Supporting Information

Gold(I)-Catalyzed Stereoselective Olefin Cyclopropanation

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General Information. Unless otherwise noted, all reagents were obtained commercially and used without further purification. Reagent grade nitromethane (NO₂Me) was obtained from Aldrich. Tertiary pivaloate **1** was prepared from 2-methyl-but-3-yn-2-ol and trimethylacetyl anhydride via the method reported by Gulhane.¹ Propargyl acetate **2** was prepared according to the method of Zimmerman.² Propargyl benzoate **3** was prepared according to the method of Emeis.³ TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates using iodine stain to visualize the reaction components. Column chromatography was carried out on Merck 60 silica gel (32-63 μ m). ¹H, ¹³C, and ³¹P NMR spectra were recorded with Bruker AV-300, AVQ-400, AVB-400, and DRX-500 spectrometers referenced to chloroform, unless otherwise noted. HPLC analyses were carried out on a Shimadzu 10A VP series system. Mass spectral and CHN data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley.

General procedure for the cyclopropanation of olefins with propargyl esters.

The gold catalyst was generated in a 1 dram vial with a threaded cap by addition of AgSbF₆ (0.05 equiv), AuPPh₃Cl (0.05 equiv), and NO₂Me (0.1 M based on the propargyl ester). After allowing the catalyst mixture to sit without stirring for 10 minutes, the appropriate olefin (4 equiv) was added. To this mixture was added a solution of the propargyl ester (1 equiv) in NO₂Me (0.1 M). The resulting mixture (0.05 M) was monitored by TLC until all starting material was consumed (20-40 minutes). The reaction mixture was concentrated and loaded directly onto a silica column; elution with hexanes/ethyl acetate resulted in isolation of analytically pure cyclopropanes.

Cyclopropane **4** was isolated as a 6:1 inseparable mixture of diastereomers in 74% yield (240.0 mg). ^1H NMR (CDCl_3 , 500 MHz) δ 7.21 (t, 2 H, $J = 7$ Hz), 7.14 (t, 1 H, $J = 7$ Hz), 7.03 (d, 2 H, $J = 7$ Hz), 2.27 (t, 2 H, $J = 7.5$ Hz), 1.47 (s, 3 H), 1.41 (s, 3 H), 1.25 (m, 1 H), 1.22 (s, 9 H), 0.99 (q, 1 H, $J = 6$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 176.8, 139.4, 137.8, 127.5, 127.2, 125.4, 123.0, 38.9, 27.2, 23.9, 21.7, 18.5, 17.2, 11.1; HRMS (EI) Calcd. For $[\text{C}_{18}\text{H}_{24}\text{O}_2]$ 272.1776, Found 272.1777.

Cyclopropane **5** was isolated and characterized as a 1.3:1 mixture of diastereomers in 62% yield (75.0 mg); spectral data was consistent with literature values.⁴ ^1H NMR (400 MHz, CDCl_3) δ 2.16 (s, 3 H), 2.14 (s, 3 H), 1.82 (s, 3 H), 1.81 (s, 3 H), 1.78-1.71 (m, 1 H), 1.64 (d, 3 H, $J = 1.3$), 1.55 (s, 3 H), 1.41 (m, 1 H), 1.02 (m, 1 H), 0.68-0.92 (m, 5 H), 0.39-0.47 (m, 2 H), 0.15-0.10 (m, 2 H), 0.06 (s, 9 H), 0.05 (s, 9H); ^{13}C (125 MHz, CDCl_3) δ 169.25, 169.12, 141.87, 140.42, 121.76, 118.86, 21.69, 20.66, 20.47, 20.29, 18.73, 18.61, 18.11, 17.78, 17.20 16.34, 14.42, 14.39, 13.87, 11.98, -1.38, -1.47; HRMS (EI) calc'd for $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Si}$: 240.1546, found: 240.1545; Anal. calc'd for $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Si}$: C, 64.95; H, 10.06. Found: C, 65.00; H, 10.12.

Cyclopropane **6** was obtained as a clear oil in 46% yield (23.7 mg) as an inseparable mixture of diastereomers. ^1H NMR (CDCl_3 , 400 MHz) δ 1.77 (s, 3 H), 1.55 (s, 3 H), 1.26 (s, 9 H), 0.76 (m, 1 H), 0.15 (q, 1 H, $J = 5.2$ Hz). The following resonances could be resolved for the minor diastereomer: 1.79 (s, 3 H), 1.50 (s, 3 H), 0.60 (pentet, 1 H, $J = 4.8$ Hz), 0.42 (pentet, 1 H, $J = 4.8$ Hz). The following resonance could not be resolved: 0.8-1.5 (m, 13 H each); ^{13}C NMR (CDCl_3 , 125 MHz) δ 176.2, 140.2, 118.8, 38.8, 31.7,

29.1, 27.3, 22.6, 18.8, 18.5, 17.5, 14.0. The following resonances could be resolved for the minor diastereomer: 176.1, 141.8, 118.8, 38.9, 31.7, 28.9, 27.3, 22.6, 18.7, 18.5, 17.8; The following resonances could not be resolved: 34.0, 29.5, 18.6, 16.7, 12.1, 10.2; Anal. calc'd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.58; H, 11.41.

Cyclopropane **7**, a clear oil, was isolated and characterized as a single diastereomer in 61% yield (23.7 mg). 1H NMR ($CDCl_3$, 400 MHz) δ 3.61 (dtd, 1 H, $J = 7.6, 3.2, 1.2$ Hz), 3.56 (dd, 1 H, $J = 7.6, 2$ Hz), 3.1 (m, 1 H), 1.85-2.05 (m, 2H), 1.84 (s, 3H), 1.81 (m, 1H), 1.54 (s, 3H), 1.49 (m, 2H), 1.29 (s, 9H), 1.14 (q, 1 H, $J = 6.4$ Hz); ($CDCl_3$, 100 MHz) δ 176.5, 139.7, 120.6, 64.4, 57.7, 39.0, 27.3, 24.8, 22.2, 19.1, 18.7, 17.9, 17.6; HRMS (EI) calc'd for $[C_{15}H_{24}O_3]$: 252.1725, found: 252.1721; See important 1H nOe correlations below for the major diastereomer:

Cyclopropane **8** was obtained as a clear oil in 68% yield (40.0 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.24 (m, 1 H), 7.05 (m, 3 H), 3.07 (dd, 1 H, $J = 17.2, 6.6$), 2.95 (d, 1 H, $J = 17.2$), 2.72 (m, 1 H), 2.21 (m, 1 H), 2.07 (m, 1 H), 1.67 (d, 3 H, $J = 1.5$), 1.27 (d, 3 H, $J = 2.0$), 1.18 (s, 9H). ^{13}C (125 MHz, $CDCl_3$) δ 176.90, 143.44, 142.41, 138.69, 125.64, 125.48, 124.91, 124.08, 123.28, 38.89, 32.54, 31.23, 27.36, 24.04, 22.48, 19.10, 16.99. HRMS (EI) calc'd for $C_{19}H_{24}O_2$: 284.1776, found: 284.1779. Anal. calc'd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.51; H, 8.76. See below for important 1H nOe correlations:

Cyclopropane **9**, a clear oil, was isolated and characterized as a 1.2:1 mixture of diastereomers in 69% yield (43.0 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.26 (m, 2 H), 7.19-7.10 (m, 4 H), 7.07-7.01 (m, 2 H), 2.71-2.50 (m, 4 H), 2.32 (d, 2 H, $J = 8.5$), 2.28-2.15 (m, 3 H), 2.11 (dd, 1 H, $J = 8.2, 4.0$), 1.87 (m, 1 H), 1.82 (s, 3 H), 1.80-1.75 (m, 3 H), 1.59 (s, 3 H), 1.57 (s, 3 H), 1.43 (s, 3 H), 1.36 (s, 9 H), 1.15 (s, 9 H); ^{13}C (125 MHz, CDCl_3) δ 176.81, 176.53, 140.69, 140.21, 137.09, 135.65, 135.32, 133.80, 130.28, 128.66, 128.40, 128.07, 126.07, 125.40, 125.35, 125.19, 121.75, 120.31, 39.08, 38.89, 27.37, 27.18, 26.62, 25.73, 23.63, 23.59, 21.96, 21.60, 20.96 (2C), 19.28, 19.14, 18.84, 18.70, 17.80, 17.11; HRMS (EI) calc'd for $\text{C}_{20}\text{H}_{26}\text{O}_2$: 298.1932, found: 298.1932.

Cyclopropane **10** was obtained as a clear oil in 73% yield (53.0 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.27-7.12 (m, 10 H), 2.67 (dd, 1 H, $J = 8.6, 8.2$), 1.86 (s, 3 H), 1.59-1.48 (m, 2 H), 1.43 (s, 3 H), 1.06 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.39, 146.09, 141.21, 138.53, 129.83, 128.40, 127.81, 127.67, 126.23, 126.01, 121.98, 38.82, 36.23, 28.09, 27.15, 19.87, 19.20, 17.83; HRMS (EI) calc'd for $\text{C}_{24}\text{H}_{28}\text{O}_2$: 348.2089, found: 348.2089.

Cyclopropane **11** was obtained as a clear oil in 73% yield (36.5 mg). ^1H NMR (CDCl_3 , 500 MHz) δ 8.09 (d, 2 H, $J = 7.5$ Hz), 7.58 (t, 1 H, $J = 7.5$ Hz), 7.48 (t, 2H, $J = 7.5$ Hz), 1.85 (s, 3 H), 1.69 (t, 1 H, $J = 7$ Hz), 1.63 (s, 3H), 1.33-1.6 (m, 8 H), 1.28 (m, 1 H), 1.16 (m, 1H), 0.59 (q, 1 H, $J = 4.5$ Hz), 0.39 (t, 1 H, $J = 4$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ

164.6, 140.5, 133.0, 130.0, 129.8, 128.4, 121.3, 36.7, 31.5, 26.5, 26.2, 25.6, 25.5, 25.1, 19.0, 17.82, 17.8; HRMS (EI) calc'd for [C₁₉H₂₄O₂]: 284.1776, found: 284.1774.

Cyclopropane **12**, a clear oil, was isolated and characterized as a 5:1 mixture of diastereomers in 84% yield (33.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.21 (m, 2 H), 7.17-7.13 (m, 3 H), 2.21 (m, 1 H), 2.03-1.21 (m, 9 H), 1.70 (s, 3 H), 1.35 (s, 3 H), 1.11 (s, 9 H); ¹³C NMR (125 MHz, CDCl₃) δ 176.30, 145.09, 139.28, 127.81, 127.58, 125.41, 120.25, 38.71, 32.11, 31.58, 31.27, 27.14, 22.99, 21.84, 21.58, 21.09, 19.02, 17.34; HRMS (EI) calc'd for [C₂₂H₃₀O₂]: 326.22458, found: 326.22534.

Cyclopropane **13**, a clear oil, was isolated and characterized as a 1.2:1 mixture of diastereomers in 69% yield (72.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 2.16 (s, 3 H), 2.15 (s, 3 H), 1.92-1.62 (m, 14 H), 1.79 (d, 3 H, *J* = 1.6), 1.75 (s, 3 H), 1.61 (s, 3 H), 1.60 (d, 3 H, *J* = 2.2), 1.27 (s, 3 H), 1.25 (m, 1 H), 1.16 (s, 3 H), 1.04 (t, 1 H, *J* = 3.7); ¹³C (125 MHz, CDCl₃) δ 169.40, 169.18, 141.30, 140.66, 121.05, 120.49, 34.79, 33.10, 31.79, 31.46, 30.96, 29.97, 28.01, 27.36, 26.95, 23.99, 23.85, 22.59, 21.96, 20.76, 20.66, 18.96, 18.91, 17.57, 17.16, 17.05; HRMS (EI) calc'd for C₂₄H₂₈O₂: 208.1463, found: 208.1466; Anal. calc'd for C₁₃H₂₀O₂: C, 74.96; H, 9.68. Found: C, 74.98; H, 9.82.

Cyclopropane **14** was obtained as a clear oil in 67% yield (34.0 mg). ¹H NMR (CDCl₃, 400 MHz) δ 1.71 (s, 3H), 1.59 (s, 3H), 1.34 (m, 1H), 1.31 (s, 9H), 1.12 (s, 6H), 1.03 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 176.1, 141.9, 122.4, 38.9, 34.8, 27.5, 24.1, 23.1,

19.5, 19.1, 17.1; Anal. calc'd for C₁₆H₂₈O₂: C, 76.14; H, 11.18. Found: C, 76.24; H, 11.48.

For this example, enantioenriched **15** was used as the starting material. Cyclopropane **16** was obtained as a clear oil in 65% yield (52.0 mg) as a single diastereomer with 0% ee. ¹H NMR (CDCl₃, 400 MHz) δ 7.3-7.1 (m, 10 H), 5.99 (s, 1 H), 2.49-2.35 (m, 2 H), 2.05 (s, 3 H), 1.46-1.41 (m, 2 H); ¹³C NMR (CDCl₃, 100 MHz) δ 168.6, 146.7, 138.1, 134.3, 128.5, 128.3, 127.9, 127.4, 127.0, 126.1, 118.4, 23.7, 23.6, 21.0, 11.0.

Cyclopropane **17** was obtained as a clear oil in 47% yield (18 mg) and 5:1 (*cis:trans*) d.r. when AuP'Bu₃Cl/AgSbF₆ was used as a catalyst. When AuPPh₃Cl/AgSbF₆ was used, **16** was obtained in 42% yield (15.8 mg) as a 1:1 mixture of diastereomers. ¹H NMR (CDCl₃, 500 MHz) *cis* δ 6.95 (d, 2 H, *J* = 9 Hz), 6.77 (d, 2 H, *J* = 9 Hz), 3.79 (s, 3 H), 2.22 (m, 2 H), 1.48 (s, 3 H), 1.41 (s, 3 H), 1.23 (s, 9 H), 1.19 (m, 1 H), 0.90 (q, 1 H, *J* = 6 Hz). The following resonances could be resolved for the minor diastereomer *trans*: δ 7.02 (d, 2 H, *J* = 8.5 Hz), 6.81 (d, 2 H, *J* = 8.5 Hz), 1.99 (m, 1 H), 1.93 (m, 1 H), 1.79 (s, 3 H), 1.55 (s, 3 H), 1.29 (s, 9 H), 1.05 (m, 2 H). ¹³C NMR (CDCl₃, 125 MHz) *cis* δ 176.3, 157.6, 138.1, 131.4, 128.2, 122.8, 113.0, 55.2, 38.9, 27.2, 23.2, 21.2, 18.6, 17.2, 11.2. The following resonances could be resolved for the minor diastereomer *trans* δ 176.5, 157.8, 140.7, 134.0, 127.0, 120.1, 113.7, 55.3, 39.0, 27.3, 22.7, 22.5, 18.7, 17.8, 14.1; HRMS (EI) Calcd. For [C₁₉H₂₆O₃] 302.1882, Found 302.1882. See below for important ¹H nOe correlations for the *cis*-diastereomer:

Cyclopropanes **18** and **19** were isolated and characterized as a 5.8:1 mixture in 81% yield (96.0 mg): ^1H NMR (400 MHz, CDCl_3) δ **all cis** 7.28-7.22 (m, 2 H), 7.19-7.15 (m, 3 H), 2.41 (m, 1 H), 2.27 (t, 1 H, $J = 9.2$), 1.64 (s, 3 H), 1.64-1.54 (m, 4 H), 1.16 (s, 9 H), 1.15 (d, 3 H, $J = 6.8$). The following resonances could be resolved for the minor diastereomer **trans-cis**: δ 1.98 (m, 1H), 1.87 (s, 3 H), 1.31 (s, 9 H), 0.90 (d, 3 H, $J = 6.8$). ^{13}C (125 MHz, CDCl_3) δ **all cis** 176.82, 138.77, 138.58, 129.27, 127.37, 125.07, 124.27, 38.89, 27.20, 26.91, 26.51, 23.16, 19.37, 18.69, 17.32, 9.97. The following resonances could be resolved for the minor diastereomer **trans-cis**: δ 176.75, 141.50, 138.10, 129.20, 128.03, 125.95, 39.01, 28.78, 27.30, 25.12, 20.61, 18.84, 17.72, 13.21. Anal. calc'd for $\text{C}_{19}\text{H}_{26}\text{O}_2$: C, 79.68; H, 9.15. Found: C, 79.56; H, 9.37. See below for important ^1H nOe correlations for the major diastereomer:

Cyclopropanes **20** and **21** were isolated and characterized as a 4.3:1 mixture in 84% yield (100.0 mg): ^1H NMR (400 MHz, CDCl_3) δ major diastereomer **20** 7.24 (m, 2 H), 7.17 (m, 1 H), 7.02 (m, 2 H), 2.05 (m, 1 H), 2.01 (dd, 1 H, $J = 8.6, 5.6$), 1.48 (s, 6 H), 1.36 (m, 1 H), 1.25 (s, 9 H), 1.24 (d, 3 H, $J = 6.4$). The following resonances could be resolved for the minor diastereomer **21**: δ 2.17 (m, 1 H), 1.84 (d, 3 H, $J = 0.8$), 1.72 (t, 1 H, $J = 5.6$),

1.64 (d, 3 H, $J = 1.6$), 1.34 (s, 9 H). ^{13}C (125 MHz, CDCl_3) δ major diastereomer **20** 176.66, 139.92, 138.18, 127.53, 127.04, 125.26, 122.82, 38.90, 32.86, 30.38, 27.23, 20.78, 18.68, 18.60, 17.17. The following resonances could be resolved for the minor diastereomer **21**: δ 142.31, 139.33, 128.30, 126.19, 125.65, 122.19, 38.92, 30.14, 28.21, 27.39, 23.50, 18.98, 17.54, 14.51; Anal. calc'd for $\text{C}_{19}\text{H}_{26}\text{O}_2$: C, 79.68; H, 9.15. Found: C, 79.76; H, 9.20. See below for important ^1H nOe correlations for the major diastereomer:

General procedure for the enantioselective cyclopropanation of styrenes with propargyl esters.

The gold catalyst was generated in a 1 dram vial with a threaded cap by addition of AgSbF_6 (0.05 equiv), $(\text{AuCl})_2(\text{Ligand})$ (0.025 equiv), and NO_2Me (0.1 M). After allowing the catalyst mixture to sit without stirring for 10 minutes, the appropriate styrene (4 equiv) was added. To this mixture was added a solution of the propargyl ester (1 equiv) in NO_2Me (0.1 M). The resulting mixture (0.05 M) was monitored by TLC until all starting material was consumed (20-40 minutes). The reaction mixture was concentrated and loaded directly onto a silica column; elution with hexanes/ethyl acetate resulted in isolation of analytically pure enantio-enriched cyclopropanes.

Cyclopropane **22** was isolated in 72% yield. The spectral data matched those reported in the literature;⁴ %ee by HPLC (Chiral Cel OD Column, 2-propanol:hexanes = 5:95 (1.0 mL/min), major isomer 4.8 min, minor isomer 5.8 min): 60% ee. Registry: 9328769.

Cyclopropane **23** was isolated in 73% yield. The spectral data matched those reported in the literature;⁴ %ee by HPLC (Chiral Pak AD Column, 2-propanol:hexanes = 5:95 (1.0 mL/min), major isomer 5.0 min, minor isomer 6.7 min): 68% ee. Registry: 9637295.

Cyclopropane **4** was isolated in 70% yield. The spectral data matched those obtained for the racemic compound; %ee by HPLC (Chiral Cel OD Column, 2-propanol:hexanes = 1:99 (1.0 mL/min), minor isomer 4.5 min, major isomer 5.1 min): 80% ee.

Cyclopropane **24** was obtained as a clear oil in 83% yield (60.0 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.17-7.08 (m, 3 H), 6.91 (m, 1 H), 2.43 (s, 3 H), 2.35 (m, 2 H), 1.67 (s, 3 H), 1.38 (s, 3 H), 1.27 (m, 1 H), 1.18 (s, 9 H), 1.11 (q, 1 H, *J* = 6.3); ¹³C NMR (125 MHz, CDCl₃) δ 176.45, 138.63, 137.62, 136.98, 129.49, 126.29, 125.63, 125.08, 121.78, 38.87, 27.23, 20.83, 20.72, 19.86, 18.75, 17.66, 10.34; HRMS (EI) calc'd for C₁₉H₂₆O₂: 286.1932, found: 286.1935; Anal. calc'd for C₁₉H₂₆O₂: C, 79.68; H, 9.15. Found: C, 80.03; H, 9.21; %ee determined by HPLC (Chiral Cel OD Column, 2-propanol:hexanes = 0.5:99.5 (1.0 mL/min), major isomer 7.0 min, minor isomer 6.2 min): 87% ee. See below for important ¹H nOe correlations:

Cyclopropane **25** was obtained as a clear oil in 82% yield (51.2 mg). ^1H NMR (CDCl_3 , 400 MHz) δ 7.24 (d, 2 H, J = 8 Hz), 6.97 (d, 2 H, J = 8 Hz), 2.24 (t, 2 H, J = 8 Hz), 1.51 (s, 3 H), 1.44 (s, 3 H), 1.31 (s, 9 H), 1.25 (m, 1 H), 1.22 (s, 9 H), 0.96 (q, 1 H, J = 6 Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 176.6, 148.3, 138.4, 136.4, 126.8, 124.3, 122.8, 38.8, 34.3, 31.4, 27.2, 23.4, 21.4, 18.6, 17.3, 18.0; Anal. calc'd for $\text{C}_{22}\text{H}_{32}\text{O}_2$: C, 80.44; H, 9.82. Found: C, 80.36; H, 9.88. In order to obtain an HPLC assay, **25** was treated with lithium aluminum hydride to form the corresponding ketone: %ee by HPLC (Regis Technologies Whelk-O 1 Column, 2-propanol:hexanes = 2:98 (1.0 mL/min), major isomer 5.7 min, minor isomer 8.3 min): 80% ee.

Cyclopropane **26** was obtained as a clear oil in 71% yield (68.6 mg). ^1H NMR (CDCl_3 , 500 MHz) δ 6.96 (s, 2 H), 2.36 (s, 3 H), 2.34 (m, 1 H), 2.07 (q, 1 H, J = 8.5 Hz), 1.91 (s, 3 H), 1.43 (s, 3 H), 1.33 (td, 1 H, J = 9, 5 Hz), 1.30 (s, 9 H), 0.81 (s, 9 H), 0.69 (m, 1 H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 148.6, 140.5, 138.1, 124.9, 124.6, 118.8, 38.7, 34.0, 31.3, 27.3, 26.8, 20.6, 19.1, 19.0, 18.4, 11.7; Anal. calc'd for $\text{C}_{24}\text{H}_{36}\text{O}_2$: C, 80.85; H, 10.18. Found: C, 80.61; H, 10.32. In order to obtain an HPLC assay, **26** was treated with lithium aluminum hydride to form a mixture of the corresponding ketone and an unidentified contaminant: %ee by HPLC of the ketone (Regis Technologies Whelk-O 1 Column, 2-propanol:hexanes = 0.3:99.7 (1.0 mL/min), major isomer 7.7 min, minor isomer 8.4 min): 94% ee; %ee by HPLC of the contaminant (Regis Technologies Whelk-O 1 Column, 2-propanol:hexanes = 0.5:99.5 (1.0 mL/min), minor isomer 4.5 min, major isomer 4.8 min): 94% ee.

Cyclopropane **27** was obtained as a clear oil in 60% yield (42.3 mg). ^1H NMR (CDCl_3 , 400 MHz) δ 7.55 (dd, 1 H, $J = 8, 1.6$ Hz), 7.22 (td, 1 H, $J = 7.6, 1.2$ Hz), 7.06 (td, 1 H, $J = 7.6, 1.6$ Hz), 6.88 (dd, 1 H, $J = 8, 1.2$ Hz), 2.65 (q, 1 H, $J = 7.2$ Hz), 2.43 (q, 1 H, $J = 8$ Hz), 1.64 (s, 3 H), 1.42 (d, 3 H, $J = 1.2$ Hz), 1.34 (m, 1 H), 1.24 (s, 9 H), 1.11 (q, 1 H, $J = 6.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 176.5, 138.3, 137.7, 132.3, 127.3, 127.1, 126.4, 126.3, 123.2, 38.9, 27.3, 23.9, 21.9, 18.9, 17.5, 11.2; HRMS (EI) calc'd for $[\text{C}_{18}\text{H}_{23}\text{BrO}_2]$: 350.0881, found: 350.0872; Anal. calc'd for $\text{C}_{18}\text{H}_{23}\text{BrO}_2$: C, 61.54; H, 6.60. Found: C, 61.28; H, 6.89; %ee by HPLC (Chiral Cel OD Column, 2-propanol:hexanes = 2:98 (1.0 mL/min), minor isomer 4.4 min, major isomer 6.1 min): 76% ee.

Cyclopropane **28** was obtained as a clear oil in 68% yield (40.7 mg). ^1H NMR (CDCl_3 , 400 MHz) δ 7.12 (m, 2 H), 7.02 (m, 1 H), 6.92 (m, 1 H), 2.25 (m, 2 H), 1.50 (s, 3 H), 1.43 (d, 3 H, $J = 1.6$ Hz), 1.27 (m, 1 H), 1.25 (s, 9 H), 0.98 (q, 1 H, $J = 6.4$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 176.7, 141.8, 137.6, 133.4, 128.7, 127.4, 125.6, 125.5, 123.6, 38.9, 27.3, 23.6, 22.0, 18.6, 17.3, 12.1; HRMS (EI) calc'd for $\text{C}_{18}\text{H}_{23}\text{ClO}_2$: 306.1387, found: 306.1387; Anal. calc'd for $\text{C}_{18}\text{H}_{23}\text{ClO}_2$: C, 70.46; H, 7.56. Found: C, 70.63; H, 7.78; %ee by HPLC (Chiral Pak AD Column, 2-propanol:hexanes = 0.5:99.5 (1.0 mL/min), major isomer 6.2 min, minor isomer 7.3 min): 76% ee.

Cyclopropane **29** was obtained as a clear oil in 75% yield (43.9 mg). ^1H NMR (CDCl_3 , 400 MHz) δ 6.97 (m, 2 H), 6.91 (m, 2 H), 2.25 (dd, 2 H, $J = 8.4, 6.4$ Hz), 1.48 (s, 3 H), 1.41 (s, 3 H), 1.25 (m, 1 H), 1.22 (s, 9 H), 0.92 (q, 1 H, $J = 6$ Hz); ^{13}C NMR (CDCl_3 , 100

MHz) δ 176.7, 162.4, 160.0, 137.9, 135.1, 128.7, 128.6, 123.2, 114.5, 114.2, 38.9, 27.3, 23.2, 21.5, 18.6, 17.3, 11.7; Anal. calc'd for $C_{18}H_{23}FO_2$: C, 74.45; H, 7.98. Found: C, 74.65; H, 8.23; %ee by HPLC (Regis Technologies Whelk-O 1 Column, 2-propanol:hexanes = 0.5:99.5 (1.0 mL/min), minor isomer 6.7 min, major isomer 7.2 min): 82% ee.

Cyclopropane **30** was obtained as a clear oil in 79% yield (54.0 mg). 1H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, 1 H, $J = 7.9$), 7.88 (dd, 1 H, $J = 9.2, 1.8$), 7.74 (d, 1 H, $J = 8.2$), 7.58-7.48 (m, 2 H), 7.42 (t, 1 H, $J = 7.4$), 7.24 (d, 1 H, $J = 7.1$), 2.78 (q, 1 H, $J = 8.5$), 2.56 (q, 1 H, $J = 8.5$), 1.74 (s, 3 H), 1.45 (m, 1 H), 1.29 (m, 1 H), 1.27 (s, 3 H), 1.06 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.41, 138.51, 134.84, 133.61, 133.54, 128.45, 126.58, 125.34, 125.25, 125.06, 124.59, 124.44, 121.67, 38.74, 27.12, 20.68, 20.24, 19.13, 17.67, 9.92; HRMS (EI) calc'd for $C_{22}H_{26}O_2$: 322.1933, found: 322.1933; Anal. calc'd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.27; H, 7.95; %ee determined by HPLC (Chiral Pak AD Column, 2-propanol:hexanes = 4:96 (1.0 mL/min), major isomer 4.5 min, minor isomer 5.5 min): 85% ee. See below for important 1H nOe correlations:

The above cyclopropane was obtained as a white solid in 24% yield (18.7 mg). 1H NMR ($CDCl_3$, 500 MHz) δ 7.11 (m, 3 H), 7.06 (s, 2 H), 6.99 (m, 2 H), 3.13 (septet, 2 H, $J = 6.5$

Hz), 2.92 (septet, 1 H, $J = 7$ Hz), 2.49 (m, 1 H), 2.38 (q, 1 H, $J = 8$ Hz), 1.52 (d, 3 H, $J = 2$ Hz), 1.37 (td, 1 H, $J = 9, 5.5$ Hz), 1.29 (m, 18 H), 1.51 (q, 1 H, $J = 6$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 169.8, 150.2, 145.1, 139.9, 138.4, 130.0, 127.3, 126.9, 125.4, 124.2, 121.0, 34.4, 31.4, 24.6, 24.2, 23.9, 22.5, 19.0, 17.5, 12.6; Anal. calc'd for $\text{C}_{29}\text{H}_{38}\text{O}_2$: C, 83.21; H, 9.15. Found: C, 83.18; H, 9.36; %ee by HPLC (Chiral Pak AD Column, 2-propanol:hexanes = 2:98 (1.0 mL/min), major isomer 4.1 min, minor isomer 5.9 min): 86% ee.

Cyclopropane **31** was isolated and characterized as a 5:1 mixture of diastereomers in 74% yield (62.9 mg). ^1H NMR (CDCl_3 , 400 MHz) *cis* δ 1.80 (s, 3 H), 1.76 (m, 1 H), 1.61 (s, 3 H), 1.30 (9 H), 1.03 (m, 1 H), 0.83 (m, 2 H), 0.10 (m, 2 H), 0.06 (s, 9 H). The following resonances could be resolved for the minor diastereomer *trans*: 1.86 (s, 3 H), 1.53 (s, 3 H), 1.28 (9 H), 0.71 (m, 1 H), 0.39 (m, 2 H), 0.05 (s, 9 H). ^{13}C NMR (CDCl_3 , 125 MHz) *cis* δ 176.5, 140.2, 121.2, 38.9, 27.4, 18.8, 17.6, 17.3, 16.2, 14.3, 11.5, -1.4. The following resonances could be resolved for the minor diastereomer *trans*: δ 141.6, 118.3, 39.0, 27.3, 21.6, 20.3, 18.6, 17.9, 14.2, 13.6, -1.5. In order to obtain an HPLC assay, **31** was treated with lithium aluminum hydride to form the corresponding ketone: %ee by HPLC (Regis Technologies Whelk-O 1 Column, 2-propanol:hexanes = 0.5:99.5 (1.0 mL/min), *cis* major isomer 5.1 min, minor isomer 5.8 min): 78% ee, (*trans* major isomer 6.4 min, minor isomer 7.3 min): 65% ee. See below for important ^1H nOe correlations for the *cis*-diastereomer:

To a solution of enolester **4** (33 mg, 0.121 mmol, 80% ee) in $\text{CCl}_4\text{:MeCN:H}_2\text{O}$ (0.2 mL:0.2 mL: 0.3 mL) was added $\text{RuCl}_3\cdot x\text{H}_2\text{O}$ (2.5 mg, 0.012 mmol)⁵. After stirring rapidly for 2 min, NaIO_4 was added in one portion. The heterogenous yellow mixture was stirred one hour and diluted with Et_2O (2 mL) to precipitate RuO_2 . MgSO_4 was added and the suspension was filtered through celite (Et_2O rinsing). The organic was concentrated to give the crude α -hydroxyketone **32** (29 mg) which was used in the next step without purification. ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.19 (m, 5 H), 3.71 (br s, 1 H), 2.85 (q, 1 H, $J = 8.8$), 2.64 (m, 1 H), 1.99 (m, 1 H), 1.51 (m, 1 H), 1.43 (s, 3 H), 1.29 (s, 3 H).

To a solution of crude **32** in MeOH (2 mL) was added a solution of NaIO_4 (180 mg, 0.84 mmol) in water (0.6 mL)⁶. The heterogenous white mixture was stirred overnight, methanol was removed and the aqueous layer was extracted with dichloromethane (3 X 5 mL) and the combined organics were dried and concentrated. The crude film was purified by column chromatography (1:1 hexanes: EtOAc) to give acid **33** (12.2 mg, 62% over two steps). The spectroscopic data obtained was consistent with those in the literature⁷: ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.22 (m, 5 H), 2.67 (q, 1 H, $J = 8.8$), 2.09 (m, 1 H), 1.71 (m, 1 H), 1.42 (m, 1 H). The absolute configuration of carboxylic acid **32** was determined to be 1R, 2S by optical rotation: $[\alpha]_D^{25} = -17^\circ$ ($c = 0.4$, CHCl_3), lit for $>98\%$ ee⁸ $[\alpha]_D^{25} = -28^\circ$ ($c = 1.02$, CHCl_3).

General procedure for the synthesis of chiral gold complexes.

Chiral gold complexes were synthesized from $(\text{SMe}_2)\text{AuCl}$ via modification of a procedure reported by Puddephat.⁹ In a 20 mL screw-top vial was dissolved $(\text{SMe}_2)\text{AuCl}$ (1 equiv) in CH_2Cl_2 , and the resulting solution was cooled in an ice bath. A solution of the desired phosphine (0.5 equiv) in CH_2Cl_2 was added dropwise, and the resulting solution was allowed to warm to room temperature and stirred for two hours. After TLC indicated complete consumption of the starting material, the reaction solution was concentrated *en vacuo* to yield the desired gold(I) complexes.

(R)-DTBM-Segphos(AuCl)₂ was obtained as a white solid in quantitative yield. ¹H NMR (CDCl_3 , 400 MHz) δ 7.57 (d, 4 H, J = 13.6 Hz), 7.33 (d, 4 H, J = 13.6 Hz), 6.90 (m, 4 H), 5.54 (d, 2 H, J = 1.4 Hz), 4.46 (d, 2 H, J = 1.4 Hz), 3.76 (s, 6 H), 3.57 (s, 6 H), 1.34 (s, 36 H), 1.30 (s, 36 H); ³¹P NMR (CDCl_3) δ 27.4 (s); ¹³C {¹H and ³¹P} NMR (CDCl_3 , 125 MHz) δ 162.54, 162.50, 149.38, 147.88, 143.82, 143.53, 134.57, 133.46, 130.18, 124.26, 122.58, 121.07, 108.25, 101.04, 64.19 (d), 53.50, 35.78 (d), 31.54 (d).; HRMS (EI) Calcd. For $[\text{C}_{74}\text{H}_{100}\text{Au}_2\text{ClO}_8\text{P}_2]$ $[\text{M}-\text{Cl}]$ 1607.5913, Found 1607.5938.

(R)-Segphos(AuCl)₂ was obtained as a white solid in quantitative yield. ¹H NMR (CDCl_3 , 400 MHz) δ 7.69-7.65 (m, 4 H), 7.57-7.51 (m, 6 H), 7.47-7.42 (m, 10 H), 6.88 (dd, 2 H, J = 8.0, 1.4 Hz), 6.83 (d, 1 H, J = 12.0 Hz), 6.80 (d, 1 H, J = 12.0 Hz), 5.54 (d,

2 H, $J = 1.2$ Hz), 5.53 (d, 2 H, $J = 1.2$ Hz) ^{31}P NMR (CDCl_3) δ 24.8 (s); HRMS (EI) Calcd. For $[\text{C}_{38}\text{H}_{28}\text{Au}_2\text{ClO}_4\text{P}_2]$ $[\text{M}-\text{Cl}]$ 1039.0483, Found 1039.0485.

(S)-(3,5-xylyl)-Binap(AuCl) $_2$ was obtained as a white solid in quantitative yield. ^1H NMR (CDCl_3 , 400 MHz) δ 8.19 (d, 2 H, $J = 8.4$ Hz), 8.02 (d, 2 H, $J = 8.4$ Hz), 7.59 (t, 2 H, $J = 7.6$ Hz), 7.43 (t, 2 H, $J = 8.8$ Hz), 7.25 (m, 2H), 7.14 (d, 4 H, $J = 6.8$ Hz), 6.96 (m, 4 H), 6.87 (s, 2 H), 6.69 (d, 4 H, $J = 13.6$ Hz), 2.21 (s, 12 H), 2.18 (s, 12 H) ^{31}P NMR (CDCl_3) δ 21.9 (s); HRMS (EI) Calcd. For $[\text{C}_{52}\text{H}_{48}\text{Au}_2\text{ClP}_2]$ $[\text{M}-\text{Cl}]$ 1163.2251, Found 1163.2237.

This compound was synthesized using equimolar amounts of $(\text{SMe}_2)\text{AuCl}$ and phosphine. (S)-MOP(AuCl) $_2$ was obtained as a white solid in quantitative yield. The spectral data obtained matched those reported in the literature¹⁰. ^1H NMR (CDCl_3 , 400 MHz) δ 8.12 (d, $J = 9$ Hz), 7.93 (d, $J = 8.1$ Hz), 7.88 (d, $J = 8.4$ Hz), 7.58-7.19 (m), 6.95 (t, $J = 7.2$ Hz), 6.56 (d, $J = 8.4$ Hz), 3.44 (s); ^{31}P NMR (CDCl_3) δ 24.6 (s).

(R)-Diop (AuCl) $_2$ was obtained as a white solid in quantitative yield. ^1H NMR (CDCl_3 , 400 MHz) δ 7.70-7.60 (m, 8 H), 7.50-7.41 (m, 12 H), 4.35- 4.29 (m, 2 H), 2.86-2.78 (m, 2 H), 2.62-2.55 (m, 2 H), 1.14 (s, 6 H); ^{31}P NMR (CDCl_3) δ 25.7 (s); HRMS (EI) Calcd. For $[\text{C}_{31}\text{H}_{32}\text{Au}_2\text{Cl}_1\text{O}_2\text{P}_2]$ $[\text{M}-\text{Cl}]$ 927.0897, Found 927.0878.

(R)-Binap(AuCl)₂ was obtained as a white solid in quantitative yield. The spectral data obtained matched those reported in the literature.¹⁰

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