Enantioselective Construction of Allylic Phosphine Oxides through Substitution of Morita-Baylis-Hillman Carbonates with Phosphine Oxides

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General Methods:

Unless stated otherwise, all reactions were carried out in flame-dried glassware. All solvents were purified and dried according to standard methods prior to use. 4 Å molecular sieves were dried at 200 °C under vacuum for 12 h before usage. Morita-Baylis-Hillman carbonates 1 were prepared according to the literature. Catalysts 3a-3e, 3i were purchased from Aldrich Chemical Company. Cinchona alkaloids catalysts 3f, 3g, 3h, 3i were prepared according to the literature. Phosphine oxides were prepared according to the literature. 41H, 13C and 31P NMR spectra were recorded on a Varian instrument (300, 75 and 121 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for 1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet or unresolved, coupling constant(s) in Hz, integration). Data for 13C and 31P NMR are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a FT-IR spectrometer and only major peaks were reported in cm⁻¹. Optical rotations were reported as follows: [α]D^0 (c: g/100 mL, in solvent). Highresolution mass spectra (HRMS) were obtained by the ESI ionization sources. The ee value determination was carried out using chiral HPLC with Daicel Chiracel OD-H, or AD column on Waters with a 996 UV-detector.

Experimental Procedures and Characterizations:


To a solution of Morita-Baylis-Hillman carbonates 1 (0.40 mmol) in the presence of 20 mol % catalyst 3e and 4Å MS (100 mg) in xylene (4.0 mL) was added phosphine oxides 2 (0.20 mmol) and the resulting solution was stirred for 60 h at 0 °C. The reaction mixture was directly purified by silica gel chromatography without work-up and fractions were collected and concentrated in vacuo to provide the pure desired products.


To a solution of Morita-Baylis-Hillman carbonates 1 (0.10 mmol) in the presence of 20 mol % DABCO in xylene (1.0 mL) was added phosphine oxides 2 (0.10 mmol) and the resulting solution was stirred for 24 h at room temperature. The reaction mixture was directly purified by silica gel chromatography without work-up and fractions were collected and concentrated in vacuo to provide the pure desired products.

(R)-methyl 2-((diphenylphosphoryl)(phenyl)methyl)acrylate (4a)

\[ \text{4a} \]

was isolated by column chromatography using silica gel in 77% yield.

\[
\begin{align*}
{^1}\text{H NMR} (300 \text{ MHz, CDCl}_3): & \delta 7.88 (t, J = 9.0 \text{ Hz, 2H}), 7.49-7.16 (m, 13H), 6.82 (s, 1H), 6.43 (s, 1H), 5.06 (d, J = 8.4 \text{ Hz, 1H}), 3.61(s, 3H); \\
{^{13}}\text{C NMR} (75 \text{ MHz, CDCl}_3): & \delta 166.8 (J = 9.75 \text{ Hz}), 136.5 (J = 2.25 \text{ Hz}), 134.7(J = 5.25 \text{ Hz}), 132.9 (J = 6.75 \text{ Hz}), 131.7 (J = 2.25 \text{ Hz}), 131.5 (J = 3.0 \text{ Hz}), 131.4 (J = 3.0 \text{ Hz}), 131.2 (J = 9.0 \text{ Hz}), 131.0 (J = 9.0 \text{ Hz}), 130.4 (J = 6.0 \text{ Hz}), 130.1 (J = 6.0 \text{ Hz}), 128.6 (J = 11.25 \text{ Hz}), 128.3 (J = 1.5 \text{ Hz}), 128.1 (J = 12 \text{ Hz}), 127.2 (J = 1.5 \text{ Hz}), 52.3, 45.6 (J = 67.5 \text{ Hz}); \\
{^{31}}\text{P NMR}(121 \text{ MHz, CDCl}_3): & \delta 31.6; \\
\text{IR:} & 3058, 2226, 1718, 1438, 1241, 1187, 1125, 699 \text{ cm}^{-1}; \\
\text{HRMS (ESI)}: & \text{C}_{23}\text{H}_{21}\text{O}_{3}\text{P}+\text{H}, \text{Calc:} 377.1301, \text{Found:} 377.1309; \\
[\alpha]_D^{\text{p}} & = -224 (c = 1.11, \text{CHCl}_3); \\
\text{HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time:} & t_{\text{major}} = 7.8, t_{\text{minor}} = 11.3, 95\% \text{ ee.}
\end{align*}
\]
(S)-methyl 2-((diphenylphosphoryl)(2-fluorophenyl)methyl)acrylate (4b)

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\[CH_3O-\]
\[P-\]
\[\text{Ph} \rightarrow \text{Ph} \]
\[\text{F} \rightarrow \text{F} \]
\[\text{COOMe} \]
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4b was isolated by column chromatography using silica gel in 74% yield.

**^1H NMR** (300 MHz, CDCl\textsubscript{3}): \(\delta\) 7.92-7.85 (m, 3H), 7.56-7.09 (m, 10H), 6.82-6.78 (m, 2H), 6.49 (d, \(J = 2.4\) Hz, 1H), 5.53 (d, \(J = 8.7\) Hz, 1H), 3.61 (s, 3H);

**^13C NMR** (75 MHz, CDCl\textsubscript{3}): \(\delta\) 166.4 (\(J = 9.75\) Hz), 160.0 (\(J = 6.75\) Hz, \(J = 245.25\) Hz), 135.8 (\(J = 2.25\) Hz), 132.4, 131.8 (\(J = 3.0\) Hz), 131.6 (\(J = 3.0\) Hz), 131.4 (\(J = 1.5\) Hz, \(J = 4.5\) Hz), 131.3 (\(J = 13.5\) Hz), 131.2, 131.1, 130.8 (\(J = 9.0\) Hz), 128.9 (\(J = 2.25\) Hz, \(J = 8.25\) Hz), 128.5 (\(J = 12.0\) Hz), 128.0 (\(J = 11.25\) Hz), 124.2 (\(J = 2.25\) Hz, \(J = 3.75\) Hz), 122.2 (\(J = 4.5\) Hz, 14.25 Hz), 114.8 (\(J = 0.75\) Hz, 22.5 Hz), 52.3, 36.5 (\(J = 2.25\) Hz, \(J = 67.5\) Hz);

**^31P NMR** (121 MHz, CDCl\textsubscript{3}): \(\delta\) 31.3 (\(J = 2.78\) Hz);

**IR:** 3059, 2951, 1719, 1489, 1438, 1233, 1190, 1125, 728, 700, 521 cm\textsuperscript{-1}.

**HRMS (ESI):** C\textsubscript{23}H\textsubscript{20}FO\textsubscript{3}P+H, Calc: 395.1207, Found: 395.1212;

**\([\alpha]_D^{20}\) = -138 (c = 1.10, CHCl\textsubscript{3});**

**HPLC:** DAICEL CHIRALCEL AD, Hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: \(t_{\text{major}} = 14.8, t_{\text{minor}} = 27.1, 81%\) ee.

(S)-methyl 2-((2-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4c)

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\[CH_3O-\]
\[P-\]
\[\text{Ph} \rightarrow \text{Ph} \]
\[\text{Cl} \rightarrow \text{Cl} \]
\[\text{COOMe} \]
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4c was isolated by column chromatography using silica gel in 83% yield.

**^1H NMR** (300 MHz, CDCl\textsubscript{3}): \(\delta\) 8.05 (d, \(J = 7.8\) Hz, 1H), 7.91-7.85 (m, 2H), 7.56-7.09 (m, 11H), 6.69 (d, \(J = 2.4\) Hz, 1H), 6.49 (d, \(J = 2.4\) Hz, 1H), 5.72 (d, \(J = 9.0\) Hz, 1H), 3.57 (s, 3H);

**^13C NMR** (75 MHz, CDCl\textsubscript{3}): \(\delta\) 166.3 (\(J = 9.0\) Hz), 135.8 (\(J = 3.0\) Hz), 134.6 (\(J = 8.25\) Hz), 133.1 (\(J = 3.75\) Hz), 132.2 (\(J = 6.75\) Hz), 131.8 (\(J = 2.25\) Hz), 131.7 (\(J = 5.25\) Hz), 131.6 (\(J = 3.0\) Hz), 131.5, 131.4 (\(J = 3.0\) Hz), 131.0 (\(J = 9.0\) Hz), 130.9 (\(J = 4.5\) Hz), 129.2 (\(J = 0.75\) Hz), 128.5 (\(J = 2.25\) Hz), 128.4, 128.0 (\(J = 11.25\) Hz), 126.9 (\(J = 1.5\) Hz), 52.2, 41.1 (\(J = 66.75\) Hz);

**^31P NMR** (121 MHz, CDCl\textsubscript{3}): \(\delta\) 31.5;

**IR:** 3059, 2950, 1721, 1473, 1438, 1233, 1190, 1125, 728, 700, 521 cm\textsuperscript{-1}.

**HRMS (ESI):** C\textsubscript{23}H\textsubscript{20}ClO\textsubscript{3}P+H, Calc: 411.0911, Found: 411.0904;

**\([\alpha]_D^{20}\) = -90 (c = 1.00, CHCl\textsubscript{3});**

**HPLC:** DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: \(t_{\text{major}} = 7.1, t_{\text{minor}} = 4.8, 76%\) ee.
(R)-methyl 2-((diphenylphosphoryl)(2-methoxyphenyl)methyl)acrylate (4d)

![Chemical Structure Image]

4d was isolated by column chromatography using silica gel in 61% yield.

\[ \text{H}^1 \text{NMR (300 MHz, CDCl}_3): \delta 7.93-7.86 (m, 2H), 7.79-7.76 (m, 1H), 7.54-7.11 (m, 9H), 6.94 (t, J = 7.2 Hz, 1H), 6.77 (d, J = 2.4 Hz, 1H), 6.57 (d, J = 8.1 Hz, 1H), 6.45 (d, J = 2.1 Hz, 1H), 5.77 (d, J = 8.7 Hz, 1H), 3.58 (s, 3H), 3.41 (s, 3H); \]

\[ \text{C}^{13} \text{NMR (75 MHz, CDCl}_3): \delta 166.7 (J = 9.75 Hz), 156.4 (J = 5.25 Hz), 136.4 (J = 2.25 Hz), 133.1, 132.9, 131.8, 131.6 (J = 3.0 Hz), 131.4, 131.3, 131.1 (J = 3.75 Hz), 131.0 (J = 4.5 Hz), 130.9 (J = 2.25 Hz), 128.4 (J = 6.0 Hz, 7.5 Hz), 127.5 (J = 12.0 Hz), 122.9 (J = 5.25 Hz), 120.5 (J = 1.5 Hz), 110.1 (J = 1.5 Hz), 55.2, 52.1, 36.6 (J = 68.25 Hz); \]

\[ \text{P}^{31} \text{NMR (121 MHz, CDCl}_3): \delta 32.1; \]

\[ \text{IR: 3057, 2950, 1720, 1491, 1438, 1247, 1185, 1126, 727, 699, 522 cm}^{-1}; \]

\[ \text{HRMS (ESI)}: \text{C}_{24}\text{H}_{23}\text{O}_{4}\text{P}+\text{H}, \text{Calc: 407.1407, Found: 407.1404; } \]

\[ \text{[d]}^{	ext{d}} \text{D}_{\text{rt}} = -143 \text{ (c = 0.80, CHCl}_3); \]

\[ \text{HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: t}_{\text{major}} = 8.3, t_{\text{minor}} = 22.9, 90\% \text{ ee.} \]

(R)-methyl 2-((3-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4e)

![Chemical Structure Image]

4e was isolated by column chromatography using silica gel in 81% yield.

\[ \text{H}^1 \text{NMR (300 MHz, CDCl}_3): \delta 7.90-7.83 (m, 2H), 7.53-7.08 (m, 12H), 6.81 (d, J = 2.4 Hz), 6.45 (d, J = 2.1 Hz, 1H), 4.99 (d, J = 8.7 Hz, 1H), 3.64 (s, 3H); \]

\[ \text{C}^{13} \text{NMR (75 MHz, CDCl}_3): \delta 166.6 (J = 9.75 Hz), 136.8 (J = 5.25 Hz), 135.9 (J = 2.25 Hz), 134.0 (J = 0.75 Hz), 132.5 (J = 8.25 Hz), 131.9 (J = 3.0 Hz), 131.7 (J = 3.0 Hz), 131.2 (J = 2.25 Hz), 131.0 (J = 6.75 Hz), 130.9 (J = 6.75 Hz), 130.8, 130.1 (J = 6.0 Hz), 129.4 (J = 1.5 Hz), 128.7 (J = 11.25 Hz), 128.3 (J = 12.0 Hz), 122.2 (J = 5.25 Hz), 127.5 (J = 2.25 Hz), 52.4, 45.4 (J = 66.75 Hz); \]

\[ \text{P}^{31} \text{NMR (121 MHz, CDCl}_3): \delta 31.3; \]

\[ \text{IR: 3056, 1717, 1591, 1438, 1238, 1185, 1130, 699, 517 cm}^{-1}; \]

\[ \text{HRMS (ESI)}: \text{C}_{23}\text{H}_{20}\text{ClO}_{3}\text{P}+\text{H}, \text{Calc: 411.0911, Found: 411.0909; } \]

\[ \text{[d]}^{	ext{d}} \text{D}_{\text{rt}} = -241 \text{ (c = 0.97, CHCl}_3); \]

\[ \text{HPLC: DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 95/5, flow rate = 0.5 mL/min, retention time: t}_{\text{major}} = 26.1, t_{\text{minor}} = 29.9, 89\% \text{ ee.} \]
(R)-methyl 2-((diphenylphosphoryl)(3-methoxyphenyl)methyl)acrylate (4f)

![Chemical Structure](image)

4f was isolated by column chromatography using silica gel in 82% yield.

**^1H NMR** (300 MHz, CDCl₃): δ 7.90-7.83 (m, 2H), 7.54-6.69 (m, 13H), 6.43 (d, J = 2.1 Hz, 1H), 5.04 (d, J = 8.7 Hz, 1H), 3.67 (s, 3H), 3.62 (s, 3H);

**^13C NMR** (75 MHz, CDCl₃): δ 166.7 (J = 9.75 Hz), 159.3 (J = 0.75 Hz), 136.3 (J = 2.25 Hz), 136.1 (J = 5.25 Hz), 132.8 (J = 6.75 Hz), 131.6 (J = 3.0 Hz, 20.25 Hz), 131.4 (J = 3.0 Hz), 131.2, 131.0 (J = 2.25 Hz), 130.9, 130.5 (J = 6.75 Hz), 129.1 (J = 1.5 Hz), 128.5 (J = 11.25 Hz), 128.1 (J = 11.25 Hz), 122.4 (J = 6 Hz), 115.2 (J = 6 Hz), 113.3 (J = 1.5 Hz), 55.1, 52.3, 45.5 (J = 67.5 Hz);

**^31P NMR** (121 MHz, CDCl₃): δ 31.4;

**IR:** 3057, 2952, 1716, 1599, 1438, 1234, 1191, 1123, 1047, 700, 519 cm⁻¹;

**HRMS (ESI):** C₂₄H₂₃O₄P⁺H, Calc: 407.1407, Found: 407.1400;

**α**Drt = -208 (c = 0.96, CHCl₃);

**HPLC:** DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_major = 10.4, t_minor = 12.1, 97% ee.

(R)-methyl 2-((diphenylphosphoryl)(4-fluorophenyl)methyl)acrylate (4g)

![Chemical Structure](image)

4g was isolated by column chromatography using silica gel in 55% yield.

**^1H NMR** (300 MHz, CDCl₃): δ 7.90-7.84 (m, 2H), 7.55-7.25 (m, 10H), 6.86 (t, J = 8.4 Hz, 2H), 6.79 (d, J = 1.8 Hz, 1H), 6.42 (d, J = 1.8 Hz, 1H), 5.01 (d, J = 8.4 Hz, 1H), 3.64 (s, 3H);

**^13C NMR** (75 MHz, CDCl₃): δ 166.6 (J = 9.75 Hz), 163.6 (J = 2.25 Hz), 160.4 (J = 2.25 Hz), 136.5 (J = 0.75 Hz), 132.6 (J = 15.0 Hz), 131.8 (J = 2.25Hz), 131.7, 131.6 (J = 2.25 Hz), 131.5 (J = 1.5 Hz), 131.3 (J = 12.0 Hz), 131.0 (J = 9.0 Hz, J = 17.25 Hz), 130.4, 128.6 (J = 11.25 Hz), 128.2 (J = 12 Hz), 115.1 (J = 2.25 Hz, J = 21.75 Hz), 52.3, 44.8 (J = 67.5 Hz);

**^31P NMR** (121 MHz, CDCl₃): δ 31.5 (J = 2.78 Hz);

**IR:** 3058, 2953, 1716, 1599, 1438, 1234, 1191, 1123, 1047, 700, 561 cm⁻¹;

**HRMS (ESI):** C₂₃H₂₀FO₃P⁺H, Calc: 395.1207, Found: 395.1209;

**α**Drt = -183 (c = 0.80, CHCl₃);

**HPLC:** DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_major = 8.8, t_minor = 9.4, 90% ee.
(R)-methyl 2-((4-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4h)

\[
\begin{align*}
\text{Cl} & \quad \text{P} \quad \text{COOMe} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

4h was isolated by column chromatography using silica gel in 84% yield.

\( ^1\text{H NMR} \) (300 MHz, CDCl\(_3\)) : \( \delta \) 7.86 (t, \( J = 7.8 \) Hz, 2H), 7.52-7.13 (m, 12H), 6.78 (d, \( J = 1.5 \) Hz, 1H), 6.43 (s, 1H), 5.00 (d, \( J = 8.4 \) Hz, 1H), 3.63 (s, 3H);

\( ^{13}\text{C NMR} \) (75 MHz, CDCl\(_3\)) : \( \delta \) 166.6 (\( J = 9.0 \) Hz), 136.2 (\( J = 2.25 \) Hz), 131.6 (\( J = 2.25 \) Hz), 131.3 (\( J = 5.25 \) Hz), 131.2, 131.1, 131.0, 130.9 (\( J = 9.0 \) Hz), 130.5 (\( J = 6.75 \) Hz), 128.6 (\( J = 11.25 \) Hz), 128.4 (\( J = 1.5 \) Hz), 128.2 (\( J = 12 \) Hz), 52.4, 45.0 (\( J = 67.5 \) Hz);

\( ^{31}\text{P NMR} \) (121 MHz, CDCl\(_3\)) : \( \delta \) 31.3;

IR: 3057, 2951, 1716, 1485, 1438, 1238, 1189, 1122, 727, 697, 547 cm\(^{-1}\);

HRMS (ESI): C_{23}H_{20}ClO_3P+H, Calc: 411.0911, Found: 411.0910;

\( [\alpha]_D^\circ = -246 \) (c = 0.98, CHCl\(_3\));

HPLC: DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: \( t_{\text{major}} = 4.6, t_{\text{minor}} = 5.2 \), 92% ee.

(R)-methyl 2-((4-bromophenyl)(diphenylphosphoryl)methyl)acrylate (4i)

\[
\begin{align*}
\text{Br} & \quad \text{P} \quad \text{COOMe} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

4i was isolated by column chromatography using silica gel in 85% yield.

\( ^1\text{H NMR} \) (300 MHz, CDCl\(_3\)) : \( \delta \) 7.86 (t, \( J = 7.8 \) Hz, 2H), 7.52-7.22 (m, 12H), 6.78 (s, 1H), 6.43 (s, 1H), 4.99 (d, \( J = 8.4 \) Hz, 1H), 3.63 (s, 3H);

\( ^{13}\text{C NMR} \) (75 MHz, CDCl\(_3\)) : \( \delta \) 166.6 (\( J = 9.0 \) Hz), 136.2 (\( J = 2.25 \) Hz), 133.8 (\( J = 5.25 \) Hz), 132.5 (\( J = 7.5 \) Hz), 131.8 (\( J = 2.25 \) Hz), 131.7, 131.6, 131.3 (\( J = 0.75 \) Hz), 131.1 (\( J = 3.75 \) Hz), 131.0 (\( J = 7.5 \) Hz), 130.9 (\( J = 9.0 \) Hz), 130.5 (\( J = 4.5 \) Hz), 128.6 (\( J = 11.25 \) Hz), 128.3 (\( J = 11.25 \) Hz), 121.4 (\( J = 2.25 \) Hz), 52.4 (\( J = 7.5 \) Hz), 45.0 (\( J = 66.75 \) Hz);

\( ^{31}\text{P NMR} \) (121 MHz, CDCl\(_3\)) : \( \delta \) 31.2;

IR: 3057, 2952, 2849, 1485, 1438, 1240, 1189, 1126, 727, 697, 550 cm\(^{-1}\);

HRMS (ESI): C_{23}H_{20}BrO_3P+H, Calc: 455.0406, Found: 455.0407;

\( [\alpha]_D^\circ = -259 \) (c = 0.99, CHCl\(_3\));

HPLC: DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: \( t_{\text{major}} = 4.7, t_{\text{minor}} = 5.3 \), 92% ee.
(R)-methyl 2-((diphenylphosphoryl)(4-methoxyphenyl)methyl)acrylate (4j)

4j was isolated by column chromatography using silica gel in 87% yield.

\[ \text{H NMR (300 MHz, CDCl}_3: \delta 7.90-7.83 (m, 2H), 7.51-7.24 (m, 10H), 6.76-6.70 (m, 3H), 6.40 (d, } J = 2.1 \text{ Hz, 1H), 4.99 (d, } J = 8.7 \text{ Hz, 1H), 3.72 (s, 3H), 3.62 (s, 3H);} \]

\[ \text{C NMR (75 MHz, CDCl}_3: \delta 166.8 (J = 9.75 \text{ Hz), 158.7 (J = 2.25 Hz), 136.7 (J = 1.5 Hz), 132.9 (J = 8.25 Hz), 131.6 (J = 2.25 Hz), 131.3 (J = 3.0 Hz), 131.1 (J = 5.25 Hz), 131.0 (J = 5.25 Hz), 130.9, 130.0 (J = 6.75 Hz), 128.5 (J = 11.25 Hz), 128.1 (J = 12 Hz), 126.5 (J = 5.25 Hz), 113.7 (J = 1.5 Hz), 55.1, 52.3, 44.7 (J = 68.25 Hz);} \]

\[ \text{P NMR (121 MHz, CDCl}_3: \delta 31.7;} \]

\[ \text{IR: 3057, 2953, 1717, 1510, 1438, 1253, 1183, 1124, 727, 700, 519 \text{ cm}^{-1};} \]

\[ \text{HRMS (ESI): C}_{24}\text{H}_{23}\text{O}_{4}\text{P}+\text{H, Calc: 407.1407, Found: 407.1403;} \]

\[ \text{[} \alpha \text{]_D^2 = -247 (c = 0.95, CHCl}_3;} \]

\[ \text{HPLC: DAICEL CHIRALCEL OD-H, Hexane/iPrOH = 70/30, flow rate = 0.5 mL/min, retention time: } t_{\text{major}} = 10.3, t_{\text{minor}} = 11.4, 95\% \text{ ee.} \]

(S)-methyl 2-((diphenylphosphoryl)(furan-2-yl)methyl)acrylate (4k)

4k was isolated by column chromatography using silica gel in 98% yield.

\[ \text{H NMR (300 MHz, CDCl}_3: \delta 7.81-7.65 (m, 4H), 7.52-7.35 (m, 6H), 7.24 (t, } J = 0.9 \text{ Hz, 1H), 6.52 (m, 2H), 6.39 (t, } J = 2.7 \text{ Hz, 1H), 6.22 (J = 1.8 Hz, 1H), 5.36 (d, } J = 10.8 \text{ Hz, 1H), 3.56(s, 3H);} \]

\[ \text{C NMR (75 MHz, CDCl}_3: \delta 166.4 (J = 6.0 \text{ Hz), 148.5 (J = 4.5 Hz), 142.1 (J = 2.25 Hz), 133.3 (J = 3.75 Hz), 132.2 (J = 18.75 Hz), 131.8, 131.8 (J = 3.0 Hz), 131.7, 131.6, 131.4 (J = 9.0 Hz), 131.1 (J = 9.0 Hz), 130.8 (J = 16.5 Hz), 128.3 (J = 12 Hz), 110.7 (J = 1.5 Hz), 109.8 (J = 4.5 Hz), 52.3, 39.9 (J = 66.0 Hz);} \]

\[ \text{P NMR (121 MHz, CDCl}_3: \delta 29.2;} \]

\[ \text{IR: 3057, 1717, 1438, 1271, 1199, 1120, 699, 526 \text{ cm}^{-1};} \]

\[ \text{HRMS (ESI): C}_{21}\text{H}_{19}\text{O}_{4}\text{P}+\text{H, Calc: 367.1094, Found: 367.1088;} \]

\[ \text{[} \alpha \text{]_D^2 = +3 (c = 1.04, CHCl}_3;} \]

\[ \text{HPLC: DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: } t_{\text{major}} = 13.4, t_{\text{minor}} = 16.6, 44\% \text{ ee.} \]
(R)-methyl 2-((dinaphthalen-1-ylphosphoryl)(phenyl)methyl)acrylate (4l)

![Chemical Structure](image)

4l was isolated by column chromatography using silica gel in 80% yield.

**1H NMR** (300 MHz, CDCl₃): δ 8.72 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 8.04-6.95 (m, 18H), 6.56 (d, J = 1.8 Hz, 1H), 5.29 (d, J = 9 Hz, 1H), 3.58 (s, 3H);

**13C NMR** (75 MHz, CDCl₃): δ 166.9 (J = 10.5 Hz), 137.0 (J = 2.25 Hz), 134.7 (J = 2.25 Hz), 134.0 (J = 2.25 Hz, J = 8.25 Hz), 133.9 (J = 9.0 Hz), 133.0 (J = 2.25 Hz), 132.7 (J = 3.0 Hz), 132.0 (J = 10.5 Hz), 131.4 (J = 9.75 Hz, J = 17.25Hz), 130.1 (J = 12.0 Hz), 129.8, 128.7, 128.5 (J = 0.75 Hz), 128.3, 128.0 (J = 1.5 Hz), 127.3, 127.1 (J = 5.25 Hz, J = 9.0 Hz), 126.8, 126.3, 126.2 (J = 3.75 Hz), 125.8, 124.1 (J = 11.25 Hz, J = 13.5 Hz), 52.3, 46.5 (J = 68.25 Hz);

**31P NMR** (121 MHz, CDCl₃): δ 38.4;

**IR:** 3059, 2230, 1714, 1505, 1438, 1241, 1174, 775, 732 cm⁻¹;

**HRMS (ESI):** C₃₁H₂₅O₃P⁺H, Calc: 477.1614, Found: 477.1606;

**[α]Drt = - 16 (c = 1.34, CHCl₃);**

**HPLC:** DAICEL CHIRALCEL AD, Hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_major = 25.4, t_minor = 42.7, 95% ee.

(R)-methyl 2-((bis(4-fluorophenyl)phosphoryl)(phenyl)methyl)acrylate (4m)

![Chemical Structure](image)

4m was isolated by column chromatography using silica gel in 63% yield.

**1H NMR** (300 MHz, CDCl₃): δ 7.91- 7.83 (m, 2H), 7.48-7.39 (m, 2H), 7.36-7.33 (dd, J = 2.1 Hz, J = 5.4 Hz, 2H), 7.22-7.15 (m, 5H), 6.99-6.92 (m, 2H), 6.79 (d, J = 2.4 Hz, 1H), 6.44 (d, J = 2.1 Hz, 1H), 4.99 (d, J = 8.4 Hz, 1H), 3.64 (s, 3H);

**13C NMR** (75 MHz, CDCl₃): δ 166.7 (J = 9.75 Hz), 165.0 (J = 3.75 Hz, J = 252 Hz), 164.7 (J = 3.75 Hz, J = 252.25 Hz), 163.1 (J = 9.75 Hz), 134.3 (J = 5.25 Hz), 133.6 (J = 8.25 Hz, J = 9.75 Hz), 133.4 (J = 9.0 Hz, J = 10.5 Hz), 130.5 (J = 6.0 Hz), 130.0 (J = 6.0 Hz), 128.5 (J = 3.0 Hz, J = 19.5 Hz), 128.4 (J = 1.5 Hz), 127.4 (J = 2.25 Hz), 127.1 (J = 3.75 Hz, J = 15.75 Hz), 116.1 (J = 12.75 Hz, J = 21.0 Hz), 115.6 (J = 12.75 Hz, J = 21.0 Hz), 52.4, 45.7 (J = 68.25 Hz);

**31P NMR** (121 MHz, CDCl₃): δ 30.6;

**IR:** 2229, 1716, 1592, 1498, 1237, 1190, 1118, 830, 542 cm⁻¹;

**HRMS (ESI):** C₂₃H₁₉F₂O₃P⁺H, Calc: 413.1113, Found: 413.1121;

**[α]Drt = - 199 (c = 1.11, CHCl₃);**

**HPLC:** DAICEL CHIRALCEL AD, Hexane/iPrOH = 80/30, flow rate = 1.0 mL/min, retention time: t_major = 8.3, t_minor = 11.7, 90% ee.
(R)-methyl 2-((dip-tolylphosphoryl)(phenyl)methyl)acrylate (4n)

![Chemical structure](image)

4n was isolated by column chromatography using silica gel in 81% yield.

**1H NMR** (300 MHz, CDCl₃): δ 7.74 (dd, J = 7.8 Hz, J = 10.5 Hz, 2H), 7.36-7.03 (m, 11H), 6.80 (d, J = 2.4 Hz, 1H), 6.42 (d, J = 1.8 Hz, 1H), 4.99 (d, J = 8.7 Hz, 1H), 3.61 (s, 3H), 2.37 (s, 3H), 2.26 (s, 3H);

**13C NMR** (75 MHz, CDCl₃): δ 166.8 (J = 9.75 Hz), 141.9 (J = 3.0 Hz), 141.6 (J = 3.0 Hz), 136.6 (J = 2.25 Hz), 134.9 (J = 5.25 Hz), 131.1 (J = 9.0 Hz), 130.9 (J = 9.0 Hz), 130.2 (J = 6.75 Hz), 130.0 (J = 5.25 Hz), 129.9 (J = 9.0 Hz), 129.2 (J = 12.0 Hz), 128.8 (J = 12.0 Hz), 128.4 (J = 6.0 Hz), 128.2 (J = 0.75 Hz), 127.0 (J = 2.25 Hz), 52.2, 45.7 (J = 67.5 Hz), 21.5, 21.4;

**31P NMR** (121 MHz, CDCl₃): δ 31.9;

**IR**: 3027, 2223, 1716, 1440, 1239, 1185, 1118, 655 cm⁻¹;

**HRMS (ESI)**: C₂₅H₂₅O₃P+H, Calc: 405.1614, Found: 405.1610;

[α]D²₀ = -216 (c = 0.98, CHCl₃);

**HPLC**: DAICEL CHIRALCEL AD, Hexane/iPrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_major = 12.3, t_minor = 9.3, 94% ee.

(R)-methyl 2-((bis(4-methoxyphenyl)phosphoryl)(phenyl)methyl)acrylate (4o)

![Chemical structure](image)

4o was isolated by column chromatography using silica gel in 94% yield.

**1H NMR** (300 MHz, CDCl₃): δ 7.77 (dd, J = 8.7 Hz, J = 10.5 Hz, 2H), 7.37-7.30 (m, 4H), 7.22-7.17 (m, 3H), 6.97 (dd, J = 2.4 Hz, J = 9.0 Hz, 2H), 6.76 (dt, J = 2.4 Hz, J = 9.0 Hz, 3H), 6.42 (d, J = 2.1 Hz, 1H), 4.95 (d, J = 8.7 Hz, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 3.62 (s, 3H);

**13C NMR** (75 MHz, CDCl₃): δ 166.8 (J = 9.75 Hz), 162.2 (J = 3.0 Hz), 161.9 (J = 3.0 Hz), 136.6 (J = 2.25 Hz), 134.9 (J = 5.25 Hz), 132.9 (J = 9.75 Hz), 132.8 (J = 10.5 Hz), 130.2 (J = 6.0 Hz), 130.0 (J = 6.0 Hz), 128.2 (J = 1.5 Hz), 127.0 (J = 1.5 Hz), 124.2 (J = 30.0 Hz), 122.8 (J = 26.25 Hz), 114.1 (J = 12.75 Hz), 113.5 (J = 12.75 Hz), 55.2, 55.1, 52.2, 46.0 (J = 67.5 Hz);

**31P NMR** (121 MHz, CDCl₃): δ 32.1;

**IR**: 3027, 2223, 1716, 1597, 1501, 1256, 1179, 1119, 1028, 732, 549 cm⁻¹;

**HRMS (ESI)**: C₂₅H₂₅O₅P+H, Calc: 437.1512, Found: 437.1519;

[α]D²₀ = -227 (c = 0.96, CHCl₃);

**HPLC**: DAICEL CHIRALCEL AD, Hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_major = 37.3, t_minor = 35.4, 94% ee.
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wR2(reflections)= 0.1017(4030)

S = 1.042

Npar= 254
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(R)-methyl 2-((diphenylphosphoryl)(phenyl)methyl)acrylate (4a)
Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.

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(S)-methyl 2-((diphenylphosphoryl)(2-fluorophenyl)methyl)acrylate (4b)
Chiralpak AD column, hexane/iPrOH (80:20), flow rate 1.0 mL/min.

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(S)-methyl 2-((2-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4c)
Chiralpak OD-H column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.
(R)-methyl 2-((diphenylphosphoryl)(2-methoxyphenyl)methyl)acrylate (4d)
Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.

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(R)-methyl 2-((3-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4e)
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(R)-methyl 2-((diphenylphosphoryl)(3-methoxyphenyl)methyl)acrylate (4f)
Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.

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(R)-methyl 2-((diphenylphosphoryl)(4-fluorophenyl)methyl)acrylate (4g)
Chiralpak OD-H column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.

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(R)-methyl 2-((4-chlorophenyl)(diphenylphosphoryl)methyl)acrylate (4h)
Chiralpak OD-H column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.

(R)-methyl 2-((4-bromophenyl)(diphenylphosphoryl)methyl)acrylate (4i)
Chiralpak OD-H column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.
(R)-methyl 2-((diphenylphosphoryl)(4-methoxyphenyl)methyl)acrylate (4j)
Chiralpak OD-H column, hexane/iPrOH (70:30), flow rate 0.5 mL/min.

(S)-methyl 2-((diphenylphosphoryl)(furan-2-yl)methyl)acrylate (4k)
Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.
(R)-methyl 2-((dinaphthalen-1-ylphosphoryl)(phenyl)methyl)acrylate (4I)

Chiralpak AD column, hexane/iPrOH (80:20), flow rate 1.0 mL/min.

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(\(R\))-methyl 2-(((4-fluorophenyl)phosphoryl)(phenyl)methyl)acrylate (4m)

Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.

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**Supplementary Material (ESI) for Chemical Communications**

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**(R)-methyl 2-((dip-tolylphosphoryl)(phenyl)methyl)acrylate (4n)**

Chiralpak AD column, hexane/iPrOH (90:10), flow rate 1.0 mL/min.

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**(R)-methyl 2-((bis(4-methoxyphenyl)phosphoryl)(phenyl)methyl)acrylate (4o)**

Chiralpak AD column, hexane/iPrOH (70:30), flow rate 1.0 mL/min.

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