Studies on Selective Nucleophilic Substitution Reactions of [(Cyclopentadienyl)(1,3- and 1,4-dichlorobenzene)Fe]$^+PF_6^-$ Complexes: Applications to the Synthesis of Polymer Monomers

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Selective displacement of chloride from cyclopentadienyl(1,4-dichlorobenzene)iron(1+) by a series of aryl oxide and amine nucleophiles is described. The methodology, coupled with decomplexation of the product organometallics, allows access to a series of para-disubstituted benzene derivatives that are of potential value in the construction of unusual polymers. Four such compounds, derived from sequential addition of 4-hydroxybenzoic ester and hydroquinone or resorcinol monophenoxide to the 1,4- and 1,3-dichlorobenzene–FeCp complexes, were subjected to polyesterification reactions. Previously unreported isoregic poly(ether–esters) were prepared and characterized.

The syntheses of diaryl ethers, unsymmetrical triaryl diethers, and unsymmetrical aniline derivatives are of current interest because of the presence of these groups in a number of important natural products and in various materials applications. Diaryl ethers are found in, for example, the angiotensin-converting enzyme inhibitor K-13[1] and the antitumor agent OF4949[2] and have been used to modify the processibility of poly(*p*-hydroxybenzoic acid).[3] Triaryl diethers are subunits in the vancomycin family of antibiotics[4] and have the potential of serving in the construction of ordered, wholly aromatic poly(ether–esters). Unsymmetrical aniline derivatives (especially para-disubstituted) have been exploited by Katz[5] and Verhoeven and Warman[6] in the development of electron transfer arrays[6a] and molecular electronic devices[6b] and in the investigation of compounds with nonlinear optical (NLO) properties.[5]

These subunits share the problem of being difficult to synthesize via traditional organic methodology. Common diaryl ether syntheses include the Ullmann reaction,[7] which requires high temperatures and often suffers from poor yields, conventional nucleophilic aromatic substitution reactions, which require the presence of an electron-withdrawing group in the ring, which must often be modified or removed, and thallium-promoted oxidative couplings,[8] which require handling highly toxic reagents. Multifunctional aniline derivatives likewise have limited availability, and because of the difficulties associated with the construction of these units, studies are limited to those few simple aniline, phenylpiperazine, and phenylmorpholine derivatives which are commercially available.

Nucleophilic substitution reactions on chloroareneiron and similar complexes have been explored by a number of groups, although issues of selectivity and demetalation have not been adequately addressed in many cases.[9] The 1,4-dichlorobenzene-FeCp system has been little investigated, though it is potentially more applicable to materials interests. A recent report from Abd-El-Aziz[10] prompts us to disclose our own, more extensive survey of the reactivity of this complex. We report herein studies on the selective construction of diaryl ethers, unsymmetrical diaryl triethers, and various substituted anilines and unsymmetrical *p*-phenylenediamine derivatives under simple and mild conditions which provide a general method for the construction of compounds of interest to both materials scientists and organic chemists. We also detail an example of one such application: the synthesis and polymerization of ordered, wholly aromatic triaryl diether hydroxy acid monomers.

Results and Discussion

The starting point for the study was the synthesis of the parent dihaloarene complexes (**1, 2**). While a general

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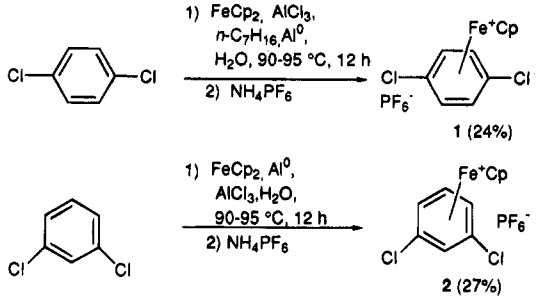
Scheme 1



method for this transformation (via a ligand exchange reaction with ferrocene) is well known,[11] the problem of aluminum-promoted reductive dechlorination of the complexed arene still hinders the synthesis. Although this dechlorination has been reported to be disfavored by lower temperatures[12] little experimental detail is available. Separation of the monochlorobenzene derivative can be accomplished by recrystallization; however, this has a devastating effect on an already disappointing yield. We have optimized conditions for the minimization of the dechlorination (ca. 50:1, dichloro/monochloro by ^{1}H NMR) during the preparation of **1** and **2** by using a combination of extremely efficient stirring, reaction temperatures less that 100 °C, and the addition of 1 equiv of water. Water has been previously implicated in some overall yield enhancements for this reaction,[13] and while we cannot speculate on its role, we have observed that it also suppresses the dechlorination. The yields remain somewhat disappointing (ca. 30%), but the combination of inexpensive starting materials and the fact that this is the first step in the sequence renders the yields tolerable.

While nucleophilic substitution reactions on **2** have been thoroughly investigated, **1** has seen much less attention, due mostly to anticipated difficulties in effecting a second nucleophilic substitution at a position para to an electron-donating aryl ether or amino group. Fortunately, this was not problematic. Optimum conditions for the selective displacement of one chloride by aryl oxide nucleophiles to give **3** and **4** were established (Figure 1). Generally, this involves stirring the phenoxide with the complex at low temperatures. One equivalent of the reactive sodium *p*-methoxyphenoxide gave approximately a 10:1 mixture of mono-/disubstituted products, which could be improved to >50:1 by recrystallization. The weaker nucleophile 4-(methoxycarbonyl)-phenoxide would not react appreciably at −78 °C, but gave a ca. 20:1 mixture of monosubstituted product **4** to unreacted starting material when the reaction was run at −15 °C in the presence of 2−3 equiv of nucleophile.

Reaction with nucleophilic secondary amines followed the same trend. Morpholine gave a 6:1 mixture of mono-/disubstituted (**5**) product when used in a 20-fold excess, at room temperature, in the presence of potassium carbonate. By using 2 equiv of amine, however, only the monosubstituted product was obtained. With the more nucleophilic piperidine, however, a 10-fold excess resulted exclusively in disubstitution and a 2-fold excess gave a 10:1 mixture of mono-/disubstitution.

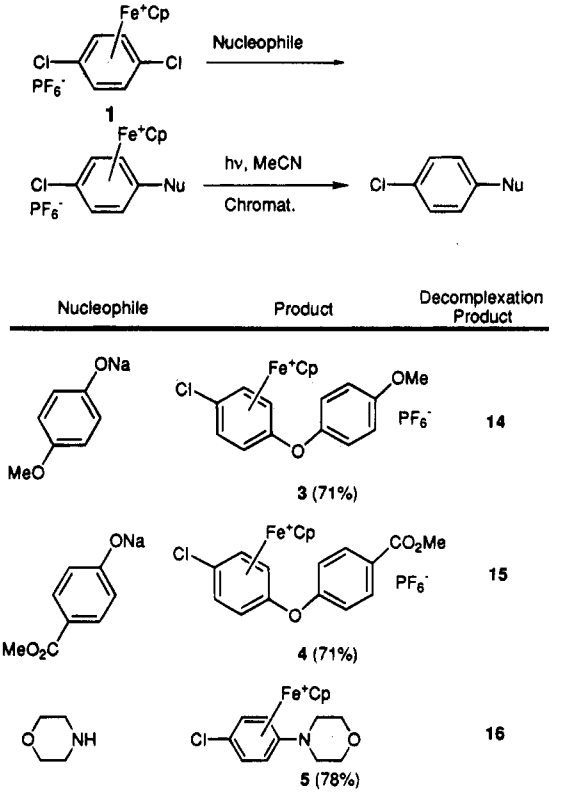


Figure 1. Selective reactions of complex **1** with nucleophiles.

Reaction of the alkoxide of benzyl alcohol with **1** gave no selectivity whatsoever. No reaction occurred at −78 °C or at −50 °C, and disubstitution occurred at −20 °C, indicating that if there is a temperature window where some selectivity is attainable, it is too narrow to be very useful.

We decided to use the morpholine and p-methoxyphenoxide derivatives to examine a range of second nucleophile substitutions. The morpholine adduct **5** was shown to be susceptible to chloride displacement by phenoxide, alkoxide, and reactive secondary amine nucleophiles (**6**−**8**) at room temperature (Figure 2). Addition of benzylamine, however, proceeded in good yield to give **9** only after stirring in refluxing THF for 2 days, in the presence of 10 equiv of the amine. *N*-Methylbenzylamine would not react under any conditions.

The *p*-methoxyphenol adduct showed similar reactivity toward phenoxides and secondary amines (Figure 3, **11**, **12**); however, when benzyl alcohol served as nucleophile, reaction times greater than *ca.* 30 min led to the formation of a highly colored, ether-soluble byproduct. The benzyloxy adduct **13** could, however, be isolated. With benzylamine, NMR signals corresponding to those expected of the product could be obtained under conditions similar to those described for **9** but never as the major signals, and the complex could not be isolated cleanly. The complex **4** likewise showed itself to be susceptible to a second phenoxide substitution, giving **10** after treatment with sodium 4-methoxyphenoxide. With the exception of **9**, all of these complexes were demetalated by photolysis in acetonitrile and gave, after chromatography, the substituted arene in 52−92% yields (Experimental Section, compounds **14**−**23**).

As expected, upon demetalation, we noticed that manipulation of solutions of the diamine **19** often resulted in the solution taking on a (frequently very intense) blue color especially in the presence of acidic media. This

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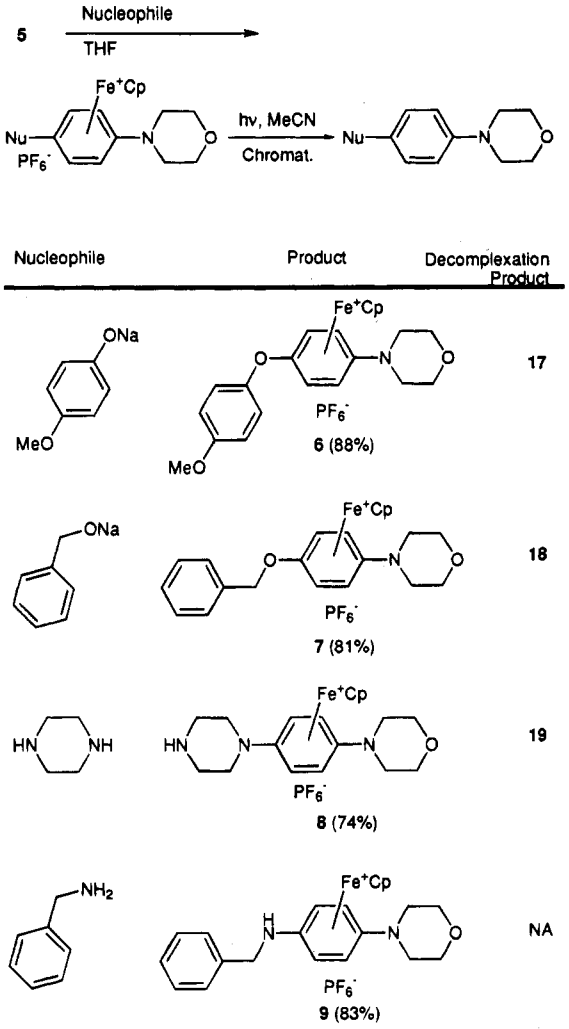

Figure 2. Second nucleophile substitutions on complex **5**.

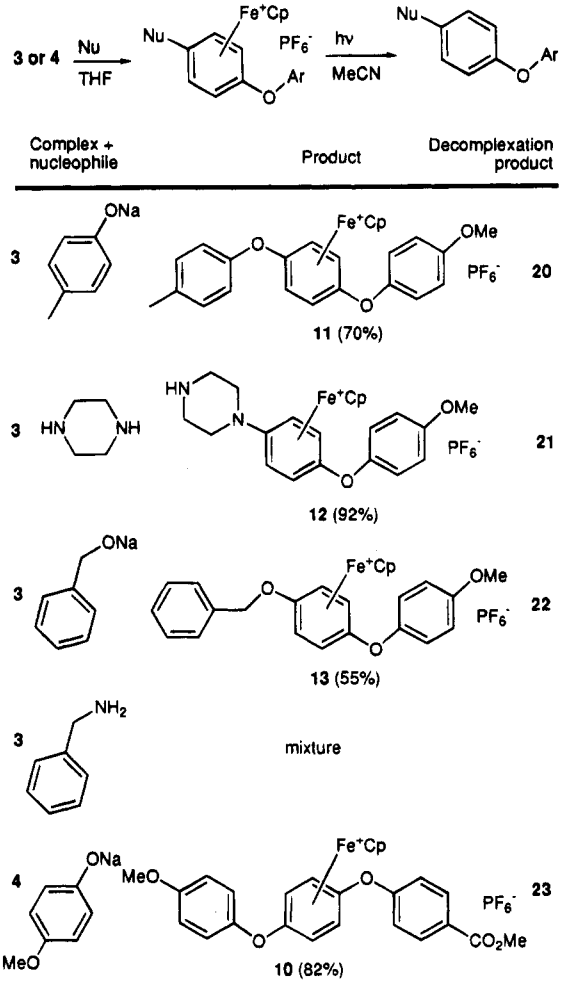

Figure 3. Second nucleophile substitutions on complex **4**.

compound is a functionalized derivative of Wurster's blue[14] (*N,N, N',N'*-tetramethyl-*p*-phenylenediamine) and displays similar electron donor properties. The point of attachment provided by the remaining nitrogen in the piperazine ring makes this a potentially useful intermediate for the synthesis of conducting polymers or other electron transfer arrays.[5,6]

The synthesis of polymers and other macromolecules with precisely defined structures is an area of strong current interest. Because of the chemoselectivity just discussed, these complexes are useful building blocks for ordered monomers, which can then be used in the synthesis of ordered, isoregic polymers, such as wholly aromatic, ordered polyaryl(ether–esters). Fully aromatic polyesters have many desirable mechanical and thermal characteristics and are often liquid crystalline. However, polyesters of, for example, *p*-hydroxybenzoic acid (PHBA) become very rigid and very insoluble at low molecular weights. This solubility problem results in polymers which are too small to be useful and too intractible to be processible, and much effort has been devoted to modification of polymers of PHBA to improve their processibility while retaining their desirable mechanical properties. The traditional solutions to this problem include copolymerization of the aromatic hydroxy acid (or diacid and diphenol) with kinked[15] or flexible spacers[16] to lower the symmetry and raise the melting entropy of the polymer, the introduction of bulky pendant groups to disrupt packing,[17] and the incorporation of carbonyl,[18] ether,[3] or other disruptor linkages to reduce the rigidity of the polymer.

The conventional routes for the incorporation of phenyl ether linkages either employ 3,4'- or 4,4'-dicarboxydiphenyl ether in a copolymerization with an aromatic diacid and a bisphenol[19] or require the presence of an electron-withdrawing group on the ring.[19] The first arrangement constrains the polymer to an ether/ester ratio of no more than 1:2, and the second is often inconvenient. Further, it is recognized that the physical properties of a polymer depend not only upon overall composition but upon its comonomer sequence,[20] and it

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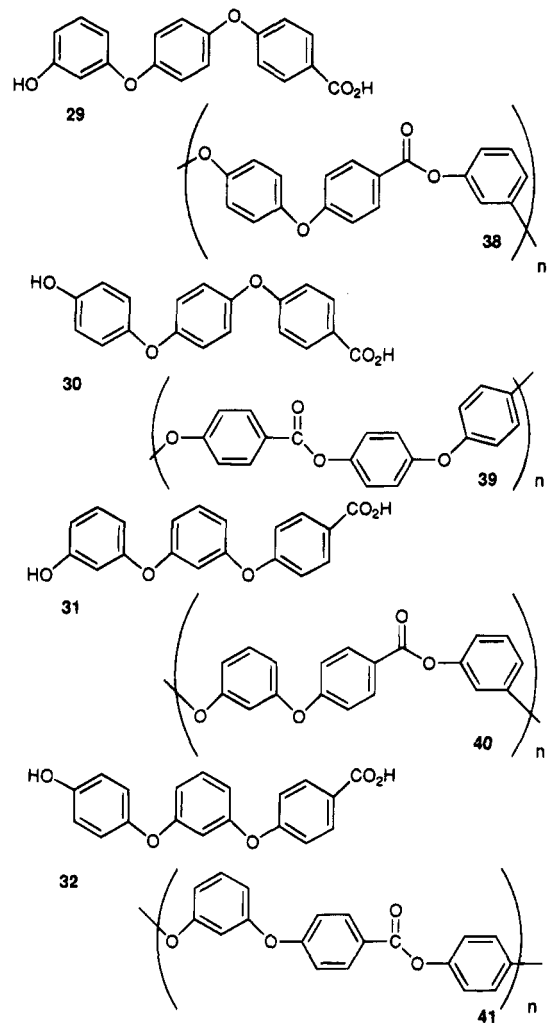

Figure 4. Structures of monomers and corresponding poly(ether–esters).

is established that ordered sequence copolyesters undergo sequence randomization, via transesterification, above their melting points.[21] Much information regarding the positional effect of aryl ester disruptors must therefore remain unassessed as the relative location of the disruptor cannot be precisely determined. If the disruptor of choice is an aliphatic spacer, the synthesis of an isoregic polymer is possible by first preparing a monomer by a Williamson reaction.[22] When the effects of strategically positioned aryl ether disruptors are of interest, however, the synthesis of the monomer becomes nontrivial.

We decided to bring the technology of transition metal mediated chemoselective S_NAr reactions to bear on this problem. The goal was the synthesis of a series of poly(ether–esters) where the ring connectivity could not be altered by transesterification, that is, where any transesterification which occurred would result in a polymer of identical comonomer sequence. The starting point was the triaryl diether **10**, recognizing that by varying the substitution of the starting dichlorobenzene complex and of the second nucleophile, we could place a disruptor at any one of various positions relative to the diphenyl ester linkage (Figure 4), which is the linkage responsible for the desirable properties of and the problems associated with aromatic polyesters. To this end, four monomers were chosen for study (**29**–**32**). Monomers **31** and **32** were prepared by a sequence analogous to those described in the preceding discussion but using complex **2** as the precursor.

From **4** or its meta-analogue **33** (which can be decomplexed to give **24** in 65% yield), it was necessary to employ the monophenoxide of either hydroquinone or resorcinol to give **34**–**37**. This was found to be possible at room temperature under conditions which were rigorously anaerobic and which employed a complex/base/phenol ratio of 1:2:4 (Schemes 2 and 3). This ratio ensured that the phenol was present in excess of the base, in order to avoid competing radical generation, and that there was sufficient base present to ensure complete reaction, even though the sodium salt of the product of the second nucleophile substitution is quite insoluble in THF. Yields for this step were in the range 67–92%. While the use of dihydroxybenzenes in S_NAr reactions with arene–iron complexes has been reported by others,[10] the reaction conditions are rather harsh if sensitive functionality is to be present, and larger excesses of the nucleophile were employed (8 equiv, 8 h reflux in THF/DMF).

Following routine decomplexation (CH_3CN, bright light, 4 h) and column chromatography the esters **25**–**28** were isolated. Their physical properties correlated closely with their assumed degree of rigidity, specifically in terms of mp; **26** melted at 172–173 °C, **25** at 123–125 °C, and **27** and **28** were oils. The trend for R_f values on TLC were the exact opposite. The ^{13}C NMR spectrum of **26** in acetone-d_6 shows nonequivalence for the two carbons ortho to the phenol moiety, presumably due to intermolecular association through hydrogen bonding. This was confirmed by noting the absence of the splitting in the ^{13}C NMR spectrum of the corresponding methyl ether **23** or in the ^{13}C NMR spectrum of **26** run in methanol-d_4.

Base hydrolysis of the esters (KOH, MeOH, H_2O, rt, 2 h) was straightforward and gave the desired hydroxyacid monomers **29**–**32** in 65–87% yield after recrystallization (EtOAc/pentane), and again the melting point trend is indicative of the degree of rigidity of the monomers and, hence, of the rigidity they can be expected to impart to their polymers. (Melting point comparison: **31**, mp = 125–26 °C); **29**, mp = 153–55 °C; **32**, mp = 182–83 °C, **30**, mp = 273–75 °C.)

With the monomers in hand, a series of polymerizations were investigated. Polymerization via the acid chloride (thionyl chloride/pyridine/DMAP, sealed tube, 120 °C, 36 h) gave fibrous, but very insoluble and difficult to characterize high molecular weight polymers; thus, we chose to restrict our initial efforts to the synthesis of lower molecular weight species (M_w *ca.* 8000, M_n *ca.* 6000, M_w/M_n *ca.* 1.3, relative to polystyrene standards) which we could more easily characterize. These were accessible using a modification of literature methods for carbodiimide-mediated polyesterifications,[23] employing dicyclohexylcarbodiimide (DCC) and (*N*,*N*-dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) in a pyridine, CH_2Cl_2, THF mixed solvent system. The polymers were isolated as white solids by precipitation into large excesses of methanol (50 mL/mL of reaction solvent), with yields at this stage of *ca.* 90%. They were recrystallized from THF/methanol until they were free of dicyclohexyl-

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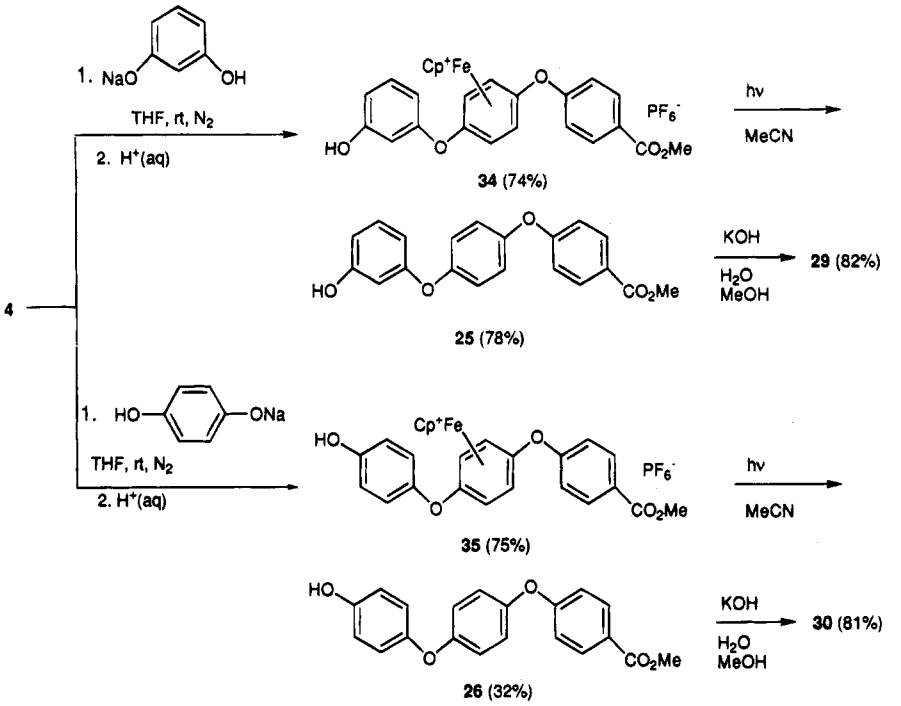
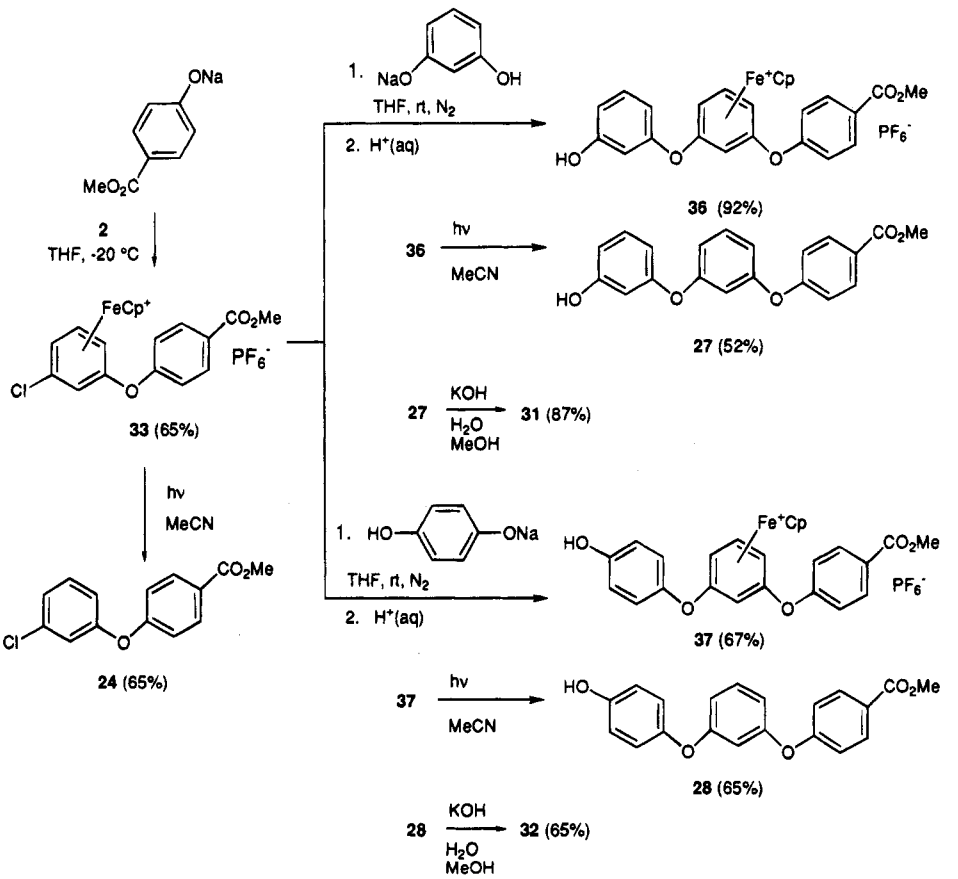
Scheme 2



Scheme 3



urea (DCU) by GPC to give the polymers **38**–**41** in final yields of about 50%. In addition to removing the DCU, the reprecipitation from methanol also served to remove low molecular weight oligomers, thus improving the polydispersity, but with accompanying yield reduction.

Gel permeation chromatography, relative to polystyrene standards, gave the molecular weights and polydispersities shown in Table 1. The actual molecular weights can be assumed to be somewhat larger than the measured weights due to the more rigid aryl(ether–ester) configuration.[15a] The polydispersity ranges from moderate to poor, but this is to be expected from condensation polymerizations. This molecular weight range, however, is well suited for those characterization tests which

Table 1. Physical Data for Polymers 38–41

polymer	M_w	M_n	M_w/M_n	TGA, dec (°C)	T_m	T_{lc-i}	melting range (°C)
38	4800	2500	1.9	393	167		200–212
39	NA	NA	NA	448	NA		280–300
40	7300	6100	1.2	431	132		140–145
41	8300	3900	2.3	426	109	159	155–170

require either dissolving the polymer (NMR, GPC) or melting it without decomposition (hot stage microscopy (HSM) and differential scanning calorimetry (DSC)).

The proton and ^{13}C NMR spectra of the polymers, while not completely assignable, are, in most cases, quite well resolved. This is an indication of both the relatively low molecular weights (<10000) of the compounds and of their isoregic composition. Thermal gravimatric analysis (TGA) shows the onset of weight loss for these polymers in the range 390–450 °C with final weight retentions of 30–40% at 700 °C (Table 1). This compares favorably with analogous polyester and poly(ether–ester) systems,[19] indicating that, as expected, the additional phenylene oxide linkage is not detrimental to thermal stability. Melting ranges (by HSM) followed the trend that would be predicted, based on the rigidity of the starting monmers, although the disparity in molecular weights may render this comparison somewhat ambiguous (Table 1).

These monomers were designed with particular interest in assessing the effect of the ordered disruptor positioning and of the additional phenylene oxide linkage on liquid crystallinity. The results have succeeded in defining a direction for further efforts. Specifically, by HSM, **38** forms a nematic phase; however, decomposition occurs close to the glass transition temperature (T_g), so DSC confirmation of the phase is not possible. The polymer **39** forms an isotropic melt, as would be expected from a diaryl ester linkage where both rings are not para-disubstituted. Poly-**40** shows very weak shear-induced ordering of the melt phase, but DSC does not confirm a liquid crystalline phase. Poly-**41** also displays shear-induced order on cooling from an isotropic melt, on both surfactant-treated and -untreated slides, lasting slightly longer than the duration of the shear, possibly characteristic of a nematic phase, for which corroboration by DSC was obtainable (Table 1). Further efforts will be directed at improving the LC properties of ordered, wholly aromatic systems, through the incorporation of naphthoate and/or 4,4′-biphenol units. Attention will likewise be given to polymerizations conducted prior to removal of the metal, in order to obtain solubility enhancements similar to those which have been observed in polymerizations of arene–ruthenium[24] and arene–chromium[25] complexes.

Conclusions

In conclusion, we have shown that highly chemoselective nucleophilic monosubstitution occurs on reaction of [(cyclopentadienyl)(1,4-dichlorobenzene)Fe]PF_6 with a variety of phenoxide and amine nucleophiles. The complexes may be prepared without aluminum-promoted reductive dechlorination. The reactivity of the second chloride to be displaced is sufficiently diminished to allow chemoselectivity in reaction with phenoxide nucleophiles, but not sufficiently diminished to obtain selectivity with the more reactive benzyl alkoxide. Likewise, piperidine gave only modest selectivity, but the weaker nucleophile morpholine was quite selective. The second chloride is sufficiently electrophilic to permit substitution by a primary amine, or a cyclic secondary amine, but not by more sterically hindered secondary amines. Methodology has been introduced for the use of hydroquinone and resorcinol monophenoxide as nucleophiles, systems which are notoriously difficult to handle. The substituted arene may be liberated from the metal cleanly and under mild conditions. It is possible to synthesize Wurster's blue derivatives by this methodology.

Another application of this methodology is to the synthesis of wholly aromatic poly(ether–esters) with precisely defined structures and potentially new mechanical properties. Four new monomers were prepared by selective phenoxide substitution, a second substitution, decomplexation, and further manipulation of the liberated organic ligand. The polymers synthesized from these monomers are isoregic and in some cases display weak, shear-induced melt-phase ordering.

Experimental Section

For general methods see ref 9b. For gel permeation chromatography molecular weights are relative to polystyrene standards. Differential scanning calorimetry was performed with a heating rate of 20 °C min^{-1}. Thermal gravimetric analysis was performed under a nitrogen atmosphere, at a heating rate of 10 °C min^{-1}. All samples for microscopy were prepared by first dissolving the polymer in THF (1 mg/mL) and passing the solution through a 0.45-μm filter. Samples were analyzed in both the presence and absence of a surfactant (HTAB).

η^6-1,4-Dichlorobenzene-η^5-cyclopentadienyliron(II) Hexafluorophosphate (1). *p*-Dichlorobenzene (40.0 g) and *n*-heptane (15 mL) were combined and heated under nitrogen with stirring until the solid had completely melted. The mixture was cooled to between 50 and 55 °C. Ferrocene (3.00 g, 16 mmol), aluminum powder (400 mg, 15 mmol), and aluminum chloride (6.00 g, 45 mmol) were added. Water (288 μL, 16 mmol) was added *via* syringe. The mixture was brought to between 95 and 100 °C and allowed to stir for 12 h. The mixture was cooled to 30 °C, and water (40 mL) was added, cautiously, to the mixture, followed by ether (30 mL). This mixture was vigorously stirred for 10 min, and the ether layer was separated and washed with water (40 mL). The aqueous fractions were combined, filtered, and extracted with ether (3 × 30 mL) to remove unreacted ferrocene. To the aqueous fraction was added a solution of saturated NH_4PF_6 dropwise until the prepicitation ceased. The yellow solid was filtered and dried *in vacuo*. Additional product was obtained by extracting the aqueous solution with CH_2Cl_2 (2 × 25 mL), drying the CH_2Cl_2 over $MgSO_4$, concentrating this to 5–10 mL, and adding ether until precipitation ceased. Total yield 1.62 g (24%). ^1H NMR δ 7.01 (4H, s), 5.48 (5H, s). Spectroscopic data are in agreement with the literature.[11]

η^6-1,3-Dichlorobenzene-η^5-cyclopentadienyliron(II) Hexafluorophosphate (2). The procedure was analogous to that for the para isomer except that *m*-dichlorobenzene (40 mL) was employed and the heptane was omitted to give the known[11] product in 27% yield. ^1H NMR δ: 7.35 (1H, s), 6.89 (2 H, d, J = 5.9 Hz), 6.81 (1 H, t, J = 5.9 Hz), 5.46 (5 H, s).

η^6-[1-Chloro-4-(4-methoxyphenoxy)benzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (3). The complex **1** (0.10 mmol, 41.3 mg) was dissolved in THF (2 mL) and cooled to −78 °C. In a separate flask, *p*-methoxyphenol (0.105 mmol, 13.0 mg) was stirred with NaH (0.2 mmol, 4.6 mg, 8.0 mg of a 60% dispersion in mineral oil) suspended in THF (1.0

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mL). The resulting solution was transferred *via* cannula to a dropping funnel atop the first flask. Additional THF (2 × 0.5 mL) was used to rinse the flask and was passed through the cannula to the dropping funnel. The phenoxide solution was added dropwise over 5 min to the solution of the complex. The reaction was stirred for 12 h and then quenched with water. After being warmed to 0 °C, the mixture was filtered through Celite and the solvent removed *in vacuo*. The residue was redissolved in CH_2Cl_2 (2 mL) and the product precipitated by addition of hexane until precipitation ceased. The solid was isolated by centrifugation and was stirred with ether and recentrifuged. The solvent was decanted and the solid dried under vacuum. This afforded a ca. 10:1 mixture of mono- to disubstituted complex in 71% yield of the monosubstituted species. This was improved to ca. 60:1 by recrystallization from refluxing EtOH (2 mL/25 mg) with very small amounts of acetone being added as necessary to completely dissolve the complex. The solution was cooled to rt and the precipitate isolated by decantation of the mother liquor. The precipitate was washed with ether (5 mL) and dried under vacuum. The mother liquor was cooled to −20 °C and additional product collected. Proton NMR showed no significant difference in purity between the two crops. The total yield following recrystallization was 51%. ^{1}H NMR δ: 7.33 (2H, d, J = 9.7 Hz), 7.13 (2H, d, J = 9.7 Hz), 6.84 (2H, d, J = 7.0 Hz), 6.46 (2H, d, J = 7.0 Hz), 5.39 (5H, s), 3.87 (3H, s). ^{13}C NMR δ: 159.1 (1C, 4°), 146.9 (1C, 4°), 134.7 (1C, 4°), 122.9 (2C, 3°), 116.5 (2C, 3°), 104.7 (1C, 4°), 87.7 (2C, 3°), 80.3 (5 C, 3°), 76.5 (2C, 3°), 56.0 (1C, 1°).

η^6-(1-Chloro-4-morpholinobenzene)-η^5-cyclopentadienyliron(II) Hexafluorophosphate (5). The complex **1** (250 mg, 0.6 mmol) and morpholine (105 mg, 1.2 mmol) were stirred with K_2CO_3 (210 mg, 1.5 mmol) in THF (2 mL) for 12 h at rt. The mixture was filtered through a cotton plug, which was washed with CH_2Cl_2. The combined filtrate and washings were concentrated to *ca.* 1 mL and were added dropwise to ether (10 mL), yielding a fine orange precipitate which was allowed to settle out. The solvent was decanted and the precipitate washed well with ether and dried *in vacuo* to give the product in 78% yield. ^{1}H NMR δ: 6.60 (2H, d, J = 6.2 Hz), 6.17 (2H, d, J = 6.2 Hz), 5.25 (5H, s), 3.83 (4H, t, J = 4.5 Hz), 3.49 (4 H, t, J = 4.5 Hz). ^{13}C NMR δ: 126.3 (1C, 4°), 102.8 (1C, 4°), 86.6 (2C, 3°), 78.0 (5C, 3°), 67.7 (2C, 3°), 66.2 (2C, 2°), 47.1 (2C, 2°).

η^6-[1-Morpholino-4-(4-methoxyphenoxy)benzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (6). *p*-Methoxyphenol (37 mg, 0.1mmol) was stirred in THF (3 mL) with sodium hydride (0.2 mmol, 8 mg of a 60% dispersion). The complex **5** was added to the solution as a solid *via* a solids addition tube and was allowed to stir for 4 h. The reaction mixture was filtered through Celite and the pad washed well with CH_2Cl_2. The solvent was removed *in vacuo* and the residue redissolved in CH_2Cl_2 (10 mL), which was washed with 1/4 saturated aqueous NH_4PF_6 (2 mL), 0.1 M NaOH (2 × 2 mL), and water (5 mL), dried over $MgSO_4$, concentrated to approximately 3 mL, added dropwise to ether (30 mL), and isolated as usual to give an orange powder in 88% yield.[26] ^{1}H NMR δ: 7.35 (2H, d, J = 9.0 Hz), 7.15 (2H, d, J = 9.0 Hz), 6.18 (2H, d, J = 7.2 Hz), 6.05 (2H, d, J = 7.2 Hz), 5.27 (5H, s), 3.92 (3H, s), 3.89 (4H, t, J = 5.1 Hz), 3.48 (4H, t, J = 5.1 Hz). ^{13}C NMR δ: 158.6 (1C, 4°), 147.8 (1C, 4°), 131.3 (1C, 4°), 124.2 (1C, 4°), 122.8 (2C, 3°), 116.3 (2C, 3°), 76.5 (5 C, 3°), 74.3 (2C, 3°), 66.6 (2C, 3°), 66.4 (2C, 2°), 56.0 (1C, 1°), 47.6 (2C, 2°).

η^6-[1-(4-Methoxyphenoxy)-4-(4-methylphenoxy)benzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (11). This procedure was strictly analogous to that for **6** except that the complex **3** was added to the phenoxide of p-cresol. This gave a yellow powder in 70% yield. ^{1}H NMR δ: 7.37 (2H, d, J = 8.6 Hz), 7.29 (2H, d, J = 9.2 Hz), 7.20 (2H, d, J = 8.6 Hz), 7.09 (2H, d, J = 9.2 Hz), 6.28 (4H, s); 5.30 (5H, s), 3.85 (3H, s), 2.38 (3H, s). ^{13}C NMR δ: 158.9 (1C, 4°), 152.2 (1C, 4°), 147.4 (1C, 4°), 137.1 (1C, 4°), 132.7 (1C, 4°), 132.0 (2C, 3°), 122.9 (2C, 3°), 121.3 (2C, 3°), 116.4 (2C, 3°), 78.7 (5C, 3°), 75.4 (2C, 3°), 75.0 (2C, 3°), 56.0 (1C, 1°), 20.8 (1C, 1°). One quaternary carbon was not detected.

η^6-[1-(Benzyloxy)-4-morpholinobenzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (7). Benzyl alcohol (0.3 mmol, 32 mg) and sodium hydride (0.2 mmol, 8 mg of 60% dispersion) were stirred in THF (3 mL) for 10 min. The complex **5** (0.1 mmol, 43 mg) was added *via* a solids addition tube. The mixture was stirred for 4 h, quenched with water (100 μL), and filtered through Celite directly into ether (30 mL). The precipitate was isolated as usual to give an orange powder in 81% yield. ^{1}H NMR δ: 7.58−7.44 (5H, m), 6.24 (2H, d, J = 7.0 Hz), 5.94 (2H, d, J = 7.0 Hz), 5.36 (2H, s), 5.12 (5H, s), 3.82 (4H, t, J = 4.5 Hz), 3.41 (4H, t, J = 4.5 Hz). ^{13}C NMR δ: 136.2 (1C, 4°), 130.9 (1C, 4°), 129.4 (2C, 3°), 129.3 (1C, 3°), 128.8 (2C, 3°), 123.5 (1C, 4°), 76.0 (5C, 3°), 72.5 (2C, 3°), 72.0 (1C, 2°), 66.7 (2C, 3°), 66.4 (2C, 2°), 47.5 (2C, 2°).

η^6-[1-(Benzyloxy)-4-(4-methoxyphenoxy)benzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (13). The procedure was analogous to that for **7** except that benzyl alcohol was employed in only a 2-fold excess and sodium hydride in only a 0.5 equiv excess relative to the complex **3** and the water quench was omitted. This gave the product in 55% yield. ^{1}H NMR δ: 7.64−7.48 (5H, m), 7.34 (2H, d, J = 9.0 Hz), 7.15 (2H, d, J = 9.0 Hz), 6.46 (2H, d, J = 7.1 Hz), 6.30 (2H, d, J = 7.1 Hz), 5.43 (2H, s), 5.26 (5H, s), 3.91 (3H, s). ^{13}C NMR δ: 158.8 (1C, 4°), 147.5 (1C, 4°), 135.9 (1C, 4°), 132.2 (1C, 3°), 129.6 (2C, 3°), 129.2 (2C, 3°), 122.9 (2C, 3°), 78.2 (5C, 3°), 74.9 (2C, 3°), 73.3 (2C, 3°), 72.5 (1C, 2°), 56.0 (1C, 1°).

η^6-[1-Morpholino-4-piperazinobenzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (8). Piperazine (0.5 mmol, 43 mg), the complex **5** (0.1 mmol, 46 mg), and potassium carbonate (0.3 mmol, 45 mg) were stirred in THF (3 mL) for 12 h at rt. The reaction mixture was filtered through Celite and washed through with CH_2Cl_2 (2 mL) directly into ether (30 mL).The precipitate was isolated as usual to give an orange solid in 74% yield. ^{1}H NMR δ: 5.86 (4H, s), 5.16 (5H, s), 3.89 (4H, t, J = 5.0 Hz), 3.43 (4H, t, J = 5.0 Hz), 3.39 (4H, t, J = 5.3 Hz), 3.04 (4H, t, J = 5.3 Hz). ^{13}C NMR δ: 123.8 (1C, 4°), 122.3 (1C, 4°), 74.4 (5C, 3°), 66.8 (2C, 3°), 66.6 (2C, 3°), 66.2 (2C, 2°), 48.5 (2C, 2°), 47.7 (2C, 2°), 46.2 (2C, 2°).

η^6-[1-(4-Methoxyphenoxy)-4-piperazinobenzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (12). The procedure was as for **8** except complex **3** was employed. Yield: 92%. ^{1}H NMR δ: 7.27 (2H, d, J = 9.1 Hz), 7.08 (2H, d, J = 9.1 Hz), 6.06 (2H, d, J = 7.3 Hz), 5.91 (2H, d, J = 7.3 Hz), 5.15 (5H, s), 3.85 (3H, s), 3.34 (4H, t, J = 4.8 Hz), 2.98 (4H, m). ^{13}C NMR δ: 158.6 (1C, 4°), 147.9 (1C, 4°), 131.2 (1C, 4°), 125.1 (1C, 4°), 123.8 (2C, 3°), 116.3 (2C, 3°), 76.4 (5C, 3°), 74.3 (2C, 3°), 66.0 (2C, 3°), 56.0 (1C, 1°), 48.8 (2C, 2°), 45.9 (2C, 2°).

η^6-[1-(*N*-Benzylamino)-4-morpholinobenzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (9). The procedure was as for **8** except benzylamine and potassium carbonate were both used in a 10-fold excess and the reaction was run in refluxing THF for 48 h. Yield: 83%. ^{1}H NMR δ: 7.53 (2H, d, J = 7.1 Hz), 7.42 (2H, apparent t, J = 7.5 Hz), 7.34 (1H, t, J = 7.3 Hz), 5.82 (2H, d, J = 7.2 Hz), 5.65 (2H, d, J = 7.2), 4.81 (5H, s), 4.51 (2H, d, J = 5.6 Hz), 4.42 (1H, br s), 3.80 (4H, t, J = 4.9 Hz), 3.28 (4H, t, J = 4.9 Hz). ^{13}C NMR δ: 138.5 (1C, 4°), 129.4 (2C, 3°), 128.5 (2C, 3°), 128.3 (1C, 3°), 122.8 (1C, 4°), 120.7 (1C, 4°), 75.0 (5C, 3°), 67.1 (2C, 3°), 66.4 (2C, 3°), 65.7 (1C, 2°), 47.6 (1C, 2°), 47.4 (2C, 2°).

η^6-[1-Chloro-4-(4-carbomethoxyphenoxy)benzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (4). Methyl 4-hydroxybenzoate (228 mg, 1.5 mmol) was stirred with NaH (2.4 mmol, 96 mg of a 60% dispersion in mineral oil) in THF (18 mL) for 10 min. The mixture was then cooled to −50 °C, and **1** was added as a solid from a solids addition tube. The mixture was warmed to −15 °C and allowed to stir for 12 h. The reaction was quenched with water (100 μL) and filtered cold through Celite and the pad washed with CH_2Cl_2 (30 mL)

(26) A number of the products of second nucleophile addition were contaminated with small amounts of unreacted starting material. While its removal can be effected by multiple recrystallization, this results in considerable loss. Consequently, the crude products were used for the decomplexation step, the product from which can be more efficiently purified by chromatography.

The solvent was removed on the rotary evaporator, and the residue was redissolved in CH_2Cl_2 (30 mL). This solution was washed with aqueous NH_4PF_6 (1.5 mL of saturated solution further diluted with 3.5 mL H_2O), 0.1 M NaOH (2 × 5 mL), and water (5 mL). The organic layer was dried over $MgSO_4$, concentrated to 10 mL, and added dropwise to ether (100 mL). The very finely divided precipitate was allowed to settle out overnight in the refrigerator, the solvent was decanted, and the precipitate was washed well with ether and dried *in vacuo* to give a yellow solid in 71% yield. ^{1}H NMR δ: 8.15 (2H, d, J = 8.2 Hz), 7.45 (2H, d, J = 8.2 Hz), 6.87 (2H, d, J = 6.4 Hz), 6.63 (2H, d, J = 6.4 Hz), 5.42 (5H, s); 3.91 (3H, s). ^{13}C NMR δ: 166.2 (1C, 4°), 158.2 (1C, 4°), 132.9 (2C, 3°), 132.3 (1C, 4°), 128.9 (1C, 4°), 121.0 (2C, 3°), 105.3 (1C, 4°), 88.0 (2C, 3°), 80.7 (5C, 3°), 78.5 (2C, 3°), 52.5 (1C, 1°). IR (cm^{-1}): 2950, 1713, 1602, 1501.

η^6-[1-Chloro-3-(4-carbomethoxyphenoxy)benzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (33). The procedure was identical to that for **4** except that the reaction was warmed from −50 to −25 °C. Yield: 65%. ^{1}H NMR δ: 8.17 (1H, d, J = 9.0 Hz), 7.47 (2H, d, J = 9.0 Hz), 7.00 (1H, t, J = 1.6 Hz), 6.76 (1H, dd, J = 6.3, 1.6 Hz), 6.73 (1H, t, J = 6.3 Hz), 6.60 (1H, dd, J = 6.3, 1.6 Hz), 5.41 (5H, s), 3.94 (3H, s). ^{13}C NMR δ: 166.2 (1C, 4°), 158.2 (1C, 4°), 133.0 (2C, 3°), 129.1 (1C, 4°), 121.2 (2C, 3°), 120.7 (1C, 4°), 107.2 (1C, 4°), 87.3 (1C, 3°), 86.9 (1C, 3°), 80.7 (5C, 3°), 80.2 (1C, 3°), 78.1 (1C, 3°), 52.6 (1C, 1°). IR (cm^{-1}): 2950, 1715, 1603, 1499.

η^6-[1-(4-Methoxyphenoxy)-4-(4-carbomethoxy)phenoxybenzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (10). The procedure was as for **6** except that the starting complex was **4**. Yield: 82%. ^{1}H NMR δ: 8.19 (2H, d, J = 8.8 Hz), 7.46 (2H, d, J = 8.8 Hz) 7.37 (2H, d, J = 9.0 Hz), 7.17 (2H, d, J = 9.0 Hz), 6.56 (2H, d, J = 7.1 Hz), 6.40 (2H, d, J = 7.1 Hz), 5.41 (5H, s), 3.97 (3H, s), 3.92 (3H, s). ^{13}C NMR δ: 166.3 (1C, 4°), 159.1 (1C, 4°), 159.0 (1C, 4°), 147.3 (1C, 4°), 133.3 (1C, 4°), 132.9 (2C, 3°), 129.8 (1C, 4°), 128.5 (1C, 4°), 122.9 (2C, 3°), 120.5 (2C, 3°), 116.5 (2C, 3°), 79.1 (5C, 3°), 77.6 (2C, 3°), 75.2 (2H, 3°), 54.0 (1C, 1°), 52.5 (1C, 1°). IR (cm^{-1}): 3093, 2954, 1718, 1606, 1506.

η^6-[1-(3-Hydroxyphenoxy)-4-(4-carbomethoxyphenoxybenzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (34). A three-necked flask was equipped with a dropping funnel and a solids addition tube. Resorcinol (88 mg, 0.8 mmol) was placed in the flask. Sodium hydride (16 mg of a 60% dispersion in mineral oil, 0.4 mmol) was placed in the solids addition tube. The complex **4** (106 mg, 0.2 mmol) was placed in the dropping funnel. After an inert atmosphere was rigorously established, THF was added *via* syringe to the resorcinol (4 mL) and to the complex (5 mL). The sodium hydride was introduced into the resorcinol solution and allowed to stir for 15 min. The solution of the complex was then added at a rate of 1 mL/min. The mixture was stirred for 2 h, during which time a yellow precipitate formed. The reaction was quenched with 10% HCl (100 μL), dissolving the precipitate. The solution was filtered through Celite, diluted with CH_2Cl_2 to 20 mL, washed with 1/4 saturated NH_4PF_6 (5 mL), 0.1 M aqueous NaOH (2 × 5 mL) and water (5 mL), dried over $MgSO_4$, concentrated to approximately 5 mL, and added dropwise to ether (50 mL). The yellow precipitate was collected and dried as for **6**, giving the product in 74% yield. ^{1}H NMR δ: 9.15 (1H, br s), 8.20 (2H, d, J = 8.7 Hz), 7.47 (2H, d, J = 8.7 Hz), 7.41 (1H, t, J = 5.1 Hz), 6.94 (1H, dm, J = 5.1 Hz), 6.84 (1H, t, J = 2.0 Hz), 6.83 (1H, dm, J = 5.1 Hz), 6.60 (2H, d, J = 7.0 Hz), 6.49 (2H, d, J = 7.0 Hz), 5.45 (5H, s), 3.97 (3H, s). ^{13}C NMR δ 166.2 (1C, 4°), 160.3 (1C, 4°), 159.0 (1C, 4°), 155.4 (1C, 4°), 132.9 (2C, 3°), 132.2 (1C, 3°), 130.0 (1C, 4°), 128.5 (1C, 4°), 120.7 (2C, 3°), 114.5 (1C, 3°), 112.1 (1C, 3°), 108.6 (1C, 3°), 107.3 (1H, 4°), 79.4 (5H, 3°), 77.8 (2C, 3°), 76.1 (2H, 3°), 52.6 (1C, 1°). IR (cm^{-1}): 3530, 2920, 1716, 1602.

η^6-[1-(4-Hydroxyphenoxy)-4-(4-carbomethoxyphenoxy)benzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (35). The procedure was identical to that for **34** except hydroquinone was used in place of resorcinol to give a yellow powder in 75% yield. ^{1}H NMR δSPCLN 8.19 (2H, d, J = 8.9 Hz), 7.46 (2H, d, J = 8.9 Hz), 7.27 (2H, d, J = 8.8 Hz), 7.06 (2H, d, J = 8.8 Hz), 6.55 (2H, d, J = 7.1 Hz), 6.39 (2H, d, J = 7.1 Hz), 5.41 (5H, s), 3.97 (3H, s). ^{13}C NMR δ: 166.3 (1C, 4°), 159.1 (1C, 4°), 157.0 (1C, 4°), 146.2 (1C, 4°), 133.6 (1C, 4°), 133.0 (2C, 3°), 129.8 (1C, 4°), 128.4 (1C, 4°), 123.1 (2C, 3°), 120.7 (2C, 3°), 117.9 (2C, 3°), 79.3 (5C, 3°), 78.0 (2C, 3°), 75.3 (2C, 3°), 52.7 (1C, 1°). IR (cm^{-1}): 3537, 2956, 1716, 1602, 1504.

η^6-[1-(3-Hydroxyphenoxy)-3-(4-carbomethoxyphenoxy)benzene]-η^5-cyclopentadienyliron(II) hexafluorophosphate (36). The procedure was as for **34** except that **33** was used in place of **4** to give the product in 92% yield. ^{1}H NMR δ: 9.03 (1H, br s), 8.20 (2H, dm, J = 8.9 Hz), 7.51 (2H, dm, J = 8.9 Hz), 7.46 (1H, t, J = 8.1 Hz), 6.92 (1H, dd, J = 8.1, 1.7 Hz), 6.89 (1H, dd, J = 8.1, 1.7 Hz), 6.86 (1H, t, J = 1.7 Hz), 6.68 (1H, t, J = 1.7 Hz), 6.59 (1H, t, J = 6.6 Hz), 6.43 (1H, dd, J = 6.6, 1.7 Hz), 6.33 (1H, dd, J = 6.6, 1.7 Hz), 5.14 (5H, s), 3.97 (3H, s). ^{13}C NMR δ: 166.3 (1C, 4°), 160.3 (1C, 4°), 158.8 (1C, 4°), 155.2 (1C, 4°), 134.0 (1C, 4°), 132.9 (2C, 3°), 132.7 (1C, 4°), 132.2 (1C, 3°), 128.6 (1C, 4°), 120.7 (2C, 3°), 114.6 (1C, 3°), 112.1 (1C, 3°), 108.6 (1C, 3°), 85.4 (1C, 3°), 79.0 (5C, 3°), 76.0 (1C, 3°), 75.1 (1C, 3°), 70.1 (1C, 3°), 52.5 (1C, 1°). IR (cm^{-1}): 3526 (OH), 3104 (CH), 2968 (Ar), 1711 (C=O), 1601 (Ar), 1513 (Ar).

η^6-[1-(4-Hydroxyphenoxy)-3-(4-carbomethoxyphenoxy)benzene]-η^5-cyclopentadienyliron(II) Hexafluorophosphate (37). The procedure was identical to that for **36** except hydroquinone was used in place of resorcinol to give the product in 67% yield. ^{1}H NMR δ: 8.81 (1H, br s), 8.19 (2H, d, J = 8.5 Hz), 7.48 (2H, d, J = 8.5 Hz), 7.30 (2H, d, J = 8.6 Hz), 7.05 (2H, d, J = 8.6 Hz), 6.56 (1H, s), 6.53 (1H, t, J = 6.0 Hz), 6.38 (1H, d, J = 6.0 Hz), 6.23 (^{1}H, d, J = 6.0 Hz), 5.37 (5H, s), 3.97 (3H, s). ^{13}C NMR δ: 166.3 (1C, 4°), 158.9 (1C, 4°), 156.8 (1C, 4°), 146.2 (1C, 4°), 133.2 (1C, 4°), 132.9 (2C, 3°), 132.1 (1C, 4°), 128.5 (1C, 4°), 123.0 (2C, 3°), 120.7 (2C, 3°), 117.8 (2C, 3°), 85.3 (1C, 3°), 78.8 (5C, 3°), 75.9 (1C, 3°), 74.2 (1C, 3°), 69.4 (1C, 3°), 52.6 (1C, 1°). IR (cm^{-1}): 3537, 2954, 1716, 1601, 1503.

General Procedure for Demetalations. (Any deviations from this procedure for a given complex are detailed with the purification and characterization data for that complex.) The complex was dissolved in acetonitrile (5 mg/mL) and irradiated (300-W sunlamp) for 3−4 h, with stirring. The resulting brown slurry was cooled to rt and added to ether (10 mL/mL CH_3CN). This was filtered through Celite and the pad washed well with ether. The solvent was removed *in vacuo* and the product purified by flash chromatography in accordance with the parameters specified for individual compounds.

1-Chloro-4-(4-methoxyphenoxy)benzene (14). Flash chromatography (SiO_2, 1:4 EtOAc/Hex, R_f = 0.8) gave the compound as an off-white solid in 80% yield, mp 49−50 °C. ^{1}H NMR δ: 7.35 (2H, d, J = 9.2 Hz), 6.96 (6H, m), 3.80 (3H, s). ^{13}C NMR δ: 158.5 (1C, 4°), 157.4 (1C, 4°), 150.4 (1C, 4°), 130.4 (2C, 3°), 127.6 (1C, 4°), 121.8 (2C, 3°), 119.6 (2C, 3°), 115.9 (2C, 3°), 55.7 (1C, 1°). HRMS: calcd for $C_{13}H_{11}ClO_2$ 234.0448, found 234.0448.

Methyl 4-(4-Chlorophenoxy)benzoate (15). Flash chromatography (SiO_2, 15% EtOAc/85% Hex, R_f = 0.45) gave the compound as a white solid in 90% yield, mp 68−69 °C. ^{1}H NMR δ: 8.03 (2H, dm, J = 6.8 Hz), 7.47 (2H, dm, J = 6.7 Hz), 7.14 (2H, dm, J = 6.7 Hz), 7.08 (2H, dm, J = 6.8 Hz), 3.87 (3H, s). ^{13}C NMR δ: 171.1 (1C, 4°), 166.5 (1C, 4°), 159.8 (1C, 4°), 137.2 (1C, 4°), 136.8 (2C, 3°), 135.3 (2C, 3°), 134.3 (1C, 4°), 130.2 (1C, 4°), 126.7 (2C, 3°), 122.6 (2C, 3°), 56.5 (1C, 1°). IR (cm^{-1}): 2920, 2851, 1721, 1604. HRMS: calcd for $C_{17}H_{11}ClO_3$ 262.0397, found 262.0401.

***N*-(4-Chlorophenyl)morpholine (16).** Flash chromatography (SiO_2, 1:9 EtOAc/Hex, R_f = 0.3) gave the compound as an off-white solid in 91% yield, mp 71−72 °C. ^{1}H NMR δ: 7.29 (2H, dd, J = 9.0 4.5 Hz), 7.02 (2H, dd, J = 9.0, 4.5 Hz), 3.83 (4H, t, J = 4.9 Hz), 3.19 (4H, t, J = 4.9 Hz). ^{13}C NMR δ: 151.3 (1C, 4°), 129.5 (2C, 3°), 124.4 (1C, 4°), 117.6 (2C, 3°), 67.2 (2C, 2°), 49.7 (2C, 2°). HRMS: calcd for $C_{10}H_{12}ClNO$ 197.0607, found 197.0606.

***N*-[4-(4-Methoxyphenoxy)phenyl]morpholine (17).** Flash chromatography (SiO_2, 1:1 EtOAc/Hex, R_f = 0.75) gave the compound as an off-white solid in 67% yield, mp 103−105 °C dec. ^{1}H NMR δ: 6.98−6.86 (8H, m), 3.77 (3H, s), 3.75 (4H, t, J = 4.8 Hz), 3.07 (4H, t, J = 4.8 Hz). ^{13}C NMR δ 120.2 (2C,

3°), 119.8 (2C, 3°), 117.9 (2C, 3°), 115.5 (2C, 3°), 67.4 (2C, 2°), 55.8 (1C, 1°), 50.7 (2C, 2°). The quaternary carbons were not detected. HRMS: calcd for $C_{17}H_{19}NO_3$ 285.1365 found 285.1353.

***N*-[4-(Benzyloxy)phenyl]morpholine (18).** Flash chromatography (SiO_2, 1:4 EtOAc/Hex, R_f = 0.25) gave the compound as a white crystalline solid in 75% yield, mp 117–118 °C. ^1H NMR δ: 7.42–7.26 (5H, m), 6.92 (2H, d, J = 3.3 Hz), 6.89 (2H, d, J = 3.3 Hz), 5.03 (2H, s), 3.86 (4H, t, J = 4.7 Hz), 3.07 (4H, t, J = 4.7 Hz). ^{13}C NMR δ: 129.2 (2C, 3°), 128.5 (1C, 3°), 128.3 (2C, 3°), 118.2 (2C, 3°), 116.2 (2C, 3°), 70.7 (1C, 2°), 67.5 (2C, 2°), 51.2 (2C, 2°). HRMS: calcd for $C_{17}H_{19}NO_2$ 269.1416, found 269.1419.

***N*-(4-*N*-Piperazinophenyl)morpholine (19).** Chromatography (basic alumina, 1:9 MeOH/$CHCl_3$, R_f = 0.5) gave the compound as a gray solid in 78% yield, mp 159–160 °C. ^1H NMR δ: 6.87 (4H, s), 3.75 (4H, t, J = 4.7 Hz), 3.02–2.87 (12H, m). ^{13}C NMR δ: 118.1 (2C, 3°), 117.8 (2C, 3°), 67.5 (2C, 2°), 52.1 (2C, 2°), 47.0 (2C, 2°). Quaternary carbons were not detected. HRMS: calcd for $C_{14}H_{21}N_3O$ 247.1685, found 247.1681.

1-(4-Methoxyphenoxy)-4-(4-methylphenoxy)benzene (20). Flash chromatography (SiO_2, 1:4 EtOAc/Hex, R_f = 0.8) gave the compound as a white solid in 60% yield, mp 83–84 °C. ^1H NMR δ: 7.17 (2H, d, J = 7.9 Hz), 7.00–6.87 (10H, m), 3.80 (3H, s), 2.23 (3H, s). ^{13}C NMR δ: 131.1 (2C, 3°), 121.0 (2C, 3°), 120.8 (2C, 3°), 119.9 (2C, 3°), 119.0 (2C, 3°), 115.7 (2C, 3°), 55.8 (1C, 1°), 28.8 (1C, 1°). The quaternary carbons were not detected. HRMS: calcd for $C_{20}H_{18}O_3$ 306.1256, found 306.1248.

***N*-[4-(4-Methoxyphenoxy)phenyl]piperazine (21).** Flash chromatography (SiO_2, 1:9 MeOH/$CHCl_3$, R_f = 0.5) gave the compound as a gummy solid in 92% yield. ^1H NMR δ: 6.98–6.76 (8H, m), 3.77 (3H, s), 3.03 (3H, t, J = 3.4 Hz), 2.93 (3H, t, J = 3.4 Hz). ^{13}C NMR δ: 156.3 (1C, 4°), 152.5 (1C, 4°), 151.7 (1C, 4°), 149.3 (1C, 4°), 120.1 (2C, 3°), 119.9 (2C, 3°), 118.1 (2C, 3°), 115.5 (2C, 3°), 55.8 (1C, 1°), 51.7 (2C, 2°), 46.9 (2C, 2°). HRMS: calcd for $C_{17}H_{20}N_2O_2$ 284.1525, found 284.1529.

1-(Benzyloxy)-4-(4-methoxyphenoxy)benzene (22). Flash chromatography (SiO_2, 1:4 EtOAc/Hex, R_f = 0.8) gave the compound as a white solid in 60% yield, mp 100–101 °C. ^1H NMR (δ) 7.49–7.32 (5H, m), 7.02–6.89 (8H, m), 5.10 (2H, s), 3.78 (3H, s). ^{13}C NMR 156.5 (1C, 4°), 155.5 (1C, 4°), 152.7 (1C, 4°), 152.3 (1C, 4°), 138.4 (1C, 4°), 129.2 (2C, 3°), 128.6 (1C, 3°), 128.4 (2C, 3°), 120.4 (2C, 3°), 120.1 (2C, 3°), 116.7 (2C, 3°), 115.6 (2C, 3°), 70.9 (1C, 2°), 55.8 (1C, 1°). HRMS: calcd for $C_{20}H_{18}O_3$ 306.1256, found 306.1267.

Methyl 4-[4-(4-Methoxyphenoxy)phenoxy]benzoate (23). Flash chromatography (SiO_2, 2:3 EtOAc/Hex, R_f = 0.4) gave the compound as a white solid in 60% yield, mp 133–34 °C. ^1H NMR δ: 8.06 (1H, dm, J = 8.7 Hz), 7.19–7.00 (10H, m), 3.92 (3H, s), 3.87 (3H, s). ^{13}C NMR δ: 166.6 (1C, 4°), 163.3 (1C, 4°), 157.1 (1C, 4°), 156.3 (1C, 4°), 151.1 (2C, 4°), 132.4 (2C, 3°), 125.2 (1C, 4°), 121.4 (2C, 3°), 119.9 (2C, 3°), 117.4 (2C, 3°), 115.8 (2C, 3°), 55.9 (1C, 1°), 52.2 (1C, 1°). IR (cm^{-1}): 2910–2980, 1717, 1505. HRMS: calcd for $C_{21}H_{18}O_5$ 350.1154, found 350.1160.

Methyl 4-(3-Chlorophenoxy)benzoate (24). Flash chromatography (SiO_2, 15% EtOAc/85% Hex, R_f = 0.4) gave the compound as a slightly yellow oil in 65% yield. ^1H NMR δ: 8.04 (2H, d, J = 8.7 Hz), 7.47 (1H, t, J = 8.1 Hz), 7.26 (1H, dd, J = 8.1, 0.7 Hz), 7.16–7.05 (4H, m), 3.87 (3H, s). ^{13}C NMR δ: 166.5 (1C, 4°), 161.7 (1C, 4°), 157.7 (1C, 4°), 135.6 (1C, 4°), 135.2 (2C, 3°), 132.3 (1C, 3°), 126.3 (1C, 4°), 125.3 (1C, 3°), 120.7 (1C, 3°), 119.0 (1C, 3°), 118.8 (2C, 3°), 52.2 (1C, 1°). IR (cm^{-1}): 2951 (Ar), 1722 (C=O), 1605, 1584 (Ar), 1503, (Ar). HRMS: calcd for $C_{14}H_{11}Cl\ O_3$ 262.0397, found 262.0398.

Methyl 4-[4-(3-Hydroxyphenoxy)phenoxy]benzoate (25). Flash chromatography (SiO_2, 15% EtOAc/Hex, R_f = 0.2) gave the compound as a white solid in 78% yield, mp 123–25 °C. ^1H NMR δ: 8.61 (1H, br s), 8.06 (2H, dm, J = 8.9 Hz), 7.26 (1H, t, J = 8.5 Hz), 7.23 (2H, d, J = 9.2 Hz), 7.18 (2H, d, J = 9.2 Hz), 7.12 (2H, dm, J = 8.9 Hz), 6.68 (1H, dd, J = 8.5, 2.0 Hz), 6.57 (1H, t, J = 2.0 Hz), 6.56 (1H, dd, J = 8.5, 2.0 Hz), 3.92 (3H, s). ^{13}C NMR δ: 166.6 (1C, 4°), 163.1 (1C, 4°), 159.7 (1C, 4°), 159.6 (1C, 4°), 154.5 (1C, 4°), 151.8 (1C, 4°), 132.4 (2C, 3°), 131.2 (1C, 3°), 125.3 (1C, 4°), 122.5 (2C, 3°), 121.5 (2C, 3°), 117.6 (2C, 3°), 111.3 (1C, 3°), 110.2 (1C, 3°), 106.5 (1C, 3°), 52.2 (1C, 1°). IR (cm^{-1}): 3384 (OH), 2922 (Ar), 1717 (C=O), 1600 (Ar), 1491 (Ar). HRMS: calcd for $C_{20}H_{16}O_5$ 336.0998, found 336.0997.

Methyl 4-[4-(4-Hydroxyphenoxy)phenoxy]benzoate (26). Flash chromatography (SiO_2, 15% EtOAc/Hex, R_f = 0.05) gave the compound as a white solid in 32% yield, mp 172–173 °C. ^1H NMR δ: 8.40 (1H, br s), 8.06 (2H, d, J = 8.7 Hz), 7.17 (2H, d, J = 9.0 Hz), 7.09 (2H, d, J = 9.0 Hz), 7.06 (2H, d, J = 9.0 Hz), 7.01 (2H, d, J =9.0 Hz), 6.94 (2H, d, J = 9.0 Hz), 3.92 (3H, s). ^{13}C NMR δ: 166.6 (1C, 4°), 163.3 (1C, 4°), 156.6 (1C, 4°), 154.8 (1C, 4°), 150.8 (1C, 4°), 150.0 (1C, 4°), 132.3 (2C, 3°), 125.1 (1C, 4°), 122.5 (2C, 3°), 121.6 (2C, 3°), 119.5 (2C, 3°), 117.4 (2C, 3°), 117.1 (1C, 3°), 117.0 (1C, 3°). IR (cm^{-1}): 3430, 2950, 1705, 1601, 1503. HRMS: calcd for $C_{20}H_{16}O_5$ 336.0998, found 336.1002.

Methyl 4-[3-(3-Hydroxyphenoxy)phenoxy]benzoate (27). Flash chromatography (SiO_2, 15% EtOAc/Hex, R_f = 0.15) gave the compound as a colorless oil in 52% yield. ^1H NMR δ: 8.64 (1H, br s), 8.08 (2H, dm, J = 8.8 Hz), 7.50 (1H, t, J = 8.2 Hz), 7.29 (1H, t, J = 8.5 Hz), 7.16 (2H, dm, J = 8.8 Hz), 6.92 (2H, dd, J = 8.2, 2.3 Hz), 6.80 (1H, t, J = 2.3 Hz), 6.69 (1H, dd, J = 8.5, 2.3 Hz), 6.60 (1H, t, J = 2.3 Hz superimposed on 1H, dd, J = 8.5, 2.3 Hz), 3.92 (3H, s). ^{13}C NMR δ: 166.6 (1C, 4°), 159.8 (2C, 4°), 158.6 (1C, 4°), 157.8 (1C, 4°), 132.4 (1C, 3°), 131.9 (1C, 3°), 131.2 (2C, 3°), 125.8 (1C, 4°), 118.4 (2C, 3°), 115.4 (1C, 3°), 115.2 (1C, 3°), 111.9 (1C, 3°), 111.0 (1C, 3°), 110.8 (1C, 3°), 107.2 (1C, 3°), 52.2 (1C, 1°). IR (cm^{-1}): 3401, 1735, 1590. HRMS calcd for $C_{20}H_{16}O_5$: 336.0998, found: 336.0996.

Methyl 4-[3-(4-Hydroxyphenoxy)phenoxy]benzoate (28). Flash chromatography (SiO_2, 15% EtOAc/Hex, R_f = 0.1) gave the compound as a colorless oil in 65% yield. ^1H NMR δ: 8.44 (1H, br s), 8.05 (2H, dm, J = 8.8 Hz), 7.40 (1H, t, J = 8.1 Hz), 7.10 (2H, dm, J = 8.8 Hz), 7.02 (2H, dm, J = 9.0 Hz), 6.95 (2H, dm, J = 9.0 Hz), 6.83–6.78 (2H, overlapping ddd, J = 8.1, 2.3, 1.0 Hz), 6.71 (1H, t, J = 2.3 Hz), 3.90 (3H, s). ^{13}C NMR δ: 166.6 (1C, 4°), 162.2 (1C, 4°), 161.5 (1C, 4°), 157.7 (1C, 4°), 155.1 (1C, 4°), 149.2 (1C, 4°), 132.4 (2C, 3°), 131.4 (1C, 3°), 125.7 (1C, 4°), 122.1 (2C, 3°), 118.3 (2C, 3°), 117.2 (2C, 3°), 114.2 (1C, 3°), 113.8 (1C, 3°), 109.6 (1C, 3°), 52.3 (1C, 1°). IR (cm^{-1}): 3400, 2952, 1719, 1592, 1506. HRMS: calcd for $C_{20}H_{16}O_5$ 336.0998, found 336.0997.

General Procedure for Ester Hydrolysis. Any deviations for a given compound are noted with the characterization data for that compound. The ester was dissolved in methanol (0.2 mmol/mL), 1 M aqueous KOH (1:1 v/v with methanol) was added, and the mixture was stirred at rt for 4 h. The solvent was removed *in vacuo* and the residue redissolved in a minimum of 0.1 M aqueous KOH. Aqueous HCl (2 M) was added dropwise until precipitation ceased and then in slight excess. The precipitate was isolated by vacuum filtration, washed with a little water, and dried *in vacuo*. The compound was recrystallized by dissolving the residue in a minimum of ethyl acetate and slowly adding pentane to the point of turbidity. The solution was centrifuged, separating a yellow oil from the solution. The solution was decanted and the process repeated two to three times until the precipitate appeared white. Pentane was then added until precipitation ceased. The mixture was cooled to −20 °C. The white crystals were isolated by suction filtration and washed with pentane.

4-[4-(3-Hydroxyphenoxy)phenoxy]benzoic Acid (29). Yield: 82%. Mp: 182–182 °C. TLC (2:3 EtOAc/Hex): R_f = 0.06. ^1H NMR δ: 8.60 (1H, br s), 8.05 (2H, dm, J = 8.9 Hz), 7.21–7.09 (5H, m), 7.06 (2H, dm, J = 8.9 Hz), 6.62 (1H, ddd, J = 8.1, 2.2, 1.0 Hz), 6.51 (1H, t, J = 2.2 Hz), 6.50 (1H, ddd, J = 8.1, 2.2, 1.0 Hz). ^{13}C NMR δ: 167.3 (1C, 4°), 163.1 (1C, 4°), 159.7 (1C, 4°), 159.6 (1C, 4°), 154.6 (1C, 4°), 152.0 (1C, 4°), 132.7 (2C, 3°), 131.2 (1C, 3°), 125.6 (1C, 4°), 122.5 (2C, 3°), 121.5 (2C, 3°), 117.6 (2C, 3°), 111.3 (1C, 3°), 110.2 (1C, 3°), 106.5 (1C, 3°). IR (cm^{-1}): 3520–3000, 2923, 2852, 1689, 1684, 1600, 1501. HRMS: calcd for $C_{19}H_{14}O_5$ 322.0841, found 322.0840.

4-[4-(4-Hydroxyphenoxy)phenoxy]benzoic Acid (30). Yield: 81%. Mp: 273–275 °C dec. TLC (2:3 EtOAc/Hex): R_f = 0.06. ^1H NMR (CD_3OD) δ: 7.87 (2H, d, J = 8.5 Hz), 6.90

(2H, d, J = 9.0 Hz), 6.89 (2H, d, J = 8.5 Hz), 6.83 (2H, d, J = 9.0 Hz), 6.77 (2H, d, J = 8.9 Hz), 6.69 (2H, d, J = 8.9 Hz). ^{13}C NMR (CD_3OD) δ: 163.8 (1C, 4°), 157.1 (1C, 4°), 155.0 (1C, 4°), 151.5 (1C, 4°), 150.6 (1C, 4°), 133.0 (2C, 3°), 122.7 (2C, 3°), 122.1 (1C, 4°), 121.8 (2C, 3°), 119.8 (2C, 3°), 117.9 (1C, 4°), 117.6 (2C, 3°), 117.2 (2C, 3°). IR (cm^{-1}): 3600–3200, 1690, 1603, 1499. HRMS: calcd for $C_{19}H_{14}O_5$ 322.0841, found 322.0846.

4-[3-(3-Hydroxyphenoxy)phenoxy]benzoic Acid (31). Yield: 87%. Mp: 125–25 °C. TLC (2:3 EtOAc/Hex): R_f = 0.13. ^{1}H NMR δ: 8.59 (1H, br s), 8.04 (2H, d, J = 8.6 Hz), 7.43 (1H, t, J = 8.2 Hz), 7.20 (1H, t, J = 8.5 Hz), 7.10 (2H, d, J = 8.6 Hz), 6.86 (2H, dd, J = 8.1, 2.2 Hz), 6.74 (1H, t, J = 2.2 Hz), 6.63 (1H, dd, J = 8.5, 2.1 Hz), 6.55 (1H, t, J = 2.1 Hz), 6.52 (1H, dd, J = 8.5, 2.1 Hz). ^{13}C NMR δ: 162.1 (1C, 4°), 159.8 (2C, 4°), 158.6 (1C, 4°), 157.9 (1C, 4°), 132.8 (2C, 3°), 131.9 (1C, 3°), 131.3 (1C, 3°), 126.2 (1C, 4°), 118.4 (2C, 3°), 115.3 (1C, 3°), 115.2 (1C, 3°), 111.8 (1C, 3°), 111.0 (1C, 3°), 110.8 (1C, 3°), 107.2 (1C, 3°). IR (cm^{-1}): 3550–3200, 2960–2855, 1679, 1591, 1506. HRMS: calcd for $C_{19}H_{14}O_5$ 322.0841, found 322.0834.

4-[3-(4-Hydroxyphenoxy)phenoxy]benzoic Acid (32). Yield: 65%. Mp: 153–155 °C. TLC (2:3 EtOAc/Hex): R_f = 0.13. ^{1}H NMR δ: 8.10 (2H, dm, J = 8.7 Hz), 7.44 (1H, t, J = 8.2 Hz), 7.13 (2H, dm, J = 8.7 Hz), 7.02 (2H, dm, J = 9.1 Hz), 6.93 (2H, dm, J = 9.1 Hz), 6.83 (2H, dd, J = 8.2, 2.3 Hz), 6.70 (1H, t, J = 2.3 Hz). ^{13}C NMR δ: 166.9 (1C, 4°), 162.7 (1C, 4°), 161.5 (1C, 4°), 157.8 (1C, 4°), 155.1 (1C, 4°), 149.1 (1C, 4°), 132.7 (2C, 3°), 131.7 (1C, 3°), 126.0 (1C, 4°), 122.2 (2C, 3°), 118.3 (2C, 3°), 117.1 (2C, 3°), 114.1 (1C, 3°), 113.8 (1C, 3°), 109.4 (1C, 3°). IR (cm^{-1}): 3450-3250, 3200–3000, 1688, 1591, 1505. HRMS: calcd for $C_{19}H_{14}O_5$ 322.0841, found 322.0841.

General Procedure for DCC Polymerizations. (Any deviations for a given compound are noted with the characterization data for that compound.) A 0.10 mmol (32 mg) sample of the hydroxy acid monomer and DPTS (0.20 mmol, 59 mg) were stirred with THF (1.5 mL), pyridine (200 μL), and CH_2Cl_2 (500 μL). The mixture was heated just to reflux and cooled to rt, and DCC (0.20 mmol, 41 mg) was added. The reaction was allowed to stir at rt for 24 h. The resulting white slurry was added slowly dropwise to 100 mL of rapidly stirred methanol. The white precipitate was isolated by centrifugation, stirred with methanol (10 mL), and again centrifuged. The resulting solid was dissolved in a minimum of THF (<3 mL), and the crystallization process was repeated until the polymer was free of dicyclohexylurea according to GPC (2–3×).

Poly[4-[4-(3-hydroxyphenoxy)phenoxy]benzoic acid] (38). Yield: 50%. Melting range: 200–210 °C (hot stage); mp 167 °C (DSC); M_w = 4800, M_n = 2500, M_w/M_n = 1.9. TGA onset of decomposition: 393 °C. ^{13}C NMR (DMF-d_7) δ: 133.5, 129.1, 128.5, 126.8, 122.5, 121.9, 117.8, 108.0. IR (cm^{-1}): 2952, 2840, 1735, 1601, 1495.

Poly[4-[4-(4-hydroxyphenoxy)phenoxy]benzoic acid] (39). This polymerization was conducted in a 1:1 DMF/pyridine solvent system. Yield: 65%; melting range 280–300 °C with decomposition at upper end (hot stage). TGA onset of decomposition: 448 °C. IR (cm^{-1}): 2960–2840, 1740, 1593, 1496. Further characterization was not possible due to the insolubility of the polymer.

Poly[4-[3-(3-hydroxyphenoxy)phenoxy]benzoic acid] (40). Yield: 45%; melting range 140–145 °C (hot stage); DSC endotherm at 132 °C; M_w = 7300; M_n = 6100; M_w/M_n = 1.2. TGA onset of decomposition: 431 °C. ^{1}H NMR (THF-d_8) δ: 8.15 (2H, d, J = 8.7 Hz), 7.39 (1H, t, J = 8.5 Hz), 7.24 (2H, d, J = 8.9 Hz), 7.15–7.06 (4H, m), 6.86 (2H, dd, J = 8.5, 2.3 Hz), 6.65 (1H, t, J = 2.3 Hz). ^{13}C NMR (THF-d_8) δ: 164.3 (1C, 4°), 162.8 (1C, 4°), 159.5 (1C, 4°), 158.6 (1C, 4°), 158.1 (1C, 4°), 155.4 (1C, 4°), 133.1 (2C, 3°), 131.8 (1C, 3°), 130.9 (1C, 3°), 125.2 (1C, 4°), 118.8 (2C, 3°), 117.8 (1C, 3°), 116.7 (1C, 3°), 115.9 (2C, 3°), 113.7 (1C, 3°), 111.8 (1C, 3°).

Poly[4-[3-(4-hydroxyphenoxy)phenoxy]benzoic acid] (41). Yield: 53%; melting range 155–170 °C (hot stage); DSC endotherms at 109 and 159 °C; M_w = 8300, M_n = 3900, M_w/M_n = 2.3. TGA onset of decomposition: 426 °C. ^{1}H NMR (THF-d_8) δ: 8.17–8.09 (2H, m), 7.43–7.33 (2H, m), 7.14–7.04 (2H, m), 7.02–6.80 (4H, m). ^{13}C NMR (THF-d_8) δ: 164.6 (1C, 4°), 162.9 (1C, 4°), 160.2 (1C, 4°), 158.0 (1C, 4°), 155.0 (1C, 4°), 148.2 (1C, 4°), 133.0 (2C, 3°), 131.8 (1C, 3°), 125.2 (1C, 4°), 124.0 (2C, 3°), 120.8 (2C, 3°), 118.5 (2C, 3°), 115.3 (1C, 3°), 115.2 (1C, 3°), 111.1 (1C, 3°). IR (cm^{-1}): 2960–2840, 1737, 1591, 1503.

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Supplementary Material Available: Copies of ^{1}H and ^{13}C NMR spectra given (75 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.