Supplementary information

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Experimental Section

General: All moisture or oxygen-sensitive reactions were carried out under nitrogen atmosphere in oven-dried flasks. The reagents had purchased from Sigma Aldrich chemicals and solvents were used purified by distillation over-drying agents that indicated THF (Na), CHCl3 (CaH2), acetone (CaSO4), C6H6 (Na), MeOH (Mg), and were transformed under nitrogen. Technical grade ethyl acetate, hexane was used for column chromatography and was distilled before use. All the reactions were monitored by thin-layer chromatography (TLC) using silica gel F254 plates. The products were purified by silica gel column chromatography on silica gel (60-120 mesh and 100-200 meshes) packed in a glass column. Optical rotations of chiral compounds measured with a digital polarimeter using 1 mL cell of 1 dm path length and FT-IR spectra recorded on KBr disc or neat. The 1H and 13C NMR spectra were recorded in CDCl3 and CD3OD on a Bruker 300, 400 and 500 MHz instruments at ambient temperature. Mass spectra recorded on Micro mass VG 7070H mass spectrometer for EI, VG Autospec mass spectrometer for FABMS and micromass Quatro LC-triple quadrupole mass spectrometer for ESI analysis.

2-methyl-2-(3-oxyxenyl)cyclohexane-1,3-dione (10): To a stirred solution of 2-methyl-1,3-cyclohexadione 7 (5.0 g, 39.63 mmol) in ethyl acetate (200 mL), was treated with triethylamine (6.62 mL, 47.55 mmol), and ethyl vinyl ketone (4.51 mL, 45.57 mmol) at room temperature. The resulting mixture was heating at 70 °C for 10 hours. Then, the mixture was cooled to room temperature and dilute with water (100 mL) and stirred for 15 min. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 x 100 mL) three times. The combined organic layers were washed with brine, dried over anhydrous Na2SO4, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel eluting with EtOAc/n-hexane (1:3) to afford the 10 (7.66 g, 92%) as a colorless oil.

(S)-5,8a-dimethyl-3,4,8a-tetrahydronaphthalene-1,6(2H,7H)-dione (11): To a stirred solution of 10 (3 g, 14.26 mmol) in DMF (210 mL) was sequentially added L-phenylalanine (2.35 g, 14.26 mmol) and D-camphor sulfonic acid (1.65 g, 7.13 mmol) at room temperature and concentrated under nitrogen atmosphere. The resulting mixture was stirring at the same temperature for 24 h. Then, the mixture was poured into cold aqueous NaHCO3 solution, and extracted with ethyl acetate (3 x 100 mL). The combined extracts were washed with brine and dried over anhydrous Na2SO4, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel eluting with EtOAc/n-hexane (1:3) to afford the chiral enone 11 (2.27 g, 83% yield, 95% ee) as a yellow oil. Rf = 0.46 (35% ether in hexane). [α]D25 = +127.44 (c = 1.64, CHCl3); IR (Neat, νmax cm−1): 2949, 1710, 1666, 1610, 1452, 1310; 13C NMR (125 MHz, CDCl3) δ: 210.1, 209.9, 64.3, 37.6, 36.9, 35.8, 29.7, 19.8, 17.5, 7.6.

(5)-5,8a-dimethyl-3,4,8a-tetrahydro-2H-spiro[naphthalene-1,2'-[1,3]dioxolan]-6(7H)-one (12): To a stirred solution of enone 11 (1.05 g, 5.46 mmol) in benzene (20 mL) was sequentially added p-toluensulfonic acid (94 mg, 0.546 mmol) and ethylene glycol (0.36 mL, 6.55 mmol) at room temperature. The resulting mixture was then stirred vigorously at 110 °C using a Dean-Stark apparatus for overnight. After cooling the resulting solution was poured into aqueous NaHCO3 at 0 °C. The organic phase was separated, and then the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined extracts were washed with brine, dried over MgSO4, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography, eluting with EtOAc/n-hexane (2:8) to afford 12 (1.16 g, 90%) as a white solid. Rf = 0.57 (35% ether in hexane). [α]D25 = +103.38 (c = 0.46, CHCl3); IR (Neat, νmax cm−1): 2951, 1665, 1337, 1163, 1092, 1029, 920; 1H NMR (500 MHz, CDCl3) δ: 5.00 – 3.89 (m, 4H), 2.74 – 2.70 (m, 1H), 2.49 – 2.35 (m, 2H), 2.23 (td, J = 13.0, 8.0, 5.5 Hz, 1H), 2.18 – 2.10 (m, 1H) 1.88 (td, J = 13.5, 8.5, 5.0 Hz, 2H), 1.83 – 1.77 (m, 4H), 1.72 – 1.57 (m, 4H), 1.32 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 211.9, 197.5, 158.1, 130.5, 50.4, 37.1, 33.1, 29.4, 27.0, 23.1, 21.3, 11.1; ESI-MS (m/z): 215 [M + Na]+.
**[8aS]-5,5,8a-trimethylhexahydro-2H-spiro[naphthalene-1,2'-[1,3] dioxolan]-6(5H)-one (13):** To a stirred reflux solution of lithium (519 mg, 74.8 mmol, 4.31 eq) in liquid ammonia (100 mL) and THF (20 mL) at −40 °C, was added a solution of 12 (4.09 g, 17.32 mmol) in dry THF (50 mL). The resulting solution was stirred at the same temperature for one hour and then, added the methyl iodide (10.78 mL, 173.2 mmol, 10.0 eq) as rapidly as possible. After stirring for 1.5 h, the reaction was quenched with solid ammonium chloride (10 g) and allowed to room temperature until all most all ammonia was evaporated. After it was poured into water (20 mL) and extracted with diethyl ether (3 × 50 mL). The combined extracts were washed with brine and dried (MgSO₄) and concentrated in vacuo. The residue was purified by column chromatography on silica gel using eluent EtOAc/Hexane (1:9) to afford 13 (2.84 g, 65% yield) as a yellow solid. *Rf* = 0.45 (25% EtOAc in hexane).

**[6S,8aS]-5,5,8a-trimethyloctahydro-2H-spiro[naphthalene-1,2'-[1,3] dioxolan]-6-ol (14):** To a stirred solution of LiAlH₄ (258 mg, 6.53 mmol) in Et₂O (20 mL) was added drop-wise 13 (1.5 g, 5.94 mmol) in Et₂O (20 mL) at 10 °C under nitrogen. The residue was purified by column chromatography on silica gel eluting with EtOAc/n-hexane (1:9) to afford 14 (1.33 g, 88%) as a white solid. *Rf* = 0.40 (25% EtOAc in hexane). [α]D = −166.6 (c = 0.44, CHCl₃); IR (Neat, fms): 3440, 2944, 2873, 1458, 1107, 1042, 951 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ: 4.39 – 3.88 (m, 3H), 3.85 – 3.80 (m, 1H), 3.24 (dd, J = 10.0, 4.5 Hz, 1H), 1.70 – 1.29 (m, 11H), 1.04 (s, 3H), 0.98 (s, 3H), 0.79 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ: 139.4, 128.0, 110.7, 109.7, 106.6, 98.9, 86.1, 71.2, 65.1, 64.7, 48.1, 43.0, 38.8, 30.3, 28.6, 27.9, 27.0, 23.0, 20.5, 16.4, 15.3; ESI-HRMS (m/z): calc'd for C₁₅H₂₀O₃ [M + Na]+ 255.1960, found 255.1968.

**[6S,8aS]-6-(benzoxyl)-5,5,8a-trimethyloctahydro-2H-spiro[naphthalene-1,2'-[1,3] dioxolane] (15):** To a flame dry two-neck flask equipped with stir bar and NaH (98 mg, 60% dispersion in mineral oil, 4.11 mmol) in DMF (4 mL) was added dropwise 14 (350 mg, 1.37 mmol) in DMF (2 mL) at 0 °C. The resulting mixture was stirred for 1 h at room temperature and was added benzyl bromide (0.24 mL, 2.05 mmol) at the same temperature. The resulting mixture was allowed to room temperature and stirred for 24 h. After that, cooling to 0 °C, the excess LAH was quenched with a minimum amount of saturated ammonium chloride solution. The mixture was purified through a pad of celite and washed with diethyl ether several times. The combined organic layer was washed with brine and dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel eluting with EtOAc/n-hexane (1:9) to afford 15 (444 mg, 94 %) as a colorless oil. *Rf* = 0.40 (10% EtOAc in hexane). [α]D = +19.03 (c = 0.60, CHCl₃); IR (Neat, fms): 3440, 2944, 2872, 1455, 1109, 1066, 949 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ: 7.36 – 7.23 (m, 5H), 4.66 (dd, J = 12.0 Hz, 1H), 4.42 (dd, J = 12.0 Hz, 1H), 3.96 – 3.88 (m, 3H), 3.86 – 3.79 (m, 1H), 2.96 (dd, J = 10.0, 5.0 Hz, 1H), 1.89 – 1.82 (m, 1H), 1.69 – 1.65 (m, 1H), 1.63-1.57 (m, 1H), 1.53 – 1.23 (m, 8H), 1.06 (s, 3H), 0.99 (s, 3H), 0.85 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ: 139.4, 128.0, 127.3, 127.1, 113.3, 86.1, 71.2, 65.1, 64.6, 48.6, 43.0, 38.8, 30.3, 28.5, 28.1, 23.1, 22.5, 20.4, 16.5, 16.3; ESI-MS (m/z): 367 [M + Na]+.
To a stirred solution of ketone 6 (1.3 g, 4.32 mmol) in THF (15 mL) was added LDA (lithium disopropylamine hydride) (5.19 mL, 5.19 mmol, 1.2 eq) in THF at 0 °C. The resulting mixture was stirred 15 min at the same temperature. After that, it was added a solution of chlorotrimethylsilane (0.65 mL, 5.19 mmol, 1.2 eq), and triethylamine (0.72 mL, 5.19, 1.2 eq) in THF (5 mL) at the same temperature. The resulting mixture was at the same temperature stirred for 1 hour. The reaction mixture was diluted with hexane (20 mL) and added saturated aqueous sodium potassium tartrate solution (20 mL) and stirred vigorously 1 hour at room temperature. The organic phase was separated, and the aqueous layer was extracted using diethyl ether (2 × 20 mL). The organic layer was washed with brine, dried over MgSO₄, and concentrated in vacuo to afford single isomer (0.9 g, 60%) as a colorless liquid. Then it was used directly next reaction without purification.

To a stirred solution of above crude silyl enol ether (1.3 g, 3.48 mmol) in THF (15 mL) containing 4 Å molecular sieves at 0 °C, was added allyl bromide (1.50 mL, 17.44 mmol, 5.0 eq) and suspension of benzyltrimethylammonium fluoride (977 mg, 5.22 mmol, 1.5 eq) in THF (2 mL). The resulting mixture was stirred 3 hours at room temperature. After the completion of the reaction filtrate and concentrate in vacuo.

The residue was purified by column chromatography to obtained allylated compound (1.01 g) with (1:1) mixture of epimers. Then it was dissolved in MeOH and added K₂CO₃ (0.5 g) and then allowed to stir at room temperature for 3 hours. After that dissolve in CH₂Cl₂ and filtrate through a pad of celite, and concentration in vacuo to afford single isomer (0.9 g, 60%) as a colorless liquid. Then it was used directly next reaction without purification.

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(3S,3aS,5aR,7S,9aS)-7-(benzoyloxy)-3,6,6,9a-tetramethyl-3a,4,5,5a,6,7,8,9,9a-decahydro-2H-cyclopenta [a] naphthalen-2-one (3): To a stirred solution of enone 16 (520 mg, 1.53 mmol) in THF (8 mL) was added LiHMDS (1.68 mL, 1.68 mmol, 1 M in THF) at 0 °C, over a period of 5 min. The resulting pale yellow solution was stirred at 0 °C for 1 hour, and then, cooled to -40 °C, and was sequentially added HMPA (0.5 mL) and MeI (0.10 mL, 1.68 mmol). The reaction mixture was allowed to warm to 0 °C and stirred for 1 hour, and then quenched with water (10 mL). The organic phase was separated, and the aqueous phase was extracted using diethyl ether (2 × 15 mL). The combined extracts were washed with water and brine and dried over Na2SO4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (3:7) to furnish the methylated enone 3 (399 mg, 74%) as a white solid. Rf = 0.4 (20% EtOAc in hexane). [α]D25 = -92.17 (c = 0.34, CHCl3); IR (Neat, νmax): 3447, 2945, 2877, 1706, 1464, 1135, 769 cm-1; 1H NMR (500 MHz, CDCl3) δ: 7.36–7.33 (m, 4H), 7.28–7.24 (m, 1H), 5.66 (d, J = 1.0 Hz, 1H), 4.68 (d, J = 11.5 Hz, 1H), 4.44 (d, J = 11.5 Hz, 1H), 2.95 (dd, J = 11.5, 4.0 Hz, 1H), 2.46–2.42 (m, 1H), 2.33–2.28 (m, 1H), 2.01–1.96 (m, 1H), 1.94–1.89 (m, 1H), 1.82 (dt, J = 12.5, 3.0 Hz, 1H), 1.78–1.73 (m, 1H), 1.67–1.53 (m, 3H), 1.71 (s, 3H), 1.15 (d, J = 7.5 Hz, 3H), 1.12–1.03 (m, 2H), 0.94 (s, 3H); 13C NMR (100 MHz, CDCl3) δ: 211.8, 191.5, 139.0, 128.2, 127.4, 127.3, 121.0, 85.7, 71.5, 52.8, 48.0, 47.0, 39.7, 39.4, 34.8, 34.4, 28.3, 22.7, 20.9, 19.6, 16.6, 14.8; ESI-MS (m/z): calcld for C24H22O2Na [M + Na]+: 353.2471, found 353.2473.

Ethyl(Z)-7-((tert-butyl(dimethyl)silyloxy)-2-methylhept-2-en-1-olate (19a): To a stirred solution of phosphonate 18 (347 mg, 1.0 mmol) in THF (8 mL) was added 18-crown-6 (275 mg, 1.04 mmol) in CH3CN and KHMDS (1.0 mL, 1.0 mmol, 1.0 M solution in THF) at -78 °C, over a period of 5 min. After being stirred at the same temperature for 20 min, and was added aldehyde 17 (216 mg, 1.0 mmol) and stirred for 1.5 hours at the same temperature. The reaction was quenched with saturated aqueous NH4Cl (10 mL) solution. The organic phase was separated, and the aqueous phase was extracted using diethyl ether (2 × 15 mL). The combined extracts were washed with water and brine and dried over Na2SO4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:20) to furnish the Z-isomer 19a (222 mg, 74%) as a pale yellow oil. Rf = 0.5 (5% EtOAc in hexane).

(Z)-7-((tert-butyl(dimethyl)silyloxy)-2-methylhept-2-en-1-ol (20): To a stirred solution of 19a (346 mg, 1.15 mmol) in CH2Cl2 (8 mL) was added DIBALH (4.6 mL, 4.6 mmol, 1 M in hexane) at 0 °C. After being stirred at the same temperature for 20 min, the mixture was allowed to warm to room temperature and stirred for 2 hours. After the reaction mixture was quenched with 10% aqueous Rochelle salt (10 mL) at 0 °C, and the mixture was warmed to room temperature and stirred for 1 hour. The organic phase was separated, and the aqueous phase was extracted using CH2Cl2 (3 × 15 mL). The combined extracts were washed with water and brine and dried over Na2SO4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:9) to furnish the 20 (285 mg, 96%) as a colorless oil. Rf = 0.3 (10% EtOAc in hexane); 1H NMR (300 MHz, CDCl3) δ: 5.29 (t, J = 7.5 Hz, 1H), 4.12 (s, 2H), 3.60 (t, J = 6.3 Hz, 2H), 2.06 (q, J = 14.7, 7.5 Hz, 2H), 1.79 (s, 3H), 1.55–1.46 (m, 2H), 1.42–1.33 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H); 13C NMR (75 MHz, CDCl3) δ: 134.4, 128.3, 63.0, 61.4, 32.3, 27.2, 26.2, 25.9, 21.1, 18.3, -53; ESI-MS (m/z): 259 [M + H]+.

(Z)-7-(benzoyloxy)-6-methylhept-5-en-1-ol (21): To a flame dried R. B flask (100 mL) charge with a magnet and NaH (60% in mineral oil) (69 mg, 2.90 mmol), was added THF (10 mL) and stirred at 0 °C. After being stirred at the same temperature for 10 min, and was sequentially added alcohol 20 (250 mg, 0.96 mmol) in THF (5 mL) and benzyl bromide (0.17 mL, 1.44 mmol). After that, the reaction mixture allowed to warm to room temperature stirred for 12 hours. The reaction mixture was quenching with H2O (10 mL) at 0°C. The mixture was warmed to room temperature and vigorously stirred for 10 min. The organic phase was separated, and the aqueous phase was extracted using ethyl acetate (3 × 15 mL). The combined extracts were washed with water and brine and dried over Na2SO4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:19) to furnish the benzyl ether (301 mg, 90%) as colorless oil. Rf = 0.5 (10% EtOAc in hexane).

A stirred solution of the above compound (300 mg, 0.86 mmol), in THF (10 mL) at 0 °C and then stirred at the same temperature for 10 min, and was added tetrabutylinammonium fluoride (TBAF) (1.29 mL, 1.29 mmol, 1 M in THF). After that, the reaction mixture allowed to warm to room temperature and was continued stirring for 6 hours. The reaction mixture was quenching with H2O (10 mL) at room temperature and vigorously stirred for 30 min. The organic phase was separated, and the aqueous phase was extracted using EtOAc (3 × 15 mL).
The combined extracts were washed with water and brine and dried over Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:5) to furnish the 21 (171 mg, 85%) as a colorless oil. Rᵣ = 0.6 (30% EtOAc in hexane). IR (Neat, νmax): 3450, 2932, 2873, 1458, 1219, 1067, 772 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ: 7.35 - 7.27 (m, 5H), 5.38 (t, J = 7.2 Hz, 1H), 4.46 (s, 2H), 4.00 (s, 2H), 3.61 (t, J = 6.3 Hz, 2H), 2.04 (q, J = 14.7, 7.5 Hz, 2H), 1.79 (s, 3H), 1.62 - 1.51 (m, 2H), 1.44 - 1.36 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: 138.3, 132.0, 129.4, 128.2, 127.6, 127.4, 76.1, 71.5, 68.3, 62.4, 32.0, 27.2, 25.9, 21; ESI-MS (m/z): calcd for C₁₅H₂₀O₃Na [M + Na]⁺ 257.1517, found 257.1505.

(Z)-7-(benzyl oxy)-6-methylhept-5-enoic acid (22): To a stirred solution of the oxalyl chloride (0.73 mL, 8.53 mmol) in CH₂Cl₂ (10 mL), was dropwise added DMSO (1.2 mL, 17.04 mmol) at -78 °C. After being stirred at the same temperature for 15 min, and was added 21 (1.0 g, 4.26 mmol) in CH₂Cl₂ (5 mL). The resulting mixture is stirred another 30 min at the same temperature. Then, Et₃N (2.0 mL, 2.0 mmol) added to reaction and stirring was continuing another 10 min at -78 °C. The reaction mixture was quenched with saturated aqueous NH₄Cl solution. The organic phase was separated, and the aqueous phase was extracted using ethyl acetate (3 × 20 mL). The combined extracts were washed with water, saturated aqueous Na₂CO₃ solution and brine and dried over Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:6) to furnish the aldehyde (821 mg, 83%) as a colorless oil. Rᵣ = 0.4 (20% EtOAc in hexane).

To a stirred solution of above aldehyde (800 mg, 3.44 mmol) in t-BuOH/2-methyl-2-butene (20 mL, 2:1) at room temperature, the mixture of NaClO₃ (622 mg, 6.88 mmol) and NaH₂PO₄ (825 mg, 6.88 mmol) dissolved in minimum amount of water and was added at the same temperature. The yellow color resulting mixture was warmed to room temperature and stirred for 2 hours. The volatile solvents were removed under reduced pressure and added H₂O (20 mL) and the aqueous layer was acidified to pH = 3 using 1 N HCl solution. The organic phase was separated, and the aqueous phase was extracted using EtOAc (3 × 20 mL). The combined extracts were washed with water, saturated aqueous Na₂CO₃ solution and brine and dried over Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:3) to afforded 22 (768 mg, 90%) as a pale yellow colorless oil. Rᵣ = 0.4 (30% EtOAc in hexane). IR (Neat, νmax): 2938, 1708, 1453, 1247, 1071, 939 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ: 7.35 - 7.27 (m, 5H), 5.35 (t, J = 7.5 Hz, 1H), 4.45 (s, 2H), 3.99 (s, 2H), 2.32 (t, J = 7.5 Hz, 2H), 2.13 - 2.03 (m, 2H), 1.79 (s, 3H), 1.74 - 1.62 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ: 179.6, 138.2, 133.1, 128.2, 127.5, 127.4, 71.58, 68.1, 33.2, 26.7, 24.6, 21.5; ESI-MS (m/z): calcd for C₁₅H₂₀O₃Na [M + Na]⁺ 271.1310, found 271.1325.

(R,Z)-4-benzyl-3-(7-(benzyl oxy)-6-methylhept-5-enoyl)oxazolidin-2-one (24): To a stirred solution of 22 (1.0 g, 4.02 mmol) in THF (15 mL) at -20 °C was added Et₃N (1.40 mL, 10.06 mmol) and Piv-Cl (0.49 mL, 4.02 mmol). After stirring at -20 °C for 1 hour, LiCl (256 mg, 6.04 mmol) followed by (R)-4-benzylazolidin-2-one 23 (712 mg, 4.02 mmol) were added at the same temperature. The resulting mixture was stirring at -20 °C for 1 hour and then at 0 °C for 2 hours. The reaction mixture was quenching with saturated aqueous NH₄Cl solution. The organic phase was separated, and the aqueous phase was extracted using ethyl acetate (3 × 20 mL). The combined extracts were washed with water, saturated aqueous Na₂CO₃ solution and brine and dried over Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:6) to afforded 24 (1.42 g, 87%) as a colorless oil. Rᵣ = 0.6 (20% EtOAc in hexane). [α]D²⁵ = -35.56 (c = 0.88, CHCl₃); IR (Neat, νmax): 2930, 1782, 1700, 1386, 1214, 1087, 771 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ: 7.37 - 7.18 (m, 10H), 5.40 (t, J = 7.2 Hz, 1H), 4.70 - 4.60 (m, 1H), 4.46 (s, 2H), 4.19 - 4.10 (m, 2H), 4.02 (s, 2H), 3.28 (dd, J = 13.2, 3.0 Hz, 1H), 2.98 - 2.85 (m, 2H), 2.73 (dd, J = 13.2, 9.6 Hz, 1H), 2.13 (q, J = 15.6, 8.1 Hz, 2H), 1.80 - 1.69 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ: 172.9, 153.3, 138.4, 135.1, 133.0, 129.3, 128.8, 128.4, 128.2, 127.5, 127.4, 127.2, 71.5, 68.3, 66.0, 55.0, 57.7, 37.7, 34.8, 26.8, 24.2, 21.5; ESI-MS (m/z): 430 [M + Na]⁺.

(R)-4-benzyl-3-((R,Z)-7-(benzyl oxy)-6-dimethylhept-5-enoyl) oxazolidin-2-one (8): To a stirred solution of 24 (950 mg, 2.33 mmol) in dry THF (10 mL) at -78 °C was added NaHMDS (4.66 mL, 2.0 mmol, 1 M solution in THF) dropwise under nitrogen atmosphere. After stirring -78 °C for 30 min, CH₂I₂ (0.43 mL, 6.99 mmol) was added into the reaction mixture. The resulting mixture was stirring another 3 hours at -78 °C. The reaction mixture was quenched with saturated aqueous NH₄Cl solution and warmed to room temperature. The organic phase was separated, and the aqueous phase was extracted using EtOAc (3 × 20 mL). The combined extracts
were washed with water, saturated aqueous Na₂CO₃ solution and brine and dried over Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:9) to afford 8 (785 mg, 80%) as a colorless oil. Rₖ = 0.4 (10% EtOAc in hexane). [α]D = -46.0 (c = 0.3, CHCl₃); IR (Neat, νmax): 2930, 1779, 1698, 1454, 1387, 1214, 771 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ: 7.36 – 7.18 (m, 10H), 5.35 (t, J = 7.2 Hz, 1H), 4.64 – 4.56 (m, 1H), 4.45 (s, 2H), 4.41 (d, J = 4.8 Hz, 2H), 3.98 (s, 2H), 3.74 – 3.63 (m, 1H), 3.24 (dd, J = 13.2, 3.3 Hz, 1H), 2.75 (dd, J = 13.2, 9.3 Hz, 1H), 2.05 (q, J = 16.5, 7.5 Hz, 2H), 1.88 – 1.77 (m, 4H), 1.50 – 1.39 (m, 1H), 1.20 (d, J = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: 176.8, 152.9, 138.4, 135.2, 132.6, 129.3, 128.8, 128.6, 128.2, 127.6, 127.4, 127.2, 71.7, 68.3, 65.8, 55.2, 37.7, 37.2, 33.2, 25.4, 21.5, 17.4; ESI-HRMS (m/z): calc for C₂₆H₃₁NO₃Na [M + Na⁺] 444.2151, found 444.2169.

(R,Z)-9-(benzoyloxy)-4,8-dimethylnona-1,7-dien-3-one (4): To a stirred solution of 8 (750 mg, 1.77 mmol) in THF/H₂O (5:1, v/v, 12 mL) at 0 °C and 30% H₂O₂ (0.32 mL, 10.67 mmol) and LiOH (105 mg, 4.42 mmol) combined, mixed, and was added into the reaction mixture at the same temperature. After being stirred at the same temperature for 1.5 hours, and the reaction mixture was warmed to room temperature and stirred another 1.5 hours. Then, the reaction was cooled to 0 °C and quenched with a saturated aqueous sodium sulfite solution and acidified with hydrochloric acid (1N aqueous, to pH = 5). The organic phase was separated, and the aqueous phase was extracted using ethyl acetate (3 × 20 mL). The combined extracts were washed with water, saturated aqueous Na₂CO₃ solution and brine and dried over Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:6) to afford carboxylic acid (450 mg, 97%) as a colorless oil. Rₖ = 0.4 (30% EtOAc in hexane).

To a stirred solution of above acid (450 mg, 1.71 mmol) in CH₂Cl₂ (12 mL) at -15 °C, were added N-methylpiperidine (0.62 mL, 5.14 mmol) and isobutyl chloroformate (0.33 mL, 2.56 mmol) and the resulting mixture stirred for 1.5 hours. To the mixture was added MeNHOMe.HCl (333 mg, 3.42 mmol) at 0 °C and quenched with a saturated aqueous sodium hydroxide solution and brine and dried over Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:1) to afford Weinreb amide (391 mg, 75%) as a colorless oil. Rₖ = 0.4 (50% EtOAc in hexane).

To a stirred solution of above Weinreb amide (300 mg, 0.98 mmol) in THF (4 mL) at 0 °C, was added vinyl magnesium bromide (1.84 mL, 2.94 mmol, 1.6 M solution in THF). The resulting mixture was stirred another 2 hours at the same temperature. The reaction mixture was quenched with a saturated aqueous NH₄Cl solution (20 mL) after that organic phase was separated, and the aqueous phase was extracted using diethyl ether (3 × 20 mL). The combined extracts were washed with water and brine and dried over Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography on silica gel eluting with EtOAc/n-hexane (1:9) to afford 4 (226 mg, 85%) as a colorless oil. Rₖ = 0.4 (10% EtOAc in hexane). [α]D = -16.66 (c = 0.44, CHCl₃); IR (Neat, νmax): 2930, 1779, 1698, 1454, 1387, 1214, 771 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ: 7.34 – 7.25 (m, 5H), 6.40 (dd, J = 17.4, 10.5 Hz, 1H), 6.23 (dd, J = 17.4, 1.5 Hz, 1H), 5.74 (dd, J = 10.2, 1.5 Hz, 1H), 5.33 (t, J = 7.5 Hz, 1H), 4.44 (s, 2H), 3.96 (s, 2H), 2.83 – 2.74 (m, 1H), 1.99 (q, J = 14.7, 7.2 Hz, 2H), 1.80 – 1.64 (m, 5H), 1.43 – 1.32 (m, 1H), 1.07 (d, J = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ: 203.6, 138.4, 135.0, 132.7, 128.6, 128.2, 127.9, 127.5, 127.4, 71.7, 68.3, 42.7, 32.9, 25.2, 21.6, 16.3; ESI-MS (m/z): 273 [M + H⁺].
$^1$H NMR spectrum of compound 11 (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 11 (75 MHz, CDCl$_3$)
$\text{H NMR spectrum of compound 12 (500 MHz, CDCl}_3\text{)}$

$\text{C NMR spectrum of compound 12 (100 MHz, CDCl}_3\text{)}$
$^{1}H$ NMR spectrum of compound 13 (500 MHz, CDCl$_3$)

$^{13}C$ NMR spectrum of compound 13 (125 MHz, CDCl$_3$)
H NMR spectrum of compound 14 (500 MHz, CDCl₃)

¹³C NMR spectrum of compound 14 (125 MHz, CDCl₃)
$^1$H NMR spectrum of compound 15 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 15 (125 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound 6 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 6 (125 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound 5 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 5 (75 MHz, CDCl$_3$)
$\mathrm{H NMR\ spectrum\ of\ compound\ 16\ (500\ MHz,\ CDCl_3)}$

$\mathrm{C NMR\ spectrum\ of\ compound\ 16\ (75\ MHz,\ CDCl_3)}$
$^1$H NMR spectrum of compound 3 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 3 (100 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound 19a (300 MHz, CDCl$_3$)
**1H NMR spectrum of compound 20 (300 MHz, CDCl₃)**

**13C NMR spectrum of compound 20 (75 MHz, CDCl₃)**
$^1$H NMR spectrum of compound 21 (300 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 21 (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound 22 (300 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 22 (75 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound 24 (300 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 24 (75 MHz, CDCl$_3$)
$^{1}H$ NMR spectrum of compound 8 (300 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 8 (75 MHz, CDCl$_3$)
$^{1}$H NMR spectrum of compound 4 (300 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 4 (125 MHz, CDCl$_3$)