Supporting Information

Versatile Synthetic Method for Sphingolipids and Functionalized Sphingosine Derivatives via Olefin Cross Metathesis

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General Methods

All commercially available reagents were used without further purification. All solvents were used after distillation. Tetrahydrofuran (THF) and diethylether were refluxed over and distilled from sodium. Dichloromethane (CH_2Cl_2) was refluxed over and distilled from P_2O_5 . Dimethylformamide (DMF) was distilled from CaH_2 under reduced pressure. Preparative separation was usually performed by column chromatography on silica gel (FUJI silysia LTD, BW-200). ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL α -400 or δ -400 spectrometer and chemical shifts were represented as δ -values relative to the internal standard TMS. Optical rotations were measured with a JASCO DIP 370 Digital Polarimeter. IR spectra were recorded on a JASCO FT/IR-5300 Fourier Transform Infrared Spectrometer. High resolution mass spectra (HRMS) were measured on a Hitachi M-4100 Tandem Mass Spectrometer or a JEOL JMS-T100LC spectrometer.

***N*-Methoxy-*N*-methyl 3-(*tert*-butyldimethylsililoxy)-(2*S*)-(N-*tert*-butyloxycarbonyl) aminopropanamide 6.** To a solution of **5** (20 g, 190.31 mmol) in dioxane (120 ml) and water (120 ml) was added triethylamine (133 ml, 952 mmol) and di-*tert*-butyldicarbonate (50 g, 228 mol) at 0 °C. After the resulting mixture was stirred at room temperature for 3h, the reaction mixture was washed hexane. Then, the water layer was added 6N HCl, and the resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude Boc protected products as a colorless oil. To a solution of Boc

protected products (190.31 mmol) obtained above in CH_2Cl_2 (360 ml) was added *N,O*-dimethylhydroxylamine hydrochloride (20.42 g, 209.3 mmol) and *N*-methyldimorpholine (23 ml, 209 mmol) at $-15\text{ }^\circ\text{C}$. Then, the resulting mixture was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (36.48 g, 209.3 mmol) over 30 min at the same temperature. After the reaction mixture was stirred at the same temperature for 1h, ice and 1N-HCl were added, and the resulting mixture was extracted with chloroform. The organic layers were combined, and washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude Weinreb amide as a colorless solid. To a solution of Weinreb amide (20.0 g, 80.6 mmol) obtained above in DMF (160 ml) was added imidazole (6.585 g, 96.72 mmol) and *tert*-butyldimethylsilyl chloride (12.76 g, 84.7 mmol) at $0\text{ }^\circ\text{C}$. After the reaction mixture was stirred at the same temperature for 10 min, ice was added, and the resulting mixture was extracted with diethyl ether. The organic layers were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude **6** (29.221 g, 93% for 3 steps) as a colorless oil.

$[\alpha]_{\text{D}}^{23.0} +19.2$ ($c = 0.93$, CHCl_3); IR (NaCl neat): 3335, 2932, 1716, 1671, 1501, 1169 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.30-5.38 (brm, 1H), 4.74 (m, 1H), 3.84 (dd, $J = 4.4, 10.0$ Hz, 1H), 3.78 (dd, $J = 5.4, 10.0$ Hz, 1H), 3.75 (s, 3H), 3.21 (s, 3H), 1.43 (s, 9H), 0.86 (s, 9H), 0.022 (s, 3H), 0.020 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 170.6, 155.2, 79.3, 63.4, 61.3, 52.3, 32.0, 28.2, 25.6, 18.1, -5.7; ESI-HRMS m/z calcd for $\text{C}_{16}\text{H}_{34}\text{N}_2\text{O}_5\text{Si}_1\text{Na}_1$ ($\text{M} + \text{Na}$) $^+$ 385.2135, found 385.2143.

1-(*tert*-Butyldimethylsilyloxy)-(2*S*)-(N-*tert*-butyloxycarbonyl)amino-3-oxo-4-

pentene 7. To a solution of **6** (20.0 g, 55.1 mmol) in THF (165 ml) was added a solution of vinyl magnesium bromide (about 220 mmol) in THF (110 ml) at room temperature. After the reaction mixture was stirred for 10 min at the same temperature, the reaction mixture was poured into 2N HCl at $0\text{ }^\circ\text{C}$. The resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude products. Column chromatography on silica gel (from 4.7% to 10.5% ethyl acetate in hexane) gave **7** (15.55 g, 92%) as a pale yellow oil.

$[\alpha]_{\text{D}}^{24.0} +63.3$ ($c = 0.62$, CHCl_3); IR (NaCl neat): 3477, 2859, 1701, 1495, 1366, 1171 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 6.55 (dd, $J = 10.7, 17.3$ Hz, 1H), 6.33 (dd, $J = 1.5,$

17.3 Hz, 1H), 5.82 (d, $J = 5.8$ Hz, 1H), 5.45 – 5.55 (brm, 1H), 4.58 (ddd, $J = 3.7, 3.7, 7.6$ Hz, 1H), 3.99 (dd, $J = 3.4, 10.3$ Hz, 1H), 3.84 (dd, $J = 4.4, 10.3$ Hz, 1H), 1.43 (s, 9H), 0.83 (s, 9H), 0.00 (s, 3H), -0.01 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 196.9, 155.3, 133.1, 129.4, 79.8, 63.4, 59.5, 28.3, 25.7, 18.2, -5.62, -5.64; ESI-HRMS m/z calcd for $\text{C}_{16}\text{H}_{31}\text{N}_1\text{O}_4\text{Si}_1\text{Na}_1$ ($\text{M} + \text{Na}$) $^+$ 352.1920, found 352.1920.

1-(*tert*-Butyldimethylsilyloxy)-(2*S*)-(N-*tert*-butyloxycarbonyl)amino-4-penten-(3*R*)-ol 8. To a solution of **7** (2.00 g, 6.07 mmol) in ethanol (12.1 ml) was added lithium tri-*tert*-butoxyaluminumhydride (3.39 g, 13.35 mmol) at -78 °C. After the reaction mixture was stirred at the same temperature for 15 min, 1N HCl was added. The resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude products. Column chromatography on silica gel (from 9% to 33% ethyl acetate in hexane) gave **8** (1.93 g, 96%) as a colorless oil.

$[\alpha]_{\text{D}}^{23.0} +24.8$ ($c = 1.45$, CHCl_3); IR (NaCl neat): 3451, 2932, 1701, 1501, 1173, 837 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.91 (ddd, $J = 4.9, 10.5, 17.3$ Hz, 1H), 5.38 (ddd, $J = 1.7, 1.7, 17.1$ Hz, 1H), 5.24 (ddd, $J = 1.7, 1.7, 10.5$ Hz, 1H), 5.21 – 5.29 (brm, 1H), 4.26 (m, 1H), 3.93 (dd, $J = 2.9, 10.5$ Hz, 1H), 3.76 (m, 1H), 3.63 (m, 1H), 3.39 – 3.46 (brm, 1H), 1.45 (s, 9H), 0.90 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.7, 137.8, 115.7, 79.3, 74.3, 63.0, 54.2, 28.2, 25.6, 18.0, -5.5, -5.8; FAB HRMS m/z calcd for $\text{C}_{16}\text{H}_{34}\text{N}_1\text{O}_4\text{Si}_1$ ($\text{M} + \text{H}$) $^+$ 332.2257, found 332.2246.

(2*S*)-(N-*tert*-Butyloxycarbonyl)amino-4-penten-1,(3*R*)-diol 11. To a solution of **8** (14.46 g, 43.63 mmol) in methanol (44 ml) was added 2N HCl (22 ml) at room temperature. After the reaction mixture was stirred at the same temperature for 15 min, brine was added, and the resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude products. Column chromatography on silica gel (from 33% to 67% ethyl acetate in hexane) gave **11** (9.19 g, 97%) as a colorless solid.

$[\alpha]_{\text{D}}^{25.8} +6.65$ ($c = 1.10$, CHCl_3); IR (NaCl neat): 3370, 2978, 11690, 1510, 1171, 1053 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.94 (ddd, $J = 5.4, 10.5, 17.3$ Hz, 1H), 5.40 (d, $J = 17.3$ Hz, 1H), 5.29 – 5.37 (brm, 1H), 5.28 (d, $J = 10.5$ Hz, 1H), 4.40 (m, 1H), 3.94 (ddd, $J = 3.7, 3.7, 11.2$ Hz, 1H), 3.73 (ddd, $J = 3.7, 7.1, 10.7$ Hz, 1H), 3.65 (m, 1H), 2.66 –

2.78 (brm, 1H), 2.38 – 2.50 (brm, 1H), 1.46 (s, 9H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 156.1, 137.3, 116.1, 79.4, 73.7, 61.7, 54.9, 28.0; FAB HRMS m/z calcd for $\text{C}_{10}\text{H}_{20}\text{NO}_4$ ($\text{M} + \text{H}$) $^+$ 218.1392, found 218.1366.

***N*-[1,(3R)-dihydroxy-4-penten-(2S)-yl]-hexadecanamide 12.** To a solution of **11** (129 mg, 0.594 mmol) in dichloromethane (2.97 ml) was added trifluoroacetic acid (1.19 ml) at 0 °C. After the reaction mixture was stirred at the same temperature for 90 min, 1N NaOH was added to neutralize pH 9. Then palmitoyl chloride (0.195 ml, 0.713 mmol) was added at the same temperature. After the reaction mixture was stirred at the same temperature for 20 min, a saturated ammonium chloride solution was added, and the resulting mixture was extracted with chloroform. The organic layers were combined, and washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude products. Column chromatography on silica gel (from 17 to 67% ethyl acetate in hexane) gave **12** (98 mg, 47%) as a colorless solid.

$[\alpha]_{\text{D}}^{23.2}$ –4.29 ($c = 0.66$, CH_3OH); IR (KBr disk): 3306, 2922, 1645, 1547, 1055, 723 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 6.24 – 6.31 (brd, 1H), 5.95 (ddd, $J = 5.2, 10.7, 17.4$ Hz, 1H), 5.41 (ddd, $J = 1.6, 1.6, 17.1$ Hz, 1H), 5.29 (ddd, $J = 1.6, 16, 10.6$ Hz, 1H), 4.40 (m, 1H), 3.93 – 4.00 (m, 2H), 3.72 (m, 1H), 2.88 – 2.90 (brm, 1H), 2.50 – 2.60 (brm, 1H), 2.24 (t, $J = 7.3$ Hz, 2H), 1.64 (tt, $J = 7.6, 7.6$ Hz, 2H), 1.25 (m, 24H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 173.8, 137.3, 116.5, 74.8, 62.3, 53.9, 36.8, 31.9, 29.7, 29.64, 29.61, 29.60, 29.49, 29.48, 29.34, 29.33, 29.26, 25.7, 22.7, 14.1; FAB HRMS m/z calcd for $\text{C}_{21}\text{H}_{42}\text{NO}_3$ ($\text{M} + \text{H}$) $^+$ 356.3164, found 356.3150.

Dimethyl (2S)-*N*-(*tert*-butyloxycarbonylamino)-(3R)-hydroxy-4-pentenylphosphate 13. To a mixture of molecular sieves 4A (40 mg), carbon tetrabromide (366 mg, 1.104 mmol) in pyridine (1.8 ml) was added trimethylphosphite (0.13 ml, 1.10 mmol) and **11** (0.200 g, 0.92 mmol) at –15 °C. Then, the reaction mixture was warmed to room temperature slowly, and then 2N HCl was added. The resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude products. Column chromatography on silica gel (from 0% to 2.0% methanol in chloroform) gave **13** (0.230 g, 77%) as a colorless oil.

$[\alpha]_{\text{D}}^{23.5}$ +14.3 ($c = 0.85$, CHCl_3); IR (NaCl neat): 3372, 2967, 1711, 1530, 1256, 1173,

1042 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.89 (ddd, $J = 5.7, 10.6, 17.0$ Hz, 1H), 5.34 (d, $J = 17.1$ Hz, 1H), 5.21 (d, $J = 10.5$ Hz, 1H), 5.15 – 5.24 (brm, 1H), 4.29 (m, 1H), 4.20 (dd, $J = 5.7, 5.7$ Hz, 1H), 4.10 (ddd, $J = 3.4, 7.1, 10.5$ Hz, 1H), 3.81 (m, 1H), 3.761 (d, $J = 11.0$ Hz, 3H), 3.757 (d, $J = 11.0$ Hz, 3H), 3.15 – 3.45 (brm, 1H), 1.41 (s, 9H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.7, 137.0, 117.0, 79.7, 72.5, 66.5 (d, $J_{\text{C-P}} = 5.7$ Hz), 54.6, 54.5 (d, $J_{\text{C-P}} = 5.7$ Hz), 28.3; FAB HRMS m/z calcd for $\text{C}_{12}\text{H}_{25}\text{NO}_7\text{P}$ ($\text{M} + \text{H}$) $^+$ 326.1368, found 326.1375.

Bromoethyl (2S)-N-(tert-butyloxycarbonylamino)-(3R)-hydroxy-4-pentenyl methyl phosphate 14. To a mixture of molecular sieves 4A, carbon tetrabromide (3.87 g, 11.7 mmol) in pyridine (20 ml) was added 2-bromoethyldimethylphosphite (1.75 ml, 11.7 mmol) and **11** (1.27 g, 5.84 mmol) in pyridine (19.2 ml) at 0 °C. After the reaction mixture was stirred at the same temperature for 3 h, precipitate was removed by filtration. The resulting mixture was extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude products. Column chromatography on silica gel (from 17% to 67% ethyl acetate in hexane) gave **14** (1.57 g, 64%) as a colorless oil.

$[\alpha]_{\text{D}}^{24.2} +9.94$ ($c = 0.89$, CHCl_3); IR (NaCl neat): 3405, 2978, 1709, 1524, 1265, 1171, 1034 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.91 (ddd, $J = 5.7, 10.5, 16.7$ Hz, 1H), 5.36 (d, $J = 17.2$ Hz, 1H), 5.24 (dd, $J = 1.2, 10.5$ Hz, 1H), 5.09 – 5.20 (brm, 1H), 4.25 – 4.40 (m, 3H), 4.22 (dd, $J = 5.5, 5.5$ Hz, 1H), 4.16 (m, 1H), 3.808 (d, $J = 11.2$ Hz, 3/2H), 3.806 (d, $J = 11.2$ Hz, 3/2H), 3.75 (m, 1H), 3.54 (t, 2H), 1.43 (s, 9H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.7, 136.9, 117.2, 79.9, 72.5, 67.0 (d, $J_{\text{C-P}} = 4.8$ Hz), 66.8 (1/2C) (d, $J_{\text{C-P}} = 5.8$ Hz), 66.7 (1/2C) (d, $J_{\text{C-P}} = 4.8$ Hz), 54.8 (d, $J_{\text{C-P}} = 5.8$ Hz), 54.6 (m), 29.4 (d, $J_{\text{C-P}} = 6.7$ Hz), 28.3; FAB HRMS m/z calcd for $\text{C}_{13}\text{H}_{26}\text{BrNO}_7\text{P}$ ($\text{M} + \text{H}$) $^+$ 418.0630, found 418.0633.

Bromoethyl (2S)-N-(1-oxohexadecyl)amino-(3R)-hydroxy-4-pentenyl methyl phosphate 15. To a solution of **14** (750 mg, 1.79 mmol) in dichloromethane (8.97 ml) were added trifluoroacetic acid (3.59 ml) at 0 °C. After the reaction mixture was stirred at the same temperature for 90 min, 1N NaOH was added to neutralize pH 9. Then parmitoyl chloride (0.592 ml, 2.15 mmol) was added at same temperature. After the reaction mixture was stirred at the same temperature for 20 min, a saturated ammonium

chloride solution was added, and the resulting mixture was extracted with chloroform. The organic layers were combined, and washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude products. Column chromatography on silica gel (from 17 to 67% ethyl acetate in hexane) gave **15** (795 mg, 80%) as a colorless solid.

$[\alpha]_D^{23.2} +5.74$ ($c = 0.93$, CHCl_3); IR (KBr disk): 3337, 2849, 1642, 1551, 1470, 1188, 1036 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 6.24 (brm, 1H), 5.89 (ddd, $J = 5.9, 10.5, 17.1$ Hz, 1H), 5.36 (d, $J = 17.1$ Hz, 1H), 5.25 (d, $J = 10.5$ Hz, 1H), 4.31 – 4.38 (m, 3H), 4.25 (m, 1H), 4.14 – 4.20 (m, 2H), 3.82 (d, $J = 11.2$ Hz, 3/2H), 3.81 (d, $J = 11.2$ Hz, 3/2H), 3.545 (dd, $J = 5.9, 5.9$ Hz, 2/2H), 3.543 (dd, $J = 5.9, 5.9$ Hz, 2/2H), 2.21 (t, $J = 7.3$ Hz, 2H), 1.61 (tt, $J = 7.3, 7.3$ Hz, 2H), 1.23 – 1.32 (m, 24H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 173.9, 136.8, 117.4, 72.7, 67.1 (m), 66.6 (d, $J_{C-P} = 5.8$ Hz), 54.9 (d, $J_{C-P} = 6.7$ Hz), 53.6 (d, $J_{C-P} = 4.8$ Hz), 3.67, 31.9, 29.68, 29.67, 29.6, 29.5, 29.4, 29.34, 29.33, 29.26, 29.25, 25.6, 22.7, 14.1.; FAB HRMS m/z calcd for $\text{C}_{24}\text{H}_{48}\text{BrNO}_6\text{P}$ ($\text{M} + \text{H}$)⁺ 556.2402, found 556.2394.

Typical experimental procedure for olefin cross metathesis reaction between olefins **B** and aminoalcohols **A**: preparation of compound **17**

1-(tert-Butyldimethylsilyloxy)-(2S)-(N-tert-butyloxycarbonyl)amino-(4E)-

ocatadecen-(3R)-ol 17. To a solution of **10** (106 mg, 0.32 mmol) in CH_2Cl_2 (4.8 ml) was added 1-pentadecene **16** (269 ml, 1.28 mmol) and Grubbs catalyst 2nd generation (8 mg, 0.01 mmol) at room temperature. After reaction mixture was stirred for 2h under reflux, solvent was removed *in vacuo* to give crude products. Column chromatography on silica gel (from 9% to 25% ethyl acetate in hexane) gave **17** (118 mg, 72%) as a colorless solid.

$[\alpha]_D^{23.8} +11.9$ ($c = 1.02$, CHCl_3); IR (NaCl neat): 3449, 2928, 1715, 1497, 1173, 839 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.75 (dtd, $J = 1.2, 6.8, 15.4$ Hz, 1H), 5.50 (ddt, $J = 1.5, 5.6, 15.4$ Hz, 1H), 5.23 (brm, 1H), 4.27 (m, 1H), 3.93 (dd, $J = 2.9, 10.2$ Hz, 1H), 3.75 (dd, $J = 2.4, 10.5$ Hz, 1H), 3.57 (m, 1H), 3.31 (brm, 1H), 2.05 (dt, $J = 7.1, 7.1$ Hz, 2H), 1.45 (s, 9H), 1.25 (m, 22H), 0.85 (m, 3H), 0.06 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.4, 133.1, 129.4, 79.4, 74.6, 63.4, 54.5, 32.3, 31.9, 29.7, 29.5, 29.3, 29.2, 28.4, 28.3, 25.8, 22.7, 18.1, 14.1, -5.6; FAB HRMS m/z calcd for $\text{C}_{29}\text{H}_{60}\text{NO}_4\text{Si}$ ($\text{M} + \text{H}$)⁺ 514.4291,

found 514.4299.

(2S)-(N-*tert*-Butyloxycarbonyl)amino-(4E)-octadecen-1,(3R)-diol 18.

$[\alpha]_D^{24.2}$ -2.34 ($c = 0.88$, CHCl_3); IR (NaCl neat): 3335, 2909, 1692, 1528, 1177, 1057, 664 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.77 (td, $J = 6.8, 15.4$ Hz, 1H), 5.52 (dd, $J = 6.3, 15.4$ Hz, 1H), 5.33 (d, $J = 7.1$ Hz, 1H), 4.29 (brm, 1H), 3.92 (ddd, $J = 3.7, 3.7, 11.5$ Hz, 1H), 3.70 (ddd, $J = 3.7, 6.8, 11.2$ Hz, 1H), 3.59 (brm, 1H), 2.60 – 2.61 (brm, 2H), 2.05 (dt, $J = 7.1, 7.1$ Hz, 2H), 1.45 (s, 9H), 1.39-1.26 (m, 22H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 156.2, 134.1, 128.9, 79.8, 74.6, 62.6, 55.4, 32.3, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 28.3, 22.7, 14.1; FAB HRMS m/z calcd for $\text{C}_{23}\text{H}_{46}\text{NO}_4$ ($\text{M} + \text{H}$) $^+$ 400.3426, found 400.3427.

Ceramide 2.

$[\alpha]_D^{24.3}$ +4.75 ($c = 0.28$, CHCl_3); IR (KBr disk): 3295, 2919, 2851, 1638, 1547, 970 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 6.28 (brd, $J = 6.8$ Hz, 1H), 5.78 (dt, $J = 6.8, 15.4$ Hz, 1H), 5.53 (dd, $J = 6.3, 15.4$ Hz, 1H), 4.31 (m, 1H), 3.95 (dd, $J = 3.7, 3.7, 11.0$ Hz, 1H), 3.90 (m, 1H), 3.70 (dd, $J = 2.7, 11.0$ Hz, 1H), 2.93 (brs, 2H), 2.23 (t, $J = 7.6$ Hz, 2H), 2.06 (m, 2H), 1.64 (tt, $J = 7.1, 7.1$ Hz, 2H), 1.40-1.26 (m, 46H), 0.88 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 170.4, 134.2, 128.8, 74.6, 62.5, 54.5, 36.8, 32.3, 31.9, 29.69, 29.65, 29.5, 29.35, 29.29, 29.23, 29.1, 25.8, 22.7, 14.1; FAB HRMS m/z calcd for $\text{C}_{34}\text{H}_{68}\text{NO}_3$ ($\text{M} + \text{H}$) $^+$ 538.5199, found 538.5222.

Dimethyl (2S)-N-(*tert*-butoxycarbonylamino)-(3R)-hydroxy-(4E)-octadecenyl phosphate 19.

$[\alpha]_D^{24.2}$ +2.47 ($c = 1.23$, CHCl_3); IR (NaCl neat): 3371.9, 2926.3, 2854.9, 1716.8, 1255.8, 1174.8, 1045.5 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.76 (td, $J = 6.8, 15.4$ Hz, 1H), 5.50 (dd, $J = 6.8, 15.3$ Hz, 1H), 5.01 (brm, 1H), 4.33 (ddd, $J = 4.6, 7.8, 10.5$ Hz, 1H), 4.10 – 4.16 (m, 2H), 3.794 (d, $J = 11.2$ Hz, 3H), 3.789 (d, $J = 11.2$ Hz, 3H), 3.78 – 3.82 (m, 1H), 2.77 (brm, 1H), 2.04 (m, 2H), 1.44 (s, 9H), 1.25 - 1.38 (m, 22H), 0.88 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.7, 134.9, 128.4, 79.7, 72.4, 66.7 (d, $J_{\text{C-P}} = 5.7$ Hz), 54.9, 54.5 (d, $J_{\text{C-P}} = 5.7$ Hz), 32.3, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 28.3, 22.7, 14.1; ESI-HRMS m/z calcd for $\text{C}_{25}\text{H}_{50}\text{N}_1\text{O}_7\text{P}_1\text{Na}_1$ ($\text{M} + \text{Na}$) $^+$ 530.3223, found 530.3211.

Bromoethyl (2S)-N-(tert-butoxycarbonylamino)-(3R)-hydroxy-(4E)-octadecenyl methylphosphate 20.

$[\alpha]_D^{22.0} +2.58$ ($c = 0,102$, CHCl_3); IR (NaCl neat): 3387, 1713, 1522, 1460, 1260, 1175, 1024 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.76 (td $J = 6.8, 15.4$ Hz, 1H), 5.50 (dd, $J = 7.1, 15.4$ Hz, 1H), 5.05 (brs, 1H), 4.36 – 4.31 (m, 3H), 4.16 (m, 2H), 3.82 (d, $J = 11.2$ Hz, 3/2H), 3.82 (d, $J = 11.2$ Hz, 3/2H), 3.79 (m, 1H), 3.55 (dd, $J = 6.1, 6.1$ Hz, 2H), 2.04 (m, 2H), 1.44 (s, 9H), 1.26 (m, 22H), 0.88 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.6, 134.9, 128.5, 79.7, 72.4, 66.9 (m, 2C), 54.7 (m, 2C), 32.3, 31.9, 29.6, 29.5, 29.3, 29.2, 29.1, 28.3, 22.6, 14.1; ESI-HRMS m/z calcd for $\text{C}_{26}\text{H}_{51}\text{Br}_1\text{N}_1\text{O}_7\text{P}_1\text{Na}_1$ ($\text{M} + \text{Na}$) $^+$ 622.2484, found 622.2460.

Bromoethyl (2S)-N-(1-oxohexadecyl)amino-(3R)-hydroxy-(4E)-octadecenyl methyl phosphate 21.

$[\alpha]_D^{22.8} -3.45$ ($c = 0,86$, CHCl_3); IR (KBr disk): 3291, 2917, 1647, 1547, 1468, 1269, 1047 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 6.32 (brd, $J = 7.1$ Hz, 1H), 5.75 (td $J = 6.8, 15.1$ Hz, 1H), 5.48 (dd, $J = 6.6, 15.4$ Hz, 1H), 4.33 (m, 3H), 4.17 (m, 3H), 3.81 (d, $J = 11.2$ Hz, 3/2H), 3.80 (d, $J = 11.2$ Hz, 3/2H), 3.55 (t, $J = 6.1$ Hz, 2H), 2.19 (dt, $J = 1.7, 7.1$ Hz, 2H), 2.03 (dt, $J = 1.7, 7.1$ Hz, 2H), 1.61 (m, 2H), 1.26 (m, 46H), 0.88 (t, $J = 6.6$ Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 173.6, 134.8, 128.5, 72.4, 67.2 (m), 66.8 (d, $J_{\text{C-P}} = 5.0$ Hz), 54.77 (d, $J_{\text{C-P}} = 5.8$ Hz, 1/2C), 54.74 (d, $J_{\text{C-P}} = 5.8$ Hz, 1/2C), 53.7 (d, $J_{\text{C-P}} = 5.8$ Hz), 36.7, 32.3, 31.9, 29.7, 29.5, 29.4, 29.37, 29.29, 29.1, 25.7, 22.6, 14.1; FAB HRMS m/z calcd for $\text{C}_{37}\text{H}_{74}\text{BrNO}_6\text{P}$ ($\text{M} + \text{H}$) $^+$ 738.4437, found 738.4456.

1-(tert-Butyldimethylsilyloxy)-(2S)-(N-tert-butyloxycarbonyl)amino-(4E)-dodecen-(3R)-ol 26.

$[\alpha]_D^{24.9} +14.1$ ($c = 0.89$, CHCl_3); IR (NaCl neat): 3449, 2930, 1715, 1499, 1175, 837 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.75 (dtd $J = 1.2, 6.6, 15.4$ Hz, 1H), 5.51 (dd, $J = 5.6, 15.4$ Hz, 1H), 4.19 (m, 1H), 3.93 (dd, $J = 2.9, 10.3$ Hz, 1H), 3.75 (m, 1H), 3.57 (m, 1H), 3.56 (m, 1H), 3.25-3.34 (brm, 1H), 2.05 (dt, $J = 6.8$ Hz, 2H), 1.44 (s, 9H), 1.25 (s, 10H), 0.90 (s, 9H), 0.88 (t, $J = 7.1$ Hz, 3H), 0.06 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.8, 133.0, 129.4, 79.4, 74.5, 63.4, 54.5, 32.3, 31.8, 29.14, 29.10, 28.3, 25.8, 25.7, 22.6, 18.1, 14.0, -5.65, -5.68; FAB HRMS m/z calcd for $\text{C}_{23}\text{H}_{48}\text{NO}_4\text{Si}$ ($\text{M} + \text{H}$) $^+$

430.3352, found 430.3370.

1-(*tert*-Butyldimethylsilyloxy)-(2*S*)-(N-*tert*-butyloxycarbonyl)amino-(4*E*)-tetradecen-(3*R*),14-diol 27.

$[\alpha]_D^{24.9} +14.2$ ($c = 0.77$, CHCl_3); IR (NaCl neat): 3447, 2930, 1698, 1505, 1173, 1103, 837 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 5.67 (dtd, $J = 1.1, 6.9, 15.3$ Hz, 1H), 5.43 (mdd, $J = 5.9, 15.6$ Hz, 1H), 5.17 (brd, $J = 8.0$ Hz, 1H), 4.11 (m, 1H), 3.86 (dd, $J = 3.0, 10.3$, Hz, 1H), 3.67 (m, 1H), 3.55 (t, $J = 6.6$ Hz, 2H), 3.49 (m, 1H), 3.36 (brm, 1H), 1.98 (dt, $J = 6.8, 6.8$ Hz, 2H), 1.48 (m, 2H), 1.21 – 1.32 (m, 14H), 0.82 (m, 9H), 0.00 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.8, 133.0, 129.5, 79.4, 74.6, 63.4, 62.9, 54.5, 32.7, 32.3, 29.5, 29.33, 29.31, 29.09, 29.05, 28.4, 25.8, 25.7, 18.1, -5.65, -5.67; ESI-HRMS m/z calcd for $\text{C}_{25}\text{H}_{51}\text{NO}_5\text{Si}_1\text{Na}_1$ ($M + \text{Na}$) $^+$ 496.3434, found 496.3421.

14-N-(7-nitrobenzo-2-oxa-1,3-diazol-4-yl)amino-1-(*tert*-butyldimethylsilyloxy)-(2*S*)-N-(*tert*-butyloxycarbonylamino)-(4*E*)-tetradecen-(3*R*)-ol 28.

$[\alpha]_D^{24.9} +1.97$ ($c = 0.91$, CHCl_3); IR (KBr disk): 3414, 2928, 1586, 1258, 1173, 839 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 8.49 (d, $J = 8.5$ Hz, 1H), 6.48-6.58 (brm, 1H), 6.18 (d, $J = 8.8$ Hz, 1H), 5.75 (dt, $J = 7.3, 14.6$ Hz, 1H), 5.51 (dd, $J = 5.9, 15.4$ Hz, 1H), 5.21-5.31 (brm, 1H), 4.20 (m, 1H), 3.94 (dd, $J = 2.9, 10.3$ Hz, 1H), 3.76 (dm, $J = 8.1$ Hz, 1H), 3.57 (m, 1H), 3.50 (dt, $J = 6.8, 6.8$ Hz, 2H), 3.38-3.44 (brm, 1H), 2.04 (dt, $J = 6.8, 6.8$ Hz, 2H), 1.81 (tt, $J = 7.3, 7.3$ Hz, 2H), 1.44 (s, 9H), 1.34 (m, 12H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.8, 144.2, 144.0, 136.5, 132.9, 129.5, 98.4, 79.4, 74.7, 63.4, 54.5, 44.0, 32.2, 29.3, 29.2, 29.1, 29.0, 28.5, 28.4, 26.9, 25.8, 18.1, -5.65, -5.68; FAB HRMS m/z calcd for $\text{C}_{31}\text{H}_{54}\text{N}_5\text{O}_7\text{Si}$ ($M + \text{H}$) $^+$ 636.3792, found 636.3778.

1-(*tert*-Butyldimethylsilyloxy)-(2*S*)-(N-*tert*-butyloxycarbonyl)amino-14-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]phenoxy- (4*E*)-tetradecen-(3*R*)-ol 29.

$[\alpha]_D^{24.5} +12.7$ ($c = 0.28$, CHCl_3); (NaCl neat): 3450, 2930, 2856, 1716, 1518, 1256, 1181, 837 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ : 7.13 (md, $J = 8.5$ Hz, 2H), 6.89 (md, $J = 8.9$ Hz, 2H), 5.75 (td, $J = 7.1, 15.3$ Hz, 1H), 5.51 (dd, $J = 7.1, 15.4$ Hz, 1H), 5.23 (brm, 1H), 4.19 (m, 1H), 3.94 (t, $J = 6.6$ Hz, 2H), 3.92 – 3.98 (m, 1H), 3.74 (m, 1H), 3.56 (m, 1H), 3.33 (brd, $J = 8.1$ Hz, 1H), 2.05 (m, 2H), 1.77 (tt, $J = 6.6, 6.6$ Hz, 2H), 1.45 (s, 9H),

1.29 – 1.42 (m, 12H), 0.90 (s, 9H), 0.072 (s, 3H), 0.068 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 160.3, 155.9, 133.1, 129.6, 128.1, 122.3 (q, $J_{\text{C-F}} = 280.0$ Hz), 114.9, 79.5, 74.7, 68.2, 63.5, 54.6, 32.4, 29.6, 29.5, 29.4, 29.23, 29.17, 28.5, 26.0, 25.9, 18.2, -5.55, -5.58; ESI-HRMS m/z calcd for $\text{C}_{33}\text{H}_{54}\text{F}_3\text{N}_3\text{O}_5\text{Si}_1\text{Na}_1$ ($\text{M} + \text{Na}$) $^+$ 680.3683, found 680.3679.

Sphingosine 3. To a solution of **18** (100 mg, 0.19 mmol) in CH_2Cl_2 (0.39 ml) was added trifluoroacetic acid (0.39 ml) at 0 °C. After the reaction mixture was stirred at the same temperature for 7h, 2N NaOH was added, and the resulting mixture was extracted with THF. The organic layers were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo* to give the crude products. Column chromatography on silica gel (from 5% methanol in chloroform to 4.3% water and 26.6% methanol in chloroform) gave **3** (46 mg, 79%) as a colorless solid.

$[\alpha]_{\text{D}}^{23.8} +5.8$ ($c = 0.51$, CHCl_3); IR (KBr disk): 3368, 2915, 1676, 1468, 1204, 1138, 1047 cm^{-1} ; ^1H NMR (CD_3OD , 400 MHz) δ : 5.67 (dt, $J = 6.8, 14.9$ Hz, 1H), 5.39 (ddm, $J = 7.3, 15.4$ Hz, 1H), 3.98 (m, 1H), 3.62 (m, 1H), 3.45 (dd, $J = 7.3, 11.0$ Hz, 1H), 2.80 (m, 1H), 1.99 (m, 2H), 1.32 (m, 2H), 1.17 – 1.26 (m, 20H), 0.80 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (CD_3OD , 100 MHz) δ : 135.6, 130.1, 73.8, 62.8, 58.1, 33.4, 33.1, 30.9, 30.79, 30.75, 30.6, 30.5, 30.35, 30.32, 23.7, 14.5; ESI-HRMS m/z calcd for $\text{C}_{18}\text{H}_{38}\text{N}_1\text{O}_2$ ($\text{M} + \text{H}$) $^+$ 300.2903, found 300.2907.

Sphingosine 1-phosphate 4. To a solution of **19** (700 mg, 1.379 mmol) in CH_2Cl_2 (6.9 ml) was added bromotrimethylsilane (1.5 ml, 11.4 mmol) at room temperature. After the reaction mixture was stirred at the same temperature for 30 min, the solvent was removed *in vacuo*. The resulting crude silyl ester was dissolved in MeOH (6.9 ml), and the solution was stirred for additional 10 min, and then the solvent was removed *in vacuo* to give crude products. Column chromatography on silica gel (from chloroform only to 4.3% water and 26.6% methanol in chloroform) gave **4** (301 mg, 57%) as a colorless solid.

IR (KBr disk): 3366, 2920, 1618, 1510, 1468, 1161, 1030 cm^{-1} ; ^1H NMR (CD_3OD , 400 MHz) δ : 5.90 (dt, $J = 6.9, 15.3$ Hz, 1H), 5.49 (dd, $J = 6.7, 15.4$ Hz, 1H), 4.35 (dd, $J = 5.7, 5.7$ Hz, 1H), 4.24 (ddd, $J = 3.7, 6.0, 11.4$ Hz, 1H), 4.12 (ddd, $J = 6.4, 8.3, 11.4$ Hz, 1H), 3.44 (m, 1H), 2.11 (dt, $J = 6.9, 6.9$ Hz, 2H), 1.28 – 1.50 (m, 22H), 0.90 (t, $J = 6.6$

Hz, 3H); ^{13}C NMR (CD_3OD , 100 MHz) δ : 136.9, 127.8, 70.4, 64.1 (m), 56.7 (d, $J_{\text{C-P}} = 6.7$ Hz), 33.3, 32.9, 30.7, 30.6, 30.5, 30.4, 30.3, 30.0, 23.6, 14.5; ESI-HRMS m/z calcd for $\text{C}_{18}\text{H}_{37}\text{N}_1\text{O}_5\text{P}_1$ ($\text{M} - \text{H}$) $^-$ 378.2409, found 378.2422.

Sphingomyelin 1. To a solution of **21** (245 mg, 0.332 mmol) in methanol (1.7 ml) was added 30% trimethylamine solution (1.7 ml) at room temperature. After the reaction mixture was stirred at 50 °C for 5h, solvent was removed *in vacuo* to give crude products. Column chromatography on silica gel (from 5% methanol in chloroform to 4.3% water and 26.6% methanol in chloroform) gave **1** (163mg, 70%) as a colorless solid.

$[\alpha]_{\text{D}}^{24.5} -1.68$ ($c = 0.28$, CH_3OH); IR (KBr disk): 3447, 2919, 1640, 1468, 1231, 1090 cm^{-1} ; ^1H NMR (CD_3OD , 400 MHz) δ : 5.71 (ddt, $J = 0.5, 6.6, 15.4$ Hz, 1H), 5.46 (ddt, $J = 1.5, 7.6, 15.4$ Hz, 1H), 4.28 (m, 2H), 3.88 – 4.14 (m, 4H), 3.63 (t, $J = 4.9$ Hz, 2H), 3.22 (s, 9H), 2.19 (m, 2H), 2.03 (dt, $J = 6.8, 6.8$ Hz, 2H), 1.59 (m, 2H), 1.26 (m, 46H), 0.90 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (CD_3OD , 100 MHz) δ : 175.8, 135.1, 131.3, 72.5, 67.5 (m), 65.9 (d, $J_{\text{C-P}} = 4.8$ Hz), 60.4 (d, $J_{\text{C-P}} = 4.8$ Hz), 55.2 (d, $J_{\text{C-P}} = 6.7$ Hz), 54.72, 54.69, 54.66, 37.4, 33.5, 33.1, 30.9, 30.73, 30.67, 30.52, 30.46, 27.2, 23.8, 14.5; ESI-HRMS m/z calcd for $\text{C}_{39}\text{H}_{79}\text{N}_2\text{O}_6\text{P}_1\text{Na}_1$ ($\text{M} + \text{Na}$) $^+$ 725.5573, found 725.5562.

15-DEC-2004 17:17:40.98

DFILE :
SF FILE : HIROKOCOMNT : KATSUMURA-LAB
EXMOD : SINGL
IRMOD : NON
POINT : 32768
FREQU : 7993.61 Hz
SCANS : 8
DUMMY : 4
ACQTM : 4.0993 sec
PD : 2.9007 sec
RGAIN : 15
PW1 : 11.00 usecOBNUC : 1H
OBFRQ : 399.65 MHz
OBSET : 134500.00 HzIRNUC : 1H
IRFRQ : 399.65 MHz
IRSET : 134500.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 27
IRBP2 : 6
IRRNS : 0ADBIT : 16
CTEMP : 26.0 C
CSPED : 12 Hz
SLVNT : CDCL3RESOL : 0.24 Hz
BF : 0.01 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 7.26 ppm
XE : 3997.53 Hz
XS : 34.27 Hz
operator

15-DEC-2004 17:43:11.38

DFILE :
SFIL : HIROKO

COMNT : KATSUMURA-LAB

EXMOD : SINGL

IRMOD : BCM

POINT : 32768

FREQU : 27100.27 Hz

SCANS : 1000

DUMMY : 4

ACQTM : 0.6046 sec

PD : 0.8000 sec

RGAIN : 23

PW1 : 10.00 usec

OBNUC : 13C

OBFRQ : 100.40 MHz

OBSET : 135500.00 Hz

IRNUC : 1H

IRFRQ : 399.65 MHz

IRSET : 134500.00 Hz

IRATN : 511

IRRPW : 50.0 usec

IRBP1 : 27

IRBP2 : 6

IRRNS : 0

ADBIT : 16

CTEMP : 26.3 C

CSPED : 10 Hz

SLVNT : CDCL3

RESOL : 0.83 Hz

BF : 2.00 Hz

T1 : 0.00 %

T2 : 0.00 %

T3 : 90.00 %

T4 : 100.00 %

REFVL : 77.00 ppm

XE : 20104.39 Hz

XS : 1055.71 Hz

operator

KATSUMURA-LAB

DFILE :
SFILE : HIROKO

```

COMNT : KATSUMURA-LAB
EXMOD : SINGL
IRMOD : NON
POINT : 32768
FREQU : 7993.61 Hz
SCANS : 8
DUMMY : 4
ACQTM : 4.0993 sec
PD : 2.9007 sec
RGAIN : 17
PW1 : 11.00 usec

```

```
OBNUC : 1H
OBFRQ : 399.65 MHZ
OBSET : 134500.00 HZ
```

```
IRNUC      : 1H
IRFRQ      : 399.65 MHz
IRSET      : 134500.00 Hz
IRATN      : 511
IRRPW      : 50.0 usec
IRBP1      : 27
IRBP2      : 6
IRHNS      : 0
```

```

ADBIT : 16
CTEMP : 26.1 c
CSPED : 14 Hz
SLVNT : CDCL3

```

RESOL :	0.24	Hz
BF	0.01	Hz
T1	0.00	%
T2	0.00	%
T3	90.00	%
T4	100.00	%
REFVL :	7.26	ppm
XE	3997.53	Hz
XS	34.27	Hz
operator

KATSUMURA-LAB

Figure 1 is a line graph titled 'Evolution of the average number of children per woman in the United States'. The vertical axis (y-axis) is labeled 'Average number of children per woman' and ranges from 0 to 10 in increments of 1. The horizontal axis (x-axis) is labeled 'Year' and ranges from 1960 to 2010 in increments of 10. A single line represents the 'U.S. average', which starts at approximately 2.1 in 1960 and decreases steadily to about 1.7 by 2010. The line is labeled 'U.S. average'.

Year	Average number of children per woman
1960	2.1
1970	2.0
1980	1.9
1990	1.8
2000	1.75
2010	1.7

```

COMNT : KATSUMURA-LAB
EXMOD : SINGL
IRMOD : BCM
POINT : 32768
FREQU : 27100.27 Hz
SCANS : 1000
DUMMY : 4
ACQTM : 0.6046 sec
PD : 0.8000 sec
RGAIN : 23

```

PW1 : 10.00 usec

```
OBNUC : 13C
OBFRQ : 100.40 MHz
OBSET : 135500.00 Hz
```

```
IRNUC : 1H
IRFRQ : 399.65 MHz
IRSET : 134500.00 Hz
IRATN : 511
IRAPW : 50.0 usec
IRBP1 : 27
IRBP2 : 6
IRNS : 0
```

```

ADBIT : 16
CTEMP : 26.5 c
CSPED : 12 Hz
SLVNT : CDCL3

```

RESOL :	0.83 Hz
BF	2.00 Hz
T1	0.00 %
T2	0.00 %
T3	90.00 %
T4	100.00 %
REFVL	77.00 ppm
XE	20104.39 Hz
XS	1054.88 Hz
operator

```

DFILE :
SSFILE : HIROKO

COMNT : KATSUMURA-LAB
EXMOD : SINGL
IRMOD : NON
POINT : 32768
FREQU : 7993.61 Hz
SCANS : 8
DUMMY : 4
ACQTM : 4.0993 sec
PPD : 2.9007 sec
RGAIN : 18

PW1 : 11.00 usec

```

```

OBNUC : 1H
OBFRQ : 399.65 MHz
OBSET : 134500.00 Hz

```

```
IRNUC      : 1H
IRFRQ      : 399.65 MHz
IRSET      : 134500.00 Hz
IRATN      : 511
IRAPW      : 50.0 usec
IRBP1      : 27
IRBP2      : 6
IRRNS      : 0
```

```

ADBIT : 16
CTEMP : 26.1 c
CSPED : 0 Hz
SLVNT : CDCL3

```

RESOL	:	0.24	Hz
BF	:	0.01	Hz
T1	:	0.00	%
T2	:	0.00	%
T3	:	90.00	%
T4	:	100.00	%
REFVL	:	0.00	ppm
XE	:	3997.53	Hz
XS	:	35.74	Hz

operator .

17-DEC-2004 18:35:46.71

DFILE :
SFIL : HIROKOCOMNT : KATSUMURA-LAB
EXMOD : SINGL
IRMOD : BCM
POINT : 32768
FREQ : 27100.27 Hz
SCANS : 1000
DUMMY : 4
ACQTM : 0.6046 sec
PD : 0.8000 sec
RGAIN : 23

PW1 : 10.00 usec

OBNUC : ¹³C
OBFRQ : 100.40 MHz
OBSET : 135500.00 HzIRNUC : ¹H
IRFRQ : 399.65 MHz
IRSET : 134500.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 27
IRBP2 : 6
IRRNS : 0ADBIT : 16
CTEMP : 26.2 C
CSPED : 13 Hz
SLVNT : CDCL3RESOL : 0.83 Hz
BF : 2.00 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 77.00 ppm
XE : 20104.39 Hz
XS : 1029.24 Hz
operator7.012
9.941
13.742
20.488
20.644
26.642
27.999
32.87054.935
55.955
60.159
61.556
73.660
76.679
77.000
77.321
79.361113.841
116.692
116.062137.255
139.427
139.822

156.071

171.151
174.105

28.21

3.142

4.443

2.128

1.0

0.907

1.04

2.024

0.989

0.983

0.947

0.958

Katsunura lab. 13C-13,1df
single pulse decoupled gated NOE

X : parts per Million : 13C

S22

11.48

8.885

1.736

1.091

0.909

1.112

1.871

0.955

1

9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

X : parts per Million : 111

abundance

28.2593

77.3147
77.0001
76.6759

54.5461
54.4889
54.3364
54.2696

66.4358
66.4930

72.4521

79.7460

116.9404

136.9917

155.6985

10.433

7.223

3.243

1.834

3.944

0.66

0.95

1.008

1

0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0

X : parts per Million : 1H

S24

abundance

abundance

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0 3.1 3.2 3.3 3.4 3.5

S30

28-JUN-2004 13:12:19.61

DFILE :
SFIL :COMT : KATSUMURA-LAB
EXMOD : SINGL
IRMOD : NON
POINT : 32768
FREQ : 7993.61 Hz
SCANS : 8
DUMMY : 4
AQTM : 4.0993 sec
PD : 2.9007 sec
RGAIN : 14
PW1 : 11.00 usecOBNUC : ¹H
OBFRQ : 399.65 MHz
OBSET : 134500.00 HzIRNUC : ¹H
IRFRQ : 399.65 MHz
IRSET : 134500.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 27
IRBP2 : 6
IRRNS : 0ADBIT : 16
CTEMP : 25.7 °C
CSPED : 14 Hz
SLVNT : CDCL₃RESOL : 0.24 Hz
BF : 0.01 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 0.00 ppm
XE : 3997.53 Hz
XS : 36.23 Hz
operator

28-JUN-2004 13:50:55.30

DFILE :
SFILE :COMNT : KATSUMURA-LAB
EXMOD : SINGL
IRMOD : BCM
POINT : 32768
FREQ : 27100.27 Hz
SCANS : 1433
DUMMY : 4
ACQTM : 0.6046 sec
PD : 0.8000 sec
RGAIN : 23

PW1 : 10.00 usec

OBNUC : ¹³C
OBFRQ : 100.40 MHz
OBSET : 135500.00 HzIRNUC : ¹H
IRFRQ : 399.65 MHz
IRSET : 134500.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 27
IRBP2 : 6
IRRNS : 0ADBIT : 16
CTEMP : 26.7 °C
CSPED : 13 Hz
SLVNT : CDCL₃RESOL : 0.83 Hz
BF : 2.00 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 77.00 ppm
XE : 20104.39 Hz
XS : 1062.33 Hz
operator

24.602

24.558

9.387

3.367

2.102

0.764

2.181

4.272

3.144

2

0.862

0.99

0.965

9-DEC-2004 14:25:43.91

DFILE :
SFIL : HIROKOCOMT : KATSUMURA-LAB
EXMOD : SINGL
IRMOD : NON
POINT : 32768
FREQU : 7993.61 Hz
SCANS : 8
DUMMY : 4
ACQTM : 4.0993 sec
PD : 2.9007 sec
RGAIN : 17

PW1 : 11.00 usec

OBNUC : 1H
OBFRQ : 399.65 MHz
OBSET : 134500.00 HzIRNUC : 1H
IRFRQ : 399.65 MHz
IRSET : 134500.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 27
IRBP2 : 6
IRRNS : 0ADBIT : 16
CTEMP : 26.1 C
CSPED : 12 Hz
SLVNT : CDCL3RESOL : 0.24 Hz
BF : 0.01 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 7.26 ppm
XE : 3997.53 Hz
XS : 34.27 Hz

operator

15-DEC-2004 18:26:29.37

DFILE : HIROKO
SFIL : HIROKO
COMT : KATSUMURA-LAB
EXMOD : SINGL
IRMOD : BCM
POINT : 32768
FREQ : 27100.27 Hz
SCANS : 1000
DUMMY : 4
ACQTM : 0.6046 sec
PD : 0.8000 sec
RGAIN : 23
PW1 : 10.00 usec

OBNUC : 13C
OBFRQ : 100.40 MHz
OBSET : 135500.00 Hz

IRNUC : 1H
IRFRQ : 399.65 MHz
IRSET : 134500.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 27
IRBP2 : 6
IRRNS : 0

ADBIT : 16
CTEMP : 26.2 C
CSPED : 12 Hz
SLVNT : CDCL3

RESOL : 0.83 Hz
BF : 2.00 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 77.00 ppm
XE : 20104.39 Hz
XS : 1060.67 Hz
operator

1.2

1.1

1.0

0.9

0.8

0.7

0.6

0.5

0.4

0.3

0.2

0.1

0

abundance

190.0

180.0

170.0

160.0

150.0

140.0

130.0

120.0

110.0

100.0

90.0

80.0

70.0

60.0

50.0

40.0

30.0

20.0

10.0

0

X : parts per Million : 13C

S43

11-JUN-2004 16:23:09.90

DFILE :
SFILE :COMNT : KATSUMURA-LAB
EXMOD : SINGL
IRMOD : NON
POINT : 32768
FREQU : 7993.61 Hz
SCANS : 8
DUMMY : 4
ACQTM : 4.0993 sec
PD : 2.9007 sec
RGAIN : 15
PW1 : 16.50 usecOBNUC : 1H
OBFRQ : 399.65 MHz
OBSET : 134500.00 HzIRNUC : 1H
IRFRQ : 399.65 MHz
IRSET : 134500.00 Hz
IRATN : 511
IRRPW : 50.0 usec
IRBP1 : 27
IRBP2 : 6
IRRNS : 0ADBIT : 16
CTEMP : 25.7 C
CSPED : 10 Hz
SLVNT : CDCL3RESOL : 0.24 Hz
BF : 0.01 Hz
T1 : 0.00 %
T2 : 0.00 %
T3 : 90.00 %
T4 : 100.00 %
REFVL : 0.00 ppm
XE : 3997.53 Hz
XS : 40.13 Hz
operator

```

DEFILE :
SFILE :

```

```

COUNT      : KATSUMURA-LAB
EXMOD       : SINGL
IRMOD       : BCM
POINT       : 32768
FREQUENCY   : 27100.27 Hz
SCANS       : 983
DUMMY       : 4
ACQTIME     : 0.6046 sec
PD          : 0.8000 sec
RGAIN       : 23

```

PW1 : 15.00 usec

```
OBNUC : 13C
OBFRQ : 100.40 MHz
OBSET : 135500.00 Hz
```

```
IRNUC      : 1H
IRFRQ      : 399.65 MHz
IRSET      : 134500.00 Hz
IRATN      : 511
IRAPW      : 50.0 usec
IRBP1      : 27
IRBP2      : 6
IRRS       : 0
```

```

ADBIT : 16
CTEMP : 26.6 c
CSPED : 10 Hz
SLVNT : CDCL3

```

```

RESOL : 0.83 Hz
BF      2.00 Hz
T1      0.00 %
T2      0.00 %
T3      90.00 %
T4      100.00 %
REFVL   77.00 ppm
XE       20104.39 Hz
XS       1059.84 Hz
operator

```

29.245

12.09

6.897

2

2.253

0.66

1.322

1.04

3.472

1.003

0.757

1.024

1.064

1.827

1.861

III X : parts per Million : III

0.4

0.3

0.2
S47

0.1

abundance

25.234

2.888

2.0

0.849

0.866

0.824

0.924

1.09

1.039

S48

X : parts per Million : 1H

Yamaguchi-13C-sphingosine-2,4,6
single pulse decoupled gated NOE

X : parts per Million : 13C