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Supporting Information

General Information. Unless otherwise noted all commercial materials were used without purification. Small scale reactions (< 10 mL) were carried out in Fisher Scientific disposable scintillation vials. Dichloromethane, toluene and ether were obtained from EMD and dried over 3 Å sieves. Gold catalysts **2** and **3** were synthesized by combining stoichiometric amounts of (Me₂S)AuCl and phosphine in dichloromethane followed by removal of solvent. Palladium catalysts were synthesized as reported by Sodeoka.¹ X-ray quality crystals of **5** were obtained by layering a dichloromethane solution of the catalyst with a small amount of ether followed by hexanes and refrigerating. Crystals obtained in this way were also used for all reactions described. Substrates **1**, **6**, **8**, **10**, **12**, **14**, **16**, **18**, **20**, **22**, **24**, **26**, **28** and **30** were prepared by alkylation of the corresponding ketoesters or diketones according to the method of Malacria.² Compound **7** has been previously reported.³ TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates. Flash chromatography was carried out on Merck 60 silica gel (32-63 μm). ¹H and ¹³C NMR spectra were recorded with Bruker AVB-400, AVQ-400, and AV-300 spectrometers and referenced to CHCl₃ (7.26 ppm). Analytical data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. The enantiomeric excess of Conia-ene products, with the exception of **27**, was determined with a Shimidzu VP Series Chiral HPLC with detection at 210, 254 and 280 nm wavelengths. The enantiomeric excess of **27** was determined by using europium tris[3-(heptafluoro-propylhydroxymethylene)-(-)-camphorate] as a chiral shift reagent.

General procedure for Pd catalyzed enantioselective Conia-ene cyclization. To a scintillation vial with magnetic stir bar was added substrate (20-60 mg, 1 equiv.), diethyl ether (0.02 M), glacial acetic acid (10 equiv.), and Yb(OTf)₃ (20 mol %) followed by **5** (10 mol %). The reaction was monitored by TLC with anisaldehyde staining until starting material was consumed. The solvent was evaporated and the yellow residue was chromatographed with hexanes and ethyl acetate to give the cyclized products described below.

1-Benzoyl-2-methylene-cyclopentanecarboxylic acid iso-propyl ester (4). ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 7.2$, 2H), 7.52 (t, $J = 7.2$, 1H), 7.41 (t, $J = 8.0$, 2H), 5.36 (t, $J = 2.0$, 1H), 5.23 (t, $J = 2.0$, 1H), 4.81 (m, 1H), 2.88 (dt, $J = 13.2$, 7.2, 1H), 2.52 (m, 2H), 2.18 (dt, $J = 13.2$, 7.2, 1H), 1.86 (m, 1H), 1.71 (m, 1H), 1.50 (d, $J = 6.0$, 3H), 0.89 (d, $J = 6.0$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.6, 171.3, 149.7, 135.6, 132.6, 128.8, 128.3, 111.5, 69.1, 67.5, 36.9, 34.5, 24.4, 21.4, 20.9. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$: C, 74.97; H, 7.40. Found: C, 74.68; H, 7.80. HPLC Chiralcel OJ column, 98:2 hexanes:isopropanol, 1.0 mL/min, t_R , 6.2 min (minor); 7.0 min (major): 89% ee.

1-Benzoyl-2-methylene-cyclopentanecarboxylic acid ethyl ester (7).³ HPLC Chiralcel OJ column, 98:2 hexanes:isopropanol, 1.0 mL/min, t_R , 8.6 min (minor); 11.5 min (major): 89% ee.

1-Benzoyl-2-methylene-cyclopentanecarboxylic acid allyl ester (9). ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 7.2$, 2H), 7.50 (t, $J = 7.2$, 1H), 7.40 (t, $J = 8.0$, 2H), 5.64 (m, 1H), 5.36 (t, $J = 2.0$, 1H), 5.21 (t, $J = 2.0$, 1H), 5.10 (m, 2H), 4.54 (m, 2H), 2.84 (m, 1H),

2.50 (m, 2H), 2.19 (m, 1H), 1.84 (m, 1H), 1.70 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.5, 171.8, 149.6, 135.6, 133.0, 131.4, 129.1, 128.7, 119.2, 112.3, 67.8, 66.4, 37.1, 34.6, 24.6. Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3$: C, 75.53; H, 6.71. Found: C, 75.63; H, 6.83. HPLC Chiralcel AD column, 99.5:0.5 hexanes:isopropanol, 1.0 mL/min, t_R , 17.1 min (minor); 21.4 min (major): 90% ee.

1-Benzoyl-2-methylene-cyclopentanecarboxylic acid tert-butyl ester (11). ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 7.2$, 2H), 7.52 (t, $J = 7.2$, 1H), 7.40 (t, $J = 7.2$, 2H), 5.35 (t, $J = 2.0$, 1H), 5.23 (t, $J = 2.0$, 1H), 2.82 (dt, $J = 13.2$, 7.2, 1H), 2.48 (m, 2H), 2.14 (m, 1H), 1.84 (m, 1H), 1.69 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.8, 170.6, 149.9, 132.5, 128.9, 128.8, 128.3, 111.3, 82.1, 68.1, 36.7, 34.6, 27.5, 24.4. Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_3$: C, 75.50; H, 7.74. Found: C, 75.58; H, 7.90. HPLC Chiralcel WHELK-O column, 98:2 hexanes:isopropanol, 1.0 mL/min, t_R , 6.4 min (minor); 7.5 min (major): 80% ee.

1-(2-Methylbenzoyl)-2-methylene-cyclopentanecarboxylic acid ethyl ester (13). ^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 7.2$, 1H), 7.28 (d, $J = 7.2$, 1H), 7.22 (t, $J = 7.2$, 1H), 7.15 (t, $J = 7.2$, 1H), 5.33 (t, $J = 2.0$, 1H), 5.24 (t, $J = 2.0$, 1H), 4.08 (m, 2H), 2.71 (m, 1H), 2.50 (m, 2H), 2.40 (s, 3H), 2.18 (m, 1H), 1.76 (m, 2H), 1.07 (t, $J = 7.2$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 201.6, 171.4, 149.7, 137.9, 137.8, 131.6, 130.4, 126.4, 125.1,

112.3, 69.7, 61.5, 37.1, 34.5, 24.5, 20.7, 13.7. Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.87; H, 7.57. HPLC Chiralcel OD column, 99:1 hexanes:isopropanol, 1.0 mL/min, t_R , 5.6 min (minor); 6.7 min (major): 93% ee.

1-(2-Iodobenzoyl)-2-methylene-cyclopentanecarboxylic acid ethyl ester (15). 1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8, 1H), 7.36 (m, 2H), 7.12 (m, 1H), 5.39 (t, J = 2.1, 1H), 5.33 (t, J = 2.1, 1H), 4.17 (m, 2H), 2.70 (m, 1H), 2.52 (m, 2H), 2.31 (m, 1H), 1.83 (m, 2H), 1.19 (t, J = 7.2, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 171.1, 149.3, 144.1, 140.8, 131.3, 127.7, 126.9, 113.5, 93.1, 69.9, 62.0, 37.2, 34.7, 24.8, 14.1. Anal. Calcd for $C_{16}H_{17}IO_3$: C, 50.02; H, 4.46. Found: C, 50.12; H, 4.61. HPLC Chiralcel WHELK-O column, 98:2 hexanes:isopropanol, 1.0 mL/min, t_R , 12.5 min (minor); 13.6 min (major): 85% ee.

1-(2-Methylbenzoyl)-2-methylene-cyclopentanecarboxylic acid allyl ester (17). 1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.2, 1H), 7.29 (t, J = 7.2, 1H), 7.22 (d, J = 7.2, 1H), 7.15 (t, J = 7.2, 1H), 5.71 (m, 1H), 5.36 (t, J = 2.0, 1H), 5.27 (t, J = 2.0, 1H), 5.24-5.14 (m, 2H), 4.53 (m, 2H), 2.71 (m, 1H), 2.51 (m, 2H), 2.41 (s, 3H), 2.21 (m, 1H), 1.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 171.2, 149.4, 137.8, 131.6, 131.4, 130.4, 126.4, 125.1, 124.5, 118.7, 112.6, 69.6, 66.2, 37.1, 34.4, 24.5, 20.8. Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.67; H, 7.37. HPLC Chiralcel AD column,

99.5:0.5 hexanes:isopropanol, 1.0 mL/min, t_R , 8.0 min (major); 16.5 min (minor): 94% ee.

1-(4-Methoxy)-benzoyl-2-methylene-cyclopentanecarboxylic acid isopropyl ester

(19). ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 9.0$, 2H), 6.88 (d, $J = 9.0$, 2H), 5.34 (t, $J = 2.0$, 1H), 5.20 (t, $J = 2.0$, 1H), 5.02 (m, 1H), 3.87 (s, 3H), 2.83 (m, 1H), 2.50 (m, 2H), 2.16 (m, 1H), 1.84 (m, 1H), 1.70 (m, 1H), 1.17 (d, $J = 6.0$, 3H) 0.92 (d, $J = 6.0$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 194.1, 171.5, 163.1, 149.7, 131.2, 128.3, 113.5, 111.5, 69.1, 67.3, 55.5, 36.9, 34.5, 24.3, 21.4, 21.1. Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_4$: C, 71.50; H, 7.33. Found: C, 71.31; H, 7.60. HPLC Chiralcel OJ column, 98:2 hexanes:isopropanol, 1.0 mL/min, t_R , 11.3 min (minor); 13.0 min (major): 86% ee.

1-(4-Nitro)-benzoyl-2-methylene-cyclopentanecarboxylic acid isopropyl ester (21).

^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 9.0$, 2H), 7.99 (d, $J = 9.0$, 2H), 5.37 (t, $J = 2.0$, 1H), 5.20 (t, $J = 2.0$, 1H), 5.01 (m, 1H), 2.86 (m, 1H), 2.52 (m, 2H), 2.14 (m, 1H), 1.89 (m, 1H), 1.72 (m, 1H), 1.18 (d, $J = 6.0$, 3H) 0.90 (d, $J = 6.0$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 194.3, 170.6, 149.9, 149.0, 140.5, 129.7, 123.6, 112.2, 69.7, 67.6, 36.6, 34.4, 24.4, 21.4, 21.0. Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_5$: C, 64.34; H, 6.03; N, 4.41. Found: C, 64.48; H, 6.18; N, 4.64. HPLC Chiralcel OJ column, 99:1 hexanes:isopropanol, 1.0 mL/min, t_R , 24.4 min (minor); 26.9 min (major): 79% ee.

1-(1-Naphthoyl)-2-methylene-cyclopentanecarboxylic acid ethyl ester (23). ^1H NMR (400 MHz, CDCl_3) δ 8.20 (d, $J = 7.6$, 1H), 7.91 (d, $J = 7.6$, 1H), 7.85 (t, $J = 7.6$, 1H), 7.53 (m, 3H), 7.40 (t, $J = 7.6$, 1H), 5.39 (t, $J = 2.0$, 1H), 5.36 (t, $J = 2.0$, 1H), 4.07 (m, 2H), 2.75 (m, 1H), 2.54 (m, 2H), 2.26 (m, 1H), 1.78 (m, 2H), 0.97 (t, $J = 7.2$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 202.0, 171.4, 149.6, 136.3, 133.8, 131.2, 130.6, 128.4, 127.5, 126.4, 125.7, 124.5, 124.0, 112.6, 70.4, 61.5, 37.3, 34.5, 24.6, 13.7. Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3$: C, 77.90; H, 6.54. Found: C, 77.87; H, 6.63. HPLC Chiralcel WHELK-O column, 98:2 hexanes:isopropanol, 1.0 mL/min, t_R , 22.0 min (minor); 25.0 min (major): 89% ee.

1-(2-Naphthoyl)-2-methylene-cyclopentanecarboxylic acid isopropyl ester (25). ^1H NMR (400 MHz, CDCl_3) δ 8.38 (s, 1H), 7.91 (m, 4H), 7.58 (m, 2H), 5.39 (t, $J = 2.0$, 1H), 5.27 (t, $J = 2.0$, 1H), 5.04 (m, 1H), 2.96 (m, 1H), 2.57 (m, 2H), 2.27 (m, 1H), 1.89 (m, 1H), 1.74 (m, 1H), 1.17 (d, $J = 6.4$, 3H), 0.84 (d, $J = 6.4$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.5, 171.4, 149.7, 135.2, 132.7, 132.3, 130.2, 129.6, 128.4, 128.1, 127.6, 126.7, 124.8, 111.6, 69.2, 67.5, 37.0, 34.5, 24.4, 21.4, 21.0. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_3$: C, 78.23; H, 6.88. Found: C, 77.54; H, 7.27. HPLC Chiralcel WHELK-O column, 98:2 hexanes:isopropanol, 1.0 mL/min, t_R , 11.0 min (minor); 12.2 min (major): 87% ee.

1-Cyclohexylcarbonyl-2-methylene-cyclopentanecarboxylic acid ethyl ester (27).

^1H NMR (400 MHz, CDCl_3) δ 5.27 (t, $J = 2.0$, 1H), 5.23 (t, $J = 2.0$, 1H), 4.20 (m, 2 H), 2.68 (m, 1H), 2.43 (m, 2H), 2.38 (m, 1H), 2.25 (m, 1H), 1.80-1.20 (m, 15H). ^{13}C NMR (100 MHz, CDCl_3) δ 208.8, 171.3, 148.5, 112.0, 70.8, 61.4, 48.1, 34.6, 33.9, 30.5, 25.7, 25.6, 23.9, 14.1. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3$: C, 72.69; H, 9.15. Found: C, 72.40; H, 9.29.

1-(1-Benzoyl-2-methylene-cyclopentyl)-ethanone (29). ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 7.2$, 2H), 7.54 (t, $J = 7.2$, 1H), 7.43 (t, $J = 8.0$, 2H), 5.42 (t, $J = 2.0$, 1H), 5.13 (t, $J = 2.0$, 1H), 2.75 (m, 1H), 2.54 (m, 2H), 2.25 (s, 3H), 2.23 (m, 1H), 1.80 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 204.9, 190.0, 149.2, 135.7, 133.1, 129.6, 128.7, 113.5, 75.7, 36.1, 34.6, 27.5, 24.5. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{O}_2$: C, 78.92; H, 7.06. Found: C 78.69; H, 6.98. HPLC Chiralcel OJ column, 98:2 hexanes:isopropanol, 1.0 mL/min, t_R , 20.4 min (minor); 27.6 min (major): 70% ee.

1-(1-Benzoyl-2-methylene-cyclopentyl)-3-methyl-butanone (31). ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, $J = 7.2$, 2H), 7.50 (t, $J = 7.2$, 1H), 7.40 (t, $J = 7.2$, 2H), 5.41 (t, $J = 2.0$, 1H), 5.12 (t, $J = 2.0$, 1H), 2.75 (m, 1H), 2.60-1.60 (m, 8H), 0.88 (d, $J = 6.9$, 3H), 0.86 (d,

$J = 6.9$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 206.0, 198.2, 148.7, 135.9, 132.9, 129.6, 128.6, 113.7, 75.6, 48.2, 36.1, 34.6, 31.9, 24.4, 24.1, 22.7. Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$: C, 79.96; H, 8.20. Found: C 79.83; H, 8.49. HPLC Chiralcel AD column, 98:2 hexanes:isopropanol, 1.0 mL/min, t_R , 6.5 min (minor); 7.9 min (major): 74% ee.

Ethyl-1,2,3,3a,9,9a-hexahydro-1-methylene-9-oxocyclopenta[b]chromene-9a-carboxylate (33). To a scintillation vial with magnetic stir bar was added **32** (50 mg, 0.185 mmol), diethyl ether (0.07 M) and glacial acetic acid (5 equiv.), followed by **5** (10 mol %). After two hours, the reaction mixture was passed through a short silica plug. The solvent was removed and conversion was determined to be 41% by ^1H NMR of the crude product. Flash chromatography (hexanes:ethyl acetate, 15:1) gave **33** (19.5 mg, 39%).

^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 7.6$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.92 (d, $J = 7.6$ Hz, 1H), 5.32 (m, 1H), 5.27 (m, 1H), 5.19 (m, 1H), 4.23 (q, $J = 6.8$ Hz, 2H), 2.69 (m, 2H), 2.22 (m, 1H), 1.92 (m, 1H), 1.26 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 187.2, 168.4, 160.0, 144.4, 136.4, 127.5, 121.6, 118.6, 118.0, 113.8, 85.3, 69.0, 62.2, 30.1, 28.8, 14.0. **Anal. Calcd. For $\text{C}_{16}\text{H}_{16}\text{O}_4$ Submitted.** HPLC Chiralcel OJ column, 93:7 hexanes:ethanol, 1.0 mL/min, t_R , 6.7 min (major); 10.6 min (minor): 82% ee.

3a-Methyl-8-oxo-2,3,3a,8-tetrahydro-1H-cyclopenta[a]indene-8a-carboxylic acid

ethyl ester (34). A mixture of **15** (88 mg, 0.23 mmol), Pd(OAc)₂ (10 mol%), triphenylphosphine (22 mol%), triethylamine (0.11 mL) and formic acid (0.03 mL) in DMF (3 mL) was stirred at 80° C for one hour. The mixture was diluted with water and extracted with ether (3 x 5 mL) and washed with water (1 x 5 mL). The organic phase was dried (MgSO₄), filtered and the solvent removed under reduced pressure. Flash chromatography (hexanes:ethyl acetate, 20:1) gave **34** (54 mg, 92% yield) as a single diastereomer. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (m, 2H), 7.49 (d, *J* = 7.8, 1H), 7.39 (t, *J* = 7.8, 1H), 4.14 (q, *J* = 7.5, 2H), 2.53 (dt, *J* = 13.2, 6.3, 1H), 2.19 (m, 1H), 1.97 (m, 1H), 1.82 (m, 1H), 1.64 (m, 1H), 1.45 (s, 3H), 1.17 (t, *J* = 7.5, 3H), 1.00 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 205.2, 171.9, 161.4, 136.4, 136.1, 128.1, 124.2, 123.8, 70.6, 61.5, 55.5, 42.7, 35.4, 24.1, 23.8, 14.4. Anal. Calcd for C₁₆H₁₈O₃: C, 74.39; H, 7.02. Found: C, 74.22; H, 7.23.

To a solution of **34** (155 mg, 0.60 mmol) in absolute ethanol (2 mL) was added sodium borohydride (34 mg, 0.90 mmol) in one portion. The reaction mixture was stirred

overnight, quenched with water (5 mL) and extracted with ethyl acetate (3 x 5 mL). The organic phase was dried, filtered and the solvent removed under reduced pressure. Flash chromatography (hexanes:ethyl acetate, 10:1) gave **35** (98 mg, 64% yield) as a single diastereomer. ^1H NMR (400 MHz, C_6D_6) δ 7.65 (m, 1H), 7.30 (m, 2H), 7.08 (m, 1H), 6.25 (bs, 1H) 4.13 (m, 2H), 3.25 (bs, 1H), 2.54 (m, 1H), 2.35 (m, 1H), 2.20 (m, 2H), 1.91 (m, 1H), 1.42 (m, 1H), 1.39 (s, 3H), 1.11 (t, $J = 7.5$, 3H).

The following nOe enhancements were observed:

^{13}C NMR (100 MHz, CDCl_3) δ 176.2, 147.6, 141.7, 128.5, 127.4, 124.0, 122.3, 77.4, 67.8, 60.7, 59.3, 40.7, 30.1, 24.2, 23.6, 14.4. Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_3$: C, 73.82; H, 7.74. Found: C, 73.49; H, 7.85.

Determination of the absolute stereochemistry of **35** using the mandelate-ester method.⁴

Signal	¹ H ppm (C ₆ D ₆)	
	major	minor
Ha	2.14	2.01
Hb	2.50	2.29
CO ₂ CH ₂ Me	4.05	3.94
CO ₂ CH ₂ CH ₃	0.98	0.92
Me	1.22	1.20

Signal	¹³ C ppm (C ₆ D ₆)	
	major	minor
Aryl	149.04	149.16
	139.13	139.28
	124.89	124.95
	122.81	122.89
CO ₂ CH ₂ Me	60.85	60.76
CO ₂ CH ₂ Me	14.21	14.14
Aliphatic	41.72	41.54
	31.50	31.45
	24.91	24.87
	24.54	24.42

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