Rapid Oligosaccharide Synthesis Using a Fluorous Protective Group

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Experimental Section

General. Part of the products was isolated by column chromatography on silica gel. Fluorous solvent FC-72 and Novec HFE-7200 were purchased from 3M Tokyo. Perfluorooctylpropanol was purchased from Daikin.

Compound 3: β -Alanine ethyl ester hydrochloride (**1**; 5.65 g, 36.8 mmol) and K_2CO_3 (17.0 g, 123 mmol) were added to a solution of compound **2**¹⁰ (7.59 g, 12.3 mmol) in dry CH_3CN (200 mL) at room temperature. After a 17 h reflux, the reaction mixture was added to water, and then extracted three times with AcOEt. The combined AcOEt layers were washed with 2M HCl, saturated aqueous $NaHCO_3$, and brine. The organic layers were dried over anhydrous Na_2SO_4 , and evaporated. The almost pure **3** (5.89 g, 83 %) thus obtained was used in the next step without further purification. The authentic sample was obtained as a colorless oil by purifying part of the sample (silica gel column chromatography; AcOEt). 1H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, J = 7.3 Hz, 3H), 1.47 (brs, 1H), 1.77 (m, 2H), 2.16 (m, 2H), 2.50 (t, J = 6.3 Hz, 2H), 2.70 (t, J = 6.8 Hz, 2H), 2.88 (t, J = 6.3 Hz, 2H), 4.15 (q, J = 7.3 Hz, 2H). HRMS (FAB): Calcd for $C_{16}H_{17}F_{17}NO_2$ ($M+H^+$): 578.0988, Found: 578.0976.

Compound 4: Jone's reagent²¹ (1.93M, 21.6 mL) was added to a solution of perfluorooctylpropanol (10.0 g, 20.9 mmol) in acetone (200 mL) at 0°C. After stirring for 4h at 0°C, the reaction mixture was added to cool water. The reaction mixture was extracted three times with AcOEt. The combined AcOEt layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated. The residue was partitioned between toluene and FC-72 ($\times 3$). The combined FC-72 layers were evaporated to give compound **4**¹¹ (9.67 g, 94 %).

Compound 5a: Triethylamine (4.27 mL, 30.6 mmol) and benzotriazol-1-yloxytripyrrolidinophosphonium hexafluorophosphate (PyBOP; 6.37 g, 12.2 mmol) were added to a solution of compound **3** (5.89 g, 10.2 mmol) and **4** (5.27 g, 10.7 mmol) in dry CH_2Cl_2 (160 mL) at room temperature. After stirring for 3h at room temperature, 5% aqueous citric acid was added to the reaction mixture. The reaction mixture was extracted three times with AcOEt. The combined AcOEt layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated. The crude product was purified by column chromatography on silica gel (hexane-AcOEt, 3:1) to give compound **5a** (9.98 g, 93%) as a white amorphous solid. 1H NMR (400 MHz, $CDCl_3$): δ = 1.27 (m, 3H), 1.87 (m, 2H), 2.10 (m, 2H), 2.61 (m, 6H), 3.45 (m, 2H), 3.64 (m, 2H), 4.16 (m, 2H); MALDI-TOF-MS: Calcd for $C_{27}H_{20}F_{34}NO_3$ ($M+H^+$): 1052.1, Found: 1051.1.

Compound 6: A sodium hydroxide aqueous solution (1M, 80 mL) was added to a solution of compound **5a** (9.98 g, 9.49 mmol) in 1,4-dioxane (160 mL) at room temperature. After stirring for 4 h at 70 °C, 2M HCl was added, and the reaction mixture was adjusted to pH 2. The reaction mixture was

extracted three times with AcOEt. The combined AcOEt layers were washed with brine, dried over anhydrous Na₂SO₄, and evaporated. The obtained compound **6** (9.52 g, 98 %) was used in the next step without further purification. The authentic sample was obtained as white needle crystals by purifying part of the sample (recrystallization from AcOEt). m.p. = 126-127°C. ¹H NMR (400 MHz, CDCl₃-CD₃OD = 5: 3): δ = 1.92 (m, 2H), 2.15 (m, 2H), 2.65 (m, 6H), 3.49 (m, 2H), 3.66 (m, 2H); MALDI-TOF-MS: Calcd for C₂₅H₁₆F₃₄NO₃ (M+H⁺): 1024.1, Found: 1024.6; Calcd for C₂₅H₁₅F₃₄NO₃Na (M+Na⁺): 1046.1, Found: 1046.5.

Compound 8: 4-(Dimethylamino)pyridine (DMAP, 1.71 g, 14.0 mmol) and *N,N'*-dicyclohexylcarbodiimide (DCC, 4.33 g, 21.0 mmol) were added to a solution of compound **7**¹³ (1.53 g, 3.51 mmol) and **6** (11.1 g, 10.8 mmol) in dry CH₂Cl₂ (75 mL). After stirring for 20 h at room temperature, toluene was added to the reaction mixture. The reaction mixture was extracted three times with FC-72. The combined FC-72 layers were evaporated to give the fluororous compound **8** (10.6 g). The fluororous compound **8** was used in the next step without further purification. The authentic sample was obtained as a white amorphous solid by purifying part of the sample (silica gel column chromatography; hexane-AcOEt, 5:2). R_f = 0.53 (Hexane : AcOEt = 2 : 1); [α]_D²⁷ = 3.9° (c = 1.03 in FC-72); ¹H NMR (400 MHz, CDCl₃): δ = 1.83 (m, 6H), 2.05 (m, 6H), 2.31-2.78 (m, 18H), 3.16 (m, 2H), 3.24-3.42 (m, 8H), 3.46 (s, 3H), 3.66 (m, 4H), 3.91 (m, 1H), 4.77 (m, 1H), 5.30 (m, 3H), 7.26 (m, 9H), 7.43 (m, 6H); MALDI-TOF-MS: Calcd for C₁₀₁H₆₇F₁₀₂N₃O₁₂Na (M+Na⁺): 3474.3, Found: 3476.8.

Compound 9: (+)-Camphorsulfonic acid (CSA, 7.14 g, 30.7 mmol) was added to a solution of compound **8** (10.6 g) in CHCl₃ (150 mL)-MeOH (75 mL). After stirring for 3 h at room temperature, toluene was added to the reaction mixture. The reaction mixture was extracted three times with FC-72. The combined FC-72 layers were evaporated to give the fluororous compound **9** (9.87 g). The fluororous compound **9** was used in the next step without further purification. The authentic sample was obtained as a colorless oil by purifying part of the sample (silica gel column chromatography; Hexane-AcOEt, 1 : 2). R_f = 0.43 (Hexane : AcOEt = 1 : 2); [α]_D²⁸ = 2.8° (c = 1.01 in FC-72); ¹H NMR (400 MHz, CDCl₃): δ = 1.87 (m, 6H), 2.05 (m, 6H), 2.47-2.73 (m, 18H), 3.40 (s, 3H), 3.42 (m, 8H), 3.67 (m, 8H), 4.72 (m, 1H), 5.30 (m, 3H); MALDI-TOF-MS: Calcd for C₈₂H₅₃F₁₀₂N₃O₁₂Na (M+Na⁺): 3232.2, Found: 3230.9; Calcd for C₈₂H₅₃F₁₀₂N₃O₁₂K (M+K⁺): 3248.2, Found: 3247.0.

Compound 11: Molecular sieves 4A powder (7.0 g) was added to a solution of compound **9** (1.35 g) and **10** (1.05 g, 2.11 mmol) in dry ether (56 mL)-dry EtOC₄F₉ (14 mL) under an argon atmosphere. After stirring for 2 h at 0 °C, TMS-OTf (230 μL, 1.27 mmol) was added to the reaction mixture at 0 °C. After stirring for 30 min at 0 °C, triethylamine (0.21 mL) was added to the reaction mixture. The

reaction mixture was filtered on Celite, and washed with AcOEt. The filtrate was then evaporated. The residue was partitioned between MeOH and FC-72 (×3). The combined FC-72 layers were evaporated to give the fluororous compound **11** (1.50 g). The fluororous compound **11** was used in the next step without further purification. The authentic sample was obtained as a white amorphous solid by purifying part of the sample (silica gel column chromatography; Hexane-AcOEt, 1 : 1). $R_f = 0.48$ (Hexane : AcOEt = 1 : 1); $[\alpha]_D^{28} = 1.7^\circ$ ($c = 1.01$ in FC-72); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 1.88$ (m, 6H), 1.97 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 2.10 (m, 6H), 2.13 (s, 3H), 2.56 (m, 18H), 3.41 (s, 3H), 3.44 (m, 6H), 3.64 (m, 7H), 3.92 (m, 3H), 4.09 (m, 1H), 4.20 (m, 1H), 4.45 (m, 1H), 4.74 (m, 1H), 5.05 (m, 1H), 5.22 (m, 4H), 5.41 (m, 1H); MALDI-TOF-MS: Calcd for $\text{C}_9\text{H}_7\text{F}_{102}\text{N}_3\text{O}_{21}\text{Na}$ ($\text{M}+\text{Na}^+$): 3562.2, Found: 3561.1; Calcd for $\text{C}_9\text{H}_7\text{F}_{102}\text{N}_3\text{O}_{21}\text{K}$ ($\text{M}+\text{K}^+$): 3578.4, Found: 3577.2.

Compound 12: A solution of sodium methoxide in methanol (28%, one drop) was added to a solution of compound **11** (1.25 g) in Et_2O (10 mL) and MeOH (10 mL) at room temperature. After stirring for 22 h at room temperature, Amberlite IR-120 (H^+ form) was added, and the reaction mixture was neutralized. After filtration, the filtrate was evaporated. The residue was partitioned between MeOH and FC-72 (×3). The combined FC-72 layers were evaporated to give the fluororous compound **5b** (1.05 g, 81% in 4 steps from **7**) as a white amorphous solid. The methanol layer was evaporated, and the residue was purified by column chromatography on silica gel ($\text{CHCl}_3\text{-MeOH-H}_2\text{O} = 6:4:1$) to give pure compound **12** (125 mg, 59% in 4 steps from **7**) as a white amorphous solid. Compound **12**: $[\alpha]_D^{28} = 34.3^\circ$ ($c = 1.09$ in MeOH); $^1\text{H NMR}$ (600 MHz, D_2O): $\delta = 3.26$ (s, 3H), 3.41 (t, $J = 7.6$ Hz, 1H), 3.51 (dd, $J = 10.0, 3.4$ Hz, 1H), 3.55 (dd, $J = 7.6, 4.1$ Hz, 1H), 3.62 (m, 5H), 3.76 (m, 3H), 4.04 (d, $J = 11.0$ Hz, 1H), 4.29 (d, $J = 7.6$ Hz, 1H), 4.60 (s, 1H); $^{13}\text{C NMR}$ (150 MHz, CD_3OD): $\delta = 55.4, 62.5, 68.5, 69.9, 70.3, 71.9, 72.4, 72.6, 73.4, 74.8, 76.7, 102.8, 105.4$; HRMS (ESI-TOF): Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_{11}\text{Na}$ ($\text{M}+\text{Na}^+$): 379.1211, Found: 379.1220.

Compound **5b**: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 1.87$ (m, 2H), 2.10 (m, 2H), 2.62 (m, 6H), 3.45 (m, 2H), 3.64 (m, 2H), 3.69 and 3.72 (each s, 3H, splits of O-Me peak); MALDI-TOF-MS: Calcd for $\text{C}_{26}\text{H}_{18}\text{F}_{34}\text{NO}_3$ ($\text{M}+\text{H}^+$): 1038.1, Found: 1038.5; Calcd for $\text{C}_{26}\text{H}_{17}\text{F}_{34}\text{NO}_3\text{Na}$ ($\text{M}+\text{Na}^+$): 1060.1, Found: 1060.2.

Compound 14: Molecular sieves 4A powder (7.2 g) was added to a solution of compound **9** (7.01 g) and **13** (7.52 g, 10.9 mmol) in dry ether (100 mL)-dry EtOC_4F_9 (60 mL) under an argon atmosphere. After stirring for 2 h at 0°C , TMS-OTf (1.20 mL, 6.63 mmol) was added to the reaction mixture at 0°C . After stirring for 40 min at 0°C , triethylamine (1.0 mL) was added to the reaction mixture. The reaction mixture was filtered on Celite, and washed with AcOEt. The filtrate was then evaporated. The residue was partitioned between MeOH and FC-72 (×3). The combined FC-72 layers were

evaporated to give the fluoros compound **14** (8.29 g). The fluoros compound **14** was used in the next step without further purification. The authentic sample was obtained as a white amorphous solid by purifying part of the sample (silica gel column chromatography; Hexane-AcOEt, 2:1). $R_f = 0.50$ (Hexane : AcOEt = 3 : 2); $[\alpha]_D^{28} = 3.5^\circ$ ($c = 1.00$ in FC-72); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 1.04$ (s, 9H), 1.85 (m, 6H), 1.90 (s, 3H), 1.98 (s, 3H), 2.05 (s, 3H), 2.09 (m, 6H), 2.47-2.81 (m, 18H), 3.41 (s, 3H), 3.47-3.68 (m, 14H), 3.73 (brs, 2H), 3.91 (m, 1H), 4.02 (m, 1H), 4.48 (m, 1H), 4.73 (brs, 1H), 5.07 (m, 2H), 5.21 (m, 3H), 5.30 (m, 1H), 7.38 (m, 6H), 7.67 (m, 4H); MALDI-TOF-MS: Calcd for $\text{C}_{110}\text{H}_{87}\text{F}_{102}\text{N}_3\text{O}_{20}\text{SiNa}$ ($\text{M}+\text{Na}^+$): 3758.4, Found: 3756.4; Calcd for $\text{C}_{110}\text{H}_{87}\text{F}_{102}\text{N}_3\text{O}_{20}\text{SiK}$ ($\text{M}+\text{K}^+$): 3774.4, Found: 3772.2.

Compound 15: To a solution of compound **14** (5.16 g) in dry THF (75 mL) was added 70% HF-pyridine (7.5 mL) at room temperature. After stirring for 17 h at room temperature, the reaction mixture was partitioned between toluene, saturated aqueous NaHCO_3 , and FC-72 ($\times 3$). The combined FC-72 layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated to give the fluoros compound **15** (4.83 g). The fluoros compound **15** was used in the next step without further purification. The authentic sample was obtained as a white amorphous solid by purifying part of the sample (silica gel column chromatography; Hexane-AcOEt, 1 : 1). $R_f = 0.16$ (Hexane : AcOEt = 1 : 1); $[\alpha]_D^{28} = 1.9^\circ$ ($c = 1.01$ in FC-72); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 1.87$ (m, 6H), 2.00 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.10 (m, 6H), 2.45-2.80 (m, 19H), 3.39 (s, 3H), 3.43-3.72 (m, 16H), 3.92 (m, 2H), 4.54 (m, 1H), 4.70 (brs, 1H), 5.00 (m, 2H), 5.25 (m, 4H). MALDI-TOF-MS: Calcd for $\text{C}_{94}\text{H}_{69}\text{F}_{102}\text{N}_3\text{O}_{20}\text{Na}$ ($\text{M}+\text{Na}^+$): 3520.3, Found: 3520.2; Calcd for $\text{C}_{94}\text{H}_{69}\text{F}_{102}\text{N}_3\text{O}_{20}\text{K}$ ($\text{M}+\text{K}^+$): 3536.2, Found: 3536.2.

Compound 16: Molecular sieves 4A powder (6.2 g) was added to a solution of compound **15** (4.35 g) and **13** (4.29 g, 6.23 mmol) in dry ether (60 mL)-dry EtOC_4F_9 (35 mL) under an argon atmosphere. After stirring for 2.5 h at 0°C , TMS-OTf (0.68 mL, 3.76 mmol) was added to the reaction mixture at 0°C . After stirring for 30 min at 0°C , triethylamine (0.57 mL) was added to the reaction mixture. The reaction mixture was filtered on Celite, and washed with AcOEt. The filtrate was then evaporated. The residue was partitioned between MeOH and FC-72 ($\times 3$). The combined FC-72 layers were evaporated to give the fluoros compound **16** (5.09 g). The fluoros compound **16** was used in the next step without further purification. The authentic sample was obtained as a white amorphous solid by purifying part of the sample (silica gel column chromatography; Hexane-AcOEt, 13 : 7). $R_f = 0.64$ (Hexane : AcOEt = 1 : 1); $[\alpha]_D^{28} = 4.5^\circ$ ($c = 1.02$ in AcOEt); $^1\text{H NMR}$ (600 MHz, CDCl_3): $\delta = 1.04$ (s, 9H), 1.88 (s, 3H), 1.90 (m, 6H), 1.93 (s, 3H), 1.98 (s, 6H), 2.05 (s, 3H), 2.06 (s, 3H), 2.08 (m, 6H), 2.56 (m, 13H), 2.72 (m, 5H), 3.30-3.80 (m, 21H), 4.07 (m, 1H), 4.50 (m, 2H), 4.74 (brs, 1H), 4.87-5.31 (m,

9H), 7.40 (m, 6H), 7.65 (m, 4H). MALDI-TOF-MS: Calcd for $C_{122}H_{103}F_{102}N_3O_{28}SiNa$ ($M+Na^+$): 4046.5, Found: 4045.1.

Compound 17: To a solution of compound **16** (2.68 g) in dry THF (40 mL) was added 70% HF-pyridine (4.0 mL) at room temperature. After stirring for 19 h at room temperature, the reaction mixture was partitioned between toluene, saturated aqueous $NaHCO_3$, and FC-72 ($\times 3$). The combined FC-72 layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated to give the fluororous compound **17** (2.62 g). The fluororous compound **17** was used in the next step without further purification. The authentic sample was obtained as a white amorphous solid by purifying part of the sample (silica gel column chromatography; Hexane-AcOEt, 4 : 5). $R_f = 0.11$ (Hexane : AcOEt = 1 : 1); $[\alpha]_D^{28} = 1.4^\circ$ ($c = 1.00$ in AcOEt); 1H NMR (400 MHz, $CDCl_3$): $\delta = 1.89$ (m, 6H), 1.97 (s, 3H), 2.00 (s, 3H), 2.03 (s, 6H), 2.04 (s, 6H), 2.05 (m, 6H), 2.46-2.88 (m, 19H), 3.40 (s, 3H), 3.43-3.71 (m, 18H), 3.91 (m, 2H), 4.00 (m, 1H), 4.50 (m, 2H), 4.72 (brs, 1H), 4.98 (m, 4H), 5.23 (m, 5H). MALDI-TOF-MS: Calcd for $C_{106}H_{85}F_{102}N_3O_{28}Na$ ($M+Na^+$): 3808.4, Found: 3807.1; Calcd for $C_{106}H_{85}F_{102}N_3O_{28}K$ ($M+K^+$): 3824.3, Found: 3823.9.

Compound 18: Molecular sieves 4A powder (3.1 g) was added to a solution of compound **17** (2.22 g) and **13** (2.02 g, 2.93 mmol) in dry ether (30 mL)-dry $EtOC_4F_9$ (18 mL) under an argon atmosphere. After stirring for 3.5 h at 0 °C, TMS-OTf (0.32 mL, 1.77 mmol) was added to the reaction mixture at 0 °C. After stirring for 40 min at 0 °C, triethylamine (0.27 mL) was added to the reaction mixture. The reaction mixture was filtered on Celite, and washed with AcOEt. The filtrate was then evaporated. The residue was partitioned between MeOH and FC-72 ($\times 3$). The combined FC-72 layers were evaporated to give the fluororous compound **18** (2.33 g). The fluororous compound **18** was used in the next step without further purification. The authentic sample was obtained as a white amorphous solid by purifying part of the sample (silica gel column chromatography; Hexane-AcOEt, 3:2). $R_f = 0.52$ (Hexane : AcOEt = 1 : 1); $[\alpha]_D^{28} = 3.3^\circ$ ($c = 1.02$ in AcOEt); 1H NMR (600 MHz, $CDCl_3$): $\delta = 1.04$ (s, 9H), 1.73-2.26 (m, 39H), 2.24-2.93 (m, 18H), 3.31-3.70 (m, 23H), 3.72-4.12 (m, 4H), 4.50 (m, 3H), 4.74 (m, 1H), 4.85-5.38 (m, 12H), 7.40 (m, 6H), 7.65 (m, 4H); MALDI-TOF-MS: Calcd for $C_{134}H_{119}F_{102}N_3O_{36}SiNa$ ($M+Na^+$): 4334.6, Found: 4337.2; Calcd for $C_{134}H_{119}F_{102}N_3O_{36}SiK$ ($M+K^+$): 4350.5, Found: 4352.2

Compound 19: To a solution of compound **18** (1.66 g) in dry THF (25 mL) was added 70% HF-pyridine (2.5 mL) at room temperature. After stirring for 20 h at room temperature, the reaction mixture was partitioned between toluene, saturated aqueous $NaHCO_3$, and FC-72 ($\times 4$). The combined FC-72 layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated. The residue was purified as a white amorphous solid by column chromatography on silica gel (Hexane-AcOEt, 3:4) to

give pure compound **19** (195 mg, 11 % in 8 steps from **7**). $R_f = 0.38$ (Hexane : AcOEt = 1 : 2); $[\alpha]_D^{28} = 0.1^\circ$ ($c = 1.85$ in AcOEt); ^1H NMR (600 MHz, CDCl_3): $\delta = 1.70\text{--}2.26$ (m, 39H), 2.37–2.92 (m, 18H), 3.31–3.81 (m, 23H), 3.87 (m, 3H), 4.04 (m, 1H), 4.51 (m, 2H), 4.60 (m, 1H), 4.72 (m, 1H), 4.84–5.09 (m, 6H), 5.12–5.38 (m, 6H); MALDI-TOF-MS: Calcd for $\text{C}_{118}\text{H}_{101}\text{F}_{102}\text{N}_3\text{O}_{36}\text{Na}$ ($\text{M}+\text{Na}^+$): 4096.4, Found: 4094.6; Calcd for $\text{C}_{118}\text{H}_{101}\text{F}_{102}\text{N}_3\text{O}_{36}\text{K}$ ($\text{M}+\text{K}^+$): 4112.4, Found: 4111.2.

Compound 20: A sodium methoxide solution in methanol (28%, one drop) was added to a solution of compound **19** (116 mg, 28.6 μmol) in Et_2O (2 mL) and MeOH (2 mL) at room temperature. After stirring for 18 h at room temperature, Amberlite IR-120 (H^+ form) was added, and the reaction mixture was neutralized. After filtration, the filtrate was evaporated. The residue was partitioned between AcOEt and H_2O ($\times 3$). The combined H_2O layers were evaporated, and the residue was purified by column chromatography on Sephadex LH-20 ($\text{MeOH} : \text{H}_2\text{O} = 1 : 1$) to give pure compound **20** (19.2 mg, 99 %) as a white amorphous solid. $[\alpha]_D^{28} = -10.4^\circ$ ($c = 1.29$ in H_2O); ^1H NMR (600 MHz, D_2O): $\delta = 3.28$ (m, 4H), 3.36 (m, 4H), 3.44 (m, 6H), 3.58 (m, 2H), 3.70 (m, 4H), 3.86 (m, 5H), 4.47 (d, $J = 8.2$ Hz, 1H), 4.48 (d, $J = 8.9$ Hz, 1H), 4.49 (d, $J = 7.7$ Hz, 1H), 4.71 (s, 1H); ^{13}C NMR (150 MHz, D_2O): $\delta = 54.88, 60.62, 66.37, 68.47, 68.63, 68.79, 69.28, 69.35, 69.52, 69.73, 70.32, 71.34, 72.94, 72.98, 74.84, 75.38, 75.46, 75.55, 75.81, 100.87, 102.76, 102.79, 102.86$; HRMS (ESI-TOF): Calcd for $\text{C}_{25}\text{H}_{44}\text{O}_{21}\text{Na}$ ($\text{M}+\text{Na}^+$): 703.2267, Found: 703.2287.

Compound 22: TBDPS-Cl (17.2 mL, 68.1 mmol) was added to a solution of compound **21**¹⁸ (10.0 g, 45.4 mmol) in pyridine (100 mL) at room temperature. After stirring for 4 h at room temperature, acetic anhydride (42.8 mL, 454 mmol) was added to the reaction mixture. After stirring for 19 h at room temperature, methanol (80 mL) was added to the reaction mixture at 0 $^\circ\text{C}$. Almost of methanol was evaporated off. The residue was added to water, and extracted three times with AcOEt. The combined AcOEt layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated. The residue was purified by column chromatography on silica gel ($\text{Hexane-EtOAc} = 3 : 1$) to give compound **22** (24.9 g, 93%) as colorless plate crystals. m.p. = 117–118 $^\circ\text{C}$. $[\alpha]_D^{23} = -22.2^\circ$ ($c = 1.01$ in CHCl_3). ^1H NMR (600 MHz, CDCl_3): $\delta = 1.03$ (s, 9H), 1.99 (s, 3H), 2.01 (s, 3H), 2.05 (s, 3H), 3.67 (m, 1H), 3.76 (m, 2H), 4.05 (dd, $J = 14.4, 6.2$ Hz, 1H), 4.30 (dd, $J = 14.4, 4.8$ Hz, 1H), 4.48 (d, $J = 8.2$ Hz, 1H), 5.05 (dd, $J = 10.3, 3.4$ Hz, 1H), 5.21 (m, 3H), 5.55 (d, $J = 3.4$ Hz, 1H), 5.81 (m, 1H), 7.41 (m, 6H), 7.62 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3): $\delta = 19.04, 20.63, 20.65, 20.78, 26.71, 61.26, 67.13, 69.24, 69.78, 71.30, 73.39, 100.06, 117.38, 127.79, 129.83, 129.90, 132.81, 133.01, 133.45, 135.57, 135.62, 169.48, 170.12, 170.21$; Anal. Calcd for $\text{C}_{31}\text{H}_{40}\text{O}_9\text{Si}$: C, 63.68; H, 6.90. Found: C, 63.50; H, 7.02.

Compound 23: Pd(PPh₃)₄ (10.0 g, 8.65 mmol) was added to a solution of compound **22** (24.6 g, 42.1 mmol) in AcOH (200 mL) under an argon atmosphere. After stirring for 1 h at 80 °C, toluene (80 mL) was added to the reaction mixture at room temperature. The reaction mixture was then evaporated. The residue was purified by column chromatography on silica gel (Hexane-EtOAc = 2 : 1) to give a deallylated compound (18.3 g, 80%). DBU (1.50 mL, 10.0 mmol) and trichloroacetonitrile (20.0 mL, 202 mmol) were added to a solution of the above deallylated compound (18.3 g, 33.6 mmol) in dry CH₂Cl₂ (50 mL) at 0 °C. After stirring for 1 h at 0 °C, the reaction mixture was purified by column chromatography on silica gel (Hexane-EtOAc = 3 : 1) to give compound **23** (20.4 g, 88%) as a white amorphous solid. $[\alpha]_D^{23} = 49.5^\circ$ (c = 1.00 in CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ = 1.00 (s, 9H), 2.02 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 3.63 (dd, *J* = 10.0, 7.8 Hz, 1H), 3.71 (dd, *J* = 10.0, 6.1 Hz, 1H), 4.31 (t, *J* = 7.3 Hz, 1H), 5.32 (dd, *J* = 11.0, 3.7 Hz, 1H), 5.46 (dd, *J* = 11.0, 3.2 Hz, 1H), 5.73 (d, *J* = 3.2 Hz, 1H), 6.55 (d, *J* = 3.7 Hz, 1H), 7.37 (m, 6H), 7.58 (m, 4H), 8.60 (brs, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 19.11, 20.61, 20.77, 26.70, 61.24, 67.22, 67.41, 67.84, 71.47, 93.56, 127.64, 127.67, 129.71, 129.76, 132.74, 132.78, 135.44, 160.84, 169.77, 169.82, 169.99; MALDI-TOF-MS: Calcd for C₃₀H₃₆Cl₃NO₉SiNa (M+Na⁺): 710.1, Found: 710.0.

Compound 25: DMAP (2.54 g, 20.8 mmol) and DCC (6.42 g, 31.1 mmol) were added to a solution of compound **24**¹⁹ (2.66 g, 5.2 mmol) and **6** (16.5 g, 16.1 mmol) in dry CH₂Cl₂ (140 mL). After stirring for 2 h at room temperature, toluene (100 mL) was added to the reaction mixture. Almost all of the CH₂Cl₂ was evaporated off, and the reaction mixture was extracted three times with FC-72. The combined FC-72 layers were evaporated to give the fluorous compound **25** (17.6 g). The fluorous compound **25** was used in the next step without further purification. The authentic sample was obtained by purifying part of the sample (silica gel column chromatography; hexane-AcOEt = 5:2). Colorless oil; *R*_f = 0.50 (Hexane : AcOEt = 2 : 1); $[\alpha]_D^{23} = -5.5^\circ$ (c = 1.01 in FC-72). ¹H NMR (400 MHz, CDCl₃): δ = 1.82 (m, 6H), 2.08 (m, 6H), 2.51 (m, 18H), 3.13 (m, 1H), 3.42 (m, 13H), 3.77 (m, 1H), 4.51 (m, 1H), 4.58 (m, 1H), 4.86 (m, 1H), 5.02 (m, 1H), 5.16 (m, 1H), 5.59 (m, 1H), 7.31 (m, 20H); MALDI-TOF-MS: Calcd for C₁₀₇H₇₁F₁₀₂N₃O₁₂Na (M+Na⁺): 3550.3, Found: 3550.4.

Compound 26: (+)-Camphorsulfonic acid (4.21 g, 18.1 mmol) and lithium chloride (769 mg, 18.1 mmol) were added to a solution of compound **25** (6.40 g) in CHCl₃ (100 mL)-MeOH (50 mL). After stirring for 3 h at room temperature, the reaction mixture was added to saturated aqueous NaHCO₃, and extracted three times with AcOEt. The combined AcOEt layers were washed with brine, dried over anhydrous Na₂SO₄, and evaporated. The residue was partitioned between toluene and FC-72 (×3). The combined FC-72 layers were evaporated to give the fluorous compound **26** (5.73 g). The fluorous compound **26** was used immediately in the next step without further purification.

Compound 27: Molecular sieves 4A powder (4.0 g) was added to a solution of compound **26** (4.39 g) and **23** (4.60 g, 6.68 mmol) in dry ether (70 mL)-dry EtOC₄F₉ (40 mL) under an argon atmosphere. After stirring for 3 h at 0 °C, TMS-OTf (726 µL, 4.01 mmol) was added to the reaction mixture at 0 °C. After stirring for 30 min at 0 °C, triethylamine (1.0 mL) was added to the reaction mixture. The reaction mixture was filtered on Celite. The filtrate was added to saturated aqueous NaHCO₃, and extracted three times with AcOEt. The combined AcOEt layers were washed with brine, dried over anhydrous Na₂SO₄, and evaporated. The residue was partitioned between MeOH and FC-72 (×3). The combined FC-72 layer was evaporated to give the fluororous compound **27** (5.05 g). The fluororous compound **27** was used in the next step without further purification. The authentic sample was obtained as a white amorphous solid by purifying part of the sample (silica gel column chromatography; Hexane-AcOEt, 2 : 1). $R_f = 0.40$ (Hexane : AcOEt = 3 : 2); $[\alpha]_D^{23} = -0.5^\circ$ (c = 1.00 in FC-72). ¹H NMR (400 MHz, CDCl₃): δ = 1.03 (s, 9H), 1.86 (m, 6H), 1.98 (s, 3H), 2.02 (s, 6H), 2.04 (m, 6H), 2.50 (m, 18H), 3.39-3.79 (m, 18H), 4.54 (m, 3H), 4.96 (m, 3H), 5.17 (m, 2H), 5.32 (m, 1H), 5.57 (d, $J = 2.4$ Hz, 1H), 7.36 (m, 11H), 7.61 (m, 4H). MALDI-TOF-MS: Calcd for C₁₁₆H₉₁F₁₀₂N₃O₂₀SiNa (M+Na⁺): 3834.4, Found: 3834.8. Calcd for C₁₁₆H₉₁F₁₀₂N₃O₂₀SiK (M+K⁺): 3850.4, Found: 3850.4.

Compound 28: To a solution of compound **27** (5.05 g) in dry THF (75 mL) was added 70% HF-pyridine (7.5 mL) at room temperature. After stirring for 9 h at room temperature, the reaction mixture was partitioned between toluene, saturated aqueous NaHCO₃, and FC-72 (×3). The combined FC-72 layers were washed with brine, dried over anhydrous Na₂SO₄, and evaporated to give the fluororous compound **28** (4.57 g). The fluororous compound **28** was used immediately in the next step without further purification.

Compound 29: Molecular sieves 4A powder (3.0 g) was added to a solution of compound **27** (2.32 g) and **23** (2.23 g, 3.25 mmol) in dry ether (27 mL)-dry EtOC₄F₉ (15 mL) under an argon atmosphere. After stirring for 2 h at 0 °C, TMS-OTf (353 µL, 1.95 mmol) was added to the reaction mixture at 0 °C. After stirring for 30 min at 0 °C, triethylamine (0.5 mL) was added to the reaction mixture. The reaction mixture was filtered on Celite. The filtrate was added to saturated aqueous NaHCO₃, and extracted three times with AcOEt. The combined AcOEt layers were washed with brine, dried over anhydrous Na₂SO₄, and evaporated. The residue was partitioned between MeOH and FC-72 (×3). The combined FC-72 layer was evaporated to give the fluororous compound **29** (2.62 g). The fluororous compound **29** was used in the next step without further purification. The authentic sample was obtained as a white amorphous solid by purifying part of the sample (silica gel column

chromatography; Hexane-AcOEt, 3 : 2). $R_f = 0.68$ (Hexane : AcOEt = 1 : 1); $[\alpha]_D^{25} = -3.3^\circ$ ($c = 1.01$ in FC-72). ^1H NMR (400 MHz, CDCl_3): $\delta = 1.03$ (s, 9H), 1.88 (m, 6H), 1.93 (s, 3H), 1.98 (s, 3H), 2.02 (s, 6H), 2.03 (s, 3H), 2.07 (s, 3H), 2.08 (m, 6H), 2.46-2.77 (m, 18H), 3.36-3.87 (m, 21H), 4.52 (m, 4H), 4.97 (m, 4H), 5.13 (m, 2H), 5.23 (m, 1H), 5.35 (m, 2H), 5.58 (d, $J = 2.4$ Hz, 1H), 7.35 (m, 11H), 7.60 (m, 4H). MALDI-TOF-MS: Calcd for $\text{C}_{128}\text{H}_{107}\text{F}_{102}\text{N}_3\text{O}_{28}\text{SiNa}$ ($\text{M}+\text{Na}^+$): 4122.5, Found: 4124.2; Calcd for $\text{C}_{128}\text{H}_{107}\text{F}_{102}\text{N}_3\text{O}_{28}\text{SiK}$ ($\text{M}+\text{K}^+$): 4138.5, Found: 4140.6.

Compound 30: To a solution of compound **29** (2.45 g) in dry THF (40 mL) was added 70% HF-pyridine (4.0 mL) at room temperature. After stirring for 9 h at room temperature, the reaction mixture was partitioned between toluene, saturated aqueous NaHCO_3 , and FC-72 ($\times 3$). The combined FC-72 layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated to give the fluororous compound **30** (2.26 g). The fluororous compound **30** was used immediately in the next step without further purification.

Compound 31: Molecular sieves 4A powder (1.5 g) was added to a solution of compound **30** (1.30 g) and **23** (1.16 g, 1.68 mmol) in dry ether (14 mL)-dry EtOC_4F_9 (7 mL) under an argon atmosphere. After stirring for 2 h at 0°C , TMS-OTf (183 μL , 1.01 mmol) was added to the reaction mixture at 0°C . After stirring for 30 min at 0°C , triethylamine (0.5 mL) was added to the reaction mixture. The reaction mixture was filtered on Celite. The filtrate was added to saturated aqueous NaHCO_3 , and extracted three times with AcOEt. The combined AcOEt layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated. The residue was partitioned between MeOH and FC-72 ($\times 3$). The combined FC-72 layer was evaporated to give the fluororous compound **31** (1.39 g). The fluororous compound **31** was used in the next step without further purification. The authentic sample was obtained as a white amorphous solid by purifying part of the sample (silica gel column chromatography; Hexane-AcOEt, 5 : 4). $R_f = 0.56$ (Hexane : AcOEt = 1 : 1); $[\alpha]_D^{25} = -1.7^\circ$ ($c = 1.38$ in CHCl_3). ^1H NMR (600 MHz, CDCl_3): $\delta = 1.02$ (s, 9H), 1.87 (m, 6H), 1.91 (s, 3H), 1.95 (s, 3H), 1.97 (s, 3H), 2.00 (s, 3H), 2.03 (s, 9H), 2.05 (s, 3H), 2.10 (m, 6H), 2.12 (s, 3H), 2.43-2.76 (m, 18H), 3.34-3.88 (m, 24H), 4.43 (m, 2H), 4.57 (m, 3H), 4.96 (m, 5H), 5.15 (m, 4H), 5.31 (d, $J = 3.4$ Hz, 1H), 5.36 (brs, 2H), 5.56 (d, $J = 3.4$ Hz, 1H), 7.28-7.44 (m, 11H), 7.60 (m, 4H); MALDI-TOF-MS: Calcd for $\text{C}_{140}\text{H}_{123}\text{F}_{102}\text{N}_3\text{O}_{36}\text{SiNa}$ ($\text{M}+\text{Na}^+$): 4410.6, Found: 4408.4; Calcd for $\text{C}_{140}\text{H}_{123}\text{F}_{102}\text{N}_3\text{O}_{36}\text{SiK}$ ($\text{M}+\text{K}^+$): 4426.6, Found: 4424.7.

Compound 32: To a solution of compound **31** (1.39 g) in dry THF (20 mL) was added 70% HF-pyridine (2.0 mL) at room temperature. After stirring for 8 h at room temperature, the reaction mixture was partitioned between toluene, saturated aqueous NaHCO_3 , and FC-72 ($\times 3$). The combined FC-72

layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated to give the fluororous compound **32** (1.30 g). The fluororous compound **32** was used immediately in the next step without further purification.

Compound 33: Molecular sieves 4A powder (1.0 g) was added to a solution of compound **32** (703 mg) and **23** (1.17 g, 1.69 mmol) in dry ether (8 mL)-dry EtOC_4F_9 (4 mL) under an argon atmosphere. After stirring for 2 h at 0 °C, TMS-OTf (92 μL , 0.51 mmol) was added to the reaction mixture at 0 °C. After stirring for 30 min at 0 °C, triethylamine (0.4 mL) was added to the reaction mixture. The reaction mixture was filtered on Celite. The filtrate was added to saturated aqueous NaHCO_3 , and extracted three times with AcOEt. The combined AcOEt layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated. The residue was partitioned between MeOH and FC-72 ($\times 3$). The combined FC-72 layer was evaporated. The residue was purified by column chromatography on silica gel (EtOC_4F_9 : Acetone = 5 : 2) to give compound **33** (285 mg, 29%, in 9 steps) as a white amorphous solid. R_f = 0.39 (EtOC_4F_9 : Acetone = 2 : 1); $[\alpha]_D^{25} = -9.9^\circ$ (c = 1.13 in CHCl_3); ^1H NMR (600 MHz, CDCl_3): δ = 1.02 (s, 9H), 1.87 (m, 6H), 1.92 (s, 3H), 1.946 (s, 3H), 1.949 (s, 3H), 1.98 (s, 3H), 2.00 (s, 3H), 2.02 (s, 12H), 2.04 (s, 3H), 2.07 (m, 6H), 2.11 (s, 3H), 2.13 (s, 3H), 2.40-2.76 (m, 18H), 3.39-3.87 (m, 27H), 4.43 (m, 3H), 4.56 (m, 3H), 4.96 (m, 6H), 5.11 (m, 4H), 5.21 (m, 1H), 5.31 (d, J = 3.4 Hz, 1H), 5.34 (m, 3H), 5.56 (d, J = 3.4 Hz, 1H), 7.28-7.44 (m, 11H), 7.60 (m, 4H); MALDI-TOF-MS: Calcd for $\text{C}_{152}\text{H}_{139}\text{F}_{102}\text{N}_3\text{O}_{44}\text{SiNa}$ ($\text{M}+\text{Na}^+$): 4698.7, Found: 4699.9. Calcd for $\text{C}_{150}\text{H}_{139}\text{F}_{102}\text{N}_3\text{O}_{44}\text{SiK}$ ($\text{M}+\text{K}^+$): 4714.7, Found: 4715.6.

Compound 34: To a solution of compound **33** (208 mg, 45 μmol) in dry THF (4 mL) was added 70% HF-pyridine (400 μL) at room temperature. After stirring for 22 h at room temperature, the reaction mixture was partitioned between toluene, saturated aqueous NaHCO_3 , and FC-72 ($\times 3$). The combined FC-72 layers were washed with brine, dried over anhydrous Na_2SO_4 , and evaporated to give the fluororous compound **34** (192 mg). The fluororous compound **34** was used immediately in the next step without further purification.

Compound 35: A sodium methoxide solution in methanol (28%, 30 μL) was added to a solution of compound **34** (187 mg) in Et_2O (6 mL) and MeOH (18 mL) at room temperature. After stirring for 2 h at room temperature, H_2O (4 mL) was added to the reaction mixture. After stirring for 1 h at room temperature, Amberlite IR-120 (H^+ form) was added, and the reaction mixture was neutralized. After filtration, the filtrate was evaporated. The residue was partitioned between H_2O and EtOC_4F_9 ($\times 2$). The H_2O layer was evaporated, and the residue was purified by column chromatography on ODS silica gel (10% MeOH) to give compound **35** (35.8 mg, 92% in 2 steps from **33**) as a white amorphous solid.

$[\alpha]_D^{25} = -16.5^\circ$ ($c = 0.41$ in H_2O); 1H NMR (600 MHz, D_2O): $\delta = 3.40$ (m, 5H), 3.50 (m, 6H), 3.62 (m, 2H), 3.78 (m, 13H), 3.90 (m, 4H), 4.29 (d, $J = 7.6$ Hz, 1H), 4.30 (d, $J = 7.6$ Hz, 1H), 4.31 (d, $J = 8.2$ Hz, 1H), 4.35 (d, $J = 7.6$ Hz, 1H), 4.36 (d, $J = 8.2$ Hz, 1H), 4.62 (d, $J = 11.7$ Hz, 1H), 4.82 (d, $J = 11.7$ Hz, 1H), 7.31 (m, 5H); ^{13}C NMR (150 MHz, D_2O): $\delta = 61.63, 69.23, 69.28, 69.75, 69.85, 69.94, 70.02, 71.29, 71.31, 71.35, 72.11, 73.18, 73.22, 73.24, 73.35, 73.40, 74.32, 74.34, 74.36, 74.49, 75.76, 102.53, 103.95, 104.01, 129.01, 129.18, 129.35, 137.45$; HRMS (ESI-TOF): Calcd for $C_{37}H_{58}O_{26}Na$ ($M+Na^+$): 941.3109, Found: 941.3148.

Compound 36: A solution of compound **35** (25.8 mg, 28 μ mol) in EtOH (3 mL)- H_2O (3 mL) was added to a suspension of 10% Pd/C (25 mg) in EtOH (0.5 mL)- H_2O (0.5 mL). After a 2h bubbling with hydrogen, the reaction mixture was filtered. The filtrate was evaporated, and the residue was purified by column chromatography on Sephadex LH-20 (50% MeOH) to give compound **36** (18.8 mg, 81 %) as a white amorphous solid. The ratio of the α/β isomers was 1:2. $[\alpha]_D^{25} = 10.9^\circ$ ($c = 0.59$ in H_2O); 1H NMR (600 MHz, D_2O): $\delta = 3.32$ -3.92 (m, 30H), 4.31 (m, 4H), 4.44 (d, $J = 8.2$ Hz, H-1 of the β isomer), 5.11 (d, $J = 4.1$ Hz, H-1 of the α isomer); ^{13}C NMR (150 MHz, D_2O): $\delta = 61.86, 69.12, 69.48, 69.62, 69.78, 70.07, 70.13, 70.24, 70.32, 71.53, 71.58, 72.65, 73.36, 73.42, 73.45, 73.60, 74.60, 75.98, 93.20, 97.27, 103.98, 104.05, 104.19, 104.24$; HRMS (ESI-TOF): Calcd for $C_{30}H_{52}O_{26}Na$ ($M+Na^+$): 851.2645, Found: 851.2664.

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13107
9000.9 Hz
16
1.455 sec
5.000 sec
7.1 us
22.0 C
D2O
4.65 ppm
0.12 Hz
200000

12

C:\Documents and Settings\

PROFILE
 COMMENT
 DATIM
 GENUC
 EXM00
 OEFRO
 OEFSE
 OEFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 FOL
 IRENUC
 CTMP
 SLMT
 EXREF
 EF
 RGAIN

C:\Documents and Settings\
 HML9_frl9_28
 13C
 single_pulse_dec
 150.92 MHz
 0.52 MHz
 1.7 Hz
 26214
 37878.2 Hz
 1500
 0.632 sec
 2.000 sec
 2.0 us
 28.5 s
 CD3OD
 49.00 ppm
 1.20 Hz
 150000

C:\Documents and Settings\
H320_fr9_10

DFILE
COMET
DATIN
OEMUC
EXMOD
OEFERQ
OEBET
OEFIN
POINT
FREQU
STANS
ACQTM
PD
POL
IERUC
CTEMP
SLWMT
EXRET
EF
RGAIN

1H
single_pulse.exe
600.17 MHz
5.30 KHz
5.5 Hz
13107
9008.9 Hz
16
1.455 sec
5.000 sec
6.5 us
24.4 c
CDCL3
0.00 ppm
1.44 Hz
200000

C:\Documents and Settings\TMM-86

Fri Mar 16 11:10:04 2001

LH

NOM

399.65 MHz

124.00 KHz

10500.0 Hz

32768

8000.0 Hz

32

4.096 sec

2.904 sec

7.8 us

LH

22.1 c

CDCL3

0.00 ppm

0.12 Hz

20

IFILE

COUNT

DATE

NAME

EXMOD

OEPRQ

OESET

OEFIN

POINT

FREQ

STANS

ACQTM

PD

POL

IRNOC

CTEMP

SLUNT

EXREF

EF

RGAIN

C:\Documents and Settings\

TMD-88 (Fr. 4-7)

Fri Mar 23 12:41:19 2001

1H

MON

399.65 MHz

124.00 KHz

10500.0 Hz

32768

8000.0 Hz

16

4.096 sec

2.904 sec

7.8 us

1H

24.7 c

CDCL3

0.00 ppm

0.12 Hz

15

DEFILE

COMMT

DATA1

ORNUC

EXMOD

ORFQ

ORSET

ORFIN

POINT

FREQU

SCANS

ACQTM

PD

POL

IRNUC

CTEMP

SLVMT

EXREF

EF

RGAIN

```
C:\Documents and Settings\
```

TM-89

Wed Apr 04 14:11:34 2001

11

ROOM

399.65 MHz

124.00 KHz

10500.0 Hz

32768

8000.0 Hz

16

4.096 sec

2.030 36F
2.904 36F

111

1.0.0.1

1
 2
 3
 4

30.27

0.0000

0.18 Hz
0.00 ppm

15
20
25

DEFILE

CONFIDENTIAL

DETIM

018271C

OFFICE
CHIEF081390
081391

1380
1381

OFFICE

POINT TO POINT

FORM
FEE-011

5073
5074

2000

UD
EATN 78

FD 100

ALL INFORMATION CONTAINED
HEREIN IS UNCLASSIFIED

DATE _____
TIME _____

DATE: 10
PAGE: 10

RESULTS

THE
WORLD

19

DFILE H:\matsumoto\11-40\HM24_fr
 CNAME HM24_fr29_37
 INSTR 1H
 PULPROG zgpg30
 EXMODE 600.17 MHz
 OBSFREQ 500.13 MHz
 OBSFREQ 5.5 Hz
 POINT 12107
 FREQ 9008.9 Hz
 SCANS 16
 ACQTIME 1.455 sec
 PD 5.000 sec
 PUL 6.5 us
 INSTRUC 1H
 CTMP 21.9 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 RF 0.12 Hz
 RGAIN 200000

INFILE
 COMMENT
 INSTRUM
 OEMUC
 EXMOD
 OEFREQ
 OESSET
 OEFIN
 POINT
 FREQU
 STANS
 ACQTM
 PD
 POL
 IEMUC
 CTEMP
 SLUNT
 EXREF
 EF
 RGAIN

H:\matsumoto\21-40\HJ_26_1
 HJ26

LH
 single_pulse.exe
 600.17 MHz
 5.30 KHz
 5.5 Hz
 10485
 7207.0 Hz
 16
 1.455 sec
 5.000 sec
 7.1 us
 23.2 c
 D2O
 4.75 ppm
 0.12 Hz
 200000

C:\Documents and Settings\
HJ_4tou

DFILE
 CDEMT
 DATIN
 OENUC
 EXMOD
 OEFRO
 OESST
 OEFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 FOL
 IIRUC
 CTMP
 SLVNT
 EXREF
 EF
 RGAIN

13C
 single_pulse_dec
 150.92 MHz
 8.52 KHz
 1.7 Hz
 26214
 27878.2 Hz
 1300
 0.692 sec
 2.000 sec
 4.0 us
 23.0 c
 D2O
 77.00 PPM
 0.83 Hz
 150000

C:\Documents and Settings\
TMR-175(Fr 2-4)

DFILE
C0001
D0110
O0000
EXMOD
O0000
O0000
O0000
POINT
FREQ
SCANS
ACQTM
PD
POL
IRNUC
CTEMP
SLVMT
EXREF
EF
RGAIN

1H
single_pulse.exe
600.17 MHz
5.30 KHz
5.5 Hz
131.07
9008.9 Hz
8
1.455 sec
4.000 sec
6.5 us
26.7 c
CDCL3
0.00 ppm
0.12 Hz
200000

22

C:\Documents and Settings\
TMM-175(Fr. 2-4)

13C
single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

0.692 sec

2.000 sec

3.0 us

27.7 °C

CDCL₃

0.00 ppm

0.86 Hz

150000

13C

single_pulse_dec

150.92 MHz

8.52 KHz

1.7 Hz

26214

37878.2 Hz

1696

C:\Documents and Settings\

H0-7(Fr.3-6)

Thu May 02 14:27:24 2002

1H

NON

399.65 MHz

124.00 KHz

10500.0 Hz

32768

8000.0 Hz

8

4.096 sec

2.904 sec

7.8 us

1H

21.6 c

CDCL3

0.00 ppm

0.12 Hz

20

DFILE

COMET

INSTR

ORNDU

EXMOD

OEPRQ

OE3ET

OEFIN

POINT

FREQU

SCANS

ACQTM

PD

POL

IRNDU

CTEMP

SLVNT

EXREF

EF

RGAIN

AcO O-TBDPS

H:\H037Fz3_5_bcm.als
 H0-37(Fz 3-5)
 Wed May 07 16:18:11 2003
 13C
 ECH
 100.40 MHz
 125.00 MHz
 10500.0 Hz
 32768
 27173.9 Hz
 347
 1.206 sec
 1.794 sec
 5.5 us
 1H
 25.9 c
 CDCL3
 77.00 ppm
 0.83 Hz
 29
 ECH

DFILE
 COMET
 DATIM
 OENUC
 EXMOD
 OEFRO
 OESST
 OEFIM
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 P01
 IPNUC
 CTIMP
 SLVMT
 EXREF
 EF
 ECH

14.255
 19.105
 20.607
 20.772
 26.695

61.235
 67.224
 67.414
 67.843
 71.473
 76.678
 77.000
 77.313
 90.867
 93.557

127.635
 127.668
 129.714
 129.755
 132.742
 132.783
 135.439

160.839
 169.765
 169.823
 169.988

C:\Documents and Settings\

H0-60

Fri May 16 16:50:44 2003

LH

NOM

399.65 MHz

124.00 KHz

10500.0 Hz

32768

8000.0 Hz

16

4.096 sec

2.904 sec

7.0 us

LH

25.3 °

CDCL3

0.00 ppm

0.12 Hz

14

DFILE

COMET

DATEM

GENUC

EXMOD

OEPRQ

OESET

OEFIN

POINT

FREQ

SCANS

ACQTM

PD

POL

IRNUC

CTEMP

SLVMT

EXREF

BF

RGAIN

C:\Documents and Settings\

27

Sat Apr 17 17:24:17 2004

1H

NOM

399.65 MHz

124.00 KHz

10500.0 Hz

32768

7992.6 Hz

16

4.099 sec

2.901 sec

8.0 us

1H

21.4 c

CDCL3

0.00 PPM

0.12 Hz

19

IFILE

COMET

DATA

DEMOD

EXMOD

OEPRQ

OESET

OEFIN

POINT

FREQ0

SCANS

ACQTM

PD

PG1

IRMOD

CTEMP

SLUNT

EXREF

BF

RGAIN

C:\Documents and Settings\
H0-22(Fr.13-20)

DPFILE
COMET
DATIN
OENUC
EXMOD
OEFERQ
OESER
OEFIN
POINT
FREQU
STANS
ACQIN
PD
POL
IRNUC
CTEMP
SLVMT
EXREF
EF
RGAIN

1H
single_pulse.exe
600.17 MHz
5.30 KHz
5.5 Hz
131.07
9008.9 Hz
16
1.455 sec
4.000 sec
6.5 us
25.1 c
CDCL3
0.00 ppm
0.12 Hz
200000

AcO-O-TBDPS

D:\Documents and Settings\
 H0-29 (Fr.10-18)
 1H
 single_pulse.ex2
 600.17 MHz
 5.30 KHz
 5.5 Hz
 13107
 9008.9 Hz
 16
 1.455 sec
 4.000 sec
 6.5 us
 26.6 s
 CDCL3
 0.00 ppm
 0.12 Hz
 200000

DFILE
 COMMENT
 DATIM
 OEMUC
 EXMOD
 OEFREQ
 OESST
 OEFIM
 POINT
 FREQU
 STANS
 ACQTM
 PD
 POL
 IEMUC
 CTIMP
 SLVMT
 EXREF
 EF
 RGAIN

C:\Documents and Settings\
H0-46(FR.13-16)

DFILE
 COUNT
 DATE
 OENUC
 EXMOD
 OEFREQ
 OESSET
 OEFIN
 POINT
 FREQU
 SCANS
 ACQTM
 PD
 POL
 IENUC
 CTMP
 SLVMT
 EXREF
 EF
 RGAIN

13C
 single_pulse_dec
 150.92 MHz
 8.52 KHz
 1.7 Hz
 26214
 37878.2 Hz
 286
 0.692 sec
 2.000 sec
 3.0 us
 23.9 c
 D2O
 77.00 ppm
 0.82 Hz
 150000

137.446
 129.345
 129.183
 129.010
 104.010
 103.953
 102.526
 75.755
 74.491
 74.357
 74.338
 74.319
 73.400
 73.352
 73.237
 73.218
 73.180
 72.107
 71.351
 71.313
 71.293
 70.020
 69.943
 69.848
 69.752
 69.283
 69.225
 61.632

C:\Documents and Settings\
 H0-47

INFILE
 COMPT
 INSTM
 OEMUC
 EXMOD
 OEFREQ
 OESSET
 OEFIN
 POINT
 FREQU
 STANS
 ALQTM
 PD
 POL
 IEMUC
 CTEMP
 SLVMT
 EXREF
 EF
 RGAIN

1H
 single_pulse.exe
 600.17 MHz
 5.30 KHz
 5.5 Hz
 13107
 9000.9 Hz
 16
 1.455 sec
 4.000 sec
 6.5 us
 22.4 c
 D2O
 4.65 ppm
 0.12 Hz
 2000000

C:\Documents and Settings\

INFILE
 COUNT
 INSTM
 OEMUC
 EXMOD
 OEFREQ
 OESSET
 OEFIN
 POINT
 FREQU
 STANS
 ALQTM
 PD
 POL
 IEMUC
 CTEMP
 SLVMT
 EXREF
 EF
 PGAIN

13C
 single_pulse_dec
 150.92 MHz
 8.52 KHz
 1.7 Hz
 22768
 47348.5 Hz
 2738
 0.692 sec
 0.000 sec
 3.0 us
 22.8 c
 D2O
 77.00 ppm
 0.86 Hz
 150000

23.247

61.010
 68.258
 68.622
 68.766
 68.919
 69.254
 69.292
 69.426
 69.484
 70.671
 70.729
 71.772
 72.481
 72.557
 72.586
 72.730
 73.745
 75.133
 92.348
 96.408
 99.951
 103.120
 103.206
 103.340
 103.398