

# Synthesis of Oligoethylene Glycol toward 44-Mer

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## Supporting Information

**General Information**-----S4

### Experimental Procedures

#### *Monoprotection and Functionalization of Tetraethylene Glycol*

Monobenzyl-protected tetraethylene glycol-----S4

Monobenzyl-protected tetraethylene glycol tosylate-----S5

Monotetrahydropyranyl-protected tetraethylene glycol-----S5

Monotetrahydropyranyl-protected tetraethylene glycol tosylate-----S5

Monotrityl-protected tetraethylene glycol-----S6

Monotrityl-protected tetraethylene glycol tosylate-----S6

Monobenzyl-protected tetraethylene glycol mesylat-----S6

Monobenzyl-protected tetraethylene glycol chloride-----S7

#### *12-Ethylene Glycol Bisbenzyl Ether and 12-Ehtylene Glycol*

12-Ethylene glycol bisbenzyl ether with tosylate-----S7

12-Ethylene glycol bisbenzyl ether with excess tosylate 1-----S7

12-Ethylene glycol bisbenzyl ether with excess tosylate 2-----S8

12-Ethylene glycol bisbenzyl ether with mesylate-----S8

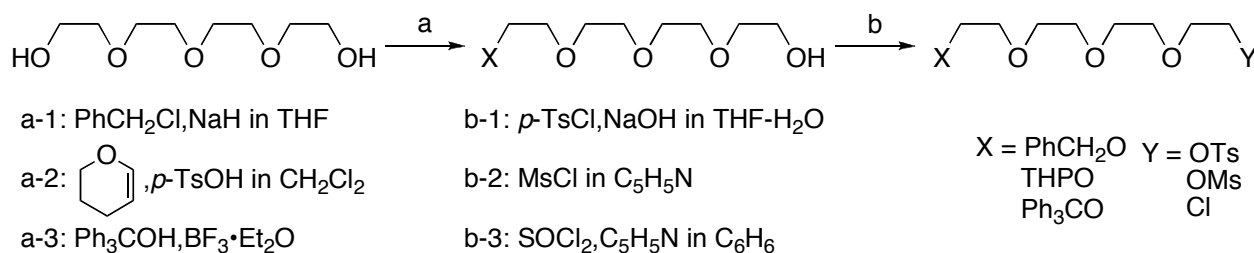
12-Ethylene glycol-----S8

*12-Ethylene Glycol Bisbenzyl Ether with Ditosylate*

Tetraethylene glycol ditosylate-----	S8
12-Ethylene glycol bisbenzyl ether with tetraethylene glycol ditosylate-----	S9
<i>Bn-OEG and OEG (7- ~ 44-Mer)</i>	
Monobenzyl-protected diethylene glycol-----	S9
Monobenzyl-protected diethylene glycol tosylate-----	S10
Monobenzyl-protected triethylene glycol-----	S10
Monobenzyl-protected triethylene glycol tosylate-----	S10
7-Ethylene glycol bisbenzyl ether-----	S11
7-Ethylene glycol-----	S11
8-Ethylene glycol bisbenzyl ether-----	S11
8-Ethylene glycol-----	S12
9-Ethylene glycol bisbenzyl ether-----	S12
9-Ethylene glycol-----	S12
10-Ethylene glycol bisbenzyl ether-----	S12
10-Ethylene glycol-----	S12
11-Ethylene glycol bisbenzyl ether-----	S13
11-Ethylene glycol-----	S13
12-Ethylene glycol bisbenzyl ether-----	S13
12-Ethylene glycol-----	S13
20-Ethylene glycol bisbenzyl ether-----	S14
20-Ethylene glycol-----	S14
28-Ethylene glycol bisbenzyl ether-----	S14
28-Ethylene glycol-----	S14
36-Ethylene glycol bisbenzyl ether-----	S15
36-Ethylene glycol-----	S15
44-Ethylene glycol bisbenzyl ether-----	S15

44-Ethylene glycol-----	S15
<i>12-Ethylene Glycol with 4-(Dodecyloxy)benzyl Protecting Group</i>	
Methyl-4-(dodecyloxy)benzoate-----	S16
4-(Dodecyloxy)benzyl alcohol-----	S16
4-(Dodecyloxy)benzyl bromide-----	S17
Mono-4-(dodecyloxy)benzyl-protected tetraethylene glycol-----	S17
Mono-4-(dodecyloxy)benzyl-protected tetraethylene glycol mesylate-----	S17
12-Ethylene glycol bis(4-(dodecyloxy)benzyl) ether with mono-4-(dodecyloxy)benzyl-protected tetraethylene glycol mesylate-----	S18
12-Ethylene glycol with 12-ethylene glycol bis(4-(dodecyloxy)benzyl) ether-----	S18

All starting chemicals were commercially available purity, and used without further purification. In purification, silica-gel (MERK, Silica gel 60, 70~230 mesh) and HPLC columns (TOSOH, TSKgel G1000H<sub>6</sub>, G1000H<sub>HR</sub>, G2000H<sub>6</sub>, G2000H<sub>HR</sub>, G3000H<sub>6</sub>, G3000H<sub>HR</sub>) were used for column chromatography (50 cm in length) and gel permeation chromatography, respectively. The exclusion-limit-molecular-weight are 1000, 10000, and 60000 for G1000, G2000, and G3000, respectively. H<sub>6</sub> HPLC columns are 60 cm in length and 21.5 mm in diameter. On the other hand, H<sub>HR</sub> HPLC columns are 30 cm in length and 21.5 mm in diameter. In purification, 0.5 ~ 1.0 g of crude products dissolved with 3 mL chloroform were loaded on HPLC columns. In cases of oligoethylene glycol bisbenzyl ether below 12-mer, TSKgel G1000H<sub>6</sub> and G1000H<sub>HR</sub> were applied for purification. When oligoethylene glycol bisbenzyl ethers were more than 12-mer, TSKgel G2000H<sub>6</sub>, G2000H<sub>HR</sub>, G3000H<sub>6</sub>, and G3000H<sub>HR</sub> were applied for purification. All yields are calculated based on less starting materials in molar.



**Monobenzyl-protected tetraethylene glycol (a-1):** To a three-necked flask, NaH (9.60 g, 400 mmol) and THF (700 mL) were placed, and then, tetraethylene glycol (77.6 g, 400 mmol) was added slowly. The mixture was heated to 100 °C, and THF solution (80 mL) of benzyl chloride (12.7 g, 100 mmol) was added dropwise. The reaction mixture was stirred for 3 hrs at 100 °C, and then, it was allowed to cool at room temperature. Methanol was added to the reaction mixture to quench excess NaH, and 5wt% aq. HCl (50 mL) was added. After evaporation of THF, the product was extracted using 5wt% aq. HCl and CHCl<sub>3</sub>. The crude product (brownish liquid, 90% yield) obtained by solvent evaporation and drying under vacuum condition was used for the subsequent reaction without purification. The formation of bisbenzyl ether in ca. 10% molar ratio was observed in <sup>1</sup>H NMR analysis. Peaks in <sup>1</sup>H NMR spectra (500 MHz, in CDCl<sub>3</sub>) for benzyl protons of tetraethylene

glycol monobenzyl and bisbenzyl ethers afforded different chemical shifts, being 4.57 and 4.56 ppm, respectively, to determine the molar ratio by a simple integration.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.7 (16H, m,  $\text{OCH}_2$ ), 4.57 (2H, s,  $\text{CH}_2\text{Ph}$ ), 7.2~7.4 (5H, m, aromatic H).

**Monobenzyl-protected tetraethylene glycol tosylate (b-1):** Monobenzyl-protected tetraethylene glycol (90% in purity, 15.8 g, 50 mmol), NaOH (7.00 g, 175 mmol), THF (35 mL), and  $\text{H}_2\text{O}$  (35 mL) were put to a three-necked flask, and the mixture was cooled at 0 °C. A THF solution (50 mL) of *p*-toluenesulfonyl chloride (11.4 g, 60 mmol) was added to the mixture dropwise, and the reaction mixture was stirred for 2 hrs at 0 °C. The reaction mixture was allowed to warm at room temperature, and stirred for additional 20 hrs. The reaction mixture was poured to 5wt% aq. HCl cooled at 0 °C, and the product was extracted with  $\text{CHCl}_3$ . The organic layer was rinsed with water, and dried with  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated, and the obtained product (brownish liquid, quantitative yield) was used for the subsequent reaction without purification after drying under vacuum condition. The crude product contained tetraethylene glycol bisbenzyl ether in ca. 10% molar ratio.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  2.44 (3H, s,  $\text{CH}_3$ ), 3.6~3.7 (14H, m,  $\text{OCH}_2$ ), 4.15 (2H, t,  $J = 4.8\text{Hz}$ ,  $\text{OCH}_2$ ), 4.56 (2H, s,  $\text{CH}_2\text{Ph}$ ), 7.2~7.4 (7H, m, aromatic H), 7.79 (2H, d,  $J = 8.3\text{Hz}$ , aromatic H).

**Monotetrahydropyranyl-protected tetraethylene glycol (a-2):** To a three-necked flask, dihydropyran (164 mg, 2 mmol), tetraethylene glycol (1.94 g, 10 mmol), and dry  $\text{CH}_2\text{Cl}_2$  (50 mL) were placed and stirred at room temperature. To the mixture, *p*-toluenesulfonic acid monohydrate (38.0 mg, 0.2 mmol) was added, and the reaction mixture was stirred for 30 min. at room temperature. The reaction mixture was poured into water, and the organic layer was separated. The organic layer was rinsed with water, and the crude product (colorless liquid, 80% yield) obtained by solvent evaporation and drying under vacuum condition was used for the subsequent reaction without purification.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  1.4~1.6 (2H, m,  $\text{CH}_2$ ), 1.7~1.9 (2H, m,  $\text{CH}_2$ ), 3.35~3.41 (1H, m,  $\text{OCH}_2$ ), 3.48~3.53 (1H, m,  $\text{OCH}_2$ ), 3.6~4.0 (18H, m,  $\text{OCH}_2$ ), 4.56~4.59 (1H, m, OCH).

**Monotetrahydropyranyl-protected tetraethylene glycol tosylate (b-1):**

Monotetrahydropyranyl-protected tetraethylene glycol (1.32 g, 5 mmol), NaOH (700 mg, 17.5 mmol), THF (35 mL), and H<sub>2</sub>O (35 mL) were put to a three-necked flask, and the mixture was cooled at 0 °C. A THF solution (50 mL) of *p*-toluenesulfonyl chloride (1.14 g, 6 mmol) was added to the mixture dropwise, and the reaction mixture was stirred for 2 hrs at 0 °C. The reaction mixture was allowed to warm at room temperature, and stirred for additional 20 hrs. The reaction mixture was poured to water, and the product was extracted with CHCl<sub>3</sub>. The organic layer was rinsed with water, and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to obtain the product. However, the NMR analysis revealed that deprotection of the tetrahydropyranyl group was occurred.

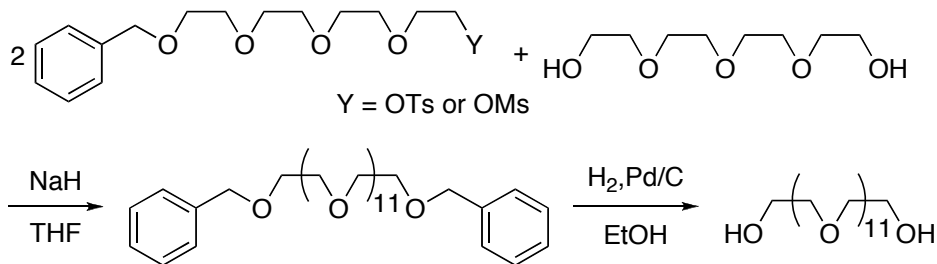
**Monotrityl-protected tetraethylene glycol (a-3):** To a three-necked flask, triphenyl methanol (520 mg, 2 mmol) and tetraethylene glycol (19.4 g, 100 mmol) were placed and stirred at room temperature. To the mixture, BF<sub>3</sub> diethyl ether complex (47%, 868 mg, 6 mmol) was added slowly, and the reaction mixture was stirred for 6 hrs at room temperature. The reaction mixture was poured to water, and the product was extracted with benzene. The organic layer was rinsed with water, and the crude product (colorless liquid, quantitative yield) obtained by solvent evaporation and drying under vacuum condition was used for the subsequent reaction without purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 3.6~3.7 (14H, m, OCH<sub>2</sub>), 7.2~7.5 (15H, m, aromatic H).

**Monotrityl-protected tetraethylene glycol tosylate (b-1):** The synthetic procedure was the same as for monotetrahydropyranyl-protected tetraethylene glycol tosylate, except for using monotrityl-protected tetraethylene glycol (2.18 g, 5 mmol) instead of monotetrahydropyranyl-protected tetraethylene glycol. NMR analysis showed that elimination of trityl group proceeded during tosylation.

**Monobenzyl-protected tetraethylene glycol mesylate (b-2):** Monobenzyl-protected tetraethylene glycol (90% in purity, 1.58 g, 5 mmol), methanesulfonyl chloride (860 mg, 7.5 mmol), and pyridine (30 mL) were put to a three-necked flask, and the mixture was stirred for 20 hrs at room temperature. The reaction mixture was poured to ice-water, and neutralized with hydrochloric acid. The product was extracted with CHCl<sub>3</sub>. The organic layer was rinsed with water, and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product (brownish liquid, 73% yield) obtained by solvent evaporation and drying under

vacuum condition was used for the subsequent reaction without purification.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.06 (3H, s,  $\text{CH}_3$ ), 3.6~3.8 (14H, m,  $\text{OCH}_2$ ), 4.3~4.4 (2H, m,  $\text{OCH}_2$ ), 4.57 (2H, s,  $\text{CH}_2\text{Ph}$ ), 7.2~7.4 (5H, m, aromatic H).

**Monobenzyl-protected tetraethylene glycol chloride (b-3):** Monobenzyl-protected tetraethylene glycol (90% in purity, 1.58 g, 5 mmol), pyridine (790 mg, 10 mmol), and  $\text{CHCl}_3$  (70 mL) were put to a three-necked flask. To the mixture,  $\text{CHCl}_3$  solution (20 mL) of thionyl chloride (1.19 g, 10 mmol) was added dropwise, and the reaction mixture was refluxed for 6 hrs. The reaction mixture was allowed to cool at room temperature, and poured to 5wt% aq. HCl. The product was extracted with  $\text{CHCl}_3$ , and the organic layer was rinsed with water. The solvent was evaporated to obtain the product. However, the NMR and GC analysis revealed that cleavage of the ethylene glycol moiety was occurred.



**12-Ethylene glycol bisbenzyl ether with tosylate:** To a three-necked flask, tetraethylene glycol (970 mg, 5 mmol), NaH (2.40 g, 100 mmol), and dry THF (200 mL) were put, and a dry THF solution (50 mL) of monobenzyl-protected tetraethylene glycol tosylate (90% in purity, 7.31 g, 15 mmol) was added to the mixture dropwise at room temperature. The reaction mixture was refluxed for 24 hrs, and then, allowed to cool at room temperature. Methanol was added to the reaction mixture to quench excess NaH. The solvent was evaporated, and the product was extracted with 5wt% aq. HCl and  $\text{CHCl}_3$ . The product obtained by solvent evaporation was purified by gel permeation chromatography (GPC) in 73% yield as colorless liquid.

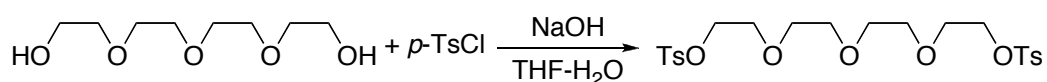
**12-Ethylene glycol bisbenzyl ether with excess tosylate 1:** The synthetic procedure was the same as for 12-ethylene glycol bisbenzyl ether with tosylate, except for using monobenzyl-protected tetraethylene glycol tosylate (90% in purity, 1.94 g, 4 mmol) instead of monobenzyl-protected

tetraethylene glycol mesylate, to give the product with 72% yield.

**12-Ethylene glycol bisbenzyl ether with excess tosylate 2:** The synthetic procedure was the same as for 12-ethylene glycol bisbenzyl ether with tosylate, except for using monobenzyl-protected tetraethylene glycol tosylate (90% in purity, 2.43 g, 5 mmol) instead of monobenzyl-protected tetraethylene glycol mesylate, to give the product with 75% yield.

**12-Ethylene glycol bisbenzyl ether with mesylate:** The synthetic procedure was the same as for 12-ethylene glycol bisbenzyl ether with tosylate, except for using monobenzyl-protected tetraethylene glycol mesylate (90% in purity, 1.21 g, 3 mmol) instead of monobenzyl-protected tetraethylene glycol mesylate, to give the product with 83% yield as colorless liquid.

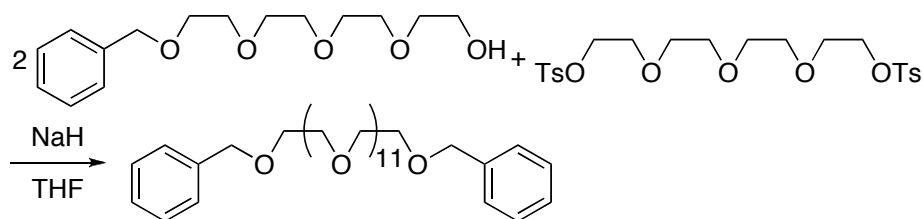
**12-Ethylene glycol:** To an autoclave, 12-ethylene glycol bisbenzyl ether (3.63 g, 5 mmol), palladium carbon (5wt%, 200 mg), and EtOH (130 mL) were put, and the autoclave was sealed. H<sub>2</sub> gas (8 atm) was introduced to the autoclave, and the reaction mixture was stirred for 24 hrs at 100 °C. The autoclave was allowed to cool at room temperature and depressurized to open. The product was obtained by filtration off palladium carbon and solvent evaporation in 98% yield as colorless liquid.



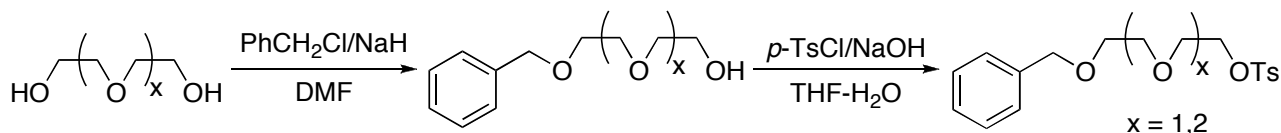
**Tetraethylene glycol ditosylate:** Tetraethylene glycol (1.94 g, 10 mmol), NaOH (1.4 g, 35 mmol), THF (35 mL), and H<sub>2</sub>O (35 mL) were put to a three-necked flask, and the mixture was cooled at 0 °C. To the mixture, a THF solution (100 mL) of *p*-toluenesulfonyl chloride (4.19 g, 22 mmol) was added dropwise, and the reaction mixture was stirred for 2 hrs at 0 °C. The reaction mixture was allowed to warm at room temperature, and stirred for additional 2 hrs. The reaction mixture was poured to 5wt% aq. HCl, and the product was extracted with C<sub>6</sub>H<sub>6</sub> twice. The organic layer was rinsed with water, and dried with Na<sub>2</sub>SO<sub>4</sub>. The crude product (colorless liquid, quantitative yield) obtained by solvent evaporation and drying under vacuum condition was used for the subsequent reaction without purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 2.44 (6H, s, CH<sub>3</sub>), 3.56 (8H, s, OCH<sub>2</sub>), 3.68 (4H, t, J = 5.0Hz, OCH<sub>2</sub>), 4.15 (4H, t, J = 4.8Hz, OCH<sub>2</sub>), 7.34 (4H, d, J = 8.4Hz, aromatic H), 7.79 (4H, d,



$J = 8.4\text{Hz}$ , aromatic H).



**12-Ethylene glycol bisbenzyl ether with tetraethylene glycol ditosylate:** To a three-necked flask, monobenzyl-protected tetraethylene glycol (90% in purity, 1.90 g, 6 mmol), NaH (960 mg, 40 mmol), and dry THF (150 mL) were put, and a dry THF solution (50 mL) of tetraethylene glycol ditosylate (1.06 g, 2 mmol) was added to the mixture dropwise at room temperature. The reaction mixture was refluxed for 24 hrs, and then, allowed to cool at room temperature. Methanol was added to the reaction mixture to quench excess NaH. The solvent was evaporated, and the product was extracted with 5wt% aq. HCl and  $\text{CHCl}_3$ . The product obtained by solvent evaporation was purified by gel permeation chromatography (GPC) in 62% yield as colorless liquid.



**Monobenzyl-protected diethylene glycol:** To a three-necked flask, NaH (9.60 g, 400 mmol) and DMF (700 mL) were placed, and then, diethylene glycol (42.4 g, 400 mmol) was added slowly. The mixture was heated to  $100\text{ }^{\circ}\text{C}$ , and DMF solution (80 mL) of benzyl chloride (12.7 g, 100 mmol) was added dropwise. The reaction mixture was stirred for 3 hrs at  $100\text{ }^{\circ}\text{C}$ , and then, it was allowed to cool at room temperature. Methanol was added to the reaction mixture to quench excess NaH, and 5wt% aq. HCl (50 mL) was added. After evaporation of DMF, the product was extracted using 5wt% aq. HCl and  $\text{CHCl}_3$ . The crude product (brownish liquid, quantitative yield) obtained by solvent evaporation and drying under vacuum condition was used for the subsequent reaction without purification. In this case, the formation of bisbenzyl ether was not recognized in  $^1\text{H}$  NMR analysis.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.8 (8H, m,  $\text{OCH}_2$ ), 4.57 (2H, s,  $\text{CH}_2\text{Ph}$ ), 7.2~7.4 (5H,

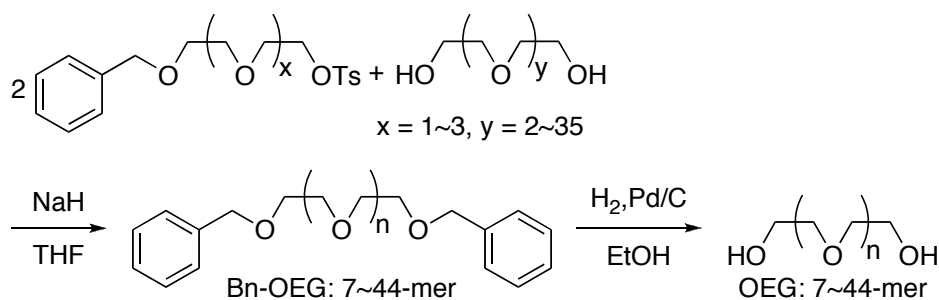
m, aromatic H).

**Monobenzyl-protected diethylene glycol tosylate:** Monobenzyl-protected diethylene glycol (9.81 g, 50 mmol), NaOH (7.00 g, 175 mmol), THF (35 mL), and H<sub>2</sub>O (35 mL) were put to a three-necked flask, and the mixture was cooled at 0 °C. A THF solution (50 mL) of *p*-toluenesulfonyl chloride (11.4 g, 60 mmol) was added to the mixture dropwise, and the reaction mixture was stirred for 2 hrs at 0 °C. The reaction mixture was allowed to warm at room temperature, and stirred for additional 20 hrs. The reaction mixture was poured to 5wt% aq. HCl cooled at 0 °C, and the product was extracted with CHCl<sub>3</sub>. The organic layer was rinsed with water, and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and the obtained product (brownish liquid, quantitative yield) was used for the subsequent reaction without purification after drying under vacuum condition. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 2.43 (3H, s, CH<sub>3</sub>), 3.55~3.65 (4H, m, OCH<sub>2</sub>), 3.70 (2H, t, J = 4.8Hz, OCH<sub>2</sub>), 4.17 (2H, t, J = 4.8Hz, OCH<sub>2</sub>), 4.53 (2H, s, CH<sub>2</sub>Ph), 7.2~7.4 (7H, m, aromatic H), 7.80 (2H, d, J = 8.3Hz, aromatic H).

**Monobenzyl-protected triethylene glycol:** The synthetic procedure was the same as for monobenzyl-protected diethylene glycol, except for using triethylene glycol (60.0 g, 400 mmol) instead of diethylene glycol, to give the product with 77% yield (brownish liquid). The formation of bisbenzyl ether in ca. 20% molar ratio was observed in <sup>1</sup>H NMR analysis. Peaks in <sup>1</sup>H NMR spectra (500 MHz, in CDCl<sub>3</sub>) for benzyl protons of triethylene glycol monobenzyl and bisbenzyl ethers afforded different chemical shifts, being 4.57 and 4.56 ppm, respectively, to determine the molar ratio by a simple integration. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 3.6~3.8 (12H, m, OCH<sub>2</sub>), 4.57 (2H, s, CH<sub>2</sub>Ph), 7.2~7.4 (5H, m, aromatic H).

**Monobenzyl-protected triethylene glycol tosylate:** The synthetic procedure was the same as for monobenzyl-protected diethylene glycol tosylate, except for using monobenzyl-protected triethylene glycol (80% in purity, 15.0 g, 50 mmol) instead of monobenzyl-protected diethylene glycol, to give the product with quantitative yield (brownish liquid). The crude product contained triethylene glycol bisbenzyl ether in ca. 20% molar ratio. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 2.42 (3H, s, CH<sub>3</sub>), 3.5~3.7 (10H, m, OCH<sub>2</sub>), 4.14 (2H, t, J = 4.6Hz, OCH<sub>2</sub>), 4.54 (2H, s, CH<sub>2</sub>Ph), 7.2~7.4 (7H, m,

aromatic H), 7.78 (2H, d, J = 8.2Hz, aromatic H).



**7-Ethylene glycol bisbenzyl ether:** To a three-necked flask, triethylene glycol (750 mg, 5 mmol), NaH (2.40 g, 100 mmol), and dry THF (200 mL) were put, and a dry THF solution (50 mL) of monobenzyl-protected diethylene glycol tosylate (5.25 g, 15 mmol) was added to the mixture dropwise at room temperature. The reaction mixture was refluxed for 24 hrs, and then, allowed to cool at room temperature. Methanol was added to the reaction mixture to quench excess NaH. The solvent was evaporated, and the product was extracted with 5wt% aq. HCl and  $\text{CHCl}_3$ . The product obtained by solvent evaporation was purified by gel permeation chromatography (GPC) in 80% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.7 (28H, m,  $\text{OCH}_2$ ), 4.56 (4H, s,  $\text{CH}_2\text{Ph}$ ), 7.2~7.4 (10H, m, aromatic H); Anal. Calcd. for  $\text{C}_{28}\text{H}_{42}\text{O}_8$ : C, 66.38; H, 8.36. Found: C, 66.02; H, 8.39; m/z: 507 ( $\text{M} + \text{H}^+$ ).

**7-Ethylene glycol:** To an autoclave, 7-ethylene glycol bisbenzyl ether (2.60 g, 5 mmol), palladium carbon (5wt%, 200 mg), and EtOH (130 mL) were put, and the autoclave was sealed.  $\text{H}_2$  gas (8 atm) was introduced to the autoclave, and the reaction mixture was stirred for 24 hrs at 100 °C. The autoclave was allowed to cool at room temperature and depressurized to open. The product was obtained by filtration off palladium carbon and solvent evaporation in 98% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.5~3.8 (28H, m,  $\text{OCH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  61.8, 70.4, 70.7 (3 carbons), 70.72, 72.7; Anal. Calcd. for  $\text{C}_{14}\text{H}_{30}\text{O}_8$ : C, 51.52; H, 9.26. Found: C, 51.89; H, 9.42; m/z: 327 ( $\text{M} + \text{H}^+$ ).

**8-Ethylene glycol bisbenzyl ether:** The synthetic procedure was the same as for 7-ethylene glycol bisbenzyl ether, except for using tetraethylene glycol (970 mg, 5 mmol) instead of triethylene glycol,

to give the product with 71% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.7 (32H, m,  $\text{OCH}_2$ ), 4.56 (4H, s,  $\text{CH}_2\text{Ph}$ ), 7.2~7.4 (10H, m, aromatic H); Anal. Calcd. for  $\text{C}_{30}\text{H}_{46}\text{O}_9$ : C, 65.43; H, 8.42. Found: C, 65.03; H, 8.48;  $m/z$ : 551 ( $\text{M} + \text{H}^+$ ).

**8-Ethylene glycol:** The synthetic procedure was the same as for 7-ethylene glycol, except for using 8-ethylene glycol bisbenzyl ether (2.82 g, 5 mmol) instead of 7-ethylene glycol bisbenzyl ether, to give the product with 91% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.5~3.8 (32H, m,  $\text{OCH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  61.8, 70.5, 70.7 (5 carbons), 72.8; Anal. Calcd. for  $\text{C}_{16}\text{H}_{34}\text{O}_9$ : C, 51.88; H, 9.25. Found: C, 51.89; H, 9.17;  $m/z$ : 371 ( $\text{M} + \text{H}^+$ ).

**9-Ethylene glycol bisbenzyl ether:** The synthetic procedure was the same as for 7-ethylene glycol bisbenzyl ether, except for using monobenzyl-protected triethylene glycol tosylate (80% in purity, 7.40 g, 15 mmol) instead of monobenzyl-protected diethylene glycol tosylate, to give the product with 79% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.7 (36H, m,  $\text{OCH}_2$ ), 4.56 (4H, s,  $\text{CH}_2\text{Ph}$ ), 7.2~7.4 (10H, m, aromatic H); Anal. Calcd. for  $\text{C}_{32}\text{H}_{50}\text{O}_{10}$ : C, 64.63; H, 8.47. Found: C, 64.68; H, 8.52;  $m/z$ : 595 ( $\text{M} + \text{H}^+$ ).

**9-Ethylene glycol:** The synthetic procedure was the same as for 7-ethylene glycol, except for using 9-ethylene glycol bisbenzyl ether (3.04 g, 5 mmol) instead of 7-ethylene glycol bisbenzyl ether, to give the product with 93% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.8 (36H, m,  $\text{OCH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  61.8, 70.4, 70.7 (5 carbons), 70.73, 72.7; Anal. Calcd. for  $\text{C}_{18}\text{H}_{38}\text{O}_{10}$ : C, 52.16; H, 9.24. Found: C, 51.86; H, 9.41;  $m/z$ : 415 ( $\text{M} + \text{H}^+$ ).

**10-Ethylene glycol bisbenzyl ether:** The synthetic procedure was the same as for 7-ethylene glycol bisbenzyl ether, except for using tetraethylene glycol (970 mg, 5 mmol) and monobenzyl-protected triethylene glycol tosylate (80% in purity, 7.40 g, 15 mmol) instead of triethylene glycol and monobenzyl-protected diethylene glycol tosylate, respectively, to give the product with 66% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.7 (40H, m,  $\text{OCH}_2$ ), 4.56 (4H, s,  $\text{CH}_2\text{Ph}$ ), 7.2~7.4 (10H, m, aromatic H); Anal. Calcd. for  $\text{C}_{34}\text{H}_{54}\text{O}_{11}$ : C, 63.93; H, 8.52. Found: C, 64.07; H, 8.57;  $m/z$ : 639 ( $\text{M} + \text{H}^+$ ).

**10-Ethylene glycol:** The synthetic procedure was the same as for 7-ethylene glycol, except for

using 10-ethylene glycol bisbenzyl ether (3.26 g, 5 mmol) instead of 7-ethylene glycol bisbenzyl ether, to give the product with 98% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.8 (40H, m,  $\text{OCH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  61.7, 70.3, 70.6 (6 carbons), 70.7, 72.9; Anal. Calcd. for  $\text{C}_{20}\text{H}_{42}\text{O}_{11}$ : C, 52.39; H, 9.23. Found: C, 51.99; H, 9.40;  $m/z$ : 459 ( $\text{M} + \text{H}^+$ ).

**11-Ethylene glycol bisbenzyl ether:** The synthetic procedure was the same as for 7-ethylene glycol bisbenzyl ether, except for using monobenzyl-protected tetraethylene glycol tosylate (90% in purity, 7.31 g, 15 mmol) instead of monobenzyl-protected diethylene glycol tosylate, to give the product with 66% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.7 (44H, m,  $\text{OCH}_2$ ), 4.56 (4H, s,  $\text{CH}_2\text{Ph}$ ), 7.2~7.4 (10H, m, aromatic H); Anal. Calcd. for  $\text{C}_{36}\text{H}_{58}\text{O}_{12}$ : C, 63.32; H, 8.56. Found: C, 63.51; H, 8.54;  $m/z$ : 683 ( $\text{M} + \text{H}^+$ ).

**11-Ethylene glycol:** The synthetic procedure was the same as for 7-ethylene glycol, except for using 11-ethylene glycol bisbenzyl ether (3.48 g, 5 mmol) instead of 7-ethylene glycol bisbenzyl ether, to give the product with 97% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.8 (44H, m,  $\text{OCH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  61.8, 70.4, 70.6 (8 carbons), 70.7, 72.6; Anal. Calcd. for  $\text{C}_{22}\text{H}_{46}\text{O}_{12}$ : C, 52.58; H, 9.22. Found: C, 52.24; H, 9.36;  $m/z$ : 503 ( $\text{M} + \text{H}^+$ ).

**12-Ethylene glycol bisbenzyl ether:** The synthetic procedure was the same as for 7-ethylene glycol bisbenzyl ether, except for using tetraethylene glycol (970 mg, 5 mmol) and monobenzyl-protected tetraethylene glycol tosylate (90% in purity, 7.31 g, 15 mmol) instead of triethylene glycol and monobenzyl-protected diethylene glycol tosylate, respectively, to give the product with 73% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.7 (48H, m,  $\text{OCH}_2$ ), 4.57 (4H, s,  $\text{CH}_2\text{Ph}$ ), 7.2~7.4 (10H, m, aromatic H); Anal. Calcd. for  $\text{C}_{38}\text{H}_{62}\text{O}_{13}$ : C, 62.79; H, 8.60. Found: C, 62.97; H, 8.46;  $m/z$ : 727 ( $\text{M} + \text{H}^+$ ).

**12-Ethylene glycol:** The synthetic procedure was the same as for 7-ethylene glycol, except for using 12-ethylene glycol bisbenzyl ether (3.63 g, 5 mmol) instead of 7-ethylene glycol bisbenzyl ether, to give the product with 97% yield as colorless liquid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.6~3.8 (48H, m,  $\text{OCH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  61.7, 70.4, 70.6 (8 carbons), 70.7, 72.8; Anal. Calcd. for  $\text{C}_{24}\text{H}_{50}\text{O}_{13}$ : C, 52.73; H, 9.22. Found: C, 52.40; H, 9.44;  $m/z$ : 547 ( $\text{M} + \text{H}^+$ ).

**20-Ethylene glycol bisbenzyl ether:** To a three-necked flask, 12-ethylene glycol (547 mg, 1 mmol), NaH (480 mg, 20 mmol), and dry THF (50 mL) were put, and a dry THF solution (20 mL) of monobenzyl-protected tetraethylene glycol tosylate (90% in purity, 1.46 g, 3 mmol) was added to the mixture dropwise at room temperature. The reaction mixture was refluxed for 24 hrs, and then, allowed to cool at room temperature. Methanol was added to the reaction mixture to quench excess NaH. The solvent was evaporated, and the product was extracted with 5wt% aq. HCl and CHCl<sub>3</sub>. The product obtained by solvent evaporation was purified by gel permeation chromatography (GPC) in 73% yield as colorless liquid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 3.5~3.7 (80H, m, OCH<sub>2</sub>), 4.55 (4H, s, CH<sub>2</sub>Ph), 7.2~7.4 (10H, m, aromatic H); Anal. Calcd. for C<sub>54</sub>H<sub>94</sub>O<sub>21</sub>: C, 60.09; H, 8.78. Found: C, 59.89; H, 8.73; m/z: 1080 (M + 2H<sup>+</sup>).

**20-Ethylene glycol:** To an autoclave, 20-ethylene glycol bisbenzyl ether (1.08 g, 1 mmol), palladium carbon (5wt%, 200 mg), and EtOH (100 mL) were put, and the autoclave was sealed. H<sub>2</sub> gas (8 atm) was introduced to the autoclave, and the reaction mixture was stirred for 24 hrs at 100 °C. The autoclave was allowed to cool at room temperature and depressurized to open. The product was obtained by filtration off palladium carbon and solvent evaporation in 93% yield as colorless waxy solid; m.p. 33~35 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 3.6~3.8 (80H, m, OCH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 61.6, 70.3, 70.6 (17 carbons), 72.6; Anal. Calcd. for C<sub>40</sub>H<sub>82</sub>O<sub>21</sub>: C, 53.44; H, 9.19. Found: C, 53.19; H, 9.12; m/z: 899 (M + H<sup>+</sup>).

**28-Ethylene glycol bisbenzyl ether:** The synthetic procedure was the same as for 20-ethylene glycol bisbenzyl ether, except for using 20-ethylene glycol (899 mg, 1 mmol) instead of 12-ethylene glycol, to give the product with 75% yield as colorless waxy solid; m.p. 29~31 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 3.5~3.7 (112H, m, OCH<sub>2</sub>), 4.54 (4H, s, CH<sub>2</sub>Ph), 7.2~7.4 (10H, m, aromatic H); Anal. Calcd. for C<sub>70</sub>H<sub>126</sub>O<sub>29</sub>: C, 58.72; H, 8.87. Found: C, 58.47; H, 8.83; m/z: 1432 (M + 2H<sup>+</sup>).

**28-Ethylene glycol:** The synthetic procedure was the same as for 20-ethylene glycol, except for using 28-ethylene glycol bisbenzyl ether (1.43 g, 1 mmol) instead of 20-ethylene glycol bisbenzyl ether, to give the product with 94% yield as colorless solid; m.p. 39~40 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 3.6~3.8 (112H, m, OCH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 61.8, 70.4, 70.7 (25 carbons), 72.7; Anal.

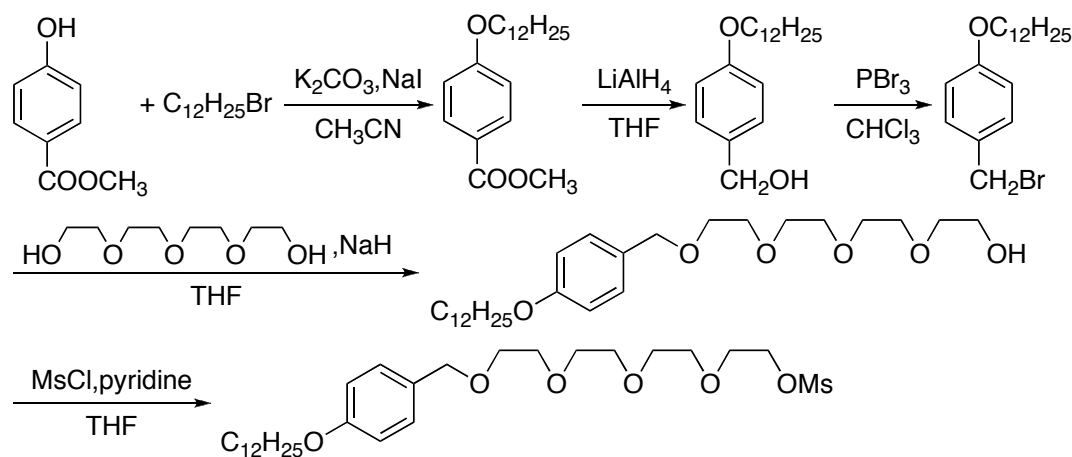
Calcd. for  $C_{56}H_{114}O_{29}$ : C, 53.74; H, 9.18. Found: C, 53.48; H, 9.14; m/z: 1251 ( $M + H^+$ ).

**36-Ethylene glycol bisbenzyl ether:** The synthetic procedure was the same as for 20-ethylene glycol bisbenzyl ether, except for using 28-ethylene glycol (1.25 g, 1 mmol) instead of 12-ethylene glycol, to give the product with 77% yield as colorless solid; m.p. 41~42 °C;  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  3.5~3.7 (144H, m,  $OCH_2$ ), 4.54 (4H, s,  $CH_2Ph$ ), 7.2~7.4 (10H, m, aromatic H); Anal. Calcd. for  $C_{86}H_{158}O_{37}$ : C, 57.90; H, 8.93. Found: C, 57.88; H, 8.97; m/z: 1784 ( $M + 2H^+$ ).

**36-Ethylene glycol:** The synthetic procedure was the same as for 20-ethylene glycol, except for using 36-ethylene glycol bisbenzyl ether (1.78 g, 1 mmol) instead of 20-ethylene glycol bisbenzyl ether, to give the product with 95% yield as colorless solid; m.p. 45~46 °C;  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  3.6~3.8 (144H, m,  $OCH_2$ );  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  61.8, 70.4, 70.7 (33 carbons), 72.7; Anal. Calcd. for  $C_{72}H_{146}O_{37}$ : C, 53.92; H, 9.17. Found: C, 53.79; H, 9.15; m/z: 1604 ( $M + 2H^+$ ).

**44-Ethylene glycol bisbenzyl ether:** The synthetic procedure was the same as for 20-ethylene glycol bisbenzyl ether, except for using 36-ethylene glycol (1.60 g, 1 mmol) instead of 12-ethylene glycol, to give the product with 69% yield as colorless solid; m.p. 45~46 °C;  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  3.6~3.7 (176H, m,  $OCH_2$ ), 4.55 (4H, s,  $CH_2Ph$ ), 7.2~7.4 (10H, m, aromatic H); Anal. Calcd. for  $C_{102}H_{190}O_{45}$ : C, 57.34; H, 8.96. Found: C, 57.03; H, 8.99; m/z: 2134 ( $M^+$ ).

**44-Ethylene glycol:** The synthetic procedure was the same as for 20-ethylene glycol, except for using 44-ethylene glycol bisbenzyl ether (2.14 g, 1 mmol) instead of 20-ethylene glycol bisbenzyl ether, to give the product with 98% yield as colorless solid; m.p. 48~49 °C;  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  3.6~3.7 (176H, m,  $OCH_2$ );  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  61.7, 70.4, 70.6 (41 carbons), 72.6; Anal. Calcd. for  $C_{88}H_{178}O_{45}$ : C, 54.03; H, 9.17. Found: C, 54.12; H, 9.17; m/z: 1956 ( $M + 2H^+$ ).



**Mehtyl-4-(docecyloxy)benzoate:** Under nitrogen atmosphere, 1-bromododecane (12.5 g, 50 mmol), methyl-4-hydroxybenzoate (11.4 g, 75 mmol), and acetonitrile (800 mL) were placed to a three-necked flask. To the mixture,  $K_2CO_3$  (69.0 g, 500 mmol) and  $NaI$  (7.50 g, 50 mmol) were added, and the reaction mixture was refluxed for 24 hrs. The reaction mixture was allowed to cool at room temperature, and the solvent was evaporated. To the obtained residue, 5wt% aq.  $NaOH$  was added, and the product was extracted with ethyl acetate. The organic layer was rinsed with 5wt% aq.  $NaOH$ , and then, with 5wt% aq.  $HCl$ . The product obtained by solvent evaporation and drying under vacuum condition (colorless solid, quantitative yield) was used for the subsequent reaction without purification.  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  0.88 (3H, t,  $J = 6.8Hz$ ,  $CH_3$ ), 1.2~1.5 (18H, m,  $CH_2$ ), 1.7~1.9 (2H, m,  $CH_2$ ), 3.89 (3H, s,  $OCH_3$ ), 4.00 (2H, t,  $J = 6.6Hz$ ,  $OCH_2$ ), 6.90 (2H, d,  $J = 9.0Hz$ , aromatic H), 7.98 (2H, d,  $J = 9.2Hz$ , aromatic H).

**4-(Dodecyloxy)benzyl alcohol:** To a three necked-flask,  $LiAlH_4$  (2.38 g, 62.5 mmol) and  $THF$  (500 mL) were placed. To the mixture, a  $THF$  solution (100 mL) of mehtyl-4-(docecyloxy)benzoate (8.00 g, 25 mmol) was added dropwise, and the reaction mixture was stirred for 1hr at room temperature. In order to quench excess  $LiAlH_4$ , methanol (50 mL) was added to the reaction mixture dropwise at 0 °C, and then, conc. aq.  $HCl$  (50 mL) was added dropwise similarly. After solvent evaporation, water was added to the obtained residue, and the product was extracted with  $CHCl_3$ . The product obtained by solvent evaporation and drying under vacuum condition (colorless solid, quantitative yield) was used for the subsequent reaction without purification.  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  0.88 (3H, t,  $J = 6.8Hz$ ,  $CH_3$ ), 1.2~1.6 (18H, m,  $CH_2$ ), 1.7~1.9 (2H, m,  $CH_2$ ), 3.95 (2H, t,  $J =$



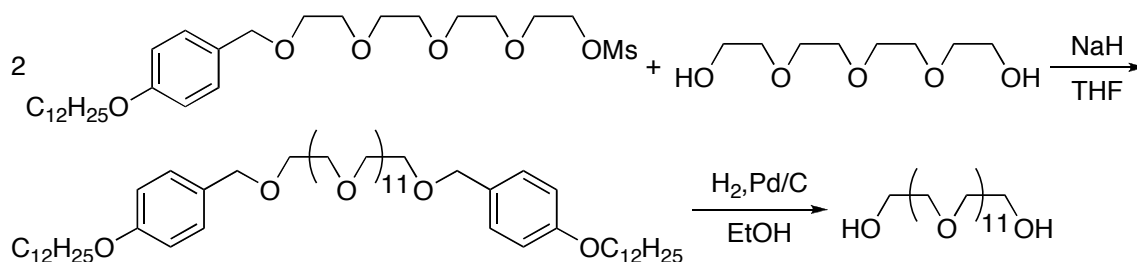
6.6Hz, OCH<sub>2</sub>), 4.61 (2H, s, PhCH<sub>2</sub>), 6.87 (2H, d, J = 8.8Hz, aromatic H), 7.28 (2H, d, J = 9.2Hz, aromatic H).

**4-(Dodecyloxy)benzyl bromide:** To a three-necked flask, 4-(dodecyloxy)benzyl alcohol (2.92 g, 10 mmol) and CHCl<sub>3</sub> (150 mL) were put, and a CHCl<sub>3</sub> solution (20 mL) of PBr<sub>3</sub> (4.06 g, 15 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 1 hr and poured into water. The organic layer was separated and dried with Na<sub>2</sub>SO<sub>4</sub>. The product obtained by solvent evaporation and drying under vacuum condition (brownish solid, quantitative yield) was used for the subsequent reaction without purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.88 (3H, t, J = 6.8Hz, CH<sub>3</sub>), 1.2~1.6 (18H, m, CH<sub>2</sub>), 1.7~1.9 (2H, m, CH<sub>2</sub>), 3.95 (2H, t, J = 6.6Hz, OCH<sub>2</sub>), 4.56 (2H, s, PhCH<sub>2</sub>), 6.88 (2H, d, J = 10.4Hz, aromatic H), 7.29 (2H, d, J = 10.8Hz, aromatic H).

**Mono-4-(dodecyloxy)benzyl-protected tetraethylene glycol:** Tetraethylene glycol (9.70 g, 50 mmol), NaH (2.40 g, 100 mmol), and THF 100mL were placed to a three-necked flask. To the mixture, a THF solution (30 mL) of 4-(dodecyloxy)benzyl bromide (3.55 g, 10 mmol) was added dropwise, and the reaction mixture was refluxed for 4 hrs. The reaction mixture was allowed to cool at room temperature, and methanol was added to quench excess NaH. The solvent was evaporated, and 5wt% aq. HCl was added to the obtained residue. The product was extracted with CHCl<sub>3</sub>, and the solvent was evaporated. The product obtained by drying under vacuum condition (brownish liquid, quantitative yield) was used for the subsequent reaction without purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.88 (3H, t, J = 6.4Hz, CH<sub>3</sub>), 1.2~1.6 (18H, m, CH<sub>2</sub>), 1.7~1.9 (2H, m, CH<sub>2</sub>), 3.5~3.8 (16H, m, OCH<sub>2</sub>), 3.94 (2H, t, J = 6.6Hz, OCH<sub>2</sub>), 4.49 (2H, s, PhCH<sub>2</sub>), 6.86 (2H, d, J = 8.4Hz, aromatic H), 7.25 (2H, d, J = 8.4Hz, aromatic H).

**Mono-4-(dodecyloxy)benzyl-protected tetraethylene glycol mesylate:** Mono-4-(dodecyloxy)benzyl-protected tetraethylene glycol (4.49 g, 10 mmol), pyridine (3.95 g, 50 mmol), and THF (100 mL) were put to a three-necked flask. To the mixture, a THF solution (20 mL) of mesyl chloride (5.75 g, 50 mmol) was added dropwise, and the reaction mixture was stirred for 24 hrs at room temperature. The solvent was evaporated, and 5wt% aq. HCl was added to the obtained residue. The product was extracted with ethyl acetate. The organic layer was rinsed with 5wt% aq.

HCl, and then, dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated, and the product was purified with gel permeation chromatography with 78% yield as brownish liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.88 (3H, t, J = 6.8Hz, CH<sub>3</sub>), 1.2~1.6 (18H, m, CH<sub>2</sub>), 1.7~1.9 (2H, m, CH<sub>2</sub>), 3.06 (3H, s, CH<sub>3</sub>), 3.5~3.8 (14H, m, OCH<sub>2</sub>), 3.94 (2H, t, J = 6.6Hz, OCH<sub>2</sub>), 4.3~4.4 (2H, m, OCH<sub>2</sub>), 4.48 (2H, s, PhCH<sub>2</sub>), 6.86 (2H, d, J = 8.4Hz, aromatic H), 7.25 (2H, d, J = 8.4Hz, aromatic H).



**12-Ethylene glycol bis(4-(dodecyloxy)benzyl) ether with mono-4-(dodecyloxy)benzyl-protected tetraethylene glycol mesylate:** To a three-necked flask, tetraethylene glycol (388 mg, 2 mmol), NaH (480 mg, 20 mmol), and dry THF (50 mL) were put, and a dry THF solution (20 mL) of mono-4-(dodecyloxy)benzyl-protected tetraethylene glycol mesylate (3.28 g, 6 mmol) was added to the mixture dropwise at room temperature. The reaction mixture was refluxed for 24 hrs, and then, allowed to cool at room temperature. Methanol was added to the reaction mixture to quench excess NaH. The solvent was evaporated, and 5wt% aq. HCl was added to the obtained residue. The product was extracted with CHCl<sub>3</sub>. The product obtained by solvent evaporation was purified by gel permeation chromatography in 95% yield as colorless liquid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 0.88 (6H, t, J = 6.6Hz, CH<sub>3</sub>), 1.2~1.6 (36H, m, CH<sub>2</sub>), 1.7~1.9 (4H, m, CH<sub>2</sub>), 3.5~3.7 (48H, m, OCH<sub>2</sub>), 3.94 (4H, t, J = 6.6Hz, OCH<sub>2</sub>), 4.48 (4H, s, PhCH<sub>2</sub>), 6.85 (4H, d, J = 8.4Hz, aromatic H), 7.24 (4H, d, J = 8.4Hz, aromatic H).

**12-Ethylene glycol with 12-ethylene glycol bis(4-(dodecyloxy)benzyl) ether:** To an autoclave, 12-ethylene glycol bis(4-(dodecyloxy)benzyl) ether (5.48 g, 5 mmol), palladium carbon (5wt%, 1.00 g), and EtOH (100 mL) were put, and the autoclave was sealed. H<sub>2</sub> gas (8 atm) was introduced to the autoclave, and the reaction mixture was stirred for 24 hrs at 100 °C. The autoclave was allowed to cool at room temperature and depressurized to open. Palladium carbon was filtrated off, and the

solvent was evaporated. To the obtained residue, 5wt% aq. HCl and ethyl acetate were added, and the aqueous layer was separated. Water and HCl were removed, and the product was obtained by drying under vacuum condition in 92% yield as colorless liquid.