Selective Arylation of Diols Using Arene–Iron Chemistry

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Chloroarene–metal complexes are attracting attention in many facets of polymer and materials chemistry, including the synthesis of metal-containing polymers[1] and oligomers,[2] the use of the organometallic moiety as a temporary solubilizing agent for the synthesis of higher molecular weight polymers than are otherwise possible,[3] the synthesis of monomers that are not accessible by traditional organic methods,[4] and the synthesis of bridged bimetallic complexes, with a variety (diphenol, dithiol, diamine) of bridging groups.[2a,5] One category of bridging groups that is absent from this list is aliphatic diols. Abd-El-Aziz has recently reported difficulty in effecting nucleophilic displacement of chloride from chloroarene–FeCp complexes with ROH under his standard reaction conditions (K_2CO_3, THF/DMF reflux).[5] There are only a few examples of the use of alkoxide nucleophiles with these complexes.[4b,6]

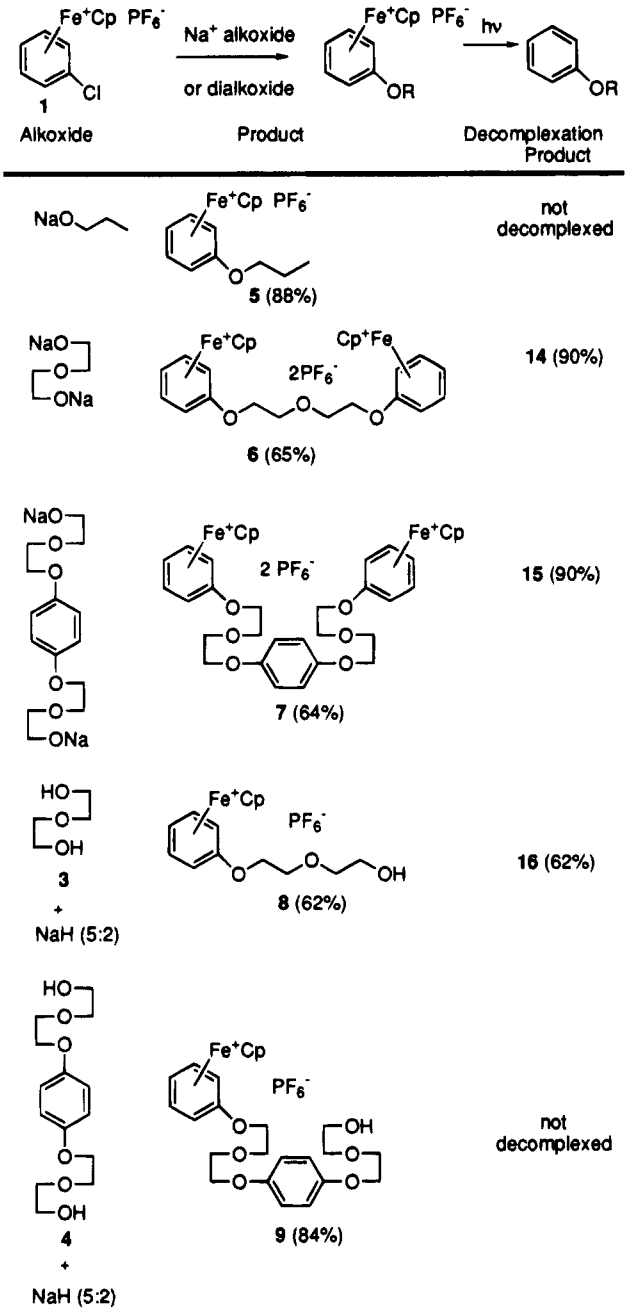
Selective functionalization at only one end of an α,ω-dinucleophile generally requires a large excess of the dinucleophile in order to avoid the formation of a mixture of all possible products. In connection with our recent studies on the applications of arene–iron complexes to polymer and materials chemistry, we have had occasion to explore the reactivity of η^6-mono- and 1,3-dichlorobenzene(cyclopentadienyl)iron(II) hexafluorophosphate (**1**, **2**) with diethylene glycol (**3**) and 1,4-bis((hydroxyethoxy)-ethoxy)benzene[7] (**4**), and we report herein our solutions to the problem of obtaining efficient displacement of chloride with alkoxide nucleophiles, as well as conditions for controlling the selectivity of the nucleophilic displacement reactions at the arene and for obtaining some control over the formation of either a mono- or diarylated derivative.

Results and Discussion

Reaction of complex **1** with 1 equiv of sodium *n*-propoxide in THF at room temperature for 2 h gave an 83% yield of the *n*-propyl ether complex **5**. Encouraged by this result, we proceeded to examine diarylation of **3** with **1**. Formation of the disodium salt at room temperature, followed by addition of 2 equiv of the complex, gave the diarylated species **6** in 65% yield, uncontaminated by the monoarylated species. Diarylation of **4** with **1** proceeded similarly and in 64% yield to give **7**. Monoarylation of these diols with **1** was accomplished under similar conditions, using an excess of the diol (2–4 equiv) to give **8** and **9** in 60 and 84% yields, respectively (Scheme 1).

The use of complex **2** requires several modifications to the above conditions. Specifically, conditions must be obtained which avoid a second nucleophilic displacement at the arene, and polymerizations must be suppressed. Therefore, it was necessary to determine conditions which were as nearly stoichiometric as possible, thereby allowing us to take advantage of the chemoselective nucleophilic displacement obtainable in the dichlorobenzene complexes by appropriate temperature manipulation.[4,8]

Scheme 1



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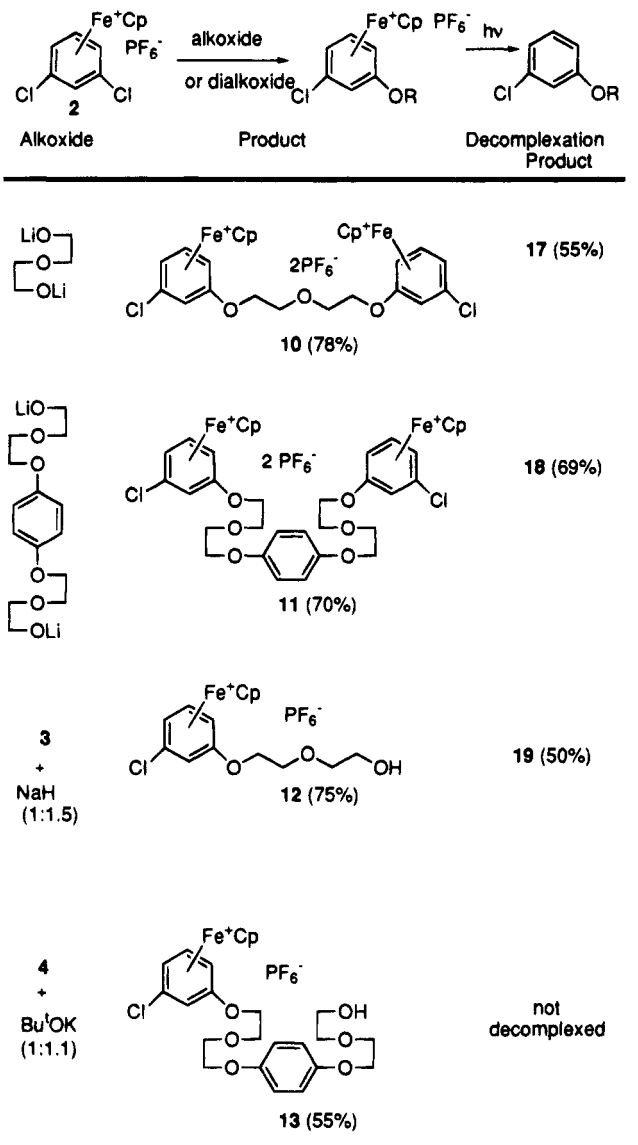
Scheme 2



Unlike the syntheses of **6** and **7**, the diarylation reactions of **3** and **4** with **2** (Scheme 2) were not straightforward. At the temperatures required to maintain control of substitution at the complex, neither the disodium alkoxides of **3** and **4** nor the corresponding monoarylated monosodium alkoxides were sufficiently soluble in THF, dioxane, or 1,2-dimethoxyethane to allow the reaction to reach completion. Phase-transfer catalysis with tetrabutylammonium bromide has previously been used with arene–chromium complexes to solve this problem;[9] however, it was unsuccessful in this case; likewise, 18-crown-6 was employed to no avail. Though the problem could be partially solved by the use of an excess of **2**, the unreacted complex was difficult to remove and the pure diarylated diol could not be isolated. It was eventually found that the dilithium alkoxides of **3** and **4** were sufficiently soluble in THF at room temperature, and their reactivity was adequately attenuated to permit nearly complete diarylation of the diol with *mono*substitution at the complex to give **10** and **11** in 74 and 81% yields, respectively.

Surprisingly, we were also able to obtain reasonable chemoselectivity for *mono*arylation of these diols with complex **2**, without employing an excess of the diol. The choice of base and reaction temperatures critically depends on the diol under consideration. For example, optimum conditions for monoarylation of **3** with **2** required 1.5 equiv of sodium hydride and a reaction temperature of −45 °C for 6 h. This gave a mixture of the monoarylated and diarylated diols **12** and **10** in an 11:1 ratio in the crude reaction mixture (obtained by integration of the signals of the cyclopentadienyl protons in the ^{1}H NMR). Reprecipitation of the product by addition of a concentrated CH_2Cl_2 solution of this mixture into hexane, in order to remove traces of unreacted **3**, also resulted in the loss of small amounts of **12**. After this purification, the ratio of **12** to **10** was *ca.* 9:1. In contrast, the lithium alkoxide would not react appreciably at lower temperatures and, when run at room temperature, gave a statistical mixture of products. The potassium alkoxide gave a 4:1 ratio of **12:10**.

While the sodium alkoxide of **3** can be monoarylated at temperatures as low as −55 °C, the corresponding reaction with **4** does not occur below −30 °C. The reaction proceeds much more cleanly with the potassium alkoxide to give **13** along with a small amount of **11** (*ca.* 8:1 by ^{1}H NMR). The reaction mixture employing the potassium alkoxide takes on a very intense green color as the reaction progresses, which does not occur with either the lithium or sodium alkoxides (Scheme 2).

We attribute the selectivity to a combination of two effects. First, monoarylated monosodium salts are rather insoluble at low temperatures; thus, diarylation occurs more slowly. Also, there is a possibility that the sodium alkoxide can be sequestered and coordinated by the remainder of the polyether chain.[10] At the low reaction temperatures, there may not be a great deal of "uncoiling" of the polyether chain; thus, the second alkoxide would be less accessible to the arene–iron complex. This could explain why reaction with **4** requires a higher temperature and proceeds more rapidly with a larger cation, such as potassium, which is not completely engulfed by the polyether residue, but is hindered enough to diminish the reactivity of the second alkoxide. With the shorter diol, **3**, the potassium alkoxide may be inadequately sequestered due to the smaller polyether chain. This would result in lower selectivity. The smaller sodium alkoxide is of appropriate size to be adequately, but not prohibitively, hindered by the smaller polyether residue of **3**. It is reasonable to expect that modest excess of the diol in question, in combination with these effects, would lead to still better product ratios.

With the exceptions of **5**, **9**, and **13**, all complexes were photolytically demetalated to give the liberated organic ligands **14**–**19** in 50–90% yields after chromatography. In cases where the mixtures of product complexes cannot be separated without considerable loss, the demetalation products can be rigorously purified.

Conclusions

We have illustrated methods for diarylation of polyether diols using arene–iron chemistry. Likewise, we have shown that it is possible to obtain monoarylated

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derivatives with some selectivity, which is not well understood but may be the result of solubility effects and/or equilibrium conformations in which the metal alkoxide is sequestered by polyether residue and is therefore less nucleophilic. This has allowed us to determine conditions for doubly selective reactions, incorporating monoarylation of a diol and monosubstitution at the complex.

Experimental Section

General. For general methods, see ref 8b. Complexes **1** and **2** were prepared using the general methods described in ref 4b. Diol **4** was prepared according to the procedure in ref 7. Yields of the major products are calculated based upon ^{1}H NMR ratios of the Cp signals, if they are well enough resolved. In other cases, the signals of the methylene proximate to the arene were used. Proton and ^{13}C NMR spectra were obtained on a Varian Gemini spectrometer, at 300 and 75 MHz, respectively. For decomplexations, yields are calculated based upon the amount of the actual precursor present in the mixture. For mixtures of mono- and bimetallic complexes, separation is very difficult and purification is postponed until the decompexation step; because of this, the complexes were not subjected to elemental analysis.

Arylation of *n*-Propanol with 1 (Compound 5). A 50 mg sample of **1** (0.13 mmol) was stirred in THF (3 mL). To this was added 1.4 mL of a 1.0 M solution of sodium *n*-propoxide in THF. The mixture was stirred for 2 h, filtered through Celite, washed through with CH_2Cl_2, and concentrated to <1 mL by rotary evaporation. This solution was added dropwise to ether, the precipitate was allowed to settle out, the solvent was decanted, and the product washed with ether and dried under vacuum to give a yellow oil in 88% yield; ^{1}H NMR (δ) 6.30 (5H, m), 5.17 (5H, s), 4.26 (2H, t, J = 6.5 Hz), 1.85 (2H, apparent hex, J = 7.0 Hz), 1.06 (3H, t, J = 7.5 Hz); ^{13}C NMR (δ) 87.6, 84.8, 77.3, 75.4, 72.0, 22.8, 10.4; the quaternary carbon was not detected.

Diarylation of Diethylene Glycol with 1 (Compound 6). Diethylene glycol (56 mg, 0.53 mmol) was stirred with NaH (26 mg, 1.08 mmol) in THF (2 mL). Complex **1** (400 mg, 1.06 mmol) was dissolved in a minimum (10 mL) of hot THF and added to the mixture via a pressure-equalizing dropping funnel. The reaction was allowed to proceed at rt for 4 h, filtered through Celite, and washed through with CH_2Cl_2. The combined filtrate and washings were concentrated to <5 mL by rotary evaporation and added dropwise to ether. The precipitate was allowed to settle out, the solvent was decanted, and the precipitate was rinsed with ether and dried *in vacuo* to give the product as a golden oil in 65% yield; ^{1}H NMR (δ) 6.45–6.05 (10H, m), 5.18 (10H, s), 4.54 (4H, dd, J = 4.3, 2.8 Hz), 4.03 (4H, dd, J = 4.3, 2.8 Hz); ^{13}C NMR (δ) 134.8, 87.5, 85.0, 77.4, 75.8, 70.2, 69.9.

Diarylation of 1,4-Bis((hydroxyethoxy)ethoxy)benzene with 1 (Compound 7). The procedure was as for compound **6**, and the product was obtained in 64% yield; ^{1}H NMR (δ) 6.87 (4H, s), 6.36 (8H, m), 6.18 (2H, m), 5.14 (10H, s), 4.46 (4H, t, J = 4.2 Hz), 4.12 (4H, t, J = 4.3 Hz), 3.95 (4H, t, J = 4.2 Hz), 3.89 (4H, t, J = 4.3 Hz); ^{13}C NMR (δ) 153.9, 134.9, 116.3, 87.5, 84.9, 77.4, 75.9, 70.6, 70.4, 69.8, 68.8.

Monoarylation of Diethylene Glycol with 1 (Compound 8). Diethylene glycol (49 mg, 47 μL, 0.5 mmol) was stirred in THF (2 mL) with NaH (8 mg of a 60% dispersion, 0.2 mmol) for 15 min. THF (3 mL), containing **1** (38 mg, 0.1 mmol), was then added from a dropping funnel. The reaction was stirred for 4 h and worked up in the usual way to give a mixture of mono- and diarylated diethylene glycol in a 10:1 ratio (by NMR integrations of Cp signals) corresponding to a 62% yield of **8**; ^{1}H NMR (δ) 6.45–6.35 (4H, m), 6.25–6.17 (1H, m), 5.18 (5H, s), 4.46 (2H, t, J = 3.9 Hz), 3.90 (2H, t, J = 3.9 Hz), 3.66 (4H, m); ^{13}C NMR (δ) 135.4, 87.5, 84.9, 77.4, 75.9, 73.7, 70.4, 69.7, 61.8.

Monoarylation of 1,4-Bis((hydroxyethoxy)ethoxy)benzene with 1 (Compound 9). The procedure was as for compound **8**, giving the product in 84% yield; ^{1}H NMR (δ) 6.97 (4H, s), 6.36 (1H, m), 6.25 (1H, m), 5.15 (5H, s), 4.47 (2H, t, J = 4.2 Hz), 4.11 (2H, t, J = 6.1 Hz), 4.05 (2H, t, J = 5.4 Hz), 3.93 (2H, t, J = 5.4 Hz), 3.90 (2H, t, J = 6.1 Hz), 3.78 (2H, t, J = 4.2 Hz), 3.63 (2H, t, J = 4.0 Hz), 3.60 (2H, t, J = 4.0 Hz), 3.24 (1H, br s); ^{13}C NMR (δ) 154.0, 153.9, 134.9, 116.3, 116.2, 87.5, 84.9, 77.3, 75.8, 73.5, 70.6, 70.4, 70.3, 69.8, 68.8, 61.9; IR (cm^{-1}) 3538 (OH), 1636, 1509 (Ar).

Diarylation of Diethylene Glycol with 2 (Compound 10). Diethylene glycol (9.5 μL, 0.1 mmol) and *n*-butyllithium (110 μL of a 2.0 M solution in pentane) were stirred in THF (5 mL). After 10 min, the complex **2** (82 mg, 0.2 mmol) was added from a solids addition tube. The reaction was stirred for 8 h, filtered through Celite, and washed through with CH_2Cl_2. The workup was as usual, giving 73 mg of a gold-brown solid that was a 6:1 mixture of monoarylated to diarylated diethylene glycol (by ratios of Cp signals) in 78% of the theoretical yield for **10**; ^{1}H NMR (δ) 6.86 (2H, s), 6.62 (2H, d, J = 6.4 Hz), 6.53 (2H, t, J = 6.4 Hz), 6.44 (2H, d, J = 6.4 Hz), 5.29 (10 H, s), 4.61 (4H, t, J = 5.4 Hz); 4.07 (4H, t, J = 5.4 Hz); ^{13}C NMR (δ) 134.9, 107.0, 86.9, 85.6, 79.8, 77.1, 75.0, 71.1, 69.9.

Diarylation of 1,4-Bis((hydroxyethoxy)ethoxy)benzene with 2 (Compound 11). The procedure was analogous to that for **10** and gave a 5:1 mixture of **11** to **13** (by ratios of the ω-methylene signal of **13** to the average of the individual methylene signals from **11**) in 70% yield of **11**; ^{1}H NMR (δ) 6.87 (10H, s), 6.86 (2H, d, J = 6.3 Hz), 6.53 (2H, t, J = 6.3 Hz), 6.48 (2H, d, J = 6.3 Hz), 5.27 (10H, s), 4.56 (4H, t, J = 4.2 Hz), 4.12 (4H, t, J = 4.2 Hz), 3.98 (4H, t, J = 4.2 Hz), 3.94 (4H, t, J = 4.2 Hz); ^{13}C NMR (δ) 154.0, 134.9, 116.3, 107.0, 86.9, 85.5, 79.8, 77.3, 75.0, 71.3, 70.7, 69.9, 68.8.

Monoarylation of Diethylene Glycol with 2 (Compound 12). Diethylene glycol (19 μL, 0.2 mmol) and sodium hydride (0.3 mmol, 12 mg of a 60% dispersion in mineral oil) were stirred in THF (5 mL) at room temperature and then at −45 °C. Complex **2** (82 mg, 0.2 mmol) was added from a solids addition tube. The reaction was allowed to proceed for 3 h, quenched with water (50 μL), and worked up as usual. Proton NMR analysis of this crude mixture indicated an 11:1 ratio of mono- to diarylated products (by ratios of the Cp signals), together with traces of unreacted **3**. This mixture was dissolved in a minimum of CH_2Cl_2, and the product was precipitated by addition of hexane. The solvent was decanted, and the solid washed with ether and dried under vacuum to give 86 mg of a golden oil consisting of a 9:1 mixture of **12** and **10** in 75% of the theoretical yield of **12**; ^{1}H NMR (δ) 6.85 (1H, s), 6.58 (1H, d, J = 6.3 Hz), 6.49 (1H, t, J = 6.3 Hz), 6.44 (1H, d, J = 6.3 Hz), 5.32 (5H, s), 4.52 (2H, t, J = 3.3 Hz), 3.91 (2H, apparent t, J = 4.3 Hz), 3.75–3.65 (4H, m); ^{13}C NMR (δ) 135.1, 107.0, 86.8, 85.5, 79.8, 77.3, 75.0, 73.7, 71.3, 69.7, 61.9.

Monoarylation of 1,4-Bis((hydroxyethoxy)ethoxy)benzene with 2 (Compound 13). Diol **4** (29 mg, 0.1 mmol) and potassium *tert*-butoxide (110 μL of a 1.0 M solution in THF) were stirred in THF (5 mL) at rt for 15 min and then at −30 °C. Complex **2** (41 mg, 0.1 mmol) was added from a solids addition tube. The reaction was stirred for 6 h, gradually turning in color from yellow to very dark green. The mixture was concentrated by rotary evaporation, redissolved in a minimum of dichloromethane, and isolated by precipitation into ether (20 mL) to give 43 mg of an 8:1 mixture of **13**:**11** in 55% of the theoretical yield of **13** (by ratios of proximal methylene signals); ^{1}H NMR (δ) 6.87 (4H, s), 6.58 (1H, d, J = 6.3 Hz), 6.50 (1H, t, J = 6.3 Hz), 6.40 (1H, d, J = 6.3 Hz), 5.26 (5H, s), 4.57 (2H, t, J = 2.3 Hz), 4.14 (4H, overlapping triplets, J = 2.3, 4.4 Hz), 4.06 (2H, t, J = 4.7 Hz), 3.98 (2H, t, J = 4.4 Hz), 3.94–3.90 (overlapping triplets, J = 4.7, 4.4 Hz), 3.81 (2H, t, J = 4.4 Hz), 3.64 (1H, br s).

General Procedure for Decomplexations. A detailed procedure for decomplexations has been described in ref 4b. Variations from this for individual compounds are described below.

Diethylene Glycol Diphenyl Ether (14). Chromatography (1:9 EtOAc:hexanes, R_f = 0.2) gave the known compound **14** in 90% yield; mp 62–64 °C (lit.[10a] mp = 65 °C). The NMR data for this compound are not readily available; therefore they are given here: ^{1}H NMR (δ) 7.19 (4H, m), 6.86 (6H, m), 4.07 (4H, t, J = 4.4 Hz), 3.87 (4H, t, J = 4.4 Hz); ^{13}C NMR (δ) 158.7 (4°), 129.4, 120.9, 114.6, 69.9, 67.3; IR (cm^{-1}) 3013, 2929, 2877, 1599, 1497; HRMS calcd for $C_{16}H_{18}O_3$ 258.1256, found 258.1265.

1,4-Bis(2-(2-phenoxyethoxy)ethoxy)benzene (15): 90% yield; ^{1}H NMR (δ) 7.23 (4H, m), 6.88 (6H, m), 6.78 (4H, s), 4.09 (4H, t, J = 4.4 Hz), 4.04 (4H, t, J = 5.1 Hz), 3.86 (4H, t, J = 5.0 Hz), 3.84 (4H, t, J = 4.4 Hz); ^{13}C NMR (δ) 159.5, 153.1, 129.4,

120.9, 115.6, 114.6, 70.0, 69.9, 68.1, 67.3; IR (cm^{-1}) 3018, 2928 (CH), 1599, 1497 (Ar); HRMS calcd for $C_{26}H_{30}O_6$ 438.2042; found 438.2039.

2-(2-Phenoxyethoxy)ethanol (16). Chromatography (30% EtOAc/Hex, R_f = 0.1) gave the known compound **16**[11] as a colorless oil in 62% yield. Its NMR data are given here as they are not readily available: ^1H NMR (δ) 7.24 (2H, m), 6.88 (3H, m), 4.08 (2H, t, J = 4.7 Hz), 3.82 (2H, t, J = 4.7 Hz), 3.71 (2H, t, J = 4.3 Hz), 3.52 (2H, t, J = 4.3 Hz), 2.06 (1H, br); ^{13}C NMR (δ) 129.5, 121.0, 114.6, 72.5, 69.7, 67.3, 61.8; IR (cm^{-1}) 3608–3493, 2927, 2873, 1599, 1497.

Bis(2-(3-chlorophenoxy)ethyl) Ether (17). The compound was isolated by chromatography in 55% yield as a colorless oil (SiO_2, 1:9 EtOAc/Hex, R_f = 0.2): ^1H NMR (δ) 7.19 (1H, t, J = 9.0 Hz), 6.95 (1H, dd, J = 9.0, 1.0 Hz), 6.94 (1H, t, J = 1.0 Hz), 6.81 (1H, dd, J = 9.0, 1.0 Hz), 4.15 (dd, J = 4.8, 0.7 Hz), 3.91 (dd J = 4.8, 0.7 Hz); ^{13}C NMR (δ) 159.4, 134.8, 130.2 ,121.2, 115.0, 113.1, 69.8, 67.7; HRMS calcd for $C_{16}H_{16}Cl_2O_3$ 326.0476, found 326.0458.

1,4-Bis(2-(2-(3-chlorophenoxy)ethoxy)ethoxy)benzene (18): 69% yield; mp 86–87 °C; TLC SiO_2, 15% EtOAc/Hex, R_f = 0.2; ^1H NMR (δ) 7.12 (2H, t, J = 8.4 Hz), 6.96 (2H, ddd, J = 8.4, 4.0, 1.1 Hz), 6.91 (2H, t, J = 1.1 Hz), 6.78 (4H, s), 6.73 (2H, ddd, J = 8.4, 4.0, 1.1 Hz), 4.07 (4H, t, J = 4.3 Hz), 4.04 (4H, t, H = 3.5 Hz), 3.85 (4H, t, J = 3.5 Hz), 3.83 (4H, t, J = 4.2 Hz); ^{13}C NMR (δ) 159.5, 153.1, 130.3, 130.2, 121.1, 115.6, 115.1, 113.1, 70.1, 69.7, 68.1, 67.7; HRMS calcd for $C_{26}H_{28}Cl_2O_6$ 506.1263, found 506.1221.

2-(2-(3-Chlorophenoxy)ethoxy)ethanol (19). Chromatography (SiO_2, 30% EtOAc/Hex, R_f = 0.1) gave the product as a colorless oil in 50% yield; ^1H NMR (δ) 7.20 (1H, t, J = 9.0 Hz), 6.98–6.78 (3H, m), 4.13 (2H, t, J = 4.8 Hz), 3.86 (2H, t, J = 4.8 Hz), 3.77 (2H, apparent q, J = 5.1 Hz), 3.68 (2H ,t, J = 4.7 Hz), 2.06 (1H, br t); ^{13}C NMR (δ) 129.8, 120.8, 114.5, 112.7, 72.1, 69.1, 67.2, 61.4; HRMS calcd for $C_{10}H_{13}ClO_3$ 216.0553, found 216.0553.

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Supplementary Material Available: Proton and ^{13}C NMR spectra for all new compounds reported (32 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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