Supporting Information

Crotylations of α -Carbonyl Radicals with Crotylstannane

Mukund P. Sibi* and Hideto Miyabe

Department of Chemistry, North Dakota State University

Fargo, North Dakota 58105-5516

Mukund.Sibi@ndsu.nodak.edu

General Experimental. Tetrahydrofuran and Dichloromethane were dried by SOLV-TEK alumina column prior to use. Flash chromatography was performed by using EM Science silica gel 60 (230-400 mesh). Reactions with air sensitive materials were carried out by standard syringe techniques. Melting points were determined by using the Fisher-Johns melting point apparatus. ^1H NMR spectra were recorded on Varian Unity/Inova-500 NB spectrometer or Varian Unity/Inova-400 NB spectrometer. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublets of doublets, ddd = doublets of doublets of doublets, m = multiplet, br = broad), coupling constant(s) and integration. ^{13}C NMR spectra were recorded on Varian Unity/Inova-500 NB spectrometer or Varian Unity/Inova-400 NB spectrometer using broad band proton decoupling. High-resolution mass spectra (HRMS) [E+] were obtained at the Mass Spectrometry Laboratory, University of South Carolina, Columbia, SC and Ohio State University, Columbus Ohio.

Preparation of acrylamides: Acrylamides were prepared using literature procedures:¹ 2-Oxazolidinone, 2-pyrrolidinone, 3,5-dimethyl-pyrazole were acylated with acryloyl chloride and triethyl amine; 2-benzoxazolinone and naphtho<1,8-cd>isothiazole-1,1-dioxide were deprotonated with *n*-butyllithium followed by addition of acryloyl chloride; 1-phenyl-2-imidazolidinone,² was treated with *n*-butyllithium followed by addition of 3-bromopropionyl chloride, then the bromide eliminated by addition of triethylamine.

3-(2-Propenoyl)-2-oxazolidinone (1).³

mp 80-81 °C; ¹H NMR (400 MHz, CDCl₃) δ 4.06 (t, *J* = 8.0 Hz, 2H), 4.43 (t, *J* = 8.0 Hz, 2H), 5.89 (dd, *J* = 10.5, 1.6 Hz, 1H), 6.54 (dd, *J* = 17.2, 1.6 Hz, 1H), 7.46 (dd, *J* = 17.2, 10.6 Hz, 1H).

1-(2-Propenoyl)-2-pyrrolidinone (4).³

¹H NMR (400 MHz, CDCl₃) δ 1.92-2.00 (m, 2H), 2.51 (t, *J* = 8.0 Hz, 2H), 3.74 (t, *J* = 7.2 Hz, 2H), 5.72 (dd, *J* = 10.5, 2.0 Hz, 1H), 6.37 (dd, *J* = 17.2, 2.0 Hz, 1H), 7.35 (dd, *J* = 17.2, 10.5 Hz, 1H).

1-Phenyl-3-(2-propenoyl)-2-imidazolidinone (5).

mp 135-136 °C; ¹H NMR (400 MHz, CDCl₃) δ 3.93 (t, *J* = 8.0 Hz, 2H), 4.02 (t, *J* = 8.0 Hz, 2H), 5.83 (dd, *J* = 10.5, 1.9 Hz, 1H), 6.52 (dd, *J* = 16.9, 1.9 Hz, 1H), 7.12-7.18 (m, 1H), 7.34-7.42 (m, 2H), 7.50-7.58 (m, 2H), 7.64 (dd, *J* = 16.9, 10.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 39.2, 41.8, 119.2, 124.6, 128.6, 129.1, 129.9, 138.8, 152.6, 165.8. Anal. Calcd for C₁₂H₁₂N₂O₂: C, 66.65, H, 5.59, N, 12.95. Found: C, 66.46, H, 5.81, N, 12.75.

3-(2-Propenoyl)-2-benzoxazolinone (6).⁴

mp 90-92 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.08 (dd, *J* = 10.5, 1.4 Hz, 1H), 6.74 (dd, *J* = 16.9, 1.4 Hz, 1H), 7.19-7.30 (m, 3H), 7.60 (dd, *J* = 16.9, 10.5 Hz, 1H), 8.05-8.13 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 109.9, 116.2, 124.9, 125.5, 127.5, 127.9, 134.1, 142.4, 151.2, 164.1.

3,5-Dimethyl-1-(2-propenoyl)pyrazole (7).⁵

¹H NMR (400 MHz, CDCl₃) δ 2.24 (s, 3H), 2.58 (s, 3H), 5.96 (dd, *J* = 10.5, 1.6 Hz, 1H), 5.99 (s, 1H), 6.60 (dd, *J* = 17.2, 1.6 Hz, 1H), 7.57 (dd, *J* = 17.2, 15.6 Hz, 1H).

2-(2-Propenoyl)-naphtho<1,8-cd>isothiazole>-1,1-dioxide (8).

mp 173-175 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.09 (dd, *J* = 10.2, 1.4 Hz, 1H), 6.76 (dd, *J* = 16.6, 1.4 Hz, 1H), 7.26 (dd, *J* = 16.6, 10.2 Hz, 1H), 7.66-7.83 (m, 3H), 8.01-8.03 (m, 1H), 8.17-8.20 (m, 1H), 8.31-8.34 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 113.9, 118.9, 120.0, 122.3,

127.8, 127.9, 128.5, 129.9, 130.6, 131.6, 132.2, 133.0, 162.6. Anal. Calcd for $C_{13}H_9NO_3S$: C, 60.22 H, 3.50, N, 5.40. Found: C, 59.91, H, 3.68, N, 5.31.

General Procedure for the reaction of 1 and 4-8: To a flask containing $Yb(OTf)_3$ (132 mg, 0.213 mol) and starting materials **1** and **4-8** (0.213 mmol) under N_2 were added THF (2 mL) and CH_2Cl_2 (4 mL), and then cooled in a dry ice/acetone bath. To this solution were added EtI (0.17 mL, 2.13 mmol), $CH_3CH=CHCH_2SnBu_3$ (0.37 mL, 1.07 mmol), and Et_3B /hexane solution (1M, 0.64 mL, 0.639 mmol). At once, O_2 (5 mL) was added. After being stirred at $-78\text{ }^\circ\text{C}$ for 3 h, the reaction was diluted with ether (20 mL). Silica gel (ca. 2.5 g) was added to the mixture, and then concentrated. The resulting powder was washed with hexanes (100 mL), and the product was eluted by washing EtOAc (60 mL). Evaporation of EtOAc yielded the crude product. Flash chromatography (hexane/EtOAc) furnished the desired compounds **3** and **9-10**. (See: Table 2)

3: a mixture of diastereomers (major isomer:minor isomer = 3.5:1); a colorless oil; 1H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, $J = 7.5$ Hz, $1/4.5 \times 3H$), 0.88 (t, $J = 7.5$ Hz, $3.5/4.5 \times 3H$), 1.01 (d, $J = 6.5$ Hz, $1/4.5 \times 3H$), 1.02 (d, $J = 7.0$ Hz, $3.5/4.5 \times 3H$), 1.18-1.27 (m, 2H), 1.42-1.58 (m, 1H), 1.53-1.73 (m, 1H), 2.41-2.51 (m, 1H), 3.82-3.91 (m, 1H), 3.93-4.05 (m, 2H), 4.34-4.41 (m, 2H), 4.91-5.04 (m, 2H), 5.70 (ddd, $J = 19.0, 10.5, 8.5$ Hz, $1/4.5 \times 1H$), 5.78 (ddd, $J = 18.5, 10.5, 8.0$ Hz, $3.5/4.5 \times 1H$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4, 16.8, 18.5, 20.7, 21.0, 31.3, 32.5, 41.0, 41.2, 42.8, 42.9, 47.2, 47.4, 61.9, 114.6, 115.2, 141.3, 141.9, 153.6 (2 peaks), 176.4, 176.7; HRMS Calcd. for $C_{12}H_{19}NO_3$: 225.1365, Found: 225.1358. Some ^{13}C resonances are missing because of the overlap of diastereomers.

9: a mixture of diastereomers (major isomer:minor isomer = 3.7 : 1); a colorless oil; 1H NMR (500 MHz, $CDCl_3$) δ 0.82 (t, $J = 7.0$ Hz, $1/4.7 \times 3H$), 0.84 (t, $J = 7.0$ Hz, $3.7/4.7 \times 3H$), 0.970 (d, $J = 7.0$ Hz, $3.7/4.7 \times 3H$), 0.973 (d, $J = 7.0$ Hz, $1/4.7 \times 3H$), 1.10-1.28 (m, 2H), 1.34-1.47 (m, 1H), 1.56-1.72 (m, 1H), 1.91-2.02 (m, 2H), 2.39-2.47 (m, 1H), 2.54-2.62 (m, 2H), 3.70-3.90 (m, 3H), 4.88-4.99 (m, 2H), 5.67 (ddd, $J = 18.5, 10.5, 8.5$ Hz, $1/4.7 \times 1H$), 5.77 (ddd, $J = 18.0, 10.5, 8.0$ Hz, $3.7/4.7 \times 1H$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5, 16.4, 17.2, 18.6, 20.7, 21.0, 30.9, 32.3, 34.4, 40.5, 41.2, 46.0 (2 peaks), 48.6 (2 peaks), 114.1, 114.8, 141.6, 142.3, 175.4 (2 peaks),

177.2, 177.6; HRMS Calcd. for $C_{13}H_{21}NO_2$: 223.1572, Found: 223.1574. Some ^{13}C resonances are missing because of the overlap of diastereomers.

10: a mixture of diastereomers (major isomer:minor isomer = 3.7 : 1); a colorless oil; 1H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, $J = 7.5$ Hz, $1/4.7 \times 3H$), 0.90 (t, $J = 7.0$ Hz, $3.7/4.7 \times 3H$), 1.04 (d, $J = 7.0$ Hz, 3H), 1.21-1.34 (m, 2H), 1.43-1.55 (m, 1H), 1.62-1.78 (m, 1H), 2.51 (dt, $J = 14.5, 7.5$ Hz, 1H), 3.84-4.01 (m, 4H), 4.02-4.11 (m, 1H), 4.91-5.05 (m, 2H), 5.73 (ddd, $J = 19.0, 10.5, 8.5$ Hz, $1/4.7 \times 1H$), 5.85 (ddd, $J = 18.0, 10.5, 8.0$ Hz, $3.7/4.7 \times 1H$), 7.13-7.80 (m, 1H), 7.36-7.42 (m, 2H), 7.54-7.58 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5 (2 peaks), 16.8, 18.9, 20.9, 21.1, 31.4, 32.8, 39.3, 39.4, 40.9, 41.5, 41.6, 47.7, 47.8, 114.2, 114.9, 119.4 (2 peaks), 124.6, 124.7, 129.3 (2 peaks), 139.0, 139.1, 142.0, 142.5, 152.8, 176.8, 177.3; HRMS Calcd. for $C_{18}H_{24}NO_2$: 300.1838, Found: 300.1833. Some ^{13}C resonances are missing because of the overlap of diastereomers.

11: a mixture of diastereomers (major isomer:minor isomer = 1.4 : 1); a colorless oil; 1H NMR (500 MHz, $CDCl_3$) δ 0.89 (t, $J = 7.5$ Hz, $1/2.4 \times 3H$), 0.91 (t, $J = 7.5$ Hz, $1.4/2.4 \times 3H$), 1.08 (d, $J = 7.0$ Hz, $1.4/2.4 \times 3H$), 1.10 (d, $J = 6.5$ Hz, $1/2.4 \times 3H$), 1.24-1.37 (m, 2H), 1.52-1.63 (m, 1H), 1.73-1.87 (m, 1H), 2.56-2.65 (m, 1H), 3.96-4.05 (m, 1H), 4.93-5.06 (m, 2H), 5.75 (ddd, $J = 17.5, 10.5, 8.0$ Hz, $1/2.4 \times 1H$), 5.85 (ddd, $J = 17.5, 10.5, 8.0$ Hz, $1.4/2.4 \times 1H$), 7.20-7.28 (m, 3H), 8.08-8.13 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.4 (2 peaks), 16.4, 18.6, 20.7, 21.0, 31.0, 32.1, 40.6, 41.1, 49.1 (2 peaks), 110.0 (2 peaks), 115.2, 115.7, 116.5, 124.0 (2 peaks), 125.5 (2 peaks), 128.1 (2 peaks), 140.7, 141.3, 142.3, 151.5, 151.6, 175.7, 175.9; HRMS Calcd. for $C_{16}H_{19}NO_3$: 273.1365, Found: 273.1360. Some ^{13}C resonances are missing because of the overlap of diastereomers.

12: a mixture of diastereomers (major isomer:minor isomer = 1.5 : 1); a colorless oil; 1H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, $J = 7.5$ Hz, $1/2.5 \times 3H$), 0.88 (t, $J = 7.5$ Hz, $1.5/2.5 \times 3H$), 1.00 (d, $J = 7.0$ Hz, $1/2.5 \times 3H$), 1.03 (d, $J = 6.5$ Hz, $1.5/2.5 \times 3H$), 1.15-1.31 (m, 2H), 1.47-1.78 (m, 2H), 2.225 (s, $1.5/2.5 \times 3H$), 2.232 (s, $1/2.5 \times 3H$), 2.52 (s, $1.5/2.5 \times 3H$), 2.54 (s, $1/2.5 \times 3H$), 2.54-2.61 (m, 1H), 3.87 (m, $1/2.5 \times 1H$), 3.94 (m, $1.5/2.5 \times 1H$), 4.87-5.04 (m, 2H), 5.72 (ddd, $J =$

19.0, 10.5, 8.5 Hz, 1/2.5 x 1H), 5.79 (ddd, $J = 17.5, 10.0, 7.5$ Hz, 1.5/2.5 x 1H), 5.94 (s, 1.5/2.5 x 1H), 5.96 (s, 1/2.5 x 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.1, 14.5 (2 peaks), 15.0 (2 peaks), 16.9, 19.0, 20.7, 20.9, 31.4, 32.8, 40.6, 41.4, 48.0, 48.2, 111.4, 111.6, 114.3, 115.0, 141.8, 142.1, 144.0 (2 peaks), 151.5, 151.6, 176.7, 177.3; HRMS Calcd. for $\text{C}_{14}\text{H}_{22}\text{N}_2\text{O}$: 234.1732, Found: 234.1727. Some ^{13}C resonances are missing because of the overlap of diastereomers.

13: a mixture of diastereomers (major isomer:minor isomer = 2.3 : 1); a white solid; mp 52-54 °C; ^1H NMR (500 MHz, CDCl_3) δ 0.91 (t, $J = 7.0$ Hz, 1/3.3 x 3H), 0.94 (t, $J = 7.5$ Hz, 2.3/3.3 x 3H), 1.180 (d, $J = 7.0$ Hz, 2.3/3.3 x 3H), 1.184 (d, $J = 6.5$ Hz, 1/3.3 x 3H), 1.36-1.95 (m, 4H), 2.65-2.77 (m, 1H), 3.29-3.34 (m, 1/3.3 x 1H), 3.37-3.43 (m, 2.3/3.3 x 1H), 4.96-5.14 (m, 2H), 5.84 (ddd, $J = 18.5, 10.5, 8.5$ Hz, 1/3.3 x 1H), 5.98 (ddd, $J = 18.5, 10.5, 8.0$ Hz, 2.3/3.3 x 1H), 7.60-8.40 (6H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 14.6 (2 peaks), 16.8, 18.9, 20.6, 20.8, 32.1, 33.7, 41.4, 42.2, 51.8, 113.9, 114.0, 115.1, 115.7, 118.8 (2 peaks), 119.8, 119.9, 122.2, 122.3, 127.9, 128.0, 128.9, 130.0, 130.7 (2 peaks), 132.0 (2 peaks), 132.1, 132.2, 141.2, 141.6, 174.0, 174.5; HRMS Calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$: 343.1242, Found: 343.1233. Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$: C, 66.45, H, 6.16, N, 4.08. Found: C, 66.37, H, 6.14, N, 3.93. Some ^{13}C resonances are missing because of the overlap of diastereomers.

General Procedure for radical addition/trapping with 1: To a flask containing $\text{Yb}(\text{OTf})_3$ (132 mg, 0.213 mol) and 3-(2-Propenoyl)-2-oxazolidinone **1** (30 mg, 0.213 mmol) under N_2 were added THF (2 mL) and CH_2Cl_2 (4 mL), and then cooled in a dry ice/acetone bath. To this solution were added RI (2.13 mmol), $\text{CH}_3\text{CH}=\text{CHCH}_2\text{SnBu}_3$ (0.37 mL, 1.07 mmol), and Et_3B /hexane solution (1M, 0.64 mL, 0.639 mmol). At once, O_2 (5 mL) was added. After being stirred at -78 °C for 3 h, the reaction was diluted with ether (20 mL). Silica gel (ca. 2.5 g) was added to the mixture, and then concentrated. The resulting powder was washed with hexanes (100 mL), and the product was eluted by washing EtOAc (60 mL). Evaporation of EtOAc yielded the crude product. Flash chromatography (hexane/EtOAc) furnished the desired compounds **14-20**. (See: Table 3)

14: a mixture of diastereomers (major isomer:minor isomer = 2.0 : 1); a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 1.01 (d, $J = 6.5$ Hz, $1/3 \times 3\text{H}$), 1.03 (d, $J = 7.0$ Hz, $2/3 \times 3\text{H}$), 1.70-2.08 (m, 2H), 2.42-2.52 (m, 1H), 3.22 (s, $1/3 \times 3\text{H}$), 3.24 (s, $2/3 \times 3\text{H}$), 3.32-3.37 (m, 2H), 3.85-4.04 (m, 3H), 4.33-4.41 (m, 2H), 4.93-5.06 (m, 2H), 5.67 (ddd, $J = 19.0, 10.5, 9.0$ Hz, $1/3 \times 1\text{H}$), 5.78 (ddd, $J = 18.0, 10.5, 8.0$ Hz, $2/3 \times 3\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 16.7, 18.5, 29.0, 30.8, 40.8, 41.5, 43.0, 43.2, 45.1 (2 peaks), 58.7 (2 peaks), 61.9, 71.5 (2 peaks), 114.9, 115.7, 141.3, 141.6, 153.7, 153.8, 176.1, 176.7; HRMS Calcd. for $\text{C}_{12}\text{H}_{19}\text{NO}_4$: 241.1314, Found: 241.1300. Some ^{13}C resonances are missing because of the overlap of diastereomers.

15: a mixture of diastereomers (major isomer:minor isomer = 2.6 : 1); a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 0.82 (d, $J = 7.0$ Hz, $1/3.6 \times 6\text{H}$), 0.84 (d, $J = 6.5$ Hz, $2.6/3.6 \times 6\text{H}$), 1.01 (d, $J = 7.5$ Hz, $1/3.6 \times 3\text{H}$), 1.02 (d, $J = 6.5$ Hz, $2.6/3.6 \times 3\text{H}$), 1.03-1.16 (m, 2H), 1.42-1.73 (m, 3H), 2.40-2.51 (m, 1H), 2.77-3.86 (m, 1H), 3.92-4.08 (m, 2H), 4.33-4.42 (m, 2H), 4.91-5.04 (m, 2H), 5.69 (ddd, $J = 18.5, 10.0, 8.5$ Hz, $1/3.6 \times 1\text{H}$), 5.78 (ddd, $J = 18.0, 10.0, 8.0$ Hz, $2.6/3.6 \times 1\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 16.9, 18.5, 22.5, 22.9, 27.0, 28.2, 28.4 (2 peaks), 36.4, 36.7, 41.0, 41.2, 42.8, 42.9, 47.5, 47.8, 61.9, 114.6, 115.2, 141.3, 141.9, 153.6 (2 peaks), 176.4, 176.7; HRMS Calcd. for $\text{C}_{14}\text{H}_{23}\text{NO}_3$: 253.1678, Found: 253.1672. Some ^{13}C resonances are missing because of the overlap of diastereomers.

16: a mixture of diastereomers (major isomer:minor isomer = 3.4 : 1); a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 0.81-0.89 (m, 3H), 1.00 (d, $J = 6.5$ Hz, $1/4.4 \times 3\text{H}$), 1.01 (d, $J = 7.0$ Hz, $3.4/4.4 \times 3\text{H}$), 1.25-1.32 (m, 6H), 1.39-1.70 (m, 2H), 2.40-2.49 (m, 1H), 3.79-3.88 (m, 1H), 3.92-4.05 (m, 2H), 4.32-4.40 (m, 2H), 4.90-5.03 (m, 2H), 5.69 (ddd, $J = 17.0, 10.5, 8.5$ Hz, $1/4.4 \times 1\text{H}$), 5.77 (ddd, $J = 17.0, 10.5, 8.0$ Hz, $3.4/4.4 \times 1\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 13.9, 14.2, 16.8, 18.5, 22.7, 27.4, 27.7, 29.1, 29.6, 32.1, 41.0, 41.2, 42.8, 42.9, 47.4, 47.6, 61.9, 62.0, 114.5, 115.1, 141.3, 142.0, 153.6, 176.3, 176.6; HRMS Calcd. for $\text{C}_{14}\text{H}_{23}\text{NO}_3$: 253.1678, Found: 253.1678. Some ^{13}C resonances are missing because of the overlap of diastereomers.

17: a mixture of diastereomers (major isomer:minor isomer = 3.0 : 1); a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 0.84-0.88 (m, 6H), 1.01 (d, $J = 6.5$ Hz, $3/4 \times 3\text{H}$), 1.02 (d, $J = 7.0$ Hz, $1/4 \times$

3H), 1.19-1.30 (m, 1H), 1.35-1.46 (m, 1H), 1.68-1.89 (m, 1H), 2.34-2.44 (m, 1H), 3.91-4.06 (m, 3H), 4.33-4.41 (m, 2H), 4.91-5.02 (m, 2H), 5.70 (ddd, $J = 19.0, 10.5, 8.5$ Hz, $1/4 \times 1H$), 5.78 (ddd, $J = 18.5, 10.5, 8.0$ Hz, $3/4 \times 1H$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.8, 18.0, 22.1, 22.2, 23.9 (2 peaks), 26.8, 38.0, 39.2, 41.6, 41.8, 42.9, 43.0, 45.2, 45.5, 61.9, 114.6, 115.2, 141.3, 141.7, 153.6, 176.4, 176.7; HRMS Calcd. for $C_{13}H_{21}NO_3$: 239.1521, Found: 239.1518. Some ^{13}C resonances are missing because of the overlap of diastereomers.

18: a mixture of diastereomers (major isomer:minor isomer = 3.5 : 1); a colorless oil; 1H NMR (500 MHz, $CDCl_3$) δ 0.73-0.92 (m, 2H), 0.99 (d, $J = 7.0$ Hz, $3.5/4.5 \times 3H$), 1.01 (d, $J = 6.5$ Hz, $1/4.5 \times 3H$), 1.02-1.33 (m, 5H), 1.52-1.77 (m, 6H), 2.32-2.43 (m, 1H), 3.90-4.07 (m, 3H), 4.31-4.40 (m, 2H), 4.90-4.99 (m, 2H), 5.68 (ddd, $J = 18.5, 10.5, 8.0$ Hz, $1/4.5 \times 1H$), 5.76 (ddd, $J = 18.5, 10.5, 8.0$ Hz, $3.5/4.5 \times 1H$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 18.0, 26.4, 26.5, 26.7 (2 peaks), 32.8, 34.4, 36.3 (2 peaks), 41.5, 41.7, 42.9, 43.0, 44.6, 44.9, 61.9, 114.6, 115.1, 141.2, 141.8, 153.6, 176.4, 176.7; HRMS Calcd. for $C_{16}H_{25}NO_3$: 279.1834, Found: 279.1831. Some ^{13}C resonances are missing because of the overlap of diastereomers.

19: a mixture of diastereomers (major isomer:minor isomer = 5.6 : 1); a colorless oil; 1H NMR (500 MHz, $CDCl_3$) δ 1.00 (d, $J = 7.0$ Hz, $5.6/6.6 \times 3H$), 1.02 (d, $J = 7.0$ Hz, $1/6.6 \times 3H$), 1.05-1.95 (m, 17H), 2.30-2.39 (m, 1H), 3.93-4.05 (m, 3H), 4.33-4.45 (m, 2H), 4.94-5.03 (m, 2H), 5.72 (ddd, $J = 18.0, 10.5, 8.0$ Hz, $1/6.6 \times 1H$), 5.78 (ddd, $J = 18.0, 10.5, 7.5$ Hz, $5.6/6.6 \times 1H$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.0, 17.6, 28.8, 32.5 (2 peaks), 37.1, 41.4, 41.6, 42.0, 42.5, 43.1, 43.2, 61.9, 114.7, 115.2, 141.0, 141.5, 153.6, 176.6, 176.8; HRMS Calcd. for $C_{20}H_{29}NO_3$: 331.2147, Found: 331.2149. Some ^{13}C resonances are missing because of the overlap of diastereomers.

20: a mixture of diastereomers (major isomer : minor isomer = 5.4 : 1); a colorless oil; 1H NMR (500 MHz, $CDCl_3$) δ 0.817 (s, $1/6.4 \times 9H$), 0.820 (s, $5.4/6.4 \times 9H$), 1.00 (d, $J = 7.0$ Hz, $5.4/6.4 \times 3H$), 1.02 (d, $J = 6.5$ Hz, $1/6.4 \times 3H$), 1.26 (dd, $J = 14.0, 1.5$ Hz, $5.4/6.4 \times 1H$), 1.34 (y/x+y 1H, dd, $J = 14.0, 1.5$ Hz, $1/6.4 \times 1H$), 1.89 (dd, $J = 14.0, 10.5$ Hz, $1/6.4 \times 1H$), 1.93 (dd, $J = 14.0, 10.5$ Hz, $5.4/6.4 \times 1H$), 2.28-2.37 (m, 1H), 3.92-4.03 (m, 3H), 4.33-4.41 (m, 2H), 4.94-5.03 (m,

2H), 5.70 (ddd, $J = 18.5, 10.5, 8.0$ Hz, $1/6.4 \times 1\text{H}$), 5.76 (ddd, $J = 18.0, 10.5, 8.0$ Hz, $5.4/6.4 \times 1\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 16.2, 17.6, 29.7, 30.7, 30.8, 41.6, 41.8, 42.3, 42.8, 43.0, 43.1, 43.2, 43.4, 61.9, 114.8, 115.4, 141.1, 141.4, 153.6, 176.8, 177.1; HRMS Calcd. for $\text{C}_{14}\text{H}_{23}\text{NO}_3$: 253.1678, Found: 253.1675. Some ^{13}C resonances are missing because of the overlap of diastereomers.

Preparation of 21 and 22: To a solution of 2-oxazolidinone (4.79 g, 55 mmol) in THF (100 mL) was added *n*-BuLi (2.5 M in hexane, 26 mL, 66 mmol) at -78°C under N_2 . After being stirred at -78°C for 30 min, 2-bromopropionyl bromide or 2-bromobutyryl bromide (55 mmol) was added dropwise to the reaction mixture at -78°C . After being stirred at -78°C for 3 h, the reaction mixture was quenched with sat. NH_4Cl . After THF was evaporated, the residue was extracted with EtOAc. The organic phase was washed with H_2O and sat. NaCl, dried over with Na_2SO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (hexane/EtOAc, 10:1) to provide the desired compounds **21** (93%) and **22** (95%).

21 ⁶: a yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 1.76-1.80 (m, 3H), 4.00-4.06 (m, 2H), 4.40-4.48 (m, 2H), 5.60-5.60 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 20.8, 38.4, 43.1, 62.5, 152.9, 169.9.

22: a white solid; mp $30\text{--}31^\circ\text{C}$; a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 1.03 (t, $J = 7.5$ Hz, 3H), 2.00-2.18 (m, 2H), 4.05-4.10 (m, 2H), 4.43-4.49 (m, 2H), 5.52 (t, $J = 7.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 12.1, 27.7, 43.1, 45.6, 62.4, 152.9, 169.5; HRMS Calcd. for $\text{C}_7\text{H}_{10}\text{BrNO}_3$: 234.9844, Found: 234.9836. Anal. Calcd for $\text{C}_7\text{H}_{10}\text{BrNO}_3$: C, 35.62, H, 4.27, N, 5.93. Found: C, 35.78, H, 4.27, N, 6.01.

Preparation of 23 and 24: To a solution of 2-bromovaleric acid or 2-bromo-3-methylbutyric acid (55 mol) in CH_2Cl_2 (100 mL) were added a catalytic amount of DMF and $(\text{COCl})_2$ (5.8 mL, 66 mL) at 0°C under N_2 . After being stirred at rt for 2 h, the reaction mixture was evaporated to give the acid chloride. To a solution of 2-oxazolidinone (4.79 g, 55 mmol) in THF (100 mL) was

added *n*-BuLi (2.5 M in hexane, 26 mL, 66 mmol) at $-78\text{ }^{\circ}\text{C}$ under N_2 . After being stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, the prepared acid chloride was added dropwise to the reaction mixture at $-78\text{ }^{\circ}\text{C}$. After being stirred at $-78\text{ }^{\circ}\text{C}$ for 3 h, the reaction mixture was quenched with sat. NH_4Cl . After THF was evaporated, the residue was extracted with EtOAc. The organic phase was washed with H_2O and sat. NaCl, dried over with Na_2SO_4 , filtered, and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (hexane/EtOAc, 10:1) to give the desired compounds **23** (51%) and **24** (62%).

23: a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 0.93 (t, $J = 7.5\text{ Hz}$, 3H), 1.32-1.55 (m, 2H), 1.95-2.09 (m, 2H), 4.03-4.08 (m, 2H), 4.42-4.48 (m, 2H), 5.59 (dd, $J = 8.0, 6.5\text{ Hz}$, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.6, 20.8, 36.1, 43.1, 43.6, 62.4, 152.9, 169.6; HRMS Calcd. for $\text{C}_8\text{H}_{12}\text{BrNO}_3$: 249.0001, Found: 248.9992.

24: a white solid; mp $58\text{--}60\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 1.03 (d, $J = 6.5\text{ Hz}$, 3H), 1.15 (d, $J = 6.5\text{ Hz}$, 3H), 1.56-1.61 (br m, 1H), 2.28-2.39 (m, 1H), 4.06-4.12 (m, 2H), 4.44-4.49 (m, 2H), 5.49 (d, $J = 8.5\text{ Hz}$, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 20.2, 20.4, 31.8, 43.1, 51.8, 62.4, 153.0, 169.3; HRMS Calcd. for $\text{C}_8\text{H}_{12}\text{BrNO}_3$: 249.0001, Found: 248.9999. Anal. Calcd for $\text{C}_8\text{H}_{12}\text{BrNO}_3$: C, 38.42, H, 4.84, N, 5.60. Found: C, 38.43, H, 4.82, N, 5.66.

General Procedure for the reaction of 21-24: To a flask containing $\text{Yb}(\text{OTf})_3$ (132 mg, 0.213 mol) and **21-24** (0.213 mmol) under N_2 were added THF (2 mL) and CH_2Cl_2 (4 mL), and then cooled in a dry ice/acetone bath. To this solution were added $\text{CH}_3\text{CH}=\text{CHCH}_2\text{SnBu}_3$ (0.37 mL, 1.07 mmol) and Et_3B /hexane solution (1M, 0.64 mL, 0.639 mmol). At once, O_2 (5 mL) was added. After being stirred at $-78\text{ }^{\circ}\text{C}$ for 3 h, the reaction was diluted with ether (20 mL). Silica gel (ca. 2.5 g) was added to the mixture, and then concentrated. The resulting powder was washed with hexanes (100 mL), and the product was eluted by washing EtOAc (60 mL). Evaporation of EtOAc yielded the crude product. Flash chromatography (hexane/EtOAc) furnished the desired compounds **25-27** and **3**. (See: Table 3)

25: a mixture of diastereomers (major isomer:minor isomer = 3.0 : 1); a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 1.01 (d, $J = 7.0$ Hz, $3/4 \times 3\text{H}$), 1.02 (d, $J = 7.0$ Hz, $1/4 \times 3\text{H}$), 1.09 (d, $J = 7.0$ Hz, $1/4 \times 3\text{H}$), 1.11 (d, $J = 7.0$ Hz, $3/4 \times 3\text{H}$), 2.45-2.56 (m, 1H), 3.68-3.74 (m, $1/4 \times 1\text{H}$), 3.78-3.85 (m, $3/4 \times 1\text{H}$), 3.92-4.05 (m, 2H), 4.33-4.42 (m, 2H), 4.91-5.05 (m, 2H), 5.67 (ddd, $J = 19.0, 10.5, 8.5$ Hz, $1/4 \times 1\text{H}$), 5.77 (ddd, $J = 18.0, 10.5, 7.5$ Hz, $3/4 \times 1\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 14.9, 16.1, 18.8, 40.8, 41.2, 42.0, 42.2, 42.9, 43.0, 62.0 (2 peaks), 114.6, 115.5, 140.8, 142.0, 153.5, 176.8, 176.9; HRMS Calcd. for $\text{C}_{10}\text{H}_{15}\text{NO}_3$: 197.1052, Found: 197.1051. Some ^{13}C resonances are missing because of the overlap of diastereomers.

26: a mixture of diastereomers (major isomer : minor isomer = 2.1 : 1); a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 0.80 (t, $J = 7.5$ Hz, $1/3.1 \times 3\text{H}$), 0.82 (t, $J = 7.5$ Hz, $2.1/3.1 \times 3\text{H}$), 0.98 (d, $J = 7.0$ Hz, $1/3.1 \times 3\text{H}$), 0.99 (d, $J = 6.5$ Hz, $2.1/3.1 \times 3\text{H}$), 1.46-1.71 (m, 2H), 2.39-2.49 (m, 1H), 3.71-3.80 (m, 1H), 3.90-4.06 (m, 2H), 4.31-4.39 (m, 2H), 4.88-5.01 (m, 2H), 5.67 (ddd, $J = 18.5, 10.5, 8.5$ Hz, $1/3.1 \times 1\text{H}$), 5.75 (ddd, $J = 18.5, 10.5, 8.0$ Hz, $2.1/3.1 \times 1\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 11.6, 12.0, 16.8, 18.6, 22.1, 23.3, 40.5, 40.8, 42.8, 42.9, 48.8, 49.1, 61.9, 114.5, 115.1, 141.3, 142.0, 153.6 (2 peaks), 176.2, 176.4; HRMS Calcd. for $\text{C}_{11}\text{H}_{17}\text{NO}_3$: 211.1208, Found: 211.1205. Some ^{13}C resonances are missing because of the overlap of diastereomers.

27: a mixture of diastereomers (major isomer : minor isomer = 1.2 : 1); a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 0.90 (d, $J = 6.5$ Hz, $1/2.2 \times 3\text{H}$), 0.92 (d, $J = 7.0$ Hz, $1.2/2.2 \times 3\text{H}$), 0.94 (d, $J = 7.0$ Hz, $1/2.2 \times 3\text{H}$), 0.95 (d, $J = 7.0$ Hz, $1.2/2.2 \times 3\text{H}$), 0.98 (d, $J = 7.0$ Hz, $1/2.2 \times 3\text{H}$), 1.02 (d, $J = 7.0$ Hz, $1.2/2.2 \times 3\text{H}$), 1.97-2.09 (m, 1H), 2.55-2.68 (m, 1H), 3.87-4.05 (m, 3H), 4.32-4.37 (m, 2H), 4.91-5.07 (m, 2H), 5.57 (ddd, $J = 18.0, 10.5, 8.0$ Hz, $1/2.2 \times 1\text{H}$), 5.82 (x/x+y 1H, ddd, $J = 19.0, 10.5, 9.0$ Hz, $1.2/2.2 \times 1\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 16.9, 18.3, 19.0, 19.3, 20.5, 20.6, 28.8, 29.1, 38.4, 38.9, 42.8 (2 peaks), 51.8, 52.2, 61.7 (2 peaks), 114.6, 114.7, 141.5, 141.8, 153.7 (2 peaks), 175.4, 175.7; HRMS Calcd. for $\text{C}_{12}\text{H}_{19}\text{NO}_3$: 225.1365, Found: 225.1359. Some ^{13}C resonances are missing because of the overlap of diastereomers.

Determination of stereochemistry

Synthesis of **28 and **29**:** To a solution of **16** or **26** (0.237 mmol) in THF (100 mL) and H₂O (0.3 mL) were added 30% H₂O₂ (0.054 mL, 0.95 mmol) and a solution of LiOH (16 mg, 0.38 mmol) in H₂O (0.35 mL) at 0 °C. After being stirred at 0 °C for 1 h, a solution of Na₂SO₃ (120 mg, 0.95 mmol) in H₂O (0.9 mL) was added to the reaction mixture at 0 °C. After being stirred at rt for 30 min, THF was evaporated. The residue was diluted with 10% NaOH, washed with Et₂O, acidified with 10% HCl, and extracted with CH₂Cl₂. The organic phase was washed with H₂O and sat. NaCl, dried over with Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by preparative TLC (CH₂Cl₂/MeOH, 25:1) to provide the desired compounds **28** (81%) or **29** (82%).

Determination of stereochemistry of **28 and **29**:** Stereochemistry of diastereomers of **28** and **29** was determined by comparison with ¹H and ¹³C NMR spectra of the reported data.⁷ These results show that the stereochemistry of major isomer of **28** and **29** is the *syn*-isomer and the stereochemistry of minor isomer of **28** and **29** is *anti*-isomer.

28: a mixture of diastereomers (major isomer : minor isomer = 3.4 : 1); a colorless oil; ¹H NMR (500 MHz, CDCl₃) δ 0.84-0.92 (m, 3H), 1.05 (d, *J* = 6.5 Hz, 1/4.4 x 3H, *anti*), 1.06 (d, *J* = 7.0 Hz, 3.4/4.4 x 3H, *syn*), 1.20-1.38 (m, 6H), 1.41-1.65 (m, 2H), 2.19 (br q, *J* = 8.0 Hz, 1/4.4 x 1H, *anti*), 2.25-2.32 (m, 3.4/4.4 x 1H, *syn*), 2.33-2.48 (m, 1H), 4.97-5.07 (m, 2H), 5.64 (ddd, *J* = 17.5, 10, 8.5 Hz, 1/4.4 x 1H, *anti*), 5.78 (ddd, *J* = 17.5, 10, 8.5 Hz, 3.4/4.4 x 1H, *syn*); ¹³C NMR (125 MHz, CDCl₃) δ 14.2 (*syn* and *anti*), 17.5 (*syn*), 18.8 (*anti*), 22.7 (*syn* and *anti*), 27.5 (*anti*), 27.6 (*syn*), 29.3 (*syn*), 30.5 (*anti*), 31.9 (*anti*), 32.0 (*syn*), 40.3 (*syn*), 40.9 (*anti*), 51.4 (*syn*), 51.6 (*anti*), 114.8 (*syn*), 115.3 (*anti*), 141.4 (*syn*), 141.6 (*anti*), 181.6 (*syn*), 181.9 (*anti*).

29: a mixture of diastereomers (major isomer : minor isomer = 2.1 : 1); a colorless oil; ^1H NMR (500 MHz, CDCl_3) δ 0.92 (t, $J = 7.5$ Hz, $1/3.1 \times 3\text{H}$, *anti*), 0.94 (t, $J = 7.5$ Hz, $2.1/3.1 \times 3\text{H}$, *syn*), 1.05 (d, $J = 6.5$ Hz, $1/3.1 \times 3\text{H}$, *anti*), 1.06 (d, $J = 7.0$ Hz, $2.1/3.1 \times 3\text{H}$, *syn*), 1.50-1.68 (m, 2H), 2.10-2.16 (m, $1/3.1 \times 1\text{H}$, *anti*), 2.19-2.25 (m, $2.1/3.1 \times 1\text{H}$, *syn*), 2.36-2.49 (m, 1H), 4.97-5.07 (m, 2H), 5.63 (ddd, $J = 18.5, 10.5, 8.5$ Hz, $1/3.1 \times 1\text{H}$, *anti*), 5.77 (ddd, $J = 18.5, 10.5, 8.0$ Hz, $2.1/3.1 \times 1\text{H}$, *syn*); ^{13}C NMR (125 MHz, CDCl_3) δ 12.2 (*anti*), 12.3 (*syn*), 17.5 (*syn*), 18.9 (*anti*), 22.4 (*syn*), 23.6 (*anti*), 40.1 (*syn*), 40.7 (*anti*), 53.1 (*syn*), 53.2 (*anti*), 114.9 (*syn*), 115.3 (*anti*), 141.3 (*syn*), 141.5 (*anti*), 181.8 (*syn*), 182.1 (*anti*).

References

1. (a) Curran, D. P.; Qi, H.; Porter, N. A.; Su, Q.; Wu, W.-X. *Tetrahedron Lett.* **1993**, *34*, 4489; (b) Pikul, S.; Corey, E. J. *Org. Synth.* **1992**, *71*, 30.
2. Anwer, B. *Tetrahedron Lett.* **1988**, *29*, 2525.
3. Reddy, P. A.; Hsiang, B. C. H.; Latifi, T. N.; Hill, M. W.; Woodward, K. E.; Rothman, S. M.; Ferrendelli, J. A.; Covey, D. F. *J. Med. Chem.* **1996**, *39*, 1898.
4. Aliev, N. A.; Ahmad, H. E. I.; Abdusamatov, A. *Chem. Nat. Compd.* **1979**, *15*, 627.
5. Kashima, C.; Fukusaka, K.; Takahashi, K.; Yokoyama, Y. *J. Org. Chem.* **1999**, *64*, 1108.
6. Ito, Y.; Sasaki, A.; Tamoto, K.; Sunagawa, M.; Terashima, S. *Tetrahedron* **1991**, *47*, 2801.
7. Eriksson, M.; Hjelmencrantz, A.; Nilsson, M.; Olsson, T. *Tetrahedron* **1995**, *51*, 12631.