Organocatalytic Enantioselective Conjugate Addition to Alkynones

Marco Bella and Karl Anker Jørgensen*

Danish National Research Foundation: Center for Catalysis, Department of Chemistry,
Aarhus University, DK-8000 Aarhus C, Denmark

Supporting Information

General Methods. The ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at 400 MHz, 100 MHz and 376 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^1H NMR ($\delta = 77.5$) for ^{13}C NMR relative to the central CDCl_3 resonance. Flash chromatography (FC) was carried out using Merck silica gel 60 (230-400 mesh). Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The enantiomeric excess (ee) of the products was determined by HPLC using a Daicel Chiralpak AS, AD, and Chiralcel OJ, OD columns (wavelength = 254 nm) with *i*-PrOH/hexane as the eluent or by chiral GC using a Chrompack CP-Chirasil Dex C β or Astec G-TA columns.

Materials. Alkynones **1b**,¹ **1c**, **1d**,² **1e**,³ **1f**, **1g** and **1h**² were all prepared according to literature procedure.³ β -Diketones **2a**, **2b**, **2e**, alkynone **1a**, [DHQ]₂PHAL, [DHQ]₂AQN, [DHQ]₂PYR, [DHQD]₂PHAL quinine, cinchonine, (*S*)-(+)-1-(2-pyrrolidinylmethyl)-pyrrolidine, Et₃N, Bu₃P, toluene, were obtained from Aldrich and used as received. *O*-Ac cinchonine, β -diketones **2c**, **2d**, **2e**, **2f** and **2g** were preparing according to standard literature procedures.

1c: Yield: 82%; ^1H NMR δ 8.13 (dd, 2H, $J(\text{H})$ 8.8 Hz, $J(\text{F})$ 5.2 Hz), 7.12 (dd, 2H, $J(\text{H})$ 8.8 Hz, $J(\text{F})$ 5.2 Hz), 3.4 (d, 1H, $J(\text{F})$ 0.8 Hz); ^{13}C NMR δ 176.24, 167.15 (d, $J(\text{F})$ 257.2 Hz), 133.10 (d, $J(\text{F})$ 2.3 Hz), 132.90 (d, $J(\text{F})$ 10.0 Hz), 116.46 (d, $J(\text{F})$ 22.0 Hz), 82.43, 81.32; ^{19}F NMR δ -102.7 (m).

1f: Yield: 85%; ^1H NMR δ 8.25 (d, 2H, J 8.4 Hz), 7.78 (d, 2H, J 8.4 Hz), 3.56 (s, 1H); ^{13}C NMR δ 176.65, 138.94, 135.96 (q, $J(F)$ 33.0 Hz), 130.39, 126.21 (q, $J(F)$ 3.8 Hz), 123.86 (q, $J(F)$ 272.4 Hz), 82.60, 80.20; ^{19}F NMR δ -63.7 (s).

1h: Yield: 83%; ^1H NMR δ 7.4-7.2 (m, 5H), 3.28 (s, 1H), 3.1-2.9 (m, 4H); ^{13}C NMR δ 186.75, 140.39, 129.06, 128.80, 126.85, 81.76, 79.34, 47.41, 30.01.

Figure 1: Structure of some of the cinchona alkaloids derivatives tested.

Screening of reaction conditions for the conjugate addition of butyn-2-one **1a** to acetyl cyclopentanone **2a** (Table 1).

The cinchona-base (5 mol%, 0.005 mmole) was placed a in a test tube and acetyl cyclopentanone **2a** (12.6 mg, 0.1 mmole), dissolved in 2 mL of toluene, was added. Butyn-2-one **1a** (10 mg, 0.116 mmole) was added via syringe and the resulting solution allowed to stir at room temperature until all the **2a** has reacted (0.5-4 h). Et₂O (10 mL)

was added to the solution and filtered through a plug of silica gel (0.5 g) to be directly analyzed by CSP-GC.

A larger scale preparation (400 mg acetyl cyclopentanone **2a**, 317 mg 2-butyne **1a** and 123 mg [DHQ]₂PHAL in 63 mL of toluene) was purified by FC. The solution was loaded on a column packed with 20 g of silica gel, toluene was removed, and then the product was separated eluting, first with pentane, followed by pentane/Et₂O 6:1; 220 mg of (*Z*)-**3a** (33% yield) and 438 mg of (*E*)-**3a** (64% yield) were obtained as transparent oils.

General procedure for the isomerization of alkynones double bond.

The crude mixture of addition products (*Z*)- and (*E*)-**3a** (0.4 mmole, 83 mg, 2:1 ratio (*Z*)/(*E*), ee = 40% (*Z*), ee = 70% (*E*)) was dissolved in 8 mL of toluene and 8 mg of Bu₃P (0.04 mmol, 10% mol) was added. The solution was immediately placed under vacuum in a hot water bath warmed up to be 40 °C and the solvent was removed by evaporation over 5 min. The resulting dark-yellowish oil was first analyzed by ¹H NMR and the (*E*)- and (*Z*)-isomer ratio was found to be >50:1, followed by purification by FC (first pentane, then pentane/Et₂O 6:1 to afford 67 mg (81% yield) of pure (*E*)-**3a** (60% ee).

3a: The ee was determined by HPLC using Chiralpak AD column (hexane/*i*-PrOH (85:15); flow rate 1.0 mL/min; (*Z*)-**3a**: $\tau_{\text{minor}} = 9.4$ min; $\tau_{\text{major}} = 11.0$ min; (*E*)-**3a**: $\tau_{\text{minor}} = 12.5$ min; $\tau_{\text{major}} = 13.6$ min) and by GC using a chiral Astec G-TA column: rate 10 °C/min, starting T = 70 °C; T final 180 °C for 10 min; (*Z*)-**3a**: $\tau_{\text{major}} = 14.1$ min, $\tau_{\text{minor}} = 14.4$ min; (*E*)-**3a**: $\tau_{\text{major}} = 15.4$ min, $\tau_{\text{minor}} = 15.5$ min.

(*E*)-**3a**: ¹H NMR δ 6.98 (d, 1H, *J* 16.4 Hz), 6.09 (d, 1H, *J* 16.4 Hz), 2.8-2.7 (m, 1H), 2.4-2.2 (m, 2H), 2.25, (s, 3H), 2.18 (s, 3H), 2.30-2.20 (m, 2H), 2.13 (s, 3H), 2.0-1.8 (m, 3H); ¹³C NMR δ 212.46, 200.35, 197.98, 143.15, 132.21, 71.92, 38.33, 31.51, 27.89, 27.55,

19.79; $[\alpha]_D^{25} = +18.2$ ($c = 1.51$ g/100 mL, CHCl_3 , 70% ee – reaction performed at room temperature).

(*Z*)-**3a**: ^1H NMR δ 6.33 (d, 1H, J 11.2 Hz), 6.30 (d, 1H, J 11.2 Hz), 2.95-2.85 (m, 1H), 2.4-2.3 (m, 2H), 2.19, (s, 3H), 2.10 (s, 3H), 2.1-1.6 (m, 3H); ^{13}C NMR 213.90, 200.76, 189.51, 143.58, 129.38, 71.93, 38.05, 33.91, 31.51, 27.44, 20.15; $[\alpha]_D^{25} = +59.6$ ($c = 2.97$ g/100 mL, CHCl_3 , 40% ee – reaction performed at room temperature); HRMS calc. (mixture of isomers) $\text{C}_{11}\text{H}_{14}\text{NaO}_3$: 217.08406; found: 217.0840.

Reaction of compound (*Z/E*)-3a** with silica gel.** Compound **3a**, 66 mg 1:2 ratio *Z/E*, ee = 40% (*Z*), ee = 70% (*E*), was dissolved in 2 mL of CH_2Cl_2 and the solution adsorbed 3 g of silica gel. The mixture was dried by rotary evaporator. After 6 h the silica was washed with Et_2O (100 mL), the solvent evaporated to afford a yellowish dense liquid. Purification by FC (pentane, then pentane: Et_2O 6:1) afforded 15 mg of compound **3a** as only the (*Z*)-isomer (yield = 68% based on only (*Z*)-**3a**, ee = 40%) and 23 mg of compound (*E*) **4a**⁴ (52% yield based on only (*E*)-**3a**).

(*E*)-**4a**: ^1H NMR δ 6.65-6.55 (m, 1H), 3.22 (d, 2H J 7.2 Hz), 2.6-2.5 (m, 2H), 2.29 (t, 2H J 8.0 Hz) 2.14, (s, 3H), 1.95-1.85 (m, 2H); ^{13}C NMR 206.85, 204.78, 140.58, 126.64, 44.76, 38.92, 30.43, 27.34, 20.03; HRMS calc. $\text{C}_9\text{H}_{12}\text{NaO}_2$: 175.0735; found: 175.0734.

General procedure for the catalytic asymmetric Michael addition to aryl alkynones.

β -Diketones (Table 2) (0.3 mmole) and $[\text{DHQ}]_2\text{PHAL}$ (0.015 mmol, 5 mol% catalyst loading) were dissolved in toluene (8 mL) and the solution was cooled to -20 °C. Alkynones (see Table 1 and 2) were dissolved in 4 mL of toluene, the solution cooled to -20 °C and added drop-wise to the β -diketone solution. The reaction mixture was stirred at -20 °C for 24 h, Et_2O (5mL) was added and the solution filtered over a plug (a Pasteur pipette which the end was filled with cotton wool and loaded with 0.5 g of silica gel). The silica was washed with additional 2 mL of Et_2O . The organic solvents were evaporated to

give pure compounds, all as pale yellow dense oils, with yields and enantiomeric excesses as reported in Table 2.

General procedure for tandem addition to alkynones-isomerization of the double bond. After the catalytic addition reaction to aryl alkynones has been stirred for 24 h, (see above procedure) the solution was transferred in a round-bottomed flask, Bu₃P (0.03 mmols, 10%) was added and the flask immediately put under vacuum and solvent removed at 40 °C. The resulting dark-yellow oils were purified by FC (note: the compounds are slightly unstable on silica) to afford only the (*E*) isomeric products as reported in Table 2.

3b: The ee was determined by HPLC using Chiralpak AS+AD columns (hexane/*i*-PrOH (90:10); flow rate 1.0 mL/min; (*Z*)-**3b**: $\tau_{\text{minor}} = 20.2$ min, $\tau_{\text{major}} = 22.5$ min; (*E*)-**3b**: $\tau_{\text{minor}} = 21.1$ min, $\tau_{\text{major}} = 24.6$ min).

Yield: 99%

(*E*)-**3b**: ¹H NMR δ 7.85-7.80 (m, 2H), 7.60-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.14 (d, 1H, *J* 16.0 Hz), 6.94 (d, 1H, *J* 16.0 Hz), 2.80 (ddd, 1H, *J* 12.0, 6.8, 6.0 Hz), 2.3-2.2 (m, 2H), 2.20 (s, 3H), 2.05-1.95 (m, 2H), 1.95-1.85 (m, 1H); ¹³C NMR δ 212.37, 200.67, 189.89, 144.19, 133.65, 129.10, 128.97, 128.85, 127.31, 72.09, 38.43, 31.92, 27.76, 19.81; $[\alpha]_{\text{D}}^{\text{rt}} = -13.2$ (*c* = 1.25 g/100mL, CHCl₃, 80% ee – reaction performed at room temperature).

(*Z*)-**3b**: ¹H NMR δ 7.85-7.80 (m, 2H), 7.60-7.55 (m, 1H), 7.50-7.45 (m, 2H), 6.97 (d, 1H, *J* 12.0 Hz), 6.68 (d, 1H, *J* 12.0 Hz), 3.05-2.95 (m, 1H), 2.35-2.25 (m, 2H), 2.26 (s, 3H), 2.1-1.8 (m, 3H); ¹³C NMR δ 214.17, 200.69, 191.17, 145.00, 137.42, 133.87, 129.10, 128.86, 127.06, 72.13, 37.93, 33.67, 27.63, 20.10; HRMS calc.: C₁₆H₁₆NaO₃ 279.0997; found: 279.1006.

3c: The ee was determined by HPLC using Chiralpak AS+AD columns (hexane/*i*-PrOH (85:15); flow rate 1.0 mL/min; (*E*)-**3c**: $\tau_{\text{minor}} = 19.5$ min, $\tau_{\text{major}} = 20.9$ min; (*Z*)-**3c**: $\tau_{\text{minor}} = 26.5$ min, $\tau_{\text{major}} = 46.9$ min).

Yield: 99%

(*E*)-**3c**: ^1H NMR δ 7.96 (dd, 2H, $J(\text{H})$ 8.8 Hz, $J(\text{F})$ 5.6 Hz), 7.23 (d, 1H, 15.6 Hz), 7.16 (dd, 2H, $J(\text{H})$ 8.8 Hz, $J(\text{F})$ 5.6 Hz), 7.00 (d, 1H, J 15.6 Hz), 2.90 (ddd, 1H, J 12.0, 6.8, 6.0 Hz), 2.35-2.25 (m, 2H), 2.29 (s, 3H), 2.1-2.0 (m, 3H); ^{13}C NMR δ 212.37, 200.60, 188.23, 165.97 (d, $J(\text{F})$ 255.6 Hz), 144.40, 133.95 (d, $J(\text{F})$ 3.0 Hz), 131.68 (d, $J(\text{F})$ 9.8 Hz), 126.93, 116.29, (d, $J(\text{F})$ 22.0 Hz), 72.11, 38.53, 32.03, 27.77, 19.86; ^{19}F NMR δ -104.9 (m); $[\alpha]_{\text{D}}^{25} = -18.5$ ($c = 1.70$ g/100mL, CHCl_3 , 80% ee – reaction performed at room temperature).

(*Z*)-**3c**: ^1H NMR δ 7.96 (dd, 2H, $J(\text{H})$ 8.8 Hz, $J(\text{F})$ 5.6 Hz), 7.16 (dd, 2H, $J(\text{H})$ 8.8 Hz, $J(\text{F})$ 5.6 Hz), 7.13 (d, 1H, J 11.6 Hz), 6.69 (d, 1H, J 11.6 Hz), 3.0-2.9 (m, 1H), 2.35-2.25 (m, 2H), 2.19 (s, 3H), 2.1-2.0 (m, 3H); ^{13}C NMR δ 214.07, 200.49, 189.64, 166.03 (d, $J(\text{F})$ 255.4 Hz), 145.21, 134.05 (d, $J(\text{F})$ 3.0 Hz), 131.71 (d, $J(\text{F})$ 9.8 Hz), 126.96, 116.20, (d, $J(\text{F})$ 22.0 Hz), 72.15, 37.93, 33.72, 27.59, 20.01; ^{19}F NMR δ -104.9. HRMS calc. : $\text{C}_{16}\text{H}_{15}\text{FNaO}_3$: 297.0902; found : 297.0895.

3d: The ee was determined by HPLC using Chiralpak AS+AD columns (hexane/*i*-PrOH (90:10); flow rate 1.0 mL/min; (*E*)-**3d**: $\tau_{\text{minor}} = 23.7$ min, $\tau_{\text{major}} = 25.8$ min; (*Z*)-**3d**: $\tau_{\text{minor}} = 45.7$ min, $\tau_{\text{major}} = 122.9$ min).

Yield: 99%

(*E*)-**3d**: ^1H NMR δ 7.80 (d, 2H, J 8.8 Hz), 7.38 (d, 2H, J 8.8 Hz), 7.15 (d, 1H, J 15.2 Hz), 6.91 (d, 1H, J 15.2 Hz), 2.80 (ddd, 1H, J 12.0, 6.8, 6.0 Hz), 2.35-2.25 (m, 2H), 2.20 (s, 3H), 2.05-1.95 (m, 2H), 1.95-1.85 (m, 1H); ^{13}C NMR δ 212.36, 200.54, 188.65, 144.79, 140.22, 135.92, 130.47, 129.51, 126.87, 72.20, 38.58, 32.06, 27.84, 19.91; $[\alpha]_D^{25} = -18.2$ ($c = 2.30$ g/100 mL, CHCl_3 , 80% ee – reaction performed at room temperature).

(*Z*)-**3d**: ^1H NMR δ 7.81 (d, 2H, J 8.8 Hz), 7.39 (d, 2H, J 8.8 Hz), 7.19 (d, 1H, J 12.0 Hz), 6.53 (d, 1H, J 12.0 Hz), 2.95-2.85 (m, 1H), 2.35-2.25 (m, 2H), 2.15 (s, 3H), 2.05-1.95 (m, 2H), 1.95-1.85 (m, 1H); ^{13}C NMR δ 214.03, 200.47, 189.99, 145.61, 140.40, 135.82, 130.35, 129.52, 126.69, 72.19, 37.98, 33.76, 27.69, 20.14; HRMS calc.: $\text{C}_{16}\text{H}_{15}\text{ClNaO}_3$ 313.0607; found: 313.0607.

3e: The ee was determined by HPLC using Chiralpak AD column (hexane/*i*-PrOH (80:20); flow rate 1.0 ml/min; (*Z*)-**3e**: $\tau_{\text{minor}} = 16.9$ min, $\tau_{\text{major}} = 18.3$ min; (*E*)-**3e**: $\tau_{\text{minor}} = 20.0$ min, $\tau_{\text{major}} = 24.7$ min).

Yield: 99%

(*E*)-**3e**: ^1H NMR δ 8.24 (d, 2H, J 8.8 Hz), 7.98 (d, 2H, J 8.8 Hz), 7.19 (d, 1H, J 15.8 Hz), 6.92 (d, 1H, J 15.8 Hz), 2.82 (ddd, 1H, J 12.0, 6.8, 6.0 Hz), 2.20-2.10 (m, 2H), 2.13 (s, 3H), 2.05-1.95 (m, 2H), 1.90-1.80 (m, 1H).

(*Z*)-**3e**: ^1H NMR δ 8.25 (d, 2H, J 8.8 Hz), 7.99 (d, 2H, J 8.8 Hz), 6.96 (d, 1H, J 12.0 Hz), 6.86 (d, 1H, J 12.0 Hz), 2.90-2.80 (m, 1H), 2.30-2.20 (m, 2H), 2.19 (s, 3H), 2.05-1.95 (m, 2H), 1.95-1.85 (m, 1H); ^{13}C NMR (mixture of isomers) δ 213.58, 212.13, 200.32, 200.10, 189.58, 188.52, 150.79, 146.29, 142.29, 141.96, 130.01, 129.93, 126.66, 126.38, 124.53, 72.32, 72.13, 38.49, 37.95, 33.87, 32.02, 27.80, 27.68, 20.08; HRMS calc.: $\text{C}_{16}\text{H}_{15}\text{NaNO}_5$ 324.0847; found: 324.0851.

3f: The ee was determined by HPLC using Chiralpak AS column (hexane/*i*-PrOH (80:20); flow rate 1.0 mL/min; (*E*)-**3f**: $\tau_{\text{minor}} = 5.7$ min, $\tau_{\text{major}} = 6.7$ min; (*Z*)-**3f**: $\tau_{\text{minor}} = 13.9$ min, $\tau_{\text{major}} = 34.4$ min).

Yield: 99%

(*E*)-**3f**: ^1H NMR δ 7.94 (d, 2H, J 8.4 Hz), 7.68 (d, 2H, J 8.4 Hz), 7.19 (d, 1H, J 15.8 Hz), 6.93 (d, 1H, J 15.8 Hz), 2.95 (ddd, 1H, J 12.0, 6.8, 6.0 Hz), 2.4-2.2 (m, 2H), 2.21 (s, 3H), 2.1-1.9 (m, 3H), 1.95-1.85 (m, 1H); ^{13}C NMR δ 212.27, 200.34, 189.16, 145.63, 140.05, 134.93 (q, $J(F)$ 32.8 Hz), 129.38, 126.95, 126.25 (q, $J(F)$ 3.8 Hz), 125.92 (q, $J(F)$ 122.0 Hz), 72.32, 38.57, 32.06, 27.54, 20.08; ^{19}F NMR δ -63.6; $[\alpha]_{\text{D}}^{\text{rt}} = -10.8$ ($c = 2.90$ g/100 mL, CHCl_3 , 85% ee – reaction performed at room temperature).

(*Z*)-**3f**: ^1H NMR δ 7.96 (d, 2H, J 8.8 Hz), 7.68 (d, 2H, J 8.8 Hz), 6.96 (d, 1H, J 11.6 Hz), 6.67 (d, 1H, J 11.6 Hz), 3.0-2.9 (m, 1H), 2.35-2.25 (m, 2H), 2.13 (s, 3H), 2.0-1.9 (m, 3H); ^{13}C NMR δ 213.81, 200.44, 190.26, 146.12, 139.05, 134.73 (q, $J(F)$ 32.8 Hz), 129.26, 126.95, 126.24 (q, $J(F)$ 3.8 Hz), 125.92 (q, $J(F)$ 122.0 Hz), 72.17, 39.19, 33.72, 27.77, 19.88; ^{19}F NMR δ -63.6. HRMS calc.: $\text{C}_{17}\text{H}_{15}\text{F}_3\text{NaO}_3$ 347.0871; found: 347.0874.

3g: The ee was determined by HPLC using Chiralpak AD column (hexane/*i*-PrOH (85:15); flow rate 1.0 mL/min; (*Z*)-**3g**: $\tau_{\text{minor}} = 12.8$ min, $\tau_{\text{major}} = 14.0$ min; (*E*)-**3g**: $\tau_{\text{minor}} = 17.6$ min, $\tau_{\text{major}} = 21.3$ min).

Yield: 99%

(*E*)-**3g**: ^1H NMR δ 7.86 (d, 2H, J 8.8 Hz), 7.10 (d, 1H, J 15.8 Hz), 6.88 (d, 2H, J 8.8 Hz), 6.86 (d, 1H, J 15.8 Hz), 3.87 (s, 3H), 2.82 (ddd, 1H, J 12.0, 6.8, 6.0 Hz), 2.30-2.20 (m, 2H), 2.13 (s, 3H), 2.0-1.4 (m, 3H).

(*Z*)-**3g**: ^1H NMR δ 7.85 (d, 2H, J 8.8 Hz), 6.96 (d, 1H, J 12.0 Hz), 6.90 (d, 2H, J 8.8 Hz), 6.55 (d, 1H, J 12.0 Hz), 3.86 (s, 3H), 2.95-2.85 (m, 1H), 2.3-2.2 (m, 1H), 2.20 (s, 3H), 2.0-1.4 (m, 4H); ^{13}C NMR (mixture of isomers) δ 214.43, 212.58, 201.01, 200.73, 189.73, 188.61, 164.24, 164.18, 144.13, 143.30, 131.43, 131.29, 130.59, 130.54, 127.27, 127.21, 114.36 (2 peaks), 72.10, 72.05, 55.97, 55.89, 38.60, 37.99, 33.75, 32.09, 27.84, 27.68, 20.15, 19.87; HRMS calc.: $\text{C}_{17}\text{H}_{18}\text{NaO}_4$ 309.1102; found: 309.1100.

3h: The ee was determined by HPLC using Chiralpak AS column (hexane/*i*-PrOH (90:10); flow rate 1.0 mL/min; (*E*)-**3h**: $\tau_{\text{major}} = 11.8$ min, $\tau_{\text{minor}} = 12.6$ min; hexane/*i*-PrOH (65:35); flow rate 1.0 mL/min; (*Z*)-**3h**: $\tau_{\text{major}} = 9.8$ min, $\tau_{\text{minor}} = 11.6$ min).

Yield: 95%

(*E*)-**3h**: ^1H NMR δ 7.9-7.8 (m, 2H), 7.32 (d, 1H, J 16 Hz), 7.1-7.0 (m, 2H), 6.70 (d, 1H, J 16 Hz), 2.2-2.6 (m, 4H), 2.08 (s, 3H), 2.0-1.7 (m, 4H).

(*Z*)-**3h**: ^1H NMR δ 7.9-7.8 (m, 2H), 7.1-7.0 (m, 2H), 6.95 (d, 1H, J 12 Hz), 6.55 (d, 1H, J 12.4 Hz), 2.2-2.6 (m, 4H), 2.05 (s, 3H), 2.0-1.7 (m, 4H); ^{13}C NMR (mixture of isomers) δ 207.18, (2 peaks) 203.24, 202.57, 189.75, 188.69, 166.16 (2 peaks) (d, $J(F)$ 257.3 Hz), 145.10, 144.61, 134.01 (d, $J(F)$ 3 Hz), 133.98 (d, $J(F)$ 3.0 Hz), 132.89, 132.79, 131.75, (d, $J(F)$ 9.8 Hz), 131.65, (d, $J(F)$ 9.8 Hz), 127.68, 126.94, 70.68, 70.33, 41.80, 40.87, 36.15, 34.97, 27.87, 27.76, 27.08, 27.05, 22.42, 22.35; ^{19}F NMR δ -104.8, (m), -105.1 (m); HRMS calc.: $\text{C}_{17}\text{H}_{17}\text{FNaO}_3$ 311.1059; found: 311.1062.

3i: The ee was determined by HPLC using Chiralpak AS column (hexane/*i*-PrOH (90:10); flow rate 1.0 mL/min; (*E*)-**3i**: $\tau_{\text{major}} = 13.0$ min, $\tau_{\text{minor}} = 15.1$ min; hexane/*i*-PrOH (50:50); flow rate 1.0 mL/min; (*Z*)-**3i**: $\tau_{\text{major}} = 10.2$ min, $\tau_{\text{minor}} = 14.5$ min).

Yield: 95%

(*E*)-**3i**: ^1H NMR δ 7.81 (d, 2H, J 8.8 Hz), 7.40 (d, 2H, J 8.8 Hz), 7.37 (d, 1H, J 16.4 Hz), 6.73 (d, 1H, J 16.4 Hz), 2.2-2.6 (m, 4H), 2.12 (s, 3H), 2.0-1.7 (m, 4H); $[\alpha]_{\text{D}}^{25} = +61.9$ ($c = 0.85$ g/100 mL, CHCl_3 , 85% ee – reaction performed at room temperature).

(*Z*)-**3i**: ^1H NMR δ 7.85 (d, 2H, J 8.8 Hz), 7.40 (d, 2H, J 8.8 Hz), 6.99 (d, 1H, J 12.4 Hz), 6.62 (d, 1H, J 12.4 Hz), 2.2-2.6 (m, 4H), 2.10 (s, 3H), 2.0-1.7 (m, 4H); ^{13}C NMR (mixture of isomers) δ 207.09, 206.84, 203.17, 203.16, 190.04, 189.03, 145.42, 144.87, 140.25, 140.02, 135.93, 135.85, 130.52, 130.38, 129.42, 129.40, 127.55, 126.84, 70.65 (2 peaks), 41.78, 40.87, 36.13, 34.93, 27.84, 27.75, 27.03, 26.97, 22.40, 22.33; HRMS calc.: $\text{C}_{17}\text{H}_{17}\text{ClNaO}_3$ 341.1154; found: 341.1151.

3j: The ee was determined by HPLC using Chiralpak AD column (hexane/*i*-PrOH (85:15); flow rate 1.0 mL/min; (*Z*)-**3j**: $\tau_{\text{major}} = 16.1$ min, $\tau_{\text{minor}} = 17.6$ min; (*E*)-**3j**: $\tau_{\text{major}} = 21.9$ min, $\tau_{\text{minor}} = 25.9$ min).

Yield: 95%

^1H NMR (mixture of isomers) δ 7.6-7.0 (m, 20 H), 4.15 (d, 1H, J 17.2 Hz), 4.05 (d, 1H, J 17.2 Hz), 3.13 (d, 1H, J 17.2 Hz), 2.70 (d, 1H, J 17.2 Hz), 2.35 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (mixture of isomers) δ 201.58, 198.90, 199.61, 194.48, 189.67, 188.37, 154.82, 153.01, 146.38, 145.05, 140.50, 140.09, 136.46, 136.16, 135.90, 135.76, 134.30, 134.00, 130.45, 130.32, 129.53, 129.41, 128.52, 128.09, 126.82, 126.71, 126.59, 126.52, 125.43, 125.18, 72.83, 72.27, 38.55, 35.73, 27.50, 27.28. HRMS calc.: $\text{C}_{20}\text{H}_{15}\text{ClNaO}_3$ 361.0607; found: 361.0570.

3k: The ee was determined by HPLC using Chiralpak AD column (hexane/*i*-PrOH (90:10); flow rate 1.0 mL/min; (*Z*)-**3k**: $\tau_{\text{major}} = 17.7$ min, $\tau_{\text{minor}} = 19.2$ min; (*E*)-**3k**: $\tau_{\text{major}} = 22.4$ min, $\tau_{\text{minor}} = 23.0$ min).

Yield: 95%

^1H NMR (mixture of isomers) δ 7.6-7.0 (m, 20 H), 4.19 (d, 1H, J 17.4 Hz), 4.04 (d, 1H, J 17.4 Hz), 3.15 (d, 1H, J 17.4 Hz), 2.70 (d, 1H, J 17.4 Hz), 2.8-2.5 (m, 4H), 0.94 (t, 3H, J 6.8 Hz), 0.92 (t, 3H, J 6.8 Hz); ^{13}C NMR (mixture of isomers) δ 202.95, 201.81, 201.48, 199.91, 189.75, 188.91, 155.05, 153.20, 146.76, 145.41, 140.52, 140.18, 136.48, 136.20, 136.02, 135.87, 134.46, 134.09, 130.53, 130.39, 129.61, 129.49, 128.68, 128.55, 126.85, 126.59, 126.53, 126.49, 125.75, 125.52, 72.86, 71.99, 38.98, 36.27, 33.61, 32.90, 8.39, 8.37; HRMS calc.: $\text{C}_{21}\text{H}_{17}\text{ClNaO}_3$ 375.0764; found: 375.0762.

3l: The ee was determined by HPLC using 2 Chiralpak AD columns (hexane/*i*-PrOH (95:5); flow rate 1.0 mL/min; (*Z*)-**3l**: $\tau_{\text{major}} = 48.7$ min, $\tau_{\text{minor}} = 51.7$ min; (*E*)-**3l**: $\tau_{\text{minor}} = 57.1$ min, $\tau_{\text{major}} = 60.1$ min).

Yield: 99%

(*E*)-**3l**: ^1H NMR δ 8.06 (d, 1H, J 8.0 Hz), 7.82 (d, 2H, J 8.0 Hz), 7.6-7.0 (m, 7H), 6.84 (d, 1H, J 15.6 Hz), 3.3-2.6 (m, 4H) 2.18 (s, 3H).

(*Z*)-**3l**: ^1H NMR δ 7.92 (d, 1H, J 8.0 Hz), 7.87 (d, 2H, J 8.0 Hz), 7.6-7.0 (m, 6H), 7.04 (d, 1H, J 12.0 Hz), 6.51 (d, 1H, J 12.0 Hz), 3.3-2.6 (m, 4H) 2.18 (s, 3H); ^{13}C NMR (mixture of isomers) δ 203.81, 202.96, 196.69, 195.16, 191.31, 190.20, 144.84, 143.96, 143.73, 137.63, 137.59, 134.83, 134.33, 133.82, 133.61, 132.30, 131.97, 131.84, 129.37, 129.23, 129.11, 129.09, 129.00, 128.64, 128.51, 128.35, 128.09, 127.99, 127.52, 127.25, 127.19, 126.21, 66.98, 66.77, 31.13, 30.93, 28.87, 28.73, 26.64, 26.10; HRMS calc.: $\text{C}_{21}\text{H}_{18}\text{NaO}_3$ 341.1154; found: 341.1154.

3m: The ee was determined by HPLC using Chiralpak AD column (hexane/*i*-PrOH (85:15); flow rate 1.0 mL/min; (*Z*)-**3m** $\tau_{\text{major}} = 15.7$ min, $\tau_{\text{minor}} = 18.0$ min; (*E*)-**3m**; $\tau_{\text{minor}} = 20.3$ min, $\tau_{\text{major}} = 22.9$ min).

Yield: 99%

(*E*)-**3m**: ^1H NMR δ 8.04 (d, 1H, J 8.0 Hz), 7.92 (d, 1H, J 8.0 Hz), 7.81 (d, 2H, J 8.8 Hz), 7.75 (d, 2H, J 8.8 Hz), 7.35 (d, 4H, J 8.8 Hz), 7.4-7.0 (m, 7H), 6.97 (*Z*, d, 1H, J 12.0 Hz), 6.80 (*E*, d, 1H, J 16.0 Hz), 6.48 (*Z*, d, 1H, J 12.0 Hz), 3.3-3.2 (m, 1H), 3.1-3.0 (m, 1H),

2.9-2.4 (m, 4H), 2.4-2.3 (m, 1H), 2.2-2.1 (m, 1H), 2.17 (s, 6H); $[\alpha]_D^{25} = -1.0$ ($c = 3.55$ g/100mL, CHCl₃, 84% ee – reaction performed at room temperature).

(*Z*)-**3m**: ¹H NMR δ 8.25 (d, 2H, J 8.8 Hz), 7.99 (d, 2H, J 8.8 Hz), 6.96 (d, 1H, J 12.0 Hz), 6.68 (d, 1H, J 12.0 Hz), 2.90-2.80 (m, 1H), 2.3-2.2 (m, 2H), 2.19 (s, 3H), 2.05-1.95 (m, 2H), 1.95-1.85 (m, 1H); ¹³C NMR (mixture of isomers) δ 203.80, 202.77, 195.36, 195.7, 190.17, 188.91, 145.37, 144.02, 143.80, 143.72, 140.23, 140.03, 135.93 (2 peaks), 134.89, 134.35, 132.02, 131.78, 130.52, 130.42, 129.41, 129.40, 129.39, 128.61, 128.52, 127.85, 127.80, 127.55, 127.24, 67.00, 66.78, 31.47, 30.97, 28.82, 28.66, 26.59, 26.08, 33.87, 32.02, 27.80, 27.68, 20.08, 19.91; HRMS calc.: C₂₁H₁₇ClNaO₃ 375.0764; found: 375.0767.

3n: The ee was determined by HPLC using Chiralcel OJ column (hexane/*i*-PrOH (80:20); flow rate 1.0 mL/min; (*E*)-**3n**: $\tau_{\text{major}} = 21.3$ min; $\tau_{\text{minor}} = 30.0$ min; (*Z*)-**3n**: $\tau_{\text{major}} = 34.1$ min, $\tau_{\text{minor}} = 43.0$ min).

Yield: 97% (*E*)-**3n**: ¹H NMR δ 8.01 (d, 1H, J 8.0 Hz), 7.5-7.1 (m, 4H), 7.23 (d, 1H, J 16.4 Hz), 6.02 (d, 1H, J 16.4 Hz), 3.2-2.5 (m, 4H); 2.23 (s, 3H), 2.21 (s, 3H).

(*Z*)-**3n**: ¹H NMR δ 7.95 (d, 1H, J 8.0 Hz), 7.5-7.1 (m, 4H), 6.37 (d, 1H, J 11.6 Hz), 6.15 (d, 1H, J 11.6 Hz), 3.2-2.5 (m, 4H); 2.16 (s, 3H), 2.11 (s, 3H); ¹³C NMR (mixture of isomers) δ 204.03, 202.35, 198.62, 198.08, 195.22, 195.07, 143.86, 143.74, 143.59, 142.58, 134.90, 134.45, 134.22, 132.84, 132.28, 131.78, 130.25, 129.37, 129.27, 128.53, 127.53, 127.30, 66.69, 66.64, 31.64, 31.56, 30.56, 28.79, 28.28, 27.75, 26.67, 26.04.

3o: The ee was determined by HPLC using Chiralcel OJ column (hexane/*i*-PrOH (80:20); flow rate 1.0 mL/min; (*E*)-**3o**: $\tau_{\text{major}} = 29.7$ min; $\tau_{\text{minor}} = 35.2$ min; (*Z*)-**3o**: $\tau_{\text{major}} = 42.5$ min, $\tau_{\text{minor}} = 50.5$ min).

Yield: 97% (*E*)-**3o**: ^1H NMR δ 7.99 (d, 1H, J 8.0 Hz), 7.5-7.1 (m, 10H), 6.02 (d, 1H, J 16.4 Hz), 2.8-2.2 (m, 8H), 2.07 (s, 3H).

(*Z*)-**3o**: ^1H NMR δ 7.94 (d, 1H, J 8.0 Hz), 7.5-7.1 (m, 9H), 6.32 (d, 1H, J 12.4 Hz), 6.17 (d, 1H, J 12.4 Hz), 2.8-2.2 (m, 8H), 2.07 (s, 3H); ^{13}C NMR (mixture of isomers) δ 203.90, 202.48, 199.97, 199.06, 195.42, 195.06, 143.78, 143.75, 143.12, 142.86, 141.26, 141.23, 134.89, 134.29, 132.31, 132.13, 132.05, 131.78, 129.95, 129.37, 128.94, 128.91, 128.80, 128.75, 128.60, 128.54, 127.53, 127.28, 126.60, 126.57, 66.95, 66.62, 47.34, 45.80, 42.50, 31.40, 30.57, 30.31, 29.97, 28.40, 26.68, 26.04.

Additional data on several combinations of alkynones/ β -dicarbonyl compounds.

(Table 3)

<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> 1 </div> <div style="text-align: center;"> 2 </div> <div style="text-align: center;"> 3 </div> </div> <p style="text-align: right;">(4)</p>							
Entry	Alkynone		β -Dicarbonyl compounds	Yield% ^a	<i>E/Z</i> ^b	<i>Ee</i> ^c <i>E/Z</i> %	
1		1a		2b 3p 94	1.1:1	82/70	
2		1a		2f 3q 90	1.0:1	77/47	
4		1h		2a 3r 94	1.4:1	70/20	
5		1h		2b 3s 95	1.5:1	72/36	
6		1a		2h 3t 95	2.5:1 ^d	72/24	

^aIsolated yield. ^bDetermined by ¹H-NMR. ^cEnantiomeric excess determined by HPLC or CSP-GC.

^dDetermined by GC.

3p: The ee was determined by HPLC using Chiralcel OJ columns (hexane/*i*-PrOH (80:20); flow rate 1.0 mL/min; (*E*)-**3p**: τ_{major} = 12.0 min; τ_{minor} = 14.0. min; (*Z*)-**3p**: τ_{major} = 15.6 min; τ_{minor} = 17.0 min).

Yield :94%

(*E*)-**3p** ^1H NMR δ 7.22 (d, 1H, J 16.0 Hz), 5.94 (d, 1H, J 16.0 Hz), 2.6-1.6 (m, 8H), 2.25 (s, 3H), 2.06 (s, 3H).

(*Z*)-**3p**: ^1H NMR δ 6.35 (d, 1H, J 12.0 Hz), 6.23 (d, 1H, J 12.0 Hz), 2.6-1.6 (m, 8H), 2.17 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (mixture of isomers) δ 207.10, 206.70, 203.40, 202.21, 198.71, 198.27, 143.86, 143.43, 132.70, 129.45, 70.56, 69.94, 41.75, 40.86, 35.98, 34.67, 31.56 (2 peaks), 27.50, 27.42, 26.99, 26.70, 22.45, 22.29; HRMS calc.: $\text{C}_{12}\text{H}_{16}\text{NaO}_3$ 231.0997; found: 231.0999.

3q: The ee was determined by HPLC using Chiralpak AS+AD columns (hexane/*i*-PrOH (95:5); flow rate 1.0 mL/min; (*Z*)-**3q**: τ_{minor} = 20.9 min, τ_{major} = 32.9. min; (*E*)-**3q**: τ_{minor} = 39.6 min, τ_{major} = 42.2 min).

Yield: 94%

(*E*)-**3q** ^1H NMR δ 7.28 (d, 1H, J 16.4 Hz), 6.04 (d, 1H, J 16.4 Hz), 2.8-1.2 (m, 10H), 2.31 (s, 3H), 2.11 (s, 3H).

(*Z*)-**3q**: ^1H NMR δ 6.78 (d, 1H, J 12.0 Hz), 6.42 (d, 1H, J 12.0 Hz), 2.6-1.6 (m, 8H), 2.22 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (mixture of isomers) δ 209.97, 209.26, 202.89, 199.90, 198.75, 198.45, 146.66, 144.58, 132.54, 128.73, 75.52, 73.55, 42.47, 40.30, 33.14, 31.40, 30.58, 30.44, 27.83, 27.70, 27.41, 27.28, 26.66, 26.61, 25.79, 24.93.

3r: The ee was determined by HPLC using Chiralcel OD column (hexane/*i*-PrOH (80:20); flow rate 1.0 mL/min; (*Z*)-**3r**: $\tau_{\text{major}} = 8.3$ min, $\tau_{\text{minor}} = 9.1$ min; (*E*)-**3r**: $\tau_{\text{major}} = 10.0$ min, $\tau_{\text{minor}} = 11.5$ min).

Yield: 94%

(*E*)-**3r**: ^1H NMR δ 7.6-7.4 (m, 2H), 7.4-7.2 (m, 3H) 7.00 (d, 1H, J 16.4 Hz), 6.13 (d, 1H, J 16.4 Hz), 3.0-2.7 (m, 5H), 2.4-1.8 (m, 5H), 2.18, (s, 3H).

(*Z*)-**3r**: ^1H NMR δ 7.6-7.4 (m, 2H), 7.4-7.2 (m, 3H) 6.35 (d, 1H, J 11.2 Hz), 6.30 (d, 1H, J 11.2 Hz), 3.0-2.7 (m, 5H), 2.4-1.8 (m, 5H), 2.10, (s, 3H); ^{13}C NMR (mixture of isomers) δ 214.00, 212.40, 200.66, 200.39, 199.83, 199.00, 143.78, 142.46, 141.17, 141.10, 131.38, 129.05, 128.94, 128.89, 128.79, 128.74, 126.62, 126.58, 72.01, 71.89, 45.69, 42.64, 38.37, 37.99, 33.82, 31.54, 30.28, 29.92, 27.61, 27.44, 20.13, 19.79.

3s: The ee was determined by HPLC using Chiralcel OJ columns (hexane/*i*-PrOH (80:20); flow rate 1.0 mL/min; (*Z*)-**3s**: $\tau_{\text{major}} = 24.3$ min, $\tau_{\text{major}} = 61.2$ min; (*E*)-**3s**: $\tau_{\text{major}} = 28.9$ min, $\tau_{\text{major}} = 32.1$ min).

Yield: 95%

(*E*)-**3r**: ^1H NMR δ 7.6-7.4 (m, 2H), 7.4-7.2 (m, 4H), 5.93 (d, 1H, J 16.0 Hz), 3.0-1.4 (m, 12H), 1.99 (s, 3H).

(*Z*)-**3s**: ^1H NMR δ 7.6-7.4 (m, 2H), 7.4-7.2 (m, 3H) 6.29 (d, 1H, J 11.2 Hz), 6.25 (d, 1H, J 11.2 Hz), 3.0-1.4 (m, 12H), 1.98 (s, 3H); ^{13}C NMR (mixture of isomers) δ 207.11,

206.86, 203.27, 202.24, 199.98, 199.24, 143.70, 143.15, 141.24, 141.17, 131.91, 129.09, 128.92, 128.87, 128.79, 128.76, 126.59, 126.55, 70.71, 69.94, 45.74, 42.19, 41.71, 40.77, 36.03, 34.67, 30.35, 30.10, 29.94, 27.51, 26.99, 26.86, 22.40, 22.31; HRMS calc. $C_{19}H_{22}NaO_3$: 321.1467; found: 321.1463.

3t: The ee was determined by CSP-GC using a Chrompack CP-Chirasil Dex C β column : rate 10 °C / min, starting T= 70 °C, T fin 200 °C for 10 min; (*Z*)-**3t**: $\tau_{\text{major}} = 9.4$ min, $\tau_{\text{minor}} = 9.5$ min; (*E*)-**3t**: $\tau_{\text{minor}} = 9.8$ min, $\tau_{\text{major}} = 9.9$ min.

Yield: 94%

(*E*)-**3t**: ^1H NMR δ 7.16 (d, 1H, J 16.4 Hz), 6.02 (d, 1H, J 16.0 Hz), 4.19 (dq, 1H, J 7.2, 2.0 Hz), 2.25 (s, 3H), 2.13 (s, 3H), 1.47 (s, 3H) 1.22 (t, 3H, J 7.2 Hz).

(*Z*)-**3t**: ^1H NMR δ 6.61 (d, 1H, J 11.6 Hz), 6.24 (d, 1H, J 11.6 Hz), 4.10 (q, 1H, J 7.2, Hz), 2.21 (s, 3H), 2.14 (s, 3H), 1.51 (s, 3H) 1.17 (t, 3H, J 7.2 Hz); ^{13}C NMR (mixture of isomers) δ 202.86, 202.02, 198.66, 198.20, 171.44, 170.80, 144.24, 144.04, 131.95, 127.63, 62.68, 62.33, 62.23, 62.01, 31.59, 27.74, 27.08, 27.03, 21.30, 19.70, 14.39, 14.36.

Determination of absolute configuration

Absolute configuration was determined with comparison with the known compound **5** and extended by analogy to the other compounds. Compound **3u** was prepared according to general procedure. Hydrogenation (H_2 , Pd/C 10%, MeOH, 85% yield) gave product **5** found to be identical to the one reported (see below).⁵

3u: The ee was determined by HPLC using Chiralcel OJ column (hexane/*i*-PrOH (95:5); flow rate 1.0 mL/min; (*Z*)-**3u**: $\tau_{\text{major}} = 7.2$ min; $\tau_{\text{minor}} = 7.8$ min; (*E*)-**3u**: $\tau_{\text{major}} = 9.3$ min; $\tau_{\text{minor}} = 10.2$ min). *E/Z* ratio (NMR) = 1:2:1; (*Z*)-**3u** = 26% ee; (*E*)-**3u** = 56% ee.

Yield: 97%

(*E*)-**3u**: ^1H NMR δ 6.94 (d, 1H, *J* 16.4 Hz), 6.02 (d, 1H, *J* 16.4 Hz), 2.8-2.7 (m, 1H), 2.4-2.2 (m, 4H), 2.21, (s, 3H), 2.30-2.20 (m, 2H), 2.0-1.8 (m, 3H), 0.88 (s, 9H).

(*Z*)-**3u**: ^1H NMR δ 6.25 (d, 1H, *J* 11.6 Hz), 6.21 (d, 1H, *J* 11.6 Hz), 2.9-2.8 (m, 1H), 2.4-2.2 (m, 4H), 2.13, (s, 3H), 2.30-2.20 (m, 2H), 2.0-1.8 (m, 3H), 0.87 (s, 9H); ^{13}C NMR (mixture of isomers) δ 213.72, 212.67, 210.55, 201.26, 198.30, 197.97, 143.49, 143.32, 132.03, 129.09, 72.73, 72.64, 51.47, 51.40, 38.26, 37.88, 33.77, 31.58, 31.42, 31.18, 30.74, 29.98, 29.80, 29.72, 29.62, 27.77, 19.92, 19.67; HRMS calc.: $\text{C}_{15}\text{H}_{22}\text{NaO}_3$ 273.1466 found: 273.1469.

5: The ee was determined by HPLC using Chiralcel OJ column (hexane/*i*-PrOH (95:5); flow rate 0.5 mL/min; $\tau_{\text{major}} = 17.7$ min; $\tau_{\text{minor}} = 22.0$ min; 42% ee. $[\alpha]_{\text{D}}^{\text{rt}} = +46.0$ ($c = 4.78$ g/100 mL, CHCl_3 , 42% ee – reaction performed at room temperature).

Concordance of sign and magnitude of optical rotation, and HPLC retention times allowed us to assign (*R*) as the absolute configuration of the product **5**. Literature: Chiralcel OJ column (hexane/*i*-PrOH (95:5); flow rate 0.44 mL/min; $\tau_{\text{major}} = 20.7$ min; $\tau_{\text{minor}} = 26.0$ min; ee 96%. $[\alpha]_{\text{D}}^{\text{rt}} = +115.4$ ($c = 0.2$ g/100 mL, CHCl_3 , 96% ee).⁵

^1H NMR δ 2.04, (s, 3H), 2.4-1.6 (m, 11H), 1.6-1.4 (m, 1H) 0.90 (s, 9H); ^{13}C NMR δ 216.36, 207.20, 205.68, 67.93, 49.46, 38.45, 38.41, 31.58, 30.62, 29.88, 29.33, 27.20, 19.25; HRMS calc.: $\text{C}_{15}\text{H}_{24}\text{NaO}_3$ 275.16231 found: 275.1620.

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