Enantioselective, Cyclopentene-Forming Annulations via NHC-Catalyzed Benzoin–Oxy-Cope Reactions

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Supporting Information

General Methods. All reactions utilizing air- or moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry Ar. Dichloroethane (DCE) and CH₂Cl₂ were distilled over CaH₂. EtOH was distilled over Mg. THF were dried by passage over activated alumina under Ar atmosphere. Cinnamaldehyde, *trans*-2-hexene-1-al, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purified by vacuum distillation prior to use. *Trans*-3-(2-furyl)acrolein was purified by sublimation. Other reagents were used without further purification. Thin layer chromatography (TLC) was performed on Merck precoated plates (silica gel 60 F₂₅₄, Art 5715, 0.25 mm) and were visualized by fluorescence quenching under UV light or by staining with phosphomolybdic acid. Silica-gel preparative thin-layer chromatography (PTLC) was performed using plates prepared from Merck Kieselgel 60 PF₂₅₄ (Art 7747). Column chromatography was performed on E. Merck Silica Gel 60 (230–400 Mesh) using a forced flow of 0.5–1.0 bar. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) were measured on a Varian Unity 400 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from residual solvent peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; ad, approximate doublet; t, triplet; q, quartet; m, multiplet; asterisks (*) indicate peaks arising from the minor diastereomers. Infrared (IR) spectra were recorded on a JASCO FT:IR-430 spectrophotometer and are reported as wavenumber (cm⁻¹). Optical rotations were measured on a JASCO DIP-1000 polarimeter operating at the sodium D line with a 100 mm path length cell, and are reported as follows: $[\alpha]_D^{25}$ (concentration (g/100 mL), solvent).

HPLC Conditions. Column, Diacel Chiralpak AD-H (4.6 × 250mm); eluent: hexanes:iPrOH and hexanes:EtOH; flow rate 1.0 mL/min; detection: 254 nm.

SFC Conditions. Column, Diacel Chiralpak AS-H, (4.6 × 250mm); eluent: CO₂: MeOH; oven temperature: 40 °C; pressure 100 bar; flow rate 2.0 mL/min; detection: 254 nm.

General procedure for NHC-catalyzed, enantioselective benzoin–oxy-Cope reactions

The reaction of *trans*-methyl-4-oxo-4-phenylbut-2-enoate and cinnamaldehyde is representative: Into an oven dried 10.0 mL vial was added the 4-oxoenoate (95.1 mg, 0.50 mmol, 1.00 equiv) and triazolium catalyst **1** (18.3 mg, 0.05 mmol, 0.10 equiv). The vial was sealed with a septum and 5.0 mL dichloroethane (0.1 M) and cinnamaldehyde (69.4 μ L, 0.55 mmol, 1.1 equiv) were added via syringe. The solution was stirred at 0 °C for 15 minutes before DBU (11.3 μ L, 0.075 mmol, 0.15 equiv) was added. The resulting solution was stirred at 0 °C at least 6 h, followed by warming to rt for 40 h total reaction time. The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography (9:1 hexanes:EtOAc) to afford the cyclopentene product as a white solid (109 mg, 78% yield, 9:1 dr).

***cis*-1,3(S)-Diphenyl-4(R)-methoxycarbonylcyclopent-1-ene** (Table 1, entry 1). Prepared according to the general procedure from cinnamaldehyde and *trans*-methyl-4-oxo-4-phenylbut-2-enoate using 10 mol % **1** as the catalyst in 78% yield (9:1 dr) as a white solid. $[\alpha]_D^{20}$ (c 1.25, CHCl₃): +139.5; mp: 107–108 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.58–7.52 (m, 2H), 7.43–7.18 (m, 8H), 6.19 (s, 1H), 4.47–4.43 (ad, 1H), 3.82–3.75 (m, 1H), 3.49–3.43 (m, 1H), 3.28 (s, 3H), 2.97–2.91 (dd, 1H, *J* = 16.1, 9.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 173.4, 142.7, 140.3, 135.7, 128.8, 128.7*, 128.3, 127.9, 127.7, 127.3*, 126.8, 126.1*, 126.0, 125.9, 54.7, 51.4, 48.8, 34.6; IR (thin film) ν 3048, 3027, 2925, 2898, 2855, 1731, 1447, 1227, 1200, 1169, 1150 cm⁻¹; HRMS (EI) for C₁₉H₁₈O₂ calcd. (M⁺): 278.1307, found: 278.1313; >99% ee (major, *cis*), 69% ee (minor, *trans*) as determined by HPLC (AD-H, 60:1 hexanes:EtOH), *t_r* (major) = 9.1 and 11.9 min, *t_r* (minor) = 8.2 and 11.1 min.

NOE Experiment

***cis*-4(*R*)-Ethoxycarbonyl-1-(4-methoxyphenyl)-3(*S*)-phenylcyclopent-1-ene** (Table 1, entry 2).

Prepared according to the general procedure from cinnamaldehyde and *trans*-ethyl-4-(4-methoxyphenyl)-4-oxobut-2-enoate using 10 mol % **1** as the catalyst in 58% yield (5:1 dr) as a white solid. $[\alpha]_D^{20}$ (c 1.00, CHCl_3): +148.8; mp: 110–111 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.50–7.49 (m, 2H), 7.47–7.15 (m, 5H), 6.93–6.89 (m, 2H), 6.03 (s, 1H), 4.42–4.38 (dt, 1H, J = 9.8, 2.8 Hz), 3.84 (s, 3H), 3.77–3.61 (m, 3H), 3.44–3.38 (m, 1H), 2.92–2.85 (dd, 1H, J = 11.4,

9.1 Hz), 0.92–0.88 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 159.4, 141.9, 140.8, 128.9, 128.6, 128.2, 127.3, 127.2, 125.0, 114.0, 60.4, 55.5, 54.7, 48.7, 34.9, 14.0; IR (thin film) ν 2932, 1730, 1606, 1513, 1256, 1197, 1177, 1037 cm^{-1} ; HRMS (EI) for $\text{C}_{21}\text{H}_{22}\text{O}_3$ calcd. (M^+): 322.1569, found: 322.1570; >99% ee (major, *cis*), 68% ee (minor, *trans*) as determined by HPLC (AD-H, 60:1 hexanes:EtOH), t_r (major) = 19.6 and 21.8 min, t_r (minor) = 13.2 and 16.2 min.

***cis*-1-(4-Bromophenyl)-4(*R*)-methoxycarbonyl-3(*S*)-phenylcyclopent-1-ene** (Table 1, entry 3).

Prepared according to the general procedure from cinnamaldehyde and *trans*-methyl-4-(4-bromophenyl)-4-oxobut-2-enoate using 10 mol % **1** as the catalyst in 50% yield (11:1 dr) as a white solid. $[\alpha]_D^{20}$ (c 1.07, CHCl_3): +113.2; mp: 91–92 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.51–7.49 (ad, 2H), 7.41–7.35 (m, 2H), 7.28–7.26 (m, 3H), 7.24–7.14 (ad, 2H), 6.16 (s, 1H), 4.43–4.41 (ad, 1H), 3.77–3.75 (m, 1H), 3.44–3.39 (m, 1H), 3.25 (s, 3H), 2.91–2.85 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 141.6, 140.0, 134.6, 131.7, 128.8, 128.6, 128.3, 127.7, 127.6, 127.5,

127.3, 121.7, 55.3*, 54.7, 52.2*, 51.4, 48.7, 37.0*, 34.6; IR (thin film) ν 2947, 1735, 1638, 1489, 1200, 1168 cm^{-1} ; HRMS (EI) for $\text{C}_{19}\text{H}_{17}\text{BrO}_2$ calcd. (M^+): 356.0412, found: 356.0407; >99% ee (major, *cis*), 79% ee (minor, *trans*) as determined by HPLC (AD-H, 60:1 hexanes:EtOH), t_r (major) = 17.3 and 20.3 min, t_r (minor) = 11.0 and 16.2 min.

***cis*-1-(Furan-2-yl)-4(*R*)-methoxycarbonyl-3(*S*)-phenylcyclopent-1-ene** (Table 1, entry 4).

Prepared according to the general procedure from cinnamaldehyde and *trans*-methyl-4-(4-furan-2-yl)-4-oxobut-2-enoate using 10 mol % **1** as the catalyst in 93% yield (>20:1 dr) as a light yellow solid. $[\alpha]_D^{20}$ (c 1.09, CHCl_3): +136.5; mp: 126–127 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (s, 1H), 7.28–7.14 (m, 6H), 6.44–6.43 (m, 1H), 6.35–6.34 (d, 1H, $J = 2.8$ Hz), 6.01 (s, 1H), 4.43–4.41 (ad, 1H, $J = 9.7$ Hz), 3.73–3.71 (dd, 1H, $J = 18.1, 18.0$ Hz), 3.35–3.29 (m, 1H), 3.23 (s, 3H), 2.85–2.78 (dd, 1H, $J = 11.5, 9.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 151.4, 142.5, 140.1, 133.0, 128.7, 128.3, 127.3, 125.4, 111.4, 107.7, 54.7, 51.4, 48.8, 33.9; IR (thin

film) ν 2906, 1728, 1453, 1440, 1363, 1201, 1171, 1159 cm^{-1} ; HRMS (EI) for $\text{C}_{17}\text{H}_{16}\text{O}_3$ calcd. (M^+): 268.1099, found: 268.1092; 98% ee (major, *cis*), as determined by HPLC (AD-H, 9:1 hexanes:iPrOH), t_r (major) = 4.8 and 5.2 min, t_r (minor) = 5.5 and 6.9 min.

***cis*-3(S)-(4-Bromophenyl)-4(R)-methoxycarbonyl-1-phenylcyclopent-1-ene** (Table 1, entry 5).

Prepared according to the general procedure from 4-bromocinnamaldehyde and *trans*-methyl-4-oxo-4-phenylbut-2-enoate using 10 mol % **1** as the catalyst in 93% yield (6:1 dr) as a light yellow solid. $[\alpha]_D^{20}$ (c 1.03, CHCl_3): +113.2; mp: 67–68 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.57–7.54 (ad, 2H), 7.52–7.31 (m, 5H), 7.20–7.04 (ad, 2H), 6.12 (s, 1H), 4.41–4.37 (dt, 1H, J = 9.8, 2.6 Hz), 3.78–3.73 (m, 1H), 3.46–3.40 (m, 1H), 3.32 (s, 3H), 2.96–2.90 (dd, 1H, J = 11.6, 9.1 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 143.2, 139.3, 135.4, 131.8, 131.3, 130.4, 129.5, 128.7, 128.1, 126.2, 126.0, 125.9, 121.1, 54.6*, 54.0, 52.3*, 51.5, 48.6, 37.1*, 34.6; IR (thin film) ν 2947, 1736, 1641, 1487, 1446, 1434, 1200, 1168 cm^{-1} ; HRMS (EI) for $\text{C}_{19}\text{H}_{17}\text{BrO}_2$ calcd.

(M^+): 356.0412, found: 356.0400; 99% ee (major, *cis*), 67% ee (minor, *trans*) as determined by HPLC (AD-H, 60:1 hexanes:EtOH), t_r (major) = 9.5 and 16.3 min, t_r (minor) = 10.8 and 13.2 min.

NOE Experiment

***cis*-4(*R*)-Methoxycarbonyl-1-phenyl-3(*S*)-(4-(trifluoromethyl)phenyl)cyclopent-1-ene** (Table 1, entry 6). Prepared according to the general procedure from 4-trifluoromethylcinnamaldehyde and *trans*-methyl-4-oxo-4-phenylbut-2-enoate using 10 mol % **1** as the catalyst in 68% yield (4:1 dr) as a white solid. $[\alpha]_D^{20}$ (c1.00, CHCl_3): +116.7; mp: 54–55 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.63–7.53 (m, 4H), 7.45–7.31 (m, 5H), 6.16 (s, 1H), 4.51–4.49 (d, 1H, J = 9.8 Hz), 3.86–3.78

(m, 1H), 3.51–3.45 (m, 1H), 3.29 (s, 3H), 3.01–2.95 (dd, 1H, $J = 11.6, 9.1$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 143.6, 135.4, 129.1, 128.8, 128.3, 128.1, 126.1, 126.0, 125.9, 125.2, 125.1, 54.9*, 54.3, 52.2*, 51.5, 48.7, 37.1*, 34.7; IR (thin film) ν 2950, 1738, 1618, 1326, 1165, 1123 cm^{-1} ; HRMS (EI) for $\text{C}_{20}\text{H}_{17}\text{F}_3\text{O}_2$ calcd. (M^+): 346.1181, found: 346.1180; 98% ee (major, *cis*), 67% ee (minor, *trans*) as determined by HPLC (AD-H, 60:1 hexanes:EtOH), t_r (major) = 6.8 and 10.9 min, t_r (minor) = 7.5 and 9.3 min.

***cis*-3(*S*)-(Furan-2-yl)-4(*R*)-methoxycarbonyl-1-phenylcyclopent-1-ene** (Table 1, entry 7).

Prepared according to the general procedure from *trans*-3-(2-furyl)acrolein and *trans*-methyl-4-oxo-4-phenylbut-2-enoate using 10 mol % **1** as the catalyst in 53% yield (5:1 dr) as a yellow solid. $[\alpha]_D^{20}$ (c 1.03, CHCl_3): +135.8; mp: 70–71 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.52–7.50 (m, 2H), 7.39–7.28 (m, 4H), 6.29–6.27 (dd, 1H, $J = 2.3, 1.8$ Hz), 6.10–6.06 (m, 2H), 4.52–4.49 (dt, 1H, $J = 10.6, 2.5$ Hz), 3.66–3.61 (dd, 1H, $J = 13.4, 8.8$ Hz), 3.51 (s, 3H), 3.42–3.38 (m, 1H), 2.91–2.85 (dd, 1H, $J = 11.4, 8.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 154.1, 143.5, 142.0,

135.6, 128.7, 128.1, 126.1, 123.6, 110.5, 107.0, 51.9, 47.8, 47.5, 34.6; IR (thin film) ν 2949, 1736, 1638, 1496, 1435, 1358, 1263, 1216, 1173 cm^{-1} ; HRMS (EI) for $\text{C}_{17}\text{H}_{16}\text{O}_3$ calcd. (M^+): 269.1099, found: 268.1090; 99% ee (major, *cis*), 82% ee (minor, *trans*) as determined by HPLC (AD-H, 60:1 hexanes:EtOH), t_r (major) = 11.2 and 18.8 min, t_r (minor) = 10.5 and 14.9 min.

***cis*-4(*R*)-Methoxycarbonyl-1-phenyl-3(*S*)-propylcyclopent-1-ene** (Table 1, entry 8). Prepared according to the general procedure but heated at 60 °C for an additional 20 h from *trans*-2-hexen-1-al and *trans*-methyl-4-oxo-4-phenylbut-2-enoate using 10 mol % **1** as the catalyst in 25% yield (14:1 dr) as yellow liquid. $[\alpha]_D^{20}$ (c 0.96, CHCl_3): +150.0; ^1H NMR (400 MHz, CDCl_3) δ 7.46–7.44 (ad, 2H), 7.35–7.25 (m, 3H), 6.18 (s, 1H), 3.74 (s, 3H), 3.43–3.39 (dd, 1H, J = 13.2, 8.9 Hz), 3.25–3.21 (m, 1H), 3.19–3.12 (br, 1H), 2.81–2.75 (dd, 1H, J = 11.3, 8.7 Hz), 1.42–1.30 (m, 4H), 0.95–0.91 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 140.9, 136.2, 128.6, 127.9, 127.6, 125.8, 51.7, 47.7, 47.1, 34.5, 33.5, 21.1, 14.5; IR (thin film) ν 2955, 2929, 2871, 1737, 1447, 1435, 1195, 1176 cm^{-1} ; HRMS (EI) for $\text{C}_{16}\text{H}_{20}\text{O}_2$ calcd. (M^+): 244.1463, found: 244.1468; 96%

ee (major, *cis*), 32% ee (minor, *trans*) as determined by HPLC (AD-H, 60:1 hexanes:EtOH), t_r (major) = 4.8 and 8.4 min, t_r (minor) = 5.3 and 5.7 min.

NOE Experiment

***trans*-3(S)-(4-Bromophenyl)-1,4(S)-diphenyl-cyclopent-1-ene (*trans*-15).** Prepared according to the general procedure from 4-bromocinnamaldehyde and *trans*-chalcone using 10 mol % **1** as the catalyst in 69% yield (9:1 dr) as light yellow liquid. $[\alpha]_D^{20}$ (c 1.17, CHCl₃): +56.9; ¹H NMR (400 MHz, CDCl₃) δ 7.56–7.54 (m, 2H), 7.42–7.37 (m, 4H), 7.34–7.30 (m, 3H), 7.27–7.22 (m,

3H), 7.04–7.00 (m, 2H), 6.22 (s, 1H), 4.11–4.09 (m, 1H), 3.40–3.31 (m, 2H), 3.05–3.03 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.0, 144.1, 142.9, 135.9, 131.7, 129.4, 128.8, 128.7, 127.9, 127.8, 127.5, 126.6, 126.0, 120.4, 60.5, 55.0, 42.1; IR (thin film) ν 3026, 2924, 2848, 1600, 1486, 1446, 1404, 1261 cm^{-1} ; HRMS (EI) for $\text{C}_{23}\text{H}_{19}\text{Br}$ calcd. (M^+): 374.0670, found: 374.0662; 55% ee (major, *trans*), 99% ee (minor, *cis*) as determined by HPLC (AD-H, 12:1 hexanes:iPrOH), t_r (major) = 5.0 and 5.4 min, t_r (minor) = 4.2 and 4.4 min.

(1*R*,2*S*,7*aS*,*E*)-4-Benzylidene-1,2-diphenyl-2,4,5,6,7,7*a*-hexahydro-1*H*-indene (cis-14).

Prepared according to the general procedure from cinnamaldehyde and *trans,trans*-dibenzylidenecyclo-hexanone using 10 mol % **1** as the catalyst in 45% yield (>20:1 dr) as a yellow solid. $[\alpha]_{\text{D}}^{20}$ (c 1.03, CHCl_3): +213.9; mp = 108–109 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.41–7.14 (m, 15H), 6.85–6.84 (ad, 1H), 5.93 (s, 1H), 4.13–4.10 (ad, 1H), 3.04–2.89 (m, 3H),

2.35–2.27 (m, 1H), 2.08–1.98 (ad, 1H), 1.91–1.87 (ad, 1H), 1.44–1.33 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.9, 144.9, 142.7, 137.7, 137.0, 129.7, 128.5, 128.4, 128.3, 128.3, 127.7, 126.7, 126.5, 126.5, 125.5, 124.1, 65.5, 58.5, 54.1, 32.4, 29.4, 25.7; IR (thin film) ν 3026, 2926, 1702, 1600, 1494, 1450 cm^{-1} ; HRMS (EI) for $\text{C}_{28}\text{H}_{26}$ calcd. (M^+): 362.2035, found: 362.2048; 72% ee (major, *cis*) as determined by SFC (AS-H, 70% $\text{MeOH}:\text{CO}_2$), t_r (major) = 8.5 and 9.8 min.

NOE experiment

NHC-Catalyzed Oxy-Cope Reactions and Control Experiments

(a)

Into an oven dried 10.0 mL flask was added the triazolium catalyst (6 mg, 0.021 mmol) and 4-hydroxy-1,4,6-triphenylhexa-1,5-dien-3-one (**8**) (72 mg, 0.21 mmol) was added as a solution in 2 mL dichloroethane. The reaction mixture was stirred at 0 °C for 15 min, before DBU (4.7 μL , 4.8 mg, 0.032 mmol) was added. After stirring overnight at rt, the reaction mixture was concentrated under reduced pressure and the residue was purified by PTLC (10:1 hexanes: EtOAc).

(b)

Into an oven dried 10.0 mL flask was added the triazolium catalyst (7.5 mg, 0.029 mmol) and 1,4,6-triphenyl-4-trimethylsilyl-hexa-1,5-dien-3-one (**10**) (59.2 mg, 0.143 mmol) was added as a solution in 2 mL 1:1 EtOH: DCE. The reaction mixture was stirred at 0 °C for 15 min, before DBU (4 μ L, 3.35 mg, 0.022 mmol) was added. After stirring overnight at rt, the reaction mixture was concentrated under the reduced pressure, and residue was purified by PTLC (15:1 hexanes: EtOAc).

1,3,6-Triphenylhex-5-ene-1,4-dione (12). Pale yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ 8.01–7.99 (2H, m), 7.67 (1H, d, J = 16 Hz), 7.59–7.57 (1H, m), 7.51–7.45 (5H, m), 7.37–7.34 (7H, m), 7.31–7.26 (1H, m), 6.82 (1H, d, J = 16 Hz), 4.75 (1H, dd, J = 4, 9.6 Hz), 4.13 (1H, dd, J = 9.6, 18 Hz), 3.23 (1H, dd, J = 4, 18 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 198.3, 198.0, 143.5, 138.4, 136.8, 134.7, 133.4, 130.6, 129.4, 129.0, 128.8, 128.5, 128.4, 127.8, 125.2, 52.5, 42.7; IR (thin film) ν 3059, 2917, 1683, 1610, 1449, 753, 719 cm⁻¹; HRMS (EI) [M]⁺ calcd. for C₂₄H₂₀O₂ 340.1463, found, 340.1470.

6-Oxo-3,4,6-triphenyl-hexanoic acid ethyl ester (retro silyl-benzoin/Stetter product). Pale yellow oil. ^1H NMR (CDCl_3 , 400 MHz) δ 7.89–7.86 (2H, m), 7.57–7.53 (1H, m), 7.45–7.41 (2H, m), 7.20–7.13 (6H, m), 7.96–7.91 (4H, m), 4.01–3.93 (2H, m), 3.81–3.76 (1H, m), 3.62–3.56 (1H, m), 3.41–3.30 (2H, m), 2.78 (1H, dd, $J = 6.4, 15.6$ Hz), 2.66 (1H, dd, $J = 9.2, 15.6$ Hz), 1.21 (1H, s), 1.07 (3H, t, $J = 7.2$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 198.4, 172.2, 140.9, 140.4, 137.0, 133.0, 128.9, 128.5, 128.0, 127.8, 127.8, 126.6, 126.5, 60.3, 46.4, 45.1, 41.7, 38.3, 14.0 cm^{-1} ; IR (thin film) ν 3028, 2979, 1731, 1685, 1450, 750, 700 cm^{-1} ; HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{26}\text{H}_{26}\text{O}_3$ 409.1780, found, 409.1777.

1,6-Diphenyl-hexa-1,5-diene-3,4-dione.¹ Piperidine (0.6 mL, 0.51 g, 60 mmol) and glacial AcOH (0.36 mL, 60 mmol) were added to a stirred solution of 2,3-butanedione (2.64 mL, 2.6 g, 30.2 mmol) and benzaldehyde (14.5 mL, 15.12 g, 142.4 mmol) in MeOH (15 mL) and the mixture heated to reflux for 5 h, after which volatile compounds were removed in vacuo. The remaining oil was placed in a freezer overnight and the orange crystals were filtered to give the product (1.28 g, 3.5%). mp = 159–161 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ 7.88 (2H, d, $J = 16$ Hz), 7.69–7.65 (4H, m), 7.50 (2H, d, $J = 16$ Hz), 7.47–1.43 (6H, m); ^{13}C NMR (CDCl_3 , 100 MHz) δ 189.0, 147.8, 134.3, 131.4, 129.0, 129.0, 119.5; IR (thin film) ν 3059, 1668, 1606, 1447, 987, 727, 688 cm^{-1} ; HRMS (EI) calcd. for $\text{C}_{18}\text{H}_{14}\text{O}_2$ $[\text{M}]^+$ 262.0994, found, 262.0986.

4-Hydroxy-1,4,6-triphenyl-hexa-1,5-dien-3-one (8). 1,6-Diphenyl-hexa-1,5-diene-3,4-dione (414 mg, 1.58 mmol) was dissolved in 16 mL THF and cooled to -78°C and phenyllithium (1.8 M, 0.87 mL, 1.58 mmol) was added. After stirring at -78°C for 30 min, the reaction was diluted

(1) Constable, E.C.; Harverson, P. *Polyhedron* **1999**, 18, 3093–3016.

with 10 mL EtOAc and poured into 15 mL sat aq NH_4Cl . The aqueous layer was extracted with an additional 3×15 mL EtOAc. The combined organic extracts were washed with 15 mL brine, dried over Na_2SO_4 . After filtration and concentration, the residue was purified by silica chromatography (20:1 hexanes: EtOAc) to give **8** (265.5mg, 50%) as a yellow oil. ^1H NMR (CDCl_3 , 400 MHz) δ 7.86 (1H, d, J = 15.6 Hz), 7.52–7.47 (6H, m), 7.43–7.34 (8H, m), 7.30–7.28 (1H, m), 7.08 (1H, d, J = 16 Hz), 6.87 (1H, d, J = 16 Hz), 6.84 (1H, d, J = 15.6 Hz), 5.02 (1H, s); ^{13}C NMR (CDCl_3 , 100MHz) δ 196.8, 145.7, 141.0, 136.3, 134.0, 132.9, 131.1, 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.1, 127.6, 127.3, 127.0, 126.9, 126.9, 120.0, 82.4; IR (thin film) ν 3439, 3059, 3026, 1681, 1607, 1065, 749, 697 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_2$ $[\text{M}+\text{Na}]^+$ 363.1361, found, 363.1352.

1,4,6-Triphenyl-4-trimethylsilanyl-hexa-1,5-dien-3-one (10). Hydroxy ketone **8** (265.5 mg, 0.78 mmol) was dissolved in 2.5 mL hexamethylphosphoramide (HMPA) at rt. Imidazole (212.4 mg, 3.12 mmol) and TMSCl (0.4 mL, 340.0 mg, 3.12 mmol) were added. After stirring overnight, the reaction mixture was poured into 5 mL pH 7 buffer and extracted with 3×5 mL Et_2O . The combined organics were washed with 5 mL brine, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by chromatography on silica (10: 1 hexanes: EtOAc) to give ketone **10** (224.0 mg, 70%) as a yellow oil. ^1H NMR (CDCl_3 , 400 MHz) δ 7.75 (1H, d, J = 16 Hz), 7.56–7.53 (4H, m), 7.45–7.41 (2H, m), 7.40–7.32 (7H, m), 7.29–7.28 (2H, m), 7.20 (1H, d, J = 16 Hz), 7.02 (1H, d, J = 16 Hz), 6.57 (1H, d, J = 16 Hz), 0.20 (9H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 198.1, 143.2, 141.0, 136.1, 134.4, 133.5, 130.6, 130.1, 128.5, 128.3, 128.1, 128.0, 127.7, 127.5, 126.7, 126.4, 121.1, 84.7, 1.8; IR (thin film) 3059, 3026, 2956, 1689, 1611, 1251, 842, 753, 703 cm^{-1} ; HRMS (ESI) calcd. for $\text{C}_{27}\text{H}_{28}\text{O}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 435.1756, found, 435.1752.

General procedure for the preparation of α,β -unsaturated aldehydes

All α,β -unsaturated aldehydes were prepared according to literature procedures.^{2,3} The corresponding aryl iodides and bromides (1.0 equiv) are allowed to react with acrolein diethyl acetal (3.0 equiv) in the presence of ⁿBuNOAc (2 equiv), K₂CO₃ (1.5 equiv), KCl (1.0 equiv), Pd(OAc)₂ (0.03 equiv) and DMF (0.25 M) at 90 °C for 2-6 h, followed by addition of 2N HCl to the reaction mixture. The reaction mixture was extracted with Et₂O, and the organic layer was concentrated and purified by column chromatography (9:1 hexanes:EtOAc) to afford the corresponding aldehydes.

4-bromocinnamaldehyde. ¹H NMR (400 MHz, CDCl₃) δ 9.72–9.70 (d, 1H, J = 7.5 Hz), 7.60–7.56 (m, 2H), 7.45–7.41 (m, 3H), 6.74–6.68 (dd, 1H, J = 16.0, 7.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 193.7, 151.4, 133.1, 132.6, 130.0, 129.2, 125.9. Other spectral data was identical to the literature values.

4-trifluoromethylcinnamaldehyde. ¹H NMR (400 MHz, CDCl₃) δ 9.78–9.75 (d, 1H, J = 7.7 Hz), 7.72–7.67 (m, 4H), 7.54–7.50 (d, 2H, J = 16.1 Hz), 6.82–6.76 (dd, 1H, J = 16.0, 7.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 193.5, 150.6, 130.7, 128.8, 126.3, 126.2. Other spectral data was identical to the literature values.

Preparation of 4-oxoenonates

All 4-oxoenonates were prepared according to literature protocols.⁴

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trans-methyl-4-oxo-4-phenylbut-2-enoate (3).⁵ ¹H NMR (400 MHz, CDCl₃) δ 8.02–8.00 (m, 2H), 7.00–7.91 (d, 1H, *J* = 15.5 Hz), 7.65–7.61 (m, 1H), 7.54–7.50 (m, 2H), 6.92–6.88 (d, 1H, *J* = 15.6 Hz), 3.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 189.6, 166.2, 136.8, 134.1, 132.3, 129.1, 120.0, 52.6. Other spectral data was identical to the literature values.

trans-ethyl-4-(4-methoxyphenyl)-4-oxobut-2-enoate.⁶ ¹H NMR (400 MHz, CDCl₃) δ 8.02–8.00 (d, 2H, *J* = 8.9 Hz), 7.99–7.90 (d, 1H, *J* = 15.5 Hz), 6.99–6.97 (d, 2H, *J* = 8.9 Hz), 6.89–6.85 (d, 1H, *J* = 15.5 Hz), 4.32–4.27 (q, 2H, *J* = 7.1 Hz), 3.89–3.87 (s, 3H), 1.36–1.33 (t, 3H, *J* = 7.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 187.8, 165.9, 164.4, 136.7, 132.0, 131.5, 129.9, 114.3, 61.5, 55.8, 14.4. Other spectral data was identical to the literature values.

trans-methyl-4-(4-bromophenyl)-4-oxobut-2-enoate.^{7,8} ¹H NMR (400 MHz, CDCl₃) δ 7.90–7.86 (m, 3H), 7.69–7.66 (m, 2H), 6.94–6.90 (d, 1H, *J* = 15.5 Hz), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 188.5, 166.1, 136.1, 135.5, 132.8, 132.5, 130.5, 129.5, 52.7. Other spectral data was identical to the literature values.

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***trans*-methyl-4-(4-furan-2-yl)-4-oxobut-2-enoate.**^{6,9} ¹H NMR (400 MHz, CDCl₃) δ 7.80–7.76 (d, 1H, *J* = 15.5 Hz), 7.71–7.70 (t, 1H, *J* = 0.8 Hz), 7.40–7.39 (d, 1H, *J* = 3.7 Hz), 7.01–6.98 (d, 1H, *J* = 15.7 Hz), 6.64–6.63 (q, 1H, *J* = 1.7 Hz), 3.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 176.6, 166.1, 153.0, 148.1, 135.9, 131.9, 119.9, 113.2, 52.6. Other spectral data was identical to the literature values.

Preparation of α,α'-bis(substituted benzylidene) cycloalkane

trans,trans-Dibenzylidenecyclohexanone was prepared according to the literature procedure.¹⁰ The synthesis was achieved by the reaction of cyclohexanone (1.0 equiv) with benzaldehyde (2.0 equiv) using Cu(OTf)₂ as catalyst.

***trans,trans*-dibenzylidenecyclohexanone (13).** ¹H NMR (400 MHz, CDCl₃) δ 7.82 (s, 2H), 7.50–7.33 (m, 10H), 2.97–2.93 (m, 4H), 1.84–1.79 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 190.6, 137.2, 136.4, 136.2, 130.6, 128.8, 128.6, 28.7, 23.2. Other spectral data was identical to the literature values.

Determination of the relative and absolute stereochemistry of the cyclopentene products

The stereochemistry was determined by single crystal x-ray analysis of the product derived from 4-bromocinnamaldehyde (see above for characterization datum): A colorless crystal of approximate dimensions 0.4 × 0.05 × 0.04 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹¹ program was used to determine the unit cell parameters and data collection (20 sec: frame, 0.3 deg.: frame for a sphere of diffraction data). The data were collected at room temperature. The raw frame data were processed using SAINT¹² program. The absorption correction was applied using program SADABS¹³. The

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structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. Hydrogen atoms were theoretically added. At convergence, GOF = 1.207 for 206 variables refined to R₁ = 0.0632 for 1415 reflections with I > 2σ(I). The absolute structure was determined from the Flack parameters¹⁴ −0.02 (2). See the corresponding CIF file for further information.

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Figure 1. ORTEP representation (50% probability level) of *cis*-3(*S*)-(4-bromophenyl)-4(*R*)-methoxycarbonyl-1-phenylcyclopent-1-ene.