Synthesis and Reactions of 3,4-Bis(trimethylsilyl)furan: Diels–Alder Cycloaddition, Friedel–Crafts Acylation, and Regiospecific Conversion to 3,4-Disubstituted Furans[1,2]

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As a versatile building block, 3,4-bis(trimethylsilyl)furan (**1**), conveniently obtained through a Diels–Alder reaction between 4-phenyloxazole and bis(trimethylsilyl)acetylene, was able to undergo Diels–Alder cycloadditions with dienophiles. In two separate experiments, extrusion of bis(trimethylsilyl)-acetylene occurred when **1** was treated with acetylenic dienophiles. Furan **1** was also found to undergo Friedel–Crafts acylations at the unsubstituted α-position in general and gave a pair of regioisomers. Moreover, **1** was converted regiospecifically to various 3,4-disubstituted furans, utilizing consecutively and repeatedly an *ipso* displacement of the trimethylsilyl group with boron trichloride and a novel palladium-catalyzed Suzuki-type coupling reaction of the resulting boroxines.

Introduction

3,4-Disubstituted furans are important building blocks of heterocyclic compounds. In nature, a number of biologically interesting marine natural products having this skeleton have recently been isolated and structurally elucidated.[3] Furthermore, 3,4-disubstituted furans also played an important role as key intermediates in organic synthesis.[4] In the literature, several methods for synthesizing this class of molecules have been recorded.[5] However, most of these methods involved the use of acyclic precursors, which were not otherwise suitable for the preparation of a diverse variety of 3,4-disubstituted furans (*vide infra*). The synthesis of structually more elaborate 3,4-disubstituted furans, nevertheless, still remains a formidable challenge to many organic chemists.

In a continuation of the study on possible routes to 3,4-disubstituted furan,[5i,j] we were interested in exploring the role of a silyl group as a potential directing group because silyl groups are well-known for their σ-donating character.[6] Their tendency to stabilize a β-carbocation through the so-called $(p\text{-}\sigma)_\pi$ overlap contributes to the *ipso*-substitution pattern, which is not common to the other ordinary substituents.[6] In light of this fact, the use of silyl substituents as directing groups has become a powerful tool in organic synthesis.[6] Our second concern was on the chemistry of furans. Although less obvious, there are ample examples to justify that the Diels–Alder adducts formed between furans and alkenyl dienophiles would incur a pronounced tendency to undergo cycloreversion reactions.[7] This phenomenon is likely due to the particularly low activation energies of both forward and reverse reactions involved.[7] In addition, furans with electron-withdrawing substituents at the β-positions were rather inactive as dienes, and in many cases, highly reactive dienophiles were required.[8]

Taking all the above observations and facts into consideration, we decided to investigate the use of 3,4-bis(trimethylsilyl)furan (**1**) as a starting material. It was hoped that **1**, with σ-donating trimethylsilyl groups at the β-positions, would function as a better diene, as compared to other furans with σ-accepting substituents, thereby allowing a smooth Diels–Alder cycloaddition. After cycloaddition, the silyl groups might then be replaced in an *ipso* manner by other electrophiles. It was also likely that **1** would serve as a building block for the regiospecific synthesis of 3,4-disubstituted furans, due to

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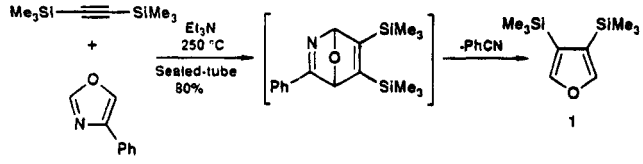
Scheme 1. Preparation of 3,4-Bis(trimethylsilyl)furan



the aforementioned *ipso* substitution tendency. We report herein the synthesis of **1**,[2a] as well as the use of **1** in Diels–Alder reactions, acylation, and regiospecific conversion to 3,4-disubstituted furans, utilizing a palladium-catalyzed Suzuki-type coupling reaction[9] of the boroxines[10] resulting from the displacement of the trimethylsilyl group with boron trichloride.

Results and Discussion

(a) Preparation of 3,4-Bis(trimethylsilyl)furan (1).[2a] Diels–Alder reaction of equimolar quantities of bis(trimethylsilyl)acetylene and 4-phenyloxazole[11] in 5 mol % triethylamine at 250 °C in a sealed tube afforded **1** as the sole product in 80% yield (Scheme 1).[5c,d,12] To prepare **1** in good yield, it was necessary to add a small amount of a proton scavenger, i.e., triethylamine, to the reaction mixture in order to suppress acid-catalyzed rearrangement of the resulting **1** to 2,4-bis(trimethylsilyl)furan.[2a]

(b) Diels–Alder Reactions of 3,4-Bis(trimethylsilyl)furan (1). After a reliable route to **1** had been secured, its reactivity was then studied. It was of particular interest to investigate the Diels–Alder cycloaddition of **1** as a diene because the trimethylsilyl groups of **1** are σ-donors. Thus, **1** was allowed to react with maleic anhydride at room temperature to provide the expected adduct 4,5-bis(trimethylsilyl)-3,6-endoxo-1,2,3,6-tetrahydrophthalic anhydride (**2**) in only 40% yield.[13] The ^{1}H NMR spectrum shows only three singlets at δ 0.25 (18H), 2.92 (2H), and 5.51 (2H), indicating an exo structure of **2**.[13] Compound **2** was also found to be rather unstable in chloroform, giving back the starting materials through a retro-Diels–Alder reaction. Surprisingly, similar cycloadditions of **1** with dimethyl acetylenedicarboxylate and 5,6-didehydrodibenzo[*a*,*e*]cyclooctene (**4**)[14] furnished dimethyl furan-3,4-dicarboxylate (**3**) and 3,4,7,8-dibenzocycloocta[1,2-*c*]furan (**5**), respectively. The ^{1}H NMR spectrum of **5** shows two singlets at δ 6.71 (2H) and 7.40 (2H) and a multiplet at δ 7.16–7.30 (8H). It is believed that the generation of a double bond between the two carbons bearing the trimethylsilyl groups in the Diels–Alder adducts is sterically unfavorable, thereby resulting in a retro-Diels–Alder reaction to afford **3** and **5**. Such steric argument was also pointed out in 1972 by Seyferth for 1,2-bis(trimethylsilyl)benzene,[12a,b] whose acid-catalyzed rearrangement was complete in 25 h at 152 °C, affording a mixture of 1,3-bis(trimethylsilyl)-benzene and 1,4-bis(trimethylsilyl)benzene in the ratio of 92:8. Sakurai's steric rationale in 1980 for a twist of the carbon–carbon double bond in tetrakis(trimethylsilyl)ethene to a torsion angle of 29.5°[12c,d] and its thermal conversion at 150° to a radical species via presumably a biradical state should convincingly validate our issue.[12e] Further evidence for this disposition was also established by the facile *Z*–*E* isomerization of (*Z*)-1,2-bis(phenyldimethylsilyl)-1,2-bis(trimethylsilyl)ethene,[12e] as well as (*Z*)-1,2-bis(*tert*-butyldimethylsilyl)-1,2-bis(trimethylsilyl)-ethene.[12f] Moreover, Sakurai also found in 1990 that the benzene ring of hexakis(trimethylsilyl)benzene in the solid state was distorted to a chair form with C–C–C–C torsion angles averaging 9.8°.[12g] In our own endeavor, **1** also rearranged efficiently to 2,4-bis(trimethylsilyl)furan in good yield, upon treatment with a catalytic amount of acid.[2a] It is clear from these reports that there has been sufficient concrete structural data[12d,f,g] to support our stereochemical ground. Therefore, it is quite likely that the cycloreversion driving force was due to an inclination of the two bulky trimethylsilyl groups to alleviate the unfavorable steric factor, and the restoration of aromaticity in the furan generation. Thus, in order to revive a strain-free state, an extrusion of bis(trimethylsilyl)-acetylene from their corresponding intermediate adducts presumably occurred as shown in Scheme 2. Noteworthy is that such a process is similar to a precedented reaction in which dicyanoacetylene was expelled from the corresponding endoxide.[15]

(c) Acylation Reactions of 3,4-Bis(trimethylsilyl)-furan (1). With the aim of utilizing the *ipso* directing effect of a trimethylsilyl group[8] in order to bring in a facile synthesis of 3,4-disubstituted furans, furan **1** was subjected to several acylation reactions. Initially, it was found that titanium(IV) chloride promoted Friedel–Crafts reaction between dichloromethyl methyl ether and **1** afforded the α-formylated **6** after hydrolysis (eq 1, Scheme 3).[16] In the cases of the Vilsmeier reaction[17] (eq 2, Scheme 3) and Friedel–Crafts acylation[18] (eq 3, Scheme 3), it appeared that α-formylation took place to form **6** and **8**, which was followed by a 3-protodesilylation step, yielding **7** and **9**. However, when aluminum chloride was used (eq 4, Scheme 3), α-acylation plus 3-

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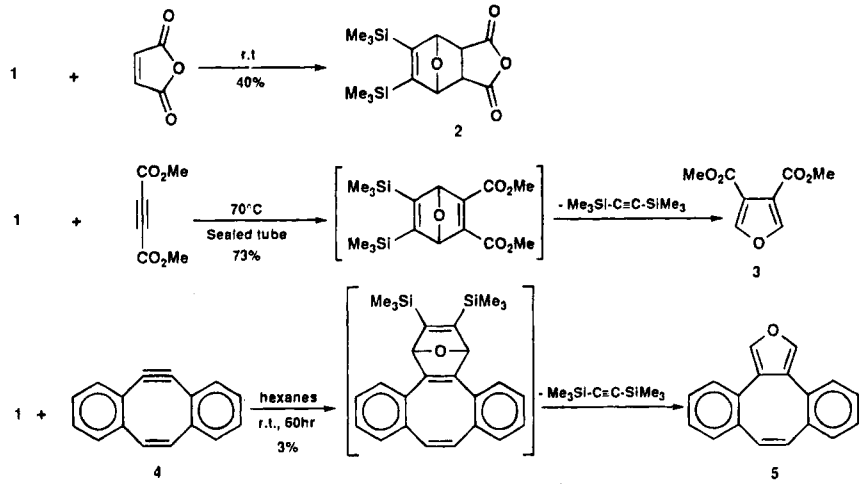
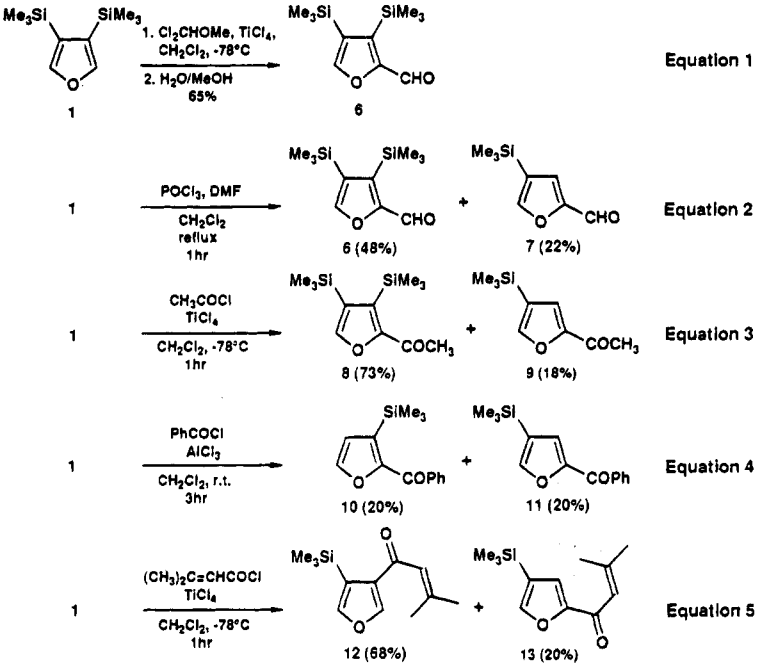
Scheme 2. Diels–Alder Reaction of 3,4-Bis(trimethylsilyl)furan



Scheme 3. Electrophilic Aromatic Substitution of 3,4-Bis(trimethylsilyl)furan



and 4-protodesilylation were observed at room temperature, affording a mixture of **10** and **11**.[19,20] Due to the fact that the Lewis acid strength is about the same for titanium(IV) chloride and aluminum chloride, it thus appeared that the undesired protodesilylation was favored at higher temperature. The only successful *ipso*-substitution pattern was observed in the acylation reaction (eq 5, Scheme 3) in which **1** was allowed to react with β,β-dimethylacryloyl chloride in the presence of titanium(IV) chloride at −78 °C, from which **12** and the α-substituted protodesilylation product **13** were obtained.[19,20]

For most electrophilic substitutions of silyl-substituted arenes with electrophiles, it was found that the rate of silyl-directed *ipso*-substitutions were generally faster than those of *ortho*-, *meta*-, and *para*-substitutions.[6,19–21] Nevertheless, in our special case, we were dealing with 3,4-bis(trimethylsilyl)furan (**1**). There was therefore always a competition for the electrophile between the β-carbon that bears a trimethylsilyl group and the furan α-carbon.[22] Obviously, the β-effect, and hence the resulting *ipso*-directing characteristic and the usual reactivity of furan, were responsible for such a predicament.[6,19–21] To make the situation more complicated, the σ-donating tendency of one of the trimethylsilyl groups[6] was likely also playing an essential role in stabilizing the β-carbocationic intermediate that was formed en route to an α-substituted product.[7,22] As can be corroborated by the transformations illustrated in Scheme 3, we can perhaps

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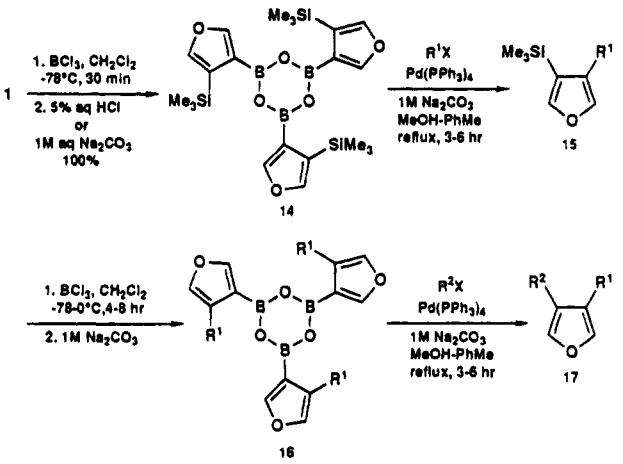
reach an agreement that the furan α-carbons were always more reactive than the silyl-substituted β-carbons. As such, the prospect of yielding *ipso*-substitution products by using this acylation route was therefore rather doubtful.

(d) Synthesis and Palladium-Catalyzed Cross-Coupling Reactions of Tris[4-(trimethylsilyl)furan-3-yl]boroxine (14). As mentioned earlier, another desired pathway for the conversion of **1** would be toward 3,4-disubstituted furans. Although several procedures were known before our own endeavors, none of them could provide furans with intricate substituents. For example, the Garst–Spencer procedure[5a] and its modification[5b] required ketones containing an α-methylene group as starting material. As a result, unsymmetrical ketones with two equally reactive α-methylene groups would likely give rise to complications, not to mention that a number of sensitive functional groups would be destroyed during the arduous reaction sequence involved in this approach. The oxazole approach,[5c,d] on the other hand, suffers from the low dienophilic reactivities of many alkynes. Indeed, the procedure is usually applicable only to furans with electron-withdrawing 3,4-substituents. The Reich approach gave only 3-substituted 4-methylfurans and is therefore not multipurpose.[5e] The same is also true for the Keay approach, which furnished either 3-substituted 4-(methoxycarbonyl)-furans[5f] or 3-substituted 4-(hydroxymethyl)furans.[5g] Our own tin protocol[5i,j] gave several 3,4-disubstituted furans with rather diverse substituents, but an efficient preparation of the starting material, namely 3,4-bis(tri-*n*-butylstannyl)furan, has not yet been secured. Interestingly, the synthesis of some structurally undemanding 3,4-disubstituted furans was disclosed in a recent report,[5k] which might be an outstanding example to demonstrate the challenge and possibly even the frustration in the regiospecific synthesis of these molecules. In view of the aforementioned situation and our own failure in synthesizing 3,4-disubstituted furans via acylation reactions (*vide supra*), we thus embarked on the development of a process in which 3,4-disubstituted furans could be produced in a more efficient routine. Needless to say, the primary aim of this undertaking was to regiospecifically incorporate various structurally complex substituents to furans. This avenue was first explored by our attempts to directly replace the trimethylsilyl groups of **1** with aryl or alkenyl groups via palladium-catalyzed coupling. This route has so far been unsuccessful, despite the fact that similar displacements on fluorinated silanes are well-documented.[23] After several unsuccessful experiments, it was eventually found that **1** underwent regiospecific *ipso* substitution[19,24] with one or two equivalents of boron trichloride from 0 °C to room temperature,[25] affording the air-stable tris[4-(trimethylsilyl)furan-3-yl]boroxine (**14**) in a quantitative yield (Scheme 4).[2a] Experimentally, it can be seen that the displacement of the silyl group of

Scheme 4. Suzuki-Type Cross-Coupling Reactions of Boroxines



1 has been made possible by using a strong Lewis acid, i.e., boron trichloride. As it turned out, the resulting dichloroboranes were easily hydrolyzed to boroxines,[26] which now play important roles in our palladium-catalyzed transformations, thus ensuring a facile entry to carbon–carbon bond formations (*vide infra*). In this connection, boron trichloride is a much better choice than boron trifluoride.

Although trimeric anhydrides of organoboronic acids, namely boroxines, have been known for more than 50 years,[10] their synthetic applications[27] have been restricted mainly to characterization and purification of the corresponding boronic acids.[28] Nevertheless, it was found that boroxine **14** smoothly underwent regiospecific Suzuki-type cross-coupling[9] catalyzed by 10 mol % of tetrakis(triphenylphosphine)palladium to furnish furans **15** (Table 1 and Scheme 4). To determine the scope and limitations of this conversion, the reaction was performed on a number of aryl and benzylic halides (entries 1–7 and 12–16), aryl and benzylic dibromides (entries 8–10 and 17–18), and an aryl tribromide (entry 11), as well as allylic bromides (entries 19 and 20). It seemed that groups of diversified electronic and steric nature did not affect the yields of the reactions. With only five exceptions (entries 10–12, 19, and 20), the yields of **15** were generally higher than 90%. As can be seen from entry 17 in Table 1, the reactivities of aryl bromide and benzyl bromide were almost the same. On the contrary, cross-coupling took place only for aryl bromide in the presence of an α-bromo ketone (entry 7, Table 1).

Expectedly, the choice of electrophiles (R^1X) as shown in Table 1 was quite restricted because the conversion of **15** eventually to **17** via **16** (Scheme 4) must involve

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Table 1. Palladium-Catalyzed Cross-Coupling Reactions of Tris[4-(trimethylsilyl)furan-3-yl]boroxine (14)

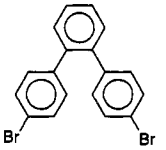
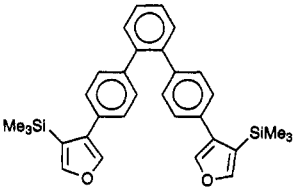
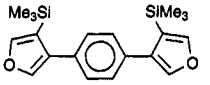
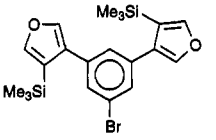
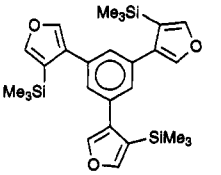
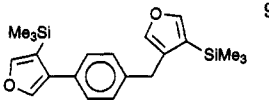
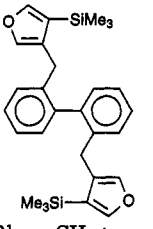
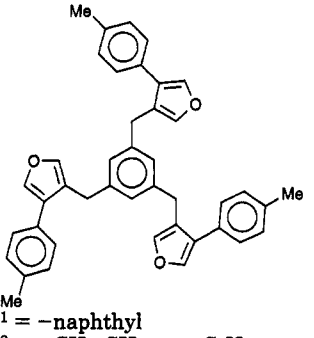
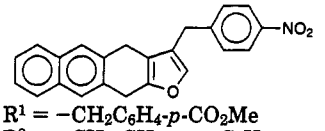
entry	R^1X	15	yield (%)
1	C_6H_5Br	**15a** $R^1 = -C_6H_5$	97
2	p-MeC_6H_4I	**15b** $R^1 = -C_6H_4$-p-Me	97
3	p-$MeCOC_6H_5Br$	**15c** $R^1 = -C_6H_4$-p-COMe	96
4	1-bromonaphthalene	**15d** R^1 = −naphthyl	98
5	p-MeC_5H_4-o-C_6H_4I	**15e** $R^1 = -C_6H_4$-o-C_6H_4-p-Me	95
6	1-bromothiophene	**15f** R^1 = −1-thienyl	96
7	p-$BrCH_2COC_6H_4Br$	**15g** $R^1 = -C_6H_4$-p-$COCH_2Br$	91
8		**15h** 	92
9	p-BrC_6H_4Br	**15i** 	90
10	1,3,5-$C_6H_3Br_3$	**15j** 	60
11	1,3,5-$C_6H_3Br_3$	**15k** 	52
12	9-bromofluorene	**15l** R^1 = −9-fluorenyl	45
13	piperonyl chloride	**15m** R^1 = −piperonyl	92
14	p-$O_2NC_6H_4CH_2Br$	**15n** $R^1 = -CH_2C_6H_4$-p-NO_2	95
15	p-$MeO_2CC_6H_4CH_2Br$	**15o** $R^1 = -CH_2C_6H_4$-p-CO_2Me	95
16	3,4,5-$(MeO)_3C_6H_2CH_2Cl$	**15p** $R^1 = -CH_2C_6H_2$-3,4,5-$(OMe)_3$	97
17	p-$BrCH_2C_6H_4Br$	**15q** 	90
18	o-$BrCH_2C_6H_4$-o-$C_6H_4CH_2Br$	**15r** 	92
19	C_6H_5-*trans*-$CH{=}CHCH_2Br$	**15s** $R^1 = -CH_2$-*trans*-$CH{=}CHC_6H_5$	53
20	MeO_2C-*trans*-$CH{=}CHCH_2Br$	**15t** $R^1 = -CH_2$-*trans*-$CH{=}CHCO_2Me$	58

Table 2. Preparation and Palladium-Catalyzed Cross-Coupling Reactions of Tris[4-(substituted)furan-3-yl]boroxines (16). Regiospecific Synthesis of 3,4-Disubstituted Furans 17

entry	16	yield (%)	R^2X	17	yield (%)
1	**16a**	72	1,3,5-$C_6H_3Br_3$	**17a** $R^1 = -C_6H_5$, R^2 = 3,5-$Br_2C_6H_3$	60
2	**16b**	67	α,α′,α″-tribromomesitylene	**17b** 	54
3	**16d**	56	*trans*-$C_5H_{11}CH{=}CHI$	**17d** R^1 = −naphthyl, $R^2 = -CH{=}CH$-*trans*-C_5H_{11}	92 92
4	**16e**	58	bromocyclooctatetraene	**17e** $R^1 = -C_6H_4$-o-C_6H_4-p-Me, R^2 = −cyclooctatetraenyl	90
5	**16n**	76	9-bromophenanthrene	**17n** $R^1 = -CH_2C_6H_4$-p-NO_2, R^2 = −9-phenanthenyl	87
6	**16n**	76	2,3-bis(bromomethyl)naphthalene	**17n′** 	61
7	**16o**	71	*trans*-$C_4H_9CH{=}CHI$	**17o** $R^1 = -CH_2C_6H_4$-p-CO_2Me, $R^2 = -CH{=}CH$-*trans*-C_4H_9	93
8	**16o**	71	p-BrC_6H_4Br	**17o′** $R^1 = -CH_2C_6H_4$-p-CO_2Me, $R^2 = -C_6H_4$-p-Br	81
9	**16p**	31	o-MeC_6H_4I	**17p** $R^1 = -CH_2C_6H_2$-3,4,5-$(OMe)_3$, $R^2 = -C_6H_4$-o-Me	78

again the use of the Lewis acid boron trichloride (*vide infra*). In light of this fact, only groups without Lewis acid sensitive functionalities could be safely employed as incipient electrophiles, whose coupling products **15** were converted in two more steps to **17** (Scheme 3, Tables 1 and 2).

Having noted the limitation in the choice of R^1, we however still managed to engage a number of aryl, benzylic, and allylic halides in the formation of **15**. While **15a−15d**, **15l**, **15s**, and **15t** were mainly synthesized with an aim as model studies in our first-stage synthetic evaluation of boroxines, **15e−15k**, **15q**, and **15r**, on the

other hand, might serve as potential precursors of non-natural molecules such as cyclophanes[29a] (*viz.* **15e**, **15g–15j**, **15q**, and **15r**) and heterocyclic oligomers[29b] (*viz.* **15f**) as well as dendrimers[29c] (*viz.* **15k**). In contrast, **15m–15p** possess molecular skeletons reminiscent of some known natural molecules,[30] and therefore their syntheses might ultimately become new entries to such compounds.

(e) Preparation of Tris[4-(substituted)furan-3-yl]-boroxines 16 and Their Palladium-Catalyzed Cross-Coupling Reactions: Regiospecific Synthesis of 3,4-Disubstituted furans 17. To achieve our final goal for the preparation of 3,4-disubstituted furans, the remaining trimethylsilyl groups of **15** were again replaced by boron trichloride, and the resulting dichloroboranes were subsequently worked up also by addition of 1 M aqueous sodium carbonate (Scheme 4). As expected, boroxines **16** were obtained, albeit in somewhat inferior yields (Table 2).[1,2a] It is important to note that the substitution of the second trimethylsilyl group in **15** by boron trichloride was less facile; therefore, the yields of these reactions were much lower than that of **14**. Again, boroxines **16** were readily converted to 3,4-disubstituted furans **17** in good yields via the Suzuki-type reaction catalyzed by 10 mol % of tetrakis(triphenylphosphine)palladium. As depicted in Table 2, the preparation of **17a**, **17d**, **17n**, and **17o** was again for model study purpose only. The intriguing generation of **17b** interestingly demonstrated the versatility of boroxines in cross-coupling reactions. It is of interest to note that the synthesis of **17e**, which contained a rather labile cyclic polyene, namely cyclooctatetraene, aptly manifested the mildness of our boroxine pathway. The formation of **17n′**, on the other hand, showed that the palladium(0) condition was able to trigger an intramolecular Heck-type coupling at the furan α-carbon.[1] Finally, the molecular skeletons of compounds **17n′**, **17o′**, and **17p** have found their partially matchable analogs in natural occurring molecules.[30] In light of this finding, it is our wish that this method can be used to assemble the frameworks of these compounds.

As can be seen in Tables 1 and 2, the alkaline condition required for the Suzuki cross-coupling step lamentably prohibited the use of acyl halides. However, this discrepancy was addressed and overcome in our tin-directed 3,4-disubstituted furan synthesis protocol.[5i] Other compounds that were notably absent from Tables 1 and 2 were 3,4-dialkynylfurans. To the best of our knowledge, the use of alkynyl electrophiles has not been reported for the Suzuki reaction.[9] To circumvent this shortcoming, we recently achieved the regiospecific synthesis of several alkynylfurans from iodofurans prepared from **1**, **16n**, and **16o**.[21a]

To conclude this section, it is important to emphasize once again that R^1 (Table 1) must be insensitive to Lewis acids, such as boron trichloride, whereas the choice of R^2 (Table 2) is less demanding, depending solely on the limitations of the Suzuki reaction.

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Conclusion

The synthesis of 3,4-bis(trimethylsilyl)furan (**1**) via oxazole cycloaddition and cycloreversion has been demonstrated. Furan **1** was able to undergo Diels–Alder reactions with dienophiles although the reactivity was lower than a similar diene reported by Garratt.[13a] In the case of acetylenic dienophiles, extrusion of bis(trimethylsilyl)acetylene occurred, and this may formulate a viable route for the synthesis of annulated furans. Furan **1** was also able to undergo regiospecific electrophilic substitution at the unsubstituted α-position, with or without protodesilylation. We have also shown that the cross-coupling reaction for boroxines was quite efficient in terms of the ease of product workup and yields. In this program, a number of 3,4-disubstituted furans, which are otherwise impossible or difficult to prepare, have been realized. Eminent examples are **17b**, **17e**, **17n**, and **17n′** (Table 2), which, to the best of our knowledge, are inaccessible through the use of other literature procedures.

Our initial attention had been so far concentrated only on the development of practical methodologies for the construction of 3,4-disubstituted furans with considerable molecular complexity. An interesting application of this boroxine chemistry has already led to the realization of several furan-3,4-diyl oligomers, which might have some implications in the study of furan polymers.[1] Syntheses of natural molecules with potential application in the pharmaceutical industry utilizing such a palladium-catalyzed silicon–boroxine protocol is also on our agenda. In due course, we hope to extend our methods to include also the regiospecific syntheses of polysubstituted thiophenes as well as pyrroles.

Experimental Section

General. Melting points were measured on a Reichert microscope apparatus and were uncorrected. NMR spectra were recorded on a Bruker-Cryospec WM 250 spectrometer. ^1H NMR (250.13 MHz) and ^{13}C NMR (62.89 MHz) chemical shifts are reported, respectively, relative to $CDCl_3$ at δ 7.24 ppm and 77.00 ppm and tetramethylsilane at δ 0.00 ppm. Coupling constants are reported in Hz. NMR spectroscopic terms were reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra (EIMS, and HRMS) were obtained with a VG Micromass 7070F spectrometer and determined at an ionizing voltage of 70 eV. Relevant data were tabulated as *m/e*. Elemental analyses were performed at the Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, China.

Unless otherwise stated, all reactions were carried out in oven-dried glassware. THF was distilled from sodium benzophenone ketyl. Methylene chloride was distilled from CaH_2. All solutions were evaporated under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using hexanes–diethyl ether as the eluent unless specified otherwise. Flash chromatography was performed using E. Merck silica gel 60 (230–400 mesh). The plates used for thin-layer chromatography (TLC) were E. Merck silica gel 60 F_{254} (0.25-mm thickness) precoated on an aluminum plate, and they were visualized under both long (365-nm) and short (254-nm) UV light.

Materials. Reagents were purchased from commercial suppliers and were used without further purification. 5,6-Didehydrodibenzo[*a,e*]cyclooctene,[14] *trans*-1-iodohexene,[31] *trans*-

(31) Negishi, E.-I.; Takahashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 3402–3408.

1-heptene,[32] 2-iodo-4'-methyl-1,1'-biphenyl,[32] 4,4'-dibromo-*o*-terphenyl,[32] piperonyl chloride,[33] bromo-cyclooctatetraene,[34] α,α',α''-tribromomesitylene,[35] 2,2'-(bromomethyl)-1,1'-biphenyl,[35] and 2,3-bis(bromomethyl)naphthalene[35] were prepared according to the literature.

***exo*-4,5-Bis(trimethylsilyl)-3,6-endoxo-1,2,3,6-tetrahydrophthalic anhydride (2).** A mixture of **1**[2a] (900 mg, 4.2 mmol) and maleic anhydride (400 mg, 4.1 mmol) was stirred under N_2 for 4 days. The resulting yellow precipitate was washed with hexanes until no more solid dissolved. The hexane solution was evaporated, and the residual white solids were recrystallized from hexanes at 0 °C to afford **2** as wool-like crystals (522 mg, 40%): mp 83–84 °C; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 18H, 2 × $SiMe_3$), 2.92 (s, 2H), 5.51 (s, 2H); MS *m/e* 212 (M^+, 98). Anal. Calcd for $C_{14}H_{22}O_4Si_2$: C, 54.15; H, 7.14. Found: C, 53.45; H, 7.05.

Dimethyl Furan-3,4-dicarboxylate (3). A mixture of **1**[2a] (110 mg, 0.5 mmol) and dimethyl acetylenedicarboxylate (120 mg, 0.8 mmol) was heated in a sealed tube at 75 °C for 7 h. The residue was purified by column chromatography (silica gel, EtOAc/hexanes, 1/4) to give **3** as white crystals (70 mg, 73%): mp 43-44 °C [lit.[36] mp 46 °C]; ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 6H), 7.92 (s, 2H); MS *m/e* 184 (M^+, 60).

3,4,7,8-Dibenzocyclooct[1,2-*c*]furan (5). A solution of 5-bromodibenzo[*a,e*]cyclooctene[14] (200 mg, 0.7 mmol) in dry THF (2 mL) was added dropwise during a period of 2 min to a stirred solution of KO-*t*-Bu (240 mg, 2.2 mmol) in dry THF (20 mL) at room temperature under N_2. The solution was stirred for 5 min, 2 *N* aqueous *HCl* (10 mL) was added, and the solution was extracted with Et_2O (2 × 20 mL). The organic layer was washed with H_2O (5 mL) and dried over $MgSO_4$. Evaporation and chromatography (alumina, grade III, hexanes) gave a yellow solution of 5,6-didehydrodibenzo[*a,e*]-cyclooctene (**4**).[14] 3,4-Bis(trimethylsilyl)furan (**1**) (200 mg, 0.94 mmol) was then added to the yellow solution. The mixture was concentrated to 5 mL and stirred under N_2 for 2.5 days. Preparative TLC (hexanes) gave **5** as a white solid (6 mg, 3%): mp 113–116 °C; ^{1}H NMR ($CDCl_3$) δ 6.71 (s, 2H), 7.16–7.30 (m, 8H), 7.40 (s, 2H); MS *m/e* 244 (M^+, 25); exact mass calcd for $C_{18}H_{12}O$ 244.0888, found 244.0861.

Preparation of 3,4-Bis(trimethylsilyl)furan-2-carbaldehyde (6). To **1**[2a] (212 mg, 1 mmol) and dichloromethyl methyl ether (127 mg, 1.1 mmol) dissolved in dry CH_2Cl_2 (10 mL) at −78 °C was added titanium(IV) chloride (1 mL, 1.0 M solution in CH_2Cl_2), and the mixture was stirred at this temperature for 1 h. The resulting red-brownish solution was hydrolyzed by addition of 50% aqueous MeOH (10 mL) at −20 °C. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL). The combined CH_2Cl_2 solution was washed with 5% $NaHCO_3$ (15 mL) and 20% NaCl (10 mL) solution, dried with $MgSO_4$, and concentrated by evaporation. Isolation of the product by column chromatography (silica gel, 50 g, hexanes/Et_2O, 8/1) afforded **6** (156 mg, 65%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 9H, $SiMe_3$), 0.42 (s, 9H, $SiMe_3$), 7.61 (s, 1H), 9.86 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$) δ 0.53, 1.31, 117.42, 126.52, 152.97, 158.24, 179.00; MS *m/e* 240 (M^+, 10). Anal. Calcd for $C_{11}H_{20}O_2Si_2$: C, 54.94; H, 8.38. Found: C, 55.00; H, 8.31.

3,4-Bis(trimethylsilyl)furan-2-aldehyde (6) and 4-(Trimethylsilyl)furan-2-aldehyde (7). A mixture of **1**[2a] (212 mg, 1 mmol) and DMF (92 mg, 1.3 mmol) in CH_2Cl_2 (2 mL) was stirred for 10 min at 0 °C. After that $POCl_3$ (184 mg, 1.2 mmol) was added slowly, and the reaction mixture was further stirred and refluxed for 2 h. After addition of ice–water (10 mL), the reaction mixture was neutralized with sodium acetate solution. The organic phase was separated, and the aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic phase was washed with $NaHCO_3$ solution (20%, 10 mL), dried over $MgSO_4$, and evaporated. Purification by chromatography on silica gel (40 g, hexanes/Et_2O, 8/1) yielded **6** (175 mg, 73%) and **7** (30 mg, 18%) as oils. Compound **7**: ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9H, $SiMe_3$), 7.26 (s, 1H), 7.58 (s, 1H), 9.66 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −1.01, 122.52, 125.00, 152.04, 153.95, 177.68; MS *m/e* 168 (M^+, 5), 167 (M^+ − 1, 100). Anal. Calcd for $C_8H_{12}O_2Si$: C, 57.10; H, 7.19. Found: C, 57.35; H, 7.48. Coupound **6** was identical in all aspects with the sample prepared previously.

2-Acetyl-3,4-bis(trimethylsilyl)furan (8) and 2-Acetyl-4-(trimethylsilyl)furan (9). To **1**[2a] (212 mg, 1 mmol) and acetyl chloride (94.2 mg, 1.2 mmol) dissolved in dry CH_2Cl_2 (10 mL) at −78 °C was added titanium(IV) chloride (1 mL, 1.0 M solution in CH_2Cl_2), and the mixture was stirred at this temperature for 2 h. Ice–water (10 mL) was then added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated. Purification by chromatography on silica gel (40 g, hexanes/Et_2O, 10/1) yielded **8** (174 mg, 73%) and **9** (32 mg, 18%) as oils. Compound **8**: ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9H, $SiMe_3$), 0.31 (s, 9H, $SiMe_3$), 2.50(s, 3H, CH_3), 7.45 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 0.47, 0.79, 27.13, 117.70, 126.76, 150.92, 158.89, 188.72; MS *m/e* 254 (M^+, 5), 239 (M^+ − Me, 100). Anal. Calcd for $C_{12}H_{22}O_2Si_2$: C, 56.67; H, 8.73. Found: C, 56.54; H, 8.71. Compound **9**: ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9H, $SiMe_3$), 2.42 (s, 3H, CH_3), 7.12 (s, 1H), 7.41 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −1.01, 25.99, 121.10, 122.09, 150.42, 153.75, 186.59; MS *m/e* 182 (M^+, 80). Anal. Calcd for $C_9H_{14}O_2Si$: C, 59.32; H, 7.75. Found: C, 59.61; H, 7.43.

2-Benzoyl-3-(trimethylsilyl)furan (10) and 2-Benzoyl-4-(trimethylsilyl)furan (11). To a solution of $AlCl_3$ (250 mg, 2 mmol) in CH_2Cl_2 (3 mL) was added a mixture of **1**[2a] (300 mg, 1.5 mmol) and benzoyl chloride (210 mg, 1.5 mmol) in CH_2Cl_2 (4 mL). The solution was stirred at room temperature under N_2 for 3 h. Ice–water (10 mL) was then added, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The CH_2Cl_2 solution was dried over $MgSO_4$. Evaporation and chromatography (alumina, grade III, hexanes) gave two major fractions. The less polar fraction was **10** (150 mg, 62%) as a pale yellow liquid and the more polar fraction was **11** (44 mg, 18%) as colorless crystals. Compound **10**: ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 9H, $SiMe_3$), 6.62 (d, 1H, J = 1.5 Hz), 7.45–7.60 (m, 3H), 7.63 (d, 1H, J = 1.5 Hz), 8.04–8.09 (m, 2H); MS *m/e* 229 (M^+ − 15, 40). Anal. Calcd for $C_{14}H_{16}O_2Si$: C, 68.81; H, 6.60. Found: C, 68.72; H, 6.84. Compound **11**: mp 44–45 °C; ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9H, $SiMe_3$), 7.21 (d, 1H, J = 0.73 Hz), 7.46–7.57 (m, 3H), 7.59 (d, 1H, J = 0.73 Hz), 7.94–7.99 (m, 2H); MS *m/e* 244 (M^+, 32). Anal. Calcd for $C_{14}H_{16}O_2Si$: C, 68.81; H, 6.60. Found: C, 68.51; H, 6.40.

3-(β,β-Dimethylacryloyl)-4-(trimethylsilyl)furan (12) and 2-(β,β-Dimethylacryloyl)-4-(trimethylsilyl)furan (13). To **1**[2a] (212 mg, 1 mmol) and β,β-dimethylacryloyl chloride (142 mg, 1.2 mmol) dissolved in dry CH_2Cl_2 (10 mL) at −78 °C was added titanium(IV) chloride (1 mL, 1.0 M solution in CH_2Cl_2), and the mixture was stirred at this temperature for 2.5 h. Ice–water (10 mL) was then added, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The CH_2Cl_2 solution was dried over $MgSO_4$ and evaporated. Purification by chromatography on silica gel (50 g, hexanes/Et_2O, 8/1) yielded **12** (150 mg, 68%) and **13** (44 mg, 20%) as oils. Compound **12**: ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9H, $SiMe_3$), 1.75 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 6.24 (d, 1H, J = 0.8 Hz), 7.09 (s, 1H), 7.85 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −0.82, 20.81, 27.39, 119.15, 122.08, 133.18, 147.69, 149.37, 154.18, 185.72; MS *m/e* 222 (M^+, 10). Anal. Calcd for $C_{12}H_{18}O_2Si$: C, 64.83; H, 8.16. Found: C, 64.43; H, 8.11. Compound **13**: ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9H, $SiMe_3$), 2.00 (d, 3H, J = 0.9 Hz, CH_3), 2.26 (s, 3H, J = 0.9 Hz, CH_3), 6.66 (d, 1H, J = 1.1 Hz), 7.14 (s, 1H), 7.44 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −0.87, 21.10, 27.98, 120.22, 121.96, 149.90, 155.31, 157.40, 179.39; MS *m/e* 222 (M^+, 5). Anal. Calcd for $C_{12}H_{18}O_2Si$: C, 64.83; H, 8.16. Found: C, 64.75; H, 7.71.

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Tris[4-(naphth-1-yl)furan-3-yl]boroxine (16d).[1,2a] To a solution of **15d** (399 mg, 1.5 mmol) in CH_2Cl_2 (100 mL) was added a solution of BCl_3 (1.0 M) in CH_2Cl_2 (3 mL) under N_2 at −78 °C. After 5 h, the reaction was quenched with 2 M Na_2CO_3 solution (5 mL) and the mixture was extracted with Et_2O (3 × 50 mL). The organic layer was dried ($MgSO_4$) and the solvent evaporated. The crude product was chromatographed on silica gel (100 g, hexanes/Et_2O, 1/1) to give **16d** (185 mg, 56%) as a semisolid: ^1H NMR ($CDCl_3$) δ 7.31−7.54 (m, 18H), 7.89−7.96 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 125.12, 125.48, 125.64, 125.77, 126.48, 126.78, 127.63, 127.75, 127.96, 128.46, 128.76, 131.43, 133.20, 133.48, 141.34, 154.72; MS *m/e* 660 (M^+, 50). Anal. Calcd for $C_{42}H_{27}O_6B_3$: C, 76.34; H, 4.12. Found: C, 75.68; H, 4.12.

The synthesis of boroxines **16a**, **16b**, **16e**, and **16n−16p** has been reported elsewhere.[1,2a]

General Procedure for the Pd-Catalyzed Cross-Coupling of Boroxines (14 or 16) with Organohalides. (a) 4-Phenyl-3-(trimethysilyl)furan (15a). To a stirred solution containing bromobenzene (236 mg, 1.5 mmol), tris[4-(trimethylsilyl)furan-3-yl]boroxine (**14**)[2a] (250 mg, 0.5 mmol), and $Pd(PPh_3)_4$ (86 mg, 0.075 mmol) in MeOH/PhMe (1:1, 30 mL) was added a 2 M Na_2CO_3 solution (4 mL). The reaction mixture was heated under reflux for 3−4 h and then poured into ice−water (50 mL). The resulting mixture was extracted with Et_2O (3 × 50 mL). The combined Et_2O extract was dried over $MgSO_4$ and the solvent evaporated. The residue was purified by chromatography on silica gel (40 g, hexanes) to give **15a** (314 mg, 97%) as an oil: ^1H NMR ($CDCl_3$) δ 0.19 (s, 9H, $SiMe_3$), 7.36−7.41 (m, 6H), 7.56 (d, 1H, *J* = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ −0.09, 119.18, 127.06, 128.15, 128.84, 131.20, 134.51, 140.11, 148.76; MS *m/e* 216 (M^+, 55). Anal. Calcd for $C_{13}H_{16}OSi$: C, 72.12; H, 7.45. Found: C, 72.55; H, 7.74.

(b) 4-(*p*-Tolyl)-3-(trimethylsilyl)furan (15b) was prepared from *p*-bromotoluene (257 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15b** (335 mg, 97%) as colorless needles: mp 42.5−43 °C; ^1H NMR ($CDCl_3$) δ 0.18 (s, 9H, $SiMe_3$), 2.40 (s, 3H, CH_3), 7.19 (d, 2H, *J* = 8.0 Hz), 7.29 (d, 2H, *J* = 8.1 Hz), 7.38 (d, 1H, *J* = 1.4 Hz), 7.52 (d, 1H, *J* = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ −0.05, 21.11, 119.22, 128.74, 128.88, 131.11, 131.32, 136.69, 140.02, 148.69; MS *m/e* 230 (M^+, 65). Anal. Calcd for $C_{14}H_{18}OSi$: C, 72.99; H, 7.88. Found: C, 72.79; H, 7.99.

(c) 4-(*p*-Acetylphenyl)-3-(trimethylsilyl)furan (15c) was prepared from *p*-bromoacetophenone (298 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15c** (372 mg, 96%) as colorless needles: mp 79−80 °C; ^1H NMR ($CDCl_3$) δ 0.18 (s, 9H, $SiMe_3$), 2.58 (s, 3H, CH_3), 7.39 (s, 1H), 7.47 (d, 2H, *J* = 8.1 Hz), 7.58 (s, 1H), 7.97 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ −0.01, 15.97, 118.46, 128.07, 128.31, 130.00, 135.66, 139.14, 140.49, 149.05, 196.70; MS *m/e* 258 (M^+, 50). Anal. Calcd for $C_{15}H_{18}O_2Si$: C, 69.73; H, 7.02. Found: C, 69.81; H, 7.15.

(d) 4-(Naphth-1-yl)-3-(trimethylsilyl)furan (15d) was prepared from 1-bromonaphthlene (311 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15d** (391 mg, 98%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.18 (s, 9H, $SiMe_3$), 7.51−7.58 (m, 4H), 7.61 (d, 1H, *J* = 1.5 Hz), 7.66 (d, 1H, *J* = 1.4 Hz), 7.91−7.96 (m, 3H); ^{13}C NMR ($CDCl_3$) δ −0.47, 121.12, 124.92, 125.80, 126.66, 127.89, 128.02, 132.19, 133.44, 133.54, 141.26, 148.14; MS *m/e* 266 (M^+, 87). Anal. Calcd for $C_{17}H_{18}OSi$: C, 76.64; H, 6.80. Found: C, 76.88; H, 6.37.

(e) 4-(4′-Methyl-1,1′-biphen-2-yl)-3-(trimethylsilyl)furan (15e) was prepared from 2-iodo-4′-methyl-1,1′-biphenyl[32] (441 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15e** (436 mg, 95%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.24 (s, 9H, $SiMe_3$), 2.46 (s, 3H, CH_3), 7.21 (d, 1H, *J* = 1.5 Hz), 7.22 (d, 2H, *J* = 7.6 Hz), 7.32 (d, 2H, *J* = 8.2 Hz), 7.46 (d, 1H, *J* = 1.5 Hz), 7.48−7.58 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −0.18, 20.95, 119.97, 126.41, 127.57, 128.46, 129.12, 129.50, 130.10, 131.57, 132.63, 136.04, 138.61, 141.33, 141.63, 147.98; MS *m/e* 306 (M^+, 90). Anal. Calcd for $C_{20}H_{22}OSi$: C, 78.38; H, 7.24. Found: C, 78.59; H, 7.08.

(f) 4-(Thiophen-2-yl)-3-(trimethylsilyl)furan (15f) was prepared from 2-bromothiophene (245 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15f** (320 mg, 96%) as a pale-yellow oil: ^1H NMR ($CDCl_3$) δ 0.18 (s, 9H, $SiMe_3$), 6.99−6.70 (m, 2H), 7.19 (m, 1H), 7.32 (d, 1H, *J* = 1.9 Hz), 7.57 (d, 1H, *J* = 1.8 Hz); ^{13}C NMR ($CDCl_3$) δ −0.34, 119.61, 123.66, 124.54, 125.94, 135.46, 141.11, 147.84, 148.79; MS *m/e* 222 (M^+, 38). Anal. Calcd for $C_{11}H_{14}OSSi$: C, 59.41; H, 6.35. Found: C, 58.97; H, 6.84.

(g) 4-[*p*-(Bromoacetyl)phenyl]-3-(trimethylsilyl)furan (15g) was prepared from 4-bromo(bromoacetyl)benzene (396 mg, 1.5 mmol) and **14**[2a] (250 mg, 1.5 mmol) to give **15g** (440 mg, 91%) as pale-yellow needles: mp 76−77 °C; ^1H NMR ($CDCl_3$) δ 0.06 (s, 9H, $SiMe_3$), 4.40 (s, 2H, CH_2), 7.27 (d, 1H, *J* = 1.7 Hz), 7.36 (d, 2H, *J* = 8.5 Hz), 7.47 (d, 1H, *J* = 1.5 Hz), 7.86 (d, 2H, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ −0.14, 39.25, 118.74, 128.26, 128.55, 129.69, 130.20, 131.76, 135.87, 139.43, 140.64, 149.22, 197.16; MS *m/e* 336 (M^+ + 22), 338 (M^+ + 2, 23). Anal. Calcd for $C_{15}H_{17}O_2BrSi$: C, 53.42; H, 5.08. Found: C, 53.10; H, 5.47.

(h) 4,4′-Bis[3-(trimethylsilyl)furan-4-yl]-*o*-terphenyl (15h) was prepared from 4,4′-dibromo-*o*-terphenyl[32] (291 mg, 0.75 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15h** (349 mg, 92%) as colorless needles: mp 151−152 °C; ^1H NMR ($CDCl_3$) δ 1.34 (s, 18H, 2 × $SiMe_3$), 8.32−8.66 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 0.00, 118.98, 119.19, 126.51, 127.52, 127.65, 127.92, 128.47, 128.58, 129.78, 130.48, 130.66, 130.90, 131.11, 131.51, 132.73, 132.87, 133.75, 139.06, 140.01, 140.39, 148.72, 149.05; MS *m/e* 506 (M^+, 100). Anal. Calcd for $C_{32}H_{34}O_2Si_2$: C, 75.84; H, 6.76. Found: C, 76.08; H, 6.55.

(i) 1,4-Bis[4-(trimethylsilyl)furan-3-yl]benzene (15i) was prepared from 1,4-dibromobenzene (177 mg, 0.75 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15i** (239 mg, 90%) as colorless needles: mp 99−99.5 °C; ^1H NMR ($CDCl_3$) δ 0.14 (s, 18H, 2 × $SiMe_3$), 7.34−7.35 (m, 6H), 7.55 (d, 2H, *J* = 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ −0.05, 119.29, 128.71, 130.90, 133.37, 140.13, 148.81; MS *m/e* 354 (M^+, 64). Anal. Calcd for $C_{20}H_{26}O_2Si_2$: C, 67.74; H, 7.39. Found: C, 67.54; H, 7.54.

(j) 1-Bromo-3,5-bis[4-(trimethylsilyl)furan-3-yl]benzene (15j) was prepared from 1,3,5-tribromobenzene (236 mg, 0.75 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15j** (194 mg, 60%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.16 (s, 18H, 2 × $SiMe_3$), 7.30 (s, 1H) 7.35 (d, 2H, *J* = 1.4 Hz), 7.47 (d, 2H, *J* = 1.4 Hz), 7.54 (d, 2H, *J* = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 0.01, 119.11, 121.99, 127.64, 129.85, 130.35, 136.53, 140.46, 149.17; MS *m/e* 432 (M^+, 34), 434 (M^+ + 2, 37). Anal. Calcd for $C_{20}H_{25}O_2BrSi_2$: C, 55.55; H, 5.83. Found: C, 56.04; H, 5.94.

(k) 1,3,5-Tris[4-(trimethylsilyl)furan-3-yl]benzene (15k) was prepared from 1,3,5-tribromobenzene (315 mg, 1 mmol) and **14**[2a] (498 mg, 1 mmol) to give **15k** (256 mg, 52%) as colorless needles: mp 57−59 °C; ^1H NMR ($CDCl_3$) δ 0.14 (s, 27H, 3 × $SiMe_3$), 7.32 (s, 3H) 7.36 (d, 3H, *J* = 1.5 Hz), 7.55 (d, 3H, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 0.07, 119.20, 128.13, 130.94, 134.49, 140.19, 148.99; MS *m/e* 492 (M^+, 22). Anal. Calcd for $C_{27}H_{36}O_3Si_3$: C, 65.83; H, 7.37. Found: C, 65.64; H, 7.28.

(l) 4-(Fluoren-9-yl)-3-(trimethylsilyl)furan (15l) was prepared from 9-bromofluorene (368 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15l** (205 mg, 45%) as a yellow solid: mp 64−65 °C; ^1H NMR ($CDCl_3$) δ −0.36 (br s, 9H, $SiMe_3$), 5.00 (s, 1H), 7.24−7.41 (m, 8H), 6.99 (d, 2H, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ −0.94, 45.68, 119.89, 125.26, 127.31, 127.44, 127.75, 140.98, 142.34, 147.69, 149.60; MS *m/e* 304 (M^+, 65). Anal. Calcd for $C_{20}H_{20}OSi$: C, 79.18; H, 6.32. Found: C, 79.03; H, 6.67.

(m) 4-Piperonyl-3-(trimethylsilyl)furan (15m) was prepared from piperonyl chloride[33] (256 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15m** (378 mg, 92%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.13 (s, 9H, $SiMe_3$), 3.72 (s, 2H, CH_2), 5.92 (s, 2H, OCH_2O), 6.64 (d, 2H, *J* = 8.5 Hz), 6.73 (d, 1H, *J* = 7.6 Hz), 7.14 (d, 1H, *J* = 1.0 Hz), 7.28 (d, 1H, *J* = 1.3 Hz); ^{13}C NMR ($CDCl_3$) δ −0.60, 31.63, 100.79, 108.05, 109.26, 119.14, 121.56, 128.12, 134.19, 141.23, 146.01, 147.76, 148.64; MS *m/e* 320 (M^+, 100). Anal. Calcd for $C_{15}H_{18}O_3Si$: C, 65.66; H, 6.61. Found: C, 65.38; H, 6.55.

(n) 4-(*p*-Nitrobenzyl)-3-(trimethylsilyl)furan (15n) was prepared from *p*-nitrobenzyl bromide (324 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15n** (392 mg, 95%) as pale-yellow needles: mp 72−73 °C; ^1H NMR ($CDCl_3$) δ 0.11 (s, 9H, $SiMe_3$), 3.93 (s, 2H, CH_2), 7.18 (d, 1H, *J* = 1.1 Hz), 6.91 (d,

1H, J = 1.3 Hz), 7.42 (d, 2H, J = 8.7 Hz), 8.11 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ −0.81, 31.52, 118.90, 123.22, 123.35, 126.02, 129.29, 129.58, 141.34, 146.58, 148.05, 148.88; MS m/e 275 (M^+, 32). Anal. Calcd for $C_{14}H_{17}O_3NSi$: C, 61.06; H, 6.22; N, 5.09. Found: C, 61.04; H, 6.16; N, 5.00.

(o) 4-[*p*-(Methoxycarbonyl)benzyl]-3-(trimethylsilyl)furan (15o) was prepared from *p*-(methoxycarbonyl)benzyl bromide (343 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15o** (410 mg, 95%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H, $SiMe_3$), 3.86 (s, 2H, CH_2), 3.91 (s, 3H, OCH_3), 7.14 (d, 1H, J = 1.1 Hz), 7.26 (d, 2H, J = 8.7 Hz), 7.30 (d, 1H, J = 1.4 Hz), 7.97 (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ −0.67, 31.87, 51.75, 119.08, 126.89, 128.36, 128.66, 129.67, 141.32, 145.69, 148.76, 166.86; MS m/e 288 (M^+, 32). Anal. Calcd for $C_{16}H_{20}O_3Si$: C, 66.63; H, 6.99. Found C, 66.24; H, 7.16.

(p) 4-(3,4,5-Trimethoxybenzyl)-3-(trimethylsilyl)furan (15p) was prepared from 3,4,5-trimethoxybenzyl chloride (325 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15p** (466 mg, 97%) as colorless needles: mp 49−49.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9H, $SiMe_3$), 3.75 (s, 2H, CH_2), 3.81 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.14 (s, 2H), 7.15 (d, 1H, J = 1.3 Hz), 7.29 (d, 1H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ −0.90, 31.88, 55.82, 60.36, 106.16, 118.81, 127.50, 135.55, 136.83, 140.95, 148.40, 153.04; MS m/e 320 (M^+, 100). Anal. Calcd for $C_{17}H_{24}O_4Si$: C, 63.72; H, 7.55. Found: C, 63.94; H, 7.91.

(q) 4″-[*p*-(3′-[(Trimethylsilyl)furan-4′-yl]benzyl]-3″-(trimethylsilyl)furan (15q) was prepared from *p*-bromobenzyl bromide (187 mg, 0.75 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15q** (248 mg, 90%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9H, $SiMe_3$), 1.06 (s, 9H, $SiMe_3$), 3.80 (s, 2H, CH_2), 7.12 (d, 1H, J = 1.5 Hz), 7.14 (d, 2H, J = 8.2 Hz), 7.25 (d, 2H, J = 7.0 Hz), 7.26 (d, 1H, J = 1.4 Hz), 7.31 (d, 1H, J = 1.4 Hz), 7.47 (d, 1H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ −0.52, −0.05, 31.65, 119.21, 127.82, 128.57, 128.87, 130.99, 132.46, 139.19, 140.10, 141.34, 148.72; MS m/e 368 (M^+, 100). Anal. Calcd for $C_{21}H_{28}O_2Si_2$: C, 68.43; H, 7.66. Found: C, 68.15; H, 7.85.

(r) 2,2′-Bis[[3-(trimethylsilyl)furan-4-yl]methyl]-1,1′-biphenyl (15r) was prepared from 2,2′-bis(bromomethyl)1,1′-biphenyl[35] (255 mg, 0.75 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15r** (316 mg, 92%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 18H, 2 × $SiMe_3$), 3.48 (s, 4H, 2 × CH_2), 6.83 (d, 2H, J = 1.2 Hz), 7.08−7.26 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −0.67, 29.74, 119.10, 126.02, 127.40, 128.28, 129.61, 129.81, 137.99, 140.67, 141.36, 148.22; MS m/e 458 (M^+, 25). Anal. Calcd for $C_{28}H_{34}O_2Si_2$: C, 73.31; H, 7.47. Found: C, 73.62; H, 7.36.

(s) 4-(Cinnamyl)-3-(trimethylsilyl)furan (15s) was prepared from cinnamyl bromide (296 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15s** (mg, 53%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 9H, $SiMe_3$), 3.44 (d, 2H, J = 5.9 Hz), 6.39−6.47 (m, 2H), 7.26−7.43 (m, 7H); ^{13}C NMR ($CDCl_3$) δ −0.39, 29.24, 119.12, 126.14, 127.11, 128.51, 131.31, 137.58, 140.49, 148.46; MS m/e 256 (M^+, 78). Anal. Calcd for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86. Found: C, 74.30; H, 7.23.

(t) 4-[3-(Methoxycarbonyl)-*trans*-2-propenyl]-3-(trimethylsilyl)furan (15t) was prepared from methyl 4-bromocrotonate (268 mg, 1.5 mmol) and **14**[2a] (250 mg, 0.5 mmol) to give **15t** (207 mg, 58%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9H, $SiMe_3$), 3.33 (dd, 2H, J = 1.6, 6.4 Hz), 3.70 (s, 3H, CH_3), 5.79 (dt, 1H, J = 1.7, 15.6 Hz), 7.06 (dt, 1H, J = 6.4, 15.7 Hz), 7.24 (s, 2H); ^{13}C NMR ($CDCl_3$) δ −0.52, 28.32, 51.19, 118.90, 122.28, 124.68, 140.69, 146.73, 148.56, 166.58; MS m/e 238 (M^+, 14). Anal. Calcd for $C_{12}H_{18}O_3Si$: C, 60.47; H, 7.61. Found: C, 60.50; H, 7.68.

(u) 3-(3′,5′-Dibromophenyl)-4-phenylfuran (17a) was prepared from 1,3,5-tribromobenzene (188 mg, 0.6 mmol) and **16a**[1,2a] (102 mg, 0.2 mmol) to give **17a** (136 mg, 60%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.18−7.22 (m, 2H), 7.29−7.34 (m, 5H), 7.55−7.58 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 122.86, 123.70, 125.85, 127.58, 128.59, 128.66, 130.11, 131.19, 132.58, 135.90, 141.10, 141.37; MS m/e 376 (M^+, 42), 378 (M^+ + 2, 82), 380 (M^+ + 4, 40). Anal. Calcd for $C_{16}H_{10}OBr_2$: C, 50.83; H, 2.67. Found: C, 51.20; H, 2.67.

(v) α,α′,α″-Tris[4-(*p*-tolylfuran-3-yl)]mesitylene (17b) was prepared from α,α′,α″-tribromomesitylene[35] (71 mg, 0.2 mmol) and **16b**[1,2a] (110 mg, 0.2 mmol) to give **17b** (60 mg, 54%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.33 (s, 9H, 3 × CH_3), 3.72 (s, 6H, 3 × CH_2), 6.80 (s, 3H), 6.91 (s, 3H), 7.09−7.27 (m, 12H), 7.46 (d, 3H, J = 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 21.05, 30.33, 123.71, 127.03, 128.14, 129.20, 129.70, 136.69, 139.83, 140.23, 141.40; MS m/e 588 (M^+, 100). Anal. Calcd for $C_{42}H_{36}O_3$: C, 85.68; H, 6.17. Found: C, 85.59; H, 6.10.

(w) 3-(Naphth-1-yl)-4-(*trans*-hept-1-en-1-yl)furan (17d) was prepared from *trans*-1-iodoheptene[31] (134 mg, 0.6 mmol) and **16d**[1,2a] (132 mg, 0.2 mmol) to give **17d** (160 mg, 92%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 3H, J = 6.4 Hz, CH_3), 0.90−1.30 (m, 6H, 3 × CH_2), 1.87 (m, 2H), 5.56 (dt, 1H, J = 7.0, 17 Hz), 5.93 (d, 1H, J = 16 Hz), 7.40−7.52 (m, 5H), 7.59 (d, 1H, J = 1.3 Hz), 7.84−7.90 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 13.86, 22.39, 28.82, 31.09, 32.96, 118.75, 123.88, 124.98, 125.29, 125.84, 125.99, 126.50, 128.01, 128.08, 130.37, 132.29, 132.72, 133.77, 139.32, 141.50; MS m/e 290 (M^+, 100). Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.86; H, 7.75.

(x) 3-Cyclooctatetraenyl-4-(4′-methyl-1,1′-biphen-2-yl)furan (17e) was prepared from bromocyclooctatetraene[34] (110 mg, 0.6 mmol) and **16e**[1,2a] (156 mg, 0.2 mmol) to give **17e** (181 mg, 90%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H, CH_3), 5.31−5.55 (m, 2H), 5.60−5.69 (m, 5H), 7.06−7.12 (m, 5H), 7.19 (d, 1H, J = 1.7 Hz), 7.34−7.38 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.07, 124.83, 126.18, 126.35, 126.95, 127.86, 128.48, 128.62, 128.97, 129.45, 130.21, 130.39, 130.93, 131.39, 131.84, 132.08, 133.86, 136.18, 138.63, 140.48, 141.60; MS m/e 336 (M^+, 100). Anal. Calcd for $C_{25}H_{20}O$: C, 89.25; H, 6.00. Found: C, 89.17; H, 6.03.

(y) 3-(*p*-Nitrobenzyl)-4-(phenanthen-9-yl)furan (17n) was prepared from 9-bromophenanthrene (154 mg, 0.6 mmol) and **16n**[1,2a] (137 mg, 0.2 mmol) to give **17n** (198 mg, 87%) as colorless needles: mp 101−102 °C; ^{1}H NMR ($CDCl_3$) δ 3.51 (s, 2H, CH_2), 6.80 (d, 2H, J = 8.5 Hz), 7.24 (s, 1H), 7.34−7.68 (m, 10H), 8.58 (t, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 30.23, 122.52, 122.85, 123.13, 124.21, 124.89, 126.41, 126.57, 126.90, 127.98, 128.40, 128.89, 130.15, 130.42, 131.25, 131.54, 140.43, 141.52, 146.31, 147.37; MS m/e 379 (M^+, 100). Anal. Calcd for $C_{25}H_{17}O_3N$: C, 79.13; H, 4.52; N, 3.69. Found: C, 79.04; H, 4.85; N, 3.60.

(z) 3-(*p*-Nitrobenzyl)-4,11-dihydroanthro[2,3-*b*]furan (17n′) was prepared from 2,3-bis(bromomethyl)naphthalene[35] (94 mg, 0.3 mmol) and **16n**[1,2a] (68 mg, 0.1 mmol) to give **17n′** (65 mg, 61%) as a pale-yellow powder: mp 174−175 °C; ^{1}H NMR ($CDCl_3$) δ 3.77 (t, 2H, J = 3.7 Hz, CH_2), 3.92 (s, 2H, CH_2), 4.17 (t, 2H, J = 3.7 Hz, CH_2), 7.24 (d, 1H, J = 3.1 Hz), 7.38−7.43 (m, 4H), 7.68−7.74 (m, 4H), 8.16 (d, 2H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 26.84, 28.24, 30.22, 114.99, 121.56, 123.79, 125.62, 127.09, 127.75, 127.99, 129.35, 131.29, 131.75, 132.19, 138.79, 146.88, 147.62, 149.31; MS m/e 355 (M^+, 100). Anal. Calcd for $C_{23}H_{17}O_3N$: C, 77.72; H, 4.82; N, 3.94. Found: C, 77.53; H, 4.76; N, 3.89.

(aa) 3-(*trans*-Hex-1-en-1-yl)-4-[*p*-(methoxycarbonyl)benzyl]furan (17o) was prepared from *trans*-1-iodohexene[31] (126 mg, 0.6 mmol) and **16o**[1,2a] (145 mg, 0.2 mol) to give **17o** (166 mg, 93%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.77 (t, 3H, J = 7.0 Hz, CH_3), 1.10−1.26 (m, 4H, 2 × CH_2), 1.97 (m, 2H, J = 6.6 Hz), 3.77 (s, 2H, CH_2), 3.81 (s, 3H, OCH_3), 5.70−5.79 (m, 1H), 5.93 (d, 1H, J = 16.2 Hz), 6.96 (d, 1H, J = 0.8 Hz), 7.18 (d, 2H, J = 8.1 Hz), 7.33 (d, 1H, J = 1.2 Hz), 7.88 (d, 2H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 13.78, 22.06, 30.40, 31.43, 32.86, 51.83, 118.64, 122.05, 124.03, 128.34, 128.55, 129.76, 132.17, 139.87, 141.13, 145.26, 166.98; MS m/e 298 (M^+, 100). Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.57; H, 7.07.

(ab) 3-(*p*-Bromophenyl)-4-[*p*-(methoxycarbonyl)benzyl]furan (17o′) was prepared from 1,4-dibromobenzene (71 mg, 0.3 mmol) and **16o**[1,2a] (72.6 mg, 0.1 mmol) to give **17o′** (90 mg, 81%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 3.88 (s, 2H, CH_2), 3.90 (s, 3H, CH_3), 7.13 (d, 2H, J = 8.6 Hz), 7.16 (d, 1H, J = 0.8 Hz), 7.22 (d, 2H, J = 8.2 Hz), 7.45 (d, 2H, J = 8.2 Hz), 7.51 (d, 1H, J = 1.6 Hz), 7.94 (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 30.22, 51.92, 121.28, 122.42, 126.08, 128.26, 128.55, 129.84, 130.13, 130.47, 130.51, 131.33, 131.75, 132.05, 140.37, 141.79, 143.25, 145.16, 166.95; MS m/e 370 (M^+, 54), 372 (M^+ + 2, 58). Accurate mass calcd for $C_{19}H_{15}O_3Br$ 370.0179, found 370.0174.

(ac) 3-(*o*-Tolyl)-4-(3′,4′,5′-trimethoxybenzyl)furan (17p) was prepared from 2-iodotoluene (65 mg, 0.3 mmol) and **16p**[1,2a] (82 mg, 0.1 mmol) to give **17p** (90 mg, 78%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.08 (s, 3H, CH_3), 3.53 (s, 2H, CH_2), 3.71 (s, 6H, 2×CH_3), 3.80 (s, 3H, CH_3), 6.16 (s, 2H), 7.08–7.23 (m, 4H), 7.28–7.30 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.99, 30.54, 56.01, 60.71, 106.09, 124.82, 125.36, 125.87, 127.59, 129.64, 130.73, 131.87, 135.63, 137.31, 139.95, 140.31, 153.00; MS *m*/*e* 338 (M^+, 100). Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55. Found: C, 74.21; H, 6.75.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for all compounds (49 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.