Supporting Information for:

**Catalytic Enantioselective Synthesis of Tetrasubstituted Tertiary Ethers. Ready Access to Fully-substituted α-Hydroxyketones, esters, and acids.**

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**Materials and Methods.** Unless otherwise stated, reactions were performed in flame-dried glassware under an argon atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Tetrabutylammonium triphenyldifluorosilicate (TBAT) was purchased from Sigma-Aldrich Chemical Company and azeotropically dried five times from acetonitrile prior to use. Trimethylsilyl chloride (TMSCl) and triethyl amine (TEA) were distilled from sodium hydride immediately prior to use. Sodium iodide was dried by heating at 90 °C (2 torr) for 12 h. Bis(3,5,3',5'-dimethoxydibenzylidenacetone)palladium(0) (Pd(dma):) was purchased from Sigma-Aldrich Chemical Company and stored in a glove box prior to use. (S)-r-Bu-PHOX was prepared by known methods.1 Cyclohexylamine, alkyl halides, triethylsilyl chloride and diallyl carbonate were used without further purification. Molecular sieves were purchased from Aldrich as activated 5 µm powder and stored in a 120 °C drying oven until immediately prior to use unless otherwise noted. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, anisaldehyde, or CAM staining. Florisil® (100-200 mesh) and ICN Silica gel (particle size 0.032-0.063 mm) were used for flash chromatography. Chiral HPLC analysis was performed with an Agilent 1100 Series HPLC utilizing chiralpak AD or chiralcel OD-H columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. with visualization at 254 nm or 220 nm. Chiral GC analysis was performed with an Agilent 6890 GC utilizing a G-TA (30 m x 0.25 cm) column (1.0 mL/min carrier gas flow). Optical rotations were measured with a Jasco P-1010 polarimeter at 589 nm.1H and 13C NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer (at 300 MHz and 75 MHz respectively), and are reported relative to Me4Si (δ 0.0). Data for 1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Data for 13C NMR spectra are reported in terms of chemical shift relative to Me4Si (δ 0.0). IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in wavenumbers (cm⁻¹). High resolution mass spectra were obtained from the Caltech Mass Spectral Facility.

**Representative Procedure for the Synthesis of 2,2-Dimethyl-1,3-dioxan-5-ones.**

![Representative Procedure for the Synthesis of 2,2-Dimethyl-1,3-dioxan-5-ones.](image)

2,2,4-Trimethyl-1,3-dioxan-5-one.

To a solution of 2,2-dimethyl-1,3-dioxan-5-one (5.0 g, 38.4 mmol, 1.0 equiv) in toluene (125 mL, 0.3 M) were added 4Å molecular sieves (5.0 g) and cyclohexylamine (8.50 mL, 74.3 mmol, 1.94 equiv) at room temperature (ca. 25 °C). The mixture was stirred for 14 h, then the molecular sieves were removed by filtration. The filtrate was concentrated under reduced pressure to give crude imine (7.95 g).

Lithium diisopropylamine was prepared in a separate flask by dropwise addition of n-BuLi (2.50 M in hexanes, 15.4 mL, 38.5 mmol, 1.0 equiv) via syringe to a solution of
diisopropylamine (5.40 mL, 38.5 mmol, 1.0 equiv) in THF (60 mL, 0.64 M) at −78 °C. The mixture was stirred at 0 °C for 10 min, and then cooled to −78 °C. A solution of the imine (7.95 g) in THF (40.0 mL) was added dropwise via syringe to the resulting LDA solution at −78 °C. The reaction mixture was warmed to −35 °C, and stirred for 2 h, after which point it was re-cooled to −78 °C, and MeI (2.39 mL, 38.4 mmol, 1.0 equiv) was added. The reaction was warmed to room temperature (ca. 25 °C) over 3 h. Saturated aq NH₄Cl (60 mL) was added to the reaction mixture and the mixture was stirred at room temperature overnight. The mixture was extracted with Et₂O (3 x 50 mL). The combined organic layers were washed with brine (30 mL), dried over MgSO₄, and filtered. Solvent was removed under reduced pressure and the residue was purified by flash chromatography (20% Et₂O in pentane on silica gel) to give 2,2,4-trimethyl-1,3-dioxane-5-one (3.93 g, 71% yield) as a pale orange oil.

**4-Methyl-2,2-dimethyl-1,3-dioxan-5-one (SI 1a).** 71% yield. Pale orange oil; Rf 0.72 (20% EtOAc in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 4.37 (qd, J = 6.9, 1.5 Hz, 1H), 4.28 (dd, J = 17.1, 1.5 Hz, 1H), 4.01 (d, J = 17.1 Hz, 1H), 3.98 (d, J = 17.0 Hz, 1H), 1.97-1.83 (m, 1H), 1.66-1.51 (m, 1H), 1.46 (s, 3H), 1.44 (s, 3H), 1.31 (d, J = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 210.2, 101.0, 71.1, 66.6, 24.1, 23.9, 14.3; IR (Neat Film NaCl) 2994, 2944, 1749, 1376, 1227, 1101 cm⁻¹; HRMS (EI+) m/z calc’d for C₇H₁₂O₃ [M]+: 144.0786, found 144.0786.

**4-Ethyl-2,2-dimethyl-1,3-dioxan-5-one (SI 1g).** 72% yield. Colorless oil; Rf 0.58 (20% EtOAc in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 4.27 (dd, J = 17.0, 1.5 Hz, 1H), 4.17-4.13 (m, 1H), 3.98 (d, J = 17.0 Hz, 1H), 1.97-1.83 (m, 1H), 1.66-1.51 (m, 1H), 1.46 (s, 3H), 1.34 (s, 3H), 0.98 (t, J = 7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.9, 100.9, 76.0, 66.9, 24.2, 23.7, 22.0, 9.7; IR (Neat Film NaCl) 2986, 2940, 2881, 1749, 1376, 1225, 1165, 1115, 1077, 1011, 867 cm⁻¹; HRMS (EI+) m/z calc’d for C₈H₁₅O₃ [M]+: 158.0943, found 158.0939.

**4-Benzyl-2,2-dimethyl-1,3-dioxan-5-one (SI 1h).** 73% yield. Yellow oil; Rf 0.54 (20% EtOAc in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.31-7.16 (m, 5H), 4.46 (ddd, J = 9.3, 3.3, 1.8 Hz, 1H), 4.26 (dd, J = 17.1, 1.8 Hz, 1H), 4.01 (d, J = 17.1 Hz, 1H), 3.24 (dd, J = 15.0, 3.3 Hz, 1H), 2.79 (dd, J = 15.0, 9.3 Hz, 1H), 1.43 (s, 3H), 1.34 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.1, 137.9, 129.4, 128.4, 126.6, 101.2, 75.8, 66.8, 34.6, 24.1, 23.7; IR (Neat Film NaCl) 3030, 2988, 2938, 2884, 1747, 1498, 1454, 1375, 1252, 1223, 1173, 1101, 1062, 748, 700 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₃H₁₆O₃ [M]+: 220.1100, found 220.1092.
4-Allyl-2,2-dimethyl-1,3-dioxan-5-one (SI 1i). 65% yield. Colorless oil; Rf 0.43 (10% EtOAc in hexanes); 1H NMR (300 MHz, CDCl3) δ 5.92-5.78 (m, 1H), 5.20-5.08 (m, 2H), 4.33-4.24 (m, 2H), 4.01 (d, J = 16.8 Hz, 1H), 2.69-2.60 (m, 1H), 2.38-2.27 (m, 1H), 1.47 (s, 3H), 1.45 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 209.2, 133.6, 117.7, 101.1, 74.6, 66.8, 32.9, 24.1, 23.8; IR (Neat Film NaCl) 2989, 1749, 1376, 1254, 1224, 1177, 1162, 1103 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₀H₁₄O₃ [M⁺]: 170.0943, found 170.0951.

2,2-Dimethyl-4-(2-methylallyl)-1,3-dioxan-5-one (SI 1c). 66% yield. Pale orange oil; Rf 0.56 (20% Et₂O in hexanes); 1H NMR (300 MHz, CDCl3) δ 4.83 (s, 1H), 4.81 (s, 1H), 4.42 (ddd, J = 9.6, 3.0, 1.2 Hz, 1H), 4.29 (ddd, J = 17.1, 1.8 Hz, 1H), 4.01 (d, J = 17.1 Hz, 1H), 2.69 (app. dd, J = 15.6, 3.0 Hz, 1H), 2.20 (dd, J = 15.8, 9.6 Hz, 1H), 1.77 (s, 3H), 1.48 (s, 3H), 1.44 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 209.5, 141.6, 112.5, 101.1, 73.8, 66.7, 36.2, 24.1, 23.8, 23.0; IR (Neat Film NaCl) 3079, 2988, 2940, 1748, 1650, 1426, 1374, 1223, 1175, 1106, 1076, 1048, 1016, 899, 833 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₀H₁₄O₃ [M⁺]: 184.1100, found 184.1101.

4-(But-3-enyl)-2,2-dimethyl-1,3-dioxan-5-one (SI 1d). 53% yield. Colorless oil; Rf 0.38 (20% Et₂O in hexanes); 1H NMR (300 MHz, CDCl3) δ 5.85-5.72 (m, 1H), 5.09-4.98 (m, 2H), 4.29-4.21 (m, 2H), 3.98 (d, J = 16.8 Hz, 1H), 2.30-2.08 (m, 2H), 2.03-1.92 (m, 1H), 1.70-1.58 (m, 1H), 1.45 (s, 3H), 1.44 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 210.0, 137.7, 115.8, 101.0, 73.8, 66.8, 29.3, 27.6, 24.1, 23.9; IR (Neat Film NaCl) 2988, 2938, 2884, 1748, 1642, 1434, 1376, 1251, 1225, 1175, 1103, 1071, 916, 864 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₀H₁₄O₃ [M⁺]: 184.1100, found 184.1131.

Synthesis of Bis(2-phenylallyl) carbonate (SI 2).

To a solution of 2-phenylallyl alcohol⁷ (2.0 g, 14.9 mmol, 1.0 equiv) and pyridine (1.2 mL, 14.9 mmol, 1.0 equiv) in Et₂O (11 mL, 1.35 M) was added dropwise diphosgene (0.45 mL, 3.73 mmol, 0.25 equiv) via syringe at 0 °C over 20 min. The mixture was stirred at room temperature (ca. 25 °C) for 20 h. The white solid was removed by filtration, and the filter cake was washed with Et₂O. The filtrate was washed with aqueous CuSO₄ (5mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by flash chromatography (10% EtOAc in hexanes on silica gel) to give carbonate (1.26 g, 57% yield) as a colorless oil. Rf 0.61 (10% EtOAc in hexanes);
1H NMR (300 MHz, CDCl₃) δ 7.44-7.23 (m, 10H), 5.55 (s, 2H), 5.38 (s, 2H), 5.04 (s, 4H); 13C NMR (75 MHz, CDCl₃) δ 155.1, 142.2, 138.0, 128.7, 128.4, 126.2, 115.9, 69.4; IR (Neat Film NaCl) 3058, 1747, 1496, 1448, 1395, 1254, 970, 912, 778, 706 cm⁻¹; HRMS (EI⁺) m/z calc’d for C₁₉H₉₆O₃ [M⁺]: 294.1256, found 294.1250.

Synthesis of Silyl Enol Ethers

Representative Procedure for the Synthesis of Trimethylsilyl Enol Ethers.

![Diagram](image)

2,2,4-Trimethyl-5-trimethylsilyloxy-1,3-diox-4-ene (SI 3a).
To a solution of 2,2,2-trimethyl-1,3-dioxan-5-one (1.0 g, 6.94 mmol, 1.0 equiv), hexamethyldisilazane (1.75 mL, 13.4 mmol, 1.9 equiv), and sodium iodide (1.17 g, 7.81 mmol, 1.1 equiv) in acetonitrile (10.0 mL, 0.7 M) was added TMSCl (1.0 mL, 7.82 mmol, 1.1 equiv) at room temperature (ca. 25 °C). After the mixture was stirred at room temperature for 16 h, pentane (20 mL) was added to the mixture. The mixture was stirred at room temperature for 2 min, and then the pentane was decanted. After additional pentane extractions (5 x 10 mL), the combined pentane layer was washed with water (3 x 30 mL) and brine (30 mL), dried over Na₂SO₄, concentrated under reduced pressure. The residue was purified by flash chromatography (2% Et₂O in pentane on Florisil®) to give 2,2,4-Trimethyl-5-trimethylsilyloxy-1,3-diox-4-ene (0.481 g, 32% yield) as a colorless oil.

![Image](image)

2,2,4-Trimethyl-5-trimethylsilyloxy-1,3-diox-4-ene (SI 3a). 32% yield. Colorless oil; Rₜ 0.25 (10% Et₂O in hexanes); 1H NMR (300 MHz, CDCl₃) δ 4.04 (q, J = 1.8 Hz, 2H), 1.76 (t, J = 1.8 Hz, 3H), 1.45 (s, 6H), 0.20 (s, 9H); 13C NMR (75 MHz, CDCl₃) δ 134.9, 125.5, 98.3, 61.1, 24.2, 14.2, 0.8; IR (Neat Film NaCl) 2995, 2958, 2939, 1384, 1370, 1276, 1254, 1224, 1151, 1120, 1072, 893, 846 cm⁻¹; HRMS (EI⁺) m/z calc’d for C₉H₁₉O₃ [M-C₃H₆Si]⁺: 143.0708, found 143.0718.

2,2-Dimethyl-4-ethyl-5-trimethylsilyloxy-1,3-diox-4-ene (SI 3g). 35% yield. Colorless oil; Rₜ 0.52 (20% Et₂O in hexanes); 1H NMR (300 MHz, CDCl₃) δ 4.03 (app. t, J = 1.2 Hz, 2H), 2.16 (q, J = 7.4 Hz, 2H), 1.43 (s, 6H), 1.00 (t, J = 7.4 Hz, 3H), 0.18 (s, 9H); 13C NMR (75 MHz, CDCl₃) δ 139.5, 124.7, 98.1, 61.1, 24.2, 20.8, 11.1, 0.7; IR (Neat Film NaCl) 2964, 1384, 1369, 1276, 1254, 1223, 1199, 1148, 1122, 1079, 1035, 894, 867, 844, 752 cm⁻¹; HRMS (EI⁺) m/z calc’d for C₉H₁₉O₃ [M-C₂H₄Si]⁺: 157.0865, found 157.0749.
**2,2-Dimethyl-4-benzyl-5-trimethylsilyloxy-1,3-diox-4-ene (SI 3h).** 16% yield. Colorless oil; R, 0.44 (10% EtOAc in hexanes); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.32-7.12 (m, 5H), 4.09 (t, J = 1.2 Hz, 2H), 3.47 (app. s, 2H), 1.35 (s, 6H), 0.17 (s, 9H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 138.9, 136.9, 128.9, 128.3, 126.4, 126.2, 98.4, 61.1, 34.0, 24.1, 0.9; IR (Neat Film NaCl) 3029, 2994, 2957, 1748, 1603, 1495, 1454, 1382, 1370, 1276, 1253, 1230, 1199, 1144, 1093, 888, 845 cm\(^{-1}\); HRMS (EI+) m/z calc’d for C\(_{16}\)H\(_{24}\)O\(_3\)Si [M\(^+\)]: 292.1495, found 292.1482.

**2,2-dimethyl-4-(2-methylallyl)-5-trimethylsilyloxy-1,3-diox-4-ene (SI 3c).** 32% yield. Colorless oil; R, 0.46 (50% EtOAc in hexanes); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 4.779 (s, 1H), 4.775 (s, 1H), 4.07 (t, J = 1.1 Hz, 2H), 2.86 (s, 2H), 1.73 (s, 3H), 1.44 (s, 6H), 0.18 (s, 9H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 142.5, 136.0, 126.6, 111.7, 98.3, 61.1, 36.2, 24.2, 22.7, 0.8; IR (Neat Film NaCl) 3077, 2994, 2902, 2838, 1749, 1653, 1454, 1382, 1370, 1276, 1253, 1229, 1198, 1146, 1096, 891, 846 cm\(^{-1}\); HRMS (EI+) m/z calc’d for C\(_{13}\)H\(_{25}\)O\(_3\)Si [M\(^+\)]: 256.1495, found 256.1500.

**Representative Procedure for the Synthesis of Triethylsilyl Enol Ethers.**

**4-Ethyl-2,2-dimethyl-5-trimethylsilyloxy-1,3-diox-4-ene (SI 4g).**

To a solution of 4-ethyl-2,2-dimethyl-1,3-dioxane-5-one (0.50 g, 3.16 mmol, 1.0 equiv), Et\(_3\)N (0.71 mL, 5.09 mmol, 1.6 equiv) and NaI (0.62 g, 4.14 mmol, 1.3 equiv) in acetonitrile (5.0 mL, 0.63 M) was added TESCl (0.69 mL, 4.11 mmol, 1.3 equiv) at room temperature (ca. 25 °C). After the mixture was stirred for 20 h, pentane (10 mL) was added. The mixture was stirred at room temperature for 2 min, and then pentane was decanted. After additional pentane extractions (5 x 10 mL), the combined pentane layers were washed with water (20 mL) and brine (20 mL), dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The residue was purified by flash chromatography (1% Et\(_2\)O in petroleum ether on silica gel) to give triethylsilyl enol ether 4b (0.659 g, 77% yield) and 4-Ethyl-2,2-dimethyl-5-trimethylsilyloxy-1,3-diox-5-ene (70.6 mg, 8% yield).

**4-Methyl-2,2-dimethyl-5-trimethylsilyloxy-1,3-diox-4-ene (4a).** 77% yield. Colorless oil; R, 0.50 (10% Et\(_2\)O in hexanes); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 4.04 (q, J = 1.9 Hz, 2H), 1.77 (t, J = 1.9 Hz, 3H), 1.43 (s, 6H), 0.98 (t, J = 8.1 Hz, 9H), 0.65 (q, J = 8.1 Hz, 6H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 134.4, 125.6, 98.2, 61.2, 24.3, 14.0, 6.9, 5.5; IR (Neat Film
Triethyl(2,2,4-trimethyl-4H-1,3-dioxin-5-yloxy)silane (SI 5a). 6% yield. Colorless oil; R, 0.55 (10% Et₂O in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 6.10 (d, J = 1.5 Hz), 4.23 (qd, J = 6.6, 1.5 Hz), 1.47 (s, 3H), 1.02-0.96 (m, 12H), 0.65 (q, J = 7.8 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 139.0, 124.8, 98.0, 61.1, 24.3, 20.7, 11.1, 6.9, 5.5; IR (Neat Film NaCl) 2952, 2877, 1383, 1276, 1221, 1198, 1147, 1121, 1079, 1012, 857, 745, 730 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₇H₂₉O₃Si [M⁺]: 281.1642, found 258.1642.

4-Ethyl-2,2-dimethyl-5-triethylsilyloxy-1,3-diox-4-ene (SI 4g). 77% yield. Colorless oil; R, 0.53 (5% Et₂O in toluene); ¹H NMR (300 MHz, CDCl₃) δ 4.14 (t, J = 1.2 Hz, 2H), 2.19 (qt, J = 7.5, 1.2 Hz, 2H), 1.43 (s, 6H), 1.02-0.96 (m, 12H), 0.65 (q, J = 7.8 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 139.0, 124.8, 98.0, 61.1, 24.3, 20.7, 11.1, 6.9, 5.5; IR (Neat Film NaCl) 2952, 2877, 1383, 1276, 1221, 1198, 1147, 1121, 1079, 1012, 857, 745, 730 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₇H₂₉O₃Si [M⁺]: 185.0634, found 185.0639.

4-Ethyl-2,2-dimethyl-5-triethylsilyloxy-1,3-diox-5-ene (SI 5g). 8% yield. Colorless oil; R, 0.57 (5% Et₂O in toluene); ¹H NMR (300 MHz, CDCl₃) δ 6.14 (d, J = 1.5 Hz, 1H), 4.08 (ddd, J = 6.6, 3.6, 1.5 Hz, 1H), 1.87-1.72 (m, 1H), 1.69-1.55 (m, 1H), 1.46 (s, 3H), 1.43 (s, 3H), 1.01-0.92 (m, 12H), 0.70-0.62 (m, 6H).

4-Benzyl-2,2-dimethyl-5-triethylsilyloxy-1,3-diox-4-ene (SI 4h). 78% yield. Colorless oil; R, 0.41 (10% Et₂O in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.31-7.12 (m, 5H), 4.10 (t, J = 1.2 Hz, 2H), 3.49 (s, 2H), 1.33 (s, 6H), 0.98 (t, J = 8.1 Hz, 9H), 0.66 (q, J = 8.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 139.0, 136.5, 128.9, 128.3, 126.5, 126.1, 98.3, 61.2, 33.8, 24.1, 6.9, 5.7; IR (Neat Film NaCl) 2956, 2877, 1454, 1382, 1370, 1276, 1226, 1198, 1145, 1093, 1016, 867, 746, 729, 731, 696 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₉H₂₉O₃Si [M⁺]: 334.1964, found 334.1978.

Triethyl(4-benzyl-2,2-dimethyl-4H-1,3-dioxin-5-yloxy)silane (SI 5h). 10% yield. Pale yellow oil; R, 0.50 (10% Et₂O in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.15 (m,
5H), 6.13 (d, J = 1.2 Hz, 1H), 4.31 (ddd, J = 8.4, 3.0, 1.2 Hz, 1H), 3.16 (dd, J = 14.4, 3.0 Hz, 1H), 2.80 (dd, J = 14.3, 8.4 Hz, 1H), 1.43 (s, 3H), 1.42 (s, 3H), 1.01 (t, J = 7.8 Hz, 9H), 0.69 (q, J = 7.8 Hz, 6H).

4-Allyl-2,2-dimethyl-5-triethysilyloxy-1,3-diox-4-ene (SI 4i). 69% yield. Colorless oil; Rf 0.58 (10% EtOAc in hexanes); 1H NMR (300 MHz, CDCl₃) δ 5.87-5.73 (m, 1H), 5.15-5.01 (m, 2H), 4.06 (t, J = 1.2 Hz, 2H), 2.96-2.91 (m, 2H), 1.44 (s, 6H), 0.99 (t, J = 8.1 Hz, 9H), 0.66 (q, J = 8.1 Hz, 6H); 13C NMR (75 MHz, CDCl₃) δ 135.8, 134.4, 126.0, 116.2, 98.3, 61.1, 32.1, 24.3, 6.9, 5.6; IR (Neat Film NaCl) 2995, 2957, 2913, 2879, 1639, 1458, 1414, 1382, 1370, 1278, 1241, 1196, 1147, 1084, 1016, 970, 909, 871, 851, 746, 731 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₃H₂₆O₃Si [M⁺]: 284.1808, found 284.1836.

(4-Allyl-2,2-dimethyl-4H-1,3-dioxin-5-yloxy)triethysilane (SI 5i). 10% yield. Pale yellow oil; Rf 0.65 (10% EtOAc in hexanes); 1H NMR (300 MHz, CDCl₃) δ 6.14 (d, J = 1.2 Hz, 1H), 5.97-5.83 (m, 1H), 5.16-5.04 (m, 2H), 4.16 (ddd, J = 7.2, 3.3, 1.2 Hz, 1H), 2.61-2.49 (m, 1H), 2.40-2.27 (m, 1H), 1.46 (s, 3H), 1.43 (s, 3H), 0.98 (t, J = 7.8 Hz, 9H), 0.67 (q, J = 7.8 Hz, 6H).

2,2-Dimethyl-6-(2-methylallyl)-4H-1,3-dioxin-5-yloxy)triethysilane (SI 4c). 46% yield. Colorless oil; Rf 0.19 (10% Et₂O in hexanes); 1H NMR (300 MHz, CDCl₃) δ 4.78 (s, 2H), 4.08 (t, J = 1.1 Hz, 2H), 2.89 (s, 2H), 1.74 (s, 3H), 1.43 (s, 6H), 0.98 (t, J = 8.1 Hz, 9H), 0.65 (q, J = 8.1 Hz, 6H); 13C NMR (75 MHz, CDCl₃) δ 142.5, 135.6, 126.7, 111.7, 98.3, 61.1, 36.0, 24.3, 22.7, 6.9, 5.6; IR (Neat Film NaCl) 2956, 2913, 2878, 1382, 1369, 1276, 1225, 1198, 1146, 1095, 1010, 851, 730 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₃H₂₆O₃Si [M –H⁺]²⁺ 297.1886, found 297.1851.

(2,2-dimethyl-4-(2-methylallyl)-4H-1,3-dioxin-5-yloxy)triethysilane (SI 5c). 15% yield. Colorless oil; Rf 0.27 (10% Et₂O in hexanes); 1H NMR (300 MHz, CDCl₃) δ 6.13 (d, J = 1.5 Hz, 1H), 4.82 (s, 1H), 4.80 (s, 1H), 4.25 (ddd, J = 9.0, 2.7, 1.5 Hz, 1H), 2.61-2.53 (m, 1H), 2.20 (dd, J = 14.7, 9.0 Hz, 1H), 1.79 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3H), 0.98 (t, J = 7.8 Hz, 9H), 0.67 (q, J = 7.8 Hz, 6H).
(6-(but-3-enyl)-2,2-dimethyl-4H-1,3-dioxin-5-yloxy)triethylsilane (SI 4d). 66% yield. Colorless oil; Rf 0.58 (10% Et2O in hexanes); 1H NMR (300 MHz, CDCl3) δ 5.90-5.77 (m, 1H), 5.07-5.0 (m, 1H), 5.0-4.93 (m, 1H), 4.05 (s, 2H), 2.30-2.13 (m, 4H), 1.43 (s, 6H), 0.98 (t, J = 7.8 Hz, 9H), 0.65 (q, J = 7.8 Hz, 6H); 13C NMR (75 MHz, CDCl3) δ 138.5, 137.2, 125.7, 114.8, 98.2, 61.1, 30.9, 27.0, 24.3, 6.9, 5.6; IR (Neat Film NaCl) 2995, 2957, 2914, 2878, 2838, 1383, 1369, 1277, 1198, 1147, 1085, 1006, 857, 745, 730 cm⁻¹; HRMS (EI+) m/z calc’d for C16H30O3Si [M]+: 298.1964, found 298.1967.

Asymmetric Alkylation Reaction

Representative Procedure for the Asymmetric Alkylation Reaction of Triethylsilyl Enol Ethers.

(R)-4- Allyl-2,2,4-trimethyl-1,3-dioxan-5-one (6a).

A 100 mL round-bottom flask was flame dried under vacuum and back-filled with argon. Pd(dmdba)2 (20.3 mg, 0.025 mmol, 0.05 equiv), (S)-t-Bu-PHOX (10.6 mg, 0.027 mmol, 0.055 equiv), and TBAT (270 mg, 0.50 mmol, 1.0 equiv) were added to the flask. The system was evacuated under vacuum and back-filled with argon (3 x). Toluene (15 mL, 0.033 M) was added by syringe and the mixture was stirred at room temperature (ca. 25 °C) for 30 min. Diallyl carbonate (75.2 μL, 0.52 mmol, 1.05 equiv) and silyl ether 4a (108 mg, 0.50 mmol, 1.0 equiv) were added. When the reaction was complete by TLC (after ca. 9 h), the reaction mixture was loaded onto a silica gel column and eluted with 2% Et2O in petroleum ether to give tetrasubstituted 6a (78.8 mg, 86% yield, 87% ee).
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Table SI 1. Substrate scope for the enantioselective alkylation.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield [%]\textsuperscript{b}</th>
<th>ee [%]</th>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield [%]\textsuperscript{b}</th>
<th>ee [%]</th>
</tr>
</thead>
</table>
| 1     | \[
\begin{array}{c}
\text{OSIEt}_3 \\
\text{4a}
\end{array}
\] | \[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{OSIEt}_3
\end{array}
\] | 86 | 87 | 6'     | \[
\begin{array}{c}
\text{OSIEt}_3 \\
\text{4a}
\end{array}
\] | \[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{PhMe}
\end{array}
\] | 73 | 94 |
| 2     | \[
\begin{array}{c}
\text{OSIEt}_3 \\
\text{4a}
\end{array}
\] | \[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{OSIEt}_3
\end{array}
\] | 79 | 93 | 7'     | \[
\begin{array}{c}
\text{OSIEt}_3 \\
\text{4a}
\end{array}
\] | \[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{PhMe}
\end{array}
\] | 93 | 88 |
| 3     | \[
\begin{array}{c}
\text{OSIEt}_3 \\
\text{4a}
\end{array}
\] | \[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{OSIEt}_3
\end{array}
\] | 85 | 86 | 8      | \[
\begin{array}{c}
\text{OSIEt}_3 \\
\text{4a}
\end{array}
\] | \[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{PhMe}
\end{array}
\] | 88 | 85 |
| 4'    | \[
\begin{array}{c}
\text{OSIEt}_3 \\
\text{4a}
\end{array}
\] | \[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{OSIEt}_3
\end{array}
\] | 73 | 82 | 9      | \[
\begin{array}{c}
\text{OSIEt}_3 \\
\text{4a}
\end{array}
\] | \[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{PhMe}
\end{array}
\] | 83 | 92 |
| 5'    | \[
\begin{array}{c}
\text{OSIEt}_3 \\
\text{OSIEt}_3
\end{array}
\] | \[
\begin{array}{c}
\text{R}^1 \\
\text{R}^2 \\
\text{OSIEt}_3
\end{array}
\] | 59 | 92 |                   |                   |                   |                   |

[a] Reactions were performed with silyl enol ether (0.5 mmol) and diallyl carbonate (1.05 equiv) in PhMe (0.033 M) unless stated otherwise. [b] Isolated yields. [c] Measured by chiral GC or HPLC. [d] Employed dimethyl carbonate (1.05 equiv). [e] Employed dichloroallyl carbonate (1.05 equiv) at 35°C. [f] Employed diphenylallyl carbonate (1.05 equiv).

**Representative Procedure for the Asymmetric Alkylation Reaction of Trimethylsilyl Enol Ethers.**

(R)-4-Allyl-2,2,4-trimethyl-1,3-dioxan-5-one (6a).

A 100 mL round-bottom flask was flame-dried under vacuum and back-filled with argon. Pd(dmdba)\textsubscript{2} (20.3 mg, 0.025 mmol, 0.05 equiv), (S)-t-Bu-PHOX (10.6 mg, 0.027 mmol, 0.055 equiv), and TBAT (94.3 mg, 0.18 mmol, 0.35 equiv) were added to the flask. The system was evacuated under vacuum and back-filled with argon (x 3). Et\textsubscript{2}O (30 mL) was added by syringe, and the mixture was stirred at room temperature (ca. 28 °C) for 30 min. Diallyl carbonate (75.2 µL, 0.52 mmol, 1.05 equiv) and silyl ether 4d (108 mg, 0.50 mmol, 1.0 equiv) were added. When the reaction was complete by TLC (after ca. 5 h), the reaction mixture was filtered through silica gel, and chased with Et\textsubscript{2}O. The filtrate was evaporated under reduced pressure (~60 mmHg), the residue was purified by flash chromatography (2% Et\textsubscript{2}O in petroleum ether on silica gel) to give tetrasubstituted 6a (76.2 mg, 83% yield, 90% ee).
**Table SI 2.** Substrate scope for the enantioselective alkylation of trimethylsilyl enol ethers. *

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield [%]</th>
<th>ee [%]</th>
<th>Yield [%]</th>
<th>ee [%]</th>
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</thead>
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<td>OSiMe$_3$</td>
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<td>93</td>
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<td>91</td>
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<tr>
<td>3</td>
<td>OSiMe$_3$</td>
<td>OSiMe$_3$</td>
<td>84</td>
<td>85</td>
<td>86</td>
<td>85</td>
</tr>
</tbody>
</table>

[a] Reactions were performed with substrate (0.5 mmol) in Et$_2$O (0.0167 M) with diallyl carbonate (1.05 equiv) unless stated otherwise. [b] Isolated yields. [c] Measured by chiral GC or HPLC. [d] Employed dimethallyl carbonate (1.06 equiv). [e] Employed dichloromallyl carbonate (1.05 equiv) at 35 °C.

(S)-4-allyl-4-methyl-2,2-dimethyl-1,3-dioxan-5-one (6a). Colorless oil; R$_f$ 0.22 (20% Et$_2$O in hexanes); $^1$H NMR (300 MHz, CDCl$_3$) δ 5.90-5.76 (m, 1H), 5.13-5.04 (m, 2H), 4.21 (s, 2H), 2.57-2.50 (m, 1H), 2.45-2.37 (m, 1H), 1.49 (s, 3H), 1.48 (s, 3H), 1.39 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 210.9, 132.6, 119.0, 100.1, 82.2, 67.1, 43.6, 26.9, 26.7, 24.4; IR (Neat Film NaCl) 3079, 2989, 2942, 1742, 1641, 1429, 1382, 1373, 1229, 1203, 1180, 1161, 1143, 1080, 1007, 919 cm$^{-1}$; HRMS (EI+) m/z calc’d for C$_{16}$H$_{18}$O$_3$ [M]$: 184.1100$, found 184.1096; $[\alpha]_D$$^{23.0}$ –68.6° (c 0.510, CH$_2$Cl$_2$, 90% ee); $[\alpha]_D$$^{27.5}$ –60.3° (c 0.845, CH$_2$Cl$_2$, 87% ee).

(S)-4-allyl-4-ethyl-2,2-dimethyl-1,3-dioxan-5-one (Table 2, entry 2). Colorless oil; R$_f$ 0.48 (20% Et$_2$O in hexanes); $^1$H NMR (300 MHz, CDCl$_3$) δ 5.89-5.70 (m, 1H), 5.14-5.02 (m, 2H), 4.17 (s, 2H), 2.60-2.39 (m, 2H), 1.91-1.64 (m, 2H), 1.49 (s, 3H), 1.48 (s, 3H), 0.88 (t, J = 7.5 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 210.8, 132.6, 118.9, 100.0, 85.2, 67.5, 41.4, 29.9, 27.0, 26.7, 7.7; IR (Neat Film NaCl) 3079, 2984, 2941, 2884, 1737, 1428, 1382, 1372, 1231, 1200, 1172, 1150, 1086, 1009, 918 cm$^{-1}$; HRMS (EI+) m/z calc’d for C$_{16}$H$_{18}$O$_3$ [M]$: 198.1256$, found 198.1258; $[\alpha]_D$$^{24.4}$ –0.20° (c 0.575, CH$_2$Cl$_2$, 93% ee).
(R)-4-allyl-4-benzyl-2,2-dimethyl-1,3-dioxan-5-one (Table 2, entry 3). Colorless oil; Rf 0.44 (20% Et2O in hexanes); 1H NMR (300 MHz, CDCl3) δ 7.29-7.18 (m, 5H), 5.97-5.83 (m, 1H), 5.17-5.10 (m, 2H); 4.05 (d, J = 18.0 Hz, 1H), 3.87 (d, J = 18.0 Hz, 1H), 3.08 (d, J = 13.5 Hz, 1H), 2.93 (d, J = 13.5 Hz, 1H), 2.63-2.45 (m, 2H), 1.50 (s, 3H), 1.27 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 210.0, 136.2, 132.4, 131.3, 128.0, 126.8, 119.3, 99.9, 85.5, 67.7, 43.2, 43.1, 27.7, 25.6; IR (Neat Film NaCl) 3077, 3031, 2990, 2939, 1736, 1496, 1454, 1426, 1382, 1372, 1231, 1196, 1102, 1052, 918 cm−1; HRMS (EI+) m/z calc’d for C18H20O3 [M]+: 260.1412, found 260.1417; [α]D26.3 +21.4° (c 0.825, CH2Cl2, 86% ee); [α]D24.2 +22.2° (c 1.055, CH2Cl2, 85% ee).

(S)-2,2,4-trimethyl-4-(2-methylallyl)-1,3-dioxan-5-one (Table 2, entry 4). Colorless oil; Rf 0.46 (20% Et2O in hexanes); 1H NMR (300 MHz, CDCl3) δ 4.88 (s, 1H), 4.72 (s, 1H), 4.27 (d, J = 17.9 Hz, 1H), 4.19 (d, J = 17.9 Hz, 1H), 2.50 (d, J = 13.7 Hz, 1H), 2.39 (d, J = 13.7 Hz, 1H), 1.81 (s, 3H), 1.51 (s, 3H), 1.48 (s, 3H), 1.43 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 211.1, 141.5, 115.4, 100.0, 83.0, 67.3, 46.8, 27.0, 26.6, 25.0, 24.6; IR (Neat Film NaCl) 2987, 2943, 2919, 1742, 1645, 1440, 1382, 1373, 1230, 1200, 1159, 1106, 1010, 896 cm−1; HRMS (EI+) m/z calc’d for C11H13O3 [M]+: 198.1256, found 198.1263; [α]D26.5 −87.7° (c 0.735, CH2Cl2, 89% ee).

(S)-4-(2-chloroallyl)-2,2,4-trimethyl-1,3-dioxan-5-one (Table 2, entry 5). Colorless oil; Rf 0.50 (20% Et2O in hexanes); 1H NMR (300 MHz, CDCl3) δ 5.30 (d, J = 1.2 Hz, 1H), 5.22 (d, J = 0.6 Hz, 1H), 4.37 (d, J = 17.7 Hz, 1H), 4.21 (d, J = 17.9 Hz, 1H), 2.91 (d, J = 14.4 Hz, 1H), 2.73 (d, J = 14.4 Hz, 1H), 1.55 (s, 3H), 1.51 (s, 3H), 1.47 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 209.9, 137.1, 117.0, 100.5, 81.3, 67.1, 48.1, 27.4, 26.2, 25.1; IR (Neat Film NaCl) 2991, 2941, 2897, 1744, 1633, 1425, 1383, 1374, 1229, 1203, 1182, 1158, 1106, 1060, 1011, 891 cm−1; HRMS (EI+) m/z calc’d for C16H19O3 [M–CH3]+: 203.0475, found 203.0484; [α]D20.7 −89.7° (c 1.030, CHCl3, 93% ee).

(S)-2,2,4-trimethyl-4-(2-phenylallyl)-1,3-dioxan-5-one (Table 2, entry 6). Colorless oil; Rf 0.23 (5% Et2O in toluene); 1H NMR (300 MHz, CDCl3) δ 7.40-7.19 (m, 5H), 5.33 (d, J = 1.5 Hz, 1H), 5.13 (s, 1H), 4.08 (d, J = 17.7 Hz, 1H), 3.95 (d, J = 17.7 Hz, 1H), 2.98 (s, 2H), 1.39 (s, 3H), 1.38 (s, 3H), 1.19 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 210.8, 144.5, 142.3, 128.1, 127.4, 127.0, 117.9, 99.9, 82.7, 67.3, 44.9, 26.5, 25.5; IR (Neat Film NaCl)
Representative Procedure for the Synthesis of \( \alpha,\beta \)-Unsaturated Esters.

\[(S,E)\]-methyl-4-(2,2,4-trimethyl-5-oxo-1,3-dioxan-4-yl)but-2-enoate (6b). To a solution of terminal olefin 6a (30.0 mg, 0.163 mmol, 1 equiv) and methyl acrylate (0.14 mL, 1.55 mmol, 9.5 equiv) in CH\(_2\)Cl\(_2\) (1.6 mL, 0.1 M) was added Grubbs second generation catalyst (2.8 mg, 0.0033 mmol, 0.02 equiv) at room temperature (ca. 25°C).
The mixture was stirred at 37 °C for 40 h. Ethyl vinyl ether (0.5 mL) was added, and it was stirred at 37 °C for 10 min. The mixture was filtered through silica gel with Et₂O/petroleum ether (1:2). After the filtrate was evaporated under reduced pressure (~60 mmHg), the residue was purified by flash column chromatography (10% Et₂O in petroleum ether on silica gel) to give α,β-unsaturated 6b (32.8 mg, 83% yield).

(S,E)-methyl 4-(2,2,4-trimethyl-5-oxo-1,3-dioxan-4-yl)but-2-enoate (6b). 83% yield. Colorless oil; R, 0.23 (20% Et₂O in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 6.92 (dt, J = 15.6, 7.8 Hz, 1H), 5.87 (dt, J = 15.6, 1.3 Hz, 1H), 4.23 (s, 2H), 3.73 (s, 3H), 2.71-2.63 (m, 1H), 2.54-2.47 (m, 1H), 1.50 (s, 3H), 1.45 (s, 3H), 1.43 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 210.1, 166.7, 143.1, 124.7, 100.5, 81.5, 66.8, 51.7, 41.3, 27.5, 26.2, 24.5; IR (Neat Film NaCl) 2992, 2951, 1727, 1659, 1437, 1374, 1338, 1274, 1231, 1197, 1180, 1155, 1117, 1008, 990 cm⁻¹; HRMS (EI⁺) m/z calc’d for C₁₂H₁₉O₅ [M+H]⁺: 243.1232, found 243.1224; [α]D²⁴⁺⁻₄⁹.⁹° (c 0.715, CH₂Cl₂, 90% ee).

(S,E)-methyl 4-(4-ethyl-2,2-dimethyl-5-oxo-1,3-dioxan-4-yl)but-2-enoate (SI 6g). 89% yield. Colorless oil; R, 0.19 (20% Et₂O in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 6.92 (dt, J = 15.6, 7.6 Hz, 1H), 5.88 (dt, J = 15.6, 1.5 Hz, 1H), 4.21 (s, 2H), 3.74 (s, 3H), 2.71-2.53 (m, 2H), 1.92-1.78 (m, 2H), 1.51 (s, 3H), 1.49 (s, 3H), 0.90 (t, J = 7.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 210.0, 166.7, 143.3, 124.6, 100.2, 84.6, 67.3, 51.7, 39.2, 30.4, 27.3, 26.4, 7.8; IR (Neat Film NaCl) 2985, 1726, 1658, 1435, 1383, 1373, 1271, 1232, 1196, 1177, 1084, 1033, 1013 cm⁻¹; HRMS (EI⁺) m/z calc’d for C₁₃H₂₁O₅ [M+H]⁺: 257.1389, found 257.1385; [α]D²⁴⁺⁻₃.₁⁴° (c 0.655, CH₂Cl₂, 94% ee).

(S,E)-methyl 4-(4-benzyl-2,2-dimethyl-5-oxo-1,3-dioxan-4-yl)but-2-enoate (SI 6h). 75% yield. Colorless oil; R, 0.19 (20% Et₂O in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.31-7.13 (m, 5H), 7.00 (ddd, J = 15.6, 8.1, 7.2 Hz, 1H), 5.89 (dt, J = 15.9, 1.5 Hz, 1H), 4.06 (d, J = 18.0 Hz, 1H), 3.86 (d, J = 15.6, 1.5 Hz, 1H), 3.74 (s, 3H), 3.06 (d, J = 13.5 Hz, 1H), 2.94 (d, J = 13.5 Hz, 1H), 2.72 (ddd, J = 14.4, 6.9, 1.2 Hz, 1H), 2.58 (ddd, J = 14.4, 8.1, 1.2 Hz, 1H), 1.48 (s, 3H), 1.32 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.3, 166.7, 142.9, 135.5, 131.1, 128.1, 127.1, 124.9, 100.3, 84.8, 67.5, 51.8, 43.8, 40.8, 27.0, 26.3; IR (Neat Film NaCl) 2992, 2950, 1725, 1658, 1435, 1385, 1374, 1271, 1234, 1198, 1171, 1114, 1098, 1054, 988, 702 cm⁻¹; HRMS (EI⁺) m/z calc’d for C₁₈H₂₂O₅ [M⁺]: 318.1467, found 318.1469; [α]D²⁷⁺⁺₁⁴.₉° (c 0.550, CH₂Cl₂, 85% ee).
Synthesis of Spiro Compounds by Ring-Closing Metathesis.

Representative Procedure for the Synthesis of Spiro Compounds 6c and 6d.

(R)-2,7,7-trimethyl-6,8-dioxaspiro[4.5]dec-2-en-10-one (6c). To a solution of diene 6h (60 mg, 0.268 mmol, 1.0 equiv) in CH₂Cl₂ (10 mL) was added Grubbs second generation catalyst (4.6 mg, 0.0054 mmol, 0.02 equiv) at room temperature. After the mixture was stirred at 35 °C for 40 h, it was concentrated under reduced pressure. The residue was purified by flash chromatography (2% Et₂O in petroleum ether on silica gel) to give the cyclopentene 6c (51.4 mg, 98% yield) as a colorless oil.

(R)-2,7,7-trimethyl-6,8-dioxaspiro[4.5]dec-2-en-10-one (6d). 95% yield. Colorless oil; Rf 0.37 (20% Et₂O in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 5.22-5.20 (m, 1H), 4.31 (s, 2H), 2.91-2.52 (m, 4H), 1.73-1.71 (m, 3H), 1.49 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 210.1, 137.1, 120.8, 100.2, 88.3, 66.8, 48.5, 45.0, 27.0, 26.8, 16.5; IR (Neat Film NaCl) 2991, 2941, 2910, 1740, 1382, 1372, 1231, 1199, 1152, 1098, 1058, 988, 846 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₁H₁₆O₃ [M⁺]: 196.1100, found 196.1095; [α]D²³¹ +19.2° (c 0.725, CH₂Cl₂, 85% ee).

(S)-2,7,7-trimethyl-6,8-dioxaspiro[4.5]dec-2-en-10-one (SI 6c). 87% yield. Colorless oil; Rf 0.37 (20% Et₂O in hexanes); [α]D²⁴⁰ -20.4° (c 0.885, CH₂Cl₂, 88% ee).

(S)-2,2-dimethyl-1,3-dioxaspiro[5.5]undec-8-en-5-one (6d). 90% yield. Colorless oil; Rf 0.24 (10% Et₂O in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 5.80-5.70 (m, 1H), 5.67-5.58 (m, 1H), 4.27 (s, 2H), 2.60-2.47 (m, 1H), 2.38-2.18 (m, 2H), 2.17-1.81 (m, 3H), 1.51 (s, 3H), 1.47 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 211.1, 126.4, 122.8, 100.5, 79.9, 66.6, 33.5, 29.9, 27.7, 26.3, 21.8; IR (Neat Film NaCl) 3030, 2991, 2938, 2911, 1739, 1429, 1382, 1372, 1259, 1230, 1200, 1155, 1099, 1062, 999, 886, 836, 778, 651 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₁H₁₆O₃ [M⁺]: 196.1100, found 196.1139; [α]D²⁰² -20.9° (c 1.045, CH₂Cl₂, 92% ee).

(S)-1,3-dihydroxy-3-methylhex-5-en-2-one (Table 3, entry 1).
To a solution of acetonide 6a (80.5 mg, 0.44 mmol, 1.0 equiv) in MeOH (4.4 mL, 0.1 M) was added p-toluenesulfonic acid monohydrate (8.3 mg, 0.044 mmol, 0.1 equiv) at room temperature (ca. 25 °C). After the mixture was stirred for 3.5 h, Et,N (0.2 mL) was added. The mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (30% EtOAc in hexanes on silica gel) to give diol 7a (57.4 mg, 90% yield) as a colorless oil.

(S)-1,3-dihydroxy-3-ethylhex-5-en-2-one (Table 3, entry 1). 90% yield. Colorless oil; R, 0.21 (33% EtOAc in hexanes); 1H NMR (300 MHz, CDCl₃) δ 5.79-5.65 (m, 1H), 5.23-5.14 (m, 2H), 4.55 (dd, J = 20.0, 5.1 Hz, 1H), 4.46 (dd, J = 20.0, 5.1 Hz, 1H), 2.92 (t, J = 5.1 Hz, 1H), 2.74 (s, 1H), 2.57-2.50 (m, 1H), 2.42-2.35 (m, 1H), 1.39 (s, 3H); 13C NMR (75 MHz, CDCl₃) δ 214.1, 131.5, 120.8, 78.2, 65.3, 44.5, 25.6; IR (Neat Film NaCl) 3413, 2980, 1721, 1641, 1414, 1370, 1169, 1019, 923 cm⁻¹; HRMS (ES+) m/z calc’d for C₁₁H₁₃O₃ [M+H]+: 145.0865, found 145.0850; [α]D³⁵ +14.2° (c 0.810, CH₂Cl₂, 90% ee).

(S)-1,3-dihydroxy-3-ethylhex-5-en-2-one (Table 3, entry 2). 97% yield; Colorless oil; R, 0.32 (33% EtOAc in hexanes); 1H NMR (300 MHz, CDCl₃) δ 5.76-5.62 (m, 1H), 5.20-5.12 (m, 2H), 4.47 (dd, J = 19.8, 4.8 Hz, 1H), 4.40 (dd, J = 19.8, 4.8 Hz, 1H), 2.94 (t, J = 4.8 Hz, 1H), 2.84 (s, 1H), 2.53-2.38 (m, 2H), 1.86-1.64 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H); 13C NMR (75 MHz, CDCl₃) δ 214.1, 131.6, 120.5, 81.1, 66.2, 43.6, 32.2, 7.7; IR (Neat Film NaCl) 3436, 2976, 1717, 1641, 1414, 1272, 1158, 1111, 1042, 922 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₃H₁₄O₃ [M]+: 158.0943, found 158.0948; [α]D²⁰ +0.37° (c 0.715, CH₂Cl₂, 93% ee).

(S)-1,3-dihydroxy-3-ethylhex-5-en-2-one (Table 3, entry 1). 91% yield. Colorless oil; R, 0.50 (33% EtOAc in hexanes); 1H NMR (300 MHz, CDCl₃) δ 7.35-7.24 (m, 3H), 7.13 (dd, J = 7.4, 1.9 Hz, 2H), 5.81-5.67 (m, 1H), 5.23-5.14 (m, 2H), 4.41 (dd, J = 20.1, 4.8 Hz, 1H), 4.07 (dd, J = 20.1, 4.8 Hz, 1H), 3.14 (d, J = 13.8 Hz, 1H), 2.92-2.86 (m, 2H), 2.65 (dd, J = 13.8, 7.4 Hz, 1H), 2.51 (s, 1H), 2.45-2.38 (dd, J = 14.1, 7.4 Hz, 1H); 13C NMR (75 MHz, CDCl₃) δ 214.5, 134.8, 131.5, 130.3, 128.9, 127.6, 120.8, 81.4, 67.2, 45.2, 43.7; IR (Neat Film NaCl) 3436, 3079, 3030, 2917, 1717, 1640, 1496, 1454, 1429, 1412, 1259, 1098, 1043, 978, 924, 759, 703 cm⁻¹; HRMS (EI+) m/z calc’d for C₁₃H₁₆O₃
[M]⁺: 220.1100, found 220.1069; [α]D²³.³ +16.1° (c 0.690 CH₂Cl₂, 86% ee).

(5)-1,3-dihydroxy-3,5-dimethylhex-5-en-2-one (Table 3, entry 4). 97% yield. Colorless oil; R, 0.36 (33% EtOAc in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 4.98-4.97 (m, 1H), 4.79 (d, J = 0.9 Hz, 1H), 4.59 (dd, J = 20.0, 4.8 Hz, 1H), 4.46 (dd, J = 20.0, 4.8 Hz, 1H), 2.96 (t, J = 4.8 Hz, 1H), 2.74 (s, 1H), 2.62 (d, J = 14.0 Hz, 1H), 2.35 (d, J = 14.0 Hz, 1H), 1.70 (s, 3H), 1.38 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 214.8, 140.8, 116.6, 78.1, 65.5, 47.9, 26.6, 24.2; IR (Neat Film NaCl) 3429, 3078, 2976, 2917, 1720, 1644, 1452, 1373, 1229, 1135, 1101, 1024, 898 cm⁻¹; HRMS (EI⁺) m/z calc’d for C₈H₁₄O₃ [M⁺]: 158.0943, found 158.0943; [α]D²¹.² -24.2° (c 0.420 CH₂Cl₂, 89% ee).

(5S)-5-chloro-1,3-dihydroxy-3-methylhex-5-en-2-one (Table 3, entry 5). 97% yield. Colorless oil; R, 0.30 (33% EtOAc in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 5.38 (d, J = 0.9 Hz, 1H), 5.28 (d, J = 0.9 Hz, 1H), 4.65 (dd, J = 19.8, 5.1 Hz, 1H), 4.54 (dd, J = 19.8, 4.8 Hz, 1H), 2.96-2.91 (m, 3H), 2.74 (d, J = 14.7 Hz, 1H), 1.42 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 213.5, 136.0, 118.4, 78.0, 65.6, 49.2, 26.3; IR (Neat Film NaCl) 3422, 2981, 2922, 1722, 1633, 1452, 1416, 1371, 1267, 1167, 1087, 1021, 981, 895 cm⁻¹; HRMS (EI⁺) m/z calc’d for C₇H₅ClO₂ [M-H₂O⁺]: 160.0291, found 160.0298; [α]D²¹.₂ -16.7° (c 1.000, CH₂Cl₂, 91% ee).

(5S)-1,3-dihydroxy-3-methyl-phenylhex-5-en-2-one (Table 3, entry 6). 92% yield. Colorless oil; R, 0.27 (33% EtOAc in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.26 (m, 5H), 5.41 (d, J = 1.2 Hz, 1H), 5.17 (d, J = 0.9 Hz, 1H), 4.41 (dd, J = 20.3, 5.0 Hz, 1H), 4.18 (dd, J = 20.3, 5.0 Hz, 1H), 3.12 (d, J = 14.0 Hz, 1H), 2.86 (d, J = 14.0 Hz, 1H), 2.66 (t, J = 5.0 Hz, 1H), 2.46 (s, 1H), 1.33 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 214.5, 143.7, 140.8, 128.9, 128.4, 126.8, 118.8, 78.7, 65.7, 45.6, 26.4; IR (Neat Film NaCl) 3431, 2977, 2931, 1719, 1625, 1494, 1445, 1406, 1369, 1142, 1021, 908, 780, 700 cm⁻¹; HRMS (EI⁺) m/z calc’d for C₁₅H₁₆O₃ [M⁺]: 220.1100, found 220.1116; [α]D²₀.₆ -9.82° (c 0.355, CH₂Cl₂, 94% ee).

(S,E)-methyl 5,7-dihydroxy-5-methyl-6-oxohept-2-enoate (Table 3, entry 7). 80% yield. Colorless oil; R, 0.58 (50% EtOAc in hexanes); ¹H NMR (300 MHz, CDCl₃) δ 6.85 (m, 1H), 5.94-5.88 (m, 1H), 4.52 (d, J = 5.1 Hz, 2H), 3.73 (s, 3H), 2.99-2.90 (m, 2H), 2.69-2.50 (m, 2H), 1.42 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 213.5, 166.6, 142.1, 125.5, 78.2, 65.1, 51.9, 42.4, 25.7; IR (Neat Film NaCl) 3436, 2954, 1721, 1658, 1439, 1339, 1280, 1204, 1021 cm⁻¹; HRMS (EI⁺) m/z calc’d for C₁₃H₁₆O₇ [M+H⁺]: 203.0919, found
203.0918; $[\alpha]_D^{18.5} -8.35^\circ$ (c 0.695, CH$_2$Cl$_2$, 92% ee).

**Synthesis of Hydroxyesters by Oxidation and Methylation.**

**Representative Procedure for the Synthesis of $\alpha$-Hydroxy Esters 8.**

![Diagram](image)

(2S)-Hydroxy-2-methyl-4-pentanoate (Table 3, entry 1). To a solution of diol 7a (53.4 mg, 0.37 mmol, 1 equiv) in THF and water (THF/H$_2$O, 2:1, 11.1 mL, 0.033 M) was added H$_2$IO$_6$ (127 mg, 0.50 mmol, 1.5 equiv) at room temperature. After the mixture was stirred at room temperature (ca. 25 °C) for 24 h, the mixture was extracted with Et$_2$O (3 x 30 mL). The organic layer was washed with water (3 mL) and brine (3 mL), dried over Na$_2$SO$_4$ and concentrated under reduced pressure. To a suspension of the residue and K$_2$CO$_3$ (27.6 mg, 0.44 mmol, 1.2 equiv) in DMF (3.7 mL, 0.1 M) was added MeI (27.6 µL, 0.44 mmol, 1.2 equiv) at room temperature (ca. 25 °C). After stirring for 1 h, water (5 mL) was added, and the reaction was extracted with Et$_2$O (3 x 30 mL). The organic layer was washed with water (3 mL) and brine (3 mL), dried over Na$_2$SO$_4$ and concentrated under reduced pressure (~80 mmHg). The residue was purified by flash chromatography (10% Et$_2$O in petroleum ether on silica gel) to give methyl ester 8a (28.9 mg, 54% yield, 90% ee).

(2S)-Hydroxy-2-methyl-4-pentanoate (Table 3, entry 1). $^8$ 54% yield. Colorless oil; R$_f$ 0.48 (20% EtOAc in hexanes); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.84-5.70 (m, 1H), 5.15 (s, 1H), 5.12-5.07 (m, 1H), 3.77 (s, 3H), 3.10 (s, 1H), 2.35-2.54 (m, 2H), 1.43 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 177.1, 132.6, 119.3, 74.7, 52.9, 44.9, 25.7; IR (Neat Film NaCl) 3504, 2982, 2955, 1736, 1642, 1455, 1437, 1372, 1271, 1227, 1170, 1143, 1069, 1000, 980, 920 cm$^{-1}$; HRMS (EI+) $m/z$ calc’d for C$_7$H$_{12}$O$_3$ [M+H]$^+$: 145.0865, found 145.0867; $[\alpha]_D^{22.7} +25.6^\circ$ (c 0.365, CH$_2$Cl$_2$, 90% ee).

(2S)-Hydroxy-2-ethyl-4-pentanoate (Table 3, entry 2). 60% yield. Colorless oil; R$_f$ 0.59 (33% EtOAc in hexanes); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.84-5.70 (m, 1H), 5.13-5.06 (m, 2H), 3.77 (s, 3H), 3.16 (s, 1H), 2.51-2.37 (m, 2H), 1.85-1.63 (m, 2H), 0.86 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 176.8, 132.7, 119.0, 78.2, 52.8, 43.8, 32.0, 8.1; IR (Neat Film NaCl) 3524, 2956, 1735, 1641, 1446, 1246, 1225, 1163, 1028, 999, 974, 919 cm$^{-1}$; HRMS (EI+) $m/z$ calc’d for C$_8$H$_{16}$O$_3$ [M+H]$^+$: 159.1021, found 159.1026; $[\alpha]_D^{20.4} +24.3^\circ$ (c 0.350, CH$_2$Cl$_2$, 93% ee).
(2S)-Hydroxy-2-benzyl-4-pentanoate (Table 3, entry 3). 85% yield. Colorless oil; Rf 0.52 (20% EtOAc in hexanes); 1H NMR (300 MHz, CDCl3) δ 7.31-7.11 (m, 5H), 5.88-5.74 (m, 1H), 5.16-5.11 (m 2H), 3.72 (s, 3H), 3.07 (d, J = 13.5 Hz, 1H), 3.07 (s, 1H), 2.95 (d, J = 13.5 Hz, 1H), 2.65-2.46 (m, 2H); 13C NMR (75 MHz, CDCl3) δ 175.7, 135.9, 132.5, 130.3, 128.4, 127.2, 119.2, 78.4, 52.7, 45.3, 43.8; IR (Neat Film NaCl) 3522, 3030, 2981, 1738, 1414, 1269, 1129, 980, 701 cm⁻¹; HRMS (EI+) m/z calc’d for C13H16O3 [M]+: 220.1100, found 220.1105; [α]D²³⁺ +41.8° (c 0.890, CH₂Cl₂, 86% ee).

Methyl (S)-2-hydroxy-2,4-dimethyl-pent-4-enoic acid methyl ester (Table 3, entry 4). 84% yield. Colorless oil; Rf 0.38 (20% EtOAc in hexanes); 1H NMR (300 MHz, CDCl3) δ 4.89-4.88 (m, 1H), 4.75 (s, 1H), 3.77 (s, 3H), 3.12 (s, 1H), 2.53 (d, J = 13.8 Hz, 1H), 2.37 (d, J = 13.8 Hz, 1H), 1.74 (s, 3H), 1.44 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 177.4, 141.4, 115.2, 74.9, 52.8, 48.2, 26.6, 24.0; IR (Neat Film NaCl) 3514, 2954, 1736, 1644, 1452, 1375, 1266, 1212, 1156, 1114, 896 cm⁻¹; HRMS (EI+) m/z calc’d for C8H14O3 [M]+: 158.0944, found 158.0946; [α]D²²⁺ +11.4° (c 0.220, CH₂Cl₂, 89% ee).

2-(2-Chloroallyl)-2-hydroxymalonic acid dimethyl ester (Table 3, entry 5). 76% yield. Colorless oil; Rf 0.48 (33% EtOAc in hexanes); 1H NMR (300 MHz, CDCl3) δ 5.33 (d, J = 0.9 Hz, 1H), 5.26 (d, J = 0.9 Hz, 1H), 3.80 (s, 3H), 3.32 (s, 1H), 2.86 (d, J = 14.3 Hz, 1H), 2.72 (d, J = 14.3 Hz, 1H), 1.47 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 176.4, 136.6, 117.2, 73.6, 53.1, 49.6, 26.4; IR (Neat Film NaCl) 3507, 2987, 2955, 1738, 1633, 1454, 1436, 1278, 1230, 1167, 887 cm⁻¹; HRMS (EI+) m/z calc’d for C13H16ClO3 [M]+: 178.0397, found 178.0399; [α]D²⁰⁺ +0.79° (c 1.190, CH₂Cl₂, 91% ee).

Methyl (S)-2-hydroxy-2-methyl-4-phenyl-4-pentanoate (Table 3, entry 6). 77% yield. Colorless oil; Rf 0.52 (33% EtOAc in hexanes); 1H NMR (300 MHz, CDCl3) δ 7.36-7.24 (m, 5H), 5.34 (d, J = 1.5 Hz, 1H), 5.17 (s, 1H), 3.18 (s, 3H), 3.07 (d, J = 13.5 Hz, 2H), 2.80 (d, J = 13.5 Hz, 1H), 1.45 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 176.4, 144.1, 141.4, 128.3, 127.7, 126.9, 118.1, 74.3, 52.3, 46.4, 26.1; IR (Neat Film NaCl) 3514, 2981, 2952, 1736, 1626, 1494, 1447, 1269, 1214, 1129, 980, 906, 778, 709 cm⁻¹; HRMS (EI+) m/z calc’d for C13H16O3 [M]+: 220.1100, found 220.1108; [α]D²⁰⁺ –4.09° (c 0.610, CH₂Cl₂, 94% ee).
Synthesis of Hydroxyacid.

(1S)-Hydroxy-cyclohex-3-ene carboxylic acid (10). To a solution of methyl ester (48.0 mg, 0.307 mmol, 1 equiv) in MeOH (3.0 mL, 0.1 M) was added 1N NaOH (0.37 mL, 0.37 mmol, 1.2 equiv) at room temperature (ca. 25 °C). After stirring for 18 h, the mixture was concentrated under reduced pressure. To the residue was added 1N HCl (1.0 mL) and the mixture was extracted with Et₂O (3 x 20 mL). The organic layer was washed with brine (5.0 mL), dried over Na₂SO₄, and concentrated under reduced pressure to give carboxylic acid (10) (41.5 mg, 95% yield, 92% ee) as a white solid: mp 79-81 °C; ¹H NMR (300 MHz, CDCl₃) δ 5.88-5.79 (m, 1H), 5.72-5.61 (m, 1H), 2.79-2.62 (m, 1H), 2.37-2.11 (m, 4H), 1.95-1.80 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 181.5, 126.6, 122.6, 72.6, 34.9, 30.6, 21.4; IR (Neat Film NaCl) 3432, 3032, 2929, 2624, 1736, 1443, 1370, 1356, 1278, 1123, 1059, 1038, 983 cm⁻¹; HRMS (EI+) m/z calc’d for C₈H₁₀O₃ [M⁺]: 156.0786, found 156.0786; [α]D²⁻⁻⁰.16° (c 0.600, CH₂Cl₂, 92% ee).
1318, 1253, 1216, 1092, 1064, 982, 939, 886, 773, 746, 650, 736 cm\(^{-1}\); HRMS (EI+) \(^{m/z}\) calc’d for C\(_8\)H\(_{12}\)O\(_3\) [M]\(^+\): 143.0708, found 143.0708; [\(\alpha\)]\(^D\)\(_{20.7}\) +31.7\(^\circ\) (c 0.310, CH\(_2\)Cl\(_2\), 92% ee).

(1S)-Hydroxy-cyclohex-3-ene carboxylic acid (10).\(^{13}\) To a solution of acetonide 6d (40 mg, 0.20 mmol, 1.0 equiv) in MeOH (4 mL, 0.05 M) was added p-toluenesulfonic acid monohydrate (3.9 mg, 0.02 mmol, 0.1 equiv) at room temperature (24 °C). After the mixture was stirred for 3 h, Et\(_3\)N (0.1 mL) was added. The mixture was concentrated under reduced pressure to give a yellow oil. The oil was diluted with EtOAc (10 mL), filtered through SiO\(_2\) (1 mL), and concentrated under reduced pressure to furnish a white solid (35 mg). The solid was dissolved in THF (0.4 mL) and water (0.2 mL), and the colorless solution was cooled to 0 °C (ice water bath). H\(_2\)IO\(_6\) (46 mg, 0.20 mmol, 1 equiv) was added to the solution. The mixture was allowed to warm to room temperature (26 °C) over 10 minutes, and then stirred for 2 h. The reaction was diluted with water (0.5 mL), and extracted with EtOAc (4 x 15 mL). Extracts were dried over Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The white solid was purified by column chromatography over silica gel (ca. 9 mL) with 2:1 Hexanes:EtOAc to give carboxylic acid 10 (16.3 mg, 56% yield, 92% ee) as a white solid.

**Determination of Absolute Stereochemistry.**

(S)-dimethyl citramalate (SI 6).\(^{14}\) Ozone was bubbled through a colorless solution of alkene (25 mg, 0.14 mmol, 1 equiv) in MeOH (0.52 mL, 0.27 M) at −78 °C until the solution turned blue (50 minutes). The blue solution was flushed with nitrogen gas until it turned colorless, at which point it was treated with sodium sulfite (79 mg, 4.5 equiv). The mixture was allowed to warm to room temperature overnight (ca. 25 °C), at which point it was diluted with Et\(_2\)O (to 30 mL), filtered, and concentrated under vacuum to a colorless oil (9.7 mg, 39% yield). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.81 (s, 3H), 3.80 (s, 3H), 2.97 (d, \(J=16.5\) Hz, 1H), 2.67 (d, \(J=16.5\) Hz, 1H), 1.44 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 176.2, 171.7, 72.8, 53.2, 52.2, 44.2, 26.5; IR (Neat Film NaCl) 3500, 2988, 2957, 2851, 1740, 1439, 1356, 1292, 1207, 1120, 1012, 983 \(\text{cm}^{-1}\); HRMS (EI+) \(^{m/z}\) calc’d for C\(_8\)H\(_{12}\)O\(_3\) [M]\(^+\): 170.0763, found 170.0750; [\(\alpha\)]\(^D\)\(_{21.6}\) +13.4\(^\circ\) (c 0.485, CHCl\(_3\)).

**Methods for the Determination of Enantiomeric Excess.**

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*Table SI 3. Methods for determination of enantiomeric excess*
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<td>O</td>
<td>O</td>
<td>HPLC</td>
<td>Chiralcel OD-H</td>
<td>1% IPA in hexanes</td>
<td>isocratic, 1.0 mL/min</td>
<td>7.256</td>
<td>6.818</td>
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<tr>
<td>7</td>
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<td>O</td>
<td>O</td>
<td>O</td>
<td>GC, G-TA</td>
<td>80 °C</td>
<td>isotherm</td>
<td></td>
<td>69.974</td>
<td>62.451</td>
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<td>GC, G-TA</td>
<td>80 °C</td>
<td>isotherm</td>
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<td>O</td>
<td>O</td>
<td>HPLC</td>
<td>CHIRALPAK AD</td>
<td>Hexanes (220nm)</td>
<td>isocratic, 1.0 mL/min</td>
<td>11.462</td>
<td>10.307</td>
<td>92</td>
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<td>O</td>
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<td>GC, G-TA</td>
<td>100 °C</td>
<td>isotherm</td>
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<td>GC, G-TA</td>
<td>100 °C</td>
<td>isotherm</td>
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<td>11</td>
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<td>O</td>
<td>O</td>
<td>GC, G-TA</td>
<td>110 °C</td>
<td>isotherm</td>
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<td>GC, G-TA</td>
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<td>isotherm</td>
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<td>O</td>
<td>Cl</td>
<td>O</td>
<td>GC, G-TA</td>
<td>100 °C</td>
<td>isotherm</td>
<td></td>
<td>14.338</td>
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</table>
HPLC
CHIRALPAK AD
3% EtOH in hexanes isocratic, 1.0 mL/min

GC, G-TA
100 °C isotherm

GC, G-TA
110 °C isotherm

GC, G-TA
85°C isotherm

References:
12) Previous preparations of the racemate have been reported: Y. Naruta, H. Uno, K. Maruyama, *Chem. Lett.* 1982, 961–964.