Supporting Information for:

Enol Ester as an Olefinic Partner in Enyne Cyclization. A Novel Tandem Cyclization to Stereo-defined Bicyclo[3.3.0]octenes

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General. ¹H and ¹³C NMR spectra were taken on a Varian Gemini-300 spectrometer at 300 and 75 MHz, respectively. CDCl₃ was used as the solvent. Chemical shifts are reported in parts per million shift (δ value) from Me₄Si (δ 0 ppm for ¹H) or based on the middle peak of the solvent (CDCl₃) (δ 77.00 ppm for ¹³C NMR) as an internal standard. Signal patterns are indicated as br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) are given in Hertz. Infrared (IR) spectra were recorded on a JASCO A-100 spectrometer and are reported in wave numbers (cm⁻¹). Ti(O-*i*-Pr)₄ was distilled and stocked under argon atmosphere. Isopropylmagnesium chloride was prepared in Et₂O as a 1.3-1.7 M solution from isopropyl chloride and magnesium turnings by the usual procedure, titrated, and stocked under an argon atmosphere. All reactions were carried out under argon. Dry solvents (THF, ethyl ether, CH₂Cl₂) were purchased from Kanto Chemicals Co. (Japan). Chemicals were purified or dried in a standard manner, if necessary.

(*E*)-1-Tridecen-6-ynyl Propanoate (2) (>99% *E*).

¹H NMR δ 0.88 (t, *J* = 6.0 Hz, 3H), 1.16 (t, *J* = 7.5 Hz, 3H), 1.22-1.66 (m, 10H), 2.06-2.19 (m, 6H), 2.38 (q, *J* = 7.5 Hz, 2H), 5.39 (dt, *J* = 12.3, 7.5 Hz, 1H), 7.11 (d, *J* = 12.5 Hz, 1H). The peaks of the (*Z*)-isomer (see below) were not seen on ¹H NMR spectra of crude and purified samples. Thus, the stereoselectivity was judged to be >99:<1 based on the limit of detection of ¹H NMR spectroscopy.

(Z)-1-Tridecen-6-ynyl Propanoate (4) (>99% Z). This was prepared as follows [Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, 99, 1993-1996]. The yields have not been optimized at all.

To a cold stirred solution of enyne **24** (4.2 g, 18.6 mmol) in CH₂Cl₂ (55 mL) were added *m*-CPBA (70 % purity, 5.9 g, 24.1 mmol) and NaHCO₃ (0.47 g, 5.57 mmol) at 0 °C. After the solution was allowed to warm to room temperature and stirred for 1 h, it was diluted with hexane. The organic phase was washed with an aqueous NaHCO₃ solution, separated, dried (Na₂SO₄), and concentrated to a crude oil, which was chromatographed on silica gel to afford epoxide **25** (3.9 g, 78%).

To a stirred solution of (*E*)-1-(trimethylsilyl)-1,2-epoxy-6-tridecyne (**25**) (0.200 g, 0.750 mmol, >99% *E*), propanoic acid (3.40 mL, 45.8 mmol), and propanoic anhydride (0.340 mL, 2.63 mmol) was added BF₃•OEt₂ (2 drops) at room temperature under argon. After being stirred overnight at the same temperature, the reaction mixture was diluted with ether, and an aqueous solution of NaHCO₃ was carefully added. The organic phase was separated and the aqueous phase was extracted with ether. The combined ethereal extracts were dried (Na₂SO₄) and concentrated to a crude oil, which was chromatographed on silica gel to afford the title compound (124 mg, 69 %) as a colorless oil.

R_f 0.54 (analytical TLC plate Merck #1.05554, hexane:ethyl acetate = 9:1).

¹H NMR δ 0.88 (t, J = 6.9 Hz, 3H), 1.18 (t, J = 7.5 Hz, 3H), 1.24-1.61 (m, 10H), 2.08-2.18 (m, 4H), 2.23 (dq, J = 12, 6.6 Hz, 2H), 2.43 (q, J = 7.5 Hz, 2H), 4.86 (q, J = 6.6 Hz, 1H), 7.04 (d, J = 6.6 Hz, 1H).

¹³C NMR δ 9.00, 14.16, 18.41, 18.85, 22.65, 23.71, 27.47, 28.63, 28.75, 29.19, 31.44, 79.56, 80.59, 113.01, 134.40, 171.36.

IR (neat) 2931, 2858, 1755 (C=O), 1671 (C=C), 1463, 1350, 1163, 1098, 1024, 750 cm⁻¹.

Anal. Calcd for C₁₆H₂₆O₂: C, 76.75; H, 10.47. Found: C, 76.54; H, 10.46.

The peaks of the (*E*)-isomer (see above) were not seen on ¹H NMR spectra of crude and purified samples. Thus, the stereoselectivity was judged to be >99:<1 based on the limit of detection of ¹H NMR spectroscopy.

(1*RS*,2*RS*,3*SR*)-3-Ethyl-4-hexyl-4-bicyclo[3.3.0]octene-2,3-diol (5). To a stirred solution of (*Z*)-1-tridecen-6-ynyl propanoate (**4**) (>99% *Z*) (35 mg, 0.140 mmol) in 1.5 mL of Et₂O were successively added Ti(*O-i*-Pr)₄ (0.052 mL, 0.175 mmol) at -30 °C and *i*-PrMgCl (1.40 M in Et₂O, 0.250 mL, 0.350 mmol) at -78 °C under argon. The solution was warmed to -50 °C over 30 min, stirred at the same temperature for 3 h, warmed to -20 °C, stirred at this temperature for 4 h, warmed to 0 °C, and finally stirred at this temperature for 1 h. Then, the reaction was terminated by the addition of water (0.2 mL). The resultant heterogeneous mixture was filtered through a short pad of Celite with the aid of additional ether. The organic phase was concentrated to an oil, careful analysis of which by ¹H NMR spectroscopy showed the presence of a single title compound without any other isomeric products. The crude product was chromatographed on silica gel (hexane-ether) to afford the title compound (27 mg, 76%) as a colorless oil.

R_f 0.22 (analytical TLC plate Merck #1.05554, hexane:ethyl acetate = 7:3).

¹H NMR δ 0.88 (t, *J* = 6.0 Hz, 3H), 0.92 (t, *J* = 7.8 Hz, 3H), 1.13-2.27 (m, 18H), 2.10 (d, *J* = 4.8 Hz, 1H), 2.68 (s, 1H), 2.73 (m, 1H), 3.98 (t, *J* = 4.8 Hz, 1H). On treatment with D₂O, the peaks at δ 2.10 and 2.68 ppm disappeared and the triplet peak at δ 3.98 ppm changed to doublet. The observed coupling constant between H¹ and H² is 4.8 Hz, which supports the depicted 1,2-stereochemistry. (Note that, if the relative stereochemistry of the 2-position is 2*SR*, the coupling constant between these protons should be around 8~9 Hz.) In addition, irradiation of the proton at δ 3.98 ppm (CH²OH) showed 8% nOe enhancement to the peak at δ 2.73 ppm (tertiary allylic H¹). Thus, the stereochemistry has been confirmed. The relative stereochemistry of the diol moiety (i.e., that between 2- and 3-positions) was deduced based on that of similar compound **20** described below.

¹³C NMR δ 8.52, 13.97, 22.55, 23.58, 23.66, 25.61, 27.00, 28.85, 29.40, 29.65, 31.63, 52.10, 76.06, 91.42, 133.20, 143.81.

IR (neat) 3421, 2960, 2926, 2852, 1458, 1378, 1170, 1095, 1067, 725, 705 cm^{-1} .

Anal. Calcd for C₁₆H₂₈O₂: C, 76.14; H, 11.18. Found: C, 76.11; H, 11.53.

(Z)-1-Tridecen-6-ynyl Isobutyrate (11) (>99% Z).

¹H NMR δ 0.88 (t, J = 6.6 Hz, 3H), 1.22 (d, J = 7.5 Hz, 6H), 1.12-1.66 (m, 10H), 2.01-2.21 (m, 4H), 2.24 (dt, J = 9, 6.9 Hz, 2H), 2.64 (quintet, J = 7.2 Hz, 1H), 4.87 (q, J = 6.9 Hz, 1H), 7.03 (d, J = 6.9 Hz, 1H).

¹³C NMR δ 14.16, 18.42, 18.85, 18.88, 22.65, 23.71, 28.64, 28.77, 29.19, 31.44, 34.02, 79.57, 80.59, 113.08, 134.54, 173.92.

IR (neat) 2932, 2859, 1752 (C=O), 1670 (C=C), 1469, 1244, 1146, 742 cm⁻¹.

Anal. Calcd for C₁₇H₂₈O₂: C, 77.22; H, 10.67. Found: C, 77.03; H, 10.78.

The peaks of the (*E*)-isomer were not seen on ¹H NMR spectra of crude and purified samples. Thus, the stereoselectivity was judged to be >99:<1 based on the limit of detection of ¹H NMR spectroscopy.

(Z)-1-Tridecen-6-ynyl 9-(Z)-Octadecenoate (oleate) (12) (>99% Z, Z).

¹H NMR δ 0.78 (t, J = 6.0 Hz, 6H), 1.04-1.64 (m, 32H), 1.80-1.98 (m, 4H), 2.03 (q, J = 6.0 Hz, 4H), 2.13 (q, J = 6.0 Hz, 2H), 2.30 (t, J = 6.0 Hz, 2H), 4.86 (q, J = 6.0 Hz, 1H), 5.35 (t, J = 5.4 Hz, 2H), 7.04 (d, J = 6.0 Hz, 1H).

¹³C NMR δ 14.00 (2 peaks), 22.58 (2 peaks), 23.61, 23.66, 24.16, 25.64, 27.05, 27.10, 27.12, 28.88, 29.18, 29.23 (2 peaks), 29.43 (2 peaks), 29.66, 29.68, 30.17, 31.64, 31.82, 37.00, 52.04, 76.49, 91.21, 129.91, 130.03, 133.49, 143.65, 170.70.

IR (neat) 2927, 2855, 1750 (C=O), 1655 (C=C), 1560, 1510, 1459, 1150 cm^{-1} .

Anal. Calcd for C₃₁H₅₄O₂: C, 81.16; H, 11.86. Found: C, 80.83; H, 11.52.

The peaks of (*E*)-1-tridecen-6-ynyl 9-(*Z*)-octadecenoate were not seen on ¹H NMR spectra of crude and purified samples. Thus, the stereoselectivity was judged to be >99:<1 based on the limit of detection of ¹H NMR spectroscopy.

(*Z*)-7-(Trimethylsilyl)-1-hepten-6-ynyl Propanoate (13) (>99% *Z*).

¹H NMR δ 0.14 (s, 9H), 1.18 (t, *J* = 7.8 Hz, 3H), 1.60 (quintet, *J* = 7.2 Hz, 2H), 2.23 (t, *J* = 6.9 Hz, 2H), 2.24 (q, *J* = 6.6 Hz, 2H), 2.43 (q, *J* = 7.5 Hz, 2H), 4.85 (q, *J* = 6.6 Hz, 1H), 7.05 (d, *J* = 6.6 Hz, 1H).

¹³C NMR δ 0.27, 9.01, 19.46, 23.65, 27.47, 28.23, 84.64, 106.95, 112.74, 134.54, 171.33.

IR (neat) 2958, 2174, 1756 (C=O), 1671 (C=C), 1249, 1162, 1098, 842, 760 cm⁻¹.

Anal. Calcd for C₁₃H₂₂O₂Si: C, 65.50; H, 9.30. Found: C, 66.05; H, 9.73.

The peaks of the (*E*)-isomer were not seen on ¹H NMR spectra of crude and purified samples. Thus, the stereoselectivity was judged to be >99:<1 based on the limit of detection of ¹H NMR spectroscopy.

(*Z*)-1-Tridecen-6-ynyl 4-Bromobutyrate (14) (>99% *Z*).

¹H NMR δ 0.88 (t, *J* = 6.6 Hz, 3H), 1.18-1.66 (m, 10H), 2.08-2.32 (m, 8H), 2.62 (t, *J* = 7.2 Hz, 2H), 3.49 (t, *J* = 6.3 Hz, 2H), 4.89 (q, *J* = 6.5 Hz, 1H), 7.04 (d, *J* = 6.5 Hz, 1H).

¹³C NMR δ 13.94, 18.21, 18.66, 22.46, 23.55, 27.37, 28.47, 28.55, 29.04, 31.28, 32.11, 32.37, 79.52, 80.69, 113.62, 134.41, 169.83.

IR (neat) 2930, 2858, 2017, 1752 (C=O), 1670 (C=C), 1162, 1128, 749 cm⁻¹.

Anal. Calcd for C₁₇H₂₇BrO₂: C, 59.48; H, 7.93. Found: C, 59.70; H, 8.35.

The peaks of the (*E*)-isomer were not seen on ¹H NMR spectra of crude and purified samples. Thus, the stereoselectivity was judged to be >99:<1 based on the limit of detection of ¹H NMR spectroscopy.

(±)-(*Z*)-3-Butyl-1-tridecen-6-ynyl Propanoate (15) (>99% *Z*).

^1H NMR δ 0.84-0.91 (m, 9H), 1.15-1.64 (m, 16H), 2.00-2.22 (m, 4H), 2.41 (q, J = 7.2 Hz, 2H), 2.65 (m, 1H), 4.55 (dd, J = 6.5, 9.9 Hz, 1H), 7.06 (d, J = 6.5 Hz, 1H).

^{13}C NMR δ 14.16, 16.90, 18.87, 22.66, 22.75, 27.51, 28.65, 29.18, 29.23, 29.44, 29.51, 31.47, 34.41, 34.92, 35.12, 76.58, 80.05, 117.81, 134.57, 171.37.

IR (neat) 2930, 2858, 2017, 1757 (C=O), 1671 (C=C), 1249, 1161, 840 cm^{-1} .

Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{O}_2$: C, 78.38; H, 11.18. Found: C, 78.45; H, 11.28.

The peaks of the (*E*)-isomer were not seen on ^1H NMR spectra of crude and purified samples. Thus, the stereoselectivity was judged to be >99:<1 based on the limit of detection of ^1H NMR spectroscopy.

($\pm$)-(Z)-1-Tridecen-6-ynyl Phenyl(methoxy)acetate (16) (>99% Z).

^1H NMR δ 0.86 (t, J = 6.6 Hz, 3H), 1.21-1.41 (m, 8H), 1.48 (quintet, J = 7.2 Hz, 2H), 2.01-2.20 (m, 6H), 3.45 (s, 3H), 4.85 (s, 1H), 4.91 (q, J = 6.9 Hz, 1H), 6.99 (d, J = 6.9 Hz, 1H), 7.33-7.42 (m, 3H), 7.43-7.52 (m, 2H).

^{13}C NMR δ 14.15, 18.41 (2 peaks), 18.86, 22.65, 23.72, 28.61 (2 peaks), 29.20, 31.44, 57.47, 80.60, 82.22, 114.43, 127.11, 128.60, 128.79 (2 peaks), 134.15, 167.59.

IR (neat) 3015, 2930, 2858, 1760 (C=O), 1670 (C=C), 1560, 1540, 1510, 1459, 668 cm^{-1} .

Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_3$: C, 77.16; H, 8.83. Found: C, 77.08; H, 8.53.

The peaks of the (*E*)-isomer were not seen on ^1H NMR spectra of crude and purified samples. Thus, the stereoselectivity was judged to be >99:<1 based on the limit of detection of ^1H NMR spectroscopy.

(1*RS*,2*RS*,3*SR*)-4-Hexyl-3-isopropyl-4-bicyclo[3.3.0]octene-2,3-diol (17).

^1H NMR δ 0.85 (d, J = 6.3 Hz, 3H), 0.86 (t, J = 6.3 Hz, 3H), 1.01 (d, J = 6.0 Hz, 3H), 1.19-2.28 (m, 18H), 2.60 (s, 1H), 2.71 (m, 1H), 4.08 (d, J = 6.0 Hz, 1H).

^{13}C NMR δ 14.22, 17.42, 17.61, 22.78, 23.65, 24.10, 26.06, 26.98, 29.16, 29.94, 31.78, 33.93, 53.38, 72.90, 93.95, 132.12, 145.19.

IR (neat) 3420, 2960, 2928, 2862, 1458, 1363, 1162, 733 cm^{-1} .

Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{O}_2$: C, 76.64; H, 11.35. Found: C, 76.65; H, 11.20.

(1*RS*,2*RS*,3*SR*)-3-(8-Heptadecenyl)-4-hexyl-4-bicyclo[3.3.0]octene-2,3-diol (18).

^1H NMR δ 0.88 (t, J = 6.0 Hz, 6H), 1.21-2.25 (m, 44H), 2.01 (s, 1H), 2.65 (s, 1H), 2.74 (m, 1H), 3.98 (d, J = 5.3 Hz, 1H), 5.34 (t, J = 5.4 Hz, 2H).

^{13}C NMR δ 14.23, 22.77, 23.80 (2 peaks), 23.85, 24.35, 25.82 (2 peaks), 27.23, 27.27 (2 peaks), 27.30 (2 peaks), 29.05, 29.40 (2 peaks), 29.60 (2 peaks), 29.83 (2 peaks), 30.34, 31.80, 31.98, 37.13, 52.12, 76.49, 91.16, 129.72, 129.84, 133.28, 143.40.

IR (neat) 3418, 2925, 2854, 1464, 1377, 1073, 724 cm^{-1} .

Anal. Calcd for $\text{C}_{31}\text{H}_{56}\text{O}_2$: C, 80.81; H, 12.25. Found: C, 80.63; H, 11.94.

(1*RS*,2*RS*,3*RS*)-3-Ethyl-4-(trimethylsilyl)-4-bicyclo[3.3.0]octene-2,3-diol (19).

^1H NMR δ 0.14 (s, 9H), 0.91 (t, J = 7.5 Hz, 3H), 1.39-2.04 (m, 7H), 2.21-2.26 (m, 2H), 2.74 (s, 1H), 2.82 (m, 1H), 3.96 (d, J = 4.5 Hz, 1H).

^{13}C NMR δ 0.05, 8.78, 23.44, 25.80, 27.21, 30.36, 55.56, 76.77, 96.00, 134.00, 162.84.

IR (neat) 3390, 2956, 2840, 1457, 1363, 1245, 1075, 836, 756 cm^{-1} .

Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Si}$: C, 64.95; H, 10.06. Found: C, 64.72; H, 10.02.

(1*RS*,2*RS*,3*SR*)-3-(3-Bromopropyl)-4-hexyl-4-bicyclo[3.3.0]octene-2,3-diol (20). To a stirred solution of (Z)-1-tridecen-6-ynyl 4-bromobutyrate (**14**) (>99% *Z*) (22 mg, 0.064 mmol) in 0.5 mL of Et_2O were successively added $\text{Ti}(\text{O}-i\text{-Pr})_4$ (0.024 mL, 0.080 mmol) at $-30\text{ }^\circ\text{C}$ and *i*-PrMgCl (1.40 M in Et_2O , 0.114 mL, 0.160 mmol) at $-78\text{ }^\circ\text{C}$ under argon. The solution was warmed to $-50\text{ }^\circ\text{C}$ over 30 min, stirred at the same temperature for 3 h, warmed to $-20\text{ }^\circ\text{C}$, stirred at this temperature for 4 h, warmed to $0\text{ }^\circ\text{C}$, and finally stirred at this temperature for 1 h. Then, the reaction was terminated by the addition of water (0.1 mL). The resultant heterogeneous mixture was filtered through a short pad of Celite with the aid of additional ether. The organic phase was concentrated to an oil, careful analysis of which by ^1H NMR spectroscopy showed the presence of a single title compound without any other isomeric products. The crude

product was chromatographed on silica gel (pre-treated twice with 5% NEt₃ in hexane (10 mL each) prior to the sample elution with hexane-ether) to give the title compound (14 mg, 63%) as a fairly unstable oil.

¹H NMR δ 0.89 (t, J = 6.0 Hz, 3H), 1.20-2.28 (m, 21H), 2.77 (m, 1H), 2.87 (s, 1H), 3.36-3.54 (m, 2H), 3.98 (d, J = 4.8 Hz, 1H).

Other physical properties have not been obtained due to the instability of this compound. Instead, its further characterization was performed in the form of **23** as described below.

(1*RS*,2*RS*,3*SR*)-4-Hexyl-3,3-(1-oxa-1,4-butylene)-4-bicyclo[3.3.0]octen-2-ol (23). To a stirred ether solution (1 mL) of crude **20**, prepared as above from (Z)-1-tridecen-6-ynyl 4-bromobutyrate (**14**) (>99% Z) (20 mg, 0.0583 mmol), Ti(O-*i*-Pr)₄ (0.021 mL, 0.073 mmol), and *i*-PrMgCl (1.47 M in Et₂O, 0.099 mL, 0.146 mmol), was added Et₃N (0.030 mL, 0.117 mmol) at room temperature under argon. Then, the reaction mixture was stirred at the same temperature for 3 h. The reaction was terminated by the addition of an aqueous NH₄Cl solution. The organic layer was separated, dried (Na₂SO₄), and concentrated to an oil, which was chromatographed on silica gel to afford the title compound (9.5 mg, 62 % overall from the enol ester **14**).

R_f 0.32 (analytical TLC plate Merck #1.05554, hexane:ethyl acetate = 7:3).

¹H NMR δ 0.88 (t, J = 6.0 Hz, 3H), 1.26 (m, 6H), 1.49 (m, 2H), 1.55-1.68 (m, 3H), 1.70-2.00 (m, 5H), 1.95 (t, J = 7.5 Hz, 2H), 2.06 (m, 1H), 2.23 (dt, J = 1.3, 8.4 Hz, 1H), 2.65 (m, 1H), 2.86 (s, 1H), 3.69 (d, J = 6.0 Hz, 1H), 3.82-4.00 (m, 2H). Irradiation of the proton at δ 2.86 ppm (OH) showed 4% nOe enhancement to the peak at δ 3.69 ppm (CH₂OH) and 1 % nOe enhancement to the peak at δ 3.90-4.00 ppm (OCH₂), respectively. Thus, the stereochemistry between 2- and 3-positions has been confirmed, which, in turn, determines the stereochemistry of the diol moiety of **20**.

^{13}C NMR δ 14.00, 22.56, 23.35, 23.66, 25.55, 26.14, 27.03, 28.57, 29.60, 31.65 (2 peaks), 52.41, 68.72, 76.85, 100.17, 130.70, 144.94.
 IR (neat) 3450, 2929, 2870, 1458, 670 cm^{-1} .

($\pm$)-(1*RS*,2*RS*,3*SR*,8*SR*)-8-Butyl-3-ethyl-4-hexyl-4-bicyclo[3.3.0]octene-2,3-diol as a >95:<5 mixture of diastereoisomers (21).

^1H NMR δ 0.84-0.96 (m, 9H), 1.20-1.52 (m, 16H), 1.74 (m, 2H), 1.89 (d, $J = 5.7$ Hz, 1H), 2.00 (m, 2H), 2.05-2.12 (m, 3H), 2.34 (dd, $J = 5.7, 10.2$ Hz, 1H), 2.70 (s, 1H), 3.98 (t, $J = 5.7$ Hz, 1H). The coupling constant between H^1 and H^8 is 10.2 Hz, which supports the depicted stereochemistry between these hydrogens. (Note that, if the 8-position is 8*RS*, the coupling constant should be around 5~6 Hz.) Thus, the stereochemistry has been confirmed.

^{13}C NMR δ 8.56, 13.98 (2 peaks), 22.56, 23.02, 23.34, 25.53, 28.69, 29.22, 29.68, 30.67, 31.64, 34.24, 34.85, 37.85, 58.60, 75.95, 91.07, 133.21, 143.70.
 IR (neat) 3420, 2955, 2926, 2856, 1457, 1378, 1099, 1066, 731 cm^{-1} .
 Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{O}_2$: C, 77.87; H, 11.76. Found: C, 78.11; H, 11.72.

The peaks of minor isomers were not seen on ^1H NMR spectra of crude and purified samples. Thus, the diastereoselectivity was judged to be >95:<5 based on the limit of detection of ^1H NMR spectroscopy.

($\pm$)-(1*RS*,2*RS*,3*SR*)-4-Hexyl-3-[phenyl(methoxy)methyl]-4-bicyclo[3.3.0]octene-2,3-diol as a 67:33 mixture of diastereoisomers (22). To a stirred solution of $\text{Ti}(\text{O}-i\text{-Pr})_4$ (0.110 mL, 0.365 mmol) in 2.0 mL of Et_2O was added $i\text{-PrMgCl}$ (1.27 M in Et_2O , 0.580 mL, 0.730 mmol) at -78°C under argon. The solution was warmed to -50°C over 30 min, and the stirring was continued for 1 h at -50°C . Then, ($\pm$)-(Z)-1-tridecen-6-ynyl phenyl(methoxy)acetate (**16**) (>99% Z) (100 mg, 0.292 mmol) in 1.0 mL of Et_2O was

added. The solution was stirred at -50 °C for 3 h, warmed to -20 °C, stirred at this temperature for 4 h, warmed to 0 °C, and finally stirred for 1 h at this temperature. The reaction was then terminated by the addition of water (0.2 mL). The resultant heterogeneous mixture was filtered through a short pad of Celite with the aid of ether. The organic phase was concentrated to a crude oil, ¹H NMR analysis of which showed the presence of diastereoisomers in a ratio of 67:33. The crude product was chromatographed on silica gel (hexane-ether) to afford the title compound of the same isomeric composition (62.7 mg, 62 %) as a colorless oil.

Major Diastereoisomer: ¹H NMR δ 0.72-2.08 (m, 22H), 3.06 (dd, J = 4.0, 10 Hz, 1H), 3.21 (d, J = 1.0 Hz, 1H), 3.29 (s, 1H), 3.43 (s, 3H), 4.98 (s, 1H), 7.28-7.48 (m, 5H).

Minor Diastereoisomer: ¹H NMR δ (only characteristic peaks are shown) 2.44 (d, J = 4.8 Hz, 1H), 2.54 (m, 1H), 3.08 (s, 1H), 3.24 (s, 3H), 4.05 (s, 1H), 4.20 (t, J = 4.8 Hz, 1H).

IR (neat) 3444, 2925, 2858, 1456, 1109, 757, 701, 668 cm⁻¹ for a 67:33 mixture of diastereoisomers.

Anal. Calcd for C₂₂H₃₂O₃: C, 76.70; H, 9.36. Found: C, 76.69; H, 9.67 for a 67:33 mixture of diastereoisomers.