A New Strategy for the Total Synthesis of Macrosphelide A and B Based on the Ring-Closing Metathesis

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Supporting Information

Experimental procedures and characterization data for all new compounds.

General Procedures. All nonaqueous reactions were carried out under Ar atmosphere. Reagents were purchased from commercial sources and used as received. Methyl (*S*)-(-)-lactate (optically pure reagent) and methyl (*S*)-(+)-3-hydroxybutyrate (> 80% ee) were purchased from Tokyo Kasei Kogyo Co., Ltd and Wako Pure Chemical Industries, Ltd, respectively. Anhydrous solvents were obtained from commercial sources or prepared by distillation over CaH₂ or P₂O₅. ¹H and ¹³C NMR spectra were obtained on a Varian Gemini 300 (300 MHz for ¹H and 75.46 MHz for ¹³C) instrument or a Varian UNITY plus 500 (500 MHz for ¹H and 125 MHz for ¹³C) instrument, using tetramethylsilane or chloroform as an internal reference. Mass spectra were measured on a JEOL D-200 or a JEOL AX 505 mass spectrometer, and the ionization method was electron impact (EI, 70 eV). IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. The optical rotations were determined on a JASCO DIP-1000 instrument. Melting points were taken with a Yanagimoto micro melting point apparatus and are uncorrected. Column chromatography was carried out by employing Cica Silica Gel 60N (spherical, neutral,

40-50 μm or 63-210 μm).

(3*R*,4*S*)-4-(*tert*-Butyldimethylsilyloxy)-3-[(2-methoxyethoxy)methoxy]-1-pentene

(9). (2-Methoxyethoxy)methyl chloride (7.1 ml, 63 mmol) was added dropwise to a stirred solution of the alcohol **7**⁵⁾ (6.8 g, 21 mmol) and *N,N*-diisopropylethylamine (16.5 ml, 95 mmol) in CH_2Cl_2 (100 ml) at 0 °C under Ar atmosphere. After continuous stirring for 24 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (25 ml), washed with water, 10% HCl, sat. NaHCO_3 , and brine successively, and dried over MgSO_4 . Evaporation of the solvent afforded a residue which was chromatographed on silica gel with hexane-EtOAc (10 : 1) to give MEM ether **9** (6.71 g, 70%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 5.71 (1H, ddd, $J=17, 10, 7.4$ Hz), 5.25 (1H, d, $J=10$ Hz), 5.24 (1H, d, $J=17$ Hz), 4.77 (1H, d, $J=6.8$ Hz), 4.68 (1H, d, $J=6.8$ Hz), 3.89-3.77 (3H, m), 3.66-3.51 (3H, m), 3.39 (3H, s), 1.14 (3H, d, $J=6.0$ Hz), 0.88 (9H, s), 0.05 (3H, s), 0.04 (3H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 135.15, 118.53, 92.74, 81.48, 71.60, 70.51, 66.70, 58.82, 25.76, 19.58, 18.04, -4.64, -4.67; IR (neat): 1644 cm^{-1} ; MS (EI) m/z 304 (M^+); HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{32}\text{O}_4\text{Si}$: 304.2070 (M^+), found: 304.2092; $[\alpha]_{\text{D}}^{25}$ -56.8 ($c=1.22$, CHCl_3).

(2*S*,3*S*)-3-(*tert*-Butyldimethylsilyloxy)-2-[(2-methoxyethoxy)methoxy]butanal (10).

Osmium tetroxide (catalytic amount) and 50% aqueous *N*-methylmorpholine *N*-oxide (6.15 ml, 26 mmol) were added to a solution of MEM ether **9** (4.00 g, 13 mmol) in acetone (60 ml) at 0 °C. After continuous stirring for 6 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (30 ml), and dried over MgSO_4 . Evaporation of the solvent left a residue which was chromatographed on silica gel with hexane-EtOAc (1 : 4) to give the diol (3.98 g, 90%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 4.86 (1H, d, $J=6.7$ Hz), 4.79 (1H, d, $J=6.7$ Hz), 4.07-4.05 (1H, m), 3.88-3.44 (8H, m), 3.40 (3H, s), 1.20 (3H, d, $J=6.3$ Hz), 0.89 (9H, s), 0.08 (6H, s); IR (neat): 3446 cm^{-1} ; MS (EI) m/z 338 (M^+); HRMS (EI) Calcd for $\text{C}_{15}\text{H}_{34}\text{O}_6\text{Si}$: 338.2125 (M^+), found: 338.2155.

A solution of sodium periodate (4.28 g, 20 mmol) and tetra-*n*-butylammonium bromide (358 mg, 1.1 mmol) in water (22 ml) was added to a solution of the diol (3.76 g, 11 mmol) in CH_2Cl_2 (23 ml) at 0 °C. After continuous stirring for 3 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (30 ml), washed with water and brine successively, and dried over MgSO_4 . Evaporation of the solvent afforded a residue which was chromatographed on silica gel with hexane-EtOAc (2 : 1) to give the aldehyde **10** (2.77 g, 81%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 9.67 (1H, d, $J=1.8$ Hz), 4.82 (2H, s), 4.19-4.10 (1H, m), 3.85 (1H, dd, $J=4.4, 1.8$ Hz), 3.82-3.70 (2H, m), 3.54-3.52 (2H, m), 3.38 (3H, s), 1.22 (3H, d, $J=6.3$ Hz), 0.87 (9H, s), 0.07 (3H, s), 0.06 (3H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 202.28, 95.79, 85.66, 71.76, 69.74, 67.69, 59.19, 25.93, 20.30, 18.23, -4.28, -4.67; IR (neat): 1736 cm^{-1} ; MS (EI) m/z 306 (M^+); HRMS (EI) Calcd for $\text{C}_{14}\text{H}_{30}\text{O}_5\text{Si}$: 306.1863 (M^+), found: 306.1860; $[\alpha]_{\text{D}}^{25}$ +11.4 ($c=1.37$, CHCl_3).

Ethyl (4*R*,5*S*)-5-(*tert*-Butyldimethylsilyloxy)-4-[(2-methoxyethoxy)methoxy]-2-hexenoate (11). DBU (1.49 ml, 11 mmol) was added to a stirred suspension of ethyl diethylphosphonoacetate (2.16 ml, 11 mmol) and LiCl (112 mg, 2.6 mmol) in MeCN (90 ml) at 0 °C under Ar atmosphere. After continuous stirring for 30 min at room

temperature, a solution of the aldehyde **10** (2.75 g, 8.9 mmol) in MeCN (10 ml) was added dropwise to the solution at 0 °C. After stirring was continued for 1 h at room temperature, the solvent was evaporated off. The residue was dissolved in ether, and the organic layer was washed successively with water, 10% HCl, sat. NaHCO₃, and brine, and dried over MgSO₄. The residue resulting from evaporation of the solvent was chromatographed on silica gel with hexane-EtOAc (2 : 1) to give the ethyl ester **11** (3.21 g, 95%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 6.84 (1H, dd, *J*=16, 6.3 Hz), 5.99 (1H, dd, *J*=16, 1.3 Hz), 4.74 (2H, dd, *J*=8.8, 6.9 Hz), 4.19 (2H, q, *J*=7.1 Hz), 4.07-4.04 (1H, m), 3.79-3.76 (2H, m), 3.65-3.64 (1H, m), 3.54-3.52 (2H, m), 3.37 (3H, s), 1.28 (3H, t, *J*=7.1 Hz), 1.16 (3H, d, *J*=6.0 Hz), 0.86 (9H, s), 0.04 (3H, s), 0.02 (3H, s); ¹³C NMR (75 MHz, CDCl₃): δ 166.04, 145.69, 123.47, 94.17, 80.11, 71.86, 70.81, 67.41, 60.58, 59.23, 26.02, 20.20, 18.31, 14.52, -4.26, -4.49; IR (neat): 1724, 1658 cm⁻¹; MS (EI) *m/z* 377 (M⁺+1), 361 (M⁺-15); HRMS (EI) Calcd for C₁₈H₃₇O₆Si: 377.2364 (M⁺+H), found: 377.2364, Calcd for C₁₇H₃₃O₆Si: 361.2047 (M⁺-CH₃), found: 361.2047; [α]_D²⁵ -41.9 (*c*=1.11, CHCl₃).

(4*R*,5*S*)-5-(*tert*-Butyldimethylsilyloxy)-4-[(2-methoxyethoxy)methoxy]-2-hexenoic Acid (6**).** A solution of the ethyl ester **11** (3.05 g, 8.1 mmol) and 0.2 M NaOH (16 ml) in MeOH/THF (3 : 1, 65 ml) was stirred for 12 h at room temperature, and then acidified with 10% HCl at 0 °C. The mixture was extracted with CHCl₃ and combined extracts were dried over MgSO₄. Evaporation of the solvent followed by chromatography on silica gel with CHCl₃-MeOH (9 : 1) afforded the carboxylic acid **6** (2.79 g, 99%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 6.98 (1H, dd, *J*=16, 6.3 Hz), 6.02 (1H, dd, *J*=11, 1.2 Hz), 4.75 (1H, d, *J*=6.9 Hz), 4.71 (1H, d, *J*=6.9 Hz), 4.11-4.08 (1H, m), 3.85-3.83 (1H, m), 3.78-3.74 (1H, m), 3.67-3.64 (1H, m), 3.56-3.53 (2H, m), 3.38 (3H, s), 1.16 (3H, d, *J*=6.3 Hz), 0.86 (9H, s), 0.04 (3H, s), 0.03 (3H, s); ¹³C NMR (75 MHz, CDCl₃): δ 170.99, 148.46, 122.62, 94.33, 80.15, 71.83, 70.74, 67.46, 59.21, 26.01, 20.22, 18.29, -4.30, -4.49; IR (neat): 2933, 1703, 1657 cm⁻¹; [α]_D²⁴ -36.3 (*c*=1.31, CHCl₃) [lit.^{2a} [α]_D²² -30.0 (*c*=0.62, CHCl₃)].

(3*R*,4*S*)-4-(*tert*-Butyldimethylsilyloxy)-3-(4-methoxybenzyloxy)-1-pentene (12**).** 4-Methoxybenzyl trifluoroacetimidate⁶⁾ (5.17 g, 22 mmol) and pyridinium *p*-toluene sulfonate (420 mg, 1.7 mmol) were added successively to a stirred solution of the alcohol **7** (2.40 g, 11 mmol) in CH₂Cl₂ (35 ml) at 0 °C under Ar atmosphere. After continuous stirring for 24 h at room temperature, the reaction mixture was diluted with CH₂Cl₂ (25 ml), washed with water, 10% HCl, sat. NaHCO₃ and brine successively, and dried over MgSO₄. Evaporation of the solvent afforded a residue which was chromatographed on silica gel with hexane-EtOAc (10 : 1) to give PMB ether **12** (1.74 g, 47%, conversion yield 95%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.22 (2H, d, *J*=8.6 Hz), 6.82 (2H, d, *J*=8.6 Hz), 5.75 (1H, ddd, *J*=17, 10, 7.4 Hz), 5.25 (1H, d, *J*=10 Hz), 5.20 (1H, d, *J*=17 Hz), 4.52 (1H, d, *J*=11 Hz), 4.30 (1H, d, *J*=11 Hz), 3.76-3.74 (1H, m), 3.76 (3H, s), 3.51 (1H, dd, *J*=7.5, 5.3 Hz), 1.13 (3H, d, *J*=6.3 Hz), 0.85 (9H, s), 0.10 (3H, s), 0.08 (3H, s); ¹³C NMR (75 MHz, CDCl₃): δ 159.01, 136.64, 130.92, 129.37, 118.56, 113.73, 85.00, 71.08, 70.32, 55.41, 26.14, 20.52, 18.40, -4.18, -4.25; IR (neat): 1613 cm⁻¹; MS (EI) *m/z* 336 (M⁺); HRMS (EI) Calcd for C₁₉H₃₂O₃Si: 336.2121 (M⁺), found: 336.2141; [α]_D²⁶ -22.3 (*c*=1.50, CHCl₃).

(3R,4S)-4-Hydroxy-3-(4-methoxybenzyloxy)-1-pentene (13). A 1 M solution of tetra-*n*-butylammonium fluoride in THF (0.58 ml, 0.58 mmol) was added to a stirred solution of the PMB ether **12** (98.0 mg, 0.29 mmol) in THF (0.6 ml) at room temperature under Ar atmosphere, and the mixture was stirred for 6 h at room temperature. The reaction mixture was diluted with ether, and the organic layer was washed with water and brine, and dried over MgSO₄. Evaporation of the solvent left a residue which was chromatographed on silica gel with hexane-EtOAc (2 : 1) to give the alcohol **13** (62 mg, 96%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.23 (2H, d, *J*=8.6 Hz), 6.87 (2H, d, *J*=8.6 Hz), 5.82 (1H, ddd, *J*=17, 10, 8.0 Hz), 5.38 (1H, dd, *J*=10, 1.9 Hz), 5.29 (1H, ddd, *J*=17, 1.9, 0.8 Hz), 4.56 (1H, d, *J*=11 Hz), 4.30 (1H, d, *J*=11 Hz), 3.86-3.84 (1H, m), 3.79 (3H, s), 3.64 (1H, dd, *J*=8.0, 3.8 Hz), 1.12 (3H, d, *J*=6.6 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 159.13, 134.69, 130.35, 129.41, 120.17, 113.83, 84.09, 70.05, 69.37, 55.39, 18.21; IR (neat): 3449, 1612 cm⁻¹; MS (EI) *m/z* 222 (M⁺); HRMS (EI) Calcd for C₁₃H₁₈O₃: 222.1256 (M⁺), found : 222.1221; [α]_D²⁴ -45.2 (*c*=1.28, CHCl₃).

(3R,4S)-3-(4-Methoxybenzyloxy)-1-penten-4-yl (3S)-3-(tert-Butyldimethylsilyl) butanoate (14). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (2.28 g, 12 mmol) was added to a stirred solution of the alcohol **13** (1.33 g, 6.0 mmol), (*S*)-3-(*tert*-butyldimethylsilyloxy)butanoic acid⁴⁾ (2.56 g, 12 mmol), and 4-dimethylamino pyridine (73.3 mg, 0.60 mmol) in CH₂Cl₂ (50 ml) at 0 °C under Ar atmosphere. After continuous stirring for 12 h at room temperature, the solvent was evaporated to leave a residue which was triturated with ether and filtered through celite. Evaporation of the solvent followed by chromatography on silica gel with hexane-EtOAc (4 : 1) afforded the ester **14** (2.49 g, 99%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.25 (2H, d, *J*=8.8 Hz), 6.87 (2H, d, *J*=8.8 Hz), 5.74 (1H, ddd, *J*=18, 11, 7.4 Hz), 5.32 (1H, d, *J*=11 Hz), 5.28 (1H, d, *J*=18 Hz), 4.97-4.95 (1H, m), 4.55 (1H, d, *J*=12 Hz), 4.35 (1H, d, *J*=12 Hz), 4.25-4.23 (1H, m), 3.80 (3H, s), 3.73-3.71 (1H, m), 2.47 (1H, dd, *J*=15, 6.3 Hz), 2.34 (1H, dd, *J*=15, 6.3 Hz), 1.22 (3H, d, *J*=6.6 Hz), 1.18 (3H, d, *J*=6.0 Hz), 0.86 (9H, s), 0.06 (3H, s), 0.05 (3H, s); ¹³C NMR (75 MHz, CDCl₃): δ 170.34, 159.10, 135.07, 130.43, 129.28, 119.43, 113.78, 81.71, 71.99, 70.32, 65.84, 55.41, 45.29, 26.04, 25.96, 24.02, 18.26, 15.65, -4.25, -4.59; IR (neat): 1737, 1613 cm⁻¹; MS (EI) *m/z* 422 (M⁺); HRMS (EI) Calcd for C₂₃H₃₈O₅Si: 422.2489 (M⁺), found: 422.2515; [α]_D²⁷ -19.7 (*c*=0.98, CHCl₃).

(3R,4S)-3-(4-Methoxybenzyloxy)-1-penten-4-yl (3S)-3-hydroxybutanoate (5). A 1 M solution of tetra-*n*-butylammonium fluoride in THF (12.0 ml, 12 mmol) was added to a stirred solution of the silyl ether **14** (2.51 g, 6.0 mmol) in THF (12 ml) at room temperature under Ar atmosphere, and the mixture was stirred for 5 h at room temperature. The solvent was evaporated off to leave a residue, which was dissolved in ether and the resulting organic layer was washed with water and brine, and dried over MgSO₄. Evaporation of the solvent left a residue which was chromatographed on silica gel with hexane-EtOAc (1 : 1) to give the alcohol **5** (1.75 g, 95%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.24 (2H, d, *J*=8.8 Hz), 6.86 (2H, d, *J*=8.8 Hz), 5.75 (1H, ddd, *J*=17, 10, 7.7 Hz), 5.34 (1H, d, *J*=10 Hz), 5.29 (1H, d, *J*=17 Hz), 5.05 (1H, dq, *J*=6.4, 4.4 Hz), 4.56 (1H, d, *J*=12 Hz), 4.33 (1H, d, *J*=12 Hz), 4.13-4.11 (1H, m), 3.79 (3H, s), 3.76-3.74 (1H, m), 3.17 (1H, br), 2.48-2.33 (2H, m), 1.22 (3H, d, *J*=6.4 Hz), 1.20 (3H, d, *J*=6.4 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 172.01, 159.09, 134.54, 130.06,

129.38, 129.33, 119.87, 113.75, 81.39, 72.04, 70.15, 64.47, 55.34, 43.53, 22.66, 15.70; IR (neat): 3449, 1730, 1613 cm^{-1} ; MS (EI) m/z 308 (M^+); HRMS (EI) Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_5$: 308.1624 (M^+), found: 308.1652; $[\alpha]_{\text{D}}^{24}$ -32.3 ($c=1.04$, CHCl_3).

(-)-1-[3-(4-Methoxybenzyloxy)-1-penten-4-yloxycarbonyl]prop-2-yl 5-(tert-Butyldimethylsilyloxy)-4-[(2-methoxyethoxy)methoxy]-2-hexenoate (15). To a solution of the carboxylic acid **6** (5.1 g, 14.6 mmol) and Et_3N (4.06 ml, 29.2 mmol) in toluene (150 ml) was added 2,4,6-trichlorobenzoyl chloride (3.03 ml, 19.4 mmol) at room temperature under Ar atmosphere, and the resulting mixture was stirred at room temperature for 1 h. The alcohol **5** (3.00 g, 9.72 mmol) and DMAP (1.43 g, 11.7 mmol) were added, and the reaction mixture was stirred for 1 h. After the reaction completed, the mixture was washed with sat. NaHCO_3 and brine, and dried over MgSO_4 . The solvent was evaporated off to leave a residue which was chromatographed on silica gel with hexane-EtOAc (2 : 1) to afford the ester **15** (6.14 g, 99%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.24 (2H, d, $J=8.8$ Hz), 6.87 (2H, d, $J=8.8$ Hz), 6.82 (1H, d, $J=16$ Hz), 5.95 (1H, dd, $J=16$, 1.2 Hz), 5.73 (1H, ddd, $J=17$, 10, 7.5 Hz), 5.32 (1H, d, $J=10$ Hz), 5.32-5.29 (1H, m), 5.28 (1H, d, $J=17$ Hz), 4.99-4.97 (1H, m), 4.71 (2H, dd, $J=9.9$, 6.9 Hz), 4.54 (1H, d, $J=12$ Hz), 4.33 (1H, d, $J=12$ Hz), 4.06-4.04 (1H, m), 3.85-3.71 (2H, m), 3.80 (3H, s), 3.67-3.60 (1H, m), 3.54-3.51 (2H, m), 3.38 (3H, s), 2.66 (1H, dd, $J=15$, 6.9 Hz), 2.48 (1H, dd, $J=16$, 6.9 Hz), 1.29 (3H, d, $J=6.3$ Hz), 1.18 (3H, d, $J=6.6$ Hz), 1.15 (3H, d, $J=6.3$ Hz), 0.87 (9H, s), 0.06 (3H, s), 0.04 (3H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 169.26, 164.96, 159.07, 145.85, 134.82, 130.24, 129.28, 123.43, 119.72, 113.75, 94.01, 81.55, 79.95, 72.15, 71.76, 70.68, 70.16, 67.49, 67.31, 59.14, 55.36, 41.31, 25.98, 20.10, 19.99, 18.23, 15.77, -4.35, -4.54; IR (neat): 1730, 1657, 1613 cm^{-1} ; MS (EI) m/z 638 (M^+); HRMS (EI) Calcd for $\text{C}_{33}\text{H}_{54}\text{O}_{10}\text{Si}$: 638.3486 (M^+), found : 638.3467; $[\alpha]_{\text{D}}^{26}$ -39.7 ($c=0.95$, CHCl_3).

(-)-1-[3-(4-Methoxybenzyloxy)-1-penten-4-yloxycarbonyl]prop-2-yl 5-Hydroxy-4-[(2-methoxyethoxy)methoxy]-2-hexenoate (16). A 1 M solution of tetra-*n*-butylammonium fluoride in THF (19.6 ml, 20 mmol) was added to a stirred solution of the silyl ether **15** (626 mg, 0.98 mmol) and acetic acid (1.23 ml, 22 mmol) in THF (45 ml) at room temperature under Ar atmosphere, and the mixture was stirred for 5 days at room temperature. The ethereal solution of the residue resulting from the evaporation of the solvent was washed with water, sat. NaHCO_3 , and brine, and dried over MgSO_4 . Evaporation of the solvent left a residue which was chromatographed on silica gel with hexane-EtOAc (1 : 2) to give the alcohol **16** (433 mg, 85%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.24 (2H, d, $J=8.2$ Hz), 6.90-6.80 (3H, m), 6.01 (1H, d, $J=16$ Hz), 5.74 (1H, ddd, $J=17$, 10, 7.4 Hz), 5.30 (1H, d, $J=10$ Hz), 5.30-5.28 (1H, m), 5.28 (1H, d, $J=17$ Hz), 4.99-4.96 (1H, m), 4.76 (1H, d, $J=7.4$ Hz), 4.69 (1H, d, $J=7.4$ Hz), 4.54 (1H, d, $J=11$ Hz), 4.32 (1H, d, $J=11$ Hz), 4.22-4.20 (1H, m), 3.95-3.62 (4H, m), 3.79 (3H, s), 3.55-3.48 (2H, m), 3.37 (3H, s), 3.16 (1H, br), 2.65 (1H, dd, $J=15$, 7.1 Hz), 2.51 (1H, dd, $J=15$, 6.0 Hz), 1.31 (3H, d, $J=5.8$ Hz), 1.18 (3H, d, $J=6.3$ Hz), 1.13 (3H, d, $J=6.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 169.13, 164.70, 158.90, 144.05, 134.61, 130.06, 129.10, 123.55, 119.54, 113.57, 94.24, 81.34, 80.60, 71.96, 71.59, 69.97, 68.87, 67.40, 58.87, 55.15, 41.09, 19.83, 17.79, 15.52, 14.23; IR (neat): 3465, 1733, 1657, 1613 cm^{-1} ; MS (EI) m/z 524 (M^+); HRMS (EI) Calcd for $\text{C}_{27}\text{H}_{40}\text{O}_{10}$: 524.2622 (M^+), found: 524.2674; $[\alpha]_{\text{D}}^{25}$ -53.1 ($c=0.87$, CHCl_3).

(-)-1-[3-(4-Methoxybenzyloxy)-1-penten-4-yloxycarbonyl]prop-2-yl 5-Acryloyloxy-4-[(2-methoxyethoxy)methoxy]-2-hexenoate (4). Acryloyl chloride (0.263 ml, 3.2 mmol) was added dropwise to a stirred solution of the alcohol **16** (425 mg, 0.81 mmol) and *N,N*-diisopropylethylamine (0.705 ml, 4.1 mmol) in CH₂Cl₂ (8 ml) at 0 °C under Ar atmosphere. After continuous stirring for 1 h at room temperature, the reaction mixture was diluted with CH₂Cl₂ (10 ml), washed with water, 10% HCl, sat. NaHCO₃, and brine successively, and dried over MgSO₄. Evaporation of the solvent afforded a residue which was chromatographed on silica gel with hexane-EtOAc (2 : 1) to give the ester **4** (444 mg, 95%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.24 (2H, d, *J*=8.6 Hz), 6.87 (2H, d, *J*=8.6 Hz), 6.80 (1H, d, *J*=16 Hz), 6.39 (1H, d, *J*=17 Hz), 6.13 (1H, d, *J*=10 Hz), 6.03 (1H, d, *J*=16 Hz), 5.83 (1H, d, *J*=10 Hz), 5.74 (1H, ddd, *J*=17, 10, 7.1 Hz), 5.34 (1H, d, *J*=10 Hz), 5.34-5.32 (1H, m), 5.28 (1H, d, *J*=17 Hz), 5.08-5.05 (1H, m), 4.98-4.96 (1H, m), 4.74 (1H, d, *J*=6.9 Hz), 4.69 (1H, d, *J*=6.9 Hz), 4.54 (1H, d, *J*=12 Hz), 4.40-4.38 (1H, m), 4.33 (1H, d, *J*=12 Hz), 3.84-3.72 (2H, m), 3.79 (3H, s), 3.66-3.60 (1H, m), 3.54-3.50 (2H, m), 3.36 (3H, s), 2.66 (1H, dd, *J*=15, 7.3 Hz), 2.51 (1H, dd, *J*=15, 6.0 Hz), 1.31 (3H, d, *J*=6.3 Hz), 1.23 (3H, d, *J*=6.6 Hz), 1.18 (3H, d, *J*=6.3 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 169.12, 165.12, 164.63, 158.97, 143.29, 134.67, 130.95, 130.11, 129.17, 128.31, 124.14, 119.62, 113.64, 93.74, 81.41, 76.52, 72.04, 71.59, 71.41, 70.03, 67.67, 59.00, 55.23, 41.15, 19.89, 15.64, 15.04; IR (neat): 1728, 1657, 1614 cm⁻¹; MS (EI) *m/z* 547 (M⁺-31); [α]_D²⁵ -50.2 (*c*=0.99, CHCl₃).

Synthesis of 3 by Ring-Closing Metathesis of 4. Grubbs' catalyst (cat. **2**) (20.4 mg, 0.024 mmol) was added to a solution of **4** (14.0 mg, 0.024 mmol) in 1,2-dichloroethane (24 ml) at room temperature under Ar atmosphere. After continuous stirring for 5 days at 80 °C, the solvent was evaporated to afford a residue which was chromatographed on silica gel with hexane-EtOAc (1 : 1) to give **3** (8.5 mg, 65%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.21 (2H, d, *J*=8.5 Hz), 6.87 (2H, d, *J*=8.5 Hz), 6.75 (1H, dd, *J*=15, 7.4 Hz), 6.74 (1H, dd, *J*=15, 7.9 Hz), 5.99 (1H, d, *J*=15 Hz), 5.91 (1H, d, *J*=15 Hz), 5.31-5.29 (1H, m), 5.02-4.97 (2H, m), 4.74 (1H, d, *J*=7.1 Hz), 4.71 (1H, d, *J*=7.1 Hz), 4.53 (1H, d, *J*=11 Hz), 4.27 (1H, d, *J*=11 Hz), 4.13-4.11 (1H, m), 3.80 (3H, s), 3.78-3.63 (3H, m), 3.57-3.54 (2H, m), 3.39 (3H, s), 2.56-2.50 (2H, m), 1.43 (3H, d, *J*=6.3 Hz), 1.29 (3H, d, *J*=6.0 Hz), 1.27 (3H, d, *J*=6.0 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 169.46, 164.31, 164.17, 159.33, 145.01, 129.62, 129.25, 124.30, 124.12, 113.86, 94.11, 79.13, 78.71, 71.91, 71.65, 71.04, 70.81, 67.75, 67.51, 59.14, 55.37, 53.61, 41.17, 19.91, 18.10, 17.98; IR (neat): 1726, 1658 cm⁻¹; MS (EI) *m/z* 550 (M⁺); HRMS (EI) Calcd for C₂₈H₃₈O₁₁: 550.2414 (M⁺), found: 550.2368; [α]_D²⁴ -76.1 (*c*=2.34, CHCl₃).

1-(3-Hydroxy-1-penten-4-yloxycarbonyl)prop-2-yl 5-Acryloyloxy-4-[(2-methoxyethoxy)methoxy]-2-hexenoate (17). A mixture of PMB ether **4** (480 mg, 0.83 mmol) and DDQ (282 mg, 1.25 mmol) in CH₂Cl₂/H₂O (18 : 1, 10 ml) was stirred at room temperature for 1 h. The precipitate formed was removed by filtration, and the filtrate was concentrated to furnish a gummy mass, which was chromatographed on silica gel with hexane-EtOAc (1 : 1) to give the alcohol **17** (368 mg, 97%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 6.85 (1H, dd, *J*=16, 6.2 Hz), 6.41 (1H, dd, *J*=16, 1.4 Hz), 6.10 (1H, dd, *J*=17, 10 Hz), 6.06 (1H, dd, *J*=16, 1.4 Hz), 5.84 (1H, dd, *J*=10, 1.4

Hz), 5.81 (1H, ddd, $J=17, 10, 5.8$ Hz), 5.37-5.35 (1H, m), 5.35 (1H, d, $J=17$ Hz), 5.25 (1H, d, $J=17$ Hz), 5.13-5.10 (1H, m), 4.98-4.95 (1H, m), 4.76 (1H, d, $J=7.0$ Hz), 4.60 (1H, d, $J=7.0$ Hz), 4.41-4.39 (1H, m), 4.24-4.22 (1H, m), 3.79-3.76 (1H, m), 3.65-3.63 (1H, m), 3.55-3.50 (2H, m), 3.38 (3H, s), 2.70 (1H, dd, $J=16, 8.0$ Hz), 2.57 (1H, dd, $J=16, 5.2$ Hz), 1.34 (3H, d, $J=6.3$ Hz), 1.25 (3H, d, $J=6.5$ Hz), 1.20 (3H, d, $J=6.3$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 169.73, 165.33, 164.99, 143.71, 135.80, 131.14, 128.41, 124.10, 117.37, 93.90, 76.67, 74.56, 73.85, 71.70, 71.54, 67.82, 67.35, 59.14, 41.41, 20.23, 15.14, 14.41.

Synthesis of 18. (Method A) Grubbs' catalyst (cat. **2**) (52 mg, 0.06 mmol) was added to a solution of **17** (285 mg, 0.62 mmol) in CH_2Cl_2 (622 ml) under Ar atmosphere. After continuous stirring for 24 h at room temperature, the solvent was evaporated to afford a residue which was chromatographed on silica gel with hexane-AcOEt (2 : 1) to give the macrocyclic alcohol **18** (207 mg, 77%) as a colorless solid. (Method B) A mixture of PMB ether **3** (8.0 mg, 0.015 mmol) and DDQ (4.95 mg, 0.022 mmol) in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (18 : 1, 0.16 ml) was stirred at room temperature for 30 min. The precipitate formed was removed by filtration, and the filtrate was concentrated to furnish a gummy mass, which was chromatographed on silica gel with hexane-EtOAc (2 : 1) to give **18** (6.2 mg, 99%) as a colorless solid. mp 94-96 °C; ^1H NMR (300 MHz, CDCl_3): δ 6.80 (1H, dd, $J=16, 5.1$ Hz), 6.72 (1H, dd, $J=16, 7.1$ Hz), 5.99 (1H, dd, $J=16, 1.4$ Hz), 5.93 (1H, d, $J=16$ Hz), 5.28-5.26 (1H, m), 4.93-4.83 (2H, m), 4.70-4.67 (2H, m), 4.15-4.05 (2H, m), 3.78-3.71 (1H, m), 3.65-3.59 (1H, m), 3.53-3.36 (2H, m), 3.35 (3H, s), 2.97 (1H, br), 2.69 (1H, dd, $J=15, 2.9$ Hz), 2.48 (1H, dd, $J=15, 8.3$ Hz), 1.37 (3H, d, $J=6.0$ Hz), 1.31 (3H, d, $J=6.8$ Hz), 1.29 (3H, d, $J=6.8$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 169.94, 164.61, 164.38, 145.77, 144.75, 124.54, 122.57, 94.01, 78.66, 73.75, 72.95, 71.67, 71.04, 67.85, 67.49, 59.16, 41.01, 19.73, 18.08, 17.72; IR (KBr): 3435, 1711, 1647 cm^{-1} ; MS (EI) m/z 430 (M^+); HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_{10}$: 430.1839 (M^+), found: 430.1882; $[\alpha]_{\text{D}}^{24}$ -31.0 ($c=0.88$, CHCl_3).

Macrosphelide A (1). Trifluoroacetic acid (0.6 ml) was added to a solution of MEM ether **18** (21.5 mg, 0.05 mmol) in CH_2Cl_2 (0.6 ml) at 0 °C under Ar atmosphere. After continuous stirring for 24 h at room temperature, the solvent was evaporated to afford a residue which was chromatographed on silica gel with CH_2Cl_2 -EtOAc (1 : 1) to give macrosphelide A (**1**) (15.4 mg, 90%) as a colorless solid. mp 144-146 °C (colorless needles from CH_2Cl_2 -hexane, lit.^{2a} mp 146-147 °C); ^1H NMR (500 MHz, CDCl_3): δ 6.88 (1H, dd, $J=16, 4.9$ Hz), 6.87 (1H, dd, $J=15, 4.5$ Hz), 6.05 (1H, dd, $J=16, 1.7$ Hz), 6.03 (1H, dd, $J=16, 1.7$ Hz), 5.40-5.37 (1H, m), 4.97-4.94 (1H, m), 4.88-4.85 (1H, m), 4.23 (1H, brs), 4.15 (1H, brs), 2.62 (1H, dd, $J=15, 9.0$ Hz), 2.57 (1H, dd, $J=15, 3.4$ Hz), 1.46 (3H, d, $J=6.4$ Hz), 1.37 (3H, d, $J=6.0$ Hz), 1.33 (3H, d, $J=6.4$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 170.19, 165.76, 164.53, 146.01, 144.97, 122.71, 122.26, 75.07, 74.80, 74.12, 73.10, 67.64, 40.94, 19.67, 18.03, 17.82; $[\alpha]_{\text{D}}^{25}$ +81.0 ($c=0.195$, MeOH) [lit.^{1b} $[\alpha]_{\text{D}}^{23}$ +84.1 ($c=0.59$, MeOH)].

Macrosphelide B (2). Pyridinium dichromate (137 mg, 0.37 mmol) was added portionwise to a stirred solution of the alcohol **18** (39.3 mg, 0.091 mmol) and molecular sieves 4A (150 mg) in CH_2Cl_2 (10 ml) at 0 °C under Ar atmosphere. After continuous stirring for 1 h at room temperature, the reaction mixture was diluted with ether (20 ml),

and filtered through celite. The filtrate was evaporated to leave a residue which was chromatographed on silica gel with hexane-EtOAc (1 : 1) to give the corresponding ketone (32.0 mg, 82%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 6.98 (1H, d, $J=16$ Hz), 6.82 (1H, dd, $J=16$, 6.0 Hz), 6.73 (1H, d, $J=16$ Hz), 6.04 (1H, dd, $J=16$, 1.4 Hz), 5.39-5.35 (1H, m), 5.17 (1H, dd, $J=14$, 7.0 Hz), 5.04-5.02 (1H, m), 4.76 (1H, d, $J=7.1$ Hz), 4.73 (1H, d, $J=7.1$ Hz), 4.27-4.24 (1H, m), 3.80-3.74 (1H, m), 3.70-3.63 (1H, m), 3.58-3.52 (2H, m), 3.38 (3H, s), 2.75 (1H, dd, $J=16$, 10 Hz), 2.62 (1H, dd, $J=16$, 2.6 Hz), 1.43 (3H, d, $J=6.3$ Hz), 1.41 (3H, d, $J=6.9$ Hz), 1.36 (3H, d, $J=6.3$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 195.85, 170.25, 164.33, 163.73, 143.85, 133.13, 132.41, 124.17, 94.21, 78.27, 75.50, 72.49, 71.70, 68.33, 67.61, 59.23, 41.14, 20.12, 17.95, 16.12; IR (neat): 1729, 1660 cm^{-1} ; MS (EI) m/z 428 (M^+); HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{28}\text{O}_{10}$: 428.1683 (M^+), found: 428.1688; $[\alpha]_{\text{D}}^{24} -74.9$ ($c=1.43$, CHCl_3).

Trifluoroacetic acid (1.5 ml) was added to a solution of the ketone (52.3 mg, 0.122 mmol) in CH_2Cl_2 (1.5 ml) at 0 °C under Ar atmosphere. After continuous stirring for 24 h at room temperature, the solvent was evaporated to afford a residue which was chromatographed on silica gel with hexane-EtOAc (1 : 1) to give macrosphelide B (**2**) (35.7 mg, 86%) as a colorless oil. ^1H NMR (300MHz, CDCl_3): δ 7.02 (1H, d, $J=16$ Hz), 6.92 (1H, dd, $J=16$, 3.7 Hz), 6.73 (1H, d, $J=16$ Hz), 6.07 (1H, dd, $J=16$, 1.8 Hz), 5.47-5.44 (1H, m), 5.10-5.00 (2H, m), 4.32 (1H, brs), 3.10 (1H, brs), 2.83 (1H, dd, $J=16$, 11 Hz), 2.62 (1H, dd, $J=16$, 2.2 Hz), 1.49 (3H, d, $J=6.9$ Hz), 1.43 (3H, d, $J=7.1$ Hz), 1.35 (3H, d, $J=6.3$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 196.18, 170.33, 165.46, 164.12, 144.15, 132.51, 132.01, 122.55, 76.92, 75.80, 74.86, 67.66, 40.58, 19.79, 17.94, 16.09; $[\alpha]_{\text{D}}^{27} +3.71$ ($c=0.335$, MeOH) [lit.^{1b)} $[\alpha]_{\text{D}}^{23} +4.10$ ($c=0.99$, MeOH)].

Pulse Sequence: s2pu1

INDEX	FREQUENCY	PPM	HEIGHT
1	10218.469	135.430	27.8
2	8969.613	118.878	24.8
3	7018.810	93.024	26.5
4	6169.149	81.763	27.6
5	5856.630	77.621	24.9
6	5824.890	77.200	26.4
7	5793.150	76.778	26.0
8	5424.475	71.893	28.7
9	5342.683	70.809	28.5
10	5054.579	66.991	26.1
11	4482.502	59.144	20.9
12	1966.012	26.056	98.6
13	1500.895	19.892	21.5
14	1384.922	18.355	17.2
15	-326.609	-4.329	26.8
16	-329.050	-4.361	18.1

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

INDEX	FREQUENCY	PPM	HEIGHT
1	15262.722	202.284	25.0
2	7227.563	95.790	29.3
3	6483.356	85.662	41.3
4	5856.630	77.621	48.4
5	5824.890	77.200	53.3
6	5793.149	76.779	56.8
7	5414.708	71.764	42.6
8	5262.111	69.741	26.9
9	5107.072	67.686	50.1
10	4466.164	59.192	38.4
11	1956.245	25.927	131.2
12	1531.415	20.297	37.4
13	1375.155	18.226	23.4
14	-322.947	-4.280	33.2
15	-352.245	-4.668	25.6

Pulse Sequence: s2pu1

INDEX	FREQUENCY	PPM	HEIGHT
1	12528.180	166.042	5.2
2	10992.441	145.688	14.8
3	9316.314	123.473	19.7
4	7105.485	94.172	12.6
5	6044.630	80.112	13.6
6	5856.630	77.621	77.3
7	5824.890	77.200	79.4
8	5743.149	76.779	71.6
9	5422.033	71.861	18.9
10	5342.683	70.809	19.0
11	5086.319	67.411	22.2
12	4571.151	60.584	16.2
13	4468.606	58.225	13.0
14	1963.570	26.024	45.3
15	1524.090	20.199	16.5
16	1381.259	18.306	10.3
17	1045.597	14.520	17.6
18	-321.726	-4.264	15.6
19	-338.817	-4.490	10.2

STANDARD 1H OBSERVE
Pulse Sequence: s2pul

INDEX	FREQUENCY	PPM	HEIGHT
1	12901.738	170.983	11.6
2	11201.184	148.455	14.4
3	9251.612	122.616	16.4
4	7117.683	94.334	15.2
5	6047.071	80.145	18.1
6	5856.630	77.621	66.2
7	5824.890	77.200	62.8
8	5783.149	76.779	58.1
9	5419.591	71.828	18.1
10	5337.789	70.744	17.1
11	5089.982	67.460	21.3
12	4467.385	59.208	21.3
13	1962.348	26.008	51.2
14	1525.311	20.216	20.6
15	1380.038	18.280	17.8
16	-324.167	-4.286	18.5
17	-336.817	-4.480	19.3

STANDARD 1H OBSERVE
Pulse Sequence: s2pu1

INDEX	FREQUENCY	PPM	HEIGHT
1	11997.142	159.004	23.3
2	10310.027	136.644	48.6
3	9877.872	130.916	18.2
4	9760.677	128.363	75.4
5	8945.137	118.555	40.1
6	8561.406	113.753	66.6
7	6413.305	84.989	46.5
8	5857.851	77.637	31.5
9	5824.890	77.200	32.4
10	5793.150	76.779	35.1
11	5363.436	71.084	47.4
12	5306.059	70.324	42.9
13	4180.502	55.406	34.5
14	1972.116	26.137	160.1
15	1548.506	20.523	38.7
16	1388.584	18.404	29.6
17	-315.622	-4.183	41.1
18	-320.505	-4.248	38.5

STANDARD 1H OBSERVE
Pulse Sequence: s2pu1

INDEX	FREQUENCY	PPM	HEIGHT
1	12006.908	159.133	23.8
2	10162.313	134.686	87.0
3	9835.145	130.350	39.5
4	9764.340	129.411	130.2
5	9067.276	120.173	75.0
6	8586.731	113.650	136.6
7	6344.941	84.092	84.6
8	5857.851	77.637	83.4
9	5824.890	77.200	60.9
10	5793.150	76.779	84.5
11	5285.306	70.049	80.1
12	5234.034	69.369	76.3
13	4567.489	60.535	8.7
14	4179.282	55.390	86.4
15	1602.220	21.235	9.8
16	1373.935	18.209	82.0
17	1087.052	14.407	8.2

STANDARD 1H OBSERVE
Pulse Sequence: s2pu1

STANDARD 1H OBSERVE

Pulse Sequence: szpu1

STANDARD 1H OBSERVE
Pulse Sequence: s2pu1

STANDARD 1H OBSERVE
Pulse Sequence: s2pul

STANDARD 1H OBSERVE
Pulse Sequence: s2pu1

INDEX	FREQUENCY	PPM	HEIGHT
1	12780.128	169.116	23.7
2	12458.596	165.120	16.1
3	12421.973	164.634	16.7
4	11994.701	158.971	18.7
5	10811.767	143.293	26.4
6	10161.093	134.670	30.9
7	9880.314	130.948	22.3
8	9816.833	130.107	16.6
9	9746.028	129.169	61.0
10	9681.327	128.311	26.0
11	9366.366	124.137	22.8
12	9025.769	119.623	21.6
13	8574.082	113.636	69.5
14	7072.525	93.735	21.1
15	6142.293	81.407	23.5
16	5856.631	77.621	35.8
17	5824.891	77.200	40.0
18	5793.150	76.778	38.7
19	5773.818	76.520	27.4
20	5435.462	72.039	26.0
21	5401.281	71.586	36.3
22	5387.852	71.408	24.2
23	5284.086	70.032	30.4
24	5105.852	67.670	26.6
25	5070.450	67.201	31.9
26	4554.061	60.357	14.7
27	4451.516	58.998	31.1
28	4167.074	55.228	35.6
29	3104.988	41.152	24.5
30	1500.896	19.892	23.8
31	1179.832	15.637	22.8
32	1134.663	15.038	22.4
33	1079.728	14.310	16.3

STANDARD 1H OBSERVE
Pulse Sequence: s2pu1

STANDARD 1H OBSERVE
Pulse Sequence: s2pu1

Chemical structure of compound **17** is shown above the spectrum. The structure is a 14-membered macrocyclic diester with two vinyl groups, two methyl groups (one wedged, one dashed), and a methoxymethyl (OMEM) group.

The ¹H NMR spectrum (400 MHz, CDCl₃) shows peaks from 0 to 7 ppm. Key features include a broad peak at ~6.5 ppm (OH), a multiplet at ~5.5 ppm (vinyl protons), a doublet at ~4.5 ppm (CH-O), a multiplet at ~3.5 ppm (CH-OMEM), a doublet at ~2.5 ppm (CH-Me), and a large peak at ~1.2 ppm (methyl groups). Integration values are shown above the peaks.

INDEX	FREQUENCY	PPM	HEIGHT
1	12806.517	169.731	8.3
2	12474.466	165.330	9.8
3	12448.829	164.980	10.3
4	10843.507	143.714	13.6
5	10246.547	135.802	13.3
6	9894.963	131.143	10.6
7	9686.651	128.408	13.6
8	9363.924	124.104	13.2
9	8656.081	117.374	12.5
10	7084.732	93.897	11.0
11	5656.630	77.621	37.4
12	5624.890	77.200	38.0
13	5793.150	76.779	34.7
14	5784.604	76.666	10.6
15	5625.903	74.563	16.3
16	5572.189	73.851	11.3
17	5409.826	71.699	15.5
18	5397.618	71.537	11.1
19	5116.839	67.816	11.7
20	5081.436	67.347	17.1
21	4482.502	59.144	16.9
22	3124.530	41.411	9.7
23	1526.532	20.232	12.3
24	1141.987	15.135	13.1
25	1087.052	14.407	14.0

STANDARD 1H OBSERVE

Pulse Sequence: s2pu1

18

INDEX	FREQUENCY	PPM	HEIGHT
1	12822.387	169.941	17.7
2	12420.752	164.618	19.9
3	12402.440	164.375	19.3
4	10998.546	145.769	20.1
5	10921.637	144.750	17.9
6	9396.885	124.541	22.9
7	9247.951	122.567	22.5
8	7093.278	94.011	20.3
9	5934.760	76.656	23.3
10	5856.630	77.621	61.9
11	5824.890	77.200	62.6
12	5793.150	76.779	58.4
13	5564.864	73.754	19.1
14	5503.826	72.945	23.1
15	5407.384	71.667	24.4
16	5359.774	71.036	21.0
17	5119.281	67.848	22.4
18	5092.423	67.492	26.6
19	4463.723	59.160	19.3
20	3094.010	41.006	18.3
21	1488.688	19.730	19.1
22	1364.169	18.080	22.8
23	1337.311	17.724	21.2

Macrosphelide A (1)

STANDARD CARBON PARAMETERS
Pulse Sequence: s2pu1

STANDARD PROTON PARAMETERS
Pulse Sequence: s2pu1

Macrosphelide B (2)

Macrosphelide B (2)

STANDARD CARBON PARAMETERS
Pulse Sequence: s2pu1