Synthesis of Lipophilic Lariat Ethers with Pendant *N*-(X)sulfonyl Carboxamide Groups

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Synthetic routes to sixteen lipophilic lariat ether *N*-(X)sulfonyl carboxamides with X = trifluoromethyl, methyl, phenyl, and *p*-nitrophenyl are described. For this new family of proton-ionizable lariat ethers in which the acidity can be 'tuned' by X group variation, the ring size is systematically varied from 12-crown-4 to 14-crown-4 to 15-crown-5 to 18-crown-6.

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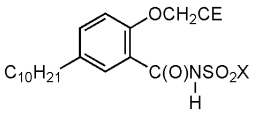
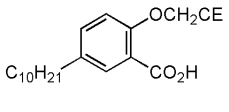
Crown ethers with a pendant proton-ionizable group are efficient reagents for the solvent extraction of alkali metal cations and their transport across bulk liquid, liquid surfactant (emulsion), polymer-supported, and polymer inclusion membranes [1-4]. Compared with crown ether ligands that do not possess acidic functions, such proton-ionizable lariat [5] ethers have the distinct advantage that transfer of the metal cation from the aqueous phase into the organic medium does not require concomitant transport of an aqueous phase anion [6]. This factor is of immense importance for potential practical separation processes in which hard, hydrophilic, aqueous-phase anions, such as chloride, nitrate and sulfate, would be involved.

Previously we have reported the synthesis of lipophilic crown ethers with a pendant carboxylic acid group or phosphonic acid monoethyl ester group, **1** and **2**, respectively [7,8]. The selectivity in competitive alkali metal cation extractions by these ligands was found to be influenced both by the size of the crown ether ring (CE) and the identity of the acidic group [9,10]. To better assess the affect of varying the acidic function, a closely related series of lariat ether *N*-(X)sulfonyl carboxamides **3** has now been prepared. By variation of the electronic properties of X, the acidity of the proton-ionizable group can be altered [11,12].

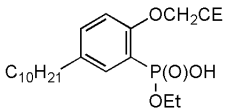


Crown Ether Ring Size	Compound with X = CF_3	CH_3	C_6H_5	*p*-$NO_2C_6H_4$
12-crown-4	**4**	**5**	**6**	**7**
14-crown-4	**8**	**9**	**10**	**11**
15-crown-5	**12**	**13**	**14**	**15**
18-crown-6	**16**	**17**	**18**	**19**

With a few exceptions, the precursor lipophilic lariat ether carboxylic acids **1** with CE = 12-crown-4, 14-crown-4, 15-crown-5, and 18-crown-6 were prepared by published methods [6]. This general route (Scheme 1) involves formation of the crown ether portion by a ring-closure reaction to provide the (benzyloxymethyl)crown ether **20**, followed by hydrogenolysis to produce the (hydroxymethyl)crown ether **21**, and preparation of the (tosyloxymethyl)crown ether **22**. Reaction of methyl 5-decylsalicylate with sodium or potassium hydride and



1



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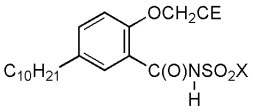


3

(CE = Crown Ether)

Results and Discussion.

For the new family of lipophilic, proton-ionizable lariat ethers **3**, the crown ether ring size is varied from 12-crown-4 (12C4) to 14-crown-4 (14C4) to 15-crown-5 (15C5) to 18-crown-6 (18C6) and the X group is changed from trifluoromethyl to methyl to phenyl to *p*-nitrophenyl in compounds **4**-**19**. (For the 14-crown-4 rings with alternating three-carbon and two-carbon bridges connecting the four oxygen atoms, attachment to the lipophilic, proton-ionizable moiety is *via* a carbon atom in a shorter bridge.)

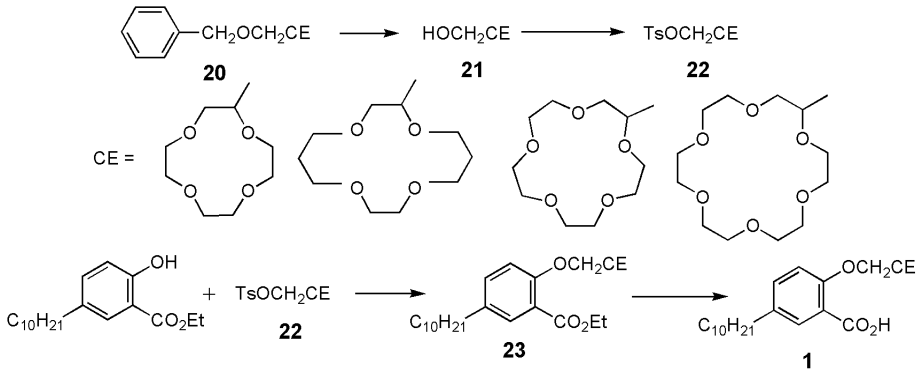
the (tosyloxymethyl)crown ether **22** gave the corresponding lariat ether ester **23** that was hydrolyzed to form the lariat ether carboxylic acid **1**. Although the use of sodium hydride provided 58-72% yields of the coupling product when the crown ether ring in **22** was 12-crown-4, 14-crown-4, and 18-crown-6, the yield for a 15-crown-5 ring size was only 35%. Changing to potassium hydride provided a markedly increased 63% yield of **23** with CE = 15-

crown-5. The lower yield of this coupling product obtained with sodium hydride as the base is attributed to strong interaction of the metal cation within the cavity of the crown ether of the lariat ether alkoxide. Ion pairing of the cavity-complexed metal ion with the alkoxide center deactivates the nucleophile, leading to diminished yield. With potassium hydride as the base, there a mismatch in the sizes of the potassium cation and the 15-crown-5 cavity, so strong ion pairing does not take place. To test this supposition, the reaction of methyl 5-decylsalicylate and hydroxymethyl-18-crown-6 was performed with potassium hydride as the base. In this case, there is a match between the crown ether cavity and the yield of coupling product should decrease compared to an analogous reaction with sodium hydride as the base. In agreement, the yield of **23** with CE = 18-crown-6 dropped to 22% with potassium hydride as the base, compared with 72% when sodium hydride was employed.

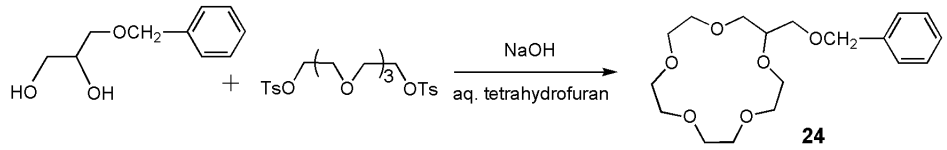
In the current research, it was found that the yield of (benzyloxymethyl)-15-crown-5 (**24**) from cyclization of 3-(benzyloxy)propane-1,2-diol [13,14] and tetraethylene glycol ditosylate was improved from 39% with sodium hydride in dimethylformamide-tetrahydrofuran [15] or 23% with potassium *tert*-butoxide in tetrahydrofuran [16] to 67% when sodium hydroxide in aqueous tetrahydrofuran was utilized (Scheme 2).

For the synthesis of (benzyloxymethyl)-18-crown-6 (**27**) (Scheme 3), the precursor diol 4-benzyloxymethyl-3,6-dioxa-1,8-octanediol (**26**) was prepared in 85% yield by direct reduction of dicarboxylic acid **25** with lithium

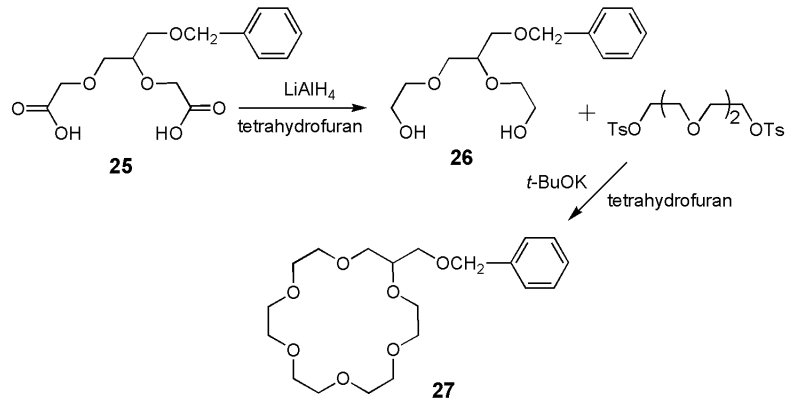
Scheme 1



Scheme 2



Scheme 3



aluminum hydride in tetrahydrofuran rather than the reported esterification of **25** followed by reduction with lithium aluminum hydride [17]. Reaction of diol **26**, the ditosylate of triethylene glycol, and potassium *tert*-butoxide in tetrahydrofuran gave a 73% yield of **27**, which is a considerable improvement over the 54% yield when the cyclization was promoted by potassium hydride in tetrahydrofuran [18].

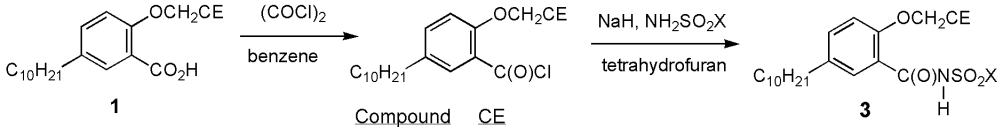
The lipophilic lariat ether carboxylic acids **1** were converted into the corresponding lariat ether acid chlorides by treatment with oxalyl chloride in benzene (Scheme 4). Subsequently the acid chlorides were reacted with sodium hydride and commercially available trifluoromethanesulfonamide, methanesulfonamide, benzenesulfonamide, or *p*-nitrobenzene sulfonamide in tetrahydrofuran to give the lipophilic lariat ether *N*-(X)sulfonyl carboxamides **3** (Scheme 4).

Melting points were determined with a Mel-Temp melting point apparatus. Infrared (ir) spectra were recorded with a Perkin-Elmer Model 1600 FT-IR spectrophotometer. Proton nuclear magnetic resonance (nmr) spectra were obtained with a Bruker AF-300 (300 MHz) spectrometer. Carbon nuclear magnetic resonance (nmr) spectra were obtained with a Varian Unity INOVA spectrometer at 126 MHz. Combustion analysis was performed by Desert Analytics Laboratory of Tucson, Arizona.

(Benzyloxymethyl)-15-crown-5 (**24**).

To 3-(benzyloxymethyl)-1,2-diol (4.00 g, 22 mmol) in 40 ml of tetrahydrofuran-water (40:1) was added sodium hydroxide (2.20 g, 55 mmol). The reaction mixture was stirred and gently heated under nitrogen at 60 °C until the base dissolved completely after which a solution of the ditosylate of tetraethylene glycol (11.00 g, 22 mmol) in 20 ml of tetrahydrofuran was added dropwise. The mixture was stirred and heated overnight. An additional amount (2.20 g) of ditosylate was added in one portion

Scheme 4



Compound	CE
28	12-crown-4
29	14-crown-4
30	15-crown-5
31	18-crown-6

The new lipophilic lariat ether *N*-(X)sulfonyl carboxamides **4**-**19** were characterized by proton magnetic resonance spectroscopy, infrared spectroscopy, and combustion analysis. Carbon nuclear magnetic resonance spectra were obtained for *N*-(trifluoromethyl)sulfonyl carboxamides **4**, **8**, **12**, and **16** with different ring sizes and *N*-(X)sulfonyl carboxamide compounds with four different X groups, but a common 15-crown-5 ring. In the proton magnetic resonance spectra of the proton-ionizable lariat ethers with a given ring size, the chemical shift for the N-H proton uniformly decreased as X was varied X = trifluoromethyl > *p*-nitrophenyl > phenyl > methyl, indicating decreasing acidity in this order. This is consistent with the effect of pH of the aqueous phase upon efficiency of alkali metal cation extraction into chloroform observed in the solvent extraction studies performed with these ligands [19].

EXPERIMENTAL

Reagents and solvents were purchased from commercial sources and used without further purification unless otherwise noted. Tetrahydrofuran was dried and purified by distillation from sodium under nitrogen with benzophenone ketyl as indicator.

and stirring and heating were continued for an additional 10 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was evaporated *in vacuo*. The residue was chromatographed on alumina with dichloromethane then dichloromethane-ethyl acetate as eluents to give 5.04 g (67%) of colorless oil. IR (neat): 1127 and 1028 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 3.64-3.66 (m, 21H), 4.55 (s, 2H), 7.32 (m, 5H).

(Benzyloxymethyl)-18-crown-6 (**27**).

To a solution of diol **26** (13.50 g, 50 mmol) in tetrahydrofuran (480 ml) was added under nitrogen potassium *t*-butoxide (12.20 g, 110 mmol). The mixture was stirred at room temperature for 1 h and a solution of the ditosylate of triethylene glycol (25.19 g, 55 mmol) in tetrahydrofuran (95 ml) was added dropwise over a 1 h-period. The reaction mixture was stirred at room temperature for 2 days and then refluxed for an additional 3 days. The solvent was evaporated *in vacuo* and the residue was chromatographed on alumina with dichloromethane as eluent to produce **27** as a pale yellow oil (14.07 g, 73 % yield). IR (neat): 1115 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 3.50-3.80 (m, 25H), 4.51 (s, 2H), 7.23-7.31 (m, 5H).

General Procedure for the Preparation of 5-(Decyl)-2-[(methoxymethyl)crown ether]benzoyl Chlorides **28**-**31**.

To the dry lipophilic lariat ether carboxylic acid (0.50 g) in 75 mL of benzene under nitrogen was added oxalyl chloride (0.64 ml). The reaction mixture was stirred and refluxed for 6 h. The

excess oxalyl chloride and benzene were evaporated *in vacuo* to produce a quantitative yield of the lipophilic lariat ether acid chloride, which was used without purification in the next step.

5-(Decyl)-2-(methoxymethyl-12-crown-4)benzoyl Chloride (**28**).

This compound was obtained as a beige oil. IR (neat): 1779 (C=O), 1139 and 1025 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H), 1.26 (m, 16H), 2.59 (t, 2H), 3.70-4.05 (m, 17H), 6.94-6.98 (d, 1H), 7.27 (dd, 1H), 7.97,7.98 (d, 1H).

5-(Decyl)-2-(methoxymethyl-14-crown-4)benzoyl Chloride (**29**).

This compound was produced as a beige oil. IR (neat): 1782 (C=O), 1128 and 1032 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.88 (t, 3H), 1.26 (m, 16H), 1.80-1.82 (m, 4H), 2.59 (t, 2H), 3.63-4.06 (m, 17H), 6.90-6.92 (d, 1H), 7.36 (dd, 1H), 7.83,7.84 (d, 1H, J = 2.2 Hz).

5-(Decyl)-2-(methoxymethyl-15-crown-5)benzoyl Chloride (**30**).

This compound was obtained as a beige oil. IR (neat): 1780 (C=O), 1137 and 1027 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.88 (t, 3H, J = 6.2 Hz), 1.26 (m, 16H), 2.59 (t, 2H), 3.64-3.94 (m, 21H), 6.89 (d, 1H), 7.36 (dd, 1H), 7.85,7.86 (d, 1H, J = 2.1 Hz).

5-(Decyl)-2-(methoxymethyl-18-crown-6)benzoyl Chloride (**31**).

This compound was produced as a beige oil. IR (neat): 1778 (C=O), 1118 and 1027 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.88 (t, 3H, J = 6.2 Hz), 1.26 (m, 16H), 2.59 (t, 2H, J = 7.5 Hz), 3.68-4.12 (m, 25H), 6.95 (d, 1H), 7.31-7.36 (m, 1H), 7.85 (s, 1H).

General Procedure for the Preparation of *N*-(X)sulfonyl 5-(Decyl)-2-(methoxymethylcrown ether)benzamides **4-19**.

Under nitrogen, sodium hydride (95%, 0.11 g, 4.6 mmol, 5.0 eq) was added to 15 ml of tetrahydrofuran. A solution of the appropriate sulfonamide (1.2 eq) in 30 ml of tetrahydrofuran 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 (1.0 eq) in 45 ml of tetrahydrofuran was added over a 10-min period and the mixture was stirred overnight at room temperature. The mixture was cooled to 0 °C and 30 ml of ice-water was carefully added dropwise to destroy the unreacted sodium hydride. The tetrahydrofuran was evaporated *in vacuo*. The residue was dissolved in 40 ml of water. The alkaline aqueous solution was extracted with dichloromethane (100 ml, then 30 ml) and the combined extracts were washed with 10 % aq. potassium carbonate (2 X 45 ml). The combined potassium carbonate washes were back extracted with dichloromethane (2 X 30 ml) and the organic extracts were combined, dried over magnesium sulfate and evaporated *in vacuo*. The residue was purified by chromatography on alumina with methanol-dichlormethane (1:10) as eluent. The resultant sodium salt was dissolved in dichloromethane (50 ml) and protonated by shaking with 50 ml of 1 *N* hydrochloric acid. The organic layer was separated, washed with water (2 X 50 ml), dried over magnesium sulfate and evaporated *in vacuo*.

N-(Trifluoromethyl)sulfonyl 5-(decyl)-2-(methoxymethyl-12-crown-4)benzamide (**4**).

This compound was obtained in 94%yield as a pale yellow oil. IR (neat): 1715 (C=O), 1372 and 1202 (S=O), 1289 and 1135 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.88 (t, 3H, J = 6.1 Hz), 1.26 (m, 16H), 2.58 (t, 2H, J = 7.9 Hz), 3.66-4.34 (m, 17H), 6.96 (d, 1H, J = 8.6 Hz), 7.36 (dd, 1H), 7.93,7.94 (d, 1H, J = 2.3 Hz), 10.98 (s, 1H). ^{13}C NMR (deuteriochloroform): _14.1, 22.7, 29.1, 29.3, 29.4, 29.5, 29.6, 31.3, 31.9, 34,7, 68.9, 69.4, 69.8, 70.3, 71.7, 113.1, 118.1, 120.6, 132.5, 136.0, 137.0, 155.4, 162.2.

Anal. Calcd for $C_{27}H_{42}F_3NO_8S$: C, 54.26; H, 7.08; N, 2.34. Found: C, 54.10; H, 7.15; N, 2.48.

N-Methylsulfonyl 5-(Decyl)-2-(methoxymethyl-12-crown-4)benzamide (**5**).

This compound was produced in 44% yield as a white solid with mp 64-65 °C. IR (deposit from deuteriochloroform solution onto a sodium chloride plate): 1686 (C=O), 1342 (S=O), 1244 and 1135 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.88 (t, 3H, J = 6.1 Hz), 1.25 (m, 16H), 2.58 (t, 2H, J = 7.8 Hz), 3.39 (s, 3H), 3.68-4.27 (m, 17H), 6.94 (d, 1H, J = 8.5 Hz), 7.26 (dd, 1H), 7.95,7.97 (d, 1H, J = 2.3 Hz), 10.52 (s, 1H).

Anal. Calcd for $C_{27}H_{45}NO_8S$: C, 59.64; H, 8.34; N, 2.58. Found: C, 59.88; H, 8.15; N, 2.65.

N-Phenylsulfonyl 5-(Decyl)-2-(methoxymethyl-12-crown-4)benzamide (**6**).

This compound was isolated in 95% yield as a pale yellow oil. IR (neat): 1691 (C=O), 1349 and 1187 (S=O), 1243 and 1135 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.84-0.90 (t, 3H), 1.23 (m, 16H), 2.48-2.52 (t, 2H), 3.68-4.27 (m, 17H), 6.90 (d, 1H, J = 8.5 Hz), 7.26 (dd, 1H), 7.55-7.59 (m, 3H), 7.84,7.85 (d, 1H, J = 2.4 Hz), 8.12-8.17 (m, 2H), 10.70 (s, 1H).

Anal. Calcd for $C_{32}H_{47}NO_8S$: C, 63.45; H, 7.82; N, 2.31. Found: C, 63.80; H, 7.97; N, 2.39.

N-(*p*-Nitrophenyl)sulfonyl 5-(Decyl)-2-(methoxymethyl-12-crown-4)benzamide (**7**).

This compound was obtained in 90 %yield as a pale yellow oil. IR (neat): 1693 (C=O), 1350 and 1186 (S=O), 1245 and 1137 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.87 (t, 3H, J = 6.1 Hz), 1.23 (m, 16H), 2.58 (t, 2H, J = 7.9 Hz), 3.71-4.25 (m, 17H), 6.91 (d, 1H, J = 8.5 Hz), 7.27 (dd, 1H), 7.79,7.81 (d, 1H, J = 2.3 Hz), 8.37 (m, 4H), 10.87 (s, 1H).

Anal. Calcd for $C_{32}H_{46}N_2O_{10}S$: C, 59.06; H, 7.12; N, 4.30. Found: C, 59.14; H, 7.28; N, 4.18.

N-(Trifluoromethyl)sulfonyl 5-(Decyl)-2-(methoxymethyl-14-crown-4)benzamide (**8**).

This compound was realized in 84%yield as a colorless oil. IR (neat): 1717 (C=O), 1375 and 1202 (S=O), 1288 and 1131 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.88 (t, 3H, J = 6.2 Hz), 1.25 (m, 16H), 1.78-1.85 (m, 4H), 2.59 (t, 2H, J = 7.3 Hz), 3.48-3.95 (m, 15H), 4.26,4.28 (d, 2H, J = 5.0 Hz), 6.96 (d, 1H, J = 8.5 Hz), 7.36-7.42 (dd, 1H), 7.94,7.96 (d, 1H, J = 2.3 Hz), 10.87 (s, 1H). ^{13}C NMR (deuteriochloroform): δ 14.1, 22.7, 29.1, 29.3, 29.4, 29.5, 29.6, 30.1, 30.3, 31.3, 31.9, 34.7, 65.3, 66.3, 67.6, 69.6, 70.1, 70.4, 70.4, 76.3, 112.8, 117.8, 118.0, 120.6, 132.6, 136.0, 137.0, 155.3, 162.0.

Anal. Calcd for $C_{29}H_{46}F_3NO_8S$: C, 55.66; H, 7.41; N, 2.24. Found: C, 55.37; H, 7.51; N, 2.24.

N-Methylsulfonyl 5-(Decyl)-2-(methoxymethyl-14-crown-4)benzamide (**9**).

This compound was produced in 64% yield as a colorless oil. IR (neat): 1724 (C=O), 1345 (S=O), 1246 and 1147 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H), 1.25 (m, 16H), 1.80-1.83 (m, 4H),

2.59 (t, 2H), 3.39 (s, 3H), 3.62-3.70 (m, 15H), 4.22-4.25 (d, 2H), 6.93 (d, 1H, J = 8.5 Hz), 7.26 (dd, 1H), 7.96,7.98 (d, 1H, J = 2.3 Hz), 10.46 (s, 1H).

Anal. Calcd for $C_{29}H_{49}NO_8S$: C, 60.92; H, 8.64; N, 2.45. Found: C, 60.95; H, 8.84; N, 2.51.

N-Phenylsulfonyl 5-(Decyl)-2-(methoxymethyl-14-crown-4)benzamide (**10**).

This compound was isolated in 72% yield as a pale yellow oil. IR (neat): 1714 (C=O), 1372 and 1202 (S=O), 1237 and 1130 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.87 (t, 3H), 1.23 (m, 16H), 1.82 (m, 4H), 2.51 (t, 2H), 3.66-3.75 (m, 15H), 4.22-4.24 (m, 2H), 6.90 (d, 1H), 7.26 (dd, 1H), 7.53-7.57 (m, 3H), 7.85,7.86 (d, 1H, J = 2.3 Hz), 8.13-8.17 (m, 2H), 10.62 (s, 1H).

Anal. Calcd for $C_{34}H_{51}NO_8S$: C, 64.43; H, 8.11; N, 2.21. Found: C, 64.32; H, 8.13; N, 2.22.

N-(*p*-Nitrophenyl)sulfonyl 5-(Decyl)-2-(methoxymethyl-14-crown-4)benzamide (**11**).

This compound was formed in 89% yield as a pale yellow solid with a mp of 68-70 °C. IR (neat): 1691 (C=O), 1351 and 1186 (S=O), 1243 and 1131 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.87 (t, 3H), 1.23 (m, 16H), 1.84 (m, 4H), 2.48-2.52 (t, 2H), 3.67-3.78 (m, 15H), 4.25 (d, 2H, J = 5.1 Hz), 6.93 (d, 1H), 7.27 (dd, 1H), 7.81,7.82 (d, 1H, J = 2.3 Hz), 8.36-8.37 (m, 4H), 10.77 (s, 1H).

Anal. Calcd for $C_{34}H_{50}N_2O_{10}S$: C, 60.16; H, 7.42; N, 4.13. Found: C, 59.77; H, 7.32; N, 4.10.

N-(Trifluoromethyl)sulfonyl 5-(Decyl)-2-(methoxymethyl-15-crown-5)benzamide (**12**).

This comound was obtained in 65% yield as a pale yellow oil. IR (neat): 1715 (C=O), 1372 and 1202 (S=O), 1289 and 1130 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.88 (t, 3H, J = 6.1 Hz), 1.26-1.66 (m, 16H), 2.58 (t, 2H, J = 7.2 Hz), 3.57-4.26 (m, 21H), 4.37-4.42 (m, 1H), 6.97 (d, 1H, J = 8.5 Hz), 7.31-7.39 (dd, 1H), 7.91,7.93 (d, 1H, J = 2.3 Hz), 11.06 (s, 1H). ^{13}C NMR (deuteriochloroform): δ 14.1, 22.7, 29.1, 29.3, 29.4, 29.5, 29.6, 31.3, 31.9, 34.7, 69.0, 69.5, 69.7, 70.3, 70.5, 70.6, 70.6, 70.6, 70.9, 71.8, 76.5, 113.3, 118.2, 132.4, 135.9, 136.9, 155.6, 162.3.

Anal. Calcd for $C_{29}H_{46}F_3NO_9S$: C, 54.28; H, 7.22; N, 2.18. Found: C, 54.12; H, 7.17; N, 2.26.

N-Methylsulfonyl 5-(Decyl)-2-(methoxymethyl-15-crown-5)benzamide (**13**).

This compound was produced in 61% yield as a colorless oil. IR (neat): 1682 (C=O), 1344 (S=O), 1245 and 1134 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.87 (t, 3H, J = 6.1 Hz), 1.25 (m, 16H), 2.58 (t, 2H, J = 8.0 Hz), 3.39 (s, 3H), 3.61-4.30 (m, 21H), 6.96 (d, 1H, J = 8.5 Hz), 7.26 (dd, 1H), 7.94,7.96 (d, 1H, J = 2.3 Hz), 10.58 (s, 1H). ^{13}C NMR (deuteriochloroform): δ 14.1, 22.7, 29.1, 29.3, 29.4, 29.5, 29.6, 31.3, 31.9, 34.8, 41.8, 69.5, 69.9, 70.3, 70.5, 70.6, 70.7, 71.0, 71.6, 76.9, 113.2, 118.9, 132.1, 135.1, 136.5, 155.6, 164.2.

Anal. Calcd for $C_{29}H_{49}NO_9S$: C, 59.26; H, 8.40; N, 2.38. Found: C, 59.29; H, 8.36; N, 2.33.

N-Phenylsulfonyl 5-(Decyl)-2-(methoxy-15-crown-5)benzamide (**14**).

This compound was realized in 84% yield as a yellow oil. IR (neat): 1693 (C=O), 1348 and 1187 (S=O), 1244 and 1133 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.87 (t, 3H, J = 6.1 Hz), 1.23 (m, 16H), 2.51 (t, 2H), 3.64-3.85 (m, 19H), 4.28 (m, 2H), 6.88-6.92 (d, 1H), 7.26 (dd, 1H), 7.53-7.58 (m, 3H), 7.83,7.84 (d, 1H, J = 2.3 Hz), 8.13-8.17 (m, 2H), 10.76 (s, 1H). ^{13}C NMR (deuteriochloroform): δ 14.1, 22.7, 29.1, 29.3, 29.4, 29.5, 29.6, 31.3, 31.9, 34.7, 69.5, 69.7, 69.9, 70.4, 70.6, 70.7, 71.5, 71.6, 96.1, 112.8, 118.8, 128.5, 128.8, 132.1, 133.6, 134.9, 136.5, 139.9, 155.4, 162.9.

Anal. Calcd for $C_{34}H_{51}NO_9S$: C, 62.84; H, 7.91; N, 2.16. Found: C, 63.03; H, 7.98; N, 2.28.

N-(*p*-Nitrophenyl)sulfonyl 5-(Decyl)-2-(methoxy-15-crown-5)benzamide (**15**).

This compound was obtained in 85% yield as a yellow oil. IR (neat): 1690 (C=O), 1350 and 1186 (S=O), 1247 and 1131 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.87 (t, 3H), 1.23 (m, 16H), 2.48-2.52 (t, 2H), 3.65-4.25 (m, 21H), 6.94 (d, 1H), 7.27 (dd, 1H), 7.78,7.79 (d, 1H, J = 2.3 Hz), 8.37 (m, 4H), 10.95 (s, 1H). ^{13}C NMR (deuteriochloroform): δ 14.1, 22.7, 29.1, 29.3, 29.4, 29.5, 29.6, 31.3, 31.9, 34.7, 69.6, 69.7, 70.1, 70.3, 70.6, 70.6, 70.6, 70.7, 71.0, 71.7, 77.0, 113.0, 118.9, 128.5, 128.7, 132.0, 133.5, 134.8, 136.4, 139.4, 155.5, 163.0.

Anal. Calcd for $C_{34}H_{50}N_2O_{11}S$: C, 58.77; H, 7.25; N, 4.03. Found: C, 58.47; H, 7.43; N, 3.87.

N-(Trifluoromethyl)sulfonyl 5-(Decyl)-2-(methoxymethyl-18-crown-6)benzamide (**16**).

This compound was isolated in 29%yield as a colorless oil. IR (neat): 1716 (C=O), 1370 and 1201 (S=O), 1290 and 1130 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.88 (t, 3H, J = 6.5 Hz), 1.26-1.57 (m, 16H), 2.58 (t, 2H, J = 7.5 Hz), 3.58-4.48 (m, 24H), 4.49-4.51 (m, 1H), 6.99,7.01 (d, 1H, J = 8.6 Hz), 7.36-7.40 (dd, 1H), 7.91,7.92 (d, 1H, J = 2.3 Hz), 11.06 (s, 1H). ^{13}C NMR (deuteriochloroform): δ 14.1, 22.7, 29.1, 29.3, 29.4, 29.5, 29.6, 31.3, 31.9, 34.7, 69.1, 69.2, 69.4, 70.6, 70.6, 70.7, 70.7, 70.9, 71.6, 76.1, 109.9, 113.4, 118.1, 120.7, 132.3, 135.9, 136.8, 155.7, 162.3.

Anal. Calcd for $C_{31}H_{50}F_3NO_{10}S$: C, 54.29; H, 7.35; N, 2.04. Found: C, 54.04; H, 7.52; N, 2.25.

N-Methylsulfonyl 5-(Decyl)-2-(methoxy-18-crown-6)benzamide (**17**).

This compound was realized in 86% yield as a colorless oil. IR (neat): 1686 (C=O), 1344 (S=O), 1247 and 1135 (C-O) cm^{-1}. ^1H NMR (deuteriochloroform): δ 0.88 (t, 3H, J = 6.5 Hz), 1.26-1.28 (m, 16H), 2.58 (t, 2H, J = 7.4 Hz), 3.39 (s, 3H), 3.62-3.88 (m, 23 H), 4.30 (m, 2H), 6.98 (d, 1H, J = 5.5 Hz), 7.26 (dd, 1H), 7.95,7.96 (d, 1H, J = 2.6 Hz), 10.56 (s, 1H).

Anal. Calcd for $C_{31}H_{53}NO_{10}S$: C, 58.93; H, 8.45; N, 2.22. Found: C, 59.26; H, 8.70; N, 2.25.

N-Phenylsulfonyl 5-(Decyl)-2-(methoxymethyl-18-crown-6)benzamide (**18**).

This compound was obtained in 89% yield as a colorless oil. IR (neat): 1690 (C=O), 1349 and 1187 (S=O), 1247 and 1120 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.87 (t, 3H, J = 6.0 Hz), 1.23 (m, 16H), 2.51 (t, 2H, J = 7.8 Hz), 3.64-3.95 (m, 23H), 4.31-4.34 (m, 2H), 6.93 (d, 1H, J = 8.5 Hz), 7.26 (dd, 1H), 7.53-7.58 (m, 3H), 7.83,7.84 (d, 1H, J = 2.2 Hz), 8.12-8.17 (m, 2H), 10.75 (s, 1H).

Anal. Calcd for $C_{36}H_{55}NO_{10}S$: C, 62.31; H, 7.99; N, 2.02. Found: C, 62.33; H, 8.34; N, 2.11.

N-(*p*-Nitrophenyl)sulfonyl 5-(Decyl)-2-(methoxymethyl-18-crown-6)benzamide (**19**).

This compound was obtained in 92% yield as a pale yellow oil. IR (neat): 1690 (C=O), 1351 and 1186 (S=O), 1248 and 1116 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.87 (t, 3H, J = 6.1 Hz), 1.23 (m, 16H), 2.48-2.52 (t, 2H), 3.63-3.95 (m, 23H), 4.35 (m, 2H), 6.94 (d, 1H), 7.27 (dd, 1H), 7.80 (d, 1H), 8.37 (m, 4H), 10.93 (s, 1H).

Anal. Calcd for $C_{36}H_{54}N_2O_{12}S$: C, 58.52; H, 7.37; N, 3.79. Found: C, 58.57; H, 7.51; N, 3.76.

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