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Intramolecular rearrangement of 1,3-bistriflate ester of thiacalix[4]arene to 1,2-counterpart: an efficient di-O-protection method for the stereoselective synthesis of *anti*-1,2-diethers

Ryuichi Serizawa,[a] Shinya Tanaka,[a] Naoya Morohashi,[a] Fumitaka Narumi[b] and Tetsutaro Hattori[a,*]

[a]*Department of Environmental Studies, Graduate School of Environmental Studies, Tohoku University, 6-6-11 Aramaki-Aoba, Aoba-ku, Sendai 980-8579, Japan*
[b]*Department of Basic Sciences, School of Science and Engineering, Ishinomaki Senshu University, 1 Shinmito, Minamisakai, Ishinomaki 986-8580, Japan*

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Abstract—A net *anti*-selective dialkylation of the proximal hydroxy groups of thiacalix[4]arene **2** is achieved for the first time via the initial protection of the two proximal hydroxy groups of compound **2** with Tf moieties by intramolecular rearrangement of easily preparable 1,3-bistriflate ester **3** to 1,2-counterpart **4**, followed by *anti*-selective dialkylation of the remaining hydroxy groups with alkyl halides or under the Mitsunobu conditions and subsequent removal of the Tf moieties.

Calix[4]arenes (e.g., **1**) are one of the most extensively utilized molecular scaffolds for designing synthetic receptors in supramolecular chemistry, which is mainly due to the easy availability of the basic macrocycles and their regio- and stereoselective functionalization methods developed for this class of compounds during the last two decades.[1] It is well known in calixarene chemistry that the dialkylation of the phenolic hydroxy groups of calix[4]arenes with alkyl halides in the presence of a base preferentially proceeds at the distal positions in a *syn* fashion by virtue of a circular intramolecular hydrogen bonding in the monoalkylated intermediate,[2] which provides a versatile access to *syn*-1,3-di-O-alkylated calix[4]arenes, while it still remains a challenge to prepare other regio- and/or stereoisomers, that is, *syn*-1,2-, *anti*-1,2-, and *anti*-1,3-diethers, under efficient regio- and stereocontrol. We have been engaged in the development of novel functional molecules based on thiacalixarenes (e.g., **2**), which have epithio linkages instead of the methylene bridges in the conventional calixarenes.[3] Recently, we have reported a facile synthesis of 1,2-di-O-alkylated calix- and thiacalix[4]arenes via 1,2-*O*-tetraisopropyldisiloxane (TIPDS)-capping by the treatment of the parent tetraol **1** and **2** with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in the presence of imidazole, followed by the dialkylation of the remaining hydroxy groups with an alkyl halide using a base and subsequent deprotection of the TIPDS moiety.[4] In the dialkylation of conventional calix[4]arene **1**, high degrees of both *syn* and *anti* stereocontrol were achieved by choosing a base, *tert*-BuOK and K_2CO_3 giving *syn* stereoisomers and Cs_2CO_3 *anti* counterparts, while thiacalixarene **2** strongly preferred to afford *syn* stereoisomers in combination with any bases. To the best of our knowledge, a general protocol for the regio- and stereoselective synthesis of *anti*-1,2-diethers of thiacalix[4]arene **2** has yet to be established,[5,6] although the development of such a method is highly desirable for designing not only synthetic receptors but also metal catalysts,[7] as the compounds have one of the simplest inherently chiral calixarene skeleton[8] with potentially high complexation ability toward metal ions originated

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* Corresponding author. Tel.: +81 22 795 7262; fax: +81 22 795 7293; e-mail: hattori@orgsynth.che.tohoku.ac.jp

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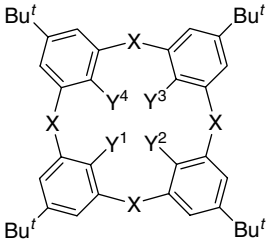
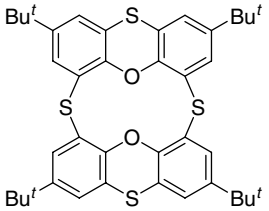
from the cooperative coordination of an epithio linkage with two neighboring phenolates to the metal center.[9] During the course of our studies on the development of an efficient method for replacing a hydroxy group of thiacalix[4]arene **2** with an amino group by an Ullmann-type amination of *syn*-1,3-bistriflate ester **3** with the aid of K_3PO_4,[10] we have encountered an interesting phenomenon that a Tf moiety of compound **3** migrates under the basic conditions to afford *syn*-1,2-bistriflate ester **4**. Ester **4**, having Tf capping groups for the two adjacent hydroxy groups, has shown high *anti* selectivity in the dialkylation of the remaining hydroxy groups. Herein, we wish to report the first successful net *anti*-selective proximal dialkylation of thiacalix[4]arenes **2** via the intramolecular rearrangement of readily available 1,3-bistriflate ester **3**.[10]



	X	Y^1	Y^2	Y^3	Y^4
1	CH_2	OH	OH	OH	OH
2	S	OH	OH	OH	OH
3	S	OTf	OH	OTf	OH
4	S	OTf	OTf	OH	OH
5	S	OTf	OH	OH	OH
6	S	OTf	OTf	OTf	OH



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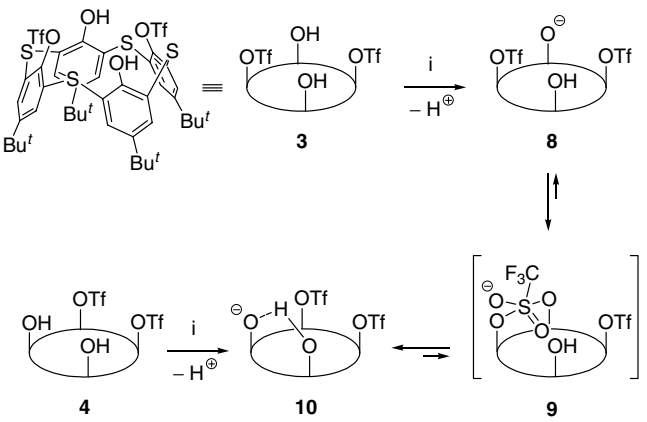
The rearrangement of 1,3-bistriflate **3** to 1,2-counterpart **4** was examined under varying reaction conditions (Table 1).[11] Treatment of **3** with 4.4 mol equiv of Hunig's base in refluxing acetone for 24 h gave the desired 1,2-bistriflate **4** in 15% yield, accompanied by the formation of monotriflate **5** (5%), tristriflate **6** (5%), and bis(phenoxathiine) **7**[10] (8%) with the recovery of the starting ester **3** (48%) (entry 1). Changing the acetone into more polar solvents accelerated the rearrangement presumably due to an increase in the nucleophilicity of the phenolate anion of ester **3** (entries 2 and 3); compound **4** was obtained in an almost quantitative yield on treatment with Hunig's base in DMSO at 60 °C for 8 h. Under the conditions, the reaction time could be reduced to 1 h without appreciable loss of the product yield (entry 4), while the use of an excess of the amine was mandatory (compare entries 5 and 6 with entry 4). Triethylamine was also effective as the base (entry 7), while DMAP did not afford 1,2-bistriflate **4** but mono- (**5**) and tristriflates **6** in 43% and 25% yields, respectively (entry 8). Inorganic bases examined were less effective than the tertiary amines for the rearrangement (entries 9–12). There are several reports on the intra- and/or intermolecular migration of sulfonyl,[12] acyl,[13] and phosphoryl groups[14] in conventional calix[4]arenes and a related compound, in which product-, regio-, and stereoselectivities largely depend on the migration groups, reagents and reaction conditions employed. For example, it was reported that *syn*-1,3-bis(diethoxyphosphoryl) ester of calix[4]arene **1**, on treatment with NaH in benzene or THF at refluxing temperature, gave *syn*-1,2-diphosphoryl ester,[14] while *syn*-1,3-bis(3,5-dinitrobenzoyl) ester of **1** with imidazole in chloroform at room temperature gave *anti*-1,2-diester.[13a] The stereochemistry of **4** obtained in this study was proved to be *syn* as evidenced by ^{1}H NMR analysis after derivatization to diether **13a** (vide infra). The complete *syn*-1,2-selectivity can be explained by an intramolecular ester-exchange mechanism depicted in Scheme 1. The monoanion (**8**) of 1,3-bistriflate **3** is in an equilibrium with that (**10**) of 1,2-bistriflate **4** via trigonal bipyramidal intermediate **9** by the S_AN mechanism or a transition state of a similar geometry by the S_N2 mechanism,[15] which explains the *syn* stereoselectivity. The position of the equilibrium between monoanions **8** and **10** lies far to the right because the latter anion is more stable due to an intramolecular hydrogen bonding. On the other hand, the intermolecular migration of the Tf moiety mediated by DMAP (vide supra) is supposed to proceed via 4-dimethylamino-1-(trifluoromethanesulfonyl)pyridium intermediate formed by the nucleo-

Table 1. Synthesis of 1,2-bistriflate **4** by the rearrangement of 1,3-bistriflate **3**

Entry	Base (mol equiv)	Solvent	Temp/°C (time/h)	Yield[a] (%)
1	Pr^i_2EtN (4.4)	Acetone	Reflux (24)	15
2	Pr^i_2EtN (4.4)	DMF	60 (24)	49[b]
3	Pr^i_2EtN (4.4)	DMSO	60 (8)	96
4	Pr^i_2EtN (4.4)	DMSO	60 (1)	94
5	Pr^i_2EtN (2.2)	DMSO	60 (1)	82
6	Pr^i_2EtN (1.1)	DMSO	60 (1)	72
7	Et_3N (4.4)	DMSO	60 (1)	91
8	DMAP (4.4)	DMSO	60 (1)	—
9	K_2CO_3 (4.4)	DMSO	60 (1)	84
10	Cs_2CO_3 (4.4)	DMSO	60 (1)	89
11	NaOH (4.4)	DMSO	60 (1)	71
12	NaOH (21.1)	DMSO	60 (1)	81

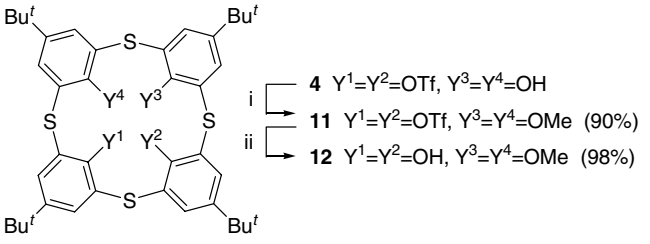
[a] Isolated yield.
[b] 1,3-Bistriflate **3** (7%), monotriflate **5** (15%), tristriflate **6** (9%), and bis(phenoxathiine) **7** (10%) were also isolated.



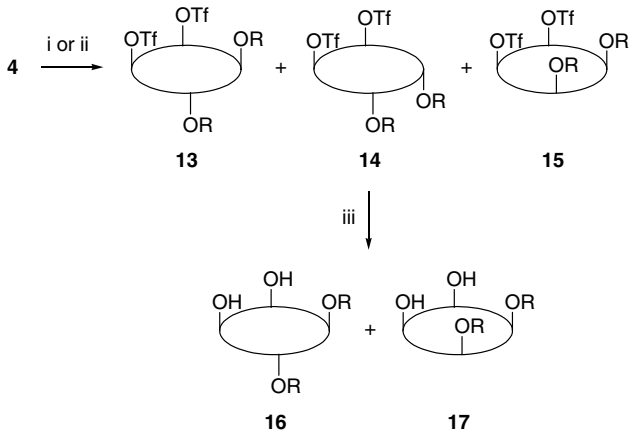
Scheme 1. Reagent: (i) Pr^i_2EtN.

philic attack of DMAP to a Tf moiety of 1,3-bistriflate **3**.[15]

We next examined the dialkylation of 1,2-bistriflate **4**. Ester **4** was treated with a large excess of iodomethane (40 mol equiv) and Cs_2CO_3 (20 mol equiv) in refluxing THF, which was the best solvent for the dialkylation of the TIPDS-capped calixarenes.[4] Under the conditions, the reaction was sluggish and accompanied by severe ester cleavage to give, after heating for 24 h, a complex mixture, from which tetramethyl ether (17%) and tri-*O*-methyl mono-Tf ester (34%) were isolated by TLC. However, changing the solvent to acetone facilitated the dialkylation to give, after the hydrolysis of the ester moieties, dimethyl ether **12**[4a] in almost quantitative yield (Scheme 2). We then tried stereoselective dialkylation by introducing bulkier substituents (Scheme 3 and Table 2).[16–18] Reaction of ester **4** with benzyl bromide was carried out in the presence of Cs_2CO_3 in refluxing acetone, after which a portion of the reaction mixture was purified by TLC to give minor stereoisomer **15a** in 19% yield and a hardly isolable 6:1 mixture of major stereoisomer **13a** and another minor one **14a** in 70% yield (entry 1). The remaining reaction mixture was hydrolyzed without purification to give *anti*- and *syn*-1,2-dibenzyl ethers **16a** and **17a** in 56% and 23% yields, respectively. Thus, the net *anti*-selective dialkylation of thiacalix[4]arene has been achieved for the first time. Other alkyl halides, 1-iodobutane and ethyl bromoacetate, also showed good *anti* selectivity (entries 2 and 3). In the case of ethyl bromoacetate, diester **13c** could be isolated without hydrolysis, which will be convenient for further derivatization. Replacement



Scheme 2. Reagents and conditions: (i) MeI, Ce_2CO_3, acetone, reflux, 4 h; (ii) NaOH, THF–EtOH–H_2O (2:1:1), reflux, 1 day.



13–17a, R=CH_2Ph; **b**, R=Bu; **c**, R=CH_2CO_2Et.

Scheme 3. Reagents and conditions: (i) RX, base, acetone, reflux; 4–8 h; (ii) ROH, PPh_3, DEAD, THF, reflux, 3 h; (iii) NaOH, THF–EtOH–H_2O (2:1:1), reflux, 1 day.

of the base with K_2CO_3 improved the stereoselectivity to an extent depending on the alkyl halide employed (entries 4–6). Although the stereocontrol mechanism is unclear at present, the formation of three stereoisomers **13–15** indicates that the alkyl group was introduced from both the same and opposite sides to the Tf moieties in regard to the mean plane of the macrocycle in each alkylation step. On the other hand, it was found that the dialkylation of **4** under the Mitsunobu conditions efficiently proceeded to give two stereoisomers **13** and **15** out of the three with a good *anti* selectivity (entries 7 and 8).

The stereochemistries of compounds **13–17** were determined by ^1H NMR analyses as exemplified by the case of the dibenzylation as follows. Individual hydrolysis of single stereoisomer **15a** and a mixture of **13a** and **14a** obtained by the reaction of **4** with benzyl bromide confirmed that these compounds yielded *syn*-, *anti*-, and *syn*-1,2-dibenzyl ethers, respectively. The ^1H NMR spectrum of the major isomer **13a** showed four singlets (9H each) for the *tert*-butyl protons and four doublets (1H each) for the OCH_2 protons.[18] The unsymmetrical spectral patterns unambiguously assign the

Table 2. Dialkylation of 1,2-bistriflate **4** and hydrolysis of a mixture of the resulting esters **13–15**

Entry	Dialkylation				Hydrolysis	
	Reagents (mol equiv)	Yield[a] (%)			Yield[a] (%)	
		13	**14**	**15**	**16**	**17**
1	$PhCH_2Br$ (8.0), Cs_2CO_3 (6.0)	60[b]	10[b]	19	56	23
2	BuI (8.0), Cs_2CO_3 (6.0)	60[b]	12[b]	9	55	14
3	$BrCH_2CO_2Et$ (8.0), Cs_2CO_3 (6.0)	51	23	13		
4	$PhCH_2Br$ (20), K_2CO_3 (20)	65[b]	6[b]	21	64	22
5	BuI (20), K_2CO_3 (20)	—[c]	—[c]	—[c]	71	22
6	$BrCH_2CO_2Et$ (20), K_2CO_3 (20)	48	19	14		
7	$PhCH_2OH$ (20), PPh_3 (6.0), DEAD (5.7)	55		21		
8	BuOH (20), PPh_3 (6.0), DEAD (5.7)	78		20		

[a] Isolated yield unless otherwise noted.
[b] Determined by ^1H NMR analysis of a mixture of **13** and **14**.
[c] Not determined.

conformation of **13a** to be partial cone, which consequently establishes the stereochemistry of the two Tf moieties of **4**, as well as that of **13a**, to be *syn*. On the other hand, the ^{1}H NMR spectra of the minor isomers **14a** and **15a** with a *syn* arrangement of the two benzyl moieties showed two singlets (18H each) for the *tert*-butyl protons and two doublets (2H each) for the OCH_2 protons,[17,18] being consistent with the symmetric structure with a σ-plane, that is, cone or 1,2-alternate conformation. It is known that the OCH_2 protons of an alkyl ether of thiacalix[4]arene **2** that adopts 1,2-alternate conformation resonate at a higher field than those of its stereoisomer of cone conformation, owing to anisotropic shielding effects by the facing benzene rings.[4b,16a] Based on the comparison of the chemical shift values of the OCH_2 signals of compound **14a** (δ 4.49 and 5.24) with those of compound **15a** (δ 5.32 and 5.65), the conformations of **14a** and **15a** are assigned to be 1,2-alternate and cone, respectively.

In conclusion, we have shown here an efficient rearrangement of 1,3-bistriflate ester (**3**) of thiacalix[4]arene to 1,2-counterpart **4**. The reaction could be applied to an otherwise difficult *anti*-selective proximal di-O-alkylation of thiacalix[4]arene.

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11. *Typical procedure for the preparation of 1,2-bistriflate* **4** *(Table 1, entry 3)*: A mixture of ester **3** (100 mg, 0.102 mmol), diisopropylethylamine ($d = 0.751$ g mL^{-1}; 77 μL, 0.447 mmol) and dry DMSO (3.0 mL) was heated at 60 °C for 8 h. After cooling, the reaction was quenched with 2 M HCl and the mixture was extracted with chloroform. The extract was washed with water and evaporated to leave a residue, which was chromatographed on silica gel with hexane–chloroform (1:1) as an eluent to give ester **4** (96.3 mg, 96%) as crystals, mp 236–237 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 [18H, s, $C(CH_3)_3$], 1.22 [18H, s, $C(CH_3)_3$], 7.24 (2H, d, $J = 2.3$ Hz, ArH), 7.36 (2H, d, $J = 2.3$ Hz, ArH), 7.53 (2H, d, $J = 2.4$ Hz, ArH), 7.55 (2H, d, $J = 2.4$ Hz, ArH), 7.72 (2H, s, OH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.82, 31.22, 34.18, 34.52, 120.18, 120.33, 129.24, 132.42, 134.16, 134.20, 135.07, 135.45, 143.85, 147.11, 151.42, 154.92; FAB-MS *m*/*z* 984 (M^+). Anal. Calcd for $C_{42}H_{46}F_6O_8S_6$: C, 51.20; H, 4.71; S, 19.53. Found: C, 51.10; H, 4.73; S, 19.67.
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17. *Typical procedure for the dialkylation of 1,2-bistriflate* **4** *with alkyl halides and the hydrolysis of the resulting esters* **13**–**15** *(Table 2, entry 4)*: A mixture of ester **4** (101 mg, 0.103 mmol), K_2CO_3 (281 mg, 2.03 mmol), and dry acetone (3.0 mL) was stirred at room temperature for 30 min. To the mixture was added benzyl bromide ($d = 1.44$ g mL^{-1}; 0.241 mL, 2.03 mmol) and the mixture was refluxed for 6 h. After cooling, the reaction was quenched with 2 M HCl and the mixture was extracted with chloroform. The extract was washed with water and evaporated to leave a residue (123.3 mg), a portion (32.4 mg) of which was purified by TLC with hexane–chloroform (3:2) as a developer to give compound **15a** (6.5 mg, 21%) and a mixture of compounds **13a** and **14a** (22.2 mg, 71%). ^{1}H NMR analysis of the mixture determined the molar ratio of **13a**:**14a** to be 23:2. Compound **14a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 [18H, s, $C(CH_3)_3$], 1.28 [18H, s, $C(CH_3)_3$], 4.49 (2H, d, $J = 11.2$ Hz, OCH_2), 5.24 (2H, d, $J = 11.2$ Hz, OCH_2), 7.28–7.39 (10H, m, Ph), 7.42 (2H, d, $J = 2.5$ Hz, ArH), 7.51 (2H, d, $J = 2.5$ Hz, ArH), 7.52 (2H, d, $J = 2.5$ Hz, ArH), 7.60 (2H, d, $J = 2.5$ Hz, ArH). For the spectral data of **13a**

and **15a**, see ref. 18. The remaining residue (90.9 mg) was heated at reflux with NaOH (283 mg) in a mixture of THF (3.0 mL), ethanol (1.5 mL), and water (1.5 mL) for 1 day. After cooling, the reaction was quenched with 2 M HCl and the mixture was extracted with chloroform. The extract was washed with water and evaporated to leave a residue, which was purified by TLC with hexane–chloroform (1:1) as a developer to give diethers **16a** (43.5 mg, 64%) and **17a** (14.7 mg, 22%). The spectral data of these diethers were identical with those reported previously.[4b]

18. *Typical procedure for the dialkylation of 1,2-bistriflate* **4** *by the Mitsunobu reaction (Table 2, entry 7)*: To an ice-cold solution of ester **4** (101 mg, 0.103 mmol) in dry THF were added triphenylphosphine (160 mg, 0.610 mmol) and a 40% solution of diethyl azodicarboxylate (DEAD) in toluene ($d = 0.958$ g mL^{-1}; 0.264 mL, 0.581 mmol) and the mixture was stirred for 10 min. To the mixture was added benzyl alcohol ($d = 1.05$ g mL^{-1}; 0.210 mL, 2.04 mmol) and the resulting mixture was refluxed for 3 h. After cooling, the reaction was quenched with 2 M HCl and the mixture was extracted with chloroform. The extract was washed with water and evaporated to leave a residue, which was purified by TLC with hexane–chloroform (2:1) as a developer to give diethers **13a** (65.3 mg, 55%) and **15a** (25.3 mg, 21%). Compound **13a**: mp 258–260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.63 [9H, s, $C(CH_3)_3$], 1.02 [9H, s, $C(CH_3)_3$], 1.30 [9H, s, $C(CH_3)_3$], 1.33 [9H, s, $C(CH_3)_3$], 4.93 (1H, d, $J = 9.4$ Hz, OCH_2), 4.96 (1H, d, $J = 10.9$ Hz, OCH_2), 5.12 (1H, d, $J = 9.4$ Hz, OCH_2), 5.42 (1H, d, $J = 10.9$ Hz, OCH_2), 6.87 (1H, d, $J = 2.5$ Hz, ArH), 7.06 (1H, d, $J = 2.5$ Hz, ArH), 7.28–7.40 (9H, m, ArH and Ph), 7.45 (1H, d, $J = 2.5$ Hz, ArH), 7.65 (1H, br, Ph), 7.67 (1H, br, Ph), 7.78 (1H, d, $J = 2.6$ Hz, ArH), 7.82 (1H, d, $J = 2.6$ Hz, ArH), 7.85 (1H, d, $J = 2.5$ Hz, ArH), 7.99 (1H, d, $J = 2.5$ Hz, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.57, 30.99, 31.00, 31.20, 34.03, 34.14, 34.32, 34.78, 76.00, 76.08, 126.61, 127.73, 127.80, 127.94, 128.24, 128.25, 128.57, 128.85, 129.47, 129.64, 129.67, 129.77, 130.77, 132.17, 132.59, 132.72, 133.43, 135.58, 135.88, 136.02, 137.18, 137.23, 137.46, 137.88, 146.12, 147.03, 147.55, 149.99, 150.15, 151.55, 157.38, 159.80; FAB-MS *m/z* 1165 [$(M+1)^+$]. Anal. Calcd for $C_{56}H_{58}F_6O_8S_6$: C, 57.71; H, 5.02. Found: C, 57.52; H, 5.00. Compound **15a**: mp 251–253 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 [18H, s, $C(CH_3)_3$], 1.09 [18H, s, $C(CH_3)_3$], 5.32 (2H, d, $J = 11.8$ Hz, OCH_2), 5.65 (2H, d, $J = 11.8$ Hz, OCH_2), 7.23–7.27 (9H, m, ArH and Ph), 7.36–7.39 (9H, m, ArH and Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.98, 31.07, 34.16, 34.53, 76.45, 127.77, 127.96, 128.82, 129.21, 130.06, 130.58, 132.05, 133.57, 134.26, 134.87, 135.62, 136.35, 146.29, 148.40, 151.01, 157.45; FAB-MS *m/z* 1165 [$(M+1)^+$]. Anal. Calcd for $C_{56}H_{58}F_6O_8S_6$: C, 57.71; H, 5.02. Found: C, 57.64; H, 5.04.