Supporting Information

Challenge toward Structural Complexity Using Asymmetric Catalysis: Target-Oriented Development of Catalytic Enantioselective Diels-Alder Reaction

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General: Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500, ECX500 or ECA500 spectrometer, operating at 500 MHz for ^1H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts were reported downfield from TMS ($= 0$) for ^1H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to the solvent used as an internal reference. Optical rotations were measured on a JASCO P-1010 polarimeter. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM). The enantiomeric excesses (ee's) were determined by HPLC. HPLC analysis was performed on JASCO HPLC systems consisting of the following: pump, 880-PU or PU-980; detector, 875-UV or UV-970, measured at 254 nm; column, DAICEL CHIRALPAK AD-H, or DAICEL CHIRALCEL OJ-H, OD-H; mobile phase, hexane/2-propanol. EI mass spectra were measured on JEOL JMS-BU20 GCmate. In general, reactions were carried out in dry solvents under an argon atmosphere, unless noted otherwise. Dry solvents of ether, tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purchased from KANTO CHEMICAL CO., INC. FeBr_3 and AgSbF_6 were purchased from Aldrich and stored in dry-box. Other reagents were purified by usual methods.

Preparation of ligand

(*R,R*)-Ph-pybox was prepared as described.¹

Ligand **4** was prepared by the modified method of the reference.²

Preparation of diene

tert-Butyldimethyl(3-methyl-1-methylene-2-butenyloxy)silane (**6a**) was prepared as described.³

6b was prepared as follows.

2-Isopropylidenebutane-1,3-diol (6b2): To a suspension of lithium aluminum hydride (38 g, 0.99 mol) in THF (1000 mL), ethyl isopropylideneacetate⁴ (**6b1**) (42 g, 0.247 mol) in THF (100 mL) was added at 0 °C. After stirring at ambient temperature for 2 h, H₂O (38 mL), 15% NaOH aqueous solution (38 mL) and H₂O (110 mL) were added carefully at 0 °C. Then the mixture was filtered through a short pad of celite and washed with CH₂Cl₂ and MeOH thoroughly. The filtrate was concentrated to give a residue, which was purified by silica gel flash chromatography (CH₂Cl₂/MeOH, 10/1) to afford **6b2** (25.0 g, 0.192 mol; 78%) as colorless liquid. ¹H NMR (CDCl₃): δ 4.89 (q, *J* = 6.4 Hz, 1H), 4.31 (d, *J* = 11.8 Hz, 1H), 4.23 (d, *J* = 11.8 Hz, 1H), 2.88 (s, 1H), 2.70 (s, 1H), 1.77 (s, 3H), 1.70 (s, 3H), 1.26 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (CDCl₃): δ 134.1, 131.4, 67.7, 58.3, 22.2, 20.6, 19.9; IR (neat, cm⁻¹): 3357; EI-MS *m/z* 130 (M⁺); EI-HRMS Calcd for C₁₁H₁₇O₂ (M⁺+H): 131.1072, Found: 131.1076.

4-Methyl-3-(triisopropylsiloxymethyl)-3-penten-2-ol (6b3): To a solution of **6b2** in DMF (400 mL), imidazole (18.7 g, 0.274 mol) and TIPSCl (47 mL, 0.219 mol) were added successively at 0 °C. After stirring at 50 °C for 20 h, water and ether were added to the mixture at 0 °C. The organic phase was separated, and the aqueous phase was further extracted three times with ether. The combined organic layer was washed with water (three times) and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/10) to afford **6b3** (45.6 g, 0.159 mol; 87 %) as colorless liquid. ¹H NMR (CDCl₃): δ 4.76 (d, *J* = 6.4 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 3.63-3.72 (brs, 1H), 1.67 (s, 3H), 1.66 (s, 3H), 1.27 (d, *J* = 6.4 Hz, 3H), 1.02-1.05 (m, 21H); ¹³C NMR (CDCl₃): δ 133.1, 128.9, 67.9, 60.6, 22.5, 20.5, 20.1, 17.9, 11.8; IR (neat, cm⁻¹): 3428; EI-MS *m/z* 271 (M⁺-Me), 268 (M⁺-H₂O), 241 (M⁺-ⁱPr-H₂O); EI-HRMS Calcd for C₁₃H₂₅OSi (M⁺-ⁱPr-H₂O): 225.1675, Found: 225.1673.

4-Methyl-3-(triisopropylsiloxymethyl)-3-penten-2-one (6b4): To a suspension of **6b3** (2.78 g, 9.70 mmol) and MS 4A (powder, 4.85 g) in CH₂Cl₂ (30 mL), NMO (1.70 g, 14.6 mmol) and TPAP (170 mg, 0.49 mmol) were added successively at 0 °C. After stirring for 0.5 h at ambient temperature, the mixture was filtered through a short pad of silica gel, and the residue was washed with EtOAc. The filtrate was concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/40) to give **6b4** (2.29 g, 8.05 mmol; 83%) as colorless liquid. ¹H NMR (CDCl₃): δ 4.50 (s, 2H), 2.31 (s, 3H), 1.83 (s, 3H), 1.77 (s, 3H), 1.03-

1.05 (m, 2H); ^{13}C NMR (CDCl_3): δ 205.3, 137.3, 137.2, 60.9, 30.6, 22.4, 21.0, 18.0, 11.9; IR (neat, cm^{-1}): 1695; EI-MS m/z 241 ($\text{M}^+ - \text{iPr}$); EI-HRMS Calcd for $\text{C}_{13}\text{H}_{25}\text{O}_2\text{Si}$ ($\text{M}^+ - \text{iPr}$): 241.1624, Found: 241.1618.

4-Methyl-2-(triisopropylsiloxy)-3-(triisopropylsiloxymethyl)penta-1,3-diene (6b): To a solution of **6b4** (2.15 g, 7.54 mmol) in CH_2Cl_2 (35 mL), 2,6-lutidine (1.3 mL, 11.3 mmol) and TIPSOTf (2.6 mL, 9.81 mmol) were added successively at -78°C . After stirring at -78°C for 1 h, excess amount of Et_3N and water were added. The organic phase was separated and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water (twice) and brine, dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/50) to afford **6b** (2.12 g, 4.81 mmol; 64%) as colorless liquid. ^1H NMR (C_6D_6): δ 4.52 (s, 2H), 4.52 (s, 1H), 4.32 (s, 1H), 1.86 (s, 3H), 1.75 (s, 3H), 1.12-1.17 (m, 42H); ^{13}C NMR (C_6D_6): δ 155.6, 133.1, 132.4, 93.7, 60.1, 22.0, 19.4, 17.5, 17.4, 12.2, 11.7; IR (neat, cm^{-1}): 1613; EI-MS m/z 440 (M^+); EI-HRMS Calcd for $\text{C}_{25}\text{H}_{52}\text{O}_2\text{Si}$ (M^+): 440.3506, Found: 440.3507.

6c was prepared as follows.

3Z-4,8-Dimethylnona-3,7-dien-2-ol (6c2): To a solution of neral⁵ (**6c1**) (5.10 g, 0.0336 mol) in ether (150 mL), MeLi (29 mL, 0.0436 mol, 1.5 M in ether) was added at -78°C . After stirring at the same temperature for 1.5 h, 1 N HCl was added slowly. The organic phase was separated and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water and brine, dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/20) to give **6c2** (5.46 g, 0.0329 mol; 98%) as colorless liquid. ^1H NMR (CDCl_3): δ 5.15 (d, $J = 8.9$ Hz, 1H), 5.04 (t, $J = 5.7$ Hz, 1H), 4.41-4.48 (m, 1H), 1.98-2.06 (m, 4H), 1.64 (s, 3H), 1.62 (s, 3H), 1.53 (s, 3H), 1.23 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (CDCl_3): δ 136.2, 131.1, 129.1, 122.8, 63.0, 31.1, 25.3, 24.4, 22.3, 22.0, 16.4; IR (neat, cm^{-1}): 3345; EI-MS m/z 168 (M^+); EI-HRMS Calcd for $\text{C}_{11}\text{H}_{20}\text{O}$ (M^+): 168.1514, Found: 168.1512.

3Z-4,8-Dimethylnona-3,7-dien-2-one (6c3): To a suspension of **6c2** (1.63 g, 9.70 mmol) and MS 4A (powder, 4.85 g) in CH_2Cl_2 (30 mL), NMO (1.70 g, 14.6 mmol) and TPAP (170 mg, 0.49 mmol) were added successively at 0°C . After stirring for 0.5 h at ambient temperature, the

mixture was filtered through a short pad of silica gel and the residue washed with EtOAc. The filtrate was concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/10) to give **6c3** (1.43 g, 8.61 mmol; 89%) as colorless liquid.

^1H NMR (CDCl_3): δ 6.03 (s, 1H), 5.08-5.14 (m, 1H), 2.55 (t, $J = 7.7$ Hz, 2H), 2.12 (s, 3H), 2.07-2.14 (m, 2H), 1.84 (s, 3H), 1.65 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (CDCl_3): δ 198.0, 158.8, 132.0, 124.1, 123.6, 33.6, 31.6, 26.6, 25.6, 25.5, 17.5; IR (neat, cm^{-1}): 1688, 1617; EI-MS m/z 166 (M^+); EI-HRMS Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$ (M^+): 166.1358, Found: 166.1352.

(2Z-3,7-Dimethyl-1-methylenoocta-2,6-dieneyloxy)triisopropylsilane (6c): To a solution of **6c3** (2.10 g, 12.7 mmol) in CH_2Cl_2 (40 mL), Hünig base (3.5 mL, 20.3 mmol) and TIPSOTf (4.4 mL, 16.4 mmol) were added successively at -78°C . After stirring for 1 h at -78°C , excess amount of Et_3N and water were added. The organic phase was separated and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water (twice) and brine, dried (Na_2SO_4) and concentrated to give a residue, which was purified by distillation (1 mmHg, 230°C , Kugelrohr) to afford **6c** (3.28 g, 10.2 mmol; 81%) as colorless liquid. ^1H NMR (C_6D_6): δ 5.75 (s, 1H), 5.24 (t, $J = 5.5$ Hz, 1H), 4.42 (s, 1H), 4.31 (s, 1H), 2.56 (t, $J = 7.5$ Hz, 2H), 2.18 (dt, $J = 5.5, 7.5$ Hz, 2H), 1.67 (s, 3H), 1.65 (s, 3H), 1.55 (s, 3H), 1.13-1.16 (m, 21H); ^{13}C NMR (C_6D_6): δ 155.2, 139.2, 130.4, 123.9, 123.4, 93.2, 32.2, 26.3, 24.9, 23.4, 17.3, 17.0, 12.3; IR (neat, cm^{-1}): 1464, 1250, 1017; EI-MS m/z 322 (M^+); EI-HRMS Calcd for $\text{C}_{20}\text{H}_{38}\text{OSi}$ (M^+): 322.2692, Found: 322.2696.

6d was prepared as follows:

3E-4,8-Dimethylnona-3,7-dien-2-ol (6d2): To a solution of geranial⁵ (**6d1**) (7.90 g, 0.0520 mol) in ether (200 mL), MeLi (45 mL, 0.0676 mol, 1.5 M in ether) was added at -78°C . After stirring for 1.5 h at the same temperature, 1 N HCl was added slowly. The organic phase was separated and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water and brine, dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/20) to give **6d2** (6.26 g, 0.0373 mol; 72%) as colorless liquid. ^1H NMR (CDCl_3): δ 5.21 (d, $J = 8.3$ Hz, 1H), 5.08 (t, $J = 7.0$ Hz, 1H), 4.52-4.60 (m, 1H), 2.06-2.11 (m, 2H), 1.96-2.01 (m, 2H), 1.67 (s, 6H), 1.59 (s, 3H), 1.22 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (CDCl_3): δ 136.4, 130.5, 128.0, 122.8, 63.6, 38.3, 25.2,

24.5, 22.4, 16.5, 15.2; IR (neat, cm^{-1}): 3346; EI-MS m/z 168 (M^+); EI-HRMS Calcd for $\text{C}_{11}\text{H}_{20}\text{O}$ (M^+): 168.1514, Found: 168.1515.

3E-4,8-Dimethylnona-3,7-dien-2-one (6d3): To a suspension of **6d2** (1.91 g, 11.4 mmol) and MS 4A (powder, 5.70 g) in CH_2Cl_2 (30 mL), NMO (2.00 g, 17.1 mmol) and TPAP (200 mg, 0.57 mmol) were added successively at 0 °C. After stirring for 0.5 h at ambient temperature, the mixture was filtered through a short pad of silica gel, and the residue was washed with EtOAc. The filtrate was concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/10) to give **6d3** (1.62 g, 9.76 mmol; 86%) as colorless liquid.

^1H NMR (CDCl_3): δ 6.04 (s, 1H), 5.02-5.08 (m, 1H), 2.15 (s, 3H), 2.10-2.14 (m, 4H), 2.10 (d, J = 1.3 Hz, 3H), 1.66 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (CDCl_3): δ 198.7, 158.1, 132.4, 123.5, 122.9, 41.1, 31.7, 26.0, 25.6, 19.2, 17.6; IR (neat, cm^{-1}): 1688, 1617; EI-MS m/z 166 (M^+); EI-HRMS Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$ (M^+): 166.1358, Found: 166.1356.

(2E-3,7-Dimethyl-1-methyleneocta-2,6-dienyloxy)triisopropylsilane (6d): To a solution of **6d3** (2.10 g, 12.7 mmol) in CH_2Cl_2 (40 mL), Hünig base (3.5 mL, 20.3 mmol) and TIPSOTf (4.4 mL, 16.4 mmol) were added successively at -78 °C. After stirring for 1 h at -78 °C, excess amount of Et_3N and water were added. The organic phase was separated and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water (twice) and brine, dried (Na_2SO_4) and concentrated to give a residue, which was purified by distillation (1 mmHg, 230 °C, Kugelrohr) to afford **6d** (3.80 g, 11.8 mmol; 93%) as colorless liquid. ^1H NMR (C_6D_6): δ 5.79 (s, 1H), 5.14 (t, J = 6.3 Hz, 1H), 4.47 (s, 1H), 4.28 (s, 1H), 2.10-2.15 (m, 2H), 2.01-2.05 (m, 2H), 1.94 (s, 3H), 1.64 (s, 3H), 1.51 (s, 3H), 1.12-1.16 (m, 21H); ^{13}C NMR (C_6D_6): δ 155.4, 138.8, 130.5, 123.5, 122.9, 93.8, 40.2, 26.0, 24.9, 17.4, 17.3, 17.0, 12.2; IR (neat, cm^{-1}): 1464, 1256, 1016; EI-MS m/z 322 (M^+); EI-HRMS Calcd for $\text{C}_{20}\text{H}_{38}\text{OSi}$ (M^+): 322.2692, Found: 322.2697.

6e and **6f** were prepared as follows.

7-Methyl-6-octen-2-ynoic acid ethyl ester (6ef2): To a solution of 6-methyl-5-hepten-1-yne⁶ (**6ef1**) (10.8 g, 0.1 mol) in THF (200 mL), ⁱPrMgCl (50 mL, 0.1 mol, 2.0 M in THF) was added at 0 °C. After 1 h, ethyl chloroformate (14.3 mL, 0.15 mol) was added to the mixture at –78 °C. The mixture was further stirred at –78 °C for 0.5 h and at 0 °C for 1 h, before 2 N HCl was added. The organic phase was separated and the aqueous phase was further extracted twice with hexane. The combined organic layer was washed with water (twice) and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/40) to afford **6ef2** (15.8 g, 87.8 mmol; 88%) as colorless liquid. ¹H NMR (CDCl₃): δ 5.10 (t, *J* = 5.8 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.27-2.31 (m, 2H), 2.20-2.23 (m, 2H), 1.66 (s, 3H), 1.58 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (CDCl₃): δ 153.7, 133.8, 121.6, 89.0, 73.0, 61.6, 26.2, 25.5, 19.1, 17.6, 13.9; IR (neat, cm^{–1}): 1712; EI-MS *m/z* 180 (M⁺); EI-HRMS Calcd for C₁₁H₁₆O₂ (M⁺): 180.1150, Found: 180.1150.

Mixture of 2Z- and 2E-2-acetyl-3,7-dimethylocta-2,6-dienoic acid ethyl ester (6e3, 6f3): To a suspension of CuI (1.24 g, 6.5 mmol) in THF (50 mL), MeLi (8.7 mL, 13 mmol, 1.5 M in ether) was added at 0 °C and stirred at the same temperature for 40 min. Then to the solution, **6ef2** (0.90 g, 5.0 mmol) was added dropwise at –78 °C and stirred at the same temperature before adding AcBr (1.85 mL, 25 mmol). The mixture was further stirred at –78 °C for 4 h, and then 1 N HCl was added to quench the reaction. The organic phase was separated and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/20) to afford inseparable mixture of **6e3** and **6f3** (1.20 g, 5.0 mmol; 100%, **6e3/6f3** = 1/7) as colorless liquid.

Mixture of 2Z- and 2E-2-(1,5-dimethylhex-4-enylidene)butane-1,3-diol (6e4, 6f4): To a suspension of lithium aluminum hydride (0.67 g, 17.6 mmol) in THF (50 mL), mixture of **6e3** and **6f3** (1.05 g, 4.41 mmol, **6e3/6f3** = 1/7) in THF (6 mL) was added at 0 °C. After 1 h, water (0.67 mL), 15% NaOH aqueous solution (0.67 mL) and water (2.01 mL) were added carefully at 0 °C. The suspension was filtered through a pad of celite, and the residue was washed with CH₂Cl₂. The filtrate was concentrated to give a residue, which was purified by silica gel flash chromatography (CH₂Cl₂/MeOH, 50/1 to 20/1) to afford inseparable mixture **6e4** and **6f4** (870 mg, 4.39 mmol; 99%, **6e4/6f4** = 1/7) as colorless liquid.

3E- and 3Z-4,8-Dimethyl-3-(triisopropylsiloxymethyl)-3,7-nonadien-2-ol (6e5, 6f5): To a solution of a mixture of **6e4** and **6f4** (760 mg, 3.84 mmol, **6e4/6f4** = 1/7) in DMF (10 mL), imidazole (392 mg, 5.76 mmol) and TIPSCl (0.992 mL, 4.99 mmol) were added at 0 °C. After stirring at ambient temperature for 24 h, water and ether were added at 0 °C successively. The organic phase was separated, and the water phase was further extracted with ether twice. The combined organic layer was washed with water (twice), brine, dried (Na₂SO₄) and concentrated

to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/50) to give **6e5** (145 mg, 0.41 mmol; 11%) and **6f5** (1.03 g, 2.90 mmol; 76 %) respectively. Z-form (**6e5**): ^1H NMR (CDCl_3): δ 5.05-5.13 (m, 1H), 4.79 (dt, $J = 6.1, 7.0$ Hz, 1H), 4.55 (d, $J = 11.6$ Hz, 1H), 4.44 (d, $J = 11.6$ Hz, 1H), 3.51 (d, $J = 7.0$ Hz, 1H), 1.99-2.11 (m, 4H), 1.72 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.34 (d, $J = 6.1$ Hz, 1H), 1.04-1.10 (m, 21H); ^{13}C NMR (CDCl_3): δ 134.0, 133.4, 132.2, 124.0, 67.7, 61.1, 34.5, 31.8, 27.1, 25.8, 23.1, 18.8, 18.2, 12.1; IR (neat, cm^{-1}): 3452; EI-MS m/z 354 (M^+); EI-HRMS Calcd for $\text{C}_{21}\text{H}_{42}\text{O}_2\text{Si}$ (M^+): 354.2954, Found: 354.2953. E-form (**6f5**): ^1H NMR (CDCl_3): δ 5.01-5.07 (m, 1H), 4.75 (dt, $J = 6.3, 6.9$ Hz, 1H), 4.54 (d, $J = 11.5$ Hz, 1H), 4.40 (d, $J = 11.5$ Hz, 1H), 3.67 (d, $J = 6.9$ Hz, 1H), 1.95-2.14 (m, 4H), 1.70 (s, 3H), 1.65 (s, 3H), 1.55 (s, 3H), 1.31 (d, $J = 6.3$ Hz, 1H), 1.02-1.07 (m, 21H); ^{13}C NMR (CDCl_3): δ 133.8, 132.5, 131.9, 123.6, 68.1, 60.5, 34.8, 31.5, 27.0, 25.6, 22.6, 17.9, 17.7, 11.8; IR (neat, cm^{-1}): 3445; EI-MS m/z 354 (M^+); EI-HRMS Calcd for $\text{C}_{21}\text{H}_{42}\text{O}_2\text{Si}$ (M^+): 354.2954, Found: 354.2952.

3Z-4,8-Dimethyl-3-(triisopropylsiloxymethyl)-3,7-nonadien-2-one (6e6): To a suspension of **6e5** (520 mg, 1.46 mmol) and MS 4A (powder, 0.73 g) in CH_2Cl_2 (15 mL), NMO (256 mg, 2.19 mmol) and TPAP (26 mg, 0.073 mmol) were added successively at 0 °C. After stirring at ambient temperature for 0.5 h, the mixture was filtered through a short pad of silica gel and the residue was washed with EtOAc. The filtrate was concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/20) to give **6e6** (470 mg, 1.33 mmol; 91%) as colorless liquid. ^1H NMR (CDCl_3): δ 5.04-5.11 (m, 1H), 4.48 (s, 2H), 2.28 (s, 3H), 2.06-2.16 (m, 4H), 1.73 (s, 3H), 1.65 (s, 3H), 1.59 (s, 3H), 1.03-1.06 (m, 21H); ^{13}C NMR (CDCl_3): δ 205.3, 139.4, 137.9, 132.2, 123.7, 61.1, 35.9, 30.9, 26.9, 25.8, 18.5, 18.0, 17.7, 12.0; IR (neat, cm^{-1}): 1697; EI-MS m/z 352 (M^+); EI-HRMS Calcd for $\text{C}_{21}\text{H}_{40}\text{O}_2\text{Si}$ (M^+): 352.2798, Found: 352.2797.

3E-4,8-Dimethyl-3-(triisopropylsiloxymethyl)-3,7-nonadien-2-one (6f6): To a suspension of **6f5** (1.95 g, 5.49 mmol) and MS 4A (powder, 2.70 g) in CH_2Cl_2 (30 mL), NMO (964 mg, 8.23 mmol) and TPAP (96 mg, 0.27 mmol) were added successively at 0 °C. After stirring at ambient temperature for 0.5 h, the mixture was filtered through a short pad of silica gel, and the residue was washed with EtOAc. The filtrate was concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/20) to give **6f6** (1.61 g, 4.56 mmol; 83%) as colorless liquid. ^1H NMR (CDCl_3): δ 5.04-5.12 (m, 1H), 4.49 (s, 2H), 2.30 (s, 3H), 2.05-2.12 (m, 4H), 1.80 (s, 3H), 1.68 (s, 3H), 1.59 (s, 3H), 1.04 (s, 18H), 1.03 (s, 3H); ^{13}C NMR (CDCl_3): δ 205.9, 139.5, 137.7, 132.6, 123.3, 60.7, 34.9, 30.9, 26.7, 25.8, 20.4, 18.1, 17.7, 12.0; IR (neat, cm^{-1}): 1695; EI-MS m/z 352 (M^+); EI-HRMS Calcd for $\text{C}_{21}\text{H}_{40}\text{O}_2\text{Si}$ (M^+): 352.2798, Found: 352.2795.

3Z-4,8-Dimethyl-2-(triisopropylsiloxy)-3-(triisopropylsiloxymethyl)nona-1,3,7-triene (6e):

To a solution of **6e** (410 mg, 1.16 mmol) in CH₂Cl₂ (10 mL), Hünig base (0.303 mL, 1.74 mmol) and TIPSOTf (0.405 mL, 1.57 mmol) were added successively at –78 °C. After stirring at –78 °C for 2 h and at 0 °C for 3h, excess amount of Et₃N and water were added. The organic phase was separated, and the aqueous phase was further extracted twice with ether. The combined organic layer was washed water (twice) and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/50) to afford **6e** (362 mg, 0.711 mmol; 61%) as colorless liquid. Stereochemistry was determined by NOE analysis. ¹H NMR (C₆D₆): δ 5.20-5.25 (m, 1H), 4.49 (s, 2H), 4.43 (s, 1H), 4.34 (s, 1H), 2.42-2.45 (m, 2H), 2.13-2.20 (m, 2H), 1.78 (s, 3H), 1.65 (s, 3H), 1.56 (s, 3H), 1.13-1.18 (m, 42H); ¹³C NMR (C₆D₆): δ 156.4, 136.8, 134.5, 131.3, 124.8, 93.7, 61.3, 36.4, 27.5, 25.8, 18.4, 18.4, 18.3, 17.6, 13.1, 12.6; IR (neat, cm⁻¹): 1464; EI-MS *m/z* 508 (M⁺); EI-HRMS Calcd for C₃₀H₆₀O₂Si₂ (M⁺): 508.4132, Found: 508.4132.

3E-4,8-Dimethyl-2-(triisopropylsiloxy)-3-(triisopropylsiloxymethyl)nona-1,3,7-triene (6f):

To a solution of **6f6** (1.60 g, 4.53 mmol) in CH₂Cl₂ (30 mL), Hünig base (1.2 mL, 6.80 mmol) and TIPSOTf (1.58 mL, 5.89 mmol) were added successively at –78 °C. After stirring at –78 °C for 2 h and at 0 °C for 3h, excess amount of Et₃N and water were added. The organic phase was separated, and the aqueous phase was further extracted twice with ether. The combined organic layer was washed water (twice) and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (AcOEt/hexane, 1/50) to afford **6f** (1.60 g, 3.14 mmol; 69%) as colorless liquid. Stereochemistry was determined by NOE analysis. ¹H NMR (C₆D₆): δ 5.20-5.24 (m, 1H), 4.53 (s, 2H), 4.51 (s, 1H), 4.31 (s, 1H), 2.26-2.30 (m, 2H), 2.14-2.20 (m, 2H), 1.90 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H), 1.13-1.17 (m, 42H); ¹³C NMR (C₆D₆): δ 156.4, 136.7, 134.6, 131.6, 124.6, 94.8, 60.6, 34.5, 27.4, 25.8, 20.7, 18.4, 18.4, 17.7, 13.1, 12.6; IR (neat, cm⁻¹): 1464; EI-MS *m/z* 508 (M⁺); EI-HRMS Calcd for C₃₀H₆₀O₂Si₂ (M⁺): 508.4132, Found: 508.4134.

Metal effect

entry	metal	additive (x mol %)	temp (°C)	time (h)	yield (%)	ee (%)
1	In(OTf) ₃	none	-40	17	44	27
2	Sc(OTf) ₃	none	-40	17	41	16
3	Cu(OTf) ₂	none	-10	46	29	38
4	Zn(OTf) ₂	none	-10	46	18	30
5	Mn(ClO ₄) ₂ ·6H ₂ O	none	-10	38	28	12
6	Co(ClO ₄) ₂ ·6H ₂ O	none	-40	110	8	5
7	Fe(ClO ₄) ₂ ·nH ₂ O	none	-40	120	6	19
8	Fe(ClO ₄) ₃ ·nH ₂ O	none	-40	21	35	76
9	InCl ₃	AgSbF ₆ (30 mol%)	-40	15	7	31
10	FeBr ₃	AgSbF ₆ (30 mol%)	-40	16	42	80
11 ^a	FeBr ₃	AgSbF ₆ (20 mol%)	-20	20	69	87
12	FeBr ₃	AgSbF ₆ (20 mol%)	-40	16	64	86

^a Filtered catalyst solution was used.

Ligand effect-1

entry	1	2	3
ligand			
yield (%)	64	12	11
ee (%)	86	-22	-8

entry	4	5	6
ligand			
yield (%)	25	25	40
ee (%)	61	86	43

Procedure of catalytic enantioselective Diels-Alder reaction using Ph-pybox

3-[4-(*tert*-Butyldimethylsiloxy)-2,2-dimethylcyclohex-3-enecarbonyl]oxazolidin-2-one (**7a**):

A suspension of (*R,R*)-Ph-pybox (17.7 mg, 0.048 mmol), FeBr₃ (11.8 mg, 0.040 mmol) and AgSbF₆ (27.5 mg, 0.080 mmol) in CH₂Cl₂ (0.8 mL) was stirred at ambient temperature for 8 h in the dark, and then dienophile **5a** (282 mg, 2.0 mmol) in CH₂Cl₂ (4.0 mL) was added. After 15 min, diene **6a** (850 mg, 4.0 mmol) was added dropwise to the mixture at -50 °C to start the reaction. After 7 h, reaction was quenched by the addition of Et₃N and water. After stirring at ambient temperature for 0.5 h, the mixture was filtered through a pad of celite. The organic phase of filtrate was separated and the water phase was further extracted with ether twice. The combined organic layer was washed with water and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/10) to afford **7a** (530 mg, 1.49 mmol; 75%) as a colorless oil. ¹H NMR (C₆D₆): δ 4.77 (s, 1H), 4.18 (dd, *J* = 2.8, 10.1 Hz, 1H), 3.10-3.17 (m, 4H), 2.00-2.19 (m, 3H), 1.76-1.82 (m, 1H), 1.21 (s, 3H), 1.18 (s, 3H), 0.98 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H); ¹³C NMR (C₆D₆): δ 173.5, 152.2, 148.1, 114.5, 59.8, 44.8, 41.6, 34.2, 29.4, 28.1, 25.4, 24.9, 22.3, 17.2, -5.3, -5.3; IR (neat, cm⁻¹): 1780, 1697; EI-MS *m/z* 353 (M⁺); EI-HRMS Calcd for C₁₈H₃₁NO₄ (M⁺): 353.2022, Found: 353.2022; [α]_D²¹ +6.28 (c = 3.15, CH₂Cl₂) (90% ee).

Conversion to determine the enantiomeric excess: To a solution of **7a** (105 mg, 0.297 mmol) in THF (2 mL), HF-Py (0.2 mL) was added dropwise at ambient temperature. After stirring for 1.5 h, the mixture was diluted with EtOAc and poured into saturated NaHCO₃ aqueous solution. The organic phase was separated and aqueous phase was further extracted twice with EtOAc. The combined organic layer was washed with saturated NaHCO₃ aqueous solution and brine, dried (NaSO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/5) to afford **7a1** (67.7 mg, 0.283 mmol; 95%) as a colorless oil.

3-[(1*R*)-2,2-Dimethyl-4-oxocyclohexanecarbonyl]oxazolidin-2-one (7a1**):** ¹H NMR (CDCl₃): δ 4.40 (t, *J* = 7.6 Hz, 2H), 4.16 (dd, *J* = 4.9, 7.9 Hz, 1H), 4.04 (d, *J* = 7.6 Hz, 2H), 2.47-2.53 (m, 1H), 2.48 (d, *J* = 13.8 Hz, 1H), 2.27-2.34 (m, 1H), 2.20 (d, *J* = 13.8 Hz, 1H), 1.99-2.12 (m, 2H), 1.03 (s, 3H), 1.02 (s, 3H); ¹³C NMR (CDCl₃): δ 209.3, 173.3, 152.3, 60.5, 53.1, 44.4, 41.7, 37.6, 37.0, 27.3, 24.0, 22.9; IR (neat, cm⁻¹): 1773, 1694; EI-MS *m/z* 239 (M⁺); EI-HRMS Calcd for C₁₂H₁₇NO₄ (M⁺): 239.1158, Found: 239.1157; [α]_D²¹ -34.8 (c = 1.69, CHCl₃) (90% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 1/1, 1.0 ml/min) *t*_R 10.4 min (major), 13.8 min (minor).

Determination of absolute configuration: To a solution of **7a1** (50 mg, 0.21 mmol; 90% ee) in benzene (30 mL), (*R,R*)-hydrobenzoin (67 mg, 0.31 mmol) and TsOH·H₂O (8 mg, 0.042 mmol) was added at ambient temperature, and the mixture was refluxed in Dean-Stark apparatus for 1 h. After cooling down to ambient temperature, saturated aqueous NaHCO₃ solution was added and the organic phase was separated, while the water phase was further extracted twice with EtOAc. The combined organic layer was washed with water and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/2) to afford **7a2** (82.0 mg, 0.188 mmol; 90%) as a white powder. A crystalline sample was obtained by recrystallization from EtOAc/hexane and subjected to X-ray analysis. **3-[(2*R*,3*R*,8*R*)-7,7-Dimethyl-2,3-diphenyl-1,4-dioxaspiro[4.5]decane-8-carbonyl]oxazolidin-2-one (**7a2**):** ¹H

Ligand effect-2

General procedure of catalytic enantioselective Diels-Alder reaction using ligand 4.

A suspension of ligand **4** (55.0 mg, 0.12 mmol), FeBr₃ (29.6 mg, 0.10 mmol), AgSbF₆ (68.8 mg, 0.20 mmol) and MS 5A (250 mg) in CH₂Cl₂ (2.5 mL) was stirred at ambient temperature for 8 h in the dark, before dienophile **5a** (212 mg, 1.5 mmol) in CH₂Cl₂ (17.5 mL) was added. After 15 min, diene **6f** (509 mg, 1.0 mmol) was added dropwise to the mixture at -70 °C to start the reaction. After 30 h, reaction was quenched by the addition of Et₃N and water. After stirring at ambient temperature for 0.5 h, the mixture was filtered through a pad of celite. The organic phase of filtrate was separated and the water phase was further extracted with ether twice. The combined organic layer was washed with water and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/10 to 1/1 then CH₂Cl₂/MeOH, 20/1) to afford **7f** (644 mg, 0.99 mmol; 99%, pure *exo* product) as a colorless oil. Enantiomeric excess was determined after appropriate conversions. Ligand **4** was recovered as a white powder (54.0 mg, 0.118 mmol; 98% recovery).

3-[(1*R*)-2,2-Dimethyl-4-(triisopropylsiloxy)-3-(triisopropylsiloxy)methyl]cyclohex-3-enecarbonyl]oxazolidin-2-one (**7b**):

7b: ¹H NMR (C₆D₆): δ 4.92 (d, *J* = 11.3 Hz, 1H), 4.70 (d, *J* = 11.3 Hz, 1H), 4.25 (dd, *J* = 2.2, 9.8 Hz, 1H), 3.08-3.13 (m, 4H), 2.12-2.31 (m, 3H), 1.87-1.95 (m, 1H), 1.67 (s, 3H), 1.57 (s, 3H), 1.16-1.20 (m, 21H), 1.11-1.14 (m, 21H), ; ¹³C NMR (CDCl₃): δ 173.6, 152.3, 144.5, 120.2, 59.8, 58.3, 46.4, 41.6, 36.5, 30.9, 28.4, 26.5, 23.8, 17.5, 17.3, 12.9, 11.5; IR (neat, cm⁻¹): 1781, 1698; EI-MS *m/z* 581 (M⁺); EI-HRMS Calcd for C₂₈H₅₂NO₅Si₂ (M⁺-Pr):

538.3384, Found: 538.3381; [δ]²¹_D -7.90 (*c* = 2.81, CH₂Cl₂) (86% ee).

Determination of enantiomeric excess was as follows: To a solution of **7b** (105 mg, 0.180 mmol) in CDCl₃ (2 mL), 30% HCl (1 μ L, MeOH solution) was added at ambient temperature. After 30 min, saturated aqueous NaHCO₃ solution was added and the organic phase was separated. The aqueous phase was further extracted with EtOAc twice. The combined organic layer was washed with water and brine, dried (NaSO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/8) to afford **7b1** (62.6 mg, 0.153 mmol; 85%) as a colorless oil.

3-[(1*R*)-6,6-Dimethyl-5-methylene-4-(triisopropylsilyloxy)-cyclohex-3-enecarbonyl]-oxazolidin-2-one (**7b1**):

7b1: ¹H NMR (CDCl₃): δ 5.78 (s, 1H), 5.11 (s, 1H), 5.04 (s, 1H), 4.34 (dd, *J* = 5.5, 8.6 Hz, 1H), 2.99-3.06 (m, 4H), 2.59-2.66 (m, 1H), 2.42-2.48 (m, 1H), 1.42 (s, 3H), 1.26 (s, 3H), 1.13-1.18 (m, 21H); ¹³C NMR (CDCl₃): δ 173.0, 152.1, 148.6, 147.4, 106.2, 102.3, 59.8, 44.8, 41.4, 37.0, 25.4, 24.6, 23.3, 17.3, 12.2; IR (neat, cm⁻¹): 1777, 1697; EI-MS *m/z* 408 (M⁺+1); EI-HRMS Calcd for C₂₂H₃₇NO₄Si (M⁺): 407.2492, Found: 407.2489; [δ]²¹_D -34.8 (*c* = 1.68, CH₂Cl₂) (86% ee);

HPLC (DAICEL CHIRALCEL OD-H, hexane/2-propanol 9/1, 0.5 ml/min) t_R 22.9 min (major), 27.5 min (minor).

3-[(1R)-4-(*tert*-Butyldimethylsiloxy)-2,2,6-trimethylcyclohex-3-enecarbonyl]oxazolidin-2-one (7c)

one (7c): ^1H NMR (C_6D_6): δ 4.78 (d, $J = 1.8$ Hz, 1H), 4.22 (d, $J = 11.3$ Hz, 1H), 3.08-3.24 (m, 4H), 2.38 (dddd, $J = 5.7, 6.4, 11.3, 11.3$ Hz, 1H), 2.08 (dd, $J = 5.7, 17.4$ Hz, 1H), 1.90 (ddd, $J = 1.8, 11.3, 17.4$ Hz, 1H), 1.22 (s, 3H), 1.16 (s, 3H), 0.99 (s, 9H), 0.94 (d, $J = 6.4$ Hz, 3H), 0.14 (s, 6H); ^{13}C NMR (CDCl_3): δ 174.7, 153.4, 148.4, 115.5, 60.8, 52.8, 42.6, 38.5, 36.3, 30.2, 29.2, 26.9, 25.9, 19.6, 18.2, -4.3, -4.4; IR (neat, cm^{-1}): 1779, 1694; EI-MS m/z 367 (M^+); EI-

HRMS Calcd for $\text{C}_{19}\text{H}_{34}\text{NO}_4\text{Si}$ ($\text{M}^+\text{+H}$): 368.2257, Found: 368.2265; $[\alpha]_D^{21} +26.0$ ($c = 3.93$, CH_2Cl_2) (85% ee).

Determination of enantiomeric excess was as follows: To a solution of **7c** (52 mg, 0.141 mmol) in THF (2 mL), HF-Py (0.2 mL) was added dropwise at ambient temperature. After stirring for 1.5 h, the mixture was diluted with EtOAc and poured into saturated NaHCO_3 aqueous solution. The organic phase was separated and the aqueous phase was further extracted twice with EtOAc. The combined organic layer was washed with saturated NaHCO_3 aqueous solution and brine, dried (NaSO_4) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/3) to afford **7c1** (30.8 mg, 0.122 mmol; 86%) as a colorless oil. The relative configuration was determined based on the coupling constant of ^1H NMR. **3-[(1R)-2,2,6-Trimethyl-4-oxocyclohexanecarbonyl]oxazolidin-2-one (7c1):** ^1H

NMR (CDCl_3): δ 4.39-4.44 (m, 2H), 4.23 (d, $J = 11.0$ Hz, 1H), 4.03-4.12 (m, 2H), 2.37-2.44 (m, 3H), 2.06-2.16 (m, 2H), 1.05 (s, 3H), 0.98 (s, 3H), 0.96 (d, $J = 11.1$ Hz, 3H); ^{13}C NMR (CDCl_3): δ 208.3, 173.3, 152.5, 60.5, 54.7, 52.6, 47.3, 41.8, 37.2, 31.2, 27.7, 21.2, 19.1; IR (neat, cm^{-1}): 1774, 1705; EI-MS m/z 253 (M^+); EI-HRMS Calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_4$ (M^+):

253.1314, Found: 253.1315; $[\alpha]_D^{21} +3.70$ ($c =$

1.54, CH_2Cl_2) (85% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 4/1, 0.5 ml/min) t_R 48.5 min (minor), 53.1 min (major).

3-[2-Methyl-2-(4-methylpent-3-enyl)-4-(triisopropylsilyloxy)cyclohex-3-

enecarbonyl]oxazolidin-2-one (7d): Enantiomeric excess and relative stereochemistry were determined after conversion shown below, because the diastereomers are only separable after allylation.

2-Methyl-2-(4-methylpent-3-enyl)-4-(triisopropylsilanyloxy)cyclohex-3-enecarboxylic acid S-ethyl ester (7d1): To a solution of EtSH (0.057 mL, 0.776 mmol) in THF (5 mL), *n*-BuLi (0.328 mL, 0.518 mmol) was added dropwise at -78°C . After stirring at 0°C for 30 min, **7d** (120 mg, 0.259 mmol) in THF (2 mL) was added at the same temperature. Then the mixture was stirred at the same temperature for 30 min before adding saturated NH_4Cl aqueous solution to quench the reaction. The organic phase was separated and the water phase was further extracted with ether twice. The combined organic layer was washed with water and brine, dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/30) to afford **7d1** (107 mg, 0.244 mmol; 94%) as inseparable diastereomixture.

[2-Methyl-2-(4-methylpent-3-enyl)-4-(triisopropylsilanyloxy)cyclohex-3-enyl]methanol (7d2): To a suspension of lithium aluminium hydride (45 mg, 1.20 mmol) in THF (3 mL), **7d1** (105 mg, 0.239 mmol) in THF (2 mL) was added at 0°C and the mixture was stirred at the same temperature for 20 min. Water (0.045 mL), 15% NaOH aqueous solution (0.045 mL) and water (0.135 mL) were added carefully. The mixture was filtered through a pad of celite, and the residue was washed with CH_2Cl_2 . The filtrate was concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/15) to afford **7d2** (86.5 mg, 0.227 mmol; 95%) as inseparable diastereomixture.

4-Hydroxymethyl-3-methyl-3-(4-methylpent-3-enyl)cyclohexanone (7d3): To the solution of **7d2** (85 mg, 0.223 mmol), HF-Py (0.3 mL) was added at ambient temperature. After stirring for 6 h, the mixture was diluted with EtOAc and poured into saturated NaHCO_3 aqueous solution. The organic phase was separated and the aqueous phase was further extracted twice with EtOAc. The combined organic layer was washed with water and brine, dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/2) to afford **7d3** (36.7 mg, 0.162 mmol; 73 %) as inseparable diastereomixture.

4-(*tert*-Butyldiphenylsiloxy)methyl-3-methyl-3-(4-methylpent-3-enyl)cyclohexanone (7d4):

To a solution of **7d3** (35 mg, 0.155 mmol) in DMF (1 mL), imidazole (63 mg, 0.930 mmol) and TBDPSCl (0.121 mL, 0.465 mmol) was added at ambient temperature. After 1 h, water and ether was added at 0 °C to quench the reaction. The organic layer was separated and the aqueous layer was further extracted with ether twice. The combined organic layer was washed with water twice and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/40) to afford **7d4** (diastereomixture) and TBDPSOH as mixture.

2-Allyl-4-(tert-butyldiphenylsilyloxymethyl)-5-methyl-5-(4-methylpent-3-enyl)cyclohexanone (7d5, 7d6): To a solution of HNⁱPr₂ (0.228 mL, 1.63 mmol) in THF (7 mL), *n*-BuLi (0.98 mL, 1.55 mmol) was added at –20 °C, and the solution was stirred at the same temperature for 40 min before adding **7d4** obtained as above in THF (3 mL) at the same temperature. After 1 h, allyl bromide (0.402 mL, 4.65 mmol) and HMPA (0.539 mL, 3.10 mmol) were added respectively at the same temperature, and the mixture was stirred for 2 h before the addition of saturated NH₄Cl aqueous solution to quench the reaction. The organic phase was separated and the aqueous phase was further extracted with ether twice. The combined organic layer was washed with water twice and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/50) to afford **7d5+7d6** (55.0 mg, 0.109 mmol; 2steps 71%) as diastereomixture. Separation by PTLC (EtOAc/hexane, 1/20) afforded less polar product **7d5** (5.7 mg, 0.0114 mmol) and more polar product **7d6** (34.4 mg, 0.0684 mmol). The relative stereochemistry of each compound was determined by NOESY analysis. **7d5**: ¹H NMR (CDCl₃): δ 7.64-7.68 (m, 4H), 7.36-7.44 (m, 6H), 5.73-5.83 (m, 1H), 5.01-5.09 (m, 2H), 4.90 (t, *J* = 7.1 Hz, 1H), 3.88 (dd, *J* = 4.3, 10.3 Hz, 1H), 3.76 (dd, *J* = 9.2, 10.3 Hz, 1H), 2.44-2.55 (m, 2H), 2.36-2.42 (m, 1H), 2.30 (d, *J* = 13.8 Hz, 1H), 2.00-2.05 (m, 1H), 1.98 (d, *J* = 13.8 Hz, 1H), 1.80-1.89 (m, 2H), 1.65-1.76 (m, 2H), 1.62 (s, 3H), 1.57 (s, 3H), 1.47 (s, 3H), 1.20 (dt, *J* = 4.6, 12.6 Hz, 1H), 1.04-1.10 (m, 1H), 1.05 (s, 9H), 0.90 (s, 3H); ¹³C NMR (CDCl₃): δ 211.4, 135.0, 134.4, 134.3, 132.1, 130.2, 128.5, 128.4, 126.5, 126.4, 122.8, 115.2, 61.2, 49.9, 44.5, 41.4, 39.3, 37.8, 32.7, 28.7, 25.6, 24.3, 24.2, 20.4, 17.9, 16.2; IR (neat, cm⁻¹): 1716; EI-MS *m/z* 502 (M⁺); EI-HRMS Calcd for C₃₃H₄₆O₂Si (M⁺): 502.3267, Found: 502.3268; [α]_D²⁴ –3.6 (c = 0.72, CHCl₃) (88% ee); HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol 250/1,

0.50 ml/min) *t*_R 16.1 min (minor), 17.2 min (major).

7d6: ¹H NMR (CDCl₃): δ 7.58-7.62 (m, 4H), 7.30-7.38 (m, 6H), 5.64-5.73 (m, 1H), 4.90-

5.02 (m, 3H), 3.81 (dd, $J = 4.3, 10.1$ Hz, 1H), 3.61 (dd, $J = 8.9, 10.1$ Hz, 1H), 2.34-2.43 (m, 2H), 2.00-2.10 (m, 4H), 1.72-1.84 (m, 4H), 1.59 (s, 3H), 1.51 (s, 3H), 1.49 (s, 3H), 1.06-1.19 (m, 2H), 0.99 (s, 9H), 0.73 (s, 3H); ^{13}C NMR (CDCl_3): δ 211.8, 134.7, 134.3, 132.2, 132.2, 130.3, 128.5, 126.4, 126.4, 122.8, 115.3, 62.1, 49.5, 45.3, 39.7, 39.6, 39.1, 33.3, 28.6, 25.6, 24.3, 21.2, 20.5, 17.9, 16.2; IR (neat, cm^{-1}): 1710; EI-MS m/z 502 (M^+); EI-HRMS Calcd for $\text{C}_{29}\text{H}_{37}\text{O}_2\text{Si}$ ($\text{M}^+ - \text{tBu}$): 445.2563, Found: 445.2559; $[\alpha]_D^{24} -25.5$ ($c = 1.66$, CHCl_3) (86% ee); HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol 250/1, 0.50 ml/min) t_R 20.6 min (major), 31.0 min (minor).

3-[(1R,2S)-2-Methyl-2-(4-methylpent-3-enyl)-4-(triisopropylsiloxy)-3-

(triisopropylsiloxymethyl)cyclohex-3-enecarbonyl]oxazolidin-2-one (7e): ^1H NMR (C_6D_6):

δ 5.30 (t, $J = 6.9$ Hz, 1H), 5.04 (d, $J = 12.0$ Hz, 1H), 4.63 (d, $J = 12.0$ Hz, 1H), 4.23 (dd, $J = 3.5, 6.3$ Hz, 1H), 3.09-3.24 (m, 4H), 2.30-2.38 (m, 1H), 2.04-2.20 (m, 7H), 1.65 (s, 3H), 1.60 (s, 3H), 1.57 (s, 3H), 1.14-1.19 (m, 42H); ^{13}C NMR (C_6D_6): δ 173.4, 152.8, 145.1, 130.4, 125.6, 120.2, 60.7, 59.0, 45.8, 42.5, 39.3, 36.3, 28.1, 27.5, 25.6, 23.9, 21.9, 17.4, 13.6, 12.7; IR (neat, cm^{-1}): 1780; EI-MS m/z 649 (M^+); EI-

HRMS Calcd for $\text{C}_{36}\text{H}_{67}\text{O}_5\text{Si}_2$ (M^+): 649.4558, Found: 649.4570; $[\alpha]_D^{26} +1.20$ ($c = 1.09$, CH_2Cl_2) (66% ee).

The relative

stereochemistry of **7e** and **7f** was determined by NOE analysis.

Determination of enantiomeric excess was as follows: To a solution of **7e** (113 mg, 0.174 mmol) in THF (3 mL), HF-Py (0.3 mL) was added dropwise at ambient temperature. After stirring for 2 h, the mixture was diluted with EtOAc and poured into saturated NaHCO_3 aqueous solution. The organic phase was separated and the aqueous phase was further extracted twice with EtOAc. The combined organic layer was washed with saturated NaHCO_3 aqueous solution and brine, dried (NaSO_4) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/2) to afford **7e1** (42.0 mg, 0.132 mmol; 76%) as a colorless oil. **3-[(1R,2S)-2-Methyl-3-methylene-2-(4-methylpent-3-enyl)-4-oxocyclohexanecarbonyl]oxazolidin-2-one (7e1):** ^1H NMR (CDCl_3): δ 5.80 (s, 1H), 5.16 (s, 1H), 5.04 (s, 1H), 4.38-4.44 (m, 2H), 4.27 (dd, $J = 4.3, 8.3$ Hz, 1H), 4.02-4.06 (m, 2H), 2.43-2.59 (m, 2H), 2.10-2.26 (m, 3H), 1.78-1.84 (m, 3H), 1.65 (s, 3H), 1.59 (s, 3H), 1.54 (s, 3H),

1.23-1.28 (m, 1H), 1.18 (s, 3H); ^{13}C NMR (CDCl_3): δ 202.3, 173.8, 153.3, 153.2, 131.9, 124.0, 117.5, 61.8, 45.8, 42.9, 42.9, 37.5, 34.7, 25.7, 23.5, 22.4, 22.3, 17.6; IR (neat, cm^{-1}): 1775, 1693; EI-MS m/z 319 (M^+); EI-HRMS Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_4$ (M^+): 319.1784, Found: 319.1785; $[\alpha]_D^{26}$ -29.0 ($c = 0.57$, CH_2Cl_2) (66% ee); HPLC (DAICEL CHIRALPAK AD-H, AD-H; hexane/2-propanol 9/1, 1.0 ml/min) t_R 33.1 min (major), 34.4 min (minor).

3-[(1*R*,2*R*)-2-Methyl-2-(4-methylpent-3-enyl)-4-(triisopropylsiloxy)-3-

(triisopropylsilyloxymethyl)cyclohex-3-enecarbonyl]oxazolidin-2-one (7f): ^1H NMR (CDCl_3):

δ 5.27 (t, $J = 6.9$ Hz, 1H), 5.01 (d, $J = 11.5$ Hz, 1H), 4.62 (d, $J = 11.5$ Hz, 1H), 4.32 (dd, $J = 3.5, 9.2$ Hz, 1H), 3.14-3.18 (m, 4H), 2.34-2.41 (m, 1H), 2.21-2.28 (m, 2H), 2.10-2.17 (m, 2H), 1.94-2.07 (m, 3H), 1.78 (s, 3H), 1.64 (s, 3H), 1.62 (s, 3H), 1.17-1.20 (m, 21H), 1.12-1.14 (m, 21H); ^{13}C NMR (CDCl_3): δ 174.3, 153.1, 146.7, 130.6, 125.3, 120.1, 60.7, 59.1, 42.7, 42.4, 40.3, 38.8, 31.7, 29.3, 25.6, 23.8, 22.2, 18.2,

18.1, 17.5, 13.6, 12.2; IR (neat, cm^{-1}): 1780; EI-MS m/z 649 (M^+); EI-HRMS Calcd for $\text{C}_{36}\text{H}_{67}\text{NO}_5\text{Si}_2$ (M^+): 649.4558, Found: 649.4564; $[\alpha]_D^{26}$ -35.1 ($c = 1.46$, CH_2Cl_2) (87% ee). The relative stereochemistry of **7e** and **7f** was determined by NOE analysis.

Determination of enantiomeric excess was as follows: To a solution of **7f** (70 mg, 0.108 mmol) in THF (3 mL), HF-Py (0.3 mL) was added dropwise at ambient temperature. After stirring for 2 h, the mixture was diluted with EtOAc and poured into saturated NaHCO_3 aqueous solution. The organic phase was separated and the aqueous phase was further extracted twice with EtOAc. The combined organic layer was washed with saturated NaHCO_3 aqueous solution and brine, dried (NaSO_4) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/2) to afford **7f1** (31.7 mg, 0.099 mmol; 92%) as a colorless oil.

3-[(1*R*,2*R*)-2-Methyl-3-methylene-2-(4-methylpent-3-enyl)-4-oxocyclohexanecarbonyl]oxazolidin-2-one (7f1): ^1H NMR (CDCl_3): δ 5.91 (s, 1H), 5.13 (s,

1H), 5.02 (t, $J = 7.2$ Hz, 1H), 4.41 (t, $J = 8.3$ Hz, 2H), 4.31 (dd, $J = 3.9, 4.3$ Hz, 1H), 4.03 (t, $J = 8.3$ Hz, 2H), 2.63-2.71 (m, 1H), 2.46-2.52 (m, 1H), 2.28-2.35 (m, 1H), 1.87-2.01 (m, 3H), 1.65 (s, 3H), 1.57 (s, 3H), 1.49-1.54 (m, 1H), 1.33-1.40 (m, 1H), 1.20 (s, 3H) ^{13}C NMR (CDCl_3): δ 200.3, 173.1, 152.1, 150.7, 131.0, 122.1, 116.8, 60.5, 42.9, 41.6, 41.4, 38.8, 34.6, 24.4, 20.7, 20.4, 20.3, 16.4; IR (neat, cm^{-1}): 1692, 1775; EI-MS

m/z 522 (M^+); EI-HRMS Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_4$ (M^+): 319.1784, Found: 319.1781; $[\alpha]_D^{26}$ $+8.29$ ($c = 0.70$, CH_2Cl_2) (87% ee); HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 9/1, 1.0 ml/min) t_R 20.9 min (major), 24.3 min (minor).

Conversion of the product

(1*R*,2*R*)-2-Methyl-2-(4-methylpent-3-enyl)-4-(triisopropylsiloxy)-3-

(triisopropylsiloxymethyl)cyclohex-3-enecarboxylic acid *S*-ethyl ester (**7f2**): To a solution of EtSH (0.12 mL, 1.62 mmol) in THF (5 mL), *n*-BuLi (0.68 mL, 1.58 M in hexane) was added dropwise at -78°C . After stirring at 0°C for 30 min, **7f** (350 mg, 0.538 mmol) in THF (4 mL) was added at 0°C , and the mixture was stirred at 0°C for 30 min before saturated NH_4Cl aqueous solution was added. The organic phase was separated and the aqueous phase was further extracted twice with ether. The combined organic layer was washed with water and brine, dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/30) to afford **7f2** (327 mg, 0.523 mmol, 97%) as a colorless oil. ^1H NMR (C_6D_6): δ 5.34 (t, $J = 6.4$ Hz, 1H), 5.09 (d, $J = 11.3$ Hz, 1H), 4.42 (d, $J = 11.3$ Hz, 1H), 2.87 (dd, $J = 2.5, 11.3$ Hz, 1H), 2.65-2.75 (m, 2H), 2.46-2.54 (m, 1H), 1.87-2.19 (m, 6H), 1.75-1.80 (m, 1H), 1.69 (s, 3H), 1.68 (s, 3H), 1.63 (s, 3H), 1.14-1.17 (m, 21H), 1.06-1.09 (m, 21H), 1.05 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (C_6D_6): δ 198.7, 145.8, 129.5, 124.2, 118.5, 58.1, 54.1, 39.8, 37.2, 28.7, 24.6, 23.8, 22.8, 22.2, 21.1, 17.2, 17.1, 13.8, 12.6, 11.3; IR (neat, cm^{-1}): 1694; EI-MS m/z 624 (M^+); EI-HRMS Calcd for $\text{C}_{35}\text{H}_{68}\text{O}_3\text{Si}_2$ (M^+): 624.4428, Found: 624.4421; $[\alpha]_D^{25} -24.2$ ($c = 1.30$, CH_2Cl_2) (87% ee).

[(1*R*,2*R*)-2-Methyl-2-(4-methylpent-3-enyl)-4-(triisopropylsiloxy)-3-

(triisopropylsiloxymethyl)cyclohex-3-enyl]methanol (**7f3**): To a suspension of lithium aluminum hydride (94 mg, 2.48 mmol), **7f2** (310 mg, 0.496 mmol) in THF (3 mL) was added at 0°C . After 10 min, water (0.094 mL), 15% NaOH aqueous solution (0.094 mL) and water

(0.282 mL) were added carefully at 0 °C. The suspension was filtered through a pad of celite and washed with CH₂Cl₂. The filtrate was concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 15/1) to afford **7f3** (268 mg, 0.473 mmol; 95%) as a colorless oil. ¹H NMR (C₆D₆): δ 5.29 (t, *J* = 6.1 Hz, 1H), 5.10 (d, *J* = 11.2 Hz, 1H), 4.42 (d, *J* = 11.2 Hz, 1H), 3.68 (dd, *J* = 3.4, 10.1 Hz, 1H), 3.21 (dd, *J* = 9.2, 10.1 Hz, 1H), 2.02-2.15 (m, 4H), 1.87-2.00 (m, 2H), 1.60-1.79 (m, 3H), 1.69 (s, 3H), 1.63 (s, 3H), 1.29 (s, 3H), 1.17-1.20 (m, 21H), 1.07-1.11 (m, 21H); ¹³C NMR (C₆D₆): δ 146.9, 129.4, 119.0, 61.7, 58.3, 40.9, 38.4, 36.7, 29.1, 24.7, 22.6, 22.6, 20.2, 17.4, 17.2, 16.6, 12.8, 11.4; IR (neat, cm⁻¹): 3307, 1647; EI-MS *m/z* 566 (M⁺); EI-HRMS Calcd for C₃₃H₆₆O₃Si₂ (M⁺): 566.4550, Found: 566.4549; [α]_D²⁵ -25.7 (c = 0.86, CH₂Cl₂) (87% ee).

(3R,4R)-4-Methoxymethoxymethyl-3-methyl-3-(4-methylpent-3-enyl)-1-

(triisopropylsiloxy)-2-(triisopropylsiloxymethyl)cyclohex-1-ene (8f): To a solution of **7f3** (225 mg, 0.397 mmol) in 1,2-dichloroethane (5 mL), Hünig base (0.414 mL, 2.38 mmol), MOMCl (0.090 mL, 1.19 mmol) and TBAI (220 mg, 0.596 mmol) were added at 0 °C. The mixture was then stirred at ambient temperature for 2 h before adding water to quench the reaction. The organic phase was separated and the aqueous phase was further extracted with ether twice. The combined organic layer was washed with water and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/100 to 1/30) to afford **8f** (225 mg, 0.368 mmol; 93%) as a colorless oil. ¹H NMR (C₆D₆): δ 5.31 (t, *J* = 7.0 Hz, 1H), 5.11 (d, *J* = 11.0 Hz, 1H), 4.54 (d, *J* = 6.4 Hz, 1H), 4.51 (d, *J* = 6.4 Hz, 1H), 4.44 (d, *J* = 11.0 Hz, 1H), 3.75 (dd, *J* = 3.4, 9.2 Hz, 1H), 3.31 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.21 (s, 3H), 2.18-2.26 (m, 1H), 2.06-2.18 (m, 3H), 1.87-2.03 (m, 3H), 1.77-1.84 (m, 1H), 1.68 (s, 3H), 1.63 (s, 3H), 1.30 (s, 3H), 1.18-1.20 (m, 21H), 1.07-1.10 (m, 21H); ¹³C NMR (C₆D₆): δ 146.8, 129.4, 124.6, 119.1, 95.8, 67.5, 58.4, 38.7, 38.5, 36.6, 29.2, 24.7, 22.7, 22.6, 20.9, 17.4, 17.2, 16.6, 12.8, 11.4; IR (neat, cm⁻¹): 1646; EI-MS *m/z* 610 (M⁺); EI-HRMS Calcd for C₃₅H₇₀O₄Si (M⁺): 610.4813, Found: 610.4808; [α]_D²³ -25.1 (c = 0.87, CH₂Cl₂) (87% ee).

4-Methoxymethoxymethyl-3-methyl-3-(4-methylpent-3-enyl)-2-

(triisopropylsiloxy)methyl)cyclohexanone (8f1): To a solution of **8f** (185 mg, 0.303 mmol) in THF (6 mL), AcOH (0.275 mL, 3.03 mmol) and TBAF (1.5 mL, 1 M in THF) were added at 0 °C. The mixture was then stirred at ambient temperature for 24 h before adding water. The organic phase was separated and the aqueous phase was further extracted with EtOAc twice. The combined organic layer was washed with water and brine, dried (Na₂SO₄) and concentrated to give a residue, which was passed through a silica gel flash chromatography (short column to remove AcOH and some polar impurity, elute: EtOAc/hexane, 1/1) to give a residue, which was used in next step without further purification. To a solution of the products in DMF (5 mL),

imidazole (103 mg, 1.52 mmol) and TIPSCl (0.181 mL, 0.909 mmol) were added at 0 °C. The mixture was then stirred at 0 °C for 2 h and at ambient temperature for 20 h before water and ether were added at 0 °C to quench the reaction. The organic phase was separated and the aqueous phase was further extracted with EtOAc twice. The combined organic layer was washed with water (twice) and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel chromatography to afford an inseparable diastereomixture **8f1** (109.3 mg, 0.240 mmol; 2steps 79%, ratio 1/1) as a colorless oil.

4-Methoxymethoxymethyl-3-methyl-6-(3-methylbut-2-enyl)-3-(4-methylpent-3-enyl)-2-

(triisopropylsiloxyethyl)cyclohexanone (9f, 10f): To a solution of diisopropylamine (0.119 mL, 0.848 mmol) in THF (4 mL), *n*-BuLi (0.515 mL, 1.58 M in hexane) was added at –20 °C. After 30 min, **8f1** (74 mg, 0.163 mmol) in THF (3 mL) was added at –20 °C. Then after 50 min, prenyl bromide (0.282 mL, 2.45 mmol) and HMPA (0.283 mL, 1.63 mmol) was added at –20 °C, and the mixture was stirred at the same temperature before adding saturated NH₄Cl aqueous solution to quench the reaction. The organic phase was separated and the aqueous phase was further extracted with ether twice. The combined organic layer was washed with water (twice) and brine, dried (Na₂SO₄) and concentrated to give a residue, which was purified by silica gel flash chromatography (EtOAc/hexane, 1/40) to afford **9f** (less polar, 35.8 mg, 0.0685 mmol; 42%) and **10f** (more polar, 36.1 mg, 0.0690 mmol; 42%) as a colorless oil. The relative stereochemistry was determined by NOE analysis. **9f**: ¹H NMR (CDCl₃): δ 5.08 (t, *J* = 6.3 Hz, 1H), 5.01 (t, *J* = 6.2

Hz, 1H), 4.71 (d, *J* = 6.4 Hz, 1H), 4.68 (d, *J* = 6.4 Hz, 1H), 3.90 (dd, *J* = 9.4, 9.4 Hz, 1H), 3.80 (dd, *J* = 4.0, 9.4 Hz,

1H), 3.64 (dd, *J* = 4.3, 10.0 Hz, 1H), 3.40 (s, 3H), 2.61 (dd, *J* = 4.3, 6.4 Hz, 1H), 2.38-2.49 (m, 2H), 2.20-2.25 (m, 1H), 1.76-1.98 (m, 4H), 1.65 (s, 6H), 1.60 (s, 3H), 1.55 (s, 3H), 1.47-1.52 (m, 1H), 1.16 (s, 3H), 1.03-1.10 (m, 23H); ¹³C NMR (CDCl₃): δ 210.2, 131.5, 130.5, 122.8, 120.9, 95.5, 65.9, 59.4, 56.7, 54.1, 45.2, 42.2, 38.7, 34.4, 29.7, 26.4, 24.5, 24.4, 22.5, 20.3, 16.8, 16.8, 16.6, 16.3, 10.7; IR (neat, cm⁻¹): 1714; EI-MS *m/z* 522 (M⁺); EI-HRMS Calcd for C₃₁H₅₈O₄Si (M⁺): 522.4104, Found: 522.4095; [α]_D²³ –18.3 (c = 0.69, CH₂Cl₂) (87% ee). **10f**: ¹H NMR (CDCl₃): δ 5.07 (t, *J* = 6.2 Hz, 1H), 5.01 (t, *J* = 6.2 Hz, 1H), 4.61 (d, *J* = 6.6 Hz, 1H), 4.59 (d, *J* = 6.6 Hz, 1H), 4.14 (dd, *J* = 6.3, 10.3 Hz, 1H), 3.68 (dd, *J* = 3.4, 9.2 Hz, 1H), 3.64 (dd, *J* = 4.0, 10.3 Hz, 1H), 3.35 (s, 3H), 3.23 (dd, *J* = 9.2, 9.2 Hz, 1H), 2.80 (dd, *J* = 4.0, 6.3 Hz, 1H), 2.34-2.44 (m, 2H), 2.14-2.29 (m, 2H), 2.00-2.10 (m, 2H), 1.64-1.79 (m, 2H), 1.67 (s, 3H), 1.65 (s,

3H), 1.63 (s, 3H), 1.61 (s, 3H), 1.48-1.55 (m, 1H), 1.37-1.45 (m, 1H), 1.02-1.05 (m, 21H), 0.64 (s, 3H); ^{13}C NMR (CDCl_3): δ 214.4, 133.7, 131.7, 124.1, 121.0, 96.7, 68.2, 57.7, 55.6, 55.3, 50.0, 43.5, 37.8, 37.1, 31.4, 30.5, 25.8, 21.7, 18.2, 18.1, 18.1, 18.0, 17.8; IR (neat, cm^{-1}): 1712; EI-MS m/z 522 (M^+); EI-HRMS Calcd for $\text{C}_{31}\text{H}_{58}\text{O}_4\text{Si}$ (M^+): 522.4104, Found: 522.4100; $[\alpha]^{24}_{\text{D}} -43.0$ ($c = 1.42$, CH_2Cl_2) (87% ee).

Enantiomeric excess' of X and X were determined by converting TIPS ether to Bz ester (1. HF-py, THF; 2. BzCl, DMAP, Py) **9f1**: ^1H NMR (CDCl_3): δ 7.97 (d, $J = 8.0$ Hz, 2H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.41 (dd, $J = 7.5$, 8.0 Hz, 2H), 5.08 (t, $J = 7.5$ Hz, 1H), 5.02 (t, $J = 7.2$ Hz, 1H), 4.74 (dd, $J = 8.0$, 11.2 Hz, 1H), 4.70 (d, $J = 6.9$ Hz, 1H), 4.66 (d, $J = 6.9$ Hz, 1H), 4.40 (dd, $J = 3.5$, 11.2 Hz, 1H), 3.92 (dd, $J = 9.2$, 9.7 Hz, 1H), 3.80 (dd, $J = 4.0$, 9.7 Hz, 1H), 3.38 (s, 3H), 2.91 (dd, $J = 3.5$, 8.0 Hz, 1H), 2.49-2.57 (m, 1H), 2.42-2.48 (m, 1H), 2.27 (ddd, $J = 1.7$, 6.3, 13.7 Hz, 1H), 2.02-2.06 (m, 1H), 1.93-1.99 (m, 1H), 1.79-1.92 (m, 1H), 1.66 (s, 6H), 1.60 (s, 3H), 1.56 (s, 3H), 1.53-1.59 (m, 1H), 1.24 (s, 3H), 1.22-1.28 (m, 1H), 1.11-1.17 (m, 1H); ^{13}C NMR (CDCl_3): δ 210.3, 166.7, 133.2, 132.9, 132.1, 130.4, 129.7, 128.4, 123.7, 121.9, 96.8, 67.2, 60.1, 56.7, 55.5, 46.7, 43.7, 39.8, 35.8, 30.9, 27.7, 25.9, 25.7, 23.7, 21.6, 17.9, 17.6; IR (neat, cm^{-1}): 1716; EI-MS m/z 470 (M^+); EI-HRMS Calcd for $\text{C}_{29}\text{H}_{42}\text{O}_5$ (M^+): 470.3032, Found: 470.3021; $[\alpha]^{24}_{\text{D}} -22.5$ ($c = 0.72$, CHCl_3) (87% ee); HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol 100/1, 1.0 ml/min) t_{R} 24.2 min (major), 28.3 min (minor). **10f1**: ^1H NMR (CDCl_3): δ 7.95 (d, $J = 6.9$ Hz, 2H), 7.50 (t, $J = 7.5$ Hz, 1H), 7.38 (dd, $J = 6.9$, 7.5 Hz, 2H), 5.07 (t, $J = 7.2$ Hz, 1H), 5.00 (t, $J = 7.5$ Hz, 1H), 4.60-4.65 (m, 3H), 4.43 (dd, $J = 3.5$, 10.9 Hz, 1H), 3.70 (dd, $J = 4.0$, 9.2 Hz, 1H), 3.36 (s, 3H), 3.26 (dd, $J = 8.6$, 9.2 Hz, 1H), 3.11 (dd, $J = 3.5$, 9.2 Hz, 1H), 2.42-2.54 (m, 3H), 2.18-2.32 (m, 2H), 2.08-2.16 (m, 2H), 1.81 (dt, $J = 5.2$, 13.8 Hz, 1H), 1.64 (s, 3H), 1.61 (s, 3H), 1.58 (s, 3H), 1.57 (s, 3H), 1.46-1.57 (m, 2H), 0.74 (s, 3H); ^{13}C NMR (CDCl_3): δ 213.1, 166.6, 134.0, 132.9, 132.2, 130.3, 129.7, 128.3, 123.6, 120.5, 96.8, 68.0, 59.5, 55.4, 51.0, 50.1, 43.8, 37.4, 36.9, 31.4, 30.7, 25.8, 25.7, 21.6, 18.1, 18.0, 17.7; IR (neat, cm^{-1}): 1718; EI-MS m/z 470 (M^+); EI-HRMS Calcd for $\text{C}_{29}\text{H}_{42}\text{O}_5$ (M^+): 470.3032, Found: 470.3041; $[\alpha]^{24}_{\text{D}} -66.0$ ($c = 1.13$, CHCl_3) (87% ee); HPLC (DAICEL CHIRALPAK AD-H, hexane/2-propanol 100/1, 1.0 ml/min) t_{R} 18.6 min (major), 23.2 min (minor).

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