Syntheses of Monofunctional Derivatives of *m*-Phenylene-16-crown-5, Bis(*m*-phenylene)-32-crown-10, and *m*-Phenylene-*p*-phenylene-33-crown-10

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A series of monofunctional bis(*m*-phenylene)-32-crown-10 and *m*-phenylene-*p*-phenylene-33-crown-10 derivatives has been synthesized. Cyclization of *m*- and *p*-bis(*ω*-chlorotetraethyleneoxy)benzenes (**6**) with 5-substituted resorcinols **1** using pseudo-high dilution conditions in DMF and either CsF or K_2CO_3 as base afforded 5-carbomethoxy-1,3-phenylene-*m*-phenylene-32-crown-10 (**7a**, 46%), 5-carbomethoxy-1,3-phenylene-*p*-phenylene-33-crown-10 (**7b**, 48%), 5-(benzyloxy)-1,3-phenylene-*m*-phenylene-32-crown-10 (**11a**, 42%) and 5-(benzyloxy)-1,3-phenylene-*p*-phenylene-33-crown-10 (**11b**, 51%). Unsubstituted *m*-phenylene-*p*-phenylene-33-crown-10 (**15**) was also made (29%) in this way. Functional group conversions of the bis-phenylene macrocycles yielded 5-carboxy-1,3-phenylene-*m*-phenylene-32-crown-10 (**8a**), 5-(hydroxymethyl)-1,3-phenylene-*m*-phenylene-32-crown-10 (**9a**), 5-(bromomethyl)-1,3-phenylene-*m*-phenylene-32-crown-10 (**10a**), 5-hydroxy-1,3-phenylene-*m*-phenylene-32-crown-10 (**12a**), 5-hydroxy-1,3-phenylene-*p*-phenylene-33-crown-10 (**12b**), 5-(phthalimidomethyl)-1,3-phenylene-*m*-phenylene-32-crown-10 (**13a**), and 5-(aminomethyl)-1,3-phenylene-*m*-phenylene-32-crown-10 (**14a**). Similarly 5-carbomethoxy-1,3-phenylene-16-crown-5 (**4**) was transformed to the corresponding acid (**16**), hydroxymethyl (**17**), formyl (**18**), bromomethyl (**19**), phthalimidomethyl (**20**), azidomethyl (**21**), and aminomethyl (**22**) derivatives. These compounds are building blocks for supramolecular assemblies (as shown by the synthesis of a Schiff base (**23**) from **18** and a diester (**24**) from 4,4′-biphenol and **17**) and useful endcapping or pendant host components of macromolecules.

Introduction

Crown ethers are an interesting class of compounds[1,2] which have spawned the new area of supramolecular chemistry.[3] As a result, several interesting new classes of molecules including cryptands,[2,3] rotaxanes,[4,5] polyrotaxanes,[4,6] and catenanes[4a,5f,7] have been made. Crown ethers have also been incorporated into polymeric backbones to study complexation,[8] photoresponsive ion-conducting behavior,[9] transport of ions[10] and enantiomerically pure amino esters,[11] chiral recognition[12] , as liquid crystalline materials,[13] and as sensor elements in conducting polymers.[14]

We have previously synthesized a number of aliphatic crown ethers ranging from 21- to 60-membered rings.[15] It is well known that aliphatic crown ethers with approximately 30-membered rings complex two metal ions[16] and that phenylene crown ethers complex large organic dications at least in part by charge transfer interaction.[16b,17] These macrocycles have been shown to undergo threading with linear polymers to generate polyrotaxanes.[4,6] Recently we also incorporated difunctional bis(*m*-phenylene)-32-crown-10 moieties into poly-

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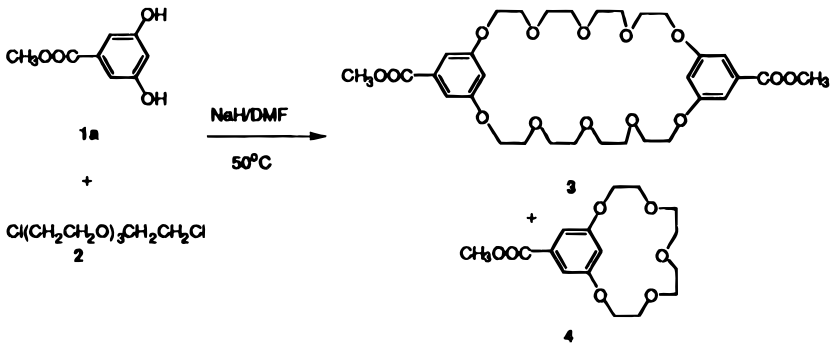
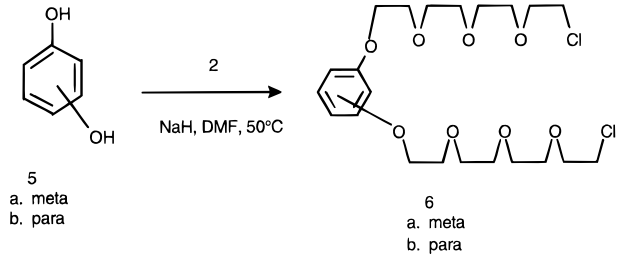
Scheme 1



meric backbones;[18,19] in the cases of polyamides,[18b] polyurethanes,[19a] and polyesters,[19b] this resulted in insoluble but swellable gels, i. e., physical cross-linking by rotaxane formation *via* self threading of the growing polymer chain through macrocycles which are part of the backbone.

Previously we reported a one-step procedure to synthesize several bis(*m*-phenylene) macrocyclic compounds.[18,20] Although this method was simple, it generally resulted in poor yields. One such reaction we reported earlier was between methyl 3,5-dihydroxybenzoate (**1a**) and tetra(ethylene glycol) dichloride (**2**) to give a 9% yield of the 2 + 2 product, 32-membered diester crown bis(5-carbomethoxy-1,3-phenylene-32-crown-10) (**3**), along with a 15% yield of the 1 + 1 product, 16-membered 5-carbomethoxy-1,3-phenylene-16-crown-5 (**4**) (Scheme 1).[18,20]

Scheme 2



We have now devised a general approach to bis-phenylene crown ethers *via* substituted 3,5-bis[ω-chloro-(oligoethyleneoxy)]benzenes.[21,22] This method allows one to tailor the ring size and number and type of functional groups by choice of the reactants for the cyclization process. Here we report the syntheses of such monosubstituted macrocycles via such a two-step method. In the first step a dichloride intermediate was prepared. Cyclization of the intermediate with a 5-substituted resorcinol produced the macrocycles. We also describe functional group conversions of 5-carbomethoxy-1,3-phenylene-16-crown-5 (**4**) and the bis-phenylene crown ethers to provide a range of building blocks for supramolecular chemistry. Of particular interest to us is their use in preparation of polymers with macrocyclic components as pendant or end groups and as building blocks for self assembled supramolecules.

Results and Discussion

A. Precursor Synthesis. The syntheses began with the preparation of the bis[ω-chlorotetra(ethyleneoxy)] derivatives **6** of resorcinol (**5a**) and hydroquinone (**5b**) as shown in Scheme 2. The dichlorides were produced in 62 and 60% yields, respectively. A four-step procedure from **5a** via synthesis (87%)[20c] and reaction of its bis-[hydroxyethoxy(ethoxy)] derivative with 2-[2′-chloroethoxy(ethoxy)]tetrahydropyran (95%), deprotection (92%), and treatment with $SOCl_2$ (85%) also gave **6a**, but the overall yield was only 64%.

B. Cyclization Reactions. In the second step the dichlorides were condensed with bis-phenols in the cyclization reaction. Scheme 3 shows the syntheses of

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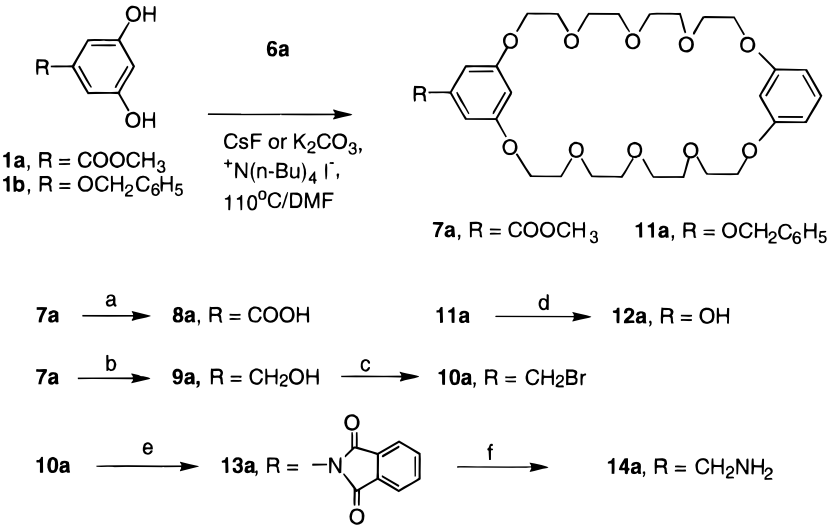
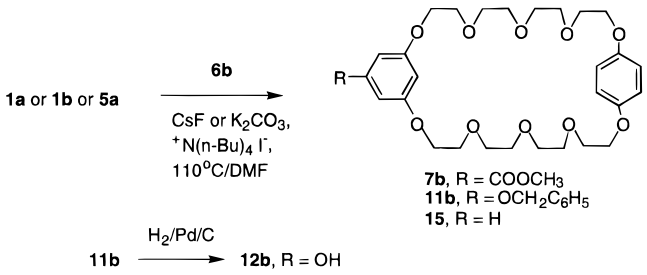
Scheme 3



a. NaOH/EtOH-H_2O. b. LAH/THF/25 °C. c. PBr_3/toluene-Et_2O. d. H_2/Pd/C.
e. K phthalimide/DMF/90°C. f. NH_2NH_2/MeOH/65°C.

Scheme 4

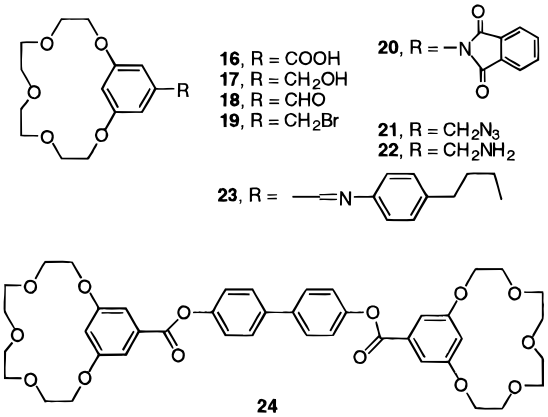


the mononfunctional bis(*m*-phenylene)-32-crown-10 derivatives by condensation of the dichloride **6a** with 5-substituted resorcinol derivatives **1a** and **1b**. The reaction utilized DMF as the solvent, tetra-*n*-butylammonium iodide (TBAI) as a phase transfer catalyst and either CsF or K_2CO_3 as the base; pseudo-high-dilution conditions were achieved by syringe pump addition of the two organic substrates. As in our previous work to produce difunctional derivatives,[21,22] these conditions produced ca. 50% yields of the carbomethoxy and benzyloxy compounds **7a** and **11a**.

Similarly, as shown in Scheme 4, reaction of the p-dichloride **6b** with methyl 3,5-dihydroxybenzoate (**1a**) produced (42%) the ester **7b** with one *m*-phenylene ring and one *p*-phenylene ring. Condensation of **1b** with **6b** yielded benzyl ether **11b** (51%). Reaction of **6b** with resorcinol (**5a**) afforded the unsubstituted *m*-phenylene-*p*-phenylene-33-crown-10 (**15**) in 29% yield.

C. Functional Group Transformations of Bis-phenylene Crown Ethers. Having successfully prepared a number of monofunctional bis-phenylene crown ethers, we were poised to make a number of useful derivatives by functional group conversions as shown in Schemes 3 and 4. The bis(*m*-phenylene) ester **7a** was hydrolyzed (79%) to the parent carboxylic acid **8a**. Ester **7a** was also subjected to reduction with lithium aluminum hydride (LAH) to afford the alcohol **9a** (92%). The alcohol **9a** was in turn converted in 92% yield to the benzylic bromide **10a** with PBr_3. The bromide **10a** was reacted with potassium phthalimide to produce the phthalimido derivative **13a** (92%). Reaction of **13a** with hydrazine afforded amine **14a** (100%). Benzyl ethers **11a** and **11b** were subjected to hydrogenolysis to afford the phenols **12a** and **12b** (92 and 85%, respectively).

D. Functional Group Conversions of 5-Carbomethoxy-1,3-phenylene-16-crown-5. We previously reported the hydrolysis of ester **4** to the parent carboxylic acid **16**.[23] In the current effort we carried out a number of functional group transformations to provide a spectrum of reactivity for inclusion in supramolecular assemblies. Ester **4** was reduced to alcohol **17** in 90% yield with LAH. Alcohol **17** was oxidized with PCC to aldehyde **18** in 85% yield. Alcohol **17** was also converted (82%) to the benzylic bromide **19**, which in turn by reaction with potassium phthalimide gave rise to the phthalimido derivative **20** (95%). Hydrazinolysis of **20** afforded (94%) the amino compound **22**. Bromide **19** also was reacted with NaN_3 to afford (98%) azide **21**, which could also be converted to the amine **22**. Condensation of amine **22** with *p*-*n*-butylaniline afforded an 86% yield of Schiff's base **23**, which we had hoped would show liquid crystalline behavior; however, **23** is not mesomorphic. For the same reason, the possible production of liquid crystalline crown ether derivatives, the diacid **16** was condensed with 4,4′-biphenol to form (80%) the diester **24**, which unfortunately did not show liquid crystalline characteristics.



Conclusions

We have prepared a number of monofunctional derivatives of bis(*m*-phenylene)-32-crown-10, *m*-phenylene-*p*-

phenylene-33-crown-10, and *m*-phenylene-16-crown-5. These compounds are useful host-type building blocks for self assembled structures. Our future publications will describe utilization of some of these hosts in supramolecular assemblies and as pendant or end groups on polymers of various chemical compositions and architectures.

Experimental Section

Materials. THF was distilled over Na/benzophenone. Otherwise, reagent grade reactants and solvents were used as received from chemical suppliers.

Measurements. Characterization techniques and instrumentation have been described.[21] Mass spectra (MS) were measured in house [low resolution (LR)], at the Washington University Mass Spectrometry Resource and at the Nebraska Center for Mass Spectrometry [LR and high resolution (HR)], typically by fast atom bombardment (FAB) using 3-nitrobenzyl alcohol matrices and other additives as specified; EI = electon impact.

m-Bis(11-chloro-3,6,9-trioxaundecyloxy)benzene (6a). NaH (9.35 g, 312 mmol, 80% in mineral oil) was added to a solution of **5a** (16.39 g, 149 mmol) in DMF (100 mL). The mixture was stirred for 3 h at 110 °C and cooled to room temperature (rt). At rt the suspension of dianion was added to a solution of **2**[1b] (344.2 g, 1488 mmol) in DMF (60 mL) over a period of 6 h, and then the mixture was stirred for 7 d at 50 °C, filtered to remove NaCl, and taken to dryness on a rotary evaporator. Excess **2** (270 mL) was removed via vacuum distillation (~125 °C/1.6 Torr). Continuous liquid−liquid extraction with petroleum ether gave 45.8 g (62%) of **6a**, an oil. IR (neat) 3070 (C=C−H), 2869 (CH), 1596 (C=C), 1121 (C−O−C). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.62 (t, J = 5.6 Hz, 4H), 3.69 (m, 12H), 3.74 (m, 8H), 3.85 (t, J = 4.8 Hz, 4H), 4.10 (t, J = 4.8 Hz, 4H), 6.49 (br s, 2H), 6.52 (t, J = 2.4 Hz, 1H), 7.16 (t, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 42.69, 67.32, 69.65, 70.575, 70.60, 70.64, 70.76, 71.29, 101.67, 106.96, 129.74, 159.88 (12 peaks as required). MS (FAB) m/z (rel int): 501.1 {[M(^{37}Cl^{35}Cl) + H]$^+$, 18%}, 499.1 {[M(^{35}Cl$_2$) + H]$^+$, 28%}, 463.2 [(M + H − Cl)$^+$, 2%], 375.1 [(M + H)$^+$ − $C_4H_8O_2$-Cl), 3%], 107 (100%); HRFAB: calcd for $C_{22}H_{37}O_8{}^{35}Cl_2$, [M + H]$^+$: 499.1865, found 499.1866 (error 0.1 ppm).

***p*-Bis(11-chloro-3,6,9-trioxa-1-undecyloxy)benzene (6b).** Application of the procedure above for **6a** using **5b** instead of **5a** gave 60% of **6b**, an oil. IR (neat): 2869 (CH), 1596 (C=C), 1121 (C−O−C). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.62 (t, J = 5.8 Hz, 4H), 3.69 (m, 12H), 3.76 (m, 8H), 3.83 (t, J = 4.8 Hz, 4H), 4.08 (t, J = 4.8 Hz, 4H), 6.84 (s, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm): 42.68, 67.97, 69.79, 70.57, 70.59, 70.63, 70.74, 71.28, 115.46, 153.01 (10 peaks as required). MS (FAB) m/z (rel int): 500.2 {[M(^{37}Cl^{35}Cl)]$^+$, 73%}, 498.2 {[M(^{35}Cl$_2$)]$^+$, 100%}, 436.2 (M$^+$ − C_2H_3Cl, 2%), 375.1 [(M$^+$ − $C_4H_8O_2Cl$), 3%]; HRFAB calcd for $C_{22}H_{36}O_8{}^{35}Cl_2$, (M)$^+$: 498.1787, found 498.1783 (error 0.8 ppm).

5-Carbomethoxy-1,3-phenylene-*m*-phenylene-32-crown-10 (7a). A solution of **6a** (17.35 g, 34.74 mmol) and **1a** (5.85 g, 34.8 mmol) in DMF (total volume = 50 mL) was added by syringe pump at a rate of 0.75 mL/h to a suspension containing CsF (53.75 g, 354 mmol) and TBAI (80 mg) in DMF (1650 mL) at 110 °C. After complete addition, the mixture was stirred at 110 °C for 5 d, cooled, taken to dryness, treated with dichloromethane (DCM), and filtered. Removal of DCM followed by flash column chromatography using Et_2O gave **7a** (9.42 g, 46%), mp 74.8−75.4 °C. IR: 2930 (CH), 1722 (C=O), 1596 (C=C), 1131 (C−O−C). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.70 (m, 16H), 3.84 (m, 8H), 3.88 (s, 3H), 4.06 (t, J = 4.8 Hz, 4H), 4.10 (J = 4.8 Hz, 4H), 6.47 (m, 2H), 6.49 (t, J = 2.4 Hz, 1H), 6.68 (t, J = 2.2 Hz, 1H), 7.11 (t, J = 8.4 Hz, 1H), 7.17 (d, J = 2.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 52.15, 67.27, 67.99, 69.52, 69.62, 71.00, 70.81, 70.84, 70.87, 101.62, 106.74, 106.99, 107.98, 129.70, 131.76, 159.71, 159.89, 166.71 (18 peaks as required). MS (FAB, LiI): m/z 735.3 [(M + Li + LiI)$^+$, 19%], 617.3 [(M + Na)$^+$, 6%], 601.4 [(M + Li)$^+$, 100%], 594.3 [(M + H)$^+$, 3%], 313.1 [(M + Li) − $C_{14}H_{19}O_6$)$^+$, 22%], 160.1 (40%). Anal. Calcd for $C_{30}H_{42}O_{12}$: C 60.58, H 7.12. Found: C 60.56, H 7.11.

5-Carbomethoxy-1,3-phenylene-*p*-phenylene-33-crown-10 (7b). Using the above procedure with **6b** and **1a** gave pure **7b** (42%), mp 76.9−77.6 °C. IR (KBr) cm^{-1}: 2950−2871 (CH), 1715 (C=O), 1602 (C=C), 1131 (C−O−C). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.69 (m, 16H), 3.82 (m, 8H) 3.89 (s, 3H), 4.04 (m, 8H), 6.63 (t, J = 2.4 Hz, 1H), 6.78 (s, 4H), 7.18 (d, J = 2.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 52.20, 67.80, 68.22, 69.54, 69.73, 70.80, 70.82, 70.86, 106.59, 107.96, 115.63, 131.81, 153.03, 159.77, 166.75 (15 peaks; theory 17). MS (FAB) m/z (rel int): 727.2 [(M − H + LiI)$^+$, 34%], 617.3 [(M + Na)$^+$, 9%], 594.3 (M$^+$, 15%), 563.3 [(M − OCH_3)$^+$, 3%], 286.0 (38%), 154.1 (100%). Anal. Calcd for $C_{32}H_{42}O_{12}$: C 60.58, H 7.12; found: C 60.55, H 7.10.

5-Carboxy-1,3-phenylene-*m*-phenylene-32-crown-10 (8a). A solution of NaOH (47 mL, 4 M) and **7a** (1.97 g, 3.32 mmol) in absolute EtOH (210 mL) was refluxed for 120 h, cooled to rt, acidified with aqueous HCl (4 M), evaporated to dryness, and diluted with $CHCl_3$ (50 mL). Filtration followed by evaporation gave **8a** (1.51 g, 79%), mp 62.7−63.5 °C. IR (neat) cm^{-1}: 3455−2439 (br, OH), 1715 (C=O), 1596 (C=C), 1131 (C−O−C). ^{1}H NMR $CDCl_3$ δ (ppm): 3.71 (m, 16H), 3.84 (m, 8H), 4.07 (J = 4.8 Hz, 4H), 4.10 (J = 4.8 Hz, 4H), 6.47 (d, J = 2.0 Hz, 1H), 6.49 (br s, 2H), 6.72 (t, J = 2.4 Hz, 1H), 7.11 (t, J = 8.4 Hz, 1H), 7.21 (d, J = 2.4 Hz, 1H). ^{13}H NMR $CDCl_3$ δ (ppm): 67.40, 67.78, 69.56, 69.63, 70.76, 70.795, 70.81, 70.84, 101.60, 107.05, 107.36, 108.50, 129.74, 131.12, 159.73, 159.88, 170.34 (17 peaks as required). MS (FAB, NaI) m/z (rel int): 775.1 [(M − H + 2Na + NaI)$^+$, 11%], 753.1 [(M + Na + NaI)$^+$, 26%], 625.2 [(M$^+$ − H + 2Na)$^+$, 100%], 603.2 [(M + Na)$^+$, 73%], 176.0 (57%). Anal. Calcd for $C_{29}H_{40}O_{12}\cdot H_2O$: C 58.18, H 7.07. Found: C 58.17, H 7.04.

5-(Hydroxymethyl)-1,3-phenylene-*m*-phenylene-32-crown-10 (9a). LAH (10.0 mL of 1.0 M THF solution, 10.0 mmol) was added to a solution of **7a** (10.17 g, 17.10 mmol) in anhydrous THF (600 mL). The mixture was stirred overnight. The unreacted LAH was destroyed using EtOAc. Addition of H_2O resulted in a cloudy suspension which became clear upon acidification with 10% HCl. The organic product was extracted with Et_2O (3 × 150 mL). The combined organic layer was evaporated to half its volume and decolorized using charcoal. Filtration followed by evaporation gave a light yellow oil which solidified upon standing. The crude material was recrystallized from EtOH to give pure **9a** (8.91 g, 92%), mp 88.2−89.6 °C. IR (KBr) cm^{-1}: 3448 (OH), 2917 (CH), 1596 (C=C), 1131 (C−O−C). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.26 (br s, 1H), 3.69 (m, 16H), 3.82 (m, 8H), 4.05 (m, 8H), 4.55 (s, 2H), 6.45 (m, 6H), 7.12 (t, J = 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ ppm: 65.17, 67.45, 67.60, 69.66, 69.68, 70.82, 100.86, 101.59, 105.47, 107.10, 129.74, 143.45, 159.91, 160.05 (14 peaks; theory 15). MS (FAB) m/z (rel int): 566.3 [M$^+$, 18%], 549.3 [(M − OH)$^+$, 23%)], 307.1 (12%), 154.0 (100%). Anal. Calcd for $C_{29}H_{42}O_{11}$: C 61.45, H 7.47. Found: C 61.59, H 7.42.

5-(Bromomethyl)-1,3-phenylene-*m*-phenylene-32-crown-10 (10a). A solution of 1.01 g (1.78 mmol) of **9a**, 2.7 mL (28 mmol) of PBr_3, 45 mL of Et_2O, and 140 mL toluene was stirred at rt for 18 h. The solvents were removed, and H_2O was added. The mixture was extracted with $CHCl_3$, and the extract was dried (Na_2SO_4) and evaporated to afford crude product. After silica gel chromatography with EtOAc, 920 mg (82%) of solid was obtained. Recrystallization from acetone-hexane yielded nearly colorless crystals, mp 63.7−65.4 °C; IR (KBr) cm^{-1}: no OH, 2944, 2877 (aliph C−H); 1596 (C=C), 1117 (C−O−C), 686 (1,3,5-subst phenyl); ^{1}H NMR ($CDCl_3$) δ (ppm): 3.69 (m, 16H), 3.83 (m, 8H), 4.06 (t, J = 4.8 Hz, 8H), 4.53 (s, 2H), 6.41 (t, J = 2.4 Hz, 1H), 6.4−6.6 (m, 5H), 7.13 (d of t, J = 8, 2 Hz, 1H). ^{1}H NMR (CD_3COCD_3) δ (ppm): 3.61 (m, 16H), 3.79 (m, 8H), 4.08 (t, J = 4.8 Hz, 8H), 4.37 (s, 2H), 6.49 (m, 4H), 6.61 (d, J = 2 Hz, 2H), 7.13 (sm, main J = 8, 1H). MS (FAB) m/z (rel int): 631.1 {[M(^{81}Br) + H]$^+$, 13%}, 629.1 {[M(^{79}Br) + H]$^+$, 14%}, 307.1 (18%), 154.0 (100%); HR FAB: calcd for $C_{29}H_{42}O_{10}{}^{79}Br$, [M(^{79}Br) + H]$^+$: 629.1913, found: 629.1971 (error 1.5 ppm).

(23) Nagvekar, D. S.; Delaviz, Y.; Prasad, A.; Merola, J. S.; Marand, H.; Gibson, H. W. *J. Org. Chem.* **1996**, *61*, 1211.

5-(Benzyloxy)-1,3-phenylene-*m*-phenylene-32-crown-10 (11a). Using the procedure given for the synthesis of **7a**, except using K_2CO_3 instead of CsF, reaction of **6a** and **1b**[24] gave **11a** (48%), an oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.70 (m, 16H), 3.83 (m, 8H), 4.03 (t, J = 4.8 Hz, 4H), 4.06 (t, J = 4.8 Hz, 4H), 4.98 (s, 2H), 6.11 (t, J = 2.2 Hz, 1H), 6.16 (d, J = 2.2 Hz, 2H), 6.49 (m, 3H), 7.12 (m, 1H), 7.37 (m, 5H). ^{13}C NMR ($CDCl_3$) δ (ppm): 67.46, 67.42, 68.13, 69.58, 69.66, 69.99, 70.79, 94.33, 94.61, 101.62, 107.12, 127.50, 127.92, 128.52, 129.74, 136.84, 159.93, 160.46, 160.54 (19 peaks; theory 20).

5-(Benzyloxy)-1,3-phenylene-*p*-phenylene-33-crown-10 (11b). Using the procedure given for the synthesis of **7a**, except using K_2CO_3 instead of CsF, reaction of **6b** and **1b**[24] gave **11b** (51%), an oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.69 (m, 16H), 3.81 (m, 8H), 4.01 (m, 8H), 4.98 (s, 2H), 6.07 (t, J = 2.2 Hz, 1H), 6.17 (d, J = 2.2 Hz, 2H), 6.79 (s, 4H), 7.40 (m, 5H). ^{13}C NMR ($CDCl_3$) δ (ppm): 67.49, 68.25, 69.60, 69.74, 70.00, 70.76, 70.80, 70.83, 94.21, 94.58, 115.68, 127.48, 127.92, 128.53, 136.84, 153.06, 160.48, 160.60 (18 peaks as required).

5-Hydroxy-1,3-phenylene-*m*-phenylene-32-crown-10 (12a). A solution of **11a** (4.20 g, 6.53 mmol) in 1:1 $CHCl_3$/MeOH (50 mL) was subjected to hydrogenolysis at 60 psi at rt with 10% Pd/C (100 mg) for 48 h, filtered, and taken to dryness under vacuum to give **12a** (3.29 g, 92%), a white solid, mp 103.1−105.0 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.69 (m, 16H), 3.77 (t, J = 4.8 Hz, 4H), 3.84 (t, J = 4.8 Hz, 4H), 4.02 (m, 8H), 6.02 (t, J = 2.2 Hz, 1H), 6.10 (d, J = 2.2 Hz, 2H), 6.46 (m, 3H), 7.10 (t, J = 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 67.22, 67.54, 69.63, 69.56, 70.60, 70.62, 70.67, 94.20, 95.57, 101.46, 107.08, 129.58, 157.99, 159.78, 160.48 (15 peaks as required). MS (FAB) m/z (rel int): 685.5 [(M − H + LiI)$^+$, 71%], 553.5 [(M + H)$^+$, 100%]. HRFAB: calcd for $C_{28}H_{41}O_{11}$, [M + H]$^+$: 553.2649, found 553.2663 (error 2.5 ppm). Anal. Calcd for $C_{28}H_{40}O_{11}$: C 60.84, H 7.30. Found: C 60.60, H 7.22.

5-Hydroxy-1,3-phenylene-*p*-phenylene-33-crown-10 (12b). Hydrogenolysis of **11b** as above for **12a** gave **12b** (85%), an oil. ^{1}H NMR (DMSO) δ (ppm): 3.55 (m, 16H), 3.69 (m, 8H), 3.93 (t, J = 4.4 Hz, 4H), 3.97 (t, J = 4.4 Hz, 4H), 5.93 (s, 3H), 6.78 (s, 4H), 9.41 (s, 1H). ^{13}C NMR (DMSO) δ (ppm): 67.01, 67.62, 68.91, 69.94, 69.99, 92.05, 94.56, 115.32, 152.46, 159.02, 160.32 (11 peaks; theory 13). MS (FAB) m/z (rel int): 575.3 [(M + Na)$^+$, 3%], 553.4 [(M + H)$^+$, 100%], 460.3 [(M − C_6H_4O)$^+$, 7%], 307.4 (87%), 133.0 (78%); MS (FAB, NaI) m/z (rel int): 725.5 [(M + Na + NaI)$^+$, 12%], 597.5 [(M − H + 2Na)$^+$, 20%], 575.5 [(M + Na)$^+$, 48%], 176.1 (100%); HRFAB: calcd for $C_{28}H_{41}O_{11}$, (M + H)$^+$: 553.2649, found: 553.2665 (error 2.9 ppm).

5-(Phthalimidomethyl)-1,3-phenylene-*m*-phenylene-32-crown-10 (13a). A solution of 780 mg (1.2 mmol) of **10a**, 243 mg (1.31 mmol) of potassium phthalimide, and 3.5 mL of DMF was held at 90 °C for 24 h, cooled, diluted with 50 mL of H_2O, and extracted with $CHCl_3$. The extract was washed with 0.1 N NaOH and evaporated to give a crude oil, which was passed through a short silica gel column with EtOAc to yield 790 mg (92%) of a colorless oil, **13a**. IR (KBr) cm^{-1}: 2778 (CH), 1769 and 1716 (C═O), 1596 (C═C), 1124 (C−O−C). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.69 (m, 16H), 3.81 (m, 8H), 4.04 (m, 8H), 4.73 (s, 2H), 6.3−6.6 (m, 6H), 7.09 (d of t, J = 8, 2 Hz, 1H), 7.77 (A_2B_2 m, 4H). MS (FAB) m/z (rel int): 868.2 [(M + Na + NaI)$^+$, 25%], 718.3 [(M + Na)$^+$, 68%], 550.7 [(M + H − phthalimido)$^+$, 6%], 325.9 (28%), 176 (100%); HR FAB: calcd for $C_{37}H_{45}NO_{12}Na$, (M + Na)$^+$: 718.2839; found: 718.2850 (error 1.5 ppm).

5-(Aminomethyl)-1,3-phenylene-*m*-phenylene-32-crown-10 (14a). A solution of 410 mg (0.59 mmol) of **13a**, 0.40 mL (8.2 mmol) of hydrazine monohydrate, and 3.0 mL of MeOH was refluxed 18 h, cooled, concentrated by rotary evaporation, and diluted with 4.0 mL of concd HCl. The mixture was boiled for 6 h, cooled, diluted with H_2O, and filtered. The solid was washed with H_2O (2 × 5 mL). The filtrate was neutralized with 2 N NaOH and extracted with DCM (3 × 20 mL). After drying (Na_2SO_4), DCM removal and vacuum drying produced 330 mg (100%) of a nearly colorless oil; IR (KBr) cm^{-1}: 3350, 3300 (b, NH_2), 2900 (CH), 1596 (C═C), 1124 (C−O−C). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.25 (br s, 2H), 3.7 (m, 18H), 3.83 (t, J = 4.6 Hz, 8H), 4.06 (m, 8H), 6.36 (m, 1 H), 6.45−6.55 (m, 6H), 7.12 (t, J = 8 Hz, 1H). MS (FAB) m/z (rel int): 566.4 [(M + H)$^+$, 100%], 549.3 [(M − NH_2)$^+$, 14%]; HR FAB: calcd for $C_{29}H_{44}NO_{10}$, (M + H)$^+$: 566.2965, found: 566.2958 (error 1.2 ppm).

***m*-Phenylene-*p*-phenylene-33-crown-10 (15).** Using the procedure given for the synthesis of **7a**, reaction **6a** and **5b** gave pure **15** (29%), an oil; lit.[5f] reported as an oil. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.69 (m, 16H), 3.82 (m, 8H), 4.03 (t, J = 4.8 Hz, 8H), 6.45 (t, J = 2.4 Hz, 1H), 6.50 (dd, J = 8.4 and 2.4 Hz, 2H), 6.79 (s, 4H), 7.13 (t, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 67.44, 68.24, 69.66, 69.74, 70.79, 70.82, 101.49, 107.03, 115.68, 129.76, 153.04, 159.98 (12 peaks; theory 13). MS (FAB) m/z (rel int): 709.1 [(M + Na + NaI)$^+$, 13%], 559.2 [(M + Na)$^+$, 100%], 132.9 (51%); HR FAB: calcd for $C_{28}H_{40}O_{10}$-Na, (M + Na)$^+$: 559.2519, found: 559.2511 (error 1.4 ppm).

5-(Hydroxymethyl)-1,3-phenylene-16-crown-5 (17). Application of the procedure described for **9a** to **4**[18,20] gave a solid (90%), mp 82.3−83.4 °C. IR (KBr) cm^{-1}: 3490 (OH), 2895 (CH), 1596 (C═C), 1171 (COC). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.62 (A_2B_2 m, 8H), 3.78 (t, J = 4.7 Hz, 4H), 4.28 (t, J = 4.7 Hz, 4H), 4.57 (s, 2H), 6.54 (d, J = 2.2 Hz, 2H), 7.02 (t, J = 2.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 64.79, 68.63, 70.23, 70.48, 70.61, 102.66, 108.28, 142.98, 160.22 (9 peaks; theory 9). MS (EI) m/z (rel int): 298.1 [(M)$^+$, 8%], 211.1 [(M + H − 2CH_2-CH_2O)$^+$, 5%], 166.1[(M − 3CH_2CH_2O)$^+$, 20%], 137.1 [(M + H − CH_2CH_2O − CO)$^+$, 30%], 140.0 [($C_7H_8O_3$)$^+$, 41%], 69.1 (100%); HR EI, calcd for $C_{15}H_{22}O_6$, (M)$^+$: 298.1416; found: 298.1429 (error 2.4 ppm).

5-Formyl-1,3-phenylene-16-crown-5 (18). To a solution of 2.01 g (6.78 mmol) of **17** in 100 mL of DCM was added 1.72 g (7.98 mmol) of PCC, and the mixture was stirred at rt for 2 h and then filtered; the inorganic solid was washed with DCM, and the organic phases were combined and evaporated to give the crude product. Silica gel chromatography with EtOAc gave a light yellow oil, which was recrystallized from acetone to afford 1.70 g (85%) of pure **18**, mp 75.8−76.5 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.58 (m, 4H), 3.66 (m, 4H), 3.81 (t, J = 4.4 Hz, 4H), 4.34 (t, J = 4.4 Hz, 4H), 7.03 (d, J = 2.0 Hz, 2H), 7.39 (t, J = 2.0 Hz, 1H) and 9.88 (s, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 68.94, 70.31, 70.674, 110.30, 110.86, 137.95, 160.75 and 191.95 (8 peaks, theory 9). MS (FAB) m/z (rel int): 429.2 [(M − H + LiI)$^+$, 8%], 297.3 [(M + H)$^+$, 100%], 253.2 [(M + H − CH_2CH_2O)$^+$, 5%], 209.2 [(M + H − 2CH_2CH_2O)$^+$, 9%], 165.1 [(M + H − 3 CH_2CH_2O)$^+$, 19%], 137.1 [(M + H − CH_2CH_2O − CO)$^+$, 30%]; HR FAB, calcd for $C_{15}H_{21}O_6$, (M + H)$^+$: 297.1338; found: 297.1336 (error 0.7 ppm).

5-(Bromomethyl)-1,3-phenylene-16-crown-5 (19). Application of the procedure described for **10a** to **17** gave **19** (82%), mp 77.4−78.0 °C. IR (KBr) cm^{-1}: 2944, 2877 (CH), 1596 (C═C), 1171 (COC), 686 (C−Br). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.63 (A_2B_2 m, 8H), 3.79 (t, J = 4.7 Hz, 4H), 4.29 (t, J = 4.7 Hz, 4H), 4.38 (s, 2H), 6.56 (d, J = 2.2 Hz, 2H), 7.06 (t, J = 2.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 33.42, 68.83, 70.36, 70.65, 70.76, 103.64, 110.72, 139.16, 160.36 (9 peaks; theory 9). MS (HR EI) m/z (rel int): calcd for $C_{15}H_{21}{}^{81}BrO_5$, (M)$^+$: 362.0552; for $C_{15}H_{21}{}^{79}BrO_5$, (M)$^+$: 360.0572; found: 362.0548 (13%, error 1.6 ppm), 360.0552 (14%, error 5.8 ppm), 281.1382 [(M − Br)$^+$, 33%, error 2.5 ppm], 149 (28%), 121 (15%), 77 (34%), 45.0 (100%).

5-(Phthalimidomethyl)-1,3-phenylene-16-crown-5 (20). Application of the procedure described for **13a** to **19** afforded pure **20** (95%), mp 130−131 °C. IR (KBr) cm^{-1}: 2880 (C−H), 1769, 1769, 1709 (C═O), 1609 (C═C), 1131 (COC). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.61 (A_2B_2 m, 8H), 3.76 (t, J = 4.7 Hz, 4H), 4.26 (t, J = 4.7 Hz, 4H), 4.74 (s, 2H), 6.56 (d, J = 2.2 Hz, 2H), 7.01 (t, J = 2.2 Hz, 1H), 7.77 (A_2B_2 m, 4H). MS (FAB, NaI) m/z (rel int): 600.0 [(M + Na + NaI)$^+$, 2%], 450.1 [(M + Na)$^+$, 100%]; HR FAB: calcd for $C_{23}H_{25}NO_7Na$, (M + Na)$^+$: 450.1529; found: 450.1515 (error 3.1 ppm).

5-(Azidomethyl)-1,3-phenylene-16-crown-5 (21). A mixture of 1.43 g (3.96 mmol) of **19**, 310 mg (4.77 mmol) of NaN_3, and 20 mL of DMF was heated at 60 °C for 20 h, cooled, poured into 75 mL of H_2O, and extracted with DCM (3 × 50 mL). The extract was washed with H_2O (2 × 50 mL) and saturated NaCl, dried (Na_2SO_4), and evaporated to give the crude product,

(24) Nagvekar, D. S.; Gibson, H. W. *Org. Prep. Proced. Int.* **1997**, *29*, 240.

which was passed through a short silica gel column with Et_2O, to give pure **21**, a colorless oil, 1.25 g (98%). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.63 (A_2B_2 m, 8H), 3.80 (t, J = 4.7 Hz, 4H), 4.22 (s, 2H), 4.30 (t, J = 4.7 Hz, 4H), 6.49 (d, J = 2.4 Hz, 2H), 7.08 (t, J = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 54.58, 68.75, 70.32, 70.62, 70.76, 103.24, 109.74, 137.01, 160.52 (9 peaks as required). MS (FAB, Gly) m/z (rel int): 323 (M^+, 18%), 281 [$(M - N_3)^+$, 22%], 219 [$(M - O(CH_2CH_2O)_2)^+$, 10%], 154 (93%), 136 (100%).

5-(Aminomethyl)-1,3-phenylene-16-crown-5 (22). Application of the procedure described for **14a** to **20** afforded (94%) a dark brown oil. Elution through a short silica gel column first with EtOAc and then again with EtOH gave the pure amine **22**, a light brown oil (62%). IR (smear) cm^{-1}: 3360 (NH), 2864 (CH), 1696 (C=C), 1158, 1065 (COC). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.63 (A_2B_2 m, 8H), 3.77 (s, 2H), 3.79 (t, J = 5.0 Hz, 4H), 4.29 (t, J = 5.0 Hz, 4H), 6.51 (d, J = 2.2 Hz, 2H), 6.99 (t, J = 2.2 Hz, 1H). MS (FAB, NaI) m/z (rel int): 576.2 {$[(M - NH_2)\cdot(M - 2H)]^+$, 100%}, 296.2 ($M^+$, 9%), 294.2 [$(M - 2H)^+$, 9%], 281.1 [$(M - NH_2)^+$, 13%], 136.0 [$(M - (CH_2CH_2O)_3CH_2CH_2)^+$, 14%]; HR FAB, calcd for $C_{30}H_{42}NO_{10}$, $[(M - NH_2)\cdot(M - 2H)]^+$: 576.2810; found: 576.2792 (error 3.5 ppm).

5-[[(*p*-*n*-Butylphenyl)imino]methyl]-1,3-phenylene-16-crown-5 (23). A solution of 507 mg (1.71 mmol) of **18**, 282 mg (1.89 mmol) of *p*-*n*-butylaniline, 1 drop of HOAc, and 10 mL of EtOH was heated under reflux in the presence of molecular seives for 24 h, filtered, and concentrated to give a yellow oil. Trituration with hexane−acetone gave a solid which was recrystallized twice from acetone−hexane, 600 mg (86%) of yellow needles, mp 65.1−66.9 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.93 (t, J = 7.2 Hz, 3H), 1.37 (m, 2H), 1.61 (m, 2H), 2.63 (t, J = 7.6 Hz), 3.7 (m, 8H), 3.83 (t, J = 4.6 Hz, 4H), 4.06 (m, 4H), 7.09 (d, J = 2 Hz, 2H), 7.16−7.26 (m, 5H), 8.47 (s, 1H). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.16, 22.89, 34.52, 35.67, 69.52, 71.06, 71.42, 71.48, 107.18, 110.53, 121.68, 129.87, 139.06, 141.47, 150.45, 159.97, 161.57 (17 peaks; theory 18). MS (FAB) m/z (rel int): 428.4 [$(M + H)^+$, 100%], 412.4 [$(M + H - CH_3)^+$, 6.2%], 398.4 [$(M + H - CH_2CH_3)^+$, 15%], 384.4 [$(M + H - CH_2CH_2CH_3)^+$, 22%]; HR FAB, calcd for $C_{25}H_{34}NO_5$, $(M + H)^+$: 428.2437; found: 428.2436 (error 0.2 ppm).

4,4′-Biphenol Diester (24) of 5-Carboxy-1,3-phenylene-16-crown-5. A mixture of 627 mg (2.00 mmol) of **16**, 186 mg (1.00 mmol) of 4,4′-biphenol, 2.53 g (12.3 mmol) of DCC, 50 mg of DMAP, and 50 mL of $CHCl_3$ was refluxed for 2 d, cooled, and filtered. After concentration of the filtrate, more dicyclohexylurea was collected. The residual oil was subjected to silica gel column chromatography to yield a colorless solid that was recrystallized twice from EtOH, 0.62 g (80%), mp 188.8−191.5 °C. NMR ($CDCl_3$) δ (ppm): 3.61 (m, 8H), 3.68 (m, 8H), 3.83 (t, J = 4.8 Hz, 8H), 4.36 (t, J = 4.8 Hz, 8H), 7.28 (t, J = 8.8 Hz, 4H), 7.39 (d, J = 2.2 Hz, 4H), 7.41 (t, J = 2.2 Hz, 2H), 7.63 (t, J = 8.8 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm): 69.04, 70.36, 70.69, 70.72, 109.63, 111.69, 121.99, 128.17, 130.79, 138.15, 150.43, 160.29, 164.90 (13 peaks as required); MS (FAB, NaI) m/z (rel int): 775.7 [$(M + H)^+$, 2%], 295.3 [$(M - C_{27}H_{27}O_8)^+$, 62%], 184.3 [$(C_6H_4C_6H_4)^+$, 75%], 154.1 (79%), 93.1 (100%); HR FAB, calcd for $C_{42}H_{47}O_{14}$, $(M + H)^+$: 775.2966; found: 775.2950 (error 2.0 ppm).

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Supporting Information Available: ^{1}H NMR spectra for **6b** (270 MHz), **10a** (270 MHz), **11a** (400 MHz), **13a** (270 MHz), **14a** (270 MHz), **20** (270 MHz), and **22** (270 MHz), and 100 MHz ^{13}C NMR spectra for **6a**, **11b**, **12b**, **17**, **18**, **19**, **21**, **23**, and **24** (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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