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The Synthesis of Anthracene Crown Ethers Derived from Benzo-crown Ethers

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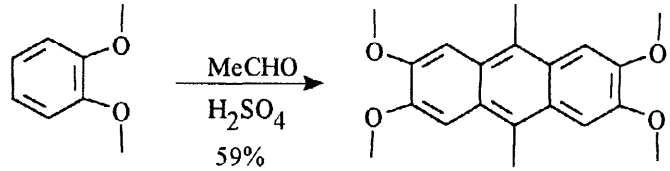
Abstract: The sulfuric acid-promoted reaction of benzo-15-crown-5 (**3**) and benzo-18-crown-6 (**6**) with aliphatic aldehydes, leading to the formation of anthracene crown ethers, was studied. A substantial substituent effect on the reaction course was found. For the isobutyl group the highest yield was obtained, while for longer and shorter alkyl groups the yield dropped down. Reaction of acetaldehyde and benzo-15-crown-5 leads to formation of compound **4** in 35% yield. Application of cyclohexanone as a carbonyl reagent caused formation of till now unknown 4,5-disubstituted crown ether **8**.

There is a great interest in the synthesis of new types of ionophores since their discovery by Pedersen.[1] New receptor molecules that respond to substrate binding by displaying characteristic optical effects are of special interest due to their potential application in the field of semiochemistry, the chemistry of molecular signalization[2]. Among the others, anthracene ionophores were shown to behave as sensitive probes for metal cations. Several anthracene crown ethers,[3-9] anthracene cryptands,[10-12] and anthracene podands[13,14] were prepared in multi-step syntheses. Unfortunately, in all these cases the desired compounds were obtained in very low yields, which limits their potential application.



1 2

Scheme 1

Since we were interested in a simple and efficient synthesis of anthracene crown ethers, we turned our attention to a sulfuric acid-promoted reaction between veratrol (**1**) and aliphatic aldehydes.[15] In this reaction 90% sulfuric acid was used and, for acetaldehyde, 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene (**2**) was obtained in a 59% yield.[15] In this reaction, instead of veratrol, benzo-crown ethers can be used and anthracene-crown ethers can be obtained. Application of concentrated sulfuric acid as a reactant can cause some problems since ethereal bonds present in starting crown ethers can be broken. Therefore appropriate choice of reaction conditions is desired.

Application of benzo-15-crown-5 (**3**) instead of veratrol according to literature procedure[15] resulted in decomposition of the reagent used. The same reaction performed in 84% sulfuric acid leads to formation of the single product **4** in 35% yield (Scheme 2).

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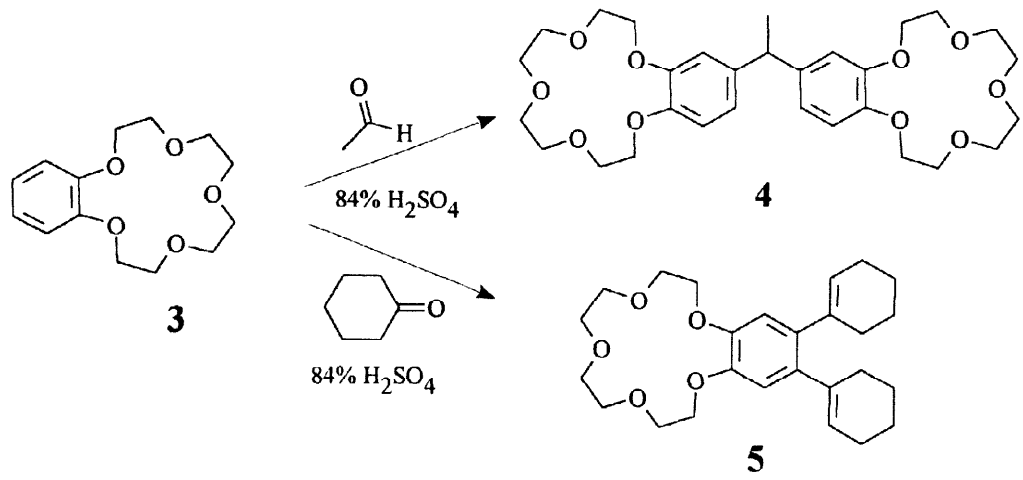
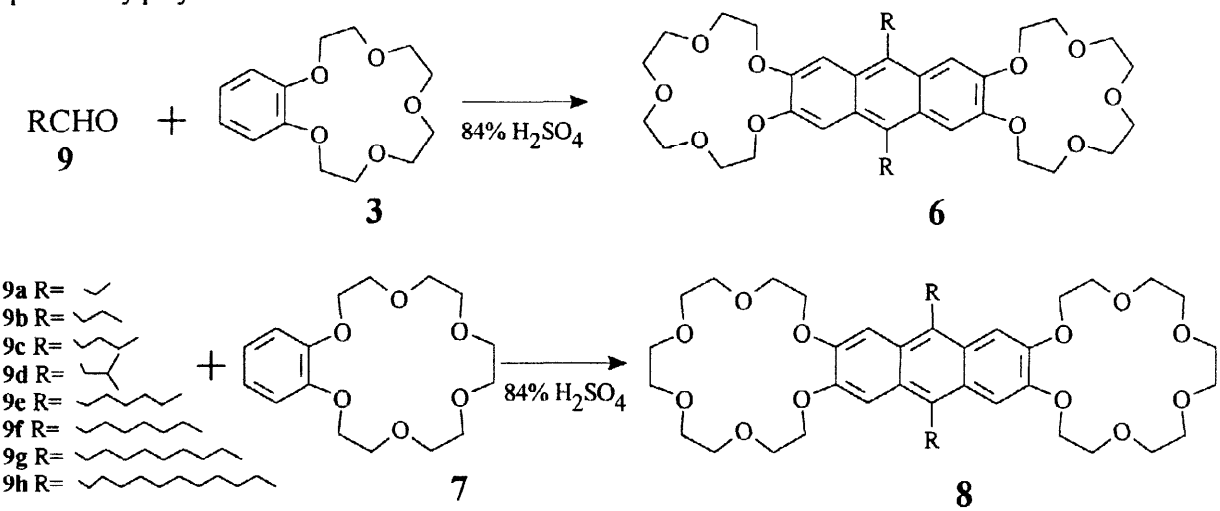


3 4 5

Scheme 2

Its structure was proved by ^1H and ^{13}C NMR as well as by mass spectrometry. We were unable to transform this compound into the anthracene crown **6**. Instead of formation of anthracene compound **6**, decomposition of **4** was observed. The same reaction performed with benzo-18-crown-6 (**7**) led to decomposition of starting materials. The same reaction performed with cyclohexanone leads to formation of the disubstituted crown **5** according to Scheme 2.
When the reaction of propionaldehyde (2 equiv.) with the benzo-15-crown-5 (1 equiv.) was performed in 84% sulfuric acid, the desired crown ether **6a** was obtained in 46% yield, as a yellowish powder (Table 1, Entry 1). Besides desired compound only polymeric material was obtained.



Scheme 3

When the reaction was performed in 90% sulfuric acid according to the literature procedure,[15] only decomposition was observed. The slight decrease of acid concentration to 80% reduced the yield to 21%. Simultaneously, formation of compound of structure **4**, accompanied by unidentified products, was detected. The reaction failed when 75% sulfuric acid was used.
The reaction is sensitive to aldehyde - crown ether stoichiometry. Larger amount of aldehyde did not improve the yield, whereas 1:1 ratio of substrates decreases the reaction yield to 20%. This reaction proceeded smoothly only at temperature below 10°C with an optimum at about 5°C. Replacement of propionaldehyde by other aldehydes, under the same experimental conditions, leads to formation of desired compounds **6** in the yield of 26 to 71% (Table 1).

Table 1 Results of reactions of benzo-crowns **3** or **7** with aliphatic aldehydes **9**

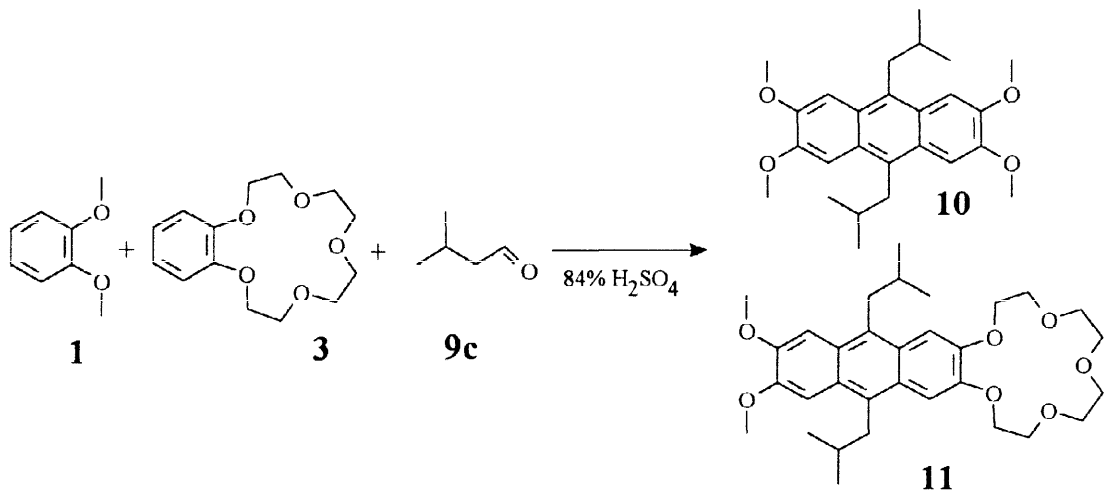
Entry	Aldehyde	Product	Yield [%]	Entry	Product	Yield [%]
1	**9a** R= $-CH_2CH_3$	**6a**	46	9	**8a**	45
2	**9b** R= $-CH_2CH_2CH_3$	**6b**	61	-	-	-
3	**9c** R= $-CH_2(CH_2)_2CH_3$	**6c**	64	10	**8c**	52
4	**9d** R= $-CH_2CH(CH_3)_2$	**6d**	71	11	**8d**	51
5	**9e** R= $-CH_2(CH_2)_4CH_3$	**6e**	49	-	-	-
6	**9f** R= $-CH_2(CH_2)_5CH_3$	**6f**	35	12	**8f**	16
7	**9g** R= $-CH_2(CH_2)_7CH_3$	**6g**	27	13	**8g**	15
8	**9h** R= $-CH_2(CH_2)_9CH_3$	**6h**	26	14	**8h**	19

For the isovaleraldehyde the highest, yield was obtained(71%, Entry 4), while for longer and shorter alkyl groups the yield dropped down (Entries 2, 3, 5, 6, 7, 8). The same reactions performed in the presence of Lewis acid ($BF_3{\cdot}Et_2O$, $TiCl_4$, $Ti(OMe)_2Cl_2$, $AlCl_3$) in polar aprotic solvents lead to decomposition of benzo-crown ether **3**.

A diminished reactivity of the second crown ether studied, benzo-18-crown-6 (**7**), was observed. The yield of reaction for valeraldehyde 52% is almost the same, for isovaleraldehyde 51%, (Entries 10 and 11). For longer aldehydes, the yields of reaction drops down to (Entries 12, 13, 14).

High symmetry of all compounds was observed in NMR spectra. ^1H NMR spectra show characteristic signals at 7.4 ppm for four equivalent aromatic protons and broad multiplets at 3.8, 4.0 and 4.3 ppm for crown ether protons. Also, two aliphatic groups present in 9,10-positions of anthracene were magnetically equivalent. In ^{13}C NMR spectra, fourteen signals of aromatic carbon appeared at 104, 125, 130, and 148 ppm while crown ether carbon atoms absorbed at 68, 69, 70, and 71 ppm.

The synthesis of anthracene-crown possessing only one crown ether ring was more complicated and the results of our studies are summarized in Scheme 4.



Scheme 4

The cross condensation of veratrol (**1**) with benzo-15-crown-5 (**3**) and acetaldehyde, or propionaldehyde failed. For isovaleraldehyde, two from three possible compounds were obtained: tetramethoxyanthracene **10** and anthracene crown **11** in the yield of 24 and 6%, respectively. Formation of symmetrical anthracene crown **6d** was not observed.

Conclusions

In conclusion, we present here the efficient synthesis of anthracene crown ethers derived from benzo-15-crown-5 and benzo-18-crown-6. The condensation reaction proceeds smoothly for propionic aldehyde and higher homologues, for acetaldehyde the only product of structure **4** was obtained. The highest yield (71%) obtained for isobutyl group for benzo-15-crown-5 drops down with the increasing number of carbon atoms of aldehyde. Cross condensation reaction

of veratrol with benzo-15-crown-5 allowed as to prepare anthracene crown **11**. Application of a cyclohexanone as a carbonyl reagent results in formation of a new class of benzo-crown **4**.
Future work will concentrate on functionalization of alkyl groups present at 9- and 10- position of anthracene together with studies on complexation of the new anthracene-crowns.

EXPERIMENTAL

General. Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were recorded using a Varian 200 Gemini spectrometer in $CDCl_3$ or $CDCl_3/C_6D_6$ with TMS as an internal standard. Liquid SIMS spectra were determined on an AMD 604 spectrometer (Cs^+, 10 keV).
Typical Experimental Procedure: To the intensively stirred, cooled to 5 ^{0}C (ice bath) solution of sulfuric acid (10 ml, 84%), a solution of respective aldehyde (10 mmol) and benzo-15-crown-15 (0.536 g, 2 mmol) in chloroform (5 ml) was added slowly, while keeping the temperature of the reaction mixture below 10 ^{0}C. The reaction mixture became dark red and was stirred at this temperature for 1 h, then the cooling bath was removed and stirring was continued until TLC indicated complete conversion of the benzo-15-crown-5 (usually 1 h). Then water (50 ml) and ammonium hydroxide was added to reach pH 11. Water phase was extracted by chloroform (3x 30 ml) and organic phases were combined and dried ($MgSO_4$). Pure anthracene crown was obtained after chromatography on silica gel using chloroform-methanol solvent mixture (95/5, v/v). Crystallization from the respective solvent gave desired compounds as yellowish powders in the yield given in Table 1.
Crown 4: unstable oil; ^{1}H NMR ($CDCl_3$) δ 1.54 (3H, d, J=7.2, -CHC**H**$_3$), 1.82-1.87 (1H, m, -C**H**CH$_3$), 3.74 (16H, brs, -OC**H**$_2$C**H**$_2$O-), 3.85-3.92 (8H, m, Ar-OCH$_2$C**H**$_2$O-), 4.05-4.12 (8H, m, ArOC**H**$_2$CH$_2$O-), 6.65-6.77 (6H, m, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 22.0, 43.5, 68.8, 68.9, 69.4, 70.3, 70.7, 113.7, 119.9, 139.7, 147.1, 148.7; L-SIMS *m/z* 585 ([M+Na]$^+$, 100%), 562 ([M]$^+$, 77%), 295 (75%), 283 (33%); HR-LSIMS m/z 585.2705 (585.2676 calcd for $C_{30}H_{42}O_{10}Na$, [M+Na]$^+$); Anal. Calcd. for $C_{30}H_{42}O_{10}$+0.5 H_2O: 63.14; H, 7.82. Found: C,63.03; H 7.58.
Crown 5: yield 37%; unstable oil: ^{1}H NMR ($CDCl_3$) δ 0.91-2.21 (18 H, m, -CH$_2$), 3.65-4.20 (16H, m, -OC**H**$_2$-), 6.88 (2H, s, Ar**H**); EI-MS *m/z* 428 ([M]$^+$, 16%), 350 (18%), 268 (19%), 136 (63%), 98 (100%); HR-MS m/z 428.2565 (428.2567 calcd for $C_{26}H_{36}O_5$, [M]$^+$); Anal. Calcd. for $C_{26}H_{36}O_5$+1.5 H_2O: C, 68.54; H, 8.63. Found: C, 68.41; H 8.75.
Crown 6a: R= -C_2H_5; mp >260°C ($CHCl_3/Et_2O$); ^{1}H NMR ($CDCl_3$) δ 1.38 (6H, t, J=7.5, C**H**$_3$CH$_2$-), 3.39 (4H, q, J=7.5, CH$_3$C**H**$_2$-), 3.81 (16H, brs, -OC**H**$_2$C**H**$_2$O-), 4.00-4.05 (8H, m, Ar-OCH$_2$C**H**$_2$O-), 4.25-4.35 (8H, m, Ar-OC**H**$_2$CH$_2$O-), 7.39 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 14.6, 21.8, 68.6, 69.5, 70.5, 71.3, 104.4, 125.2, 130.6, 148.8; L-SIMS *m/z* 637 ([M+Na]$^+$, 100%), 614 ([M]$^+$, 97%); HRMS m/z 614.3100 (614.3091 calcd for $C_{34}H_{46}O_{10}$, [M]$^+$); Anal. Calcd. for $C_{34}H_{46}O_{10}$+H_2O: C, 64.54; H, 7.65. Found: C, 64.34; H 7.50.
Crown 6b: R= -$CH_2CH_2CH_3$, mp 240.0-241.5°C (dioxane/hexane); ^{1}H NMR ($CDCl_3$) δ 1.11 (6H, t, J=7.4, -CH_2CH_2C**H**$_3$), 1.65-1.85 (4H, m, -CH_2C**H**$_2$CH$_3$), 3.34 (4H, t, J=7.7, -C**H**$_2$CH$_2$CH$_3$), 3.81 (16H, brs, -OC**H**$_2$C**H**$_2$O-), 3.98-4.04 (8H, m, Ar-OCH$_2$C**H**$_2$O-), 4.26-4.34 (8H, m, ArOC**H**$_2$CH$_2$O-), 7.38 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 14.9, 23.6, 30.7, 68.4, 69.4, 70.4, 71.2, 104.6, 125.6, 129.3, 148.5; L-SIMS *m/z* 665 ([M+Na]$^+$, 90%), 642 ([M]$^+$,100%); HRMS m/z 642.3401 (642.3404 calcd for $C_{36}H_{50}O_{10}$, [M]$^+$); Anal. Calcd. for $C_{36}H_{50}O_{10}$+0.5H_2O: C, 66.34; H, 7.89. Found: C, 66.27; H 7.97.
Crown 6c: R= -$CH_2(CH_2)_2CH_3$; mp 235-237°C (PhMe/MeOH); ^{1}H NMR ($CDCl_3$) δ 1.03 (6H, d, J=7.2, -$CH_2(CH_2)_2$C**H**$_3$), 1.50-1.81 (8H, m, CH_2(C**H**$_2$)$_2$CH$_3$), 3.65 (4H, t, J=7.9, C**H**$_2$(CH$_2$)$_2$CH$_3$), 3.82 (16H, brs, -OC**H**$_2$C**H**$_2$O-), 3.91-4.05 (8H, m, Ar-OCH$_2$C**H**$_2$O-), 4.25-4.32 (8H, m, ArOC**H**$_2$C**H**$_2$O-), 7.38 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 14.1, 23.3, 28.2, 32.5, 68.4, 69.5, 70.4, 71.3, 104.5, 125.5, 129.4, 148.6; L-SIMS m/z 693([M+Na]$^+$, 94%), 670 ([M]$^+$,100%); HRMS m/z 670.3727 (670.3717 calcd for $C_{36}H_{50}O_{10}$, [M]$^+$); Anal. Calcd. for $C_{38}H_{54}O_{10}$+0.5H_2O: C, 67.13; H, 8.45. Found: C, 66.81; H 8.19.
Crown 6d: R= -$CH_2CH(CH_3)_2$; mp 242-243.5°C ($CHCl_3$/MeOH); ^{1}H NMR ($CDCl_3$) δ 1.03 (12H, d, J=4.2, -CH_2CH(C**H**$_3$)$_2$), 2.10-2.24 (2H, m, -CH_2C**H**(CH$_3$)$_2$), 3.28 (4H, d, J=7.0, -C**H**$_2$CH(CH$_3$)$_2$), 3.82 (16H, brs, -OC**H**$_2$C**H**$_2$O-), 3.98-4.05 (8H, m, Ar-OCH$_2$C**H**$_2$O-), 4.25-4.32 (8H, m, ArOC**H**$_2$C**H**$_2$O-), 7.40 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 23.4, 30.6, 37.3, 68.4, 69.5, 70.4, 71.3, 105.1, 126.2, 128.8, 148.3; L-SIMS *m/z* 693([M+Na]$^+$, 90%), 670 ([M]$^+$,100%); Anal. Calcd. for $C_{38}H_{54}O_{10}$: C, 68.03; H, 8.11. Found: C, 68.04; H 8.20.
Crown 6e: R= -$CH_2(CH_2)_4CH_3$, mp 246.5-247.5°C (dioxane/Me_2CO); ^{1}H NMR ($CDCl_3$) δ 0.91 (6H, t, J=7.0 Hz, -CH_2(CH$_2$)$_5$C**H**$_3$), 1.20-1.82 (16H, -CH_2(C**H**$_2$)$_5$CH$_3$), 3.35 (4H, t, J=8.0, -C**H**$_2$(CH$_2$)$_5$CH$_3$), 3.82 (16H, brs, -OC**H**$_2$C**H**$_2$O-), 3.99-4.05 (8H, m, Ar-OCH$_2$C**H**$_2$O-), 4.26-4.37 (8H, m, ArOC**H**$_2$CH$_2$O-), 7.38 (4H, s, Ar**H**); ^{13}C

NMR ($CDCl_3$) δ 14.1, 22.7, 28.6, 29.9, 30.2, 31.8, 68.4, 69.5, 70.4, 71.3, 104.5, 125.5, 129.4, 148.6; L-SIMS *m/z* 765 ($[M+K]^+$, 98%), 749 ($[M+Na]^+$, 100%), 726 ($[M]^+$, 82%); %); HRMS m/z 726.4401 (726.4340 calcd for $C_{42}H_{62}O_{10}$, $[M]^+$); Anal. Calcd. for $C_{42}H_{62}O_{10}$: C, 69.39; H, 8.60. Found: C, 69.43, H 8.71.

Crown 6f: R= $-CH_2(CH_2)_5CH_3$, mp 186.0-187.5°C (PhMe/MeOH); ^1H NMR ($CDCl_3$) δ 0.89 (6H, t, J=7.0, $-CH_2(CH_2)_5\mathbf{CH_3}$), 1.25-1.72 (20H, $-CH_2(\mathbf{CH_2})_5CH_3$), 3.35 (4H, t, J=8.0, $-\mathbf{CH_2}(CH_2)_5CH_3$), 3.82 (16H, brs, $-OCH_2\mathbf{CH_2}O-$), 3.79-3.99 (8H, m, Ar-$OCH_2\mathbf{CH_2}O-$), 4.28-4.31 (8H, m, Ar$O\mathbf{CH_2}CH_2O-$), 7.38 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 14.6, 22.7, 29.1, 29.9, 30.8, 32.3, 32.4, 68.9, 70.0, 70.9, 71.8, 104.5, 124.1, 126.0, 149.1; L-SIMS *m/z* 1548 ($[M+K]^+$, 4%), 793 ($[M+K]^+$, 19%), 754 ($[M]^+$, 100%); HRL-SIMS m/z 754.4699 (754.4656 calcd for $C_{44}H_{66}O_{10}$, $[M]^+$); Anal. Calcd. for $C_{44}H_{66}O_{10}+0.5\ H_2O$: C, 69.16; H, 8.84. Found: C, 68.85, H 8.81.

Crown 6g: R= $-CH_2(CH_2)_7CH_3$, mp 160.5-162.5°C ($CHCl_3$/MeOH); ^1H NMR ($CDCl_3$) δ 0.88 (6H, t, J=6.6, $-CH_2(CH_2)_7\mathbf{CH_3}$), 1.15-1.57 (24H, m, $-CH_2CH_2(\mathbf{CH_2})_6CH_3$), 1.70-1.82 (4H, m, $-CH_2\mathbf{CH_2}(CH_2)_6CH_3$), 3.35 (4H, t, J=8.0, $-\mathbf{CH_2}(CH_2)_8CH_3$), 3.82 (16H, brs, $-OCH_2\mathbf{CH_2}O-$), 4.00-4.05 (8H, m, Ar-$OCH_2\mathbf{CH_2}O-$), 4.27-4.34 (8H, m, Ar$O\mathbf{CH_2}CH_2O-$), 7.38 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.6, 29.4, 29.5, 29.6, 30.3, 31.9, 68.5, 69.5, 70.5, 71.3, 104.5, 125.5, 129.5, 148.6; L-SIMS *m/z* 749 ($[M+K]^+$, 11%), 833 ($[M+Na]^+$,100%), 810 ($[M]^+$, 11%); HRL-SIMS m/z 810.5281 (810.5281 calcd for $C_{48}H_{74}O_{10}$, $[M]^+$); Anal. Calcd. for $C_{48}H_{74}O_{10}+H_2O$ C, 69.54; H, 9.24. Found: C, 69.09, H 9.31.

Crown 6h: R= $-CH_2(CH_2)_9CH_3$; mp 159-162°C ($CHCl_3$/MeOH); ^1H NMR ($CDCl_3$) δ 0.88 (6H, t, J=6.5 $-CH_2(CH_2)_9\mathbf{CH_3}$), 1.18-1.60 (32H, m, $-CH_2CH_2(\mathbf{CH_2})_8CH_3$), 1.70-1.8 (4H, m, $-CH_2\mathbf{CH_2}(CH_2)_8CH_3$), 3.33 (4H, t, J=6.6, $-\mathbf{CH_2}(CH_2)_9CH_3$), 3.82 (16H, brs, $-OCH_2\mathbf{CH_2}O-$), 4.00-4.05 (8H, m, Ar-$OCH_2\mathbf{CH_2}O-$), 4.27-4.35 (8H, m, Ar$O\mathbf{CH_2}CH_2O-$), 7.36 (4H, s, Ar**H**);; ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.6, 29.4, 29.5, 29.6, 29.7, 30.3, 31.9, 68.5, 69.5, 70.5, 71.3, 104.5, 125.5, 129.5, 148.5; L-SIMS *m/z* 906($[M+K]^+$, 22%), 890 ($[M+Na]^+$, 100%), 867 ($[M]^+$, 38%); Anal. Calcd. for $C_{52}H_{82}O_{10}+0.5H_2O$: C, 71.28; H, 9.55. Found: C,71.38; H 9.64.

Crown 8a: R= $-C_2H_5$; mp 231-233°C ($CHCl_3$/MeOH); ^1H NMR ($CDCl_3$) δ 1.39 (6H, t, J=7.4, $\mathbf{CH_3}CH_2-$), 3.41 (4H, q, J=7.4, $CH_3\mathbf{CH_2}-$), 3.71 (8H, brs, $-OCH_2\mathbf{CH_2}O-$), 3.74-3.79 (8H, m, $-\mathbf{CH_2}OCH_2CH_2O\mathbf{CH_2}-$), 3.81-3.88 (8H, m, $ArOCH_2CH_2O\mathbf{CH_2}-$) 4.01-4.08 (8H, m, Ar-$OCH_2\mathbf{CH_2}O-$), 4.31-4.37 (8H, m, Ar-$O\mathbf{CH_2}CH_2O-$), 7.41 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 14.6, 21.8, 68.9, 69.5, 70.7, 70.8, 70.9, 104.5, 125.2, 130.6, 148.6; EI-MS *m/z* 758 ($[M+K]^+$, 12%), 702 ($[M]^+$, 100%); Anal. Calcd. for $C_{38}H_{54}O_{12}$: C, 64.94; H, 7.74. Found: C, 64.77; H 7.90.

Crown 8c: R= $-CH_2(CH_2)_2CH_3$; mp 160.4-162.1°C (PhMe/MeOH); ^1H NMR ($CDCl_3$) δ 1.03 (6H, d, J=7.1, $-CH_2(CH_2)_2\mathbf{CH_3}$), 1.50-1.81 (8H, m, $CH_2(\mathbf{CH_2})_2CH_3$), 3.37 (4H, t, J=7.9, $\mathbf{CH_2}(CH_2)_2CH_3$), 3.72-3.77 (16H, brs, $-\mathbf{CH_2}OCH_2CH_2O\mathbf{CH_2}$), 3.82-3.86 (8H, m, $Ar-OCH_2CH_2O\mathbf{CH_2}-$) 4.00-4.06 (8H, m, Ar-$OCH_2\mathbf{CH_2}O-$), 4.28-4.34 (8H, m, Ar$O\mathbf{CH_2}CH_2O-$), 7.40 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 14.1, 23.3, 28.3, 32.5, 68.7, 69.5, 70.7, 70.8, 70.9, 104.6, 125.5, 129.4, 148.5; EI-MS m/z 758($[M]^+$, 100%); HRMS m/z $C_{42}H_{62}O_{12}$ 758.4397 (758.4241 calcd for $C_{42}H_{62}O_{12}$, $[M]^+$); Anal. Calcd. for $C_{42}H_{62}O_{12}+0.5H_2O$: C, 65.78; H, 8.15. Found: C, 65.51; H 8.44.

Crown 8d: R= $-CH_2CH(CH_3)_2$; mp 197.1-199.4°C ($CHCl_3$/MeOH); ^1H NMR ($CDCl_3$) δ 1.03 (12H, d, J=6.6, $-CH_2CH(\mathbf{CH_3})_2$), 2.10-2.22 (2H, m, $-CH_2\mathbf{CH}(CH_3)_2$), 3.27 (4H, d, J=6.8, $-\mathbf{CH_2}CH(CH_3)_2$,), 3.72-3,79 (16H, m, $-\mathbf{CH_2}OCH_2CH_2O-$), 3.81-3.87 (8H, m, Ar-$OCH_2CH_2O\ \mathbf{CH_2}-$) 4.00-4.05 (8H, m, Ar-$OCH_2\mathbf{CH_2}O-$), 4.30-4.38 (8H, m, Ar$O\mathbf{CH_2}CH_2O-$), 7.42 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 23.4, 30.5, 37.3, 68.4, 69.5, 70.7, 70.8, 71.0, 105.1, 126.2, 128.8, 148.1; EI-MS *m/z* 758($[M]^+$, 100%), 715 (22%); HR-MS m/z 758.4219 (758.4241 calcd for $C_{22}H_{62}O_{12}$, $[M]^+$); Anal. Calcd. for $C_{42}H_{64}O_{12}+1.5H_2O$: C, 64.18; H, 8.30. Found: C, 64.23; H 8.30.

Crown 8f: R= $-CH_2(CH_2)_5CH_3$; mp 162.0-163.5°C (PhMe/MeOH); ^1H NMR ($CDCl_3$) δ 0.90 (6H, t, J=6.7, $-CH_2(CH_2)_5\mathbf{CH_3}$), 1.25-1.62 (16H, m, $-CH_2CH_2(\mathbf{CH_2})_4CH_3$), 1.70-1.82 (4H, m, $-CH_2\mathbf{CH_2}(CH_2)_4CH_3$) 3.58 (4H, t, J=6.8, $-\mathbf{CH_2}(CH_2)_5CH_3$),), 3.72-3.80 (16H, brs, $-CH_2OCH_2\mathbf{CH_2}OCH_2-$), 3.83-3.88 (8H, m, Ar-$OCH_2CH_2O\mathbf{CH_2}-$), 4.02-4.08 (8H, m, Ar-$OCH_2\mathbf{CH_2}O-$), 4.28-4.37 (8H, m, Ar$O\mathbf{CH_2}CH_2O-$), 7.40 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.6, 29.3, 30.3, 31.9, 68.7, 69.5, 70.7, 70.8, 71.0, 104.6, 125.5, 129.5, 148.5; L-SIMS *m/z* 865 ($[M+Na]^+$, 85%), 8424 ($[M]^+$, 100%); HRL-SIMS m/z 842.5246 (842.5180 calcd for $C_{48}H_{74}O_{12}$, $[M]^+$); Anal. Calcd. for $C_{48}H_{74}O_{12}+0.25\ H_2O$: C, 68.08; H, 8.85. Found: C, 67.81, H 8.71.

Crown 8g: R= $-CH_2(CH_2)_7CH_3$; mp 146.3-147.8°C (Et_2O/MeOH); ^1H NMR ($CDCl_3$) δ 0.88 (6H, t, J=6.6, $-CH_2(CH_2)_7\mathbf{CH_3}$), 1.15-1.57 (24H, m, $-CH_2CH_2(\mathbf{CH_2})_6CH_3$), 1.70-1.82 (4H, m, $-CH_2\mathbf{CH_2}(CH_2)_6CH_3$), 3.35 (4H, t, J=8.0, $-\mathbf{CH_2}(CH_2)_8CH_3$), 3.72-3.87 (16H, m, $-\mathbf{CH_2}OCH_2CH_2O\mathbf{CH_2}-$), 4.00-4.05 (8H, m, Ar-$OCH_2\mathbf{CH_2}O-$), 4.27-4.34 (8H, m, Ar$O\mathbf{CH_2}CH_2O-$), 7.38 (4H, s, Ar**H**); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.6, 29.4, 29.6, 30.3, 31.9, 68.6, 69.5, 70.6,

70.8, 70.9, 104.4, 125.4, 129.4, 148.4; EI-MS *m/z* 899 ([M+H]$^+$, 100%), 867 (6%); HR-MS m/z 899.5831 (899.5885 calcd for $C_{52}H_{83}O_{12}$, [M+H]$^+$); Anal. Calcd. for $C_{52}H_{82}O_{12}$+2H_2O C, 66.78; H, 9.27. Found: C, 66.78, H 9.06.

Crown 8h: R= -$CH_2(CH_2)_9CH_3$; mp 132.1-134.9°C (PhMe/MeOH); ^{1}H NMR ($CDCl_3$) δ 0.88 (6H, t, J=6.8 -$CH_2(CH_2)_9CH_3$), 1.20-1.60 (32H, m, -$CH_2CH_2(CH_2)_8CH_3$), 1.70-1.8 (4H, m, -$CH_2CH_2(CH_2)_8CH_3$), 3.49 (4H, t, J=6.6, -$CH_2(CH_2)_9CH_3$), 3.72-8.87 (16H, m, -$CH_2OCH_2CH_2OCH_2$-); 4.01-4.06 (8H, m, ArOCH_2CH_2O-), 4.28-4.34 (8H, m, Ar-OCH_2CH_2O-), 7.38 (4H, s, ArH); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.7, 28.6, 29.4, 29.5, 29.6, 29.7, 30.3, 31.9, 68.4, 69.5, 70.6, 70.8, 70.9, 104.5, 125.5, 129.5, 148.4; EI-IMS *m/z* 955([M]$^+$, 100%), 899 (10%), 813 (9%); HR-MS m/z 954.6472 (954.6432 $C_{56}H_{90}O_{12}$ calcd for [M]$^+$); Anal. Calcd. for $C_{56}H_{90}O_{12}$+0.5H_2O: C, 69.74; H, 9.51. Found: C, 69.87; H 9.77.

Cross condensation experiment; To the intensively stirred, cooled to 5 °C (ice bath) solution of sulfuric acid (10 ml, 84%), a solution of isovaleraldehyde (0.86g, 10 mmol, 5 equiv.), benzo-15-crown-15 (0.536 g, 2 mmol) and veratrol (0.28g, 2 mmol), in chloroform (5 ml) was added slowly, while keeping the temperature of the reaction mixture below 10 °C. The reaction mixture became dark red and was stirred at this temperature for 3 h, then the cooling bath was removed and stirring was continued for 1 h. Then water (50 ml) and ammonium hydroxide were added to reach pH 11. The aqueous phase was extracted with chloroform (3x30 ml) and organic phases were combined and dried ($MgSO_4$). Chromatography on silica gel using chloroform-methanol solvent gradient (from pure chloroform to chloroform-methanol mixture 95/5, v/v) resulted in separation of 0.098g (24% yield) of anthracene **10** and 0.032g (6% yield) of anthracene-crown **11**.

Anthracene 10: ^{1}H NMR ($CDCl_3$) δ 1.08 (12H, d, J=6.7, -$CH_2CH(CH_3)_2$), 2.14-2.23 (2H, m, -$CH_2CH(CH_3)_2$), 3.34 (4H, d, J=6.9, -$CH_2CH(CH_3)_2$), 4.05 (6H, s, ArOCH_3), 7.43 (4H, s, ArH); ^{13}C NMR ($CDCl_3$) δ 23.4, 30.6, 37.3, 55.5, 103.1, 126.0, 128.8, 148.4; EI-MS *m/z* 410 ([M]$^+$, 62%), 367 (100%); Anal. Calcd. for $C_{26}H_{34}O_4$+H_2O: C, 72.87; H, 8.47. Found: C, 72.84; H 8.34.

Crown 11: ^{1}H NMR ($CDCl_3$) δ 1.05 (12H, d, J=6.6, -$CH_2CH(CH_3)_2$), 2.10-2.23 (2H, m, -$CH_2CH(CH_3)_2$), 3.31 (4H, d, J=6.8, -$CH_2CH(CH_3)_2$), 3.80-3.84 (8H, brs, -Ar$OCH_2CH_2OCH_2CH_2$-), 3.98-4.07 (12H, m, Ar-OCH_2CH_2O-, ArOCH_3), 4.27-4.32 (4H, m, ArOCH_2CH_2O-), 7.41 (4H, s, ArH); ^{13}C NMR ($CDCl_3$) δ 23.4, 30.6, 37.3, 55.5, 68.3, 69.5, 70.4, 71.3, 103.1, 105.0, 125.9, 126.2, 128.8, 148.2, 148.4; EI-MS *m/z* 540 ([M]$^+$, 100%), 497 (82%); HR-MS m/z 540.3088 (540.3087 $C_{32}H_{24}O_7$ calcd, [M]$^+$); Anal. Calcd. for $C_{32}H_{24}O_7$+H_2O: C, 66.64; H, 8.39. Found: C, 66.30; H 8.11.

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