PDC mediated tandem oxidative-Wittig Olefination

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Supporting Information

1. General remarks Flash chromatography was performed on silica gel (230–400 mesh). IR spectra were recorded on Shimadzu FT-IR spectrophotometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a Bruker instrument. Chemical shift (ppm) are relative to the internal standard Me_4Si (0 ppm).

2. General Procedure

To a magnetically stirred suspension of pyridinium dichromate (1.85 mmol), Wittig reagent (1.85 mmol) in anhyd CH_2Cl_2 (10 mL), alcohol (1.85 mmol) in anhyd CH_2Cl_2 (10 mL) was added in one portion. The reaction mixture was stirred at r.t. for 24h. Et_2O (30 mL) was added to the reaction mixture and filtered. The residue was washed with ether (2 X 5 mL) and dried over anhydrous Na_2SO_4 . The combined filtrate was then evaporated to give the crude product. Further purification by column chromatography using petroleum ether as an eluent gave the product.

3. Spectral data

Ethyl (2E)-3-phenylprop-2-enoate¹ (3a). Yield 0.15g (90%), Colourless oil; ^1H NMR (400 MHz, CDCl_3); δ = 1.36 (t, 3H, J = 7.2 Hz, CH_3), 4.29 (q, 2H, J = 7.2 Hz, CH_2), 6.46 (d, 1H, J = 16 Hz, CH), 7.42–7.71 (m, 2H, Ar-H), 7.53–7.58 (m, 2H, Ar-H), 6.46 (d, 1H, J = 16 Hz, CH); ^{13}C NMR (100 MHz, CDCl_3); δ = 14.3 (CH_3), 60.5 (CH_2), 118.3 (CH), 128.1 (2 x CH), 128.9 (2 x CH), 130.23 (CH), 134.5 (Cq), 144.6 (Cq), 167.0 (Cq). ν_{max} (thin flim); 1705, 1637, 1203 cm^{-1} .

Ethyl (2E)-3-(4-nitrophenyl)prop-2-enoate² (3b). Yield 0.23g (82%), yellow solid; ^1H NMR (400 MHz, CDCl_3); δ = 1.28 (t, 3H, J = 7.2 Hz, CH_3), 4.22 (q, 2H, J = 7.2 Hz, OCH_2), 6.49 (d, 1H, J = 16 Hz, CH), 7.59–7.66 (m, 3H, Ar-H and =CH), 8.18 (m, 2H, Ar-H), ^{13}C NMR (100 MHz, CDCl_3); δ = 14.3 (CH_3), 60.0 (CH_2), 122.6 (CH), 124.2 (2 x CH), 128.6 (2 x CH), 140.6 (Cq), 141.6 (CH), 148.4 (Cq), 166.2 (Cq). ν_{max} (KBr); 1710, 1643, 1253 cm^{-1} .

Ethyl (2E)-3-(4-methoxyphenyl)prop-2-enoate³ (3c). Yield 0.24g (81%), Colourless oil; ¹H NMR (400 MHz, CDCl₃); δ = 1.25 (t, 3H, J = 7.2 Hz, CH₃), 3.77 (s, 3H, OCH₃), 4.17 (q, 2H, J = 7.2 Hz, OCH₂), 6.24 (d, 1H, J = 16 Hz, CH), 6.83 (d, 2H, J = 8.8 Hz, Ar-H), 7.41 (d, 2H, J = 8.8 Hz, Ar-H), 7.575 (d, 1H, J = 16 Hz, CH), ¹³C NMR (100 MHz, CDCl₃) δ = 14.3 (CH₃), 55.2 (OCH₃), 60.2 (CH₂), 114.2 (2 x CH), 115.6 (CH), 121.3 (Cq), 129.6 (2 x CH), 144.2 (CH), 161.3 (Cq), 167.4 (Cq); ν_{max} (thin flim); 1707, 1602, 1170 cm⁻¹.

Ethyl (2E)-3-(furan-2-yl)prop-2-enoate² (3d). brown oil, yield 0.33g (99%); ¹H NMR (400 MHz, CDCl₃) δ = 1.252 (t, 3H, J = 7.2 Hz, CH₃), 4.17 (q, 2H, J = 7.2 Hz, OCH₂), 6.24 (d, 1H, J = 16 Hz, CH), 6.39 (m, 1H, Ar-H), 6.54 (d, 1H, Ar-H), 7.35 (d, 1H, J = 16 Hz, CH), 7.41 (d, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃); δ = 14.3 (CH₃), 60.4 (OCH₂), 112.2 (CH), 114.7 (CH), 115.9 (CH), 130.9 (CH), 144.7 (CH), 150.9 (Cq), 167.0 (Cq); ν_{max} (thin flim); 1712, 1639, 1209 cm⁻¹.

(3E)-4-(furan-2-yl)but-3-en-2-one² (3e). Yield, 0.27g (97%), Colourless oil; ¹H NMR (400 MHz, CDCl₃); δ = 2.265 (s, 3H, CH₃), 6.42 (m, 1H, Ar-H), 6.55 (d, 1H, J = 16 Hz, CH), 6.59 (m, 1H, Ar-H), 7.19 (d, 1H, J = 16 Hz, CH), 7.43 (m, 1H, Ar-H); ¹³C NMR (100 MHz, CDCl₃) δ = 27.6 (CH₃), 112.5 (CH), 115.7 (CH), 124.1 (CH), 129.4 (CH), 145.0 (CH), 150.8 (Cq), 197.8 (Cq); ν_{max} (thin flim); 1685, 1610, 1170 cm⁻¹.

Ethyl (2E)-4-(4-methoxyphenyl)but-2-enoate⁴ (3f). Yield 0.17g, (60%), Colourless oil; ¹H NMR (400 MHz, CDCl₃); δ = 1.20 (t, 3H, J = 7.2 Hz, CH₃), 3.34 (d, 2H, CH₂), 3.74 (s, 3H, OCH₃), 4.15 (q, 2H, J = 7.2 Hz, OCH₂), 5.76 (td, 1H, J = 16 Hz, J = 1.6 Hz, CH), 6.79 (m, 2H, Ar-H), 7.01 (m, 3H, Ar-H); ¹³C NMR (100 MHz, CDCl₃); δ = 14.3 (CH₃), 37.6 (CH₂), 55.2 (OCH₃), 60.3 (OCH₂), 114.1 (2 x CH), 122.1 (CH), 129.7 (Cq), 129.8 (2 x CH), 147.8 (CH), 158.4 (Cq), 166.6 (Cq); ν_{max} (thin flim); 1716, 1604, 1174 cm⁻¹.

Ethyl (2E)-non-2-enoate¹ (3g). Yield 0.28g (87%), Colourless oil; ¹H NMR (400 MHz, CDCl₃); δ = 1.19–1.26 (m, 11H, C₈H₁₁), 1.38 (t, 3H, J = 7.2 Hz, CH₃), 2.09 (m, 2H, CH₂), 4.12 (q, 2H, J = 7.2 Hz, CH₂), 5.73 (td, 1H, J = 16 Hz, 1.6 Hz, CH), 6.89 (td, 1H, J = 16 Hz, 6.8 Hz, CH); ¹³C NMR (100 MHz, CDCl₃); δ = 14.04 (CH₃), 14.25 (CH₃), 22.54 (CH₂), 27.96 (CH₂), 28.99 (CH₂), 31.43 (CH₂), 32.19 (CH₂), 60.11 (CH₂), 121.16 (CH), 149.5 (CH), 166.8 (Cq); ν_{max} (thin flim); 1720, 1654, 1174 cm⁻¹.

Diethyl (2E,6E)-octa-2,6-dienedioate⁵ (3h). Yield 0.31g (62%); Colourless oil; ¹H NMR (400 MHz, CDCl₃); δ = 1.30 (t, 6H, J = 7.2 Hz, CH₃), 2.39 (d, 4H, CH₂), 4.24 (q, 4H, J = 7.2 Hz, OCH₂), 5.87 (d, 1H, J = 16 Hz, CH), 6.95 (d, 1H, J = 16 Hz, CH); ¹³C NMR (100 MHz, CDCl₃) δ = 14.2 (2 x CH₃), 30.4 (2 x CH₂), 60.3 (2 x OCH₂), 122.3 (2 x CH), 133.6 (2 x Cq), 146.9 (2 x Cq); ν_{max} (thin flim); 1720, 1654, 1182 cm⁻¹.

Diethyl (2E,4E)-hexa-2,4-dienedioate¹ (3i). Yield 0.25 (40%); low melting solid; ¹H NMR (400 MHz, CDCl₃); δ = 1.32 (d, 6H, J = 6 Hz, CH₃), 4.24 (t, 4H, J = 6 Hz, OCH₂), 6.20 (m, 2H, CH), 7.32 (m, 2H, CH); ¹³C NMR (100 MHz, CDCl₃) δ = 14.2 (2xCH₃), 60.8 (2 x OCH₂), 128.3 (2 x CH), 140.8 (2 x CH), 165.9 (2 x Cq); $\nu_{\max}$ (KBr); 1730, 1714, 1176 cm⁻¹.

Ethyl (2E)-4-methylpent-2-enoate² (3j). Yield 0.25g (66%); Colourless oil; ¹H NMR (400 MHz, CDCl₃); δ = 1.00 (d, 6H, J = 6.8 Hz, CH₃), 1.22 (t, 3H, J = 7.2 Hz, CH₃), 2.39 (m, 1H, CH), 4.12 (q, 2H, J = 7.2 Hz, CH₂), 5.71 (dd, 1H, J = 16 Hz, J = 1.6 Hz, CH), 6.89 (dd, 1H, J = 16 Hz, J = 1.6 Hz, CH); ¹³C NMR (100 MHz, CDCl₃) δ = 14.2 (CH₃), 23.9 (CH), 29.8 (2 x CH₃), 60.5 (OCH₂), 117.9 (CH), 154.6 (CH), 167.0 (Cq); $\nu_{\max}$ (thin flim); 1705, 1654, 1157 cm⁻¹.

Ethyl (2E,4E)-5-phenylpenta-2,4-dienoate² (3k). Yield 0.22g (73%); Colourless oil; ¹H NMR (400 MHz, CDCl₃); δ = 1.34 (t, 3H, J = 7.2 Hz, CH₃), 4.25 (q, 2H, J = 7.2 Hz, OCH₂), 6.01 (d, 1H, J = 16 Hz, CH), 6.90 (d, 1H, J = 8.4 Hz, CH), 7.3–7.50 (m, 7H, Ar-H and vinylic); ¹³C NMR (100 MHz, CDCl₃) δ = 14.3 (CH₃), 60.3 (OCH₂), 121.3 (CH), 126.2 (CH), 127.4 (2 x CH), 128.8 (2 x CH), 129.0 (CH), 136.0 (Cq), 140.4 (CH), 144.6 (CH), 167.1 (Cq); $\nu_{\max}$ (thin flim); 1718, 1510, 1176 cm⁻¹.

Ethyl (2E)-penta-2,4-dienoate⁶ (3l). Yield 0.30g (70%); Colourless oil; ¹H NMR (400 MHz, CDCl₃); δ = 1.22 (t, 3H, J = 7.2 Hz, CH₃), 4.16 (q, 2H, J = 7.2 Hz, CH₂), 5.42 (d, 1H, J = 10 Hz, CH), 5.52 (dd, 1H, J = 17 Hz, 0.4 Hz, CH), 5.82 (dd, 1H, J = 15.2 Hz, 0.4 Hz, CH), 6.38 (m, 1H, CH), 7.19 (m, 1H, J = 11 Hz, CH); ¹³C NMR (100 MHz, CDCl₃); δ = 14.2 (CH₃), 60.6 (OCH₂), 122.9 (CH), 125.5 (CH), 134.7 (CH), 144.7 (CH), 166.9 (Cq); $\nu_{\max}$ (thin flim); 1720, 1651, 1178 cm⁻¹.

Ethyl (2E)-pent-2-en-4-ynoate⁶ (3m). Yield 0.25g (56%); Colourless oil; ¹H NMR (400 MHz, CDCl₃); δ = 1.35 (t, 3H, J = 7.2 Hz, CH₃), 3.26 (s, 1H, CH) 4.14 (q, 2H, J = 7.2 Hz, OCH₂), 6.25 (d, 1H, J = 16 Hz, CH), 6.64 (d, 1H, J = 16 Hz, CH); ¹³C NMR (100 MHz, CDCl₃); δ = 14.2 (CH₃), 60.95 (OCH₂), 80.2 (Cq), 85.81 (CH), 123.9 (CH), 132.5 (CH), 164.4 (Cq); $\nu_{\max}$ (thin flim); 1720, 1651, 1178 cm⁻¹.

tert-Butyl 2-[(1E)-3-ethoxy-3-oxoprop-1-en-1-yl]pyrrolidine-1-carboxylate⁷ (3n). Yield, 0.21g (84%); [α]_D²¹=79 (c = 1 MeOH); Colourless oil; ¹H NMR (400 MHz, CDCl₃); δ = 1.21 (t, 3H, J = 7.2 Hz, CH₃), 1.36 (s, 9H, CH₃), 1.80 (m, 2H, CH₂), 2.02 (m, 2H, CH₂), 3.35 (t, 2H, J = 5.2 Hz, CH₂), 4.12 (q, 2H, J = 7.2 Hz, OCH₂), 4.352 (br, 1H, CH), 5.75 (d, 1H, J = 15.6 Hz, CH), 6.75 (dd, 1H, J = 15.6 Hz, J = 5.6 Hz, CH); ¹³C NMR (100 MHz, CDCl₃) δ = 14.2

(CH₃), 22.9 (CH₂), 28.2 (3 x CH₃), 31.7 (CH₂), 46.2 (CH₂), 57.8 (CH), 60.4 (OCH₂), 79.7 (Cq), 120.4 (CH), 148.5 (CH), 154.3 (Cq), 166.5 (Cq); ν_{max} (thin film); 1720, 1693, 1168 cm⁻¹.

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4. Spectra

Ethyl (2*E*)-3-phenylprop-2-enoate (3a).

Ethyl (2E)-3-(4-nitrophenyl)prop-2-enoate (3b).

Ethyl (2E)-3-(4-methoxyphenyl)prop-2-enoate (3c).

Ethyl (2E)-3-(furan-2-yl)prop-2-enoate (3d).

(3E)-4-(furan-2-yl)but-3-en-2-one (3e).

Ethyl (2E)-4-(4-methoxyphenyl)but-2-enoate (3f).

Ethyl (2*E*)-non-2-enoate (3g).

diethyl (2*E*,4*E*)-hexa-2,4-dienedioate (3i).

Ethyl (2E)-4-methylpent-2-enoate (3j).

Ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate (k).

Ethyl (2*E*)-penta-2,4-dienoate (3l).

Ethyl (2*E*)-pent-2-en-4-ynoate (m).

***tert*-Butyl 2-[(1*E*)-3-ethoxy-3-oxoprop-1-en-1-yl]pyrrolidine-1-carboxylate (n).**