CH_2-(1)), 1.32 (tdd, J = 7.1, 3.0, 1.0 \text{ Hz, } 12\text{H, }4\text{CH}_3-(5)); \[^{13}C \text{NMR} (101 \text{ MHz, CDCl}_3) \delta_C/\text{ppm}: 136.1 (\text{C(3)}), 81.2 (\text{C(2)}), 63.9 (\text{C(4)}), 40.0 (\text{C(1)}), 16.3 (\text{C(5)}); \[^{31}P \text{NMR} (162 \text{ MHz, CDCl}_3) \delta_P/\text{ppm}: -1.53; \text{HRMS (ESI) } m/z \text{ calcd for } C_{13}H_{26}O_8P_2Na[M+Na]^+: 395.09951, \text{found: } 395.09958; \text{IR (ATR) } \nu (\text{cm}^{-1}) \text{ thin film, CHCl}_3: 2984.8 (w), 1445.1 (w), 1371.8 (w), 1262.7 (m), 1165.9 (w), 1028.0 (s), 978.1 (s), 804.2 (w), 754.9 (w). [\alpha]^{25}_{589} = -123.2 (c=1.0 \text{ in CHCl}_3, >99\% \text{ ee})\]
**2-Substituted Bisphosphates**

![Diagram showing the general synthesis of 2-substituted diphosphates]

*Scheme S2.* General synthesis of 2-substituted diphosphates

**2,2-Dimethylcyclopentane-1,3-dione**

![Diagram showing the synthesis of 2,2-dimethylcyclopentane-1,3-dione]

2-Methyl-1,3-cyclopentanedione (2.50 g, 22.23 mmol, 1.0 eq) was dissolved in 1,4-dioxane (18.75 mL) and water (6.5 mL) before addition of KOH (1.31 g, 23.41 mmol, 1.05 eq) and methyl iodide (1.53 mL, 24.53 mmol, 1.1 eq). The resulting mixture was heated to reflux at left to stir for 12 hours. The reaction mixture was poured over water (50 mL) and extracted with EtOAc (3 x 50 mL). The organic extracts were combined, washed with brine (50 mL), dried (MgSO₄) and evaporated *in vacuo* to give a yellow oil. The yellow oil was purified by flash chromatography (10-20-30% EtOAc in petroleum ether) to give 2,2-dimethylcyclopentane-1,3-dione (1.765 g, 63%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δH/ppm: 2.76 (s, 4H), 1.10 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δc/ppm: 216.4, 52.7, 34.6, 20.3. Consistent with data in the literature.⁷
2-Allyl-2-methylcyclopentane-1,3-dione

2-Methyl-1,3-cyclopentanedione (2.50 g, 22.30 mmol, 1 eq) was dissolved in 1M aq. NaOH (25.0 mL) before addition of allyl bromide (3.86 mL, 44.60 mmol, 2.0 eq). The resulting mixture was vigorously stirred (1000 rpm) at room temperature for 40 hours. The reaction mixture was extracted with EtOAc (3 x 20 mL). The organic extracts were combined, washed with brine (20 mL), dried (MgSO\(_4\)) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (5-10% EtOAc in petroleum ether) to give 2-benzyl-2-methylcyclopentane-1,3-dione (2.55 g, 75%) as a yellow oil.

\(^{1}\text{H NMR (400 MHz, CDCl}_3\) \(\delta_\text{H}/\text{ppm: 5.54 (ddt, } J = 16.1, 10.9, 7.5 \text{ Hz, 1H), 5.05 – 5.03 (m, 1H), 5.02 – 4.98 (m, 1H), 2.77 – 2.59 (m, 4H), 2.30 (dt, } J = 7.5, 1.1 \text{ Hz, 2H), 1.07 (s, 3H);}^{13}\text{C NMR (101 MHz, CDCl}_3\) \(\delta_c/\text{ppm: 216.3, 131.6, 119.9, 56.8, 40.1, 35.5, 18.9. Consistent with data in the literature.}^8\)

2-BenzyI-2-methylcyclopentane-1,3-dione

2-Methyl-1,3-cyclopentanedione (1.50 g, 13.4 mmol, 1 eq) was dissolved in 1M aq. NaOH (15.0 mL) before addition of benzyl bromide (3.20 mL, 26.8 mmol, 2.0 eq). The resulting mixture was vigorously stirred (1000 rpm) at room temperature for 44 hours. The reaction mixture was extracted with EtOAc (3 x 20 mL). The organic extracts were combined, washed with brine (20 mL), dried (MgSO\(_4\)) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (5-10-15% EtOAc in petroleum ether) to give 2-benzyl-2-methylcyclopentane-1,3-dione (2.025 g, 75%) as an off-white solid.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)/ppm: 7.25 – 7.18 (m, 3H), 7.06 – 7.01 (m, 2H), 2.95 (s, 2H), 2.54 (dd, \(J = 19.2, 7.3\) Hz, 2H), 2.05 (dd, \(J = 18.4, 6.2\) Hz, 2H), 1.20 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\)/ppm: 217.6, 135.9, 129.7, 128.7, 127.4, 58.4, 43.2, 35.6, 20.2. Consistent with data in the literature.\(^8\)

2-(2-Chlorobenzyl)-2-methylcyclopentane-1,3-dione

\[
\begin{align*}
\text{O} & \quad \text{Me} \\
\text{O} & \quad \text{Me} \\
\text{O} & \quad \text{Me} \\
\end{align*}
\]

2-Methyl-1,3-cyclopentanedione (2.50 g, 22.30 mmol, 1 eq) was dissolved in 1M aq. NaOH (25.0 mL) before addition of 2-chlorobenzyl bromide (5.80 mL, 44.60 mmol, 2.0 eq). The resulting mixture was vigorously stirred (1000 rpm) at room temperature for 96 hours. The reaction mixture was extracted with EtOAc (3 x 20 mL). The organic extracts were combined, washed with brine (20 mL), dried (MgSO\(_4\)) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (5-10-20% EtOAc in petroleum ether) to give 2-benzyl-2-methylcyclopentane-1,3-dione (1.453 g, 28%) as a yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)/ppm: 7.35 – 7.30 (m, 1H), 7.19 – 7.14 (m, 2H), 7.12 – 7.08 (m, 1H), 3.10 (s, 2H), 2.67 – 2.48 (m, 4H), 1.18 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\)/ppm: 215.8, 134.7, 133.4, 132.0, 130.0, 128.9, 126.9, 57.2, 39.1, 35.7, 18.6. Consistent with data in the literature.\(^8\)

2-((Benzyloxy)methyl)-2-methylcyclopentane-1,3-dione

\[
\begin{align*}
\text{Bn} & \quad \text{O} \\
\text{O} & \quad \text{Me} \\
\text{O} & \quad \text{TMS} \\
\end{align*}
\]

2-((Benzyloxy)methyl)-2-methyl-1,3-dioxolane (synthesised according to reference [10]) (1.00 g, 4.81 mmol, 1.0 eq) and 1,2-bis(trimethylsiloxy)cyclobutene (1.85 mL, 7.21 mmol, 1.50 eq) were dissolved in CH\(_2\)Cl\(_2\) (8.0 mL) and cooled to 0 °C before
dropwise addition of boron trifluoride diethyl etherate (0.89 mL, 7.21 mmol, 1.50 eq). The resulting solution was left to stir at room temperature for 16 hours. The reaction mixture was poured over water (50 mL) and extracted with CH$_2$Cl$_2$ (3 x 50 mL). The organic extracts were combined, washed with brine (50 mL), dried (MgSO$_4$) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (10-15% EtOAc in petroleum ether) to give 2-((benzyloxy)methyl)-2-methylcyclopentane-1,3-dione (188 mg, 17%) as a colourless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ$_H$/ppm: 7.36 – 7.25 (m, 3H), 7.21 – 7.17 (m, 2H), 4.39 (s, 2H), 3.61 (s, 2H), 2.86 – 2.67 (m, 4H), 1.00 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ$_c$/ppm: 216.8, 137.4, 128.5, 127.9, 127.5, 75.4, 73.7, 56.4, 36.4, 15.2. Consistent with data in the literature.$^9$

$^{2',3'}$-Dihydrospiro[cyclopentane-1,1'-indene]-2,5-dione

1-Indanone (514 mg, 3.89 mmol, 1.0 eq) and 1,2-bis(trimethylsiloxy)cyclobutene (1.50 mL, 5.84 mmol, 1.50 eq) were dissolved in CH$_2$Cl$_2$ (7.0 mL) and cooled to 0 °C before dropwise addition of boron trifluoride diethyl etherate (0.72 mL, 5.84 mmol, 1.50 eq). The resulting solution was left to stir at room temperature for 24 hours. The reaction mixture was poured over water (50 mL) and extracted with CH$_2$Cl$_2$ (3 x 50 mL). The organic extracts were combined, washed with brine (50 mL), dried (MgSO$_4$) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (10-20% EtOAc in petroleum ether) to give $^{2',3'}$-dihydrospiro[cyclopentane-1,1'-indene]-2,5-dione (454 mg, 58%) as a pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ$_H$/ppm: 7.31 – 7.27 (m, 1H), 7.23 (td, $J = 7.5$, 1.2 Hz, 1H), 7.15 (t, $J = 7.5$ Hz, 1H), 6.90 (d, $J = 7.6$ Hz, 1H), 3.18 (t, $J = 7.5$ Hz, 2H), 3.11 – 2.83 (m, 4H), 2.40 (t, $J = 7.5$ Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ$_c$/ppm: 213.3, 145.0, 140.8, 128.5, 127.1, 125.6, 122.6, 70.0, 35.7, 33.0, 31.8. Consistent with data in the literature.$^{10}$
Spiro[chromane-4,1’-cyclopentane]-2’,5’-dione

[Chemical structure image]

Spiro[chromane-4,2’-[1,3]dioxolane] (961 mg, 5.00 mmol, 1.0 eq) and 1,2-bis(trimethylsiloxy)cyclobutene (1.93 mL, 7.50 mmol, 1.50 eq) were dissolved in CH$_2$Cl$_2$ (8.0 mL) and cooled to 0 °C before dropwise addition of boron trifluoride diethyl etherate (0.92 mL, 7.50 mmol, 1.50 eq). The resulting solution was left to stir at room temperature for 18 hours. The reaction mixture was poured over water (50 mL) and extracted with CH$_2$Cl$_2$ (3 x 50 mL). The organic extracts were combined, washed with brine (50 mL), dried (MgSO$_4$) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (10-20% EtOAc in petroleum ether) to give spiro[chromane-4,1’-cyclopentane]-2’,5’-dione (471 mg, 43%) as a colourless, crystalline solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ/ppm: 7.21 – 7.15 (m, 1H), 6.91 (dd, $J = 8.3$, 1.1 Hz, 1H), 6.85 (td, $J = 7.7$, 1.3 Hz, 1H), 6.57 (dd, $J = 7.7$, 1.6 Hz, 1H), 4.35 – 4.31 (m, 2H), 3.11 – 2.90 (m, 4H), 2.10 – 2.06 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ/ppm: 213.7, 155.5, 129.5, 128.1, 121.2, 118.2, 117.8, 61.1, 57.2, 35.6, 29.3. Consistent with data in the literature.$^{10}$

2,2-Dimethylcyclopent-4-ene-1,3-dione

[Chemical structure image]

Synthesised according to general procedure 3 using 2,2-Dimethylcyclopentane-1,3-dione on a 13.62 mmol scale. Purified by flash chromatography (10-15-20% EtOAc in petroleum ether) to give 2,2-Dimethylcyclopent-4-ene-1,3-dione as a pale yellow oil (568 mg, 34% yield). NOTE: Product volatile.

$^1$H NMR (400 MHz, CDCl$_3$) δ/ppm: 7.17 (s, 2H), 1.12 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ/ppm: 207.8, 147.2, 46.5, 19.7. Consistent with data in the literature.$^{11}$
2-Allyl-2-methylcyclopent-4-ene-1,3-dione

Synthesised according to general procedure 3 using 2-allyl-2-methylcyclopentane-1,3-dione on a 16.30 mmol scale. Purified by flash chromatography (2-5-10% EtOAc in petroleum ether) to give 2-allyl-2-methylcyclopent-4-ene-1,3-dione as a bright yellow oil (761 mg, 31% yield). **NOTE**: Product volatile.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 7.20 (s, 2H), 5.44 (ddt, $J$ = 16.9, 10.1, 7.5 Hz, 1H), 5.01 – 4.92 (m, 2H), 4.97 – 4.95 (m, 1H), 2.34 (d, $J$ = 7.5 Hz, 2H), 1.11 (s, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ppm: 207.2, 148.4, 131.5, 119.7, 50.6, 38.8, 18.6. Consistent with data in the literature.$^8$

2-Benzyl-2-methylcyclopent-4-ene-1,3-dione

Synthesised according to general procedure 3 using 2-benzyl-2-methylcyclopentane-1,3-dione on a 16.81 mmol scale. Purified by flash chromatography (5-10-15% EtOAc in petroleum ether) to give 2-benzyl-2-methylcyclopent-4-ene-1,3-dione as a bright yellow solid (2.99 g, 89% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 7.18 – 7.12 (m, 3H), 6.98 (s, 2H), 6.94 – 6.91 (m, 2H), 2.99 (s, 2H), 1.25 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ppm: 207.4, 148.9, 135.7, 129.8, 127.2, 52.7, 41.1, 19.5. Consistent with data in the literature.$^8$
2-(2-Chlorobenzyl)-2-methylcyclopent-4-ene-1,3-dione

Synthesised according to general procedure 3 using 2-(2-chlorobenzyl)-2-methylcyclopentane-1,3-dione on a 5.93 mmol scale. Purified by flash chromatography (5-10-15% EtOAc in petroleum ether) to give 2-(2-chlorobenzyl)-2-methylcyclopent-4-ene-1,3-dione as a bright yellow solid (1.14 g, 82% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ$_{H}$/ppm: 7.29 – 7.25 (m, 1H), 7.14 – 7.08 (m, 2H), 7.10 (s, 2H), 7.06 – 7.02 (m, 1H), 3.14 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ$_{C}$/ppm: 206.4, 148.4, 134.5, 133.4, 132.0, 130.1, 128.7, 126.7, 51.5, 37.6, 18.6. Consistent with data in the literature.$^8$

2-((Benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-dione

Synthesised according to general procedure 3 using 2-((Benzyloxy)methyl)-2-methylcyclopentane-1,3-dione on a 0.81 mmol scale. Purified by flash chromatography (5-10% EtOAc in petroleum ether) to give 2-((Benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-dione as a yellow oil (118 mg, 63% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ$_{H}$/ppm: 7.35 – 7.25 (m, 3H), 7.34 (s, 2H), 7.18 – 7.15 (m, 2H), 4.39 (s, 2H), 3.66 (s, 2H), 1.06 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ$_{C}$/ppm: 206.3, 149.3, 137.5, 128.5, 127.8, 127.4, 73.5, 72.1, 51.4, 14.9. Consistent with data in the literature.$^9$
2',3'-Dihydrospiro[cyclopent-4-ene-1,1'-indene]-2,5-dione

Synthesised according to general procedure 3 using 2',3'-Dihydrospiro[cyclopent-4-ene-1,1'-indene]-2,5-dione on a 2.25 mmol scale. Purified by flash chromatography (5-10-15% EtOAc in petroleum ether) to give 2',3'-Dihydrospiro[cyclopent-4-ene-1,1'-indene]-2,5-dione as a bright yellow solid (343 mg, 77% yield).

\[ \text{H NMR (400 MHz, CDCl}_3 \] \( \delta \) H/ppm: 7.49 (s, 2H), 7.31 (dp, \( J = 7.5, 1.0 \) Hz, 1H), 7.24 (td, \( J = 7.5, 1.1 \) Hz, 1H), 7.12 (tq, \( J = 7.5, 1.0 \) Hz, 1H), 6.78 (dd, \( J = 7.5, 0.4 \) Hz, 1H), 3.23 (t, \( J = 7.4 \) Hz, 2H), 2.41 (t, \( J = 7.4 \) Hz, 2H); \[ \text{C NMR (101 MHz, CDCl}_3 \] \( \delta \) c/ppm: 204.3, 150.3, 145.5, 140.2, 128.6, 126.9, 125.3, 122.3, 63.3, 60.4, 32.0, 31.8, 14.2. Consistent with data in the literature.\(^\text{12}\)

Spiro[chromane-4,1’-cyclopent-4-ene]-2’,5’-dione

Synthesised according to general procedure 3 using Spiro[chromane-4,1’-cyclopentane]-2’,5’-dione on a 2.13 mmol scale. Purified by flash chromatography (10-20-30% EtOAc in petroleum ether) to give Spiro[chromane-4,1’-cyclopent-4-ene]-2’,5’-dione as a bright yellow solid (413 mg, 91% yield).

\[ \text{H NMR (400 MHz, CDCl}_3 \] \( \delta \) H/ppm: 7.48 (s, 2H), 7.23 – 7.10 (m, 1H), 6.92 (dd, \( J = 8.3, 1.3 \) Hz, 1H), 6.81 (td, \( J = 7.5, 1.3 \) Hz, 1H), 6.60 (dd, \( J = 7.8, 1.6 \) Hz, 1H), 4.43 (t, \( J = 5.3 \) Hz, 2H), 2.10 (t, \( J = 5.3 \) Hz, 2H); \[ \text{C NMR (101 MHz, CDCl}_3 \] \( \delta \) c/ppm: 204.5, 155.9, 149.9, 129.6, 127.0, 121.1, 118.2, 117.3, 61.9, 50.3, 28.0. Consistent with data in the literature.\(^\text{11}\)
(1R,2S,3S)-2-Benzyl-2-methylcyclopent-4-ene-1,3-diol

Synthesised according to general procedure 4 using 2-Benzyl-2-methylcyclopent-4-ene-1,3-dione on a 5.00 mmol scale. Purified by flash chromatography (40-50% EtOAc in petroleum ether) to give (1R,2S,3S)-2-Benzyl-2-methylcyclopent-4-ene-1,3-diol as a colourless, crystalline solid (489 mg, 48% yield). Stereochemistry confirmed by 2D NOESY.

1H NMR (500 MHz, CDCl₃) δ/ppm: 7.44 – 7.40 (m, 2H, 2ArH-(9)), 7.29 (t, J = 7.5 Hz, 2H, 2ArH(8)), 7.21 (tt, J = 7.3, 1.3 Hz, 1H, ArH-(10)), 6.19 (dd, J = 1.5, 0.9 Hz, 2H, 2CH-(3)), 4.02 (d, J = 7.2 Hz, 2H, 2CH-(2)), 2.97 (s, 2H, CH₂-(6)), 2.27 (d, J = 7.5 Hz, 2H, 2OH-(4)), 0.72 (s, 3H, CH₃-(5)); 13C NMR (101 MHz, CDCl₃) δ/ppm: 139.5 (C(7)), 137.2 (C(3)), 130.7 (C(8)), 128.2 (C(9)), 126.0 (C(10)), 82.1 (C(2)), 48.4 (C(1)), 36.7 (C(6)), 24.1 (C(5)); HRMS (ESI) m/z calcd for C₁₃H₁₆O₂Na [M+Na]⁺: 227.10425, found: 227.10421; IR (ATR) ν (cm⁻¹) thin film, CHCl₃: 3275.6 (br. m), 2961.1 (w), 2911.1 (w), 1461.0 (w), 1343.4 (w), 1293.5 (w), 1147.5 (w), 1098.8 (w), 1029.2 (m), 981.4 (m), 931.7 (m), 744.2 (m), 700.15 (m), 623.5 (m). Melting point: 99-102 °C.
**Cis-2,2-dimethylcyclopent-4-ene-1,3-diol**

![Chemical Structure]

Synthesised according to general procedure 4 using 2,2-dimethylcyclopent-4-ene-1,3-dione on a 3.72 mmol scale. Purified by flash chromatography (1-2% MeOH in EtOAc) to give cis-2,2-dimethylcyclopent-4-ene-1,3-diol (single diastereomer) as a colourless, crystalline solid (337 mg, 71% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 6.00 (d, $J = 1.1$ Hz, 2H), 4.05 (d, $J = 6.8$ Hz, 2H), 2.14 (d, $J = 7.2$ Hz, 2H), 1.02 (s, 3H), 1.01 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ppm: 136.1, 82.9, 46.0, 26.9, 16.7. Consistent with data in the literature.$^{13}$

**$(1R,2S,3S)$-2-Allyl-2-methylcyclopent-4-ene-1,3-diol**

![Chemical Structure]

Synthesised according to general procedure 4 using 2-allyl-2-methylcyclopent-4-ene-1,3-dione on a 5.07 mmol scale. Purified by flash chromatography (40-50% EtOAc in petroleum ether) to give $(1R,2S,3S)$-2-allyl-2-methylcyclopent-4-ene-1,3-diol as a colourless, crystalline solid (334 mg, 43% yield). Stereochemistry confirmed by 2D NOESY.
\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta/\text{ppm}: 6.07\) (d, \(J = 1.6\) Hz, 2H, 2CH-(3)), 6.00 (ddt, \(J = 17.3, 10.1,\) 7.3 Hz, 1H, CH-(7)), 5.15 (ddt, \(J = 17.3, 2.7,\) 1.4 Hz, 1H, CHH\(^{\text{H}}\)-(8)), 5.10 (ddt, \(J = 10.1, 2.2,\) 1.1 Hz, 1H, CHH\(^{\text{H}}\)-(8)), 4.00 (d, \(J = 0.7\) Hz, 2H, 2CH-(2)), 2.74 (s, 2H, 2OH-(4)), 2.33 (d, \(J = 7.3\) Hz, 2H, CH\(_2\)-(6)), 0.88 (s, 3H, CH\(_3\)-(5)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta/\text{ppm}: 136.5\) (C(3)), 136.1 (C(7)), 117.4 (C(8)), 82.4 (C(2)), 47.0 (C(1)), 35.9 (C(6)), 24.5 (C(5)); HRMS (ESI) m/z calcld for C\(_9\)H\(_{14}\)O\(_2\)Na \([\text{M+Na}]^+:\) 177.08860, found: 177.08862; IR (ATR) \(\nu/\text{cm}^{-1}\) thin film, CHCl\(_3\): 3309.2 (br. m), 2970.6 (w), 2910.1 (w), 1638.0 (w), 1453.8 (w), 1399.1 (w), 1298.3 (w), 1245.3 (w), 1116.1 (w), 1072.7 (m), 1031.7 (m), 997.9 (m), 987.5 (m), 953.7 (m), 902.5 (m), 828.1 (m), 778.0 (m). Melting point: 70–72 °C.

\((1R,2S,3S)-2-(2\text{-Chlorobenzyl})-2\text{-methylcyclopent-4-ene-1,3-diol}\)

![Chemical Structure Diagram](image)

Chemical Formula: C\(_{13}\)H\(_{16}\)ClO\(_2\)
Molecular Weight: 238.7110

Synthesised according to general procedure 4 using 2-(2-chlorobenzyl)-2-methylcyclopent-4-ene-1,3-dione on a 2.14 mmol scale. Purified by flash chromatography (40–50% EtOAc in petroleum ether) to give \((1R,2S,3S)-2-(2\text{-chlorobenzyl})-2\text{-methylcyclopent-4-ene-1,3-diol}\) as a colourless, crystalline solid (188 mg, 37% yield). Stereochemistry confirmed by 2D NOESY.

\(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta/\text{ppm}: 7.76\) (dd, \(J = 7.7,\) 1.8 Hz, 1H, ArH-(11)), 7.35 (dd, \(J = 7.9,\) 1.5 Hz, 1H, ArH-(8)), 7.19 (td, \(J = 7.6,\) 1.5 Hz, 1H, ArH-(10)), 7.13 (td, \(J = 7.7,\) 1.8 Hz, 1H, ArH-(11)), 7.04 (dd, \(J = 7.9,\) 1.5 Hz, 1H, ArH-(8)), 7.00 (td, \(J = 7.6,\) 1.5 Hz, 1H, ArH-(10)), 6.97 (td, \(J = 7.7,\) 1.8 Hz, 1H, ArH-(11)), 6.93 (dd, \(J = 7.9,\) 1.5 Hz, 1H, ArH-(8)), 6.88 (td, \(J = 7.6,\) 1.5 Hz, 1H, ArH-(10)), 6.85 (td, \(J = 7.7,\) 1.8 Hz, 1H, ArH-(11)), 6.81 (dd, \(J = 7.9,\) 1.5 Hz, 1H, ArH-(8)), 6.77 (td, \(J = 7.6,\) 1.5 Hz, 1H, ArH-(10)), 6.73 (td, \(J = 7.7,\) 1.8 Hz, 1H, ArH-(11)), 6.69 (dd, \(J = 7.9,\) 1.5 Hz, 1H, ArH-(8)), 6.65 (td, \(J = 7.6,\) 1.5 Hz, 1H, ArH-(10)), 6.62 (td, \(J = 7.7,\) 1.8 Hz, 1H, ArH-(11)), 6.58 (dd, \(J = 7.9,\) 1.5 Hz, 1H, ArH-(8)), 6.55 (td, \(J = 7.6,\) 1.5 Hz, 1H, ArH-(10)), 6.51 (td, \(J = 7.7,\) 1.8 Hz, 1H, ArH-(11)), 6.47 (dd, \(J = 7.9,\) 1.5 Hz, 1H, ArH-(8)), 6.44 (td, \(J = 7.6,\) 1.5 Hz, 1H, ArH-(10)), 6.41 (td, \(J = 7.7,\) 1.8 Hz, 1H, ArH-(11)), 6.37 (dd, \(J = 7.9,\) 1.5 Hz, 1H, ArH-(8)), 6.34 (td, \(J = 7.6,\) 1.5 Hz, 1H, ArH-(10)), 6.31 (td, \(J = 7.7,\) 1.8 Hz, 1H, ArH-(11)), 6.28 (dd, \(J = 7.9,\) 1.5 Hz, 1H, ArH-(8)), 6.25 (td, \(J = 7.6,\) 1.5 Hz, 1H, ArH-(10)), 6.22 (td, \(J = 7.7,\) 1.8 Hz, 1H, ArH-
= 7.6, 1.8 Hz, 1H, ArH-(9)), 6.20 (dd, J = 1.5, 0.9 Hz, 2H, 2CH-(3)), 4.09 – 4.05 (m, 2H, 2CH-(2)), 3.20 (s, 2H, CH₂-(6)), 2.55 – 2.51 (m, 2H, 2OH-(4)), 0.71 (s, 3H, CH₃-(5)); ¹³C NMR (101 MHz, CDCl₃) δ/c/ppm: 137.7 (C(7)), 137.3 (C(3)), 135.2 (C(12)), 132.3 (C(8)), 129.6 (C(11)), 127.4 (C(10)), 126.9 (C(9)), 82.0 (C(2)), 49.1 (C(1)), 31.7 (C(6)), 22.3 (C(5)); HRMS (ESI) m/z calcd for C₁₃H₁₅O₂ClNa [M+Na]+: 261.06528, found: 261.06531; IR (ATR) ν (cm⁻¹) thin film, CHCl₃: 3315.1 (br. w), 2980.1 (s), 2888.1 (m), 1611.2 (w), 1582.1 (m), 1251.8 (m), 1151.6 (m), 1087.0 (m), 1040.8 (m), 954.6 (m), 820.7 (w), 750.6 (m), 679.0 (w). Melting point: 126-127 °C.

(1R,2S,3S)-2-((Benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-diol

Synthesised according to general procedure 4 using 2-((benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-dione on a 1.27 mmol scale. Purified by flash chromatography (40-50% EtOAc in petroleum ether) to give (1R,2S,3S)-2-((benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-diol as a colourless oil (137 mg, 46% yield). Stereochemistry confirmed by 2D NOESY.

¹H NMR (500 MHz, CDCl₃) δH/ppm: 7.38 – 7.28 (m, 5H, 5ArH-(9-11)), 5.95 (d, J = 1.0 Hz, 2H, 2CH-(3)), 4.51 (s, 2H, CH₂-(7)), 4.20 (d, J = 8.1 Hz, 2H, 2CH-(2)), 3.72 (s, 2H, CH₂-(6)), 2.79 (d, J = 8.8 Hz, 2H, 2OH-(4)), 1.10 (s, 3H, CH₃-(5)); ¹³C NMR (101 MHz, CDCl₃) δ/c/ppm: 137.4 (C(8)), 135.7 (C(3)), 128.7 (C(10)), 128.1 (C(11)), 127.8 (C(9)), 83.7 (C(2)), 73.6 (C(6)), 73.0 (7)), 49.1 (C(1)), 23.3 (C(5)); HRMS
(ESI) m/z calcd for C_{14}H_{18}O_{3}Na\{M+Na\}^{+}: 257.11482, found: 257.11469; IR (ATR) ν (cm\(^{-1}\)) thin film, CHCl\(_3\): 3384.8 (br. m), 2980.5 (s), 2885.4 (m), 1454.3 (w), 1382.8 (m), 1251.4 (w), 1144.4 (m), 1073.6 (m), 1030.6 (m), 955.8 (m), 736.7 (w), 698.1 (w).

\((1S,2R,5S)-2',3'-\text{Dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-diol}\)

Synthesised according to general procedure 4 using \(2',3'-\text{Dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-dione}\) on a 1.72 mmol scale. Purified by flash chromatography (3% MeOH in CH\(_2\)Cl\(_2\)) to give \((1S,2R,5S)-2',3'-\text{Dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-diol}\) as a colourless, crystalline solid (158 mg, 46% yield, NOTE: Mixture of both cis-diastereomers and trans-diastereomer obtained. Unable to remove trans by chromatography; used crude in next step). Stereochemistry confirmed by 2D NOESY.

Analytical data for \((1S,2R,5S)-2',3'-\text{Dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-diol}\)

\(^1\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta_{\text{H}}/\text{ppm}\): 7.43 – 7.37 (m, 1H, ArH-(8)), 7.34 – 7.31 (m, 1H, ArH-(11)), 7.31 – 7.25 (m, 1H, ArH-(10)), 7.24 – 7.17 (m, 1H, ArH-(9)), 6.17 (d, \(J = 0.7\) Hz, 2H, 2CH-(3)), 4.53 (d, \(J = 8.7\) Hz, 2H, 2CH-(2)), 2.99 (t, \(J = 7.4\) Hz, 2H, CH\(_2\)-(6)), 2.25 (t, \(J = 7.4\) Hz, 2H, CH\(_2\)-(5)), 1.69 (d, \(J = 9.0\) Hz, 2H, 2OH-(4)); \(^{13}\text{C}\)}
NMR (101 MHz, CDCl₃) δ/ppm: 147.3 (C(12)), 140.0 (C(7)), 136.8 (C(3)), 128.3 (C(8)), 126.4 (C(10)), 126.2 (C(9)), 125.7 (C(11)), 82.1 (C(2)), 66.3 (C(1)), 36.6 (C(5)), 31.1 (C(6)); HRMS (ESI) m/z calcd for C₁₃H₁₄O₂Na [M+Na]⁺: 225.08860, found: 225.08861; IR (ATR) ν (cm⁻¹) thin film, CHCl₃: 3355.8 (br. m), 1479.3 (w), 1293.3 (m), 1031.2 (m), 987.5 (m), 738.4 (m), 632.0 (m). Melting point: 126-130 °C.

(2'R,4S,5'S)-Spirop[chromane-4,1'-cyclopentan]-3'-ene-2',5'-diol

Synthesised according to general procedure 4 using spiro[chromane-4,1'-cyclopent-4-ene]-2',5'-dione on a 1.87 mmol scale. Purified by flash chromatography (2-3% MeOH in CH₂Cl₂) to give (2'R,4S,5'S)-spiro[chromane-4,1'-cyclopentan]-3'-ene-2',5'-diol as a colourless, crystalline solid (121 mg, 30% yield, NOTE: Mixture of both cis-diastereomers and trans-diastereomer obtained. Unable to remove unknown impurity) Stereochemistry confirmed by 2D NOESY.

Analytical data for (2'R,4S,5'S)-Spirop[chromane-4,1'-cyclopentan]-3'-ene-2',5'-diol

¹H NMR (500 MHz, CDCl₃) δ/ppm: 7.30 (dd, J = 7.8, 1.6 Hz, 1H, ArH-(11)), 7.19 (ddd, J = 8.3, 7.2, 1.7 Hz, 1H, ArH-(9)), 6.92 (dd, J = 8.3, 1.2 Hz, 1H, ArH-(8)), 6.86 (ddd, J = 7.8, 7.2, 1.4 Hz, 1H, ArH-(10)), 6.04 (s, 2H, 2CH-(3)), 4.53 (d, J = 10.0 Hz, 2H, 2CH-(2)), 4.34 (t, J = 5.4 Hz, 2H, CH₂-(6)), 2.26 (t, J = 5.4 Hz, 2H, CH₂-(5)), 1.72 (d, J = 10.0 Hz, 2H, 2OH-(4)); ¹³C NMR (101 MHz, CDCl₃) δ/ppm: 157.3
(C(7)), 135.9 (C(3)), 129.4 (C(9)), 128.4 (C(11)), 120.2 (C(10)), 118.8 (C(8)), 117.9 (C(12)), 83.7 (C(2)), 63.7 (C(6)), 54.6 (C(1)), 34.5 (C(5)); HRMS (ESI) m/z calcd for C_{13}H_{14}O_3Na [M+Na]^+ : 241.08352, found: 241.08354; IR (ATR) ν (cm\(^{-1}\)) thin film, CHCl\(_3\): 3326.1 (br. m), 1488.0 (w), 1303.5 (w), 1225.4 (m), 1063.9 (m), 1042.7 (m), 1014.3 (w), 973.7 (w), 756.9 (m), 643.9 (w). Melting point: 125-137 °C.

(1R,2S,3S)-2-Benzyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (4a)

![Chemical structure](image)

Chemical Formula: C\(_{21}\)H\(_{30}\)O\(_3\)P\(_2\)
Molecular Weight: 476.4425

Synthesised according to general procedure 5 using (1R,2S,3S)-2-benzyl-2-methylcyclopent-4-ene-1,3-diol on a 12.24 mmol scale. Purified by flash chromatography (1-2-3% MeOH in EtOAc) to give (1R,2S,3S)-2-benzyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (4a) as a colourless oil (4.61 g, 79%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ ppm: 7.35 – 7.30 (m, 2H, ArH-(7)), 7.27 – 7.22 (m, 2H, ArH-(8)), 7.17 (tt, J = 7.2, 1.4 Hz, 1H, ArH-(9)), 6.33 (s, 2H, 2CH-(3)), 4.66 – 4.63 (m, 2H, 2CH-(2)), 4.16 – 4.03 (m, 8H, 4CH\(_2\)-(10)), 2.98 (s, 2H, CH\(_2\)-(5)), 1.31 (qd, J = 7.1, 1.0 Hz, 12H, 4CH\(_3\)-(11)), 0.81 (s, 3H, CH\(_3\)-(4)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ ppm: 138.3 (C(6)), 136.0 (C(3)), 130.7 (C(7)), 128.2 (C(8)), 126.2 (C(9)), 86.2 (C(2)), 63.9 (C(10)), 48.6 (C(1)), 36.2 (C(5)), 24.0 (C(4)), 16.3 (C(11)); \(^{31}\)P
NMR (162 MHz, CDCl3) δ/ppm: -2.00; HRMS (ESI) m/z calcd for C17H35O8P2 [M+H]+: 477.17291, found: 477.17285; IR (ATR) ν (cm⁻¹) thin film, CHCl3: 2985.8 (w), 1368.0 (w), 1260.7 (m), 1162.4 (w), 1021.5 (s), 987.6 (s), 911.1 (m), 821.3 (w), 756.2 (w).

_Cis-2,2-dimethylcyclopent-4-ene-1,3-bis(diethyl phosphate) (5a)_

Synthesised according to general procedure 5 using _cis-2,2-dimethylcyclopent-4-ene-1,3-diol_ on a 1.66 mmol scale. Purified by flash chromatography (2-3-4% MeOH in CH2Cl2) to give _cis-2,2-dimethylcyclopent-4-ene-1,3-bis(diethyl phosphate) (5a)_ as a colourless oil (458 mg, 69%).


\[ \text{Chemical Formula: C}_{15}\text{H}_{30}\text{O}_{8}\text{P}_{2} \]

Molecular Weight: 400.3445

\[ ^1H \text{ NMR (400 MHz, CDCl3) } \delta/\text{ppm: } 6.01 \text{ (s, 2H, 2CH-(3))}, \quad 4.71 \text{ (d, } J = 6.4 \text{ Hz, 2H, 2CH-(2))}, \quad 4.06 \text{ (ddq, } J = 10.6, 8.0, 7.1 \text{ Hz, 8H, 4CH}_2\text{-(6)}), \quad 1.29 \text{ (tdd, } J = 7.1, 4.4, 1.0 \text{ Hz, 12H, 4CH}_3\text{-(7)}), \quad 1.17 \text{ (s, 3H, CH}_3\text{-(4)}), \quad 1.00 \text{ (s, 3H, CH}_3\text{-(5))}; \]

\[ ^13\text{C NMR (101 MHz, CDCl3) } \delta/\text{ppm: } 133.9 \text{ (C(3))}, \quad 86.6 \text{ (C(2))}, \quad 63.8 \text{ (C(6))}, \quad 47.5 \text{ (C1)}, \quad 25.9 \text{ (C(4))}, \quad 17.3 \text{ (C5)}, \quad 16.2 \text{ (C(7))}; \]

\[ ^31\text{P NMR (162 MHz, CDCl3) } \delta/\text{ppm: } -1.65; \]

HRMS (ESI) m/z calcd for C15H30O8P2 [M+H]+: 401.14887, found: 401.14848; IR (ATR) ν (cm⁻¹) thin film, CHCl3: 2984.7 (w), 1368.2 (w), 1262.4 (m), 1165.7 (w), 1023.2 (s), 997.1 (s), 951.4 (s), 912.1 (m), 818.4 (w), 755.3 (w).
(1R,2S,3S)-2-Allyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (6a)

\[
\begin{align*}
\text{Chemical Formula: } & C_{17}H_{32}O_8P_2 \\
\text{Molecular Weight: } & 426.3825
\end{align*}
\]

Synthesised according to general procedure 5 using (1R,2S,3S)-2-allyl-2-methylcyclopent-4-ene-1,3-diol on a 1.82 mmol scale. Purified by flash chromatography (2-3% MeOH in EtOAc) to give (1R,2S,3S)-2-allyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (6a) as a colourless oil (632 mg, 81%).

\[\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3\text{) } & \delta_H/\text{ppm: } 6.22 \text{ (d, } J = 0.8 \text{ Hz, } 2H, 2\text{CH-(3))}, 5.89 \text{ (ddt, } J = 17.3, 10.2, 7.2 \text{ Hz, } 1H, \text{CH-(6)}), 5.13 - 5.08 \text{ (m, } 1H, \text{CHH}^-\text{(7)}), 5.08 - 5.05 \text{ (m, } 1H, \text{CHH}^-\text{(7)}), 4.68 \text{ (d, } J = 5.6 \text{ Hz, } 2H, 2\text{CH-(2)}), 4.15 - 4.01 \text{ (m, } 8H, 4\text{CH}_2\text{-(8))}, 2.37 \text{ (d, } J = 7.2 \text{ Hz, } 2H, \text{CH}_2\text{-(5))}, 1.31 \text{ (qd, } J = 7.0, 1.0 \text{ Hz, } 12H, 4\text{CH}_3\text{-(9))}, 1.00 \text{ (s, } 3H, \text{CH}_3\text{-(4))}; \\
\text{13C NMR (101 MHz, CDCl}_3\text{) } & \delta_C/\text{ppm: } 135.3 \text{ (C(3))}, 134.8 \text{ (C(6))}, 117.9 \text{ (C(7))}, 86.2 \text{ (C(2))}, 63.9 \text{ (C(8))}, 47.6 \text{ (C(1))}, 35.7 \text{ (C(5))}, 24.3 \text{ (C(4))}, 16.2 \text{ (C(9))}; \\
\text{31P NMR (162 MHz, CDCl}_3\text{) } & \delta_P/\text{ppm: } -1.85; \\
\text{HRMS (ESI) } m/z \text{ calcd for } C_{17}H_{32}O_8P_2[M+Na]^+: \text{ 449.146.46, found: 449.14596; IR (ATR) } \nu/\text{(cm}^{-1})\text{ thin film, CHCl}_3: 2986.5 \text{ (w), } 1382.2 \text{ (w), } 1251.9 \text{ (m), } 1156.7 \text{ (w), } 1023.2 \text{ (s), } 996.4 \text{ (s), } 949.6 \text{ (s), } 913.2 \text{ (m), } 816.9 \text{ (w), } 754.4 \text{ (w).}
\end{align*}\]
(1R,2S,3S)-2-(2-Chlorobenzyl)-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (7a)

Synthesised according to general procedure 5 using (1R,2S,3S)-2-(2-chlorobenzyl)-2-methylcyclopent-4-ene-1,3-diol on a 0.79 mmol scale. Purified by flash chromatography (2-3% MeOH in EtOAc) to give (1R,2S,3S)-2-(2-chlorobenzyl)-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (7a) as a colourless oil (324 mg, 80%).

$\text{\textbf{1H NMR (400 MHz, CDCl}_3\text{)} \delta_{\text{H}}/\text{ppm: } 7.58 \text{ (dd, } J = 7.6, 1.8 \text{ Hz, } 1\text{H, ArH-(10))}, \text{ 7.34 } \text{ (dd, } J = 7.8, 1.5 \text{ Hz, } 1\text{H, ArH-(7))}, \text{ 7.18 } \text{ (td, } J = 7.6, 1.5 \text{ Hz, } 1\text{H, ArH-(9))}, \text{ 7.12 } \text{ (td, } J = 7.8, 1.8 \text{ Hz, } 1\text{H, ArH-(8))}, \text{ 6.36 } \text{ (s, } 2\text{H, 2CH-(3))}, \text{ 4.72 } - \text{ 4.69 } \text{ (m, } 2\text{H, 2CH-(2))}, \text{ 4.18 } - \text{ 4.04 } \text{ (m, } 8\text{H, 4CH_2-(12))}, \text{ 3.23 } \text{ (s, } 2\text{H, CH_2-(5))}, \text{ 1.33 } \text{ (qd, } J = 7.1, 1.0 \text{ Hz, } 12\text{H, 4CH_3-(13))}, \text{ 0.82 } \text{ (s, } 3\text{H, CH_3-(4))}; \text{ \textbf{13C NMR (101 MHz, CDCl}_3\text{)} \delta_{\text{C}}/\text{ppm: } 136.6 \text{ (C(11))}, \text{ 136.0 } \text{ (C(3))}, \text{ 135.4 } \text{ (C(6))}, \text{ 131.4 } \text{ (C(7))}, \text{ 129.7 } \text{ (C(10))}, \text{ 127.6 } \text{ (C(9))}, \text{ 127.0 } \text{ (C(8))}, \text{ 86.1 } \text{ (C(2))}, \text{ 63.9 } \text{ (C(12))}, \text{ 48.9 } \text{ (C(1))}, \text{ 31.2 } \text{ (C(5))}, \text{ 22.3 } \text{ (C(4))}, \text{ 16.3 } \text{ (C(13))}; \text{ \textbf{31P NMR (162 MHz, CDCl}_3\text{)} \delta_{\text{p}}/\text{ppm: } -2.06; \text{ HRMS (ESI) } m/z \text{ calcld for C}_{21}\text{H}_{34}\text{O}_8\text{ClP}_2[M+H]^+: 511.14120, \text{ found: 511.14102}; \text{ IR (ATR) } \nu/\text{cm}^{-1}\text{ thin film, CHCl}_3\text{: } 2986.9 \text{ (w), } 1369.9 \text{ (w), } 1262.2 \text{ (m), } 1163.4 \text{ (w), } 1023.0 \text{ (s), } 995.4 \text{ (s), } 952.1 \text{ (s), } 909.9 \text{ (m), } 816.7 \text{ (w), } 756.5 \text{ (w).}
(1R,2S,3S)-2-((Benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (8a)

Synthesised according to general procedure 5 using (1R,2S,3S)-2-((benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-diol on a 0.59 mmol scale. Purified by flash chromatography (2-3-4% MeOH in EtOAc) to give (1R,2S,3S)-2-((benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (8a) as a colourless oil (242 mg, 81%).

\[ \text{Chemical Formula: } C_{25}H_{46}O_9P_2 \]
Molecular Weight: 506.4685

\[ \text{1H NMR (400 MHz, CDCl}_3 \text{) } \delta/\text{ppm: } 7.33 \text{ – 7.25 (m, 4H, 4ArH-(8, 9)), 7.25 \text{ – 7.19 (m, 1H, ArH-(10)), 6.24 \text{ – 6.20 (m, 2H, 2CH-(3)), 4.76 \text{ – 4.73 (m, 2H, 2CH-(2)), 4.51 (s, 2H, CH}_2-(6)), 4.06 \text{ – 3.95 (m, 8H, 4CH}_2-(11)), 3.62 (s, 2H, CH}_2-(5)), 1.23 (qd, } J = 7.1, 1.0 \text{ Hz, 12H, 4CH}_3-(12)), 1.15 (s, 3H, CH}_3-(4)); \]
\[ \text{13C NMR (101 MHz, CDCl}_3 \text{) } \delta/\text{ppm: } 138.7 \text{ (C(7)), 135.3 (C(3)), 128.2 (C(9)), 127.4 (C(10)), 127.3 (C(8)), 85.8 (C(2)), 73.4 (C(5)), 69.7 (C(6)), 63.7 (C(11)), 48.4 (C(1)), 22.6 (C(4)), 16.1 (C(12));} \]
\[ \text{31P NMR (162 MHz, CDCl}_3 \text{) } \delta/\text{ppm: } -1.83; \text{ HRMS (ESI) } m/z \text{ calcld for } C_{27}H_{37}O_9P_2 [M+H]^+ \text{: } 507.19073, \text{ found: } 507.19021; \text{ IR (ATR) } \nu \text{ (cm}^{-1}) \text{ thin film, CDCl}_3 \text{: } 2980.8 \text{ (w), 1392.9 (w), 1262.5 (m), 1164.6 (w), 1098.7 (w), 1072.2 (w), 1021.0 (s), 965.3 (s), 919.7 (w), 879.9 (w), 742.3 (w), 700.0 (w).} \]
(1S,2R,5S)-2',3'-Dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-bis(diethyl phosphate) (9a)

Synthesised according to general procedure 5 using (1S,2R,5S)-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-diol on a 0.72 mmol scale. Purified by flash chromatography (1-2-3% MeOH in EtOAc) to give (1S,2R,5S)-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-bis(diethyl phosphate) (9a) as a colourless oil (221 mg, 65%).

$^1$H NMR (400 MHz, CDCl$_3$) δ$_H$/ppm: 7.32 (d, $J = 7.6$ Hz, 1H, ArH-(7)), 7.18 – 7.14 (m, 1H, ArH-(10)), 7.12 (td, $J = 7.1$, 1.3 Hz, 1H, ArH-(9)), 7.05 (td, $J = 7.6$, 7.1, 0.8 Hz, 1H, ArH-(8)), 6.26 – 6.25 (m, 2H, 2CH-(3)), 5.11 – 5.08 (m, 2H, 2CH-(2)), 3.90 – 3.79 (m, 4H, 2CH$_2$-(12)), 3.63 – 3.54 (m, 4H, 2CH$_2$-(12)), 2.97 (t, $J = 7.3$ Hz, 2H, CH$_2$-(5)), 2.31 (t, $J = 7.3$ Hz, 2H, CH$_2$-(4)), 1.20 – 1.15 (m, 6H, 2CH$_3$-(13)), 1.06 – 1.01 (m, 6H, 2CH$_3$-(13)); $^{13}$C NMR (101 MHz, CDCl$_3$) δ$_C$/ppm: 145.4 (C(11)), 139.9 (C(6)), 135.2 (C(3)), 128.4 (C(7)), 127.4 (C(9)), 125.2 (C(8)), 124.1 (C(10)), 85.6 (C(2)), 63.9 (C(1)), 63.6 (C(12)), 37.5 (C(4)), 30.7 (C(5)), 16.0 (C(13)); $^{31}$P NMR (162 MHz, CDCl$_3$) δ$_P$/ppm: -2.29; HRMS (ESI) m/z calcd for C$_{21}$H$_{33}$O$_8$P$_2$ [M+H]$^+$ : 475.16452, found: 475.16455; IR (ATR) ν (cm$^{-1}$) thin film, CHCl$_3$: 2981.6 (w), 1262.6 (m), 1165.4 (w), 1009.2 (s), 953.5 (s), 902.6 (w), 883.4 (w), 818.6 (w), 803.3 (w), 760.3 (w).
(2'R,4S,5'S)-Spiro[chromane-4,1'-cyclopentan]-3'-ene-2',5'-bis(diethyl phosphate) (10a)

Synthesised according to general procedure 5 using (2'R,4S,5'S)-spiro[chromane-4,1'-
cyclopentan]-3'-ene-2',5'-dial on a 0.57 mmol scale. Purified by flash chromatography
(3-4-5% MeOH in EtOAc) to give (2'R,4S,5'S)-spiro[chromane-4,1'-cyclopentan]-3'-
ene-2',5'-bis(diethyl phosphate) (10a) as a colourless oil (193 mg, 69%).

\[ \text{Chemical Formula: C}_{21}\text{H}_{33}\text{O}_{9}\text{P}_{2} \]
\[ \text{Molecular Weight: 490.4255} \]

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3\text{) } & \delta_{\text{H}}/\text{ppm: 7.17 (dd, } J = 7.9, 1.5 \text{ Hz, 1H, ArH-(10))}, 7.03 \\
& (\text{td, } J = 7.1, 1.7 \text{ Hz, 1H, ArH-(8))}, 6.76 - 6.69 \text{ (m, 2H, 2ArH-(7, 9))}, 6.19 \text{ (s, 2H,} \\
& 2\text{CH-(3))}, 5.10 \text{ (dd, } J = 7.2, 1.0 \text{ Hz, 2H, 2CH-(2))}, 4.30 \text{ (t, } J = 5.4 \text{ Hz, 2H,} \\
& \text{CH}_{2}-(5))}, 3.91 - 3.81 \text{ (m, 4H, 2CH}_{2}-(12))}, 3.63 - 3.53 \text{ (m, 4H, 2CH}_{2}-(12))}, 2.32 \text{ (t, } J = 5.4 \text{ Hz,} \\
& 2\text{H, CH}_{2}-(4))}, 1.19 \text{ (td, } J = 7.1, 1.1 \text{ Hz, 6H, 2CH}_{3}-(13))}, 1.03 \text{ (td, } J = 7.1, 1.1 \text{ Hz, 6H,} \\
& 2\text{CH}_{3}-(13)); 13\text{C NMR (101 MHz, CDCl}_3\text{) } \delta_{\text{C}}/\text{ppm: 155.7 (C(6))}, 134.3 \text{ (C(3))}, 132.1 \\
& (\text{C(10)}), 128.2 \text{ (C(8))}, 118.7 \text{ (C(9))}, 118.0 \text{ (C(11))}, 116.9 \text{ (C(7))}, 86.7 \text{ (C(2))}, 63.8 \\
& (\text{C(12)}), 63.1 \text{ (C(5))}, 52.3 \text{ (C(1))}, 34.8 \text{ (C(4))}, 16.0 \text{ (C(13))}); 31\text{P NMR (162 MHz,} \\
& \text{CDCl}_3\text{) } \delta_{\text{P}}/\text{ppm: -2.29; HRMS (ESI) } m/z \text{ calcd for C}_{21}\text{H}_{33}\text{O}_{9}\text{P}_{2}[\text{M+H}]^+: 491.15943,} \\
& \text{found: 491.15935; IR (ATR) } \nu/(\text{cm}^{-1}) \text{ thin film, CHCl}_3: 2981.5 \text{ (w), 1490.2} \text{ (w),} \\
& 1450.9 \text{ (w), 1308.6 \text{ (m), 1261.2} \text{ (w), 1009.0} \text{ (s), 957.5} \text{ (s), 889.0} \text{ (w), 818.3} \text{ (w), 803.8} \text{ (w),} \\
& 754.5 \text{ (m).} \n\end{align*}
\]
Heterocyclic Bisphosphates

1,1'-Oxybis(but-3-en-2-ol)

1,4-Anhydroerythritol (1.37 mL, 16.7 mmol, 1 eq) was dissolved in CH₂Cl₂ (35 mL) and cooled to 0 °C before addition of PhI(OAc)₂ (8.05 g, 25.0 mmol, 1.5 eq). The resulting mixture was allowed to warm to room temperature and stir for 2 hours. The mixture was cooled to −78 °C and vinylmagnesium bromide (1.0 M in THF, 100 mL, 100 mmol, 6 eq) was added slowly via canula. The resulting mixture was warmed to 0 °C and left to stir for 1 hour and then poured over sat. aq. NH₄Cl (150 mL). The mixture was extracted with EtOAc (3 x 100 mL). The organic extracts were combined, washed with brine (150 mL), dried (MgSO₄) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (40-50% EtOAc in petroleum ether) to give 1,1'-oxybis(but-3-en-2-ol) (1.644 g, 62%) as a colourless oil.

¹H NMR (500 MHz, CDCl₃) δ/ppm: 5.81 (dddd, J = 17.2, 10.6, 5.7, 3.4 Hz, 2H), 5.34 (d, J = 17.2 Hz, 2H), 5.17 (dd, J = 10.6, 1.4 Hz, 2H), 4.36 – 4.31 (m, 2H), 3.57 (dd, J = 10.0, 3.1 Hz, 1H), 3.53 (dd, J = 10.1, 3.1 Hz, 1H), 3.45 (s, 2H), 3.42 (dd, J = 10.1, 7.9 Hz, 1H), 3.37 (dd, J = 10.0, 8.2 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ/ppm: 136.6, 116.6, 75.4, 71.6. Consistent with data in the literature.
**Cis-2,3,6,7-tetrahydrooxepine-3,6-diol**

To a solution of 1,1'-oxybis(but-3-en-2-ol) (1.36 g, 8.60 mmol, 1.0 eq) in 1,2-dichloroethane (860 ml) was added Grubbs Catalyst 2nd Generation (146 mg, 0.172 mmol, 2 mol%). The resulting solution was left to stir at 60 °C for 24 hours. Another portion of Grubbs Catalyst 2nd Generation (146 mg, 0.172 mmol, 2 mol%) was added and the reaction was left to stir at 60 °C for a further 24 hours. The reaction mixture was concentrated *in vacuo* to give a brown oil. The brown oil was purified by flash chromatography (75% EtOAc in petroleum ether) to give *cis*-2,3,6,7-tetrahydrooxepine-3,6-diol (less polar, eluted first, 204 mg, 18%) and *trans*-2,3,6,7-tetrahydrooxepine-3,6-diol (more polar, eluted second, 203 mg, 18%) as brown oils. *Cis*-diol characterised.

1H NMR (400 MHz, CDCl3) δ H/ppm: 5.91 (dd, J = 3.1, 1.5 Hz, 2H), 4.14 (s, 2H), 3.88 (dd, J = 12.4, 5.1 Hz, 4H), 3.63 (dd, J = 12.4, 2.3 Hz, 2H); 13C NMR (126 MHz, CDCl3) δ c/ppm: 133.5, 76.2, 69.9. Consistent with data in the literature.¹⁶

**Tetraethyl ((3R,6S)-2,3,6,7-tetrahydrooxepine-3,6-diy) bis(phosphate) (11a)**

*Cis*-2,3,6,7-tetrahydrooxepine-3,6-diol (204 mg, 1.57 mmol, 1.0 eq) was dissolved in THF (10 mL) before addition of DABCO (527 mg, 4.70 mmol, 3.0 eq). The resulting solution was cooled to 0 °C before dropwise addition of diethyl chlorophosphate (0.68 mL, 4.70 mmol, 3.0 eq). The resulting mixture was allowed to warm to room temperature and stir for 17 hours before being poured over sat. aq. NaHCO₃ (50 mL). The mixture was extracted with EtOAc (3 x 50 mL). The organic extracts were combined, washed with brine (100 mL), dried (MgSO₄) and evaporated *in vacuo* to
give a yellow oil. The yellow oil was purified by flash chromatography (0-1-2% MeOH in CH₂Cl₂) to give tetraethyl ((3R,6S)-2,3,6,7-tetrahydrooxepine-3,6-diyl) bis(phosphate) (11a) (289 mg, 46%) as a colourless oil.

\[ \text{tert-Butyl (3R,4S)-3,4-dihydroxypyrrolidine-1-carboxylate} \]

To a solution of N-Boc-2,5-dihydro-1H-pyrrole (2.50 g, 14.77 mmol, 1 eq) in acetone (24 mL) and water (6 mL) was added NMO (2.60 g, 22.19 mmol, 1.5 eq) followed by potassium osmate(VI) dihydrate (163 mg, 0.44 mmol, 0.03 eq). The resulting orange/brown suspension was left to stir at room temperature overnight. The resulting mixture was quenched by addition of sat. aq. Na₂S₂O₅ (100 mL). The mixture was extracted with EtOAc (3 x 100 mL). The organic extracts were combined, washed with brine (150 mL), dried (MgSO₄) and evaporated in vacuo to give a yellow oil. The yellow oil was purified by flash chromatography (0-10% MeOH in CH₂Cl₂) to give tert-butyl (3R,4S)-3,4-dihydroxypyrrolidine-1-carboxylate (2.98 g, 99%) as a clear amorphous solid.
$^1$H NMR (500 MHz, CDCl$_3$) δ$_H$/ppm: 4.20 – 4.15 (m, 2H), 3.77 (s, 2H), 3.50 (dd, $J$ = 11.0, 5.2 Hz, 2H), 3.29 (dd, $J$ = 11.0, 4.0 Hz, 2H), 1.41 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ$_C$/ppm: 155.0, 80.1, 71.0, 50.5, 28.6. Consistent with data in the literature.$^{15}$

tert-Butyl bis(2-hydroxybut-3-en-1-yl)carbamate

$^1$H NMR (500 MHz, CDCl$_3$) δ$_H$/ppm: 5.88 – 5.72 (m, 2H), 5.38 – 5.24 (m, 2H), 5.14 (d, $J$ = 10.6 Hz, 2H), 4.58 – 4.28 (m, 2H), 4.00 (s, 2H), 3.74 – 2.77 (m, 4H), 1.45 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ$_C$/ppm: 157.1, 156.4, 138.3, 138.1, 115.9, 80.6, 72.8, 72.2, 72.1, 57.4, 57.1, 55.7, 55.4, 28.5, 28.5. Consistent with data in the literature.$^{16}$
**tert-Butyl (3R,6S)-3,6-dihydroxy-2,3,6,7-tetrahydro-1H-azepine-1-carboxylate**

![Chemical structure](image)

To a solution of tert-butyl bis(2-hydroxybut-3-en-1-yl)carbamate (3.09 g, 12.01 mmol, 1.0 eq) in CH₂Cl₂ (400 ml) was added Grubbs Catalyst 2nd Generation (307 mg, 0.36 mmol, 3 mol%). The resulting solution was left to stir at room temperature for 5 days. The reaction mixture was concentrated *in vacuo* to give a brown oil. The brown oil was purified by flash chromatography (75% EtOAc in petroleum ether) to give tert-butyl cis-3,6-dihydroxy-2,3,6,7-tetrahydro-1H-azepine-1-carboxylate (less polar, eluted first, 472 mg, 17%) and tert-butyl trans-3,6-dihydroxy-2,3,6,7-tetrahydro-1H-azepine-1-carboxylate (more polar, eluted second, 469 mg, 17%) as brown oils. Both obtained as a mixture of rotamers. *Cis*-diol characterised.

^{1}H NMR (400 MHz, CDCl₃) δ/ppm: 5.75 (s, 2H), 4.40 – 4.24 (m, 2H), 3.87 (br. s, 1H), 3.82 – 3.71 (m, 2H), 3.30 (br. s, 1H), 3.22 – 3.14 (m, 2H), 1.44 (s, 9H); ^{13}C NMR (126 MHz, CDCl₃) δ/ppm: 155.8, 133.9, 80.7, 69.0, 53.3, 28.4. Consistent with data in the literature.¹⁶

**tert-Butyl (3R,6S)-3,6-bis((diethoxypyrophosphoryl)oxy)-2,3,6,7-tetrahydro-1H-azepine-1-carboxylate (12a)**

![Chemical structure](image)

To a solution of tert-butyl cis-3,6-dihydroxy-2,3,6,7-tetrahydro-1H-azepine-1-carboxylate (470 mg, 2.05 mmol, 1.0 eq) in CH₂Cl₂ (8.2 mL) was added NEt₃ (0.86 mL, 6.15 mmol, 3.0 eq) and DMAP (124 mg, 1.01 mmol, 0.5 eq). The resulting solution was cooled to 0 °C before dropwise addition of diethylchlorophosphosphate (0.89 mL, 6.15 mmol, 3.0 eq). The resulting mixture was left to stir at room temperature for 16 hours. The mixture was then quenched with H₂O (20 mL) and extracted with
CH₂Cl₂ (3 x 20 mL). The organic extracts were combined, washed with brine (50 mL), dried (MgSO₄) and evaporated \textit{in vacuo} to give a yellow oil. The yellow oil was purified by flash chromatography (50-100% EtOAc in heptane) to give \textit{tert}-Butyl (3R,6S)-3,6-bis((diethoxyphosphoryl)oxy)-2,3,6,7-tetrahydro-1H-azepine-1-carboxylate (12a) as a pale yellow oil (494 mg, 48% yield). Obtained as a mixture of rotamers.

![Chemical structure of 12a](image)

\(^1\)H NMR (400 MHz, DMSO-\textit{d₆}, 338K) \(\delta/\text{ppm:} 5.83 \text{ (s, 2H, 2CH-(3))}, 4.92 - 4.86 \text{ (m, 2H, 2CH-(2))}, 4.11 - 4.03 \text{ (m, 8H, 4CH₂-(4))}, 4.02 \text{ (dd,} J=13.6,4.3 \text{ Hz, 2H, 2CHH'-(1)}), 3.22 \text{ (dd,} J=13.6,9.5 \text{ Hz, 2H, 2CHH'-(1)}), 1.46 \text{ (s, 9H, 3CH₃-(8))}, 1.29 \text{ (t,} J=6.9 \text{ Hz, 12H, 4CH₃-(5))}; \(^{13}\)C NMR (126 MHz, CDCl₃) \(\delta/\text{ppm:} 154.41 \text{ (C(6))}, 131.95 \text{ (C(3))}, 131.69 \text{ (C(3))}, 81.00 \text{ (C(2))}, 74.18 \text{ (C(1))}, 73.79 \text{ (C(1))}, 64.13 \text{ (C(4))}, 52.12 \text{ (C(7))}, 51.33 \text{ (C(7))}, 28.39 \text{ (C(8))}, 16.25 \text{ (C(5))}; \(^{31}\)P NMR (162 MHz, CDCl₃) \(\delta/\text{ppm:} -1.50\); HRMS (ESI) \(m/z\) calcd for C₁₉H₃₇NO₁₀P [M+H]: 501.18927, found: 501.19836; IR (ATR) \(\nu \text{ (cm}^{-1} \text{)}\) thin film, CHCl₃: 2888.4 (w), 1693.7 (s), 1465.7 (w), 1367.8 (w), 1254.0 (m), 1027.8 (s), 989.6 (m), 806.3 (w), 701.2 (w)
Desymmetrization Products

Dimethyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate

Synthesised according to general procedure 1b, using *meso*-4-cyclopentene-1,3-bisdimethylphosphate and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (20-50% EtOAc in petroleum ether) to give dimethyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate as a yellow oil (71 mg, 55%).

HPLC analysis indicated an enantiomeric excess of 86% [Chiralpak® IA; flow: 1 mL/min; hexane/iPrOH: 94:6; λ = 210 nm; major enantiomer, \( t_R = 8.075 \) min; minor enantiomer, \( t_R = 10.003 \) min].

\begin{align*}
\text{1H NMR (400 MHz, CDCl}_3) \delta_{\text{H}}/\text{ppm:} & \quad 7.33 – 7.24 (m, 2H, ArH-(12)), 7.21 – 7.14 (m, 3H, ArH-(11, 13)), 5.77 – 5.58 (m, 2H, 2CH-(3, 4)), 4.68 (tt, \( J = 6.3, 2.9 \) Hz, 1H, CH-(1)), 3.74 (dd, \( J = 11.1, 0.9 \) Hz, 6H, 2CH_3-(14)), 2.87 – 2.71 (m, 2H, CHH’-(2), CHH’-(5)), 2.66 – 2.57 (m, \( J = 7.7 \) Hz, 2H, CH_2-(9)), 2.54 – 2.44 (m, \( J = 17.8 \) Hz, 1H, CHHH’-(2)), 1.73 – 1.58 (m, 2H, CH_2-(6)), 1.53 – 1.27 (m, 4H, 2CH_2-(7, 8))); \\
\text{13C NMR (101 MHz, CDCl}_3) \delta_{\text{c}}/\text{ppm:} & \quad 142.7 (C(10)), 132.8 (C(4)), 128.5 (C(12)), 128.4 (C(11)), 127.3 (C(3)), 125.8 (C(13)), 83.5 (C(1)), 54.3 (C(14)), 53.06 (C(5)), 39.9 (C(2)), 36.0
\end{align*}
(C(9)), 32.7 (C(6)), 31.7 (C(8)), 27.2 (C(7)); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$/ppm: 0.76; HRMS (ESI) $m/z$ calcld for C$_{17}$H$_{25}$O$_4$P [M+H]$^+$: 325.149, found: 325.1569; IR (ATR) $\nu$ (cm$^{-1}$) thin film, CHCl$_3$: 2929.8 (w), 2584.7 (w), 1453.9 (w), 1218.4 (m), 1186.0 (w), 1035.0 (s), 922.3 (w), 848.1 (m), 750.0 (w), 700.8 (w); $[\alpha]_25^{{\text{589}}} = -72.6$ (c=1.0 in CHCl$_3$, 86% ee).

Diethyl ((1$R$,2$R$)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate (1b)

![Chemical Structure](image)

Chemical Formula: C$_{18}$H$_{26}$O$_4$P
Molecular Weight: 352.4108

Synthesised according to general procedure 1b, using meso-4-cyclopentene-1,3-bisdiethylphosphate (1a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (20-40% EtOAc in petroleum ether) to give 1b as a yellow oil (93 mg, 66%).

HPLC analysis indicated an enantiomeric excess of 90% [Chiralpak® IA; flow: 1.0 mL/min; hexane/iPrOH: 95:5; $\lambda$ = 210 nm; major enantiomer, $t_R$ = 8.687 min; minor enantiomer, $t_R$ = 10.302 min].

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 7.31 – 7.22 (m, 2H, ArH-(12)), 7.22 – 7.13 (m, 3H, ArH-(11, 13)), 5.66 (dq, $J = 6.0$, 1.8 Hz, 2H, 2CH-(3, 4)), 4.67 (tt, $J = 6.4$, 3.0 Hz, 1H, CH-(1)), 4.09 (p, $J = 7.2$ Hz, 4H, 2CH$_2$-(14)), 2.86 – 2.69 (m, 2H, $CHH'$.-(2),
CH-(5)), 2.67 – 2.57 (m, J = 7.7 Hz, 2H, CH2-(9)), 2.53 – 2.46 (m, 1H, CHH’-(2)), 1.72 – 1.56 (m, 2H, CH2-(6)), 1.56 – 1.38 (m, 4H, 2CH2-(7, 8)), 1.33 (t, J = 7.3 Hz, 6H, 2CH3-(15)); 13C NMR (101 MHz, CDCl3) δ/ppm: 142.7 (C(10)), 132.7 (C(4)), 128.4 (C(12)), 128.3 (C(11)), 127.3 (C(3)), 125.7 (C(13)), 83.1 (C(1)), 63.6 (C(14)), 53.0 (C(5)), 39.9 (C(2)), 35.9 (C(9)), 32.6 (C(6)), 31.7 (C(8)), 27.2 (C(7)), 16.3 (C(15)); 31P NMR (162 MHz, CDCl3) δ/ppm: -1.45; HRMS (ESI) m/z calcd for C19H29O4P [M+H]+ : 353.1803, found: 353.1883; IR (ATR) ν (cm\(^{-1}\)) thin film, CHCl3: 2930.2 (w), 2586.7 (w), 1453.8 (w), 1369.2 (w), 1262.6 (m), 1165.9 (w), 1028.6 (s), 976.8 (m), 820.8 (w), 748.9 (w), 700.4 (w); [α]\(^{25}\) = -65.6 (c=1.0 in CHCl3, 90% ee).

**Diisopropyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate**

![Chemical structure](attachment:chemical_structure.png)

**Chemical Formula:** C\(_{20}\)H\(_{30}\)O\(_5\)P

**Molecular Weight:** 380.4648

Synthesised according to general procedure 1b, using meso-4-cyclopentene-1,3-bisdiisopropylphosphatate and 4-phenyl-1-buten as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (30-40% EtOAc in petroleum ether) to give diisopropyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate as a yellow oil (69 mg, 45%).

HPLC analysis indicated an enantiomeric excess of 84% [Chiralpak® IA; flow: 1 mL/min; hexane/iPrOH: 96:4; λ = 210 nm; major enantiomer, t\(_R\) = 7.985 min; minor enantiomer, t\(_R\) = 10.348 min].

S50
$^1$H NMR (400 MHz, CDCl$_3$) δ/ppm: 7.30 – 7.24 (m, 2H, ArH-(12)), 7.20 – 7.13 (m, 3H, 2ArH-(11, 13)), 5.65 (dq, J = 6.0, 1.9 Hz, 2H, 2CH-(3, 4)), 4.69 – 4.57 (m, 3H, 3CH-(1, 14)), 2.81 – 2.70 (m, 2H, CHH$^\cdot$(2), CH-(5)), 2.64 – 2.57 (m, 2H, CH$_2$-(9)), 2.50 (dd, J = 17.5, 1.8 Hz, 1H, CHH$^\cdot$(2)), 1.64 – 1.58 (m, 2H, CH$_2$-(6)), 1.53 – 1.38 (m, 4H, 2CH$_2$-(7, 8)), 1.32 (d, J = 6.3 Hz, 12H, 4CH$_3$-(15)); $^{13}$C NMR (101 MHz, CDCl$_3$) δ/c/ppm: 142.7 (C(10)), 132.7 (C(4)), 128.5 (C(12)), 128.4 (C(11)), 127.4 (C(3)), 125.8 (C(13)), 82.9 (C(1)), 72.3 (C(14)), 53.0 (C(5)), 39.9 (C(2)), 36.0 (C(9)), 32.8 (C(6)), 31.8 (C(8)), 27.3 (C(7)), 23.8 (C(15)); $^{31}$P NMR (162 MHz, CDCl$_3$) δ$\nu$/ppm: -3.05; HRMS (ESI) m/z calcd for C$_{21}$H$_{33}$O$_4$NaP$^{[M+Na]^+}$: 403.2009, found: 403.2002; IR (ATR) ν (cm$^{-1}$) thin film, CHCl$_3$: 2980.6 (m), 2931.3 (w), 1454.3 (w), 1385.4 (w), 1260.3 (m), 1143.1 (w), 999.2 (s), 700.1 (w).; [$\alpha$]$^{25}_{D89}$ = -63.1 (c=1.0 in CHCl$_3$, 84% ee).

Diphenyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate

Chemical Formula: C$_{22}$H$_{28}$O$_4$P
Molecular Weight: 448.4988

Synthesised according to general procedure 1b, using *meso*-4-cyclopentene-1,3-bisdiphenylphosphate and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10% EtOAc in petroleum ether with 1% NEt$_3$) on silica which was pre-washed with 2% NEt$_3$ in petroleum ether solution
to give diphenyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate as a yellow oil (121 mg, 68%).

HPLC analysis indicated an enantiomeric excess of 70% [Chiralpak® IA; flow: 1 mL/min; hexane/iPrOH: 90:10; λ = 210 nm; major enantiomer, tR = 13.473 min; minor enantiomer, tR = 17.902 min].

\[ \text{H NMR (400 MHz, CDCl}_3 \text{)} \delta \text{H/ppm: 7.35 – 7.12 (m, 15H, ArH-(11, 12, 13, 15, 16, 17)), 5.65 (dq, J = 6.0, 1.8 Hz, 2H, 2CH-(3, 4)), 4.94 – 4.88 (m, J = 6.4, 3.8, 2.9 Hz, 1H, CH-(1)), 2.82 – 2.71 (m, 2H, CHH'-(2), CH-(5)), 2.58 – 2.53 (m, 2H, CH2-(9)), 2.53 – 2.46 (m, 1H, CHH'-(2)), 1.62 – 1.52 (m, 2H, CH2-(6)), 1.43 – 1.25 (m, 4H, 2CH2-(7, 8)); }^{13}\text{C NMR (101 MHz, CDCl}_3 \text{)} \delta \text{C/ppm: 150.6 (C(14)), 142.6 (C(10), 132.6 (C(4)), 129.8 (C(12)), 128.4 (C(11)), 128.3 (C(13)), 127.1 (C(3)), 125.7 (C(16)), 125.3 (C(17)), 120.2 (C(15)), 85.1 (C(1)), 52.9 (C(5)), 39.7 (C(2)), 35.8 (C(9)), 32.4 (C(6)), 31.6 (C(8)), 27.1 (C(7)); }^{31}\text{P NMR (162 MHz, CDCl}_3 \text{)} \delta \text{P/ppm: -12.3; HRMS (ESI) m/z calcld for C}_{27}\text{H}_{29}\text{O}_4\text{NaP [M+Na]}^+: 471.1696, found: 471.1688; IR (ATR) \nu (\text{cm}^{-1}) \text{ thin film, CHCl}_3: 2929.9 (w), 2856.3 (w), 1591.2 (w), 1489.3 (m), 1455.3 (w), 1286.5 (m), 1221.1 (w), 1190.9 (s), 1163.1 (w), 1022.4 (m), 948.6 (s), 753.9 (m), 689.2 (m); }^{[\alpha]}_{D}^{25} = -36.1 (c=1.0 \text{ in CHCl}_3, 70\% \text{ ee).} \]
Diethyl ((1R,2R)-2-(4-phenylbutyl)cyclohex-3-en-1-yl) phosphate (2b)

Sythesised according to general procedure 1b, using meso-5-cyclohexene-1,4-bisdiethylphosphate (2a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (40-50% EtOAc in petroleum ether) to give 2b as a yellow oil (102 mg, 79%).

HPLC analysis indicated an enantiomeric excess of 91% [Chiralpak® IB; flow: 1 mL/min; hexane/iPrOH: 98:2; λ = 210 nm; major enantiomer, tR = 9.164 min; minor enantiomer, tR = 9.966 min].

1H NMR (400 MHz, CDCl3) δ/ppm: 7.31 – 7.23 (m, 2H, ArH-(13)), 7.20 – 7.13 (m, 3H, ArH-(12, 14)), 5.69 – 5.61 (m, 1H, CH-(1)), 5.54 – 5.47 (m, 1H, CH-(5)), 4.33 (dtd, J = 9.4, 6.7, 2.9 Hz, 1H, CH-(1)), 4.09 (p, J = 7.1 Hz, 4H, 2CH2-(15)), 2.61 (t, J = 7.7 Hz, 2H, CH2-(10)), 2.30 – 2.20 (m, 1H, CH-(6)), 2.20 – 2.13 (m, 1H, CHH’- (3)), 2.13 – 2.07 (m, 1H, CHH’-(3)), 2.07 – 1.99 (m, 1H, CHH’-(2)), 1.87 – 1.76 (m, 1H, CHH’-(2)), 1.68 – 1.34 (m, 6H, 3CH2-(7, 8, 9)), 1.32 (tdd, J = 7.1, 2.8, 1.0 Hz, 6H, 2CH3-(16)); 13C NMR (101 MHz, CDCl3) δ/ppm: 142.7 (C(11)), 128.5 (C(13)), 128.4 (C(12)), 128.1 (C(5)), 126.4 (C(4)), 125.7 (C(14)), 78.4 (C(1)), 63.6 (C(15)), 63.1 (C(15))
41.8 (C(6)), 36.0 (C(10)), 32.5 (C(7)), 31.9 (C(9)), 27.8 (C(2)), 26.1 (C(8)), 23.3 (C(3)), 16.2 (C(16)); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$/ppm: -1.47; HRMS (ESI) m/z calcd for C$_{20}$H$_{31}$O$_4$NaP [M+Na]$^+$ : 389.18522, found: 389.18602; IR (ATR) $\nu$ (cm$^{-1}$) thin film, CHCl$_3$: 2981.0 (w), 2931.1 (w), 2858.5 (w), 1262.0 (m), 1030.7 (s), 1010.4 (s), 967.4 (m), 817.8 (w), 784.2 (w), 700.0 (w); $[\alpha]^{25}_{D89} = -70.2$ (c=1.0 in CHCl$_3$, 95% ee).

**Diethyl ((1R,2R)-2-(4-phenylbutyl)cyclohept-3-en-1-yl) phosphate (3b)**

![Chemical structure of 3b]

Chemical Formula: C$_{24}$H$_{35}$O$_4$P
Molecular Weight: 380.4648

Synthesised according to general procedure 1b, using *meso*-6-cycloheptene-1,5-bisdiethylphosphate (3a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (40-50% EtOAc in petroleum ether) to give 3b as a yellow oil (92 mg, 60%).

HPLC analysis indicated an enantiomeric excess of 92% [Chiralpak® IC; flow: 1 mL/min; hexane/iPrOH: 96:4; $\lambda$ = 210 nm; major enantiomer, $t_R$ = 26.044 min; minor enantiomer, $t_R$ = 29.793 min].
$^1$H NMR (400 MHz, CDCl$_3$) δ/ppm: 7.30 – 7.24 (m, 2H, ArH-(14)), 7.21 – 7.14 (m, 3H, ArH-(13, 15)), 5.84 (dtd, J = 11.2, 6.3, 1.6 Hz, 1H, CH-(5)), 5.41 (dd, J = 11.2, 4.6 Hz, 1H, CH-(6)), 4.26 (qd, J = 8.1, 3.1 Hz, 1H, CH-(1)), 4.08 (pd, J = 7.4, 3.1 Hz, 4H, 2CH$_2$-(16)), 2.60 (td, J = 8.1, 2.3 Hz, 2H, CH$_2$-(11)), 2.57 – 2.49 (m, 1H, CH-(7)), 2.25 – 2.18 (m, 1H, CHH’-(2)), 2.09 (q, J = 6.0 Hz, 2H, CHH’-(4)), 1.97 – 1.88 (m, 1H, CHH’-(2)), 1.78 – 1.69 (m, 1H, CHH’-(3)), 1.68 – 1.57 (m, 3H, 2CH$_2$-(8, 9)), 1.54 – 1.38 (m, 3H, CHH’-(3), 3CH$_2$-(9, 10)), 1.32 (tt, J = 7.1, 1.2 Hz, 6H, 2CH$_3$-(17)) 1.32 - 1.24 (m, 1H, CH$_2$-(10)); $^{13}$C NMR (101 MHz, CDCl$_3$) δ/ppm: 142.8 (C(12)), 133.0 (C(5)), 131.4 (C(6)), 128.5 (C(13)), 128.4 (C(14)), 125.7 (C(15)), 79.5 (C(1)), 63.6 (C(16)), 44.5 (C(7)), 36.4 (C(2)), 36.0 (C(11)), 31.84 (C(9)), 31.76 (C(8)), 28.1 (C(4)), 26.7 (C(10)), 23.0 (C(3)), 16.3 (C(17)); $^{31}$P NMR (162 MHz, CDCl$_3$) δ/ppm: -1.74; HRMS (ESI) m/z calced for C$_{21}$H$_{33}$O$_4$NaP [M+Na]$^+$ : 403.20087, found: 403.20154; IR (ATR) ν (cm$^{-1}$) thin film, CHCl$_3$: 2930.1 (w), 2858.0 (w), 1453.3 (w), 1392.8 (w), 1261.0 (m), 1032.3 (s), 997.3 (s), 802.3 (w), 748.7 (w), 699.9 (w); [$\alpha$]$^2$$_{589}$ = -41.3 (c=1.0 in CHCl$_3$, 92% ee).

Diethyl ((1R,2R)-2-ethylcyclopent-3-en-1-yl) phosphate (1c)

Synthesised according to general procedure 1b, using meso-4-cyclopentene-1,3-bisdiethylphosphate (1a) and ethylene as the alkene partner (hydrozirconation and reaction carried out under an ethylene atmosphere). Purified by flash chromatography (30-50% EtOAc in petroleum ether) to give 1c as a yellow oil (81 mg, 82%).

The product was derivatised according to general procedure 2 for HPLC analysis.

HPLC analysis indicated an enantiomeric excess of 90% [Chiralpak® ID; flow: 0.7 mL/min; hexane/iPrOH: 99:1; $\lambda$ = 210 nm; minor enantiomer, $t_R$ = 14.157 min; major enantiomer, $t_R$ = 14.785 min].
1H NMR (500 MHz, CDCl3) δH/ppm: 5.68 – 5.65 (m, 1H, CH-(4)), 5.64 – 5.61 (m, 1H, CH-(3)), 4.66 (tt, J = 6.6, 3.1 Hz, 1H, CH-(1)), 4.08 (dt, J = 14.6, 7.1, 3.2 Hz, 4H, 2CH2-(8)), 2.77 – 2.72 (m, 1H, CHH-´-(2)), 2.73 – 2.67 (m, 1H, CH-(5)), 2.51 – 2.44 (m, 1H, CHH-´-(2)), 1.52 – 1.39 (m, 1H, CHH-´-(6)), 1.39 – 1.33 (m, 1H, CHH-´-(6)), 1.31 (tdd, J = 7.1, 2.3, 1.0 Hz, 6H, CH3-(9)), 0.93 (t, J = 7.5 Hz, 3H, 2CH3-(7));

13C NMR (126 MHz, CDCl3) δc/ppm: 132.5 (C(4)), 127.3 (C(3)), 82.9 (C(1)), 63.7 (C(8)), 54.6 (C(5)), 40.0 (C(2)), 25.6 (C(6)), 16.3 (C(9)), 11.8 (C(7));

31P NMR (202 MHz, CDCl3) δp/ppm: -1.46; HRMS (ESI) m/z calcd for C21H33O4NaP [M+Na]+ : 271.10697, found: 271.10697; IR (ATR) ν (cm−1) thin film, CHCl3: 2980.1 (w), 1460.5 (w), 1392.7 (w), 1263.4 (m), 1166.2 (w), 1026.8 (s), 974.6 (s), 887.0 (w), 820.82 (w), 715.4 (w); [α]25 589 = -71.1 (c=1.0 in CHCl3, 90% ee). Optical rotation value consistent with those found in the literature.5

Diethyl ((1R,2R)-2-ethylcyclohex-3-en-1-yl) phosphate (2c)

Synthesised according to general procedure 1b, using meso-5-cyclopentene-1,4-bisdieethylphosphate (2a) and ethylene as the alkene partner (hydrozirconation and reaction carried out under an ethylene atmosphere). Purified by flash chromatography (30-50% EtOAc in petroleum ether) to give 2c as a yellow oil (83 mg, 79%).

The product was derivatised according to general procedure 2 for HPLC analysis.
HPLC analysis indicated an enantiomeric excess of 97% [Chiralpak® ID; flow: 0.7 mL/min; hexane/iPrOH: 99:1; λ = 210 nm; major enantiomer, \(t_R = 13.323\) min; minor enantiomer, \(t_R = 14.305\) min].

\[
\begin{align*}
\text{H} & \quad \text{NMR} \quad (500 \text{ MHz, CDCl}_3) \quad \delta_{H/\text{ppm}}: \quad 5.69 - 5.63 \quad (m, \quad 1\text{H, CH-(4)}), \quad 5.54 - 5.48 \quad (m, \quad 1\text{H, CH-(5)}), \quad 4.36 - 4.30 \quad (m, \quad 1\text{H, CH-(1)}), \quad 4.14 - 4.05 \quad (m, \quad 4\text{H, 2CH}_2-(9)), \quad 2.23 - 2.17 \quad (m, \quad 1\text{H, CH-(6)}), \quad 2.17 - 2.13 \quad (m, \quad 1\text{H, CHH}^--(3)), \quad 2.12 - 2.07 \quad (m, \quad 1\text{H, CHH}^--(3)), \\
& \quad 2.07 - 2.01 \quad (m, \quad 1\text{H, CHH}^--(2)), \quad 1.84 - 1.76 \quad (m, \quad 1\text{H, CHH}^--(2)), \quad 1.65 - 1.55 \quad (m, \quad 1\text{H, CH}- (7)), \quad 1.42 - 1.35 \quad (m, \quad 1\text{H, CH}- (7)), \quad 1.33 \quad (td, \quad J = 7.1, \quad 1.0 \text{ Hz, 6H, 2CH}_3-(10)), \\
& \quad 0.93 \quad (t, \quad J = 7.5 \text{ Hz, 3H, CH}_3-(8)); \quad \text{\textsuperscript{13}C NMR} \quad (126 \text{ MHz, CDCl}_3) \quad \delta_{c/\text{ppm}}: \quad 128.0 \quad (C(5)), \quad 126.5 \quad (C(4)), \quad 78.0 \quad (C(1)), \quad 63.7 \quad (C(9)), \quad 43.3 \quad (C(6)), \quad 28.0 \quad (C(2)), \quad 25.2 \quad (C(7)), \quad 23.5 \quad (C(3)), \quad 16.3 \quad (C(10)), \quad 10.7 \quad (C(8)); \\
& \quad \text{\textsuperscript{31}P NMR} \quad (202 \text{ MHz, CDCl}_3) \quad \delta_{\text{ppm}}: \quad -1.49; \quad \text{HRMS} \quad (ESI) \quad m/z \quad \text{calcld for C}_{21}\text{H}_{33}\text{O}_{4}\text{NaP}[\text{M+Na}]^+: \quad 285.12262, \quad \text{found:} \quad 285.12257; \quad \text{IR (ATR)} \quad \nu \quad (\text{cm}^{-1}) \quad \text{thin film, CDCl}_3: \quad 3024.8 \quad (w), \quad 2934.2 \quad (w), \quad 1444.3 \quad (w), \quad 1262.7 \quad (m), \quad 1166.6 \quad (w), \quad 1100.9 \quad (w), \quad 1026.5 \quad (s), \quad 1008.2 \quad (s), \quad 987.3 \quad (m), \quad 819.0 \quad (w), \quad 726.3 \quad (w), \quad 682.0 \quad (w); \\
& \quad [\alpha]_{25}^{D89} = -51.8 \quad (c=1.0 \text{ in CHCl}_3, \quad 97\% \text{ ee}). \quad \text{Optical rotation value consistent with those found in the literature.}^5
\end{align*}
\]

Diethyl ((1R,2R)-2-hexylcyclopent-3-en-1-yl) phosphate (1d)

\[
\begin{align*}
\text{Synthesised according to general procedure 1b, using meso-4-cyclopentene-1,3-bisdiethylphosphate (1a) and 1-hexene as the alkene partner (hydrozirconation time}
\end{align*}
\]
20 mins). Purified by flash chromatography (20-40% EtOAc in petroleum ether) to give 1d as a yellow oil (78 mg, 64%).

GC analysis indicated an enantiomeric excess of 90% [Astec Chiraldex β-DA (Supelco) column; initial temperature 140 °C, initial hold time 5 min, progress rate 0.5 °C/min, final temperature 160 °C, final hold time 15 min; Flow rate 2 mL/min; minor enantiomer, t_R = 46.800 min; major enantiomer, t_R = 47.341 min].

\[1H \text{ NMR (400 MHz, CDCl}_3\] \(\delta_h/\text{ppm}: 5.71 - 5.66 \text{ (m, 1H, CH-(4)), 5.66 - 5.62 \text{ (m, 1H, CH-(3))}, 4.67 \text{ (tt, } J = 6.4, 3.0 \text{ Hz, 1H, CH-(1))}, 4.10 \text{ (pd, } J = 7.2, 2.7 \text{ Hz, 4H, 2CH}_2-(12)), 2.80 - 2.71 \text{ (m, 2H, CHH'-(2), CH-(5))}, 2.54 - 2.45 \text{ (m, 1H, CHH'-(2))}, 1.33 \text{ (tdd, } J = 7.1, 2.2, 1.0 \text{ Hz, 6H, 2CH}_3-(13)), 1.47 - 1.18 \text{ (m, 10H, 5CH}_2-(6, 7, 8, 9, 10)), 0.90 - 0.84 \text{ (m, 3H, CH}_3-(11))\]; \(^{13}C \text{ NMR (101 MHz, CDCl}_3\] \(\delta_c/\text{ppm}: 132.9 \text{ (C(4)), 127.2 \text{ (C(3)), 83.2 \text{ (C(1))}, 63.7 \text{ (C(12)), 53.2 \text{ (C(5))}, 40.0 \text{ (C(2)), 32.9 \text{ (C(6)), 31.9 \text{ (C(9)), 29.6 \text{ (C(8)), 27.5 \text{ (C(7)), 22.8 \text{ (C(10)), 16.3 \text{ (C(13)), 14.2 \text{ (C(11))};}^{31}P \text{ NMR (162 MHz, CDCl}_3\] \(\delta_p/\text{ppm: } -1.46; \text{ HRMS (ESI) } m/z \text{ calcd for C}_{15}H_{29}O_4NaP} [M+Na]^+: 327.16957, \text{ found: 327.16953} ; \text{ IR (ATR) } \nu (\text{cm}^{–1}) \text{ thin film, CHCl}_3\]: 2926.9 (w), 2856.2 (w), 1459.2 (w), 1392.7 (w), 1263.7 (m), 1165.8 (w), 1030.2 (s), 973.6 (m), 820.6 (w), 712.4 (w); \([\alpha]^{25}_{589} = -63.5 \text{ (c=1.0 in CHCl}_3, 90\% \text{ ee).} \]
Diethyl ((1R,2R)-2-hexylcyclohex-3-en-1-yl) phosphate (2d)

Synthesised according to general procedure 1b, using meso-5-cyclohexene-1,4-bisdiethylphosphate (2a) and 1-hexene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (20-40% EtOAc in petroleum ether) to give 2d as a yellow oil 111 mg, 87%.

GC analysis indicated an enantiomeric excess of 97% [Astec Chiraldex β-DA (Supelco) column; initial temperature 160 °C, initial hold time 5 min, progress rate 0.1 °C/min, final temperature 165 °C, final hold time 10 min; Flow rate 2 mL/min; minor enantiomer, $t_R = 44.980$ min; major enantiomer, $t_R = 45.671$ min].

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 5.68 – 5.60 (m, 1H, CH-(4)), 5.56 – 5.48 (m, 1H, CH-(5)), 4.33 (dt, $J = 9.3, 6.7, 2.9$ Hz, 1H, CH-(1)), 4.16 – 4.03 (m, 4H, 2CH$_2$-(13)), 2.29 – 2.20 (m, 1H, CH-(6)), 2.20 – 2.12 (m, 1H, CHH‘-(3)), 2.11 – 2.06 (m, 1H, CHH‘-(3)), 2.06 – 1.97 (m, 1H, CHH‘-(2)), 1.86 – 1.75 (m, 1H, CHH‘-(2)), 1.59 – 1.16 (m, 10H, 5CH$_2$-(7, 8, 9, 10, 11)), 1.33 (td, $J = 7.1, 1.0$ Hz, 6H, 2CH$_3$-(14)), 0.91 – 0.84 (m, 3H, CH$_3$-(12)); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ppm: 128.3 (C(5)), 126.3 (C(4)), 78.4 (C(1)), 63.6 (C(13)), 41.8 (C(6)), 32.7 (C(7)), 31.9 (C(10)), 29.7 (C(9)), 27.7 (C(2)), 26.3 (C(8)), 23.3 (C(3)), 22.8 (C(11)), 16.3 (C(14)), 14.2 (C(12));

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$/ppm: -1.49; HRMS (ESI) $m$/z calcld for C$_{16}$H$_{31}$O$_3$NaP [M+Na]$^+$ : 341.18522, found: 341.18537; IR (ATR) $\nu$ (cm$^{-1}$) thin film, CHCl$_3$: 2928.1
Diethyl ((1R,2R)-2-tetradecylcyclopent-3-en-1-yl) phosphate (1e)

\[
\text{C}_{14}\text{H}_{29}\text{OP(OEt)}_2
\]

Chemical Formula: \(\text{C}_{29}\text{H}_{45}\text{O}_4\text{P}\)  
Molecular Weight: 416.5828

Synthesised according to general procedure 1b, using meso-4-cyclopentene-1,3-bisdiethylphosphate (1a) and 1-tetradecene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (15-35% EtOAc in petroleum ether) to give 1e as a yellow oil (92 mg, 55%).

The product was derivatised according to general procedure 2 for HPLC analysis.

HPLC analysis indicated an enantiomeric excess of 90% [Chiralpak® IC; flow: 0.7 mL/min; hexane/iPrOH: 99:1; \(\lambda = 210\) nm; major enantiomer, \(t_R = 11.584\) min; minor enantiomer, \(t_R = 12.143\) min].

\begin{align*}
\text{1}^\text{H} \text{ NMR} & \quad (400 \text{ MHz, CDCl}_3) \ \delta/\text{ppm} \quad \text{H} & \quad 5.71 - 5.66 \text{ (m, 1H, CH-(4))}, 5.65 - 5.61 \text{ (m, 1H, CH-(3))}, 4.66 \text{ (tt, } J = 6.4, 3.0 \text{ Hz, 1H, (CH-(1))}, 4.09 \text{ (pd, } J = 7.2, 2.7 \text{ Hz, 4H, 2CH}_2-(20)), 2.81 - 2.71 \text{ (m, 2H, CHH} \wedge '-(2), \text{CH-(5))}, 2.53 - 2.44 \text{ (m, 1H, CHH}_\wedge '-'(2)), 1.37 - 1.30 \text{ (m, 6H, 2CH}_3-(21)), 1.46 - 1.21 \text{ (m, 26H, 13CH}_2-(6-18)), 0.92 - 0.83 \text{ (m, 3H, CH}_3-(19)); \\
\text{13}^\text{C} \text{ NMR} & \quad (101 \text{ MHz, CDCl}_3) \ \delta/\text{ppm} \quad \text{C} & \quad 132.9 \text{ (C(4))}, 127.2 \text{ (C(3))}, 83.3
\end{align*}
(C(1)), 63.7 (C(20)), 53.2 (C(5)), 40.0 (C(2)), 32.9 (C(6)), 32.1 (C(7-18), 29.9 (C(7-18)), 29.8 (C(7-18)), 29.8 (C(7-18)), 29.8 (C(7-18)), 29.7 (C(7-18), 29.5 (C(7-18)), 27.6 (C(7-18)), 22.8 (C(7-18)), 16.3 (C(21)), 14.3 (C(19)); $^{31}$P NMR (162 MHz, CDCl$_3$) δ/ppm: -1.46; HRMS (ESI) m/z calcd for C$_{23}$H$_{46}$O$_4$NaP [M+Na]$^+$ : 439.29477, found: 439.29420; IR (ATR) ν (cm$^{-1}$) thin film, CHCl$_3$: 2923.1 (m), 2853.2 (w), 1465.9 (w), 1369.6 (w), 1264.1 (m), 1166.2 (w), 1030.3 (s), 974.4 (m), 820.6 (w), 712.6 (w); $[\alpha]_{25}^{2589} = -56.0$ (c=1.0 in CHCl$_3$, 90% ee).

Diethyl ((1$R$,2$R$)-2-tetradecylocyclohex-3-en-1-yl) phosphate (2e)

![Chemical structure](image)

Chemical Formula: C$_{29}$H$_{46}$O$_4$P
Molecular Weight: 430.6068

Synthesised according to general procedure 1b, using meso-5-cyclohexene-1,4-bisdiethylphosphate (2a) and 1-tetradecene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (15-35% EtOAc in petroleum ether) to give 2e as a yellow oil (128 mg, 74%).

The product was derivatised according to general procedure 2 for HPLC analysis.

HPLC analysis indicated an enantiomeric excess of 95% [Chiralpak® IC; flow: 0.7 mL/min; hexane/iPrOH: 99:1; $\lambda$ = 210 nm; major enantiomer, $t_R$ = 11.101 min ; minor enantiomer, $t_R$ = 11.933 min].
$^1$H NMR (400 MHz, CDCl$_3$) δ/ ppm: 5.68 – 5.62 (m, 1H, CH-(4)), 5.55 – 5.49 (m, 1H, CH-(5)), 4.33 (dt, $J = 9.3, 6.7, 2.9$ Hz, 1H, CH-(1)), 4.10 (pd, $J = 7.2, 3.2$ Hz, 4H, 2CH$_2$-(21)), 2.29 – 2.21 (m, 1H, CH-(6)), 2.21 – 2.12 (m, 1H, CHH$^-$-(3)), 2.12 – 2.06 (m, 1H, CHH$^-$-(3)), 2.03 – 1.98 (m, 1H, CHH$^-$-(2)), 1.86 – 1.75 (m, 1H, CHH$^-$-(2)), 1.46 – 1.21 (m, 26H, 13CH$_2$-(7-19)) 1.33 (td, $J = 7.1, 1.0$ Hz, 6H, 2CH$_3$-(22)), 0.92 – 0.84 (m, 3H, CH$_3$-(20)); $^{13}$C NMR (101 MHz, CDCl$_3$) δ/ ppm: 128.3 (C(5)), 126.3 (C(4)), 78.4 (C(1)), 63.6 (C(21)), 41.8 (C(6)), 32.8 (C(7)), 32.1 (C(8-19)), 30.0 (C(8-19)), 29.8 (C(8-19), 29.8 (C(8-19)), 29.8 (C(8-19)), 29.7 (C(8-19)), 29.5 (C(8-19)), 27.7 (C(2)), 26.4 (C(8-19)), 23.3 (C(3)), 22.8 (C(8-19)), 16.3 (C(22)), 14.3 (C(20)); $^{31}$P NMR (162 MHz, CDCl$_3$) δ/ ppm: -1.49; HRMS (ESI) m/z calc'd for C$_{24}$H$_{47}$O$_4$NaP [M+Na]+: 453.31042, found: 453.31042; IR (ATR) ν (cm$^{-1}$) thin film, CHCl$_3$: 2923.5 (m), 2853.4 (m), 1466.1 (w), 1264.3 (w), 1166.7 (w), 1034.2 (s), 1012.2 (s), 976.8 (m), 817.6 (w), 724.2 (w); $[\alpha]_{25}^{289} = -44.5$ (c=1.0 in CHCl$_3$, 95% ee).

Diethyl ((1R,2R)-2-isopentylcyclopent-3-en-1-yl) phosphate (1f)

![Diagram of 1f]

Synthesised according to general procedure 1b, using meso-4-cyclopentene-1,3-bisdiethylphosphate (1a) and 3-methyl-1-butene (reagent bottle under an Ar atmosphere and cooled to -78 °C before adding to flask B) as the alkene partner (hydrozirconation time 30 mins). Purified by flash chromatography (15-40% EtOAc in petroleum ether) to give 1f as a yellow oil (70 mg, 60%).

GC analysis indicated an enantiomeric excess of 90% [Astec Chiraldex β-DA (Supelco) column; initial temperature 120 °C, initial hold time 5 min, progress rate 2 °C/min, final temperature 170 °C, final hold time 10 min; Flow rate 3 mL/min; minor enantiomer, $t_R = 27.398$ min; major enantiomer, $t_R = 27.708$ min].
\[^1\]H NMR (400 MHz, CDCl\(_3\)) \(\delta /\text{ppm:} 5.70 - 5.66 (m, 1H, CH-(4)), 5.66 - 5.61 (m, 1H, CH-(3)), 4.66 (tt, \(J = 6.5, 3.0 \text{ Hz, 1H, CH-(1)}), 4.16 - 4.03 (m, 4H, 2CH\(_2\)-(10)), 2.80 - 2.70 (m, 2H, \text{CHH}'-(2), \text{CH-(5)}), 2.53 - 2.44 (m, 1H, \text{CHH}'-(2)), 1.57 - 1.47 (m, 1H, CH-(8)), 1.47 - 1.16 (m, 4H, 2CH\(_2\)-(6, 7)) 1.33 (tdd, \(J = 7.1, 2.2, 1.0 \text{ Hz, 6H, 2CH\(_3\)-(11)})), 0.86 (dd, \(J = 6.7, 1.2 \text{ Hz, 6H, 2CH\(_3\)-(9)}); ^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta /\text{ppm:} 132.9 (\text{C(4)}), 127.2 (\text{C(3)}), 83.3 (\text{C(1)}), 63.7 (\text{C(10)}), 53.3 (\text{C(5)}), 40.0 (\text{C(2)}), 36.7 (\text{C(7)}), 30.6 (\text{C(8)}), 28.3 (\text{C(6)}), 22.7 (\text{C(9)}), 16.2 (\text{C(11)}); ^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta /\text{ppm:} -1.47; \text{HRMS (ESI) } m/z \text{ calcd for C}_{14}\text{H}_{26}\text{O}_{4}\text{NaP [M+Na]}^+: 313.15392, \text{found:} 313.15373; \text{IR (ATR) } \nu (\text{cm}^{-1}) \text{ thin film, CHCl}_3: 2928.1 (w), 2869.4 (w), 1468.3 (w), 1367.5 (w), 1263.8 (m), 1167.4 (w), 1029.3 (s), 977.0 (m), 820.9 (w), 712.0 (w); [\alpha]^{25}_{\text{D}} = -75.9 (c=1.0 \text{ in CHCl}_3, 90\% \text{ ee}).

**Diethyl ((1R,2R)-2-isopentylcyclohex-3-en-1-yl) phosphate (2f)**

![Chemical Structure](image)

Chemical Formula: C\(_{14}\)H\(_{26}\)O\(_4\)P
Molecular Weight: 304.3668

Synthesised according to general procedure 1b, using meso-5-cyclohexene-1,4-bisdiethylphosphate (2a) and 3-methyl-1-butene (reagent bottle under an Ar atmosphere and cooled to -78 °C before adding to flask B) as the alkene partner (hydrozirconation time 30 mins). Purified by flash chromatography (15-40% EtOAc in petroleum ether) to give 2f as a yellow oil (95 mg, 78%).

GC analysis indicated an enantiomeric excess of 96% [Astec Chiraldex ß-DA (Supelco) column; initial temperature 120 °C, initial hold time 5 min, progress rate 2
°C/min, final temperature 170 °C, final hold time 10 min; Flow rate 3 mL/min; minor enantiomer, \( t_R = 33.344 \) min; major enantiomer, \( t_R = 33.699 \) min.

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta \text{H/ppm: 5.68 – 5.61 (m, 1H, CH-(4)), 5.54 – 5.48 (m, 1H, CH-(5)), 4.33 (dt, } J = 9.3, 6.7, 2.9 \text{ Hz, 1H, CH-(1)}, 4.10 (pd, } J = 7.2, 3.9 \text{ Hz, 4H, 2CH}_{2}-(11)), 2.27 – 2.18 (m, 1H, CH-(6)), 2.18 – 2.12 (m, 1H, CHH’-(3)), 2.12 – 2.05 (m, 1H, CHH’-(3)), 2.05 – 1.99 (m, 1H, CHH’-(2)), 1.86 – 1.74 (m, 1H, CHH’- (2)), 1.61 – 1.45 (m, 2H, CHH’-(7), CH-(9)), 1.36 – 1.12 (m, 3H, CHH’-(7) CH_{2}-(8)), 1.33 (td, } J = 7.1, 1.0 \text{ Hz, 6H, 2CH}_{3}-(10)), 0.87 (dd, } J = 6.6, 1.8 \text{ Hz, 6H, 2CH}_{3}-(12)); \]

\[ \text{C NMR (101 MHz, CDCl}_3\text{) } \delta \text{c/ppm: 128.3 (C(5)), 126.3 (C(4)), 78.4 (C(1)), 63.6 (C(13)), 42.0 (C(6)), 35.5 (C(8)), 30.5 (C(9)), 28.4 (C(7)), 27.8 (C(2)), 23.3 (C(3)), 22.7 (C(10)), 16.3 (C(12)); \]

\[ \text{P NMR (162 MHz, CDCl}_3\text{) } \delta \text{p/ppm: -1.49; HRMS (ESI) } m/z \text{ calcd for C}_35\text{H}_49\text{O}_4\text{NaP [M+Na]}^+: 327.16957, \text{ found: 327.16949; IR (ATR) } \nu \text{ (cm}^{-1}) \text{ thin film, CHCl}_3: 2955.5 (w), 1458.1 (w), 1367.8 (w), 1263.6 (m), 1166.4 (w), 1011.0 (s), 973.9 (m), 817.5 (w), 726.0 (w); [\alpha]^{25}_{389} = -76.8 (c=1.0 \text{ in CHCl}_3, 96\% \text{ ee}). \]

**Diethyl (1R,2R)-2-(3,3-dimethylbuty1)cyclopent-3-en-1-yl) phosphate (1g)**

![Diethyl (1R,2R)-2-(3,3-dimethylbuty1)cyclopent-3-en-1-yl) phosphate (1g)](image)

Synthesised according to general procedure 1b, using *meso*-4-cyclopentene-1,3-bisdiethylphosphate (1a) and 3,3-dimethyl-1-butene as the alkene partner.
(hydrozirconation time 1hr 15 mins). Purified by flash chromatography (20-40% EtOAc in petroleum ether) to give 1g as a yellow oil (59 mg, 48%).

GC analysis indicated an enantiomeric excess of 91% [Astec Chiraldex β-DA (Supelco) column; initial temperature 120 °C, initial hold time 5 min, progress rate 4 °C/min, final temperature 170 °C, final hold time 5 min; Flow rate 3 mL/min; minor enantiomer, \( t_R = 22.524 \text{ min}; \) major enantiomer, \( t_R = 22.903 \text{ min} \)].

\[ \begin{align*}
\text{1H NMR} & \quad (400 \text{ MHz, CDCl}_3) \quad \delta_{\text{H}}/\text{ppm}: 5.70 - 5.66 (\text{m, 1H, CH-(4)}), 5.65 - 5.61 (\text{m, 1H, CH-(3)}), 4.66 (\text{tt, } J = 6.5, 3.0 \text{ Hz, 1H, CH-(1)}), 4.09 (\text{pd, } J = 7.1, 3.0 \text{ Hz, 4H, 4CH}_2-(10)), 2.80 - 2.67 (\text{m, 2H, CHH}^--(2), \text{CH-(5)}), 2.53 - 2.45 (\text{m, 1H, CHH}^--(2)), 1.33 (\text{tdd, } J = 7.1, 2.3, 0.9 \text{ Hz, 6H, 2CH}_3-(11)), 1.44 - 1.17 (\text{m, 4H, 2CH}_2-(6, 7)), 0.85 (\text{s, 9H, 3CH}_3-(9));
\end{align*} \]

\[ \begin{align*}
\text{13C NMR} & \quad (101 \text{ MHz, CDCl}_3) \quad \delta_{\text{C}}/\text{ppm}: 132.9 \text{ (C(4))}, 127.2 \text{ (C(3))}, 83.2 \text{ (C(1))}, 63.7 \text{ (C(10))}, 53.7 \text{ (C(5))}, 41.7 \text{ (C(8))}, 40.0 \text{ (C(2))}, 30.3 \text{ (C(7))}, 29.4 \text{ (C(9))}, 27.8 \text{ (C(6))}, 16.3 \text{ (C(11))};
\end{align*} \]

\[ \begin{align*}
\text{31P NMR} & \quad (162 \text{ MHz, CDCl}_3) \quad \delta_{\text{P}}/\text{ppm}: -1.49; \text{HRMS (ESI) m/z calcd for C}_{15}\text{H}_{29}\text{O}_4\text{NaP}[M+Na]^+ : 327.16957, \text{found: 327.16945}; \text{IR (ATR) } \nu (\text{cm}^{-1}) \text{ thin film, CHCl}_3: 2952.4 \text{ (w), 2866.8 (w), 1476.1 (w), 1364.6 (w), 1263.0 (m), 1166.9 (w), 1033.9 (s), 1011.9 (s), 979.8 (m), 817.6 (w), 725.7 (w); } [\alpha]^{25}_{\text{D}} = -35.2 \text{ (c=1.0 in CHCl}_3, 91\% \text{ ee).}
\end{align*} \]

**Diethyl (1R,2R)-2-(3,3-dimethylbutyl)cyclohex-3-en-1-yl) phosphate (2g)**

\[ \begin{align*}
\text{Chemical Formula: } & \quad \text{C}_{16}\text{H}_{28}\text{O}_4\text{P} \\
\text{Molecular Weight: } & \quad 318.3938
\end{align*} \]

Synthesised according to general procedure 1b, using *meso*-5-cyclohexene-1,4-bisdieethylphosphate (2a) and 3,3-dimethyl-1-butene as the alkene partner.
(hydrozirconation time 1hr 15 mins). Purified by flash chromatography (20-40% EtOAc in petroleum ether) to give 2g as a yellow oil (80 mg, 63%).

GC analysis indicated an enantiomeric excess of 96% [Astec ChiralDex β-DA (Supelco) column; initial temperature 120 °C, initial hold time 5 min, progress rate 4 °C/min, final temperature 170 °C, final hold time 15 min; Flow rate 3 mL/min; minor enantiomer, \( t_R = 28.911 \) min; major enantiomer, \( t_R = 29.547 \) min].

\[
\begin{align*}
\text{1H NMR} & \quad (400 MHz, CDCl}_3 \quad \delta_H/\text{ppm} : 5.68 - 5.62 (m, 1H, CH-(4)), 5.53 - 5.47 (m, 1H, CH-(5)), 4.34 (dtd, J = 9.3, 6.7, 2.9 Hz, 1H, CH-(1)), 4.15 - 4.05 (m, 4H, 2CH_2-(11)), 2.24 - 2.17 (m, 1H, CH-(6)), 2.17 - 2.12 (m, 1H, CHH^--(3)), 2.11 - 2.06 (m, 1H, CHH^--(3)), 2.06 - 2.00 (m, 1H, CHH^--(2)), 1.87 - 1.72 (m, 1H, CHH^--(2)), 1.60 - 1.47 (m, 1H, CHH^--(7)), 1.37 - 1.28 (m, 6H, 2CH_3-(12)), 1.37 - 1.08 (m, 3H, CHH^--(7), CH_2-(8)), 0.86 (s, 9H, 3CH_3-(10)); \\
\text{13C NMR} & \quad (101 MHz, CDCl}_3 \quad \delta_C/\text{ppm} : 128.3 (C(5)), 126.3 (C(4)), 78.4 (C(1)), 63.6 (C(11)), 42.3 (C(6)), 40.4 (C(9)), 30.4 (C(8)), 29.5 (C(10)), 27.9 (C(2)), 27.4 (C(7)), 23.4 (C(3)), 16.3 (C(12)); \\
\text{31P NMR} & \quad (162 MHz, CDCl}_3 \quad \delta_P/\text{ppm} : -1.49; \\
\text{HRMS (ESI) m/z} & \quad \text{calcd for C}_{16}H_{31}O_4NaP[M+Na]^+ : 341.18522, \quad \text{found: 341.18521}; \\
\text{IR (ATR) } \nu/\text{cm}^{-1} & \quad \text{thin film, CHCl}_3: 2952.8 \quad (w), 2867.0 \quad (w), 1475.9 \quad (w), 1393.6 \quad (w), 1364.6 \quad (w), 1262.9 \quad (m), 1166.5 \quad (w), 1033.0 \quad (s), 1011.9 \quad (s), 979.0 \quad (m), 817.6 \quad (w), 725.6 \quad (w); \\
\left[\alpha\right]^{25}_{589} & \quad = -58.5 \quad (c=1.0 \quad \text{in CHCl}_3, \quad 96\% \quad \text{ee}).
\end{align*}
\]
Diethyl (1R,2R)-2-(2-cyclohexylethyl)cyclopent-3-en-1-yl phosphate (1h)

\[
\text{Chemical Formula: C}_{17}\text{H}_{31}\text{O}_{4}\text{P}
\]

Molecular Weight: 330.4848

Synthesised according to general procedure 1b, using meso-4-cyclopentene-1,3-bisdiethylphosphate (1a) and vinylcyclohexane as the alkene partner (hydrozirconation time 30 mins). Purified by flash chromatography (15-40% EtOAc in petroleum ether) to give 1h as a yellow oil (74 mg, 56%).

GC analysis indicated an enantiomeric excess of 91% [Astec ChiralDEX β-DA (Supelco) column; initial temperature 180 °C, initial hold time 5 min, progress rate 0.5 °C/min, final temperature 205 °C, final hold time 10 min; Flow rate 2 mL/min; minor enantiomer, t<sub>R</sub> = 35.635 min; major enantiomer, t<sub>R</sub> = 36.243 min].

\[
\begin{align*}
\text{1H NMR} & \quad (400 \text{ MHz, CDCl}_3) \delta/\text{ppm}: 5.70 - 5.65 (\text{m, 1H, CH-(4)}), 5.65 - 5.61 (\text{m, 1H, CH-(3)}), 4.66 (\text{tt, } J = 6.5, 2.9 \text{ Hz, 1H, CH-(1)}), 4.16 - 4.03 (\text{m, 4H, 2CH}_2-(12)), 2.79 - 2.69 (\text{m, 2H, CHH'-(2), CH-(5)}), 2.53 - 2.44 (\text{m, 1H, CHH'-(2)}), 1.73 - 1.58 (\text{m, 5H, CH-(8), 2CH}_2-(9)), 1.48 - 1.04 (\text{m, 8H, 4CH}_2-(6, 7, 10)), 1.33 (\text{ddd, } J = 7.1, 2.5, 1.0 \text{ Hz, 6H, 2CH}_3-(13)), 0.86 (\text{m, 2H, CH}_2-(11)); \\
\text{13C NMR} & \quad (101 \text{ MHz, CDCl}_3) \delta/\text{ppm}: 132.9 (\text{C(4)}), 127.2 (\text{C(3)}), 83.3 (\text{C(1)}), 63.7 (\text{C(12)}), 53.4 (\text{C(5)}), 39.9 (\text{C(2)}), 38.0 (\text{C(9)}), 35.2 (\text{C(7)}), 33.5 (\text{C(8)}), 30.1 (\text{C(6)}), 26.8 (\text{C(11)}), 26.5 (\text{C(10)}), 16.3 (\text{C(13)}); \\
\text{31P NMR} & \quad (162 \text{ MHz, CDCl}_3) \delta/\text{ppm}: -1.47; \text{HRMS (ESI) } m/z \text{ calcld for C}_{17}\text{H}_{31}\text{O}_4\text{NaP[M+Na]}^+ : 353.18522, \text{found: 353.18493}; \text{IR (ATR) } \nu (\text{cm}^{-1}) \text{ thin film, CHCl}_3: 2981.1 (\text{w}), 2922.0 (\text{m}), 2851.3 (\text{w}), 1448.1 (\text{w}), 1369.5 (\text{m}), 1263.4 (\text{m}),
\end{align*}
\]
1165.6 (w), 1029.3 (s), 974.7 (m), 820.6 (w), 712.0 (w); [α]^{25}_D = -73.4 (c=1.0 in CHCl₃, 91% ee).

**Diethyl (1R,2R)-2-(2-cyclohexylethyl)cyclohex-3-en-1-yl phosphate (2h)**

![Chemical Structure Image]

Chemical Formula: C₁₉H₂₉O₇P
Molecular Weight: 344.4318

Synthesised according to general procedure 1b, using meso-5-cyclopentene-1,4-bisdiethylphosphate (2a) and vinylcyclohexane as the alkene partner (hydrozirconation time 30 mins). Purified by flash chromatography (15-40% EtOAc in petroleum ether) to give 2h as a yellow oil (94 mg, 64%).

GC analysis indicated an enantiomeric excess of 95% [Astec ChiralDEX β-DA (Supelco) column; initial temperature 180 °C, initial hold time 5 min, progress rate 0.5 °C/min, final temperature 205 °C, final hold time 10 min; Flow rate 2 mL/min; minor enantiomer, t<sub>R</sub> = 46.528 min; major enantiomer, t<sub>R</sub> = 47.237 min].

![1H NMR Image]

1H NMR (400 MHz, CDCl₃) δ/ppm: 5.69 – 5.61 (m, 1H, CH-(4)), 5.54 – 5.47 (m, 1H, CH-(5)), 4.33 (dtd, J = 9.3, 6.7, 2.9 Hz, 1H, CH-(1)), 4.17 – 4.03 (m, 4H, 2CH₂-(11)), 2.25 – 2.18 (m, 1H, CH-(6)), 2.18 – 2.12 (m, 1H, CHH⁻(3)), 2.12 – 2.05 (m, 1H, CHH⁻(3)), 2.05 – 1.98 (m, 1H, CHH⁻(2)), 1.86 – 1.75 (m, 1H, CHH⁻(2)), 1.74 – 1.50 (m, 7H, CH-(9), CHH⁻(7), 2CH₂-(10)), 1.33 (dt, J = 7.1, 1.0 Hz, 6H, 2CH₃-
(14)), 1.31 – 1.09 (m, 7H, CHH\textsuperscript{3}-(7), 3CH\textsuperscript{2}-(8, 11)), 0.94 – 0.79 (m, 2H, CH\textsubscript{2}-(12)); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta_{C}/\text{ppm}: 128.3\) (C(5)), 126.3 (C(4)), 78.4 (C(1)), 63.7 (C(13)), 42.0 (C(6)), 38.1 (C(10)), 34.0 (C(8)), 33.5 (C(9)), 30.0 (C(6)), 27.8 (C(2)), 26.8 (C(12)), 26.5 (C(11)), 23.3 (C(3)), 16.3 (C(14)); \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}) \(\delta_{P}/\text{ppm}: -1.49\); HRMS (ESI) \(m/z\) calcd for C\textsubscript{18}H\textsubscript{33}O\textsubscript{4}NaP [M+Na\textsuperscript{+}] : 367.20087, found: 367.20042; IR (ATR) \(\nu (\text{cm}^{-1})\) thin film, CHCl\textsubscript{3}: 2980.56 (w), 2922.3 (m), 2850.9 (w), 1447.8 (w), 1393.3 (w), 1263.2 (m), 1165.7 (w), 1034.3 (s), 1011.9 (s), 817.8 (w), 725.6 (w); \(\alpha\)\textsubscript{25}\textsuperscript{589} = -66.2 (c=1.0 in CHCl\textsubscript{3}, 96% ee).

\((1R,2R)-2-(6-chlorohexyl)cyclopent-3-en-1-yl diethyl phosphate (1i)\)

\[
\begin{align*}
\text{Cl} & \quad \text{OP(\text{OEt})}_2 \\
\text{Cyclic Structure} & \\
\text{1i} & \\
\text{Chemical Formula: C}_{19}\text{H}_{38}\text{ClO}_4\text{P} \\
\text{Molecular Weight: 338.8088}
\end{align*}
\]

Synthesised according to general procedure 1b, using \textit{meso}-4-cyclopentene-1,3-bisdiethylphosphate (1a) and 6-chloro-1-hexene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (20-40% EtOAc in petroleum ether) to give \textit{1i} as a yellow oil (61 mg, 45%).

The product was derivatised according to general procedure 2 for HPLC analysis.

HPLC analysis indicated an enantiomeric excess of 91\% [Chiralpak® IC; flow: 0.8 mL/min; hexane/iPrOH: 98:2; \(\lambda = 210\) nm; minor enantiomer, \(t_R = 17.579\) min ; major enantiomer, \(t_R = 18.652\) min].
Synthesised according to general procedure 1b, using meso-5-cyclohexene-1,4-bisdiethylphosphate (2a) and 6-chloro-1-hexene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (20-40% EtOAc in petroleum ether) to give 2i as a yellow oil (95 mg, 67%).

The product was derivatised according to general procedure 2 for HPLC analysis.

HPLC analysis indicated an enantiomeric excess of 95% [Chiralpak® IC; flow: 0.8 mL/min; hexane/iPrOH: 98:2; λ = 210 nm; major enantiomer, tR = 25.573 min; minor enantiomer, tR = 27.726 min].
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 5.69 – 5.62 (m, 1H, CH-(4)), 5.55 – 5.47 (m, 1H, CH-(5)), 4.32 (dtd, $J = 9.4$, 6.7, 2.9 Hz, 1H, CH-(1)), 4.10 (pd, $J = 7.1$, 3.2 Hz, 4H, 2CH$_2$-(13)), 3.52 (t, $J = 6.7$ Hz, 2H, CH$_2$-(12)), 2.29 – 2.21 (m, 1H, CH-(6)), 2.21 – 2.12 (m, 1H, CHH′-(3)), 2.12 – 2.05 (m, 1H, CHH′-(3)), 2.05 – 1.98 (m, 1H, CHH′-(2)), 1.86 – 1.75 (m, 1H, CHH′-(2)), 1.79 – 1.71 (m, 2H, CH$_2$-(11)), 1.59 – 1.25 (m, 8H, 4CH$_2$-(7, 8, 9, 10)) 1.33 (td, $J = 7.1$, 1.1 Hz, 6H, 2CH$_3$-(14)); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ppm: 128.1 (C(5)), 126.4 (C(4)), 78.3 (C(1)), 63.7 (C(13)), 45.2 (C(12)), 41.7 (C(6)), 32.7 (C(11)), 32.6 (C(7)), 29.2 (C(8-10)), 27.8 (C(2)), 26.9 (C(8-10)), 26.2 (C(8-10)), 23.4 (C(3)), 16.3 (C(14)); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$/ppm: -1.46; HRMS (ESI) $m/z$ calcd for C$_{16}$H$_{30}$O$_4$ClNaP [M+Na]$^+$ : 375.14636, found: 35.14624; IR (ATR) $\nu$ (cm$^{-1}$) thin film, CHCl$_3$: 2930.6 (w), 2856.2 (w), 1444.0 (w), 1274.0 (w), 1167.1 (w), 1030.0 (s), 821.1 (w), 713.8 (w); $[\alpha]^{25}_{D}$ = -61.3 (c=1.0 in CHCl$_3$, 95% ee).

(1$R$,2$R$)-2-(4-((tert-butyldiphenylsilyl)oxy)butyl)cyclopent-3-en-1-yl diethyl phosphate (1j)

Synthesised according to general procedure 1b, using meso-4-cyclopentene-1,3-bisdieuthylphosphate (1a) and (but-3-en-1-yloxy)(tert-butyl)diphenylsilane as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (15-40% EtOAc in petroleum ether) to give 1j as a yellow oil (109 mg, 51%).
HPLC analysis indicated an enantiomeric excess of 89% [Chiralpak® ID; flow: 1.0 mL/min; hexane/iPrOH: 97:3; λ = 210 nm; major enantiomer, tR = 21.054 min; minor enantiomer, tR = 24.276 min].

$^1$H NMR (400 MHz, CDCl$_3$) δ H/ppm: 7.70 – 7.63 (m, 4H, ArH-(14)), 7.46 – 7.34 (m, 6H, ArH-(13, 15)), 5.71 – 5.61 (m, 2H, 2CH-(3, 4)), 4.65 (tt, J = 6.4, 2.9 Hz, 1H, CH-(1)), 4.09 (p, J = 7.1 Hz, 4H, 2CH$_2$-(16)), 3.65 (t, J = 6.5 Hz, 2H, CH$_2$-(9)), 2.80 – 2.70 (m, 2H, CHH’-(2), CH-(5)), 2.54 – 2.46 (m, 1H, CHH’-(2)), 1.64 – 1.51 (m, 2H, CH$_2$-(6)), 1.48 – 1.26 (m, 4H, 2CH$_2$-(7, 8)), 1.32 (tdd, J = 7.1, 2.8, 1.0 Hz, 6H, 2CH$_3$-(17)), 1.04 (s, 9H, 3CH$_3$-(11)); $^{13}$C NMR (101 MHz, CDCl$_3$) δ c/ppm: 135.7 (C(12)), 134.2 (C(15)), 132.7 (C(4)), 128.7 (C(13)), 127.7 (C(14)), 127.3 (C(3)), 83.2 (C(1)), 63.9 (C(9)), 63.7 (C(16)), 53.1 (C(5)), 39.9 (C(2)), 32.8 (C(8)), 32.7 (C(6)), 27.0 (C(11)), 23.8 (C(7)), 19.4 (C(10)), 16.3 (C(17)); $^{31}$P NMR (162 MHz, CDCl$_3$) δ P/ppm: -1.47; HRMS (ESI) m/z calcld for C$_{29}$H$_{43}$OsNaPSi [M+Na$^+$]: 553.25096, found: 553.25022; IR (ATR) ν (cm$^{-1}$) thin film, CHCl$_3$: 3069.8 (w), 2931.9 (w), 2857.9 (w), 2361.5 (w), 1473.0 (w), 1428.4 (w), 1391.0 (w), 1263.5 (w), 1166.1 (w), 1110.4 (m), 1031.7 (s), 977.2 (m), 822.8 (w), 741.3 (w), 703.6 (m), 613.9 (w); [α]$^2$$_{589}$ = -46.2 (c=1.0 in CHCl$_3$, 89% ee).
(1R,2R)-2-(4-((tert-butyldiphenylsilyl)oxy)butyl)cyclohex-3-en-1-yl diethyl phosphate (2j)

Synthesised according to general procedure 1b, using meso-5-cyclohexene-1,4-bisdiethylphosphate (2a) and (but-3-en-1-yloxy)(tert-butyl)diphenylsilane as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (15-40% EtOAc in petroleum ether) to give 2j as a yellow oil (139 mg, 64%).

HPLC analysis indicated an enantiomeric excess of 92% [Chiralpak® IC; flow: 0.8 mL/min; hexane/iPrOH: 96:4; λ = 210 nm; major enantiomer, tR = 18.135 min; minor enantiomer, tR = 19.126 min].

1H NMR (400 MHz, CDCl3) δH/ppm: 7.69 – 7.64 (m, 4H, ArH-(15)), 7.45 – 7.34 (m, 6H, ArH-(14, 16)), 5.69 – 5.63 (m, 1H, CH-(4)), 5.55 – 5.49 (m, 1H, CH-(5)), 4.32 (dtd, J = 9.1, 6.6, 2.8 Hz, 1H, CH-(1)), 4.09 (pd, J = 7.2, 2.2 Hz, 4H, 2CH2-(17)), 3.40 (t, J = 6.8 Hz, 2H, CH2-(10)), 2.28 – 2.20 (m, 1H, CH-(6)), 2.20 – 2.13 (m, 1H, CHH’-(3)), 2.13 – 2.05 (m, 1H, CHH’-(3)), 2.05 – 1.98 (m, 1H, CHH’-(2)), 1.87 – 1.76 (m, 1H, CHH’-(2)), 1.65 – 1.24 (m, 6H, 3CH2-(7, 8, 9)), 1.31 (qd, J = 7.1, 1.0
Hz, 6H, 2CH$_3$-(18)), 1.04 (s, 9H, 3CH$_3$-(12)); $^{13}$C NMR (101 MHz, CDCl$_3$) δ/ppm: 135.7 (C(13)), 134.2 (C(16)), 129.6 (C(14)), 128.0 (C(5)), 127.7 (C(15)), 126.4 (C(4)), 78.4 (C(1)), 63.9 (C(10)), 63.7 (C(17)), 41.8 (C(6)), 32.9 (C(9)), 32.5 (C(7)), 27.7 (C(2)), 27.0 (C(12)), 23.3 (C(3)), 22.7 (C(8)), 19.4 (C(11)), 16.3 (C(18)); $^{31}$P NMR (162 MHz, CDCl$_3$) δ/ppm: -1.49; HRMS (ESI) m/z calcd for C$_{30}$H$_{45}$O$_3$NaPSi$^+$: 567.26661, found: 567.26490; IR (ATR) ν (cm$^{-1}$) thin film, CHCl$_3$: 3069.8 (w), 2931.9 (w), 2857.9 (w), 2361.5 (w), 1473.0 (w), 1428.4 (w), 1391.0 (w), 1361.8 (w), 1263.5 (w), 1166.1 (w), 1110.4 (m), 1031.7 (s), 977.2 (m), 822.8 (w), 741.3 (w), 703.6 (m), 613.9 (w); [α]$^{25}_{	ext{D}}$ = -43.3 (c=1.0 in CHCl$_3$, 95% ee).

**(1R,2R)-2-(4-((tert-butyldiphenylsilyl)oxy)butyl)cyclohept-3-en-1-yl diethyl phosphate (3j)**

![Chemical Structure](image)

Chemical Formula: C$_{30}$H$_{45}$O$_3$PSi
Molecular Weight: 558.7708

Synthesised according to general procedure 1b, using meso-6-cycloheptene-1,5-bisdiethylphosphate (3a) and (but-3-en-1-yloxy)(tert-butyl)diphenylsilane as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (20-40% EtOAc in petroleum ether) to give 3j as a yellow oil (134 mg, 60%).

HPLC analysis indicated an enantiomeric excess of 91% [Chiralpak® IC; flow: 1.0 mL/min; hexane/iPrOH: 96:4; λ = 210 nm; major enantiomer, t$_R$ = 15.451 min; minor enantiomer, t$_R$ = 16.874 min].
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 7.69 – 7.63 (m, 4H, ArH-(16)), 7.45 – 7.33 (m, 3H, ArH-(15, 17)), 5.84 (dtd, $J =$ 11.2, 6.2, 1.5 Hz, 1H, CH-(5)), 5.41 (dd, $J =$ 11.2, 5.3 Hz, 1H, CH-(6)), 4.25 (qd, $J =$ 7.9, 3.1 Hz, 1H, CH-(1)), 4.08 (p, $J =$ 7.1 Hz, 4H, 2CH$_2$-(18)), 3.65 (t, $J =$ 6.4 Hz, 2H, CH$_2$-(11)), 2.58 – 2.48 (m, 1H, CH-(7)), 2.24 – 2.16 (m, 1H, CHH’-(2)), 2.09 (q, $J =$ 5.9 Hz, 2H, CHH’-(4)), 1.99 – 1.88 (m, 1H, CHH’-(2)), 1.79 – 1.69 (m, 1H, CHH’-(3)), 1.64 – 1.21 (m, 6H, 3CH$_2$-(8, 9, 10)), 1.31 (qd, $J =$ 7.1, 1.0 Hz, 6H, 2CH$_3$-(19)), 1.04 (s, 9H, 3CH$_3$-(13)); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ppm: 135.7 (C(14)), 134.2 (C(17)), 133.0 (C(5)), 131.4 (C(6)), 129.6 (C(15)), 127.7 (C(16)), 79.5 (C(1)), 64.0 (C(11)), 63.6 (C(18)), 44.6 (C(7)), 36.3 (C(2)), 32.9 (C(10)), 31.6 (C(8)), 28.1 (C(4)), 27.00 (C(13)), 23.2 (C(9)), 23.0 (C(3)), 19.4 (C(12)), 16.3 (C(19)); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$/ppm: -1.76; HRMS (ESI) m/z calcd for C$_{31}$H$_{47}$O$_5$NaPSi [M+Na$^+$]: 581.28226, found: 581.28170; IR (ATR) $\nu$ (cm$^{-1}$) thin film, CHCl$_3$: 2931.3 (w), 2858.4 (w), 1472.9 (w), 1428.3 (w), 1390.6 (w), 1261.5 (m), 1166.0 (w), 1110.1 (m), 1033.5 (s), 998.1 (s), 822.4 (w), 741.6 (w), 703.1 (m), 613.6 (w); [$\alpha$]$^{25}_{D99}$ = -20.7 (c=1.0 in CHCl$_3$, 91% ee).
Diethyl ((1R,2R)-2-(4-methoxyphenethyl)cyclopent-3-en-1-yl) phosphate (1k)

![Chemical structure of 1k]

Synthesised according to general procedure 1b, using meso-4-cyclopentene-1,3-bisdiethylphosphate (1a) and 4-methoxystyrene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (25-50% EtOAc in petroleum ether) to give 1k as a yellow oil (99 mg, 70%). **NOTE:** Compound unstable in air and should be stored under an Ar atmosphere in a freezer.

HPLC analysis indicated an enantiomeric excess of 91% [Chiralpak® ID; flow: 1.0 mL/min; hexane/iPrOH: 90:10; λ = 210 nm; major enantiomer, t\textsubscript{R} = 22.170 min; minor enantiomer, t\textsubscript{R} = 24.908 min].

**1H NMR (400 MHz, CDCl\textsubscript{3})** δ/ppm: 7.10 (d, J = 8.7 Hz, 2H, ArH-(10)), 6.81 (d, J = 8.7 Hz, 2H, ArH-(9)), 5.74 – 5.69 (m, 1H, CH-(4)), 5.69 – 5.65 (m, 1H, CH-(3)), 4.74 (tt, J = 6.4, 3.0 Hz, 1H, CH-(1)), 4.09 (pd, J = 7.4, 3.2 Hz, 4H, 2CH\textsubscript{2}-(13)), 3.78 (s, 3H, CH\textsubscript{3}-(12)), 2.85 – 2.74 (m, 2H, CHH\textsuperscript{′}-(2), CH-(5)), 2.63 (t, J = 7.4 Hz, 2H, CH\textsubscript{2}-(7)), 2.56 – 2.47 (m, 1H, CHH\textsuperscript{′}-(2)), 1.78 – 1.54 (m, 2H, CHH\textsuperscript{′}-(6)), 1.32 (tdd, J = 7.1, 2.6, 1.0 Hz, 6H, 2CH\textsubscript{3}-(14)); **13C NMR (101 MHz, CDCl\textsubscript{3})** δ/ppm: 157.9 (C(11)), 134.2 (C(9)), 132.5 (C(4)), 129.4 (C(10)), 127.6 (C(3)), 113.9 (C(8)), 83.1 (C(1)), 63.7 (C(13)), 55.4 (C(12)), 52.6 (C(5)), 39.9 (C(2)), 34.9 (C(7)), 32.9 (C(6)), 16.3
Diethyl ((1R,2R)-2-(4-methoxyphenethyl)cyclohex-3-en-1-yl) phosphate (2k)

Synthesised according to general procedure 1b, using meso-5-cyclohexene-1,4-bisdiethylphosphate (2a) and 4-methoxystyrene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (25-50% EtOAc in petroleum ether) to give 2k as a yellow oil (103 mg, 70%). NOTE: Compound unstable in air and should be stored under an Ar atmosphere in a freezer.

SFC analysis indicated an enantiomeric excess of 99% [Chiralpak® IG; flow: 1.5 mL/min; MeOH/CO₂: 1% to 30%; λ = 210 nm; major enantiomer, tᵣ = 3.393 min; minor enantiomer, tᵣ = 3.462 min].

¹H NMR (400 MHz, CDCl₃) δH/ppm: 7.11 (d, J = 8.6 Hz, 2H, ArH-(11)), 6.81 (d, J = 8.6 Hz, 2H, ArH-(10)), 5.73 – 5.67 (m, 1H, CH-(4)), 5.57 (dd, J = 10.0, 1.8 Hz, 1H,
CH-(5), 4.40 (dtd, J = 9.3, 6.7, 2.9 Hz, 1H, CH-(1)), 4.08 (pd, J = 7.2, 2.2 Hz, 4H, 2CH2-(14)), 3.77 (s, 3H, CH2-(13)), 2.70 (ddd, J = 13.8, 10.6, 5.5 Hz, 1H, CHH´-(8)), 2.55 (ddd, J = 13.8, 10.4, 6.1 Hz, 1H, CHH´-(8)), 2.36 – 2.27 (m, 1H, CH-(6)), 2.27 – 2.16 (m, 1H, CHH´-(3)), 2.16 – 2.07 (m, 1H, CHH´-(3)), 2.07 – 2.01 (m, 1H, CHH´-(2)), 1.89 – 1.77 (m, 2H, CHH´-(2) CHH´-(7)), 1.68 – 1.57 (m, 1H, CHH´-(7)), 1.31 (qd, J = 7.1, 1.0 Hz, 6H, 2CH3-(15)); 13C NMR (101 MHz, CDCl3) δ/ppm: 157.8 (C(12)), 134.4 (C(10)), 129.3 (C(11)), 127.8 (C(5)), 126.8 (C(4)) 113.9 (C(9)), 78.4 (C(1)), 63.7 (C(14)), 55.4 (C(13)), 41.3 (C(6)), 34.8 (C(8)), 31.6 (C(7)), 27.8 (C(2)), 23.4 (C(3)), 16.3 (C(18)); 31P NMR (162 MHz, CDCl3) δ/ppm: -1.44; HRMS (ESI) m/z calcd for C19H29O5NaP [M+Na]+: 391.16448, found: 391.16517; IR (ATR) ν (cm⁻¹) thin film, CHCl3: 3649.5 (w), 2980.7 (m), 2360.3 (w), 1612.1 (w), 1512.6 (m), 1457.5 (w), 1392.8 (w), 1247.5 (m), 1176.5 (w), 1032.5 (s), 972.5 (m), 818.1 (w), 726.4 (w); [α]25^289 = -55.9 (c=1.0 in CHCl3, 97% ee).

Diethyl ((1R,2R)-2-(4-methoxyphenethyl)cyclohept-3-en-1-yl) phosphate (3k)

![Chemical Formula: C19H29O5P](image_url)

Synthesised according to general procedure 1b, using meso-6-cycloheptene-1,5-bisdiethylphosphate (3a) and 4-methoxystyrene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (25-50% EtOAc in petroleum ether) to give 3k as a yellow oil (80 mg, 52%). NOTE: Compound unstable in air and should be stored under an Ar atmosphere in a freezer.

HPLC analysis indicated an enantiomeric excess of 94% [Chiralpak® IA; flow: 1.0 mL/min; hexane/iPrOH: 93:7; λ = 210 nm; major enantiomer, tR = 11.108 min; minor enantiomer, tR = 11.960 min].
H NMR (400 MHz, CDCl₃) δH/ppm: 7.10 (d, J = 6.1 Hz, 2H, ArH-(12)), 6.81 (d, J = 8.7 Hz, 2H, ArH-(11)), 5.91 (dd, J = 11.2, 5.3 Hz, 1H, CH-(6)), 4.31 (qd, J = 7.9, 3.0 Hz, 1H, CH-(1)), 4.11 – 4.02 (m, 4H, 2CH₂-(15)), 3.78 (s, 3H, CH₃-(14)), 2.71 (ddd, J = 13.8, 10.7, 4.9 Hz, 1H, CHH´-(9)), 2.63 – 2.55 (m, 1H, CH-(7)), 2.50 (ddd, J = 13.8, 10.4, 6.4 Hz, 1H, CHH´-(9)), 2.24 – 2.17 (m, 1H, CHH´-(2)), 2.11 (q, J = 5.6 Hz, 2H, CHH´-(4)), 1.98 – 1.84 (m, 2H, CHH´-(2), CHH´-(8)), 1.78 – 1.66 (m, 2H, CHH´-(3), CHH´-(8)), 1.55 – 1.42 (m, 1H, CHH´-(3)), 1.30 (ddd, J = 10.9, 7.1, 1.0 Hz, 6H, 2CH₃-(16)); ¹³C NMR (101 MHz, CDCl₃) δc/ppm: 157.8 (C(13)), 134.5 (C(12)), 133.4 (C(5)), 131.1 (C(6)), 129.4 (C(11)), 113.8 (C(10)), 79.2 (C(1)), 63.6 (C(15)), 55.4 (C(14)), 44.0 (C(7)), 36.4 (C(2)), 34.0 (C(9)), 32.2 (C(8)), 28.1 (C(4)), 23.0 (C(3)), 16.3 (C(16)); ³¹P NMR (162 MHz, CDCl₃) δp/ppm: -1.73; HRMS (ESI) m/z calcd for C₂₀H₃₁O₅NaP [M+Na]⁺: 405.18013, found: 405.17959; IR (ATR) ν (cm⁻¹) thin film, CHCl₃: 2932.2 (w), 1612.0 (w), 1512.6 (m), 1444.4 (w), 1392.8 (w), 1246.9 (m), 1177.9 (w), 1032.7 (s), 998.9 (s), 819.5 (w), 700.5 (w); [α]²⁵ρ₈₉ = -34.3 (c=1.0 in CHCl₃, 94% ee).

(1R,2R)-2-(2-bromophenethyl)cyclopent-3-en-1-yl diethyl phosphate (1l)

Chemical Formula: C₁₇H₂₆BrO₅P
Molecular Weight: 403.2528

Synthesised according to general procedure 1b, using meso-4-cyclopentene-1,3-bisdiethylphosphate (1a) and 2-bromostyrene as the alkene partner (hydrozirconation
time 20 mins). Purified by flash chromatography (25-50% EtOAc in petroleum ether) to give **11** as a yellow oil (85 mg, 53%).

HPLC analysis indicated an enantiomeric excess of 83% [Chiralpak® ID; flow: 1.0 mL/min; hexane/iPrOH: 90:10; λ = 210 nm; major enantiomer, t<sub>R</sub> = 17.193 min; minor enantiomer, t<sub>R</sub> = 18.143 min].

![Chemical structure](image)

**1H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sup>H</sup>/ppm: 7.56 – 7.50 (m, 1H, ArH-(12)), 7.28 – 7.21 (m, 2H, ArH-(9, 10)), 7.10 – 7.05 (m, 1H, ArH-(11)), 5.78 (d, J = 6.0, 1.9 Hz, 1H, CH-(4)), 5.73 (d, J = 6.0, 2.0 Hz, 1H, CH-(3)), 4.82 (tt, J = 6.5, 3.1 Hz, 1H, CH-(1)), 4.09 (pd, J = 7.1, 3.2 Hz, 4H, 2CH<sub>2</sub>-(14)), 2.94 – 2.74 (m, 4H, CHH′-(2), CHH′-(5), CHH′-(7)), 2.57 (dd, J = 17.5, 2.0 Hz, 1H, CHH′-(2)), 1.82 – 1.59 (m, 2H, CHH′-(6)).

**13C NMR** (101 MHz, CDCl<sub>3</sub>) δ<sup>c</sup>/ppm: 141.4 (C(8)), 132.9 (C(4)), 132.3 (C(12)), 130.5 (C(10)), 127.9 (C(3)), 127.8 (C(9)), 127.6 (C(11)), 124.4 (C(13)), 82.9 (C(1)), 63.8 (C(14)), 52.9 (C(5)), 40.0 (C(2)), 34.2 (C(7)), 33.0 (C(6)), 16.3 (C(15)); **31P NMR** (162 MHz, CDCl<sub>3</sub>) δ<sup>P</sup>/ppm: -1.48; HRMS (ESI) m/z calc for C<sub>17</sub>H<sub>24</sub>O<sub>7</sub>BrNaP [M+Na]<sup>+</sup>: 425.04878, found: 425.04845; IR (ATR) ν (cm<sup>-1</sup>) thin film, CHCl<sub>3</sub>: 3649.2 (w), 3059.2 (w), 2980.7 (m), 2362.7 (w), 1471.8 (w), 1440.7 (w), 1392.4 (w), 1263.4 (m), 1164.2 (w), 1027.2 (s), 970.6 (m), 821.2 (w), 753.1 (w), 658.2 (w); [α]<sup>25</sup><sub>89</sub> = -66.9 (c=1.0 in CHCl<sub>3</sub>, 83% ee).
(1R,2R)-2-(2-bromophenethyl)cyclohex-3-en-1-yl diethyl phosphate (2l)

Synthesised according to general procedure 1b, using meso 5-cyclohexene-1,4-bisdiethylphosphate (2a) and 2-bromostyrene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (25-50% EtOAc in petroleum ether) to give 2l as a yellow oil (102 mg, 61%).

HPLC analysis indicated an enantiomeric excess of 91% [Chiralpak® IA; flow: 0.7 mL/min; hexane/iPrOH: 99:1; λ = 210 nm; major enantiomer, tR = 45.337 min; minor enantiomer, tR = 54.833 min].

1H NMR (400 MHz, CDCl3) δH/ppm: 7.50 (dd, J = 8.0, 1.2 Hz, 1H, ArH-(13)), 7.28 – 7.18 (m, 2H, ArH-(10, 11)), 7.08 – 7.00 (m, 1H, ArH-(12)), 5.77 – 5.67 (m, 1H, CH-(4)), 5.67 – 5.62 (m, 1H, CH-(5)), 4.42 (dtd, J = 9.7, 7.0, 3.0 Hz, 1H, CHH´-(8)), 2.85 (ddd, J = 13.6, 11.2, 5.4 Hz, 1H, CHH´-(8)), 2.75 (ddd, J = 13.6, 10.9, 5.6 Hz, 1H, CHH´-(8)), 2.41 – 2.31 (m, 1H, CH-(6)), 2.26 – 2.16 (m, 1H, CHH´-(3)), 2.16 – 2.09 (m, 1H, CHH´-(3)), 2.09 – 2.03 (m, 1H, CHH´-(2)), 1.96 – 1.78 (m, 2H, CHH´-(2) CHH´-(7)), 1.69 – 1.55 (m, 1H, CHH´-(7)), 1.31 (qd, J =
7.0, 1.0 Hz, 6H, 2CH3-(16)); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \textsuperscript{\&}ppm: 141.7 (C(9)), 132.9 (C(13)), 130.5 (C(11)), 127.7 (C(5)), 127.6 (C(10)), 127.6 (C(12)), 126.9 (C(4)) 124.5 (C(14)), 78.0 (C(1)), 63.7 (C(15)), 41.7 (C(6)), 33.0 (C(8)), 32.8 (C(7)), 27.8 (C(2)), 23.5 (C(3)), 16.3 (C(16)); \textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3}) \textsuperscript{\&}ppm: -1.49; HRMS (ESI) \textsuperscript{\&}z calcd for C\textsubscript{18}H\textsubscript{26}O\textsubscript{4}BrNaP [M+Na]\textsuperscript{+}: 439.06443, found: 439.06403; IR (ATR) \textnu (cm\textsuperscript{-1}) thin film, CHCl\textsubscript{3}: 2983.7 (w), 2932.2 (w), 2360.5 (w), 1472.0 (w), 1439.0 (w), 1262.8 (m), 1165.5 (w), 1023.1 (s), 979.7 (m), 818.1 (w), 752.3 (w); [\alpha]^{25}_{589} = -44.4 (c=1.0 in CHCl\textsubscript{3}, 91\% ee).
(1S,2R,5R)-2-benzyl-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (4b)

![Chemical Structure](image)

Synthesised according to general procedure 1c, using (1R,2S,3S)-2-benzyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (4a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-20-30% EtOAc in petroleum ether) to give 4b as a yellow oil (127 mg, 70%).

HPLC analysis indicated an enantiomeric excess of 94% [Chiralpak® IC; flow: 1.0 mL/min; hexane/iPrOH: 95:5; λ = 210 nm; major enantiomer, t_R = 14.330 min; minor enantiomer, t_R = 15.586 min].

\[ ^1H \text{NMR} \text{ (400 MHz, CDCl}_3 \text{) } \delta_{\text{H}}/\text{ppm}: 7.31 - 7.22 \text{ (m, 4H, 4ArH-(12, 17)}, 7.22 - 7.12 \text{ (m, 6H, 6ArH-(11, 13, 18, 19)}, 5.57 \text{ (d, } J = 6.3 \text{ Hz, 1H, CH-(3)}), 5.32 \text{ (dd, } J = 6.3, 2.3 \text{ Hz, 1H, CH-(4)}), 4.33 \text{ (dd, } J = 8.4, 7.4 \text{ Hz, 1H, CH-(1)}), 4.23 - 4.11 \text{ (m, 4H, 2CH}_2-(20)), 2.85 \text{ (d, } J = 13.0 \text{ Hz, 1H, CHH}-^-(15)), 2.79 - 2.72 \text{ (m, 1H, CH-(5)}), 2.66 - 2.60 \text{ (m, 2H, CH}_2-(9)), 2.65 \text{ (d, } J = 13.0 \text{ Hz, 1H, CHH}-^-(15)), 1.85 - 1.74 \text{ (m, 1H, CHH}^--(6)), 1.71 - 1.61 \text{ (m, 2H, CH}_2-(8)), 1.56 - 1.46 \text{ (m, 1H, CHH}^--(6)), 1.43 - 1.33 \text{ (m, 2H, CH}_2-(7)), 1.39 \text{ (td, } J = 7.1, 1.1 \text{ Hz, 3H, CH}_3-(21)), 1.36 \text{ (td, } J = 7.1, 1.1 \text{ Hz, 3H, } \]
CH₃-(21)), 1.13 (s, 3H, CH₃-(14)); ¹³C NMR (101 MHz, CDCl₃) δ/ppm: 142.8 (C(10)), 138.8 (C(16)), 137.5 (C(4)), 130.9 (C(17)), 129.8 (C(3)), 128.5 (C(12)), 128.4 (C(11)), 127.7 (C(18)), 126.0 (C(19)), 125.8 (C(13)), 91.2 (C(1)), 63.9 (C(20)), 50.6 (C(2)), 50.1 (C(5)), 41.0 (C(15)), 36.0 (C(9)), 32.2 (C(6)), 31.8 (C(8)), 27.3 (C(7)), 24.5 (C(14)), 16.4 (C(21)); ³¹P NMR (162 MHz, CDCl₃) δ/ppm: -1.15;
HRMS (ESI) m/z calcd for C₂₇H₃₇O₄NaP[M+Na]⁺: 479.23217, found: 479.23213; IR (ATR) v (cm⁻¹) thin film, CHCl₃: 2928.8 (w), 2857.3 (w), 1263.9 (m), 1027.6 (s), 972.6 (m), 745.9 (m), 701.4 (m); [α]²⁵θ = -44.3 (c=1.0 in CHCl₃, 94% ee).

(1S,2R,5R)-2-Benzyl-5-(3-(benzyloxy)propyl)-2-methylcyclopent-3-en-1-yl
diethyl phosphate (4c)

Synthesised according to general procedure 1c, using (1R,2S,3S)-2-benzyl-2-
methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (4a) and allyl benzyl ether as the
alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography
(10-30% EtOAc in heptane) to give 4c as a yellow oil (127 mg, 67%).

SFC analysis indicated an enantiomeric excess of 89% [Chiralpak® IG; flow: 1.5
mL/min; MeOH/CO₂: 1% to 30%; λ = 210 nm; minor enantiomer, tᵣ = 3.597 min;
major enantiomer, tᵣ = 3.855 min].
\[^1\text{H} \text{NMR} (500 \text{ MHz, CDCl}_3) \delta_{\text{H/ppm}}: 7.26 (d, J = 4.4 \text{ Hz}, 4\text{H, 4ArH-(11, 12)}) , 7.23 – 7.19 (m, 1\text{H, ArH-(13)}), 7.19 – 7.15 (m, 2\text{H, 2ArH-(18)}), 7.14 – 7.10 (m, 1\text{H, ArH-(19)}), 7.09 – 7.05 (m, 2\text{H, 2ArH-(17)}), 5.51 (d, J = 6.3 \text{ Hz}, 1\text{H, CH-(3)}), 5.26 (dd, J = 6.3, 2.3 \text{ Hz}, 1\text{H, CH-(4)}), 4.43 (s, 2\text{H, CH}_2-(9)) , 4.27 (dd, J = 8.4, 7.4 \text{ Hz}, 1\text{H, CH-(1)}) , 4.14 – 4.04 (m, 4\text{H, 2CH}_2-(20)) , 3.43 (t, J = 6.5 \text{ Hz}, 2\text{H, CH}_2-(8)) , 2.78 (d, J = 13.0 \text{ Hz}, 1\text{H, CHH'}-(15)) , 2.74 – 2.68 (m, 1\text{H, CH-(5)}) , 2.59 (d, J = 13.0 \text{ Hz}, 1\text{H, CHH'}-(15)) , 1.81 – 1.73 (m, 1\text{H, CHH'}-(6)) , 1.73 – 1.65 (m, 1\text{H, CHH'}-(7)) , 1.64 – 1.55 (m, 1\text{H, CHH'}-(7)) , 1.40 – 1.34 (m, 1\text{H, CHH'}-(6)) , 1.31 (td, J = 7.1, 1.0 \text{ Hz}, 3\text{H}, \text{CH}_3-(21)) , 1.27 (td, J = 7.1, 1.0 \text{ Hz}, 3\text{H}, \text{CH}_3-(21)) , 1.06 (s, 3\text{H}, \text{CH}_3-(14)); \[^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3) \delta_{\text{C/ppm}}: 138.8 (C(16)) , 138.7 (C(10)) , 137.7 (C(4)) , 130.9 (C(17)) , 129.7 (C(3)) , 128.5 (C(18)) , 127.7 (C(12)) , 127.7 (C(11)) , 127.6 (C(13)) , 126.0 (C(19)) , 91.1 (C(1)) , 73.0 (C(9)) , 70.6 (C(8)) , 63.9 (C(20)) , 50.7 (C(2)) , 50.0 (C(5)) , 41.1 (C(15)) , 28.9 (C(6)) , 27.8 (C(7)) , 24.5 (C(14)) , 16.3 (C(21)); \[^{31}\text{P NMR} (162 \text{ MHz, CDCl}_3) \delta_{\text{P/ppm}}: -1.19; \text{ HRMS (ESI) } \text{m/z} \text{ calcld for } \text{C}_{27}\text{H}_{37}\text{O}_5\text{NaP [M+Na]}^+: 495.22708, \text{ found: } 495.22637; \text{ IR (ATR) } \nu (\text{cm}^{-1}) \text{ thin film, CHCl}_3: 2930.5 (w), 1453.5 (w), 1262.4 (w), 1102.1 (w), 1025.6 (s), 974.3 (w), 742.3 (w), 702.0 (w); [\alpha]_{\text{D}}^{25} = -98.6 (c=1.0 \text{ in CHCl}_3, 89\% \text{ ee}).

(1\text{S,2R,5R})-2-\text{Benzyl}-5-(4-\text{bromobutyl})-2-\text{methylcyclopent-3-en-1-yl diethyl phosphate (4d)}

Synthesised according to general procedure 1c, using (1\text{R,2S,3S})-2-benzyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (4a) and 4-bromobut-1-ene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-30\% EtOAc in heptane) to give 4d as a yellow oil (81 mg, 44\%). The product was derivatised according to general procedure 2 for HPLC analysis.
HPLC analysis indicated an enantiomeric excess of 90% [Chiralpak® IC; flow: 0.8 mL/min; hexane/iPrOH: 98:2; λ = 210 nm; major enantiomer, $t_R = 22.900$ min; minor enantiomer, $t_R = 25.200$ min].

\[
\begin{align*}
\text{Br} & \quad 7 \\
6 & \quad 5 \\
12 & \quad 13 \\
9 & \quad 10 \\
8 & \quad 11
\end{align*}
\]

$^1$H NMR (500 MHz, CDCl$_3$) δH/ppm: 7.20 – 7.15 (m, 2H, 2ArH-(14)), 7.14 – 7.10 (m, 1H, ArH-(15)), 7.08 – 7.05 (m, 2H, 2ArH-(13)), 5.50 (d, $J = 6.3$ Hz, 1H, CH-(3)), 5.27 (dd, $J = 6.3$, 2.4 Hz, 1H, CH-(2)), 4.28 – 4.24 (m, 1H, CH-(1)), 4.15 – 4.06 (m, 4H, 2CH$_2$-(16)), 3.35 (td, $J = 6.8$, 1.2 Hz, 2H, CH$_2$-(9)), 2.78 (d, $J = 13.0$ Hz, 1H, CHH′-(11)), 2.72 – 2.66 (m, 1H, CH-(5)), 2.58 (d, $J = 13.0$ Hz, 1H, CHH′-(11)), 1.86 – 1.78 (m, 2H, CH$_2$-(8)), 1.75 – 1.66 (m, 1H, CHH′-(6)), 1.57 – 1.48 (m, 1H, CHH′-(7)), 1.47 – 1.38 (m, 1H, CHH′-(7)), 1.35 – 1.29 (m, 6H, 2CH$_3$-(17)), 1.33 – 1.26 (m, 1H, CHH′-(6)) 1.06 (s, 3H, CH$_3$-(10)); $^{13}$C NMR (126 MHz, CDCl$_3$) δC/ppm: 138.7 (C(12)), 137.8 (C(4)), 130.9 (C(13)), 129.5 (C(15)), 127.8 (C(14)), 126.1 (C(15)), 91.0 (C(1)), 64.0 (C(16)), 50.7 (C(2)), 50.0 (C(5)), 41.1 (C(15)), 33.8 (C(9)), 33.0 (C(8)), 31.5 (C(6)), 26.1 (C(7)), 24.6 (C(10)), 16.4 (C(17)); $^{31}$P NMR (162 MHz, CDCl$_3$) δP/ppm: -1.13; HRMS (ESI) $m/z$ calcd for C$_{21}$H$_{32}$O$_4$BrNaP [M+Na$^+$]: 483.10933, found: 483.10854; IR (ATR) v (cm$^{-1}$) thin film, CHCl$_3$: 2931.0 (w), 1453.7 (w), 1263.0 (m), 1023.2 (s), 972.0 (m), 746.8 (w), 703.8 (w); [$\alpha$]$^{25}_{D89}$ = -75.5 (c=1.0 in CHCl$_3$, 90% ee).
(1S,2R,5R)-2-Benzyl-5-(2-bromo-5-fluorophenethyl)-2-methylcyclopent-3-en-1-yl diethyl phosphate (4e)

Synthesised according to general procedure 1c, using (1R,2S,3S)-2-benzyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (4a) and 2-bromo-5-fluorostyrene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-30% EtOAc in heptane) to give 4e as a yellow oil (112 mg, 53%).

SFC was performed on a Waters SFC 15 system equipped with a Waters 2998 PDA (UV) detector and Waters SQD2 mass spectrometer using a Daicel Chiralpak IA column (10 x 250 mm, 5 μm). Mobile phase was 90% CO₂ and 10% methanol with 20mM NH₃. The flow rate was 10 mL/min, the back pressure was 120 bar, and the column temperature was 40 °C. The PDA detector range was 210 – 400 nm.

SFC analysis indicated an enantiomeric excess of 86; minor enantiomer, t<sub>R</sub> = 4.80 min; major enantiomer, t<sub>R</sub> = 5.14 min].
$^1$H NMR (500 MHz, CDCl$_3$) δ/ppm: 7.39 (dd, $J = 8.8$, 5.4 Hz, 1H, ArH-(10)), 7.19 – 7.15 (m, 2H, 2ArH-(18)), 7.14 – 7.10 (m, 1H, ArH-(19)), 7.09 – 7.06 (m, 2H, 2ArH-(17)), 6.90 (dd, $J = 9.4$, 3.1 Hz, 1H, ArH-(13)), 6.71 (td, $J = 8.3$, 3.0 Hz, 1H, ArH-(11)), 5.57 (d, $J = 6.3$ Hz, 1H, CH-(3)), 5.32 (dd, $J = 6.3$, 2.3 Hz, 1H, CH-(4)), 4.35 – 4.31 (m, 1H, CH-(1)), 4.15 – 4.04 (m, 4H, 2CH$_2$-(20)), 2.80 (d, $J = 13.1$ Hz, 1H, CHH’-(15)), 2.78 – 2.66 (m, 3H, CH-(5), CH$_2$-(7)), 2.59 (d, $J = 13.0$ Hz, 1H, CHH’-(15)), 2.02 – 1.94 (m, 1H, CHH’-(6)), 1.63 – 1.54 (m, 1H, CHH’-(6)), 1.31 (td, $J = 7.1$, 1.0 Hz, 3H, CH$_3$-(21)), 1.28 (td, $J = 7.1$, 1.0 Hz, 3H, CH$_3$-(21)), 1.08 (s, 3H, CH$_3$-(14)); $^{13}$C NMR (126 MHz, CDCl$_3$) δ/ppm: 162.1 (C(12)), 143.7 (C(8)), 138.7 (C(16)), 138.1 (C(4)), 133.9 (C(10)), 130.9 (C(17)), 129.3 (C(3)), 127.8 (C(18)), 126.1 (C(19)), 118.5 (C(9)), 117.3 (C(13)), 114.8 (C(11)), 90.8 (C(1)), 64.0 (C(20)), 50.8 (C(2)), 49.8 (C(5)), 41.1 (C(15)), 34.2 (C(7)), 32.3 (C(6)), 24.6 (C(14)), 16.4 (C(21)); $^{31}$P NMR (162 MHz, CDCl$_3$) δ/ppm: -1.05; HRMS (ESI) m/z calcd for C$_{25}$H$_{32}$O$_4$BrFP [M+H]$^+$: 525.1200, found: 525.0913; IR (ATR) ν (cm$^{-1}$) thin film, CHCl$_3$: 2980.6 (m), 1470.0 (w), 1392.1 (w), 1261.6 (w), 1155.3 (w), 1025.2 (s), 964.5 (m), 808.3 (w), 744.6 (w), 703.6 (w); [$\alpha$]$^2$$_{589} = -101.1$ (c=1.0 in CHCl$_3$, 86% ee).

(1S,2R,5R)-2-Benzyl-5-(4-(dibenzylamino)butyl)-2-methylcyclopent-3-en-1-yl diethyl phosphate (4f)

![Chemical Structure](image.png)

**Chemical Formula:** C$_{39}$H$_{54}$NO$_4$P  
**Molecular Weight:** 575.7298

Synthesised according to general procedure 1c, using (1R,2S,3S)-2-benzyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (4a) and N,N-dibenzylbut-3-en-1-amine as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-30% EtOAc in heptane) to give 4f as a yellow oil (145 mg, 63%).

SFC was performed on a Waters UPC system equipped with a PDA (UV) detector and QDa (MS) detector using a Daicel Chiralpak IA column (3.0 x 50 mm, 3 μm).
Mobile phase A was CO\textsubscript{2} and mobile phase B was methanol with 20mM NH\textsubscript{3}. A gradient from 5% to 50% mobile phase B over 3.5 minutes was used, followed by an increase to 60% over 0.05 minutes, a hold at 60% for 0.4 minutes and return to 5%. The total flow was 2 mL/min, the back pressure was 140 bar, and the column temperature was 40 °C. The PDA detector range was 210 – 400 nm.

The product was derivatised according to general procedure 2 (reduction only) for SFC analysis.

SFC analysis indicated an enantiomeric excess of 86%; minor enantiomer, \( t_\text{R} = 2.03 \) min; major enantiomer, \( t_\text{R} = 2.21 \) min].

\begin{figure}[ht]
\centering
\includegraphics[width=0.5\textwidth]{structure.png}
\end{figure}

\begin{table}
\centering
\begin{tabular}{l}
\hline
\textbf{H NMR (500 MHz, CDCl\textsubscript{3})} \hline
\hline
\text{\( \delta \text{u/ppm} \)} & \text{H} & \text{J (Hz)} & \text{multiplicity} & \text{chemical shift} \\
\hline
7.30 & d & 7.2 & 4H, 4ArH-(12) & 7.23 \\
7.20 – 7.14 & m & 4H, 4ArH & 7.14 (s, 1H, ArH-(20)), 7.09 – 7.06 (m, 2H, 2ArH-(18)), 5.47 (d, \textit{J} = 6.3 Hz, 1H, CH-(3)), 5.25 (dd, \textit{J} = 6.3, 2.4 Hz, 1H, CH-(4)), 4.21 (dd, \textit{J} = 8.4, 7.4 Hz, 1H, CH-(1)), 4.13 – 4.02 (m, 4H, 2CH\textsubscript{2}-(21)), 3.55 – 3.45 (m, 4H, 2CH\textsubscript{2}-(10)), 2.78 (d, \textit{J} = 13.0 Hz, 1H, CHH\textsuperscript{\textdagger}-(15)), 2.66 – 2.61 (m, 1H, CH-(5)), 2.58 (d, \textit{J} = 13.0 Hz, 1H, CHH\textsuperscript{\textdagger}-(15)), 2.37 (t, \textit{J} = 7.6 Hz, 2H, CH\textsubscript{2}-(9)), 1.66 – 1.58 (m, 1H, CHH\textsuperscript{\textdagger}-(6)), 1.56 – 1.40 (m, 2H, CH\textsubscript{2}-(8)), 1.37 – 1.27 (m, 1H, CHH\textsuperscript{\textdagger}-(7)), 1.30 (td, \textit{J} = 7.1, 1.0 Hz, 3H, CH\textsubscript{3}-(22)), 1.26 (td, \textit{J} = 7.1, 1.0 Hz, 3H, CH\textsubscript{3}-(22)), 1.24 – 1.18 (m, 1H, CHH\textsuperscript{\textdagger}-(6)), 1.05 (s, 3H, CH\textsubscript{3}-(15)); \textsuperscript{13}C \\
\hline
\end{tabular}
\end{table}

S89
NMR (126 MHz, CDCl₃) δ/ppm: 138.7 (C(17)), 137.3 (C(4)), 130.8 (C(18)), 129.7 (C(3)), 128.8 (C(12)), 128.2 (C(13)), 127.6 (C(14), 127.6 (C(19)), 126.8 (C(11)), 125.9 (C(20)), 91.1 (C(1)), 63.8 (C(21)), 58.3 (C(10)), 53.4 (C(9)), 50.5 (C(2)), 50.1 (C(5)), 40.9 (C(16)), 32.2 (C(6)), 27.2 (C(8)), 25.2 (C(7)), 24.4 (C(15)), 16.2 (C(22)); ³¹P NMR (162 MHz, CDCl₃) δ/ppm: -1.22; HRMS (ESI) m/z calcd for C₃₅H₄₇O₄NP [M+H]⁺: 576.32372, found: 576.32325; IR (ATR) ν (cm⁻¹) thin film, CHCl₃: 2930.4 (w), 1453.2 (w), 1262.9 (m), 1026.9 (s), 973.3 (m), 745.7 (m), 700.8 (m); [α]²⁵ 589 = -94.0 (c=1.0 in CHCl₃, 86% ee).

(1S,5R)-2,2-Dimethyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (5b)

Chemical Formula: C₃₅H₄₇O₄P
Molecular Weight: 380.4648

Synthesised according to general procedure 1c, using cis-2,2-dimethylcyclopent-4-ene-1,3-bis(diethyl phosphate) (5a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-20-30% EtOAc in petroleum ether) to give 5b as a yellow oil (112 mg, 74%).

HPLC analysis indicated an enantiomeric excess of 91% [Chiralpak® ID; flow: 0.8 mL/min; hexane/iPrOH: 96:4; λ = 210 nm; major enantiomer, t_R = 18.136 min; minor enantiomer, t_R = 18.920 min].
1H NMR (400 MHz, CDCl3) δH/ppm: 7.30 – 7.24 (m, 2H, 2ArH-(12)), 7.20 – 7.14 (m, 3H, 3ArH-(11, 13)), 5.47 (s, 1H, CH-(3/4)), 5.47 (s, 1H, CH-(3/4)), 4.22 (dd, J = 8.3, 6.7 Hz, 1H, CH-(1)), 4.12 (h, J = 7.1 Hz, 4H, 2CH2-(15)), 2.79 – 2.71 (m, 1H, CH-(5)), 2.64 – 2.59 (m, 2H, CH2-(9)), 1.82 – 1.71 (m, 1H, CHH´-(6)), 1.71 – 1.59 (m, 2H, CH2-(8)), 1.53 – 1.44 (m, 1H, CHH´)-(6)), 1.43 – 1.29 (m, 2H, CH2-(8)), 1.34 (td, J = 7.1, 1.0 Hz, 6H, 2CH3-(16)), 1.16 (s, 3H, CH3-(14)), 1.02 (s, 3H, CH3-(14)); 13C NMR (101 MHz, CDCl3) δc/ppm: 142.7 (C(10)), 139.4 (C(4)), 128.9 (C(3)), 128.5 (C(12)), 128.3 (C(11)), 125.7 (C(13)), 90.5 (C(1)), 63.7 (C(15)), 50.5 (C(5)), 47.1 (C(2)), 36.0 (C(9)), 32.5 (C(6)), 31.8 (C(8)), 27.3 (C(7)), 27.3 (C(14)), 21.6 (C(14)), 16.3 (C(16)); 31P NMR (162 MHz, CDCl3) δP/ppm: -1.20; HRMS (ESI) m/z calcld for C21H33O4NaP [M+Na]+ : 403.20087, found: 403.20079; IR (ATR) ν (cm⁻¹) thin film, CHCl3: 2980.31 (w), 2929.6 (w), 2858.9 (w), 1263.6 (w), 1027.3 (s), 970.6 (m), 747.1 (w), 700.0 (w); [α]D 25 = -61.6 (c=1.0 in CHCl3, 91% ee).

(1S,2R,5R)-2-Allyl-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (6b)

![Diagram of 6b](attachment:diagram.png)

Chemical Formula: C22H36O4P
Molecular Weight: 406.5028

Synthesised according to general procedure 1c, using (1R,2S,3S)-2-allyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (6a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-20-30% EtOAc in petroleum ether) to give 6b as a yellow oil (143 mg, 88%).

HPLC analysis indicated an enantiomeric excess of 94% [Chiralpak® ID; flow: 1.0 mL/min; hexane/iPrOH: 95:5; λ = 210 nm; major enantiomer, tR = 12.123 min; minor enantiomer, tR = 12.992 min].
$^1$H NMR (400 MHz, CDCl$_3$) δ/ppm: 7.30 – 7.24 (m, 2H, 2ArH-(12)), 7.20 – 7.14 (m, 3H, 3ArH-(11, 13)), 5.87 – 5.74 (m, 1H, CH-(16)), 5.55 (dd, J = 6.2, 0.9 Hz, 1H, CH-(3)), 5.48 (dd, J = 6.2, 2.2 Hz, 1H, CH-(4)), 5.05 – 5.02 (m, 1H, CHH’-(18)), 5.01 – 4.98 (m, 1H, CHH’-(17)), 4.27 (dd, J = 8.4, 7.0 Hz, 1H, CH-(1)), 4.17 – 4.07 (m, 4H, 2CH$_2$-(18)), 2.78 – 2.71 (m, 1H, CH-(5)), 2.62 (td, J = 8.0, 2.1 Hz, 2H, CH$_2$-(9)), 2.28 (dd, J = 13.5, 7.1 Hz, 1H, CHH’-(15)), 2.12 (dd, J = 13.5, 7.8 Hz, 1H, CHH’-(15)), 1.82 – 1.73 (m, 1H, CHH’-(6)), 1.69 – 1.60 (m, 2H, CH$_2$-(8)), 1.53 – 1.45 (m, 1H, CHH’-(6)), 1.44 – 1.29 (m, 2H, CH$_2$-(7)), 1.37 – 1.31 (m, 6H, 2CH$_3$-(19)), 1.15 (s, 3H, CH$_3$-(19)); $^{13}$C NMR (101 MHz, CDCl$_3$) δ/ppm: 142.8 (C(10)), 137.3 (C(4)), 135.4 (C(16)), 130.0 (C(3)), 128.5 (C(12)), 128.4 (C(11)), 125.7 (C(13)), 117.3 (C(17)), 91.0 (C(1)), 63.8 (C(18)), 50.8 (C(5)), 50.1 (C(2)), 40.1 (C(15)), 36.0 (C(9)), 32.6 (C(6)), 31.8 (C(8)), 27.3 (C(7)), 25.0 (C(14)), 16.3 (C(19)); $^{31}$P NMR (162 MHz, CDCl$_3$) δ/ppm: -1.18; HRMS (ESI) m/z calcd for C$_{23}$H$_{35}$O$_4$NaP [M+Na]$^+$: 429.21644, found: 429.21652; IR (ATR) ν (cm$^{-1}$) thin film, CHCl$_3$: 2980.0 (w), 2929.2 (w), 2857.9 (w), 1263.3 (m), 1025.9 (s), 963.8 (m), 748.9 (m), 699.8 (w); [α]$^{25}_{\text{S}}$ = -83.5 (c=1.0 in CHCl$_3$, 94% ee).
(1S,2R,5R)-2-(2-chlorobenzyl)-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (7b)

Synthesised according to general procedure 1c, using ((1R,2S,3S)-2-(2-chlorobenzyl)-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (7a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-20-30% EtOAc in petroleum ether) to give 7b as a yellow oil (154 mg, 79%).

HPLC analysis indicated an enantiomeric excess of 94% [Chiralpak® ID; flow: 1.0 mL/min; hexane/iPrOH: 95:5; λ = 210 nm; major enantiomer, tR = 19.110 min; minor enantiomer, tR = 19.878 min].

1H NMR (400 MHz, CDCl3) δ/ppm: 7.35 – 7.31 (m, 1H, ArH-(20)), 7.30 – 7.25 (m, 2H, 2ArH-(12)), 7.25 – 7.22 (m, 1H, ArH-(19)), 7.21 – 7.16 (m, 3H, 3ArH-(11, 13, 19)), 7.16 – 7.12 (m, 2H, 2ArH-(17, 19)), 5.55 (d, J = 6.3 Hz, 1H, CH-(3)), 5.40 (dd, J = 6.3, 2.3 Hz, 1H, CH-(4)), 4.34 (dd, J = 8.6, 7.5 Hz, 1H, CH-(1)), 4.25 – 4.13 (m, 4H, 2CH2-(22)), 3.03 (d, J = 13.2 Hz, 1H, CHH´-(15)), 2.94 (d, J = 13.2 Hz, 1H, CHH´-(15)), 2.87 – 2.78 (m, 1H, CH-(5)), 2.63 (dt, J = 7.7, 2.0, 1.7 Hz, 2H, CH2-(9)), 1.86 – 1.76 (m, 1H, CHH´-(6)), 1.71 – 1.61 (m, 2H, CH2-(8)), 1.56 – 1.46 (m, 1H, CHH´-
(6), 1.44 – 1.32 (m, 2H, CH$_2$-(7)), 1.38 (dt, $J = 8.2, 7.1$, 1.0 Hz, 6H, 2CH$_3$-(23)),
1.18 (s, 3H, CH$_3$-(14)); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ppm: 142.8 (C(10)), 137.2
(C(4)), 137.0 (C(16)), 135.4 (C(21)), 132.8 (C(20)), 130.0 (C(3)), 129.7 (C(19)),
128.5 (C(12)), 128.4 (C(11)), 127.6 (C(17)), 126.1 (C(18)), 125.8 (C(13)), 91.2
(C(1)), 63.9 (C(22)), 51.4 (C(2)), 50.2 (C(5)), 36.9 (C(15)), 36.0 (C(9)), 32.2 (C(6)),
31.8 (C(8)), 27.3 (C(7)), 24.7 (C(14)), 16.4(C(23)); $^{31}$P NMR (162 MHz, CDCl$_3$)
$\delta$/ppm: -1.13; HRMS (ESI) m/z calcd for C$_{27}$H$_{36}$O$_4$ClNaP [M+Na]$^+$: 513.19319,
found: 513.19327; IR (ATR) $\nu$ (cm$^{-1}$) thin film, CHCl$_3$: 2980.7 (w), 2929.7 (w),
2857.6 (w), 1263.9 (m), 1027.3 (s), 971.7 (m), 749.2 (m), 699.7 (w); $[\alpha]^{25}_{D89} = -81.2$
(c=1.0 in CHCl$_3$, 94% ee).

(1$S$,2$S$,5$R$)-2-((benzyloxy)methyl)-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl
diethyl phosphate (8b)

![Chemical Structure of 8b](image)

Synthesised according to general procedure 1c, using (1$R$,2$S$,3$S$)-2-
((benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (8a) and 4-
phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by
flash chromatography (10-25-35% EtOAc in petroleum ether) to give 8b as a yellow
oil (128 mg, 66%).

HPLC analysis indicated an enantiomeric excess of 90% [Chiralpak® ID; flow: 1.0
mL/min; hexane/iPrOH: 95:5; $\lambda = 210$ nm; major enantiomer, $t_R = 18.954$ min; minor
enantiomer, $t_R = 20.164$ min].
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$/ppm: 7.25 – 7.22 (m, 4H, 4ArH-(12, 19)), 7.22 – 7.16 (m, 3H, 3ArH-(11, 13)), 7.12 – 7.07 (m, 3H, 3ArH-(18, 20)), 5.58 – 5.54 (m, 1H, CH-(3)), 5.51 (dd, $J = 6.1$, 2.0 Hz, 1H, CH-(4)), 4.43 (d, $J = 2.8$ Hz, 2H, CH$_2$-(16)), 4.23 (dd, $J = 8.5$, 6.6 Hz, 1H, CH-(1)), 4.04 – 3.94 (m, 4H, 2CH$_2$-(21)), 3.45 (d, $J = 9.0$ Hz, 1H, CHH’-(15)), 3.33 (d, $J = 9.0$ Hz, 1H, CHH’-(15)), 2.83 – 2.77 (m, 1H, CH-(5)), 2.58 – 2.51 (m, 2H, CH$_2$-(9)), 1.74 – 1.64 (m, 1H, CHH’-(6)), 1.62 – 1.51 (m, 2H, CH$_2$-(8)), 1.45 – 1.36 (m, 1H, CHH’-(6)), 1.36 – 1.25 (m, 2H, CH$_2$-(7)), 1.21 (qd, $J = 6.9$, 1.1 Hz, 6H, 2CH$_3$-(22)), 1.14 (s, 3H, CH$_3$-(14)); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$/ppm: 142.8 (C(10)), 138.9 (C(17)), 135.9 (C(4)), 131.2 (C(3)), 128.5 (C(12)), 128.4 (C(11)), 128.3 (C(19)), 127.4 (C(18)), 127.4 (C(20)), 125.7 (C(13)), 90.5 (C(1)), 74.2 (C(15)), 73.5 (C(16)), 63.8 (C(21)), 51.5 (C(2)), 51.4 (C(5)), 36.0 (C(9)), 32.8 (C(6)), 31.8 (C(8)), 27.3 (C(7)), 23.0 (C(14)), 16.3 (C(22)); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$/ppm: -1.15; HRMS (ESI) $m/z$ calcd for C$_{28}$H$_{39}$O$_3$NaP [M+Na]$^+$: 509.24273, found: 509.24260; IR (ATR) $\nu$ (cm$^{-1}$) thin film, CHCl$_3$: 2980.7 (w), 2929.4 (w), 2857.0 (w), 1263.3 (m), 1100.2 (w), 1027.0 (s), 972.9 (m), 748.1 (w), 698.9 (w); $[\alpha]^{25}_{D}$ = -83.4 (c=1.0 in CHCl$_3$, 90% ee).
Diethyl ((1S,4R,5S)-4-(4-phenylbutyl)-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-en-5-yl) phosphate (9b)

Synthesised according to general procedure 1c, using (1S,2R,5S)-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-bis(diethyl phosphate) (9a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-20-30% EtOAc in petroleum ether) to give 9b as a yellow oil (112 mg, 61%).

HPLC analysis indicated an enantiomeric excess of 90% [Chiralpak® ID; flow: 1.0 mL/min; hexane/iPrOH: 95:5; λ = 210 nm; major enantiomer, t_R = 21.376 min; minor enantiomer, t_R = 23.910 min].

^1H NMR (400 MHz, CDCl_3) δ_H/ppm: 7.32 – 7.27 (m, 2H, 2ArH-(12), 7.23 – 7.18 (m, 4H, 4ArH-(11, 13, 17), 7.18 – 7.14 (m, 3H, 3ArH-(18, 19, 20), 5.81 (dd, J = 6.0, 2.0 Hz, 1H, CH-(3)), 5.63 (dd, J = 6.0, 1.7 Hz, 1H, CH-(4)), 4.59 (dd, J = 8.6, 4.7 Hz, 1H, CH-(1)), 3.87 – 3.74 (m, 2H, CH_2-(22)), 3.50 – 3.36 (m, 2H, CH_2-(22)), 3.17 – 3.07 (m, 1H, CHH`-(15)), 2.99 – 2.93 (m, 1H, CH-(5)), 2.92 – 2.83 (m, 1H, CHH`-(15)), 2.66 (t, J = 7.7 Hz, 2H, CH_2-(9)), 2.24 – 2.17 (m, 2H, CH_2-(14)), 1.85 – 1.74 (m, 1H,
CHH’-(6)), 1.73 – 1.64 (m, 2H, CH2-(8)), 1.60 – 1.40 (m, 3H, CH2-(7), CHH’-(6)), 1.19 (td, J = 7.1, 1.1 Hz, 3H, CH3-(23)), 1.02 (td, J = 7.1, 1.1 Hz, 3H, CH3-(23)); 13C NMR (101 MHz, CDCl3) δ/ppm: 144.6 (C(21)), 143.8 (C(16)), 142.7 (C(10)), 136.6 (C(4)), 132.0 (C(3)), 128.5 (C(12)), 128.4 (C(11)), 127.1 (C(17)), 126.0 (C(20)), 125.9 (C(18)), 125.7 (C(13)), 124.4 (C(19)), 88.7 (C(1)), 64.5 (C(2)), 63.5 (C(22)), 63.2 (C(22)), 52.7 (C(5)), 39.1 (C(14)), 36.0 (C(9)), 33.7 (C(15)), 31.8 (C(8)), 31.0 (C(6)), 27.5 (C(7)), 16.0 (C(23)); 31P NMR (162 MHz, CDCl3) δ/ppm: -1.97; HRMS (ESI) m/z calcd for C27H36O4P [M+H]+: 455.23457, found: 455.23463; IR (ATR) ν (cm⁻¹) thin film, CHCl3: 2980.8 (w), 2929.9 (w), 2856.9 (w), 1275.1 (w), 1262.7 (w), 1029.1 (s), 971.2 (m), 772.1 (w), 748.6 (w), 700.0 (w); [α]25° = -111.9 (c=1.0 in CHCl3, 90% ee).

Diethyl (4S,4'R,5'S)-4'-(4-phenylbutyl)spiro[chromane-4,1'-cyclopentan]-2'-ene-5'-yl) phosphate (10b)

![Chemical structure of 10b](image)

Chemical Formula: C27H36O4P
Molecular Weight: 470.5458

Synthesised according to general procedure 1c, using (2'R,4S,5'S)-spiro[chromane-4,1'-cyclopentan]-3'-ene-2',5'-bis(diethyl phosphate) (10a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-20-30% EtOAc in petroleum ether) to give 10b as a yellow oil (107 mg, 57%).

HPLC analysis indicated an enantiomeric excess of 91% [Chiralpak® ID; flow: 1.0 mL/min; hexane/iPrOH: 95:5; λ = 210 nm; major enantiomer, tR = 30.321 min; minor enantiomer, tR = 41.961 min].
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta_{H}/ppm\): 7.30 – 7.26 (m, 2H, 2ArH-(12)), 7.21 – 7.16 (m, 3H, 3ArH-(11, 13)), 7.11 – 7.06 (m, 2H, 2ArH-(18,20)), 6.82 (td, \(J = 7.5, 1.3\) Hz, 1H, ArH-(19)), 6.78 (dd, \(J = 8.7, 1.4\) Hz, 1H, ArH-(17)), 5.87 (dd, \(J = 6.0, 2.1\) Hz, 1H, CH-(3)), 5.54 (dd, \(J = 6.0, 1.9\) Hz, 1H, CH-(4)), 4.46 (dd, \(J = 8.8, 4.1\) Hz, 1H, CH-(1)), 4.42 (td, \(J = 11.6, 2.2\) Hz, 1H, CHH´-(15)), 4.27 (dt, \(J = 11.3, 3.7\) Hz, 1H, CHH´-(15)), 3.83 (p, \(J = 7.2\) Hz, 2H, CH\(_2\)-(22)), 3.53 (dp, \(J = 10.1, 7.1\) Hz, 1H, CHH´-(22)), 3.43 (dp, \(J = 10.1, 7.1\) Hz, 1H, CHH´-(22)), 2.97 – 2.92 (m, 1H, CH-(5)), 2.64 (t, \(J = 7.7\) Hz, 2H, CH\(_2\)-(9)), 2.19 – 2.11 (m, 1H, CHH´-(14)), 1.85 – 1.77 (m, 2H, CHH´-(14), CHH´-(6)), 1.72 – 1.63 (m, 2H, CH\(_2\)-(8)), 1.54 – 1.43 (m, 3H, CHH´-(6), CH\(_2\)-(7)), 1.19 (td, \(J = 7.1, 1.0\) Hz, 3H, CH\(_3\)-(23)), 1.03 (td, \(J = 7.1, 1.0\) Hz, 3H, CH\(_3\)-(23)); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta_{C}/ppm\): 154.7 (C(16)), 142.7 (C(10)), 136.7 (C(4)), 133.0 (C(3)), 130.7 (C(20)), 128.5 (C(12)), 128.4 (C(11)), 128.3 (C(18)), 125.8 (C(13)), 122.0 (C(21)), 119.8 (C(19)), 116.8 (C(17)), 89.9 (C(1)), 63.7 (C(22)), 63.4 (C(22)), 62.9 (C(15)), 53.8 (C(5)), 52.7 (C(2)), 36.0 (C(9)), 35.3 (C(14)), 34.3 (C(6)), 31.7 (C(8)), 27.6 (C(7)), 16.1 (C(23)); \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta_{P}/ppm\): -2.29; HRMS (ESI) \(m/z\) calcd for C\(_{27}\)H\(_{35}\)O\(_5\)NaP [M+H]\(^+\): 493.21143, found: 493.21134; IR (ATR) \(\nu\) (cm\(^{-1}\)) thin film, CHCl\(_3\): 2980.7 (w), 2929.6 (w), 2857.1 (w), 1488.3 (w), 1452.0 (w), 1261.4 (w), 1224.3 (w), 1027.8 (s), 975.3 (m), 755.0 (w), 700.2 (w); [\(\alpha\)]\(^{25}\)\(_{S89}\) = -62.9 (c=1.0 in CHCl\(_3\), 91\% ee).
Diethyl ((3S,4R)-4-(4-phenylbutyl)-2,3,4,7-tetrahydroxepin-3-yl) phosphate (11b)

Synthesised according to general procedure 1c, using tetraethyl ((3R,6S)-2,3,6,7-tetrahydroxepine-3,6-diyl) bis(phosphate) (11a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-30-40% EtOAc in petroleum ether) to give 11b as a yellow oil (109 mg, 71%).

SFC analysis indicated an enantiomeric excess of 92% [Chiralpak® IG; flow: 1.5 mL/min; MeOH/CO₂: 1% to 30%; λ = 210 nm; minor enantiomer, t<sub>R</sub> = 2.584 min; major enantiomer, t<sub>R</sub> = 2.680 min].

<sup>1</sup>H NMR (400 MHz, CDCl₃) δ/ppm: 7.30 – 7.24 (m, 2H, 2ArH-(13)), 7.19 – 7.14 (m, 3H, 3ArH-(12, 14)), 5.61 – 5.55 (m, 1H, CH-(4)), 5.50 – 5.44 (m, 1H, CH-(5)), 4.40 (tt, J = 7.9, 3.6 Hz, 1H, CH-(1)), 4.33 (dq, J = 16.7, 2.4 Hz, 1H, CHH´-3)), 4.16 (dt, J = 4.0, 1.6 Hz, 1H, CHH´-3)), 4.13 – 4.04 (m, 4H, 2CH₂-(15)), 3.97 (dd, J = 4.9, 3.6 Hz, 2H, CH₂-(2)), 2.89 – 2.80 (m, 1H, CH-(6)), 2.61 (t, J = 7.6 Hz, 2H, CH₂-(10)), 1.74 – 1.60 (m, 3H, CH₁-(9), CHH´-(8)), 1.57 – 1.43 (m, 2H, CHH´-(7, 8)), 1.41 – 1.35 (m, 1H, CHH´-(7)), 1.32 (tdd, J = 7.1, 3.6, 1.0 Hz, 6H, 2CH₃-(16)); <sup>13</sup>C NMR
(101 MHz, CDCl3) δ/ppm: 142.7 (C(11)), 130.1 (C(5)), 129.7 (C(4)), 128.5 (C(12)), 128.4 (C(13)), 125.8 (C(14)), 81.0 (C(1)), 73.2 (C(2)), 70.9 (C(3)), 63.9 (C(15)), 41.9 (C(6)), 36.0 (C(10)), 32.1 (C(8)), 31.7 (C(9)), 26.8 (C(7)), 16.3 (C(16)); 31P NMR (162 MHz, CDCl3) δ/ppm: –1.58; HRMS (ESI) m/z calc’d for C20H32O5P [M+H]+: 383.19819, found: 383.19822; IR (ATR) ν (cm−1) thin film, CHCl3: 3025.9 (w), 2926.1 (w), 2855.6 (w), 1496.7 (w), 1274.1 (w), 1103.1 (w), 1029.9 (s), 748.7 (w), 699.7 (w); [α]25° = -46.0 (c=1.0 in CHCl3, 92% ee).

tert-Butyl (3S,4R)-3-((diethoxyphosphoryl)oxy)-4-(4-phenylbutyl)-2,3,4,7-tetrahydro-1H-azepine-1-carboxylate (12b)

![Chemical structure of 12b](image)

Chemical Formula: C25H40NO6P
Molecular Weight: 481.57

Synthesised according to general procedure 1c, using tert-butyl (3R,6S)-3,6-bis((diethoxyphosphoryl)oxy)-2,3,6,7-tetrahydro-1H-azepine-1-carboxylate (12a) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (10-30-40% EtOAc in petroleum ether) to give 12b as a yellow oil (140 mg, 73%). Obtained as a mixture of rotamers.

SFC was performed on a Waters UPC system equipped with a PDA (UV) detector and QDa (MS) detector using a Lux Cellulose 2 column (3.0 x 50 mm, 3 μm). Mobile phase A was CO2 and mobile phase B was IPA with 20mM NH3. A gradient from 5% to 50% mobile phase B over 3.5 minutes was used, followed by an increase to 60% over 0.05 minutes, a hold at 60% for 0.4 minutes and return to 5%. The total flow was 2 mL/min, the back pressure was 140 bar, and the column temperature was 40 °C. The PDA detector range was 210 – 400 nm.
SFC analysis indicated an enantiomeric excess of 93%, major enantiomer, $t_R = 2.27\text{min}$; minor enantiomer, $t_R = 2.77\text{min}$.

$^1$H NMR (500 MHz, DMSO-$d_6$, 338K) $\delta_{\text{H}}$/ppm: 7.26 (t, $J = 7.6$ Hz, 2H, 2ArH- (13)), 7.19 – 7.13 (m, 3H, 3ArH-(12, 14)), 5.71 – 5.66 (m, 1H, CH-(4)), 5.52 – 5.46 (m, 1H, CH-(5)), 4.37 – 4.29 (m, 1H, CH-(1)), 4.08 – 4.00 (m, 2H, 2CH$_2$-(18)), 3.98 – 3.89 (m, 2H, CH$_2$-(3)), 3.89 – 3.83 (m, 1H, CHH´-(2)), 3.56 (dd, $J = 14.7$, 5.2 Hz, 1H, CHH´-(2)), 2.59 (t, $J = 7.6$ Hz, 2H, CH$_2$-(10)), 2.62 – 2.54 (m, 1H, CH-(6)), 1.64 – 1.57 (m, 3H, CH$_2$-(9), CHH´-(7)), 1.42 (s, 9H, 3CH$_3$-(17)), 1.46 – 1.31 (m, 3H, CH$_2$-(8), CHH´-(7)), 1.27 (td, $J = 7.2$, 5.9 Hz, 6H, 2CH$_3$-(19)); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta_{\text{c}}$/ppm: 155.3, 142.6, 131.0, 130.3, 128.9, 128.6, 128.5, 128.4, 125.8, 80.3, 79.9, 79.0, 63.9, 50.6, 46.8, 46.6, 42.3, 36.0, 32.5, 32.1, 31.7, 28.5, 26.9, 16.3; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta_{\text{P}}$/ppm: –1.60; HRMS (ESI) m/z calcd for C$_{25}$H$_{41}$O$_6$NP [M+H]$^+$ : 482.26660, found: 482.26662; IR (ATR) $\nu$ (cm$^{-1}$) thin film, CHCl$_3$: 2928.9 (w), 2856.8 (w), 1694.3 (s), 1248.3 (m), 1166.8 (m), 1131.0 (w), 1008.6 (s), 749.4 (w), 699.9 (w); [$\alpha$]$^{25}_{\text{D}}$$_{899}$ = -94.1 (c=1.0 in CHCl$_3$, 93% ee).
Diethyl ((1S,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate (14)

Synthesised according to general procedure 1b, using (1S,3S)-cyclopent-4-ene-1,3-diyld tetraethyl bis(phosphate) (13) and 4-phenyl-1-butene as the alkene partner (hydrozirconation time 20 mins). Purified by flash chromatography (20-40% EtOAc in petroleum ether) to give 14 as a yellow oil (91 mg, 65%).

HPLC analysis indicated an enantiomeric excess of >99% [Chiralpak® IA; flow: 1.0 mL/min; hexane/iPrOH: 95:5; λ = 210 nm; minor enantiomer, t<sub>R</sub> = 9.663 min; major enantiomer, t<sub>R</sub> = 10.616 min].

<sup>1</sup>H NMR (400 MHz, CDCl₃) δ<sub>H</sub>/ppm: 7.30 – 7.24 (m, 2H, ArH-(12)), 7.20 – 7.15 (m, 3H, ArH-(11, 13)), 5.72 – 5.67 (m, 2H, 2CH-(3, 4)), 4.99 (dtd, J = 6.8, 5.7, 3.7 Hz, 1H, CH-(1)), 4.14 – 4.03 (m, 4H, 2CH₂-(14)), 2.74 – 2.66 (m, 1H, CH-(5)), 2.65 – 2.58 (m, 4H, 2CH₂-(2, 9)), 1.71 – 1.59 (m, 3H, CH₂-(8), CHH´-(6)), 1.50 – 1.40 (m, 3H, CH₂-(7), CHH´-(6)), 1.32 (td, J = 7.1, 1.0 Hz, 6H, 2CH₃-(15)); <sup>13</sup>C NMR (101 MHz, CDCl₃) δ<sub>c</sub>/ppm: 142.8 (C(10)), 133.2 (C(4)), 128.5 (C(11)), 128.4 (C(12)), 127.4 (C(3)), 125.8 (C(13)), 79.8 (C(1)), 63.7 (C(14)), 49.1 (C(5)), 39.9 (C(2)), 36.1 (C(9)), 32.0 (C(6)), 28.1 (C(8)), 27.8 (C(7)), 16.3 (C(15)); <sup>3</sup>¹P NMR (162 MHz,
CDCl₃ δppm: 7.26; HRMS (ESI) m/z calcd for C₁₉H₂₉O₄NaP [M+Na]^+ : 375.16957, found: 375.16960; IR (ATR) ν (cm⁻¹) thin film, CHCl₃: 2981.3 (w), 2932.2 (w), 2857.9 (w), 2360.2 (w), 1603.9 (w), 1454.2 (w), 1393.0 (w), 1262.5 (m), 1165.6 (w), 1029.5 (s), 973.5 (m), 819.8 (w), 746.5 (w), 700.2 (w); [α]²⁵º⁸⁹ = -36.1 (c=1.0 in CHCl₃, >99% ee).
Derivatisation Products

(1R,2R)-2-ethylcyclopent-3-en-1-ol (15)

![Chemical Structure](image)

Chemical Formula: C_{12}H_{22}O
Molecular Weight: 192.320

To a solution of 3 (98 µL, 0.4 mmol, 1.0 eq) in Et₂O was added LiAlH₄ (1.0 M in Et₂O, 0.89 mL, 0.89 mmol, 2.2 eq) at 0 °C. The mixture was left to stir at room temperature for 90 mins before quenching with dropwise addition of H₂O, until effervescence stopped. The resulting residue was suspended in CH₂Cl₂ and filtered through celite, washing the filter pad with CH₂Cl₂. The filtrate was evaporated in vacuo and purified on silica (40% Et₂O in pentane) to give 15 as a colourless oil (43 mg, 96%; NOTE: Product is volatile and should not be dried by high vacuum. Rotary evaporator at 35 °C, 150 mbar was sufficient).

The product was derivatised according to general procedure 2 (esterification process only) for HPLC analysis.

HPLC analysis indicated an enantiomeric excess of 90% [Chiralpak® ID; flow: 0.7 mL/min; hexane/iPrOH: 99:1; λ = 210 nm; minor enantiomer, tᵣ = 14.157 min; major enantiomer, tᵣ = 14.785 min].

H NMR (500 MHz, CDCl₃) δH/ppm: 5.68 – 5.65 (m, 1H, CH-(4)), 5.64 – 5.61 (m, 1H, CH-(3)), 4.66 (tt, J = 6.6, 3.1 Hz, 1H, CH-(1)), 4.08 (ddt, J = 14.6, 7.1, 3.2 Hz, 4H, 2CH₂-(8)), 2.77 – 2.72 (m, 1H, CHH’-(2)), 2.73 – 2.67 (m, 1H, CH-(5)), 2.51 – 2.44 (m, 1H, CHH’-(2)), 1.52 – 1.39 (m, 1H, CHH’-(6)), 1.39 – 1.33 (m, 1H, CHH’-(6), 1.31 (tdd, J = 7.1, 2.3, 1.0 Hz, 6H, CH₃-(9)), 0.93 (t, J = 7.5 Hz, 3H, 2CH₃-(7));

C NMR (126 MHz, CDCl₃) δc/ppm: 132.5 (C(4)), 127.3 (C(3)), 82.9 (C(1), 63.7 (C(8)), 54.6 (C(5)), 40.0 (C(2)), 25.6 (C(6)), 16.3 (C(9)), 11.8 (C(7)). Consistent with data found in the literature.¹⁴
Diethyl ((1R,4aR,10aR)-1,4,4a,9,10,10a-hexahydropyphenanthren-1-yl) phosphate (16)

A 10 mL round bottomed flask was charged with Pd(OAc)₂ (12 mg, 0.054 mmol, 0.15 eq), 1,3-bis(diphenylphosphino)propane (45 mg, 0.108 mmol, 0.30 eq) and K₂CO₃ (199 mg, 1.44 mmol, 4.0 eq). The flask was purged with Ar 3 times and capped with a rubber septum. The mixture was suspended in toluene (4 mL), before adding 2l (119 µL, 0.36 mmol, 1.0 eq). The flask was wrapped in parafilm to prevent loss of solvent, and stirred at 110 °C (dark brown mixture forms) for 21 hours. The reaction mixture was cooled to room temperature, poured over H₂O (50 mL) and extracted with CH₂Cl₂ (3 x 50 mL). The organic layers were combined, washed with brine (50 mL), dried (MgSO₄) and evaporated in vacuo to give a brown oil. The oil was purified on silica (20-30-40% EtOAc in petroleum ether) to give 16 as a yellow oil (97 mg, 80%).

HPLC analysis indicated an enantiomeric excess of 91% [Chiralpak® IA; flow: 1.0 mL/min; hexane/iPrOH: 95:5; λ = 210 nm; major enantiomer, tᵣ = 8.687 min; minor enantiomer, tᵣ = 11.302 min].

H NMR (500 MHz, CDCl₃) δH/ppm: 7.25 (d, J = 7.6 Hz, 1H, ArH-(11)), 7.18 (td, J = 7.4, 1.5 Hz, 1H, ArH-(13)), 7.13 (td, J = 7.4, 1.5 Hz, 1H, ArH-(12)), 7.08 (d, J = 7.3
Hz, 1H, ArH-(14)), 5.78 – 5.71 (m, 1H, CH-(4)), 5.55 – 5.48 (m, 1H, CH-(3)), 4.70 (dq, J = 7.6, 3.8 Hz, 1H, CH-(1)), 4.16 – 4.06 (m, 4H, CH₂-(15)), 3.69 (m, 1H, CH-(5)), 2.88 – 2.74 (m, 2H, CH₂-(8)), 2.44 – 2.38 (m, 1H, CH-(6)), 2.36 (m, 2H, CH₂-(2)), 1.75 – 1.56 (m, 2H, CH₂-(7)), 1.33 (ddt, J = 11.1, 7.1, 1.0 Hz, 6H, CH₃-(16)); ¹³C NMR (126 MHz, CDCl₃) δc/ppm: 138.8 (C(10)), 136.6 (C(9)), 131.5 (C(4)), 129.3 (C(11)), 129.1 (C(14)), 126.4 (C(13)), 126.1 (C(12)), 120.8 (C(3)), 76.3 (C(1)), 63.8 (C(15)), 37.6 (C(6)), 35.7 (C(5)), 28.9 (C(8)), 28.6 (C(2)), 22.6 (C(7)), 16.3 (C(16)); ³¹P NMR (162 MHz, CDCl₃) δp/ppm: -1.21; HRMS (ESI) m/z calcld for C₁₈H₂₆O₄P [M+H]⁺: 337.15632, found: 337.15604; IR (ATR) ν (cm⁻¹) thin film, CHCl₃: 2982.2 (w), 2929.8 (w), 1488.9 (w), 1448.1 (w), 1392.8 (w), 1261.4 (m), 1165.4 (w), 1028.8 (s), 1009.0 (s), 818.7 (w), 775.1 (w), 744.9 (m), 679.0 (w); [α]²⁵ 589 = -80.3 (c=1.0 in CHCl₃, 91% ee).

(1S,2R,3R,4S,5R)-2-benzyl-3,4-dihydroxy-2-methyl-5-(4-phenylbutyl)cyclopentyl diethyl phosphate (17)

To a solution of 4b (100 mg, 0.22 mmol, 1.0 eq, 94% ee) in acetone (350 µL) and H₂O (90 µL) was added NMO (39 mg, 0.33 mmol, 1.50 eq) and K₂OsO₄·H₂O (3 mg, 0.008 mmol, 4 mol%) at rt. The resulting heterogeneous mixture was stirred for 21 hours at rt. The reaction mixture was quenched with sat. aq. Na₂S₂O₃ (1 mL) and stirred for a further 20 minutes. The mixture was extracted with EtOAc (3 x 2 mL). The organic layers were combined, dried (MgSO₄) and evaporated in vacuo to give a yellow oil. The yellow oil was purified on silica (30-70% EtOAc in heptane) to give 17 as a yellow oil (107 mg, 75%, 94% ee). Other diastereomer observed in crude NMR at a 4:1 ratio in favour of the isolated product.
SFC was performed on a Waters UPC system equipped with a PDA (UV) detector and QDa (MS) detector using a Daicel Chiralpak IC column (3.0 x 50 mm, 3 μm). Mobile phase A was CO\(_2\) and mobile phase B was methanol with 20mM NH\(_3\). A gradient from 5% to 50% mobile phase B over 3.5 minutes was used, followed by an increase to 60% over 0.05 minutes, a hold at 60% for 0.4 minutes and return to 5%. The total flow was 2 mL/min, the back pressure was 140 bar, and the column temperature was 40 °C. The PDA detector range was 210 – 400 nm.

SFC analysis indicated an enantiomeric excess of 94%; major enantiomer, \(t_R = 1.65\) min; minor enantiomer, \(t_R = 2.20\) min.

\[\text{H NMR (500 MHz, CDCl}_3\] \(\delta\)H/ppm: 7.31 – 7.26 (m, 4H, 4ArH-(12, 18), 7.25 – 7.20 (m, 3H, 3ArH-(17, 19)), 7.20 – 7.15 (m, 3H, 3ArH-(11, 13)), 4.46 (t, J = 9.0 Hz, 1H, CH-(1)), 4.18 – 4.09 (m, 5H, CH-(4)), 2CH\(_2\)-(20)), 4.03 (d, J = 4.5 Hz, 1H, CH-(3)), 2.77 (d, J = 13.5 Hz, 1H, CHH’-(15)), 2.70 – 2.57 (m, 2H), 2.65 (d, J = 12.1 Hz, 1H, CHH’-(15)), 1.97 – 1.89 (m, 1H, CH-(5)), 1.75 – 1.62 (m, 4H, 2CH\(_2\)-(6, 8)), 1.60 – 1.50 (m, 1H, CHH’-(7)), 1.42 – 1.30 (m, 1H, CHH’-(7)), 1.36 (m, 6H, 2CH\(_3\)-(21)), 1.14 (s, 3H, CH\(_3\)-(14)); \(\text{C NMR (126 MHz, CDCl}_3\] \(\delta\)C/ppm: 142.8 (C(10)), 138.4 (C(16)), 130.6 (C(17)), 128.5 (C(12)), 128.3 (C(11)), 128.3 (C(18)), 126.5 (C(19)), 125.7 (C(13)), 91.0 (C(1)), 76.9 (C(3)), 71.4 (C(4)), 64.0 (C(20)), 46.3 (C(5)), 46.2 (C(2)), 41.8 (C(15)), 36.0 (C(9)), 31.8 (C(8)), 27.8 (C(7)), 26.6 (C(6)), 21.2 (C(14)), 16.3 (C(21)); \(\text{P NMR (162 MHz, CDCl}_3\] \(\delta\)P/ppm: 1.23; HRMS (ESI) m/z calcld for C\(_{27}\)H\(_{39}\)O\(_6\)NaP [M+Na\(^+\)]: 513.23765, found: 513.23778; IR (ATR) \(\nu\) (cm\(^{-1}\)) thin film, CHCl\(_3\): 3360.5 (br. w), 3026.6 (w), 2933.1 (w), 1248.7 (w), 1024.2 (s), 981.0 (w), 754.9 (w), 701.2 (w); \([\alpha]_{25}^{\text{D}}\) = -42.9 (c=1.0 in CHCl\(_3\), 94% ee).
Supplementary Figures 2 - 67

Supplementary Figure 2 - *Meso*-4-cyclopentene-1,3-bisdimethylphosphate

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Supplementary Figure 3 - *Meso*-4-cyclopentene-1,3-bisdiethylphosphate (1a)

$^3$P NMR (162 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
Supplementary Figure 4 - Mes0-4-cyclopentene-1,3-bisdiisopropylphosphate

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

Supplementary Figure 5 - Meso-4-cyclopentene-1,3-bis(diphenylphosphate)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
Supplementary Figure 6 - *Meso*-5-cyclohexene-1,4-bisdiethylphosphate (2a)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
**Supplementary Figure 7** - *Meso*-6-cycloheptene-1,5-bisdiethylphosphate (3a)

**1H NMR (400 MHz, CDCl₃)**

**31P NMR (162 MHz, CDCl₃)**
$^{13}$C NMR (101 MHz, CDCl$_3$)

3a

$^{31}$P NMR (162 MHz, CDCl$_3$)

3a
Supplementary Figure 8 - (1S,3S)-Cyclopent-4-ene-1,3-diyl tetraethyl bis(phosphate) (13)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)
Supplementary Figure 9 - (1R,2S,3S)-2- Allyl-2-methylcyclopent-4-ene-1,3-diol

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Supplementary Figure 10 - (1R,2S,3S)-2- Allyl-2-methylcyclopent-4-ene-1,3-diol
$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Supplementary Figure 11 - (1R,2S,3S)-2-(2-Chlorobenzyl)-2-methylcyclopent-4-ene-1,3-diol

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Supplementary Figure 12 - (1R,2S,3S)-2-((Benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-diol $^1$H NMR (500 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Supplementary Figure 13 - \((1S,2R,5S)-2',3'-\text{Dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-diol}\) \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\))

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\))
Supplementary Figure 1 - (2'R,4S,5'S)-Spiro[chromane-4,1'-cyclopentan]-3'-ene-2',5'-diol  $^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Supplementary Figure 15 - (1R,2S,3S)-2-Benzyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (4a) $^1$H NMR (400 MHz, CDCl₃)

$^{13}$C NMR (101 MHz, CDCl₃)
Supplementary Figure 16 - Cis-2,2-dimethylcyclopent-4-ene-1,3-bis(diethyl phosphate) (5a) $^1$H NMR (400 MHz, CDCl₃)

$^{31}$P NMR (162 MHz, CDCl₃)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
Supplementary Figure 1 - (1R,2S,3S)-2-Allyl-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (6a)  
$^{1}$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
Supplementary Figure 18 - (1R,2S,3S)-2-(2-Chlorobenzyl)-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (7a) \(^1\)H NMR (400 MHz, CDCl\(_3\))
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
Supplementary Figure 19 - (1R,2S,3S)-2-((Benzyloxy)methyl)-2-methylcyclopent-4-ene-1,3-bis(diethyl phosphate) (8a) $^1$H NMR (400 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

Supplementary Figure 20 - (1$S$,2$R$,5$S$)-2',3'-Dihydrospiro[cyclopentane-1,1'-inden]-3-ene-2,5-bis(diethyl phosphate) (9a) $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
Supplementary Figure 21 - (2'R,4S,5'S)-Spiro[chromane-4,1'-cyclopentan]-3'-ene-2',5'-bis(diethyl phosphate) (10a) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

Supplementary Figure 22 - Tetraethyl (3R,6S)-2,3,6,7-tetrahydrooxepine-3,6-diyl) bis(phosphate) (11a) $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
Supplementary Figure 23 - tert-Butyl (3R,6S)-3,6-bis((diethoxyphosphoryl)oxy)-2,3,6,7-tetrahydro-1H-azepine-1-carboxylate (12a) ¹H NMR (400 MHz, DMSO-d₆, 338K)

¹H NMR (400 MHz, DMSO-d₆, 338K)

¹³C NMR (101 MHz, CDCl₃)
$^{31}$P NMR (162 MHz, CDCl$_3$)

![Chemical Structure](image)

12a
Supplementary Figure 24 - Dimethyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}\text{P NMR (162 MHz, CDCl}_3\text{)}$

HPLC Trace
Supplementary Figure 25 - Diethyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate (1b) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 26 - Diisopropyl ((1R,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate. \(^1\)H NMR (400 MHz, CDCl\(_3\)).

\(^1\)C NMR (101 MHz, CDCl\(_3\)).
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 27 - Diphenyl ((1\textit{R},2\textit{R})-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 28 - Diethyl ((1R,2R)-2-(4-phenylbutyl)cyclohex-3-en-1-yl) phosphate (2b) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 29 - Diethyl ((1R,2R)-2-(4-phenylbutyl)cyclohept-3-en-1-yl) phosphate (3b) $^1$H NMR (400 MHz, CDCl₃)

$^{13}$C NMR (101 MHz, CDCl₃)
$^{31}\text{P NMR (162 MHz, CDCl}_3\text{)}$

$\begin{align*}
\text{(EtO)}_2\text{PO}_\text{Ph} \rightarrow \\
3b
\end{align*}$

HPLC Trace

$\begin{align*}
\text{(EtO)}_2\text{PO}_\text{Ph} \rightarrow \\
3b
\end{align*}$
Supplementary Figure 30 - Diethyl ((1R,2R)-2-ethylcyclopent-3-en-1-yl) phosphate (1c) $^1$H NMR (500 MHz, CDCl$_3$)

$^1$C NMR (126 MHz, CDCl$_3$)
$^{31}$P NMR (202 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 31 - Diethyl ((1R,2R)-2-ethylcyclohex-3-en-1-yl) phosphate (2c) \(^1\)H NMR (500 MHz, CDCl\(_3\))

\[
\begin{array}{c}
\text{O} \\
\text{(EtO)}_2\text{PO}_2 \\
\text{Et} \\
\text{2c}
\end{array}
\]

\(\text{\(^{13}\)C NMR (126 MHz, CDCl\(_3\))}

\[
\begin{array}{c}
\text{O} \\
\text{(EtO)}_2\text{PO}_2 \\
\text{Et} \\
\text{2c}
\end{array}
\]
$^{31}$P NMR (202 MHz, CDCl$_3$)

HPLC Trace

$\text{O}_2\text{N}$

O$_2$N

Et

$\text{O}^ -$
Supplementary Figure 32 - Diethyl ((1R,2R)-2-hexylcyclopent-3-en-1-yl) phosphate (1d) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure32.png}
\caption{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure32.png}
\caption{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})}
\end{figure}
$^{31}$P NMR (162 MHz, CDCl$_3$)

GC Trace
Supplementary Figure 33 - Diethyl ((1R,2R)-2-hexylcyclohex-3-en-1-yl) phosphate (2d) \(^1\)H NMR (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR (101 MHz, CDCl\(_3\))
$^{31}$P NMR (162 MHz, CDCl$_3$)

![NMR Spectrum]

GC Trace

![GC Trace]

2d
Supplementary Figure 34 - Diethyl ((1R,2R)-2-tetradecyclocpent-3-en-1-yl) phosphate (1e) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace

$\text{C}_{14}\text{H}_{29} \text{OP(OME)}_2$

$1e$

$\text{C}_{14}\text{H}_{29} \text{OP} \text{NO}_2$

$1e'$
Supplementary Figure 35 - Diethyl ((1R,2R)-2-tetradecylcyclohex-3-en-1-yl) phosphate (2e) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)

\[ \text{(EtO)$_2$PO$_4$} \]

\[ \text{C$_{14}$H$_{29}$} \]

\[ 2e \]
$^{31}\text{P NMR (162 MHz, CDCl}_3\text{)}$

![Chemical structure](image)

HPLC Trace

![HPLC trace](image)
Supplementary Figure 36 - Diethyl ((1R,2R)-2-isopentylcyclopent-3-en-1-yl) phosphate (1f) \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})

\begin{align*}
\text{\textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3})}
\end{align*}
$^{31}$P NMR (162 MHz, CDCl$_3$)

![Chemical Structure](image)

GC Trace

![GC Trace](image)
Supplementary Figure 37 - Diethyl ((1R,2R)-2-isopentylcyclohex-3-en-1-yl) phosphate (10b) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

[Chemical structure image]

GC Trace

[GC trace image]

S166
Supplementary Figure 38 - Diethyl (1R,2R)-2-(3,3-dimethylbutyl)cyclopent-3-en-1-yl) phosphate (1g) ¹H NMR (400 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)
$^{31}$P NMR (162 MHz, CDCl$_3$)

GC Trace

1g
Supplementary Figure 39 - Diethyl (1R,2R)-2-(3,3-dimethylbutyl)cyclohex-3-en-1-yl) phosphate (2g) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

![NMR Spectrum]

GC Trace

![GC Trace]

S170
Supplementary Figure 40 - Diethyl (1R,2R)-2-(2-cyclohexylethyl)cyclopent-3-en-1-yl phosphate (1h) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

GC Trace
Supplementary Figure 41 - Diethyl (1R,2R)-2-(2-cyclohexylethyl)cyclohex-3-en-1-yl phosphate (2h) Suplementary Figure 41 - Diethyl (1R,2R)-2-(2-cyclohexylethyl)cyclohex-3-en-1-yl phosphate (2h) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

$\text{(EtO)$_2$PO$_2$}$

GC Trace

$\text{(EtO)$_2$PO$_2$}$
Supplementary Figure 42 - (1R,2R)-2-(6-chlorohexyl)cyclopent-3-en-1-yl diethyl phosphate (II)  $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

1i

HPLC Trace

1i'

S176
Supplementary Figure 43 - (1R,2R)-2-(6-chlorohexyl)cyclohex-3-en-1-yl diethyl phosphate (2i) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}\text{P NMR (162 MHz, CDCl}_3\text{)}$

\[ \text{Cl} \quad \text{(EtO)$_2$PO$_2$N} \quad \text{Cl} \\
\quad \text{2i} \]

HPLC Trace

\[ \text{Cl} \quad \text{O$_2$N} \quad \text{O$_2$} \\
\quad \text{1i'} \]
Supplementary Figure 44 - (1R,2R)-2-(4-((tert-butyldiphenylsilyl)oxy)butyl)cyclopent-3-en-1-yl diethyl phosphate (1j) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}\text{P NMR (162 MHz, CDCl}_3$)

HPLC Trace
Supplementary Figure 45 - (1R,2R)-2-(4-((tert-butyldiphenylsilyl)oxy)butyl)cyclohex-3-en-1-yl diethyl phosphate (2j) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 46 - (1R,2R)-2-(4-((tert-butyldiphenylsilyl)oxy)butyl)cyclohept-3-en-1-yl diethyl phosphate (3j) \( ^1\)H NMR (400 MHz, CDCl\textsubscript{3})

\( ^{13}\)C NMR (101 MHz, CDCl\textsubscript{3})
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 47 - Diethyl ((1R,2R)-2-(4-methoxyphenethyl)cyclopent-3-en-1-yl) phosphate (1k)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 48 - Diethyl ((1R,2R)-2-(4-methoxyphenethyl)cyclohex-3-en-1-yl) phosphate (2k) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 49 - Diethyl (1R,2R)-2-(4-methoxyphenethyl)cyclohept-3-en-1-yl) phosphate (3k) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 50 - (1R,2R)-2-(2-bromophenethyl)cyclopent-3-en-1-yl diethyl phosphate (II) \(^1\)H NMR (400 MHz, CDCl\(_3\))

\[
\begin{array}{c}
\text{Br} \quad \text{O} \\
\text{OP(OEt)}_2 \\
\text{II}
\end{array}
\]

\[13\text{C NMR (101 MHz, CDCl}_3\text{)}
\]

\[
\begin{array}{c}
\text{Br} \quad \text{O} \\
\text{OP(OEt)}_2 \\
\text{II}
\end{array}
\]
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 51 - (1R,2R)-2-(2-bromophenethyl)cyclohex-3-en-1-yl diethyl phosphate (2I) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)
Supplementary Figure 52 - (1S,2R,5R)-2-Benzyl-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (4b) 1H NMR (400 MHz, CDCl3)

13C NMR (101 MHz, CDCl3)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace

4b
Supplementary Figure 53 - (1S,2R,5R)-2-Benzyl-5-(3-(benzyloxy)propyl)-2-methylcyclopent-3-en-1-yl diethyl phosphate (4c) $^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

SFC Trace
Supplementary Figure 54 - \((1S,2R,5R)-2\text{-}2\text{-}benzyl\text{-}5\text{-}4\text{-}\text{bromobutyl}\text{-}2\text{-}methylocyclopent\text{-}3\text{-}en\text{-}1\text{-}yl\text{ diethyl phosphate (4d)}\) \(^1\text{H} \text{NMR (500 MHz, CDCl}_3\))

\[ \text{\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Supplementary Figure 54.}
\end{figure}} \]

\(^{13}\text{C} \text{NMR (126 MHz, CDCl}_3\))

\[ \text{\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Supplementary Figure 54.}
\end{figure}} \]
$^{31}\text{P NMR (162 MHz, CDCl}_3\text{)}$

$^{31}\text{P NMR (162 MHz, CDCl}_3\text{)}$

$^{31}\text{P NMR (162 MHz, CDCl}_3\text{)}$

HPLC Trace

HPLC Trace

HPLC Trace

HPLC Trace
Supplementary Figure 55 - (1S,2R,5R)-2-Benzyl-5-(2-bromo-5-fluorophenethyl)-2-methylcyclopent-3-en-1-yl diethyl phosphate (4e) $^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

SFC Trace

4e
Supplementary Figure 56 - (1S,2R,5R)-2-Benzyl-5-(4-(dibenzylamino)butyl)-2-methylcyclopent-3-en-1-yl diethyl phosphate (4f) $^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

![SFC Trace image]

**4f**
Supplementary Figure 57 - (1S,5R)-2,2-Dimethyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (5b) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 58 - \((1S,2R,5R)-2\text{-Allyl-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (6b)}\) \(^1\)H NMR (400 MHz, CDCl\(_3\))

\[^1\]C NMR (101 MHz, CDCl\(_3\))
$^3\text{P NMR (162 MHz, CDCl}_3\text{)}$

HPLC Trace

$\text{Ph}$

$\text{Me}$

$\text{O}$

$\text{O}$

$\text{OP(OEt)}_2$

$6b$
Supplementary Figure 59 - (1S,2R,5R)-2-(2-chlorobenzyl)-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (7b) \( ^1\)H NMR (400 MHz, CDCl\(_3\))

\[
\begin{align*}
\text{H NMR} (400 MHz, CDCl}_3
\end{align*}
\]

\[
\begin{align*}
\text{13C NMR (101 MHz, CDCl}_3
\end{align*}
\]
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 60 - (1S,2S,5R)-2-((benzyloxy)methyl)-2-methyl-5-(4-phenylbutyl)cyclopent-3-en-1-yl diethyl phosphate (8b) $^1$H NMR (400 MHz, CDCl₃)

$^1$H NMR (400 MHz, CDCl₃)

$^{13}$C NMR (101 MHz, CDCl₃)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 61 - Diethyl ((1S,4R,5S)-4-(4-phenylbutyl)-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-en-5-yl) phosphate (9b) $^1$H NMR (400 MHz, CDCl$_3$)

$^1$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace

S214
Supplementary Figure 62 - Diethyl ((4S,4'R,5'S)-4'-((4-phenylbutyl)spiro[chromane-4,1'-cyclopentan]-2'-en-5'-yl) phosphate (10b) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 63 - Diethyl ((3S,4R)-4-(4-phenylbutyl)-2,3,4,7-tetrahydrooxepin-3-yl) phosphate (11b) $^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

SFC Trace
Supplementary Figure 64 - tert-Butyl (3S,4R)-3-((diethoxyphosphoryl)oxy)-4-(4-phenylbutyl)-2,3,4,7-tetrahydro-1H-azepine-1-carboxylate (12b) ¹H NMR (500 MHz, DMSO-dma, 338K)

¹³C NMR (101 MHz, CDCl₃)
$^{31}$P NMR (162 MHz, CDCl$_3$)

SFC Trace
Supplementary Figure 65 - Diethyl ((1S,2R)-2-(4-phenylbutyl)cyclopent-3-en-1-yl) phosphate (14) $^1$H NMR (500 MHz, CDCl$_3$) 

$^{13}$C NMR (162 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace

\[
\begin{align*}
&\text{Ph} \\
P &\text{OP(OEt)$_2$}
\end{align*}
\]

14
Supplementary Figure 66 - Diethyl ((1R,4aR,10aR)-1,4,4a,9,10,10a-
hexahydrophenanthren-1-yl) phosphate (16) $^1$H NMR (500 MHz, CDCl₃)

$^{13}$C NMR (126 MHz, CDCl₃)
$^{31}$P NMR (162 MHz, CDCl$_3$)

HPLC Trace
Supplementary Figure 67 - (1S,2R,3R,4S,5R)-2-benzyl-3,4-dihydroxy-2-methyl-5-(4-phenylbutyl)cyclopentyl diethyl phosphate (17) $^1$H NMR (500 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

SFC Trace

![Chemical Structure Image]
Supplementary References

[1] Buchwald, S. L., LaMaire, S. J. & Nielsen, R.B. *Org. Synth.* **71**, 77-82 (1993).

[2] Menard, F., Perez, D., Roman, D. S., Chapman, T. M. & Lautens, M. *J. Org. Chem.* **75**, 4056-4068 (2010).

[3] Feng, K., Wu, L., Zhang, L. & Tung, C. *Tetrahedron*, **63**, 4907-4911 (2007).

[4] Shiramizu, M. & Toste, D. F. *Angew. Chem. Int. Ed.* **52**, 12905-12909 (2013).

[5] Piarulli, U., Claverie, C., Daubos, P., Gennari, C., Minnaard, A. J. & Feringa, B. L. *Org. Lett.* **5**, 4493-4496 (2003).

[6] Holec, C., Sandkuhl, D., Rother, D., Kroutil, W. & Pietruszka, J. *ChemCatChem* **7**, 3125-3130 (2015).

[7] Agosta, W. C. & Smith, A. B. *J. Org. Chem.* **35**, 3856-3860 (1970).

[8] Manna, M. S. & Mukherjee, S. *Chem. Sci.* **5**, 1627-1633 (2014).

[9] Aikawa, K., Okamoto, T. & Mikami, M. *J. Am. Chem. Soc.* **134**, 10329-10332 (2012).

[10] Crane, S. N. & Burnell, D. J. *J. Org. Chem.* **63**, 1352-1355 (1998).

[11] Brun, O., Agramunt, J., Raich, L., Rovira, C., Pedroso, E. & Grandas, A. *Org. Lett.* **18**, 4836-4839 (2016).

[12] Evans, J. C., Klix, R. C. & Bach, R. D. *J. Org. Chem.* **53**, 5519-5527 (1988).

[13] Miyaoka, H., Sagawa, S., Nagaoka, H. & Y. Yamada, Y. *Tetrahedron: Asymmetry*, **6**, 587-594 (1995).

[14] Ito, M., Matsumii, M., Murugesh, M. G. & Kobayashi, Y. *J. Org. Chem.* **66**, 5881-5889 (2001).

[15] Brawn, R. A., Guimaraes, C. R. W., McClure, K. F. and Liras, S. *Org. Lett.*, **14**, 4802-4805 (2012).

[16] Hartman, G. D. and Kuduk, S. WO Patent Application, 2015109130 (2015)