Formal Total Synthesis of Fostriecin

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4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8501, Japan***Experimental Section**

To an ice-cold solution of *i*-Pr₂NH (21.5 mL, 153.6 mmol) in THF (110 mL) was added *n*-BuLi (64.0 mL, 2.10 M in hexane, 134.4 mmol) dropwise. After 15 min at 0 °C, the solution was cooled to -60 °C, and EtOAc (13.2 mL, 134.8 mmol) was added dropwise. Stirring was continued at -60 °C for 30 min, and a solution of methacrolein (10.0 mL, 120 mmol) in THF (10 mL) was added slowly. The solution was stirred between -60 °C and -30 °C for additional 50 min, and then poured into an ice-cold mixture of saturated NH₄Cl and EtOAc. After being stirred vigorously for a few minutes, the layers were separated, and the aqueous layer was extracted with EtOAc twice. The combined organic layers were dried over MgSO₄ and concentrated to afford a yellow residue, which was distilled under reduced pressure to furnish *rac*-18 (17.3 g, 91%): B.p. 75–80 °C (4 Torr); IR (neat) 3463, 1734, 1163, 1025 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.28 (t, *J* = 7 Hz, 3 H), 1.76 (s, 3 H), 2.54 (dd, *J* = 16, 8 Hz, 1 H), 2.59 (dd, *J* = 16, 5 Hz, 1 H), 3.08 (br s, 1 H), 4.18 (q, *J* = 7 Hz, 2 H), 4.44–4.51 (m, 1 H), 4.88 (br s, 1 H), 5.03 (br s, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ 14.3, 18.3, 40.2, 60.9, 71.6, 111.4, 145.5, 172.4.

To a mixture of 4A molecular sieves (760 mg) and $\text{Ti}(i\text{-PrO})_4$ (2.97 mL, 10.1 mmol) in CH_2Cl_2 (25 mL) was added L-(+)-DIPT (2.55 mL, 12.1 mmol) dropwise at -20°C . The mixture was stirred at -20°C for 20 min, and a solution of *rac*-18 (4.0 g, 25.3 mmol) in CH_2Cl_2 (5 mL) was injected. The mixture was stirred for additional 20 min at -20°C , and then cooled to -40°C . A solution of TBHP in CH_2Cl_2 (5.68 mL, 4.45 M, 25.3 mmol) was added dropwise. The reaction was carried out at -20°C for 24 h, and quenched by addition of Me_2S (3.5 mL, 47.7 mmol). After 30 min at -20°C , 10% tartaric acid (5 mL), NaF (15 g, 357 mmol), and Celite (5 g) were added successively. The resulting mixture was stirred at room temperature for 30 min and filtered through a pad of Celite with Et_2O . The filtrate was concentrated to afford a crude compound, which was purified by chromatography on silica gel (hexane/ EtOAc) to furnish *(R)*-16 (1.94 g, 49%). The enantiomeric excess of *(R)*-16 was $> 98\%$ by ^1H NMR spectroscopy of the corresponding ester derived from S-(+)-MTPACl. *(R)*-16: $[\alpha]_D^{32} +29$ (c 0.25, CHCl_3).

A solution of *(R)*-16 (1.06 g, 6.70 mmol), benzyl trichloroacetimidate (3.79 g, 13.4 mmol), and 10-camphorsulfonic acid (156 mg, 0.67 mmol) in CH_2Cl_2 (25 mL) was stirred at room temperature for 25 h, and then diluted with saturated NaHCO_3 . The mixture was extracted with CH_2Cl_2 twice. The combined organic layers were dried over MgSO_4 and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/ EtOAc) to furnish 17 (1.73 g, 93%): IR (neat) 1737, 1613, 1514, 1248, 1068 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.22 (t, $J = 7$ H, 3 H), 1.72 (br s, 3 H), 2.45 (dd, $J = 15, 5$ Hz, 1 H), 2.66 (dd, $J = 15, 9$ Hz, 1 H), 3.77 (s, 3 H), 4.06–4.28 (m, 4 H), 4.36–4.48 (m, 1 H), 4.99 (br s, 1 H), 5.02 (br s, 1 H), 6.85 (d, $J = 9$ Hz, 2 H), 7.22 (d, $J = 9$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.3, 16.8, 40.0, 55.2, 60.4, 70.0, 79.4, 113.6, 114.3, 129.3, 130.3, 143.2, 159.0, 170.8; $[\alpha]_D^{32} +25$ (c 0.195,

CHCl₃).

To an ice-cold solution of **17** (2.26 g, 8.12 mmol) in THF (20 mL) was added LiAlH₄ (231 mg, 6.09 mmol) portionwise. The mixture was stirred for 1 h at r.t., and excess hydride was quenched at 0 °C by addition of H₂O (0.4 mL). After addition of NaF (12 g), the resulting slurry was stirred at room temperature for 30 min, and filtered through a pad of Celite with EtOAc. The filtrate was concentrated to obtain a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford the corresponding alcohol (1.78 g, 93%): IR (neat) 3421, 1613, 1513, 1248, 1036 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.62–1.99 (m, 2 H), 1.73 (s, 3 H), 2.56 (br s, 1 H), 3.64–3.76 (m, 2 H), 3.79 (s, 3 H), 3.96 (dd, *J* = 9, 4 Hz, 1 H), 4.20 (d, *J* = 11 Hz, 1 H), 4.46 (d, *J* = 11 Hz, 1 H), 4.98 (br s, 2 H), 6.87 (d, *J* = 9 Hz, 2 H), 7.24 (d, *J* = 8 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ 17.1, 36.4, 55.3, 61.0, 69.7, 82.2, 113.5, 113.8, 129.4, 130.3, 144.2, 159.1; [α]_D²⁷ +63 (c 0.218, CHCl₃).

To a solution of (COCl)₂ (0.986 mL, 11.3 mmol) in CH₂Cl₂ (35 mL) was added DMSO (1.60 mL, 22.5 mmol) at –60 °C. After 15 min of stirring at –60 °C, the above alcohol (1.78 g, 7.53 mmol) in CH₂Cl₂ (5 mL) was added dropwise. The solution was kept between –60 °C and –40 °C for 30 min with stirring, and then Et₃N (7.35 mL, 52.7 mmol) was added. After 10 min, the mixture was warmed to 0 °C, stirred for additional 30 min, and diluted with saturated NaHCO₃. The organic phase was separated, and the aqueous phase was extracted with CH₂Cl₂ twice. The combined extracts were dried over MgSO₄ and evaporated to obtain crude aldehyde **18**, which was used for the next reaction without further purification. Aldehyde **18**: ¹H NMR (300 MHz, CDCl₃) δ 1.73 (s, 3 H), 2.44 (ddd, *J* = 15, 4, 2 Hz, 1 H), 2.74 (ddd, *J* = 16, 9, 3 Hz,

1 H), 3.79 (s, 3 H), 4.23 (d, $J = 11$ Hz, 1 H), 4.29 (dd, $J = 9, 4$ Hz, 1 H), 4.46 (d, $J = 11$ Hz, 1 H), 5.01–5.07 (m, 2 H), 6.87 (d, $J = 9$ Hz, 2 H), 7.22 (d, $J = 9$ Hz, 2 H), 9.70 (dd, $J = 3, 2$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 17.0, 47.8, 55.3, 69.8, 77.5, 113.8, 114.4, 129.4, 130.0, 143.0, 159.1, 200.8.

To a mixture of LiCl (431 mg, 10.2 mmol) and DBU (1.69 mL, 11.3 mmol) in MeCN (20 mL) was added $(\text{EtO})_2\text{P}(=\text{O})\text{CH}_2\text{CO}_2\text{Et}$ (1.96 mL, 9.79 mmol) at 0 °C. After 30 min of stirring at 0 °C, a solution of crude **18** in MeCN (5 mL) was added. The mixture was stirred at 0 °C for 30 min and then at r.t. for another 30 min, before dilution with saturated NaHCO_3 . The organic phase was separated, and the aqueous phase was extracted with EtOAc twice. The combined extracts were dried over MgSO_4 and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish the corresponding ester (2.26 g, 99% from the above alcohol): IR (neat) 1718, 1653, 1612, 1514, 1249, 1038 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.27 (t, $J = 7$ Hz, 4 H), 1.71 (s, 3 H), 2.30–2.61 (m, 2 H), 3.78 (s, 3 H), 3.70–3.88 (m, 1 H), 4.12–4.26 (m, 3 H), 4.44 (d, $J = 11$ Hz, 1 H), 4.96 (br s, 1 H), 5.00 (br s, 1 H), 5.84 (dt, $J = 16, 1.5$ Hz, 1 H), 6.86 (d, $J = 9$ Hz, 2 H), 6.91 (dd, $J = 16, 7$ Hz, 1 H), 7.23 (d, $J = 9$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.3, 16.7, 36.8, 55.2, 60.1, 69.6, 81.3, 113.7, 114.3, 122.9, 129.2, 130.3, 143.4, 145.4, 159.0, 166.1; $[\alpha]_D^{30} +44$ (c 0.373, CHCl_3).

To a solution of the above ester (2.26 g, 7.42 mmol) in THF (30 mL) was added DIBAL (20 mL, 0.93 M in hexane, 18.6 mmol) dropwise at –78 °C. After being stirred at –78 °C for 2 h, the solution was poured into 1 N HCl (90 mL) at 0 °C, and the resulting mixture was stirred vigorously for a few minutes. The organic phase was separated and the aqueous phase was extracted with EtOAc twice. The combined organic phases were dried over MgSO_4 and concentrated to afford a residue which was purified by chromatography on silica gel (hexane/EtOAc) to furnish allylic alcohol **19** (1.80 g, 92%): IR (neat) 3393, 1612, 1513, 1248, 1036 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.70 (s, 3 H), 2.18–2.30 (m, 1 H), 2.34–2.46 (m, 1 H), 3.70–3.90 (m, 1 H), 3.78 (s, 1 H), 4.03 (d, $J = 5$ Hz, 1 H), 4.19 (d, $J = 11.5$ Hz, 1 H), 4.43 (d, $J = 11.5$ Hz, 1 H), 4.92 (br s, 1 H),

4.97 (br s, 1 H), 5.54–5.72 (m, 2 H), 6.86 (d, $J = 8.5$ Hz, 2 H), 7.23 (d, $J = 8.5$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.9, 36.7, 55.3, 63.6, 69.6, 82.5, 113.7, 114.0, 128.9, 129.3, 130.6, 131.0, 144.0, 159.0; $[\alpha]_D^{25} +50$ (c 0.507, CHCl_3).

To a mixture of 4A molecular sieves (34 mg) and $\text{Ti}(i\text{-PrO})_4$ (0.067 mL, 0.228 mmol) in CH_2Cl_2 (8 mL) was added D-(-)-DIPT (0.057 mL, 0.273 mmol) dropwise at -20°C . The mixture was stirred at -20°C for 30 min, and a solution of **19** (300 mg, 1.14 mmol) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred for additional 30 min at -20°C and then cooled to -40°C . A solution of TBHP in CH_2Cl_2 (0.387 mL, 4.45 M, 1.72 mmol) was added dropwise to it. The reaction was carried out at -20°C for 6 h, and quenched with Me_2S (0.15 mL, 2.04 mmol). After 30 min at -20°C , 10% tartaric acid (0.15 mL), NaF (0.5 g, 11.9 mmol), and Celite (0.2 g) were added. The resulting mixture was stirred at room temperature for 1 h and filtered through a pad of Celite with Et_2O . The filtrate was concentrated to afford an oily residue, which was purified by chromatography on silica gel (hexane/ EtOAc) to furnish **20** (293 mg, 92%, diastereomeric ratio = 23 : 1): IR (neat) 3433, 1612, 1513, 1248, 1035 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.61 (ddd, $J = 14, 7, 4.5$ Hz, 1 H), 1.71 (s, 3 H), 1.93 (ddd, $J = 14, 9, 5$ Hz, 1 H), 2.60 (t, $J = 6$ Hz, 1 H), 2.86–2.93 (m, 1 H), 3.05 (ddd, $J = 7, 4.5, 2$ Hz, 1 H), 3.45–3.58 (m, 1 H), 3.77 (s, 3 H), 3.68–3.90 (m, 1 H), 3.95 (dd, $J = 9, 4$ Hz, 1 H), 4.21 (d, $J = 11$ Hz, 1 H), 4.44 (d, $J = 11$ Hz, 1 H), 4.96–5.04 (m, 2 H), 6.86 (d, $J = 8$ Hz, 2 H), 7.23 (d, $J = 8$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.8, 36.8, 53.6, 55.2, 59.0, 61.9, 69.7, 80.2, 113.6, 113.7, 129.2, 130.4, 144.0, 158.9; $[\alpha]_D^{28} +72$ (c 0.19, CHCl_3).

A mixture of epoxy alcohol **20** (1.58 g, 5.68 mmol), PPh_3 (2.23 g, 8.50 mmol), and NaHCO_3 (106 mg, 1.26 mmol) in CCl_4 (15 mL) was heated under reflux for 6 h and

most of the volatile material was removed by evaporation. The residue obtained was diluted with EtOAc/hexane (1 : 5), and the resulting mixture was filtered through a pad of Celite. The filtrate was concentrated, and the crude product was purified by chromatography on silica gel (hexane/EtOAc) to furnish epoxy chloride **21** (1.40 g, 83%): IR (neat) 1612, 1515, 1248, 1082, 1035 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.60 (ddd, $J = 14, 7, 4$ Hz, 1 H), 1.71 (s, 3 H), 1.96 (ddd, $J = 14, 9, 4.5$ Hz, 1 H), 2.95–3.06 (m, 2 H), 3.44–3.58 (m, 2 H), 3.78 (s, 3 H), 3.93 (dd, $J = 9, 4$ Hz, 1 H), 4.21 (d, $J = 11$ Hz, 1 H), 4.44 (d, $J = 11$ Hz, 1 H), 4.97–5.04 (m, 2 H), 6.87 (d, $J = 9$ Hz, 2 H), 7.24 (d, $J = 9$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 16.9, 36.8, 44.8, 55.3, 56.6, 57.6, 69.8, 80.1, 113.7, 113.9, 129.3, 130.4, 144.0, 159.0; $[\alpha]_D^{32} +62$ (c 0.192, CHCl_3).

To a solution of epoxy chloride **21** (770 mg, 2.59 mmol) in THF (10 mL) was added *n*-BuLi (7.16 mL, 1.45 M in hexane, 10.4 mmol) dropwise at -30 $^{\circ}\text{C}$. The solution was warmed to 0 $^{\circ}\text{C}$ over 1 h and poured into a mixture of saturated NH_4Cl and EtOAc. After being stirred vigorously for a few minutes, the layers were separated, and the aqueous layer was extracted with EtOAc twice. The combined organic layers were dried over MgSO_4 and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish **22** (615 mg, 91%): IR (neat) 3433, 3292, 1613, 1514, 1249, 1075, 1036 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.73 (s, 3 H), 1.78 (ddd, $J = 15, 7, 3$ Hz, 1 H), 2.10 (ddd, $J = 15, 10, 3$ Hz, 1 H), 2.43 (d, $J = 2$ Hz, 1 H), 3.65 (d, $J = 8$ Hz, 1 H), 3.77 (s, 3 H), 4.24 (d, $J = 11$ Hz, 1 H), 4.30 (dd, $J = 10, 3$ Hz, 1 H), 4.44 (d, $J = 11$ Hz, 1 H), 4.50–4.60 (m, 1 H), 5.00 (s, 1 H), 5.04 (s, 1 H), 6.86 (d, $J = 8$ Hz, 2 H), 7.25 (d, $J = 8$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ 17.2, 40.5, 55.2, 60.3, 70.1, 72.9, 80.4, 84.6, 113.7, 113.8, 129.5, 129.9, 143.5, 159.1; $[\alpha]_D^{29} +83$ (c 0.24, CHCl_3).

A solution of alcohol **22** (750 mg, 2.88 mmol), TBSCl (651 mg, 4.32 mmol), and imidazole (588 mg, 8.64 mmol) in DMF (10 mL) was stirred at r.t. for 2 h and diluted with saturated NaHCO_3 and Et_2O at 0 °C. After being stirred vigorously for a few minutes, the layers were separated, and the aqueous layer was extracted with Et_2O twice. The combined organic layers were dried over MgSO_4 and concentrated to afford an oil, which was purified by chromatography on silica gel (hexane/ EtOAc) to furnish the corresponding silyl ether (1.01 g, 94%): IR (neat) 3309, 1614, 1515, 1249, 1095 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.10 (s, 3 H), 0.15 (s, 3 H), 0.90 (s, 9 H), 1.71 (s, 3 H), 1.84 (ddd, $J = 14, 10, 4$ Hz, 1 H), 2.00 (ddd, $J = 14, 10, 4$ Hz, 1 H), 2.34 (d, $J = 2$ Hz, 1 H), 3.78 (s, 3 H), 3.98 (dd, $J = 10, 3$ Hz, 1 H), 4.14 (d, $J = 11$ Hz, 1 H), 4.38 (d, $J = 11$ Hz, 1 H), 4.55 (ddd, $J = 10, 4, 2$ Hz, 1 H), 4.97 (s, 1 H), 4.99 (s, 1 H), 6.86 (d, $J = 9$ Hz, 2 H), 7.23 (d, $J = 9$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.8, -4.1, 17.0, 18.3, 26.0, 43.9, 55.3, 59.4, 69.9, 72.2, 79.2, 85.8, 113.5, 113.8, 129.3, 130.7, 144.5, 159.1; $[\alpha]_D^{29} +50$ (c 0.178, CHCl_3).

A stream of O_3 in O_2 was gently bubbled into a solution of the above compound (960 mg, 2.56 mmol) in n -PrOH (15 mL) at -78 °C for 30 min. Excess O_3 remaining in the solution was purged by bubbling argon at -78 °C, and then Me_2S (0.94 mL, 12.8 mmol) was added. After being stirred at room temperature overnight the solution was concentrated, and the residue was purified by chromatography on silica gel (hexane/ EtOAc) to furnish keton **6** (820 mg, 85%): IR (neat) 3286, 1716, 1515, 1251, 1098, 838 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.11 (s, 3 H), 0.17 (s, 3 H), 0.91 (s, 9 H), 1.89–2.08 (m, 2 H), 2.16 (s, 3 H), 2.39 (d, $J = 2$ Hz, 1 H), 3.80 (s, 3 H), 4.02 (dd, $J = 9, 4$ Hz, 1 H), 4.35 (d, $J = 11$ Hz, 1 H), 4.47 (d, $J = 11$ Hz, 1 H), 4.59 (ddd, $J = 9, 4, 2$ Hz, 1 H), 6.88 (d, $J = 9$ Hz, 2 H), 7.26 (d, $J = 9$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.8, -4.1, 18.3, 25.6, 26.0, 41.3, 55.4, 58.9, 72.4, 72.9, 81.4, 85.0, 113.9, 129.5, 129.6, 159.4, 210.0; $[\alpha]_D^{29} +54$ (c 0.14, CHCl_3).

To an ice-cold solution of aldehyde **25** (6.50 g, 50.7 mmol) in THF (70 mL) was added allylmagnesium chloride (87 mL, 0.70 M in THF, 61 mmol) dropwise. The solution was stirred at 0 °C for 30 min and poured into a mixture of saturated NH_4Cl and EtOAc. The resulting mixture was stirred vigorously for a few minutes. The organic layer was separated, and the aqueous layer was extracted with EtOAc twice. The combined organic layers were dried over MgSO_4 and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish *rac*-**26** (8.64 g, 100%): IR (neat) 3391, 1641, 1249, 992 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.04 (s, 9 H), 2.07 (br s, 1 H), 2.16–2.38 (m, 2 H), 4.06–4.17 (m, 1 H), 5.04–5.14 (m, 2 H), 5.69–5.86 (m, 1 H), 5.85 (dd, $J = 19$, 1.5 Hz, 1 H), 6.03 (dd, $J = 19$, 5 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ -1.4, 41.5, 73.2, 118.1, 129.5, 134.4, 147.8.

To a mixture of 4A molecular sieves (264 mg) and $\text{Ti}(i\text{-PrO})_4$ (0.776 mL, 2.64 mmol) in CH_2Cl_2 (8 mL) was added D-(-)-DIPT (0.648 mL, 3.08 mmol) dropwise at -20 °C. The mixture was stirred for 20 min at -20 °C, and a solution of *rac*-**26** (1.50 g, 8.81 mmol) in CH_2Cl_2 (2 mL) was added slowly. The mixture was stirred for additional 30 min at -20 °C and cooled to -40 °C. A solution of TBHP in CH_2Cl_2 (2.97 mL, 4.45 M, 13.2 mmol) was added dropwise, and the mixture was stirred for 6 h at -20 °C. Me_2S (1.1 mL, 15.0 mmol) was added to it. After 30 min at -20 °C, 10% tartaric acid (1.5 mL), NaF (4.5 g, 107 mmol), and Celite (2 g) were also added. The resulting mixture was stirred vigorously at r.t. for 30 min and filtered through a pad of Celite with Et_2O . The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to elute (*S*)-**26** (680 mg, 45%) and epoxide **27** (755 mg, 46%). Enantiomeric excesses of (*S*)-**26** and **27** were both > 99% by ^1H NMR spectroscopy of the corresponding esters derived from S-(+)-MTPACl. (*S*)-**26**: $[\alpha]_D^{27} -111$ (c 0.056, CHCl_3). **27**: IR (neat) 3458, 1250, 842 cm^{-1} ; ^1H NMR

(300 MHz, CDCl_3) δ 0.03 (s, 9 H), 2.20–2.40 (m, 3 H), 2.84 (t, $J = 4$ Hz, 1 H), 3.79–3.87 (m, 1 H), 5.04–5.16 (m, 2 H), 5.84 (ddt, $J = 17, 10, 7$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ -3.6, 38.5, 47.7, 58.0, 68.7, 117.8, 133.6; $[\alpha]_D^{27}$ -3 (c 0.54, CHCl_3).

To an ice-cold solution of *i*-Pr₂NH (4.51 mL, 32.2 mmol) in THF (25 mL) was added *n*-BuLi (11.3 mL, 2.10 M in hexane, 23.6 mmol) slowly. After 20 min at 0 °C, Bu₃SnH (4.23 mL, 16.1 mmol) was added dropwise, and the solution was stirred at 0 °C for additional 30 min. To this was added a solution of **27** (2.0 g, 10.7 mmol) in THF (5 mL). After 2 h at 0 °C, the resulting solution was poured into an ice-cold mixture of saturated NH₄Cl and hexane. The mixture was stirred vigorously for a few minutes. The organic layer was separated, and the aqueous layer was extracted with hexane twice. The combined organic layers were dried over MgSO₄ and concentrated to afford the crude vinyl stannane **28**, which was used for the next reaction without further purification: ^1H NMR (300 MHz, CDCl_3) δ 0.80–1.02 (m, 15 H), 1.24–1.66 (m, 12 H), 1.74 (d, $J = 5$ Hz, 1 H), 2.24–2.40 (m, 2 H), 4.10–4.20 (m, 1 H), 5.09–5.17 (m, 2 H), 5.74–5.89 (m, 1 H), 6.02 (dd, $J = 19, 5$ Hz, 1 H), 6.18 (dd, $J = 19, 1.2$ Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 9.7, 13.9, 27.4, 29.2, 41.9, 74.1, 118.0, 127.9, 134.3, 149.9.

To a solution of the above crude vinyl stannane **28** in Et₂O (30 mL) was added I₂ (3.54 g, 14.0 mmol) at 0 °C. The resulting dark brown solution was stirred at 0 °C for 30 min, and saturated Na₂S₂O₃ was added with vigorous stirring. The organic phase was separated, and the aqueous phase was extracted with Et₂O twice. The combined organic phases were dried over MgSO₄ and concentrated to afford a residue which was purified by chromatography on silica gel (hexane/EtOAc) to furnish vinyl iodide **29**.

(2.35 g, 98% from epoxide **27**): IR (neat) 3365, 1641, 1607, 947, 920 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.18–2.37 (m, 3 H), 4.05–4.16 (m, 1 H), 5.08–5.18 (m, 2 H), 5.67–5.84 (m, 1 H), 6.34 (dd, $J = 14$, 1.2 Hz, 1 H), 6.56 (dd, $J = 14$, 9 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 41.1, 73.3, 77.4, 118.8, 133.1, 147.5; $[\alpha]_D^{29} +25$ (c 0.232, CHCl_3).

A solution of alcohol **29** (2.50 g, 11.2 mmol), TESCl (2.43 mL, 14.5 mmol), and imidazole (1.52 g, 22.3 mmol) in DMF (25 mL) was stirred at r.t. for 1.5 h and poured into a mixture of saturated NaHCO_3 and Et_2O at 0 $^\circ\text{C}$ with vigorous stirring. The organic layer was separated, and the aqueous layer was extracted with Et_2O twice. The combined organic layers were dried over MgSO_4 and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/ EtOAc) to furnish **3** (3.77 g, 100%): IR (neat) 1083, 1004, 742 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.47–0.64 (m, 6 H), 0.90–0.99 (m, 9 H), 2.22–2.29 (m, 2 H), 4.12 (dq, $J = 1.5$, 6 Hz, 1 H), 5.02–5.12 (m, 2 H), 5.68–5.85 (m, 1 H), 6.24 (dd, $J = 14$, 1.5 Hz, 1 H), 6.54 (dd, $J = 14$, 6 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 5.1, 6.6, 7.0, 42.4, 74.9, 76.2, 117.6, 133.8, 148.5; $[\alpha]_D^{32} +18$ (c 0.677, CHCl_3).

To a mixture of 4A molecular sieves (793 mg) and $\text{Ti}(i\text{-PrO})_4$ (2.33 mL, 7.92 mmol) in CH_2Cl_2 (15 mL) was added L-(+)-DIPT (1.94 mL, 9.23 mmol) dropwise at -20 $^\circ\text{C}$. After 30 min at -20 $^\circ\text{C}$, a solution of (S) -**26** (4.50 g, 26.4 mmol) in CH_2Cl_2 (5 mL) was added slowly. The mixture was stirred for additional 20 min at -20 $^\circ\text{C}$, and cooled to -40 $^\circ\text{C}$. A solution of TBHP in CH_2Cl_2 (11.9 mL, 4.45 M, 53 mmol) was added to it.

The resulting mixture was stirred at $-20\text{ }^{\circ}\text{C}$ for 6 h, and Me_2S (5 mL, 69 mmol) was added. After 30 min at $-20\text{ }^{\circ}\text{C}$, 10% tartaric acid (4 mL), NaF (12 g, 286 mmol), and Celite (5 g) were added successively. The resulting mixture was stirred at r.t. for 1 h and filtered through a pad of Celite with Et_2O . The filtrate was concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/ EtOAc) to furnish *ent*-**27** (4.68 g, 95%): $[\alpha]_{\text{D}}^{27} +3$ (*c* 0.355, CHCl_3). The IR, ^1H NMR, and ^{13}C NMR spectra of the product were identical with those measured for **27**.

To an ice-cold solution of epoxide *ent*-**27** (355 mg, 1.91 mmol) in THF (5 mL) were added PPh_3 (1.10 g, 4.19 mmol), 3,5-dinitrobenzoic acid (848 mg, 4.0 mmol) and diisopropyl azodicarboxylate (0.749 mL, 3.81 mmol). The solution was stirred at r.t. for 3 h, and then diluted with saturated NaHCO_3 and hexane. After vigorous stirring for a few minutes, the organic phase was separated and the aqueous phase was extracted with hexane twice. The combined extracts were dried over MgSO_4 and purified by chromatography on silica gel (EtOAc /hexane) to afford the corresponding ester (680 mg, 93%): ^1H NMR (300 MHz, CDCl_3) δ 0.05 (s, 9 H), 2.19 (d, $J = 3.5$ Hz, 1 H), 2.60 (t, $J = 7$ Hz, 2 H), 3.08 (dd, $J = 7.5, 3.5$ Hz, 1 H), 4.86 (q, $J = 7$ Hz, 1 H), 5.06–5.22 (m, 2 H), 5.77 (ddt, $J = 17, 10, 7$ Hz, 1 H), 9.09–9.18 (m, 3 H); ^{13}C NMR (75 MHz, CDCl_3) δ -3.6, 36.4, 49.8, 56.1, 78.9, 119.1, 122.3, 129.4, 131.6, 133.7, 148.5, 161.6.

A mixture of the above ester (480 mg, 1.26 mmol) in THF (5 mL) and 2 N NaOH (3.2

mL, 6.40 mmol) was stirred at r.t. for 2 h and diluted with Et₂O. The phases were separated, and the aqueous phase was extracted with Et₂O twice. The combined organic phases were dried over MgSO₄ and concentrated to obtain an oil, which was purified by chromatography on silica gel (EtOAc/hexane) to afford alcohol **30** (220 mg, 94%): IR (neat) 3542, 1642, 1250 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.04 (s, 9 H), 2.19 (d, *J* = 4 Hz, 1 H), 2.27–2.44 (m, 2 H), 2.54 (br s, 1 H), 2.82 (dd, *J* = 5, 4 Hz, 1 H), 3.38–3.47 (m, 1 H), 5.04–5.18 (m, 2 H), 5.81 (ddt, *J* = 17, 10, 7 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ -3.5, 39.2, 49.5, 59.0, 72.6, 117.9, 133.6; [α]_D³² -20 (c 0.315, CHCl₃).

To an ice-cold solution of *i*-Pr₂NH (7.90 mL, 56.4 mmol) in THF (25 mL) was added *n*-BuLi (22.4 mL, 2.10 M in hexane, 47 mmol) slowly. After 15 min at 0 °C, Bu₃SnH (9.85 mL, 37.6 mmol) was added dropwise. The solution was stirred at 0 °C for additional 30 min, and **30** (3.50 g, 18.8 mmol) in THF (5 mL) was added to it. The solution was stirred at 0 °C for 4 h, and poured into an ice-cold mixture of saturated NH₄Cl and hexane. The mixture was stirred vigorously for a few minutes. The organic layer was separated, and the aqueous layer was extracted with hexane twice. The combined organic layers were dried over MgSO₄ and concentrated to afford the crude vinyl stannane **28**, which was used for the next reaction without further purification. The ¹H NMR and ¹³C NMR spectra of **28** thus synthesized were identical with those obtained above.

To an ice-cold solution of the above vinyl stannane **28** in Et₂O (30 mL) was added I₂ (6.20 g, 24.4 mmol). After being stirred at 0 °C for 30 min, saturated Na₂S₂O₃ was added, and the mixture was stirred vigorously for a few minutes. The organic phase was separated and the aqueous phase was extracted with Et₂O twice. The combined organic phases were dried over MgSO₄ and concentrated to afford a residue which was purified by chromatography on silica gel (hexane/EtOAc) to furnish vinyl iodide **29** (3.53 g, 84% from epoxide **30**). The ¹H NMR and ¹³C NMR spectra of **29** thus synthesized were identical with those presented above.

A solution of alcohol **29** (3.53 g, 15.8 mmol), TESCl (3.43 mL, 20.5 mmol), and

imidazole (2.15 g, 31.6 mmol) in DMF (40 mL) was stirred at r.t. for 1.5 h and poured into a mixture of saturated NaHCO_3 and Et_2O at 0 °C with vigorous stirring. The organic layer was separated, and the aqueous layer was extracted with Et_2O twice. The combined organic layers were dried over MgSO_4 and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/ EtOAc) to furnish **3** (4.98 g, 93%). The ^1H NMR and ^{13}C NMR spectra of **3** thus synthesized were identical with those described above.

To a mixture of magnesium turnings (503 mg, 0.0207 atom) in THF (4 mL) was added a solution of allyl bromide (2.34 mL, 27.7 mmol) in THF (1 mL). The mixture was kept refluxing for 20 min and cooled to room temperature, thus affording a slurry of MgBr_2 in THF. In another flask was charged vinyl iodide **3** (933 mg, 2.76 mmol) in THF (15 mL), and $n\text{-BuLi}$ (1.28 mL, 2.10 M in hexane, 2.69 mmol) was added to it slowly at -78 °C. After 20 min at -78 °C, a slurry of above MgBr_2 in THF was added. The mixture was stirred at -78 °C for additional 30 min, and ketone **6** (2.0 g, 10.7 mmol) in THF (1 mL) was added dropwise. After being stirred 1 h between -78 °C and -50 °C, the mixture was poured into an ice-cold mixture of saturated NH_4Cl and EtOAc . The mixture was stirred vigorously for a few minutes. The organic layer was separated, and the aqueous layer was extracted with EtOAc twice. The combined organic layers were dried over MgSO_4 and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/ EtOAc) to furnish **7** (739 mg, 91%, diastereomeric ratio = > 50 : 1): IR (neat) 3482, 3310, 1515, 1250, 1085 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.14 (s, 3 H), 0.19 (s, 3 H), 0.60 (q, J = 8 Hz, 6 H), 0.92 (s, 9 H), 0.95 (t, J = 8 Hz, 9 H), 1.26 (s, 3 H), 1.75–1.86 (m, 1 H), 1.94–2.06 (m, 1 H), 2.20 (s, 1 H), 2.18–2.36 (m, 2 H), 2.42 (d, J = 2 Hz, 1 H), 3.53 (dd, J = 9, 3 Hz, 1 H), 3.79 (s, 3 H), 4.19 (q, J = 6 Hz, 1 H), 4.52–4.68 (m, 3 H), 4.99–5.09 (m, 2 H), 5.68–5.88 (m, 3 H), 6.87 (d, J = 9 Hz, 2 H), 7.25 (d, J = 9 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.6, -3.7, 5.2, 7.1, 18.3, 23.9, 26.0, 40.8, 43.2, 55.3, 60.1, 72.9, 73.0, 74.2, 75.1, 82.0, 85.6, 113.8, 116.9, 129.0, 130.8, 132.1, 134.2, 134.8, 159.1; $[\alpha]_D^{29} +21$ (c 0.154, CHCl_3).

To an ice-cold solution of HF (0.015 mL, 55% in H₂O, 0.474 mmol) and MeOH (0.099 mL, 2.45 mmol) in MeCN (20 mL) was added **7** (287 mg, 0.488 mmol) in MeCN (5 mL). After 5 min at 0 °C, the solution was diluted with saturated NaHCO₃ and EtOAc. The organic layer was separated, and the aqueous layer was extracted with EtOAc twice. The combined organic layers were dried over MgSO₄ and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to obtain diol **31** (227 mg, 98%): IR (neat) 3409, 3308, 1514, 1250, 1092, 837 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.14 (s, 3 H), 0.19 (s, 3 H), 0.92 (s, 9 H), 1.26 (s, 3 H), 1.82 (ddd, *J* = 14, 9, 4 Hz, 1 H), 1.99 (ddd, *J* = 14, 9, 3 Hz, 1 H), 2.04 (br s, 1 H), 2.22–2.39 (m, 2 H), 2.40–2.46 (m, 2 H), 3.53 (dd, *J* = 8, 3 Hz, 1 H), 3.79 (s, 3 H), 4.14–4.24 (m, 1 H), 4.50–4.60 (m, 1 H), 4.60 (s, 2 H), 4.98–5.14 (m, 2 H), 5.75–5.88 (m, 3 H), 6.87 (d, *J* = 9 Hz, 2 H), 7.24 (d, *J* = 9 Hz, 2 H); ¹³C NMR (75 MHz, CDCl₃) δ -4.6, -3.8, 18.3, 24.1, 26.0, 40.7, 42.0, 55.3, 60.2, 71.2, 73.1, 74.0, 75.1, 81.9, 85.6, 113.8, 118.1, 129.0, 130.6, 131.4, 134.1, 135.3, 159.1; [α]_D²⁵ +30 (c 0.115, CHCl₃).

To an ice-cold solution of diol **31** (1.09 g, 2.30 mmol) and diisopropylethylamine (2.0 mL, 11.5 mmol) in CH₂Cl₂ (110 mL) was added a solution of acryloyl chloride (0.557 mL, 6.89 mmol) in CH₂Cl₂ (2 mL) dropwise. After 3 h of stirring at 0 °C, the solution was diluted with saturated NaHCO₃. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ twice. The combined organic layers were dried over MgSO₄ and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish ester **32** (1.03 g, 85%): IR (neat) 3523, 3288, 1724, 1515, 1250, 1192, 1092 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.14 (s, 3 H), 0.19 (s, 3 H),

0.92 (s, 9 H), 1.24 (s, 3 H), 1.70–2.10 (m, 2 H), 2.40–2.48 (m, 4 H), 3.52 (dd, $J = 8, 3$ Hz, 1 H), 3.80 (s, 3 H), 4.50–4.60 (m, 1 H), 4.57 (s, 2 H), 5.02–5.16 (m, 2 H), 5.44 (q, $J = 6$ Hz, 1 H), 5.66–5.96 (m, 4 H), 6.11 (dd, $J = 17, 11$ Hz, 1 H), 6.39 (dd, $J = 17, 2$ Hz, 1 H), 6.88 (d, $J = 9$ Hz, 2 H), 7.24 (d, $J = 9$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.5, -3.7, 18.4, 24.1, 25.9, 39.2, 40.7, 55.4, 60.2, 73.1, 73.4, 74.1, 75.1, 81.7, 85.5, 113.9, 118.1, 126.9, 128.7, 129.1, 130.6, 133.0, 137.9, 159.2, 165.2; $[\alpha]_D^{29} +31$ (c 0.205, CHCl_3).

To an ice-cold solution of **32** (1.03 g, 1.95 mmol) in CH_2Cl_2 (15 mL) were added 2,6-lutidine (1.36 mL, 11.7 mmol) in CH_2Cl_2 (2 mL) and TESOTf (1.32 mL, 5.85 mmol) in CH_2Cl_2 (3 mL) dropwise. After 30 min at 0 °C, the resulting solution was diluted with saturated NaHCO_3 . The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 twice. The combined organic layers were dried over MgSO_4 and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish silyl ester **33** (1.12 g, 89%): IR (neat) 3303, 1727, 1514, 1249, 1188, 1095 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.13 (s, 3 H), 0.17 (s, 3 H), 0.53–0.64 (m, 6 H), 0.92 (s, 9 H), 0.86–0.99 (m, 9 H), 1.37 (s, 3 H), 1.54–1.65 (m, 1 H), 1.89–1.99 (m, 1 H), 2.37 (d, $J = 2$ Hz, 1 H), 2.44 (t, $J = 7$ Hz, 2 H), 3.51 (dd, $J = 9, 3$ Hz, 1 H), 3.80 (s, 3 H), 4.49–4.57 (m, 1 H), 4.52 (d, $J = 11$ Hz, 1 H), 4.75 (d, $J = 11$ Hz, 1 H), 5.04–5.14 (m, 2 H), 5.43 (q, $J = 7$ Hz, 1 H), 5.60–5.89 (m, 4 H), 6.10 (dd, $J = 17, 11$ Hz, 1 H), 6.38 (dd, $J = 17, 2$ Hz, 1 H), 6.87 (d, $J = 9$ Hz, 2 H), 7.25 (d, $J = 9$ Hz, 2 H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.5, -3.7, 7.0, 7.3, 18.4, 23.8, 26.1, 39.2, 41.1, 55.4, 60.1, 72.6, 73.4, 74.4, 78.2, 83.0, 86.2, 113.7, 118.2, 127.2, 128.7, 128.9, 130.4, 131.4, 133.0, 137.4, 159.0, 165.2; $[\alpha]_D^{26} +40$ (c 0.63, CHCl_3).

To a solution of **33** (1.12g, 1.74 mmol) in CH_2Cl_2 (240 mL) were added $\text{Ti}(\text{O}-i\text{-Pr})_4$ (0.153 mL, 0.52 mmol) in CH_2Cl_2 (5 mL) and $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}$ (143 mg, 0.174 mmol) in CH_2Cl_2 (5 mL) successively. The mixture was refluxed at 60 °C (oil bath temp.) overnight, and then concentrated to afford a residue which was purified by chromatography on silica gel (hexane/EtOAc) to furnish lactone **34** (886 mg, 83%): IR (neat) 3294, 1734, 1514, 1248, 1086 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.13 (s, 3 H), 0.18 (s, 3 H), 0.63 (q, $J = 8$ Hz, 6 H), 0.92 (s, 9 H), 0.97 (t, $J = 8$ Hz, 9 H), 1.41 (s, 3 H), 1.56–1.67 (m, 1 H), 1.88–2.04 (m, 1 H), 2.40 (d, $J = 2$ Hz, 1 H), 2.40–2.46 (m, 2 H), 3.53 (dd, $J = 9$, 3 Hz, 1 H), 3.79 (s, 3 H), 4.51–4.59 (m, 2 H), 4.69 (d, $J = 11$ Hz, 1 H), 4.93 (q, $J = 6$ Hz, 1 H), 5.80 (dd, $J = 16$, 6 Hz, 1 H), 5.92 (d, $J = 16$ Hz, 1 H), 6.03 (dt, $J = 10$, 2 Hz, 1 H), 6.82–6.91 (m, 1 H), 6.87 (d, $J = 8$ Hz, 2 H), 7.25 (d, $J = 8$ Hz, 2 H).

To a solution of lactone **34** (840 mg, 1.37 mmol) in acetone (10 mL) were added AgNO_3 (255 mg, 1.50 mmol) and *N*-iodosuccinimide (369 mg, 1.64 mmol). After being stirred at r.t. for 3 h, the mixture was diluted with saturated H_2O and EtOAc at 0 °C with vigorous stirring. The organic layer was separated, and the aqueous layer was extracted with EtOAc twice. The combined organic layers were dried over MgSO_4 and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish iodide **35** (840 mg, 83%): IR (neat) 1723, 1514, 1249, 1086, 757 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.11 (s, 3 H), 0.16 (s, 3 H), 0.62 (q, $J = 8$ Hz, 6 H), 0.91 (s, 9 H), 0.97 (t, $J = 8$ Hz, 9 H), 1.39 (s, 3 H), 1.53–1.65 (m, 1 H), 1.88–1.99 (m, 1 H), 2.38–2.48 (m, 2 H), 3.49 (dd, $J = 9$, 3 Hz, 1 H), 3.78 (s, 3 H), 4.47–4.71 (m, 3 H), 4.95 (dt, $J = 9$, 6 Hz, 1 H), 5.79 (dd, $J = 16$, 6 Hz, 1 H), 5.90 (d, $J = 16$ Hz, 1 H), 6.02 (d, $J = 10$ Hz, 1 H), 6.82–6.90 (m, 3 H), 7.24 (d, $J = 8$ Hz, 2 H); ^{13}C NMR (75

MHz, CDCl₃) δ -4.7, -4.0, 6.9, 7.3, 18.2, 24.4, 25.9, 29.8, 40.7, 55.2, 61.6, 74.1, 77.6, 77.8, 82.4, 96.2, 113.6, 121.4, 126.0, 128.9, 130.7, 137.9, 144.5, 158.8, 163.7; $[\alpha]_D^{26}$ +46 (*c* 0.135, CHCl₃).

To an ice-cold mixture of PMB ether **35** (586 mg, 0.791 mmol) in CH₂Cl₂/H₂O (18 : 1, 9.5 mL) was added DDQ (215 mg, 0.95 mmol) in one portion. The mixture was stirred at 0 °C for 3 h, and diluted with saturated NaHCO₃. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ twice. The combined organic layers were dried over MgSO₄ and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to furnish alcohol **36** (403 mg, 82%): IR (neat) 3509, 1717, 1251, 1081, 1009 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.08 (s, 3 H), 0.11 (s, 3 H), 0.56 (q, *J* = 8 Hz, 6 H), 0.85 (s, 9 H), 0.91 (t, *J* = 8 Hz, 9 H), 1.31 (s, 3 H), 1.46 (ddd, *J* = 14, 10.5, 3 Hz, 1 H), 1.82 (dd, *J* = 14, 7 Hz, 1 H), 2.37–2.45 (m, 2 H), 2.90 (br s, 1 H), 3.70 (d, *J* = 10.5 Hz, 1 H), 4.75 (dd, *J* = 7, 3 Hz, 1 H), 4.87–4.97 (m, 1 H), 5.76 (dd, *J* = 16, 5 Hz, 1 H), 5.86 (d, *J* = 16 Hz, 1 H), 6.00 (dt, *J* = 10, 2 Hz, 1 H), 6.81–6.90 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃) δ -5.2, -4.6, 6.9, 7.2, 18.2, 22.8, 25.8, 29.7, 39.2, 62.8, 75.0, 76.8, 77.4, 95.4, 121.5, 126.5, 137.4, 144.4, 163.7; $[\alpha]_D^{27}$ +59 (*c* 0.105, CHCl₃).

To a solution of **36** (403 mg, 0.649 mmol) in THF (5 mL) and *i*-PrOH (5 mL) were added triethylamine (0.136 mL, 0.976 mmol) and *o*-nitrobenzenesulfonylhydrazide (154 mg, 0.716 mmol). After being stirred at r.t. overnight, the mixture was diluted with saturated NaHCO₃ and EtOAc. The organic layer was separated, and the aqueous layer was extracted with EtOAc twice. The combined organic layers were dried over

MgSO₄ and concentrated to afford an oil, which was purified by chromatography on silica gel (hexane/EtOAc) to obtain vinyl iodide **2** (356 mg, 88%). The IR, ¹H NMR, and ¹³C NMR spectra were identical with those kindly provided by T. Imanishi and K. Miyashita of Osaka University.