Electronic Supplementary Information

A Novel Molecular Tube Fully Modified at One End: Selective Inclusion of \textit{cis}-Unsaturated Fatty Acid Esters

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Contents

1. Materials and Methods S3
   1-1. Synthesis of 1 S4
   1-2. Synthesis of 2 S5
   1-3. Synthesis of 3 S5
   1-4. Spectral Data of 2 S6
   1-5. Spectral Data of 3 S8
   1-6. Determination of Association Constants by NMR Titration S9
   1-7. Experimental Procedure for Job Plots S9

2. MALDI-TOF MS Spectra of the Products Obtained by the Desilylation of 1 under Various Conditions S10

3. $^1$H-NMR Spectral Changes Observed for 2 upon Addition of Long-Chain Fatty Acid Esters in Methanol-$d_4$ and Titration Curves for Their Complex Formation S11

4. Job Plots for Complexes between 2 and Long-Chain Fatty Acid Esters in Methanol-$d_4$ S16

5. NOESY Spectra of Complexes between 2 and Long-Chain Fatty Acid Esters in Methanol-$d_4$ S18

6. $^1$H-NMR Spectral Changes for 2 or 3 upon Addition of Long-Chain Fatty Acid Esters in Methanol-$d_4$/DMSO-$d_6$ (7/3) and Titration Curves for Their Complex Formation S19

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7. Job Plots for Complexes between 3 and Long-Chain Fatty Acid Esters in Methanol-d₄/DMSO-d₆ (7/3)  

S21

8. Association Constants between 2 or 3 and Various Long-Chain Fatty Acid Methyl Esters in Methanol-d₄/ 
DMSO-d₆ (7/3) at 25 °C  

S22

9. Reference  

S22
1. Materials and Methods

Boron trifluoride diethyl ether complex and dichloromethane were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Tetrabutylammonium fluoride was purchased from Sigma-Aldrich (Japan). Tetramethylammonium fluoride and 1,4-dioxane were purchased from Wako Pure Chemical Industries, Ltd. (Japan). These reagents were used without further purification. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra were recorded on a JEOL NMR system (400 MHz). The following abbreviations were used for chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. NMR signal assignments were based on additional 2D-NMR spectroscopy (e.g., COSY and HSQC). Infrared (IR) spectra were obtained with a Spectrum 100FT-IR spectrometer (Perkin Elmer). MALDI-TOF MS spectra were measured by Bruker Autoflex III. Melting points were measured with BUCHI Melting point B-545. Elemental analysis was performed with Perkin Elmer 240C. HPLC was performed using a Shimadzu Prominence HPLC system equipped with a Soft 400 ELSD detector.
1-1. Synthesis of 1

Scheme S1. Synthesis of 1.

1 was prepared according to our previously reported method.\textsuperscript{[1]} The structure was confirmed by the \textsuperscript{1}H NMR spectrum.

Figure S1. \textsuperscript{1}H NMR spectrum of 1 in chloroform-\textit{d} at 25 °C.
1-2. Synthesis of 2

1 (20 mg, 4.4 µmol) and tetramethylammonium fluoride (TMAF, 8.6 mg, 92 µmol) were dissolved in 1,4-dioxane (2.0 mL). The reaction mixture was stirred for 8 h at 100 °C. After the solvent was removed in vacuo, the resulting solid was purified by silica gel column chromatography (chloroform/methanol, in a gradient 10:1 to 6:1) to give compound 2 (8.0 mg, 48% yield).

Scheme S2. Synthesis of 2.

1-3. Synthesis of 3

1 (0.1 g, 22 µmol) was dissolved in dichloromethane (10.0 mL). Into this solution, boron trifluoride diethyl ether complex (60 µL, 0.48 mmol) was added, and the reaction mixture was stirred for 4 h at room temperature. After the solvent was removed in vacuo, the resulting solid was washed with acetone (10 mL×3) and hexane (10 mL×3), and dried at 80 °C in vacuo to give compound 3 (60 mg, 91% yield).

Scheme S3. Synthesis of 3.
1-4. Spectral Data of 2

$R_f$ 0.5 (CHCl₃/MeOH = 4/1); mp: 273 °C (decomp); $^1$H NMR (400 MHz, methanol-$d_4$): $\delta$ 0.07 (d, $J = 2.8$ Hz, 42H), $\delta$ 0.88 (s, 63H), $\delta$ 3.34-3.46 (m, 28H), $\delta$ 3.63-3.85 (m, 35H), $\delta$ 4.07 (d, $J = 8.8$ Hz, 7H), $\delta$ 4.15-4.25 (m, 28H), $\delta$ 4.93 (m, 28H), $\delta$ 5.21-5.25 (m, 28H), $\delta$ 7.14-7.18 (m, 14H), $\delta$ 7.23-7.27 (m, 7H), $\delta$ 7.66 (s, 7H); $^{13}$C NMR (100 MHz, methanol-$d_4$): $\delta$ -5.74, -4.47, 19.26, 26.63, 61.84, 72.90, 73.18, 75.33, 75.43, 77.44, 77.50, 83.22, 83.45, 84.34, 85.00, 103.76, 129.19, 129.64, 129.82, 131.38, 138.99, 139.01; MALDI-TOF MS: $m/z$ = 3808 [M+Na]$^+$. Anal. Calcd for C₁₅₂H₂₈₀O₇₀Si₇•6H₂O: C, 56.15; H, 7.56. Found: C, 56.24; H, 7.59; FT-IR (cm⁻¹): 3406, 2926, 2855, 1462, 1360, 1251, 1158, 1083, 1039, 833, 777.

Figure S2. $^1$H NMR spectrum of 2 in methanol-$d_4$ at 25 °C.

Figure S3. $^{13}$C NMR spectrum of 2 in methanol-$d_4$ at 25 °C.
**Figure S4.** HPLC chromatogram of 2. Column: NACALAI TESQUE, COSMOSIL 5SL-II Packed Column (250 mm × 4.6 mm i.d.); mobile phase: chloroform/methanol = 2/1 (v/v); flow rate: 1.5 ml min\(^{-1}\); temperature: 25 °C; detector: ELSD.
1-5. Spectral Data of 3

mp: 270 °C (decomp); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.26-3.41 (m, 28H), $\delta$ 3.58-3.70 (m, 28H), $\delta$ 4.02 (t, $J = 9.6$ Hz, 14H), $\delta$ 4.21 (d, $J = 9.6$ Hz, 14H), $\delta$ 4.63 (s, 14H), $\delta$ 4.84 (m, 14H), $\delta$ 5.04 (d, $J = 9.6$ Hz, 14H), $\delta$ 7.13 (d, $J = 8.0$ Hz, 14H), $\delta$ 7.22 (t, $J = 7.2$ Hz, 7H) , $\delta$ 7.52 (s, 7H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 59.91, 71.32, 73.58, 75.20, 81.68, 83.14, 101.42, 127.80, 128.20, 137.55; MALDI-TOF MS: $m/z = 3008 [M+Na]^+$; Anal. Caled for C$_{140}$H$_{182}$O$_{70}$$\cdot$9H$_2$O: C, 53.43; H, 6.41. Found: C, 53.43; H, 6.44; FT-IR (cm$^{-1}$): 3389, 2920, 1360, 1322, 1247, 1155, 1083, 1010, 948, 854, 754, 700.

**Figure S5.** $^1$H NMR spectrum of 3 in DMSO-$d_6$ at 25 °C.

**Figure S6.** $^{13}$C NMR spectrum of 3 in DMSO-$d_6$ at 25 °C.
1-6. Determination of Association Constants by NMR Titration

A solution of the host molecule (5.0 × 10^{-4} M, 0.5 mL) was titrated in a NMR tube with increasing amounts of guest stock solution (200 mM). 6 or more solutions with different host-guest concentration ratios were analyzed. Four of $^1$H NMR spectra obtained are shown in each figure. The titration curves (changes in the chemical shift of the host protons ($\Delta \delta$) against the guest/host concentration ratio) were analyzed by a non-linear least-squares curve fitting method to give the association constants between the hosts and the guests.

1-7. Experimental Procedure for Job Plots

Job plots were carried out by monitoring the changes in the chemical shift of the host protons ($\Delta \delta$) in a series of solutions with varying host/guest ratios but the total concentrations of the host and guest being kept constant (0.4 or 2.0 mM). The relative concentration of the host-guest complex estimated from the $\Delta \delta \cdot [\text{host}]$ value was plotted against ([host]/([host] + [guest])).
2. MALDI-TOF MS Spectra of the Products Obtained by the Desilylation of 1 under Various Conditions

![Figure S7](image1)

**Figure S7.** MALDI-TOF MS spectra of the products of the desilylation of 1 with TMAF in 1,4-dioxane at 100 °C for (a) 2 h and (b) 18 h.

![Figure S8](image2)

**Figure S8.** MALDI-TOF MS spectrum of the product of the desilylation of 1 with TBAF (14 eq.) in THF for 8 h at 60 °C.
3. **$^1$H-NMR Spectral Changes Observed for 2 upon Addition of Long-Chain Fatty Acid Esters in Methanol-$d_4$ and Titration Curves for Their Complex Formation**

**Figure S9.** (a) $^1$H NMR spectral changes observed for 2 ($5.0 \times 10^{-4}$ M) upon addition of methyl myristate in methanol-$d_4$ at 25 ºC. (b) $^1$H NMR titration curve for complex formation between 2 and methyl myristate in methanol-$d_4$ at 25 ºC. The proton signal of 2 at 4.2 ppm was used for titration.

**Figure S10.** (a) $^1$H NMR spectral changes observed for 2 ($5.0 \times 10^{-4}$ M) upon addition of methyl palmitate in methanol-$d_4$ at 25 ºC. (b) $^1$H NMR titration curve for complex formation between 2 and methyl palmitate in methanol-$d_4$ at 25 ºC. The proton signal of 2 at 4.2 ppm was used for titration.
Figure S11. (a) $^1$H NMR spectral changes observed for 2 ($5.0 \times 10^{-4}$ M) upon addition of methyl stearate in methanol-$d_4$ at 25 ºC. (b) $^1$H NMR titration curve for complex formation between 2 and methyl stearate in methanol-$d_4$ at 25 ºC. The proton signal of 2 at 4.2 ppm was used for titration.

Figure S12. (a) $^1$H NMR spectral changes observed for 2 ($5.0 \times 10^{-4}$ M) upon addition of methyl elaidate in methanol-$d_4$ at 25 ºC. (b) $^1$H NMR titration curve for complex formation between 2 and methyl elaidate in methanol-$d_4$ at 25 ºC. The proton signal of 2 at 4.2 ppm was used for titration.
Figure S13. (a) $^1$H NMR spectral changes observed for 2 (5.0 $\times$ 10^{-4} M) upon addition of methyl linoelaidate in methanol-$d_4$ at 25 °C. (b) $^1$H NMR titration curve for complex formation between 2 and methyl linoelaidate in methanol-$d_4$ at 25 °C. The proton signal of 2 at 4.2 ppm was used for titration.

Figure S14. $^1$H NMR titration curve for complex formation between 2 and methyl oleate in methanol-$d_4$ at 25 °C. The proton signal of 2 at 4.2 ppm was used for titration.
Figure S15. (a) $^1$H NMR spectral changes observed for 2 (5.0 × 10$^{-4}$ M) upon addition of methyl linoleate in methanol-$d_4$ at 25 ºC. (b) $^1$H NMR titration curve for complex formation between 2 and methyl linoleate in methanol-$d_4$ at 25 ºC. The proton signal of 2 at 4.2 ppm was used for titration.

Figure S16. (a) $^1$H NMR spectral changes observed for 2 (5.0 × 10$^{-4}$ M) upon addition of methyl eicosapentaenoate in methanol-$d_4$ at 25 ºC. (b) $^1$H NMR titration curve for complex formation between 2 and methyl eicosapentaenoate in methanol-$d_4$ at 25 ºC. The proton signal of 2 at 4.2 ppm was used for titration.
Figure S17. (a) $^1$H NMR spectral changes observed for 2 (5.0 × 10^{-4} M) upon addition of methyl docosahexaenoate in methanol-$d_4$ at 25 °C. (b) $^1$H NMR titration curve for complex formation between 2 and methyl docosahexaenoate in methanol-$d_4$ at 25 °C. The proton signal of 2 at 4.2 ppm was used for titration.
4. Job Plots for Complexes between 2 and Long-Chain Fatty Acid Esters in Methanol-$d_4$

**Figure S18.** Job plot for complex between 2 and methyl elaidate in methanol-$d_4$ at 25 °C.

**Figure S19.** Job plot for complex between 2 and methyl oleate in methanol-$d_4$ at 25 °C.
Figure S20. Job plot for complex between 2 and methyl linoleate in methanol-$d_4$ at 25 ºC.

Figure S21. Job plot for complex between 2 and methyl docosahexaenoate in methanol-$d_4$ at 25 ºC.
5. NOESY Spectra of Complexes between 2 and Long-Chain Fatty Acid Esters in Methanol-\(d_4\)

**Figure S22.** The partial 400 MHz NOESY spectrum of a complex of 2 with methyl linoleate in methanol-\(d_4\) at 25 ºC.

**Figure S23.** The partial 400 MHz NOESY spectrum of a complex of 2 with methyl docosahexaenoate in methanol-\(d_4\) at 25 ºC.
6. $^1$H-NMR Spectral Changes Observed for 2 or 3 upon Addition of Long-Chain Fatty Acid Esters in Methanol-$d_4$/DMSO-$d_6$ (7/3) and Titration Curves for Their Complex Formation

**Figure S24.** (a) $^1$H NMR spectral changes observed for 2 ($5.0 \times 10^{-4}$ M) upon addition of methyl elaidate in methanol-$d_4$/DMSO-$d_6$ (7/3) at 25 ºC. (b) $^1$H NMR titration curve observed for 2 ($5.0 \times 10^{-4}$ M) upon addition of methyl elaidate in methanol-$d_4$/DMSO-$d_6$ (7/3) at 25 ºC. The proton signal of 2 at 7.6-7.7 ppm was used for titration.

**Figure S25.** (a) $^1$H NMR spectral changes observed for 2 ($5.0 \times 10^{-4}$ M) upon addition of methyl oleate in methanol-$d_4$/DMSO-$d_6$ (7/3) at 25 ºC. (b) $^1$H NMR titration curve observed for 2 ($5.0 \times 10^{-4}$ M) upon addition of methyl oleate in methanol-$d_4$/DMSO-$d_6$ (7/3) at 25 ºC. The proton signal of 2 at 7.6-7.7 ppm was used for titration.
Figure S26. (a) $^1$H NMR spectral changes observed for 3 ($5.0 \times 10^{-4}$ M) upon addition of methyl elaidate in methanol-$d_4$/DMSO-$d_6$ (7/3) at 25 °C. (b) $^1$H NMR titration curve for complex formation between 3 and methyl elaidate in methanol-$d_4$/DMSO-$d_6$ (7/3) at 25 °C. The proton signal of 3 at 7.6-7.7 ppm was used for titration.

Figure S27. (a) $^1$H NMR spectral changes observed for 3 ($5.0 \times 10^{-4}$ M) upon addition of methyl oleate in methanol-$d_4$/DMSO-$d_6$ (7/3) at 25 °C. (b) $^1$H NMR titration curve for complex formation between 3 and methyl oleate in methanol-$d_4$/DMSO-$d_6$ (7/3) at 25 °C. The proton signal of 3 at 7.6-7.7 ppm was used for titration.
7. Job Plots for Complexes between 3 and Long-Chain Fatty Acid Esters in Methanol-$d_4$/DMSO-$d_6$ (7/3)

**Figure S28.** Job plot for complex between 3 and methyl elaidate in methanol-$d_4$/DMSO-$d_6$ (7/3) at 25 ºC.

**Figure S29.** Job plot for complex between 3 and methyl oleate in methanol-$d_4$/DMSO-$d_6$ (7/3) at 25 ºC.
8. Association Constants between 2 or 3 and Various Long-Chain Fatty Acid Methyl Esters in Methanol-\textit{d}_4/DMSO-\textit{d}_6 (7/3) at 25 °C

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9. Reference