Supporting Information

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General. Where appropriate, reactions were performed in flame-dried glassware under argon atmosphere. All extracts were dried over MgSO4 and concentrated by rotary evaporation below 30 °C at 25 Toor unless otherwise noted. Commercial reagents and solvents were used as supplied with following exceptions. N,N-Dimethylformamide (DMF), dichloromethane (CH2Cl2), acetonitrile (MeCN), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) were distilled from CaH2. Methanol (MeOH) was distilled from sodium. Thin-layer chromatography (TLC) was performed using glass-packed silica gel plates (0.2 or 0.5 mm thickness). Column chromatography was performed using silica gel (particle size 100-210 µm (regular), 40-50 µm (flush)). Optical rotations were recorded on a digital polarimeter at ambient temperature. Infrared spectra were measured on a Fourier transform infrared spectrometer. 1H NMR (400 and 500 MHz) and 13C NMR (100 MHz) spectra were measured using CDCl3, C6D6, or CD3OD, as solvent, and chemical shifts are reported as δ values in ppm based on internal CHCl3 (7.26 ppm, 1H; 77.0 ppm, 13C), C6H6 (7.15 ppm, 1H; 128.0 ppm, 13C), H2O (4.65 ppm, 1H), or MeOH (49.9 ppm, 13C). HRMS spectra were taken in EI or FAB mode.

Preparation of the Right Hand Segment

(2R,6R)-7-(Benzyloxy)-2,6-dimethylhept-3-yn-1-ol (8). To a solution of (R)-2-methylbut-3-ynyloxy)((tert-butyldiphenyl)silane (6)11 (35.0 g, 109 mmol) in THF (785 ml) was added n-BuLi (1.58 M in hexane, 60.0 ml, 94.1 mmol) at –78 °C over 5 min, and the mixture was allowed to warm to 0 °C and stirred for 30 min. A solution of (S)-3-(benzyloxy)-2-methylpropyl trifluoromethanesulfonate (7)12 (22.6 g, 72.4 mmol) and DMPU (155 ml) in THF (145 ml) was added at –78 °C over 15 min, and stirring was continued at the same temperature for 30 min. The reaction was quenched with saturated NaHCO3, and the reaction mixture was extracted with CDCl3, C6D6, or CD3OD, as solvent, and chemical shifts are reported as δ values in ppm based on internal CHCl3 (7.26 ppm, 1H; 77.0 ppm, 13C), C6H6 (7.15 ppm, 1H; 128.0 ppm, 13C), H2O (4.65 ppm, 1H), or MeOH (49.9 ppm, 13C). HRMS spectra were taken in EI or FAB mode.

1H NMR (400 and 500 MHz) and 13C NMR (100 MHz) spectra were measured using CDCl3, C6D6, or CD3OD, as solvent, and chemical shifts are reported as δ values in ppm based on internal CHCl3 (7.26 ppm, 1H; 77.0 ppm, 13C), C6H6 (7.15 ppm, 1H; 128.0 ppm, 13C), H2O (4.65 ppm, 1H), or MeOH (49.9 ppm, 13C). HRMS spectra were taken in EI or FAB mode.
128.2 (2), 127.4, 127.4 (2), 82.6, 80.6, 74.3, 73.0, 67.1, 33.3, 29.6, 23.0, 17.4, 16.6; FTIR (neat) 3400, 1456, 1369, 1095 cm⁻¹; MS (EI) m/z 91 (100), 187, 215, 246 (M⁺); HRMS (EI) calcd for C₁₆H₂₂O₂ (M⁺) 246.1620, found 246.1600.

**[(E,2S,6R)-7-(Benzyloxy)-3-iodo-2,6-dimethylhept-3-en-1-ol](11).** A mixture of 8 (3.05 g, 12.4 mmol) and 1,1,3,3-tetramethyldisilazane (TMDS) (2.40 ml, 13.6 mmol) was stirred at 0 °C for 5 min and at rt for 1 h. The reaction mixture was concentrated to give hydroxymethylsilylether 9 (3.82 g), a colorless oil: 1H NMR (400 MHz, C₆D₆) δ 7.29-7.07 (m, 5H), 4.87–4.83 (m, 1H), 4.32 (s, 2H), 3.72 (dd, J = 5.6, 9.8 Hz, 1H), 3.48 (dd, J = 7.6, 9.5 Hz, 1H), 3.28 (dd, J = 6.8, 8.8 Hz, 1H), 3.21 (dd, J = 5.7, 8.8 Hz, 1H), 2.70–2.62 (m, 1H), 2.32 (ddd, J = 2.2, 5.6, 16.3 Hz, 1H), 2.18 (ddd, J = 2.2, 6.8, 16.3 Hz, 1H), 1.99-1.91 (m, 1H), 1.19 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.8 Hz, 3H), 0.12 (d, J = 2.7 Hz, 6H).

To a solution of crude 9 (3.82 g) in THF (25 ml) was added Pr(DVDS) (0.10 M in xylene, 0.4 ml, 0.04 mmol) at 0 °C, and the mixture was stirred at rt for 1 h and concentrated to give siloxane 10 (3.90 g) as a yellow oil: 1H NMR (400 MHz, C₆D₆) δ 7.30-7.07 (m, 5H), 5.72 (t, J = 7.1 Hz, 1H), 4.33 (s, 2H), 3.89 (dd, J = 5.0, 9.5 Hz, 1H), 3.79 (d, J = 9.5 Hz, 1H), 3.21 (dd, J = 5.9, 8.8 Hz, 1H), 3.16 (dd, J = 5.9, 8.8 Hz, 1H), 2.69-2.62 (m, 1H), 2.32 (dt, J = 7.0, 14.0 Hz, 1H), 1.95 (dt, J = 7.1, 14.0 Hz, 1H), 1.89–1.80 (m, 1H), 1.05 (d, J = 7.3 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H), 0.29 (s, 3H), 0.19 (s, 3H).

To a solution of crude 10 (3.90 g) in DMF (41 ml) and MeOH (8.3 ml) was added CsF (2.80 g, 18.60 mmol) at 0 °C, and the mixture was stirred under ultrasonication at 0 °C for 30 min until it became a clear solution. Iodine (3.15 g, 12.4 mmol) was added to this solution at 0 °C and the mixture was stirred at rt for 1 h. The reaction mixture was diluted with Et₂O, washed with saturated Na₂S₂O₃, H₂O, and brine, dried, and concentrated. The residue was subjected to flash chromatography (SiO₂, 150 g, hexane/AcOEt = 10/1) to give 11 (3.79 g, 82%) as a colorless oil: [α]D₂² = -1.7 (c 1.20, CHCl₃); 1H NMR (400 MHz, C₆D₆) δ 7.29-7.07 (m, 5H), 6.31 (t, J = 7.8 Hz, 1H), 4.28 (d, J = 12.0 Hz, 1H), 4.24 (d, J = 12.0 Hz, 1H), 3.38–3.32 (m, 1H), 3.16–3.10 (m, 1H), 3.07 (d, J = 5.5, 9.3 Hz, 1H), 3.02 (dd, J = 6.3, 9.3 Hz, 1H), 2.13 (ddd, J = 6.3, 7.7, 14.1 Hz, 1H), 2.12-2.03 (m, 1H), 1.82 (dt, J = 14.1, 7.6 Hz, 1H), 1.65-1.57 (m, 1H), 0.75 (d, J = 6.6 Hz, 6H); 13C NMR (100 MHz, C₆D₆) δ 142.1, 138.3, 128.2 (2), 127.4 (3), 111.3, 74.8, 73.0, 67.1, 40.1, 35.5, 33.7, 17.5, 16.9; FTIR (neat) 3417, 1454, 1367, 1090 cm⁻¹; MS (EI) m/z 91 (100), 217, 247, 374 (M⁺); HRMS (EI) calcd for C₁₆H₂₂O₂ (M⁺) 374.0743, found 374.0727.

**Dimethyl 2-((E,2S,6R)-7-(benzyloxy)-3-iodo-N,2,6-trimethylhept-3-enoylamino)malonate (5).** To a solution of 11 (9.87 g, 26.4 mmol) in acetone (130 ml) was added Jones’ reagent (5.8 M, 27.3 ml, 158 mmol) at −10 °C over 15 min. After stirring at −10 °C for 2 h, the reaction was quenched with 2-propanol (25 ml) and the reaction mixture was extracted with Et₂O. The ethereal layer was washed with H₂O, basified with 3 M NaOH at 0 °C, and extracted with H₂O. Combined aqueous layer was acidified to pH 1 by the addition of 3 M HCl at 0 °C, and extracted with Et₂O. The extract was washed with brine, dried, and concentrated to give the corresponding carboxylic acid (8.97 g) as a pale yellow oil.

To a solution of crude carboxylic acid (8.97 g) in CH₂Cl₂ (130 ml) was added SOCl₂ (5.8 M, 27.3 ml, 158 mmol) at −10 °C over 15 min. After being stirred at rt for 18 h, the reaction mixture was concentrated to give the corresponding acid chloride (9.50 g).

To a solution of dimethyl 2-(methylamino)malonate[8] (10.6 g, 66.0 mmol) in toluene (130 ml) at 0 °C was added a solution of crude acid chloride (9.50 g) in toluene (130 ml). After
being stirred at 0 °C for 3 h, the reaction mixture was diluted with Et₂O, washed with 0.5 M HCl, H₂O, saturated NaHCO₃, dried, and concentrated. The residue was purified by flash chromatography (SiO₂ 350 g, hexane/AcOEt = 5/1 to 4/1) to give 5 (8.73 g, 62%) as an yellow oil: [α]D²⁵ +31.0 (c 1.21, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.26 (m, 5H), 6.36 (t, J = 6.6 Hz, 1H), 6.04 (s, 1H), 4.49 (s, 2H), 3.79 (s, 3H), 3.79 (s, 3H), 3.65 (q, J = 6.6 Hz, 1H), 3.34 (dd, J = 5.4, 9.3 Hz, 1H), 3.26 (dd, J = 7.0, 9.3 Hz, 1H), 3.04 (s, 3H), 2.31 (dt, J = 15.6, 5.9 Hz, 1H), 2.04 (dd, J = 15.6, 8.3 Hz, 1H), 1.95-1.86 (m, 1H), 1.22 (d, J = 6.6 Hz, 3H), 1.89 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 172.2, 166.7, 166.4, 141.7, 138.2, 128.2 (2), 127.5, 127.4 (2), 100.0, 74.6, 73.0, 60.2, 52.8, 52.7, 43.8, 35.3, 33.4, 33.2, 17.3, 16.9; FTIR (neat) 1753, 1664, 1446, 1205, 1110, 1031 cm⁻¹; MS (EI) m/z 91 (100), 160, 162, 404, 440, 500, 531 (M⁺); HRMS (EI) calc’d for C₂₂H₉₅NO₆ (M⁺) 531.1118, found 531.1113.

(R,E)-Dimethyl 3-((R)-4-(benzoxly)-3-methylbutylidene)-1,4-dimethyl-5-oxypyrrolidine-2,2-dicarboxylate (4). To a solution of 5 (2.91g, 5.48 mmol) in DMF (247 ml) and H₂O (27 ml) were added n-Bu,NBr (1.17 g, 5.48 mmol), K₂CO₃ (3.03 g, 21.9 mmol), Pd(OAc)₂ (61.5 mg, 0.274 mmol), and triphenylphosphine (287 mg, 1.10 mmol) and the mixture was degassed. After being heated for 1.5 h, the reaction mixture was cooled to rt and extracted with Et₂O. The extract was washed with H₂O, dried, concentrated, and chromatographed (SiO₂ 130 g, hexane/AcOEt = 5/1 to 3/1) to give 4 (1.87 g, 84%) as a pale yellow oil: [α]D²⁵ +0.2 (c 1.25, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.27 (m, 5H), 5.88 (dt, J = 2.1, 6.5 Hz, 1H), 4.48 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.29 (d, J = 5.9 Hz, 2H), 3.14 (q, J = 7.1 Hz, 1H), 2.93 (s, 3H), 2.30-2.22 (m, 1H), 2.08-2.01 (m, 1H), 1.91 (sex, J = 6.6 Hz, 1H), 1.33 (d, J = 7.3 Hz, 3H), 0.95 (d, J = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 176.6, 167.8, 167.5, 138.3, 133.0, 129.2, 128.2 (2), 127.40, 127.39 (2), 75.5, 74.6, 73.0 (2), 53.19, 53.16, 38.3, 33.9, 32.7, 28.3, 17.5, 17.1; FTIR (neat) 3489, 1749, 1444, 1377, 1250, 1066 cm⁻¹; MS (EI) m/z 91, 182, 238, 344 (100), 403 (M⁺); HRMS (EI) calc’d for C₂₂H₂₉NO₆ (M⁺) 403.1995, found 403.1996.

(3R,3aS,4S,6aR)-Methyl 4-((R)-3-(benzoxly)-2-methylpropyl)-hexahydro-3a-hydroxy-1,3-dimethyl-2,6-dioxo-1H-furo[3,4-b]pyrrrole-6a-carboxylate (3). To a solution of 4 (1.78 g, 4.41 mmol) in THF (35 ml) and H₂O (11 ml) were added NMO (2.27 g, 19.4 mmole) and OsO₄ (0.15 M in H₂O, 12.0 ml, 1.76 mmol). After being stirred at rt for 48 h, the reaction mixture was diluted with Et₂O, washed with saturated Na₂S₂O₅, H₂O, and brine, dried, and concentrated. The residue was subjected to flash chromatography (SiO₂ 80 g, hexane/AcOEt = 3/1) to give 3 (1.57 g, 88%) as a colorless oil: [α]D²⁵ +17.0 (c 1.17, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.28 (m, 5H), 4.55 (d, J = 12.0 Hz, 1H), 4.50 (d, J = 12.0 Hz, 1H), 4.37 (t, J = 7.0 Hz, 1H), 4.24 (s, 1H), 3.86 (s, 3H), 3.42 (dd, J = 4.4, 9.0 Hz, 1H), 3.25 (t, J = 8.7 Hz, 1H), 2.92 (s, 3H), 2.53 (q, J = 7.4 Hz, 1H), 2.06 (ddd, J = 5.7, 6.8, 14.6 Hz, 1H), 1.92-1.82 (m, 1H), 1.76 (dt, J = 14.6, 6.5 Hz, 1H), 1.15 (d, J = 7.6 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.2, 167.7, 166.2, 137.2, 128.5 (2), 128.0, 127.9 (2), 86.5, 82.0, 75.8, 75.1, 73.4, 53.5, 45.3, 32.6, 30.3, 27.3, 18.4, 11.0; FT-IR (neat) 3352, 2956, 1782, 1693, 1454, 1365, 1269, 1085 cm⁻¹; MS (EI) m/z 91, 185(100), 405 (M⁺); HRMS (EI) calc’d for C₂₂H₂₉NO₆ (M⁺) 405.1788, found 405.1787.
**(3R,3aS,4S,6aS)-4-((R)-3-(Benzyloxy)-2-methylpropyl)-dihydro-3a-hydroxy-6a-(hydroxymethyl)-1,3-dimethyl-1H-furo[3,4-b]pyrrole-2,6(3H,6aH)-dione (12).** To a solution of 3 (270 mg, 0.667 mmol) in THF (16 ml) was added 4 M LiOH (3.6 ml), and the mixture was stirred at rt for 20 min. The reaction mixture was washed with EtOAc, acidified with 1 M HCl to pH 1, and extracted with EtO. The extract was washed with brine, dried, and concentrated to give the corresponding carboxylic acid (245 mg) as a colorless solid.

To a solution of DMF (78 μl, 1.00 mmol) in CH₂Cl₂ (1.0 ml) was added (COCl)₂ (252 μl, 2.94 mmol) and the reaction mixture was stirred at 0 °C for 1 h. After evaporation of the solvent, the residue was dissolved in MeCN (1.0 ml) and THF (1.7 ml), and a solution of the carboxylic acid (245 mg) in THF (2.7 ml) was added at 0 °C. After stirred for 1 h, NaBH₄ (2.00 M in DMF, 1.0 ml, 2.00 mmol) was added at −78 °C, and the mixture was allowed to warm to rt over 12 h. The reaction was quenched with 1 M HCl at 0 °C, and the reaction mixture was extracted with EtO. The extract was washed with saturated NaHCO₃, dried, concentrated, and chromatographed (SiO₂, 20 g, hexane/AcOEt = 2/1) to give **12** (142.8 mg, 57%); [α]D³⁵ +44.5° (c 1.14, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.29 (m, 5H), 4.53 (s, 2H), 4.45 (s, 1H), 4.32 (J = 7.0 Hz, 1H), 3.99 (dd, J = 6.6, 12.3 Hz, 1H), 3.91 (dd, J = 5.5, 12.3 Hz, 1H), 3.43 (dd, J = 4.6, 9.0 Hz, 1H), 3.33 (t, J = 6.1 Hz, 1H), 3.28 (t, J = 8.4 Hz, 1H), 2.87 (s, 3H), 2.50 (q, J = 7.6 Hz, 1H), 2.01 (ddd, J = 5.6, 6.8, 14.4 Hz, 1H), 1.89-1.82 (m, 1H), 1.74 (ddd, J = 6.1, 7.2, 14.4 Hz, 1H), 1.21 (d, J = 7.8 Hz, 3H), 1.01 (d, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.2, 171.5, 137.2, 128.5 (2), 128.0, 127.9 (2), 86.6, 80.7, 75.2, 73.5, 71.8, 58.9, 45.6, 32.4, 30.2, 26.1, 18.4, 11.6; FTIR (neat) 3394, 2943, 1768, 1679, 1457, 1389, 1232, 1078, 1108 cm⁻¹; MS (EI) m/z 91, 157 (100), 377 (M⁺); HRMS (EI) calcd for C₂₉H₂₇NO₆Si (M⁺) 463.2070, found 463.2069.

**(3R,3aS,4S,6aS)-4-((R)-3-(Benzyloxy)-2-methylpropyl)-6a-(tert-butyl(dimethyl)siloxy)methyl)-dihydro-3a-hydroxy-1,3-dimethyl-1H-furo[3,4-b]pyrrole-2,6(3H,6aH)-dione (12).** To a solution of 12 (30.8 mg, 0.082 mmol) in CH₂Cl₂ (1.0 ml) was added TBSOTf (35 μl, 0.163 mmol), and the mixture was stirred for 30 min. The reaction mixture was diluted with EtOAc, washed with H₂O, dried, and concentrated. The residue was purified by preparative TLC (SiO₂, hexane/AcOEt = 1/1) to give the corresponding mono-TBS ether (35.0 mg, 87%) as colorless crystals: mp 104-105 °C (EtOH); [α]D⁰ +31.2° (c 1.14, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.26 (m, 5H), 4.50 (s, 2H), 4.32 (dd, J = 4.4, 8.5 Hz, 1H), 4.07 (d, J = 11.0 Hz, 1H), 3.89 (s, 1H), 3.96 (d, J = 11.0 Hz, 1H), 3.40 (dd, J = 4.8, 9.3 Hz, 1H), 3.30 (dd, J = 6.3, 9.0 Hz, 1H), 2.84 (s, 3H), 2.45 (q, J = 7.6 Hz, 1H), 1.99-1.89 (m, 2H), 1.73-1.66 (m, 1H), 1.24 (d, J = 7.6 Hz, 3H), 1.02 (d, J = 6.6 Hz, 3H), 0.89 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 175.1, 171.0, 138.0, 128.3 (2), 127.6 (3), 86.8, 80.3, 75.0, 73.2, 71.4, 59.8, 45.1, 32.2, 30.4, 25.9, 25.8 (3), 18.2, 18.1, 11.6, -5.5, -5.7; FTIR (neat) 3294, 1763, 1662, 1456 cm⁻¹; MS (EI) m/z 91(100), 434, 491 (M⁺); HRMS (EI) calcd for C₂₉H₄₁NO₆Si (M⁺) 491.2703, found 491.2698.

**Protection of 12 as its Dioxasilane.** To a solution of 12 (82.0 mg, 0.277 mmol) in 1,2-dichloroethane (2.5 ml) were added 2,6-lutidine (267 μl, 2.290 mmol) and diisopropyl bis(trifluoromethanesulfonate) (225 μl, 0.762 mmol), and the mixture was refluxed for 2 h. The reaction mixture was diluted with EtOAc, washed with H₂O, 0.5 M HCl, and saturated NaHCO₃, dried, and concentrated. The residue was purified by column chromatography (SiO₂ 6.2 g, hexane/AcOEt = 3/1) to give the corresponding dioxasilane (135.5 mg, 100%) as a colorless oil: [α]D³⁵ +50.7° (c 1.025, CHCl₃); ¹H NMR (300 MHz, S-4
CDCl$_3$) δ 7.39-7.23 (m, 5H), 4.47 (d, $J = 13.8$ Hz, 3H), 4.35 (dd, $J = 2.9$, 4.5 Hz, 1H), 3.94 (d, 11.4 Hz, 1H), 3.42 (dd, $J = 5.0$, 9.3 Hz, 1H), 3.31 (dd, $J = 6.0$, 9.3 Hz, 1H), 2.87 (s, 3H), 2.51 (q, $J = 7.5$ Hz, 2H), 2.11-1.86 (m, 2H), 1.81-1.55 (m, 1H), 1.28 (d, $J = 7.5$ Hz, 3H), 1.05-0.96 (m, 17H); $^1$C NMR (100 MHz, CDCl$_3$) δ 174.5, 171.1, 138.3, 128.4 (2), 127.7, 127.6 (2), 85.6, 82.3, 74.7, 67.4, 61.2, 45.3, 32.5, 30.7, 25.9, 18.0, 16.8, 16.6, 13.6, 11.7; FTIR (neat) 1780, 1705, 1462, 1377, 1209, 1093 cm$^{-1}$; MS (EI) m/z 91(100), 269, 327, 383, 418, 446, 489 (M$^+$); HRMS (EI) calc'd for C$_{26}$H$_{39}$NO$_5$Si (M$^+$) 489.2527, found 489.2542.

Debenzylation. A solution of the cyclic silyl ether of 12 (118.6 mg, 0.242 mmol) in MeOH (2.0 ml) was stirred with 10% Pd/C (12 mg) at rt under H$_2$ atmosphere. After 1.5 h, the reaction mixture was filtered through Celite pad and concentrated to give the corresponding primary alcohol (96.7 mg, 100%) as a colorless oil, which was used for the next reaction without purification; [α]$_D^{22}$ +44.8 (c 1.74, CHCl$_3$); $^1$H NMR (300 MHz, CDCl$_3$) δ 4.49 (d, $J = 10.8$ Hz, 1H), 4.37 (d, $J = 10.5$ Hz, 1H), 3.94 (d, $J = 11.4$ Hz, 1H), 3.62 (dd, $J = 4.2$, 10.5 Hz, 1H), 3.51 (dd, $J = 5.7$, 10.5 Hz, 1H), 2.88 (s, 3H), 2.58 (q, $J = 7.5$, 1H), 2.03-1.60 (m, 4H), 1.30 (d, $J = 7.8$ Hz, 3H), 1.14-0.95 (m, 17H); $^1$C NMR (100 MHz, CDCl$_3$) δ 175.6, 171.9, 86.5, 83.3, 68.4, 68.0, 62.2, 46.1, 33.6, 32.7, 26.9, 18.4, 17.8, 17.7, 17.6, 17.5, 14.5, 14.2, 12.8; FTIR (neat) 3440, 1784, 1710, 1466, 1388, 1091 cm$^{-1}$; MS (EI) m/z 189, 244 (100), 256, 328, 356, 399 (M$^+$); HRMS (EI) calc'd for C$_{16}$H$_{31}$NO$_5$Si (M$^+$) 399.2077, found 399.2059.

Aldehyde 13. To a solution of the primary alcohol (92.4 mg, 0.231 mmol) in CH$_2$Cl$_2$ (2.0 ml) was added Dess-Martin periodinane (146.9 mg, 347 μmol), and the mixture was stirred at rt for 4.5 h. The reaction was quenched with saturated Na$_2$S$_2$O$_4$ at 0 °C and the reaction mixture was extracted with Et$_3$O. The extract was washed with NaHCO$_3$, dried, concentrated. The residue was subjected to flash chromatography (SiO$_2$, 2.0 g, hexane/ACOEt = 3/1) to give aldehyde 13 (76.4 mg, 83%) as a pale yellow oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 9.68 (s, 1H), 4.69 (d, $J = 11.8$ Hz, 1H), 4.30 (d, $J = 10.8$ Hz, 1H), 3.95 (d, $J = 11.7$ Hz, 1H), 2.87 (s, 3H), 2.81-2.61 (m, 2H), 2.24 (dd, $J = 8.7$, 15.2 Hz, 1H), 1.74 (dd, $J = 10.5$, 15.2 Hz, 1H), 1.32 (d, $J = 7.8$ Hz, 3H), 1.26 (d, $J = 7.3$ Hz, 3H), 1.93-1.17 (m, 14 H).

Nozaki-Hiyama-Kishi Reaction of 13 with 14. A mixture of NiCl$_2$ (3.0 mg, 23 μmol) and CrCl$_2$ (56.9 mg, 463 μmol) in THF-DMSO (3:1) (3.0 ml) was stirred for 10 min. To this mixture were added a solution of 13 (46.0 mg, 116 μmol) in THF-DMSO (3:1) (0.6 ml), and 14 (85.0 mg, 197 μmol). After stirring at rt for 20 h, the reaction was quenched with H$_2$O at 0 °C, and the reaction mixture was filtered through Celite pad. The filtrate was extracted with AcOEt, dried, and concentrated. The residue was again reacted with 14 (85.0 mg, 197 μmol) using NiCl$_2$ (3.0 mg, 23 μmol) and CrCl$_2$ (56.9 mg, 463 μmol) in THF-DMSO (3:1) (3.6 ml) in the same manner as described above. After being stirred at rt for 16 h, the reaction was quenched with H$_2$O filtered through Celite pad, extracted with AcOEt, dried, and concentrated. The residue was purified by preparative TLC (hexane/ACOEt = 1/1) to give recovered 13 (6.4 mg, 14%) and 15, a colorless oil, (59.7 mg, 73%; 85% based on recovered 13) as a 1:1 epimeric mixture; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.77 (d, $J = 7.3$ Hz, 2H), 7.61 (d, $J = 7.3$ Hz, 2H), 7.40 (t, $J = 7.3$ Hz,
Oxidation of 15. To a solution of 15 (59.7 mg, 85 mmol) in CH₂Cl₂ (2 ml) was added Dess-Martin periodinane (54.0 mg, 127 mmol), and the mixture was stirred at rt for 2 h. The reaction was quenched with saturated Na₂S₂O₃ at 0 °C, the reaction mixture was extracted with Et₂O. The extract was washed with saturated NaHCO₃, dried, and concentrated. The residue was purified by preparative TLC (hexane/AcOEt = 1/1) to afford the corresponding ketone (51.8 mg, 87%) as a colorless oil: [α]ᵢ° +18.0 (c 1.04, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 7.8 Hz, 2H), 7.59 (d, J = 7.3 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.31 (d, J = 7.3 Hz, 2H), 7.20 (dd, J = 11.0, 15.4 Hz, 1H), 6.4-6.6 (m, 3H), 4.99 (brs, 1H), 4.47 (d, J = 11.7, 3H), 4.22 (t, J = 6.4 Hz, 1H), 4.07 (d, J = 9.3 Hz, 1H), 3.93 (d, J = 11.7 Hz, 2H), 3.86-3.70 (m, 1H), 3.08 (t, J = 6.8 Hz, 1H), 2.84 (s, 3H), 2.63 (q, J = 7.6 Hz, 1H), 2.30 (t, J = 12.2 Hz, 1H), 1.71 (t, J = 12.9 Hz, 1H), 1.30 (d, J = 7.3 Hz, 3H), 1.21 (d, J = 7.3 Hz, 2H), 1.13-0.96 (m, 14 H); ¹³C NMR (100 MHz, CDCl₃) δ 202.1, 174.5, 170.9, 143.8 (2), 142.3, 141.3 (2), 140.2, 129.2, 128.4, 127.7 (2), 127.0 (2), 124.9 (2), 120.0 (2), 85.2, 82.3, 67.4, 66.8, 61.2, 60.3, 47.2, 44.9, 40.4, 31.1, 25.9, 23.7, 22.9, 21.0, 18.7, 16.8, 14.2, 13.6, 13.3, 11.8; FTIR (neat) 3530, 1780, 1705, 1597, 1526, 1458, 1458, 1086 cm⁻¹; MS (FAB) m/z 89, 137, 154 (100), 289, 307, 391, 460, 505, 613, 700 (M⁺); HRMS (FAB) calcd for C₅₉H₆₈N₂O₇Si (M⁺) 700.3180, found 700.3115.

Compound 16. To a solution of the ketone (40.0 mg, 57 µmol) in THF (2 ml) was added L-Selectride (1 M solution in THF, 63 µl, 63 µmol) at −78 °C, and the mixture was stirred at −78 °C for 30 min. The reaction was quenched with saturated NH₄Cl, and the reaction mixture was extracted with AcOEt, dried, and concentrated. The residue was purified by flash chromatography (SiO₂ 1.2g, hexane/AcOEt = 2/1 to 1/1) to give 16 (38.4 mg, 96%) as a colorless oil: [α]ᵢ° -6.3 (c 0.814, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 7.3 Hz, 2H), 7.60 (d, J = 7.3 Hz, 2H), 7.39 (t, J = 7.3 Hz, 2H), 7.30 (t, J = 7.3 Hz, 2H), 5.76-5.58 (m, 2H), 5.38 (brs, 1H), 4.49 (d, J = 11.7 Hz, 1H), 4.40 (d, J = 7.3 Hz, 1H), 4.38-4.30 (m, 1H), 4.23 (t, J = 6.8 Hz, 1H), 4.04 (brs, 1H), 3.91 (d, J = 11.7 Hz, 2H), 3.86-3.72 (m, 1H), 2.86 (s, 3H), 2.52 (q, J = 7.8 Hz, 1H), 2.05 (dd, J = 6.36, 15.1 Hz, 1H), 1.97-1.81 (m, 2H), 1.69-1.52 (m, 1H), 1.27 (d, J = 7.32 Hz, 3H), 1.12-0.95 (m, 17H); ¹³C NMR (100 MHz, CDCl₃) δ 175.6, 171.9, 157.2, 144.9 (2), 142.2 (2), 135.5, 131.8, 131.2, 128.6 (2), 127.9 (2), 126.0 (2), 120.8 (2), 87.5, 83.2, 68.5, 67.6, 62.2, 48.2, 45.9, 43.5, 36.8, 31.7, 26.9, 18.6, 17.8, 17.5, 14.5, 14.2, 13.0; FTIR (neat) 3216, 1781, 1704, 1454, 1249, 1089 cm⁻¹; MS (FAB) m/z 55, 136, 178, 179(100), 270, 368, 463, 507, 685, 702 (M⁺); HRMS (FAB) calcd for C₅₉H₆₈N₂O₇Si (M⁺) 702.3337, found 702.3300.
Right hand segment 2. To a solution of 16 (38.4 mg, 54.7 μmol) in MeCN (3.3 ml) was added a mixture of 46% HF-pyridine-H₂O (1:4:2) (1.2 ml), and the mixture was stirred at rt for 20 min. The reaction was quenched with saturated NaHCO₃, and the reaction mixture was extracted with AcOEt, dried, and concentrated to give the corresponding triol (39.3 mg) as a yellow viscous oil, which was used for the next reaction without purification.

Crude triol (39.3 mg) was dissolved in pyridine (2ml) and Ac₂O (0.1 ml, 1.06 mmol) was added. After being stirred at rt for 16 h, the reaction mixture was diluted with Et₂O, washed with H₂O, dried, and concentrated. The residue was purified by preparative TLC (SiO₂, hexane/AcOEt = 1/10) to give 2 (34.1 mg, 92%) as a colorless viscous oil: [α]D⁰ +3.0 (c 1.65, CH₂Cl₂) (lit.¹⁰ [α]D² +3.6 (c 0.6, CH₂Cl₂)); ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 6.22 (dd, J = 10.5, 15.1 Hz, 1H), 6.13 (dd, J = 10.8, 14.7 Hz, 1H), 5.74 (dt, J = 6.9, 15.1 Hz, 1H), 5.57 (dd, J = 7.1, 15.1 Hz, 1H), 5.24 (brs, 1H), 5.20 (t, J = 6.0 Hz, 1H), 4.71 (d, J = 13.0 Hz, 1H), 4.41 (d, J = 6.9 Hz, 2H), 4.30 (q, J = 4.3 Hz, 1H), 4.26 (d, J = 12.8 Hz, 1H), 4.23 (t, J = 6.9 Hz, 1H), 3.88-3.77 (m, 2H), 2.88 (s, 3H), 2.61 (s, 1H), 2.42 (q, J = 7.7 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 1.99-1.88 (m, 2H), 1.67-1.58 (m, 1H), 1.25 (d, J = 7.6 Hz, 3H), 1.02 (d, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.5, 170.3, 170.2, 169.7, 156.3, 143.9 (2), 141.3 (2), 132.7, 131.3, 130.5, 128.7, 127.7 (2), 127.0 (2), 125.1 (2), 120.0 (2), 86.7, 80.2, 71.4, 66.8, 57.8, 47.3, 44.2, 42.6, 40.9, 34.0, 30.5, 26.1, 20.9, 11.0; FT-IR (neat) 3340, 2937, 1770, 1703, 1528, 1450, 1382, 1232, 1018, 740 cm⁻¹; MS (FAB) m/z 69, 137, 154 (100), 289, 307, 391, 460, 550, 615, 674 (M⁺); HRMS (FAB) calcd for C₇₃H₄₂N₂O₁₀Si (M⁺) 674.2840, found 674.2855. The spectral data were identical with those reported.⁶

Preparation of the Left Hand Segment

Oxazole-2-thiol. To a suspension of KSCN (7.57 g, 39.5 mmol) in MeCN (167 ml) was added concentrated HCl (8.14 g). After stirring at rt for 30 min, the precipitates were removed by filtration through Celite pad. To the resulting solution of HSCN was added 2,2-diethoxyethanol (18) (7.00 g, 52.2 mmol) and the mixture was refluxed for 4 h. After being cooled to rt, the reaction mixture was concentrated and chromatographed (SiO₂, hexane/AcOEt = 2/3) to give oxazole-2-thiol (5.25 g, 100%): ¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 1H), 6.92 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 137.4, 116.0; FTIR (CDCl₃) 3123, 2170, 1588, 1481, 1259, 1481, 1259, 1169, 1087 cm⁻¹; HRMS (FAB) calcd for C₇₃H₄₂N₂O₁₀Si (M⁺+H) 102.0013, found 102.0024.

2-(Butylthio)oxazole (19). To a suspension of KH, prepared by washing oil-dispersed KH (35% in oil, 8.7 g, 73.9 mmol) with hexane, in THF (200 ml) was added a solution of oxazole-2-thiol (5.0 g 49.3 mmol) in THF (200 ml) at -60 °C, and the mixture was stirred at the same temperature for 30 min. To this mixture was added n-BuLi (16.1 ml, 147.4 mmol), and the mixture was allowed to warm gradually to rt and stirring was continued for 2 h. The reaction was quenched by the addition of saturated NH₄Cl (50 ml) and H₂O (40 ml) and the reaction mixture was extracted with Et₂O, dried, and concentrated. The residue was purified by column chromatography (SiO₂ 300 g, hexane/AcOEt = 20/1) to give 19 (6.0 g, 79%) as a yellow oil: ¹H NMR (400 MHz CDCl₃) δ 7.64 (s, 1H), 7.10 (s, 1H), 3.17 (m, J = 7.3 Hz, 2H), 1.74 (q, J = 7.3 Hz, 2H), 1.47 (sextet, J = 7.3 Hz, 2H), 0.94 (t, 3.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 139.7, 128.2, 32.2, 31.5, 21.7, 13.5; FTIR (neat) 3128, 2961 1488, 1318, 1161, 1096 cm⁻¹; HRMS (FAB) calcd for C₁₁H₁₁NOS (M⁺) 157.0561,
found 157.0559.

2-Butylthio-5-(3-trimethylsilyl-prop-2-ynyl)oxazole (20). To a solution of 19 (6.0 g, 38.2 mmol) in THF (60 ml) was added t-BuLi (1.41 M in hexane, 29.8 ml, 42.0 mmol) at –78 °C. After stirring for 30 min, the solution was transferred into a suspension of CuCN (1.52 g, 17.1 mmol) and LiCl (1.42 g, 33.8 mmol) in THF (120 ml) at –78 °C, and stirring continued at –78 °C for 30 min. To this mixture was added (3-bromoprop-1-ynyl)trimethylsilane (10.8 ml, 76.4 mmol), and the mixture was stirred at rt for 2 h. The reaction was quenched with saturated NH₄Cl, and the reaction mixture was extracted with Et₂O, washed with brine, dried, and concentrated. The residue was purified by column chromatography (SiO₂ g, hexane/ Et₂O = 95/5) to afford 20 (9.3 g, 94%) as a yellow oil: ¹H NMR (400 MHz, CDCl₃) δ 6.87 (s, 1H), 3.61 (s, 2H), 3.15 (t, 2H, J = 7.3 Hz), 1.74 (quint, J = 7.3 Hz, 2H), 1.47 (sextet, J = 7.3 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H), 0.15 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 148.6, 124.9, 99.3, 87.2, 32.4, 31.7, 21.9, 17.9, 13.7, –0.07; FTIR (neat) 3126, 2962, 2183, 1929, 1608, 1497, 1254, 1497 cm⁻¹; HRMS (FAB) calc'd. for C₇H₂₃NOSSi (M⁺) 267.1114, found: 267.1125. The spectral data were identical with those reported.[⁵]

5-(3-(Trimethylsilyl)prop-2-ynyl)oxazole. Raney-Ni (W2) (40 g) was deactivated by heating at reflux in EtOH-acetone (1:1) (500 ml) for 1 h. To this suspension of Raney-Ni was added 20 (8.0 g, 29.9 mmol), and the mixture was refluxed for 36 h. The reaction mixture was filtered through Celite, and the filtrate was combined, washed with Et₂O and acetone. The filtrate and washing were combined, concentrated, and chromatographed (SiO₂ 250 g, hexane/AcOEt = 90/10) to afford 5-(3-(trimethylsilyl)prop-2-ynyl)oxazole (4.93 g, 92%) as a colorless oil: ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.00 (s, 1H), 3.66 (s, 2H), 0.18 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 150.8, 147.7, 123.4, 99.2, 87.5, 23.4, 17.7; FTIR (neat) 3132, 2959, 2185, 1604, 1511, 1254, 1103, 1031 cm⁻¹; HRMS (EI) calc'd for C⁹H₁₃NO (M⁺) 179.0766, found 179.0751. The spectral data were identical with those reported.[⁵]

5-(Prop-2-ynyl)oxazole (21). To a solution of 5-(3-(trimethylsilyl)prop-2-ynyl)oxazole (4.6 g, 25.6 mmol) in CH₂Cl₂-MeOH-H₂O (7:4:1) (445 ml) was added Ag(OTf) (1.3 g, 5.1 mmol), and the mixture was stirred at rt for 36 h. The reaction was quenched with saturated NH₄Cl and the reaction mixture was extracted with CH₂Cl₂, dried, and concentrated. The residue was purified by column chromatography (SiO₂ 120 g, hexane/ Et₂O = 10/1 to 3/1) to give 21 (2.0 g, 73%) as a colorless oil: bp 70-72 (20 mmHg); ¹H NMR (400 MHz CDCl₃) δ 7.82 (s, 1H), 7.0 (s, 1H), 3.7 (s, 2H), 2.17 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 150.6, 147.0, 123.3, 70. 16.2; FTIR (neat) 3728, 1699, 1539, 1262, 1107 cm⁻¹; HRMS (EI) calc'd for C₆H₅NO (M⁺) 107.0371, found 107.0325.

5-((E,Z)3-(Tributylstannyl)allyl)oxazole (22). A mixture of 21 (200 mg, 1.88 mmol), n-Bu₂SnH (1.0 ml, 3.76 mmol), and AIBN (46.4 mg, 0.282 mg) was heated at 90 °C for 14 h, and chromatographed (SiO₂ 50 g, hexane/Et₂N = 50:1) to hexane/AcOEt 20/1) to give a 6:1 E,Z-Mixture of 22 (657 mg, 88%): The spectral data for the E-isomer; ¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 2H), 6.78 (s, 2H), 6.54-6.61 (m, 1H), 5.95-6.16 (m, 3H), 3.52 (d, J = 2.9 Hz, 2H), 3.41 (d, J = 1 Hz, 2H), 1.46-1.54 (m, 12H), 1.26-1.38 (m, 12H), 0.93 (t, 30H); ¹³C NMR (100 MHz, CDCl₃) δ 151 (150.2), 141.5 (141.4), 132.8 (132.4), 122.4 (122.23), 33.7, 29.0, 27.2, 13.7, 9.4; FTIR (neat) 3124, 2959, 2186, 1598, 1509, 1376, 1103 cm⁻¹; HRMS (EI) calc'd for
Stille coupling of 22 with 23 giving 24. To a stirred solution of PdCl₂(MeCN)₂ (3.84 mg, 16.2 µmol) in degassed DMF (4 ml) at rt were added a solution of (R,4Z,6Z)-methyl 3-(tert-butylidimethylsilyl)oxy-7-iodo-2,2,4-trimethylhepta-4,6-dienoate (23) (240 mg, 0.540 mmol) in degassed DMF (2 ml) and subsequently a solution of 22 (261.6 mg, 0.652 mmol) in degassed DMF (2 ml). After being stirred at rt for 4 d, the reaction mixture was diluted with 10% NH₄OH (8 ml) and stirring was continued for several minutes. The mixture was extracted with AcOEt, washed with brine, dried, concentrated, and chromatographed (SiO₂ 20 g, hexane/AcOEt = 3:1) to give 24 (179 mg, 79%), a pale yellow oil, as an inseparable 6:1 E/Z-mixture: The spectral data for the E-isomer; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 6.81 (s, 1H), 6.68 (dd, J = 14.6, 11.2 Hz, 1H), 6.41 (d, J = 12.2 Hz, 1H), 6.25 (dd, J = 11.0, 11.9 Hz, 1H), 5.96 (dd, J = 10.8, 11.2 Hz, 1H), 5.77 (dt, J = 7.3, 14.6 Hz, 1H), 5.00 (s, 1H), 3.63 (s, 3H), 3.52 (d, 2H, J = 6.8 Hz), 1.84 (s, 3H), 1.22 (s, 3H), 1.10 (s, 3H), 0.87 (s, 9H), 0.02 (s, 3H), −0.04 (s, 3H); ¹³C NMR (100 MHz CDCl₃) δ 177.0, 150.9, 150.3, 139.0, 128.3, 127.5, 126.0, 124.3, 122.5, 122.3, 73.8, 51.7, 49.4, 29.0, 25.7, 22.3, 21.2, 20.1, 20.1, 18.0, HRMS (EI) calcd for C₂₃H₄₇NO₄Si (M⁺) 419.2528, found 419.2488. The spectral data were identical with those reported.[iv]

(R,4Z,6Z,8E)-Methyl 3-Hydroxy-2,2,4-trimethyl-10-(oxazol-5-yl)deca-4,6,8-trienoate (25). To a solution of 24 (170 mg, 0.41 mmol) in MeCN (10 ml) was added 47% HF (0.8 ml) at 0 °C, and the mixture was stirred at rt for 6 h. The reaction mixture was basified with saturated NaHCO₃ at 0 °C, extracted with AcOEt, washed with brine, dried, and concentrated. The residue was purified by column chromatography (SiO₂, 10 g, hexane/AcOEt = 2:1) followed by recrystallization from hexane to give 25 (100 mg, 80%) as colorless needles: mp 102-102 °C (lit.⁴ mp 102-102 °C); [α]D²¹ +100.6 (c 0.7, CH₂Cl₂) (lit.⁴ [α]D +102.1 (c 1.0, CH₂Cl₂)); ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 6.81 (s, 1H), 6.67 (dd, J = 15.2, 11.2 Hz, 1H), 6.44 (d, J = 11.7 Hz, 1H), 6.21 (dd, J = 11.1, 11.7 Hz, 1H), 5.96 (dd, J = 11.1, 12.1 Hz, 1H), 5.77 (dd, J = 7.0, 14.5 Hz, 1H), 4.77 (dd, J = 6.4 Hz, 1H), 3.72 (s, 3H), 3.52 (d, 2H, J = 6.8 Hz, 2H), 3.33 (d, J = 6.8 Hz, 1H), 1.80 (s, 3H), 1.27 (s, 3H), 1.16 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 178.3, 150.7, 150.4, 137.7, 128.5, 128.2, 127.9, 124.9, 124.8, 122.5, 74.6, 52.2, 46.9, 29.0, 24.31, 21.0, 19.7; FT-IR (neat) 3747, 2951, 2246, 1736, 1512, 1469, 1142, 833, 649, 493 cm⁻¹; HRMS (EI) calcd for C₁₇H₂₃NO₄ (M⁺) 305.1681; found 305.1621. The spectral data were identical with those reported.[iv]

(R,4Z,6Z,8E)-3-Acetoxo-2,2,4-trimethyl-10-(oxazol-5-yl)deca-4,6,8-trienoic acid (1). To a solution of 25 (60 mg, 0.196 mmol) in THF-MeOH-H₂O (3:1:1) (4.8 ml) was added LiOH (28 mg, 0.57 mmol) at 0 °C, and the mixture was stirred at rt for 24 h. The reaction mixture was acidified by 10% HCl at 0 °C and extracted with AcOEt. The extract was washed with brine, dried, and concentrated to give the corresponding hydroxy acid (50 mg) as a pale yellow oil, which was used for the next reaction without purification.

To a solution of crude hydroxy acid (50 mg) in pyridine (162 µl) was added Ac₂O (162 µl, 1.70 mmol) at 0 °C, and the mixture was stirred at rt for 20 h. A solution of NaHCO₃ (142 mg) in MeOH (1.0 ml) was added to the reaction mixture and stirring was continued for 1 h. The reaction mixture was extracted with AcOEt, washed with brine, dried, concentrated, and
chromatographed (SiO2, 2 g, CHCl3/MeOH = 1/19) to give 1 (65 mg, 100%) as a yellow oil:  
1H NMR (400 MHz, CDCl3) δ 7.80 (s, 1H), 6.82 (s, 1H), 6.63 (dd, J = 7.0, 14.4 Hz, 1H), 6.52 (d, J = 12.2 Hz, 1H), 6.36 (dd, J = 11.0, 11.5 Hz, 1H), 6.01 (s, 1H), 5.98 (dd, J = 11.0, 11.6 Hz, 1H), 5.77 (dt, J = 7.0, 14.4 Hz, 1H), 3.51 (d, J = 6.8 Hz, 2H), 2.05 (s, 3H), 1.82 (s, 3H), 1.26 (s, 3H), 1.22 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 180.4, 170, 150.8, 150.6, 133.2, 128.7, 128.6, 126.4, 124.3, 122.3, 75.8, 47.3, 29.0, 23.1, 21.0, 20.8, 20.7; FTIR (neat) 3528, 2923, 2532, 1749, 1512, 1471, 1370, 1271 cm⁻¹; HRMS (EI) calcd for C13H23NO5 (M+) 333.1603, found 333.1573. The spectral data were identical with those reported.⁴

**Compound 26.** To a solution of 2 (28.4 mg, 40 µmol) in CH2Cl2 (0.5 mL) was added DBU (12.4 µL, 80 µmol) at rt and the mixture was stirred at rt for 30 min to afford the corresponding free amine. To a solution of carboxylic acid 1 (14.0 mg, 40 µmol) in CH2Cl2 (0.5 mL) was added N,N-bis(2-oxo-3-oxazolidinyl)phosphorodiamidic chloride (12.0 mg, 40 µmol) and Et3N (14 µL, 120 µmol). The mixture was stirred at rt for 3 h to give mixed anhydride. The above-mentioned solution of the free amine was transferred to the anhydride, and the mixture was stirred at rt for 1 h. The reaction mixture was extracted with CH2Cl2, washed with H2O and brine, dried, and concentrated. The residue was purified by preparative TLC (CHCl3/MeOH = 10:1) to give (18.3 mg, 60%) of 26 as a pale yellow oil: [α]D ²³ +48.9 (c 0.7, CH2Cl2) (lit.⁴ [α]D +43.3 (c 0.6, CH2Cl2)); 1H NMR (500 MHz, CDCl3) δ 7.81 (s, 1H), 6.90 (s, 1H), 6.62 (dd, J = 14.0, 12.5 Hz, 1H), 6.48 (br d, J = 12.0 Hz, 1H), 6.34 (dd, J = 11.0, 12.0 Hz, 1H), 6.12-6.20 (m, 3H), 5.99 (t, J = 11.0 Hz, 1H), 5.86 (s, 1H), 5.80 (dt, J = 7.0, 15.0 Hz, 1H), 5.66 (dt, J = 8.0, 14.5 Hz, 1H), 5.56 (dd, J = 7.0, 8.0 Hz, 1H), 5.20 (t, J = 5.0 Hz, 1H), 4.71 (d, J = 13.0 Hz, 1H), 4.30 (dd, J = 4.8, 8.5 Hz, 1H), 4.24 (d, J = 13.0 Hz, 1H), 3.87-3.93 (m, 2H), 3.52 (br d, J = 7.0 Hz, 1H), 2.86 (s, 3H), 2.41 (q, J = 8.0 Hz, 1H), 2.08 (s, 9H), 1.89-1.96 (m, 2H), 1.79 (s, 3H), 1.65 (s, 3H), 1.26 (d, J = 7.5 Hz, 3H), 1.22 (s, 3H), 1.21 (s, 3H), 1.02 (d, J = 7.0 Hz, 3H); 13C NMR (100 MHz CDCl3) δ 174.9, 174.6, 170.2, 170.1, 169.8, 169.6, 150.9, 150.5, 133.4, 132.7, 131.2, 130.8, 128.8, 128.7, 128.2, 126.5, 124.3, 122.4, 86.7, 80.3, 77.5, 77.4, 71.3, 57.8, 46.8, 44.4, 41.5, 34.0, 30.6, 29.7, 29.0, 26.2, 23.7, 21.8, 21.2, 20.9, 16.4, 11.0; FTIR (CDCl3) 3370, 1740, 1531, 1428, 1371, 1242 cm⁻¹; HRMS (FAB) calcd for C20H28NO4Na [(M+Na)+] 790.3552, found 790.3539. The spectral data were identical with those reported.⁴

**Completion of the Total Synthesis**

**Neooxazolomycin.** To a solution of 30 (6.0 mg 8.0 µmol) in THF-H2O (3:1) (0.5 mL) at 0 °C was added LiOH (3.3 mg 80.0 µmol). After being stirred at rt for 1 h, the reaction mixture was acidified to pH 1-2 by the addition of 0.1 M HCl at 0 °C. The reaction mixture was extracted with AcOEt, washed with brine, dried and concentrated. The residue was purified by preparative TLC (CHCl3/MeOH = 10:1) to give neooxazolomycin (3.0 mg, 59%) as a pale yellow oil: [α]D ²³ +23.8 (c 0.08, MeOH), [α]D ²³ +36.3 (c 0.08, CH2Cl2); 1H NMR (500 MHz, CD3OD) δ 8.10 (s, 1H), 6.86 (s, 1H), 6.72 (dd, J = 12.0, 14.5 Hz, 1H), 6.46 (d, J = 11.7 Hz, 1H), 6.28 (t, J = 11.5 Hz, 1H), 6.22 (d, J = 14.4 Hz, 2H), 5.96 (t, J = 11.3 Hz, 1H), 5.79 (dt, J = 7.3, 15.1 Hz, 1H), 5.64-5.72 (m, 2H), 4.71 (s, 1H), S-10
4.62 (br s, 1H), 4.38 (dd, J = 3.7, 9.4 Hz, 1H), 3.96 (t, J = 6.4 Hz, 1H), 3.96 (d, J = 12.6 Hz, 1H), 3.86 (d, J = 5.6 Hz, 2H), 3.77 (d, J = 12.4 Hz, 1H), 3.56 (d, J = 8.9 Hz, 2H), 2.83 (s, 3H), 2.44 (dd, J = 7.3, 15.1 Hz, 1H), 1.95 (dt, J = 4.8, 14.8 Hz, 1H), 1.80 (s, 3H), 1.74-1.82 (m, 1H), 1.55 (dt, J = 8.0, 15.0 Hz, 1H), 1.25 (d, J = 8.0 Hz, 3H), 1.25 (s, 3H), 1.06 (s, 3H), 0.97 (d, J = 6.9 Hz, 3H); $^{13}$C NMR (125 MHz CDCl$_3$) $\delta$ 178.4, 173.2, 158.3, 153.1, 152.8, 140.0, 135.3, 132.3, 132.1, 130.6, 129.7, 129.5, 129.0, 125.7, 125.2, 122.6, 88.8, 81.6, 77.4, 75.5, 74.3, 56.9, 46.9, 45.9, 42.1, 37.5, 32.2, 29.6, 26.3, 26.0, 22.1, 20.1, 17.4, 11.6; FTIR (CDCl$_3$) 3370, 1740, 1531, 1428, 1371, 1242 cm$^{-1}$; HRMS (FAB) calcld for C$_{34}$H$_{48}$N$_{2}$O$_{9}$ [(M+H)$^+$] 642.3390, found 642.3401. The spectral data were identical with those reported.$^{[4]}$

Preparation of (R,4Z,6Z)-Methyl 3-(tert-Butyldimethylsilyloxy)-7-ido-2,2,4-trimethylhepta-4,6-dienoate (23)

(Z)-3-Iodo-2-methylprop-2-en-ol. To a suspension of propargyl alcohol (2.0 g, 35.6 mmol) and CuI (6.78 g, 35.6 mmol) in Et$_2$O (100 ml) was added MeMgBr (1.65 M in Et$_2$O, 45 ml, 74.8 mmol) at −5°C. The mixture was gradually allowed to warm to rt and stirred for 2 h. After addition of ICl (5.78 g, 35.6 mmol) at −5°C, the mixture was gradually allowed to warm to rt and stirring was continued for additional 16 h. The reaction was quenched with saturated NH$_4$Cl at 0°C. The reaction mixture was filtered through Celite pad and the filtrate was extracted with Et$_2$O. The extract was washed with brine, dried, concentrated, and chromatographed (SiO$_2$ 150 g, hexane/AcOEt = 5/1) to give (Z)-3-iodo-2-methylprop-2-en-ol$^{[6]}$ (4.60 g, 65%) as a pale yellow oil: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.99 (s, 1H), 4.20 (s, 2H), 1.98 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.1, 74.9, 68.1, 21.6; FTIR (neat) 3419, 2911, 2187, 2012, 1618, 1283, 1137, 1046 cm$^{-1}$; HRMS (EI) calcld for C$_{12}$H$_{18}$O (M$^+$) 197.9541, found 197.9515.

(Z)-2-Methyl-5-(trimethylsilyl)pent-2-en-4-yn-1-ol. To a solution of (Z)-3-iodo-2-methylprop-2-en-ol (4.0 g, 20.2 mmol) in degassed THF (102 ml) were added (trimethylsilyl)acrylene (5.6 ml, 40.8 mmol), diisopropylamine (24 ml, 153.7 mmol), PdCl$_2$(PPh$_3$)$_2$ (288.2 mg, 0.4 mmol), and CuI (272 mg, 1.6 mmol) at rt. After being stirred at rt for 1 h under ultrasonication, the reaction mixture was diluted with Et$_2$O, washed with saturated NaHCO$_3$, dried, and concentrated. The residue was purified by column chromatography (SiO$_2$ 180 g, hexane/AcOEt = 10/1 to 5/1) to afford (Z)-2-methyl-5-(trimethylsilyl)pent-2-en-4-yn-1-ol (3.46 g, 100%) as a red brown oil: $^1$HNMR
(400 MHz CDCl₃) δ 5.41 (s, 1H), 4.36 (d, J = 6.4 Hz, 2H), 1.88 (s, 3H), 0.19 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 151.9, 106.7, 101.6, 64.1, 20.3; FTIR (neat) 3393, 2143, 1629, 1448, 1254, 1100 cm⁻¹; HRMS (EI) calcd for C₁₉H₂₀OSi (M⁺) 168.1034, found 168.0964.

(Z)-2-Methyl-5-(trimethylsilyl)pent-2-en-4-ynal. To a solution of (Z)-2-methyl-5-(trimethylsilyl)pent-2-en-4-yn-1-ol (2.0 g, 11.8 mmol) in hexane-CH₂Cl₂ (1:1) (60 ml) was added activated MnO₂ (14.4 g, 177 mmol) at rt. After stirring at rt for 24 h, the reaction mixture was filtered through Celite pad and concentrated to give (Z)-2-methyl-5-(trimethylsilyl)pent-2-en-4-ynal (1.8 g, 92%) as a brown oil, which was used for the next reaction without further purification: ¹H NMR (400 MHz, CDCl₃) δ 10.25 (s, 1H), 6.53 (s, 1H), 1.86 (s, 3H), 0.22 (s, 9H). ¹³C NMR (100 MHz CDCl₃) δ 192.5, 147.4, 125.8, 106.5, 92.3, 15.5; FTIR (neat) 3557, 3357, 2138, 1697, 1257, 1100 cm⁻¹.

(R)-3-((S)-1-Hydroxy-3-methylbutan-2-yl)-5,5-dimethyl-6-((Z)-5-(trimethylsilyl)pent-2-en-4-yn-2-yl)-1,3-oxazinan-2,4-dione. LiAlH₄ (342 mg, 9.0 mmol) was added portionwise to a suspension of anhydrous SnCl₄ (3.42 g, 18.0 mmol), dried at 120 °C for 2 h in vacuo prior to use, in THF (18 ml) at rt. After stirring at rt for 20 min, a dark gray material was precipitated. To this suspension was added (S)-3-((2-bromo-2-methylpropanoyl)-4-isopropylloxazolidin-2-one (3.0 g, 10.8 mmol) in THF (18 ml) at rt, and the mixture was stirred at rt for 45 min. A solution of (Z)-2-methyl-5-(trimethylsilyl)pent-2-en-4-ynal (1.5 g, 9 mmol) in THF (18 ml) was then added at rt, and stirring was continued at rt for 16 h. The reaction was quenched with H₂O at 0 °C, and most of the THF was evaporated. The residue was extracted with Et₂O, washed with brine, dried, concentrated, and chromatographed (SiO₂ 150 g, hexane/AcOEt = 10/1 to 5/1) to give (R)-3-((S)-1-hydroxy-3-methylbutan-2-yl)-5,5-dimethyl-6-((Z)-5-(trimethylsilyl)pent-2-en-4-yn-2-yl)-1,3-oxazinan-2,4-dione (2.87 g, 87%) as a colorless solid; [α]₀²³ +8.1 (c 1.0, CH₂Cl₂) (lit. [α]₀⁺8.1 (c 1.0, CH₂Cl₂)); ¹H NMR (400 MHz, CDCl₃) δ 5.66 (s, 1H), 5.50 (s, 1H), 4.42 (ddd, 1H, J = 2.7, 7.9, 10.6 Hz), 4.08 (m, 1H), 3.82 (br d, 1H, J = 12.2 Hz), 2.75 (br d, 1H, J = 7.8 Hz), 2.43-2.28 (m, 1H), 1.94 (s, 3H), 1.33 (s, 3H), 1.25 (s, 3H), 1.06 (d, 3H, J = 6.8 Hz), 0.86 (d, 3H, J = 6.84 ), 0.15 (s, 9H); ¹³C NMR (400 MHz, CDCl₃) δ 175.9, 152.2, 144.4, 113.7, 102.3, 101.5, 81.2, 62.8 43.6, 26.1, 22.3, 22.3, 20.1, 19.4; FTIR (neat), 3559, 1712, 1479, 1260 cm⁻¹; HRMS (EI) calcd for 365.2202 (M⁺) found: 365.2018. The spectral data were identical with those reported.[8]

(R,Z)-Methyl 3-Hydroxy-2,2,4-trimethylhept-4-en-6-ynoate. To a solution of 21 (2.20 g, 6.03 mmol) in THF (90 ml) and H₂O (30 ml) were added 30% H₂O₂ (4.10 g, 36.1 mmol) and LiOH (506 mg, 12.1 mmol) at 0 °C, and the mixture was stirred at rt for 24 h. The reaction was quenched with 1.5 M Na₂SO₃ at 0 °C, and most of the THF was evaporated. The residue was diluted with H₂O, washed with CH₂Cl₂, acidified to pH 1, and extracted with AcOEt. The extract was washed with brine, dried, and concentrated to give a yellow oily residue (1.40 g).

The residue (1.40 g) was dissolved in THF-MeOH-H₂O (3:1:1) (90 ml) and LiOH (568 mg, 13.6 mmol) was added. After being stirred at rt for 24 h, the reaction mixture was concentrated, extracted with AcOEt, washed with brine, dried, and concentrated to give the corresponding hydroxy acid as a yellow oil (1.20 g), which was used for the next reaction without purification.

To a solution of crude hydroxy acid (1.20 g) in Et₂O (30 ml) was added ethereal CH₂N₂ at 0 °C, and the mixture was stirred at 0 °C for 10 min. The reaction mixture was concentrated and chromatographed (SiO₂ 40 g, hexane/AcOEt = 7/1) to give (R,Z)-methyl 3-hydroxy-2,2,4-trimethylhept-4-en-6-ynoate (700 mg, 60%) as a colorless oil: [α]₀²² -18.3 (c 1.1, S-12)
\[ \text{CH}_2\text{Cl}_2 \] (lit.\[^{[4]}\] \( \alpha \)_D = -26.6 (c 0.94, \text{CH}_2\text{Cl}_2)); \^1\text{HNMR} (400 \text{ MHz, CDCl}_3) \delta 5.47 (s, 1H), 5.30 (s, 1H), 4.87 (d, 1 H, \( J = 7.3 \) Hz), 3.73 (s, 3H), 3.61 (d, 1H, \( J = 7.3 \) Hz), 3.07 (d, 1H, \( J = 1.9 \) Hz), 1.75 (s, 3H), 1.35 (s, 3H), 1.18 (s, 3H); \(^{13}\text{C} \) (400 \text{ MHz CDCl}_3) \delta 178.2, 151.4, 108.7, 81.8, 80.5, 52.1, 46.5, 24.4, 20.6, 18.1; FTIR (neat) 3494, 2094, 1735, 1469, 1142, 1050 cm\(^{-1}\). HRMS (EI) calcld for \( \text{C}_{11}\text{H}_{16}\text{O}_3 \) (M\(^+\)) 196.1162, found 196.1092.

\[ \text{OTBS} \text{CO}_2\text{Me} \]

**\( (R,Z) \)-Methyl 3-(tert-Buthyldimethylsilyloxy)-2,2,4-trimethylhept-4-en-6-ynoate.** To a solution of \( (R,Z) \)-methyl 3-hydroxy-2,2,4-trimethylhept-4-en-6-ynoate (600 mg, 3.1 mmol) in \( \text{CH}_2\text{Cl}_2 \) (13 ml) were added 2,6-lutidine (1.4 ml, 12.4 mmol) and TBSOTf (2.7 ml, 7.9 mmol) at 0 °C. The mixture was allowed to warm to rt and stirred for additional 0.5 h. The reaction was quenched with saturated NH\(_4\)Cl at 0 °C, and the reaction mixture was extracted with \( \text{CH}_2\text{Cl}_2 \). The extract was washed with brine, dried, concentrated, and chromatographed (SiO\(_2\) 30 g, hexane/AcOEt = 100/1) to give \( (R,Z) \)-methyl 3-(tert-buthyldimethylsilyloxy)-2,2,4-trimethylhept-4-en-6-ynoate (900 mg, 94 %) as a colorless oil: \( \alpha \)_D = +15.3 (c 1.1, \text{CH}_2\text{Cl}_2) \) (lit.\[^{[6]}\] \( \alpha \)_D = +114.3 (c 1.2, \text{CH}_2\text{Cl}_2)); \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 5.44 (s, 1H), 5.15 (s, 1H), 3.66 (s, 3H), 3.13 (d, 1H, \( J = 1.5 \) Hz), 1.80 (s, 3H), 1.21 (s, 3H), 1.18 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), -0.02 (s, 3H); \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 177.2, 153.1, 108.8, 82.2, 80.9, 52.0, 49.4, 26.9, 22.9, 21.0, 18.9, 18.3; FTIR (neat) 3311, 1735, 1468, 1256, 1136, 1083 cm\(^{-1}\); HRMS (EI) calcld for \( \text{C}_{15}\text{H}_{20}\text{O}_3\text{Si} \) (M\(^+\)) 310.1965, found 310.1938. The spectral data were identical with those reported.\[^{[4]}\]

\[ \text{OTBS} \text{CO}_2\text{Me} \]

**\( (R,Z) \)-Methyl 3-(tert-Buthyldimethylsilyloxy)-7-iodo-2,2,4-trimethylhept-4-en-6-ynoate.** To a solution of \( (R,Z) \)-methyl 3-(tert-buthyldimethylsilyloxy)-2,2,4-trimethylhept-4-en-6-ynoate (600 mg, 1.94 mmol) in THF (10 ml) was added n-BuLi (1.6 M in hexane, 1.34 ml, 2.14 mmol) at –78 °C. After stirring at –78 °C for 1 h, a solution of I\(_2\) (984 mg, 3.88 mmol) in THF (2 ml) was added and stirring was continued at –78 °C for 1 h. The mixture was allowed to warm to rt, and the reaction was quenched with saturated Na\(_2\)S\(_2\)O\(_3\) at 0 °C. The reaction mixture was extracted with AcOEt, washed with brine, dried, concentrated, and chromatographed (SiO\(_2\) 50 g, hexane/AcOEt = 7/1) gave \( (R,Z) \)-methyl 3-(tert-buthyldimethylsilyloxy)-7-iodo-2,2,4-trimethylhept-4-en-6-ynoate (841 mg, 99%) as a pale yellow oil: \( \alpha \)_D = +93.4 (c 1.0, \text{CH}_2\text{Cl}_2) \) (lit.\[^{[6]}\] \( \alpha \)_D = +97.6 (c 1.3, \text{CH}_2\text{Cl}_2)); \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 5.55 (s, 1H), 5.10 (s, 1H), 3.67 (s, 3H), 1.80 (s, 3H), 1.20 (s, 3H), 1.16 (s, 3H), 0.88 (s, 9H), 0.06 (s, 3H), 0.01 (s, 3H); \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 176.7, 154.0, 109.6, 91.4, 76.5, 51.8, 49.0, 25.7, 22.4, 20.9, 18.4, 18.0; FTIR (neat) 1736, 1468, 1388, 1255, 1137, 1079, 1000 cm\(^{-1}\); HRMS (EI) calcld for \( \text{C}_{15}\text{H}_{20}\text{O}_3\text{Si} \) (M\(^+\)) 436.0931, found 436.0922. The spectral data were identical with those reported.\[^{[4]}\]

\[ \text{OTBS} \text{CO}_2\text{Me} \]

**\( (R,4Z,6Z) \)-Methyl 3-(tert-Butyldimethylsilyloxy)-7-ido-2,2,4-trimethylecta-4,6-dienoate (23).** To a solution of \( (R,Z) \)-methyl 3-(tert-buthyldimethylsilyloxy)-7-ido-2,2,4-trimethylecta-4-en-6-ynoate (800 mg, 1.84 mmol) in THF-i-ProH (1:1) (10 ml) were added Et\(_3\)N (0.384 ml, 2.76 mmol) and \( p \)-nitrobenzenesulfonyl hydrazide\[^{[7]}\] (654 mg, 3.00 mmol) at rt. The mixture was stirred under dark at rt for 12 h. The reaction mixture was diluted with AcOEt, washed with H\(_2\)O and brine, dried, and concentrated. The residue was purified by flash chromatography (SiO\(_2\) 15 g, hexane/AcOEt = 100/1) to give the recovered starting material (120 mg, 15%) and 23 (600 mg, 74 %) as a pale yellow oil: \( \alpha \)_D = +77.5 (c 1.35, \text{CH}_2\text{Cl}_2) \) (lit.\[^{[4]}\] \( \alpha \)_D = +78.2 (c 1.1, \text{CH}_2\text{Cl}_2)); \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.00 (br d, \( J = 8.3 \) Hz), 6.25

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(d, 1H, J = 6.3 Hz), 6.12 (d, 1H, J = 10.3 Hz), 4.91 (br s, 1H), 3.63 (s, 3H), 1.84 (s, 3H), 1.23 (s, 3H), 1.10 (s, 3H), 0.88 (s, 9H), 0.02 (s, 3H), −0.04 (s, 3H); FTIR (neat) 1741, 1469, 1386, 1260, 1091, 1012 cm⁻¹; HRMS (EI) caled for C₁₇H₁₃O₃Si (M⁺) 438.1087, found 438.1072. The spectral data were identical with those reported.\(^\text{[3]}\)

**Preparation of (9H-Fluoren-9-yl)methyl (2E,4E)-5-Iodopenta-2,4-dienylcarbamate (14)**

\[
\begin{align*}
\text{HO} & \quad \underline{\text{THP}} \\
\xrightarrow{\text{phthalimide, } \text{Ph₃P, DIPAD}} & \quad \xrightarrow{\text{NH₂NH₂·H₂O, EtOH, reflux}} \\
\text{FmocCl, NaHCO₃} & \quad \xrightarrow{\text{dioxane, 10 °C}} \\
\text{THF, -20 °C} & \quad \xrightarrow{\text{PPTS, MeOH, reflux}} \\
\text{100%} & \quad \xrightarrow{\text{92%}} \\
\text{1) TEMPO, Ph₂(OAc)₂, CH₂Cl₂} & \quad \xrightarrow{\text{64%}} \\
\text{2) CrCl₃·CH₃Cl, THF} & \quad \xrightarrow{\text{64%}} \\
\end{align*}
\]

**2-((E)-4-(Tetrahydro-2H-pyran-2-yl oxy)but-2-enyl)isoindoline-1,3-dione.** To a solution of (E)-4-(tetrahydro-2H-pyran-2-yl oxy)but-2-en-1-ol\(^\text{[8]}\) (5.00 g, 29.0 mmol) in THF (137 ml) were added triphenylphosphine (9.14 g, 34.8 mmol), phthalimide (5.12 g, 34.8 mmol), and diisopropyl azodicarboxylate (DIAD) (6.75 ml, 34.8 mmol) at -20 °C. After stirring at rt for 1 h, SiO₂ (54 g) was added, and the mixture was concentrated. The residue was subjected to column chromatography (SiO₂ 270 g, hexane/AcOEt = 10/1 to 6/1) to afford 2-((E)-4-(tetrahydro-2H-pyran-2-yl oxy)but-2-en-1-yl)isoindoline-1,3-dione (8.74 g, 100%) as a colorless solid: \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.86 (d, \(J = 2.9\) Hz, 1H), 7.84 (d, \(J = 2.9\) Hz, 1H), 7.72 (d, \(J = 2.9\) Hz, 1H), 7.71 (d, \(J = 2.9\) Hz, 1H), 5.84-5.81 (m, 2H), 4.61 (t, \(J = 3.4\) Hz, 1H), 4.30 (d, \(J = 4.6\) Hz, 2H), 4.23-4.19 (m, 1H), 3.97-3.93 (m, 1H), 3.86-3.80 (m, 1H), 3.50-3.46 (m, 1H), 1.82-1.50 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 167.7 (2), 134.2, 133.8, 132.1, 130.4, 125.5, 123.5, 123.2 (2), 97.9, 66.6, 62.1, 39.1, 30.5, 25.5, 19.4; FTIR (neat) 3801, 3464, 1699, 1606, 1389, 1190, 1024, 802, 715 cm⁻¹; MS (EI) m/z 85, 200 (100), 217, 301 (M⁺).

**2-((E)-4-(Tetrahydro-2H-pyran-2-yl oxy)but-2-en-1-amine.** To a solution of 2-((E)-4-(tetrahydro-2H-pyran-2-yl oxy)but-2-en-1-yl)isoindoline-1,3-dione (8.50 g, 28.2 mmol) in EtOH (320 ml) was added hydrazine monohydrate (2.0 ml, 42.3 mmol), and the mixture was refluxed for 1 h. Most of the EtOH was removed in vacuo, and the residue was dissolved in CHCl₃ and filtered through Celite pad. The filtrate was concentrated and chromatographed (SiO₂ 150 g, CHCl₃/MeOH = 20/1) to give (E)-4-(tetrahydro-2H-pyran-2-yl oxy)but-2-en-1-amine (2.58 g, 54%) as a pale yellow solid: \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 5.89-5.83 (m, 1H), 5.75-5.68 (m, 1H), 4.65 (t, \(J = 3.5\) Hz, 1H), 4.25 (dd, \(J = 1.2, 12.2\) Hz, 0.5H), 4.23 (dd, \(J = 1.0, 12.2\) Hz, 0.5H), 3.99-3.94 (m, 1H), 3.91-3.85 (m, 1H), 3.54-3.49 (m, 1H), 3.32 (dd, \(J = 1.0, 5.5\) Hz, 2H), 1.88-1.45 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\) 134.6, 125.9, 97.9, 67.3, 62.2, 43.6, 30.6, 25.4, 19.5; FTIR (neat) 1566, 1442, 1124, 1026 cm⁻¹; MS (FAB) m/z 43, 69, 70, 85 (100), 172 (M⁺+H).
(9H-Fluoren-9-yl)methyl (E)-4-(Tetrahydro-2H-pyran-2-yloxy)but-2-enylcarbamate. To a solution of (E)-4-(tetrahydro-2H-pyran-2-yloxy)but-2-en-1-amine (2.00 g, 11.7 mmol) in 1,4-dioxane (117 ml) were added NaHCO₃ (2.94 g, 35.0 mmol) and 9-fluorenylmethyl chloroformate (5.43 g, 17.5 mmol). After being stirred at rt for 5 h, the reaction mixture was extracted with Et₂O, washed with saturated NaHCO₃ and brine, dried, and concentrated. The residue was purified by column chromatography (SiO₂300 g, hexane/ACOEt = 10/1 to 6/1) to give (9H-fluoren-9-yl)methyl (E)-4-(tetrahydro-2H-pyran-2-yloxy)but-2-enylcarbamate (4.36 g, 95%) as a colorless solid: ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 7.3 H, 2H), 7.40 (t, J = 7.3 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 5.75 (s, 2H), 4.85 (s, 1H), 4.63 (s, 1H), 4.41 (d, J = 6.8 Hz, 2H), 4.23 (d, J = 11.5 Hz, 1H), 4.22 (s, 1H), 3.95 (d, J = 11.5 Hz, 1H), 3.88-3.83 (m, 3H), 3.52-3.48 (m, 1H), 1.87-1.52 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 143.7 (2), 141.1 (2), 128.8, 128.4, 127.5 (2), 126.9 (2), 124.8 (2), 119.8 (2), 98.0, 66.8, 66.6, 62.1, 47.2, 30.5, 25.4, 19.4; FTIR (neat) 3327, 1714, 1529, 1450, 1246, 1130, 1074, 1024 cm⁻¹; MS (EI) m/z 178 (100), 393 (M⁺); HRMS (EI) calc'd for C₂₄H₂₇NO₄ (M⁺) 393.1940, found 393.1936.

(9H-Fluoren-9-yl)methyl (E)-4-Hydroxybut-2-enylcarbamate. To a solution of (9H-fluoren-9-yl)methyl (E)-4-(tetrahydro-2H-pyran-2-yloxy)but-2-enylcarbamate (4.30 g, 10.9 mmol) in MeOH (36 ml) was added PPTS (550 mg, 2.19 mmol), and the mixture was refluxed for 24 h. The after being cooled to rt, reaction mixture was diluted with Et₂O, washed with saturated NaHCO₃ and brine, dried, concentrated, and chromatographed (SiO₂ 175 g, hexane/ACOEt = 100/1 to 80/1) to give (9H-fluoren-9-yl)methyl (E)-4-hydroxybut-2-enylcarbamate (3.10 g, 92%) as colorless crystals: mp 115-116 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 7.3 H, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 5.80-5.71 (m, 2H), 4.84 (bs, 1H), 4.43 (d, J = 6.6 Hz, 2H), 4.23-4.20 (m, 1H), 4.15 (bs, 1H), 3.83 (bs, 2H), 1.41 (bs, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.1, 143.8 (2), 141.2 (2), 131.0, 127.7, 127.6 (2), 126.9 (2), 124.8 (2), 119.8 (2), 66.6, 62.8, 47.2, 42.3; FTIR (neat) 3315, 1685, 1514, 1444, 1261, 1146, 1092 cm⁻¹; MS (EI) m/z 178 (100), 309 (M⁺); HRMS (EI) calc'd for C₁₉H₁₉NO₃ (M⁺) 309.1365, found 309.1355.

(9H-Fluoren-9-yl)methyl (2E,4E)-5-Iodopenta-2,4-dienylcarbamate (14). To a solution of (9H-fluoren-9-yl)methyl (E)-4-hydroxybut-2-enylcarbamate (500 mg, 1.62 mmol) in CH₂Cl₂ (16 ml) were added PhI(OAc)₂ (1.72 g, 5.34 mmol) and TEMPO (50.5 mg, 0.32 mmol). After being stirred at rt for 4.5 h, the reaction mixture was diluted with CH₂Cl₂, washed with saturated Na₂S₂O₃ and brine, dried, and concentrated to give the corresponding aldehyde (1.70 g), which was used for the next reaction without purification.

To a suspension of CrCl₃ (2.79 g, 22.9 mmol) in THF (30 ml) at 0 °C were added CH₃I (2.09 g, 5.28 mmol) and crude aldehyde (1.70 g), and the mixture was stirred at rt for 1.5 h. The reaction was quenched with saturated Na₂S₂O₃ (30 ml), and the reaction mixture was extracted with AcOEt. The extract was washed with brine, dried, and concentrated. The residue was purified by column chromatography (SiO₂ 30 g, hexane/ACOEt = 40/1 to 10/1) to give 14 (450 mg, 64%) as pale yellow crystals (CHCl₃): ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 7.6 Hz, 2H), 7.58 (d, J = 7.1 H, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.32-7.29 (m, 1H), 7.00 (dd, J = 10.5, 14.4 Hz, 1H), 6.32 (d, J = 14.4 Hz, 1H), 6.10-6.04 (m, 1H), 5.75-5.65 (m, 1H), 4.82 (bs, 1H), 4.43 (d, J = 6.7 Hz, 2H), 4.22 (t, J = 6.7 Hz, 1H), 3.8 (bs, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 144.1, 143.8 (2), 141.2 (2), 131.4, 130.3, 127.6 (2), 127.0 (2), 124.9 (2), 120.2 (2), 79.6, 66.7, 47.3, 42.3; FTIR (neat) 3317, 3053, 1687, 1531, 1442, 1263, 1146, 1146 cm⁻¹; MS (EI) m/z 178 (100), 256, 367, 431 (M⁺); HRMS (EI) calc'd for C₂ₙH₁₈NIO₂ (M⁺) 431.0382, found 431.0381.
References