

Selective Bridging of *p*-*tert*-Butylcalix[6]arene with Polyethylene Glycol Ditosylates

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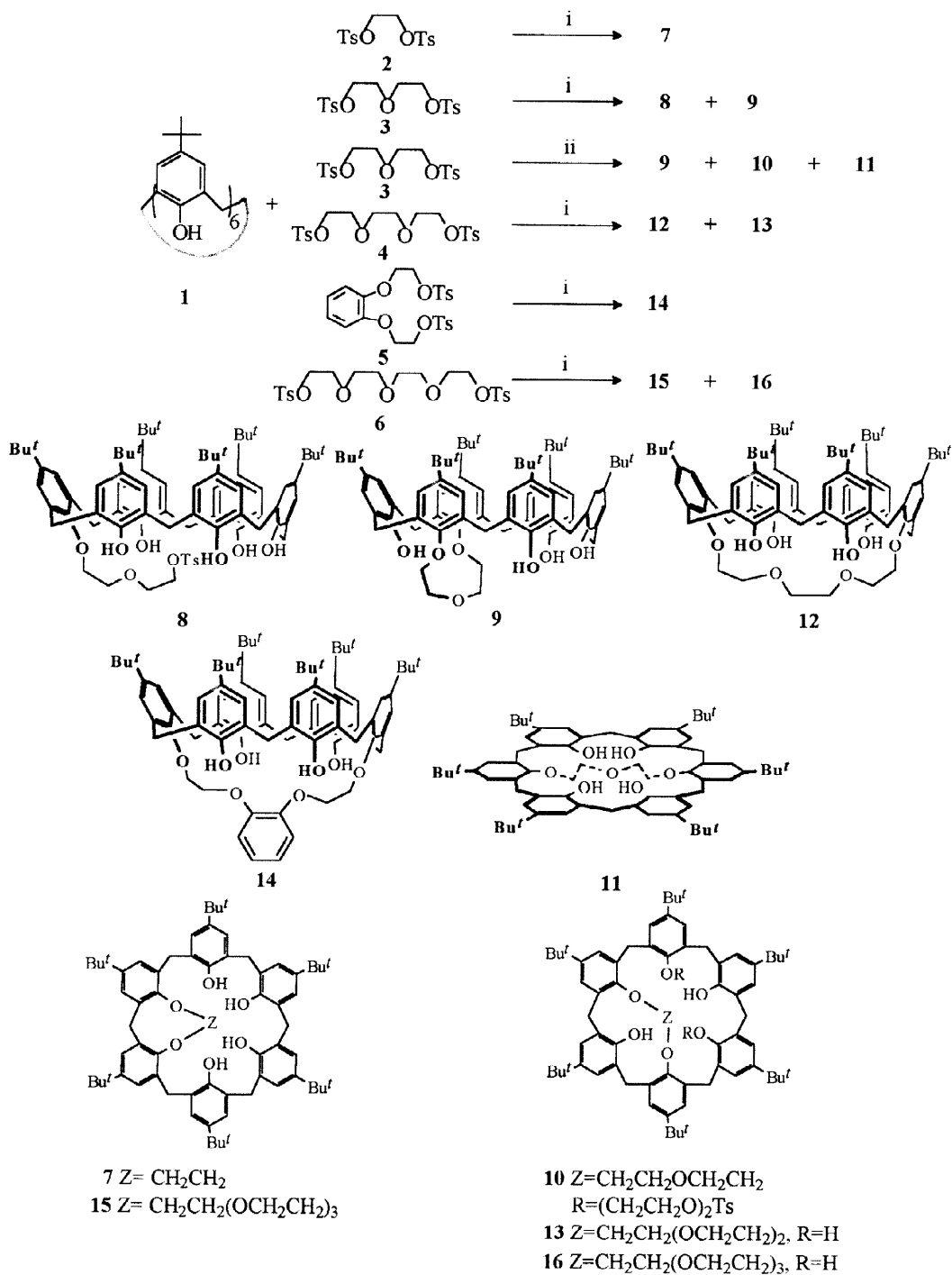
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Abstract: A convenient method for preparing various *p*-*tert*-butylcalix[6]crowns and related compounds has been developed. By refluxing *p*-*tert*-butylcalix[6]arene with ethylene glycol ditosylate or polyethylene glycol ditosylates using K_2CO_3 as a base in acetonitrile, 1,2-ethylenecalix[6]arene, 1,3- and 1,4-calix[6]crown-3, 1,3- and 1,4-calix[6]crown-4, 1,4-calix[6]benzocrown-4, 1,2- and 1,3-calix[6]crown-5 were obtained selectively. A rather flattened (o, o, o, o, o, o) conformation, adopted by the constrained 1,4-calix[6]crown-3 at ambient temperature, was observed for the first time. © 1999 Elsevier Science Ltd. All rights reserved.

Calixcrowns¹ are a family of calixarenes in which the phenolic oxygens are linked via intramolecular poly(oxyethylene) chains. The first member, *p*-*tert*-butylcalix[4]crown-6, was reported as early as 1983.² Since then, a variety of calix[4]crowns selectively bridged at lower-rim-1,2- or 1,3-positions have been prepared, and the synthetic methods have been investigated in detail.³⁻⁹ However, in contrast to the extensive research of calix[4]crowns, little is known about calix[6]crowns.

In 1995, Ungaro and co-workers¹⁰ prepared the first calix[6]crown: lower-rim 1,4-*p*-*tert*-butylcalix[6]crown-5 and 1,4-calix[6]crown-5, by selective bridging of parent macrocycles in the presence of *t*-BuOK in benzene. Just recently,¹¹ we have succeeded in synthesizing the first example of lower-rim 1,3-calix[6]crowns, i.e. 1,3-calix[6]crown-3 (**9**) and its derivative (**10**) by using Na_2CO_3 as the base in acetonitrile at reflux. We have found that this reaction is very sensitive to the type and quantity of base used, as well as the combination of bases and solvent. We therefore think it is necessary to investigate the reaction of *p*-*tert*-butylcalix[6]arene with polyethylene glycol ditosylates systematically.

In this paper, we wish to report our investigation of the condensation of *p*-*tert*-butylcalix[6]arene with ethylene glycol ditosylate, as well as di-, tri- and tetra- ethylene glycol ditosylates. In selected conditions, a series of lower-rim 1,2-, 1,3- and 1,4-bridged *p*-*tert*-butylcalix[6]arenes, i.e. 1,2-, 1,3- and 1,4- *p*-*tert*-butylcalix[6]crown-*n* have been prepared in low to reasonable yields.



Scheme 1. Reagents and Conditions: (i) K₂CO₃ (8-10 equiv.)/MeCN, reflux, 2 days.

(ii) K₂CO₃ (40-50 equiv.)/MeCN, reflux, 2 days.

Our investigation is outlined in Scheme 1. In most cases, the reactants were refluxed in acetonitrile in the presence of 8-10 equiv. of K₂CO₃ for two days. The products were isolated by column chromatography.

RESULTS AND DISCUSSION

As shown in Scheme 1, reacting *p*-*tert*-butylcalix[6]arene (**1**) with ethylene glycol ditosylate (**2**) gave the expected 1,2-ethylene bridged *p*-*tert*-butylcalix[6]arene (**7**). Using diethylene glycol ditosylate (**3**) instead of ethylene glycol ditosylate (**2**), monotosyloxyethoxyethoxy-*p*-*tert*-butylcalix[6]arene (**8**) and 1,3-calix[6]crown-3 (**9**) were obtained. Further increasing the amount of K₂CO₃ used to 40–50 equiv., the reaction became very complex, and 1,4-calix[6]crown-3 (**11**) was isolated as well as compound **9** and its derivative **10**. These results are somewhat different from that of the same reaction carried out using very large excess Na₂CO₃ as the base.¹¹ In the latter case, **8**, **9** and **10** but no **11** can be isolated in high yields under selected conditions. It is worth noting that any further functionalization of compound **11** failed in the presence of either strong base such as NaH or weak base such as K₂CO₃, and most of **11** decomposed into *p*-*tert*-butylcalix[6]arene. This fact indicates that **11** is unstable under the reaction conditions due to its inherent steric strain arising from the short diethylene glycolic spacer bridged at the lower-rim 1,4-position of *p*-*tert*-butylcalix[6]arene.

The reaction of **1** with triethylene glycol ditosylate (**4**) gave 1,4-calix[6]crown-4 (**12**) and 1,3-calix[6]crown-4 (**13**) in 20% and 11% yields, respectively. However, by using more rigid 1,2-bistosyloxyethoxybenzene (**5**) instead of **4**, only 1,4-calix[6]benzocrown-4 (**14**) was isolated.

The most striking example is the reaction of **1** with tetraethylene glycol ditosylate (**6**). Considering **6** has the longest chain among the polyethylene glycol ditosylates used, one may reasonably expect that the 1,4-calix[6]crown-5 be the main or sole product, especially as this is the case when using *t*-BuOK as base as Ungaro and co-workers reported.¹⁰ But in fact, the major product isolated was 1,3-calix[6]crown-5 (**16**) (19% yield), accompanied by an unexpected minor product, i.e. 1,2-calix[6]crown-5 (**15**) (3% yield). None of the expected 1,4-calix[6]crown-5 was isolated under these experimental conditions. Such a paradoxical phenomenon is very difficult to explain, especially as compared with the reaction of **1** with **4** or **5** under similar experimental conditions.

The structures of all the isolated compounds **7–16** were fully characterized by elemental analysis, ¹H NMR spectrometry and FAB mass spectrometry. For example, the ¹H NMR spectrum of **15** shows three singlets (ratio 1 : 1 : 1) for the *tert*-butyl groups, three pairs of doublets (ratio 1 : 1 : 1) for the aromatic protons, and two singlets (ratio 1 : 1) for the phenolic hydroxyl protons, which certainly indicates that in compound **15** the calix[6]arene moiety is intramolecularly bridged by the tetraethylene glycolic spacer at the adjacent phenolic hydroxyl positions, i.e. lower-rim 1,2-position. At ambient temperature, the compounds **8**, **9**, **12** and **14** adopt cone conformation, as indicated from the characteristics of their ¹H NMR spectra. Such

spectral characteristic evidences for cone conformation adopted by *p*-*tert*-butylcalix[6]arenes have been generally observed.^{12, 13} However, no defined conformations of the compounds **7**, **10**, **13**, **15** and **16** can be postulated from their ¹H NMR spectra.

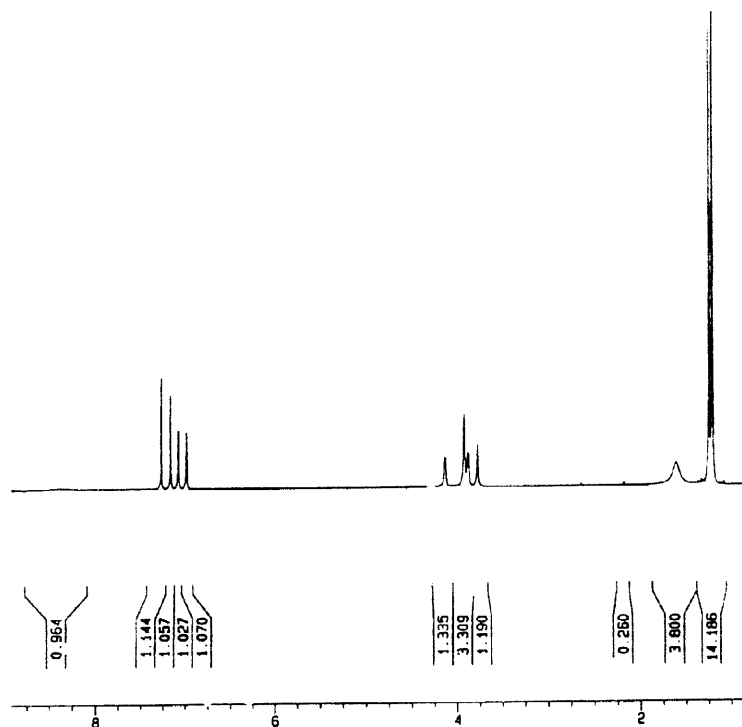


Figure 1. ¹H NMR spectrum of **11** in CDCl₃, 25 °C, 500 MHz.

It is worthy to note the unique conformation of compound **11** at room temperature. The ¹H NMR spectrum of **11** (Figure 1) shows two singlets at δ 1.20 (36H) and 1.24 (18H) for the *tert*-butyl groups, two singlets at δ 3.77 (4H) and 3.92 (8H) for the methylene protons in the calix[6]arene skeleton, two singlets at δ 3.89 (4H) and 4.13 (4H) for the protons in the crown ether moiety, one pair of doublets at δ 6.98 (4H) and 7.07 (4H) as well as one singlet at δ 7.16 (4H) for aromatic protons, and one broad singlet at δ 8.41 (4H) for the phenolic hydroxyl protons, which indicate that **11** is constrained in a special flattened (o, o, o, o, o, o) conformation.¹³ Such a conformation is so flattened that it even gives rise to *the same chemical environment of the two protons in one ArCH₂Ar*. To the best of our knowledge, such a conformation is observed here for the first time for a calix[6]arene.

Examination of CPK molecular models reveals that compounds **7-16** are well preorganized to complex cations. The percentage extraction of **7-16** towards picrate salts from water into CHCl₃ at 25 °C are summarized in Table 1. It is worthy to note that among the ten host molecules, **9**, **13** and **15** show Li⁺, Na⁺ and K⁺ selectivity, respectively, and **8** shows high Et₂NH₂⁺ selectivity. The Li⁺ selectivity of **9** is rarely

observed in calixarene chemistry.^{14, 15} To the best of our knowledge, **8** may be the first example of an ionophore with high Et₂NH₂⁺ selectivity in calixarene chemistry. Comparing the ion extraction abilities of three pairs of positional isomers, **9** with **11**, **12** with **13** and **15** with **16**, it can be concluded that: (i) the average ion extraction abilities of the 1,3-*p-tert*-butylcalix[6]crown-3 (**9**) is higher than that of its 1,4-isomer **11**. (ii) the 1,4-*p-tert*-butylcalix[6]crown-4 (**12**) shows higher extraction abilities than that of its 1,3-isomer **13** except Na⁺ and Et₂NH₂⁺. (iii) the 1,2-*p-tert*-butylcalix[6]crown-5 (**15**) shows higher extraction abilities than that of its 1,3-isomer **16**. In addition, compound **15** shows K⁺ selectivity but **16** does not.

Table 1 Percentage extraction (%E) of picrate salts from water into CHCl₃ at 25 °C.^a Arithmetic mean of several experiments-standard deviation on the mean: $\sigma_{N-1} \leq 1$.

Host	%E						
	Li ⁺	Na ⁺	K ⁺	NH ₄ ⁺	<i>n</i> -PrNH ₃ ⁺	Me ₂ NH ₂ ⁺	Et ₂ NH ₂ ⁺
7	2.7	2.4	2.0	0.7	0.7	1.0	0.3
8	4.5	5.2	4.1	3.3	1.0	0.8	11.8
9	6.6	3.4	3.3	3.2	3.3	4.0	5.9
10	6.9	4.6	3.2	5.4	7.5	4.6	12.5
11	1.8	2.5	1.8	1.6	1.7	2.0	4.2
12	2.6	6.5	4.5	3.6	2.5	3.7	5.3
13	1.7	8.7	3.9	2.8	1.8	2.8	5.3
14	1.2	3.9	4.1	4.0	2.9	3.8	5.6
15	1.6	6.8	18.0	3.4	2.8	4.6	5.2
16	1.5	5.6	6.7	1.7	1.2	1.2	3.3

^a1.00 ml of 0.005 mol dm⁻³ receptor solution in CHCl₃ was shaken (10 min) with 1.00 ml of 0.005 mol dm⁻³ picrate salt solution in H₂O and the percentage extraction was measured from the resulting absorbance at 380 nm.

CONCLUSIONS

We believe that the procedures described in this paper open an avenue to the preparation of the little-known calix[6]crowns. More host molecules with special ion and molecular recognition abilities may be expected by further functionalization of those described above.

EXPERIMENTAL SECTION

Melting points were recorded on a Gallenkamp melting point apparatus in open capillaries and are

uncorrected. ^1H NMR spectra were recorded on Bruker-ARX500 instruments at ambient temperature. TMS was used as an internal standard. Fast atom bombardment mass spectra were obtained from a Kratos MS80RF mass spectrometry service, with *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were performed by the Analytical Laboratory of the Department of Chemistry. Infrared spectra were recorded on Nicolet 170SX FT-IR spectrophotometer. UV-Vis measurements were recorded on Shimadzu-240 UV-Vis spectrophotometer equipped with two thermostatted cell compartments. All solvents were purified by standard procedures. Petroleum ether refers to the fraction with b.p. 60–90 °C. All other chemicals were analytically pure and used without further purification.

General procedures for the preparation of 7-16: A mixture of *p*-*tert*-butylcalix[6]arene (**1**) (4.86 g, 5 mmol) and ethylene glycol ditosylate (**2**) or polyethylene glycol ditosylates (**3**)-(6) (molar ratio 1 : 1.1) was stirred and refluxed in the presence of K_2CO_3 (the amount was listed in Scheme 1) in acetonitrile under nitrogen for two days. The solvent was evaporated. 100 ml of 2 N HCl was added by portions. Then 100 ml of CHCl_3 was added and the mixture was stirred at room temperature for half an hour. The organic phase was separated and washed three times with 50 ml of brine. The organic phase was separated again, dried over MgSO_4 and filtered. The solvent was evaporated again. The residue was purified by column chromatography, followed by recrystallization to give pure products.

Compound 7: the eluent for column chromatography was dichloromethane : petroleum ether (1 : 1, v/v), the product (1.75 g, 35%) was recrystallized from petroleum ether as a white powder, m.p. 220–221 °C; [Found: C, 81.81; H, 8.61. $\text{C}_{68}\text{H}_{86}\text{O}_6$ requires C, 81.72; H, 8.67]; R_f (dichloromethane : petroleum ether = 1 : 1, v/v) 0.30; ν_{max} (Nujol) 3500–3100 (br), 2957, 2905, 2868, 1640, 1484, 1391, 1362, 1293, 1250, 1202, 1117, 1055, 1029, 943, 916, 872, 817, 792, 744, 663, 634, 595, 539, 463, 446 cm^{-1} ; δ_{H} (500 MHz, CDCl_3) 1.20 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.26 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.28 (s, 18H, $\text{C}(\text{CH}_3)_3$), 3.45 (bs, 4H, OCH_2CH_2), 3.50 (d, 4H, $J=14.0\text{Hz}$, ArCH_2Ar), 3.64 (bs, 1H, ArCH_2Ar), 4.12 (d, 1H, $J=13.8\text{Hz}$, ArCH_2Ar), 4.48 (bs, 1H, ArCH_2Ar), 4.75 (d, 1H, $J=13.8\text{Hz}$, ArCH_2Ar), 4.84 (d, 4H, $J=14.0\text{Hz}$, ArCH_2Ar), 7.05 (bs, 4H, ArH), 7.09 (s, 4H, ArH), 7.13 (s, 4H, ArH), 8.44 (s, 2H, ArOH), 8.90 (bs, 2H, ArOH); m/z (FAB-MS) 999 (MH^+ , 100%).

Compound 8: the eluent for column chromatography was dichloromethane : petroleum ether (1 : 3, v/v), the product (0.91 g, 15%) was recrystallized from cyclohexane as a white powder, m.p. 227 °C (dec.); [Found: C, 76.19; H, 8.06. $\text{C}_{77}\text{H}_{98}\text{SO}_{10}$ requires C, 76.08; H, 8.03]; R_f (dichloromethane : petroleum ether = 1 : 1, v/v) 0.58; ν_{max} (Nujol) 3500–3050 (br), 2957, 2905, 2868, 1599, 1485, 1452, 1363, 1293, 1243, 1199, 1179, 1143, 1117, 1097, 1048, 1022, 987, 921, 873, 817, 769, 715, 662, 634, 582, 554, 521, 501, 465 cm^{-1} ; δ_{H} (500 MHz, CDCl_3) 1.15 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.22 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.26 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.28 (s, 18H, $\text{C}(\text{CH}_3)_3$),

4.13 (s, 4H, OCH₂CH₂), 6.98 (d, 4H, *J*=2.1Hz, ArH), 7.07 (d, 4H, *J*=2.1Hz, ArH), 7.16 (s, 4H, ArH), 8.41 (bs, 4H, ArOH); *m/z* (FAB-MS) 1043 (MH⁺, 30%).

Compound 12 and 13: the eluent for column chromatography was a gradient from dichloromethane : petroleum ether (2 : 1, v/v) to neat dichloromethane, both of the products **12** (1.09 g, 20%) and **13** (0.60 g, 11%) were recrystallized from CH₂Cl₂ / MeOH as colorless crystals. Compound **12**: m.p. 258 °C (dec.); [Found: C, 79.67; H, 8.67. C₇₂H₉₄O₈ requires C, 79.52; H, 8.71]; R_f (dichloromethane) 0.30; ν_{max} (Nujol) 3600-3000 (br), 2957, 2904, 2868, 1747, 1715, 1599, 1484, 1363, 1292, 1243, 1203, 1118, 1052, 997, 922, 872, 817, 751, 638, 599, 549, 429 cm⁻¹; δ_H (500 MHz, CDCl₃) 1.14 (s, 18H, C(CH₃)₃), 1.30 (s, 36H, C(CH₃)₃), 3.38 (d, 2H, *J*=12.5Hz, ArCH₂Ar), 3.49 (d, 4H, *J*=12.8Hz, ArCH₂Ar), 3.93 (d, 2H, *J*=12.5Hz, ArCH₂Ar), 4.04 (t, 4H, *J*=7.4Hz, OCH₂CH₂), 4.14 (t, 4H, *J*=7.4Hz, OCH₂CH₂), 4.21 (s, 4H, OCH₂CH₂), 4.40 (d, 4H, *J*=12.8Hz, ArCH₂Ar), 6.97 (s, 4H, ArH), 7.11 (d, 4H, *J*=2.1Hz, ArH), 7.13 (d, 4H, *J*=2.1Hz, ArH), 7.85 (s, 4H, ArOH); *m/z* (FAB-MS) 1086 (M⁺, 100%), 1125 (M+K⁺, 10%). Compound **13**: m.p. 198 °C (dec.); [Found: C, 79.48; H, 8.80. C₇₂H₉₄O₈ requires C, 79.52; H, 8.71]; R_f (dichloromethane) 0.27; ν_{max} (Nujol) 3700-3000 (br), 2958, 2903, 2867, 1597, 1482, 1393, 1363, 1293, 1244, 1203, 1118, 1046, 933, 873, 818, 733, 688, 622, 586, 537, 427 cm⁻¹; δ_H (500 MHz, CDCl₃) 1.20 (s, 9H, C(CH₃)₃), 1.22 (s, 18H, C(CH₃)₃), 1.26 (s, 9H, C(CH₃)₃), 1.28 (s, 18H, C(CH₃)₃), 3.55 (d, 2H, *J*=14.2Hz, ArCH₂Ar), 3.58-4.15 (m, 20H, OCH₂CH₂ and ArCH₂Ar), 4.29 (d, 2H, *J*=14.2Hz, ArCH₂Ar), 6.95 (s, 2H, ArH), 7.02 (d, 2H, *J*=2.3Hz, ArH), 7.05 (d, 2H, *J*=2.2Hz, ArH), 7.08 (d, 2H, *J*=2.2Hz, ArH), 7.10 (d, 2H, *J*=2.3Hz, ArH), 7.11 (s, 3H, ArH and one ArOH), 7.25 (s, 1H, ArOH), 7.31 (bs, 2H, ArOH); *m/z* (FAB-MS) 1087 (MH⁺, 100%).

Compound 14: the eluent for column chromatography was a gradient from dichloromethane : petroleum ether (2 : 1, v/v) to neat dichloromethane, the product (1.13 g, 20%) was recrystallized from CH₂Cl₂ / MeOH as colorless crystals, m.p. 210-212 °C; [Found: C, 80.43; H, 8.39. C₇₆H₉₄O₈ requires C, 80.39; H, 8.34]; R_f (dichloromethane) 0.60; ν_{max} (Nujol) 3600-3050 (br), 2957, 2867, 1708, 1598, 1482, 1363, 1292, 1260, 1200, 1116, 1064, 985, 930, 873, 818, 746, 675, 635, 575, 531, 468, 429 cm⁻¹; δ_H (500 MHz, CDCl₃) 1.09 (s, 18H, C(CH₃)₃), 1.19 (s, 36H, C(CH₃)₃), 3.27 (d, 2H, *J*=13.9Hz, ArCH₂Ar), 3.38 (d, 4H, *J*=13.5Hz, ArCH₂Ar), 3.91 (d, 2H, *J*=13.9Hz, ArCH₂Ar), 4.32 (d, 4H, *J*=13.5Hz, ArCH₂Ar), 4.37 (t, 4H, *J*=5.0Hz, OCH₂CH₂), 4.50 (t, 4H, *J*=5.0Hz, OCH₂CH₂), 6.87 (s, 4H, ArH), 6.94 (s, 4H, ArH), 6.99 (s, 8H, ArH), 8.40 (s, 4H, ArOH); *m/z* (FAB-MS) 1135 (MH⁺, 20%).

Compound 15 and 16: the eluent for column chromatography was a gradient from neat dichloromethane to dichloromethane : diethyl ether (50 : 1, v/v). **15** (0.17 g, 3%) and **16** (1.07 g, 19%) were recrystallized from CH₂Cl₂ / MeOH as a white powder and colorless crystals, respectively. Compound **15**: m.p.

2.08 (s, 3H, ArCH₃), 3.46 (d, 2H, *J*=14.0Hz, ArCH₂Ar), 3.52 (d, 2H, *J*=13.9Hz, ArCH₂Ar), 3.56 (d, 2H, *J*=14.5Hz, ArCH₂Ar), 3.92 (d, 2H, *J*=13.9Hz, ArCH₂Ar), 4.00 (d, 2H, *J*=14.0Hz, ArCH₂Ar), 4.03 (bs, 4H, OCH₂CH₂), 4.21 (bs, 4H, OCH₂CH₂), 4.33 (d, 2H, *J*=14.5Hz, ArCH₂Ar), 6.93 (d, 2H, *J*=8.0Hz, ArH), 7.01 (s, 2H, ArH), 7.07 (s, 4H, ArH), 7.08 (s, 2H, ArOH), 7.11 (s, 2H, ArOH), 7.12 (s, 4H, ArH), 7.14 (s, 2H, ArH), 7.26 (s, 1H, ArOH), 7.64 (d, 2H, *J*=8.0Hz, ArH); *m/z* (FAB-MS) 1215 (MH⁺, 80%).

Compound 9: the eluent for column chromatography was dichloromethane : petroleum ether (10 : 1, v/v), the product was recrystallized from petroleum ether as a white powder. When the amount of base was 8-10 equiv., the yield was 13%; when the amount of base was 40-50 equiv., the yield was 17%. Compound 9: m.p. 172-173 °C; [Found: C, 80.78; H, 8.64. C₇₀H₉₀O₇ requires C, 80.57; H, 8.69]; R_f (dichloromethane) 0.41; *v*_{max} (Nujol) 3550-3100 (br), 3030, 2958, 2905, 2867, 2775, 2689, 1771, 1751, 1713, 1602, 1485, 1459, 1393, 1362, 1292, 1246, 1204, 1144, 1120, 1089, 1052, 1025, 991, 944, 918, 876, 818, 796, 739, 713, 662, 593, 520, 465, 428 cm⁻¹; δ_H (500 MHz, CDCl₃) 1.10 (s, 9H, C(CH₃)₃), 1.15 (s, 9H, C(CH₃)₃), 1.25 (s, 18H, C(CH₃)₃), 1.27 (s, 18H, C(CH₃)₃), 3.44 (d, 2H, *J*=15.1Hz, ArCH₂Ar), 3.51 (d, 2H, *J*=14.3Hz, ArCH₂Ar), 3.52 (d, 2H, *J*=15.1Hz, ArCH₂Ar), 3.97 (bs, 4H, OCH₂CH₂), 4.17 (d, 2H, *J*=14.3Hz, ArCH₂Ar), 4.27 (d, 2H, *J*=15.1Hz, ArCH₂Ar), 4.60 (bs, 4H, OCH₂CH₂), 5.21 (d, 2H, *J*=15.1Hz, ArCH₂Ar), 6.92 (bs, 1H, ArOH), 7.07 (s, 2H, ArH), 7.08 (s, 4H, ArH), 7.09 (s, 2H, ArOH), 7.12 (s, 2H, ArH), 7.14 (s, 4H, ArH), 8.17 (bs, 1H, ArOH); *m/z* (FAB-MS) 1042 (M⁺, 70%).

Compound 10 and 11: the amount of base was 40-50 equiv., the eluent for column chromatography was dichloromethane : diethyl ether (20 : 1, v/v), **10** (0.30 g, 4%) and **11** (0.45 g, 8.6%) were recrystallized from CH₂Cl₂ / MeOH as white powder and colorless crystals, respectively. Compound 10: m.p. 255 °C (dec.); [Found: C, 72.25; H, 7.78. C₉₂H₁₁₈S₂O₁₅ requires C, 72.31; H, 7.78]; R_f (dichloromethane : diethyl ether = 8 : 1, v/v) 0.34; *v*_{max} (Nujol) 3650-3050 (br), 2958, 2904, 2868, 1703, 1602, 1580, 1483, 1416, 1392, 1361, 1321, 1266, 1247, 1206, 1124, 1093, 1043, 1027, 991, 951, 920, 887, 827, 787, 740, 681, 582, 541 cm⁻¹; δ_H (500 MHz, CDCl₃) 0.88 (s, 18H, C(CH₃)₃), 0.91 (s, 18H, C(CH₃)₃), 1.19 (s, 9H, C(CH₃)₃), 1.24 (s, 9H, C(CH₃)₃), 2.11 (s, 6H, ArCH₃), 3.25 (bs, 4H, OCH₂CH₂), 3.51 (bs, 4H, ArCH₂Ar), 3.60-3.75 (m, 12H, OCH₂CH₂), 4.10-4.25 (m, 16H, OCH₂CH₂ and ArCH₂Ar), 6.73 (bs, 4H, ArH), 6.98 (bs, 10H, ArH and ArOH), 7.07 (s, 4H, ArH), 7.19 (bs, 4H, ArH); *m/z* (FAB-MS) 1527 (MH⁺, 64%). Compound 11: m.p. 248 °C (dec.); [Found: C, 76.89; H, 8.51; N, 5.39. C₇₀H₉₀O₇·5MeCN requires C, 76.95; H, 8.47; N, 5.61]; R_f (dichloromethane : diethyl ether = 8 : 1, v/v) 0.32; *v*_{max} (Nujol) 3580-3050 (br), 2959, 2904, 2868, 1682, 1599, 1482, 1393, 1362, 1293, 1241, 1203, 1118, 1045, 932, 874, 817, 792, 587, 540 cm⁻¹; δ_H (500 MHz, CDCl₃) 1.20 (s, 36H, C(CH₃)₃), 1.24 (s, 18H, C(CH₃)₃), 3.77 (s, 4H, ArCH₂Ar), 3.89 (s, 4H, OCH₂CH₂), 3.92 (s, 8H, ArCH₂Ar),

272–274 °C; [Found: C, 78.50; H, 8.71. C₇₄H₉₈O₉ requires C, 78.55; H, 8.73]; R_f (dichloromethane : diethyl ether = 10 : 1, v/v) 0.26; ν_{max} (Nujol) 3650–3000 (br), 2958, 2904, 2867, 1602, 1484, 1362, 1294, 1245, 1203, 1117, 1051, 986, 937, 874, 794, 746, 718, 675, 577, 541, 469, 426 cm⁻¹; δ_H (500 MHz, CDCl₃) 1.08 (s, 18H, C(CH₃)₃), 1.20 (s, 18H, C(CH₃)₃), 1.31 (s, 18H, C(CH₃)₃), 3.45 (d, 2H, J=12.2Hz, ArCH₂Ar), 3.67 (d, 1H, J=11.4Hz, ArCH₂Ar), 3.68–3.98 (m, 22H, OCH₂CH₂ and ArCH₂Ar), 4.45 (d, 2H, J=12.2Hz, ArCH₂Ar), 4.74 (d, 1H, J=11.4Hz, ArCH₂Ar), 6.79 (d, 2H, J=2.3Hz, ArH), 6.93 (d, 2H, J=2.3Hz, ArH), 7.02 (d, 2H, J=2.0Hz, ArH), 7.06 (d, 2H, J=2.0Hz, ArH), 7.98 (d, 2H, J=2.4Hz, ArH), 7.14 (d, 2H, J=2.4Hz, ArH), 7.88 (bs, 2H, ArOH), 8.60 (bs, 2H, ArOH); m/z (FAB-MS) 1131 (MH⁺, 90%), 1153 (M+Na⁺, 80%), 1169 (M+K⁺, 10%).

Compound **16**: m.p. 196–197 °C; [Found: C, 78.61; H, 8.75. C₇₄H₉₈O₉ requires C, 78.55; H, 8.73]; R_f (dichloromethane : diethyl ether = 10 : 1, v/v) 0.24; ν_{max} (Nujol) 3850, 3740–3050 (br), 2959, 2904, 2867, 1752, 1712, 1600, 1484, 1362, 1293, 1243, 1204, 1117, 1045, 991, 941, 875, 818, 793, 756, 672, 614, 575, 540, 447 cm⁻¹; δ_H (500 MHz, CDCl₃) 0.98 (s, 18H, C(CH₃)₃), 1.21 (s, 9H, C(CH₃)₃), 1.25 (s, 18H, C(CH₃)₃), 1.30 (s, 9H, C(CH₃)₃), 3.50 (bs, 2H, ArCH₂Ar), 3.58 (bs, 2H, ArCH₂Ar), 3.62 (bs, 2H, ArCH₂Ar), 3.67–3.80 (m, 12H, OCH₂CH₂), 3.96 (s, 4H, OCH₂CH₂), 4.45 (bs, 2H, ArCH₂Ar), 4.48 (bs, 2H, ArCH₂Ar), 4.50 (bs, 2H, ArCH₂Ar), 6.55 (d, 2H, J=2.2Hz, ArH), 6.90 (d, 2H, J=2.2Hz, ArH), 6.96 (d, 2H, J=1.8Hz, ArH), 7.10 (d, 2H, J=1.8Hz, ArH), 7.12 (s, 2H, ArH), 7.14 (s, 2H, ArH), 7.55 (s, 1H, ArOH), 8.02 (bs, 2H, ArOH), 8.80 (bs, 1H, ArOH); m/z (FAB-MS) 1131 (MH⁺, 100%), 1153 (M+Na⁺, 10%).

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