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Synthetic routes to forty-four dibenzocrown ether alcohols are reported. The new crown ether compounds are based on a *sym*-dibenzo-16-crown-5 platform. Most have a hydroxy group and an alkyl, aryl, aralkyl, alkenyl, alkynyl, or perfluoroalkyl group on the central carbon of the three-carbon bridge. Others have substituted benzene rings and either a hydroxy or $-O(CH_2)_nOH$ group attached to the central carbon of the three-carbon bridge.

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Introduction.

Crown ether alcohols are valuable synthetic intermediates for the preparation of lariat ethers with neutral [1] and proton-ionizable groups [1-7], biscrown ethers [8] and polymer-bound crown ethers [9,10]. Pendant arms with additional neutral or anionic coordination sites often provide substantially increased metal ion binding compared to the parent crown ether [1].

For some time, we have been involved in the synthesis of lariat ether carboxylic acids and studies of their metal ion separation properties [2-7,11-24]. Lariat ether carboxylic acids are effective chelating agents for alkali, alkali earth, and lanthanide metal cations [11-24]. When such ligands are employed, the ionized group on the side arm provides the counteranion necessary for the transport of the metal ion into the organic layer in a metal ion separation process [11-24].

For the preparation of such lariat ether carboxylic acids, lariat ether alcohols were used as precursors [2-7]. Lipophilic groups were introduced to avoid ligand loss from the organic phase during the extraction of metal ions from aqueous solutions [12]. Also, attachment of an alkyl group to the crown ether carbon that bears the acidic sidearm was found to produce enhanced selectivity in metal ion separation processes [4,16].

We now report the preparation of forty-four new crown alcohols based upon a *sym*-dibenzo-16-crown-5 platform. Most of these lariat ether alcohols have a hydroxy group and an alkyl, aryl, aralkyl, alkenyl, alkynyl, or perfluoroalkyl group attached to the central carbon of the three-carbon bridge (Tables 1-4). Others have substituted benzene rings and a hydroxy or $O(CH_2)_nOH$ group attached to the central carbon of the three-carbon bridge (Tables 5 and 6). Several previously reported dibenzo-16-crown-5 lariat ether alcohols are included in these tables for comparison.

Results and Discussion.

For the preparation of the lariat ether alcohols shown in Tables 1-6, several different approaches were utilized.

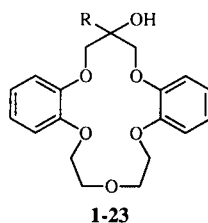
The *sym*-(hydroxy)(R)dibenzo-16-crown-5 compounds **2-34** with R = alkyl, aryl and aralkyl (Tables 1 and 2), crown alcohols **35** and **36** (Table 3) and lariat ether alcohols **45-48** (Table 4) were synthesized as shown in Scheme I. The Grignard reagent was prepared by reaction of the appropriate alkyl, aryl or aralkyl bromide with magnesium turnings in tetrahydrofuran followed by addition of a solution of *sym*-(keto)dibenzo-16-crown-5 (**63**) in tetrahydrofuran.

Yields for these Grignard reactions were very high (71-97%) with the exception of *sym*-(hydroxy)(2,2-dimethylpropyl)dibenzo-16-crown-5 (**8**) which was realized in only a 29% yield. In the reaction mixture for **8**, thin layer chromatographic (tlc) analysis showed the presence of a considerable amount of unreacted ketone **63**. This suggests that the Grignard reagent (neopentylmagnesium bromide) was too bulky for facile approach to the carbonyl carbon.

Initially, there was also a problem with the preparation of *sym*-(hydroxy)(2-methyl-1-propenyl)dibenzo-16-crown-5 (**35**). Although a mixture of 1-bromo-2-methyl-1-propene, magnesium turnings, and tetrahydrofuran was refluxed overnight, the corresponding Grignard reagent did not form due to the low reactivity of the vinyl bromide. As an alternative, activated magnesium turnings were used. A crystal of iodine was added to the magnesium turnings in tetrahydrofuran and the mixture was subjected to ultrasonication until the color of the mixture changed from brown to turbid gray. With this modification, the formation of the Grignard reagent was successful and an 86% yield of the desired lariat ether alcohol was realized.

The synthetic strategy for the preparation of lariat ether alcohols **37-41** (Table 3) which contain a geminal hydroxy and 1-alkynyl group is shown in Scheme II. Propylmagnesium bromide was prepared by reaction of magnesium turnings with 1-bromopropane in tetrahydrofuran and then the appropriate 1-alkyne was added. The reaction mixture was stirred for three hours at room temperature, followed by the addition of ketone **63**. Lariat ether alcohols **37-41** were obtained in very high yields (94-96%).

Table 1
Yields, Melting Points, ¹H NMR and IR Spectra, and Analytical Data for Crown Ether Alcohols 1-23



Compound	R	Yield (%)	mp (°C)	¹ H NMR (deuteriochloroform) δ (ppm)	IR (cm ⁻¹) [a]	Molecular Formula	Analysis %	
							Calcd./Found	C H
1	H	60 [b]						
2	CH ₃	92 [c]						
3	C ₂ H ₅	89 [c]						
4	C ₃ H ₇	84 [d]						
5	CH(CH ₃) ₂	88	125-126	1.13 (d, 6H), 2.42 (m, 1H), 3.83-4.31 (m, 12H), 6.83-6.99 (m, 8H)	3510 (OH), 1122 (C-O)	C ₂₂ H ₂₈ O ₆	68.02 68.11	7.26 7.14
6	C ₄ H ₉	90 [e]						
7	C ₅ H ₁₁	84	124-126	0.70-0.76 (t, 3H, J = 6 Hz), 1.22 (s, 6H), 1.82-1.98 (m, 2H), 3.20 (br s, 1H), 3.70-4.33 (m, 12H), 6.87 (s, 8H)	3480 (OH), 1120 (C-O)	C ₂₄ H ₃₂ O ₆	69.21 69.16	7.74 7.72
8	CH ₂ C(CH ₃) ₃	29	102-103	1.12 (s, 9H), 1.88 (s, 2H), 3.07 (s, 1H), 3.90-4.29 (m, 12H), 6.87-6.95 (m, 8H)	3501 (OH), 1124 (C-O)	C ₂₄ H ₃₂ O ₆	69.21 69.24	7.74 7.83
9	C ₆ H ₁₃	88	126-127	0.88-0.94 (t, 3H, J = 6 Hz), 1.41-1.60 (m, 8H), 1.60-1.69 (m, 2H), 3.22 (s, 1H), 3.81-4.26 (m, 12H), 6.84-7.00 (m, 8H)	3512 (OH), 1121 (C-O)	C ₂₅ H ₃₄ O ₆	69.74 69.63	7.96 7.61
10	c-C ₆ H ₁₁	77 [f]						
11	C ₇ H ₁₅	89	81-82	0.85-0.91 (t, 3H, J = 6 Hz), 1.28 (s, 10H), 1.82-1.95 (m, 2H), 3.29 (s, 1H), 3.89-4.26 (m, 12H), 6.83-7.00 (m, 8H)	3511 (OH), 1213 (C-O)	C ₂₆ H ₃₆ O ₆	70.24 70.44	8.16 8.29
12	C ₈ H ₁₇	91 [e]						
13	CH ₂ CH(C ₂ H ₅)C ₄ H ₉	71	[g]	0.86-0.96 (m, 6H), 1.22-1.61 (m, 11H), 3.25 (br s, 1H), 3.90-4.25 (m, 12H), 6.84-7.00 (m, 8H)	3560 (OH), 1257 (C-O)	C ₂₇ H ₃₈ O ₆	70.74 70.33	8.30 8.10
14	C ₉ H ₁₉	92	113-114	0.88-0.94 (t, 3H, J = 6 Hz), 1.27-1.60 (m, 14H), 1.82 (m, 2H), 3.24 (s, 1H), 3.90-4.27 (m, 12H), 6.86-6.98 (m, 8H)	3545 (OH), 1234 (C-O)	C ₂₈ H ₄₀ O ₆	71.16 70.93	8.53 8.53
15	C ₁₀ H ₂₁	90 [f]						
16	C ₁₁ H ₂₃	97	113-114	0.88-0.94 (t, 3H, J = 6 Hz), 1.25-1.60 (m, 18H), 1.82 (m, 2H), 3.26 (s, 1H), 3.92-4.27 (m, 12H), 6.66-6.98 (m, 8H)	3520 (OH), 1228 (C-O)	C ₃₀ H ₄₄ O ₆	71.97 71.81	8.86 9.03
17	C ₁₂ H ₂₅	77	83-84	0.77-0.83 (t, 3H, J = 6 Hz), 1.23 (s, 20H), 1.83 (m, 2H), 3.23 (s, 1H), 3.77-4.33 (m, 12H), 6.90 (s, 8H)	3430 (OH), 1255 (C-O)	C ₃₁ H ₄₆ O ₆	72.34 72.20	9.01 9.06
18	C ₁₃ H ₂₇	96	93-95	0.84-0.90 (t, 3H, J = 6 Hz), 1.18-1.26 (s, 22H), 1.82-1.87 (m, 2H), 3.26 (s, 1H), 3.89-4.26 (m, 12H), 6.82-6.97 (m, 8H)	3489 (OH), 1257, 1121 (C-O)	C ₃₂ H ₄₈ O ₆	72.69 73.00	9.15 9.17
19	C ₁₄ H ₂₉	79 [e]						
20	C ₁₅ H ₃₁	95	79-80	0.70-0.76 (t, 3H, J = 6 Hz), 1.25 (s, 26H), 1.93 (m, 2H), 3.21 (s, 1H), 3.75-4.33 (m, 12H), 6.87 (s, 8H)	3455 (OH), 1253, 1122 (C-O)	C ₃₄ H ₅₂ O ₆	73.34 73.01	9.41 9.45

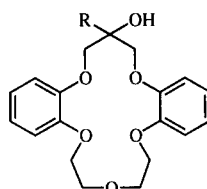
Table 1 (continued)

Compound	R	Yield (%)	mp (°C)	¹ H NMR (deuteriochloroform) δ (ppm)	IR (cm ⁻¹) [a]	Molecular Formula	Analysis %	
							Calcd./Found	C H
21	C ₁₆ H ₃₃	75	76-77	0.80-0.86 (t, 3H, J = 6 Hz), 1.28 (s, 28H), 1.90-2.20 (m, 2H), 3.23 (s, 1H), 3.77-4.30 (m, 12H), 6.87 (s, 8H)	3460 (OH), 1260, 1125 (C-O)	C ₃₅ H ₅₄ O ₆	73.65 73.48	9.54 9.40
22	C ₁₈ H ₃₇	89 [f]	71-72	0.77-0.83 (t, 3H, J = 6 Hz), 1.29 (s, 36H), 1.87 (m, 2H), 3.26 (s, 1H), 3.77-4.30 (m, 12H), 6.87 (s, 8H)	3458 (OH), 1258, 1122 (C-O)	C ₃₉ H ₆₂ O ₆	74.72 74.79	9.97 10.14
23	C ₂₀ H ₄₁	70						

[a] Deposited from dichloromethane solution onto a sodium chloride plate; [b] Reference 25; [c] Reference 5; [d] Reference 21; [e] Reference 3; [f] Reference 6; [g] Oil.

Table 2

Yields, Melting Points, ¹H NMR and IR Spectra, and Analytical Data for Crown Ether Alcohols 24-34



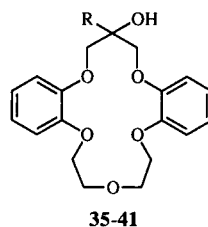
24-34

Compound	R	Yield (%)	mp (°C)	¹ H NMR (deuteriochloroform) δ (ppm)	IR (cm ⁻¹) [a]	Molecular Formula	Analysis %	
							Calcd./Found	C H
24	C ₆ H ₅	90 [b]						
25	2-(CH ₃)C ₆ H ₄	87	135-137	2.66 (s, 3H), 3.75 (s, 1H), 3.94-3.98 (m, 4H), 4.12-4.22 (m, 4H), 4.49-4.52 (d, 2H, J = 9 Hz), 4.56-4.59 (d, 2H, J = 9 Hz), 6.82-6.96 (m, 8H), 7.16-7.22 (m, 3H), 7.81-7.84 (m, 1H)	3546 (OH), 1257, 1123 (C-O)	C ₂₆ H ₂₈ O ₆ * 0.25 H ₂ O	70.82 70.73	6.41 6.69
26	3-(CH ₃)C ₆ H ₄	78	98-100	2.39 (s, 3H), 3.78 (s, 1H), 3.97-4.01 (m, 4H), 4.17-4.23 (m, 4H), 4.36-4.39 (d, 2H, J = 9 Hz), 4.46-4.49 (d, 2H, J = 9 Hz), 6.80-6.95 (m, 8H), 7.12-7.14 (d, 1H, J = 6 Hz), 7.25-7.32 (m, 1H), 7.50-7.53 (d, 1H, J = 9 Hz), 7.57 (s, 1H)	3562 (OH), 1256, 1123 (C-O)	C ₂₆ H ₂₈ O ₆	71.54 71.31	6.46 6.46
27	4-(CH ₃)C ₆ H ₄	80	128-130	2.36 (s, 3H), 3.69 (s, 1H), 3.96-3.99 (m, 4H), 4.15-4.20 (m, 4H), 4.41 (s, 4H), 6.79-6.93 (m, 8H), 7.20-7.23 (d, 2H, J = 9 Hz), 7.63-7.66 (d, 2H, J = 9 Hz)	3553 (OH), 1257, 1123 (C-O)	C ₂₆ H ₂₈ O ₆	71.54 71.33	6.46 6.67
28	3,5-(CH ₃) ₂ C ₆ H ₃	89	115-117	2.35 (s, 6H), 3.84 (s, 1H), 3.96-4.00 (m, 4H), 4.16-4.20 (m, 4H), 4.31-4.36 (d, 2H, J = 10 Hz), 4.45-4.50 (d, 2H, J = 10 Hz), 6.80-6.95 (m, 9H), 7.34 (s, 2H)	3566 (OH), 1256, 1123 (C-O)	C ₂₇ H ₃₀ O ₆	71.98 72.08	6.71 6.70
29	4-(CH ₂ =CH)C ₆ H ₄	90	134-135	3.74 (s, 1H), 3.96-4.03 (m, 4H), 4.16-4.23 (m, 4H), 4.43 (s, 4H), 5.22-5.28 (d, 1H, J = 12 Hz), 5.73-5.81 (d, 1H, J = 16 Hz), 6.65-6.98 (m, 9H), 7.44-7.48 (d, 2H, J = 8 Hz), 7.71-7.75 (d, 2H, J = 8 Hz)	3546 (OH), 1629 (C=C)	C ₂₇ H ₂₈ O ₆	72.31 72.28	6.29 6.18
30	4-(CH ₂ =C(CH ₃))C ₆ H ₄	73	151-152	2.16 (s, 3H), 3.76 (s, 1H), 3.97-4.01 (m, 4H), 4.17-4.23 (m, 4H), 4.43 (s, 4H), 5.06 (s, 1H), 5.40 (s, 1H), 6.80-6.93 (m, 8H), 7.49-7.53 (d, 2H, J = 8 Hz), 7.71-7.75 (d, 2H, J = 8 Hz)	3485 (OH), 1123 (C-O)	C ₂₈ H ₃₀ O ₆	72.71 72.47	6.54 6.52
31	(CH ₂) ₂ C ₆ H ₅	92	122-124	2.16-2.25 (m, 2H), 2.82-2.90 (m, 2H), 3.25 (s, 1H), 3.83-4.03 (m, 4H), 4.10-4.20 (m, 6H), 4.24-4.29 (d, 2H, J = 10 Hz), 6.86-7.00 (m, 8H), 7.22-7.44 (m, 5H)	3460 (OH), 1122 (C-O)	C ₂₇ H ₂₉ O ₆	72.15 71.96	6.50 6.74

Table 2 (continued)

Compound	R	Yield (%)	mp (°C)	¹ H NMR (deuteriochloroform) δ (ppm)	IR (cm ⁻¹) [a]	Molecular Formula	Analysis %	
							Calcd./Found	C H
32	(CH ₂) ₃ C ₆ H ₅	95	[c]	1.89 (m, 4H), 2.64-2.71 (t, 2H, J = 6 Hz), 3.36 (s, 1H), 3.85-3.89 (m, 4H), 4.01-4.22 (m, 8H), 6.83-6.94 (m, 8H), 7.16-7.27 (m, 5H)	3473 (OH), 1125 (C-O)	C ₂₈ H ₃₂ O ₆	72.40 72.39	6.94 6.88
33	(CH ₂) ₄ C ₆ H ₅	81	87-88	1.53-1.94 (m, 6H), 2.56-2.69 (m, 2H), 3.28 (s, 1H), 3.84-4.23 (m, 12H), 6.82-7.05 (m, 8H), 7.15-7.29 (m, 5H)	3455 (OH), 1122 (C-O)	C ₂₉ H ₃₄ O ₆	72.79 73.12	7.16 7.27
34	(CH ₂) ₅ C ₆ H ₅	97	[c]	1.41-1.90 (m, 10H), 2.58-2.66 (t, 2H, J = 8 Hz), 3.25 (s, 1H), 3.86-4.25 (m, 12H), 6.83-7.00 (m, 8H), 7.14-7.31 (m, 5H)	3450 (OH), 1122 (C-O)	C ₃₀ H ₃₆ O ₆	73.15 73.04	7.37 7.44

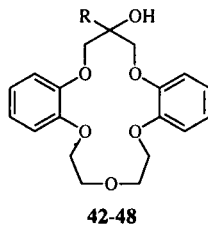
[a] Deposit from dichloromethane solution onto a sodium chloride plate; [b] Reference 6; [c] Oil.

Table 3
Yields, Melting Points, ¹H NMR and IR Spectra, and Analytical Data for Crown Ether Alcohols 35-41

Compound	R	Yield (%)	mp (°C)	¹ H NMR (deuteriochloroform) δ (ppm)	IR (cm ⁻¹) [a]	Molecular Formula	Analysis %	
							Calcd./Found	C H
35	CH=C(CH ₃) ₂	86	90-92	1.80 (s, 3H), 1.98 (s, 3H), 3.37 (s, 1H), 3.90-4.30 (m, 12H), 6.84-6.99 (m, 8H)	3510 (OH), 1122 (C-O)	C ₂₃ H ₂₈ O ₆	68.98 69.28	7.05 7.28
36	(CH ₂) ₈ CH=CH ₂	56	82-83	1.32-2.05 (m, 16H), 3.26 (br s, 1H), 3.90-4.26 (m, 12H), 4.90-5.04 (m, 2H), 5.70-5.90 (m, 1H), 6.89-7.00 (m, 8H)	3462 (OH), 1640 (C=C), 1263, 1046 (C-O)	C ₂₉ H ₄₀ O ₆	71.87 71.88	8.32 8.37
37	C≡C(CH ₂) ₃ CH ₃	96	91-93	0.91 (t, 3H, J = 6 Hz), 1.40-1.50 (m, 4H), 2.23-2.26 (t, 2H, J = 6 Hz), 3.72 (s, 1H), 3.89-3.95 (m, 4H), 4.14-4.21 (m, 6H), 4.37-4.42 (d, 2H, J = 10 Hz), 6.84-7.05 (m, 8H)	3424 (OH), 2245 (C≡C)	C ₂₅ H ₃₀ O ₆	70.42 70.30	7.04 7.25
38	C≡C(CH ₂) ₅ CH ₃	94	66-67	0.88 (t, 3H, J = 6 Hz), 1.05-1.54 (m, 8H), 2.25 (t, 2H, J = 6 Hz), 3.69 (s, 1H), 3.89-3.98 (m, 4H), 4.07-4.21 (m, 6H), 4.37-4.42 (d, 2H, J = 10 Hz), 6.84-7.05 (m, 8H)	3440 (OH), 2244 (C≡C), 1123 (C-O)	C ₂₇ H ₃₄ O ₆	71.34 71.59	7.54 7.43
39	C≡C(CH ₂) ₇ CH ₃	94	72-73	0.87 (t, 3H, J = 6 Hz), 1.26-1.57 (m, 12H), 2.25 (t, 2H, J = 6 Hz), 3.69 (s, 1H), 3.87-4.01 (m, 4H), 4.09-4.25 (m, 6H), 4.37-4.42 (d, 2H, J = 10 Hz), 6.84-7.05 (m, 8H)	3440 (OH), 2244 (C≡C), 1123 (C-O)	C ₂₉ H ₃₈ O ₆	72.17 72.24	7.94 7.72
40	C≡C(CH ₂) ₉ CH ₃	96	98-100	0.88 (t, 3H, J = 6.4 Hz), 1.13-1.63 (m, 4H), 2.26 (t, 2H, J = 6.9 Hz), 3.67 (s, 1H), 3.79-4.02 (m, 4H), 4.07-4.26 (m, 6H), 4.40 (d, 2H, J = 9.6 Hz), 6.81-7.07 (m, 8H)	3423 (OH), 2245 (C≡C), 1258, 1124 (C-O)	C ₃₁ H ₄₂ O ₆	72.91 73.00	8.29 8.35
41	C≡C(CH ₂) ₁₁ CH ₃	95	79-81	0.86 (t, 3H, J = 6.4 Hz), 1.12-1.62 (m, 4H), 2.26 (t, 2H, J = 6.9 Hz), 3.67 (s, 1H), 3.81-4.03 (m, 4H), 4.07-4.29 (m, 6H), 4.40 (d, 2H, J = 9.6 Hz), 6.77-7.11 (m, 8H)	3438 (OH), 2246 (C≡C), 1258, 1124 (C-O)	C ₃₃ H ₄₆ O ₆	73.57 73.51	8.61 8.75

[a] Deposit from dichloromethane solution onto a sodium chloride plate.

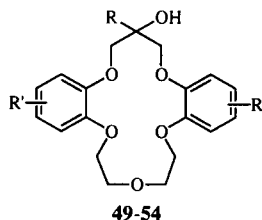
Table 4
Yields, Melting Points, ^1H NMR and IR Spectra, and Analytical Data for Crown Ether Alcohols **42-48**



Compound	R	Yield (%)	mp (°C)	^1H NMR (deuteriochloroform) δ (ppm)	IR (cm $^{-1}$) [a]	Molecular Formula	Analysis %	
							Calcd./Found C	H
42	C ₃ F ₇	60	77-78	3.57-4.23 (m, 8H), 4.53 (s, 4H), 6.93 (m, 8H)	3515 (OH), 1250, 1215, 1120 (C-O, C-F)	C ₂₂ H ₂₁ F ₇ O ₆	51.37 50.95	4.11 4.12
43	C ₆ F ₁₃	28	70-72	3.70-4.32 (m, 8H), 4.37 (s, 1H), 4.50 (s, 4H), 6.90 (s, 8H)	3513 (OH), 1320-1100 (C-O, C-F)	C ₂₅ H ₂₁ O ₆ F ₁₃ ^a H ₂ O	44.00 44.42	3.40 3.41
44	C ₈ F ₁₇	33	96-98	3.73-4.30 (m, 8H), 4.50 (s, 4H), 6.90 (s, 8H)	3509 (OH), 1300-1120 (C-O, C-F)	C ₂₇ H ₂₁ O ₆ F ₁₇	42.42 42.53	2.77 2.83
45	C ₆ F ₅	48 [b]						
46	2-(CF ₃) ₂ C ₆ H ₄	90	216-217	3.90 (s, 1H), 3.94-4.12 (m, 4H), 4.17-4.25 (m, 4H), 4.34-4.39 (d, 2H, J = 10 Hz), 4.73-4.78 (d, 2H, J = 10 Hz), 6.77-6.87 (m, 8H), 7.36-7.43 (t, 1H, J = 8 Hz), 7.52-7.60 (t, 1H, J = 8 Hz), 7.80-7.84 (d, 1H, J = 8 Hz), 8.15-8.19 (d, 1H, J = 8 Hz)	3457 (OH), 1125 (C-O)	C ₂₆ H ₂₅ F ₃ O ₆	63.67 64.04	5.14 5.22
47	3-(CF ₃)C ₆ H ₄	75 [b]						
48	3,5-(CF ₃) ₂ C ₆ H ₃	68 [b]						

[a] Deposit from dichloromethane solution onto a sodium chloride plate; [b] Reference 26.

Table 5
Yields, Melting Points, ^1H NMR and IR Spectra, and Analytical Data for Crown Ether Alcohols **49-54**



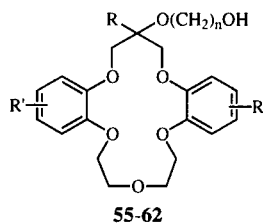
Compound	R	R ¹	Yield (%)	mp (°C)	^1H NMR (deuteriochloroform) δ (ppm)	IR (cm $^{-1}$) [a]	Molecular Formula	Analysis %	
								Calcd./Found C	H
49	H	C(CH ₃) ₃	93	175-177	2.27 (s, 18H), 3.57 (br s, 1H), 3.74-4.40 (m, 13H), 6.78-7.13 (m, 6H)	3515 (OH), 1124 (C-O)	C ₂₇ H ₃₈ O ₆	70.71 70.58	8.35 8.40
50	CH ₃	C(CH ₃) ₃	64	[b]	0.80-1.40 (m, 21H), 3.52-4.23 (m, 12H), 4.78 (br s, 1H), 6.82-7.21 (s, 6H)	3383 (OH), 1120 (C-O)	C ₂₈ H ₄₀ O ₆	71.16 70.91	8.53 8.53

Table 5 (continued)

Compound	R	R ¹	Yield (%)	mp (°C)	¹ H NMR (deuteriochloroform) δ (ppm)	IR (cm ⁻¹) [a]	Molecular Formula	Analysis %	
								Calcd./Found	C H
51	C ₃ H ₇	C(CH ₃) ₃	53	77-78	0.97-1.04 (t, 3H, J = 6 Hz), 1.27 (s, 18H), 1.52-1.59 (m, 2H), 1.81-1.86 (m, 2H), 3.25-3.29 (d, 1H, J = 8 Hz), 3.87-3.92 (m, 4H), 3.99-4.29 (m, 8H), 6.77-6.99 (m, 6H)	3476 (OH), 1267-1146 (C-O)	C ₃₀ H ₄₄ O ₆	71.97 72.35	8.86 9.06
52	H	NO ₂	100	168-170	3.70-4.40 (m, 13H), 7.00-8.40 (m, 6H)	3420 (OH), 1480, 1310 (NO ₂), 1105 (C-O)	C ₁₉ H ₂₀ N ₂ O ₁₀	52.30 52.21	4.62 4.80
53	H	NH ₂	50	182-183	3.30-4.30 (m, 13H), 4.35-5.60 (m, 5H), 5.90-7.00 (m, 6H)	3310 (NH ₂ and OH), 1125 (C-O)	C ₁₉ H ₂₄ N ₂ O ₆	60.63 60.67	6.43 6.52
54	H	F	33 [c]						

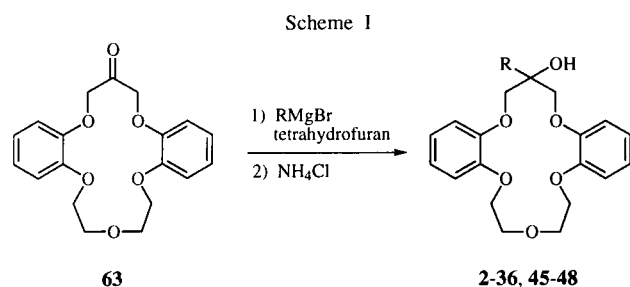
[a] Deposit from dichloromethane solution onto a sodium chloride plate; [b] Oil; [c] Reference 26.

Table 6

Yields, Melting Points, ¹H NMR and IR Spectra, and Analytical Data for Crown Ether Alcohols 55-62

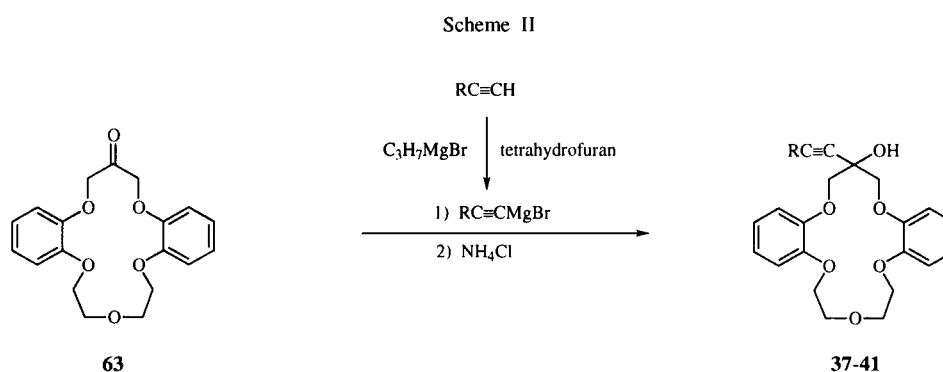
Compound	R	R ¹	n	Yield (%)	mp (°C)	¹ H NMR (deuteriochloroform) δ (ppm)	IR (cm ⁻¹) [a]	Molecular Formula	Analysis %	
									Calcd./Found	C H
55	H	H	2	95 [b]						
56	H	C(CH ₃) ₃	2	96	67-68	1.27 (m, 18H), 3.05 (br s, 1H), 3.45-4.23 (m, 17H), 6.85-7.12 (m, 6H)	3420 (OH), 1122 (C-O)	C ₂₉ H ₄₂ O ₇ * 1.15 CH ₂ Cl ₂	60.32 60.38	7.43 7.30
57	CH ₃	H	2	92	[c]	1.52 (s, 3H), 2.69 (br t, 1H), 3.72-3.75 (m, 2H), 3.77-3.95 (m, 6H), 4.08-4.18 (m, 6H), 4.30-4.35 (d, 2H, J = 10 Hz), 6.81-6.88 (m, 8H)	3402 (OH), 1256, 1123 (C-O)	C ₂₂ H ₂₈ O ₇	65.33 65.35	6.98 6.85
58	C ₁₀ H ₂₁	H	2	91	[c]	0.85-0.91 (t, 3H, J = 6 Hz), 1.27 (m, 16H), 1.84-1.92 (m, 2H), 2.62-2.68 (t, 1H), 3.70-3.78 (m, 2H), 3.90-3.94 (m, 6H), 4.08-4.17 (m, 6H), 4.38-4.43 (d, 2H, J = 10 Hz), 6.81-6.97 (m, 8H)	3239 (OH), 1256, 1129 (C-O)	C ₃₁ H ₄₆ O ₇	70.16 70.30	8.74 8.80
59	H	H	3	26 [d]						
60	H	C(CH ₃) ₃	3	97	[c]	0.92-1.54 (m, 18H), 1.90 (m, 2H), 3.33 (br s, 1H), 3.55-4.42 (m, 17H), 6.72-7.14 (m, 6H)	3295 (OH), 1122 (C-O)	C ₃₀ H ₄₄ O ₇ * 0.5 H ₂ O	68.66 68.55	8.47 8.63
61	CH ₃	H	3	53	[c]	1.51 (s, 3H), 1.77-1.88 (m, 2H), 3.09 (t, 1H), 3.77-4.17 (m, 14H), 4.30-4.35 (d, 2H, J = 10 Hz), 6.81-6.98 (m, 8H)	3283 (OH), 1125 (C-O)	C ₂₃ H ₃₀ O ₇	66.01 65.88	7.23 7.35
62	C ₁₀ H ₂₁	H	3	91	[c]	0.88-0.94 (t, 3H, J = 6 Hz), 1.15-1.18 (m, 16H), 1.68-2.20 (m, 4H), 3.74-4.51 (m, 16H), 6.83-7.02 (m, 8H)	3314 (OH), 1256, 1129 (C-O)	C ₃₂ H ₄₈ O ₇ * 1.25 H ₂ O	67.76 67.80	8.53 8.68

[a] Deposit from dichloromethane solution onto a sodium chloride plate; [b] Reference 6; [c] Oil; [d] Reference 2.

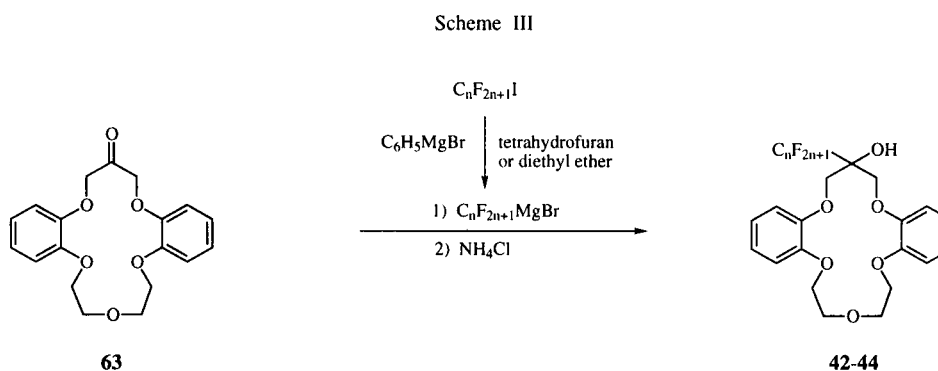


with iodine-activated magnesium turnings to give the corresponding Grignard reagent. Treatment of these Grignard reagents with **63** provided the corresponding lariat ether alcohols **45-48**.

Lariat ether alcohols **49-54** that contain substituents on the benzene rings and a hydroxy group or a geminal hydroxy and an alkyl group on the central carbon of the three-carbon bridge (Table 5) were prepared as shown in Schemes IV through VII.



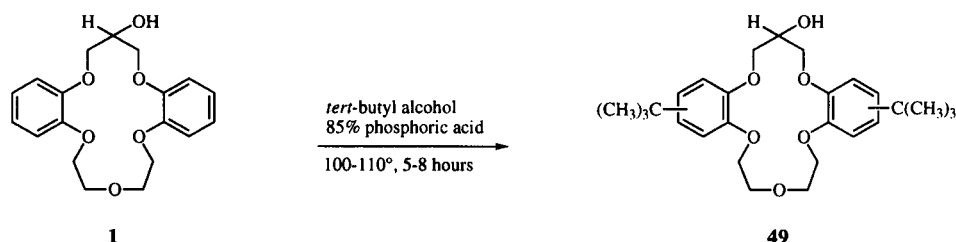
For the preparation of lariat ether alcohols **42-44** with geminal hydroxy and perfluoroalkyl groups on the central carbon of the three-carbon bridge (Table 4), a similar approach was employed [27] (Scheme III). Phenylmagnesium bromide was cooled in a dry ice/acetone bath (-78°) and the perfluoroalkyl iodide was added. The reaction mixture was stirred for one to two hours. After the addition of ketone **63**, the reaction mixture was allowed to come to room temperature and stirring was continued overnight providing lariat ether alcohols **42-44**.



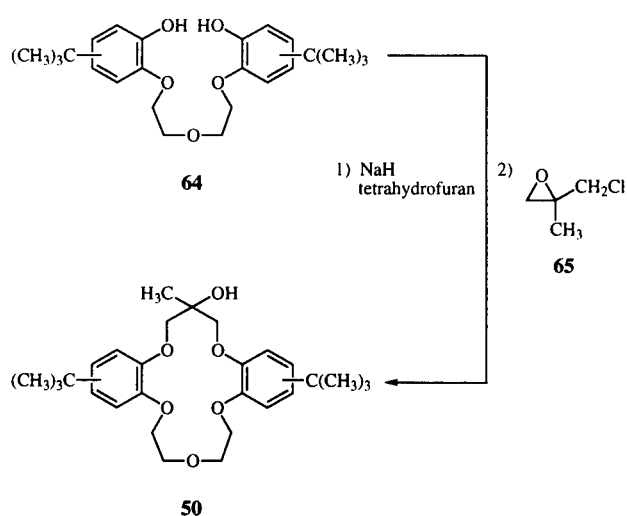
Although perfluoroalkyl iodides did not react with iodine-activated magnesium turnings, trifluoromethylphenyl bromides and iodopentafluorobenzene reacted readily

Lipophilic lariat ether alcohol **49** was prepared as depicted in Scheme IV by adaptation of a reported method for attachment of *tert*-butyl groups to the aromatic

Scheme IV



Scheme V

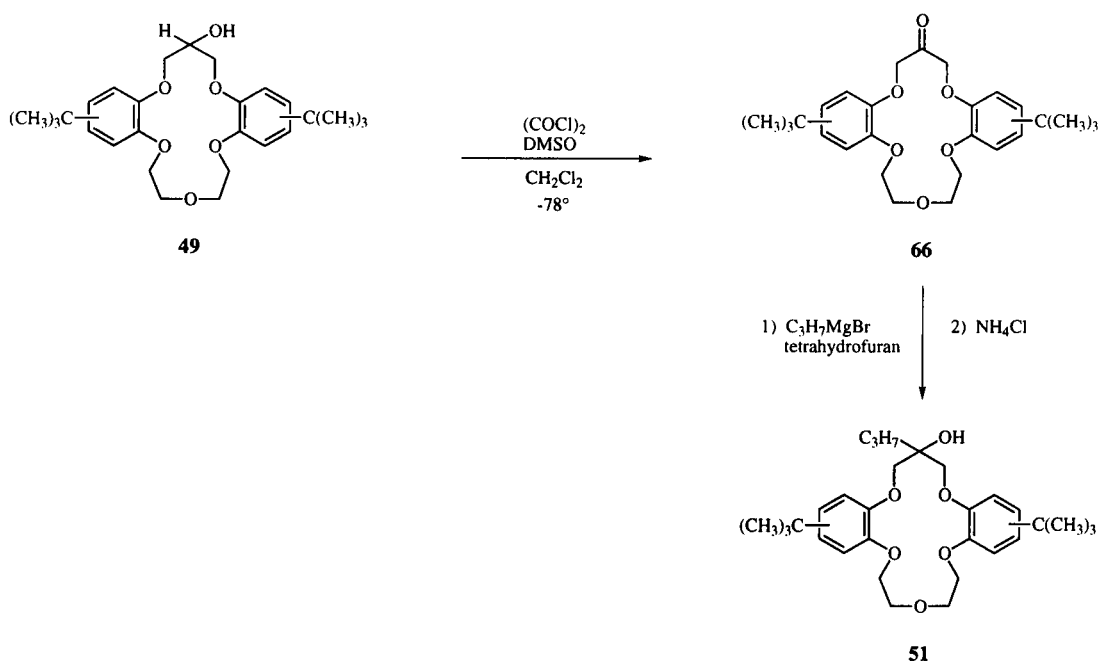


rings of benzo- and dibenzocrown ethers [28]. Thus lariat ether alcohol **1** was reacted with *tert*-butyl alcohol and 85% phosphoric acid at 100–110° to give the lipophilic lariat ether alcohol **49** in 93% yield. This yield represents a substantial increase over the 59% yield reported for an alternative synthetic route to **49** [29].

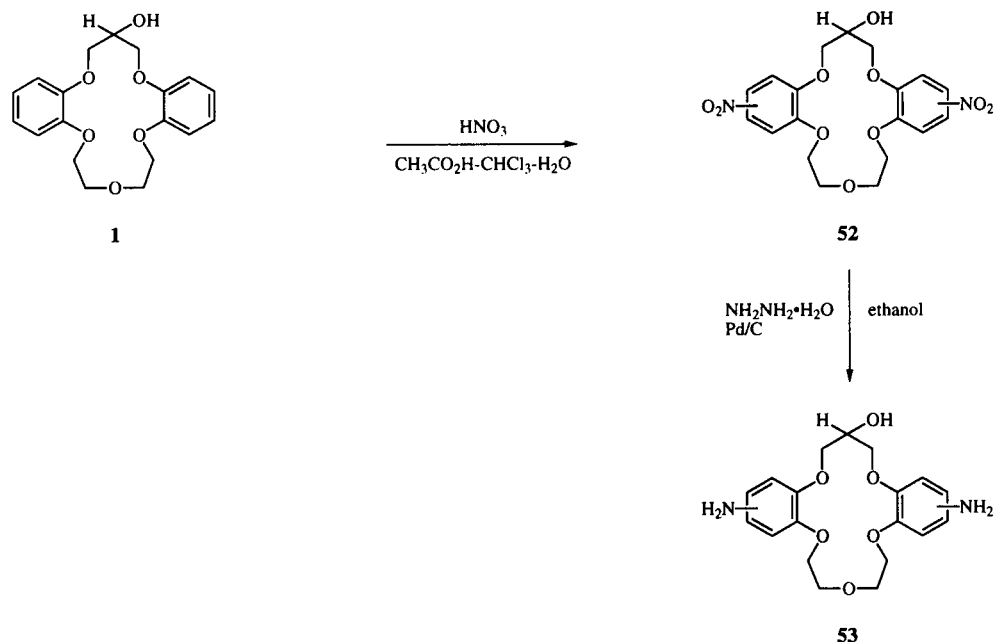
Lariat ether alcohol **50** that has geminal hydroxy and methyl groups on the central carbon of the three-carbon bridge and a *tert*-butyl group attached to each benzene ring was prepared by reaction of bisphenol **64** [29] with sodium hydride in tetrahydrofuran followed by the addition of 2-methyl-2-chloromethyloxirane (**65**) [30] (Scheme V). This highly lipophilic lariat ether alcohol was isolated in 64% yield.

An analogous lipophilic lariat ether alcohol **51** with geminal hydroxyl and propyl groups was prepared as shown in Scheme VI. Swern oxidation [31] of lariat ether alcohol **49** gave a 77% yield of lariat ether ketone **66**. Reaction of **66** with propylmagnesium bromide in tetrahy-

Scheme VI



Scheme VII



drofuran provided lariat ether alcohol **51** in 53% yield. Apparently the two *tert*-butyl group substituents in lariat ether ketone **66** sterically hindered approach of the Grignard reagent to the carbonyl carbon resulting in a lower yield of **51** than the 84% obtained from reaction of propylmagnesium bromide with *sym*-(keto)dibenzo-16-crown-5 (**63**).

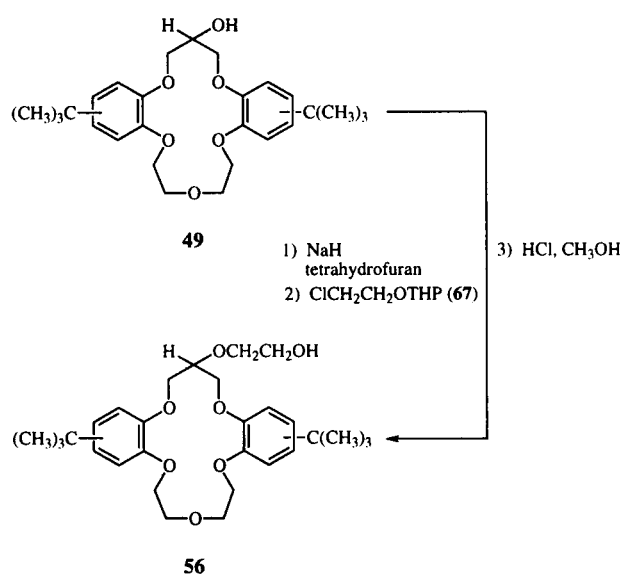
The preparation of lariat ether alcohols **52** and **53** with nitro and amino groups, respectively, on their benzene rings is shown in Scheme VII. Reaction of lariat ether alcohol **1** with nitric acid in acetic acid-chloroform-water [32] solution gave *sym*-(hydroxy)di[4(5)nitrobenzo]-16-crown-5 (**52**) in quantitative yield. The presence of at least two positional isomers was indicated by tlc.

Although the reduction of di(nitrobenzo)-18-crown-6 to the corresponding diamine by catalytic hydrogenation in *N,N*-dimethylformamide or *N,N*-dimethylacetamide was reported [32], attempted catalytic hydrogenation of **52** in *N,N*-dimethylformamide, 2-methoxyethanol or ethanol gave a dark-colored product which could not be purified by recrystallization, sublimation, or column chromatography. Subsequently it was found that **52** could be reduced to the corresponding diamino derivative **53** in 50% yield with 85% hydrazine hydrate as the hydrogen source and ethanol as the solvent.

Synthetic approaches to lariat ether alcohols containing $-\text{O}(\text{CH}_2)_n\text{OH}$ groups are presented in Schemes VIII-X. Lariat ether alcohol **56** with $n = 2$ and a *tert*-butyl group on each benzene ring was prepared in 66% yield by addition of tetrahydropyranyl (THP)-protected ethylene

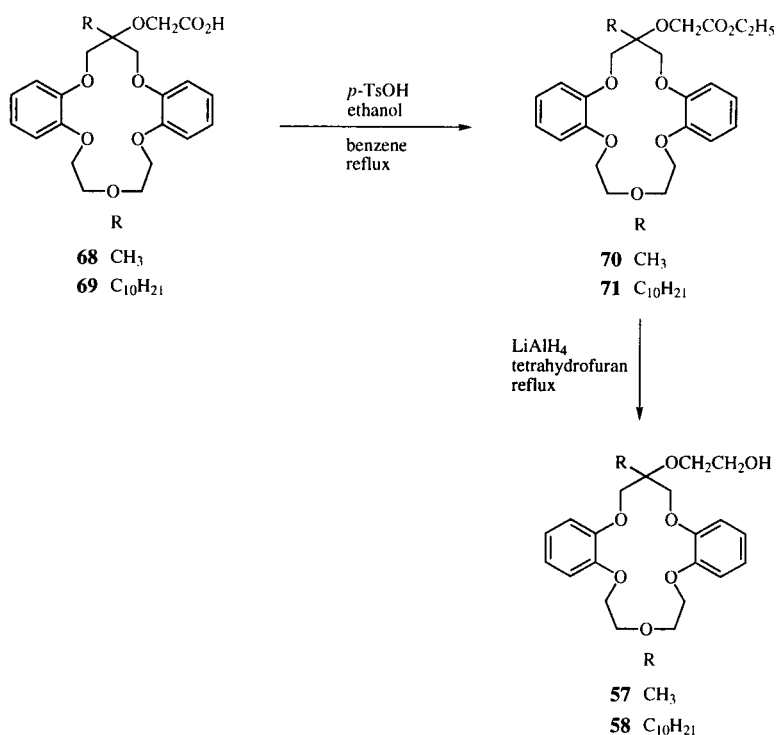
chlorohydrin (**67**) [33] to the sodium alkoxide of lariat ether alcohol **49**, followed by removal of the THP group with 10% hydrochloric acid-methanol to give **56** in 96% yield (Scheme VIII).

Scheme VIII



Esterification of the carboxylic acid functions in lariat ether carboxylic acids **68** and **69** [5,6] with ethanol and *p*-toluenesulfonic acid in benzene gave the corresponding lariat ether esters **70** and **71** in 94 and 98% yields, respectively. Reduction of the ester functions of **70** and **71** with lithium aluminum hydride in tetrahydrofuran provided lariat ether alcohols **57** and **58** in 92% and 91% yields, respectively (Scheme IX).

Scheme IX

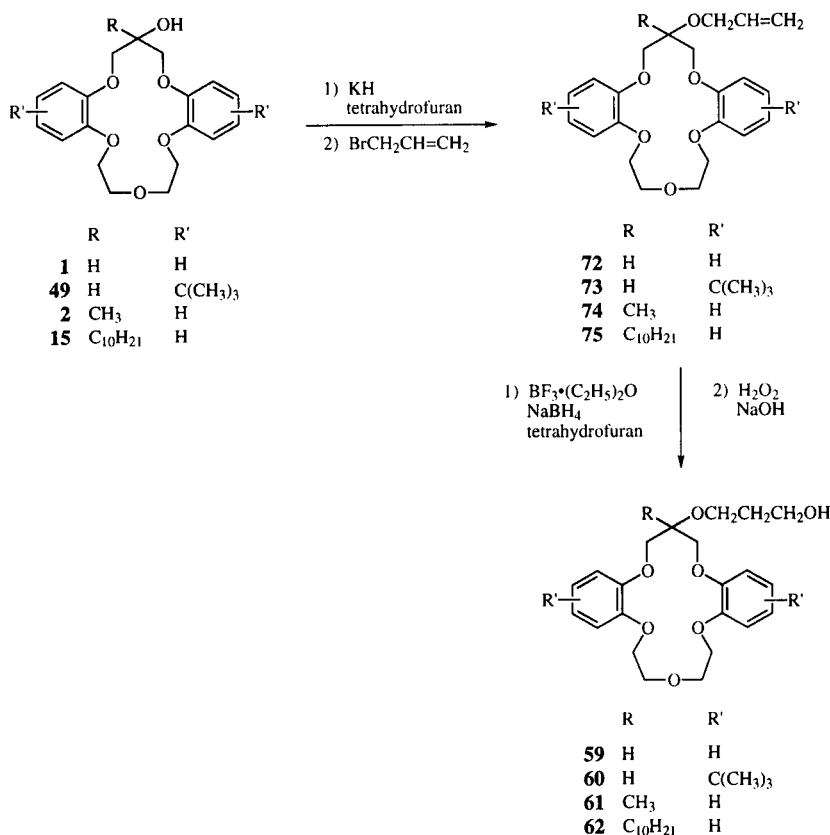


Lariat ether carboxylic acids can also be directly reduced to the corresponding alcohols by treatment with borane-tetrahydrofuran complex or lithium aluminum hydride [8].

The synthesis of lariat ether alcohols **59-62** which have a OCH₂CH₂CH₂OH side arm was accomplished by the addition of allyl bromide to the alkoxides of lariat ether alcohols **1**, **49**, **2** and **15**, respectively, to give the corresponding allyloxy lariat ethers **72-75** in very good yields. Hydroborationoxidation [34] of **72-75** provided lariat ether alcohols **59-62** in good yields (Scheme X).

As mentioned in the Introduction, some of these lariat ether alcohols have been used to prepare the corresponding lariat ether carboxylic acids [2-7]. Some lariat ether alcohols were used as monomers for the preparation of polymers with pendant crown ether units [35,36]. Lariat ether alcohol **53** with an amino group on each benzene ring was coupled with diacid chlorides to form polyamides with pendant functional groups [35]. Lariat ether alcohol **29** with a styryl group on the three-carbon bridge was readily polymerized with the radical initiator azobis(isobutyronitrile) to form a homopolymer [36].

Scheme X



EXPERIMENTAL

Unless specified otherwise, reagent grade reactants and solvents were used as received from commercial suppliers. Tetrahydrofuran was dried and purified by distillation from sodium and with benzophenone ketyl as indicator. *sym*-(Keto)dibenzo-16-crown-5 (**63**) [3], *sym*-hydroxydibenzo-16-crown-5 (**1**) [25], bis[2-(4- or 5-*tert*-butyl-2-hydroxyphenoxy)ethyl] ether (**64**) [29], 2-methyl-2-chloromethyloxirane (**65**) [30], *sym*-(methyl)dibenzo-16-crown-5-oxyacetic acid (**68**) [5], *sym*-(decyl)dibenzo-16-crown-5-oxyacetic acid (**69**) [6], and tetrahydropyranyl ethylene chlorohydrin (**67**) [33] were prepared by reported procedures.

The infrared (ir) spectra were obtained with a Perkin Elmer Model 1600 spectrophotometer and are reported in reciprocal centimeters (cm⁻¹). The proton nuclear magnetic resonance (¹H nmr) spectra were recorded with an IBM AF-200 spectrometer in deuteriochloroform and chemical shifts are reported in parts per million downfield (δ) from tetramethylsilane. Melting points were measured with a Mel-Temp melting point apparatus and are uncorrected. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

General Procedure for the Preparation of Lariat Ether Alcohols **2-36** and **45-48**.

A mixture of magnesium turnings (20 mmoles), the corresponding alkyl, aryl or aralkyl or alkenyl bromide (20 mmoles)

and 40 ml of dry tetrahydrofuran was refluxed under nitrogen until all of the magnesium turnings were consumed. (In the preparation of **24-28**, **33**, and **45-48**, the reaction mixture was stirred at room temperature for 2 hours.) After cooling to room temperature, a solution of 3.44 g (10 mmoles) of *sym*-(keto)dibenzo-16-crown-5 (**63**) in 40 ml of tetrahydrofuran was added dropwise during a period of 1 hour, followed by refluxing for 6 hours. (In the preparation of **24-28**, **33**, and **45-48**, the reaction mixture was stirred at room temperature for 2 hours.) After cooling to 0°, 20 ml of 5% ammonium chloride was added and stirring was continued overnight. The tetrahydrofuran was evaporated and the aqueous solution was extracted with diethyl ether (2 x 50 ml). The combined organic layers were dried over sodium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel with dichloromethane and then diethyl ether as eluents. The solid product was stirred for 1 hour in pentane. Spectral and combustion analysis data for **2-34** are given in Tables 1 and 2; **35** and **36** in Table 3; and **45-48** in Table 4.

General Procedure for the Preparation of *sym*-(1-Alkynyl)-(hydroxy)dibenzo-16-crown-5 Compounds **37-41**.

To magnesium turnings (0.282 g, 11.6 mmoles) under nitrogen, propyl bromide (1.41 g, 11.6 mmoles) in 15 ml of dry tetrahydrofuran was added and the mixture stirred at room temperature for 1.5-2 hours. The mixture was cooled to 0° and the appropriate 1-alkyne (12.8 mmoles) in 4 ml of dry tetrahydrofu-

ran was added, followed by stirring at 20-25° for 3 hours. The mixture was cooled to 0° and **63** (2.00 g, 5.81 mmoles) in 50 ml of dry tetrahydrofuran was added dropwise over a period of 30 minutes. The mixture was stirred at room temperature for 18 hours, cooled to 0° and 100 ml of 10% aqueous ammonium chloride was added. The tetrahydrofuran was evaporated *in vacuo* and an additional 50 ml of 10% aqueous ammonium chloride was added. The aqueous layer was extracted with ethyl acetate (2 x 100 ml). The combined organic layers were washed with 30 ml of water, dried over magnesium sulfate, and evaporated *in vacuo*. The crude product was purified by recrystallization from diethyl ether. Spectral and combustion analysis data for **37-41** are recorded in Table 3.

General Procedure for the Preparation of *sym*-(Hydroxy)(perfluoroalkyl)dibenzo-16-crown-5 Compounds **42-44**.

Phenylmagnesium bromide prepared from a 0.60 g (24 mmoles) of magnesium and 3.78 g (24 mmoles) of bromobenzene in 60 ml of diethyl ether was cooled in a dry ice/acetone bath. The perfluoro-1-iodoalkane (21 mmoles) in 140 ml of diethyl ether was added during a 30 minute period. After stirring for another 30 minutes, a suspension of 4.00 g (11.6 mmoles) of **63** in 100 ml of diethyl ether was added dropwise over a 30 minute period. The reaction mixture was stirred at -78° for 2-3 hours and allowed to warm to room temperature with stirring overnight. After cooling to 0°, 20 ml of 5% ammonium chloride was added and stirring was continued overnight. The diethyl ether layer was separated and the aqueous layer was extracted twice with diethyl ether. The combined organic layers were dried over magnesium sulfate and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel with dichloromethane as eluent and then recrystallized from hexane. Spectral and combustion analysis data for **42-44** are listed in Table 4.

sym-(Hydroxy)di[4(5)-*tert*-butylbenzo]-16-crown-5 (**49**).

A mixture of 5.12 mmoles of **1**, 1.85 g (24.9 mmoles) of *tert*-butyl alcohol, and 7.75 g of 85% phosphoric acid was stirred for 8 hours at 100-110°. During the reaction, two liquid layers formed. To the reaction mixture was added 10 g of crushed ice. The reaction mixture was extracted with dichloromethane (3 x 50 ml). The combined dichloromethane layers were washed with saturated aqueous sodium bicarbonate (2 x 50 ml) and water (2 x 50 ml), dried over magnesium sulfate, and evaporated *in vacuo* to give a yellowish oil. The oil was crystallized from hexane to give the desired product as a white solid. See Table 5 for spectral and combustion analysis data for **49**.

sym-(Hydroxy)(methyl)-bis[4(5)-*tert*-butylbenzo]-16-crown-5 (**50**).

Under nitrogen, 1.00 g (25 mmoles) of sodium hydride (60% dispersion in mineral oil) was washed with dry pentane to remove the protecting oil and was suspended in 100 ml of dry tetrahydrofuran. To the stirred mixture, **64** (5.00 g, 12.5 mmoles) was added and the mixture was stirred for 1 hour. A solution of 2-methyl-2-chloromethyloxirane (**65**) (1.37 g, 12.5 mmoles) in 25 ml of dry tetrahydrofuran was added dropwise followed by stirring at 40° for 2 hours and refluxing for 20 hours. Water (150 ml) was added to the cooled reaction mixture, the tetrahydrofuran was removed *in vacuo*, and the resultant basic mixture was extracted with dichloromethane (3 x 100 ml). The combined dichloromethane layers were washed with water, dried over

magnesium sulfate, and evaporated *in vacuo* to give the crude product which was purified by column chromatography on silica gel with dichloromethane and diethyl ether as eluents to give 3.70 g (65%) of **50** as a yellow oil. Spectral and combustion analysis data are shown in Table 5.

sym-(Keto)di[4(5)-*tert*-butylbenzo]-16-crown-5 (**66**).

To a stirred solution of 5.96 g (49.3 mmoles) of oxalyl chloride in 15 ml of dichloromethane was added 4.89 g (62.6 mmoles) of dimethyl sulfoxide in 5 ml of dichloromethane at -78° under nitrogen. The reaction mixture was stirred for an additional 10 minutes at -78°. To the reaction mixture was added 15.66 mmoles of **49** in 20 ml of dichloromethane and the mixture was stirred for 30 minutes at -78°. To the reaction mixture was added 15.85 g (157 mmoles) of triethylamine. The mixture was stirred for 30 minutes at -78°, allowed to warm to 0° for 30 minutes, and diluted with dichloromethane (50 ml). After quenching with water (30 ml), the aqueous layer was separated and extracted with dichloromethane (2 x 50 ml). The dichloromethane extracts and the original organic layer were combined and washed consecutively with 10% aqueous hydrochloric acid (2 x 50 ml), brine (1 x 50 ml), and water (50 ml). The organic solution was dried over magnesium sulfate and evaporated *in vacuo* to give a yellowish oil which was chromatographed on silica gel with ethyl acetate as eluent to give a colorless oil. The oil was crystallized from hexane to give a 77% yield of a white solid with mp 180-181°; ir (deposit from dichloromethane solution on a sodium chloride plate): ν 1742 (C=O), 1219, 1057 (C-O) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 1.27-1.28 (m, 18H), 3.91-3.94 (m, 4H), 4.17 (m, 4H), 4.96-5.07 (m, 4H), 6.90-7.10 (m, 6H).

Anal. Calcd. for $\text{C}_{27}\text{H}_{36}\text{O}_6$: C, 71.03; H, 7.95. Found: C, 71.01; H, 7.87.

sym-(Hydroxy)(propyl)di[4(5)-*tert*-butylbenzo]-16-crown-5 (**51**).

A mixture of magnesium turnings (0.21 g, 8.70 mmoles), 1-bromopropane (8.70 mmoles), and 50 ml of dry tetrahydrofuran was refluxed under nitrogen until all of the magnesium turnings were consumed. After cooling to 0°, 4.35 mmoles of **66** in 20 ml of dry tetrahydrofuran was added over a period of 1 hour with a syringe pump. The mixture was refluxed for 6 hours, cooled to 0°, and 10 ml of 5% aqueous ammonium chloride was added slowly. The tetrahydrofuran was evaporated *in vacuo* and water and dichloromethane (50 ml each) were added to the residue. The organic layer was separated, washed with 5% aqueous sodium bicarbonate (3 x 30 ml), brine (2 x 30 ml), and water (50 ml). The dichloromethane solution was dried over magnesium sulfate and evaporated *in vacuo* to give a white solid which was recrystallized from pentane. Spectral and combustion analysis data for **51** are given in Table 5.

sym-(Hydroxy)di[4(5)-nitrobenzo]-16-crown-5 (**52**).

To a stirred solution of **1** (1.00 g, 2.89 mmoles) in 5 ml of glacial acetic acid and 5 ml of chloroform was added 1.3 ml of concentrated nitric acid, followed by 1.0 ml of water. After stirring for 1 hour at room temperature (or at 4-5°), the reaction mixture was allowed to stand at room temperature for 1 hour, poured into 400 ml of water, and filtered. The filtered material was washed several times with water and dried *in vacuo* to produce 1.28 g (100%) of **52** with mp 168-170°. This procedure was also used on a larger scale (10 times) with similar results.

Spectral and combustion analysis data are recorded in Table 5.

sym-(Hydroxy)di[4(5)-aminobenzo]-16-crown-5 (**53**).

To **52** (10.00 g, 22.9 mmoles) was added to 300 ml of ethanol (incomplete solution). The 5% Pd/C catalyst (1.20 g) and then 70 ml of 85% hydrazine hydrate were added. The mixture was refluxed for 25 hours and filtered while hot. After allowing the filtrate to stand overnight, white needles were filtered, washed with ethanol, and dried *in vacuo* to give 4.30 g (50%) of **53** with mp 182-183°. The compound was very hygroscopic. See Table 5 for spectral and combustion analysis data for **53**.

2-*sym*-Di[4(5)-*tert*-butylbenzo]-16-crown-5-oxy}-ethanol (**56**).

Under nitrogen, 0.40 g (9.8 mmoles) of sodium hydride (60% mineral oil dispersion) was washed with dry pentane to remove the mineral oil and was suspended in 200 ml of dry tetrahydrofuran. To the stirred mixture, 3.00 g (6.4 mmoles) of *sym*-(hydroxy)-di[4(5)-*tert*-butylbenzo]-16-crown-5 (**49**) was added. After stirring for 1 hour, a solution of 1.00 g (6.54 mmoles) of tetrahydropyranyl-protected ethylene chlorohydrin (**67**) in 25 ml of tetrahydrofuran was added and the mixture was refluxed for 24 hours. To the cooled reaction mixture, 100 ml of water was added dropwise and the tetrahydrofuran was removed *in vacuo*. Extraction of the residual aqueous layer with dichloromethane (3 x 50 ml), drying over magnesium sulfate and evaporation gave an oil which was purified by column chromatography on silica gel with diethyl ether as eluent to give a 66% yield of the tetrahydropyranyl ether of 2-*sym*-di[4(5)-*tert*-butylbenzo]-16-crown-5-oxy}-ethanol (**56**). The protecting group was removed by stirring with 100 ml of a 10% hydrochloric acid in methanol solution for 12 hours under nitrogen. Following neutralization by addition of 10% aqueous potassium carbonate, the methanol was removed *in vacuo*. Extraction of the resultant aqueous phase with dichloromethane (2 x 100 ml), drying over magnesium sulfate, and evaporation gave an oil which was purified by column chromatography on alumina with dichloromethane as the eluent. A 96% yield of extremely hygroscopic 2-*sym*-di[4(5)-*tert*-butylbenzo]-16-crown-5-oxy}-ethanol (**56**) was obtained as a white solid with mp 67-68°. Spectral and combustion analysis data for **56** are given in Table 6.

General Procedure for the Preparation of Ethyl [*sym*-(Alkyl)-dibenzo-16-crown-5-oxy]acetates **70** and **71**.

The appropriate lariat ether carboxylic acid **68** or **69** (3.64 mmoles) was dissolved in ethanol-benzene (1:1, v/v, 200 ml). To the solution was added 0.20 g of *p*-toluenesulfonic acid and the reaction mixture was refluxed for 5 hours with continuous circulation of the condensing vapors through a Soxhlet thimble that contained anhydrous sodium sulfate. The solvents were evaporated *in vacuo* and 100 ml of dichloromethane was added to the residue. The solution was washed with saturated aqueous sodium bicarbonate (2 x 50 ml) and water (2 x 50 ml), dried over magnesium sulfate, and evaporated *in vacuo* to give a yellowish oil. The oily product was purified by column chromatography on silica gel with ethyl acetate as eluent to give the desired product.

Ethyl [*sym*-(Methyl)dibenzo-16-crown-5-oxy]acetate (**70**).

This compound was obtained in 94% yield as a colorless oil; ir (deposit from dichloromethane on a sodium chloride plate): ν 1756, 1728 (C=O), 1257, 1122 (C-O) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 1.17-1.25 (t, 3H, J = 8 Hz), 1.58 (s, 3H), 3.93-3.99 (m, 5H), 4.05-4.19 (m, 7H), 4.38-4.43 (d, 2H, J = 10 Hz), 4.74 (s, 2H), 6.81-6.95 (m, 8H).

Anal. Calcd. for $\text{C}_{24}\text{H}_{30}\text{O}_8$: C, 64.56; H, 6.77. Found: C, 64.20; H, 6.68.

Ethyl [*sym*-(Decyl)dibenzo-16-crown-5-oxy]acetate (**71**).

A white solid with mp 88-89° was isolated in 97% yield; ir (deposit from dichloromethane solution on a sodium chloride plate): ν 1758, 1728 (C=O), 1257, 1123 (C-O) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 0.85-0.91 (t, 3H, J = 6 Hz), 1.16-1.33 (m, 19H), 1.95 (m, 2H), 3.91-3.99 (m, 5H), 4.05-4.19 (m, 7H), 4.44-4.49 (d, 2H, J = 10 Hz), 4.76 (s, 2H), 6.80-6.99 (m, 8H).

Anal. Calcd. for $\text{C}_{33}\text{H}_{48}\text{O}_8$: C, 69.21; H, 8.45. Found: C, 69.20; H, 8.40.

General Procedure for the Preparation of 2-*sym*-(Alkyl)-dibenzo-16-crown-5-oxy]ethanol Compounds **57** and **58**.

A mixture of diester **70** or **71** (40.35 mmoles), lithium aluminum hydride (4.13 g, 109 mmoles), and dry tetrahydrofuran (200 ml) was refluxed for 3 hours under nitrogen. The reaction mixture was cooled in an ice-bath while the following additions were made slowly and consecutively: 12 ml of aqueous tetrahydrofuran (1:5, v/v); 10 ml of 15% aqueous sodium hydroxide; and 20 ml of aqueous tetrahydrofuran (1:1, v/v). The resulting mixture was allowed to stand overnight at room temperature, after which the precipitated inorganic material was filtered and washed with hot tetrahydrofuran. The combined filtrate and washings were evaporated *in vacuo* and 100 ml of dichloromethane was added to the aqueous residue. The organic layer was separated, washed with water (3 x 50 ml), dried over magnesium sulfate, and evaporated *in vacuo* to give a colorless oil. The crude products were chromatographed on silica gel with ethyl acetate as eluent. Spectral and combustion analysis data for **57** and **58** are given in Table 6.

General Procedure for Preparation of Allyloxy Lariat Ether Alcohols **73-75**.

The protecting mineral oil was removed by washing potassium hydride (4.26 g of 35% dispersion in mineral oil, 69.3 mmoles) with dry pentane under nitrogen and dry tetrahydrofuran (200 ml) was added. A solution of 13.9 mmoles of the appropriate lariat ether alcohol in 200 ml of dry tetrahydrofuran was added dropwise and the reaction mixture was stirred for 1 hour at room temperature. A solution of allyl bromide (2.49 g, 20.8 mmoles) in 20 ml of dry tetrahydrofuran was added dropwise during a period of 1 hour and the reaction was stirred for 10 hours at room temperature. Water (5 ml) was added carefully to decompose the unreacted potassium hydride. After the tetrahydrofuran was evaporated *in vacuo* ethyl acetate and water (100 ml of each) were added to the residue. The organic layer was separated and washed with 5% hydrochloric acid (3 x 50 ml). The dichloromethane layer was dried over magnesium sulfate, filtered, and evaporated *in vacuo* to give the crude product.

sym-(Allyloxy)-di[4(5)-*tert*-butylbenzo]-16-crown-5 (**73**).

Column chromatography on alumina with dichloromethane as eluent provided a colorless oil in 75% yield; ir (deposit from dichloromethane solution on a sodium chloride plate): ν 3074, 1647, 1587 (C=C), 1122 (C-O) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 0.92-1.54 (m, 18H), 3.55-4.49 (m, 15H), 3.55-4.49 (m, 15H), 5.10-6.15 (m, 3H), 6.52-7.14 (m, 6H).

Anal. Calcd. for $\text{C}_{30}\text{H}_{42}\text{O}_6$: C, 72.26; H, 8.49. Found: C, 72.33; H, 8.52.

3-[*sym*-(Methyl)dibenzo-16-crown-5-oxy]-1-propene (74).

Recrystallization from ethanol gave a 92% yield of a white solid with mp 93-94°; ir (deposit from dichloromethane solution on a sodium chloride plate): ν 1595 (C=C), 1125 (C-O) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 1.55 (s, 3H), 3.90-3.92 (m, 4H), 4.13-4.34 (m, 10H), 5.10-5.36 (m, 2H), 5.93-6.07 (m, 1H), 6.81-6.91 (m, 8H).

Anal. Calcd. for $\text{C}_{23}\text{H}_{28}\text{O}_6$: C, 68.98; H, 7.05. Found: C, 68.93; H, 7.00.

3-[*sym*-(Decyl)dibenzo-16-crown-5-oxy]-1-propene (75).

Column chromatography on silica gel with dichloromethane as eluent provided a colorless oil in 98% yield; ir (neat); ν 1596 (C=C), 1225, 1140 (C-O) cm^{-1} ; ^1H nmr (deuteriochloroform): δ 0.88-0.94 (t, 3H, $J = 6$ Hz), 1.15-1.58 (m, 16H), 1.90-2.02 (m, 2H), 5.13-5.42 (m, 2H), 5.88-6.05 (m, 1H), 6.82-7.06 (m, 8H).

Anal. Calcd. for $\text{C}_{32}\text{H}_{46}\text{O}_6$: C, 72.97; H, 8.80. Found: C, 72.99; H, 8.88.

General Procedure for the Preparation of Lariat Ether Alcohols 59-62.

To a solution of sodium borohydride (0.236 g, 6.24 mmoles) in 30 ml of tetrahydrofuran was added 2.50 g (6.24 mmoles) of the allyloxy lariat ether in 20 ml of dry tetrahydrofuran. Boron trifluoride etherate (0.77 ml, 6.24 mmoles) was added dropwise during a 20 minute period at 0°, followed by stirring for 10 hours at room temperature. To the reaction mixture were added dropwise 5 ml of 6*N* aqueous sodium hydroxide and 6 ml of 30% aqueous hydrogen peroxide at 0°. The reaction mixture was stirred for an additional 3 hours at room temperature and dichloromethane (30 ml) and water (20 ml) were added. The mixture was shaken and the organic layer was separated and washed with 5% aqueous sodium bicarbonate (3 x 30 ml), dried over magnesium sulfate, and evaporated *in vacuo*. Column chromatography of the residue on silica gel with dichloromethane as eluent provided the desired product as a colorless oil. Spectral and combustion analysis data for 59-62 are given in Table 6.

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