Supporting Information

Enantioselective Alkylation of β -Keto Esters by Phase-Transfer Catalysis using Chiral Quaternary Ammonium Salts

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1. General procedure for the alkylation of β -keto esters. To a stirred solution of β -keto ester (0.3 mmole), KOH (101 mg, 1.8 mmol) and cinchonium salt **3a** (19 mg, 0.03 mmol) in toluene (3 mL) was added alkyl halide (0.45 mmol) at room temperature. Reaction mixture was stirred for 2-72 h at room temperature. The mixture was diluted with saturated NH_4Cl solution (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered, concentrated, and purified by flash chromatography to afford the α -alkylated β -keto ester.

2. Characterization of alkylated β -keto esters

2-Allyl-2-(methoxycarbonyl)-1-tetralone (2a).¹ R_f 0.37 (EtOAc:Hexane = 1:8); $[\alpha]_D^{25} - 33.65$ (c 0.91, CHCl_3 , 68% ee); ^1H NMR (200 MHz, CDCl_3) δ 8.05 (d, $J = 7.8$ Hz, 1H), 7.44-7.52 (m, 1H), 7.20-7.35 (m, 2H), 5.72-5.93 (m, 1H), 5.09-5.19 (m, 2H), 3.67 (s, 3H), 2.81-3.16 (m, 2H), 2.66-2.78 (m, 2H), 2.47-2.62 (m, 1H), 2.04-2.22 (m, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 195.0, 172.1, 143.3, 133.6, 133.5, 132.0, 128.9, 128.1, 126.8, 119.0, 57.5, 52.5, 38.8, 30.6, 25.9; HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$) 267.0997, found 267.1003; R_t HPLC (hexane:*iso*-PrOH = 95:5, 254 nm, 1.0 mL/min) Chiralcel OD-H column, $t_R = 7.68$ min (minor), $t_R = 7.97$ min (major).

2-Benzyl-2-(methoxycarbonyl)-1-tetralone (2b). R_f 0.43 (EtOAc:Hexane = 1:5); $[\alpha]_D^{27} - 3.9$ (c 1.0 CHCl_3 , 66% ee); ^1H NMR (200 MHz, CDCl_3) δ 8.08 (d, $J = 8.6$ Hz, 1H), 7.49-7.41 (m, 2H), 7.34-7.15 (m, 6H), 3.66 (s, 3H), 3.46 (d, $J = 13.4$ Hz, 1H), 3.31 (d, $J = 13.5$ Hz, 1H), 3.08-3.00 (m, 1H), 2.91-2.80 (m, 1H), 2.55-2.44 (m, 1H), 2.06-1.91 (m, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 194.5, 171.8, 143.2, 136.4, 133.5, 132.1, 130.7, 128.7, 128.1, 126.8, 126.7, 125.1, 58.7, 52.5, 40.1, 30.4, 26.0; HRMS calcd for $\text{C}_{19}\text{H}_{18}\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$) 317.1154, found 317.1159; R_t HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralpak AD column, $t_R = 6.65$ min (major), $t_R = 6.93$ min (minor).

2-*p*-Nitrobenzyl-2-(methoxycarbonyl)-1-tetralone (2c). R_f 0.15 (EtOAc:Hexane = 1:9); $[\alpha]_D^{28}$ -15.0 (c 1.0 CHCl₃, 99% ee); ¹H NMR (200 MHz, CDCl₃) δ 8.13-8.05 (m, 3H), 7.47-7.26 (m, 4H), 7.18 (d, J = 7.6 Hz, 1H), 3.66 (s, 3H), 3.56 (d, J = 13.5 Hz, 1H), 3.37 (d, J = 13.4 Hz, 1H), 3.09-3.00 (m, 1H), 2.93-2.82 (m, 1H), 2.57-2.45 (m, 1H), 2.05-1.90 (m, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 194.0, 171.5, 147.0, 144.4, 142.9, 133.8, 132.0, 131.7, 128.8, 128.2, 127.0, 123.2, 58.7, 52.7, 39.9, 31.0, 26.0; HRMS calcd for C₁₉H₁₇NO₅Na ([M+Na]⁺) 362.1004, found 362.1010; R_t HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralpak AD column, t_R = 11.40 min (major), t_R = 13.68 min (minor).

2-*trans*-Cinnamyl-2-(methoxycarbonyl)-1-tetralone (2d).¹ R_f 0.34 (EtOAc:Hexane = 1:8); $[\alpha]_D^{25}$ -6.40 (c 0.63, CHCl₃, 59% ee); ¹H NMR (200 MHz, CDCl₃) δ 8.08 (d, J = 7.7 Hz, 1H), 7.44-7.52 (m, 1H), 7.16-7.36 (m, 7H), 6.49 (d, J = 6.5 Hz, 1H), 6.15-6.30 (m, 1H), 3.68 (s, 3H), 2.95-3.08 (m, 2H), 2.88 (d, J = 7.4 Hz, 2H), 2.57 (dt, J = 4.8, 13.7 Hz, 1H), 2.12-2.27 (m, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 195.1, 172.1, 143.2, 137.2, 133.9, 133.6, 131.9, 128.8, 128.4, 128.1, 127.3, 126.8, 126.2, 125.1, 57.8, 52.5, 38.1, 30.6, 25.9; HRMS calcd for C₂₁H₂₀O₃Na ([M+Na]⁺) 320.1412, found 320.1409; R_t HPLC (hexane:*iso*-PrOH = 95:5, 254 nm, 1.0 mL/min) Chiralcel OD-H column, t_R = 8.10 min (minor), t_R = 8.58 min (major).

2-Benzyl-2-(ethoxycarbonyl)-1-tetralone (2e). R_f 0.30 (EtOAc:Hexane = 1:9); $[\alpha]_D^{25}$ -7.9 (c 1.0, CHCl₃, 84% ee); ¹H NMR (200 MHz, CDCl₃) δ 8.07 (d, J = 9.1 Hz, 1H), 7.48-7.40 (m, 1H), 7.33-7.14 (m, 7H), 4.12 (q, J = 7.3 Hz, 2H), 3.47 (d, J = 13.5 Hz, 1H), 3.29 (d, J = 13.4 Hz, 1H), 3.11-3.00 (m, 1H), 2.91-2.78 (m, 1H), 2.54-2.43 (m, 1H), 2.05-1.90 (m, 1H), 1.14 (t, J = 7.3 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 194.6, 171.4, 143.1, 136.6, 133.4, 132.3, 130.8, 128.6, 128.1, 126.7, 61.5, 58.6, 39.9, 30.4, 26.0, 14.0; HRMS calcd for C₂₀H₂₀O₃Na ([M+Na]⁺) 331.1310, found 331.1319; R_t HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 0.5 mL/min) Chiralcel OD-H column, t_R = 11.95 min (minor), t_R = 12.54 min (major).

2-Ethyl-2-(ethoxycarbonyl)-1-tetralone (2f).² R_f 0.36 (EtOAc:Hexane = 1:9); $[\alpha]_D^{25}$ -15.4 (c 1.0, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ 8.04 (d, J = 8.6 Hz, 1H), 7.52-7.42 (m, 1H), 7.36-7.30 (m, 1H), 7.23-7.17 (m, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.04-3.01 (m, 1H), 2.96-2.93 (m, 1H), 2.62-2.52 (m, 1H), 2.21-1.92 (m, 3H), 1.17 (t, J = 7.3 Hz, 3H), 0.99 (t, J = 7.5 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 195.1, 171.3, 140.7, 136.5, 132.7, 128.4, 128.2, 125.6, 61.6, 57.6, 30.4, 25.9, 20.8, 14.0, 9.1; HRMS calcd for C₁₅H₁₈O₃Na ([M+Na]⁺) 269.1154, found 269.1161; R_t HPLC (hexane:*iso*-PrOH = 98:2, 254 nm, 1.0 mL/min) Chiralcel OD-H column, t_R = 6.34min (minor), t_R = 7.00 min (major).

2-Allyl-2-(ethoxycarbonyl)-1-tetralone (2g).³ R_f 0.27 (EtOAc:Hexane = 1:9); $[\alpha]_D^{25}$ -26.9 (c 1.0, CHCl₃, 60% ee); ¹H NMR (200 MHz, CDCl₃) δ 8.05 (d, J = 8.5 Hz, 1H), 7.51-7.43 (m, 1H), 7.34-7.20 (m, 2H), 5.95-5.74 (m, 1H), 5.13 (dd, J = 8.6, 10.42, 2H), 4.14 (q, J = 7.2 Hz, 2H), 3.09-2.94 (m, 2H), 2.74-2.70 (m, 2H), 2.59-2.48 (m, 1H), 2.21-2.07 (m, 1H), 1.17 (t, J = 7.2 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 195.0, 171.4, 143.1, 133.4, 128.9, 128.7, 128.0, 127.0, 126.7, 118.8, 61.3, 57.2, 38.5, 30.4, 25.8, 14.0; HRMS calcd for C₁₆H₁₈O₃Na ([M+Na]⁺) 181.1154, found 281.1161; R_t HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralcel OJ column, t_R = 5.97 min (major), t_R = 8.10 min (minor).

2-*p*-Nitrobenzyl-2-(ethoxycarbonyl)-1-tetralone (2h). R_f 0.14 (EtOAc:Hexane = 1:9); $[\alpha]_D^{25}$ -17.3 (c 1.0, CHCl₃, 96% ee); ¹H NMR (200 MHz, CDCl₃) δ 8.15-8.04 (m, 3H), 7.47-7.42 (m, 3H), 7.33 (d, J = 7.5 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 4.12 (q, J = 7.3 Hz, 2H), 3.57 (d, J = 13.4 Hz, 1H), 3.36 (d, J = 13.4 Hz, 1H), 3.10-3.01 (m, 1H), 2.94-2.83 (m, 1H), 2.56-2.45 (m, 1H), 2.04-1.89 (m, 1H), 1.12 (t, J = 7.3 Hz, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 194.1, 171.0, 146.9, 144.5, 142.8, 133.7, 131.7, 128.7, 128.0, 126.8, 123.1, 61.8, 58.5, 39.6, 30.9, 26.0, 13.9; HRMS calcd for C₂₀H₁₉NO₅Na ([M+Na]⁺) 376.1161, found 376.1171; R_t HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralpak AD column, t_R = 10.64 min (major), t_R = 12.26 min (minor).

2-Benzyl-2-(benzyloxycarbonyl)-1-tetralone (2i). R_f 0.3 (EtOAc:Hexane = 1:9); $[\alpha]_D^{30}$ -

7.3 (c 1.0 CHCl₃, 67% ee); ¹H NMR (200 MHz, CDCl₃); δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.48-7.40 (m, 1H), 7.34-7.08 (m, 7H), 5.14 (d, *J* = 12.5 Hz, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 3.47 (d, *J* = 13.7 Hz, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.01-2.90 (m, 1H), 2.86-2.73 (m, 1H), 2.53-2.42 (m, 1H), 2.05-1.90 (m, 1H); ¹³C NMR (50 MHz, CDCl₃); δ 194.4, 171.2, 143.1, 136.4, 135.4, 133.4, 132.3, 130.7, 128.7, 128.4, 128.1, 127.8, 127.4, 126.7, 66.9, 58.6, 39.8, 30.4, 25.9; HRMS calcd for C₂₅H₂₂O₃Na ([M+Na]⁺) 393.1467, found 393.1472; *R_f* HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralpak AD column, *t_R* = 9.00 min (minor), *t_R* = 9.51 min (major).

2-Allyl-2-(benzyloxycarbonyl)-1-tetralone (2j).⁴ *R_f* 0.27 (EtOAc:Hexane = 1:15); [α]_D²⁵ -18.2 (c 1.0, CHCl₃, 47% ee); ¹H NMR (200 MHz, CDCl₃) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.50-7.43 (m, 1H), 7.34-7.11 (m, 7H), 5.88-5.71 (m, 1H), 5.23-5.00 (m, 4H), 3.03-2.89 (m, 2H), 2.85-2.71 (m, 2H), 2.59-2.47 (m, 1H), 2.22-2.07 (m, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 194.8, 171.2, 140.9, 140.3, 139.5, 132.7, 128.7, 128.4, 128.2, 127.4, 127.3, 125.6, 67.1, 60.9, 31.8, 29.2, 26.4; HRMS calcd for C₂₁H₂₀O₃Na ([M+Na]⁺) 343.1310, found 343.1318; *R_f* HPLC (hexane:*iso*-PrOH = 98:2, 254 nm, 1.0 mL/min) Chiralcel OD-H column, *t_R* = 8.24 min (minor), *t_R* = 8.89 min (major).

2-Benzyl-2-(*t*-butoxycarbonyl)-1-tetralone (2k). *R_f* 0.27 (EtOAc:Hexane = 1:15); [α]_D²⁷ -13.9 (c 1.0 CHCl₃, 75% ee); ¹H NMR (200 MHz, CDCl₃) δ 8.05 (d, *J* = 9.2 Hz, 1H), 7.47-7.39 (m, 2H), 7.32-7.14 (m, 6H), 3.49 (d, *J* = 13.5 Hz, 1H), 3.21 (d, *J* = 13.4 Hz, 1H), 3.08-3.00 (m, 1H), 2.90-2.80 (m, 1H), 2.48-2.37 (m, 1H), 2.02-1.87 (m, 1H), 1.29 (s, 9H); ¹³C NMR (50 MHz, CDCl₃) δ 193.2, 170.7, 142.7, 136.8, 133.0, 132.8, 130.9, 128.5, 127.9, 127.8, 126.5, 82.2, 59.1, 39.5, 30.8, 27.7, 26.1; HRMS calcd for C₂₂H₂₄O₃Na ([M+Na]⁺) 359.1623, found 359.1632; *R_f* HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralpak AD column, *t_R* = 4.20 min (major), *t_R* = 4.68 min (minor).

2-*p*-Nitrobenzyl-2-(*t*-butoxycarbonyl)-1-tetralone (2l). *R_f* 0.31 (EtOAc:Hexane = 1:6); [α]_D²⁷ -39.4 (c 0.5 CHCl₃, 99% ee); ¹H NMR (200 MHz, CDCl₃) δ 8.10 (d, *J* = 6.8 Hz, 2H),

8.03 (d, $J = 9.2$ Hz, 1H), 7.50-7.41 (m, 3H), 7.34-7.27 (m, 1H), 7.17 (d, $J = 7.6$ Hz, 1H), 3.54 (d, $J = 13.5$ Hz, 1H), 3.30 (d, $J = 13.6$ Hz, 1H), 3.10-3.02 (m, 1H), 2.93-2.82 (m, 1H), 2.50-2.40 (m, 1H), 2.02-1.87 (m, 1H), 1.26 (s, 9H); ^{13}C NMR (50 MHz, CDCl_3) δ 194.7, 171.1, 146.8, 144.9, 142.4, 133.4, 132.6, 131.8, 128.5, 127.8, 126.7, 123.1, 82.9, 59.0, 39.4, 31.5, 27.6, 26.1; HRMS calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$) 404.1474, found 404.1479; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralpak AD column, $t_R = 6.30$ min (major), $t_R = 7.44$ min (minor).

2-Benzyl-2-(ethoxycarbonyl)-1-indanone (2m). R_f 0.45 (Aceton:Hexane = 1:9); $[\alpha]^{25}_D +12.4$ (c 1.0, CHCl_3 , 63% ee); ^1H NMR (200 MHz, CDCl_3) δ 7.74 (d, $J = 7.6$ Hz, 1H), 7.57-7.50 (m, 1H), 7.37-7.30 (m, 3H), 7.22-7.12 (m, 4H), 4.18 (q, $J = 7.3$ Hz, 2H), 3.63 (d, $J = 17.4$ Hz, 1H), 3.49 (d, $J = 14.0$ Hz, 1H), 3.28 (d, $J = 13.9$ Hz, 1H), 3.16 (d, $J = 17.4$ Hz, 1H), 1.21 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 202.2, 170.7, 153.2, 136.4, 135.2, 130.0, 128.2, 127.5, 126.7, 126.1, 124.6, 61.8, 39.6, 35.4, 29.6, 14.0; HRMS calcd for $\text{C}_{19}\text{H}_{18}\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$) 317.1154, found 317.1162; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralpak AD column, $t_R = 6.59$ min (minor), $t_R = 7.73$ min (major).

2-*p*-Nitrobenzyl-2-(ethoxycarbonyl)-1-indanone (2n). R_f 0.17 (EtOAc:Hexane = 1:9); $[\alpha]^{28}_D +32.9$ (c 1.0, CHCl_3 , 65% ee); ^1H NMR (200 MHz, CDCl_3) δ 8.08-8.01 (m, 2H), 7.75 (d, $J = 8.1$ Hz, 1H), 7.61-7.54 (m, 1H), 7.40-7.31 (m, 4H), 4.18 (q, $J = 7.3$ Hz, 2H), 3.65 (d, $J = 17.4$ Hz, 1H), 3.55 (d, $J = 14.0$ Hz, 1H), 3.41 (d, $J = 13.9$ Hz, 1H), 3.09 (d, $J = 17.4$ Hz, 1H), 1.20 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 201.5, 170.3, 159.2, 152.7, 147.0, 144.2, 135.7, 130.9, 128.0, 126.2, 124.8, 123.4, 62.1, 61.1, 39.2, 35.6, 14.0; HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_5\text{Na}$ ($[\text{M}+\text{Na}]^+$) 362.1004, found 362.1009; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralpak AD column, $t_R = 14.3$ min (minor), $t_R = 15.03$ min (major).

2-Allyl-2-(ethoxycarbonyl)-1-indanone (2o).⁵ R_f 0.24 (MC:Hexane = 1:1); $[\alpha]^{29}_D +68.1$ (c 0.5, CHCl_3 , 57% ee); ^1H NMR (200 MHz, CDCl_3) δ 7.77 (d, $J = 7.6$ Hz, 1H), 7.66-7.59 (m,

1H), 7.54-7.35 (m, 2H), 5.75-5.55 (m, 1H), 5.17-5.02 (m, 2H), 4.16 (q, $J = 7.2$ Hz, 2H), 3.65 (d, $J = 17.5$ Hz, 1H), 3.14 (d, $J = 17.5$ Hz, 1H), 2.75 (dd, $J = 6.3, 72.0$ Hz, 1H), 2.75 (dd, $J = 6.3, 43.6$ Hz, 1H), 1.21 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 202.2, 170.7, 153.1, 135.3, 135.1, 132.7, 127.7, 126.4, 124.7, 119.2, 61.6, 59.9, 39.0, 35.9, 14.0; HRMS calcd for $\text{C}_{15}\text{H}_{16}\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$) 267.0997, found 267.1004; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Whelk-O1 column, $t_R = 7.00$ min (minor), $t_R = 8.85$ min (major).

2-Benzyl-2-(methoxycarbonyl)-1-indanone (2p).⁶ R_f 0.32 (Aceton:Hexane = 1:4); $[\alpha]_D^{28} +84.8$ (c 1.0 CHCl_3 , 63% ee); ^1H NMR (200 MHz, CDCl_3) δ 7.75 (d, $J = 8.8$ Hz, 1H), 7.59-7.51 (m, 1H), 7.38-7.34 (m, 2H), 7.26-7.12 (m, 5H), 3.72 (s, 3H), 3.63 (d, $J = 17.5$ Hz, 1H), 3.50 (d, $J = 13.9$ Hz, 1H), 3.29 (d, $J = 13.9$ Hz, 1H), 3.18 (d, $J = 17.4$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 202.1, 171.2, 153.1, 136.3, 135.3, 130.9, 129.9, 128.3, 127.6, 126.8, 126.2, 124.7, 61.7, 52.8, 39.7, 35.4; HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$) 303.0997, found 303.1002; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralpak AD column, $t_R = 9.23$ min (minor), $t_R = 11.30$ min (major).

2-Benzyl-2-(benzyloxycarbonyl)-1-indanone (2q). R_f 0.24 (Acetone:Hexane = 1:15); $[\alpha]_D^{29} +60.2$ (c 1.0 CHCl_3 , 44% ee); ^1H NMR (200 MHz, CDCl_3) δ 7.74 (d, $J = 8.5$ Hz, 1H), 7.57-7.50 (m, 1H), 7.35-7.22 (m, 7H), 7.16-7.07 (m, 5H), 5.16 (s, 2H), 3.63 (d, $J = 17.4$ Hz, 1H), 3.51 (d, $J = 14.0$ Hz, 1H), 3.30 (d, $J = 14.0$ Hz, 1H), 3.16 (d, $J = 17.4$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 201.8, 170.4, 153.0, 135.2, 129.8, 128.4, 128.2, 128.1, 127.7, 127.5, 126.7, 126.1, 124.6, 67.2, 61.7, 39.6, 35.3; HRMS calcd for $\text{C}_{24}\text{H}_{20}\text{O}_3\text{Na}$ ($[\text{M}+\text{Na}]^+$) 379.1310, found 379.1319; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Chiralpak AD column, $t_R = 10.35$ min (minor), $t_R = 12.13$ min (major).

2-Benzyl-2-(ethoxycarbonyl)cyclopentanone (5a).⁷ R_f 0.25 (EtOAc:Hexane = 1:15); $[\alpha]_D^{25} +9.89$ (c 1.65, EtOH, 58% ee); ^1H NMR (CDCl_3 , 200 MHz) δ 1.26 (t, $J = 7.2$ Hz, 3H), 1.86-2.01 (m, 2H), 2.03-2.12 (m, 2H), 2.30-2.46 (m, 2H), 3.11 (d, $J = 17.7$ Hz, 2H),

4.18 (q, $J = 7.2$ Hz, 2H), 7.11-7.14 (m, 2H), 7.23-7.28 (m, 3H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 14.0, 19.4, 31.7, 38.3, 38.9, 61.4, 61.5, 126.8, 128.3, 130.0, 136.6, 171.0, 214.9; MS (70 eV) m/z 246.13 (M^+ , 59.3 %) 78, 90 (100), 91, 115, 130, 173; Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$: C, 73.75; H, 6.60. Found: C, 73.65; H, 6.71; R_f HPLC (hexane:*iso*-PrOH = 98:2, 254 nm, 0.5 mL/min) Chiralpak AD column, $t_R = 13.1$ min (major), $t_R = 14.2$ min (minor).

2-(*o*-Nitrobenzyl)-2-(ethoxycarbonyl)cyclopentanone (5b). R_f 0.17 (EtOAc:Hexane = 1:15); $[\alpha]_D^{25} +8.33$ (c 1.65, EtOH, 50% ee); ^1H NMR (CDCl_3 , 200 MHz) δ 1.23 (t, $J = 7.3$ Hz, 3H), 1.77-1.95 (m, 2H), 1.98-2.22 (m, 2H), 2.35-2.49 (m, 2H), 3.43 (d, $J = 14.0$ Hz, 1H), 3.73 (d, $J = 14.0$ Hz, 1H), 4.16 (q, $J = 7.3$ Hz, 2H), 7.28-7.60 (m, 3H), 7.81 (d, $J = 8.5$ Hz, 1H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 14.0, 19.6, 33.5, 34.5, 38.1, 61.2, 61.8, 124.8, 128.0, 132.1, 132.8, 133.0, 150.3, 172.6, 214.1; MS (70 eV) m/z 291.11 (M^+ , 0.71 %) 55 (100), 77, 115, 144, 190; Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_3$: C, 77.12; H, 6.60; N, 4.81. Found: C, 77.10; H, 6.69; N, 4.78; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1 mL/min) Chiralpak AS column, $t_R = 7.3$ min (major), $t_R = 7.8$ min (minor).

2-(*p*-Nitrobenzyl)-2-(ethoxycarbonyl)cyclopentanone (5c). R_f 0.14 (EtOAc:Hexane = 1:15); $[\alpha]_D^{25} +7.27$ (c 1.65, EtOH, 97% ee); ^1H NMR (CDCl_3 , 200 MHz) δ 1.26 (t, $J = 7.1$ Hz, 3H), 1.70-1.92 (m, 2H), 2.01-2.17 (m, 2H), 2.40-2.54 (m, 2H), 3.17 (d, $J = 13.6$ Hz, 1H), 3.33 (d, $J = 13.7$ Hz, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 7.34 (d, $J = 8.6$ Hz, 2H), 8.14 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 14.0, 19.4, 32.1, 38.0, 38.5, 61.2, 61.9, 123.5, 131.1, 144.5, 169.7, 212.1; MS (70 eV) m/z 291.11 (M^+ , 0.03 %) 91 (100), 115, 190, 218, 245; Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_3$: C, 77.12; H, 6.60; N, 4.81. Found: C, 77.14; H, 6.71; N, 4.76; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 0.4 mL/min) Chiralpak AS column, $t_R = 26.2$ min (major), $t_R = 27.4$ min (minor).

2-(*p*-Chlorobenzyl)-2-(ethoxycarbonyl)cyclopentanone (5d). R_f 0.22 (EtOAc:Hexane = 1:15); $[\alpha]_D^{25} +18.52$ (c 1.65, EtOH, 57% ee); ^1H NMR (CDCl_3 , 200 MHz) δ 1.25 (t, $J = 7.1$ Hz, 3H), 1.84-1.98 (m, 2H), 2.01-2.08 (m, 2H), 2.31-2.44 (m, 2H), 3.12 (d, $J = 7.1$ Hz, 2H),

4.17 (q, $J = 7.1$ Hz, 2H), 7.07 (d, $J = 8.3$ Hz, 2H), 7.23 (d, $J = 10.7$ Hz, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 14.0, 19.3, 31.8, 38.2, 38.7, 61.3, 61.7, 128.4, 131.6, 132.8, 135.1, 170.8, 214.6; MS (70 eV) m/z 280.09 (M^+ , 1.91 %) 77, 95 (100), 115, 185, 124, 221; Anal. Calcd for $\text{C}_{15}\text{H}_{17}\text{ClO}_3$: C, 64.17; H, 6.10. Found: C, 64.21; H, 6.20; R_f HPLC (hexane: *iso*-PrOH = 90:10, 254 nm, 0.4 mL/min) Chiralpak AS column, $t_R = 12.5$ min (major), $t_R = 13.1$ min (minor).

2-(Benzyl)-2-(ethoxycarbonyl)cyclohexanone (5e).⁸ R_f 0.17 (EtOAc:Hexane = 1:15); $[\alpha]_D^{25} -34.07$ (c 1.65, EtOH, 61% ee); ^1H NMR (CDCl_3 , 200 MHz) δ 1.08 (t, $J = 7.0$ Hz, 3H), 1.27-1.62 (m, 4H), 1.63-1.91 (m, 1H), 1.95-2.29 (m, 3H), 2.77 (d, $J = 13.7$ Hz, 1H), 3.21 (d, $J = 13.7$ Hz, 1H), 4.03 (q, $J = 7.0$ Hz, 2H), 7.00-7.07 (m, 2H), 7.12-7.18 (m, 3H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 13.8, 22.4, 27.5, 35.8, 40.3, 41.1, 61.1, 62.0, 126.5, 127.9, 130.2, 136.5, 170.9, 205.2; MS (70 eV) m/z 260.14 (M^+ , 0.02 %) 77, 90 (100), 91, 115, 185; Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$: C, 73.82; H, 7.74. Found: C, 73.79; H, 7.80; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Whelk-O1 column, $t_R = 22.1$ min (minor), $t_R = 23.2$ min (major).

2-(*p*-Nitrobenzyl)-2-(ethoxycarbonyl)cyclohexanone (5f). R_f 0.08 (EtOAc:Hexane = 1:15); $[\alpha]_D^{25} -36.2$ (c 1.65, EtOH, 87% ee); ^1H NMR (CDCl_3 , 200 MHz) δ 1.17 (t, $J = 7.2$ Hz, 3H), 1.46-1.79 (m, 4H), 2.05-2.06 (m, 1H), 2.39-2.52 (m, 3H), 2.95 (d, $J = 13.4$ Hz, 1H), 3.39 (d, $J = 13.5$ Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 2H), 7.33 (d, $J = 10.9$ Hz, 2H), 8.10 (d, $J = 10.9$ Hz, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 13.9, 22.5, 27.5, 36.5, 40.2, 41.2, 61.5, 62.1, 123.1, 131.3, 144.7, 148.9, 165.1, 206.8; MS (70 eV) m/z 305.13 (M^+ , 82.2 %) 55, 116, 214 (100), 232; Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_3$: C, 62.94; H, 6.27; N, 4.59. Found: C, 63.02; H, 6.31; N, 4.51; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.2 mL/min) Whelk-O1 column, $t_R = 9.2$ min (minor), $t_R = 9.9$ min (major).

2-(*p*-Chlorobenzyl)-2-(ethoxycarbonyl)cyclohexanone (5g). R_f 0.22 (EtOAc:Hexane = 1:15); $[\alpha]_D^{25} -8.96$ (c 1.65, EtOH, 77% ee); ^1H NMR (CDCl_3 , 200 MHz) δ 1.17 (t, $J = 7.2$

Hz, 3H), 1.38–1.71 (m, 4H), 1.90–2.03 (m, 2H), 2.37–2.48 (m, 2H), 2.83 (d, $J = 13.7$ Hz, 1H), 3.25 (d, $J = 13.8$ Hz, 1H), 4.06 (q, $J = 7.2$ Hz, 2H), 7.01 (d, $J = 10.9$ Hz, 2H), 7.20 (d, $J = 8.3$ Hz, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 13.9, 22.5, 27.5, 36.1, 39.7, 41.2, 61.3, 62.1, 128.1, 131.7, 132.5, 135.1, 170.9, 208.8; MS (70 eV) m/z 294.10 (M^+ , 10.7 %) 89, 115, 124 (100), 125, 207; Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{ClO}_3$: C, 65.19; H, 6.50. Found: C, 65.10; H, 6.58; R_f HPLC (hexane: *iso*-PrOH = 90:10, 254 nm, 0.8 mL/min) Chiralcel OJ column, t_R = 9.1 min (major), t_R = 10.1 min (minor).

2-Allyl-2-(ethoxycarbonyl)cyclohexanone (5h).⁹ R_f 0.30 (EtOAc:Hexane = 1:15); $[\alpha]_D^{25}$ –79.36 (c 0.5, CHCl_3 , 59% ee); ^1H NMR (200 MHz, CDCl_3) δ 5.64–5.85 (m, 1H), 4.99–5.09 (m, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 2.61 (dd, $J = 7.0, 13.9$ Hz, 1H), 2.42–2.52 (m, 3H), 2.33 (dd, $J = 7.8, 14.0$ Hz, 1H), 1.98–2.12 (m, 1H), 1.39–1.82 (m, 4H), 1.25 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 206.6, 171.0, 133.2, 117.8, 60.8, 60.5, 40.7, 39.0, 35.5, 27.3, 22.2, 13.9; Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_3$: C, 68.54; H, 8.63. Found: C, 68.22; H, 8.69; R_f HPLC (hexane:*iso*-PrOH = 99:1, 210 nm, 0.5 mL/min) Whelk-O1 column, t_R = 14.48 min (minor), t_R = 15.04 min (major).

2-*trans*-Cinnamyl-2-(ethoxycarbonyl)cyclohexanone (5i).¹ R_f 0.45 (EtOAc:Hexane = 1:6); $[\alpha]_D^{25}$ –57.43 (c 1.31, CHCl_3 , 57% ee); ^1H NMR (200 MHz, CDCl_3) δ 7.15–7.35 (m, 5H), 6.38 (d, $J = 15.8$ Hz, 1H), 6.09–6.24 (m, 1H), 4.17 (q, $J = 6.9$ Hz, 2H), 2.75 (dd, $J = 6.7, 13.7$ Hz, 1H), 2.43–2.57 (m, 4H), 1.98–2.06 (m, 1H), 1.44–1.79 (m, 4H), 1.21 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 207.8, 171.6, 137.2, 133.2, 128.4, 127.2, 126.1, 125.1, 61.4, 41.2, 38.5, 36.0, 27.5, 22.5, 14.1; Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3$: C, 75.50; H, 7.74. Found: C, 75.09; H, 7.82; R_f HPLC (hexane:*iso*-PrOH = 95:5, 254 nm, 1.0 mL/min) Chiralcel OD-H column, t_R = 5.49 min (minor), t_R = 6.26 min (major).

2-Allyl-2-(methoxycarbonyl)cyclohexanone (5j).⁹ R_f 0.30 (EtOAc:Hexane = 1:15); $[\alpha]_D^{25}$ –89.15 (c 0.38, CHCl_3 , 53% ee); ^1H NMR (200 MHz, CDCl_3) δ 5.64–5.85 (m, 1H), 4.99–5.07 (m, 2H), 3.71 (s, 3H), 2.62 (dd, $J = 6.9, 13.8$ Hz, 1H), 2.41–2.53 (m, 3H), 2.33 (dd, $J =$

7.9, 13.8 Hz, 1H), 1.98-2.11 (m, 1H), 1.14-1.79 (m, 4H); ^{13}C NMR (50 MHz, CDCl_3) δ 206.5, 171.5, 133.2, 117.8, 60.7, 51.8, 40.7, 39.0, 35.4, 27.2, 22.1; Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}_3$: C, 67.32; H, 8.22. Found: C, 67.25; H, 8.27; R_f HPLC (hexane:*iso*-PrOH = 99:1, 210 nm, 1.0 mL/min) Whelk-O1 column, t_R = 8.03 min (minor), t_R = 8.42 min (major).

2-Benzyl-2-(methoxycarbonyl)cyclohexanone (5k).¹⁰ R_f 0.35 (EtOAc:Hexane = 1:6); $[\alpha]_D^{25}$ -67.00 (c 0.89, CHCl_3 , 53% ee); ^1H NMR (200 MHz, CDCl_3) δ 7.15-7.36 (m, 3H), 7.04-7.11 (m, 2H), 3.64 (s, 3H), 3.32 (d, J = 13.7 Hz, 1H), 2.86 (d, J = 13.7 Hz, 1H), 2.23-2.53 (m, 3H), 1.95-2.05 (m, 1H), 1.38-1.77 (m, 4H); ^{13}C NMR (50 MHz, CDCl_3) δ 207.1, 171.4, 136.5, 130.1, 128.0, 126.6, 62.2, 41.3, 40.4, 35.6, 27.5, 22.4; Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$: C, 73.15; H, 7.37. Found: C, 73.05; H, 7.41; R_f HPLC (hexane:*iso*-PrOH = 50:1, 254 nm, 1.0 mL/min) Whelk-O1 column, t_R = 9.06 min (minor), t_R = 9.98 min (major).

2-(Benzyl)-2-(methoxycarbonyl)cyclohexanone (5l).¹⁰ R_f 0.25 (EtOAc:Hexane = 1:15); $[\alpha]_D^{25}$ -37.5 (c 1.65, EtOH, 57% ee); ^1H NMR (CDCl_3 , 200 MHz) δ 1.27-1.62 (m, 4H), 1.63-1.91 (m, 1H), 1.95-2.29 (m, 3H), 2.86 (d, J = 13.8 Hz, 1H), 3.32 (d, J = 13.7 Hz, 1H), 3.73 (s, 1H), 7.00-7.07 (m, 2H), 7.12-7.18 (m, 3H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 27.5, 28.9, 29.8, 32.6, 38.0, 60.2, 62.5, 125.7, 128.3, 128.5, 138.6, 174.1, 207.8; Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{NO}_3$: C, 73.15; H, 7.37. Found: C, 73.09; H, 7.41; R_f HPLC (hexane:*iso*-PrOH = 90:10, 254 nm, 1.0 mL/min) Whelk-O1 column, t_R = 12.0 min (minor), t_R = 12.8 min (major).

2-Allyl-2-(benzyloxycarbonyl)cyclohexanone (5m).¹¹ R_f 0.28 (EtOAc:Hexane = 1:12); $[\alpha]_D^{25}$ -57.53 (c 0.36, CHCl_3 , 53% ee); ^1H NMR (200 MHz, CDCl_3) δ 7.24-7.43 (m, 5H), 5.59-5.81 (m, 1H), 5.15 (d, J = 1.6 Hz, 2H), 4.93-5.01 (m, 2H), 2.62 (dd, J = 6.8, 13.6 Hz, 1H), 2.29-2.53 (m, 4H), 1.93-2.04 (m, 1H), 1.39-1.76 (m, 4H); ^{13}C NMR (50 MHz, CDCl_3) δ 207.2, 171.4, 133.3, 128.7, 128.5, 128.4, 118.5, 67.0, 61.1, 41.2, 39.3, 35.8, 27.6, 22.5; Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$: C, 74.97; H, 7.40. Found: C, 74.69; H, 7.45; R_f HPLC (heptane:*iso*-PrOH = 99.5:0.5, 254 nm, 1.0 mL/min) Chiralcel OD-H column, t_R = 22.64 min (minor), t_R = 23.70 min (major).

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