Enantioselective Synthesis of Allenic Esters via Ylide Route

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Supplementary 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-d₃. 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-d₃. 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) B. L. Hodous and G. C. Fu, *J. Am. Chem. Soc.*, 2002, **124**, 1578; (b) B. L. Hodous and G. C. Fu, *J. Am. Chem. Soc.*, 2002, **124**, 10006; (c) B. L. Hodous and G. C. Fu, *J. Am. Chem. Soc.*, 2005, **127**, 6176; (d) L. M. Baigrie, H. R. Seiklay and T. T. Tidnell, *J. Am. Chem. Soc.*, 1985, **107**, 5391.

Part I Experimental Part

1. General procedure for the preparation of phosphonium salts.

1.1 (2S, 5S)-1,2,5-triphenyl phospholane $3^{2,3}$



To a slurry of Li₂PPh·Et₂O (4.7g, 24 mmol) in THF (110 mL) at -78 was added dropwise (1R,4R)-1,4-bis(methanesulfonyloxy)-1,4-diphenylbutane⁴ (7.9g, 20mmol) in THF (60 mL). Upon complete addition, the mixture was allowed to stir at -78 for 1h. The reaction was then slowly warmed to 25 and stirring was continued for 16h. The resulting mixture was filtered through a short silica gel column under N₂ and concentrated to a semi-solid. Extraction with n-hexane (100 mL) and filtration, followed by concentration in vacuo yielded the crude product as pale yellow oil, which was used directly for the following reaction without further purification.

Yield: 54%. White powder. ¹H NMR (300 MHz, CDCl₃/TMS) δ 2.00-2.15 (m, 1H), 2.24-2.41 (m, 2H), 2.68-2.85 (m, 1H), 3.76-3.87 (m, 1H), 4.01-4.10 (m, 1H), 6.88 (d, *J* = 7.5 Hz, 2H), 7.00-7.22 (m, 9H), 7.29-7.40 (m, 4H); ³¹P NMR (121.5 MHz, CDCl₃) δ 21.8.

1.2 (2S, 5S)-(-)-1-r-oxo-1, 2-c, 5-triphenyl phospholane **8**³

To a vigorously stirred solution of (2S, 5S)-1,2,5-triphenyl phospholane (3.16g, 10mmol) in petroleum ether (20 mL) at -15 was added dropwise 10% H_2O_2 (20 mmol) within 1h. After stirred at -15 for 4h, the reaction mixture was diluted with 40 mL of CHCl₃. The aqueous layer was extracted with CHCl₃ (3×30 mL). The combined organic extracts were washed with H_2O , dried (Na₂SO₄), and concentrated in vacuo. The residual oil was purified by flash column chromatography (CH₂Cl₂/CH₃OH = 100/1) to afford the title compound.

Yield: 3.0g (89%), White powder. ¹H NMR (300 MHz, CDCl₃/TMS) δ 2.18-2.34 (m, 1H), 2.47-2.81 (m, 3H), 3.50-3.60 (m, 1H), 3.82-3.98 (m, 1H), 7.01-7.49 (m, 15H); ³¹P NMR (121.5 MHz, CDCl₃) δ 54.2.

² M. J. Burk, J. E. Feaster and R. L. Harlow, *Tetrahedron: Asymmetry*, 1991, 2, 569.

³ F. Guillen, M. Rivard, M. Toffano, J.-Y. Legros, J.-C. Daran and J.-C. Fiaud, *Tetrahedron*, 2002, **58**, 5895.

⁴ D. J. Aldous, W. M. Dutton and P. G. Steel, *Tetrahedron: Asymmetry*, 2000, 11, 2455.

1.3 Preparation of pure (2S,5S)-1,2,5-triphenyl phospholane $3^{2,3}$

Pure (2S,5S)-1,2,5-triphenyl phospholane **3** was obtained by reduction of the corresponding oxide **8**.

1.4 General procedure for the preparation of phosphonium salts 4a and 4b



A mixture of phosphine **3** (10 mmol) and $BrCH_2COOR$ (10.5 mmol) in Et_2O (5 mL) was stirred at 25°C for 15h. The solid was collected, washed with ether, and dried in vacuo to give phosphonium salt **4**.

(2S, 5S) -1-ethoxycarbonylmethyl -1,2,5-triphenyl phospholanium; bromide 4a

Yield: 93%. White powder. m.p. 94-96°C, $[\alpha]_D^{20} = -87.5^\circ$ (c = 1.0, CHCl₃). IR (KBr) v/cm⁻¹ 2849 (m), 1735 (vs), 1601 (m), 1496 (m), 1454 (m), 1437 (s), 1309 (m), 762 (m), 701 (s); ¹H NMR (300 MHz, CDCl₃/TMS) δ 0.90 (t, *J* = 7.2 Hz, 3H), 2.41-2.69 (m, 1H), 2.70-3.01 (m, 2H), 3.15-3.37 (m, 1H), 3.71 (q, *J* = 7.2 Hz, 2H), 4.30 (dd, *J* = 13.5, 17.1 Hz, 1H), 4.52 (dd, *J* = 11.4, 17.1 Hz, 1H), 4.92-5.23 (m, 1H), 5.78-6.00 (m, 1H), 7.06-7.74 (m, 15H); ¹³C NMR (75 MHz, CDCl₃) δ 163.37 (d, *J* = 4.6 Hz), 133.83 (d, *J* = 4.0 Hz), 132.50 (d, *J* = 8.0 Hz), 131.87 (d, *J* = 5.3 Hz), 131.75 (d, *J* = 4.9 Hz), 129.15 (d, *J* = 12.4 Hz), 128.92 (d, *J* = 5.0 Hz), 128.83 (d, *J* = 2.7 Hz), 128.58 (d, *J* = 5.7 Hz), 128.26 (d, *J* = 1.7 Hz), 127.92 (d, *J* = 2.6 Hz), 127.60 (d, *J* = 3.2 Hz), 115.89 (d, *J* = 75.5 Hz), 61.93, 44.43 (d, *J* = 41.9 Hz), 41.92 (d, *J* = 43.6 Hz), 31.41, 31.30, 28.04 (d, *J* = 48.7 Hz), 13.1; ³¹P NMR (121.5 MHz, CDCl₃) δ 42.1; MS (ESI, positive mode, *m*/z) 403.3 (M-Br⁻). Anal. Calcd for C₂₆H₂₈BrO₂P: C, 64.60; H, 5.84; Br, 16.53; P, 6.41. Found: C, 64.14; H, 5.93; Br, 16.53; P, 6.08.

(2S, 5S) -1-t-butoxycarbonylmethyl -1,2,5-triphenyl phospholanium; bromide 4b

Yield: 93%. White powder. m.p. 117-120°C, $[\alpha]_D^{20} = -89.5^\circ$ (c = 1.0, CHCl₃). IR (KBr) v/cm⁻¹ 2979 (w), 2868 (w), 1728 (s), 1601 (m), 1495 (m), 1454 (m), 1151 (s), 762 (s), 733 (m), 702 (s); ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.02 (s, 9H), 2.40-2.62 (m, 1H), 2.67-3.04 (m, 2H), 3.10-3.31 (m, 1H), 4.03 (dd, *J* = 12.3, 17.7 Hz, 1H), 4.57 (dd, *J* = 11.1, 17.7 Hz, 1H), 4.96-5.20 (m, 1H), 5.81-6.02(m, 1H), 7.04-7.84 (m, 15H); ¹³C NMR (75 MHz, CDCl₃) δ 162.24 (d, *J* = 4.1 Hz), 133.88 , 132.46 (d, *J* = 5.7 Hz), 132.31 , 131.85 (d, *J* = 5.7 Hz), 129.35 (d, *J* = 2.9 Hz), 129.21, 129.13, 128.61 (d, *J* = 5.1 Hz).

Hz), 128.47, 128.09, 127.78, 116.5 (d, J = 75.5 Hz), 83.96, 44.44 (d, J = 42.9 Hz), 41.86 (d, J = 44.0 Hz), 32.54 (d, J = 8.0 Hz), 30.98 (d, J = 8.0 Hz), 28.95 (d, J = 48.7 Hz), 27.0; ³¹P NMR (121.5 MHz, CDCl₃) δ 42.6; MS (ESI, positive mode, m/z) 431.2 (M-Br⁻). Anal. Calcd for C₂₈H₃₂BrO₂P: C, 65.76; H, 6.31; Br, 15.62; P, 6.06. Found: C, 65.39; H, 6.47; Br, 15.48; P, 6.26.

.2. General procedure for preparation of allenic esters.

2.1 general procedure



To a solution of phosphonium salt 4 (0.2 mmol) in 1 mL of THF was added NaHMDS (1M in THF, 0.2 mL). After stirred for 1h at room temperature, the reaction mixture was cooled to -78 and stirred at this temperature for 2h. Ketene (0.2 mmol) was added, and the mixture was stirred for further 48h at -78 . After quenched with several drops of water, the reaction mixture was diluted with petroleum ether, and then filtered. The filtrate was concentrated, and the resulting oil was purified by flash chromatography (petroleum ether/ethyl acetate = 40/1) to give chiral allenic ester 6. The filter cake was submitted to column chromatography to recover phosphine oxide 8. **2.2** *In situ* procedure



Preparation of ketene *in situ.* To a solution of Et_3N (61 mg, 0.6 mmol) in 1 mL of trifluoromethyl-benzene (BTF) was added 2-phenyl-4-pentenoyl chloride (78 mg, 0.4 mmol). After stirred for 2h at room temperature, the reaction mixture was filtered under N₂, and the filtrate was concentrated in vacuo. The resulting light yellow oil was diluted with 0.5 mL of THF.

Preparation of allenic esters. The procedure is similar to that described in 2.1.

2.3 One pot procedure



To a solution of phosphonium salt **4** (0.2 mmol) in 1 mL of THF was added NaHMDS (1M in THF, 0.2ml). After stirred for 1h at room temperature, the reaction mixture was cooled to -20 . Et₃N (31 mg, 0.3 mmol) and acid chloride (0.24 mmol) was added in turn, and the resulting mixture was stirred at -20 for 24h. After quenched with several drops of water, the reaction mixture was diluted with petroleum ether, and then filtered. The filtrate was concentrated and the resulting oil was purified by flash chromatography (petroleum ether/ethyl acetate = 40/1) to give chiral allenic ester **6**. The filter cake was submitted to column chromatography to recover phosphine oxide **8**.

S-4-Phenyl-hexa-2,3-dienoic acid ethyl ester 6a⁵

Yield: 80%. Straw yellow oil. $[\alpha]_D^{20} = +124.2^{\circ}$ (c = 0.74, CHCl₃), 81% ee (determined by HPLC: Chiralcel AD Column, 1/100 ⁱPrOH/hexane, 0.8 mL/min, 254 nm). IR (KBr) v/cm⁻¹ 2973 (s), 2876 (w), 1946 (s), 1717 (vs), 1598 (m), 1494 (s), 1452 (s), 1150 (vs), 761 (s), 693 (m); 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 1)

5-Methyl-4-phenyl-hexa-2,3-dienoic acid ethyl ester 6b

Yield: 76%. Straw yellow oil. $[\alpha]_D^{20} = +66.0^{\circ}$ (c = 0.78, CHCl₃), 71% ee (determined by HPLC: Chiralcel AD Column, 0.3/100 ⁱPrOH/hexane, 1.0 mL/min, 254 nm). IR (KBr) v/cm⁻¹ 2967 (m), 2931 (m), 1948 (m), 1719 (s), 1494 (w), 1450 (m), 1384 (m), 1251 (s), 766 (m), 695 (m); 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); ¹³C NMR

⁵ W. Runge, Naturforsch. B Anorg. Chem. Org. Chem., 1977, 32, 1296.

(75 MHz, CDCl₃) δ 212.8, 166.0, 134.2, 128.6, 127.7, 127.0, 117.5, 91.6, 60.7, 28.9, 21.9, 21.8, 14.2; MS (EI, *m*/z, rel. intensity) 230 (15), 215 (56), 187 (59), 142 (57), 115 (100), 105 (64), 77 (47), 43 (83). HRMS (MALDI/DHB) M+Na⁺ Calcd for C₁₅H₁₈O₂Na⁺¹: 253.1208. Found: 253.1199. (Table 1, Entry 2)

6-Methyl-4-phenyl-hepta-2,3-dienoic acid ethyl ester 6c

Yield: 71%. Straw yellow oil. $[\alpha]_D^{20} = +50.7^{\circ}$ (c = 0.74, CHCl₃), 85% ee (determined by HPLC: Chiralcel AD-H Column, 0.3/100 ⁱPrOH/hexane, 0.8 mL/min, 254 nm). IR (KBr) v/cm⁻¹ 2957 (vs), 2931 (vs), 2870 (s), 1947 (s), 1721 (vs), 1494 (m), 1256 (m), 1148 (m), 694 (m); ¹H NMR (300 MHz, CDCl₃/TMS) δ 0.99 (d, *J* = 6.6 Hz, 6H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.84 (sep, *J* = 6.6 Hz, 1H), 2.30-2.54 (m, 2H), 4.16-4.29 (m, 2H), 5.88 (t, *J* = 2.4 Hz, 1H), 7.24-7.38 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 214.1, 165.9, 134.3, 128.6, 127.7, 126.7, 109.2, 90.0, 60.8, 39.5, 26.7, 22.6, 22.4, 14.3; MS (EI, *m*/z, rel. intensity) 244 (5), 229 (9), 173 (56), 129 (100), 115 (65), 43 (69), 41 (48). HRMS (MALDI/DHB) M+Na⁺ Calcd for C₁₆H₂₀O₂Na⁺¹: 267.1361. Found: 267.1356. Anal. Calcd for C₁₆H₂₀O₂: C, 78.65; H, 8.25. Found: C, 79.36; H, 8.47. (Table 1, Entry 3)

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

Yield: 46%. Straw yellow oil. $[\alpha]_D^{20} = +52.0^{\circ}$ (c = 0.84, CHCl₃), 61% ee (determined by HPLC: Chiralcel AS Column, hexane, 1.0 mL/min, 254 nm).IR (KBr) v/cm⁻¹ 2981 (m), 1946 (m), 1717 (vs), 1575 (m), 1451 (m), 1253 (s), 1148 (s), 917 (m), 758 (m), 693 (m); 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); ¹³C NMR (75 MHz, CDCl₃) δ 213.9, 165.6, 134.2, 133.6, 128.6, 127.8, 126.5, 117.3, 108.8, 91.1, 60.9, 34.2, 14.2; MS (EI, *m*/z, rel. intensity) 228 (3), 199 (42), 155 (100), 129 (36), 115 (63), 77 (55). Anal. Calcd for C₁₅H₁₆O₂: C, 78.92; H, 7.06. Found: C, 78.94; H, 7.10. (Table 1, Entry 4)

S-4,5-Diphenyl-penta-2,3-dienoic acid ethyl ester 6e

Yield: 51%. Straw yellow oil. $[\alpha]_D^{20} = +116.0^{\circ}$ (c = 0.82, CHCl₃), 52% ee (determined by HPLC: Chiralcel AS Column, 0.5/100 ⁱPrOH/hexane, 0.8 mL/min, 254 nm). IR (KBr) v/cm⁻¹ 2980 (m), 1947 (m), 1716 (s), 1594 (w), 1495 (m), 1453 (m), 1398 (m), 1253 (m), 1146 (m), 697 (m); ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.31 (t, J = 7.2Hz, 3H), 3.90 (d, J = 2.4 Hz, 2H), 4.14-4.27 (m, 2H), 5.87 (t, J = 2.4 Hz, 1H), 7.20-7.41(m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 214.6, 165.5, 137.9, 133.4, 128.7, 128.6, 128.3, 127.8, 126.7, 126.5, 109.4, 90.7, 60.9, 36.7, 14.2; MS (EI, *m*/z, rel. intensity) 278 (7), 249 (47), 205 (64), 91 (84), 57 (100). Anal. Calcd for C₁₉H₁₈O₂: C, 81.99; H, 6.52. Found: C, 82.07; H, 6.77. (Table1, Entry 5)

4-(4-Methoxy-phenyl)-hexa-2,3-dienoic acid ethyl ester 6f

Yield: 78%. Straw yellow oil. $[\alpha]_D^{20} = +150.0^{\circ}$ (c = 0.85, CHCl₃), 91% ee (determined by HPLC: Chiralcel AD-H Column, 0.5/100 ⁱPrOH/hexane, 1.0 mL/min, 254 nm). IR (KBr) v/cm⁻¹ 2971 (s), 2935 (s), 2876 (m), 1944 (s), 1719 (vs), 1607 (s), 1512 (s), 1252 (s), 1036 (m), 833 (s), 793 (m); 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* = 3.3Hz, 1H), 6.88 (d, *J* = 9.0, 2H), 7.31 (d, *J* = 9.0Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 213.6, 166.0, 159.2, 127.6, 126.2, 114.0, 111.9, 91.5, 60.7, 55.3, 23.0, 14.2, 12.2; MS (EI, *m*/z, rel. intensity) 246 (69), 217 (61), 173 (100), 158 (55), 115 (53). Anal. Calcd for C₁₅H₁₈O₃: C, 73.15; H, 7.37. Found: C, 73.08; H, 7.39. (Table 1, Entry 6)

4-(4-Chloro-phenyl)-hexa-2,3-dienoic acid ethyl ester 6g

Yield: 75%. Straw yellow oil. $[\alpha]_D^{20} = +108.2^{\circ}$ (c = 0.90, CHCl₃), 85% ee (determined by HPLC: Chiralcel AD-H Column, 0.3/100 ⁱPrOH/hexane, 0.8 mL/min, 254 nm). IR (KBr) v/cm⁻¹ 2973 (vs), 2935 (vs), 2876 (s), 1947 (vs), 1722 (vs), 1491 (s), 1418 (m), 1380 (m), 832 (m); 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); ¹³C NMR (75 MHz, CDCl₃) δ 213.4, 165.6, 133.5, 132.7, 128.7, 127.6, 111.5, 91.9, 60.9, 22.9, 14.2, 12.1; MS (EI, *m*/z, rel. intensity) 250 (13), 235 (14), 207 (33), 142(93), 141 (100), 115 (40). Anal. Calcd for C₁₄H₁₅ClO₂: C, 67.07; H, 6.03. Found: C, 67.35; H, 6.19. (Table 1, Entry 7)

4-Ethyl-octa-2,3-dienoic acid ethyl ester 6h⁶

Yield: 51%. Straw yellow oil. $[\alpha]_D^{20} = -50.3^\circ$ (c = 0.85, CHCl₃), 63% ee (determined by HPLC: Chiralcel AD-H Column, 0.1/100 ⁱPrOH/hexane, 1.0 mL/min, 220 nm). ¹H NMR (300 MHz,

⁶ G. R.Harvey, K. W. Ratts, J. Org. Chem., 1966, **31**, 3907.

CDCl₃/TMS) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2, 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 8)

Tetradeca-2,3-dienoic acid ethyl ester 6i

Yield: 52%. Straw yellow oil. $[\alpha]_D^{20} = -66.6^\circ$ (c = 0.92, CHCl₃), 55% ee (determined by HPLC: Chiralcel AD Column, 0.2/100 ⁱPrOH/hexane, 0.8 mL/min, 220 nm). IR (KBr) v/cm⁻¹ 2926 (vs), 2855 (s), 1961 (m), 1720 (vs), 1465 (m), 1418 (m), 1252 (m), 1156 (m), 1042 (m), 871 (w); 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); ¹³C NMR (75 MHz, CDCl₃) δ 212.3, 166.3, 95.4, 88.2, 60.7, 31.9, 29.57, 29.55, 29.33, 29.30, 28.91, 28.69, 27.46, 22.66, 14.21, 14.08; MS (EI, *m*/z, rel. intensity) 254 (17), 253 (100), 125 (11), 109 (7), 95 (11), 81 (26), 43 (6), 41 (9). Anal. Calcd for C₁₆H₂₈O₂: C, 76.14; H, 11.18. Found: C, 75.97; H, 11.43. (Table 1, Entry 9)

4-Phenyl-hexa-2,3-dienoic acid tert-butyl ester 6j

Yield: 51%. Straw yellow oil. $[\alpha]_D^{20} = +170.9^{\circ}$ (c = 0.82, CHCl₃), 92% ee (determined by HPLC: Chiralcel AD Column, 0.2/100 ⁱPrOH/hexane, 0.8 mL/min, 254 nm). IR (KBr) v/cm⁻¹ 2973 (vs), 2933(s), 1946(m), 1717(vs), 1597(w), 1494 (m), 1446 (m), 1368 (m), 1259 (m), 1139 (s); ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.17 (t, *J* = 7.2Hz, 3H), 1.48 (s, 9H), 2.46-2.58 (m, 2H), 5.85 (t, *J* = 3.0 Hz, 1H), 7.24-7.45 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 213.0, 165.2, 134.6, 128.5, 127.6, 126.4, 111.9, 93.0, 80.8, 28.1, 23.0, 12.3; MS (EI, *m*/z, rel. intensity) 244 (1), 189 (5), 143 (17), 128 (12), 57 (100), 43 (6), 41 (5). Anal. Calcd for C₁₆H₂₀O₂: C, 78.65; H, 8.25. Found: C, 78.71; H, 8.40.

3. Determination of the absolute configurations of allenic ester 6a and 6e

$$\begin{array}{c} R^2 \\ R^1 \\ \mathbf{6} \\ \mathbf{0} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{DMAP} \\ \mathsf{CH}_3\mathsf{OH} \end{array} \xrightarrow{\mathbf{R}^2} \begin{array}{c} \mathsf{R}^2 \\ \mathsf{R}^1 \\ \mathbf{9} \\ \mathbf{0} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \end{array} \xrightarrow{\mathbf{R}^2} \begin{array}{c} \mathsf{R}^2 \\ \mathsf{R}^1 \\ \mathbf{9} \\ \mathsf{O} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \end{array} \xrightarrow{\mathbf{R}^2} \begin{array}{c} \mathsf{R}^2 \\ \mathsf{R}^1 \\ \mathsf{S} \\ \mathsf{O} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \mathsf{R}^1 \\ \mathsf{S} \\ \mathsf{O} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \mathsf{CH}_3\mathsf{OH} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{R}^2 \\ \mathsf{R}^1 \\ \mathsf{S} \\ \mathsf{S} \\ \mathsf{O} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \mathsf{CH}_3\mathsf{OH} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{R}^2 \\ \mathsf{R}^1 \\ \mathsf{S} \\ \mathsf{S} \\ \mathsf{O} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \mathsf{CH}_3\mathsf{OH} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{R}^2 \\ \mathsf{R}^1 \\ \mathsf{S} \\ \mathsf{S} \\ \mathsf{O} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \mathsf{CH}_3\mathsf{OH} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \xrightarrow{\mathbf{0}} \\ \mathsf{CH}_3\mathsf{OH} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \mathsf{CH}_3\mathsf{OH} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \end{array} \xrightarrow{\mathbf{0}} \begin{array}{c} \mathsf{CH}_3\mathsf{OH} \\ \xrightarrow{\mathbf{0}} \end{array} \xrightarrow$$

To a solution of chiral allenic ester **6** (0.2 mmol) in 1mL of CH₃OH was added DMAP (24.4g, 0.2mmol). After stirred for 24h at room temperature, the reaction mixture was diluted with petroleum ether and then filtered through a short silica gel column. The filtrate was concentrated and the resulting oil was purified by flash chromatography (petroleum ether/ethyl acetate = 40/1) to give chiral allenic ester **9**. The absolute configurations of **9a** and **9e** were assigned by comparison with specific rotation data in the literature .⁷

S-4-Phenyl-hexa-2,3-dienoic acid methyl ester 9a⁷

Yield: 98%. Straw yellow oil. $[\alpha]_D^{20} = +25.7^{\circ}$ (c = 0.98, CCl₄),. ¹H NMR (300 MHz, CDCl₃/TMS) δ 1.17 (t, *J* = 7.2 Hz, 3H), 2.48-2.63 (m, 2H), 3.75 (s, 3H), 5.98 (t, *J* = 3.3Hz, 1H), 7.22-7.40 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 213.6, 166.3, 134.0, 128.5, 127.8, 126.3, 112.3, 91.3, 52.0, 22.8, 12.1; Anal. Calcd for C₁₃H₁₄O₂: C, 77.20; H, 6.98. Found: C, 77.34; H, 7.02.

S-4,5-Diphenyl-penta-2,3-dienoic acid methyl ester 9e⁷

Yield: 98%. Straw yellow oil. $[\alpha]_D^{20} = +27.9^{\circ}$ (c = 0.50, CHCl₃), ¹H NMR (300 MHz, CDCl₃/TMS) δ 3.76 (s, 3H), 3.90 (d, *J* = 2.4 Hz, 2H), 5.87 (t, *J* = 2.4 Hz, 1H), 7.19-7.40 (m, 10H).

Part II

Copies of NMR Spectra of All New Compounds and Copies of HPLC Spectra of chiral allenic esters.

⁷ J. Yamazaki, T. Watanabe and K. Tanaka, *Tetrahedron: Asymmetry*, 2001, **12**, 669.

(2S, 5S)-1,2,5-triphenyl phospholane 3





(2S, 5S)-(-)-1-r-oxo-1, 2-c, 5-triphenyl phospholane 8







Phosphonium salt 4a





Phosphonium salt 4b





Allenic ester 6a



Allenic ester 6b





Allenic ester 6c





Allenic ester 6d





Allenic ester 6e





Allenic ester 6f

Allenic ester 6g

Allenic ester 6h

Allenic ester 6i

Allenic ester 6j

Allenic ester 9a

Allenic ester 9e

cy034	4201				
Peak	Time	Area	Height	Area	Norm. Area
#	[min]	[uV*sec]	[uV]	[%]	[%]
1	9.2533	8.3167e+06	4.637e+05	90.3176	90.3176
2	10.5300	891579.5171	5.523e+04	9.6824	9.6824
		9.2083e+06	5.189e+05	100.0000	100.0000

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lcy049	97rac				
Peak	Time	Area	Height	Area	Norm. Area
#	[min]	[uV*sec]	[uV]	[%]	[%]
1	8.9717	1.5313e+07	9.699e+05	50.0015	50.0015
2	10.4917	1.5312e+07	6.320e+05	49.9985	49.9985
		3.0625e+07	1.602e+06	100.0000	100.0000

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					-
lcy06	5401				
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	5.6033 6.2033	1.1400e+06 195595.0627	1.795e+05 2.760e+04	85.3555 14.6445	85.3555 14.6445
		1.3356e+06	2.071e+05	100.0000	100.0000

				Chu	an- ring
lcy06	54rac				
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1 2	5.6100 6.2100	1.7201e+06 1.7306e+06	2.705e+05 2.420e+05	49.8476 50.1524	49.8476 50.1524
		3.4507e+06	5.126e+05	100.0000	100.0000

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Allenic ester 6c

92.3380

100.0000

7.6620

92.3380

7.6620

1 12.4106 4.7732e+06 2.508e+05

2 17.4239 396071.4781 1.298e+04

5.1693e+06 2.638e+05 100.0000

Allenic ester 6d

100.0000

1.4087e+06 1.997e+04 100.0000

34920	01				
Peak	Time	Area	Height	Area	Norm. Area
#	[min]	[u∀*sec]	[uV]	[%]	[%]
1	11.5717	1.1642e+07	3.579e+05	75.8395	75.8395
2	13.5350	3.7087e+06	9.626e+04	24.1605	24.1605
		1.5350e+07	4.541e+05	100.0000	100.0000

0492r	ac				
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	11.6117	1.2992e+07	4.026e+05	49.8463	49.8463
2	13.5317	1.3072e+07	3.289e+05	50.1537	50.1537
		2.6065e+07	7.315e+05	100.0000	100.0000

Allenic ester 6e

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Allenic ester 6f

lcy069201

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J,	

Allenic ester 6g

lcy0671rac

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Peak	Time	Area	Height	Area	Norm. Area
#	[min]	[uV*sec]	[u∨]	[%]	[%]
1	7.9467	4.5107e+06	3.468e+05	50.0642	50.0642
2	10.1733	4.4992e+06	2.659e+05	49.9358	49.9358
		9.0099e+06	6.127e+05	100.0000	100.0000

Chuan-Ying, L	i.
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lcy06	7101				
Peak #	Time [min]	Area [u∀*sec]	Height [uV]	Area [%]	Norm. Area [%]
1	7.9300	6.0931e+06 488740.3311	4.648e+05 2.870e+04	92.5744 7.4256	92.5744 7.4256
		6.5818e+06	4.935e+05	100.0000	100.0000

Allenic ester 6h

Peak

#

Time

[min]

Area

[uV*sec]

1 10.2867 6.3285e+06 3.632e+05

2 11.2117 1.4435e+06 1.092e+05

Height

[uV]

7.7719e+06 4.723e+05 100.0000

Area

[%]

81.4273

18.5727

S46

Norm. Area

[%]

81.4273

18.5727

100.0000

lcy061201						
Peak	Time	Area	Height	Area	Norm. Area	
#	[min]	[u∀*sec]	[u∨]	[%]	[%]	
1	7.5948	4.2679e+06	5.292e+05	77.4230	77.4230	
	8.4495	1.2445e+06	1.419e+05	22.5770	22.5770	
		5.5124e+06	6.711e+05	100.0000	100.0000	

icyou	12100					
Peak	Time	Area	Height	Area	Norm. Area	
#	[min]	[uV*sec]	[uV]	[%]	[%]	
1	7.6516	6.1282e+06	7.489e+05	50.0761	50.0761	
2	8.5071	6.1096e+06	6.682e+05	49.9239	49.9239	
		1.2238e+07	1.417e+06	100.0000	100.0000	

1	
ICVUB1	L/rac

Chuan-Ying, Li

	Chuan-Ying, Li							
lcy063	cy0634-1							
Peak #	Time [min]	Area [uV*sec]	Height [u∨]	Area [%]	Norm. Area [%]			
1 2	11.9550 16.3550	4.7582e+06 186513.2938	2.397e+05 7086.3980	96.2281 3.7719	96.2281 3.7719			
		4.9448e+06	2.468e+05	100.0000	100.0000			

S48

dia	16.38 1.16.38
 11111111111111111111111111111111111111	

8

icy0004-lac							
Peak	Time	Area	Height	Area	Norm. Area		
#	[min]	[u∀*sec]	[uV]	[%]	[%]		
1	11.5550	5.5061e+06	2.537e+05	49.8905	49.8905		
2	16.2483	5.5302e+06	1.955e+05	50.1095	50.1095		
		1.1036e+07	4.492e+05	100.0000	100.0000		

Less	0024 m	
ICY	0034-18	1C

Allenic ester 6j

Chuan-Ying, I	Li
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