Supporting Information

Inverting External Asymmetric Induction via Selective Energy Transfer Catalysis: A Strategy to β-Chiral Phosphonate Antipodes

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anie_201911651_sm_miscellaneous_information.pdf
Supporting Information

| Section                                | Page |
|----------------------------------------|------|
| General Information                    | 1    |
| Experimental Section                   | 3    |
| HPLC traces                            | 37   |
| NMR Spectra of Key Compounds           | 55   |
| References                             | 138  |
General Information

All chemicals were purchased as reagent grade and used without further purification. Solvents for purification (extraction and chromatography) were purchased as technical grade and distilled on the rotary evaporator prior to use. For column chromatography SiO2 (40-63 µm for Flash-Chromatography, VWR Chemicals) was used as stationary phase. Analytical thin layer chromatography (TLC) was performed on aluminium foil pre-coated with SiO2-60 F254 (Merck) and visualised with a UV-lamp (254 nm) and KMnO4 or CAM solution. Concentration in vacuo was performed at ~10 mbar and 40 °C, drying at ~10-2 mbar and room temperature. NMR spectra were measured by the NMR service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster on a Bruker BZH 200/52, Bruker AV300, Bruker AV400, Agilent DD2 500 or an Agilent DD2 600 spectrometer at room temperature. The chemical shifts are referenced to the residual solvent peak as internal standard. Spectra of other nuclides as 13C and 31P are referenced according to the proton resonance of TMS as the primary reference for the unified chemical shift scale. The resonance multiplicity is abbreviated as: s (singlet), d (doublet), t (triplet), q (quadruplet), p (pentet), sext (sextet), hept (heptet), m (multiplet) and b (broad). Assignments of unknown compounds are based on DEPT, COSY (HH), HMBC, HSQC and NOESY spectra. Alkene configuration is assigned based on coupling constants and NOESY spectra. IR spectra were recorded on a PerkinElmer 100 FT-IR spectrometer, selected absorption bands are reported in wavenumbers (cm⁻¹) and intensities are reported as: w (weak), m (medium), s (strong) and b (broad). High-resolution mass spectra (HR-ESI) were measured by the MS service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster. Optical rotations were measured on a JASCO P2000 polarimeter. Enantiomeric ratios were determined on an Agilent Infinity 1260 HPLC system using a diode array detector (DAD). The chiral stationary phase and the eluent ratio of n-hexane and i-propanol is given specifically for each compound. The column temperature measured 25 to 35 °C. UV/vis absorption spectra were measured on an Agilent Cary 60 UV-Vis Spectrophotometer, baseline correction was performed with the corresponding solvent. Isomerisation reactions were performed utilizing a UVA LED (365 nm, emission spectrum: Figure S1), a Winger WEPUV3-S2 UV Power LED Star (402 nm, emission spectrum: Figure S2) and a Winger WEPRB3-S1 Power LED Star royalblue (450 nm, emission spectrum: Figure S3). The distance between the reaction vessels and the UV-lamp was set at approximately 0.5 cm for all reactions. Hydrogenation reactions were performed in a Berghof High Pressure Reactor using hydrogen gas.
Figure S1: Emission spectrum of the utilised UVA LED (365 nm).

Figure S2: Emission spectrum of the utilised Winger WEPUV3-S2 UV Power LED Star (402 nm).

Figure S3: Emission spectrum of the utilised Winger WEPRB3-S1 Power LED Star royalblue (450 nm).
Experimental Section

Procedures and Analytical Data

General Procedure A for the Synthesis of $E$-Vinylphosphonates

In a flame-dried schlenk tube under argon atmosphere sodium hydride (60% in mineral oil) was dissolved in dry tetrahydrofuran (10 mL) at 0 °C. Tetraalkyl methylenediphosphonate was added dropwise and the solution was stirred under argon atmosphere at 0 °C for 1 h. The specified acetophenone derivative was added via syringe and the solution was heated at 60 °C and stirred for 3 days. After the mixture was cooled to room temperature, water (30 mL) and ethyl acetate (40 mL) were added. The layers were separated and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was removed in vacuo. Purification by column chromatography yielded the $E$-vinylphosphonates.

Diethyl ($E$)-(2-phenylprop-1-en-1-yl)phosphonate ($E$-1):

Prepared according to general procedure A from acetophenone (1.00 mL, 8.57 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (2.70 mL, 10.9 mmol, 1.27 eq.) with sodium hydride (60% in mineral oil, 0.50 g, 12.5 mmol, 1.46 eq.) in 66 h. Purification by column chromatography (SiO$_2$, n-pentane/ethyl acetate: 6/4) yielded $E$-vinylphosphonate $E$-1 as yellow oil (0.87 g, 3.42 mmol, 40%).

$R_f = 0.25$ (SiO$_2$, n-pentane/ethyl acetate: 3/7); $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.48 - 7.44$ (m, 2H, H7), 7.38 - 7.33 (m, 3H, H8, H9), 5.89 (dd, $J = 16.5$, 1.1 Hz, 1H, H3), 4.12 (dq, $J = 7.9$, 7.1 Hz, 4H, H2), 2.50 (dd, $J = 3.3$, 1.1 Hz, 3H, H5), 1.35 (t, $J = 7.1$ Hz, 6H, H1) ppm; $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 158.3$ (d, $J_{CP} = 8.0$ Hz, C4), 141.9 (d, $J_{CP} = 23.6$ Hz, C6), 129.2 (C8/C9), 128.6 (C8/C9), 126.1 (C7), 113.7 (d, $J_{CP} = 190.2$ Hz, C3), 61.6 (d, $J_{CP} = 5.6$ Hz, C2), 19.4 (d, $J_{CP} = 7.0$ Hz, C5), 16.5 (d, $J_{CP} = 6.4$ Hz, C1) ppm;

$^{31}$P NMR (243 MHz, CDCl$_3$): $\delta = 18.14$ ppm; IR (ATR): $\tilde{\nu} = 3474$ (w), 2982 (w), 2906 (w), 1608 (m), 1574 (w), 1495 (w), 1444 (m), 1391 (w), 1325 (w), 1244 (m), 1163 (w), 1098 (w), 1050 (s), 1024 (s), 957 (s), 823 (m), 790 (m), 753 (m), 696 (m) cm$^{-1}$; HR-ESI-MS: $m/z$: 277.0969 ([M+Na]$^+$, calcd. for C$_{13}$H$_{19}$NaO$_3$P$: 277.0964), 531.2039 ([M$_2$+Na]$^+$, cald. for C$_{26}$H$_{38}$NaO$_6$P$_2$: 531.2036); analytical data in agreement with literature.$^{[1]}$
Diethyl (E)-(2-(4-fluorophenyl)prop-1-en-1-yl)phosphonate (E-2):

Prepared according to general procedure A from 4'-fluoroacetophenone (0.18 mL, 1.48 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.32 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.69 eq.) in 65 h. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 4/1) yielded E-vinylphosphonate E-2 as yellow oil (251 mg, 0.92 mmol, 62%).

\[ R_f = 0.47 (SiO₂, ethyl acetate); \]
\[ ^1H NMR \text{ (500 MHz, CDCl}_3) : \delta = 7.46 - 7.39 \text{ (m, 2H, H7), 7.04 - 6.98 \text{ (m, 2H, H8), 5.82 (dd, J = 16.1, 1.2, 0.7 Hz, 1H, H3), 4.10 (ddq, J = 7.7, 7.1, 0.6 Hz, 4H, H2), 2.45 (dt, J = 3.3, 0.8 Hz, 3H, H5), 1.32 (tt, J = 7.0, 0.6 Hz, 6H, H1) ppm; } \]
\[ ^13C NMR \text{ (126 MHz, CDCl}_3) : \delta = 163.4 \text{ (d, J}_{\text{CF}} = 249.2 \text{ Hz, C9), 156.9 (d, J}_{\text{CP}} = 8.3 \text{ Hz, C4), 137.9 (dd, J}_{\text{CP}} = 24.0, J_{\text{CS}} = 3.4 \text{ Hz, C6), 127.9 (d, J}_{\text{CS}} = 8.3 \text{ Hz, C7), 115.5 (d, J}_{\text{CP}} = 21.5 \text{ Hz, C8), 113.6 (dd, J}_{\text{CP}} = 191.0, J_{\text{CS}} = 1.4 \text{ Hz, C3), 61.6 (d, J}_{\text{CS}} = 5.7 \text{ Hz, C2), 19.4 (d, J}_{\text{CP}} = 7.0 \text{ Hz, C5), 16.5 (d, J}_{\text{CS}} = 6.5 \text{ Hz, C1) ppm; } \]
\[ ^19F NMR \text{ (282 MHz, CDCl}_3) : \delta = -112.34 \text{ (tt, J = 8.4, 5.3 Hz) ppm; } \]
\[ ^31P NMR \text{ (202 MHz, CDCl}_3) : \delta = 17.85 \text{ (ddttq, J = 15.8, 11.7, 7.9, 3.7 Hz) ppm; IR (ATR): } \]
\[ \tilde{\nu} = 3457 \text{ (w), 2983 (w), 2917 (w), 2850 (w), 1601 (m), 1509 (m), 1444 (w), 1392 (w), 1323 (w), 1236 (s), 1163 (m), 1098 (w), 1051 (s), 1024 (s), 957 (s), 810 (s), 745 (w), 718 (w) cm}^{-1}; \]
\[ \text{HR-ESI-MS: m/z: 295.0879 ([M+Na]², calcd. for C}_{13}H_{18}FNaO}_2P^+: 295.0870, 567.1847 ([M+Na]², calcd. for C}_{26}H_{36}F_2NaO}_6P^2+: 567.1847); \]
\[ \text{analytical data in agreement with literature.}^{[1]} \]

Diethyl (E)-(2-(4-chlorophenyl)prop-1-en-1-yl)phosphonate (E-3):

Prepared according to general procedure A from 4'-chloroacetophenone (0.19 mL, 1.49 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.31 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.68 eq.) in 64 h. Purification by column chromatography (SiO₂, n-pentane/ethyl acetate: 4/1) yielded E-vinylphosphonate E-3 as yellow oil (210 mg, 0.73 mmol, 49%).

\[ R_f = 0.31 (SiO₂, n-pentane/ethyl acetate: 1/1); \]
\[ ^1H NMR \text{ (500 MHz, CDCl}_3) : \delta = 7.40 - 7.35 \text{ (m, 2H, H8), 7.33 - 7.28 \text{ (m, 2H, H7), 5.86 (dd, J = 16.1, 0.9 Hz, 1H, H3), 4.10 (p, J = 7.1 Hz, 4H, H2), 2.45 (dd, J = 3.3, 0.8 Hz, 3H, H5), 1.33 (t, J = 7.1 Hz, 6H, H1) ppm; } \]
\[ ^13C NMR \text{ (126 MHz, CDCl}_3) : \delta = 156.7 (d, J}_{\text{CF}} = 8.3 \text{ Hz, C4), 140.2 (d, J}_{\text{CP}} = 24.0 \text{ Hz, C6), 135.2 (C9), 128.7 (d, J}_{\text{CP}} = 0.7 \text{ Hz, C7), 127.4 (C8), 114.2 (d, J}_{\text{CP}} = 190.8 \text{ Hz, C3), 61.7 (d, J}_{\text{CS}} = 5.6 \text{ Hz, C2), 19.2 (d, J}_{\text{CP}} = 6.9 \text{ Hz, C5), 16.5 (d, J}_{\text{CS}} = 6.4 \text{ Hz, C1) ppm; } \]
\[ ^31P NMR \text{ (202 MHz, CDCl}_3) : \delta = 17.61 \text{ ppm; IR (ATR): } \tilde{\nu} = 3477 \text{ (w), 2983 (w), 2906 (w), 1610 (m), 1592 (w), 1489 (m), 1443 (w), 1392 (w), 1321 (w), 1246 (s), 1163 (w), 1094 (m), 1051 (s), 1025 (s), 958 (s), 812 (s), 767 (m), 742 (w), 662 (m) cm}^{-1}; \]
\[ \text{HR-ESI-MS: m/z: 311.0576 ([M+Na]², calcd. for C}_{13}H_{18}ClNaO}_2P^+: 311.0576); \]
\[ \text{analytical data in agreement with literature.}^{[1]} \]
Diethyl (E)-2-([4-bromophenyl])prop-1-en-1-ylphosphonate (E-4):

Prepared according to **general procedure A** from 4'-bromoacetophenone (298 mg, 1.51 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.29 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.67 eq.) in 64 h. Purification by column chromatography (SiO$_2$, n-pentane/ethyl acetate: 4/1) yielded E-vinylphosphonate **E-4** as yellow oil (186 mg, 0.56 mmol, 37%).

R$_f$ = 0.54 (SiO$_2$, ethyl acetate); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.49 - 7.45 (m, 2H, H7), 7.34 - 7.30 (m, 2H, H8), 5.87 (dq, $J$ = 15.9, 1.1 Hz, 1H, H3), 4.11 (dq, $J$ = 7.8, 7.1 Hz, 4H, H2), 2.45 (dd, $J$ = 3.3, 1.1 Hz, 3H, H5), 1.34 (td, $J$ = 7.1, 0.5 Hz, 6H, H1) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ = 156.8 (d, $J_{CP} = 8.2$ Hz, C4), 140.8 (d, $J_{CP} = 24.1$ Hz, C6), 131.7 (q, $J_{CP} = 0.7$ Hz, C7), 127.7 (C8), 123.5 (C9), 114.3 (d, $J_{CP} = 190.7$ Hz, C3), 61.7 (d, $J_{CP} = 5.6$ Hz, C2), 19.2 (d, $J_{CP} = 7.0$ Hz, C5), 16.5 (d, $J_{CP} = 6.3$ Hz, C1) ppm; $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ = 17.57 (dddp, $J$ = 15.8, 11.7, 8.0, 4.2 Hz) ppm; IR (ATR): $\tilde{\nu}$ = 3456 (w), 2982 (w), 2908 (w), 1609 (m), 1585 (w), 1486 (m), 1442 (w), 1394 (m), 1320 (w), 1246 (s), 1163 (w), 1097 (m), 1050 (s), 1024 (s), 959 (s), 808 (s), 761 (m) cm$^{-1}$; HR-ESI-MS: m/z: 355.0086 ([M+Na]$^+$, calcd. for C$_{13}$H$_{18}$BrNaO$_4$P$: 355.0069), 689.0243 ([M+Na]$^+$, calcd. for C$_{36}$H$_{50}$BrNaO$_{3}$P$: 689.0226); analytical data in agreement with literature.$^{[1]}$

Diethyl (E)-2-([4-(trifluoromethyl)phenyl])prop-1-en-1-ylphosphonate (E-5):

Prepared according to **general procedure A** from 4'-trifluoromethylacetophenone (282 mg, 1.50 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.30 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.67 eq.) in 67 h. Purification by column chromatography (SiO$_2$, cyclohexane/ethyl acetate: 7/3) yielded E-vinylphosphonate **E-5** as yellow oil (119 mg, 0.37 mmol, 25%).

R$_f$ = 0.53 (SiO$_2$, ethyl acetate); $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.61 (d, $J$ = 8.7 Hz, 2H, H8), 7.54 (d, $J$ = 8.2 Hz, 2H, H7), 5.92 (dq, $J$ = 15.7, 1.1 Hz, 1H, H3), 4.13 (dq, $J$ = 8.1, 7.0 Hz, 4H, H2), 2.50 (dd, $J$ = 3.3, 1.1 Hz, 3H, H5), 1.35 (t, $J$ = 7.1 Hz, 6H, H1) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ = 156.6 (d, $J_{CP} = 8.2$ Hz, C4), 145.5 (d, $J_{CP} = 24.0$ C6), 131.1 (q, $J_{CS} = 32.7$ Hz, C9), 126.5 (C7), 125.6 (q, $J_{CS} = 3.8$ Hz, C8), 124.0 (q, $J_{CS} = 272.1$ Hz, C10), 116.1 (d, $J_{CP} = 190.3$ Hz, C3), 61.8 (d, $J_{CP} = 5.6$ Hz, C2), 19.4 (d, $J_{CP} = 6.9$ Hz, C5), 16.5 (d, $J_{CP} = 6.4$ Hz, C1) ppm; $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ = -62.78 ppm; $^{31}$P NMR (202 MHz, CDCl$_3$):
\[ \delta = 16.95 \ (ddtq, J = 15.8, 11.7, 7.9, 4.2, 3.7 \text{ Hz}) \text{ ppm}; \text{IR (ATR): } \tilde{\nu} = 3506 \ (w), 2983 \ (w), 2917 \ (w), 2850 \ (w), 1615 \ (w), 1572 \ (w), 1445 \ (w), 1409 \ (w), 1393 \ (w), 1322 \ (s), 1248 \ (m), 1166 \ (m), 1119 \ (s), 1080 \ (w), 1052 \ (s), 1025 \ (s), 959 \ (s), 859 \ (w), 825 \ (m), 732 \ (w) \text{ cm}^{-1}; \text{HR-ESI-MS: } m/z: 345.0843 ([M+Na]^+, \text{calcd. for C}_{14}H_{18}F_{3}NaO_{3}P^+: 345.0838), 667.1794 ([M+Na]^+, \text{calld. for C}_{28}H_{36}F_{6}NaO_{6}P_{2}^+: 667.1784); \text{analytical data in agreement with literature.}\]

**Diethyl (E)-(2-(4-tolyl)prop-1-en-1-yl)phosphonate (E-6):**

Prepared according to **general procedure A** from 4'-methylacetophenone (0.20 mL, 1.49 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.31 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.68 eq.) in 64 h. Purification by column chromatography (SiO\textsubscript{2}, n-pentane/ethyl acetate: 85/15) yielded E-vinylphosphonate **E-6** as yellow oil (211 mg, 0.79 mmol, 53%).

\[ R_t = 0.32 \ (SiO_2, \text{n-pentane/ethyl acetate: 1/1}); ^1\text{H NMR} \ (500 MHz, CDCl_3): \delta = 7.39 - 7.35 \ (m, 2H, H8), 7.18 - 7.14 \ (m, 2H, H7), 5.87 \ (dq, J = 16.6, 0.9 Hz, 1H, H3), 4.11 \ (dq, J = 7.9, 7.1 Hz, 4H, H2), 2.47 \ (dd, J = 3.2, 1.0 Hz, 3H, H5), 2.35 \ (s, 3H, H10), 1.36 - 1.32 \ (m, 6H, H1) \text{ ppm; } ^{13}\text{C NMR} \ (126 MHz, CDCl_3): \delta = 158.1 \ (d, J_{CP} = 8.1 \text{ Hz}, C4), 139.4 \ (C9), 138.9 \ (d, J_{CP} = 23.7 \text{ Hz}, C6), 129.3 \ (d, J_{CP} = 0.8 \text{ Hz}, C7), 126.0 \ (C8), 112.5 \ (d, J_{CP} = 190.6 \text{ Hz}, C3), 61.5 \ (d, J_{CP} = 5.6 \text{ Hz}, C2), 21.3 \ (C10), 19.3 \ (d, J_{CP} = 7.1 \text{ Hz}, C5), 16.5 \ (d, J_{CP} = 6.5 \text{ Hz}, C1) \text{ ppm; } ^{31}\text{P NMR} \ (202 MHz, CDCl_3): \delta = 18.55 \ (ddtq, J = 15.8, 11.6, 7.9, 3.8 \text{ Hz}) \text{ ppm; IR (ATR): } \tilde{\nu} = 3448 \ (w), 2981 \ (w), 2920 \ (w), 1606 \ (m), 1567 \ (w), 1513 \ (w), 1443 \ (w), 1391 \ (w), 1322 \ (w), 1246 \ (s), 1164 \ (w), 1097 \ (w), 1051 \ (s), 1025 \ (s), 957 \ (s), 831 \ (m), 806 \ (s), 746 \ (w) \text{ cm}^{-1}; \text{HR-ESI-MS: } m/z: 291.1121 ([M+Na]^+, \text{calcd. for C}_{14}H_{17}NaO_{2}P^+: 291.1121), 559.2341 ([M+Na]^+, \text{calld. for C}_{28}H_{36}NaO_{6}P_{2}^+: 559.2349); \text{analytical data in agreement with literature.}\]

**Diethyl (E)-(2-(4-(tert-butyl)phenyl)prop-1-en-1-yl)phosphonate (E-7):**

Prepared according to **general procedure A** from 4'-tert-butylacetophenone (0.27 mL, 1.48 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.32 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.69 eq.) in 67 h. Purification by column chromatography (SiO\textsubscript{2}, cyclohexane/ethyl acetate: 9/1) yielded E-vinylphosphonate **E-7** as yellow oil (151 mg, 0.49 mmol, 33%).

\[ R_t = 0.63 \ (SiO_2, ethyl acetate); ^1\text{H NMR} \ (500 MHz, CDCl_3): \delta = 7.44 - 7.41 \ (m, 2H, H8), 7.40 - 7.34 \ (m, 2H, H7), 5.90 \ (dq, J = 16.6, 1.1 Hz, 1H, H3), 4.11 \ (dq, J = 8.0, 7.1 Hz, 4H, H2), 2.49 \ (dd, J = 3.3, 1.0 Hz, 3H, H5), 1.37 - 1.30 \ (m, 15H, H1, H11) \text{ ppm; } ^{13}\text{C NMR} \ (126 MHz, CDCl_3): \delta = 158.0 \ (d, J_{CP} = 8.0 \text{ Hz}, C4), 152.6 \text{ ppm.}\]
Diethyl (E)-(2-(3-bromophenyl)prop-1-en-1-yl)phosphonate (E-8):

Prepared according to general procedure A from 3’-bromoacetophenone (0.46 mL, 3.47 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (1.04 mL, 4.53 mmol, 1.31 eq.) with sodium hydride (60% in mineral oil, 0.10 mmol, 1.00 eq.) and tetramethyl methylene diphosphonate (0.45 mL, 2.04 mmol, 1.00 eq.) in cyclohexane/ethyl acetate: 9/1 yielded E-vinylphosphonate E-8 as yellow oil (678 mg, 2.04 mmol, 59%).

Rt = 0.34 (SiO2, ethyl acetate); 1H NMR (600 MHz, CDCl3): δ = 7.59 (t, J = 1.9 Hz, 1H, H7), 7.48 (ddd, J = 7.9, 1.9, 1.0 Hz, 1H, H9), 7.38 (ddd, J = 7.8, 1.8, 1.0 Hz, 1H, H11), 7.24 (t, J = 7.9 Hz, 1H, H10), 5.88 (dt, J = 15.9, 1.1 Hz, 1H, H3), 4.13 (p, J = 7.1 Hz, 4H, H2), 2.47 (dd, J = 3.3, 1.0 Hz, 3H, H5), 1.36 (t, J = 7.0 Hz, 6H, H1) ppm; 13C NMR (151 MHz, CDCl3): δ = 156.6 (d, JCP = 8.3 Hz, C4), 144.1 (d, JCP = 23.9 Hz, C6), 132.1 (C9), 130.2 (C10), 129.3 (C7), 124.8 (C11), 122.8 (d, JCP = 1.1 Hz, C8), 115.1 (d, JCP = 190.3 Hz, C3), 61.8 (d, JCP = 5.6 Hz, C2), 19.4 (d, JCP = 6.9 Hz, C5), 16.5 (d, JCP = 6.5 Hz, C1) ppm; 31P NMR (243 MHz, CDCl3): δ = 17.25 (ddq, J = 15.8, 8.0, 3.9 Hz) ppm; IR (ATR): ν = 3475 (b), 2982 (w), 2929 (w), 1711 (w), 1611 (w), 1591 (w), 1558 (w), 1477 (w), 1443 (w), 1392 (w), 1368 (w), 1319 (w), 1299 (w), 1243 (m), 1163 (w), 1097 (w), 1048 (s), 1019 (s), 954 (s), 884 (w), 931 (s), 779 (s), 746 (m), 688 (m), 669 (m) cm⁻¹; HR-ESI-MS: m/z: 355.0077 ([M+Na]⁺, calcd. for C13H13BrNaO3P⁺: 355.0069), 689.0251 ([M₂+Na]⁺, cald. for C26H36Br2NaO6P₂⁺: 689.0226).

Dimethyl (E)-(2-phenylprop-1-en-1-yl)phosphonate (E-9):

Prepared according to general procedure A from acetophenone (0.17 mL, 1.46 mmol, 1.00 eq.) and tetramethyl methylene-diphosphonate (0.45 g, 1.94 mmol, 1.33 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.71 eq.) in 68 h. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 3/2) yielded E-vinylphosphonate E-9 as orange oil (136 mg, 0.60 mmol, 41%).
Diisopropyl (E)-(2-phenylprop-1-en-1-yl)phosphonate (E-10):

Prepared according to general procedure A from acetophenone (0.17 mL, 1.46 mmol, 1.00 eq.) and tetraisopropylmethylenediphosphonate (0.62 mL, 1.95 mmol, 1.34 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.71 eq.) in 66 h. Purification by column chromatography (SiO$_2$, cyclohexane/ethyl acetate: 7/3) yielded E-vinylphosphonate E-10 as orange oil (154 mg, 0.55 mmol, 38%).

R$_f$ = 0.27 (SiO$_2$, cyclohexane/ethyl acetate: 1/1); $^1$H NMR (500 MHz, CDCl$_3$): δ = 7.47 - 7.43 (m, 2H, H6), 7.38 - 7.32 (m, 3H, H8, H9), 5.91 (dq, J = 16.4, 1.0 Hz, 1H, H3), 4.71 (dhept, J = 8.2, 6.2 Hz, 2H, H2), 2.49 (dd, J = 3.3, 1.1 Hz, 3H, H5), 1.34 (dd, J = 15.2, 6.2 Hz, 12H, H1) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): δ = 157.1 (d, J$_{CP}$ = 8.0 Hz, C4), 142.2 (d, J$_{CP}$ = 23.7 Hz, C6), 129.1 (C9), 128.6 (d, J$_{CP}$ = 0.7 Hz, C7), 126.1 (C8), 115.5 (d, J$_{CP}$ = 190.7 Hz, C3), 70.2 (d, J$_{CP}$ = 5.7 Hz, C2), 24.2 (dd, J$_{CP}$ = 10.9, 4.3 Hz, C1), 19.3 (d, J$_{CP}$ = 6.9 Hz, C5) ppm; $^{31}$P NMR (202 MHz, CDCl$_3$): δ = 15.93 (dt, J = 16.3, 8.2, 3.8 Hz) ppm; IR (ATR): ̃v = 3456 (w), 2978 (w), 2933 (w), 1607 (w), 1575 (w), 1495 (w), 1445 (w), 1385 (w), 1374 (w), 1324 (w), 1245 (m), 1178 (w), 1110 (m), 976 (s), 886 (m), 814 (m), 753 (m), 695 (m) cm$^{-1}$; HR-ESI-MS: m/z: 305.1288 ([M+Na]$^+$, calcd. for C$_{15}$H$_{13}$NaO$_3$P$^+$: 305.1277), 587.2675 ([M$_2$+Na]$^+$, calcd. for C$_{30}$H$_{30}$NaO$_6$P$_2$$^+$: 587.2662); analytical data in agreement with literature.[2]

Diethyl (E)-(2-(naphthalen-2-yl)prop-1-en-1-yl)phosphonate (E-11):

Prepared according to general procedure A from 2-acetonaphtone (255 mg, 1.50 mmol, 1.00 eq.) and tetraethylmethylenediphosphonate (0.48 mL, 1.95 mmol, 1.30 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.67 eq.) in...
67 h. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 4/1) yielded E-vinylphosphonate **E-11** as orange oil (153 mg, 0.50 mmol, 33%).

Rᵣ = 0.67 (SiO₂, ethyl acetate); **¹H NMR** (600 MHz, CDCl₃): δ = 7.93 (d, J = 1.6 Hz, 1H, H7), 7.85 (d, J = 5.6, 4.1 Hz, 1H, H8), 7.84 - 7.81 (m, 2H, H11, H12), 7.60 (dd, J = 8.6, 1.9 Hz, 1H, H13), 7.52 - 7.47 (m, 2H, H9, H10), 6.06 (dd, J = 16.3, 1.0 Hz, 1H, H3), 4.16 (p, J = 7.1 Hz, 4H, H2), 2.62 (dd, J = 3.2, 1.0 Hz, 3H, H5), 1.38 (t, J = 7.1 Hz, 6H, H1) ppm; **¹³C NMR** (151 MHz, CDCl₃): δ = 157.9 (d, Jₑ₋ₑ = 8.1 Hz, C4), 139.0 (d, Jₑ₋ₑ = 23.7 Hz, C6), 133.7 (C15), 133.2 (C14), 128.7 (C8), 128.3 (C12), 127.7 (C11), 126.9 (C10), 126.7 (C9), 125.7 (C7), 123.7 (C13), 114.1 (d, Jₑ₋ₑ = 190.6 Hz, C3), 61.7 (d, Jₑ₋ₑ = 5.6 Hz, C2), 19.4 (d, Jₑ₋ₑ = 7.0 Hz, C5), 16.6 (d, Jₑ₋ₑ = 6.6 Hz, C1) ppm; **³¹P NMR** (243 MHz, CDCl₃): δ = 18.25 ppm; **IR (ATR):** ν = 3477 (w), 3056 (w), 2981 (w), 2926 (w), 2852 (w), 1607 (m), 1574 (w), 1505 (w), 1442 (w), 1389 (w), 1367 (w), 1349 (w), 1316 (w), 1240 (s), 1163 (w), 1131 (w), 1097 (w), 1050 (s), 1024 (s), 957 (s), 882 (m), 813 (s), 748 (m) cm⁻¹; **HR-ESI-MS:** m/z: 327.1117 ([M⁺Na⁺], calcd. for C₁₇H₁₃NaO₃P⁺: 327.1121), 631.2350 ([M₂⁺Na⁺⁺], calcd. for C₃₄H₃₂Na₈O₆P₂⁺: 631.2349); analytical data in agreement with literature.[¹]

**Diethyl (E)-(2-(4-methoxyphenyl)prop-1-en-1-yl)phosphonate (E-12):**

![Diethyl (E)-(2-(4-methoxyphenyl)prop-1-en-1-yl)phosphonate (E-12)](image)

Prepared according to **general procedure A** from 4'-methoxyacetophenone (225 mg, 1.50 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.30 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.67 eq.) in 67 h. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 4/1) yielded E-vinylphosphonate **E-12** as orange oil (174 mg, 0.61 mmol, 41%).

Rᵣ = 0.55 (SiO₂, ethyl acetate); **¹H NMR** (500 MHz, CDCl₃): δ = 7.44 - 7.40 (m, 2H, H7), 6.88 - 6.84 (m, 2H, H8), 5.83 (dd, J = 16.4, 1.0 Hz, 1H, H3), 4.10 (dq, J = 7.9, 7.1 Hz, 4H, H2), 3.80 (s, 3H, H10), 2.46 (dd, J = 3.2, 0.9 Hz, 3H, H5), 1.33 (t, J = 7.1 Hz, 6H, H1) ppm; **¹³C NMR** (126 MHz, CDCl₃): δ = 160.6 (C9), 157.4 (d, Jₑ₋ₑ = 8.2 Hz, C4), 133.9 (d, Jₑ₋ₑ = 23.9 Hz, C6), 127.4 (C7), 113.9 (C8), 111.3 (d, Jₑ₋ₑ = 191.7 Hz, C3), 61.5 (d, Jₑ₋ₑ = 5.5 Hz, C2), 55.4, 19.1 (d, Jₑ₋ₑ = 7.1 Hz, C5), 16.5 (d, Jₑ₋ₑ = 6.4 Hz, C1) ppm; **³¹P NMR** (202 MHz, CDCl₃): δ = 18.88 ppm; **IR (ATR):** ν = 3447 (w), 2981 (w), 2907 (w), 2840 (w), 1602 (s), 1571 (w), 1513 (s), 1442 (m), 1418 (w), 1391 (w), 1327 (w), 1291 (m), 1245 (s), 1182 (m), 1164 (m), 1097 (w), 1050 (s), 1025 (s), 957 (s), 822 (s), 805 (s), 744 (w), 714 (w) cm⁻¹; **HR-ESI-MS:** m/z: 307.1079 ([M⁺Na⁺], calcd. for C₁₄H₁₂NaO₃P⁺: 307.1070), 591.2266 ([M₂⁺Na⁺⁺], calcd. for C₂₈H₃₂Na₈O₆P₂⁺: 591.2247); analytical data in agreement with literature.[¹]
Diethyl (E)-styrylphosphonate (E-13):

Prepared according to general procedure A from benzaldehyde (0.15 mL, 1.50 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 2.50 mmol, 1.67 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 1.95 mmol, 1.30 eq.) in 63 h. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 1/9) yielded E-vinylphosphonate E-13 as yellow oil (288 mg, 1.20 mmol, 80%).

Rₚ = 0.59 (SiO₂, ethyl acetate); ¹H NMR (500 MHz, CDCl₃): δ = 7.55 - 7.45 (m, 3H, H4, H6), 7.41 - 7.34 (m, 3H, H7, H8), 6.25 (t, J = 17.6 Hz, 1H, H3), 4.18 - 4.07 (m, 4H, H2), 1.34 (td, J = 7.1, 0.6 Hz, 6H, H1) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 148.8 (d, Jₐₙ = 6.7 Hz, C4), 135.0 (d, Jₐₙ = 23.2 Hz, C5), 130.3 (C8), 129.0 (d, Jₐₙ = 0.9 Hz, C7), 127.8 (d, Jₐₙ = 0.9 Hz, C6), 114.1 (dd, Jₐₙ = 191.2, 1.0 Hz, C3), 61.9 (d, Jₐₙ = 5.5 Hz, C2), 16.5 (d, Jₐₙ = 6.4 Hz, C1) ppm; ³¹P NMR (202 MHz, CDCl₃): δ = 19.46 (ddt, J = 22.6, 17.7, 8.1 Hz) ppm; IR (ATR): ν = 3476 (w), 1982 (w), 2852 (w), 1616 (m), 1577 (w), 1449 (w), 1392 (w), 1243 (m), 1197 (w), 1163 (w), 1097 (w), 1051 (s), 1023 (s), 960 (s), 857 (m), 828 (m), 790 (m), 743 (m), 691 (m) cm⁻¹; HR-ESI-MS: m/z: 263.0814 [(M+Na)⁺, calcd. for C₁₂H₁₁NaO₃P⁺: 263.0808], 503.1729 [(M₂+Na)²⁺, calcd. for C₂₄H₂₃NaO₆P₂⁺: 503.1723]; analytical data in agreement with literature.[¹]

Diethyl (E)-(2-phenylbut-1-en-1-yl)phosphonate (E-14):

Prepared according to general procedure A from propiophenone (0.20 mL, 1.50 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.30 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 1.67 mmol, 1.67 eq.) in 66 h. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 6/4) yielded E-vinylphosphonate E-14 as yellow oil (158 mg, 0.59 mmol, 39%).

Rₚ = 0.50 (SiO₂, ethyl acetate); ¹H NMR (500 MHz, CDCl₃): δ = 7.42 - 7.38 (m, 2H, H8), 7.38 - 7.33 (m, 3H, H9, H10), 5.74 (d, J = 17.2 Hz, 1H, H3), 4.12 (p, J = 7.1 Hz, 4H, H2), 3.00 (qd, J = 7.4, 2.1 Hz, 2H, H5), 1.34 (t, J = 7.1 Hz, 6H, H1), 1.02 (t, J = 7.5 Hz, 3H, H6) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 165.0 (d, Jₐₙ = 8.7 Hz, C4), 140.8 (d, Jₐₙ = 23.8 Hz, C7), 129.0 (C9/C10), 128.6 (C9/C10), 126.65 (C8), 113.4 (d, Jₐₙ = 189.8 Hz, C3), 61.6 (d, Jₐₙ = 5.6 Hz, C2), 26.0 (d, Jₐₙ = 6.8 Hz, C5), 16.5 (d, Jₐₙ = 6.5 Hz, C1), 13.6 (d, Jₐₙ = 2.3 Hz, C6) ppm; ³¹P NMR (202 MHz, CDCl₃): δ = 17.86 (dp, Jₐₙ = 15.8, 7.7 Hz) ppm; IR (ATR): ν = 3503 (w), 2978 (w), 2934 (w), 1606 (m), 1574 (w), 1495 (w), 1444 (w), 1391 (w), 1306 (w), 1241 (s), 1163 (w), 1097 (w), 1050 (s), 1024 (s), 958 (s), 835 (m), 788 (m), 760 (m), 698 (m) cm⁻¹; HR-ESI-MS: m/z: 291.1128 [(M+Na)⁺, calcd. for C₁₄H₁₃NaO₃P⁺: 291.1121], 559.2362 [(M₂+Na)²⁺, calcd. for C₂₄H₂₄NaO₆P₂⁺: 559.2349]; analytical data in agreement with literature.[¹]
Diethyl (E)-(2-(2-tolyl)prop-1-en-1-yl)phosphonate (E-15):

Prepared according to general procedure A from 2'-methylacetophenone (1.30 mL, 9.88 mmol, 3.06 eq.) and tetraethyl methylenediphosphonate (0.80 mL, 3.23 mmol, 1.00 eq.) with sodium hydride (60% in mineral oil, 0.17 g, 4.25 mmol, 1.32 eq.) in tetrahydrofuran (20 mL) in 67 h. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 9/1) yielded E-vinylphosphonate E-15 as red oil (433 mg, 1.61 mmol, 50%).

Rₚ = 0.65 (SiO₂, ethyl acetate); ¹H NMR (600 MHz, CDCl₃): δ = 7.21 - 7.13 (m, 3H, H8, H9, H10), 7.06 (dd, J = 7.3, 1.4 Hz, 1H, H11), 5.50 (dq, J = 18.7, 1.2 Hz, 1H, H3), 4.13 (ddq, J = 7.8, 7.1, 0.7 Hz, 4H, H2), 2.37 (dd, J = 3.3, 1.2 Hz, 3H, H5), 2.29 (s, 3H, H12), 1.35 (td, J = 7.0, 0.4 Hz, 6H, H1) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 161.3 (d, JCP = 6.8 Hz, C4), 144.3 (d, JCP = 23.4 Hz, C6), 133.5 (d, JCP = 0.9 Hz, C7), 130.5 (C8), 127.8 (C9), 126.8 (d, JCP = 1.4 Hz, C11), 125.9 (C10), 116.4 (d, JCP = 184.1 Hz, C3), 61.5 (d, JCP = 5.5 Hz, C2), 19.7 (C12), 16.5 (d, JCP = 6.4 Hz, C1) ppm; ³¹P NMR (243 MHz, CDCl₃): δ = 17.00 ppm; IR (ATR): v = 3456 (w), 2981 (w), 2910 (w), 1487 (w), 1443 (w), 1391 (w), 1313 (w), 1247 (s), 1163 (w), 1097 (w), 1051 (s), 1025 (s), 957 (s), 833 (m), 794 (m), 749 (m) cm⁻¹; HR-ESI-MS: m/z: 291.1147 ([M+Na]⁺, calcd. for C₁₄H₁₂NaO₂P⁺: 291.1121), 559.2362 ([M₂+Na]⁺, calcd. for C₂₉H₂₉NaO₄P₂⁺: 559.2349); analytical data in agreement with literature.[1]

Diethyl (E)-(2-(2-fluorophenyl)prop-1-en-1-yl)phosphonate (E-16):

Prepared according to general procedure A from 2'-fluoroacetophenone (0.18 mL, 1.48 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.32 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.69 eq.) in 68 h. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 4/1) yielded E-vinylphosphonate E-16 as orange oil (229 mg, 0.84 mmol, 57%).

Rₚ = 0.51 (SiO₂, ethyl acetate); ¹H NMR (600 MHz, CDCl₃): δ = 7.31 - 7.24 (m, 2H, H9, H11), 7.11 (td, J = 7.6, 1.2 Hz, 1H, H10), 7.05 (ddd, J = 11.0, 8.2, 1.1 Hz, 1H, H8), 5.77 (dd, J = 17.0, 1.2 Hz, 1H, H3), 4.15 - 4.10 (m, 4H, H2), 2.46 (dt, J = 3.3, 1.4 Hz, 3H, H5), 1.35 (t, J = 7.1 Hz, 6H, H1) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 159.4 (d, JCP = 248.6 Hz, C7), 154.9 (dd, JCP = 8.6, JCP = 1.1 Hz, C4), 131.1 (dd, JCP = 24.5, JCP = 13.3 Hz, C6), 130.2 (d, JCP = 8.5 Hz, C9), 129.1 (dd, JCP = 3.7, JCP = 1.1 Hz, C11), 124.3 (d, JCP = 3.6 Hz, C10), 117.9 (dd, JCP = 186.7, JCP = 2.9 Hz, C3), 116.2 (d, JCP = 22.6 Hz, C8), 61.7 (d, JCP = 5.6 Hz, C2), 20.8 (dd, JCP = 6.9, JCP = 3.6 Hz, C5), 16.5 (d, JCP = 6.4 Hz, C1) ppm; ¹⁹F NMR (564 MHz, CDCl₃): δ = -114.47 (dddd, J = 12.9, 7.2, 3.5, 1.8 Hz) ppm; ³¹P NMR (243 MHz, CDCl₃): δ = 16.69 (dddd, J = 15.9, 11.7, 7.9, 4.2 Hz) ppm; IR (ATR): v = 3457 (w), 2982 (w), 2908 (w), 1615 (w), 1575 (w), 1488 (m), 1446 (m), 1392 (w), 1323 (w), 1247 (s), 1206 (w), 1163 (w), 1112 (w), 1098 (w), 1051 (s), 1024 (s), 960 (s),
836 (m), 805 (m), 759 (m) cm⁻¹; **HR-ESI-MS**: m/z: 295.0869 ([M+Na⁺], calcd. for C₁₃H₁₃FNaO₃P⁺: 295.0870), 567.1853 ([M₂+Na⁺], calcd. for C₂₆H₃₆F₃NaO₆P₂⁺: 567.1847).

**Diethyl (E)-(2-(2-chlorophenyl)prop-1-en-1-yl)phosphonate (E-17):**

Prepared according to **general procedure A** from 2'-chloroacetophenone (0.20 mL, 1.54 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.27 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.62 eq.) in 65 h. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 7/3) yielded E-vinylphosphonate **E-17** as orange oil (258 mg, 0.89 mmol, 58%).

Rᵣ = 0.46 (SiO₂, ethyl acetate); **¹H NMR** (600 MHz, CDCl₃): δ = 7.38 - 7.34 (m, 1H, H8), 7.25 - 7.21 (m, 2H, H9, H10), 7.18 - 7.14 (m, 1H, H11), 5.58 (dq, J = 17.6, 1.2 Hz, 1H, H3), 4.16 - 4.10 (m, 4H, H2), 2.42 (dd, J = 3.4, 1.2 Hz, 3H, H5), 1.35 (td, J = 7.1, 0.5 Hz, 6H, H1) ppm; **¹³C NMR** (151 MHz, CDCl₃): δ = 158.6 (d, Jₑₜ = 8.0 Hz, C4), 143.1 (d, Jₑₜ = 24.5 Hz, C6), 130.9 (d, Jₑₜ = 1.4 Hz, C7), 129.9 (C8), 129.2 (C9), 128.7 (d, Jₑₜ = 1.7 Hz, C11), 127.0 (C10), 118.0 (d, Jₑₜ = 183.8 Hz, C3), 61.7 (d, Jₑₜ = 5.5 Hz, C2), 21.4 (d, Jₑₜ = 6.5 Hz, C5), 16.5 (d, Jₑₜ = 6.4 Hz, C1) ppm; **¹⁹F NMR** (243 MHz, CDCl₃): δ = 16.31 (ddqt, J = 15.2, 11.4, 7.5, 3.4 Hz) ppm; **IR (ATR):** ν = 3467 (w), 2982 (w), 2907 (w), 1624 (w), 1590 (w), 1565 (w), 1471 (w), 1429 (w), 1392 (w), 1316 (w), 1246 (s), 1163 (w), 1129 (w), 1096 (w), 1023 (s), 959 (s), 837 (m), 822 (m), 793 (w), 756 (m), 682 (w) cm⁻¹; **HR-ESI-MS**: m/z: 311.0588 ([M+Na⁺], calcd. for C₁₃H₁₃ClNaO₃P⁺: 311.0574), 599.1261 ([M₂+Na⁺], calcd. for C₂₆H₃₆Cl₂NaO₆P₂⁺: 599.1256).

**Diethyl (E)-(2-(2-bromophenyl)prop-1-en-1-yl)phosphonate (E-18):**

Prepared according to **general procedure A** from 2'-bromoacetophenone (0.20 mL, 1.48 mmol, 1.00 eq.) and tetraethyl methylenediphosphonate (0.48 mL, 1.95 mmol, 1.32 eq.) with sodium hydride (60% in mineral oil, 0.10 g, 2.50 mmol, 1.69 eq.) in 65 h. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 7/3) yielded E-vinylphosphonate **E-18** as orange oil (309 mg, 0.93 mmol, 63%).

Rᵣ = 0.46 (SiO₂, ethyl acetate); **¹H NMR** (600 MHz, CDCl₃): δ = 7.56 - 7.54 (m, 1H, H8), 7.28 (td, J = 7.5, 1.2 Hz, 1H, H10), 7.17 - 7.13 (m, 2H, H9, H11), 5.55 (dq, J = 17.6, 1.2 Hz, 1H, H3), 4.14 (dq, J = 8.0, 7.1 Hz, 4H, H2), 2.41 (dd, J = 3.4, 1.3 Hz, 3H, H5), 1.36 (td, J = 7.1, 0.5 Hz, 6H, H1) ppm; **¹³C NMR** (151 MHz, CDCl₃): δ = 160.0 (d, Jₑₜ = 7.9 Hz, C4), 145.1 (d, Jₑₜ = 24.6 Hz, C6), 133.1 (C8), 129.3 (C9), 128.6 (d, Jₑₜ = 1.7 Hz, C11), 127.6 (C10), 120.3 (d, Jₑₜ = 1.6 Hz, C7), 117.9 (d, Jₑₜ = 183.4 Hz, C3), 61.7 (d, Jₑₜ = 5.5 Hz, C2), 21.6 (d, Jₑₜ = 6.3 Hz, C5), 16.5 (d, Jₑₜ = 6.5 Hz, C1) ppm; **¹⁹F NMR** (243 MHz, CDCl₃):
δ = 16.28 (dd, J = 11.6, 6.8 Hz) ppm; IR (ATR): ν = 3475 (w), 2982 (w), 1624 (w),
1561 (w), 1467 (w), 1425 (w), 1392 (w), 1315 (w), 1246 (s), 1163 (w), 1097 (w), 1051 (s), 1023 (s), 958 (s), 837 (m), 792 (w), 754 (s), 661 (w)

General procedure B for the isomerisation of E-vinylphosphonates

The specified E-vinylphosphonate (0.10 mmol, 1.00 eq.) and anthracene (0.09 mg, 0.005 mmol,
5 mol%) were dissolved in acetonitrile (1.5 mL) and the solution was stirred under UV light irradiation
at 365 nm at ambient temperature for 18 h. After removal of the solvent, E- and Z-isomer were isolated
by column chromatography. Yields were determined by mass recovery; Z:E ratios were determined by
integration of peaks in the 31P NMR spectrum and confirmed by integration the olefinic proton peaks
in the 1H NMR spectrum of both isomers.

Diethyl (Z)-(2-phenyl-1-en-1-yl)phosphonate (Z-1):

According to general procedure B, E-1 (25.0 mg, 0.10 mmol) was converted to
Z-1. Purification by column chromatography (SiO2, ethyl acetate) yielded a
yellow oil (24.9 mg, quant., Z-1: E-1 = 92:8).

A representative example of the reaction was repeated on a 1 mmol scale:

E-vinylphosphonate 1 (254.6 mg, 1.00 mmol, 1.00 eq.) and anthracene (8.9 mg, 0.05 mmol,
5 mol%) were dissolved in acetonitrile (10 mL) and the solution was stirred under UV light irradiation
at 365 nm at ambient temperature for 18 h. The solvent was removed in vacuo and purification by
column chromatography (SiO2, ethyl acetate) yielded a yellow oil (2246.5 mg, 97%, Z-1: E-1 = 83:17).
Diethyl (Z)-(2-(4-fluorophenyl)prop-1-en-1-yl)phosphonate (Z-2):

According to general procedure B, E-2 (27.2 mg, 0.10 mmol) was converted to Z-2. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 1/9) yielded a yellow oil (25.6 mg, 94%, Z-2: E-2 = 92:8).

Rᵣ = 0.43 (SiO₂, ethyl acetate); ¹H NMR (500 MHz, CDCl₃): δ = 7.38 (dd, J = 8.3, 5.3, 2.6 Hz, H7), 7.06 - 6.99 (m, 2H, H8), 5.71 (dq, J = 16.9, 1.3 Hz, 1H, H3), 3.90 - 3.75 (m, 4H, H2), 2.23 - 2.18 (m, 3H, H5), 1.13 - 1.07 (m, 6H, H1) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 162.8 (d, Jᵥ = 124.7 Hz, C9), 157.9 (d, Jᵥ = 4.4 Hz, C4), 136.5 (dd, Jᵥ = 7.6, Jᵥ = 3.4 Hz, C6), 129.4 (dd, Jᵥ = 8.2, Jᵥ = 1.8 Hz, C7), 115.3 (d, Jᵥ = 191.2 Hz, C3), 115.0 (d, Jᵥ = 21.5 Hz, C8), 61.5 (dd, Jᵥ = 6.0 Hz, C2), 28.5 (d, Jᵥ = 22.9 Hz, C5), 16.2 (d, Jᵥ = 6.7 Hz, C1) ppm; ¹⁹F NMR (370 MHz, CDCl₃): δ = -113.40 (tt, J = 8.7, 5.4 Hz) ppm; ³¹P NMR (202 MHz, CDCl₃): δ = 15.86 (dp, J = 15.6, 7.7 Hz) ppm; IR (ATR): ν = 3457 (w), 2982 (w), 2908 (w), 1602 (m), 1508 (s), 1479 (w), 1441 (w), 1392 (w), 1375 (w), 1345 (w), 1227 (s), 1192 (w), 1162 (m), 1098 (w), 1051 (s), 1026 (s), 958 (s), 842 (s), 818 (m), 785 (m), 741 (w), 730 (w), 666 (m) cm⁻¹; HR-ESI-MS: m/z: 295.0878 ([M+Na]+), calcd. for C₁₃H₁₃FNaO₃P⁺: 295.0870, 567.1855 ([M₂+Na]⁺), calcd. for C₂₆H₃₆Cl₂NaO₆P₂⁺: 567.1847.

Diethyl (Z)-(2-(4-chlorophenyl)prop-1-en-1-yl)phosphonate (Z-3):

According to general procedure B, E-3 (28.9 mg, 0.10 mmol) was converted to Z-3. Purification by column chromatography (SiO₂, n-pentane/ethyl acetate: 15/85) yielded a yellow oil (25.8 mg, 89%, Z-3:E-3 = 90:10).

Rᵣ = 0.21 (SiO₂, n-pentane/ethyl acetate: 1/1); ¹H NMR (500 MHz, CDCl₃): δ = 7.35 - 7.29 (m, 4H, H7, H8), 5.73 (dq, J = 16.8, 1.4 Hz, 1H, H3), 3.91 - 3.76 (m, 4H, H2), 2.22 - 2.18 (m, 3H, H5), 1.11 (t, J = 7.1 Hz, 6H, H1) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 157.7 (d, Jᵥ = 4.3 Hz, C4), 139.0 (d, Jᵥ = 7.6 Hz, C6), 134.4 (C9), 128.9 (d, Jᵥ = 1.9 Hz, C7), 128.2 (C8), 115.7 (d, Jᵥ = 191.0 Hz, C3), 61.5 (d, Jᵥ = 6.0 Hz, C2), 28.3 (d, Jᵥ = 22.9 Hz, C5), 16.2 (d, Jᵥ = 6.7 Hz, C1) ppm; ³¹P NMR (202 MHz, CDCl₃): δ = 15.60 (dp, J = 15.7, 7.7 Hz) ppm; IR (ATR): ν = 3466 (w), 2981 (w), 2908 (w), 1619 (w), 1594 (w), 1490 (m), 1440 (w), 1393 (w), 1237 (s), 1163 (w), 1091 (m), 1051 (s), 1026 (s), 959 (s), 837 (s), 791 (m), 756 (m) cm⁻¹; HR-ESI-MS: m/z: 311.0577 ([M+Na]+), calcd. for C₁₃H₁₃ClNaO₃P⁺: 311.0574, 599.1247 ([M₂+Na]⁺), calcd. for C₂₆H₃₆Cl₂NaO₆P₂⁺: 599.1256.
Diethyl (Z)-(2-(4-bromophenyl)prop-1-en-1-yl)phosphonate (Z-4):

According to general procedure B, E-4 (33.3 mg, 0.10 mmol) was converted to Z-4. Purification by column chromatography (SiO₂, n-pentane/ethyl acetate: 1/9) yielded a yellow oil (29.0 mg, 87%, Z-4:E-4 = 89:11).

Rᵣ = 0.49 (SiO₂, ethyl acetate); ¹H NMR (600 MHz, CDCl₃): δ = 7.48 - 7.44 (m, 2H, H8), 7.28 - 7.24 (m, 2H, H7), 5.72 (dd, J = 16.8, 1.5 Hz, 1H, H3), 3.91 - 3.76 (m, 4H, H2), 2.19 - 2.18 (m, 3H, H5), 1.10 (t, J = 7.1 Hz, 6H, H1) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 157.7 (d, JCP = 4.2 Hz, C4), 139.5 (d, JCP = 7.6 Hz, C6), 131.2 (C8), 129.2 (d, JCP = 1.7 Hz, C7), 122.5 (C9), 115.7 (d, JCP = 191.1 Hz, C3), 61.5 (d, JCP = 6.1 Hz, C2), 28.3 (d, JCP = 22.8 Hz, C5), 16.2 (d, JCP = 6.9 Hz, C1) ppm; ³¹P NMR (243 MHz, CDCl₃): δ = 15.55 (dp, J = 15.6, 7.7 Hz) ppm; IR (ATR): 𝜈 = 3456 (w), 2979 (w), 2908 (w), 1616 (w), 1588 (w), 1487 (m), 1440 (w), 1392 (w), 1238 (s), 1163 (w), 1097 (w), 1076 (m), 1050 (s), 1026 (s), 958 (s), 833 (m), 793 (m), 746 (m) cm⁻¹; HR-ESI-MS: m/z: 355.0068 ([M+Na]⁺, calcd. for C₁₃H₁₈BrNaO₃P⁺: 355.0069), 689.0234 ([M₂+Na]⁺, calcd. for C₂₆H₃₆Br₂Na₂O₇P₂⁺: 689.0226).

Diethyl (Z)-(2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)phosphonate (Z-5):

According to general procedure B, E-5 (32.2 mg, 0.10 mmol) was converted to Z-5. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 1/19) yielded a yellow oil (28.9 mg, 90%, Z-5:E-5 = 94:6).

Rᵣ = 0.45 (SiO₂, ethyl acetate); ¹H NMR (600 MHz, CDCl₃): δ = 7.60 (d, J = 8.5 Hz, 2H, H8), 7.48 (d, J = 8.0 Hz, 2H, H7), 5.79 (dq, J = 16.8, 1.4 Hz, 1H, H3), 3.91 - 3.74 (m, 4H, H2), 2.23 - 2.22 (m, 3H, H5), 1.08 (t, J = 7.1 Hz, 6H, H1); ¹³C NMR (151 MHz, CDCl₃): δ = 157.4 (d, JCP = 4.1 Hz, C4), 144.4 (dq, JCP = 7.6, JCF = 1.4 Hz, C6), 130.4 (q, JCF = 32.6 Hz, C9), 127.9 (d, JCF = 1.8 Hz, C7), 125.0 (q, JCF = 3.7 Hz, C8), 124.1 (q, JCF = 271.8 Hz, C10), 116.6 (d, JCP = 191.0 Hz, C3), 61.6 (d, JCP = 6.1 Hz, C2), 28.4 (d, JCP = 22.7 Hz, C5), 16.1 (d, JCP = 6.7 Hz, C1) ppm; ¹⁹F NMR (564 MHz, CDCl₃): δ = -62.77 ppm; ³¹P NMR (243 MHz, CDCl₃): δ = 15.05 (dp, J = 15.6, 7.7 Hz) ppm; IR (ATR): 𝜈 = 3457 (w), 2920 (m), 2851 (w), 1613 (w), 1571 (w), 1443 (w), 1405 (w), 1325 (s), 1242 (m), 1166 (m), 1126 (s), 1078 (m), 1054 (s), 1029 (s), 963 (m), 848 (m), 798 (w), 738 (w), 715 (w) cm⁻¹; HR-ESI-MS: m/z: 345.0835 ([M+Na]⁺, calcd. for C₁₄H₁₆F₃NaO₃P⁺: 345.0838), 667.1774 ([M₂+Na]⁺, calcd. for C₂₆H₃₆F₆Na₂O₇P₂⁺: 667.1784).
Diethyl (Z)-(2-(4-tolyl)prop-1-en-1-yl)phosphonate (Z-6):

According to general procedure B, E-6 (26.8 mg, 0.10 mmol) was converted to Z-6. Purification by column chromatography (SiO₂, ethyl acetate) yielded a yellow oil (19.6 mg, 73%, Z-6:E-6 = 80:20). Rᵣ = 0.49 (SiO₂, ethyl acetate); ¹H NMR (500 MHz, CDCl₃): δ = 7.31 - 7.28 (m, 2H, H7), 7.17 - 7.13 (m, 2H, H8), 5.68 (dq, J = 17.3, 1.4 Hz, 1H, H3), 3.90 - 3.74 (m, 4H, H2), 2.33 (s, 3H, H10), 2.21 (t, J = 1.2 Hz, 3H, H5), 1.09 (t, J = 7.1 Hz, 6H, H1) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 159.2 (d, J_CP = 4.7 Hz, C4), 138.3 (C9), 137.6 (d, J_CP = 7.4 Hz, C6), 128.7 (C8), 127.4 (d, J_CP = 1.7 Hz, C7), 114.3 (d, J_CP = 191.3 Hz, C3), 61.4 (d, J_CP = 6.0 Hz, C2), 28.5 (d, J_CP = 23.2 Hz, C5), 21.3 (C10), 16.2 (d, J_CP = 6.8 Hz, C1) ppm; ³¹P NMR (202 MHz, CDCl₃): δ = 16.42 ppm; IR (ATR): ν̃ = 3460 (w), 2981 (w), 2926 (w), 1611 (w), 1512 (w), 1441 (w), 1391 (w), 1237 (s), 1187 (w), 1163 (w), 1098 (w), 1052 (s), 1027 (s), 957 (s), 854 (m), 826 (m), 783 (m), 742 (w) cm⁻¹; HR-ESI-MS: m/z: 291.1124 ([M+Na]⁺, calcd. for C₁₄H₂₁NaO₃P⁺: 291.1121), 559.2351 ([M₂+Na]⁺, cald. for C₂₈H₄₂NaO₆P₂⁺: 559.2349).

Diethyl (Z)-(2-(4-(tert-butyl)phenyl)prop-1-en-1-yl)phosphonate (Z-7):

According to general procedure B, E-7 (31.0 mg, 0.10 mmol) was converted to Z-7. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 1/4) yielded a yellow oil (28.6 mg, 92%, Z-7:E-7 = 87:13). Rᵣ = 0.52 (SiO₂, ethyl acetate); ¹H NMR (600 MHz, CDCl₃): δ = 7.38 - 7.32 (m, 4H, H7, H8), 5.68 (dq, J = 17.4, 1.4 Hz, 1H, H3), 3.86 - 3.71 (m, 4H, H2), 2.23 - 2.21 (m, 3H, H5), 1.29 (s, 9H, H11), 1.03 (td, J = 7.1, 0.6 Hz, 6H, H1) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 159.0 (d, J_CP = 4.5 Hz, C4), 151.6 (C9), 137.6 (d, J_CP = 7.4 Hz, C6), 127.3 (d, J_CP = 1.7 Hz, C7), 124.9 (C8), 114.4 (d, J_CP = 191.7 Hz, C3), 61.4 (d, J_CP = 6.0 Hz, C2), 34.7 (C10), 31.4 (C11), 28.3 (d, J_CP = 23.3 Hz, C5), 16.1 (d, J_CP = 7.0 Hz, C1) ppm; ³¹P NMR (243 MHz, CDCl₃): δ = 16.45 (dt, J = 17.3, 7.5 Hz) ppm; IR (ATR): ν̃ = 3457 (w), 2963 (w), 2869 (w), 1617 (w), 1511 (w), 1464 (w), 1441 (w), 1392 (w), 1364 (w), 1342 (w), 1237 (m), 1202 (w), 1162 (w), 1113 (w), 1098 (w), 1052 (s), 1025 (s), 956 (s), 838 (m), 789 (m), 756 (w) cm⁻¹; HR-ESI-MS: m/z: 333.1593 ([M+Na]⁺, calcd. for C₁₇H₂₇NaO₃P⁺: 333.1590), 643.3293 ([M₂+Na]⁺, cald. for C₃₄H₄₃NaO₆P₂⁺: 643.3288).
Diethyl (Z)-(2-(3-bromophenyl)prop-1-en-1-yl)phosphonate (Z-8):

According to general procedure B, E-8 (33.3 mg, 0.10 mmol) was converted to Z-8. Purification by column chromatography (SiO₂, ethyl acetate) yielded a yellow oil (20.4 mg, 61%, Z-8:E-8 = 91:9).

Rᵣ = 0.29 (SiO₂, ethyl acetate); ¹H NMR (500 MHz, CDCl₃): δ = 7.51 (t, J = 1.8 Hz, 1H, H11), 7.45 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H, H9), 7.33 (ddd, J = 7.7, 1.7, 1.1 Hz, 1H, H7), 7.23 (t, J = 7.8 Hz, 1H, H10), 5.76 (dq, J = 16.9, 1.5 Hz, 1H, H3), 3.95 – 3.77 (m, 4H, H2), 2.22 – 2.20 (m, 3H, H5), 1.13 (td, J = 7.1, 0.6 Hz, 6H, H1) ppm; ¹³C NMR (126 MHz, CDCl₃): δ = 157.3 (d, JCP = 4.0 Hz, C4), 142.7 (d, JCP = 7.6 Hz, C6), 131.3 (C9), 130.4 (d, JCP = 1.8 Hz, C11), 129.7 (C10), 126.2 (d, JCP = 1.9 Hz, C7), 122.1 (C8), 116.3 (d, JCP = 191.3 Hz, C3), 61.6 (d, JCP = 6.0 Hz, C2), 28.4 (d, JCP = 22.8 Hz, C5), 16.3 (d, JCP = 6.9 Hz, C1) ppm; ³¹P NMR (202 MHz, CDCl₃): δ = 15.34 (dp, J = 15.7, 7.8 Hz) ppm; IR (ATR): ν = 3467 (b), 2980 (w), 2906 (w), 1622 (w), 1592 (w), 1559 (w), 1473 (w), 1410 (w), 1392 (w), 1373 (w), 1336 (w), 1234 (m), 1192 (w), 1163 (w), 1097 (w), 1049 (s), 1021 (s), 956 (s), 853 (m), 795 (m), 739 (w), 696 (m), 661 (w) cm⁻¹; HR-ESI-MS: m/z: 355.0072 ([M+Na]⁺, calcd. for C₁₃H₁₆BrNaO₃P⁺: 355.0069), 689.0249 ([M₂+Na]⁺, cald. for C₂₆H₃₆Br₂Na₂O₄P₂⁺: 689.0226).

Dimethyl (Z)-(2-phenylprop-1-en-1-yl)phosphonate (Z-9):

According to general procedure B, E-9 (22.6 mg, 0.10 mmol) was converted to Z-9. Purification by column chromatography (SiO₂, n pentane/ethyl acetate: 1/9) yielded a yellow oil (22.0 mg, 97%, Z-9:E-9 = 92:8).

Rᵣ = 0.43 (SiO₂, ethyl acetate); ¹H NMR (600 MHz, CDCl₃): δ = 7.38 - 7.33 (m, 4H, H6, H7), 7.32 - 7.29 (m, 1H, H8), 5.70 (dd, J = 17.6, 1.3 Hz, 1H, H2), 3.42 (dd, J = 11.1, 0.4 Hz, 6H, H1), 2.23 (ddd, J = 1.5, 1.0, 0.5 Hz, 3H, H4) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 159.9 (d, JCP = 4.8 Hz, C3), 140.5 (d, JCP = 7.6 Hz, C5), 128.5 (C8), 128.1 (C7), 127.2 (d, JCP = 1.7 Hz, C6), 113.8 (d, JCP = 192.2 Hz, C2), 52.0 (d, JCP = 6.1 Hz, C1), 28.5 (d, JCP = 23.1 Hz, C4) ppm; ³¹P NMR (243 MHz, CDCl₃): δ = 18.87 ppm; IR (ATR): ν = 3475 (w), 2951 (w), 2850 (w), 1616 (w), 1599 (w), 1494 (w), 1441 (w), 1374 (w), 1341 (w), 1237 (m), 1182 (w), 1023 (s), 922 (w), 864 (m), 803 (s), 764 (m), 747 (m), 699 (s) cm⁻¹; HR-ESI-MS: m/z: 249.0663 ([M+Na]⁺, calcd. for C₁₃H₁₆NaO₃P⁺: 249.0651), 475.1412 ([M₂+Na]⁺, cald. for C₂₆H₃₆Na₂O₄P₂⁺: 475.1410).
Diisopropyl (Z)-(2-phenylprop-1-en-1-yl)phosphonate (Z-10):

According to general procedure B, E-10 (28.2 mg, 0.10 mmol) was converted to Z-10. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 1/9) yielded an orange oil (28.0 mg, 99%, Z-10:E-10 = 90:10). 

$R_f = 0.55$ (SiO₂, ethyl acetate); $^1H$ NMR (600 MHz, CDCl₃): $\delta = 7.42 - 7.39$ (m, 2H, H7), 7.34 - 7.30 (m, 2H, H8), 7.30 - 7.26 (m, 1H, H9), 5.71 (dq, $J = 17.3$, 1.3 Hz, 1H, H3), 4.47 (ddt, $J = 12.4$, 7.6, 6.2 Hz, 2H, H2), 2.23 - 2.19 (m, 3H, H5), 1.16 (d, $J = 6.2$ Hz, 6H, H1), 1.04 (d, $J = 6.2$ Hz, 6H, H1') ppm; $^{13}$C NMR (151 MHz, CDCl₃): $\delta = 158.2$ (d, $J_{CP} = 4.2$ Hz, C4), 140.8 (d, $J_{CP} = 7.4$ Hz, C6), 128.3 (C9), 127.9 (C8), 127.7 (d, $J_{CP} = 1.7$ Hz, C7), 116.5 (d, $J_{CP} = 193.0$ Hz, C3), 70.2 (d, $J_{CP} = 6.4$ Hz, C2), 28.6 (d, $J_{CP} = 23.1$ Hz, C5), 24.0 (d, $J_{CP} = 4.0$ Hz, C1), 23.7 (d, $J_{CP} = 5.2$ Hz, C1') ppm; $^{31}$P NMR (243 MHz, CDCl₃): $\delta = 13.96$ (dt, $J = 16.4$, 7.8 Hz) ppm; IR (ATR): $\tilde{\nu} = 3449$ (w), 2977 (w), 2922 (w), 2851 (w), 1617 (w), 1597 (w), 1585 (w), 1513 (w), 1439 (w), 1390 (w), 1323 (w), 1234 (s), 1163 (w), 1129 (w), 1097 (w), 1052 (s), 1026 (s), 958 (s), 874 (w), 842 (w), 822 (m), 784 (m), 750 (m) cm⁻¹; HR-ESI-MS: m/z: 305.1286 ([M+Na]⁺, calcd. for C₁₅H₂₃NaO₃P⁺: 305.1277), 587.2676 ([M₂+Na]⁺, calcd. for C₃₀H₆₆NaO₆P₂⁺: 587.2662); analytical data in agreement with literature.[4]

Diethyl (Z)-(2-(naphthalen-2-yl)prop-1-en-1-yl)phosphonate (Z-11):

According to general procedure B, E-11 (30.4 mg, 0.10 mmol) was converted to Z-11. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 1/9) yielded an orange oil (27.6 mg, 91%, Z-11:E-11 = 66:34).

$R_f = 0.63$ (SiO₂, ethyl acetate); $^1H$ NMR (300 MHz, CDCl₃): $\delta = 7.91$ (d, $J = 1.9$ Hz, 1H, H7), 7.88 - 7.78 (m, 3H, H8, H11, H12), 7.53 - 7.43 (m, 3H, H9, H10, H13), 5.83 (dp, $J = 17.3$, 1.4 Hz, 1H, H3), 3.93 - 3.64 (m, 4H, H2), 2.34 - 2.30 (m, 3H, H5), 1.00 (t, $J = 7.1$ Hz, 6H, H1) ppm; $^{13}$C NMR (151 MHz, CDCl₃): $\delta = 159.1$ (d, $J_{CP} = 4.4$ Hz, C4), 138.0 (d, $J_{CP} = 7.6$ Hz, C6), 133.2 (C15), 132.9 (C14), 128.4 (C8), 127.7 (C11/C12), 127.6 (C11/C12), 126.8 (d, $J_{CP} = 2.0$ Hz, C7), 126.5 (C9/C10), 126.4 (C9/C10), 125.3 (d, $J_{CP} = 1.6$ Hz, C13), 115.4 (d, $J_{CP} = 191.9$ Hz, C3), 61.5 (d, $J_{CP} = 6.1$ Hz, C2), 28.5 (d, $J_{CP} = 23.1$ Hz, C5), 16.1 (d, $J_{CP} = 6.6$ Hz, C1) ppm; $^{31}$P NMR (243 MHz, CDCl₃): $\delta = 16.21$ ppm; IR (ATR): $\tilde{\nu} = 3456$ (w), 3056 (w), 2981 (w), 2926 (w), 2853 (w), 1615 (w), 1598 (w), 1504 (w), 1439 (w), 1390 (w), 1323 (w), 1234 (s), 1163 (w), 1129 (w), 1097 (w), 1052 (s), 1026 (s), 958 (s), 874 (w), 842 (w), 822 (m), 784 (m), 750 (m) cm⁻¹; HR-ESI-MS: m/z: 327.1127 ([M+Na]⁺, calcd. for C₁₁H₂₁NaO₃P⁺: 327.1121), 631.2359 ([M₂+Na]⁺, calcd. for C₃₄H₆₆NaO₆P₂⁺: 631.2349).
Diethyl (Z)-(2-(4-methoxyphenyl)prop-1-en-1-yl)phosphonate (Z-12):

According to general procedure B, E-12 (28.4 mg, 0.10 mmol) was converted to Z-12. Purification by column chromatography (SiO₂, ethyl acetate) yielded a yellow oil (23.7 mg, 83%, Z-12:E-12 = 58:42).

\[ R_t = 0.48 \text{(SiO}_2\text{, ethyl acetate)}; \text{ } \text{H NMR (600 MHz, CDCl}_3\text{): } \delta = 7.41 - 7.37 \text{ ppm; } \text{C NMR (151 MHz, CDCl}_3\text{): } \delta = 160.0 \text{ (C9), 158.8 \text{ (d, } J_{CP} = 4.7 \text{ Hz, C4), 132.8 \text{ (d, } J_{CP} = 7.6 \text{ Hz, C6), 129.1 \text{ (d, } J_{CP} = 1.7 \text{ Hz, C7), 113.7 \text{ (d, } J_{CP} = 191.3 \text{ Hz, C3)}, 113.4 \text{ (C8), 61.5 \text{ (d, } J_{CP} = 6.0 \text{ Hz, C2), 55.4 \text{ (C10), 28.3 \text{ (d, } J_{CP} = 23.2 \text{ Hz, C5), 16.2 \text{ (d, } J_{CP} = 6.7 \text{ Hz, C1) ppm; } \text{P NMR (243 MHz, CDCl}_3\text{): } \delta = 15.95 \text{ ppm; analytical data in agreement with literature.}^{[5]} \]

Diethyl (Z)-styrylphosphonate (Z-13):

According to general procedure B, E-13 (24.0 mg, 0.10 mmol) was converted to Z-13. Purification by column chromatography (SiO₂, n-pentane/ethyl acetate: 15/85) yielded a yellow oil (21.9 mg, 91%, Z-13:E-13 = 50:50).

\[ R_t = 0.59 \text{(SiO}_2\text{, ethyl acetate); } \text{H NMR (600 MHz, CDCl}_3\text{): } \delta = 7.69 - 7.64 \text{ (m, 2H, H6), 7.40 - 7.31 \text{ (m, 3H, H7, H8), 7.30 - 7.19 \text{ (m, 1H, H4), 5.79 \text{ (dd, } J = 15.5 \text{, 14.2 Hz, 1H, H3), 4.02 - 3.92 \text{ (m, 4H, H2), 1.16 \text{ (td, } J = 7.1 \text{, 0.5 Hz, 6H, H1) ppm; } \text{C NMR (151 MHz, CDCl}_3\text{): } \delta = 148.5 \text{ (d, } J_{CP} = 2.0 \text{ Hz, C4), 135.4 \text{ (d, } J_{CP} = 8.9 \text{ Hz, C5), 129.7 \text{ (d, } J_{CP} = 1.8 \text{ Hz, C6), 129.4 \text{ (C7/C8), 128.2 \text{ (C7/C8), 116.7 \text{ (d, } J_{CP} = 185.4 \text{ Hz, C3), 61.8 \text{ (d, } J_{CP} = 5.9 \text{ Hz, C2), 16.2 \text{ (d, } J_{CP} = 6.6 \text{ Hz, C1) ppm; } \text{P NMR (243 MHz, CDCl}_3\text{): } \delta = 15.95 \text{ ppm; analytical data in agreement with literature.}^{[5]} \]

Diethyl (Z)-(2-phenylbut-1-en-1-yl)phosphonate (Z-14):

According to general procedure B, E-14 (26.8 mg, 0.10 mmol) was converted to Z-14. Purification by column chromatography (SiO₂, n-pentane/ethyl acetate: 1/9) yielded a yellow oil (25.4 mg, 95%, Z-14:E-14 = 96:4).

\[ R_t = 0.48 \text{(SiO}_2\text{, ethyl acetate); } \text{H NMR (500 MHz, CDCl}_3\text{): } \delta = 7.35 - 7.26 \text{ ppm; } \text{C NMR (126 MHz, CDCl}_3\text{): } \delta = 164.7 \text{ (d, } J_{CP} = 4.1 \text{ Hz, 1H), 1.09 - 1.01 \text{ (m, 9H, H1, H6) ppm; } \text{P NMR (243 MHz, CDCl}_3\text{): } \delta = 15.95 \text{ ppm; analytical data in agreement with literature.}^{[5]} \]
Diethyl (Z)-(2-(2-tolyl)prop-1-en-1-yl)phosphonate (Z-15):

According to general procedure B, **E-15** (26.8 mg, 0.10 mmol) was converted to **Z-15**. Purification by column chromatography (SiO₂, ethyl acetate) yielded a yellow oil (19.1 mg, 71%, **Z-15**: **E-15** = 93:7).

\[ R_f = 0.64 \text{ (SiO₂, ethyl acetate); } ^1H \text{ NMR (600 MHz, CDCl₃): } \delta = 7.18 - 7.12 \text{ (m, 3H, H8, H9, H10)}, 7.06 \text{ (dt, } J = 6.5, 1.5 \text{ Hz, 1H, H11}), 5.81 \text{ (dq, } J = 19.1, 1.5 \text{ Hz, 1H, H3}), 3.79 \text{ (dp, } J = 10.1, 7.2 \text{ Hz, 2H, H2}), 3.73 - 3.53 \text{ (m, 2H, H2'), 2.26 (s, 3H, H12)}, 2.12 - 2.11 \text{ (m, 3H, H5)}, 1.08 \text{ (t, } J = 7.1 \text{ Hz, 6H, H11}) \text{ ppm; } ^{13}C \text{ NMR (151 MHz, CDCl₃): } \delta = 159.4 \text{ (d, } J_{CP} = 4.7 \text{ Hz, C4}), 140.8 \text{ (d, } J_{CP} = 7.3 \text{ Hz, C6}), 134.3 \text{ (d, } J_{CP} = 1.5 \text{ Hz, C7}), 129.9 \text{ (C8/C9/C10)}, 127.6 \text{ (C8/C9/C10)}, 127.2 \text{ (d, } J_{CP} = 2.2 \text{ Hz, C11}), 125.5 \text{ (C8/C9/C10)}, 116.4 \text{ (d, } J_{CP} = 193.5 \text{ Hz, C3}), 61.2 \text{ (d, } J_{CP} = 6.1 \text{ Hz, C2}), 28.5 \text{ (d, } J_{CP} = 23.7 \text{ Hz, C5}), 19.3 \text{ (C12)}, 16.2 \text{ (d, } J_{CP} = 6.5 \text{ Hz, C1}) \text{ ppm; } ^{31}P \text{ NMR (243 MHz, CDCl₃): } \delta = 15.51 \text{ ppm; IR (ATR): } \tilde{\nu} = 3449 \text{ (w), 2979 (w), 2909 (w), 1627 (w), 1600 (w), 1488 (w), 1440 (w), 1391 (w), 1369 (w), 1335 (w), 1239 (s), 1163 (w), 1098 (w), 1053 (s), 1027 (s), 959 (s), 855 (m), 803 (m), 785 (m), 762 (s), 727 (m), 698 (w) cm}^{-1}; \text{ HR-ESI-MS: } m/z: 291.1135 ([M+Na]^+, \text{ calcd. for } C_{16}H_{16}NaO}_3P^+: 291.1121), 559.2355 ([M₂+Na]^+, \text{ calcd. for } C_{28}H_{26}NaO}_6P_2^+: 559.2349); \text{ analytical data in agreement with literature.}^{[4]}

Diethyl (Z)-(2-(2-fluorophenyl)prop-1-en-1-yl)phosphonate (Z-16):

According to general procedure B, **E-16** (27.2 mg, 0.10 mmol) was converted to **Z-16**. Purification by column chromatography (SiO₂, cyclohexane/ethyl acetate: 1/9) yielded a yellow oil (24.8 mg, quant., **Z-16**: **E-16** = 99:1).

\[ R_f = 0.49 \text{ (SiO₂, ethyl acetate); } ^1H \text{ NMR (600 MHz, CDCl₃): } \delta = 7.33 - 7.25 \text{ (m, 2H, H9, H11)}, 7.12 \text{ (tt, } J = 7.5, 0.9 \text{ Hz, 1H, H10}), 7.04 \text{ (dd, } J = 10.2, 8.2 \text{ Hz, 1H, H8}), 5.84 \text{ (dq, } J = 17.3, 1.2 \text{ Hz, 1H, H3}), 3.91 - 3.76 \text{ (m, 4H, H2'}), 2.20 \text{ (s, 3H, H5)}, 1.12 \text{ (t, } J = 7.1 \text{ Hz, 6H, H11}) \text{ ppm; } ^{13}C \text{ NMR (151 MHz, CDCl₃): } \delta = 158.9 \text{ (dd, } J_{CP} = 246.3, J_{CP} = 1.7 \text{ Hz, C7}), 154.2 \text{ (d, } J_{CP} = 3.4 \text{ Hz, C4}), 130.1 \text{ (dd, } J_{CP} = 3.8, J_{CP} = 2.0 \text{ Hz, C11}), 129.8 \text{ (d, } J_{CP} = 8.1 \text{ Hz, C9}), 128.5 \text{ (dd, } J_{CP} = 16.1, J_{CP} = 7.6 \text{ Hz, C6}), 123.8 \text{ (d, } J_{CP} = 3.5 \text{ Hz, C10}), 117.8 \text{ (d, } J_{CP} = 190.7 \text{ Hz, C3}), 115.4 \text{ (d, } J_{CP} = 21.7 \text{ Hz, C8}), 61.4 \text{ (d, } J_{CP} = 6.1 \text{ Hz, C2}), 27.8
(d, \( J_{CP} = 22.5 \) Hz, C5), 16.2 (d, \( J_{CP} = 6.6 \) Hz, C1) ppm; \(^{19}\)F NMR (564 MHz, CDCl\(_3\)): \( \delta = -115.54 \) (ddd, \( J = 10.1, 7.2, 5.5 \) Hz) ppm; \(^{31}\)P NMR (243 MHz, CDCl\(_3\)): \( \delta = 14.78 \) ppm; IR (ATR): \( \tilde{\nu} = 3475 \) (w), 2983 (w), 2908 (w), 1732 (w), 1630 (w), 1609 (w), 1576 (w), 1489 (m), 1444 (m), 1392 (w), 1372 (w), 1339 (w), 1239 (s), 1223 (s), 1182 (w), 1163 (w), 1105 (w), 1052 (s), 1025 (s), 961 (s), 853 (m), 830 (m), 1239 (s), 1182 (w), 1163 (w), 1105 (w), 1052 (s), 1025 (s), 961 (s), 853 (m), 830 (m), 1105 (w), 1052 (s), 1025 (s), 961 (s), 853 (m), 830 (m), 787 (m), 760 (s), 697 (w) cm\(^{-1}\); HR-ESI-MS: \( m/z: 295.0879 \) ([M+Na]\(^+\), calcd. for \( \text{C}_{13}\text{H}_{18}\text{FNaO}_{3}\text{P}^+: 295.0870\)), 567.1851 ([M+Na]\(^+\), calld. for \( \text{C}_{26}\text{H}_{36}\text{F}_{2}\text{NaO}_{6}\text{P}_{2}^+: 567.1847\)).

Diethyl (Z)-(2-(2-chlorophenyl)prop-1-en-1-yl)phosphonate (Z-17):

According to general procedure B, E-17 (28.9 mg, 0.10 mmol) was converted to Z-17. Purification by column chromatography (SiO\(_2\), cyclohexane/ethyl acetate: 1/9) yielded a yellow oil (26.3 mg, 91%), Z\(-17\): E-17 = 96:4.

![Z-17](image)

\( R_1 = 0.33 \) (SiO\(_2\), ethyl acetate); \(^{1}\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 7.35 \) (dd, \( J = 7.4, 2.1 \) Hz, 1H, H8), 7.25 - 7.19 (m, 3H, H9, H10, H11), 5.83 (dd, \( J = 17.8, 1.4 \) Hz, 1H, H3), 3.85 (s, 4H, H2), 2.18 (s, 3H, H5), 1.11 (s, 6H, H1) ppm; \(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \( \delta = 157.1 \) (d, \( J_{CP} = 3.5 \) Hz, C4), 139.8 (d, \( J_{CP} = 7.6 \) Hz, C6), 131.2 (d, \( J_{CP} = 2.1 \) Hz, C7), 129.5 (d, \( J_{CP} = 2.0 \) Hz, C11), 129.3 (C8), 129.1 (C9/C10), 126.6 (C9/C10), 117.5 (d, \( J_{CP} = 191.2 \) Hz, C3), 61.4 (d, \( J_{CP} = 6.1 \) Hz, C2), 27.4 (d, \( J_{CP} = 22.4 \) Hz, C5), 16.2 (d, \( J_{CP} = 6.7 \) Hz, C1) ppm; \(^{31}\)P NMR (243 MHz, CDCl\(_3\)): \( \delta = 14.69 \) ppm; IR (ATR): \( \tilde{\nu} = 3449 \) (w), 2981 (w), 2917 (w), 2851 (w), 1629 (w), 1592 (s), 1472 (w), 1429 (w), 1392 (w), 1370 (w), 1337 (w), 1240 (m), 1163 (w), 1053 (s), 1026 (s), 959 (s), 853 (w), 790 (m), 753 (m), 669 (w) cm\(^{-1}\); HR-ESI-MS: \( m/z: 311.0575 \) ([M+Na]\(^+\), calcd. for \( \text{C}_{13}\text{H}_{18}\text{ClNaO}_{3}\text{P}^+: 311.0574\)), 599.1257 ([M+Na]\(^+\), calcd. for \( \text{C}_{26}\text{H}_{36}\text{ClNaO}_{6}\text{P}_{2}^+: 599.1256\)).

Diethyl (Z)-(2-(2-bromophenyl)prop-1-en-1-yl)phosphonate (Z-18):

According to general procedure B, E-18 (33.3 mg, 0.10 mmol) was converted to Z-18. Purification by column chromatography (SiO\(_2\), ethyl acetate) yielded a yellow oil (28.4 mg, 85%), Z\(-18\): E-18 = 84:16.

![Z-18](image)

\( R_1 = 0.34 \) (SiO\(_2\), ethyl acetate); \(^{1}\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.55 - 7.51 \) (m, 1H, H8), 7.28 (td, \( J = 7.5, 1.2 \) Hz, 1H, H10), 7.20 (dd, \( J = 7.6, 1.7 \) Hz, 1H, H11), 7.13 (ddd, \( J = 8.0, 7.4, 1.8 \) Hz, 1H, H9), 5.81 (dq, \( J = 17.7, 1.4 \) Hz, 1H, H3), 3.78 (d, \( J = 108.0 \) Hz, 4H, H2), 2.18 - 2.17 (m, 3H, H5), 1.11 (d, \( J = 39.2 \) Hz, 6H, H1) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 158.2 \) (d, \( J_{CP} = 3.4 \) Hz, C4), 141.8 (d, \( J_{CP} = 7.6 \) Hz, C6), 132.5 (C8), 129.4 (d, \( J_{CP} = 2.1 \) Hz, C11), 129.2 (C9), 127.1 (C10), 120.7 (d, \( J_{CP} = 2.2 \) Hz, C7), 117.3 (d, \( J_{CP} = 191.7 \) Hz, C3), 61.4 (d, \( J_{CP} = 5.0 \) Hz, C2), 27.5 (d, \( J_{CP} = 22.6 \) Hz, C5), 16.2 (d, \( J_{CP} = 6.7 \) Hz, C1) ppm; \(^{31}\)P NMR (243 MHz, CDCl\(_3\)): \( \delta = 14.53 \) ppm; IR (ATR): \( \tilde{\nu} = 3408 \) (w), 2978 (w), 2917 (w), 2850 (w), 1627 (w), 1589 (w), 1468 (w), 1427 (w), 1391 (w), 1369 (w), 1337 (w), 1240 (m), 1163 (w), 1098
(w), 1053 (s), 1024 (s), 961 (s), 853 (w), 821 (w), 790 (m), 759 (m), 655 (w) cm⁻¹; **HR-ESI-MS:** m/z: 355.0068 ([M+Na]⁺, calcd. for C₁₈H₁₄BrNaO₅P⁺: 355.0069), 689.0234 ([M₂+Na]⁺, calcd. for C₂₆H₂₆Br₂NaO₆P₂⁺: 689.0226).

**General Procedure C for the Hydrogenation of Vinylphosphonates**

In a glovebox, Rh(COD)₂BF₄ (1.3 mg, 0.0032 mmol, 3.2 mol%) and (Sₕ,Sₗ)-WalPhos (2.3 mg, 0.0035 mmol, 3.5 mol%) were added to a vial and dissolved in DCM (1 mL). After stirring for 15 min, the specified vinylphosphonate (0.10 mmol, 1.00 eq.) was added and the vial was transferred to an autoclave. The autoclave was charged with H₂ (10 bar) and the solution was stirred at room temperature for 24 h. After carefully releasing the pressure and evaporation of the solvent, n-pentane (3 mL) was added and filtration through a plug of silica or a glass microfiber filter with subsequent elution with n-pentane (2 x 2 mL) yielded the products as clear oils. The enantiomeric ratios were determined by HPLC analysis using a chiral stationary phase.

**Diethyl (R/S)-(2-phenylpropyl)phosphonate ((R/S)-19):**

According to **general procedure C**, hydrogenation of **E-1** (25.4 mg, 0.100 mmol) afforded (+)-19 as colourless oil (24.8 mg, 0.097 mmol, 97%, e.r. = 97:03); hydrogenation of **Z-1** (25.4 mg, 0.100 mmol) afforded (-)-19 as colourless oil (23.0 mg, 0.090 mmol, 90%, e.r. = 01:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (98/2, 1.0 mL/min) as the eluent with detection at 210 nm.

Hydrogenation of **E-1**: tᵣ = 13.05 min (minor enantiomer), 14.03 min (major enantiomer); **ODR** (CHCl₃, c 1.0): [α]₁⁰⁵ₑ = +17.3°; hydrogenation of **Z-1**: tᵣ = 12.90 min (major enantiomer), 14.14 min (minor enantiomer); **ODR** (CHCl₃, c 1.0): [α]₁⁰⁵ₑ = -22.0°.

**¹H NMR** (400 MHz, CDCl₃): δ = 7.33 - 7.26 (m, 2H, H₈), 7.24 - 7.15 (m, 3H, H₇, H₉), 4.05 - 3.83 (m, 4H, H₂), 3.20 (dq, J = 11.1, 7.0 Hz, 1H, H₄), 2.18 - 1.95 (m, 2H, H₃), 1.38 (d, J = 6.9 Hz, 3H, H₅), 1.22 (dt, J = 16.4, 7.0 Hz, 6H, H₁) ppm; **¹³C NMR** (101 MHz, CDCl₃): δ = 146.8 (d, JCP = 11.9 Hz, C₆), 128.6 (C₈), 126.8 (C₇), 125.6 (C₉), 61.5 (dd, JCP = 17.2, 6.4 Hz, C₂), 34.8 (d, JCP = 3.5 Hz, C₄), 34.4 (d, JCP = 138.4 Hz, C₃), 23.6 (d, JCP = 9.5 Hz, C₅), 16.4 (dd, JCP = 6.1, 1.6 Hz, C₁) ppm; **³¹P NMR** (162 MHz, CDCl₃): δ = 30.25 ppm; **IR (ATR):** ν̅ = 3480 (b), 3029 (w), 2981 (w), 2932 (w), 2907 (w), 1614 (b), 1604 (w), 1495 (w), 1479 (w), 1454 (w), 1392 (w), 1368 (w), 1288 (w), 1240 (m), 1163 (w), 1097 (w), 1052 (s), 1022 (s), 955 (s), 855 (w), 830 (w), 781 (m), 762 (m), 699 (s) cm⁻¹; **HR-ESI-MS:** m/z: 279.1134 ([M+Na]⁺, calcd. for
C_{13}H_{21}NaO_{3}P^{+}: 279.1121), 535.2356 ([M_{2}Na]^{+}, cald. for C_{26}H_{42}NaO_{6}P_{2}^{2+}: 535.2349); analytical data in agreement with literature.\[1\]

As a representative example the reaction was repeated on a 1 mmol scale:

In a glovebox, Rh(COD)_{2}BF_{4} (13.0 mg, 0.032 mmol, 3.2 mol%) and \((S_{C},S_{P})\)-WalPhos (23.0 mg, 0.035 mmol, 3.5 mol%) were added to a flask and dissolved in DCM (10 mL). After stirring for 15 min, vinylphosphonate \(E\)-1 or \(Z\)-1 (254.3 mg, 1.00 mmol, 1.00 eq.) was added and the flask was transferred to an autoclave. The autoclave was charged with H_{2} (10 bar) and the solution was stirred at room temperature for 24 h. After carefully releasing the pressure and evaporation of the solvent, \(n\)-pentane (5 mL) was added and filtration through a glass microfiber filter with subsequent elution with \(n\)-pentane (2 x 5 mL) yielded the products \(\pm\)-19 (252.7 mg, 0.99 mmol, 99%, e.r. = 97:03) and \((-\cdash\)-19 (246.5 mg, 0.96 mmol, 96%, e.r. = 01:99) as colourless oils. The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and \(n\)-hexane/i-propanol (98/2, 1.0 mL/min) as the eluent with detection at 210 nm.

Hydrogention of \(E\)-1: \(t_{R}\) = 11.75 min (minor enantiomer), 13.69 min (major enantiomer); hydrogention of \(Z\)-1: \(t_{R}\) = 12.58 min (major enantiomer), 15.40 min (minor enantiomer).

As a representative example the reaction was repeated using the opposite catalyst enantiomer

According to general procedure C, using \((R_{C},R_{P})\)-WalPhos instead of \((S_{C},S_{P})\)-WalPhos, hydrogention of \(E\)-1 (25.4 mg, 0.100 mmol) afforded \((-\cdash\)-19 as colourless oil (24.6 mg, 0.096 mmol, 96%, e.r. = 03:97); hydrogention of \(Z\)-1 (25.4 mg, 0.100 mmol) afforded \(\cdash\)-19 as colourless oil (25.4 mg, 0.099 mmol, 99%, e.r. = 99:01). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and \(n\)-hexane/i-propanol (98/2, 1.0 mL/min) as the eluent with detection at 210 nm.

Hydrogention of \(E\)-1: \(t_{R}\) = 11.05 min (major enantiomer), 13.58 min (minor enantiomer); ODR (CHCl3, c 1.0): \([\alpha]_{D}^{27} = -19.4^\circ\); hydrogention of \(Z\)-1: \(t_{R}\) = 11.50 min (minor enantiomer), 13.48 min (major enantiomer); ODR (CHCl3, c 1.0): \([\alpha]_{D}^{29} = +19.7^\circ\).

Diethyl \((R/S)-(2-(4-fluorophenyl)propyl)phosphonate ((R/S)-20):

According to general procedure C, hydrogention of \(E\)-2 (27.2 mg, 0.100 mmol) afforded \(\cdash\)-20 as colourless oil (26.8 mg, 0.096 mmol, 98%, e.r. = 97:03); hydrogention of \(Z\)-2 (27.2 mg, 0.100 mmol) afforded \((-\cdash\)-20 as colourless oil (26.0 mg, 0.095 mmol, 95%, e.r. = 02:98). The enantiomeric ratios were
determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (98/2, 1.0 mL/min) as the eluent with detection at 210 nm. Hydrogenation of E-2: t<sub>r</sub> = 10.75 min (minor enantiomer), 11.57 min (major enantiomer); ODR (CHCl₃, c 1.0): [α]<sub>D</sub> = +10.2°; hydrogenation of Z-2: t<sub>r</sub> = 10.00 min (major enantiomer), 10.92 min (minor enantiomer); ODR (CHCl₃, c 1.0): [α]<sub>D</sub> = -19.0°.

1<sup>H</sup> NMR (500 MHz, CDCl₃): δ = 7.18 (dd, J = 8.6, 5.4 Hz, 2H, H7), 6.97 (t, J = 8.6 Hz, 2H, H8), 4.06 - 3.85 (m, 4H, H2), 3.20 (s, 1H, H4), 2.15 - 1.95 (m, 2H, H2), 1.36 (d, J = 6.6 Hz, 3H, H5), 1.22 (dd, J = 21.8, 6.7 Hz, 6H, H1) ppm; 13<sup>C</sup> NMR (126 MHz, CDCl₃): δ = 161.5 (d, J<sub>CP</sub> = 244.2 Hz, C9), 142.4 (C6), 128.2 (d, J<sub>CP</sub> = 7.8 Hz, C7), 115.3 (d, J<sub>CP</sub> = 21.2 Hz, C8), 61.5 (d, J<sub>CP</sub> = 16.1 Hz, C2), 34.9 (d, J<sub>CP</sub> = 141.0 Hz, C3), 34.2 (C4), 23.9 (d, J<sub>CP</sub> = 7.2 Hz, C5), 16.5 (C1) ppm; 19<sup>F</sup> NMR (282 MHz, CDCl₃): δ = -116.87 ppm; 31<sup>P</sup> NMR (121 MHz, CDCl₃): δ = 29.90 ppm; IR (ATR): ν = 3650 (b), 3476 (b), 1604 (w), 1510 (s), 1480 (w), 1456 (w), 1393 (w), 1287 (w), 1222 (s), 1160 (m), 1098 (w), 1052 (s), 1023 (s), 955 (s), 832 (s), 777 (m), 737 (w), 713 (w), 685 (w) cm⁻¹; HR-ESI-MS: m/z: 297.1045 ([M+Na]<sup>+</sup>), calcd. for C₁₃H₇FNaO₆P<sup>+</sup>: 297.1026, 571.2173 ([M₂+Na]<sup>+</sup>), calcd. for C₂₆H₄₀F₂NaO₆P₂<sup>+</sup>: 571.2160; analytical data in agreement with literature.[1]

Diethyl (R/S)-(2-{4-chlorophenyl}propyl)phosphonate ((R/S)-21):

According to general procedure C, hydrogenation of E-3 (29.0 mg, 0.100 mmol) afforded (+)-21 as colourless oil (29.1 mg, 0.100 mmol, quant., e.r. = 97:03); hydrogenation of Z-3 (28.9 mg, 0.100 mmol) afforded (-)-21 as colourless oil (27.0 mg, 0.093 mmol, 93%, e.r. = 01:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (99.5/0.5, 0.5 mL/min) as the eluent with detection at 230 nm. Hydrogenation of E-3: t<sub>r</sub> = 29.16 min (minor enantiomer), 30.60 min (major enantiomer); ODR (CHCl₃, c 1.0): [α]<sub>D</sub> = +23.1°; hydrogenation of Z-3: t<sub>r</sub> = 24.62 min (major enantiomer), 26.47 min (minor enantiomer); ODR (CHCl₃, c 1.0): [α]<sub>D</sub> = -26.1°.

1<sup>H</sup> NMR (500 MHz, CDCl₃): δ = 7.29 - 7.25 (m, 2H, H8), 7.18 - 7.14 (m, 2H, H7), 4.06 - 3.88 (m, 4H, H2), 3.20 (dt, J = 17.8, 6.7 Hz, 1H, H4), 2.13 - 1.95 (m, 2H, H3), 1.37 (d, J = 6.9 Hz, 3H, H5), 1.24 (dt, J = 20.7, 7.0 Hz, 6H, H1) ppm; 13<sup>C</sup> NMR (126 MHz, CDCl₃): δ = 145.2 (d, J<sub>CP</sub> = 11.0 Hz, C6), 132.1 (C9), 128.7 (C8), 128.2 (C7), 61.5 (dd, J<sub>CP</sub> = 14.4, 5.8 Hz, C2), 34.5 (d, J<sub>CP</sub> = 138.9 Hz, C3), 34.3 (d, J<sub>CP</sub> = 2.6 Hz, C4), 23.7 (d, J<sub>CP</sub> = 9.8 Hz, C5), 16.5 (C1) ppm; 31<sup>P</sup> NMR (202 MHz, CDCl₃): δ = 29.74 ppm; IR (ATR): ν = 3445 (b), 2981 (w), 2931 (w), 2908 (w), 1647 (b), 1493 (w), 1456 (w), 1411 (w), 1392 (w), 1368 (w), 1297 (w), 1227 (m), 1163 (w), 1095 (m), 1052 (s), 1023 (s), 1013 (s), 956 (s), 825 (m), 759 (w), 718 (w), 657 (m) cm⁻¹;
HR-ESI-MS: \(m/z\) 313.0738 ([M+Na]⁺, calcd. for C₁₁H₂₀ClNaO₃P⁺: 313.0731), 603.1569 ([M₂+Na]⁺, calcd. for C₂₆H₄₀Cl₂NaO₆P₂⁺: 603.1577); analytical data in agreement with literature.[¹]

Diethyl (R/S)-(2-{(4-bromophenyl)propyl}phosphonate ((R/S)-22):

According to general procedure C, hydrogenation of E-4 (33.3 mg, 0.100 mmol) afforded (+)-22 as colourless oil (31.2 mg, 0.093 mmol, 93%, e.r. = 97:03); hydrogenation of Z-4 (33.3 mg, 0.100 mmol) afforded (-)-22 as colourless oil (31.6 mg, 0.094 mmol, 94%, e.r. = 01:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (99.5/0.5, 1 mL/min) as the eluent with detection at 230 nm.

Hydrogenation of E-4: \(t_R = 20.01\) min (minor enantiomer), 21.05 min (major enantiomer); ODR (CHCl₃, c 1.0): \([\alpha]_{D}^{25} = +22.7^\circ\); hydrogenation of Z-4: \(t_R = 19.60\) min (major enantiomer), 21.48 min (minor enantiomer); ODR (CHCl₃, c 1.0): \([\alpha]_{D}^{25} = -25.3^\circ\).

³H NMR (500 MHz, CDCl₃): \(\delta = 7.43 - 7.39\) (m, 2H, H8), 7.12 - 7.08 (m, 2H, H7), 4.04 - 3.86 (m, 4H, H2), 3.17 (dq, \(J = 11.2, 7.0\) Hz, 1H, H4), 2.02 (dd, \(J = 18.0, 15.3, 7.1\) Hz, 2H, H3), 1.35 (d, \(J = 6.9\) Hz, 3H, H5), 1.22 (dt, \(J = 20.4, 7.0\) Hz, 6H, H1) ppm; ¹³C NMR (126 MHz, CDCl₃): \(\delta = 145.7\) (d, \(J_{CP} = 11.3\) Hz, C6), 131.6 (C8), 128.6 (C7), 120.2 (C9), 61.5 (dd, \(J_{CP} = 14.1, 6.4\) Hz, C2), 34.4 (d, \(J_{CP} = 3.3\) Hz, C4), 34.4 (d, \(J_{CP} = 138.8\) Hz, C3), 23.6 (d, \(J_{CP} = 9.9\) Hz, C5), 16.5 (dd, \(J_{CP} = 6.1, 3.8\) Hz, C1) ppm; ³¹P NMR (202 MHz, CDCl₃): \(\delta = 29.61\) ppm; IR (ATR): \(\nu = 3454\) (b), 2980 (w), 2932 (w), 2907 (w), 1647 (b), 1592 (w), 1489 (w), 1456 (w), 1408 (w), 1392 (w), 1368 (w), 1297 (w), 1227 (m), 1163 (w), 1096 (w), 1051 (s), 1023 (s), 1008 (s), 956 (s), 822 (m), 751 (w), 715 (w) cm⁻¹.

HR-ESI-MS: \(m/z\): 357.0229 ([M+Na]⁺, calcd. for C₁₁H₂₀BrNaO₃P⁺: 357.0226), 693.0534 ([M₂+Na]⁺, calcd. for C₂₆H₄₀Br₂NaO₆P₂⁺: 693.0539); analytical data in agreement with literature.[¹]

Diethyl (R/S)-(2-{(4-trifluoromethyl)phenyl)propyl}phosphonate ((R/S)-23):

According to general procedure C, hydrogenation of E-5 (32.2 mg, 0.10 mmol) afforded (+)-23 as colourless oil (32.0 mg, 0.099 mmol, 99%, e.r. = 98:02); hydrogenation of Z-5 (32.2 mg, 0.10 mmol) afforded (-)-23 as colourless oil (32.4 mg, 0.10 mmol, quant., e.r. > 01:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (99.2/0.8, 0.4 mL/min) as the eluent with detection at 210 nm.
Hydrogention of E-5: $t_R = 46.65$ min (minor enantiomer), 49.01 min (major enantiomer); ODR (CHCl$_3$, c 1.0): $[\alpha]_{D}^{23} = +17.1^\circ$; hydrogention of Z-5: $t_R = 43.65$ min (major enantiomer), 47.60 min (minor enantiomer); ODR (CHCl$_3$, c 1.0): $[\alpha]_{D}^{23} = -21.3^\circ$.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.55$ (d, $J = 8.0$ Hz, 2H, H8), 7.34 (d, $J = 8.1$ Hz, 2H, H7), 4.03 - 3.86 (m, 4H, H2), 3.27 (dq, $J = 11.2$, 7.0 Hz, 1H, H4), 2.06 (dq, $J = 18.2$, 15.3, 7.2 Hz, 2H, H3), 1.39 (dd, $J = 6.9$, 0.8 Hz, 3H, H5), 1.20 (dt, $J = 30.5$, 7.1 Hz, 6H, H1) ppm; $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 150.7$ (dd, $J_{CP} = 11.0$, 1.3 Hz, C6), 128.9 (q, $J_{CS} = 32.3$ Hz, C9), 127.3 (C7), 125.6 (q, $J_{CS} = 3.8$ Hz, C8), 124.3 (q, $J_{CS} = 271.9$ Hz, C10), 61.6 (dd, $J_{CP} = 9.6$, 6.6 Hz, C2), 34.9 (d, $J_{CP} = 3.7$ Hz, C4), 34.2 (d, $J_{CP} = 139.6$ Hz, C3), 23.6 (d, $J_{CP} = 10.5$ Hz, C5), 16.4 (dd, $J_{CP} = 8.2$, 6.2 Hz, C1) ppm; $^{19}$F NMR (564 MHz, CDCl$_3$): $\delta = -62.48$ ppm; $^{31}$P NMR (243 MHz, CDCl$_3$): $\delta = 29.26$ ppm; IR (ATR): $\nu = 3455$ (b), 2983 (w), 2935 (w), 2908 (w), 1619 (w), 1456 (w), 1422 (w), 1393 (w), 1369 (w), 1325 (s), 1295 (w), 1162 (m), 1119 (s), 1067 (s), 957 (s), 835 (m), 794 (m), 776 (w), 718 (w) cm$^{-1}$; HR-ESI-MS: $m/z$: 347.1011 ([M$\text{Na}^+$]$^-$, calcd. for C$_{14}$H$_{20}$F$_3$NaO$_5$P$^+$: 347.0994), 671.2117 ([M$_2$Na]$^+$, calcd. for C$_{26}$H$_{40}$FeNaO$_6$P$_2^+$: 671.2097); analytical data in agreement with literature.$^{[1]}$

Diethyl (R/S)-(2-(4-tolyl)propyl)phosphonate ((R/S)-24): According to general procedure C, hydrogention of E-6 (26.8 mg, 0.10 mmol) afforded (+)-24 as colourless oil (25.7 mg, 0.095 mmol, 95%, e.r. = 97:03); hydrogention of Z-6 (26.8 mg, 0.10 mmol) afforded (-)-24 as colourless oil (24.5 mg, 0.091 mmol, 91%, e.r. = 02:98). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralpak AS-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (97/3, 1.0 mL/min) as the eluent with detection at 220 nm.

Hydrogention of E-6: $t_R = 18.98$ min (major enantiomer), 21.94 min (minor enantiomer); ODR (CHCl$_3$, c 1.0): $[\alpha]_{D}^{23} = +19.3^\circ$; hydrogention of Z-6: $t_R = 19.19$ min (minor enantiomer), 21.31 min (major enantiomer); ODR (CHCl$_3$, c 1.0): $[\alpha]_{D}^{23} = -24.0^\circ$.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.13 - 7.08$ (m, 4H, H7, H8), 4.04 - 3.87 (m, 4H, H2), 3.22 - 3.12 (m, 1H, H4), 2.31 (s, 3H, H10), 2.13 - 1.96 (m, 2H H3), 1.37 (d, $J = 7.0$ Hz, 3H, H5), 1.23 (dt, $J = 18.6$, 7.1 Hz, 6H, H1) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 143.9$ (d, $J_{CP} = 12.5$ Hz, C6), 136.0 (C9), 129.3 (C8), 126.6 (C7), 61.4 (dd, $J_{CP} = 23.1$, 6.5 Hz, C2), 34.5 (d, $J_{CP} = 138.0$ Hz, C3), 34.4 (d, $J_{CP} = 3.6$ Hz, C4), 23.6 (d, $J_{CP} = 9.0$ Hz, C5), 21.1 (C10), 16.5 (dd, $J_{CP} = 6.2$, 2.6 Hz, C1) ppm; $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta = 30.31$ (dddd, $J = 26.1$, 18.4, 11.0, 7.7 Hz) ppm; IR (ATR): $\nu = 3477$ (b), 2980 (w), 2929 (w), 1636 (b), 1516 (w), 1456 (w), 1392 (w), 1285 (w), 1240 (m), 1163 (w), 1097 (w), 1052 (s), 1021 (s), 955 (s), 816 (m), 778 (m), 735 (w), 719 (w) cm$^{-1}$; HR-ESI-MS: $m/z$: 293.1293 ([M$\text{Na}^+$]$^-$, calcd. for C$_{14}$H$_{23}$NaO$_5$P$^+$: 293.1277), 563.2683 ([M$_2$Na]$^+$, calcd. for C$_{26}$H$_{40}$FeNaO$_6$P$_2^+$: 563.2662); analytical data in agreement with literature.$^{[1]}$
Diethyl (R/S)-(2-(4-(tert-butyl)phenyl)propyl)phosphonate ((R/S)-25):

According to general procedure C, hydrogention of E-7 (31.0 mg, 0.10 mmol) afforded (+)-25 as colourless oil (27.2 mg, 0.087 mmol, 87%, e.r. = 97:03); hydrogention of Z-7 (31.0 mg, 0.10 mmol) afforded (-)-25 as colourless oil (30.6 mg, 0.098 mmol, 98%, e.r. = 01:99). The enantiomeric ratios were determined by HPLC analysis using a ReproSil Chiral OM (0.46 cm * 25 cm) column and n-hexane/i-propanol (98/2, 1.0 mL/min) as the eluent with detection at 230 nm.

Hydrogention of E-7: $t_R = 8.99$ min (major enantiomer), 9.91 min (minor enantiomer); ODR (CHCl₃, c 1.0): $[\alpha]_D^{20} = +20.6^\circ$; hydrogention of Z-7: $t_R = 8.98$ min (minor enantiomer), 9.87 min (major enantiomer); ODR (CHCl₃, c 1.0): $[\alpha]_D^{20} = -22.2^\circ$.

$^1$H NMR (500 MHz, CDCl₃): $\delta = 7.33 - 7.29$ (m, 2H, H8), 7.18 - 7.14 (m, 2H, H7), 4.05 - 3.83 (m, 4H, H2), 3.19 (dq, $J = 11.1$, 7.0 Hz, 1H, H4), 2.16 - 1.97 (m, 2H, H3), 1.38 (d, $J = 6.9$ Hz, 3H, H5), 1.30 (s, 9H, H11), 1.21 (dt, $J = 24.3$, 7.0 Hz, 6H, H1) ppm; $^{13}$C NMR (126 MHz, CDCl₃): $\delta = 149.3$ (C9), 143.7 (d, $J_{CP} = 12.0$ Hz, C6), 126.4 (C7), 125.5 (C8), 61.4 (dd, $J_{CP} = 24.9$, 6.4 Hz, C2), 34.5 (d, $J_{CP} = 137.8$ Hz, C3), 34.5 (C10), 34.3 (d, $J_{CP} = 3.5$ Hz, C4), 31.5 (C11), 23.6 (d, $J_{CP} = 9.5$ Hz, C5), 16.4 (dd, $J_{CP} = 6.3$, 2.8 Hz, C1) ppm;

$^{31}$P NMR (202 MHz, CDCl₃): $\delta = 30.35$ ppm; IR (ATR): $\tilde{\nu} = 3485$ (b), 2963 (m), 2906 (w), 2871 (w), 1716 (w), 1648 (b), 1511 (w), 1458 (w), 1393 (w), 1366 (w), 1241 (m), 1163 (w), 1113 (w), 1098 (w), 1053 (s), 1023 (s), 956 (s), 828 (m), 785 (m), 748 (w), 719 (w), 668 (w) cm⁻¹; HR-ESI-MS: m/z: 335.1773 [(M+Na)+, calcd. for C₁₀H₂₃NaO₃P⁺: 335.1747, 647.3625 [(M₂+Na)+, calcd. for C₃₆H₅₈NaO₆P₂⁺: 647.3601].

Diethyl (R/S)-(2-(3-bromophenyl)propyl)phosphonate ((R/S)-26):

According to general procedure C, hydrogention of E-8 (33.3 mg, 0.10 mmol) afforded (+)-26 as colourless oil (32.1 mg, 0.096 mmol, 96%, e.r. = 97:03); hydrogention of Z-8 (33.3 mg, 0.10 mmol) afforded (-)-26 as colourless oil (31.1 mg, 0.093 mmol, 93%, e.r. = 01:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (95/5, 1.0 mL/min) as the eluent with detection at 220 nm.

Hydrogention of E-8: $t_R = 5.59$ min (minor enantiomer), 6.38 min (major enantiomer); ODR (CHCl₃, c 1.0): $[\alpha]_D^{20} = +20.4^\circ$; hydrogention of Z-8: $t_R = 5.56$ min (major enantiomer), 6.43 min (minor enantiomer); ODR (CHCl₃, c 1.0): $[\alpha]_D^{20} = -24.7^\circ$.

Rᵣ = XXX (SiO₂, ethyl acetate); $^1$H NMR (500 MHz, CDCl₃): $\delta = 7.36$ (q, $J = 1.3$ Hz, 1H, H7), 7.34 - 7.30 (m, 1H, H9), 7.18 - 7.14 (m, 2H, H10, H11), 4.05 - 3.87 (m, 4H, H2), 3.17 (d, $J = 11.2$, 7.0 Hz, 1H, H4), 2.13 - 1.94 (m, 2H, H3), 1.37 (d, $J = 6.8$ Hz, 3H, H5), 1.23 (dt, $J = 17.6$, 7.0 Hz, 6H, H1) ppm; $^{13}$C NMR (126 MHz,
CDCl₃): δ = 149.1 (d, JCP = 11.5 Hz, C6), 130.2 (C10), 130.0 (C7), 129.6 (C9), 125.6 (C11), 122.6 (C8), 61.6 (dd, JCP = 13.4, 6.6 Hz, C2), 34.7 (d, JCP = 3.6 Hz, C4), 34.3 (d, JCP = 139.3 Hz, C3), 23.6 (d, JCP = 9.9 Hz, C5), 16.5 (dd, JCP = 6.2, 2.6 Hz, C1) ppm; 31P NMR (202 MHz, CDCl³): δ = 29.46 ppm; IR (ATR): ν = 3658 (b), 3475 (b), 2979 (w), 2930 (w), 1906 (w), 1727 (b), 1594 (w), 1568 (w), 1477 (w), 1455 (w), 1428 (w), 1392 (w), 1368 (w), 1342 (w), 1241 (m), 1164 (w), 1097 (w), 1052 (s), 1022 (s), 997 (m), 955 (s), 880 (w), 855 (w), 782 (m), 724 (w), 694 (m), 666 (w) cm⁻¹; HR-ESI-MS: m/z: 359.0204 [(M+Na)+, calcd. for C₁₃H₁₃BrNaO₃P⁺: 359.0205), 693.0559 [(M₂+Na)+, calcd. for C₂₆H₃₆Br₂NaO₆P₂⁺: 693.0539].

**Dimethyl (R/S)-(2-phenylpropyl)phosphonate ((R/S)-27):**

According to general procedure C, hydrogenation of E-9 (22.6 mg, 0.10 mmol) afforded (±)-27 as colourless oil (20.0 mg, 0.088 mmol, 88%, e.r. = 97:03); hydrogenation of Z-9 (22.6 mg, 0.10 mmol) afforded (−)-27 as colourless oil (20.5 mg, 0.090 mmol, 90%, e.r. = 01:99). The enantiomeric ratios were determined by HPLC analysis using a ReproSil Chiral OM (0.46 cm * 25 cm) column and n-hexane/i-propanol (97/3, 1.0 mL/min) as the eluent with detection at 210 nm.

Hydrogenation of E-9: tR = 22.53 min (minor enantiomer), 25.07 min (major enantiomer); ODR (CHCl₃, c 0.93): [α]D²⁸ = +22.7°; hydrogenation of Z-9: tR = 22.63 min (major enantiomer), 25.57 min (minor enantiomer); ODR (CHCl₃, c 0.74): [α]D²⁸ = -19.5°.

1H NMR (500 MHz, CDCl₃): δ = 7.30 (t, J = 7.7 Hz, 2H, H7), 7.24 - 7.18 (m, 3H, H6, H8), 3.59 (ddd, J = 39.2, 10.8, 0.7 Hz, 6H, H1), 3.20 (dq, J = 11.2, 7.0 Hz, 1H, H3), 2.15 - 2.00 (m, 2H, H2), 1.38 (dt, J = 6.9, 0.7 Hz, 3H, H4) ppm; 13C NMR (126 MHz, CDCl₃): δ = 146.6 (d, JCP = 12.0 Hz, C5), 128.7 (C7), 126.8 (C6), 126.6 (C8), 52.2 (dd, JCP = 32.1, 6.6 Hz, C1), 34.7 (d, JCP = 3.5 Hz, C5), 33.5 (d, JCP = 138.3 Hz, C2), 23.6 (d, JCP = 9.6 Hz, C4) ppm; 31P NMR (162 MHz, CDCl₃): δ = 32.91 ppm; IR (ATR): ν = 3471 (b), 3029 (w), 2957 (w), 2851 (w), 1637 (b), 1604 (w), 1495 (w), 1454 (w), 1406 (w)1378 (w), 1358 (w), 1287 (w), 1241 (m), 1183 (w), 1053 (s), 1023 (s), 914 (w), 841 (m), 799 (s), 763 (m), 721 (w), 699 (s) cm⁻¹; HR-ESI-MS: m/z: 251.0820 [(M+Na)+, calcd. for C₁₃H₁₃NaO₃P⁺: 251.0808), 479.1738 [(M₂+Na)+, calcd. for C₂₆H₃₆Br₂NaO₆P₂⁺: 479.1723); analytical data in agreement with literature.[6]

**Diethyl (R/S)-(2-(4-methoxyphenyl)propyl)phosphonate ((R/S)-28):**

According to general procedure C, hydrogenation of E-12 (28.4 mg, 0.10 mmol) afforded (±)-28 as colourless oil (23.7 mg, 0.83 mmol, 83%, e.r. = 95:05); hydrogenation of Z-12 (28.4 mg, 0.10 mmol) afforded (−)-28 as colourless oil (24.8 mg, 0.87 mmol, 87%, e.r. = 01:99). The enantiomeric ratios were
determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (98/2, 1.0 mL/min) as the eluent with detection at 220 nm.

Hydrogenation of E-12: $t_r = 18.65$ min (minor enantiomer), 20.52 min (major enantiomer); ODR (CHCl₃, c 1.0): $[\alpha]_{D}^{20} = +21.3^\circ$; hydrogenation of Z-12: $t_r = 18.44$ min (major enantiomer), 20.90 min (minor enantiomer); ODR (CHCl₃, c 0.75): $[\alpha]_{D}^{27} = -19.7^\circ$.

$^1$H NMR (400 MHz, CDCl₃): δ = 7.14 (d, $J = 8.6$ Hz, 2H, H7), 6.84 (d, $J = 8.5$ Hz, 2H, H8), 4.05 – 3.87 (m, 4H, H2), 3.78 (s, 3H, H10), 3.17 (dq, $J = 13.4$, 6.8 Hz, 1H, H4), 2.16 – 1.93 (m, 2H, H3), 1.36 (d, $J = 6.8$ Hz, 3H, H5), 1.24 (dt, $J = 16.3$, 6.9 Hz, 6H, H1) ppm; $^{13}$C NMR (101 MHz, CDCl₃): δ = 158.2 (C9), 139.0 (d, $J_{CP} = 11.9$ Hz, C6), 127.7 (C7), 61.5 (dd, $J = 19.2$, 6.0 Hz, C2), 55.4 (C10), 16.5 (d, $J_{CP} = 5.4$ Hz, C1) ppm; $^{31}$P NMR (162 MHz, CDCl₃): δ = 30.31 ppm; IR (ATR): ν = 3478 (b), 2932 (w), 2904 (w), 2349 (w), 2302 (w), 1611 (w), 1584 (w), 1513 (s), 1456 (w), 1392 (w), 1293 (w), 1244 (s), 1179 (m), 1098 (w), 1051 (s), 1023 (s), 1045 (w), 987 (m), 807 (m), 747 (m), 711 (w), 684 (w) cm⁻¹; HR-ESI-MS: m/z: 309.1237 ([M+Na]⁺, calcd. for C₁₄H₂₃NaO₄P⁺: 309.1226), 595.2574 ([M₂+Na]⁺, calcd. for C₂₉H₄₆NaO₈P₂⁺: 595.2560); analytical data in agreement with literature.[1]

Diethyl (R/S)-(2-(naphthalen-2-yl)propyl)phosphonate ((R/S)-29):

According to general procedure C, hydrogenation of E-11 (30.3 mg, 0.10 mmol) afforded (+)-29 as colourless oil (30.4 mg, 0.10 mmol, quant., e.r. = 97:03); hydrogenation of Z-11 (30.5 mg, 0.10 mmol) afforded (-)-29 as colourless oil (30.6 mg, 0.10 mmol, quant, e.r. = 01:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (98/2, 1.0 mL/min) as the eluent with detection at 230 nm.

Hydrogenation of E-11: $t_r = 22.67$ min (minor enantiomer), 27.04 min (major enantiomer); ODR (CHCl₃, c 1.0): $[\alpha]_{D}^{25} = +21.4^\circ$; hydrogenation of Z-11: $t_r = 22.62$ min (major enantiomer), 27.74 min (minor enantiomer); ODR (CHCl₃, c 1.0): $[\alpha]_{D}^{25} = -28.0^\circ$.

$^1$H NMR (600 MHz, CDCl₃): δ = 7.81 - 7.77 (m, 3H), 7.66 (d, $J = 1.8$ Hz, 1H, H7), 7.47 - 7.40 (m, 2H), 7.37 (dd, $J = 8.5$, 1.8 Hz, 1H, H13), 4.06 - 3.85 (m, 4H, H2), 3.40 (dq, $J = 11.1$, 6.9 Hz, 1H, H4), 2.26 - 2.07 (m, 2H, H3), 1.48 (d, $J = 6.9$ Hz, 3H, H5), 1.23 (t, $J = 7.1$ Hz, 3H, H1), 1.16 (t, $J = 7.1$ Hz, 3H, H1') ppm; $^{13}$C NMR (151 MHz, CDCl₃): δ = 144.2 (d, $J_{CP} = 12.2$ Hz, C6), 133.7 (C14), 132.4 (C15), 128.3, 127.7 (C7), 127.7, 126.1, 125.5 (C10), 125.4 (C13), 125.0 (C7), 61.5 (dd, $J_{CP} = 19.2$, 6.6 Hz, C2), 34.9 (d, $J_{CP} = 3.1$ Hz, C4) 34.4 (d, $J_{CP} = 138.0$ Hz, C3), 23.5 (d, $J_{CP} = 9.2$ Hz, C5), 16.4 (t, $J_{CP} = 6.6$ Hz, C1) ppm; $^{31}$P NMR (202 MHz, CDCl₃): δ = 30.13 ppm; IR (ATR): ν = 3476 (b), 3053 (w), 2979 (m), 2932 (w), 2904 (w), 2349 (w), 2309
Diethyl (R/S)-(2-phenylbutyl)phosphonate ((R/S)-30):

According to general procedure C, hydrogenation of E-14 (26.8 mg, 0.10 mmol) afforded (+)-30 as colourless oil (26.5 mg, 0.098 mmol, 98%, e.r. = 97:03); hydrogenation of Z-14 (26.7 mg, 0.10 mmol) afforded (-)-30 as colourless oil (24.2 mg, 0.090 mmol, 90%, e.r. = 01:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (98/2, 1.0 mL/min) as the eluent with detection at 210 nm.

Hydrogenation of E-14: t_R = 8.10 min (minor enantiomer), 9.68 min (major enantiomer); ODR (CHCl_3, c 1.0): [α]_D^20 = +8.0°; hydrogenation of Z-14: t_R = 8.03 min (major enantiomer), 9.75 min (minor enantiomer); ODR (CHCl_3, c 1.0): [α]_D^20 = -13.2°.

R_R = 0.50 (SiO_2, ethyl acetate); ^1H NMR (400 MHz, CDCl_3): δ = 7.33 - 7.27 (m, 2H, H9), 7.24 - 7.17 (m, 3H, H8, H10), 4.03 - 3.73 (m, 4H, H2), 2.99 - 2.87 (m, 1H, H4), 2.21 - 2.03 (m, 2H, H3), 1.86 (ddt, J = 14.6, 7.3, 5.0 Hz, 1H, H5), 1.64 (ddq, J = 14.5, 9.8, 7.3 Hz, 1H, H5'), 1.18 (dt, J = 25.1, 7.0 Hz, 6H, H1), 0.77 (t, J = 7.3 Hz, 3H, H6) ppm; ^31P NMR (126 MHz, CDCl_3): δ = 144.5 (d, J_CP = 7.8 Hz, C7), 128.4 (C9), 127.7 (C8), 126.5 (C10), 61.4 (dd, J_CP = 18.6, 6.0 Hz, C2), 42.0 (d, J_CP = 2.9 Hz, C4), 33.0 (d, J_CP = 139.0 Hz, C3), 30.9 (d, J_CP = 12.5 Hz, C5), 16.4 (dd, J_CP = 6.0, 2.5 Hz, C1), 11.9 (C6) ppm; ^31P NMR (162 MHz, CDCl_3): δ = 30.57 ppm; IR (ATR): ν = 3479 (b), 3063 (w), 3029 (w), 2973 (w), 2932 (w), 2875 (w), 2301 (w), 1643 (b), 1604 (w), 1495 (w), 1455 (w), 1392 (w), 1368 (w), 1292 (w), 1241 (m), 1163 (w), 1098 (w), 1054 (s), 1023 (s), 955 (s), 872 (w), 853 (w), 803 (m), 756 (m), 699 (s) cm⁻¹; HR-ESI-MS: m/z: 293.1290 ([M+Na]^+), calcd. for C_{16}H_{25}NaO_3P^+: 293.1277, 563.2670 ([M_2+Na]^+), calcd. for C_{28}H_{46}NaO_6P_2^+: 563.2662; analytical data in agreement with literature.^[1]

Diethyl (R/S)-(2-(2-fluorophenyl)propyl)phosphonate ((R/S)-31):

According to general procedure C, hydrogenation of E-16 (27.2 mg, 0.10 mmol) afforded (+)-31 as colourless oil (27.4 mg, 0.100 mmol, quant, e.r. = 94:06); hydrogenation of Z-16 (27.2 mg, 0.10 mmol) afforded (-)-31 as colourless oil (26.9 mg, 0.098 mmol, 98%, e.r. > 01:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (99/1, 1.0 mL/min) as the eluent with detection at 254 nm.

30
Hydrogenation of **E-16**: $t_e = 10.60$ min (minor enantiomer), 11.65 min (major enantiomer); **ODR** (CHCl$_3$, c 1.0): $[\alpha]^{26}_D = +18.4^\circ$; hydrogenation of **Z-16**: $t_e = 10.37$ min (only enantiomer); **ODR** (CHCl$_3$, c 1.0): $[\alpha]^{26}_D = -15.0^\circ$.

$^1$H NMR (500 MHz, CDC$_3$): $\delta = 7.22$ (td, $J = 7.6, 1.8$ Hz, 1H, H9), 7.17 (dddd, $J = 8.2, 7.1, 5.2, 1.7$ Hz, 1H, H9), 7.07 (td, $J = 7.5, 1.3$ Hz, 1H, H10), 6.99 (dddd, $J = 10.8, 8.1, 1.2$ Hz, 1H, H8), 4.05 - 3.90 (m, 4H, H2), 3.46 (dq, $J = 11.5, 7.0$ Hz, 1H, H4), 2.19 (dddd, $J = 18.3, 15.3, 6.6$ Hz, 1H, H3), 2.06 (dddd, $J = 18.0, 15.3, 7.7$ Hz, 1H, H3'), 1.40 (d, $J = 7.0$ Hz, 3H, H5), 1.22 (td, $J = 7.0, 2.6$ Hz, 6H, H1) ppm; $^{13}$C NMR (126 MHz, CDC$_3$): $\delta = 160.8$ (d, $J_{CP} = 245.6$ Hz, C7), 133.1 (dd, $J_{CP} = 13.8, 11.4$ Hz, C6), 128.5 (d, $J_{CP} = 5.2$ Hz, C11), 128.0 (d, $J_{CP} = 8.4$ Hz, C9), 124.3 (d, $J_{CP} = 3.5$ Hz, C10), 115.7 (d, $J_{CP} = 22.5$ Hz, C8), 61.5 (dd, $J_{CP} = 9.0, 6.4$ Hz, C2), 32.8 (d, $J_{CP} = 139.3$ Hz, C3), 29.2 (dd, $J_{CP} = 3.6, J_{CP} = 1.9$ Hz, C4), 22.1 (dd, $J_{CP} = 9.8, J_{CP} = 1.4$ Hz, C5), 16.4 (dd, $J_{CP} = 6.2, 1.6$ Hz, C1) ppm; $^{19}$F NMR (282 MHz, CDC$_3$): $\delta = -117.98$ ppm; $^{31}$P NMR (202 MHz, CDC$_3$): $\delta = 29.86$ ppm; IR (ATR): $\nu = 3478$ (b), 2981 (w), 2934 (w), 1717 (w), 1616 (w), 1584 (w), 1492 (m), 1453 (w), 1392 (w), 1368 (w), 1230 (m), 1052 (s), 1022 (s), 957 (s), 854 (w), 823 (m), 805 (w), 755 (s) cm$^{-1}$; HR-ESI-MS: $m/z$: 297.1026 (calcd. for C$^{13}$H$_{26}$FNaO$_3$P$: 297.1026$), 571.2185 ([M+Na]$^+$, calcd. for C$_{26}$H$_{40}$F$_2$NaO$_6$P$_2$: 571.2160).

Diethyl (R/S)-(2-(2-toly)propyl)phosphonate ((R/S)-32):

According to general procedure C, hydrogenation of **E-15** (26.8 mg, 0.10 mmol) afforded (+)-32 as colourless oil (25.2 mg, 0.093 mmol, 93%, e.r. = 93:07); hydrogenation of **Z-15** (26.8 mg, 0.10 mmol) afforded (-)-32 as colourless oil (24.6 mg, 0.091 mmol, 91%, e.r. > 0:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (98/2, 1.0 mL/min) as the eluent with detection at 210 nm.

Hydrogenation of **E-15**: $t_e = 9.55$ min (minor enantiomer), 18.32 min (major enantiomer); **ODR** (CHCl$_3$, c 1.0): $[\alpha]^{27}_D = +13.9^\circ$; hydrogenation of **Z-15**: $t_e = 9.58$ min (only enantiomer); **ODR** (CHCl$_3$, c 1.0): $[\alpha]^{27}_D = -15.7^\circ$.

$^1$H NMR (500 MHz, CDC$_3$): $\delta = 7.21 - 7.15$ (m, 2H, H10, H11), 7.12 (dd, $J = 7.4, 1.4$ Hz, 1H, H8), 7.08 (dddd, $J = 7.8, 6.1, 2.1$ Hz, 1H, H9), 4.07 - 3.86 (m, 4H, H2), 3.55 - 3.43 (m, 1H, H4), 2.37 (s, 3H, H12), 2.19 - 1.98 (m, 2H, H3), 1.35 (d, $J = 6.7$ Hz, 3H, H5), 1.23 (dt, $J = 13.3, 6.6$ Hz, 6H, H1) ppm; $^{13}$C NMR (126 MHz, CDC$_3$): $\delta = 145.0$ (d, $J_{CP} = 10.0$ Hz, C6), 135.1 (C7), 130.5 (C8), 126.4 (C10), 126.1 (C9), 125.3 (C11), 61.5 (d, $J_{CP} = 16.2$ Hz, C2), 34.1 (d, $J_{CP} = 136.7$ Hz, C3), 29.5 (C4), 23.0 (d, $J_{CP} = 6.4$ Hz, C5), 19.6 (C12), 16.5 (d, $J_{CP} = 3.0$ Hz, C1) ppm; $^{31}$P NMR (162 MHz, CDC$_3$): $\delta = 30.58$ ppm; IR (ATR): $\nu = 3476$ (b), 2974 (w), 2929 (w), 1651 (b), 1605 (w), 1491 (w), 1456 (w), 1392 (w), 1287 (w), 1231 (m), 1163 (w), 1097 (w), 1050 (s), 1022 (s), 955 (s), 854 (w), 831 (w), 810 (w), 758 (s), 727 (m) cm$^{-1}$; HR-ESI-MS: $m/z$: 31.
Diethyl (R/S)-(2-(2-chlorophenyl)propyl)phosphonate ((R/S)-33):

According to general procedure C, hydrogenation of E-17 (28.9 mg, 0.10 mmol) afforded (+)-33 as colourless oil (27.5 mg, 0.095 mmol, 95%, e.r. = 96:04); hydrogenation of Z-17 (28.9 mg, 0.10 mmol) afforded (-)-33 as colourless oil (27.5 mg, 0.095 mmol, 95%, e.r. > 01:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (97/3, 1.0 mL/min) as the eluent with detection at 230 nm.

Hydrogenation of E-17: \( t_e = 8.53 \text{ min} \) (minor enantiomer), 13.40 min (major enantiomer); ODR (CHCl\(_3\), c 1.0): \( [\alpha]_{D}^{27} = +0.2^\circ \); hydrogenation of Z-17: \( t_e = 8.41 \text{ min} \) (major enantiomer), 13.82 min (minor enantiomer); ODR (CHCl\(_3\), c 1.0): \( [\alpha]_{D}^{27} = -0.7^\circ \).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.33 \) (dd, \( J = 7.9, 1.3 \text{ Hz} \), 1H, H8), 7.26 (dd, \( J = 7.8, 1.9 \text{ Hz} \), 1H, H11), 7.22 (ddd, \( J = 7.5, 6.9, 1.3 \text{ Hz} \), 1H, H10), 7.13 (ddd, \( J = 8.0, 7.1, 1.9 \text{ Hz} \), 1H, H9), 4.08 - 3.96 (m, 4H, H2), 3.77 - 3.67 (m, 1H, H4), 2.17 (dd, \( J = 18.7, 15.4, 5.5 \text{ Hz} \), 1H, H3), 2.00 (ddd, \( J = 17.9, 15.3, 8.6 \text{ Hz} \), 1H, H3′), 1.39 (d, \( J = 7.0 \text{ Hz} \), 3H, H5), 1.25 (dt, \( J = 15.9, 7.0 \text{ Hz} \), 6H, H1) ppm; \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \( \delta = 143.8 \) (d, \( J_{CP} = 13.2 \text{ Hz} \), C6), 133.3 (C7), 129.8 (C8), 127.6 (C9), 127.5 (C11), 127.2 (C10), 61.6 (dd, \( J_{CP} = 16.0, 6.5 \text{ Hz} \), C2), 33.0 (d, \( J_{CP} = 139.0 \text{ Hz} \), C3), 30.9 (d, \( J_{CP} = 3.1 \text{ Hz} \), C4), 21.9 (d, \( J_{CP} = 7.5 \text{ Hz} \), C5), 16.5 (t, \( J_{CP} = 6.4 \text{ Hz} \), C1) ppm; \(^{31}\)P NMR (202 MHz, CDCl\(_3\)): \( \delta = 29.62 \) ppm; IR (ATR): \( \nu = 3474 \) (b), 2980 (w), 2934 (w), 2907 (w), 1640 (b), 1572 (w), 1476 (w), 1442 (w), 1392 (w), 1368 (w), 1281 (w), 1246 (m), 1163 (w), 1127 (w), 1098 (w), 1022 (s), 956 (s), 833 (w), 787 (m), 753 (s), 731 (w), 684 (m), 674 (w) cm\(^{-1}\);

HR-ESI-MS: \( m/z: 313.0741 \) ([M+Na]\(^+\), calcd. for C\(_{13}\)H\(_{26}\)ClNaO\(_{3}\)P\(^\cdot\): 313.0731), 603.1588 ([M\(_2\)+Na]\(^+\), calcd. for C\(_{26}\)H\(_{46}\)ClNaO\(_{6}\)P\(_2\): 603.1577).

Diethyl (R/S)-(2-(2-bromophenyl)propyl)phosphonate ((R/S)-34):

According to general procedure C, hydrogenation of E-18 (33.3 mg, 0.10 mmol) afforded (-)-34 as colourless oil (31.5 mg, 0.094 mmol, 94%, e.r. = 96:04); hydrogenation of Z-18 (33.3 mg, 0.10 mmol) afforded (+)-34 as colourless oil (31.5 mg, 0.089 mmol, 89%, e.r. > 01:99). The enantiomeric ratios were determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and n-hexane/i-propanol (95/5, 1.0 mL/min) as the eluent with detection at 230 nm.
Hydrogenation of **E-18**: \( t_r = 6.89 \text{ min (minor enantiomer), } 13.57 \text{ min (major enantiomer)} \); **ODR** (CHCl3, c 1.0): \( [\alpha]_D^{28} = -5.3^\circ \); hydrogenation of **Z-18**: \( t_r = 6.93 \text{ min (only enantiomer)} \); **ODR** (CHCl3, c 1.0): \( [\alpha]_D^{20} = +5.4^\circ \).

1H NMR (500 MHz, CDCl3): \( \delta = 7.52 \) (dd, \( J = 8.0, 1.2 \text{ Hz, 1H, H8} \)), 7.29 - 7.26 (m, 2H, H10), 7.24 (dd, \( J = 7.8, 2.2 \text{ Hz, 1H, H11} \)), 7.05 (ddd, \( J = 8.0, 6.8, 2.2 \text{ Hz, 1H, H9} \)), 4.08 - 3.98 (m, 4H, H2), 3.70 (ddd, \( J = 12.3, 8.8, 7.0, 5.4 \text{ Hz, 1H, H4} \)), 2.16 (ddd, \( J = 18.8, 15.3, 5.4 \text{ Hz, 1H, H3} \)), 1.99 (ddd, \( J = 17.8, 15.3, 8.7 \text{ Hz, 1H, H3'} \)), 1.38 (d, \( J = 6.9 \text{ Hz, 3H, H5} \)), 1.26 (dt, \( J = 13.6, 6.2 \text{ Hz, 2H, H2} \)), 3.20 (tq, \( J = 3.98, 4.5 \text{ Hz, 6H, H1} \)).

**Diisopropyl (R/S)-(2-phenylpropyl)phosphonate ([(R/S)-35]:**

According to **general procedure C**, hydrogenation of **E-10** (2802 mg, 0.10 mmol) afforded **(+)-35** as colourless oil (28.5 mg, 0.10 mmol, quant.); hydrogenation of **Z-10** (28.2 mg, 0.10 mmol) afforded **(-)-35** as colourless oil (28.5 mg, 0.10 mmol, quant.). The enantiomeric ratios could not be determined by HPLC analysis due to decomposition of the products during the analysis.

Hydrogenation of **E-10**: **ODR** (CHCl3, c 1.0): \( [\alpha]_D^{28} = +17.5^\circ \).

Hydrogenation of **Z-10**: **ODR** (CHCl3, c 1.0): \( [\alpha]_D^{27} = -20.0^\circ \).

1H NMR (500 MHz, CDCl3): \( \delta = 7.31 - 7.27 \) (m, 2H, H8), 7.23 - 7.17 (m, 3H, H7, H9), 4.64 (tq, \( J = 13.6, 9.8, 6.2 \text{ Hz, 2H, H2} \)), 3.20 (tq, \( J = 14.1, 7.1 \text{ Hz, 1H, H4} \)), 2.12 - 1.94 (m, 2H, H3), 1.39 (d, \( J = 7.0 \text{ Hz, 3H, H5} \)), 1.28 (dd, \( J = 6.1, 4.5 \text{ Hz, 6H, H1} \)), 1.23 (dd, \( J = 17.8, 6.1 \text{ Hz, 6H, H1'} \)) ppm; 13C NMR (126 MHz, CDCl3): \( \delta = 147.2 \) (d, \( J_{CP} = 12.9 \text{ Hz, C6} \)), 128.6 (C8), 126.8 (C7), 126.4 (C9), 70.0 (dd, \( J_{CP} = 10.0, 6.2 \text{ Hz, C2} \)), 35.8 (d, \( J_{CP} = 139.5 \text{ Hz, C3} \)), 35.0 (d, \( J_{CP} = 3.4 \text{ Hz, C4} \)), 24.1 (dd, \( J_{CP} = 14.5, 6.9, 3.9 \text{ Hz, C1} \)), 23.5 (d, \( J_{CP} = 8.0 \text{ Hz, C5} \)) ppm; 31P NMR (162 MHz, CDCl3): \( \delta = 28.23 \) ppm; IR (ATR): \( \tilde{\nu} = 3454 \text{ (b), 3029 (w), 2978 (w), 2934 (w), 2876 (w), 1495 (w) 1455 (w), 1385 (w), 1374 (w), 1245 (m), 1226 (m), 1177 (w), 1141 (w), 1107 (m), 1005 (s), 974 (s), 896 (m), 886 (m), 805 (w), 760 (m), 699 (s) cm}^{-1}; HR-ESI-MS: \( m/z: 307.1449 [(M+Na)^+] \), calcd. for C15H20NaO3P^+: 307.1434), 591.2989 [(M+Na)^+] \), calcd. for C36H50NaO6P2^+: 591.2975).
“One-pot” Isomerisation and Hydrogenation of Vinylphosphonate E-1

*E-vinylphosphonate  E-1* (25.4 mg, 0.10 mmol, 1.00 eq.) and anthracene (0.9 mg, 0.005 mmol, 5 mol%) were dissolved in acetonitrile (1.5 mL) and the solution was stirred under UV light irradiation at 365 nm at ambient temperature for 18 h. The solution was filtered through a syringe filter (PTFE, 0.2 µm), added to a vial and the solvent was evaporated. In a glovebox, a pre-stirred solution of Rh(COD)BF₄ (1.3 mg, 0.0032 mmol, 3.2 mol%) and (S₃C₃S₃)-WalPhos (2.3 mg, 0.0035 mmol, 3.5 mol%) in DCM (1 mL) was added and the vial was transferred to an autoclave. The autoclave was charged with H₂ (10 bar) and the solution was stirred at room temperature for 24 h. After carefully releasing the pressure and evaporation of the solvent, *n*-pentane (3 mL) was added and filtration through a glass microfiber filter with subsequent elution with *n*-pentane (2 x 2 mL) yielded the product (-)-19 as clear oil (22.3 mg, 0.087 mmol, 87%, e.r. = 07:93). The enantiomeric ratio was determined by HPLC analysis using a Daicel Chiralcel OJ-H (0.46 cm * 25 cm) column and *n*-hexane/i-propanol (98/2, 1.0 mL/min) as the eluent with detection at 210 nm: *t*ₘ = 11.63 min (major enantiomer), 13.67 min (minor enantiomer); ODR (CHCl₃, c 0.75): [α]₂⁰° = -12.5°.
Catalyst Screening for the \( E \rightarrow Z \) Isomerisation of Vinylphosphonates

Vinylphosphonate \( E-1 \) (25.4 mg, 0.10 mmol, 1.00 eq.) and the specified catalyst (0.005 mmol, 5 mol%) were dissolved in acetonitrile (1.5 mL) and the solution was stirred under UV or visible light irradiation at the given wavelength at ambient temperature for 18 h. After removal of the solvent, \( E-1 \) and \( Z-1 \) were isolated by column chromatography (SiO\(_2\), ethyl acetate). Yields were determined by mass recovery; \( Z:E \) ratios were determined by integration of peaks in the \( ^{31}P \) NMR spectrum and confirmed by integration the olefinic proton peaks in the \( ^{1}H \) NMR spectrum of both isomers.

| entry | catalyst | irradiation wavelength/ nm | isolated yield/ % | \( Z:E \) ratio |
|-------|----------|----------------------------|-------------------|----------------|
| 1     | Ir(ppy)\(_3\) | 450                        | quant.            | 13:87          |
| 2     | (-)-riboflavin | 402                        | quant.            | 66:34          |
| 3     | benzil     | 402                        | 98                | 25:75          |
| 4     | thioxanthone | 402                        | 94                | 86:14          |
| 5     | benzophenone | 365                        | quant.            | 86:14          |
| 6     | anthracene | 365                        | quant.            | 92:08          |

Table S1: Catalyst screening for the \( E \rightarrow Z \) isomerisation of vinylphosphonates.

Reaction Optimisation for the \( E \rightarrow Z \) Isomerisation of Vinylphosphonates

Vinylphosphonate \( E-1 \) (25.4 mg, 0.10 mmol, 1.00 eq.) and anthracene (0.9 mg, 0.005 mmol, 5 mol%) were dissolved in the specified solvent (1.5 mL) and the solution was stirred under UV light irradiation at 365 nm at ambient temperature. After removal of the solvent, \( E-1 \) and \( Z-1 \) were isolated by column chromatography (SiO\(_2\), ethyl acetate). Yields were determined by mass recovery; \( Z:E \) ratios were determined by integration of peaks in the \( ^{31}P \) NMR spectrum and confirmed by integration the olefinic proton peaks in the \( ^{1}H \) NMR spectrum of both isomers.

| entry | solvent     | irradiation time/ h | atmosphere | isolated yield/ % | \( Z:E \) ratio |
|-------|-------------|---------------------|------------|-------------------|----------------|
| 1     | acetonitrile | 18                  | air        | quant.            | 92:08          |
| 2     | cyclohexane  | 18                  | air        | quant.            | 38:62          |
| 3\(^a\) | dichloromethane | 18                | air        | n.d.              | 84:16          |
| 4     | toluene     | 18                  | air        | quant.            | 68:32          |
| 5     | acetonitrile | 3                   | air        | 98                | 66:34          |
| 6\(^a\) | acetonitrile | 24                  | air        | n.d.              | 90:10          |
| 7     | acetonitrile | 18                  | oxygen     | 94                | 83:17          |
| 8     | acetonitrile | 18                  | argon      | 84                | 91:09          |

\(^a\) \( Z:E \) ratio determined from crude reaction mixture.
Control Experiments for the $E \rightarrow Z$ Isomerisation of Vinylphosphonates

According to general procedure B, control experiments with vinylphosphonate $E$-1 (25.4 mg, 0.10 mmol, 1.00 eq.) and anthracene (0.9 mg, 0.005 mmol, 5 mol%) were performed in the dark, without catalyst, and in the dark without catalyst. $E$-1 and $Z$-1 were isolated by column chromatography (SiO$_2$, ethyl acetate). Yields were determined by mass recovery; $Z:E$ ratios were determined by integration of peaks in the $^{31}$P NMR spectrum and confirmed by integration the olefinic proton peaks in the $^1$H NMR spectrum of both isomers.

Table S3: Control experiments for the $E \rightarrow Z$ isomerisation of vinylphosphonates.

| entry | catalyst   | irradiation wavelength/ nm | isolated yield/ % | $Z:E$ ratio |
|-------|------------|----------------------------|-------------------|-------------|
| 1     | anthracene | -                          | 96                | 0:100       |
| 2     | -          | 365                        | quant.            | 02:98       |
| 3     | -          | -                          | quant.            | 01:100      |

Verification of the Photostationary State

According to general procedure B, control experiments with vinylphosphonates $E$- and $Z$-4 (33.3 mg, 0.10 mmol, 1.00 eq.) and anthracene (0.9 mg, 0.005 mmol, 5 mol%) were performed. $E$-4 and $Z$-4 were isolated by column chromatography (SiO$_2$, ethyl acetate). Yields were determined by mass recovery; $Z:E$ ratios were determined by integration of peaks in the $^{31}$P NMR spectrum and confirmed by integration the olefinic proton peaks in the $^1$H NMR spectrum of both isomers.

Table S4: Isomerisation of vinylphosphonates $E$- and $Z$-4.

| entry | starting geometry | isolated yield/ % | $Z:E$ ratio |
|-------|-------------------|-------------------|-------------|
| 1     | $E$ only          | 87                | 89:11       |
| 2     | $Z$ only          | 85                | 90:10       |
| 3     | $E:Z$ 1:1         | 85                | 90:10       |

The $Z:E$ ratios resulting from exposure of vinylphosphonate $Z$-4 or a 1:1 mixture of $E$- and $Z$-4 to the standard isomerisation conditions verify that the obtained $Z:E$ ratios represent photostationary state compositions.
Diethyl (2-phenylpropyl)phosphonate (19):

HPLC trace: racemic sample: 19

| Peak RetTime Type Width Area Height Area |
|-----------------|---------------|---------|---------|----------|
| 1 13.496 MM 0.3417 6897.60693 336.47971 49.9193 |
| 2 14.711 MM 0.3816 6919.90283 302.26364 50.0807 |

HPLC trace: Hydrogenation of the E-isomer: (+)-19

| Peak RetTime Type Width Area Height Area |
|-----------------|---------------|---------|---------|----------|
| 1 13.048 MM 0.3221 509.63739 26.37405 3.1766 |
| 2 14.026 MM 0.3756 1.55338e4 869.20227 96.8234 |

HPLC trace: Hydrogenation of the Z-isomer: (-)-19

| Peak RetTime Type Width Area Height Area |
|-----------------|---------------|---------|---------|----------|
| 1 12.655 MM 0.3376 1.31582e4 649.64325 98.7821 |
| 2 14.160 MM 0.3987 162.23425 6.95633 1.2179 |
Hydrogenation on a 1.0 mmol scale

Diethyl (2-phenylpropyl)phosphonate (19):

HPLC trace: Hydrogenation of the E-isomer: (+)-19

HPLC trace: Hydrogenation of the Z-isomer: (-)-19
Hydrogenation using the opposite catalyst enantiomer

Diethyl (2-phenylpropyl)phosphonate (19):

HPLC trace: Hydrogenation of the E-isomer using $(R_c,R_p)$-Walphos: $(-)$-19

HPLC trace: Hydrogenation of the Z-isomer using $(R_c,R_p)$-Walphos: $(+)$-19

One-pot Isomerisation and Hydrogenation: Diethyl (2-phenylpropyl)phosphonate: $(-)$-19
Diethyl (2-(4-fluorophenyl)propyl)phosphonate (20):

HPLC trace: racemic sample: 20

| Peak RetTime | Type  | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|--------------|-------|-------------|--------------|-------------|---------|
| 1            | BV    | 0.3389      | 1.21530e4    | 574.19360   | 49.8414 |
| 2            | VB    | 0.3754      | 1.22303e4    | 521.84021   | 50.1596 |

HPLC trace: Hydrogenation of the E-isomer: (+)-20

| Peak RetTime | Type  | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|--------------|-------|-------------|--------------|-------------|---------|
| 1            | MM    | 0.2847      | 319.60501    | 18.71310    | 2.9325  |
| 2            | MM    | 0.3185      | 1.05790e4    | 553.56372   | 97.0675 |

HPLC trace: Hydrogenation of the Z-isomer: (-)-20

| Peak RetTime | Type  | Width [min] | Area [mAU*s] | Height [mAU] | Area [%] |
|--------------|-------|-------------|--------------|-------------|---------|
| 1            | MM    | 0.2816      | 3824.58062   | 226.37099   | 98.0286 |
| 2            | MM    | 0.3099      | 76.91286     | 4.13630     | 1.9714  |
Diethyl (2-(4-chlorophenyl)propyl)phosphonate (21):

HPLC trace: racemic sample: 21

HPLC trace: Hydrogenation of the $E$-isomer: (+)-21

HPLC trace: Hydrogenation of the $Z$-isomer: (-)-21
Diethyl (2-(4-bromophenyl)propyl)phosphonate (22):

HPLC trace: racemic sample: 22

HPLC trace: Hydrogenation of the E-isomer: (+)-22

HPLC trace: Hydrogenation of the Z-isomer: (-)-22
Diethyl (2-(4-(trifluoromethyl)phenyl)propyl)phosphonate (23):

HPLC trace: racemic sample: 23

HPLC trace: Hydrogenation of the E-isomer: (+)-23

HPLC trace: Hydrogenation of the Z-isomer: (-)-23
Diethyl (2-(4-tolyl)propyl)phosphonate (24):

HPLC trace: racemic sample: 24

HPLC trace: Hydrogenation of the E-isomer: (+)-24

HPLC trace: Hydrogenation of the Z-isomer: (-)-24
Diethyl (2-(4-(tert-buty1)phenyl)propyl)phosphonate (25):

HPLC trace: racemic sample: 25

| Peak | RetTime | Type | Width | Area   | Height | Area   | %    |
|------|---------|------|-------|--------|--------|--------|------|
| 1    | 9.011   | MM   | 0.2368| 403.48837 | 28.39643 | 53.0753 |      |
| 2    | 9.915   | MM   | 0.2674| 356.73038 | 22.23635 | 46.9247 |      |

HPLC trace: Hydrogenation of the E-isomer: (+)-25

| Peak | RetTime | Type | Width | Area   | Height | Area   | %    |
|------|---------|------|-------|--------|--------|--------|------|
| 1    | 8.988   | MM   | 0.2443| 1200.03809 | 81.88293 | 96.9341 |      |
| 2    | 9.914   | MM   | 0.2735| 37.95551 | 2.31282 | 3.0659  |      |

HPLC trace: Hydrogenation of the Z-isomer: (-)-25

| Peak | RetTime | Type | Width | Area   | Height | Area   | %    |
|------|---------|------|-------|--------|--------|--------|------|
| 1    | 8.982   | MM   | 0.2215| 17.72525 | 1.33403 | 1.2919  |      |
| 2    | 9.865   | MM   | 0.2725| 1354.33411 | 82.84174 | 98.7081 |      |
Diethyl (2-(3-bromophenyl)propyl)phosphonate (26):

HPLC trace: racemic sample: 26

HPLC trace: Hydrogenation of the E-isomer: (+)-26

HPLC trace: Hydrogenation of the Z-isomer: (-)-26
Dimethyl (2-phenylpropyl)phosphonate (27):

HPLC trace: racemic sample: 27

HPLC trace: Hydrogenation of the E-isomer: (+)-27

HPLC trace: Hydrogenation of the Z-isomer: (-)-27
Diethyl (2-(4-methoxyphenyl)propyl)phosphonate (28):

HPLC trace: racemic sample: 28

HPLC trace: Hydrogenation of the E-isomer: (+)-28

HPLC trace: Hydrogenation of the Z-isomer: (-)-28
Diethyl (2-(naphthalen-2-yl)propyl)phosphonate (29):

HPLC trace: racemic sample: 29

| Peak RetTime | Type | Width | Area     | Height   | Area     | %      |
|--------------|------|-------|----------|----------|----------|--------|
| 1            | 22.890 | MM    | 0.8326   | 3.00792e4 | 602.14160 | 49.5128 |
| 2            | 27.736 | MM    | 1.0973   | 3.06711e4 | 465.83661 | 50.4872 |

HPLC trace: Hydrogenation of the E-isomer: (+)-29

| Peak RetTime | Type | Width | Area     | Height   | Area     | %      |
|--------------|------|-------|----------|----------|----------|--------|
| 1            | 22.671 | MM    | 0.7617   | 912.96643 | 19.97685 | 3.2872 |
| 2            | 27.041 | MM    | 1.0793   | 2.63608e4 | 414.59750 | 96.7128 |

HPLC trace: Hydrogenation of the Z-isomer: (-)-29

| Peak RetTime | Type | Width | Area     | Height   | Area     | %      |
|--------------|------|-------|----------|----------|----------|--------|
| 1            | 22.617 | MM    | 0.8634   | 3.76070e4 | 725.96863 | 98.6563 |
| 2            | 27.741 | MM    | 1.0034   | 512.21191 | 8.50805  | 1.3437 |
Diethyl (2-phenylbutyl)phosphonate (30):

**HPLC trace: racemic sample:** 30

![HPLC trace image]

| Peak | RetTime | Type | Width | Area       | Height | Area [mAU] | %    |
|------|---------|------|-------|------------|--------|------------|------|
| 1    | 8.712   | MM   | 0.3349| 1.12395e4  | 559.31256 | 49.6190    |      |
| 2    | 10.582  | MM   | 0.4046| 1.14121e4  | 469.85471 | 50.3810    |      |

**HPLC trace: Hydrogenation of the E-isomer:** (+)-30

![HPLC trace image]

| Peak | RetTime | Type | Width | Area       | Height | Area [mAU] | %    |
|------|---------|------|-------|------------|--------|------------|------|
| 1    | 8.096   | MM   | 0.2614| 609.73364  | 38.87682 | 3.2227     |      |
| 2    | 9.676   | MM   | 0.3516| 1.83101e4  | 867.93365 | 96.7773    |      |

**HPLC trace: Hydrogenation of the Z-isomer:** (-)-30

![HPLC trace image]

| Peak | RetTime | Type | Width | Area       | Height | Area [mAU] | %    |
|------|---------|------|-------|------------|--------|------------|------|
| 1    | 8.030   | MM   | 0.2790| 2.31342e4  | 1382.21948| 99.2520    |      |
| 2    | 9.752   | MM   | 0.4057| 174.35568  | 7.16207 | 0.7480     |      |
Diethyl (2-(2-fluorophenyl)propyl)phosphonate (31):

HPLC trace: racemic sample: 31

HPLC trace: Hydrogenation of the E-isomer: (++)-31

HPLC trace: Hydrogenation of the Z-isomer: (--)-31
Diethyl (2-(2-tolyl)propyl)phosphonate (32):

HPLC trace: racemic sample: 32

HPLC trace: Hydrogenation of the E-isomer: (+)-32

HPLC trace: Hydrogenation of the Z-isomer: (-)-32
Diethyl (2-(2-chlorophenyl)propyl)phosphonate (33):

**HPLC trace: racemic sample: 33**

```
Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*s] [mAU] %
-- ---------- -- ---------- ---------- ----------
1 8.439 MM 0.2491 3950.54126 264.32837 50.0810
2 13.787 MM 0.5487 3937.76099 119.61113 49.9190
```

**HPLC trace: Hydrogenation of the E-isomer: (+)-33**

```
Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*s] [mAU] %
-- ---------- -- ---------- ---------- ----------
1 8.526 MM 0.2438 126.09103 8.61867 3.8181
2 13.396 MM 0.5858 3176.38135 90.37035 96.1819
```

**HPLC trace: Hydrogenation of the Z-isomer: (-)-33**

```
Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*s] [mAU] %
-- ---------- -- ---------- ---------- ----------
1 8.407 MM 0.2599 2563.59082 164.41252 95.5924
2 13.892 MM 0.5108 10.49185 3.42362e-1 0.4076
```
Diethyl (2-(2-bromophenyl)propyl)phosphonate (34):

HPLC trace: racemic sample: 34

HPLC trace: Hydrogenation of the E-isomer: (-)-34

HPLC trace: Hydrogenation of the Z-isomer: (+)-34
NMR Spectra of Key Compounds

$^1$H NMR (600 MHz, CDCl$_3$): \textit{E-1}

$^{13}$C NMR (151 MHz, CDCl$_3$): \textit{E-1}
$^{31}$P NMR (162 MHz, CDCl$_3$): $E$-1

$^1$H NMR (500 MHz, CDCl$_3$): $E$-2
$^{13}$C NMR (126 MHz, CDCl$_3$): $E$-2

$^{19}$F NMR (470 MHz, CDCl$_3$): $E$-2
$^{31}$P NMR (202 MHz, CDCl$_3$): \textit{E-2}

$^{1}$H NMR (600 MHz, CDCl$_3$): \textit{E-3}
$^{13}$C NMR (126 MHz, CDCl$_3$): **E-3**

$^{31}$P NMR (202 MHz, CDCl$_3$): **E-3**
$^1$H NMR (500 MHz, CDCl$_3$): $E$-4

$^{13}$C NMR (126 MHz, CDCl$_3$): $E$-4
\(^{31}\text{P NMR (202 MHz, CDCl}_3\): E-4

\[^1\text{H NMR (500 MHz, CDCl}_3\): E-5\]
$^{13}$C NMR (126 MHz, CDCl$_3$): E-5

$^{19}$F NMR (470 MHz, CDCl$_3$): E-5
$^{31}$P NMR (202 MHz, CDCl$_3$): $E$-5

$^1$H NMR (500 MHz, CDCl$_3$): $E$-6
$^{13}$C NMR (126 MHz, CDCl$_3$): $E$-6

$^{31}$P NMR (162 MHz, CDCl$_3$): $E$-6
$^1$H NMR (500 MHz, CDCl$_3$): $E$-7

$^{13}$C NMR (126 MHz, CDCl$_3$): $E$-7
$^{31}$P NMR (202 MHz, CDCl$_3$): $E$-7

$^1$H NMR (600 MHz, CDCl$_3$): $E$-8
$^{13}$C NMR (151 MHz, CDCl$_3$): E-8

$^{31}$P NMR (243 MHz, CDCl$_3$): E-8
$^1$H NMR (600 MHz, CDCl$_3$): $E$-9

$^{13}$C NMR (151 MHz, CDCl$_3$): $E$-9
$^{31}$P NMR (162 MHz, CDCl$_3$): $E$-9

$^1$H NMR (500 MHz, CDCl$_3$): $E$-10
$^{13}$C NMR (126 MHz, CDCl$_3$): **E-10**

$^{31}$P NMR (202 MHz, CDCl$_3$): **E-10**
$^1$H NMR (600 MHz, CDCl$_3$): **E-11**

![H NMR spectrum of E-11](image)

$^{13}$C NMR (151 MHz, CDCl$_3$): **E-11**

![C NMR spectrum of E-11](image)
$^{31}$P NMR (243 MHz, CDCl$_3$): \textbf{E-11}

$^1$H NMR (500 MHz, CDCl$_3$): \textbf{E-12}
$^{13}$C NMR (126 MHz, CDCl$_3$): \textbf{E-12}

$^{31}$P NMR (121 MHz, CDCl$_3$): \textbf{E-12}
$^1$H NMR (500 MHz, CDCl$_3$): E-13

$^{13}$C NMR (126 MHz, CDCl$_3$): E-13
$^{31}$P NMR (202 MHz, CDCl$_3$): **E-13**

$^1$H NMR (500 MHz, CDCl$_3$): **E-14**
$^{13}$C NMR (126 MHz, CDCl$_3$): **E-14**

$^{31}$P NMR (202 MHz, CDCl$_3$): **E-14**
$^1$H NMR (600 MHz, CDCl$_3$): \textit{E-15}

$^{13}$C NMR (151 MHz, CDCl$_3$): \textit{E-15}
$^{31}\text{P NMR (121 MHz, CDCl}_3\text{): E-15}$

$^{1}\text{H NMR (600 MHz, CDCl}_3\text{): E-16}$
$^{13}$C NMR (151 MHz, CDCl$_3$): \textbf{E-16}

$^{19}$F NMR (564 MHz, CDCl$_3$): \textbf{E-16}
$^{31}$P NMR (243 MHz, CDCl$_3$): $E$-16

$^1$H NMR (600 MHz, CDCl$_3$): $E$-17
$^{13}$C NMR (151 MHz, CDCl$_3$): **E-17**

$^{31}$P NMR (243 MHz, CDCl$_3$): **E-17**
$^1$H NMR (600 MHz, CDCl$_3$): $E$-18

$^{13}$C NMR (151 MHz, CDCl$_3$): $E$-18
$^{31}$P NMR (243 MHz, CDCl$_3$): **E-18**

$^1$H NMR (600 MHz, CDCl$_3$): **Z-1**
$^{13}$C NMR (151 MHz, CDCl$_3$): Z-1

$^{31}$P NMR (121 MHz, CDCl$_3$): Z-1
$^1$H NMR (500 MHz, CDCl$_3$): Z-2

$^{13}$C NMR (126 MHz, CDCl$_3$): Z-2
$^{19}$F NMR (470 MHz, CDCl$_3$): Z-2

$^{31}$P NMR (202 MHz, CDCl$_3$): Z-2
$^1$H NMR (500 MHz, CDCl$_3$): Z-3

$^{13}$C NMR (101 MHz, CDCl$_3$): Z-3
$^{31}$P NMR (202 MHz, CDCl$_3$): Z-3

$^1$H NMR (600 MHz, CDCl$_3$): Z-4
$^{13}$C NMR (151 MHz, CDCl$_3$): Z-4

$^{31}$P NMR (243 MHz, CDCl$_3$): Z-4
$^{19}$F NMR (564 MHz, CDCl$_3$): Z-5

$^{31}$P NMR (243 MHz, CDCl$_3$): Z-5
$^1$H NMR (500 MHz, CDCl$_3$): Z-6

$^{13}$C NMR (126 MHz, CDCl$_3$): Z-6
$^{31}$P NMR (162 MHz, CDCl$_3$): \textbf{Z-6}

$^1$H NMR (600 MHz, CDCl$_3$): \textbf{Z-7}
$^{13}$C NMR (151 MHz, CDCl$_3$): Z-7

$^{31}$P NMR (243 MHz, CDCl$_3$): Z-7
$^1$H NMR (500 MHz, CDCl$_3$): Z-8

$^{13}$C NMR (126 MHz, CDCl$_3$): Z-8
$^{31}$P NMR (202 MHz, CDCl$_3$): Z-8

$^1$H NMR (600 MHz, CDCl$_3$): Z-9
$^{13}\text{C NMR (151 MHz, CDCl}_3\text{): Z-9}$

$^{31}\text{P NMR (162 MHz, CDCl}_3\text{): Z-9}$
$^1$H NMR (600 MHz, CDCl$_3$): Z-10

$^{13}$C NMR (151 MHz, CDCl$_3$): Z-10
$^{31}$P NMR (243 MHz, CDCl$_3$): Z-10

$^1$H NMR (300 MHz, CDCl$_3$): Z-11
$^{13}$C NMR (151 MHz, CDCl$_3$): Z-11

$^{31}$P NMR (121 MHz, CDCl$_3$): Z-11
$^1$H NMR (600 MHz, CDCl$_3$): Z-12

$^{13}$C NMR (151 MHz, CDCl$_3$): Z-12
$^{31}$P NMR (162 MHz, CDCl$_3$): Z-12

$^1$H NMR (600 MHz, CDCl$_3$): (E/Z)-13 (1:1)
$^{13}$C NMR (151 MHz, CDCl$_3$): (E/Z)-13 (1:1)

$^{31}$P NMR (162 MHz, CDCl$_3$): Z-13
$^1$H NMR (500 MHz, CDCl$_3$): **Z-14**

$^{13}$C NMR (126 MHz, CDCl$_3$): **Z-14**
$^{31}$P NMR (202 MHz, CDCl$_3$): Z-14

$^1$H NMR (600 MHz, CDCl$_3$): Z-15
$^{13}$C NMR (151 MHz, CDCl$_3$): Z-15

$^{31}$P NMR (121 MHz, CDCl$_3$): Z-15
$^1$H NMR (600 MHz, CDCl$_3$): Z-16

$^{13}$C NMR (151 MHz, CDCl$_3$): Z-16
$^{19}$F NMR (564 MHz, CDCl$_3$): Z-16

$^{31}$P NMR (121 MHz, CDCl$_3$): Z-16
$^1$H NMR (600 MHz, CDCl$_3$): Z-17

$^{13}$C NMR (151 MHz, CDCl$_3$): Z-17
$^{31}$P NMR (121 MHz, CDCl$_3$): **Z-17**

$^1$H NMR (500 MHz, CDCl$_3$): **Z-18**
$^{13}$C NMR (126 MHz, CDCl$_3$): Z-18

$^{31}$P NMR (243 MHz, CDCl$_3$): Z-18
$^1$H NMR (400 MHz, CDCl$_3$): 19

$^{13}$C NMR (101 MHz, CDCl$_3$): 19
$^{31}$P NMR (162 MHz, CDCl$_3$): 19

$^1$H NMR (500 MHz, CDCl$_3$): 20
$^{13}$C NMR (126 MHz, CDCl$_3$): 20

$^{19}$F NMR (162 MHz, CDCl$_3$): 20
$^{31}$P NMR (162 MHz, CDCl$_3$): 20

$^1$H NMR (500 MHz, CDCl$_3$): 21
$^{13}$C NMR (126 MHz, CDCl$_3$): 21

$^{31}$P NMR (162 MHz, CDCl$_3$): 21
$^1$H NMR (500 MHz, CDCl$_3$): 22

$^{13}$C NMR (126 MHz, CDCl$_3$): 22
$^{31}$P NMR (162 MHz, CDCl$_3$): 22

$^1$H NMR (500 MHz, CDCl$_3$): 23
$^{13}$C NMR (151 MHz, CDCl$_3$): 23

$^{19}$F NMR (564 MHz, CDCl$_3$): 23
$^{31}$P NMR (121 MHz, CDCl$_3$): 23

$^1$H NMR (500 MHz, CDCl$_3$): 24
$^{13}$C NMR (126 MHz, CDCl$_3$): 24

$^{31}$P NMR (202 MHz, CDCl$_3$): 24
$^1$H NMR (500 MHz, CDCl$_3$): 25

$^{13}$C NMR (126 MHz, CDCl$_3$): 25
$^{31}\text{P NMR (121 MHz, CDCl}_3\text{): 25}$

$^1\text{H NMR (500 MHz, CDCl}_3\text{): 26}$
$^{13}$C NMR (126 MHz, CDCl$_3$): 26

$^{31}$P NMR (202 MHz, CDCl$_3$): 26
$^1$H NMR (500 MHz, CDCl$_3$): 27

$^{13}$C NMR (126 MHz, CDCl$_3$): 27
$^{31}$P NMR (162 MHz, CDCl$_3$): 27

$^1$H NMR (400 MHz, CDCl$_3$): 28
$^{13}$C NMR (101 MHz, CDCl$_3$): 28

$^{31}$P NMR (162 MHz, CDCl$_3$): 28
$^1$H NMR (500 MHz, CDCl$_3$): 29

$^{13}$C NMR (126 MHz, CDCl$_3$): 29
$^{31}$P NMR (121 MHz, CDCl$_3$): 29

$^1$H NMR (400 MHz, CDCl$_3$): 30
$^{13}$C NMR (101 MHz, CDCl$_3$): 30

$^{31}$P NMR (121 MHz, CDCl$_3$): 30
$^1$H NMR (500 MHz, CDCl$_3$): 31

$^{13}$C NMR (126 MHz, CDCl$_3$): 31
$^{19}$F NMR (564 MHz, CDCl$_3$): 31

$^{31}$P NMR (162 MHz, CDCl$_3$): 31
$^1$H NMR (500 MHz, CDCl$_3$): 32

$^{13}$C NMR (126 MHz, CDCl$_3$): 32
$^{31}$P NMR (162 MHz, CDCl$_3$): 32

$^1$H NMR (500 MHz, CDCl$_3$): 33
$^{13}$C NMR (126 MHz, CDCl$_3$): 33

$^{31}$P NMR (162 MHz, CDCl$_3$): 33
$^1$H NMR (500 MHz, CDCl$_3$): 34

$^{13}$C NMR (126 MHz, CDCl$_3$): 34
$^{31}$P NMR (162 MHz, CDCl$_3$): 34
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