Iron Porphyrin-catalyzed Olefination of Ketenes with Diazoacetate for the Enantioselective Synthesis of Allenes

Chuan-Ying Li,^a Xiao-Bing Wang,^b Xiu-Li Sun,^a Yong Tang^{a*},

Jun-Cheng Zheng, Zheng-Hu Xu^a, Yong-Gui Zhou^{b*} and Li-Xin Dai^a

^aState Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry,
Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

^b. Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

Supporting Information

General Information All reaction flasks were dried by flame. And all reactions were carried out under N₂ unless otherwise noted. All solvents were purified according to standard methods unless otherwise noted.

¹H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal TMS signal at 0.0 ppm or chloroform signal at 7.26 ppm as a standard. The data are reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, sep = septuplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration).

¹³C NMR spectra were recorded on a VARIAN Mercury 75.5 MHz spectrometer in chloroform-d. All signals are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ³¹P NMR spectra were recorded on a VARIAN Mercury 121.5 MHz spectrometer in chloroform-d₃.

Ketenes were synthesized according to literature procedure.¹

¹ (a) Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 1578; (b) Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 10006; (c) Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 6176; (d) Baigrie, L. M.; Seiklay, H. R.; Tidnell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 5391.

Part I Experimental Part

1. General procedure for the preparation of allene 1a - 1j in table 1 (Method A).

1.1 Typical procedure

To a stirred solution of Fe(TCP)Cl (1.7 mg, 0.002 mmol), Ph₃P (125.8 mg, 0.48 mmol), ketene (0.4 mmol) in 2 mL of toluene at 0 °C under N₂ was added EDA (55 mg, 0.48 mmol) in one portion. After being stirred at 0 °C ca. 8 h, the reaction mixture was purified by flash chromatography to give the product.

1.2 *In situ* procedure

Preparation of ketene *in situ*. To a solution of Et₃N (61 mg, 0.6 mmol) in trifluoromethylbenzene (BTF, 1 mL) was added acyl chloride (0.4 mmol). After being stirred for 2 h at room temperature, the reaction mixture was filtered under N₂ and the filtrate was concentrated in vacuo. The resulting oil (light yellow) was diluted with 0.5 mL of THF for use.

Synthesis of allene 1e or 1f. The procedure is similar to that described in 1.1.

4-Phenyl-penta-2,3-dienoic acid ethyl ester 1a²

Yield: >99%. Pale yellow oil. ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.29 (t, *J* = 7.2 Hz, 3H), 2.21 (d, *J* = 3.0 Hz, 3H), 4.22 (q, *J* = 7.2 Hz, 2H), 5.89 (q, *J* = 3.0 Hz, 1H), 7.25-7.41 (m, 5H). (Table 1, Entry 1).

² Runge, W.; Kresze, G.; Ruch, E. *Justus Liebigs Annalen der Chemie* **1975**, 1361.

4-Phenyl-hexa-2,3-dienoic acid ethyl ester 1b³

Yield: >99%. Pale yellow oil. ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.18 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 6.9 Hz, 3H), 2.51-2.59 (m, 2H), 4.17-4.26 (m, 2H), 5.96 (t, *J* = 3.6 Hz, 1H), 7.25-7.41 (m, 5H). (Table 1, Entry 2).

5-Methyl-4-phenyl-hexa-2,3-dienoic acid ethyl ester 1c⁴

Yield: > 99%. Pale yellow oil. ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.16 (d, *J* = 2.4 Hz, 3H), 1.18 (d, *J* = 2.1 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.81-2.98 (m, 1H), 4.14-4.28 (m, 2H), 5.92 (d, *J* = 2.7 Hz, 1H), 7.24-7.40 (m, 5H). (Table 1, Entry 3).

4-Phenyl-Octa-2,3-dienoic acid ethyl ester 1d

Yield: 98%. Pale yellow oil. IR (KBr) ν/cm⁻¹ 2958 (m), 1945 (m), 1720 (vs), 1494 (m), 1148 (s); ¹H NMR (300 MHz, CDCl₃/TMS) δ 0.92 (t, *J* = 7.5 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.39-1.57 (m, 4H), 2.51-2.58 (m, 2H), 4.17-4.28 (m, 2H), 5.91 (t, *J* = 3 Hz, 1H), 7.24-7.41 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 213.7, 165.8, 134.1, 128.5, 127.7, 126.4, 110.4, 90.7, 60.8, 29.5, 29.4, 22.2, 14.2, 13.8; MS (EI, *m/z*, rel. intensity) 244 (2.2), 202 (15.4), 129 (100.0), 115 (66.1), 91 (42.4); Anal. Calcd for C₁₆H₂₀O₂: C, 78.65; H, 8.25. Found: C, 78.47; H, 8.31. (Table 1, Entry 4).

4-Phenyl-hepta-2,3,6-trienoic acid ethyl ester 1e⁴

Yield: 53%. Pale yellow oil. ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.28 (t, *J* = 6.9 Hz, 3H), 3.29-3.33 (m, 2H), 4.17-4.26 (m, 2H), 5.13(dd, *J* = 1.5, 10.5 Hz, 1H), 5.23 (dd, *J* = 1.5, 17.1 Hz, 1H), 5.88-6.00 (m, 2H), 7.26-7.42 (m, 5H). (Table 1, Entry 9).

4-Phenyl-octa-2,3,7-trienoic acid ethyl ester 1f

Yield: 75%. Pale yellow oil. IR (KBr) ν/cm⁻¹ 2980 (w), 1947 (m), 1718 (vs), 1494 (w), 1149 (m); ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.29 (t, *J* = 7.2 Hz, 3H), 2.29-2.36 (m, 2H), 2.60-2.67 (m, 2H), 4.17-4.28 (m, 2H), 4.99-5.11 (m, 2H), 5.84-5.98 (m, 2H), 7.25-7.41 (m, 5H); ¹³C NMR

³ Wadsworth, W. S.; Emmons, W. D. *J. Am. Chem. Soc.* **1961**, 83, 1733.

⁴ Li, C.-Y.; Sun, X.-L.; Jing, Q.; Tang, Y. *Chem. Commun.* **2006**, 2980.

(75 MHz, CDCl₃) δ 213.6, 165.7, 137.4, 134.0, 128.6, 127.8, 126.4, 115.3, 110.0, 91.3, 60.9, 31.6, 29.1, 14.2; MS (EI, *m/z*, rel. intensity) 242 (4.4), 213 (8.6), 169 (97.3), 141 (100.0), 115 (71.4), 91 (90.1); HRMS (EI) Calcd for C₁₆H₁₈O₂: 242.1307. Found: 242.1297; Anal. Calcd for C₁₆H₁₈O₂: C, 79.31; H, 7.49. Found: C, 79.93; H, 7.52. (Table 1, Entry 10).

4-(4-Chloro-phenyl)-hexa-2,3-dienoic acid ethyl ester 1g⁴

Yield: 98%. Pale yellow oil. ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.16 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.46-2.58 (m, 2H), 4.17-4.26 (m, 2H), 5.96 (t, *J* = 3.3 Hz, 1H), 7.31 (s, 4H). (Table 1, Entry 5).

4-(4-Methoxy-phenyl)-hexa-2,3-dienoic acid ethyl ester 1h⁴

Yield: 92%. Pale yellow oil. ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.16 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.50-2.55 (m, 2H), 3.80 (s, 3H), 4.15-4.26 (m, 2H), 5.94 (t, *J* = 3.3 Hz, 1H), 6.88 (d, *J* = 9.0, 2H), 7.31 (d, *J* = 9.0 Hz, 2H). (Table 1, Entry 6).

4-*o*-Tolyl-hexa-2,3-dienoic acid ethyl ester 1i

Yield: 95%. Pale yellow oil. IR (KBr) ν /cm⁻¹ 2972 (m), 2934 (m), 2859 (w), 1956 (m), 1719 (vs), 1486 (m), 1407 (m), 1251 (m), 1149 (m), 760 (m), 721 (w); ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.12 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 2.42 (dq, *J* = 7.2, 3.0 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 5.68 (t, *J* = 3.0 Hz, 1H), 7.17-7.24 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 210.3, 166.2, 136.1, 135.1, 130.4, 128.0, 127.6, 125.8, 110.9, 88.7, 60.6, 26.8, 20.1, 14.2, 12.1; MS (EI, *m/z*, rel. intensity) 230 (2.7), 201 (44.8), 157 (44.8), 142 (35.3), 141 (33.3), 129 (86.4), 128 (32.9), 115 (35.6), 45 (100.0); Anal. Calcd for C₁₅H₁₈O₂: C, 78.23; H, 7.88. Found: C, 78.22; H, 7.97. (Table 1, Entry 7).

2-Isobutyl-penta-2,3-dienedioic acid diethyl ester 1j

Yield: 83%. Pale yellow oil. IR (KBr) ν /cm⁻¹ 2959 (s), 1958 (s), 1716 (s), 1467 (m), 1146 (m); ¹H NMR (300 MHz, CDCl₃/TMS) δ 0.92 (d, *J* = 6.3 Hz, 6H), 1.24 (t, *J* = 6.9 Hz, 3H), 1.25 (t, *J* = 6.9 Hz, 3H), 1.71-1.85 (m, 1H), 2.10-2.29 (m, 2H), 4.14-4.25 (m, 4H), 5.89 (t, *J* = 2.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 218.7, 165.3, 164.2, 103.6, 91.2, 61.4, 61.2, 37.4, 27.1, 22.2, 22.1,

14.10, 14.08; MS (EI, *m/z*, rel. intensity) 241 (0.8), 166 (68.9), 125 (53.8), 97 (84.4), 79 (82.0), 43 (100.0); HRMS (EI) Calcd for C₁₃H₂₀O₄: 240.1362. Found: 240.1369. (Table 1, Entry 8).

2. General procedure for the preparation of allene 1k – 1o in table 1 (Method B).

To a stirred solution of Fe(TCP)Cl (1.7 mg, 0.002 mmol), Ph₃P (125.8 mg, 0.48 mmol) in toluene (2 mL) at room temperature under N₂ was added EDA (55 mg, 0.48 mmol) in one portion. After the ylide was formed completely (about 10 h), the reaction mixture was cooled to -20 °C, and Et₃N (48.6 mg, 0.48 mmol) and acyl chloride (0.4 mmol) were added in turns, after 24 h, the reaction mixture was purified by flash chromatography to give the product.

Nona-2,3-dienoic acid diethyl ester 1k⁵

Yield: 77%. Pale yellow oil. ¹H NMR (300 MHz, CDCl₃/TMS) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.26-1.35 (m, 4H), 1.42-1.52 (m, 2H), 2.09-2.17 (m, 2H), 4.16-4.23 (m, 2H), 5.55-5.62 (m, 2H). (Table 1, Entry 11).

Tetradeca-2,3-dienoic acid ethyl ester 1l⁴

Yield: 80%. Pale yellow oil. ¹H NMR (300 MHz, CDCl₃/TMS) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.22-1.38 (m, 17H), 1.40-1.48 (m, 2H), 2.10-2.14 (m, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 5.55-5.62 (m, 2H). (Table 1, Entry 12).

4-Phenyl-buta-2,3-dienoic acid ethyl ester 1m⁶

Yield: 56%. ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.29 (t, *J* = 6.9 Hz, 3H), 4.23 (q, *J* = 6.9 Hz, 2H), 6.01 (d, *J* = 6.3 Hz, 1H), 6.25 (d, *J* = 6.3 Hz, 1H), 7.23-7.48 (m, 5H). (Table 1, Entry 13).

4-Bromo-penta-2,3-dienoic acid ethyl ester 1n

⁵ Marshall, J. A.; Wolf, M. A.; Wallace, E. M. *J. Org. Chem.* **1997**, 62, 367.

⁶ Suarez, A.; Fu, G. C. *Angew. Chem., Int. Ed.* **2004**, 43, 3580.

Yield: 59%. IR (KBr) ν/cm^{-1} 2983 (m), 2926 (w), 1956 (w), 1723 (s), 1405 (m), 1386 (m), 1258 (s), 1154 (s), 1065 (s), 1035 (m), 839 (m), 611 (m); ^1H NMR (300 MHz, CDCl_3/TMS) δ 1.28 (t, $J = 7.2$ Hz, 3H), 2.33 (d, $J = 3$ Hz, 3H), 4.21 (q, $J = 7.2$ Hz, 2H), 5.52 (q, $J = 3$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 207.7, 163.9, 91.2, 90.7, 61.3, 23.7, 14.1; MS (EI, m/z , rel. intensity) 207 (4.5), 177 (8.6), 100 (100.0), 98 (41.9), 57 (45.4), 51 (45.5), 47 (75.0), 45 (64.9), 43 (58.7), 41 (72.3); Anal. Calcd for $\text{C}_7\text{H}_9\text{BrO}_2$: C, 41.00; H, 4.42. Found: C, 41.29; H, 4.57. (Table 1, Entry 14).

4-Ethyl-octa-2,3-dienoic acid ethyl ester **10**⁷

Yield: 74%. ^1H NMR (300 MHz, CDCl_3/TMS) δ 0.89 (t, $J = 7.2$ Hz, 3H), 1.03 (t, $J = 7.2$ Hz, 3H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.31-1.48 (m, 4H), 1.99-2.18 (m, 4H), 4.17 (q, $J = 7.2$ Hz, 2H), 5.57 (t, $J = 3.0$ Hz, 1H). (Table 1, Entry 15).

3. Enantioselective Synthesis of Allenes.

To a stirred solution of $\text{Fe}(\text{TCP})\text{Cl}$ (0.9 mg, 0.001 mmol), (*S*)-MeO-BiPhep-Type **4** (141 mg, 0.2 mmol) in toluene (2 mL) at room temperature under N_2 was added EDA (45.6 mg, 0.4 mmol) in four portions every 30 minutes. After ca. 6 h, the resulting mixture was concentrated and NaBr (20.6 mg, 0.2 mmol), THF (2 mL) were added, followed by cooling to -65°C and then ketene (0.2 mmol) was syringed. After 72 h, the reaction mixture was diluted with petroleum ether and filtered quickly. The filtrate was concentrated, and the resulting oil was purified by flash chromatography (petroleum ether/ethyl acetate = 100/1 $\sim$ 40/1) to give chiral allenic ester **1**. The filter cake was submitted to column chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ = 150/1 $\sim$ 30/1) to recover phosphine **4** and phosphine oxide **7** and **9**.

4-Phenyl-penta-2,3-dienoic acid ethyl ester **1a**

Yield: 72%. Pale yellow oil. 93% ee (determined by HPLC: Chiralcel AD-H Column, 0.3/100

⁷ G. R. Harvey, K. W. Ratts, *J. Org. Chem.*, 1966, **31**, 3907.

ⁱPrOH/hexane, 0.8 mL/min, 254 nm). (Table 2, Entry 1).

4-Phenyl-hexa-2,3-dienoic acid ethyl ester 1b

Yield: 90%. Pale yellow oil. 97% ee (determined by HPLC: Chiralcel AD-H Column, 0.3/100

ⁱPrOH/hexane, 0.8 mL/min, 254 nm). (Table 2, Entry 2).

4-Phenyl-hepta-2,3-dienoic acid ethyl ester 1r

Yield: 87%. Pale yellow oil. 93% ee (determined by HPLC: Chiralcel OJ Column, 0.2/100

ⁱPrOH/hexane, 0.8 mL/min, 254 nm). IR (KBr) ν/cm^{-1} 2960 (m), 1946 (m), 1719 (vs), 1494 (m), 1148 (s); ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.01 (t, *J* = 7.5 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.55-1.63 (m, 2H), 2.43-2.61 (m, 2H), 4.16-4.27 (m, 2H), 5.92 (t, *J* = 3 Hz, 1H), 7.26-7.40 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 213.7, 165.9, 134.1, 128.6, 127.7, 126.5, 110.2, 90.8, 60.8, 31.8, 20.7, 14.2, 13.7; MS (EI, *m/z*, rel. intensity) 230 (5.2), 201 (26.1), 173 (39.5), 115 (100.0), 91 (38.4); HRMS (EI) Calcd for C₁₅H₁₈O₂: 230.1307. Found: 230.1310. (Table 2, Entry 3).

4-*o*-Tolyl-hexa-2,3-dienoic acid ethyl ester 1i

Yield: 86%. Pale yellow oil. , 97% ee (determined by HPLC: Chiralcel OJ Column, 0.3/100

ⁱPrOH/hexane, 0.8 mL/min, 254 nm). (Table 2, Entry 4).

4-(4-Methoxy-phenyl)-hexa-2,3-dienoic acid ethyl ester 1h

Yield: 81%. Pale yellow oil. 96% ee (determined by HPLC: Chiralcel AD-H Column, 0.3/100

ⁱPrOH/hexane, 0.8 mL/min, 254 nm). (Table 2, Entry 5).

4-(4-Chloro-phenyl)-hexa-2,3-dienoic acid ethyl ester 1g

Yield: 83%. Pale yellow oil. 97% ee (determined by HPLC: Chiralcel AD-H Column, 0.3/100

ⁱPrOH/hexane, 0.8 mL/min, 254 nm). (Table 2, Entry 6).

4-(4-Bromo-phenyl)-hexa-2,3-dienoic acid ethyl ester 1s

Yield: 80%. Pale yellow oil. 98% ee (determined by HPLC: Chiralcel AD-H Column, 0.5/100

ⁱPrOH/hexane, 0.8 mL/min, 254 nm). IR (KBr) ν/cm^{-1} 2972 (m), 1946 (m), 1720 (vs), 1488 (m),

1150 (s); ^1H NMR (300 MHz, CDCl_3/TMS) δ 1.16 (t, $J = 7.2$ Hz, 3H), 1.28 (t, $J = 6.9$ Hz, 3H), 2.48-2.56 (m, 2H), 4.16-4.27 (m, 2H), 5.96 (t, $J = 3.3$ Hz, 1H), 7.25 (d, $J = 8.4$ Hz, 2H), 7.46 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 213.3, 165.5, 133.2, 131.6, 127.9, 121.7, 111.6, 92.0, 60.9, 22.8, 14.2, 12.1; MS (EI, m/z , rel. intensity) 295 (3.5), 187 (26.5), 142 (100.0), 128 (49.4), 63 (25.0); HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{15}\text{BrO}_2$: 294.0255. Found: 294.0255. (Table 2, Entry 7).

Chiral monophosphane oxide **7**

yield: 83%. White powder. $[\alpha]_{\text{D}}^{20} = -19.0^\circ$ ($c = 0.84$, CHCl_3). IR (KBr) ν/cm^{-1} 3002 (m), 2834 (m), 1712 (w), 1589 (vs), 1462 (vs), 1045 (s), 694 (s); ^1H NMR (300 MHz, CDCl_3/TMS) δ 3.03 (s, 3H), 3.22 (s, 3H), 3.62-3.66 (m, 12H), 6.53 (d, $J = 8.4$ Hz, 1H), 6.70-6.94 (m, 11H), 7.03-7.26 (m, 10H); ^{13}C NMR (75 MHz, CDCl_3) δ 158.97 (d, $J = 6.6$ Hz), 158.73 (d, $J = 8.0$ Hz), 156.39 (d, $J = 9.8$ Hz), 140.79 (d, $J = 14.0$ Hz), 138.70 (d, $J = 14.9$ Hz), 136.21, 134.96 (d, $J = 19.7$ Hz), 133.73, 128.97, 128.79, 128.67, 128.58, 128.45, 127.79 (d, $J = 15.2$ Hz), 126.56, 126.30, 126.01, 125.59, 125.39, 125.16, 124.29, 124.16, 123.95, 123.83, 119.29 (d, $J = 23.1$ Hz), 117.84 (d, $J = 18.7$ Hz), 117.31 (d, $J = 8.4$ Hz), 116.64 (d, $J = 10.2$ Hz), 116.06 (d, $J = 10.1$ Hz), 113.43 (d, $J = 10.0$ Hz), 113.15 (d, $J = 2.9$ Hz), 110.08, 54.98, 54.89, 54.83, 54.46, 54.31; ^{31}P NMR (121.5 MHz, CDCl_3) δ 29.60, -13.06; MS (ESI, positive mode, m/z) 719.4 ($\text{M}+\text{H}^+$). HRMS (MALDI/DHB) $\text{M}+\text{H}^+$ Calcd for $\text{C}_{42}\text{H}_{41}\text{O}_7\text{P}_2^+$: 719.2343. Found: 719.2322.

4. Synthesis of (S)-MeO-BiPhep-Type 4.

4.1 Synthesis of compound **11**

In the presence of a trace amount of iodine, 1-bromo-3-methoxybenzene **10** (70.1 g, 0.375 mol) was added dropwise to a suspension of magnesium turnings (10.0g, 0.412 mol) in THF (50 mL) with vigorously stirring under nitrogen atmosphere. The resulting gray suspension was refluxed for 1.5 h. The reaction mixture was cooled to room temperature, and PCl_3 (10.9 mL, 0.125 mol)

was added dropwise, followed by refluxing for 2 h. H₂O (150 mL) was added after the mixture was cooled to rt. THF was removed and the aqueous layer was extracted with CH₂Cl₂. The organic layer was cooled to 0 °C, and then hydrogen peroxide (45 mL, 30%) was added slowly. After the reaction was complete, the reaction mixture was treated with a saturated aqueous NaHSO₃ solution. The organic layer was separated, dried, filtered, concentrated under reduced pressure to afford compound **11**. Yield: 40.6 g (**88%**) as a white solid. ¹H-NMR (CDCl₃, 400 MHz): δ 3.79(s, 9H), 7.16-7.05 (m, 6H), 7.36-7.27 (m, 6H). ³¹P NMR (CDCl₃, 167 MHz): δ 30.25. ¹³C-NMR (CDCl₃, 100 MHz) δ 159.7 (d, *J* = 14.7 Hz), 133.9 (d, *J* = 103 Hz), 129.8 (d, *J* = 14.3 Hz), 124.5 (d, *J* = 10.0 Hz), 118.4, 116.9 (d, *J* = 10.6 Hz), 55.6. HRMS Calcd for C₂₁H₂₁O₄P [M+Na]⁺: 391.1075 Found: 391.1084.

4.2 Synthesis of racemic compound **9**

To a solution of **11** (23.8 g, 64.6 mmol) in dry THF (75 mL) at -20 °C was added dropwise LDA solution (prepared from 12.5 mL of *i*-Pr₂NH and *n*-BuLi in 50 mL of THF below -20 °C). After the addition, the resulting solution was stirred for further 2 h at -20 °C and then a suspension of anhydrous FeCl₃ (12.6 g, 77.3 mmol) in THF at -78 °C was added under N₂. The reaction mixture was warmed to room temperature and was stirred overnight. The solution was concentrated in vacuo, and the residue was diluted with CH₂Cl₂ and treated with 30 mL of ammonia water. After stirring for 30 minutes, the resulting suspension was filtered, and the filter cake was washed with CH₂Cl₂. The organic layer was washed with water and brine, dried, filtered, and concentrated. The resulting solid was purified by flash chromatography to afford pure *rac*-**9** (13.6 g, 57.4%) as a white solid. *R*_f = 0.55 (EtOAc), ¹H-NMR (CDCl₃, 400 MHz): δ 3.18 (s, 3H), 3.60 (s, 3H), 3.78 (s, 3H), 6.91-6.83 (m, 3H), 7.18-7.02 (m, 2H), 7.32-7.22 (m, 6H). ³¹P-NMR (CDCl₃, 167 MHz): δ 30.47. ¹³C-NMR (CDCl₃, 100 MHz): δ 159.4 (d, *J* = 14.8 Hz), 157.5 (d, *J* = 14.3 Hz), 137.9, 136.8, 135.8, 134.8, 134.8, 131.9, 130.9, 129.2, 129.1 (dd, *J* = 9.7 and 9.9 Hz),

127.8 (d, $J = 15.2$ Hz), 125.5 (d, $J = 12.5$ Hz), 124.9 (d, $J = 9.5$ Hz), 124.6 (d, $J = 9.9$ Hz), 117.9, 117.5 (dd, $J = 10.5$ and 11.2 Hz), 113.0, 55.6, 55.5, 54.9. HRMS Calcd for $C_{42}H_{40}O_8P_2$ $[M+Na]^+$: 757.2096 Found: 757.2081.

4.3 Resolution of compound 9

To a solution of *rac*-**9** (10.9 g, 14.8 mmol) in 10 mL of acetone was added (-)-DBTA (8.720 g, 24.3 mmol). The mixture was stirred at 10 °C overnight and filtered. The resulting solid was washed with acetone and was dissolved in CH_2Cl_2 . 150 mL of NaOH solution (2N) was added. The organic layer was washed with water and brine, dried, filtered, and concentrated to give a white solid (5.10 g). Yield: 46.8%. $[\alpha]_D^{25} = -106.0$ (c 1.12, $CHCl_3$), HPLC: Chiracel AD-H, Hexane / *i*-PrOH = 60 / 40, 0.8 mL / min, 245 nm), 5.2 min (*S*) and 11.9 min (*R*), ee > 99.0%.

4.4 Synthesis of (*S*)-MeO-BiPhep-Type 4.

To a solution of compound **9** (6.9 g, 9.39 mmol), and 13.1 mL of *N,N*-dimethylaniline (93.9 mmol) in 100 mL of dry toluene was added dropwise 9.5 mL of trichlorosilane (93.9 mmol) at room temperature. After being refluxed overnight, the reaction mixture was cooled to 0 °C, and 200 mL of degassed 30% aqueous NaOH was added and stirred for 30 minutes. The organic layer was isolated, washed with degassed water, 1N hydrochloric acid twice, and degassed distilled water again. The mixture was dried and concentrated in vacuo. The resulting residue was purified by flash chromatography to afford pure (-)-**4** (5.8 g, 87.8%) as a white solid. $R_f = 0.21$ (H/EA = 5/1), $[\alpha]_D^{25} = -26.2$ (c 1.67, $CHCl_3$). 1H -NMR ($CDCl_3$, 400 MHz): δ 3.20 (s, 3H), 3.61 (s, 3H), 3.70 (s, 3H), 6.87-6.70 (m, 8H), 7.16-7.11 (m, 1H), 7.23-7.18 (m, 1H), 7.28-7.24 (m, 1H). ^{31}P -NMR

(CDCl₃, 167 MHz): δ -12.6. ¹³C-NMR (CDCl₃, 100 MHz): δ 159.3, 157.5, 140.5, 139.1, 138.6, 133.3, 132.9, 129.2, 128.8, 126.7, 125.7, 125.6, 119.5, 119.4, 118.4, 118.3, 113.9, 111.0, 113.0, 55.2, 55.1, 54.9. HRMS Calcd for C₄₂H₄₀O₆P₂ [M+Na]⁺: 725.2198 Found: 725.2173.

4.5 Reduction of compound 7.

To a three-necked flask equipped with a thermometer, a condenser, a stirring bar, and a dropping funnel were added 3.3 g of compound **7** (4.6 mmol), 50 mL of dry toluene, and 3.0 mL of N, N-dimethylaniline (23.0 mmol) under nitrogen, followed by 2.3 mL of trichlorosilane (23.0 mmol) at room temperature. The resulting mixture was then refluxed overnight. The reaction mixture was cooled to 0 °C, and 50 mL of degassed 30% aqueous NaOH was added. After stirring for 30 minutes, the organic layer was isolated, washed with degassed distilled water, and 1N hydrochloric acid twice, and then with degassed distilled water again. The mixture was dried and concentrated in vacuo. The resulting residue was purified by flash chromatography to afford pure (-)-**4** (2.75 g, 85.2%) as a white solid.

5. Effects of Ylides on Yields and Selectivities of Allene **1b**

5.1 Synthesis of phosphonium salt **5a**

A mixture of phosphine **4** (281 mg, 0.4 mmol) and BrCH₂COOEt (50.1 mg, 0.3 mmol) in benzene (3 mL) was stirred at 25 °C for 48h. The solid was collected, washed with benzene, and dried in vacuo to give phosphonium salt **5a** (240 mg). Yield: 92.1%. White powder. $[\alpha]_D^{20} = -3.6^\circ$ (c = 0.76, CHCl₃). IR (KBr) ν/cm^{-1} 3061 (m), 2939 (m), 2181 (s), 1733 (vs), 1592 (vs), 639 (m);

^1H NMR (300 MHz, CDCl_3/TMS) δ 0.99 (t, J = 6.9 Hz, 3H), 2.13 (br, d, J = 12.9 Hz, 2H), 3.08 (s, 3H), 3.16 (s, 3H), 3.72 (s, 6H), 3.81-3.91 (m, 8H), 6.70-6.90 (m, 8H), 7.06-7.36 (m, 10H), 7.52-7.68 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 162.99 (d, J = 4.6 Hz), 159.35 (d, J = 16.9 Hz), 159.00 (d, J = 8.6 Hz), 158.53 (d, J = 9.1 Hz), 156.00 (d, J = 9.1 Hz), 138.92 (d, J = 10.8 Hz), 136.23 (d, J = 10.4 Hz), 135.38 (d, J = 8.6 Hz), 130.69, 129.21 (d, J = 7.4 Hz), 128.63 (d, J = 7.7 Hz), 127.58, 126.02 (d, J = 6.8 Hz), 125.19 (d, J = 28.3 Hz), 119.67, 119.23, 118.95, 118.50, 113.52 (d, J = 29.6 Hz), 111.13, 62.52, 55.37, 55.29, 54.56, 54.52, 54.38, 54.22, 31.15 (d, J = 51.7 Hz), 12.87; ^{31}P NMR (121.5 MHz, CDCl_3) δ 22.97 (d, J = 1.9 Hz), -12.18; MS (ESI, positive mode, m/z) 789.3 ($\text{M}-\text{Br}^-$). HRMS (MALDI/DHB) $\text{M}-\text{Br}^-$ Calcd for $\text{C}_{46}\text{H}_{47}\text{O}_8\text{P}_2^+$: 789.2754. Found: 789.2741.

5.2 Synthesis of phosphonium salt **5b**

A mixture of phosphine **4** (211 mg, 0.3 mmol) and $\text{BrCH}_2\text{COOEt}$ (200 mg, 1.2 mmol) in CH_2Cl_2 (2 mL) was stirred at 35 °C for 24h. The reaction mixture was diluted with 5 mL of benzene and the suspension was filtered. The resulting solid was washed with benzene, and dried in vacuo to give phosphonium salt **5b** (280 mg). Yield: 90.1%. White powder. $[\alpha]_{\text{D}}^{20} = +40.9^\circ$ (c = 0.89, CHCl_3). IR (KBr) ν/cm^{-1} 3063 (m), 2980 (s), 2185 (vs), 1732 (vs), 1593 (vs), 1037 (s); ^1H NMR (300 MHz, CDCl_3/TMS) δ 1.07 (t, J = 7.2 Hz, 6H), 2.25 (brs, 4H), 3.19 (s, 6H), 3.87 (s, 12H), 3.96-4.07 (m, 4H), 7.04-7.32 (m, 13H), 7.42-7.60 (m, 7H), 7.71-7.79 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 164.46 (d, J = 3.5 Hz), 159.65 (d, J = 3.3 Hz), 159.42 (d, J = 3.3 Hz), 157.08 (d, J = 15.0 Hz), 131.85 (d, J = 16.3 Hz), 131.10, 130.89, 130.66, 127.70, 125.87, 125.82, 125.75, 125.70, 125.00 (d, J = 10.1 Hz), 120.31, 119.65, 119.41, 119.13, 118.64, 118.24, 117.47, 62.80, 55.76, 55.62, 55.00, 33.16 (d, J = 54.5 Hz), 13.18; ^{31}P NMR (121.5 MHz, CDCl_3) δ 23.15; MS (ESI, positive mode, m/z) 875.5 ($\text{M}-\text{H}^+2\text{Br}^-$). HRMS (MALDI/DHB) $\text{M}-\text{H}^+2\text{Br}^-$ Calcd for $\text{C}_{50}\text{H}_{53}\text{O}_{10}\text{P}_2^+$: 875.3089. Found: 875.3109.

5.3 Synthesis of allene **1b** with phosphonium salt **5a**

To a mixture of phosphonium salt **5a** (174 mg, 0.2 mmol) and THF (1 mL) was added NaH (4.8 mg, 0.2 mmol), and the resulting mixture was stirred at room temperature for 4 h. The reaction mixture was cooled to -65 °C, and 2-phenyl-but-1-en-1-one **2b** (29.2 mg, 0.2 mmol) was added. After 72 h, the reaction mixture was diluted with petroleum ether, filtered quickly. The filtrate was concentrated, and the resulting oil was purified by flash chromatography (petroleum ether/ethyl acetate = 100/1) to give chiral allenic ester **1b** (38 mg, 88%, 96% ee).

5.4 Synthesis of allene **1b** with phosphonium salt **5b**

To a mixture of phosphonium salt **5b** (207 mg, 0.2 mmol) and THF (1 mL) was added 9.6 mg NaH (0.4 mmol), and the resulting mixture was stirred at room temperature for 4 h. The reaction mixture was cooled to -65 °C, and 2-phenyl-but-1-en-1-one **2b** (29.2 mg, 0.2 mmol) was added. After 72 h, the reaction mixture was diluted with petroleum ether, filtered quickly. The filtrate was concentrated, and the resulting oil was purified by flash chromatography (petroleum ether/ethyl acetate = 100/1) to give chiral allenic ester **1b** (16 mg, 37%, -20% ee).

Part II

Allenic ester 1a

Allenic ester 1b

Allenic ester 1c

Allenic ester 1d

Allenic ester 1c

Allenic ester 1f

Allenic ester 1g

Allenic ester 1h

Allenic ester 1i

Allenic ester 1j

Allenic ester 1k

Allenic ester 11

Allenic ester 1m

Allenic ester 1n

Allenic ester 1o

Allenic ester 1r

Allenic ester 1s

Chiral phosphine 4

Compound 11

³¹P (XW-1-22 in CDCl₃)

s

Compound 9

31P NMR (XW-1-29 in CDCl3)

Compound 7

Chemical structure of compound **2** is shown above the spectrum. The structure is a biphenyl derivative with two methoxy groups (MeO) and two PAR_2 groups. One PAR_2 group is attached to a carbon atom that is also bonded to a COOEt group and a positive charge. The other PAR_2 group is attached to a carbon atom that is also bonded to a bromine atom (Br^-).

The ^1H NMR spectrum (CDCl₃) shows the following peaks and integration values:

- Peak at 3.77 ppm (integration 3.77)
- Peak at 7.97 ppm (integration 10/18)
- Peak at 8.16 ppm (integration 8.16)
- Peak at 6.23 ppm (integration 6.23)
- Peak at 2.91 ppm (integration 2.91)
- Peak at 3.00 ppm (integration 3.00)
- Peak at 1.68 ppm (integration 1.68)
- Peak at 2.83 ppm (integration 2.83)

Compound 5b

Allenic ester 1a

lo.	R. Time	PeakHeight	PeakArea	PerCent
1	15.710	171530.1	5581730.8	50.0309
2	17.710	128037.1	5574827.0	49.9691
tal		299567.2	11156557.7	100.0000

No.	R. Time	PeakHeight	PeakArea	PerCent
1	15.960	239339.7	7865254.4	96.3861
2	18.043	7438.3	294899.9	3.6139
Total		246778.0	8160154.3	100.0000

Allenic ester 1b

Chuan-Ying, Li

LCY1084rac

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	10.2400	6.3121e+06	3.369e+05	50.4675	50.4675
2	12.1200	6.1952e+06	2.286e+05	49.5325	49.5325
		1.2507e+07	5.655e+05	100.0000	100.0000

Chuan-Ying, Li

LCY108401

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	10.2417	1.3137e+07	6.549e+05	98.4437	98.4437
2	12.3117	207688.3777	1.411e+04	1.5563	1.5563
		1.3345e+07	6.690e+05	100.0000	100.0000

Allenic ester 1r

Chuan-Ying, Li

LCY1135rac

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	11.3597	1.0493e+07	4.650e+05	49.5305	49.5305
2	12.5011	1.0692e+07	4.089e+05	50.4695	50.4695
		2.1186e+07	8.739e+05	100.0000	100.0000

Chuan-Ying, Li

LCY113501

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	11.1432	1.9146e+07	8.465e+05	96.6370	96.6370
2	12.3260	666289.9933	2.777e+04	3.3630	3.3630
		1.9812e+07	8.743e+05	100.0000	100.0000

Allenic ester 1i

序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	11.960	80422.7	2529659.1	50.2834
2	2	Unknown	13.710	77783.8	2501144.6	49.7166
合计:				158206.5	5030803.7	100.0000

序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	11.857	1814.6	34154.8	1.2654
2	2	Unknown	13.543	83294.3	2665049.6	98.7346
合计:				85108.9	2699204.4	100.0000

Allenic ester 1h

R. Time	PeakHeight	PeakArea	PerCent
31.793	379179.1	29278463.8	50.2988
42.543	171651.6	28930617.4	49.7012
	550830.7	58209081.2	100.0000

No.	R. Time	PeakHeight	PeakArea	PerCent
1	31.710	256336.1	19508306.6	98.2102
2	44.127	2618.7	355532.5	1.7898
total		258954.8	19863839.1	100.0000

Allenic ester 1g

R. Time	PeakHeight	PeakArea	PerCent
15.627	335212.3	11453566.3	49.9095
18.960	235574.0	11495098.3	50.0905
	570786.2	22948664.6	100.0000

No.	R. Time	PeakHeight	PeakArea	PerCent
1	15.460	353717.9	13135777.6	98.3490
2	18.960	4849.6	220514.5	1.6510
Total		358567.4	13356292.1	100.0000

Allenic ester 1s

Chuan-Ying, Li

LCY113401

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	0.0207	523.6553	434.7793	0.0026	0.0026
2	11.9024	1.0217e+07	4.337e+05	50.2200	50.2200
3	14.4418	1.0127e+07	3.521e+05	49.7775	49.7775
		2.0344e+07	7.862e+05	100.0000	100.0000

Chuan-Ying, Li

LCY1134rac

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	11.7050	1.4098e+07	4.993e+05	98.9117	98.9117
2	14.3233	155115.7984	5903.8553	1.0883	1.0883
		1.4253e+07	5.052e+05	100.0000	100.0000