JOC Article

Controlling the Scholl Reaction

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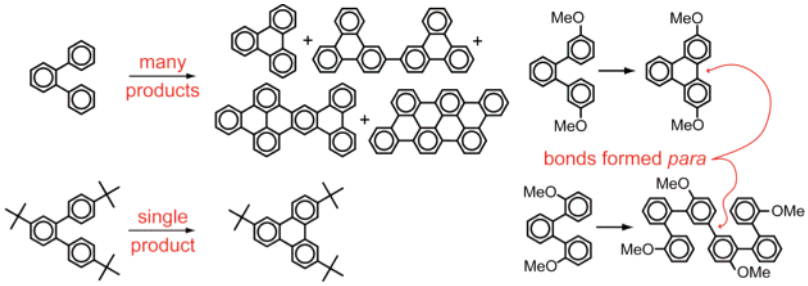

Guidelines for the application of the Scholl reaction were developed. Labeling experiments demonstrate that the Scholl reaction fails in small, unsubstituted oligophenylenes (e.g., *o*-terphenyl) due to oligomerization of the products (e.g., triphenylene). Incorporation of suitably placed blocking groups (e.g., *t*-butyl) suppresses oligomerization. The well-established directing group effects in electrophilic aromatic substitution predict the outcome of Scholl reactions of substituted substrates. Activating *o*,*p*-directing groups (e.g., MeO) direct bond formation *o*,*p*, either intramolecularly or intermolecularly. Deactivating *o*,*p*-directing groups (e.g., Br) also direct bond formation *o*,*p* but yields are lower. Deactivating *m*-directors (e.g., NO_2) suppress reaction. $MoCl_5$ and $PhI(OOCCF_3)_2/BF_3{\cdot}Et_2O$ are general and effective reagents for the Scholl oxidation. Calculations (B3LYP/6-31G(d)) predict the Scholl reaction in alkoxyarenes to proceed via arenium cations, not radical cations. Suzuki—Miyaura couplings were used to generate 12 substituted *o*-terphenyl derivatives.

Introduction

The Scholl oxidation, which generates a new C—C bond between two unfunctionalized aryl vertices, has not been a mainstay of organic synthesis because its outcome has been somewhat unpredictable. Its use has been essentially limited to the preparation of hexaalkoxytriphenylenes,[1,2] which are widely studied as discotic liquid crystals, and to the preparation of large polycyclic aromatic hydrocarbons (PAHs) from branched phenylene precursors,[3−5] an area dominated by Müllen and coworkers. In this work, we aimed to develop a practical set of guidelines for the rational application of the Scholl reaction.

The Scholl reaction holds much promise, as illustrated by comparison with the widely used Suzuki—Miyaura coupling. The Suzuki—Miyaura reaction requires an aryl halide and an aryl boronic acid or ester, which can be difficult to purify and whose preparation requires an additional step; the Scholl oxidation requires no functionality. The Suzuki—Miyaura

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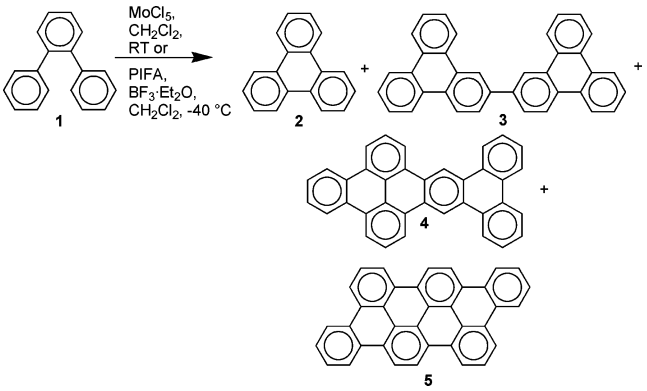
coupling requires expensive palladium catalysts, whereas the Scholl reaction can use inexpensive reagents, even iron salts. The Suzuki−Miyaura coupling is rarely used in cascade sequences (although it is effective for polymerizations[6]), but in contrast the Scholl reaction has been used to make 126 bonds in a single step.[3]

A strong acid, often a Lewis acid, and an oxidant are necessary;[7] a single reagent often serves both roles. Brønsted acids, which are usually present as impurities in Lewis acids and are necessarily formed as a byproduct of the Scholl reaction, accelerate the reaction.[8] The following cocktails have all been reported in the literature: $FeCl_3$ in CH_2Cl_2,[9] $CuCl_2$[5], or $Cu(OSO_2CF_3)_2$[3] with $AlCl_3$ in CS_2, $MoCl_5$ with or without $TiCl_4$ in CH_2Cl_2,[10−12] $(CF_3COO)_2I^{III}C_6H_5$ (PIFA)[13] with $BF_3{\cdot}Et_2O$ in CH_2Cl_2, $Pb(OAc)_4/BF_3{\cdot}Et_2O$ MeCN,[14,15] $Tl(O_2CCF_3)_3$ in CF_3CO_2H,[15] and $Tl(O_2CCF_3)_3/BF_3{\cdot}Et_2O$ in organic solvents.[15]

Radical cation based[7,16] and arenium cation based mechanisms have been proposed[7,17] for the Scholl reaction. In an excellent paper, Kochi discusses the difficulties of distinguishing acid vs electron-transfer catalysis.[18] Feng, Wu, Enkelmann, and Müllen recently reported that topology and substituents (iodine, *t*-butyl) influence the cyclization of hexa-*peri*-hexabenzocoronene precursors.[19] They attribute this effect to substituents perturbing the spin density of putative radical cation intermediates. Recent computational mechanistic studies[20,21] suggest that the arenium cation mechanism has lower key transition state barriers than the radical cation mechanism in polyphenyl benzenes. The energetically favored arenium cation mechanism involves the formation of an arenium cation, its electrophilic attack on an arene, deprotonation (or possibly decomplexation of a Lewis acid), and oxidative dehydrogenation to restore aromaticity.

SCHEME 1. Products of the Scholl Reaction of *o*-Terphenyl



Results

We first evaluated common Scholl conditions using a simple reaction, the conversion of unfunctionalized *o*-terphenyl **1** to triphenylene **2** (Scheme 1). When using $FeCl_3$, the optimized yield was ∼20%. Chlorinated solvents (CH_2Cl_2, $CHCl_3$, CCl_4, CH_2ClCH_2Cl) gave faster reactions than CH_3NO_2 or hexane. When using $MoCl_5$ in CH_2Cl_2,[2,10,11] the optimized yield was also ∼20%. Aside from triphenylene, unreacted *o*-terphenyl and insoluble oligomeric products were present. In a typical optimized reaction, about 25% of the reaction mixture was triphenylene and unreacted *o*-terphenyl. The remaining 75% was yellow insoluble powder. Vacuum sublimation of this powder afforded clean 2,2′-bistriphenylene **3**. The MALDI-MS of the residue showed two compounds having a mass 2 or 4 Da less that of **3**, indicating that annulation had occurred. These compounds likely correspond to **4** and **5**, based on the propensity of the Scholl reaction to give fully fused products.[20,21] Higher oliomers were also evident. Reactions using $C_6H_5I(O_2CCF_3)_2/BF_3{\cdot}Et_2O$ (PIFA/BF_3) instead of $MoCl_5$ gave similar results. High dilution conditions (0.5 mg/mL) did not improve the performance of this reaction. Less oligomeric product (10%) was formed, but the conversion of **1** to **2** was lower (10%).

The Scholl oxidation of terphenyl homologues also failed to produce products in good yield. *o*-Quaterphenyl **6**, 1,2,3-triphenylbenzene **7**, and *o*-quinquephenyl **8** afforded only trace amounts of their annulated PAH counterparts **9**, **9**, or **10** respectively, using either $MoCl_5$ or PIFA/$BF_3{\cdot}Et_2O$. These experiments are summarized in Scheme 2.

The reactions in Schemes 1 and 2 produced much oligomeric material. To determine if dimeric products arise from terphenyl coupling, triphenylene coupling, or cross-coupling, the oxidation of a 1:1 mixture of ^{13}C-labeled *o*-terphenyl ($C_6H_5-C_6H_4-{}^{13}C_6H_5$) and unlabeled triphenylene was performed using substoichiometric oxidant (10 mol % with respect to both reactants). MALDI-MS revealed that the dimeric products are unlabeled.

Blocking groups are commonly used to direct electrophilic aromatic substitution. We exploited this effect to suppress dimerization. Oxidation of 4,3′,4″-tri(*t*-butyl)-*o*-terphenyl **11** by PIFA/$BF_3{\cdot}Et_2O$ gave 2,7,10-tri(*t*-butyl)triphenylene **12** in good yield (86%) (Scheme 3), but use of $MoCl_5$ gave an intractable reaction mixture. The oxidation of 4,4″-di-*t*-butylterphenyl **13** by PIFA/$BF_3{\cdot}Et_2O$ gave 3,7-di(*t*-butyl)triphenylene **14** and its dimer **15**, which was crystallographically characterized.

Methoxy groups are effective *o*,*p*-directors. We find that methoxy groups influence the Scholl reaction, and oxidation of

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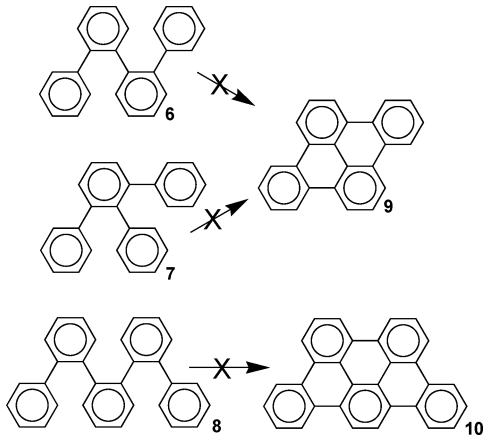
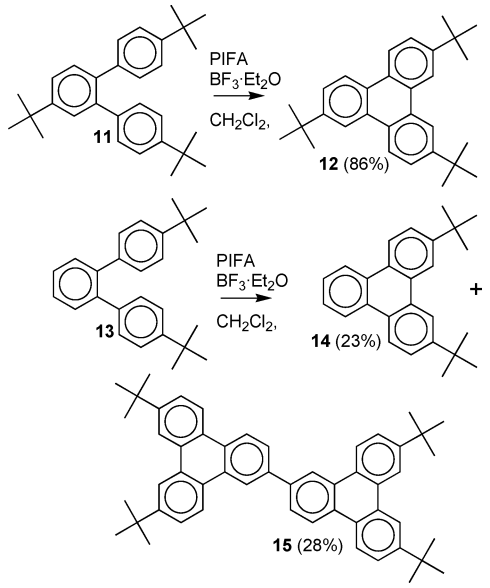
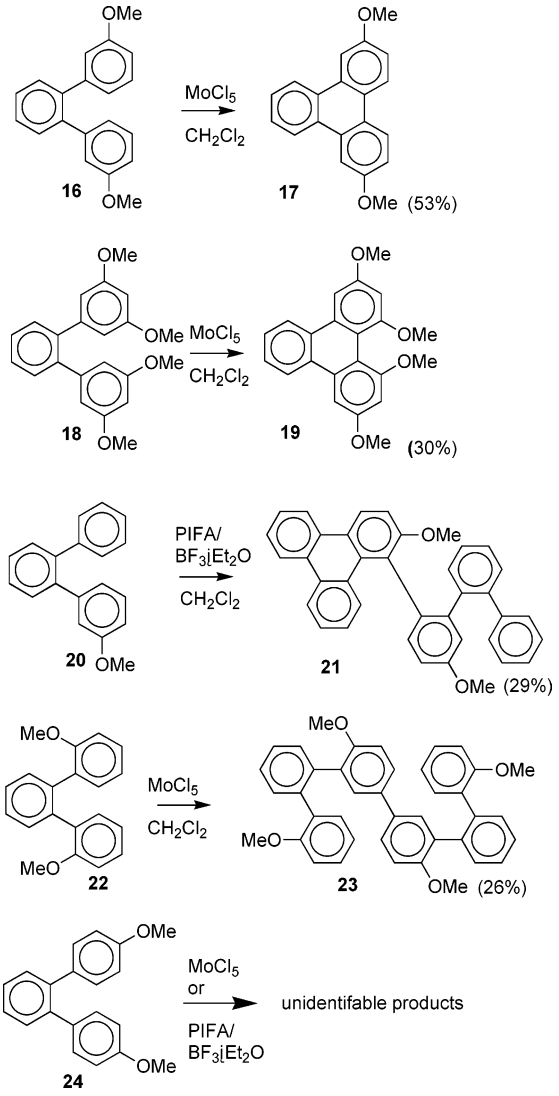
SCHEME 2. Small, Unsubstituted Oligophenyl Arenes that Do Not Fuse Cleanly



SCHEME 3. Oxidation of *tert*-Butylated Terphenyls



SCHEME 4. Oxidation of Methoxylated Terphenyl Derivatives



3,3″-dimethoxy-*o*-terphenyl **16** with $MoCl_5$ in CH_2Cl_2 gave 2,7-dimethoxytriphenylene **17** in 53% isolated yield (Scheme 4). The oxidation of the tetramethoxy derivative **18** using the same conditions gave the 1,3,10,12-tetramethoxytriphenylene **19** in 30% isolated yield. The best results were obtained with 3 equiv of $MoCl_5$ and a 45 min reaction time. PIFA/BF_3·Et_2O gave lower conversion and more oligomeric material.

The Scholl oxidation of 3-methoxy-*o*-terphenyl **20** using $MoCl_5/CH_2Cl_2$ gave an intractable mixture in which neither of the possible corresponding products, 1- or 2-methoxytriphenylene, was observed. The use of PIFA/BF_3·Et_2O at −78 °C gave the terphenyl/triphenylene dimer **21**. Single-crystal X-ray diffraction analysis established connectivity.

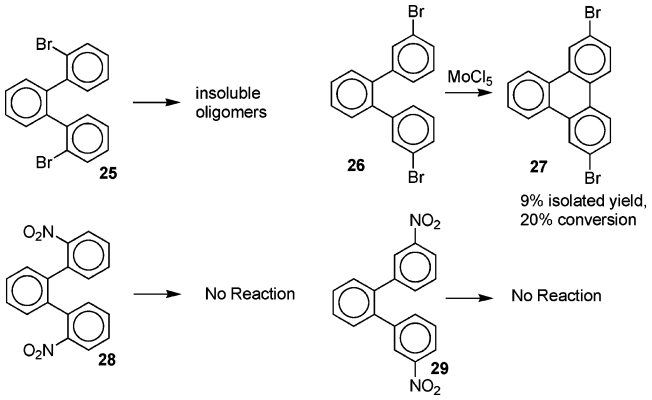
The oxidation of 2,2″-dimethoxy-*o*-terphenyl **22** failed to produce 1,8-dimethoxytriphenylene. From the complex reaction mixture, we isolated the dimer of the starting compound, tetramethoxysexiphenyl **23**, as the major product in 26% yield, the structure of which was determined by X-ray diffraction analysis. Attempts to oxidize 4,4″-dimethoxy-*o*-terphenyl **24** gave only intractable reaction mixtures.

The influence of deactivating substituents was examined. Bromine atoms, which are weakly deactivating, *o*,*p*-directing substituents, are similar to methoxy groups. Oxidation of 2,2″-dibromo-*o*-terphenyl **25** using $MoCl_5$ did not produce detectable quantities of 1,8-dibromotriphenylene under any conditions—only insoluble oligomers and starting material were recovered. The oxidation of 3,3″-dibromo-*o*-terphenyl **26** using $MoCl_5/CH_2Cl_2$ gave a mixture of the starting compound and 2,7-dibromotriphenylene **27** with conversion of about 20% (GC-MS) in an isolated yield of 9% (Scheme 5). Reaction optimization was unsuccessful. Nitro groups, which are strongly deactivating, *m*-directing substituents, inhibit the Scholl reaction. Both 2,2″-(**28**) and 3,3″-dinitroterphenyl (**29**) failed to react (**28** PIFA/BF_3·Et_2O; **29**, PIFA/BF_3·Et_2O and $MoCl_5$).

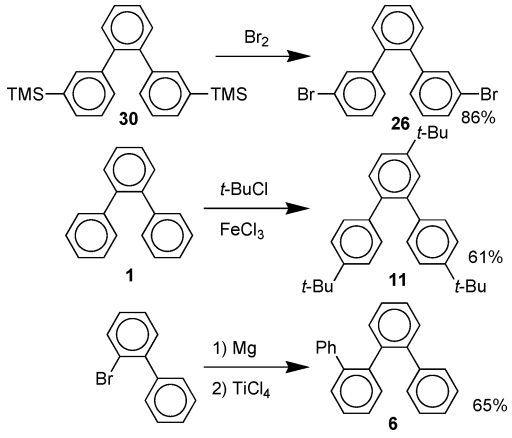
The Suzuki−Miyaura coupling provided a general route to prepare the substituted terphenyls. Symmetrically substituted terphenyls were prepared from *o*-diiodobenzene and a substituted phenylboronic acid. Unsymmetrical terphenyls were prepared from 2-iodobiphenyl and a substituted phenylboronic acid or from 2-biphenylboronic acid and an aryl halide. The syntheses are compiled in Table 1.

Three substituted *o*-terphenyls were prepared by alternative methods (Scheme 6). Suzuki−Miyara coupling was ineffective for the preparation of **26**. *ipso*-Bromination of **30** afforded **26**.

SCHEME 5. Deactivated Substrates



SCHEME 6. Other Methods Used for the Synthesis of Substituted Terphenyls



Friedel−Crafts alkylation of *o*-terphenyl introduced three *t*-butyl groups. *o*-Quaterphenyl was prepared according to literature methods.[22]

Discussion

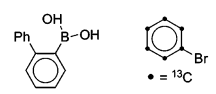
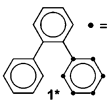
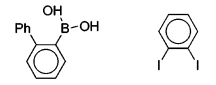
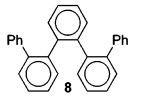
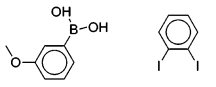
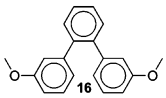
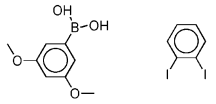
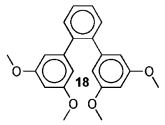
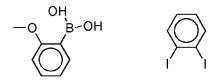
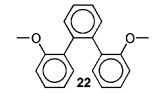
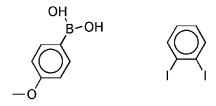
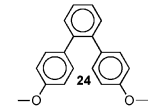
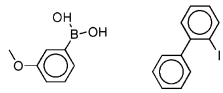
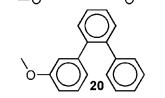
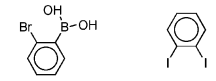
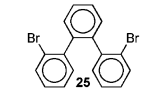
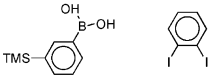
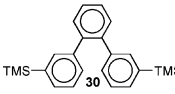
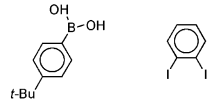
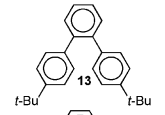
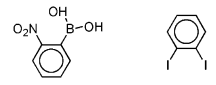
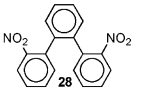
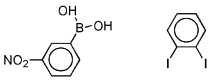
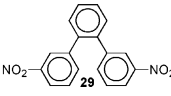
In previous computational and experimental work,[20,21] we addressed the question, why does the Scholl reaction work well in large phenylene dendrimers? Here, we address the complementary question: Why does the Scholl reaction not work well in small phenylene oligomers, such as *o*-terphenyl? The answer is that oligomerization of products is faster than cyclization of reactants.

This is demonstrated by the labeling experiment shown in Scheme 7. This experiment relies on observations from the oxidation of unlabeled parent *o*-terphenyl—the oligomeric products do not contain terphenyl units, only triphenylene units. This could stem either from exclusive oligomerization of triphenylene or from oligomerization of reactants to give putative sexiphenyl or terphenyl−triphenylene intermediates, which rapidly cyclize. To distinguish these scenarios, a 1:1 mixture of ^{13}C-labeled terphenyl **1*** and unlabeled triphenylene **2** was oxidized. The use of a substoichiometric oxidant (10 mol % with respect to both reactants) was necessary to minimize the formation of labeled triphenylene, which would complicate the analysis, from terphenyl. Each dimerization scenario will give isotopically unique products: (a) terphenyl−terphenyl coupling will give two labeled rings; (b) terphenyl−triphenylene coupling will give a single labeled ring; and (c) triphenylene−triphenylene coupling will give no labeled rings. The MALDI-MS of the insoluble products shows a dominant (>95%) peak at 450. Within the uncertainty of the approximation that only unlabeled triphenylene is present, triphenylene−triphenylene dimerization occurs exclusively. The Scholl oxidation of *o*-terphenyl fails because the product oligomerizes.

The vast majority of successful Scholl oxidations on unsubstituted phenylenes produces insoluble products. This is because the products precipitate from solution, minimizing their propensity to oligomerize. This observation supports the conclusion that oligomerization occurs through the products, not the reactants. If the reactants did oligomerize rapidly, these successful reactions would also be plagued by the production of oligomers, but they are not. It logically follows that reactants do not oligomerize rapidly.

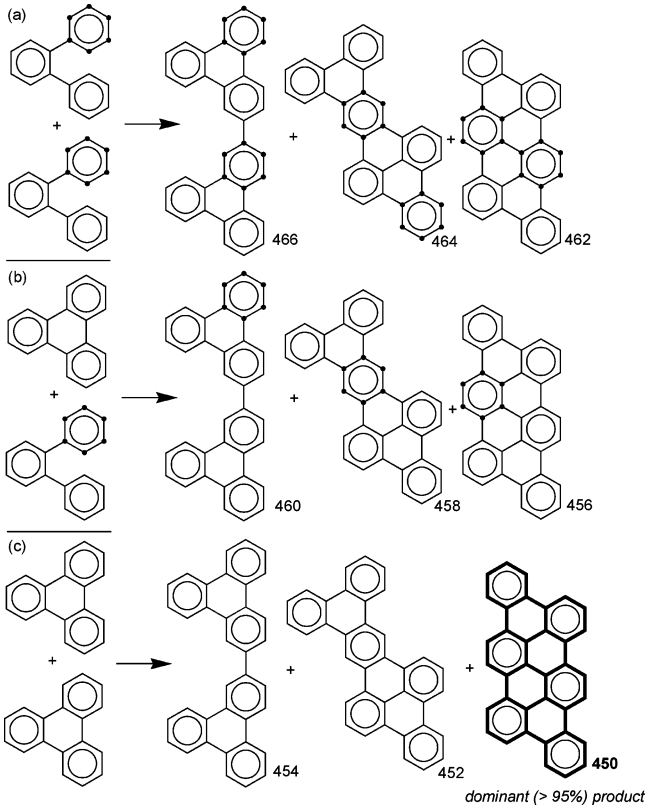
Precipitation, however, does not completely prevent the formation of oligomers. In the oxidation of hexaphenylbenzene

TABLE 1. Suzuki−Miyaura Routes to Terphenyls

reactants	product	conditions	yield
		DMF/H_2O, $Ba(OH)_2$, $PdCl_2(dppf)$	77%
		diglyme/H_2O, NaOH, $Pd(PPh_3)_4$	87%
		DME/H_2O, NaOH, $Pd(PPh_3)_4$	80%
		diglyme/H_2O, NaOH, $Pd(PPh_3)_4$	91%
		DME/H_2O, NaOH, $Pd(PPh_3)_4$	62%
		diglyme/H_2O, NaOH, $Pd(PPh_3)_4$	78%
		diglyme/H_2O, NaOH, $Pd(PPh_3)_4$	67%
		$PhNO_2/H_2O$, NaOH, $Pd(PPh_3)_4$	60%
		diglyme/H_2O, NaOH, $Pd(PPh_3)_4$	40%
		DME/H_2O, NaOH, $Pd(PPh_3)_4$	72%
		DMF/H_2O, $Ba(OH)_2$, $PdCl_2(dppf)$	26%
		DMF/H_2O, $Ba(OH)_2$, $PdCl_2(dppf)$	40%

(22) Inoue, A.; Kitagawa, K.; Shinokubo, H.; Oshima, K. *Tetrahedron* **2000**, *56*, 9601−9605.

SCHEME 7. Possible Outcomes of the Labeling Experiment[a]



[a] Only a single isotopomer is shown.

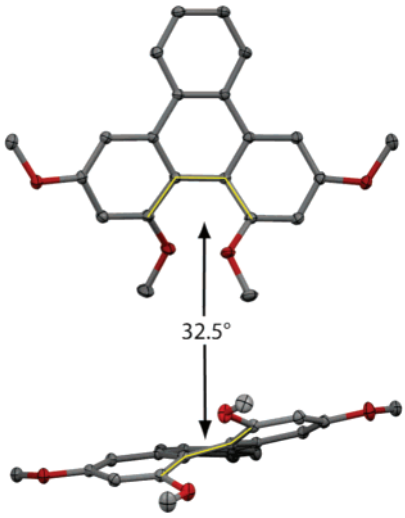


FIGURE 1. Thermal ellipsoid plots of the X-ray structure of **19** from two perspectives. Hydrogen atoms are omitted for clarity.

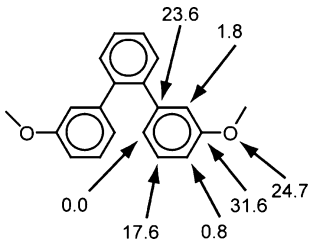


FIGURE 2. Relative proton affinities (kcal/mol) in **16**.

to hexa-*peri*-hexabenzocoronene, MALDI-MS reveals the formation of oligomers.[21] This could be the result of slow oligomerization of reactants, of the dilute products, or of any of the numerous intermediates.

It is interesting that in the oxidation of *o*-terphenyl **1** (Scheme 1), 1,2′- or 1,1′-bistriphenylene was not observed—only 2,2′-bistriphenylene **3** could be identified. The prosaic explanation is that the 2,2′-isomer **3** is formed faster that the 1,2′- or the 1,1′-isomer. However, a more appealing hypothesis exists. The 2,2′-isomer **3** cannot undergo intramolecular Scholl oxidation. In contrast, the 1,2′- and 1,1′-isomers can undergo intramolecular Scholl oxidation, to form **4** and **5**, respectively. This intramolecular fusion may occur faster than dimerization. Such behavior, a slippery slope effect, has been noted previously.[20,21] The failure to observe 1,2′- or 1,1′-bistriphenylene may be because they cyclize rapidly to form **4** and **5**.

t-Butyl groups can inhibit vicinal reactions, and this effect has been used to direct aryl halogenation.[23] In the Scholl oxidation, *t*-butyl groups inhibit oligomerization (Scheme 3). Oxidation of tri(*t*-butyl)terphenyl **11** gave triphenylene **12** in high yield (85%) without formation of dimeric products. This contrasts with oxidation of di(*t*-butyl)terphenyl **13**, which gave only modest yields (23%) of triphenylene **14**, along with significant amounts (28%) of dimer **15**, with coupling occurring at the open ring. For both reactions, the electronic effect of the *t*-butyl groups on the formation of the new bond is negligible because the mildly *o*,*p*-directing *t*-butyl groups are *meta* to the new bonds.

If the Scholl reaction proceeds by electrophilic aromatic substitution, as calculations suggest, directing group effects should be manifest. This effect has been used, perhaps fortuitously, to control the Scholl reaction, e.g. the oxidation of veratrole is commonly used to make hexaalkoxytriphenylenes.[12,24] Permethoxylated hexa-*peri*-hexabenzocorone has been prepared by Scholl oxidation of hexakis(3,4,5-trimethoxyphenyl)benzene.[25] The methoxy group and probably other activating *o*,*p*-directors that are compatible with acidic oxidants can control the outcome of the Scholl reaction. As evidenced by the clean formation of **17** (53%) and the formation of tetramethoxy triphenylene **19** (30%) and dimers **21** (29%) and **23** (26%) (Scheme 4), aryl−aryl bonds form readily in two situations: *para* to two methoxy groups or *para* to one methoxy and *ortho* to another methoxy. We see no evidence for the expected formation of bonds *ortho* to two methoxy groups, but it is difficult to design test substrates that cannot react through rotamers to give isomeric products. Bonds are not formed *meta* to a methoxy group. In substrates with suitably located directing groups, intramolecular cyclization competes effectively with oligomerization.

The Scholl reaction can introduce significant molecular strain. Tetramethoxytriphenylene **19** (Figure 1, Scheme 4) possesses 19 kcal/mol of strain, considering **2** and **17** to be unstrained (B3LYP/6-31G*).

(23) Harvey, R. G.; Pataki, J.; Cortez, C.; Raddo, P. D.; Yang, C. X. *J. Org. Chem.* **1991**, *56*, 1210−1217.

(24) Simoni, D.; Giannini, G.; Baraldi, P. G.; Romagnoli, R.; Roberti, M.; Rondanin, R.; Baruchello, R.; Grisolia, G.; Rossi, M.; Mirizzi, D.; Invidiata, F. P.; Grimaudo, S.; Tolomeo, M. *Tetrahedron Lett.* **2003**, *44*, 3005−3008.

(25) Wang, Z.; Dötz, F.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 1247−1250.

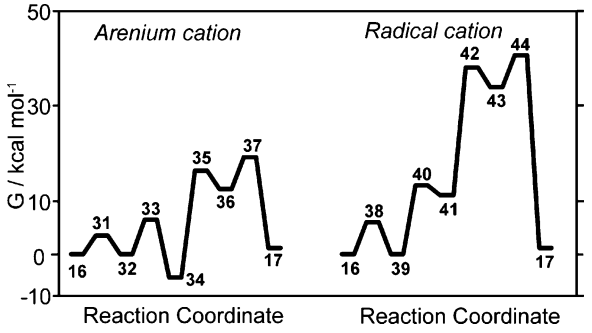


FIGURE 3. Comparison of arenium cation and radical cation reaction coordinate diagrams for the conversion of **16** to **17**.

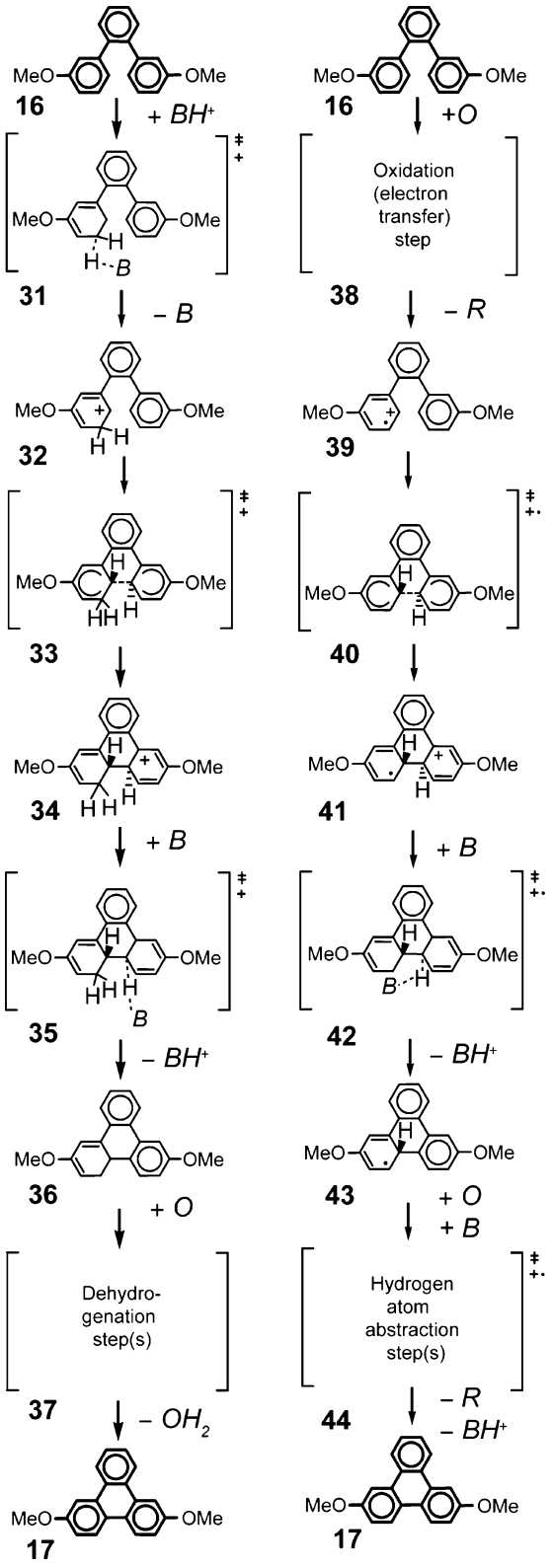
The arenium cation pathway is preferred over a radical cation pathway in the conversion of unsubstituted *o*-terphenyl to triphenylene.[20,21] However, a radical cation pathway is the accepted mechanism for Scholl oxidation of aryl ethers.[26] Does the presence of ether functionalities change the nature of the mechanism? We addressed this point as we have done before, by calculating the reaction pathways (B3LYP/6-31(d), some transition-state energies are based on literature values).[20,21] To enable the direct comparison, we make the thermodynamic assumptions that the initial steps are thermoneutral and that the net energetic outcomes are equal (see ref 21 for discussion). The reaction coordinate diagrams are shown in Figure 3. The arenium cation pathway gives lower C−C bond forming activation barriers by 7 kcal/mol. The penultimate intermediates, dihydroterphenyl **36** or radical **43**, define the energies of the rate-determining transition state. The arenium cation pathway is favored by 22 kcal/mol.

The nature of the C−C bond forming transition state for radical cation **40** is complex and involves a change in electronic symmetry. The details of this elementary step will be reported separately.[27]

Surprisingly, the oxygen atoms are not the most basic sites in **16** (Figure 2), carbon 5 is. These results are similar to proton affinity calculations (B3LYP/6-311++G(d,p)) on anisole,[28] where the *para* carbon is the most basic. Protonation of carbon 6, however, does not place positive charge at position 6, which is required for the intramolecular electrophilic attack. We have previously reported[21] that protonation *ortho* to the new bond, which does put positive charge at the electrophilic position, provides the lowest-energy transition-state barrier in the conversion of **1** to **2**. The same consideration applies to the conversion of **16** to **17**. Because the tautomers are in rapid equilibrium, the Curtin−Hammett principle applies and reaction will occur through the lowest-energy transition state. These findings are summarized in Figure 3 and Scheme 8. The arenium ion mechanism is energetically preferred for the conversion of **16** to **17**.

Deactivating groups were also considered (Scheme 5). Bromides, which are deactivating but *o*,*p*-directing, work like methoxy but in lower yields. The nitro group is a strongly deactivating *m*-director. Not surprisingly, no reaction was observed when 2,2′- or 3,3′-dinitro-*o*-terphenyl (**28** or **29**) was treated with $MoCl_5$ or PIFA/BF_3·Et_2O. The electron-withdrawing nitro group could inhibit either the generation of the arenium

SCHEME 8. Arenium Cation (Left) and Radical Cation (Right) Mechanisms for the Conversion of 16 to 17



cation or its intramolecular attack with the adjacent phenyl ring, both of which are necessary for reaction.

A few points of the terphenyl syntheses merit discussion. Diglyme, which is not widely used in Suzuki reactions, was notably effective (Table 1). $Pd(dppf)_2$ worked well for the

(26) Musgrave, O. C. *Chem. Rev.* **1969**, *69*, 499−531.
(27) Rempala, P.; King, B. T. to be submitted for publication.
(28) Nam, P.-C.; Nguyen, M. T.; Chandra, A. K. *J. Phys. Chem. A* **2006**, *110*, 4509−4515.

preparation of both unsubstituted ^{13}C-labeled terphenyl **1*** and nitrated terphenyls[29] **28** and **29**.

Conclusions

The Scholl reaction fails in small, unfunctionalized arenes because the products oligomerize. This can be suppressed by blocking groups. Oligomerization is less severe in large dendritic polyphenylenes because the insoluble products precipitate from solution. Suitably placed *t*-butyl groups suppress oligomerization. Electronic directing groups can be used to control the Scholl reaction. *o*,*p*-Directing, activating functionality should be present on both aryl moieties, arranged *o*,*p* or, preferably, *p*,*p* to the nascent bond. The Scholl reaction does not form bonds *meta* to an *o*,*p*-activating group. *m*-Directing, deactivating functionality suppresses the Scholl reaction. In alkoxyarenes, as in unsubstituted arenes, the Scholl reaction proceeds by an arenium cation pathway.

Experimental

General Methods. All reactions were performed under N_2 using conventional vacuum-line techniques. Catalysts were dispensed in a glove box under Ar. Anhydrous (<50 ppm) THF and Et_2O were dispensed in a glove box from commercially available kegs using a custom delivery system. CH_2Cl_2 was distilled from CaH_2 and stored over 4 Å molecular sieves. All other reagents were commercially available and used without further purification. Analytical HPLC was performed using MeOH/H_2O on a C_{18} column, a photodiode array, and evaporative light scattering detectors.

General Suzuki Reaction Method. *o*-Diiodobenzene (1 equiv) is stirred with the corresponding boronic acid (2−3 equiv) and Pd(PPh_3)$_4$ (10−12 mol %) in a mixture of equal volumes of diethylene glycol dimethyl ether (diglyme) or DME and 2.5 M NaOH (referred to as solvent/base). Solutions were degassed by freeze−pump−thaw cycles or by a dynamic vacuum before the addition of catalyst.

General Oxidation Procedure with $MoCl_5$. To a solution of *o*-terphenyl (100 mg, 0.43 mmol) in 10 mL of CH_2Cl_2 was added $MoCl_5$ (1−2 equiv, assuming 2e$^-$ oxidation). The reaction was stirred under N_2 at room temperature for 2 h. The reaction was quenched with MeOH (10 mL) and stirred for an additional hour. The resulting mixture was diluted with CH_2Cl_2 and MeOH, and insoluble materials were removed by filtration. The solids were thoroughly washed with CH_2Cl_2, air-dried (24 h), and massed. This material was analyzed using MALDI-TOF. The organics were washed with H_2O and dried over $MgSO_4$, and the solvent was removed. The composition of the resulting reaction mixture was analyzed by HPLC, GC/MS, and ^1H NMR. The products were isolated by SiO_2 chromatography.

General Oxidation Procedure with PIFA and BF_3·Et_2O. To a solution of *o*-terphenyl (100 mg, 0.43 mmol) in CH_2Cl_2 (8 mL) was added dropwise a solution of the equimolar mixture of PIFA and BF_3·Et_2O (1.5−2.5 equiv/bond) in CH_2Cl_2 (2 mL) under N_2 at −40 °C. The reaction mixture was stirred for 2 h and then warmed to −10 °C over 1.5 h. The reaction was quenched by MeOH and an aqueous solution of Na_2SO_3. The resulting mixture was diluted with CH_2Cl_2 and MeOH, and insoluble materials were removed by filtration. The solids were thoroughly washed with CH_2Cl_2, air-dried (24 h), and massed. This material was analyzed using MALDI-TOF. The organics were washed with H_2O and dried over $MgSO_4$, and the solvent was removed. The composition of the resulting reaction mixture was analyzed by HPLC, GC/MS, and ^1H NMR. The products were isolated by SiO_2 chromatography.

(29) Franc, C.; Denonne, F.; Cuisinier, C.; Ghosez, L. *Tetrahedron Lett.* **1999**, *40*, 4555−4558.

o*-Terphenyl-$^{13}C_6$ (1*).** In DMF−H_2O (3:1, 40 mL), 2-biphenyl boronic acid (220 mg, 1.1 mmol) was added to Ba(OH)$_2$·8H_2O (630 mg, 2.0 mmol) and bromobenzene-$^{13}C_6$ (163 mg, 1.0 mmol). After addition of $PdCl_2$dppf (60 mg, 0.1 mmol), the solution was heated to 80 °C for 2 h. The solution was filtered through a pad of SiO_2, and the filtrate was extracted with hexane and H_2O. The organic layer was dried over $MgSO_4$, and solvent removal gave pure **1 (181 mg, 77%).

[2,2′]Bitriphenylenyl (3).[30] See general oxidation procedure. A mixture of *o*-terphenyl (1.5 g, 6.51 mmol) and $MoCl_5$ (3.79 g, 13.8 mmol) in CH_2Cl_2 (100 mL) was stirred for 2 h. Sublimation of the insoluble material at 150 °C/160 mTorr gave **3** as a yellow powder (1.137 g, 75%): ^1H NMR 500 MHz (DMSO-d_6) δ 7.76 (m, 4H), 8.33 (dd, J = 8.5, 2.0 Hz, 1H), 8.86 (m, 2H), 8.90 (m, 1H), 8.97 (d, J = 9.0 Hz, 1H,), 9.18 (m, 1H), 9.33 (dd, J = 8.5, 2.0 Hz, 1H); ^{13}C NMR 125 MHz (DMSO-d_6) δ 121.9, 123.6, 123.6, 123.7, 124.4, 124.4, 126.8, 127.6, 127.6, 127.7, 127.8, 128.6, 129.0, 129.3, 129.3, 129.4, 129.8, 138.9; MALDI for $C_{36}H_{22}$ calcd 454.17, found 454.18.

***o*-Quaterphenyl (6).** Analogous to the reported procedure.[22] Mg turnings (0.017 g, 0.687 mmol) in THF (2 mL) were stirred with 2-bromobiphenyl (0.152 g, 0.654 mmol) overnight at room temperature under N_2. Additional THF (4 mL) was added, and the solution was cooled to −78 °C. To the reaction was added $TiCl_4$ (140 mg, 0.654 mmol) dropwise, and the mixture was stirred at 0 °C for 0.5 h. The mixture was poured into a saturated NH_4Cl solution, extracted with EtOAc (3 × 10 mL), and dried over Na_2SO_4. The solvent was removed, and the residue was chromatographed (SiO_2/hexane) to give **6** as a white solid (77 mg, 65%): mp 115−116 °C (lit.[31] mp 117.8 °C); GC/MS (EI) 306.

***o*-Quinquephenyl (8).**[32] See general Suzuki reaction method. A mixture of 2-biphenylboronic acid (0.180 g, 0.910 mmol), *o*-diiodobenzene (0.154 g, 0.455 mmol), and Pd(PPh_3)$_4$ (0.064 g, 0.055 mmol) was stirred in a mixture of NaOH, water, and diglyme (7 mL of 2.5 M NaOH, 30 mL of diglyme) at 50 °C for 3 h. Conventional workup with toluene/water, silica gel chromatography (4:1 hexane/CH_2Cl_2), and recrystallization (hexane) afforded **8** (156 mg, 87%) as a white solid: mp 162−164 °C (lit.[32] mp 152.4 °C); GC/MS (EI) 383.

4,4′,4″-Tri-*t*-butyl-*o*-terphenyl (11). *o*-Terphenyl (10.0 g, 43.5 mmol) and *t*-BuCl (56.0 g, 605 mmol) were stirred in CH_2Cl_2 (150 mL). A solution of $FeCl_3$ (5 mg) in nitromethane (0.5 mL) was added dropwise, and the solution was stirred for 1 h. The green mixture was quenched with H_2O, and the organics were extracted. Chromatography (SiO_2, hexane/benzene 1:1) and recrystallization from $(CH_3)_2CO$ afforded **11** (10.52 g, 61%) as colorless crystals: mp 131−132 °C; ^1H NMR 500 MHz ($CDCl_3$) δ 1.26 (s, 9H, CMe_3), 1.27 (s, 9H, CMe_3), 1.36 (s, 9H, CMe_3), 7.04 (m, 4H), 7.18 (m, 4H), 7.33 (m, 1H), 7.39 (m, 2H); ^{13}C NMR 125 MHz ($CDCl_3$) δ 31.3, 31.4, 31.5, 34.4, 34.4, 34.6, 124.2, 124.6, 124.6, 127.7, 129.5, 129.6, 130.2, 137.7, 138.5, 139.2, 140.1, 148.9, 149.1, 149.5; IR (NaCl plates) 2963, 2903, 2868, 2744, 2712, 2404, 1907, 1790, 1668, 1604, 1516, 1509, 1487, 1461, 1393, 1362, 1269, 1253, 1217, 1202, 1118, 1046, 1025, 1015, 1004, 946, 923, 897, 870, 834, 824, 759 cm^{-1}. Anal. calcd for $C_{30}H_{38}$: C, 90.39; H, 9.61. Found: C, 90.58; H, 9.46.

2,6,11-Tri-*t*-butyl-triphenylene (12). See general oxidation procedure. A solution of **21** (1.00 g, 2.51 mmol) in CH_2Cl_2 (10 mL) was stirred, and a solution of PIFA (2.70 g, 6.28 mmol) and BF_3·Et_2O (1.07 g, 7.54 mmol) in CH_2Cl_2 (5 mL) was added dropwise at −78 °C under nitrogen. The reaction mixture was stirred for 2 h and allowed to warm to −7 °C over 1 h. Workup and chromatography (SiO_2, petroleum ether/benzene 10:1) and subse-

(30) Shih, H.-T.; Shih, H.-H.; Cheng, C.-H. *Org. Lett.* **2001**, *3*, 811−814.

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quent removal of iodobenzene under a high vacuum afforded 0.858 g (86%) of **12** as a yellow oil, which crystallized from petroleum ether at −30 °C. An analytical sample was obtained by sublimation at 150 °C/60 mTorr (63 mg, 6.3%): mp 114−118 °C; ^{1}H NMR 500 MHz ($CDCl_3$) δ 1.49 (s, 9H, CMe_3), 1.50 (s, 9H, CMe_3), 1.51 (s, 9H, CMe_3), 7.68 (m, 3H), 8.52 (d, J = 8.5 Hz, 1H), 8.53 (d, J = 8.5 Hz, 1H), 8.60 (m, 2H), 8.64 (d, J = 2.0 Hz, 1H), 8.65 (d, J = 1.5 Hz, 1H); ^{13}C APT NMR 125 MHz ($CDCl_3$) δ 31.4 (CH_3), 31.46 (CH_3), 31.50 (CH_3), 35.00 (CMe_3), 35.01 (CMe_3), 118.85 (CH), 118.95 (CH), 119.03 (CH), 122.85 (CH), 122.98 (CH), 122.99 (CH), 124.7 (CH), 124.86 (CH), 124.94 (CH), 127.2 (C), 127.6 (C), 127.9 (C), 129.1 (C), 129.3 (C), 129.7 (C), 149.2 (C), 149.3 (C), 149.4 (C); IR (NaCl plates) 2963, 2903, 2868, 2360, 2342, 1762, 1614, 1510, 1490, 1479, 1459, 1413, 1400, 1362, 1268, 1238, 1216, 1202, 1141, 1119, 1044, 1031, 1004, 909, 880, 836, 815, 759 cm^{-1}; GC/MS (EI) 297, 282. Anal. calcd for $C_{30}H_{36}$: C, 90.85; H, 9.15. Found: C, 90.91; H, 9.19.

4,4″-Di(*t*-butyl)-*o*-terphenyl (13). See general Suzuki reaction method. To *o*-diiodobenzene (4.95 g, 15.0 mmol) in 450 mL of DME and aqueous base was added 4-*t*-butylphenylboronic acid (8.00 g, 44.9 mmol). The solution was degassed, and $Pd(PPh_3)_4$ (2.13 g, 1.85 mmol) was added. The reaction was stirred at 80 °C for 18 h. The reaction mixture was filtered and extracted with petroleum ether, and the organics were washed with H_2O several times. After solvent removal, the residue was recrystallized from MeCN to give **13** as colorless prisms (3.72 g, 72%): mp 76−79 °C; ^{1}H NMR 500 MHz ($CDCl_3$) δ 1.25 (s, 9H, CMe_3), 7.03 (m, 2H), 7.17 (m, 2H), 7.33 (m, 1H), 7.38 (m, 1H); ^{13}C APT NMR 125 MHz ($CDCl_3$) δ 31.3 (CH_3), 34.4 ($C(CH_3)_3$), 124.6 (CH), 127.2 (CH), 129.5 (CH), 130.5 (CH), 138.6 (C), 140.5 (C), 149.2 (C); IR (NaCl plates) 3057, 3026, 2903, 2867, 2711, 2360, 1907, 1791, 1665, 1612, 1598, 1512, 1478, 1462, 1442, 1398, 1363, 1269, 1241, 1217, 1202, 1161, 1113, 1105, 1059, 1025, 1006, 944, 922, 875, 835, 762, 743 cm^{-1}. Anal. calcd for $C_{26}H_{30}$: C, 91.17; H, 8.83. Found: C, 91.26; H, 8.99.

2,11-Di(*t*-butyl)triphenylene (14) and 7,7′,10,10′-Tetra(*t*-butyl)-[2,2′]-bitriphenylenyl (15). See general oxidation procedure. To a solution of **13** (0.500 g, 1.46 mmol) in CH_2Cl_2 (40 mL) was added dropwise a solution of PIFA (0.942 g, 2.19 mmol) and BF_3·Et_2O (0.311 g, 2.19 mmol) in CH_2Cl_2 (10 mL) at −78 °C under nitrogen. The reaction mixture was stirred for 3.5 h and allowed to warm to −40 °C over 1 h. The reaction was quenched with MeOH (5 g). Chromatography (SiO_2, petroleum ether/benzene 9:1) gave two bands.

Band 1 gave 0.189 g of **14** accompanied by starting material. Further purification by fractional crystallization from heptane afforded **14** (0.116 g, 23%) as pure colorless prisms: mp 167−169 °C; ^{1}H NMR 500 MHz ($CDCl_3$) δ 1.52 (s, 9H, CMe_3), 7.61 (m, 1H), 7.72 (dd, J = 8.5, 2.0 Hz, 1H), 8.58 (d, J = 8.5 Hz, 1H), 8.61 (m, 1H), 8.67 (d, J = 2.0 Hz, 1H); ^{13}C NMR 125 MHz ($CDCl_3$) δ 31.5 (CH_3), 35.0 (CMe_3), 118.9, 123.1, 123.2, 125.0, 126.7, 127.6, 129.5, 129.6, 149.7; IR (NaCl plates) 2962, 2903, 2868, 2366, 1613, 1512, 1479, 1461, 1401, 136172, 1264, 1201, 1110, 1044, 879, 819, 766 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{28}$ 340.2191, found 340.2188.

Band 2 gave 0.140 g of **15** (28%) by recrystallization from MeOH/CHCl as colorless needles: mp 366−371 °C (decomp.); ^{1}H NMR 500 MHz ($CDCl_3$) δ 1.47 (s, 18H, CMe_3), 7.68 (m, 2H), 7.95 (dd, J = 8.5, 1.5 Hz, 1H), 8.55 (d, J = 8.5 Hz, 1H), 8.65 (m, 4H), 8.91 (d, J = 1.5 Hz, 1H); ^{13}C APT NMR 125 MHz ($CDCl_3$) δ 31.4, 31.5, 35.1, 119.0 (CH), 119.1 (CH), 121.8 (CH), 123.3 (CH), 123.8 (CH), 125.1 (CH), 125.2 (CH), 126.1 (CH), 127.5 (C), 127.7 (C), 128.3 (CH), 128.8 (C), 129.7 (C), 129.91 (C), 129.94 (C), 139.5 (C), 149.8 (C), 149.9 (C); IR (NaCl plates) 2360, 1614, 1509, 1479, 1393, 1362, 1264, 878, 809 cm^{-1}; HRMS calcd for $C_{52}H_{54}$ 678.4226, found 678.4236.

3,3″-Dimethoxy-*o*-terphenyl (16). See general Suzuki reaction method. 3-Methoxyphenyl boronic acid (3.04 g, 20 mmol) and *o*-diiodobenzene (3.30 g, 10.0 mmol) were combined in 600 mL of DME and aqueous base. After degassing, $Pd(PPh_3)_4$ (1.16 g, 1.00 mmol) was added and the reaction was heated to 85 °C for 4 h. The mixture was separated by Et_2O extraction. After removal of solvent, the residue was chromatographed (SiO_2, hexane/CH_2Cl_2 3:1). Recrystallization from hexane gave 2.39 g (80% yield) of **16** as a white solid: mp 89−91 °C; ^{1}H NMR 500 MHz ($(CD_3)_2CO$) δ 3.59 (s, 3H, OMe), 6.66 (m, 1H), 6.73 (m, 2H), 7.13 (t, J = 8.0 Hz, 1H), 7.40 (s, 2H); ^{13}C NMR 125 MHz ($(CD_3)_2CO$) δ 55.4, 113.4, 116.1, 122.9, 128.5, 129.9, 131.3, 141.4, 144.0, 160.3; IR (NaCl plates) 3058, 3001, 2956, 2938, 2834, 2493, 2044, 1931, 1841, 1745, 1603, 1579, 1468, 1424, 1318, 1288, 1250, 1217, 1179, 1116, 1087, 1047, 1022, 995, 951, 874, 857, 789, 760, 734, 704 cm^{-1}; UV−vis (hexane) λ_{max} (log ϵ) 221 (3.73), 279 (3.69); GC/MS (EI) 290. Anal. calcd for $C_{20}H_{18}O_2$: C, 82.72; H, 6.26. Found: C, 82.62; H, 6.51.

2,7-Dimethoxytriphenylene (17). See general oxidation procedure. A solution of **16** (201 mg, 0.694 mmol) and $MoCl_5$ (189 mg, 0.694 mmol) in CH_2Cl_2 (15 mL) was stirred for 22 h. A second portion of $MoCl_5$ (189 mg) was added, and the reaction was stirred for an additional 6.5 h. After workup, the yellow crude product was purified by sublimation at 150 °C/160 mTorr to give **17** as a white solid (106 mg, 53%): mp 153−155 °C; ^{1}H NMR 500 MHz (DMSO-d_6) δ 4.04 (s, 3H, OMe), 7.30 (dd, J = 9.0, 2.5 Hz, 1H), 7.69 (m, 1H), 8.19 (d, J = 2.5 Hz, 1H), 8.61 (d, J = 9.5 Hz, 1H), 8.77 (m, 1H); ^{13}C NMR 125 MHz (DMSO-d_6) δ 55.8, 106.4, 117.3, 124.5, 124.7, 125.4, 128.2, 130.8, 131.0, 159.5; IR (NaCl plates) 2963, 2836, 2433, 2366, 2343, 1613, 1498, 1452, 1427, 1282, 1250, 1218, 1180, 1048, 1018, 842, 812, 761 cm^{-1}; UV−vis (hexane) λ_{max} (log ϵ) 264 (5.02), 288 (4.33), 299 (4.23); GC/MS (EI) 288. Anal. calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.27; H, 5.62.

3,3″,5,5″-Tetramethoxy-*o*-terphenyl (18). See general Suzuki reaction method. To *o*-diiodobenzene (7.98 g, 24.2 mmol) was added 3,5-dimethoxyphenylboronic acid (11.01 g, 60.5 mmol) in 500 mL of diglyme/base. The solution was degassed before the addition of $Pd(PPh_3)_4$ (1.40 g, 1.20 mmol). The reaction was heated to 80 °C for 18 h and then extracted with toluene, washed with water to remove diglyme, and evaporated. The residue was chromatographed (SiO_2, toluene/CH_2Cl_2 4:1). The product was recrystallized from ethanol to give **18** as a white solid (7.70 g, 91% yield): mp 100−101 °C; ^{1}H NMR 500 MHz, (C_6D_6) δ 3.23 (s, 6H, OMe), 6.46 (t, J = 2.5 Hz, 1H), 6.56 (d, J = 2.5 Hz, 2H), 7.20 (m, 1H), 7.46 (m, 1H); ^{13}C APT NMR 125 MHz ($CDCl_3$) δ 55.3 (OCH_3), 99.2 (CH), 107.9 (CH), 127.6 (CH), 130.2 (CH), 140.5 (C), 143.5 (C), 160.2 (C); IR (NaCl plates) 3000, 2938, 2836, 1591, 1458, 1416, 1349, 1335, 1304, 1269, 1249, 1204, 1154, 1063, 1028, 992, 928, 876, 838, 762 cm^{-1}; UV−vis (hexane) λ_{max} (log ϵ) 207 (5.17), 273 (4.64); GC/MS (EI) 350. Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.46; H, 6.58.

1,3,10,12-Tetramethoxytriphenylene (19). See general oxidation procedure. A solution of **18** (250 mg, 0.713 mmol), $MoCl_5$ (585 mg, 2.14 mmol), and $TiCl_4$ (406 mg, 2.14 mmol) in CH_2Cl_2 (25 mL) was stirred for 45 min. Removal of solvent and chromatography (SiO_2, benzene) and crystallization from MeOH gave colorless crystals of **19** (75 mg, 30%): mp 152−153 °C; ^{1}H NMR 500 MHz ($CDCl_3$) δ 3.98 (s, 3H, OMe), 4.01 (s, 3H, OMe), 6.72 (d, J = 2.0 Hz, 1H), 7.56 (d, J = 1.5 Hz, 1H), 7.58 (m, 1H), 8.44 (m, 1H); ^{13}C NMR APT 125 MHz ($CDCl_3$) δ 55.5 (OMe), 55.8 (OMe), 97.0 (CH), 98.4 (CH), 113.1 (C), 123.5 (CH), 127.2 (CH), 130.5 (C), 132.1 (C), 158.7 (C), 158.8 (C); IR (NaCl plates) 1602, 1542, 1466, 1413, 1361, 1279, 1205, 1159, 1117, 1072, 1027, 936, 824, 761 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{20}O_4$ 348.1362, found 348.1358.

3-Methoxy-*o*-terphenyl (20). See general Suzuki reaction method. To a solution of 2-iodobiphenyl (3.25 g, 11.6 mmol) in 330 mL of diglyme/aqueous base was added 3-methoxyphenylboronic acid (1.93 g, 12.7 mmol). After degassing, $Pd(PPh_3)_4$ (0.686 g, 0.6 mmol) was added and the reaction was heated to 50 °C for 36 h. Additional $Pd(PPh_3)_4$ (0.679 g, 0.6 mmol) was added, and

the solution was heated to 80 °C for 2 days. Benzene was added, and the mixture was washed with H_2O to remove diglyme. Removal of solvent and chromatography (SiO_2, hexane/CH_2Cl_2 9:1) gave pure **20** as a colorless oil (2.03 g, 67%): ^{1}H NMR 500 MHz ($CDCl_3$) δ 3.61 (s, 3H, OMe), 6.68 (m, 1H), 6.77 (m, 2H), 7.13−7.26 (m, 6H), 7.42−7.48 (m, 4H); ^{13}C APT NMR 125 MHz ($CDCl_3$) δ 55.0 (OMe), 112.6 (CH), 115.2 (CH), 122.3 (CH), 126.4 (CH), 127.4 (CH), 127.5 (CH), 127.9 (CH), 128.8 (CH), 129.8 (CH), 130.4 (CH), 130.5 (CH), 140.4 (C), 140.6 (C), 141.6 (C), 142.8 (C), 159.0 (C); IR (NaCl plates) 3058, 2937, 2833, 1601, 1577, 1488, 1471, 1435, 1417, 1319, 1297, 1243, 1209, 1179, 1046, 1021, 1008, 995, 863, 777, 761, 751, 700; UV−vis (hexane) λ_{max} (log ϵ) 208 (5.05), 279 (4.74); GC/MS (EI) 260. Anal. calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.67; H, 6.57.

2-Methoxy-1-(5-methoxy-*o*-terphenyl-2-yl)triphenylene (21). See general oxidation procedure. To a solution of **20** (600 mg, 2.31 mmol) in CH_2Cl_2 (50 mL) was added dropwise a solution of PIFA (1.49 g, 3.46 mmol) and BF_3·Et_2O (0.492 g, 3.46 mmol) in CH_2Cl_2 (10 mL) at −78 °C. The reaction mixture was stirred for 3 h at −78 °C and allowed to warm to −40 °C over 1.5 h. Chromatography (petroleum ether/benzene 8.5:1.5), crystallization (CH_2Cl_2−MeOH), and recrystallization (*o*-xylene) afforded colorless crystals of **21** (175 mg, 29%): mp 271−273 °C; ^{1}H NMR 500 MHz (1,2-dichlorobenzene-d_4, 60 °C) δ 3.34 (s, 3H, OMe), 3.47 (s, 3H, OMe), 6.63 (m, 1H), 6.74 (s, 1H), 6.84 (m, 2H), 6.90−7.02 (m, 4H), 7.09−7.21 (m, 6H), 7.34 (t, J = 7.5 Hz, 1H), 7.46 (m, 2H), 7.79 (d, J = 9.0 Hz, 1H), 8.37 (m, 4H); ^{13}C NMR APT/DEPT 125 MHz (1,2-dichlorobenzene-d_4, 60 °C) δ 54.89 (OMe), 54.94 (OMe), 111.4 (CH), 114.6 (CH), 118.1 (CH), 122.9 (CH), 123.1 (CH), 123.3 (CH), 123.6 (CH), 125.1(C), 125.4 (CH), 126.0 (CH), 126.2 (CH), 126.31 (C), 126.33 (CH), 126.5 (CH), 126.9 (CH), 127.3 (CH), 127.5 (CH), 127.8 (CH), 129.2 (CH), 129.5 (C), 129.95 (CH), 130.00 (CH), 130.1 (CH), 130.4 (CH), 130.6 (C), 130.9 (C), 131.4 (C), 131.6 (C), 131.8 (C), 133.7 (CH), 139.6 (C), 140.4 (C), 141.5 (C), 141.8 (C), 156.4 (C), 158.7 (C); IR (NaCl plates) 2993, 2936, 2833, 1604, 1589, 1555, 1494, 1461, 1449, 1427, 1406, 1383, 1341, 1300, 1266, 1250, 1206, 1174, 1127, 1087, 1044, 1012, 893, 862, 816, 804, 779, 771, 753, 744, 722, 701 cm^{-1}; HRMS (EI) calcd for $C_{38}H_{28}O_2$ 516.2089, found 516.2084.

2,2″-Dimethoxy-*o*-terphenyl (22). A mixture of *o*-diiodobenzene (1.14 g, 3.47 mmol) and 2-methoxyphenyl boronic acid (1.05 g, 6.94 mmol) in 600 mL of DME/aqeous base was degassed. Pd(PPh_3)$_4$ (400 mg, 0.35 mmol) was added, and the reaction was stirred at 85 °C for 2 h. Extraction (hexane/water), chromatography (SiO_2, hexane/CH_2Cl_2 2:1), and crystallization (EtOH) gave **22** (621 mg, 62%) as a white solid: mp 109−111 °C; ^{1}H NMR 500 MHz ($CDCl_3$) δ 3.51 (s, 3H, OMe), 6.74 (d, J = 8.0 Hz, 1H), 6.86 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 6.5 Hz, 1H), 7.18 (dt, J = 8.0, 2.0 Hz, 1H), 7.44 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 54.9, 110.1, 119.7, 127.0, 128.0, 130.5, 130.9, 131.4, 138.3, 156.2; IR (NaCl plates) 3059, 3023, 2935, 2833, 1600, 1581, 1495, 1465, 1432, 1247, 1237, 1181, 1122, 1052, 1030, 1009, 932, 798, 740 cm^{-1}; GC/MS (EI) 290; HRMS (EI) for $C_{20}H_{18}O_2$ calcd 290.1307, found 290.1303. Anal. calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.73; H, 6.25.

2,2‴″,4‴,4‴″-Tetramethoxy-[1,1′;2′,1″;3″,1‴;2‴,1‴″;2‴,1‴″]-sexiphenyl (23). See general oxidation procedure. To a solution of **22** (500 mg, 1.72 mmol) in CH_2Cl_2 (125 mL) was added $MoCl_5$ (475 mg, 1.74 mmol), and the reaction mixture was stirred for 40 min at 0 °C. Workup and chromatography (petroleum ether/CH_2Cl_2 1:1) gave recovered **22** (69 mg, 14%) and **23** (29 mg, 26%) as colorless crystals (hexane): mp 204−206 °C; ^{1}H NMR 500 MHz ($CDCl_3$) δ 3.39 (br s, 3H, OMe), 3.49 (br s, 3H, OMe), 6.68 (m, 2H), 6.80 (m, 1H), 7.12 (br m, 4H), 7.41 (m, 4H); ^{13}C APT NMR 125 MHz ($CDCl_3$, 60 °C) δ 55.0 (CH_3), 55.2 (CH_3), 110.6 (CH), 110.8 (CH), 120.0 (CH), 125.86 (CH), 126.90 (CH), 127.0 (CH), 128.10 (CH), 130.2 (CH), 130.57 (CH), 130.59 (CH) (at 25 °C signals 130.57 and 130.59 observed as a singlet), 131.3 (C), 131.4, 131.6, 132.7 (C), 138.5 (C), 138.6 (C) (at 25 °C signals 138.47 and 138.63 observed as a multiplet), 155.5 (C), 156.5 (C); IR (NaCl plates) 3007, 2935, 2833, 1601, 1492, 1475, 1461, 1432, 1249, 1249, 1180, 1144, 1124, 1064, 1027, 808 cm^{-1}; HRMS (EI) calcd for $C_{40}H_{34}O_4$ 578.2457, found 578.2447.

4,4″-Dimethoxy-*o*-terphenyl (24).[33] See general Suzuki reaction method. To *o*-diiodobenzene (237 mg, 0.70 mmol) in 60 mL of diglyme/aqueous base was added 4-methoxyphenylboronic acid (213 mg, 1.4 mmol). The solution was degassed, and Pd(PPh_3)$_4$ (99 mg, 0.085 mmol) was added. The reaction was stirred and heated to 80 °C for 1.25 h. Hexane extraction and chromatography (SiO_2, hexane/CH_2Cl_2 1:1), gave **24** as a white solid (0.160 g, 78%): mp 107−108 °C; ^{1}H NMR 500 MHz ($CDCl_3$) δ 3.77 (s, 3H, OMe), 6.75 (m, 2H), 7.04 (m, 2H), 7.35 (m, 2H); ^{13}C NMR 75 MHz ($CDCl_3$) δ 55.5, 113.8, 127.3, 130.8, 131.2, 134.6, 140.5, 158.7; GC/MS (EI) 290.

2,2″-Dibromo-*o*-terphenyl (25).[34] *o*-Diiodobenzene (1.75 g, 5.3 mmol), 2-bromophenylboronic acid (10.36 g, 52 mmol), PPh_3 (3.42 g, 13 mmol), and Pd(PPh_3)$_4$ (485 mg, 0.53 mmol) were combined with 300 mL of nitrobenzene and 320 mL of 2.5 M NaOH. The yellow/green solution was heated to 60 °C for 24 h. The mixture was extracted with H_2O, hexane, and brine. The organic layer was cooled to −20 °C to crystallize out much of the nitrobenzene. Evaporation of the solid gave a yellow oil, which was washed through a silica plug using hexanes. Evaporation of the solvent gave a yellow oil. Residual nitrobenzene was removed by bulb-to-bulb vacuum distillation at 60 °C with a collection bulb cooled by N_2(l) in liquid nitrogen. Hexane was added to the residue, and the solution was filtered through silica gel using hexane. Solvent was removed, giving **25** (1.8 g, 90%) as an oil. The product was contaminated by <1% of 2-bromo-*o*-terphenyl. Analytically pure product was isolated by preparative HPLC (C_{18}, water/MeOH 6:4), yielding **25** (1.19 g, 60% yield) as an opaque oil: ^{1}H NMR 300 MHz (DMSO-d_6) δ 7.53 (m, 2H), 7.46 (dd, J = 3.0, 3.3 Hz, 2H), 7.33 (m, 1H), 7.28 (dd, J = 4.5, 6.0 Hz, 1H), 7.11 (m, 6H); EI-MS *m*/*z* (rel. abundance) 388 (M^+), 308 (M^+ − 1Br), 228 (M^+ − 2Br).

3,3″-Dibromo-*o*-terphenyl (26).[35] A solution of Br_2 (3.91 g, 24.4 mmol) in CCl_4 (14 mL) was added to **30** (0.852 g, 2.27 mmol) in CCl_4 at 0 °C. The reaction was stirred for 35 min and quenched by the addition of 14 mL of saturated Na_2SO_3. The aqueous layer was extracted with CH_2Cl_2. The solvent was removed, and the resulting oily residue was recrystallized from ethanol to give **26** as a white solid (0.762 g, 86% yield): mp 90−91 °C (lit.[35] mp 90.9 °C); ^{1}H NMR 500 MHz ($CDCl_3$) δ 6.95 (m, 1H), 7.05 (t, J = 7.5 Hz, 1H), 7.32−7.36 (m, 2H), 7.39 (m, 1H), 7.42 (m, 1H); ^{13}C NMR 125 MHz ($CDCl_3$) δ 122.1, 128.1, 128.7, 129.4, 129.8, 130.5, 132.6, 139.0, 143.1; GC/MS (EI) 388, 228 (M^+ − 2Br).

2,7-Dibromotriphenylene (27). See general oxidation procedure. A solution of **26** (150 mg, 0.387 mmol) and $MoCl_5$ (212 mg, 0.776 mmol) in CH_2Cl_2 (15 mL) was stirred for 12 h. The crude product was chromatographed (SiO_2, petroleum ether) to afford 0.090 g (30% mass recover). Fractional crystallization from MeCN gave **27** (14 mg, 9%) as colorless crystals: mp 220−223 °C; ^{1}H NMR 500 MHz ($CDCl_3$) δ 7.68 (m, 1H), 7.71 (dd, J = 8.5, 2.0 Hz, 1H), 8.37 (d, J = 9.5 Hz, 1H), 8.50 (m, 1H), 8.70 (d, J = 2.0 Hz, 1H); ^{13}C NMR 125 MHz ($CDCl_3$) δ 122.1, 123.4, 124.9, 126.3, 127.9, 128.1, 128.9, 130.4, 131.4; IR (NaCl plates) 2918, 1594, 1571, 1486, 1435, 1413, 1087, 998, 858, 799, 757 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{10}Br_2$ 385.9129, found 385.9126.

2,2″-Dinitro-*o*-terphenyl (28). *o*-Diiodobezene (500 mg, 1.5 mmol), 2-nitrophenyl boronic acid (501 mg, 3.0 mmol), $Ba(OH)_2$·$8H_2O$ (950 mg, 3.0 mmol), and 60 mL of DMF−H_2O (4:1) were combined. After degassing, $PdCl_2$dppf (100 mg, 0.1 mmol) was

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added and the solution was stirred at 60 °C for 8 h. Filtration, thorough extraction (EtOAc/H_2O), chromatography (SiO_2, hexane/EtOAc 85:15), and evaporation gave yellow crystals. Recrystallization from EtOAc gave **28** (100 mg, 26% yield): ^{1}H NMR 500 MHz ($(CD_3)_2CO$) δ 7.20 (m, 3H), 7.35 (m, 7H), 7.72 (m, 1H), 7.93 (m, 1H); ^{13}C NMR 125 MHz ($(CD_3)_2CO$) δ 123.3, 124.2, 128.6, 129.0, 129.3, 129.7, 130.9, 133.0, 133.4; IR (NaCl plates) 2360, 2342, 1596, 1571, 1521, 1433, 1348, 1312, 1104, 1007, 855, 786, 769, 747, 706, 669 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 231 (5.40); GC/MS (EI) 320. Anal. calcd for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78. Found: C, 67.66; H, 3.79.

3,3″-Dinitro-*o*-terphenyl (29).[35] Prepared similarly as above using 3-nitrophenyl boronic acid (501 mg, 3.0 mmol) and heating to 80 °C for 8 h. After chromatography, crystallization gave **29** as yellow crystals (195 mg, 40% yield): ^{1}H NMR 500 MHz ($(CD_3)_2CO$) δ 7.56 (m, 2H), 7.62 (m, 6H), 8.06 (m, 2H), 8.13 (m, 2H); ^{13}C NMR 125 MHz ($(CD_3)_2CO$) δ 122.0, 124.6, 129.2, 129.8, 130.9, 136.5, 138.6, 142.7, 148.4; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 232 (5.26); GC/MS (EI) 320.

3,3″-Bis(trimethylsilyl)-*o*-terphenyl (30). See general Suzuki reaction method. To *o*-diiodobenzene (1.70 g, 5.2 mmol) in 100 mL of diglyme/base were added 3-trimethylsilylphenylboronic acid (3.00 g, 15.5 mmol) and $Pd(PPh_3)_4$ (586 mg, 0.5 mmol). After 16 h at 60 °C, additional $Pd(PPh_3)_4$ (0.290 g, 0.25 mmol) was added. After 1 day at 80 °C, the solution was extracted with toluene and the organics were washed with water (8 × 80 mL). Removal of solvent, chromatography (SiO_2/hexane), and recrystallization from MeOH gave **30** as a colorless solid (0.781 g, 40%): mp 83−84 °C; ^{1}H NMR 500 MHz (C_6D_6) δ 0.09 (s, 9H, $SiMe_3$), 7.13 (m, 1H), 7.22 (m, 1H), 7.25−7.29 (m, 2H), 7.31 (m, 1H), 7.43 (m, 1H); ^{13}C NMR 125 MHz (C_6D_6) δ −1.2, 127.8, 127.9, 130.5, 130.8, 131.6, 136.0, 139.7, 141.4, 141.6; IR (NaCl plates) 3021, 2955, 1463, 1384, 1261, 1248, 1121, 1023, 857, 837, 796, 750 cm^{-1}; GC/MS (EI) 375; UV−vis (hexane) λ_{max} (log ϵ) 216 nm (4.71). Anal. calcd for $C_{24}H_{30}Si_2$: C, 76.94; H, 8.07. Found: C, 76.87; H, 8.08.

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Note added in proof. After revision of this manuscript, a lower energy (ΔG, by 5 kcal/mol) rotamer of the radical cation of 3,3″-dimethoxy-*o*-terphenyl (**39**) was located. This does not affect conclusions about the preference for the arenium ion mechanism.

Supporting Information Available: Crystallographic information files for **13**−**15**, **17**−**19**, **21**, **23**, **28**, and **29**, ^{1}H and ^{13}C spectra of all synthesized compounds, coordinates of calculated structures **16**, **17**, and **31**−**44**, and computational methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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