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Supporting Information

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Total Synthesis and Complete Assignment of the Stereostructure of a Marine Bromochloro Triterpene Polyether (+)-Intricatetraol

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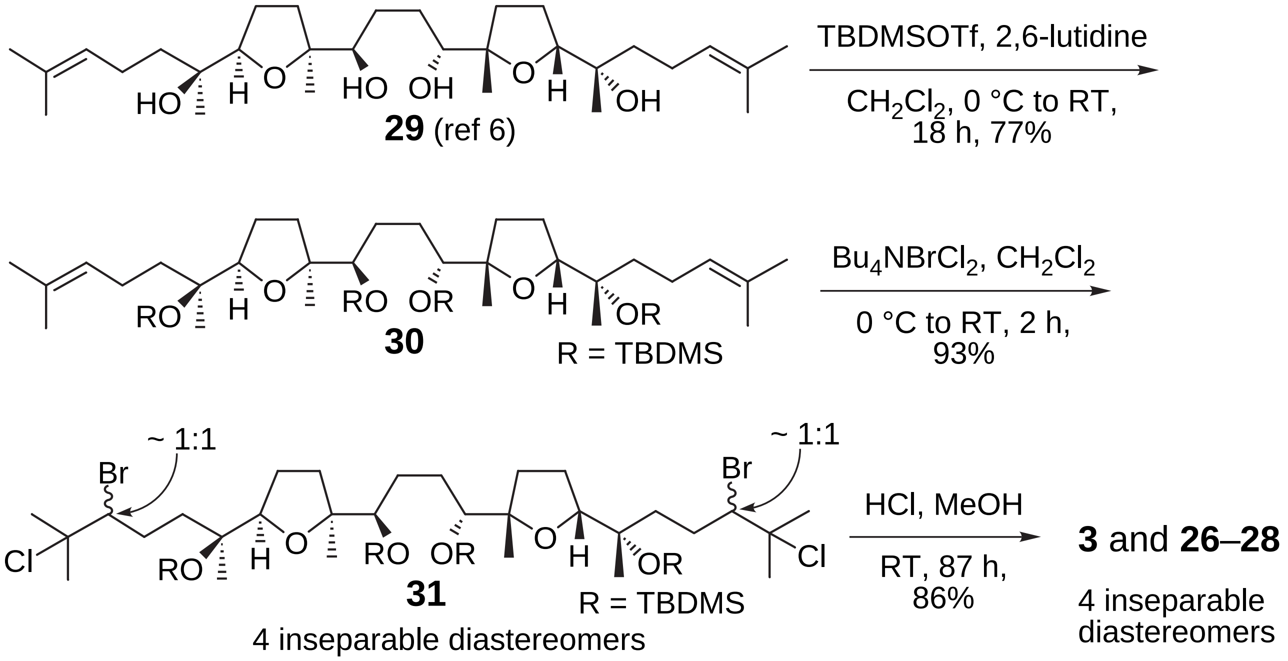
[5] d) R. W. Fuller, J. H. Cardellina II, J. Jurek, P. J. Scheuer, B. Alvarado-Lindner, M. McGuire, G. N. Gray, J. R. Steiner, J. Clardy, E. Menez, R. H. Shoemaker, D. J. Newman, K. M. Snader, M. R. Boyd, *J. Med. Chem.* **1994**, *37*, 4407–4411.

[18] D. J. Pasto, R. T. Taylor in *Organic Reactions, Vol. 40* (Eds.: L. A. Paquette, P. Beak, E. Ciganek, S. Hanessian, L. Hegedus, R. C. Kelly, S. V. Ley, L. E. Overman, H. J. Reich, C. Sih, A. B. Smith III, M. Uskokovic), Wiley, New York, **1991**, pp. 91–155.

Further discussion on the possibility of other diastereomers

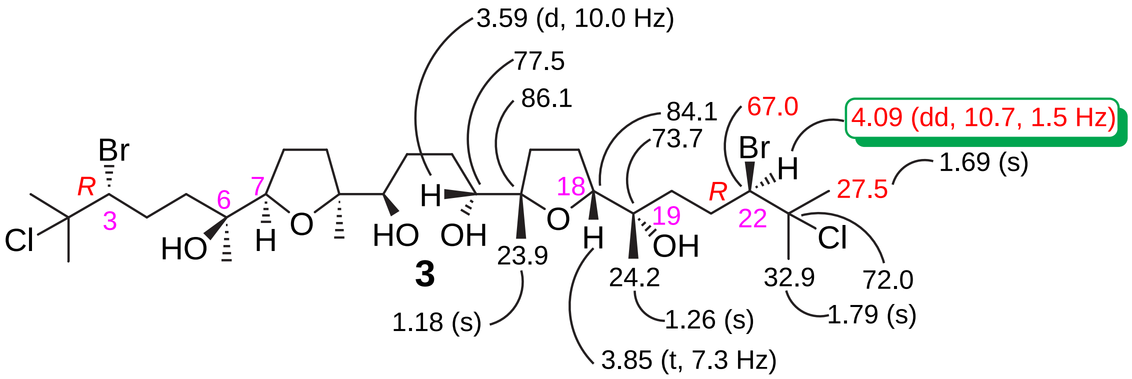
1) About the possibility of the epimer at C3 (C22)

A principal question from the referees is whether the synthetic compound **3** with *R* configuration at the C3 (C22) can spectroscopically be differentiated from the diastereomer with *S* configuration at the C3 (C22) or not. We have reported the synthesis of tetraol **29**, a degradation product of natural (+)-intricatetraol (**1**) in reference 6. For the total synthesis of (+)-intricatetraol (**1**), we have nonstereoselectively synthesized four diastereomers **3** and **26**–**28** from the tetraol **29** as shown in Scheme 5. Unfortunately, the four diastereomers **3** and **26**–**28** were obtained as an inseparable mixture. Four diastereomers **3** and **26**–**28** in the ^{1}H and ^{13}C NMR spectra of the mixture looked like almost two kinds of diastereomers. That is, we think that the NMR spectra of the left half in **27** and the right half in **28** are almost the same as those of C_2 symmetric **26** with *S* configuration at the C3 (C22) and the NMR spectra of the right half in **27** and the left half in **28** are almost the same as those of C_2 symmetric **3** with *R* configuration at the C3 (C22). Anyway, the compound **3** with *R* configuration at the C3 (C22) could clearly be differentiated from the compound **26** with *S* configuration at the C3 (C22) as shown in the chemical shifts, 4.09 ppm in the ^{1}H NMR and 67.0 ppm in the ^{13}C NMR of **3** and 3.99 ppm in the ^{1}H NMR and 66.4 ppm in the ^{13}C NMR of **26**, at the C3 (C22) position in the NMR spectra.



Scheme 5. Nonstereoselective syntheses of four diastereomers **3** and **26**–**28**.

400 MHz ^1H and 100 MHz ^{13}C NMR in $CDCl_3$



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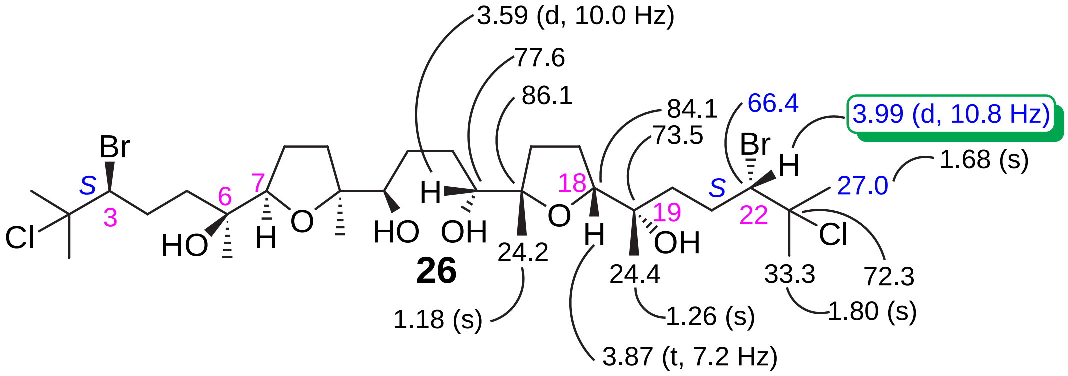

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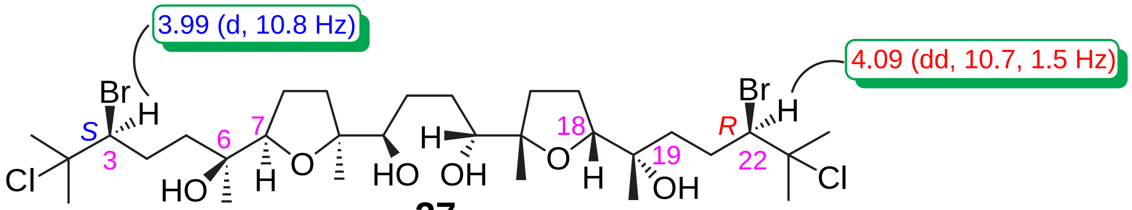
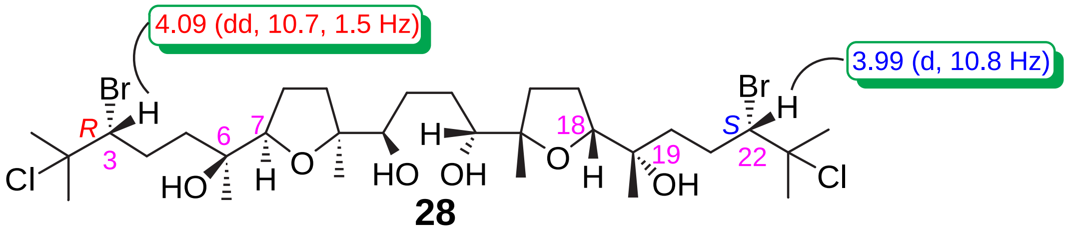


27



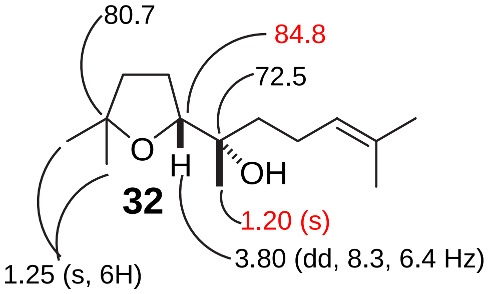
28

2) About the possibility of the epimer at C6 (C19)

Another question from the Referee 2 is whether the synthetic compound **3** with *erythro* configuration between C6 and C7 (C18 and C19) can spectroscopically be differentiated from the epimer with *threo* configuration between C6 and C7 (C18 and C19) or not. Although we have not synthesized the epimer itself, we show our deposited data of closely related compounds **32**–**35** synthesized in our laboratory below (Y. Morimoto, T. Iwai, *J. Am. Chem. Soc.* **1998**, *120*, 1633–1634).

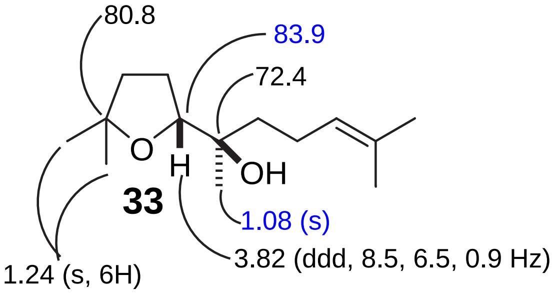
400 MHz ^{1}H and 100 MHz ^{13}C NMR in $CDCl_3$

erythro



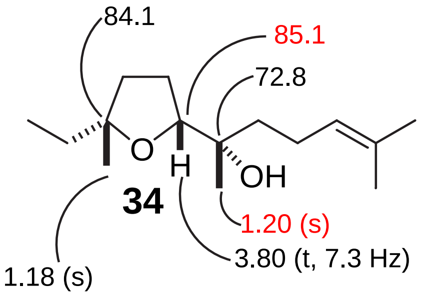
32

threo



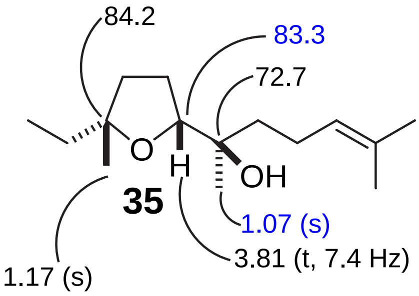
33

erythro



34

threo



35

The *erythro* compounds **32** and **34** can clearly be differentiated from the corresponding *threo* compounds **33** and **35**, respectively, in the NMR spectra, especially in the red and blue chemical shifts.

Therefore, we believe it is hardly possible that the stereochemistries of (+)-intricatetraol are epimeric at C3 (C22) and/or C6 (C19) positions.

Experimental Section

Allylic Alcohol 11. To a solution of the known chiral diol **10**[9] (738 mg, 2.47 mmol) and pyridinium *p*-toluenesulfonate (31.0 mg, 0.124 mmol) in 25.0 mL of dichloromethane was added dropwise *p*-anisaldehyde dimethyl acetal (0.631 mL, 3.71 mmol) at 0 °C under a nitrogen atmosphere, and the mixture was stirred at room temperature for 16 h. A saturated aqueous solution of sodium bicarbonate (20 mL) was added to the solution, and the aqueous layer was extracted with dichloromethane (15 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo to afford the crude benzylidene acetal which was taken to the next step without further purification.

To a solution of the above crude benzylidene acetal in 25.0 mL of methanol was added potassium carbonate (410 mg, 2.97 mmol), and the mixture was stirred under a nitrogen atmosphere at room temperature for 7 h. After the organic layer was evaporated in vacuo, water (20 mL) was added to the residue and the aqueous layer was extracted with dichloromethane (20 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was subjected to column chromatography (dichloromethane/acetone = 99:1 to 90:10) on 5 g of silica gel to furnish allylic alcohol **11** (917 mg, 99.1% yield based on diol **10**) in a 7:3 mixture at the benzylic position as a colorless oil: R_f = 0.26 (hexane/ethyl acetate = 70:30); $[\alpha]_D^{27}$ = +3.80 (c = 0.83 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): δ = 7.44–7.36 (m, 2H), 6.92–6.86 (m, 2H), 5.96 (s, 0.3H), 5.77 (s, 0.7H), 5.45–5.37 (m, 1H), 5.21–5.12 (m, 1H), 4.19–4.10 (m, 2H), 3.80 (s, 3H), 3.70 (dd, J = 9.4, 3.5 Hz, 0.7H), 3.70–3.65 (m, 0.3H), 2.30–1.99 (m, 6H), 1.78–1.46 (m, 2H), 1.68 (s, 2.1H), 1.67 (s, 0.9H), 1.62 (s, 3H), 1.36 (s, 0.9H), 1.35 (s, 2.1H), 1.24 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 28 °C): δ = 160.3, 160.0, 139.6, 134.7, 132.4, 130.4, 128.2, 127.6, 124.4, 124.3, 123.48, 123.45, 113.74, 113.68, 101.6, 101.0, 85.3, 83.3, 81.1, 80.0, 59.4, 55.30, 55.28, 39.5, 39.4, 36.7, 36.6, 29.3, 28.2, 28.1, 26.2, 25.6, 25.3, 23.6, 20.3, 16.3, 16.03, 15.99 ppm; IR (film): ν = 3420, 2974, 2916, 2855, 1616, 1516, 1373, 1304, 1248, 1171, 1155, 1070, 1034, 1003, 829 cm^{-1}; MS (FAB): *m/z* (%): 375.2 (26) $[M + H]^+$, 374 (14) $[M^+]$, 373.2 (26) $[M - H]^+$, 357.2 (5), 288.2 (7), 221.2 (18), 154.1 (39), 153 (33), 137.1 (100), 135.1 (53), 81.0 (24), 71.0 (20); HR-MS (FAB): calcd for $C_{23}H_{34}O_4$ $[M^+]$: 374.2457; found: 374.2458; HR-MS (FAB): calcd for $C_{23}H_{33}O_4$ $[M - H]^+$: 373.2379; found: 373.2401.

Epoxy Alcohol 12. To a suspension of 4 Å molecular sieves (5.20 g) in 25.0 mL of dichloromethane were sequentially added freshly distilled titanium tetraisopropoxide (51.0 μL, 0.173 mmol) and (+)-diethyl L-tartrate (50.0 mg, 0.243 mmol) in 0.5 mL of dichloromethane at –20 °C under a nitrogen atmosphere with stirring. The reaction mixture was stirred at –20 °C as *tert*-butyl hydroperoxide (1.12 mL, 3.90 mmol, 3.70 M in dichloromethane) was added dropwise over ca. 5 min. The resulting mixture was stirred at –20 °C for 30 min. A solution of allylic alcohol **11** (1.30 g, 3.47 mmol) dissolved in 10.0 mL of dichloromethane was then added dropwise over a period of 10 min, and the mixture was stirred for an additional 21 h at –20 °C. The catalyst was quenched with 5 mL of water and the mixture was stirred at 0 °C for 30 min. Hydrolysis of the tartrate was effected by adding 1.0 mL of a 30% aqueous solution of sodium hydroxide saturated with sodium chloride and stirring rigorously at 0 °C for 30 min. The lower organic phase was removed and combined with four 10 mL dichloromethane extractions of the aqueous phase. The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 70:30) on 30 g of silica gel to provide epoxy alcohol **12** (1.29 g, 95.3% yield) as a colorless oil: R_f = 0.38 (hexane/ethyl acetate = 70:30); $[\alpha]_D^{27}$ = +2.99 (*c* = 0.80 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C, TMS): δ = 7.44–7.35 (m, 2H), 6.92–6.86 (m, 2H), 5.96 (s, 0.3H), 5.77 (s, 0.7H), 5.21–5.12 (m, 1H), 3.82–3.73 (m, 1H), 3.799 (s, 0.9H), 3.797 (s, 2.1H), 3.70 (dd, *J* = 9.5, 3.2 Hz, 0.7H), 3.70–3.60 (m, 1.3H), 2.96 (dd, *J* = 6.6, 4.4 Hz, 0.7H), 2.94 (dd, *J* = 6.6, 4.6 Hz, 0.3H), 2.31–1.99 (m, 5H), 1.81–1.39 (m, 4H), 1.63 (s, 2.1H), 1.62 (s, 0.9H), 1.36 (s, 0.9H), 1.35 (s, 2.1H), 1.30 (s, 2.1H), 1.28 (s, 0.9H), 1.24 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 28 °C): δ = 160.3, 135.01, 134.96, 132.2, 130.3, 128.1, 127.6, 123.8, 123.7, 113.70, 113.65, 101.5, 101.0, 85.2, 83.2, 81.1, 80.0, 62.9, 61.32, 61.29, 61.00, 60.98, 55.2, 38.40, 38.37, 36.7, 36.6, 28.05, 27.97, 25.6, 25.3, 23.6, 23.52, 23.51, 20.2, 16.70, 16.67, 15.95, 15.89 ppm; IR (film): ν = 3440, 2972, 2936, 2856, 1616, 1516, 1437, 1387, 1369, 1304, 1248, 1171, 1155, 1111, 1070, 1034, 1011, 829, 735 cm^{-1}; MS (EI): *m/z* (%): 390 (3) [M^+], 359 (3), 288 (18), 220 (8), 163 (10), 152 (24), 137 (82), 135 (100), 108 (33), 81 (37), 71 (66), 69 (34); HR-MS (EI): calcd for $C_{23}H_{34}O_5$ [M^+]: 390.2407; found: 390.2407.

Diepoxy Alcohol 14. Alkene **12** (1.26 g, 3.23 mmol) was dissolved in acetonitrile (16.0 mL) and dimethoxymethane (32.0 mL). To the solution were added ketone **13**[11] (501 mg, 1.94 mmol), tetrabutylammonium hydrogen sulfate (88.0 mg, 0.259 mmol), and buffer (32.0 mL, 0.05 M solution of $Na_2B_4O_7 \cdot 10H_2O$ in 4 × 10^{-4} M aqueous Na_2(EDTA)). A solution of Oxone (5.48

g, 8.92 mmol) in aqueous Na_2(EDTA) (4×10^{-4} M, 25.0 mL) and a solution of potassium carbonate (5.18 g, 37.5 mmol) in water (25.0 mL) were added dropwise separately to the solution at 0 ℃ over a period of 2 h via additional funnels, and the mixture was stirred at the same temperature for another 30 min. The reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (50 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 80:20 for ketone **13** and 70:30 to 50:50 for diepoxy alcohol **14**) on 30 g of silica gel to afford diepoxy alcohol **14** (1.15 g, 87.2% yield) as a colorless oil: R_f = 0.56 (ethyl acetate); $[\alpha]_D^{26}$ = −4.81 (*c* = 0.84 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 27 ℃, TMS): δ = 7.43–7.34 (m, 2H), 6.92–6.86 (m, 2H), 5.94 (s, 0.3H), 5.76 (s, 0.7H), 3.86–3.60 (m, 3H), 3.80 (s, 3H), 3.00–2.92 (m, 1H), 2.81–2.71 (m, 1H), 2.18 (s, 0.3H), 2.17 (s, 0.7H), 1.97–1.45 (m, 8H), 1.37 (s, 0.9H), 1.35 (s, 2.1H), 1.31 (s, 2.1H), 1.30 (s, 0.9H), 1.28 (s, 0.9H), 1.27 (s, 2.1H), 1.24 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 28 ℃): δ = 160.3, 132.1, 130.2, 128.1, 127.6, 113.73, 113.72, 101.6, 101.1, 85.7, 83.9, 81.2, 80.1, 63.4, 63.3, 62.3, 61.3, 60.9, 60.5, 55.3, 36.3, 36.2, 35.1, 35.0, 29.3, 25.6, 25.3, 25.2, 24.3, 23.5, 20.1, 16.9, 16.8, 16.41, 16.35 ppm; IR (film): ν = 3447, 2972, 2934, 2872, 1616, 1516, 1456, 1437, 1387, 1369, 1304, 1248, 1221, 1171, 1159, 1111, 1070, 1034, 1011, 982, 866, 831 cm^{-1}; MS (FAB): *m/z* (%): 407 (4) $[M + H]^+$, 406 (5) $[M^+]$, 405.2 (11) $[M - H]^+$, 271.2 (23), 253.2 (13), 235.2 (15), 155.1 (18), 137 (82), 135.0 (100), 109.0 (24), 81 (24), 71.0 (39), 43.0 (41); HR-MS (FAB):

calcd for $C_{23}H_{33}O_6$ [M – H]$^+$: 405.2278; found: 405.2278.

Triol 15. A solution of diepoxy alcohol **14** (570 mg, 1.40 mmol) in 4.20 mL of 1,4-dioxane and 4.20 mL of a 1 M aqueous solution of lithium hydroxide was stirred at 100 °C for 7 h. The mixture was cooled to room temperature, and water (15 mL) was added to the mixture. The resulting mixture was extracted with chloroform (15 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 75:25 to 70:30 for bicyclic ether **16** and 30:70 to ethyl acetate/methanol = 95:5 for triol **15**) on 20 g of silica gel to provide bicyclic ether **16** (129 mg, 22.6% yield) and triol **15** (401 mg, 67.3% yield) as each colorless oil.

Triol 15: R_f = 0.28 (ethyl acetate); $[\alpha]_D^{27}$ = +13.1 (c = 1.04 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 26 °C, TMS): δ = 7.44–7.34 (m, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.94 (s, 0.3H), 5.77 (s, 0.7H), 3.88–3.60 (m, 4H), 3.80 (s, 3H), 3.78 (s, 1H), 3.60–3.35 (m, 2H), 2.22–1.45 (m, 8H), 1.39 (s, 0.9H), 1.36 (s, 2.1H), 1.26 (s, 6H), 1.18 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 26 °C): δ = 160.3, 160.1, 132.0, 130.2, 128.2, 127.7, 113.7, 101.5, 101.1, 86.2, 84.50, 84.48, 84.38, 84.1, 84.0, 81.3, 80.2, 76.8, 73.45, 73.41, 69.5, 63.3, 55.3, 53.8, 35.7, 35.5, 32.6, 31.7, 26.3, 25.6, 25.3, 24.1, 24.0, 23.7, 23.6, 23.5, 20.2 ppm; IR (film): ν = 3398, 2974, 2934, 2876, 1616, 1518, 1456, 1375, 1304, 1248, 1221, 1171, 1088, 1070, 1034, 1018, 982, 916, 831, 735 cm^{-1}; MS (FAB): m/z (%): 425.2 (7) [M + H]$^+$, 424 (4) [M^+], 423.1 (5) [M – H]$^+$, 271.2 (82), 137.1 (94), 135.1 (54), 81.0 (64), 55.0 (100), 43.0 (86); HR-MS (FAB):

calcd for $C_{23}H_{37}O_7$ [*M* + H]$^+$: 425.2539; found: 425.2512; HR-MS (FAB): calcd for $C_{23}H_{36}O_7$ [*M*$^+$]: 424.2461; found: 424.2458; HR-MS (FAB): calcd for $C_{23}H_{35}O_7$ [*M* − H]$^+$: 423.2383; found: 423.2365.

Bicyclic Ether 16: R_f = 0.62 (ethyl acetate); $[\alpha]_D^{26}$ = −1.02 (*c* = 0.87 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.44–7.36 (m, 2H), 6.93–6.87 (m, 2H), 4.03–3.97 (m, 0.3H), 4.00 (dd, *J* = 9.6, 3.3 Hz, 0.7H), 3.81 (s, 0.9H), 3.80 (s, 2.1H), 3.77–3.68 (m, 2H), 3.55 (dd, *J* = 13.3, 4.3 Hz, 0.7H), 3.53 (dd, *J* = 13.5, 4.3 Hz, 0.3H), 3.33 (ddd, *J* = 11.2, 4.1, 1.2 Hz, 0.7H), 3.35–3.29 (m, 0.3H), 2.68 (d, *J* = 11.2 Hz, 1H), 2.22–1.99 (m, 2H), 1.79 (t, *J* = 8.3 Hz, 2H), 1.65–1.46 (m, 4H), 1.40 (s, 3.9H), 1.37 (s, 2.1H), 1.28 (s, 0.9H), 1.27 (s, 2.1H), 1.25 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C): δ = 160.4, 160.1, 136.2, 130.2, 128.2, 127.7, 113.74, 113.72, 101.6, 101.1, 86.1, 85.8, 84.32, 84.29, 84.0, 81.2, 80.1, 79.8, 75.64, 75.63, 70.7, 69.5, 64.3, 55.3, 53.8, 34.7, 32.9, 32.8, 31.7, 29.2, 25.74, 25.68, 25.66, 25.4, 24.9, 24.8, 24.0, 23.9, 23.65, 23.60, 20.2 ppm; IR (film): ν = 3440, 2972, 2934, 1616, 1518, 1456, 1371, 1304, 1248, 1221, 1171, 1132, 1111, 1088, 1069, 1032, 993, 912, 831, 735 cm^{-1}; MS (FAB): *m/z* (%): 407 (8) [*M* + H]$^+$, 406 (4) [*M*$^+$], 405 (7) [*M* − H]$^+$, 271.2 (26), 137.1 (55), 83.0 (59), 57.0 (100), 55.0 (95); HR-MS (FAB): calcd for $C_{23}H_{35}O_6$ [*M* + H]$^+$: 407.2433; found: 407.2408; HR-MS (FAB): calcd for $C_{23}H_{34}O_6$ [*M*$^+$]: 406.2355; found: 406.2346; HR-MS (FAB): calcd for $C_{23}H_{33}O_6$ [*M* − H]$^+$: 405.2277; found: 405.2263.

Alkene 17. To a solution of triol **15** (900 mg, 2.12 mmol) and 4-(dimethylamino)pyridine (13.0 mg, 0.106 mmol) in 20.0 mL of dichloromethane were successively added triethylamine (0.50 mL, 3.60

mmol) and *tert*-butyldimethylsilyl chloride (505 mg, 3.18 mmol) at room temperature under a nitrogen atmosphere, and the mixture was stirred at the same temperature for 26 h. Water (20 mL) was added to the solution, and the aqueous layer was extracted with dichloromethane (15 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 80:20 to 70:30) on 30 g of silica gel to afford the TBDMS ether (1.09 g, 95.5% yield) as a colorless oil: R_f = 0.58 (ethyl acetate).

To a solution of the TBDMS ether (1.13 g, 2.09 mmol) and *N*,*N*-diisopropylethylamine (5.47 mL, 31.4 mmol) in 20.0 mL of dichloromethane was added dropwise chloromethyl methyl ether (1.99 mL, 20.9 mmol) at 0 °C under a nitrogen atmosphere, and the mixture was then stirred at room temperature for 36 h. Water (20 mL) was added to the solution, and the aqueous layer was extracted with dichloromethane (15 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 95:5 to 80:20) on 30 g of silica gel to afford the diMOM ether (1.26 g, 96.1% yield) as a colorless oil: R_f = 0.49 (hexane/ethyl acetate = 70:30).

To a solution of the diMOM ether (1.26 g, 2.01 mmol) in 20.0 mL of tetrahydrofuran was added dropwise tetrabutylammonium fluoride (2.62 mL, 2.62 mmol, 1 M in tetrahydrofuran) at 0 °C under a nitrogen atmosphere, and the mixture was stirred at room temperature for 15 h. Water (30 mL) was added to the solution, and the aqueous layer was extracted with dichloromethane (20 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography (hexane/ethyl acetate = 70:30 to 40:60) on 20 g of silica gel to furnish the primary alcohol (1.03 g, 100% yield) as a colorless oil: R_f = 0.20 (hexane/ethyl acetate = 50:50).

To a solution of the primary alcohol (1.03 g, 2.01 mmol) and triethylamine (1.69 mL, 12.1 mmol) in 10.0 mL of dichloromethane and 10.0 mL of dimethyl sulfoxide was added portionwise sulfur trioxide pyridine complex (1.32 g, 8.05 mmol) at 0 ℃ under a nitrogen atmosphere, and the mixture was stirred at 0 ℃ for 30 min. After water (40 mL) was added to the solution, the dichloromethane was evaporated in vacuo and the residual aqueous layer was extracted with ether (25 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 80:20 to 50:50) on 20 g of silica gel to give the aldehyde (1.03 g, 99.8% yield) as a colorless oil: R_f = 0.51 (hexane/ethyl acetate = 50:50).

To a suspension of methyltriphenylphosphonium bromide (2.20 g, 6.03 mmol) in 10.0 mL of tetrahydrofuran at 0 ℃ under a nitrogen atmosphere was added dropwise sodium hexamethyldisilazide (5.62 mL, 5.62 mmol, 1 M in tetrahydrofuran), and the solution was stirred at 0 ℃ for 1 h. A solution of the aldehyde (1.03 g, 2.01 mmol) in 10.0 mL of tetrahydrofuran was added dropwise to the solution, and the mixture was stirred at 0 ℃ for an additional 1 h. Water (25 mL) was added to the solution, and the aqueous layer was extracted with ether (30 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The reside was purified by column chromatography (hexane/ethyl acetate = 90:10 to 70:30) on 30 g of silica gel to provide alkene **17** (919 mg, 90.0% yield) as a colorless oil: R_f = 0.39 (hexane/ethyl acetate = 70:30); $[\alpha]_D^{26}$ = −14.5 (c = 0.99 in chloroform); ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C, TMS): δ = 7.41 (d, J = 8.8 Hz, 1.4H), 7.38 (d, J = 8.8 Hz, 0.6H), 6.89 (d, J = 8.8 Hz, 2H), 5.95 (s, 0.3H), 5.85–5.65 (m, 1H), 5.76 (s, 0.7H), 5.31–5.20 (m, 2H), 4.81 (d, J = 7.2 Hz, 1H), 4.74–4.63 (m, 2H), 4.57 (d, J = 6.6 Hz, 0.7H), 4.56 (d, J = 6.8 Hz, 0.3H), 3.94 (t, J = 7.2 Hz, 1H), 3.89 (d, J = 7.0 Hz, 0.7H), 3.88 (d, J = 7.0 Hz, 0.3H), 3.80 (s, 3H), 3.71–3.63 (m, 1H), 3.37 (s, 5.1H), 3.35 (s, 0.9H), 2.15–1.47 (m, 8H), 1.37 (s, 0.9H), 1.35 (s, 2.1H), 1.24 (s, 3.9H), 1.21 (s, 2.1H), 1.15 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C): δ = 160.3, 160.0, 135.0, 132.3, 130.4, 128.1, 127.6, 118.5, 113.6, 101.4, 100.9, 94.5, 91.4, 86.3, 84.3, 84.0, 82.50, 82.46, 82.3, 81.2, 80.0, 78.7, 55.7, 55.4, 55.2, 34.3, 33.7, 33.6, 29.2, 26.25, 26.20, 25.6, 25.4, 23.5, 23.3, 23.2, 22.0, 21.9, 20.2, 19.33, 19.26 ppm; IR (film): ν = 2974, 2936, 2889, 2839, 1614, 1518, 1464, 1371, 1302, 1248, 1217, 1171, 1148, 1094, 1036, 920, 829 cm^{-1}; MS (FAB): m/z (%): 508 (10) $[M^+]$, 507.2 (16) $[M - H]^+$, 311.2 (61), 135.0 (46), 45.0 (100); HR-MS (FAB): calcd for $C_{28}H_{44}O_8$ $[M^+]$: 508.3036; found: 508.3015; HR-MS (FAB): calcd for $C_{28}H_{43}O_8$ $[M - H]^+$: 507.2958; found: 507.2985.

Diol 18. To a solution of benzylidene acetal **17** (560 mg, 1.10 mmol) in a 17:1 mixture of dichloromethane and water (total 10.8 mL), respectively, was added portionwise 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (390 mg, 1.65 mmol) at room temperature, and the mixture was stirred at the same temperature for 2 h. The reaction mixture was filtrated through a pad of Celite under reduced pressure, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 80:20 to 50:50) on 15 g of silica gel to provide a 3:7 mixture of regioisomeric benzoate esters.

To a solution of the above 3:7 mixture of regioisomeric benzoate esters in 11.0 mL of tetrahydrofuran was added dropwise lithium aluminum hydride (3.30 mL, 3.30 mmol, 1 M in tetrahydrofuran) at 0 ℃ under a nitrogen atmosphere, and the mixture was stirred at 0 ℃ for 1.5 h. To the reaction mixture were successively added a small amount of methanol and water, and the mixture was diluted with ether. After the mixture was stirred at room temperature for 1 h, the mixture was filtrated through a pad of Celite under reduced pressure and the filtrate was concentrated in vacuo. The residue was subjected to flash column chromatography (hexane/ethyl acetate = 70:30 to 30:70) on 20 g of silica gel to provide diol **18** (411 mg, 95.6% yield based on benzylidene acetal **17**) as a colorless oil: R_f = 0.14 (hexane/ethyl acetate = 50:50); $[\alpha]_D^{26}$ = −30.5 (c = 0.81 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 24 ℃, TMS): δ = 5.78 (ddd, J = 17.5, 10.3, 6.8 Hz, 1H), 5.29 (ddd, J = 10.6, 1.8, 0.8 Hz, 1H), 5.27 (ddd, J = 17.1, 1.8, 1.1 Hz, 1H), 4.85 (d, J = 7.3 Hz, 1H), 4.69 (d, J = 6.6 Hz, 1H), 4.68 (d, J = 7.3 Hz, 1H), 4.58 (d, J = 6.6 Hz, 1H), 3.95 (dd, J = 8.1, 6.8 Hz, 1H), 3.89 (d, J = 7.1 Hz, 1H), 3.39 (s, 3H), 3.38 (s, 3H), 3.35 (ddd, J = 10.7, 4.3, 2.1 Hz, 1H), 2.91 (d, J = 4.6 Hz, 1H), 2.20 (s, 1H), 2.00 (ddd, J = 12.1, 9.3, 5.2 Hz, 1H), 1.95–1.55 (m, 6H), 1.46–1.32 (m, 1H), 1.21 (s, 3H), 1.19 (s, 3H), 1.161 (s, 3H), 1.157 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 27 ℃): δ = 134.9, 118.8, 94.6, 91.3, 84.1, 82.3, 82.2, 79.3, 78.5, 73.0, 55.8, 55.6, 34.2, 33.2, 26.35, 26.33, 25.0, 23.3, 22.2, 19.4 ppm; IR (film): ν = 3422, 2974, 2936, 2887, 1508, 1458, 1375, 1213, 1148, 1096, 1036, 920 cm^{-1}; MS (FAB): *m/z* (%): 391.2 (1.4) $[M + \text{H}]^+$, 359.2 (12), 341.2 (5), 249.2 (16), 71.0 (27), 45.0 (100), 43.0 (27); HR-MS (FAB): calcd for $C_{20}H_{39}O_7$ $[M + \text{H}]^+$: 391.2696; found: 391.2696.

Epoxide 19. To a solution of diol **18** (82.7 mg, 0.212 mmol) and pyridine (50.0 μL, 0.619 mmol) in 2.10 mL of dichloromethane was added dropwise methanesulfonyl chloride (35.0 μL, 0.424 mmol) at 0 °C under a nitrogen atmosphere, and the mixture was stirred at room temperature for 2 h. An additional pyridine (0.50 mL, 6.19 mmol) was added to the solution, and the mixture was stirred at the same temperature for 12 h. To the solution were successively added 4.20 mL of methanol and potassium carbonate (439 mg, 3.18 mmol), and the mixture was stirred at the same temperature for an additional 3 h. Water (15 mL) was added to the solution, and the aqueous layer was extracted with dichloromethane (10 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was subjected to column chromatography (hexane/ethyl acetate = 95:5 to 85:15) on 3 g of silica gel to furnish epoxide **19** (71.0 mg, 90.0% yield) as a colorless oil: R_f = 0.63 (hexane/ethyl acetate = 50:50); $[\alpha]_D^{26}$ = −37.9 (*c* = 0.95 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.79 (ddd, *J* = 17.1, 10.7, 7.1 Hz, 1H), 5.28 (ddd, *J* = 10.7, 1.9, 0.8 Hz, 1H), 5.26 (ddd, *J* = 17.1, 2.0, 1.0 Hz, 1H), 4.82 (d, *J* = 7.3 Hz, 1H), 4.69 (d, *J* = 6.6 Hz, 1H), 4.67 (d, *J* = 7.3 Hz, 1H), 4.58 (d, *J* = 6.6 Hz, 1H), 3.95 (t, *J* = 7.3 Hz, 1H), 3.89 (d, *J* = 7.1 Hz, 1H), 3.38 (s, 3H), 3.37 (s, 3H), 2.71 (t, J = 6.2 Hz, 1H), 1.98 (ddd, J = 11.7, 9.4, 5.7 Hz, 1H), 1.94–1.46 (m, 7H), 1.31 (s, 3H), 1.26 (s, 3H), 1.21 (s, 3H), 1.15 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C): δ = 135.0, 118.6, 94.6, 91.4, 84.2, 82.7, 82.3, 78.6, 64.5, 58.3, 55.7, 55.4, 34.4, 33.3, 26.1, 24.9, 23.0, 21.9, 19.1, 18.6 ppm; IR (film): ν = 2978, 2955, 2934, 2887, 1558, 1506, 1456, 1375, 1213, 1148, 1097, 1036, 920 cm^{-1}; MS (FAB): m/z (%): 373.2 (3) $[M + H]^+$, 341.2 (15), 311.2 (51), 249.2 (16), 154.0 (36), 137.1 (27), 136.0 (27), 71.0 (21), 45.0 (100), 43.0 (17); HR-MS (FAB): calcd for $C_{20}H_{37}O_6$ $[M + H]^+$: 373.2590; found: 373.2591.

Bromohydrin 20. To a solution of epoxide **19** (93.0 mg, 0.250 mmol) in 2.0 mL of tetrahydrofuran was added an excess of freshly prepared dilithium tetrabromonickelate (3.12 mL, 2.50 mmol, 0.8 M in tetrahydrofuran)[14] at room temperature under a nitrogen atmosphere, and the mixture was stirred at the same temperature for 56 h. The reaction mixture was treated with phosphate buffer (5 mL, pH 7.4) and extracted with dichloromethane (5 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 80:20 to 70:30) on 5 g of silica gel to afford bromohydrin **20** (86.5 mg, 76.4% yield) as a colorless oil: R_f = 0.18 (hexane/ethyl acetate = 70:30); $[\alpha]_D^{25}$ = +11.9 (c = 0.68 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.79 (ddd, J = 16.7, 11.1, 7.2 Hz, 1H), 5.32–5.24 (m, 2H), 4.80 (d, J = 7.1 Hz, 1H), 4.73 (d, J = 7.3 Hz, 1H), 4.70 (d, J = 6.6 Hz, 1H), 4.59 (d, J = 6.8 Hz, 1H), 4.02 (dd, J = 10.7, 2.0 Hz, 1H), 3.93 (dd, J = 8.2, 6.7 Hz, 1H), 3.89 (d, J = 7.3 Hz, 1H), 3.39 (s, 3H), 3.37 (s, 3H), 2.18 (s, 1H), 2.14–2.05 (m, 1H), 2.01 (ddd, J = 12.1, 9.3, 5.2 Hz, 1H), 1.94–1.54 (m, 6H), 1.36 (s, 3H), 1.34 (s, 3H), 1.21 (s, 3H), 1.16 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 28 °C): δ = 135.0, 118.7, 94.7, 91.5, 84.2, 82.8, 82.4, 78.8, 72.8, 72.6, 55.7, 55.5, 35.7, 34.3, 28.0, 26.8, 26.5, 25.8, 22.2, 19.5 ppm; IR (film): ν = 3445, 2978, 2937, 2887, 1448, 1375, 1217, 1148, 1097, 1036, 918 cm^{-1}; MS (FAB): m/z (%): 455 (1) $[M - H]^+$, 453.0 (1) $[M - H]^+$, 393 (25), 391.0 (25), 45.0 (100), 43.0 (26); HR-MS (FAB): calcd for $C_{20}H_{36}O_6{}^{81}Br$ $[M - H]^+$: 453.1675; found: 453.1666; HR-MS (FAB): calcd for $C_{20}H_{36}O_6{}^{79}Br$ $[M - H]^+$: 451.1695; found: 451.1686.

Alkene 21. To a solution of bromohydrin **20** (102 mg, 0.225 mmol) in 2.20 mL of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)pyrimidinone was added dropwise thionyl chloride (30.0 μL, 0.405 mmol) at 0 °C under a nitrogen atmosphere, and the mixture was stirred at the same temperature for 30 min. Water (10 mL) was added to the solution, and the aqueous layer was extracted with ether (5 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was subjected to column chromatography (hexane/ethyl acetate = 99:1 to 90:10) on 4 g of silica gel to provide the crude mixture which was taken to the next step.

To a solution of the above crude mixture in 2.0 mL of methanol was added dropwise 12 N aqueous hydrochloric acid (50.0 μL, 0.609 mmol), and the mixture was stirred at room temperature for 66 h. An appropriate amount of triethylamine was added to the solution to neutralize the solution, and the organic solvents were evaporated in vacuo. Water (5 mL) was added to the residue, and the aqueous layer was extracted with dichloromethane (5 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 95:5 for allylic bromide **23** to 70:30 for alkene **21**) on 5 g of silica gel to give allylic bromide **23** (21.3 mg, 27.2% yield based on bromohydrin **20**) as a colorless oil and alkene **21** (47.2 mg, 54.6% yield based on bromohydrin **20**) as a white needles.

Alkene 21: R_f = 0.29 (hexane/ethyl acetate = 70:30); m.p. 108–109 °C (diethyl ether/hexane); $[\alpha]_D^{28}$ = +34.1 (c = 0.69 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, TMS): δ = 5.86 (ddd, J = 17.0, 10.6, 6.4 Hz, 1H), 5.38 (dt, J = 17.2, 1.6 Hz, 1H), 5.23 (dt, J = 10.6, 1.5 Hz, 1H), 4.13 (d, J = 6.3 Hz, 1H), 4.09 (dd, J = 10.9, 1.6 Hz, 1H), 3.88 (t, J = 7.3 Hz, 1H), 2.76 (br s, 1H), 2.57 (br s, 1H), 2.53–2.44 (m, 1H), 2.18 (ddd, J = 12.4, 9.3, 5.4 Hz, 1H), 2.06–1.87 (m, 2H), 1.87–1.72 (m, 2H), 1.79 (s, 3H), 1.69 (s, 3H), 1.57–1.46 (m, 2H), 1.28 (s, 3H), 1.19 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 136.8, 117.4, 85.3, 84.4, 78.6, 73.6, 72.0, 66.9, 37.0, 33.0, 31.6, 28.8, 27.4, 26.5, 24.4, 24.2 ppm; IR (KBr): ν = 3231, 2982, 2936, 2901, 2870, 1458, 1387, 1371, 1231, 1219, 1153, 1101, 1078, 1067, 1030, 986, 962, 937, 916, 897, 862, 768 cm^{-1}; MS (FAB): m/z (%): 383.1 (8) $[M - H]^+$, 381 (3) $[M - H]^+$, 367.1 (100), 365 (78), 327.1 (36), 325.1 (28), 81.0 (46), 43.0 (81); HR-MS (FAB): calcd for $C_{16}H_{27}O_3{}^{37}Cl^{79}Br$ $[M - H]^+$: 383.0803; found: 383.0800; HR-MS (FAB): calcd for $C_{16}H_{27}O_3{}^{35}Cl^{81}Br$ $[M - H]^+$: 383.0812; found: 383.0800; HR-MS (FAB): calcd for $C_{16}H_{27}O_3{}^{35}Cl^{79}Br$ $[M - H]^+$: 381.0832; found: 381.0814.

Anal. Calcd for $C_{16}H_{28}O_3BrCl$: C, 50.08; H, 7.35. Found: C, 50.20; H, 7.36.

Allylic Bromide 23: R_f = 0.54 (hexane/ethyl acetate = 70:30); $[\alpha]_D^{27}$ = −12.6 (*c* = 1.47 in chloroform); ^1H NMR (400 MHz, $CDCl_3$, 24 °C, TMS): δ = 5.79 (ddd, *J* = 17.0, 10.6, 6.4 Hz, 1H), 5.37 (ddd, *J* = 17.2, 1.9, 1.5 Hz, 1H), 5.18 (ddd, *J* = 10.6, 1.9, 1.2 Hz, 1H), 5.03–4.98 (m, 1H), 4.77 (s, 1H), 4.36 (dd, *J* = 9.6, 5.7 Hz, 1H), 4.19 (s, 1H), 4.10 (d, *J* = 6.3 Hz, 1H), 4.05 (t, *J* = 7.7 Hz, 1H), 2.19 (ddd, *J* = 12.9, 7.3, 6.1 Hz, 1H), 2.08–1.99 (m, 1H), 1.99–1.91 (m, 2H), 1.89–1.77 (m, 2H), 1.77–1.66 (m, 1H), 1.71 (s, 3H), 1.64 (s, 1H), 1.49 (dt, *J* = 12.4, 8.8 Hz, 1H), 1.32 (s, 3H), 1.17 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C): δ = 145.3, 136.7, 117.2, 110.3, 86.2, 85.1, 84.5, 84.1, 79.2, 34.5, 31.3, 30.8, 27.9, 25.6, 24.9, 18.0 ppm; IR (film): ν = 3443, 3077, 2970, 2932, 2871, 1653, 1456, 1373, 1300, 1260, 1154, 1065, 1004, 921, 897, 874, 842, 787 cm^{-1}; MS (FAB): *m/z* (%): 268 (24) $[M + H - Br]^+$, 267.2 (100), 249.2 (32), 209.1 (97), 125.1 (84), 81.0 (38), 43.0 (66); HR-MS (FAB): calcd for $C_{16}H_{28}O_3$ $[M + H - Br]^+$: 268.2039; found: 268.2043.

Bromohydrin 22. To a solution of epoxide **19** (83.2 mg, 0.223 mmol) in 4.50 mL of dichloromethane was added magnesium bromide etherate (1.15 g, 4.46 mmol) at −78 °C under a nitrogen atmosphere, and the mixture was stirred at the same temperature for 4 h. Water (5 mL) was added to the solution, and the mixture was allowed to warm to room temperature. The aqueous layer was extracted with dichloromethane (5 mL × 3). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 90:10 for epoxide **19** to 85:15 for bromohydrin

22) on 5 g of silica gel to afford the recovered epoxide **19** (40.1 mg, 48.2% yield) and bromohydrin **22** (45.5 mg, 44.9% yield) as each colorless oil.

Bromohydrin 22: R_f = 0.29 (hexane/ethyl acetate = 70:30); $[\alpha]_D^{26}$ = −40.8 (*c* = 0.43 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 5.78 (ddd, *J* = 17.1, 10.7, 7.1 Hz, 1H), 5.29 (ddd, *J* = 10.7, 2.0, 0.7 Hz, 1H), 5.27 (ddd, *J* = 17.1, 1.7, 1.0 Hz, 1H), 4.83 (d, *J* = 7.6 Hz, 1H), 4.75 (d, *J* = 7.6 Hz, 1H), 4.69 (d, *J* = 6.8 Hz, 1H), 4.58 (d, *J* = 6.8 Hz, 1H), 3.96 (dd, *J* = 8.1, 6.6 Hz, 1H), 3.88 (d, *J* = 7.3 Hz, 1H), 3.388 (s, 3H), 3.386 (s, 3H), 3.45–3.28 (m, 1H), 2.84 (br s, 1H), 2.07–1.48 (m, 8H), 1.79 (s, 3H), 1.75 (s, 3H), 1.18 (s, 3H), 1.16 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 27 °C): δ = 134.9, 118.8, 94.6, 91.5, 84.3, 83.0, 82.3, 79.6, 79.2, 74.1, 55.8, 55.6, 34.3, 32.5, 30.5, 29.8, 26.5, 25.8, 22.0, 19.6 ppm; IR (film): ν = 3446, 3079, 2973, 2935, 2889, 2822, 1643, 1456, 1373, 1297, 1213, 1146, 1095, 1036, 919, 819, 637 cm^{-1}; MS (FAB): *m/z* (%): 455 (1) $[M + H]^+$, 453.2 (1) $[M + H]^+$, 423.2 (4), 421.2 (4), 393 (3), 391.1 (4), 361.1 (3), 359 (3), 331.1 (8), 329.1 (8), 154.1 (21), 136.1 (21), 45.0 (100), 43.0 (21); HR-MS (FAB): calcd for $C_{20}H_{38}O_6{}^{81}Br$ $[M + H]^+$: 455.1832; found: 455.1844; HR-MS (FAB): calcd for $C_{20}H_{38}O_6{}^{79}Br$ $[M + H]^+$: 453.1851; found: 453.1855.

Alkene 25. To a solution of alkene **21** (42.2 mg, 0.110 mmol) in 2.20 mL of dichloromethane was added Grubbs catalyst **24** (4.70 mg, 5.50 μmol) at room temperature under a nitrogen atmosphere, and the mixture was stirred at 40 °C for 7 h. The solution was cooled to room temperature, and the organic solvent was evaporated in vacuo. The residue was subjected to column chromatography (hexane/ethyl acetate = 50:50 to 0:100) on 2 g of silica gel to provide alkene **25** (35.0 mg, 86.0% yield) as a solid: R_f = 0.48 (hexane/ethyl acetate = 30:70); m.p. 157-158 °C (dichloromethane/hexane); $[\alpha]_D^{28}$ = +38.5 (*c* = 0.39 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C, TMS): δ = 5.69 (dd, *J* = 4.4, 2.0 Hz, 2H), 4.41 (br s, 2H), 4.11–4.05 (m, 2H), 4.07 (dd, *J* = 11.1, 1.3 Hz, 2H), 3.87 (t, *J* = 7.3 Hz, 2H), 3.57 (br s, 2H), 2.48–2.38 (m, 2H), 2.20 (ddd, *J* = 12.5, 8.8, 5.1 Hz, 2H), 2.11–1.99 (m, 2H), 1.97–1.87 (m, 2H), 1.83–1.65 (m, 4H), 1.79 (s, 6H), 1.69 (s, 6H), 1.56–1.41 (m, 2H), 1.27 (s, 6H), 1.13 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 26 °C): δ = 132.6, 85.4, 84.4, 78.4, 73.8, 72.0, 67.0, 37.5, 32.9, 31.7, 28.9, 27.6, 26.5, 25.0, 24.3 ppm; IR (KBr): ν = 3393, 2980, 2936, 2876, 1456, 1389, 1371, 1101, 1032, 972, 957, 579 cm^{-1}; MS (FAB): *m/z* (%): 743 (2.2) $[M + H]^+$, 741 (5.6) $[M + H]^+$, 739.23 (6) $[M + H]^+$, 737.24 (2.3) $[M + H]^+$, 707 (2.8), 705 (7.5), 703.21 (8.3), 701.20 (3.4), 327.1 (100), 325.1 (78), 154.1 (82), 136.1 (59), 43.0 (85); HR-MS (FAB): calcd for $C_{30}H_{53}O_6{}^{35}Cl_2{}^{79}Br_2$ $[M + H]^+$: 737.1586; found: 737.1575. Anal. Calcd for $C_{30}H_{52}O_6Br_2Cl_2$: C, 48.73; H, 7.09. Found: C, 48.94; H, 7.07.

Synthetic (+)-Intricatetraol (3). To a solution of alkene **25** (35.0 mg, 47.3 μmol) in 0.950 mL of methanol were added dipotassium azodicarboxylate freshly prepared[18] (92.0 mg, 0.473 mmol) and acetic acid (56.0 mg, 0.947 mmol) in 0.20 mL of methanol six times at room temperature under a nitrogen atmosphere, and the mixture was stirred at the same temperature for 70 h. After the organic solvent was evaporated in vacuo, water (3 mL) was added to the residue and the aqueous layer was extracted with dichloromethane (3 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/ethyl acetate = 70:30 for intricatetraol (**3**) to 50:50 for alkene **25**) on 3 g of silica gel to give synthetic (+)-intricatetraol (**3**) (19.7 mg, 56.2% yield) and the recovered alkene **25** (10.9 mg, 31.1% yield).

Synthetic (+)-Intricatetraol (3): R_f = 0.58 (hexane/ethyl acetate = 30:70); $[\alpha]_D^{23}$ = +51.3 (c = 0.41 in chloroform); ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, TMS): δ = 4.09 (dd, J = 10.7, 1.5 Hz, 2H), 3.85 (t, J = 7.3 Hz, 2H), 3.59 (d, J = 10.0 Hz, 2H), 2.52–2.42 (m, 2H), 2.22–2.13 (m, 2H), 2.05–1.86 (m, 4H), 1.86–1.63 (m, 6H), 1.79 (s, 6H), 1.69 (s, 6H), 1.58–1.36 (m, 6H), 1.26 (s, 6H), 1.18 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 86.1, 84.1, 77.5, 73.7, 72.0, 67.0, 37.1, 32.9, 31.7, 29.4, 28.9, 27.5, 26.5, 24.2, 23.9 ppm; IR (film): ν = 3400, 2974, 2934, 2872, 1373, 1103, 1045, 957, 905 cm^{-1}; MS (FAB): m/z (%): 747 (0.1) $[M + H]^+$, 745 (0.4) $[M + H]^+$, 743 (1.2) $[M + H]^+$, 741.0 (1.4) $[M + H]^+$, 739 (0.5) $[M + H]^+$, 109.0 (31), 95 (45), 81.0 (57), 69 (89), 57 (90), 55.0 (100), 43.0 (64), 41 (53); HR-MS (FAB): calcd for $C_{30}H_{55}O_6{}^{35}Cl_2{}^{79}Br_2$ $[M + H]^+$: 739.1743; found: 739.1764.