Synthesis of geminal-substituted, sterically congested, proton-ionizable dibenzo-14-crown-4, dibenzo-16-crown-5, dibenzo-19-crown-6 and dibenzo-22-crown-7 lariat ethers

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Abstract

Proton-ionizable dibenzo-14-crown-4, -16-crown-5, -19-crown-6 and -22-crown-7 lariat ethers with different lipophilic geminal alkyl groups and different proton-ionizable groups are synthesized. For each lariat ether platform, butyl, heptyl and decyl groups were incorporated as the geminal lipophilic groups. Carboxylic acid, *N*-(trifluoromethane)sulfonyl carboxamide and sodium 3-propanesulfonate groups are incorporated on the platforms as proton-ionizable functions.

Keywords: Lariat ether, synthesis, proton-ionizable groups, ion flotation

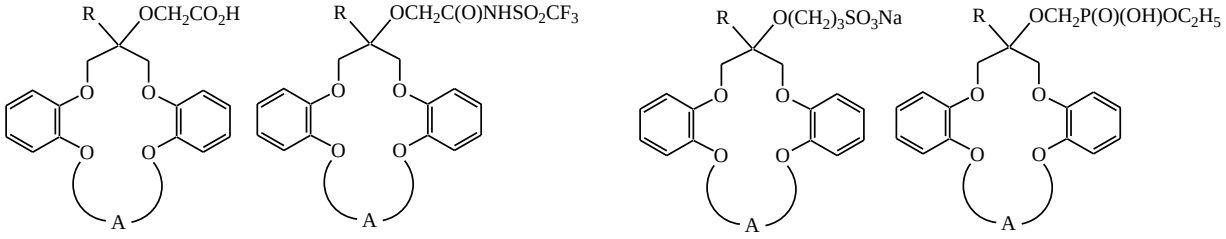
Introduction

Ionic recognition is a major field of application for supramolecular chemistry. Due to their special properties in selectively binding metal ions, anions, neutral molecules, and non-metal cations, crown ethers have established important roles in a variety of applications.[1]

Ion flotation could be an important method for removing hazardous metal ions from liquid nuclear wastes, if suitable collectors are identified.[2] Ion flotation is capable of recovering the collector and metal ions as a compact scum. But effective collectors are limited in number. Ion flotation experiments conducted with lariat ethers **6**, **18** and **37** (Figure 1) showed that proton-ionizable lariat ethers derived from dibenzo-16-crown-5 can be good collectors for flotation removal of Sr(II), Cs(I),[2] Cd(II) and Zn(II).[3] Among other factors, it was found that structural variation within the proton-ionizable lariat ether collector can influence the efficiency and selectivity of metal ion flotation. During the metal ion separation process, the presence of lipophilic groups is important in reducing loss of the macrocyclic ligand from an organic phase

into a contacting aqueous phase.[4] The attachment site of the lipophilic group also influences the selectivity of the lariat ether toward metal ions. It was found that ligands with a geminal lipophilic group were more selective extractants compared with analogues having the lipophilic group on the proton-ionizable side arm.[4c]

Results obtained from the initial screening studies were sufficiently promising to warrant the preparation of series of proton-ionizable lariat ethers with systematic structural variation. In this work, the synthesis of series of proton-ionizable lariat ethers **1-41** (Figure 1) will be described.



		A	R		
1	**13**	$CH_2CH_2CH_2$	C_4H_9	**25**	
2	**14**	$CH_2CH_2CH_2$	C_7H_{15}	**26**	
3	**15**	$CH_2CH_2CH_2$	$C_{10}H_{21}$	**27**	
4	**16**	CH_2OCH_2	C_4H_9	**28**	**37**
5	**17**	CH_2OCH_2	C_7H_{15}	**29**	**38**
6	**18**	CH_2OCH_2	$C_{10}H_{21}$	**30**	**39**
7	**19**	$(CH_2OCH_2)_2$	C_4H_9	**31**	
8	**20**	$(CH_2OCH_2)_2$	C_7H_{15}	**32**	
9	**21**	$(CH_2OCH_2)_2$	$C_{10}H_{21}$	**33**	**40**
10	**22**	$(CH_2OCH_2)_3$	C_4H_9	**34**	
11	**23**	$(CH_2OCH_2)_3$	C_7H_{15}	**35**	
12	**24**	$(CH_2OCH_2)_3$	$C_{10}H_{21}$	**36**	**41**

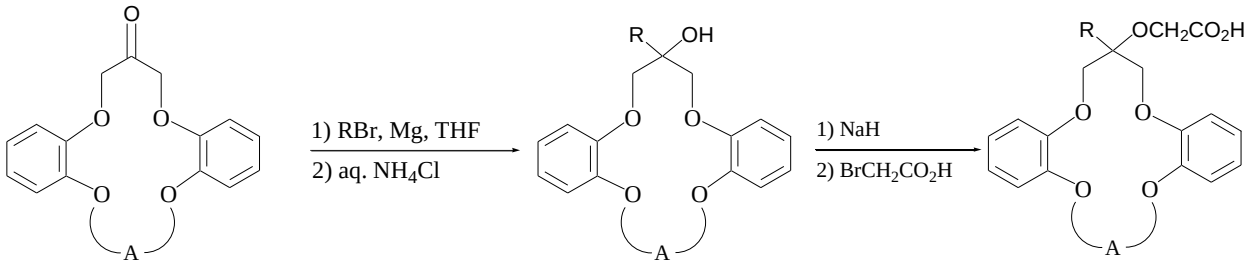
Figure 1. Structures of target proton-ionizable lariat ethers.

The proton-ionizable lariat ethers prepared in this work are based on dibenzo-14-crown-4, -16-crown-5, -19-crown-6 and -22-crown-7 platforms. Butyl, heptyl and decyl groups are used as lipophilic substituents geminal to the proton-ionizable groups. The proton-ionizable groups are varied to include carboxylic acid, *N*-(trifluoromethane)sulfonyl carboxamide, sodium 3-propanesulfonate and monoethyl methylphosphonate functions.

Results and Discussion

Preparation of *sym*-(*R*)-dibenzocrownoxyacetic acids

The preparation of *sym*-(hydroxyl)(*R*)-dibenzocrown ethers **46-57** is shown in Scheme 1. The precursor *sym*-(keto)dibenzocrown ethers **42-45** were prepared using a developed method[5] and converted into *sym*-(hydroxyl)(R)-dibenzocrown ethers **46-57** via Grignard reactions.



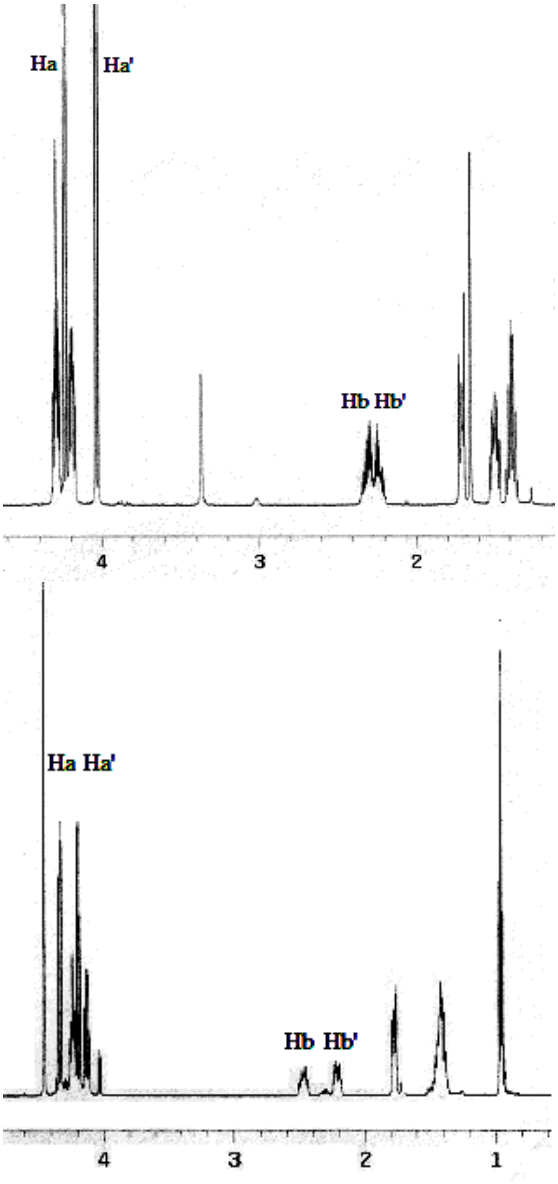
	A
42	$CH_2CH_2CH_2$
43	CH_2OCH_2
44	$(CH_2OCH_2)_2$
45	$(CH_2OCH_2)_3$

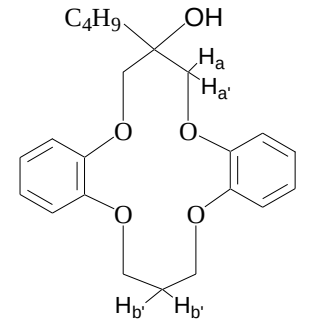
	A	R	
46	$CH_2CH_2CH_2$	C_4H_9	**1**
47	$CH_2CH_2CH_2$	C_7H_{15}	**2**
48	$CH_2CH_2CH_2$	$C_{10}H_{21}$	**3**
49	CH_2OCH_2	C_4H_9	**4**
50	CH_2OCH_2	C_7H_{15}	**5**
51	CH_2OCH_2	$C_{10}H_{21}$	**6**
52	$(CH_2OCH_2)_2$	C_4H_9	**7**
53	$(CH_2OCH_2)_2$	C_7H_{15}	**8**
54	$(CH_2OCH_2)_2$	$C_{10}H_{21}$	**9**
55	$(CH_2OCH_2)_3$	C_4H_9	**10**
56	$(CH_2OCH_2)_3$	C_7H_{15}	**11**
57	$(CH_2OCH_2)_3$	$C_{10}H_{21}$	**12**

Scheme 1. Preparation of *sym*-(Hydroxyl)(R)-dibenzocrownoxyacetic acids.

Lariat ether alcohols **46-57** were treated with NaH followed by addition of bromoacetic acid to give the target *sym*-(R)-dibenzocrownoxyacetic acids **1-12** in 36-100 % yields.

When the hydroxyl group was replaced by an oxyacetic acid group, the conformation of the compound became more rigid. As a result, the two protons on the center carbon of the three-carbon bridge are further from each other in the NMR spectrum. A comparison of the NMR spectral patterns for the protons of interest between unsubstituted compound **1** and compound **46** is shown in Figure 2.





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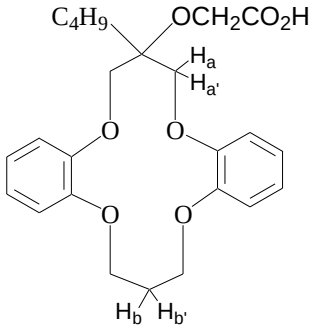

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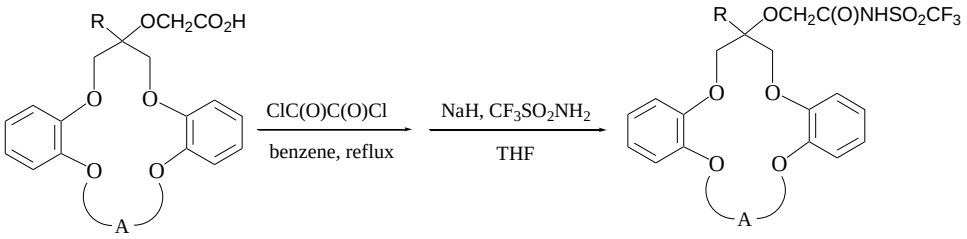
Figure 2. ^{1}H NMR spectra of methylene groups on the crown ring for compounds **1** and **46.**

Preparation of *N*-(trifluoromethane)sulfonyl *sym*-(*R*)-dibenzocrownoxyacetamides

sym-(*R*)-dibenzocrown-oxyacetic acids **1-12** were treated with oxalyl chloride in benzene to form the corresponding acid chlorides (Scheme 2). The conversions were verified by IR spectroscopy with the appearance of the strong carbonyl group absorption at around 1810 cm^{-1} for an acid chloride and the disappearance of the carbonyl group absorption for a carboxylic acid at 1745 cm^{-1}. The crude acid chlorides were used directly in the next step. After reacting trifluoromethanesulfonamide with NaH in THF, the acid chloride was added to the reaction mixture to form the target *N*-(trifluoromethane)sulfonyl *sym*-(R)-dibenzocrown-oxyacetamides **13-24** in 60-80 % yields.

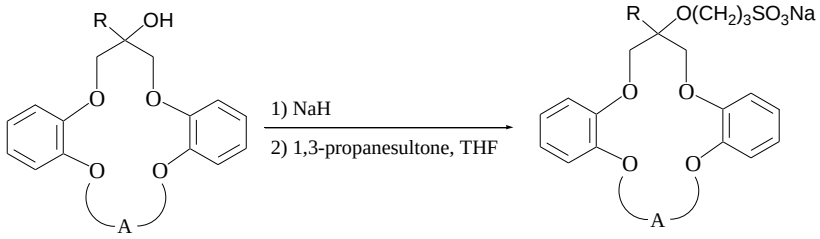
Preparation of Sodium [*sym*-(R)-dibenzocrownoxy]-3-propanesulfonates

Sodium [*sym*-(*R*)-dibenzocrownoxy]-3-propanesulfonates **25-36** were synthesized in a one-step reaction[6] from lariat ether alcohols **46-57**, respectively, as shown in Scheme 3. Reaction of lariat ether alcohols **46-57** with NaH and 1,3-propanesultone followed by workup and purification gave sodium lariat ether sulfonates **25-36** in 61-74 % yields.



	A	R	
1	$CH_2CH_2CH_2$	C_4H_9	**13**
2	$CH_2CH_2CH_2$	C_7H_{15}	**14**
3	$CH_2CH_2CH_2$	$C_{10}H_{21}$	**15**
4	CH_2OCH_2	C_4H_9	**16**
5	CH_2OCH_2	C_7H_{15}	**17**
6	CH_2OCH_2	$C_{10}H_{21}$	**18**
7	$(CH_2OCH_2)_2$	C_4H_9	**19**
8	$(CH_2OCH_2)_2$	C_7H_{15}	**20**
9	$(CH_2OCH_2)_2$	$C_{10}H_{21}$	**21**
10	$(CH_2OCH_2)_3$	C_4H_9	**22**
11	$(CH_2OCH_2)_3$	C_7H_{15}	**23**
12	$(CH_2OCH_2)_3$	$C_{10}H_{21}$	**24**

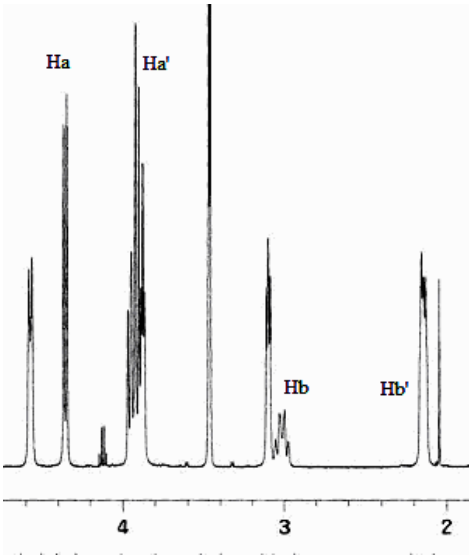
Scheme 2. Preparation of *N*-(trifluoromethane)sulfonyl *sym*-(R)-dibenzocrown-oxyacetamides.



	A	R	
46	$CH_2CH_2CH_2$	C_4H_9	**25**
47	$CH_2CH_2CH_2$	C_7H_{15}	**26**
48	$CH_2CH_2CH_2$	$C_{10}H_{21}$	**27**
49	CH_2OCH_2	C_4H_9	**28**
50	CH_2OCH_2	C_7H_{15}	**29**
51	CH_2OCH_2	$C_{10}H_{21}$	**30**
52	$(CH_2OCH_2)_2$	C_4H_9	**31**
53	$(CH_2OCH_2)_2$	C_7H_{15}	**32**
54	$(CH_2OCH_2)_2$	$C_{10}H_{21}$	**33**
55	$(CH_2OCH_2)_3$	C_4H_9	**34**
56	$(CH_2OCH_2)_3$	C_7H_{15}	**35**
57	$(CH_2OCH_2)_3$	$C_{10}H_{21}$	**36**

Scheme 3. Preparation of sodium 3-[*sym*-(R)--dibenzocrown-oxy]propanesulfonates.

Complexation of the sodium ion by the crown ether ring has a substantial influence on the chemical shifts of the two protons on the center carbon of the three-carbon bridge. This effect can be seen in Figure 3 in which part of the proton NMR spectrum of compound **27** is shown. Compared with compounds **3** and **48**, the chemical shifts of the two protons of interest are differentiated even further (nearly 1 ppm apart).



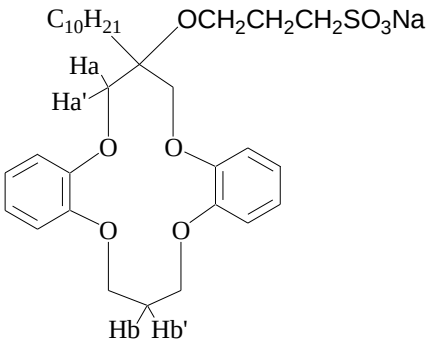


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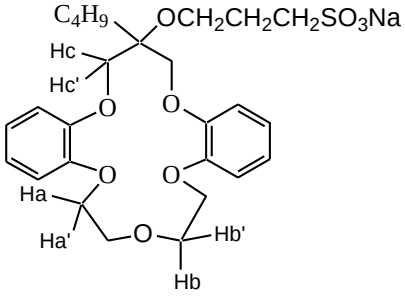
Figure 3. [1]H NMR spectra of methylene groups on the crown ether ring for compound **27**.



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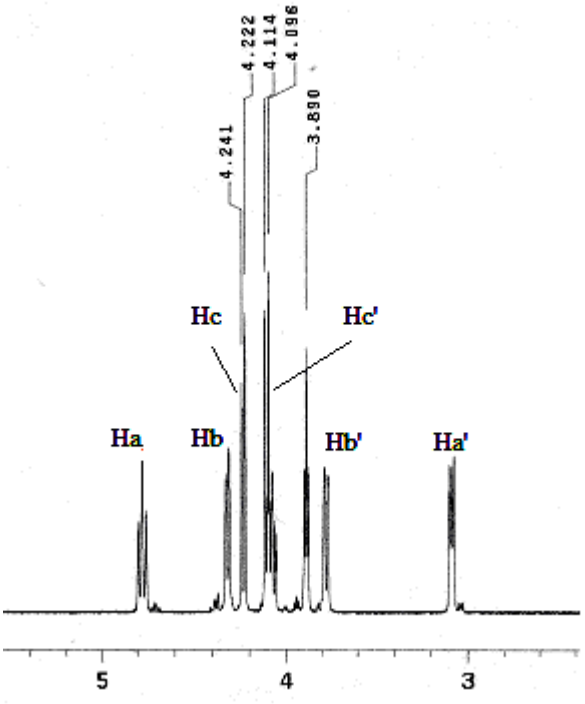


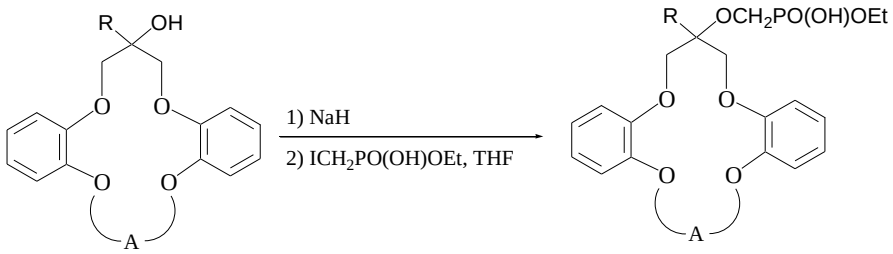
Figure 4. [1]H NMR spectrum for methylene groups on the crown ether ring for compound **28.**

The sodium ion in compounds **25-30** can form complexes with the crown ether structures. The compounds have relatively rigid conformations as reflected in their proton NMR spectra (Figure 4). Pseudo-equatorial hydrogens and pseudo-axial hydrogens on the crown ether ring showed diastereotopic splitting patterns in the spectra.

Preparation of monoethyl lariat ether phosphonates

Proton-ionizable lariat ethers with a more acidic pendent functional group, such as a phosphonic acid, would allow metal ion separations to be performed from lower pH environments than those in which lariat ether carboxylic acids are effective.

Reaction of lariat ether alcohols **49-51**, **54** and **57** with NaH and monoethyl iodomethylphosphonate in THF at room temperature followed by acidic workup gave lariat ether phosphonic acid monoethyl esters **37-41** in 43-49 % yields (Scheme 4). The method used in this work was based on literature methods.[6] In the reported method, ethyl acetate was used to wash out impurities. In the present case, the desired products would dissolve in ethyl acetate, so column chromatography was used in the purification. Due to the lower yields encountered in preparing this type of proton-ionizable lariat ether, only the selected larger ring sizes were synthesized.



	A	R	
49	CH_2OCH_2	C_4H_9	**37**
50	CH_2OCH_2	C_7H_{15}	**38**
51	CH_2OCH_2	$C_{10}H_{21}$	**39**
54	$(CH_2OCH_2)_2$	$C_{10}H_{21}$	**40**
57	$(CH_2OCH_2)_3$	$C_{10}H_{21}$	**41**

Scheme 4. Preparation of monoethyl lariat ether oxymethylphosphonates.

Conclusions

Proton-ionizable dibenzo-14-crown-4, -16-crown-5, -19-crown-6 and -22-crown-7 lariat ethers with different lipophilic geminal alkyl groups and different proton-ionizable groups have been synthesized. New compounds are characterized by NMR and IR spectroscopy and by combustion analysis. For each lariat ether platform, butyl, heptyl and decyl groups were incorporated as the geminal lipophilic groups. The proton-ionizable group was varied to include

carboxylic acid, *N*-(trifluoromethane)sulfonyl carboxamide and sodium 3-propanesulfonate. The monoethyl phosphonate unit was successfully attached onto the dibenzo-16-crown-5 platform and on selected dibenzo-19-crown-6 and -22-crown-7 platforms. Systematic study of the ion extraction ability of these compounds will help determine the effect of structural change in the collector on the selectivity and efficiency of metal ion separation by ion flotation.

Experimental Section

General. Melting points were determined with a Mel-Temp melting point apparatus. Infrared (IR) spectra were recorded with a Perkin-Elmer Model 1600 FT-IR spectrometer as deposits from CH_2Cl_2 solution on NaCl plates. The ^1H and ^{13}C NMR spectra were recorded with a Varian Unity INOVA 500 MHz FT-NMR (^1H 500 MHz and ^{13}C 126 MHz) spectrometer in $CDCl_3$ with Me_4Si as internal standard unless mentioned otherwise. Chemical shifts (δ) are given in ppm downfield from TMS and coupling constants (J) values are given in Hz. Elemental analysis was performed by Desert Analytics Laboratory/Columbia Analytical Services of Tucson, Arizona. Analytical TLC was performed on Analtech Uniplate silica gel or alumina plates. Silica gel 150 (Mallinckrodt SiliCAR®, 60-200 mesh) was used for column chromatography.
Reagents were obtained from commercial suppliers and used directly, unless otherwise noted. Acetonitrile (MeCN) was dried over CaH_2 and distilled immediately before use. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled just before use. Cs_2CO_3 was activated by heating at 150 ºC overnight under high vacuum and stored in a desiccator.

General procedure for preparation of *sym*-(hydroxy)(R)-dibenzocrown ethers 46-57
To magnesium turnings (48 mmol) under nitrogen, the appropriate 1-bromoalkane (43.6 mmol) in 30 mL of dry THF was added and the mixture was stirred at room temperature for 2 h. The *sym*-(keto)dibenzo-crown ether (**42-45**) (14.5 mmol) in 125 mL of THF was added dropwise over a period of 45 min. The mixture was stirred at room temperature overnight. The reaction mixture was cooled to 0 ºC and 100 mL of 10 % NH_4Cl was added. The THF was evaporated in vacuo and an additional 50 mL of 10 % aqueous NH_4Cl was added. The aqueous layer was extracted with CH_2Cl_2 (100 mL, then 30 mL). The combined organic layers were washed with water (2 x 100 mL), dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by recrystallization or column chromatography.

***sym*-(Butyl)(hydroxy)dibenzo-14-crown-4 (46)** was purified by chromatography on silica gel with hexanes-EtOAc (4:1) as eluent to give a white solid (72 %) with mp 87-89 ºC. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3370 (O-H), 1253 and 1119 (C-O). ^1H NMR ($CDCl_3$): δ 0.95 (t, J= 7.0 Hz, 3H), 1.34-1.43 (m, 2H), 1.45-1.53 (m, 2H), 1.68-1.74 (m, 2H), 2.18-2.36 (m, 2H), 3.37 (s, 1H), 4.03 (d, J= 9.0 Hz, 2H), 4.16-4.22 (m, 2H), 4.24 (d, J= 9.0 Hz,

2H), 4.26-4.32 (m, 2H), 6.87-6.98 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.1, 23.4, 24.9, 29.3, 34.7, 67.6, 72.9, 74.3, 115.2, 117.3, 121.7, 122.6, 149.4, 149.8. Anal. Calcd for $C_{22}H_{28}O_5$: C, 70.94; H, 7.58. Found: C, 70.81; H, 7.68.

***sym*-(Heptyl)(hydroxy)dibenzo-14-crown-4 (47)** was purified by chromatography on silica gel with hexanes-EtOAc (4:1) as eluent to give a white solid (61 %) with mp 88-90 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3368 (O-H), 1253 and 1120 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J*= 7.0 Hz, 3H), 1.23-1.38 (m, 8H), 1.46-1.55 (m, 2H), 1.68-1.74 (m, 2H), 2.18-2.38 (m, 2H), 3.40 (s, 1H), 4.03 (d, *J*= 9.0 Hz, 2H), 4.16-4.22 (m, 2H), 4.23 (d, *J*= 9.0 Hz, 2H), 4.25-4.32 (m, 2H), 6.87-6.98 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 22.7, 29.3, 29.3, 30.3, 31.8, 35.0, 67.6, 73.0, 74.3, 115.2, 117.3, 121.7, 122.6, 149.4, 149.8. Anal. Calcd for $C_{25}H_{34}O_5$: C, 72.43; H, 8.27. Found: C, 72.67; H, 8.24.

***sym*-(Decyl)(hydroxy)dibenzo-14-crown-4 (48)[7]** was purified by chromatography on silica gel with hexanes-EtOAc (4:1) as eluent to give a white solid (80 %) with mp 72-73 °C (lit.[7] mp 71.5-72.5 °C). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J*= 7.0 Hz, 3H), 1.23-1.59 (m, 16H), 1.68-1.80 (m, 2H), 2.18-2.38 (m, 2H), 3.48 (s, 1H), 4.03 (d, *J*= 9.0 Hz, 2H), 4.16-4.22 (m, 2H), 4.23 (d, *J*= 9.0 Hz, 2H), 4.25-4.32 (m, 2H), 6.87-6.98 (m, 8H).

***sym*-(Butyl)(hydroxy)dibenzo-16-crown-5 (49)[8]** was recrystallized from hexanes/ CH_2Cl_2 to give a white solid (71 %) with mp 105-107 °C (lit.[8] mp 108-109 °C). ^{1}H NMR ($CDCl_3$): δ 0.94 (t, *J*= 7.0 Hz, 3H), 1.19-1.55 (m, 4H), 1.81-1.89 (m, 2H), 3.21 (s, 1H), 3.90-4.26 (m, 12H), δ 6.84-6.99 (m, 8H).

***sym*-(Heptyl)(hydroxy)dibenzo-16-crown-5 (50)[9]** was recrystallized from Et_2O to give a white solid (68 %) with mp 98-99 °C (lit.[8] mp 81-82 °C). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, *J*= 7.0 Hz, 3H), 1.19-1.55 (m, 10H), 1.81-1.89 (m, 2H), 3.37 (s, 1H), 3.90-4.26 (m, 12H), 6.84-6.99 (m, 8H).

***sym*-(Decyl)(hydroxy)dibenzo-16-crown-5 (51)[8]** was recrystallized from hexanes/CH_2Cl_2 to give a white solid (83 %) with mp 87-89 °C (lit.[8] mp 95-96 °C). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, *J*= 7.0 Hz, 3H), 1.19-1.55 (m, 4H), 1.81-1.89 (m, 2H), 3.37 (s, 1H), 3.90-4.26 (m, 12H), δ 6.84-6.99 (m, 8H).

***sym*-(Butyl)(hydroxy)dibenzo-19-crown-6 (52)**[6] was purified by chromatography on silica gel with hexanes and then hexanes-EtOAc (2:1) as eluents to give a light yellow oil in 95 % yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3313 (O-H), 1256 and 1127 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.86-0.92 (t, J=7.0 Hz, 3H), 1.26-1.62 (m, 4H), 1.69-1.86 (m, 2H), 3.46 (s, 1H), 3.76-3.87 (m, 8H), 4.11-4.16 (m, 8H), 6.88-6.93 (m, 8H).

***sym*-(Heptyl)(hydroxy)dibenzo-19-crown-6 (53)** was purified by chromatography on silica gel with hexanes and then hexanes-EtOAc (7:1) as eluents to give a a light yellow oil in 93 % yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3473 (O-H), 1257 and 1123 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.85-0.89 (t, J=7.0 Hz, 3H), 1.23-1.51 (m, 10H), 1.71-1.86 (m, 2H), 3.42 (s, 1H), 3.76-3.88 (m, 8H), 4.09-4.15 (m, 8H), 6.86-6.97 (m, 8H). Anal. Calcd for $C_{28}H_{40}O_7$: C, 68.83; H, 8.25. Found: C, 68.70; H, 8.10.

***sym*-(Decyl)(hydroxy)dibenzo-19-crown-6 (54)**[7] was purified by chromatography on silica gel with hexanes and then hexanes-EtOAc (7:1) as eluents to give a golden oil in 70% yield. IR

(deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3313 (O-H), 1256 and 1125 (C-O). ^1H NMR ($CDCl_3$): δ 0.85-0.90 (t, 3 H, J=7.0 Hz), 1.23-1.77 (m, 16 H), 1.75-1.81 (m, 2 H), 3.38 (s, 1 H), 3.74-3.88 (m, 8 H), 4.09-4.18 (m, 8 H), 6.85-6.97 (m, 8 H).

***sym*-(Butyl)(hydroxy)dibenzo-22-crown-7** (**55**) was purified by chromatography on silica gel with hexanes-EtOAc (8:1) as eluents to give a yellowish oil (71%). IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 3460 (br, O-H), 1256 and 1123 (C-O). ^1H NMR (500 MHz, $CDCl_3$): δ 0.91 (t, *J* =7.3 Hz, 3H), 1.2-1.5 (m, 4H), 1.68 (m, 2H), 3.59 (s, 1H), 3.62-3.78 (m, 8H), 3.86 (m, 4H), 4.00-4.02 (d, *J* = 9.5 Hz, 2H), 4.12-4.15 (m, 4H), 4.22-4.24 (d, *J* = 9.5 Hz, 2H), 6.80-7.00 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 149.7, 149.5, 122.3, 121.7, 117.2, 114.9, 73.5, 73.2, 71.1, 70.5, 69.9, 69.2, 53.4, 34.0, 25.2, 23.4, 14.1. Anal. Calcd. for $C_{27}H_{38}O_8$: C, 66.12; H, 7.76. Found: C, 66.06; H, 7.74.

***sym*-(Heptyl)(hydroxy)dibenzo-22-crown-7** (**56**) was purified by chromatography on alumina with hexanes-EtOAc (12:1) as eluent to give a yellowish oil (72%). IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 3450 (br, O-H), 1256 and 1123 (C-O). ^1H NMR (500 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.20-1.32 (m, 8H), 1.45-1.49 (m, 2H), 1.73-1.77 (m, 2H), 3.56 (s, 1H), 3.60-3.75 (m, 8H), 3.82-3.84 (m, 4H), 4.00 (d, *J* = 9.5 Hz, 2H), 4.12-4.15 (m, 4H), 4.23 (d, *J* = 9.5 Hz, 2H), 6.87-6.94 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 149.7, 149.5, 122.3, 121.7, 117.2, 114.9, 73.5, 73.2, 71.2, 70.5, 69.9, 69.3, 34.3, 32.0, 30.3, 29.3, 23.0, 22.7, 14.1. Anal. Calcd. for $C_{30}H_{44}O_8$: C, 67.67; H, 8.27. Found: C, 67.86; H, 8.18.

***sym*-(Decyl)(hydroxyl)dibenzo-22-crown-7** (**57**) was purified by chromatography on alumina with hexanes-EtOAc (12:1) as eluent to give a yellowish oil (75%). IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 3450 (br, O-H), 1256 and 1123 (C-O). ^1H NMR ($CDCl_3$): δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.20-1.32 (m, 14H), 1.40-1.50 (m, 2H), 1.70-1.80 (m, 2H), 3.48 (s, 1H), 3.60-3.75 (m, 8H), 3.82-3.84 (m, 4H), 4.01 (d, *J* = 9.5 Hz, 2H), 4.12-4.15 (m, 4H), 4.23 (d, *J* = 9.5 Hz, 2H), 6.87-6.94 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 149.7, 149.5, 122.3, 121.7, 117.3, 114.8, 73.5, 71.2, 70.5, 69.9, 69.3, 53.4, 34.3, 31.9, 30.3, 29.7, 29.6, 29.3, 23.0, 22.7, 14.1. Anal. Calcd. for $C_{33}H_{50}O_8$: C, 68.99; H, 8.71. Found: C, 69.34; H, 8.30.

General procedure for *sym*-(R)-dibenzocrownoxyacetic acids 1-12

NaH (2.10 g, 87.5 mmol) was added to 41 mL of THF under nitrogen. After the mixture was stirred for 30 min, the lariat ether alcohol **46-57** (8.7 mmol) dissolved in 64 mL of THF was added dropwise over a 1-h period. The reaction mixture was stirred for an additional hour and 1.64 g (16.7 mmol) (11.80 mmol of bromoacetic acid was used for synthesis of compounds **10-12**) of the bromoacetic acid (dried with a benzene azotrope.) dissolved in 64 mL of THF was added dropwise over a period of 3-4 h. The reaction mixture was stirred overnight. The reaction was quenched by careful addition of water followed by evaporation of the THF in vacuo. To the residue, 90 mL of water was added and the aqueous mixture was acidified to pH 1 with aqueous 6 N HC1 and then extracted with CH_2C1_2 (2 x 64 mL). The combined organic layers were washed with water, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by column chromatography.

***sym*-(Butyl)dibenzo-14-crown-4-oxyacetic acid (1)** was purified by chromatography on silica gel with MeOH-CH_2Cl_2 (1:50) as eluent to give an oil (58 %). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3373 (OH), 1742 (C=O), 1257 and 1122 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.96 (t, *J*= 7.0 Hz, 3H), 1.34-1.50 (m, 4H), 1.74-1.80 (m, 2H), 2.18-2.26 (m, 1H), 2.42-2.52 (m, 1H), 4.10-4.16 (m, 2H), 4.20 (d, *J*= 10.0 Hz, 2H), 4.21-4.27 (m, 2H), 4.34 (d, *J*= 10.0 Hz, 2H), 4.45 (s, 2H), 6.84-6.98 (m, 8H), 9.90 (brs, 2H). ^{13}C NMR ($CDCl_3$): *δ* 14.0, 23.1, 25.0, 29.1, 32.0, 53.4, 61.8, 68.0, 71.5, 80.0, 113.4, 117.1, 121.1, 123.0, 148.1, 150.0, 171.5. Anal. Calcd for $C_{24}H_{30}O_7$: C, 66.96; H, 7.02. Found: C, 66.95; H, 7.38.

***sym*-(Heptyl)dibenzo-14-crown-4-oxyacetic acid (2)** was purified by chromatography on silica gel with MeOH-CH_2Cl_2 (1:50) as eluent to give an oil (55 %). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3387 (OH), 1744 (C=O), 1252 and 1121 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.90 (t, *J*= 7.0 Hz, 3H), 1.24-1.40 (m, 8H), 1.40-1.49 (m, 2H), 1.73-1.80 (m, 2H), 2.17-2.26 (m, 1H), 2.43-2.54 (m, 1H), 4.10-4.16 (m, 2H), 4.19 (d, *J*= 10.0 Hz, 2H), 4.22-4.28 (m, 2H), 4.34 (d, *J*= 10.5 Hz, 2H), 4.44 (s, 2H), 6.84-6.99 (m, 8H), 9.83 (brs, 1H). ^{13}C NMR ($CDCl_3$): *δ* 14.1, 22.6, 22.8, 29.1, 29.2, 30.0, 31.8, 32.4, 61.9, 68.0, 71.5, 80.0, 113.4, 117.1, 121.1, 123.0, 148.1, 150.0, 171.3. Anal. Calcd for $C_{27}H_{36}O_7$: C, 68.62; H, 7.68. Found: C, 68.70; H, 7.84.

***sym*-(Decyl)dibenzo-14-crown-4-oxyacetic acid (3)[10]** was purified by chromatography on silica gel with MeOH-CH_2Cl_2 (1:50) as eluent to give an oil (50 %). ^{1}H NMR ($CDCl_3$): δ 0.90 (t, *J*= 7.0 Hz, 3H), 1.24-1.41 (m, 14H), 1.40-1.49 (m, 2H), 1.73-1.80 (m, 2H), 2.17-2.26 (m, 1H), 2.43-2.54 (m, 1H), 4.10-4.16 (m, 2H), 4.19 (d, *J*= 10.0 Hz, 2H), 4.22-4.28 (m, 2H), 4.34 (d, *J*= 10.5 Hz, 2H), 4.44 (s, 2H), 6.84-6.99 (m, 8H), 9.85 (brs, 1H).

***sym*-(Butyl)dibenzo-16-crown-5-oxyacetic acid (4)[11]** was recrystallized from hexanes/CH_2Cl_2 to give a white solid (66 %) with mp 148-150 ºC (lit.[11] mp 145-146 ºC). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J*= 7.0 Hz, 3H), 1.20-1.58 (m, 4H), 1.95 (t, *J*= 7.5 Hz, 2H), 3.80-4.24 (m, 10H), 4.59 (d, *J*= 10.0 Hz, 2H), 4.84 (s, 2H), 6.81-7.00 (m, 8H), 9.85 (brs, 1H).

***sym*-(Heptyl)dibenzo-16-crown-5-oxyacetic acid (5)[12]** was recystallized using hexanes/CH_2Cl_2 to give a white solid (72 %) with mp 102-103 ºC (lit.[12] mp 102-103 ºC). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J*= 7.0 Hz, 3H), 1.20-1.59 (m, 10H), 1.96 (t, *J*= 7.5 Hz, 2H), 3.81-4.24 (m, 10H), 4.59 (d, *J*= 10.0 Hz, 2H), 4.84 (s, 2H), 6.81-7.00 (m, 8H), 9.87 (brs, 1H).

***sym*-(Decyl)dibenzo-16-crown-5-oxyacetic acid (6)[8]** was recystallized from hexanes/CH_2Cl_2 to give a white solid (60 %) with mp 105-106 ºC (lit.[8] mp 109-110 ºC). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J*= 7.0 Hz, 3H), 1.20-1.58 (m, 16H), 1.95 (t, *J*= 7.5 Hz, 2H), 3.82-4.22 (m, 10H), 4.59 (d, *J*= 10.0 Hz, 2H), 4.84 (s, 2H), 6.79-7.00 (m, 8H), 9.83 (brs, 1H).

***sym*-(Butyl)dibenzo-19-crown-6-oxyacetic acid (7)** was purified by chromatography on silica gel with MeOH-CH_2Cl_2 (1:50, 1:25, 1:10, and then 1:2) as eluents to give a golden, pasty solid with mp of 69-73 °C in 93% yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3313 (OH), 1736 (C=O), 1256 and 1125 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.95-1.00 (t, J=7.0 Hz, 3H), 1.41-1.46 (m, 4H), 1.90-1.97 (m, 2H), 3.68-4.17 (m, 12H), 4.37-4.40 (d, J=10.0 Hz, 2H), 4.54 (s, 2H), 6.86-6.92 (m, 8H), 9.90 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.0, 23.2,25.4, 29.7, 32.0, 55.9,

62.0, 68.4, 69.7, 70.8, 71.4, 76.7, 77.0, 77.3, 80.2, 96.1, 113.4, 118.3, 120.8, 121.2, 123.3, 148.0, 150.2. 171.4. Anal Calcd.for $C_{27}H_{36}O_9$: C, 64.27; H, 7.19. Found: C, 64.45; H, 7.55.

***sym*-(Heptyl)dibenzo-19-crown-6-oxyacetic acid (8)** was purified by chromatography on silica gel with MeOH-CH_2Cl_2 (1:50, 1:25, 1:10, and then 1:2) as eluents to give a white, sticky solid with mp of 60-67 °C in 100% yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3375 (OH), 1746 (C=O), 1257 and 1122 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.88-0.92 (t, J=7.0 Hz, 3H), 1.31-1.48 (m, 10H), 1.91-1.98 (m, 2H), 3.65-4.20 (m, 14H), 4.37-4.43 (d, J=10.0 Hz, 2H), 4.55 (s, 2H), 6.80-7.00 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 30.9, 62.6, 67.9, 68.5, 69.5, 76.7, 77.0, 77.3, 96.1, 113.1, 114.5, 121.6, 122.5, 147.5, 148.2, 173.4. Anal Calcd. For $C_{30}H_{42}O_9$: C, 65.91; H, 7.74. Found: C, 66.26; H, 7.67.

***sym*-(Decyl)dibenzo-19-crown-6-oxyacetic acid (9)** was purified by chromatography on silica gel with MeOH-CH_2Cl_2 ((1:50, 1:25, 1:10, and then 1:2) as eluents to give white crystals with mp 65-70 °C in 36% yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3367 (OH), 1758 (C=O), 1257 and 1123 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.87-0.90 (t, J = 7.0 Hz, 3H), 1.25-1.46 (m, 16H), 1.92-1.95 (m, 2H), 3.71 (m, 2H), 4.00-4.02 (d, J=10.0 Hz, 2H), 4.08-4.12 (m, 2H), 4.14-4.18 (m, 2H), 4.38-4.41 (d, J=10.0 Hz, 2H), 4.55 (s, 2H), 6.86-6.99 (m, 8H), 9.87 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 29.6, 62.0, 68.4, 69.7, 70.8, 76.8, 77.0, 77.3, 80.3, 113.4, 118.3, 121.2, 123.4, 148.0, 150.3, 171.4. Anal Calcd. for $C_{33}H_{48}O_9$: C, 67.32; H, 8.22. Found: C, 67.35; H, 7.85.

***sym*-(Butyl)dibenzo-22-crown-7-oxyacetic acid** (**10**) was purified by chromatography on silica gel with EtOAc and then MeOH as eluents to give a yellowish oil (89%). IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 3401 (br, O-H), 1750 (C=O), 1256 and 1127 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.92 (m, 3H), 1.20-1.48 (m, 4H), 1.80-1.95 (m, 2H), 3.50-3.90 (m, 12H), 4.12 (t, *J* = 4.3 Hz, 4H), 4.25-4.34 (m, 8H), 4.39 (s, 2H), 6.87-7.01 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 149.7, 148.4, 122.7, 121.4, 117.0, 114.0, 109.9, 96.1, 70.8, 70.6, 70.3, 69.7, 61.3, 53.4, 30.2, 29.7, 25.1, 23.1, 14.0. Anal. Calcd. for $C_{29}H_{40}O_{10}$: C, 63.50; H, 7.30. Found: C, 63.79; H, 7.55.

***sym*-(Heptyl)dibenzo-22-crown-7-oxyacetic acid** (**11**) was purified by chromatography on silica gel with EtOAc and then MeOH as eluents to give a yellowish oil (60%). IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 3340 (br, O-H), 1760 (C=O), 1265 and 1121 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.87 (t, *J* = 7.1 Hz, 3H), 1.20-1.48 (m, 10H), 1.82-1.91 (m, 2H), 3.54-3.65 (m, 8H), 3.80-3.85 (m, 4H), 4.10-4.14 (m, 4H), 4.18-4.27 (m, 4H), 4.39 (s, 2H), 6.82-7.00 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 149.4, 122.7, 121.5, 116.5, 113.8, 96.1, 70.4, 68.3, 31.8, 31.6, 30.0, 29.2, 22.6, 14.1. Anal. Calcd. for $C_{32}H_{46}O_{10}$ •0.1CH_2Cl_2: C, 64.34; H, 7.77. Found: C, 64.04; H, 7.78.

***sym*-(Decyl)dibenzo-22-crown-7-oxyacetic acid** (**12**) was purified by chromatography on silica gel with EtOAc and then MeOH as eluents to give a yellowish oil (91%). IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 3366 (br, O-H), 1754 (C=O), 1249 and 1120 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.20-1.35 (m, 14H), 1.38-1.45 (m, 2H), 1.80-1.90 (m, 2H), 3.55-3.62 (m, 4H), 3.65-3.70 (m, 4H), 4.11 (t, *J* = 4.2 Hz, 4H), 4.20-4.25 (m, 4H), 4.39 (s, 2H), 6.82-6.97 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 171.4, 149.7, 148.5, 122.7, 121.4, 114.0, 70.9,

70.7, 70.2, 69.7, 68.5, 61.2, 31.9, 30.1, 29.6, 29.5, 29.3, 22.7, 14.1. Anal. Calcd. for $C_{35}H_{52}O_{10}$•0.1CH_2Cl_2: C, 66.46; H, 8.23. Found: C, 66.35; H, 8.13.

General procedure for preparation of *N*-(trifluoromethane)sulfonyl *sym*-(R)-dibenzo-crownoxyacetamides 13-24

Oxalyl chloride (1.4 mL, 16.3 mmol) was added to the *sym*-(R)-dibenzocrownoxyacetic acid (**1-12**) (2.6 mmol) in 150 mL of dry benzene under nitrogen. The reaction mixture was stirred at reflux for 6 h. The excess oxalyl chloride and benzene were evaporated in vacuo to give a solid. Under nitrogen, NaH (0.34 g, 14.2 mmol) was added to 15 mL of THF. A solution of trifluoromethanesulfonamide (0.54 g, 3.6 mmol) in 60 mL of THF was added over a 10-min period and the mixture was stirred at room temperature for 1.5 h. A solution of the lariat ether acid chloride in 90 mL of THF was added over a 10-min period and the reaction mixture was stirred overnight at room temperature. The mixture was cooled to 0 ºC and 30 mL of ice water was carefully added to destroy the unreacted NaH. The THF was evaporated in vacuo. The residue was dissolved in 40 mL of water and extracted with CH_2C1_2 (100 mL, 30 mL). The combined extracts were washed with 10 % aq. K_2CO_3 (2 x 45 mL). The combined K_2CO_3 washes were back extracted with CH_2C1_2 (2 x 30 mL). The organic layer was washed with 1 N HCl (30 mL) and water (2 x 50 mL), dried over $MgSO_4$ and evaporated in vacuo.

***N*-(Trifluoromethane)sulfonyl *sym*-(butyl)dibenzo-14-crown-4-oxyacetamide (13)** was obtained as white solid (62 %) with mp 112-115 ºC. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1767 (C=O), 1390 and 1201 (SO_2), 1248 and 1127 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.98 (t, *J*= 7.0 Hz, 3H), 1.36-1.48 (m, 4H), 1.74-1.83 (m, 2H), 2.18-2.26 (m, 1H), 2.43-2.54 (m, 1H), 4.08-4.17 (m, 4H), 4.20-4.28 (m, 2H), 4.50 (d, *J*= 10.5 Hz, 2H), 4.82 (s, 2H), 6.84-7.02 (m, 8H), 9.91 (s, 2H). ^{13}C NMR ($CDCl_3$): *δ* 14.0, 23.2, 25.5, 29.1, 33.3, 53.4, 65.4, 68.3, 72.3, 80.5, 112.8, 118.9, 121.1, 123.7, 147.7, 150.3, 168.8. Anal. Calcd for $C_{25}H_{30}O_8F_3NS$: C, 53.47; H, 5.38; N, 2.49. Found: C, 53.52; H, 5.63; N, 2.38.

***N*-(Trifluoromethane)sulfonyl *sym*-(heptyl)dibenzo-14-crown-4-oxyacetamide (14)** was obtained as a pale yellow solid (72 %) with mp 97-99 ºC. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3285 (NH), 1756 (C=O), 1320 and 1203 (SO_2), 1250 and 1135 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, *J*= 7.0 Hz, 3H), 1.26-1.48 (m, 10H), 1.74-1.81 (m, 2H), 2.16-2.26 (m, 1H), 2.43-2.55 (m, 1H), 4.06-4.17 (m, 4H), 4.20-4.28 (m, 2H), 4.49 (d, *J*= 10.0 Hz, 2H), 4.81 (s, 2H), 6.84-7.02 (m, 8H), 9.89 (s, 2H). ^{13}C NMR ($CDCl_3$): *δ* 14.1, 22.6, 23.4, 25.6, 29.1, 29.1, 30.1, 31.7, 33.7, 53.4, 65.3, 68.4, 72.3, 80.5, 112.8, 118.8, 121.1, 123.7, 147.7, 150.3. Anal. Calcd for $C_{28}H_{36}O_8F_3NS$·0.2C_6H_5: C, 56.63; H, 6.05; N, 2.32. Found: C, 56.63; H, 6.45; N, 2.38.

***N*-(Trifluoromethane)sulfonyl *sym*-(decyl)dibenzo-14-crown-4-oxyacetamide (15)** was obtained as a white solid (80 %) with mp 82-83 ºC. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J*= 7.0 Hz, 3H), 1.26-1.48 (m, 16H), 1.74-1.81 (m, 2H), 2.16-2.26 (m, 1H), 2.43-2.55 (m, 1H), 4.06-4.17 (m, 4H), 4.20-4.28 (m, 2H), 4.49 (d, *J*= 10.0 Hz, 2H), 4.81 (s, 2H), 6.84-7.02 (m, 8H), 9.89 (s, 2H). A portion of the product was dissolved in CH_2Cl_2 and the solution was shaken with 5% Na_2CO_3. The organic layer was dried over Na_2SO_4 and evaporated in vacuo to give a white solid with mp

233-234°C. Anal. Calcd for $C_{31}H_{41}O_8F_3NSNa$: C, 55.26; H, 6.19; N, 2.10. Found: C, 55.58; H, 6.05; N, 2.13.

***N*-(Trifluoromethane)sulfonyl *sym*-(butyl)dibenzo-16-crown-5-oxyacetamide (16)** was obtained as a white solid (79 %), with mp 55-57 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (t, *J*= 7.0 Hz, 3H), 1.20-1.60 (m, 4H), 1.94 (t, *J*= 7.5 Hz, 2H), 3.79-4.18 (m, 10H), 4.63 (d, *J*= 10.0 Hz, 2H), 4.99 (s, 2H), 6.82-7.00 (m, 8H), 10.09 (s, 1H). Anal. Calcd for $C_{26}H_{32}O_9F_3NS$: C, 52.79; H, 5.45; N, 2.37. Found: C, 52.69; H, 5.37; N, 2.26.

***N*-(Trifluoromethane)sulfonyl *sym*-(heptyl)dibenzo-16-crown-5-oxyacetamide (17)** was obtained as a white solid (47 %) with mp 51-52 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 (t, *J*= 7.0 Hz, 3H), 1.20-1.60 (m, 10H), 1.95 (t, *J*= 7.5 Hz, 2H), 3.79-4.18 (m, 10H), 4.63 (d, *J*= 10.0 Hz, 2H), 4.99 (s, 2H), 6.82-7.00 (m, 8H), 10.09 (s, 1H). Anal. Calcd for $C_{29}H_{38}O_9F_3NS$: C, 54.97; H, 6.04; N, 2.21. Found: C, 55.09; H, 6.21; N, 2.08.

***N*-(Trifluoromethyl)sulfonyl *sym*-(decyl)dibenzo-16-crown-5-oxyacetamide (18)[13]** was obtained as a solid (67 %), with mp 90-91 °C (lit.[13] mp 100 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, *J*= 7.0 Hz, 3H), 1.20-1.60 (m, 16H), 1.95 (t, *J*= 7.5 Hz, 2H), 3.79-4.18 (m, 10H), 4.63 (d, *J*= 10.0 Hz, 2H), 4.99 (s, 2H), 6.82-7.00 (m, 8H), 10.09 (s, 1H).

***N*-(Trifluoromethyl)sulfonyl *sym*-(butyl)dibenzo-19-crown-6-oxyacetamide (19)** was obtained as a white solid with mp of 88-90 °C in 80 % yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1763 (C=O), 1380 and 1126 (SO_2), 1256 and 1126 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.98-1.01 (t, J=7.0 Hz, 3H), 1.43-1.49 (m, 4H), 1.98-2.02 (m, 2H), 3.72-3.96 (m, 10H), 4.05-4.20 (m, 4H). 4.43-4.45 (d, J=10.0 Hz, 2H), 4.82 (s, 2H), 6.86-7.02 (m, 8H), 10.28 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.1, 23.3, 26.0, 30.9, 33.5, 64.8, 67.6, 69.9, 70.5, 71.5, 76.7, 77.0, 77.3, 79.9, 113.0, 118.6, 121.4, 123.7, 147.7, 150.2, 169.0. Anal. Calcd. for $C_{28}H_{36}O_{10}NSF_3$: C, 52.91; H, 5.71; N, 2.20. Found: C, 52.82; H, 5.80; N, 1.98.

***N*-(Trifluoromethyl)sulfonyl *sym*-(heptyl)dibenzo-19-crown-6-oxyacetamide (20)** was obtained as a colorless, sticky substance in 82 % yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1760 (C=O), 1368 and 1126 (SO_2), 1257 and 1124 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.89-0.92 (t, J=7.0 Hz, 3H), 1.26-1.51 (m, 10H), 1.97-2.01 (m, 2H), 3.71-3.96 (m, 10H), 4.08-4.20 (m, 4H), 4.43-4.45 (d, J=10.0 Hz, 2H), 4.81 (s, 2H), 6.86-7.01 (m, 8H), 10.46 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 23.8, 29.2, 30.1, 31.8, 33.6, 53.4, 64,8, 67.6, 69.9. 70.5. 71.5, 76.8, 77.0, 77.3, 79.3, 79.9, 113.0, 118.5. 121.3. 123.6, 147.7, 150.2, 169.0. Anal Calcd. for $C_{31}H_{42}O_{10}NSF_3$: C. 55.56; H, 6.41 Found: C, 55.50; H, 6.27.

***N*-(Trifluoromethyl)sulfonyl *sym*-(decyl)dibenzo-19-crown-6-oxyacetamide (21)** was obtained as a yellow oil in 79 % yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1764 (C=O), 1367 and 1126 (SO_2), 1256 and 1126 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.88-0.90 (t, J=7.0 Hz, 3H), 1.26-1.50 (m, 16H), 1.98-2.01 (m, 2H), 3.73-3.94 (m, 10H), 4.10-4.18 (m, 4H), 4.43-4.45 (d, J=10.0 Hz, 2H), 4.81 (s, 2H), 6.86-7.02 (m, 8H), 10.28 (s, H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.7, 23.8, 29.3, 29.5. 29.6. 31.9, 33.8, 64.8, 67.6, 69.9, 70.5, 71.4, 76.7, 77.0, 77.3, 79.9, 113.1, 117.8, 118.7, 120.4, 121.4, 123.7, 147.7, 150.2, 169.0. Anal Calcd. for $C_{34}H_{48}O_{10}NSF_3$: C, 56.73; H, 6.72; N, 1.95. Found: C. 56.57; H, 6.82; N, 1.93.

***N*-Trifluoromethanesulfonyl *sym*-(butyl)dibenzo-22-crown-7-oxyacetamide** (**22**) was purified by chromatography on silica gel with EtOAc as eluent to provide a yellowish solid in 64% yield with mp 45-47 °C. IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 3340 (N-H), 1777 (C=O), 1257 and 1061 (SO_2), 1210 and 1120 (C-O). ^1H NMR ($CDCl_3$): δ 0.94 (t, *J* = 7.1 Hz, 3H), 1.30-1.50 (m, 4H), 1.85-1.90 (m, 2H), 3.48-3.60 (m, 6H), 3.62-3.70 (m, 2H), 3.80-3.84 (m, 4H), 4.09-4.30 (m, 8H), 4.64 (s, 2H), 6.84-6.97 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 169.2, 149.5, 148.5, 122.6, 121.5, 116.6, 114.1, 96.1, 80.1, 70.5, 70.5, 70.3, 70.0, 69.2, 67.8, 64.0, 53.4, 31.9, 25.3, 23.2, 14.0. Anal. Calcd. for $C_{30}H_{40}O_{11}SNF_3$: C, 53.02; H, 5.89; N, 2.06. Found: C, 53.23; H, 5.95; N, 1.99.

***N*-Trifluoromethanesulfonyl *sym*-(heptyl)dibenzo-22-crown-7-oxyacetamide** (**23**) was purified by chromatography on silica gel with EtOAc as eluent to provide a yellowish oil in 70 % yield. IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 1774 (C=O), 1259 and 1060 (SO_2), 1220 and 1121 (C-O). ^1H NMR ($CDCl_3$): δ 0.87-0.91 (m, 3H), 1.20-1.50 (m, 10H), 1.83-1.87 (m, 2H), 3.48-3.67 (m, 8H), 3.80-3.84 (m, 4H), 4.09-4.30 (m, 8H), 4.64 (s, 2H), 6.84-6.97 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 169.2, 149.5, 148.5, 122.6, 121.5, 116.6, 114.1, 80.1, 70.5, 70.4, 70.3, 69.9, 67.8, 64.0, 53.4, 32.2, 31.8, 31.6, 30.1, 29.2, 23.1, 22.6, 14.1, 14.1. Anal. Calcd. for $C_{33}H_{46}O_{11}SNF_3$: C, 54.92; H, 6.38; N, 1.94. Found: C, 55.04; H, 6.64; N, 1.93.

***N*-Trifluoromethanesulfonyl *sym*-(decyl)dibenzo-22-crown-7-oxyacetamide** (**24**) was purified by chromatography on silica gel with EtOAc as eluent to provide a yellowish oil in 71% yield. IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 3450 (N-H), 1773 (C=O), 1264 and 1060 (SO_2), 1220 and 1127 (C-O). ^1H NMR ($CDCl_3$): δ 0.88 (t, *J* = 7.1 Hz, 3H), 1.20-1.33 (m, 14H), 1.45-1.47 (m, 2H), 1.84-1.86 (m, 2H), 3.48-3.67 (m, 8H), 3.70-3.84 (m, 4H), 4.08-4.30 (m, 8H), 4.63 (s, 2H), 6.82-6.97 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 169.2, 149.5, 148.5, 122.6, 121.5, 116.6, 114.1, 80.1, 70.5, 70.5, 70.3, 69.9, 67.8, 64.0, 53.4, 32.2, 31.9, 30.1, 29.6, 29.6, 29.5, 29.3, 23.1, 22.7, 14.1. Anal. Calcd. for $C_{36}H_{52}O_{11}SNF_3$: C, 56.62; H, 6.82; N, 1.83. Found: C, 56.77; H, 6.87; N, 1.73.

General procedure for preparation of sodium [*sym*-(R)-dibenzocrownoxy]-3-propanesulfonates 25-36

The lariat ether alcohol (**46**-**57**) (2.88 mmol) in 50 mL of THF was dropped into a mixture of 0.35g (14.38 mmol) of NaH in 10 mL of THF under nitrogen. The mixture was stirred for 2 h at room temperature and 0.43 g (3.48 mmol) of 1,3-propanesultone in 5 mL of dry THF was added over 30 min with a syringe pump. The mixture was stirred for 6 h (12h for **34**-**36**) at room temperature. After cooling to 0 °C, ice water was carefully added to destroy the unreacted NaH and the THF was evaporated in vacuo. Then 50 mL of CH_2C1_2 was added and the mixture was filtered. The filtrate was evaporated in vacuo. The residue was purified by recrystallization or column chromatography.

Sodium [*sym*-(butyl)dibenzo-14-crown-4-oxy]-3-propanesulfonate (25) was purified by chromatography on silica gel using CH_2C1_2-MeOH (40:1) as eluent to give a white solid (71 %) with mp 236-238 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1217 and 1080 (SO_2), 1251 and 1124 (C-O). ^1H NMR ($CDCl_3$): δ 0.98 (t, *J*= 7.0 Hz, 3H), 1.36-1.48 (m,

4H), 1.62-1.71 (m, 2H), 2.08-2.18 (m, 3H), 3.00-3.15 (m, 3H), 3.83-3.98 (m, 6H), 4.20-4.28 (m, 2H), 4.37 (d, *J*= 9.5 Hz, 2H), 4.54-4.62 (m, 2H), 6.78-6.83 (m, 2H), 6.85-6.97 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 13.9, 23.3, 24.9, 26.1, 28.0, 30.9, 46.4, 53.4, 59.3, 68.9, 71.9, 110.3, 111.2, 121.1, 121.7, 146.3, 147.1. Anal. Calcd for $C_{25}H_{33}O_8SNa \bullet 0.2H_2O$: C, 57.72; H, 6.47. Found: C, 57.76; H, 6.69.

Sodium [*sym*-(heptyl)dibenzo-14-crown-4-oxy]-3-propanesulfonate (26) was purified by chromatography on silica gel using CH_2C1_2-MeOH (40:1) as eluent to give a white solid (70 %) with mp 114-118 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1224 and 1042 (SO_2), 1252 and 1130 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, *J*= 7.0 Hz, 3H), 1.26-1.49 (m, 10H), 1.63-1.71 (m, 2H), 2.11-2.20 (m, 3H), 2.92-3.05 (m, 1H), 3.10 (t, *J*= 6.5 Hz, 2H), 3.83-3.98 (m, 6H), 4.35 (d, *J*= 9.5 Hz, 2H), 4.53-4.62 (m, 2H), 6.78-6.83 (m, 2H), 6.85-6.97 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 22.8, 28.1, 29.1, 30.1, 31.2, 31.7, 46.6, 68.9, 71.8, 76.6, 110.3, 111.2, 121.1, 121.8, 146.2, 147.0. Anal. Calcd for $C_{28}H_{39}O_8SNa$: C, 60.20; H, 7.04. Found: C, 59.82; H, 6.94.

Sodium [*sym*-(decyl)dibenzo-14-crown-4-oxy]-3-propanesulfonate (27) was purified by chromatography on silica gel using CH_2C1_2-MeOH (40:1) as eluent to give a white solid (68 %) with mp 88-90 °C. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J*= 7.0 Hz, 3H), 1.22-1.49 (m, 16H), 1.63-1.71 (m, 2H), 2.10-2.20 (m, 3H), 2.92-3.07 (m, 1H), 3.10 (t, *J*= 6.5 Hz, 2H), 3.84-3.98 (m, 6H), 4.36 (d, *J*= 9.5 Hz, 2H), 4.53-4.62 (m, 2H), 6.78-6.83 (m, 2H), 6.85-6.97 (m, 6H). Anal. Calcd for $C_{31}H_{45}O_8SNa$: C, 61.98; H, 7.55. Found: C, 61.90; H, 7.45.

Sodium [*sym*-(butyl)dibenzo-16-crown-5-oxy]-3-propanesulfonate (28) was recrystallized from CH_2C1_2-Et_2O to give a white solid (72 %) with mp 222-223 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1253 and 1128 (C-O) , 1041 and 1213 (SO_2). ^{1}H NMR ($CDCl_3$): δ 0.97 (t, *J*= 7.0 Hz, 3H), 1.36-1.45 (m, 4H), 1.65 (t, *J*= 8.0 Hz, 2H), 2.06-2.12 (m, 2H), 3.06-3.11 (m, 2H), 3.75-3.81 (m, 2H), 3.89 (t, *J*= 6.0 Hz, 2H), 4.04-4.13 (m, 4H), 4.23 (d, *J*= 9.5 Hz, 2H), 4.28-4.34 (m, 2H), 4.74-4.81 (m, 2H), 6.86-6.92 (m, 4H), 6.93-7.02 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 13.9, 21.2, 23.3, 24.9, 27.6, 32.4, 49.7, 61.5, 66.6, 67.0, 73.2, 75.9, 109.9, 111.7, 112.0, 121.2, 122.2, 146.8, 147.1. Anal. Calcd for $C_{26}H_{35}O_9SNa$: C, 57.13; H, 6.45. Found: C, 57.08; H, 6.62.

Sodium [*sym*-(heptyl)dibenzo-16-crown-5-oxy]-3-propanesulfonate (29) was recrystallized from CH_2C1_2-Et_2O to give a white solid (60 %) with mp 188-191 °C. ^{1}H NMR ($CDCl_3$): δ 0.90 (t, *J*= 7.0 Hz, 3H), 1.19-1.81 (m, 12H), 2.06-2.18 (m, 2H), 3.08 (t, *J*= 6.0 Hz, 2H), 3.75-3.81 (m, 2H), 3.88 (t, *J*= 6.0 Hz, 2H), 4.04-4.13 (m, 4H), 4.23 (d, *J*= 9.5 Hz, 2H), 4.28-4.35 (m, 2H), 4.74-4.81 (m, 2H), 6.86-7.02 (m, 8H). Anal. Calcd for $C_{29}H_{41}O_9SNa$: C, 59.17; H, 7.02. Found: C, 59.02; H, 6.90.

Sodium [*sym*-(decyl)dibenzo-16-crown-5-oxy]-3-propanesulfonate (30)[6] was recrystallized from CH_2C1_2-Et_2O to give a white solid (67 %) with mp 155-156 °C (lit.[6] mp 157-159 °C). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, *J*= 7.0 Hz, 3H), 1.19-1.51 (m, 16H), 1.51-1.76 (m, 2H), 2.06-2.18 (m, 2H), 3.08 (t, *J*= 6.0 Hz, 2H), 3.75-3.81 (m, 2H), 3.88 (t, *J*= 6.0 Hz, 2H), 4.04-4.13 (m, 4H), 4.23 (d, *J*= 9.5 Hz, 2H), 4.28-4.35 (m, 2H), 4.74-4.81 (m, 2H), 6.86-7.02 (m, 8H).

Sodium 3-[*sym*-(butyl)dibenzo-19-crown-6-oxy]propanesulfonate (**31**) was purified by chromatography on silica gel using CH_2C1_2-MeOH (4:1) as eluent to give a white solid with mp of 75-78 °C in 77 % yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1256 and 1216 (C-O), 1046 (SO_2). ^{1}H NMR ($CDCl_3$): δ 0.92-0.95 (t, J=7.0 Hz, 3H), 1.34-1.36 (m, 4H). 1.56-1.59 (m, 2H), 2.13-2.17 (m, 2H) 3.07-3.09 (t, J=6.0 Hz, 2H), 3.34-3.39 (m, 2H), 3.60-3.63 (m, 2H), 3.95-3.99 (m, 6H) 4.17-4.40 (m, 8H), 6.81-7.02 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 13.9, 23.2, 24.8, 26.3, 30.9, 46.2, 59.3, 68.0, 69.3, 69.4, 75.2, 114.5, 116.0, 122.0, 123.3, 147.6, 149.1. Anal Calcd. for $C_{28}H_{39}O_{10}SNa$:C, 56.25; H, 6.71. Found: C, 56.19; H, 6.83.

Sodium 3-[*sym*-(heptyl)dibenzo-19-crown-6-oxy]propanesulfonate (**32**) was purified by chromatography on silica gel using CH_2C1_2-MeOH (4:1) as eluent to give a white solid with mp of 66-70 °C in 82 % yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1256 and 1212 (C-O), 1044 (SO_2). ^{1}H NMR ($CDCl_3$): δ 0.88-0.91 (t, J=7.0 Hz, 3H), 1.26-1.37 (m, 10H), 1.55-1.59 (m, 2H), 2.14-2.21 (m, 2H), 3.08-3.10 (t, J=6.0 Hz, 2H), 3.36-3.39 (m, 2H), 3.61-3.64 (m, 2H), 3.96-4.01 (m, 6H), 4.19-4.40 (m, 8H), 6.82-7.03 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 26.3, 30.9, 46.2, 53.4, 59.3, 68.0, 69.5, 76.7, 77.0, 77.3, 96.1, 114.5, 116.0, 122.0, 123.3, 147.5, 149.0. Anal Calcd. for $C_{31}H_{45}O_{10}NaS$: C, 58.18; H, 7.21. Found: C, 58.11; H, 7.16.

Sodium 3-[*sym*-(decyl)dibenzo-19-crown-6-oxy]propanesulfonate (**33**) was purified by chromatography on silica gel using CH_2C1_2-MeOH (4:1) as eluent to give a white sticky substance in 93 % yield. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1256 and 1217 (C-O), 1043 (SO_2). ^{1}H NMR ($CDCl_3$): δ 0.86-0.89 (t, J=7.0 Hz, 3H), 1.21-1.35 (m, 16H), 1.57-1.62 (m, 2H), 2.09-2.15 (m, 2H) 3.03-3.16 (t, J=6.0 Hz, 2H), 3.42-3.68 (m, 2H), 3.64-3.67 (m, 2H), 3.87-4.00 (m, 6H) 4.10-4.34 (m, 8H) 6.83-7.00 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 26.1, 29.4, 46.7, 53.4, 59.7, 68.0, 69.3, 76.8, 77.0, 77.3, 114.3, 116.2, 121.8, 123.1, 147.8. 149.1. Anal Calcd. for $C_{34}H_{51}O_{10}NaS$: C, 56.76; H, 7.19. Found: C, 56.59; H. 7.25.

Sodium 3-[*sym*-(butyl)dibenzo-22-crown-7-oxy]propanesulfonate (**34)** was purified by chromatography on silica gel with CH_2Cl_2-MeOH (10:1) as eluent to give a yellowish solid in 72 % yield with mp 44-46 °C. IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 1210 and 1039 (SO_2), 1253 and 1120 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.94 (t, *J* = 6.9 Hz, 3H), 1.30-1.41 (m, 4H), 1.60-1.72 (m, 10H), 2.08-2.14 (m, 2H), 3.02 (t, *J* = 6.2 Hz, 2H), 3.50-3.62 (m, 4H), 3.80-3.90 (m, 6H), 3.94-4.00 (m, 2H), 4.01-4.13 (m, 6H), 4.19-4.22 (m, 2H), 4.38 (d, *J* = 10.0 Hz, 2H), 6.89-6.99 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 148.6, 147.4, 128.3, 122.9, 121.7, 115.4, 113.5, 96.1, 77.7, 72.3, 69.7, 69.5, 68.5, 68.4, 53.4, 46.6, 26.0, 24.7, 23.2, 13.9. Anal. Calcd. for $C_{30}H_{43}O_{11}SNa \bullet 0.5H_2O$: C, 55.89; H, 6.88. Found: C, 55.59; H, 6.86.

Sodium 3-[*sym*-(heptyl)dibenzo-22-crown-7-oxy]propanesulfonate (**35**) was purified by chromatography on silica gel with CH_2Cl_2-MeOH (10:1) as eluent to give a yellowish solid in 61% yield with mp 50-52 °C. IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 1217 and 1052 (SO_2), 1263 and 1132 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.20-1.41 (m, 10H), 1.62-1.69 (m, 2H), 2.08-2.13 (m, 2H), 3.01 (t, *J* = 6.2 Hz, 2H), 3.55-3.62 (m, 4H), 3.80-3.90 (m, 6H), 3.95-4.00 (m, 2H), 4.01-4.13 (m, 6H), 4.19-4.23 (m, 2H), 4.38 (d, *J* = 10.1 Hz, 2H), 6.88-6.99 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 148.6, 147.5, 122.9, 121.7, 115.5, 113.6,

96.1, 77.7, 72.2, 69.7, 69.5, 68.5, 68.4, 59.8, 46.7, 31.7, 30.6, 30.1, 29.1, 26.0, 22.6, 14.1. Anal. Calcd. for $C_{33}H_{49}O_{11}SNa$: C, 58.58; H, 7.25. Found: C, 58.14; H, 7.45.

Sodium 3-[*sym*-(decyl)dibenzo-22-crown-7-oxy]propanesulfonate (**36**) was purified by chromatography on silica gel with CH_2Cl_2-MeOH (10:1) as eluent to give in 74% yield a yellowish solid with mp 65-67 °C. IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 1214 and 1044 (SO_2), 1255 and 1120 (C-O). ^1H NMR ($CDCl_3$): δ 0.89 (t, *J* = 7.1 Hz, 3H), 1.20-1.41 (m, 16H), 1.63-1.69 (m, 2H), 2.08-2.11 (m, 2H), 3.01 (t, *J* = 6.1 Hz, 2H), 3.55-3.62 (m, 4H), 3.80-3.90 (m, 6H), 3.96-4.01 (m, 2H), 4.01-4.13 (m, 6H), 4.20 (m, 2H), 4.38 (d, *J* = 10.0 Hz, 2H), 6.88-6.99 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 148.6, 147.4, 122.9, 121.7, 115.4, 113.5, 96.1, 77.7, 72.3, 69.7, 69.5, 68.5, 68.4, 46.6, 31.9, 29.5, 29.4, 29.3, 22.7, 14.1. Anal. Calcd. for $C_{36}H_{55}O_{11}SNa\bullet 0.1H_2O$: C, 58.68; H, 7.80. Found: C, 58.26; H, 7.44.

General procedure for preparation of monoethyl lariat ether oxymethylphosphonates 37-41

A solution of *sym*-(R)-(hydroxy)dibenzocrown ether (**49-51**, **54** and **57**) (1.75 mmol) in 100 mL of THF was added to 0.21 g (8.75 mmol) of NaH. (After removal of the protecting mineral oil by washing with hexanes under nitrogen, KH (8.75 mmol) was added instead of NaH for compound **41**). The mixture was stirred for 2 h at room temperature. Monoethyl iodomethylphosphonate (0.66 g, 2.64 mmol) in 10 mL of dry THF was added dropwise during a period of 1 h. The reaction mixture was stirred for 10 h at room temperature. The reaction was quenched by careful addition of water and the solvent was evaporated in vacuo. For compounds **37-39**, the residue was dissolved in CH_2Cl_2 (200 mL), washed with 6 N HCl, dried over $MgSO_4$ and evaporated *in vacuo*. For compounds **40** and **41**, ethyl acetate (100 ml) and water (100 ml) were added and the aqueous layer was separated. The aqueous layer was washed with ethyl acetate (3 × 100 ml) to remove the unreacted lariat ether alcohol and organic impurities. The aqueous layer was acidified to pH = 1 with 6 N HCl and 100 ml of CH_2Cl_2 was added. The organic layer was separated, washed with 5 % HCl (3 × 50 ml) and brine (2 × 50 ml). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography.

Monoethyl *sym*-(butyl)dibenzo-16-crown-5-oxymethylphosphonate (37) was purified by chromatography on silica gel with MeOH/CH_2Cl_2 (50:1) as eluent to give a white solid (49 %) with mp 132-134 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1251 (P=O), 1217 and 1128 (C-O). ^1H NMR ($CDCl_3$): *δ* 0.96 (t, *J*= 7.0 Hz, 3H), 1.26 (t, *J*= 7.0 Hz, 3H), 1.36-1.48 (m, 4H), 1.94 (t, *J*= 7.5 Hz, 2H), 3.85-3.89 (m, 2H), 3.98-4.04 (m, 4H), 4.11-4.18 (m, 6H), 4.45-4.52 (m, 4H), 6.79-6.87 (m, 4H), 6.88-6.95 (m, 4H). ^{13}C NMR ($CDCl_3$): *δ* 14.1, 16.4, 16.4, 23.3, 25.6, 32.4, 62.5, 62.5, 67.4, 69.6, 72.2, 112.7, 117.5, 121.0, 122.8, 128.3, 148.0, 150.3. Anal. Calcd for $C_{26}H_{37}O_9P$: C, 59.53; H, 7.11. Found: C, 59.60; H, 7.04.

Monoethyl *sym*-(heptyl)dibenzo-16-crown-5-oxymethylphosphonate (38) was purified by chromatography on silica gel with MeOH/CH_2Cl_2 (50:1) as eluent to give a white solid (49 %) with mp 113-115 °C. IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1252 (P=O), 1218 and 1121 (C-O). ^1H NMR ($CDCl_3$): *δ* 0.89 (t, *J*= 7.0 Hz, 3H), 1.24 (t, *J*= 7.0 Hz, 3H), 1.25-

1.48 (m, 10H), 1.92 (t, *J*= 8.5 Hz, 2H), 3.84-3.89 (m, 2H), 3.97-4.04 (m, 4H), 4.10-4.18 (m, 6H), 4.42-4.52 (m, 4H), 6.80-6.87 (m, 4H), 6.88-6.95 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 14.1, 16.4, 16.4, 22.7, 23.4, 29.3, 30.2, 31.9, 32.6, 67.4, 69.6, 72.2, 112.7, 117.5, 121.0, 122.7, 128.3, 148.1, 150.4. Anal. Calcd for $C_{29}H_{43}O_9P$: C, 61.47; H, 7.65. Found: C, 61.75; H, 7.41.

Monoethyl *sym*-(decyl)dibenzo-16-crown-5-oxymethylphosphonate (39) was purified by chromatography on silica gel with MeOH/CH_2Cl_2 (50:1) as eluent to give a yellow oil (43 %). IR (deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 1255 (P=O), 1215 and 1126 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.88 (t, *J*= 7.0 Hz, 3H), 1.25 (t, *J*= 7.5 Hz, 3H), 1.22-1.48 (m, 16H), 1.92 (t, *J*= 8.0 Hz, 2H), 3.84-3.89 (m, 2H), 3.96-4.05 (m, 4H), 4.10-4.18 (m, 6H), 4.42-4.52 (m, 4H), 6.79-6.87 (m, 4H), 6.88-6.95 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 14.1, 16.4, 16.4, 22.7, 23.4, 29.4, 29.6, 29.6 29.7, 30.3, 31.9, 32.7, 62.5, 67.3, 69.9, 72.2, 96.1, 112.7, 117.5, 121.0, 122.8, 128.3, 148.0, 150.3. Anal. Calcd for $C_{32}H_{49}O_9P$: C, 63.14; H, 8.11. Found: C, 62.95; H, 8.05.

Monoethyl *sym*-(decyl)dibenzo-19-crown-6-oxymethylphosphonic Acid (40) was obtained as a yellow oil (36% yield: 44% of starting material was recovered by column chromatography): IR(deposit from CH_2Cl_2 solution on a NaCl plate) ν_{max}/cm^{-1}: 3600-1600 (P-OH, with broad maxima at 3450, 2200, 1654); 1257 (P=O); 1125 (C-O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.88 (t, *J*=6.7 Hz, 3H), 1.20-1.50 (m, 19H), 1.81-1.93 (m, 2H), 3.79-3.93 (m, 8H), 4.09-4.19 (m, 10H), 4.27 (d, *J*=10.3 Hz, 2H), 6.82-6.95 (m, 8H), 8.87 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 14.1, 16.4 (d, $J_{C\text{-}P}$=6.1 Hz), 22.4, 22.6, 29.3, 29.5, 29.6, 29.6, 30.2, 30.4, 31.9, 58.1 (d, $J_{C\text{-}P}$=170.5 Hz), 62.4 (d, $J_{C\text{-}P}$=6.5 Hz), 68.7, 69.8, 70.9, 71.7, 79.8 (d, $J_{C\text{-}P}$=13.5 Hz), 113.5, 117.5, 121.2, 122.5, 148.6, 149.9; Anal. Calcd. for $C_{34}H_{53}O_{10}P\bullet 0.6H_2O$: C, 61.54; H, 8.23. Found: C, 61.50; H, 8.27.

Monoethyl *sym*-(decyl)dibenzo-22-crown-7-oxymethylphosphonic acid (**41**) was purified by chromatography on silica gel with CH_2Cl_2-MeOH (10:1) as eluent to give a yellowish oil in 14% yield. IR (deposit from $CDCl_3$ solution onto a NaCl plate) ν_{max}/cm^{-1}: 3395 (O-H), 1259 (P=O), 1220, 1128 (C-O). ^{1}H NMR ($CDCl_3$): δ 0.89 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.25-1.36 (m, 14H), 1.36-1.43 (m, 2H), 1.62-1.64 (m, 2H), 3.46-3.52 (m, 2H), 3.54-3.59 (m, 4H), 3.75-3.81 (m, 2H), 3.87-4.00 (m, 8H), 4.02-4.07 (m, 2H), 4.10-4.15 (m, 2H), 4.18-4.23 (m, 2H), 4.46 (d, *J* = 9.5 Hz, 2H), 6.86-7.00 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 149.1, 147.3, 122.9, 121.5, 115.9, 113.1, 77.6, 77.5, 71.8, 70.4, 69.9, 68.4, 68.3, 59.9, 59.8, 58.2, 57.0, 53.4, 31.8, 30.4, 30.0, 29.5, 29.5, 29.4, 29.2, 22.6, 22.3, 17.1, 17.0, 14.0. Anal. Calcd. for $C_{36}H_{57}O_{11}P\bullet 0.5CH_2Cl_2$: C, 59.30; H, 7.91; Found: C, 59.22; H, 8.14.

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