Synthetic Applications of 3,4-Bis(trimethylsilyl)thiophene: Unsymmetrically 3,4-Disubstituted Thiophenes and 3,4-Didehydrothiophene†,‡

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3,4-Bis(trimethylsilyl)thiophene (**1a**) was synthesized by three routes: (a) 1,3-dipolar cycloaddition; (b) modification of 3,4-dibromothiophene; and (c) intermolecular thiazole−alkyne Diels−Alder reaction. 3,4-Bis(trimethylsilyl)thiophene (**1a**) can function as a versatile building block for the construction of unsymmetrically 3,4-disubstituted thiophenes utilizing its stepwise regiospecific mono-*ipso*-substitution followed by palladium-catalyzed cross-coupling reactions. In this manner, thiophenes **15**, **16**, **17a**−**j**, **19a,b**, **20**, **22a**−**c**, **23a,b**, **24a**−**d**, **25a**−**c**, and **27a**−**j** were prepared. The thiophene-3,4-diyl dimer **28** and thiophene-3,4-diyl tetramer **29** were also realized by palladium-catalyzed self-coupling reaction of organoboroxines. The stannylthiophene **31**, formed by conversion of the C−Si bond to a C−Sn bond *via* boroxine **26c** underwent both carbonylative coupling and lithiation followed by quenching with electrophiles to afford unsymmetrically 3,4-disubstituted thiophenes **33** and **36a**−**c** as well. Moreover, 3,4-bis(trimethylsilyl)thiophene (**1a**) can be used as the starting material for the generation of the highly strained cyclic cumulene 3,4-didehydrothiophene (**2**), whose existence was substantiated by its trapping reaction with several alkenes.

Introduction

Thiophenes occur abundantly as structural units in many natural and non-natural molecules and enjoy potential applications in flavor[1] and pharmaceutical[2] industries, in conducting polymer design,[3] as well as in nonlinear optical materials.[4] Moreover, in the preparation of a wide range of cyclic and acyclic nonthiophene molecules, thiophene derivatives are excellent synthetic intermediates because of the unique electronic properties of sulfur as well as the steric constraints of a five-membered ring. For example, thiophenes can undergo Diels−Alder reactions through their 1,1-dioxide derivatives.[5]

Because of their synthetic importance, thiophenes have been popular targets for synthetic chemists. Consequently, the scope of the synthesis and applications of thiophenes has broadened enormously in the past two decades. However, the inclination of thiophene to endure both metalation and electrophilic substitution preferentially at α-positions[6] has made the synthesis of 3-substituted[7] and 3,4-disubstituted thiophenes an exceedingly arduous assignment. Although several approaches to 3,4-disubstituted thiophenes such as Hinsburg condensation,[8] intramolecular reductive carbonyl coupling of diketo sulfides,[9] modification of 3,4-dibromothiophene,[10] condensation of olefins with sulfur or sulfur dioxide,[11] and thermolysis of di-1-alkenyl disulfides,[12] *via* (*n*-butylthio)-methylene ketones[13] and *via* α-oxoketene dithioacetals,[14]

† Dedicated to Professor Dr. Dieter Seebach on the occasion of his 60th birthday.

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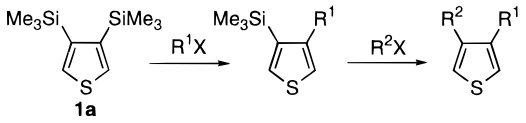
Scheme 1



are available, they are generally not suitable for thiophenes with elaborate substituents. We report herein full details of our strategy for synthesizing several unsymmetrically 3,4-disubstituted thiophenes utilizing 3,4-bis(trimethylsilyl)thiophene (**1a**) as a building block. The use of 3,4-bis(trimethylsilyl)thiophene (**1a**) as the precursor for the generation of 3,4-didehydrothiophene (**2**) is also described.

Results and Discussion

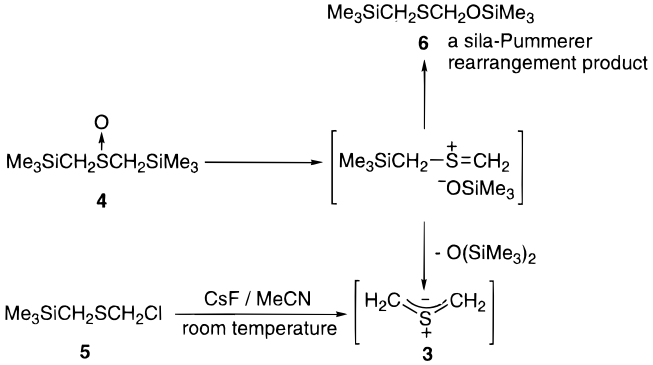
(a) Synthesis of 3,4-Bis(trimethylsilyl)thiophene (1a). Recently, the successful conversions of 3,4-bis(trimethylsilyl)furan to 3,4-disubstituted furans, involving the concomitant functions of silyl groups as protecting groups[15] and as *ipso*-substitution directors,[16] have been achieved.[17] Encouraged by these results, we are interested in synthesizing 3,4-bis(trimethylsilyl)thiophene (**1a**) in which both the C-3 and C-4 trimethylsilyl groups can be modified and manipulated for later synthetic applications. Possessing a strong directing effect, the trimethylsilyl groups of **1a** should be easily replaced by other groups, preferably in a stepwise manner (Scheme 1).

The first synthesis of 3,4-bis(trimethylsilyl)thiophene (**1a**) was reported by Shepherd,[18] who employed sequential low-temperature lithiations followed by silylations starting from 3,4-dibromothiophene.[19] The first lithiation was performed with *n*-butyllithium, and the second lithiation step involved treatment of 3-bromo-4-(trimethylsilyl)thiophene with 2 equiv of *tert*-butyllithium.

We independently explored the synthesis of **1a** *via* three routes: (1) 1,3-dipolar cycloaddition, (2) silylation utilizing an ultrasonic technique, and (3) intermolecular thiazole-alkyne Diels−Alder reaction.

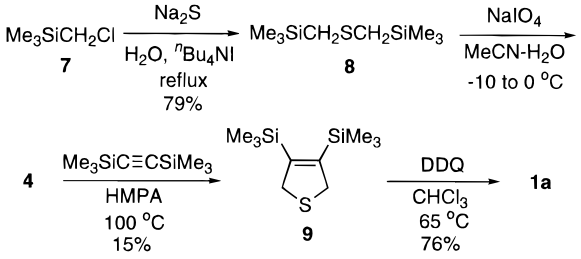
(1) 1,3-Dipolar Cycloaddition. Thiocarbonyl ylides[20] are useful reactive intermediates for the synthesis of heterocycles containing a sulfur atom. The parent thiocarbonyl ylide, namely thioformaldehyde *S*-methylide (**3**), can be generated by two methods:[21,22] one involved the release of disiloxane from bis(trimethylsilylmethyl) sulfoxide (**4**) through a pathway related to the sila-Pummerer rearrangement,[23] the other involved the 1,3-elimination of chloromethyl (trimethylsilyl)methyl sulfide (**5**) catalyzed by cesium fluoride in acetonitrile at room temperature (Scheme 2).

Scheme 2



The thiocarbonyl ylide **3** is able to undergo cycloadditions with conjugated dipolarophiles to lead to di- or tetrahydrothiophenes. In considering the fluoride-induced desilylation, we chose the former strategy to accomplish the synthesis of the silylated thiophene **1a** using bis(trimethylsilyl)acetylene as a dipolarophile. Our synthetic approach was shown below (Scheme 3).

Scheme 3



Bis[(trimethylsilyl)methyl] sulfide (**8**),[24] readily prepared by the reaction of (chloromethyl)trimethylsilane (**7**) with sodium sulfide in water at reflux in the presence of phase-transfer catalyst tetrabutylammonium iodide, was oxidized by sodium periodate[25] at lower temperature (−10 to 0 °C) to give the sulfoxide **4**. Treatment of **4** with bis(trimethylsilyl)acetylene at 100 °C in HMPA gave the 1,3-dipolar cycloadduct **9**, which was treated with DDQ[26] in chloroform at 65 °C to produce 3,4-bis(trimethylsilyl)thiophene (**1a**).

Although the synthesis of the building block **1a** was successfully realized by this route, the yield of the key

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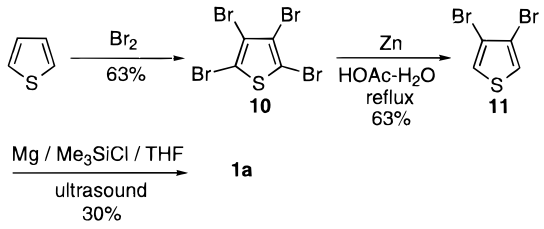
Scheme 4



1,3-dipolar cycloaddition step is low, i.e., 10% from sulfide **8**. All efforts to improve the yield were unfruitful. For example, change of the reaction temperature only led to inferior yields. This unsatisfactory outcome may result from the low reactivity of the dipolarophile bis(trimethylsilyl)acetylene, which carries bulky trimethylsilyl groups, thus making the formation of the sila-Pummerer rearrangement product a major pathway.

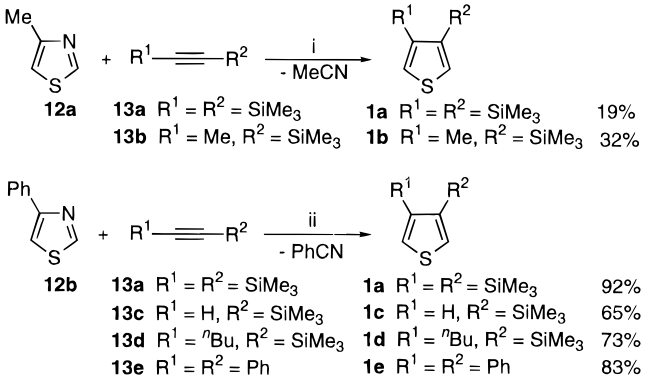
To overcome the yield limitation, new pathways were therefore required.

(2) Modification of 3,4-Dibromothiophene. Silylation of halothiophenes is a common access to silylthiophenes. Several methods leading to silylated thiophenes have been established, which involved organolithium,[18,27] organosodium,[28] and organomagnesium[27a,29] routes. Very recently, an electrochemical pathway was also reported.[30] Among the numerous approaches, we were especially interested in the synthesis of 3-(trimethylsilyl)thiophene through the reaction between 3-bromothiophene with chlorotrimethylsilane and magnesium in THF under ultrasonication due to its simplicity and convenience.[29b] This prompted us to study the possibility of synthesizing 3,4-bis(trimethylsilyl)thiophene (**1a**) employing the sonochemical cross-coupling of 3,4-dibromothiophene (**11**) with Me_3SiCl (Scheme 4).

3,4-Dibromothiophene (**11**) was easily obtained by bromination[31] of thiophene followed by selective dehalogenation[19] with Zn-dust in acetic acid. No reaction took place when a mixture of **11**, Me_3SiCl, and magnesium turnings (molar ratio **11**:Me_3SiCl:Mg = 1:2.25:2.25) in THF in a sealed tube was kept under ultrasonication (output power 35 W) even for 4 days. While magnesium powder was used instead of magnesium turnings under the same conditions, surprisingly, the reaction occurred slowly and was complete in about 7 days. The yield is, however, modest, usually only 30%. This seems to arise also from the steric effect of two bulky β-substituents in thiophene rings. It should be noted that a stronger ultrasonic irradiation source (Branson SONIFIER 450) did not seem to initiate the reaction and, therefore, resulted in the recovery of the starting material **11**.

(3) Intermolecular Diels–Alder Cycloaddition–Cycloreversion. Owing to the low reactivity of thiazoles toward Diels–Alder cycloaddition,[32] only a few examples are known in which thiophene rings were assembled *via* a crucial intramolecular thiazole–alkyne cycloaddition.[33] The intermolecular version of these reactions had hitherto been unexplored. After a great deal of experimentation, however, it was eventually found that at the temperature range of 320–360 °C alkynes **13** were able to react with 4-methylthiazole (**12a**)[34a] or 4-phenylthiazole (**12b**),[34b] with the latter being much more competent in terms of yields, providing 3-substituted or 3,4-disubstituted thiophenes **1** after extrusion of acetonitrile or benzonitrile (Scheme 5). In this way, 3,4-bis(trimethylsilyl)thiophene (**1a**) was obtained in an inferior yield by reacting **12a** with bis(trimethylsilyl)-acetylene (**13a**) in Et_3N at 360 °C or in 92% yield from a similar reaction between **12b** and **13a** in DBU at 325 °C. Noteworthy is that thiazole **12b** constantly gave much better yields of **1**. We still lack an explanation for this observation, but it is likely due to the detrimental pressure effect in the sealed tube caused by the lower-boiling acetonitrile formed in the cycloreversion. The thermal reaction between **12b** and **13a** is quite amenable to a large-scale production of **1a**, which was generated routinely in about an 8 g quantity in one single run (see Experimental Section). A base was somehow needed to play the role as a proton scavenger because **1a** can undergo a facile acid-catalyzed rearrangement.[35] Higher temperatures and longer reaction times made the rearrangement to occur more easily. Reaction of thiazole **12a** and acetylene **13b** in DBU at 340 °C again only gave **1b** in unsatisfactory yield. Nevertheless, **12b** reacted with **13c** and **13d** in the presence of DBU to produce in good yields **1c** and **1d**, respectively. The preparation of **1e** from **12b** and **13e**, on the other hand, did not require a base. It is noteworthy that the aforementioned reactions did not occur when the temperatures were lower than 300 °C.

Scheme 5[a]



[a] Reagents and conditions: (i) sealed tube, 340–360 °C, Et_3N or DBU; (ii) sealed tube, 325–340 °C, DBU.

(b) Preparation of Unsymmetrically 3,4-Disubstituted Thiophenes. The use of the trimethylsilyl group to assist in the iodination of aromatic species has been well-documented. For example, a method of iodinating aryltrimethylsilanes using iodine or iodine monochloride and a silver salt to activate the electrophile was reported by Jacob.[36] This mild method was also used to

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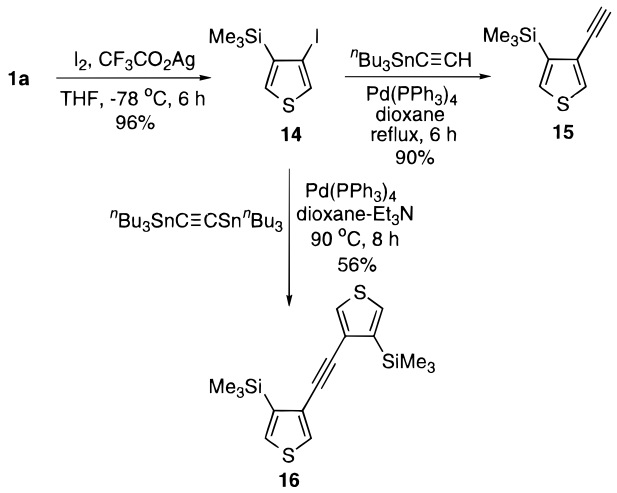
Scheme 6



convert silylated furans to their corresponding iodinated products in our laboratory.[17c] Such practice was also applied to thiophene **1a**. A regiospecific mono-*ipso*-iodination cleanly converted **1a** into iodide **14**, when **1a** was treated with iodine and silver trifluoroacetate in THF at −78 °C (Scheme 6). To avoid the formation of the side product diiodide, it is necessary to maintain the reaction temperature at −78 °C.

With the aim to test the versatility of our strategy for the synthesis of 3,4-disubstituted thiophenes, the coupling reaction[37] of 3-iodo-4-(trimethylsilyl)thiophene (**14**) with organostannanes was examined. It was found that **14** underwent a smooth cross-coupling reaction with ethynyltributyltin to give 3-ethynyl-4-(trimethylsilyl)-thiophene (**15**) in 90% yield. The reaction made use of tetrakis(triphenylphosphine)palladium(0) as catalyst and dioxane as solvent. Under similar conditions, reaction of **14** with bis(tributylstannyl)acetylene provided alkyne **16** (Scheme 6). It should be noted that the trimethylsilyl group of **16** is very acid sensitive due to the strong rearrangement tendency;[35] for this reason, it is necessary to add triethylamine to the reaction solvent and the chromatography eluent in order to secure pure **16**.

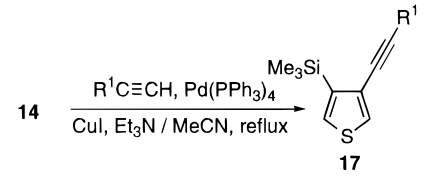
3-Iodo-4-(trimethylsilyl)thiophene (**14**) was also transformed to **17** by the Sonogashira coupling reaction[38] with various terminal alkynes. The results are summarized in Table 1. This is a convenient route for the synthesis of 3-alkynyl-4-(trimethylsilyl)thiophenes. All these reactions were performed under the same conditions: iodide **14** (1 equiv), alkynes (1.5 equiv), $Pd(PPh_3)_4$ (0.1 equiv), CuI (0.2 equiv), Et_3N−MeCN (v/v 2.5:1) as mixed solvent, reflux temperature. The yields are usually high.

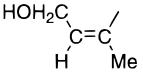
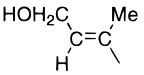
The remaining trimethylsilyl group of **17c** was replaced by iodine in merely 30% yield under more rigorous conditions,[16c,37] presumably due to alkyne interference. All attempts to improve the yield such as changing solvents or anions of the silver salts, and using iodine monochloride instead of iodine, were unfruitful. Further Sonogashira reaction[38] of the resulting iodide **18** gave 3,4-dialkynylthiophenes **19** in much better yields (Scheme 7).

To widen the scope of our strategy, iodide **14** was initially converted to **20** by Suzuki coupling reaction.[39] Thus, **14** coupled with phenylboronic acid in the presence of $Pd(PPh_3)_4$ catalyst and 2 M Na_2CO_3 in methanol−toluene to give **20** in 77% yield. Subsequent regiospecific iodination of **20** produced another key intermediate **21** in 67% yield (Scheme 8).

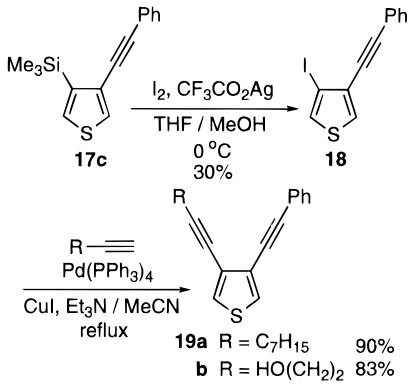
3-Iodo-4-phenylthiophene (**21**) underwent a smooth Heck-type cross-coupling reaction[40] with terminal alkenes to lead to alkenyl-substituted thiophenes **22**. The reactions were carried out either under typical Heck conditions or under phase-transfer[41] conditions. All coupling

Table 1. Sonogashira Coupling Reaction of 14 with Terminal Alkynes

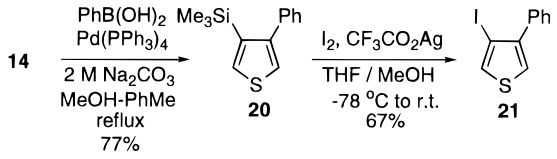


Entry	R^1	Product	(Yield)
1	*n*-C_5H_{11}-	**17a**	(88%)
2	*n*-C_7H_{15}-	**17b**	(89%)
3	Ph-	**17c**	(85%)
4		**17d**	(88%)
5		**17e**	(93%)
6	$HOCH_2CH_2$-	**17f**	(92%)
7	$HO(CH_2)_4$-	**17g**	(91%)
8	$PhCH_2N(Me)CH_2$-	**17h**	(91%)
9		**17i**	(74%)
10		**17j**	(68%)

Scheme 7



Scheme 8

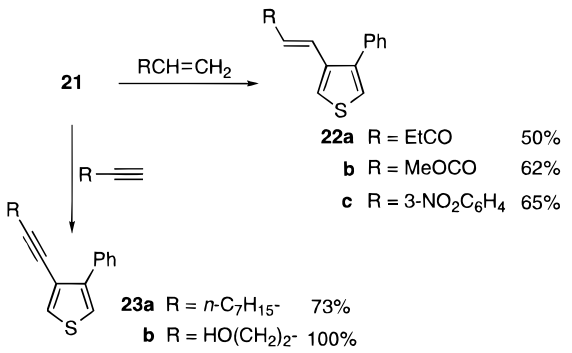


(37) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508−524.

(38) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470. (b) Cassar, L. *J. Organomet. Chem.* **1975**, *93*, 253−257. (c) Alvarez, A.; Guzmán, A.; Ruiz, A.; Velarde, E.; Muchowski, J. M. *J. Org. Chem.* **1992**, *57*, 1653−1656. (c) Rossi, R.; Carpita, A.; Bellina, F. *Org. Prep. Proced. Int.* **1995,** *27*, 129−160. (d) Furstner, A.; Seidel, G. *Tetrahedron* **1995**, *51*, 11165−11176.

(39) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513−519. Martin, A. R.; Yang, Y.-H. *Acta Chem. Scand.* **1993**, *47*, 221−230. Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419−422. Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483. Kubiak, G. G.; Confalone, P. N. *Tetrahedron Lett.* **1990**, *31*, 3845−3848. Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972−980.

Scheme 9[a]



[a] Reagents and conditions: for **22a** and **22b**, $Pd(OAc)_2$, Et-COCH=CH_2 or MeO_2CCH=CH_2, K_2CO_3, $^nBu_4NI$, DMF, 80−90 °C; for **22c**, $Pd(OAc)_2$, 3-$NO_2C_6H_4CH$=CH_2, PPh_3, Et_3N, reflux temperature; for **23**, terminal alkynes, $Pd(PPh_3)_4$, CuI, Et_3N/MeCN, reflux.

products were found to possess *trans*- configurations (Scheme 9).

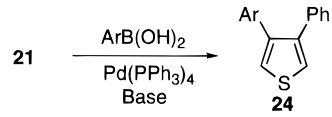
3-Alkynyl-4-phenylthiophenes **23** were readily obtained in high yields by the Sonogashira coupling reaction[38] of 3-iodo-4-phenylthiophene (**21**) with terminal alkynes (Scheme 9). Due to the possible poisoning of the palladium catalyst caused by the thiophene sulfur, more palladium catalyst (about 10% mol) had to be used. An insufficient amount of catalyst did not lead to reaction.

Several 3-phenyl-4-arylthiophenes **24** were prepared by the Suzuki cross-coupling reaction[39] of 3-iodo-4-phenylthiophene (**21**) with areneboronic acids in good yields. As such, this procedure provides a general route to unsymmetrical 3,4-diarylthiophenes. For example, 3-phenyl-4-(4′-methylphenyl)thiophene (**24a**) was isolated in 76% yield by reaction of **21** with 4-methylphenylboronic acid in the presence of $Pd(PPh_3)_4$ catalyst and 2 M aqueous Na_2CO_3 in refluxing MeOH−PhMe (Table 2, entry 1). Under similar conditions, the coupling reaction utilizing mesitylboronic acid did not occur due to the steric hindrance of the two *o*-methyl groups. The reaction did not proceed well even when a stronger base $Ba(OH)_2$ was used.[42a] Eventually, it was found that the base ^{t}BuOK[42b] could lead to the coupling reaction in acceptable yield (56%), affording **24d** as a highly sterically hindered thiophene (Table 2, entry 4).

Previous reports[17c,d] from our laboratory have unequivocally demonstrated the usefulness of organoboroxines for the synthesis of 3,4-disubstituted furans. To further extend this pathway, we would like to investigate the possibility of 3,4-disubstituted thiophene synthesis from organoboroxines. As can be seen in Scheme 10, the alkynylthiophenes **17** were first hydrogenated to **25** with 10% Pd−C catalyst in almost quantitative yields. Then, alkylthiophenes **25** were converted to boroxines **26** by treatment with boron trichloride and subsequent hydrolysis of the resulting dichloroboranes.

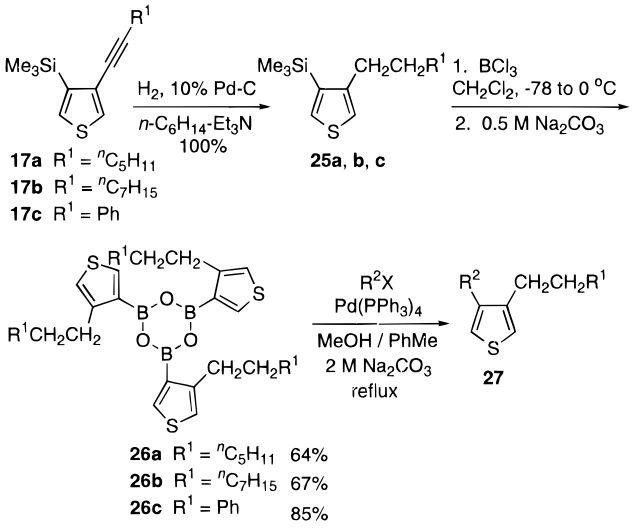
The Suzuki-type coupling reaction[17b,39] of boroxines **26** with aryl, vinyl, and benzylic halides readily took place

Table 2. Suzuki Coupling Reaction of 21 with Areneboronic Acids



Entry	$ArB(OH)_2$	Base	Solvent	Product	Yield
1	Me-C6H4-B(OH)2	Na_2CO_3	MeOH-PhMe	**24a**	76%
2	MeO-C6H4-B(OH)2	Na_2CO_3	MeOH-PhMe	**24b**	90%
3	1-naphthyl-B(OH)2	Na_2CO_3	MeOH-PhMe	**24c**	78%
4	2,6-Me2-C6H3-B(OH)2	^{t}BuOK	^{t}BuOH	**24d**	56%

Scheme 10



(Scheme 10, Table 3). For example, **27a** was obtained in 87% yield by reaction of the boroxine **26a** with 9-bromophenanthrene in the presence of $Pd(PPh_3)_4$ catalyst and 2 M Na_2CO_3 aqueous solution in reflux methanol−toluene (Table 3, entry 1). When **26a** was allowed to react with 1,4-dibromobenzene under similar conditions, two coupling products **27b** and **27c** were isolated in 21% and 49% yields, respectively (Table 3, entry 2). Somewhat surprisingly, the reaction of 2 equiv of boroxine **26a** with 3,4-dibromothiophene afforded the monocoupling product **27e** and the hydrolytic deboration product **27f** without any detectable amount of the biscoupling product (Table 3, entry 4). On the other hand, the cross coupling of boroxine **26b** and (*E*)-*β*-bromostyrene gave the corresponding product **27i** with complete retention of the alkene configuration (Table 3, entry 7). In this way, a number of unsymmetrically 3,4-disubstituted thiophenes have been realized, which is in keeping with our own route to 3,4-disubstituted furans.[17bde,43]

The cross-coupling of boroxine **26c** with 9,10-bis(bromomethyl)phenanthrene using palladium catalyst in

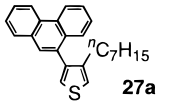
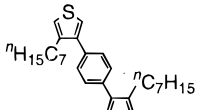
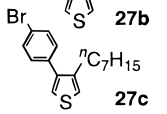
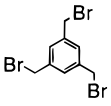
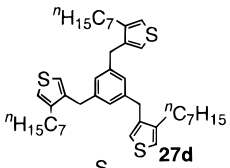
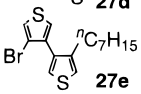
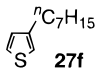
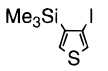
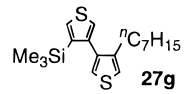
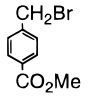
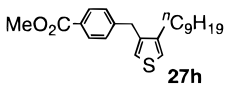
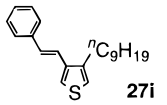
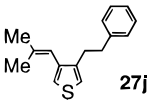
(40) Heck, R. F. In *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985; Chapter 6, pp 179−321. Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133−1136. Daves, G. D., Jr. In *Advances in Metal−Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: London, 1991; Vol. 2, pp 59−99. Cabri, W.; Candiani, I.; Bedeschi, A. *J. Org. Chem.* **1992**, *57*, 3558−3563.

(41) Jeffery, T. *Tetrahedron Lett.* **1985**, *26*, 2667−2670. Jeffery, T. *Tetrahedron Lett.* **1990**, *31*, 6641−6644.

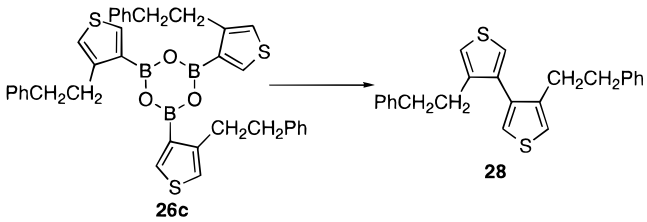
(42) (a) Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213−222. Campi, E. M.; Jackson, W. R.; Marcuccio, S. M.; Naeslund, C. G. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2395. (b) Zhang, H.-C.; Chan, K. S. *Tetrahedron Lett.* **1996**, *37*, 1043−1044.

(43) Kaufmann, D. *Chem. Ber.* **1987**, *120*, 901−905.

Table 3. Suzuki-Type Reaction of Boroxines 26 with Halides

Entry	R^1	R^2X	Product	Yield (%)
1	$^nC_5H_{11}$		 **27a**	87
2	$^nC_5H_{11}$		 **27b**	21
			 **27c**	49
3	$^nC_5H_{11}$		 **27d**	83
4	$^nC_5H_{11}$		 **27e**	69
			 **27f**	94
5	$^nC_5H_{11}$		 **27g**	98
6	$^nC_7H_{15}$		 **27h**	95
7	$^nC_7H_{15}$		 **27i**	50
8	Ph		 **27j**	90

Scheme 11[a]

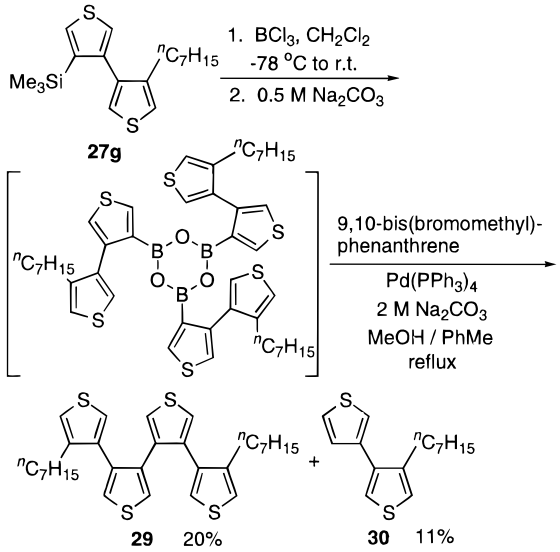


[a] Reagents and conditions: 9,10-bis(bromomethyl)phenanthrene, $Pd(PPh_3)_4$, 2 M Na_2CO_3, MeOH/PhMe, reflux, 44% yield.

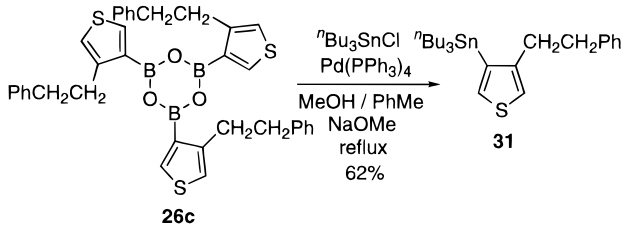
the presence of 2 M Na_2CO_3 was also attempted. However, no desired cross-coupling product was isolated. The only identifiable product obtained was the dimeric thiophene **28** in 44% yield (Scheme 11). It was with no surprise because similar outcomes were encountered in our former work concerning furans.[17d]

Inspired by the successful synthesis of the thiophene-3,4-diyl dimer **28**, the regiospecific preparation of a thiophene-3,4-diyl tetramer was subsequently sought. Thus, as shown in Scheme 12, the dimer **27g**, prepared from the cross-coupling of a boroxine and a halide as shown in Table 3, was converted to its corresponding boroxine, and subsequent coupling reaction gave the

Scheme 12



Scheme 13



quaterthiophene **29** in 20% yield and the reduction product **30** in 11% yield. Consequently, the palladium-catalyzed self-coupling reaction of boroxines is expected to provide a new entry to thiophene-3,4-diyl oligomers, which are difficult or even impossible to realize otherwise.

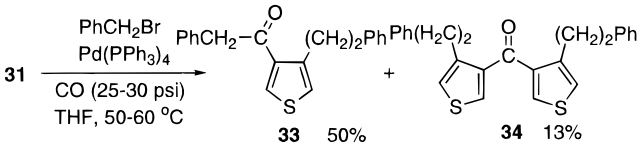
In order to further broaden the synthetic scope of our silicon protocol strategy, it is desirable that the trimethylsilyl group can be converted to a tri-*n*-butylstannyl group; thus, the resulting tin compound can serve as a key intermediate for a regiospecific synthesis of 3,4-disubstituted thiophenes. For this purpose, tris[4-(phenylethyl)thiophene-3-yl]boroxine (**26c**), prepared from the corresponding 3-(phenylethyl)-4-(trimethylsilyl)thiophene (**25c**) after displacement of the C−Si bond by the C−B bond, was chosen in our attempts to replace the boroxine unit directly *via* palladium-catalyzed Suzuki coupling[17f] with tri-*n*-butylstannyl chloride. A combination of $Pd(PPh_3)_4$ as catalyst (10 mol %), NaOMe as base, and methanol−toluene as solvent was found to be effective in furnishing tri-*n*-butylstannyl-substituted thiophene **31** (Scheme 13).

It is noteworthy that thiophene **31** is acid-sensitive. When **31** was slowly chromatographed through a column packed with silica gel, an almost complete protodestannylation occurred, yielding 3-(phenylethyl)thiophene (**32**). For this reason, **31** had to be isolated by flash chromatography on silica gel using hexanes containing 1% (v/v) of triethylamine as eluent.

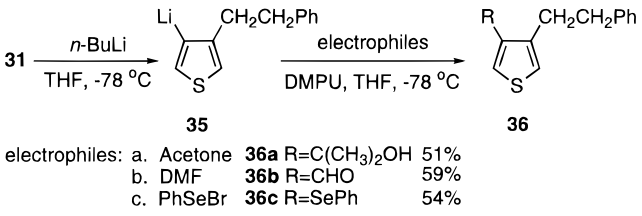
The carbonylative coupling reaction[44] of 3-(phenylethyl)-4-(tri-*n*-butylstannyl)thiophene (**31**) with halides resulted in the introduction of a carbonyl functional group at the coupling juncture of the two partners. The reaction was performed under a CO pressure of 25−30 psi. Thus, when 3-(phenylethyl)-4-(tri-*n*-butylstannyl)-

(44) Goure, W. F.; Wright, M. E.; Davis, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500−7506.

Scheme 14



Scheme 15



thiophene (**31**) was allowed to react with benzyl bromide under an atmosphere of CO (25−30 psi), catalyzed by Pd(PPh$_3$)$_4$ in THF at 50−60 °C, the carbonylated product **33** was obtained in 50% yield and was accompanied by 13% yield of bis[4-(phenylethyl)thiophene-3-yl] ketone (**34**) (Scheme 14). As a result, a synthetic entry to 3-alkyl-4-acylthiophenes was therefore established. We believe that this conversion is also suitable for other aryl halides. The formation of **34** was likely due to the low CO pressure, which implied that the stannylthiophene **31** could possibly participate in an oxidative-addition-like reaction with palladium in the presence of carbon monoxide.

Another pathway from which 3,4-unsymmetrically substituted thiophenes could be made was by soliciting a tin−lithium exchange reaction.[45,46] The lithiation of 3-(phenylethyl)-4-(tri-*n*-butylstannyl)thiophene (**31**) with *n*-butyllithium was carried out at −78 °C to ensure that the β-lithiothiophene formed would not undergo rearrangement[47] to the α-lithiothiophene. The tin−lithium exchange reaction was monitored by TLC with the appearance of tetrabutyltin and disappearance of the starting organostannane. It is worthy to note that organostannanes generally show large bright spots on TLC plates in an iodine chamber. The lithiation was very fast, usually reaching completion within 15 min (Scheme 15).

To make sure that the β-lithiothiophene **35** was indeed formed, the reaction solution was quenched with an excess of acetone, and as a result, the product thiophene **36a** was isolated in 51% yield. Similarly, the trapping reaction of **35** toward electrophiles DMF and phenylselenenyl bromide resulted in the formation of aldehyde **36b** and selenide **36c** in 59% and 54% yields, respectively (Scheme 15).

(c) 3,4-Didehydrothiophene. Structural limitations in organic compounds have posed a longstanding challenge to chemists.[48] Cyclic cumulenes[49] are a fundamental class of strained hydrocarbons for which limiting ring sizes are as yet unknown. Because of such curiosity, considerable efforts have been devoted toward the synthetic exploration of strained cyclic cumulenes in the last decade. In the literature, the isolable 1,2,3-cyclononatriene[50] as well as the fugitive 1,2,3-cycloheptatriene[51] and 1,2,3-cyclohexatriene[52] have been registered. Very recently, 1,2,3-cyclooctatriene as a reactive intermediate has also been reported.[53] Within this series, 1,2,3-cyclopentatriene still remains unknown, but its structural features and energetics have been studied by computation.[50a]

On the other hand, five-membered hetarynes have also aroused widespread synthetic endeavor[54] and theoretical curiosity[55] because of their inherent strain. Although both 2,3-didehydrothiophene (**37**)[56] and 3,4-didehydrothiophene (**2**),[57] the most mentioned of the five-membered hetarynes, had been suggested as reactive intermediates by Wittig in the early 1960's, the validity of such a claim was soon questioned.[54bc,58] Subsequently, the hetaryne **37** was generated from flash vacuum thermolysis (FVT) of thiophene-2,3-dicarboxylic anhydride and accordingly trapped.[59] By way of contrast, evidence for the existence of 3,4-didehydrothiophene (**2**) has never been obtained despite many experimental attempts.[54c,59ac,60−64] Thus, the question has remained open for over 30 years.

37

2

Recently, the use of phenyl[*o*-(trimethylsilyl)phenyl]-iodonium triflate as a precursor for the efficient formation of benzyne under mild and neutral conditions was reported by Kitamura and Yamane.[65] Encouraged by

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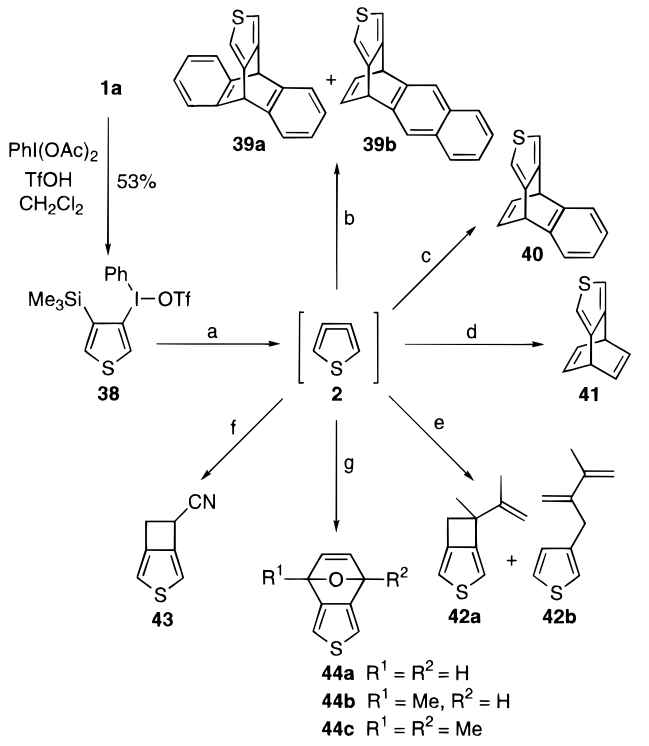
Scheme 16[a]



[a] Reagents and conditions: (a) KF, 18-crown-6, CH_2Cl_2, room temperature; (b) anthracene; (c) naphthalene; (d) benzene; (e) 2,3-dimethyl-1,3-butadiene; (f) acrylonitrile; (g) furan, 2-methylfuran, or 2,5-dimethylfuran.

their result, we were interested in exploring the generation of 3,4-didehydrothiophene (**2**) by virtue of this method, which involved the fluoride-induced vicinal elimination of the trimethylsilyl group and a good leaving group.[66]

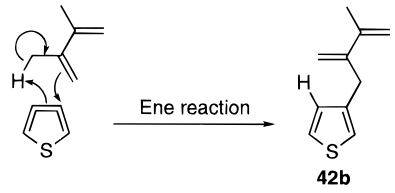
The precursor of **2**, a diaryliodonium salt,[67] namely, phenyl[4-(trimethylsilyl)thien-3-yl]iodonium triflate (**38**), was prepared from 3,4-bis(trimethylsilyl)thiophene (**1a**) according to the literature procedure.[65] Thus, treatment of **1a** with iodobenzene diacetate in the presence of trifluoromethanesulfonic acid gave **38** in 53% yield (Scheme 16). The crystalline product **38** is quite stable (mp 169−172 °C) at room temperature and can be stored for extended periods.

The identity of **38** is unequivocally vindicated by its ^{1}H NMR spectrum, which exhibited absorptions at δ 0.28 (s, 9H) for the trimethylsilyl protons, 7.43 (t, J = 6.5, 6.5 Hz, 2H), 7.52 (dd, J = 6.7, 1.1 Hz, 1H), and 7.80 (d, J = 6.4 Hz, 2H) for the phenyl protons, 7.55 (d, J = 2.9 Hz, 1H) and 8.51 (d, J = 2.9 Hz, 1H) for the 5- and 2-position protons of the thiophene ring, respectively. The structure of **38** was also supported by its ^{13}C NMR, mass spectrum, and a correct elemental analysis.

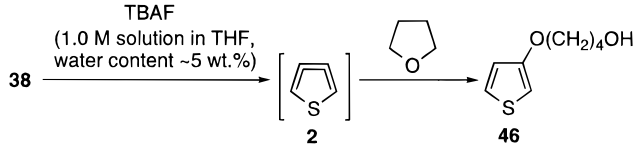
Addition of anhydrous potassium fluoride to a dichloromethane solution of **38** in the presence of 18-crown-6 as anticipated generated cumulene **2**, whose presence was convincingly endorsed by its trapping reactions with several alkenes as shown in Scheme 16.

Such a trapping exercise was first explored by generating **2** at room temperature in the presence of anthracene. In this manner, a chromatographically inseparable mixture of the known 9,10-adduct **39a**[68] and the 1,4-adduct **39b** was given in a total yield of only 10%. The structures and ratio (2.7:1) of **39a** and **39b** were confirmed by ^{1}H- and ^{13}C-NMR spectral analyses. Careful partial recrystallization of a mixture of **39a** and **39b** from MeOH nonetheless afforded a pure sample of **39a**, mp 267−268 °C (lit.[68] mp 268 °C). Lower reaction temperatures were found to cause no significant effect on the yield and ratio of the products. In a similar manner, when naphthalene was used as a trapping reagent, adduct **40** was isolated in a meager 6% yield. Compelling evidence for **2**'s remarkable reactivity was obtained by its reaction with benzene, which yielded the adduct **41** in a low 7% yield. Moreover, the reaction of **2** with 2,3-dimethyl-1,3-butadiene unexpectedly gave in 27% total yield a chromatographically separable mixture (silica gel, *n*-pentane) of a [2 + 2] adduct **42a**, as well as an ene reaction product **42b**, in the ratio of 1:1. The isolation of **42b** is consistent with the observation that ene reaction generally competes with cycloaddition in a trapping process comprising a distorted π-system and an alkene having allylic hydrogen atoms (Scheme 17).[69] The [2 + 2]-cycloaddition was also performed by reaction of **2** with acrylonitrile, and expectedly, the [2 + 2] adduct **43** was obtained in 13% yield. In other Diels−Alder reactions, furan, 2-methylfuran, and 2,5-dimethylfuran were all proved to react readily with **2** to supply adducts **44a**, **44b**, and **44c**, in 31%, 17%, and 13% yields, respectively. The disappointingly low yields of the aforementioned trapping reactions were most probably due to the side reaction in which **2** reacted also with the iodobenzene generated from **38** through the elimination reaction.

Scheme 17



Scheme 18



It appeared that **2** did not dimerize to provide cyclobuta[1,2-*c*:3,4-*c*′]dithiophene (**45**),[70] even for the condition in which no trapping reagent was involved. However, interestingly, when an 1 M ^{n}Bu$_4$NF in THF solution was used instead of KF and 18-crown-6, an unexpected product **46** was isolated in 6% yield. This result implies that **2** may possibly possess some degree of diradical character and is able to cleave the C−O bond of a THF molecule (Scheme 18). Further studies on this aspect will be attractive.

In summary, evidence for 3,4-didehydrothiophene (**2**) as an intermediate has been procured by the formation of its [2 + 2]- and [4 + 2]-cycloaddition adducts with alkenes. It is believed that the five-membered **2** is the smallest cyclic cumulene ever characterized.

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Conclusion

In this study, we have described the efficient and stepwise procedures for the realization of a number of unsymmetrically 3,4-disubstituted thiophenes utilizing 3,4-bis(trimethylsilyl)thiophene (**1a**) as a precursor.

3,4-Bis(trimethylsilyl)thiophene (**1a**) underwent consecutive regiospecific mono-*ipso*-iodination and palladium-catalyzed cross-coupling reactions such as the Stille reaction, Sonogashira reaction, Heck reaction, and Suzuki reaction to provide a number of unsymmetrically 3,4-disubstituted thiophenes.

The silylthiophenes were also converted to the corresponding boroxines by an *ipso* replacement of a boron moiety, which underwent a smooth Suzuki-type cross-coupling reaction with organohalides to furnish 3,4-disubstituted thiophenes with diverse substituents as well.

By utilization of the palladium-catalyzed self-coupling reaction of organoboroxines, thiophene-3,4-diyl dimer **28** and thiophene-3,4-diyl tetramer **29** were realized.

Tris[4-(phenylethyl)thiophene-3-yl]boroxine (**26c**) was converted successfully to 3-(phenylethyl)-4-(tri-*n*-butylstannyl)thiophene (**31**) through the palladium-catalyzed cross-coupling reaction with tri-*n*-butylstannyl chloride. The stannylthiophene (**31**) underwent carbonylative coupling reaction to give thienyl ketones. On the other hand, regiospecific lithiation of **31** provided the intermediate β-lithiothiophene **35**, which was quenched by several electrophiles to afford various unsymmetrically 3,4-disubstituted thiophenes.

As an important application, 3,4-bis(trimethylsilyl)-thiophene (**1a**) was successfully converted to phenyl[4-(trimethylsilyl)thien-3-yl]iodonium triflate (**38**). This iodonium salt **38** was then treated with fluoride to generate 3,4-didehydrothiophene (**2**), which was trapped by its [2 + 2]- and [4 + 2]-cycloaddition reactions with several alkenes.

Experimental Section

3,4-Bis(trimethylsilyl)thiophene (1a). Method A. (a) Bis(trimethylsilylmethyl)sulfoxide (4).[21] To a solution of acetonitrile (3 mL) containing bis[(trimethylsilyl)methyl] sulfide (**8**)[24a] (206 mg, 1 mmol) in a 50-mL round-bottomed flask was added an aqueous solution of sodium metaperiodate (257 mg, 1.2 mmol) in water (3 mL) at −10 °C by ice−salt bath cooling. The solution was stirred at −10 to 0 °C for 12 h, and then the cold solution was filtered and extracted with cold dichloromethane (3 × 5 mL). The dichloromethane extracts were dried (Na_2SO_4) and concentrated under vacuum to yield **4** as a colorless oil that is pure enough to be used in the subsequent reaction without further purification: ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 18H), 2.14 (d, J = 13.4 Hz, 2H), 2.45 (d, J = 13.7 Hz, 2H). The spectroscopic data coincide with the previous report.[21]

(b) 3,4-Bis(trimethylsilyl)-2,5-dihydrothiophene (9). In a flame dried 100-mL three-necked round-bottomed flask equipped with a water condenser and a dropping funnel was added a solution of **4** (666 mg, 3 mmol) and bis(trimethylsilyl)-acetylene (**13a**) (340 mg, 2 mmol) in dry HMPA (2 mL) (distilled from CaH_2) rapidly from a dropping funnel to dry HMPA (2 mL), and the resulting solution was warmed at 100 °C and stirred at this temperature for half an hour under nitrogen atmosphere. The cooled reaction mixture was diluted with benzene (40 mL), washed with brine (4 × 15 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (50 g, hexanes) to give **9** (69 mg, 15%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.21 (s, 18H), 4.06 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 0.84, 50.44, 150.77; MS m/z 230 (M^+, 21); high-resolution MS Calcd for $C_{10}H_{22}SSi_2$ m/z 230.0982, found 230.0981.

(c) 3,4-Bis(trimethylsilyl)thiophene (1a). To dihydrothiophene **9** (230 mg, 1 mmol) in chloroform (8 mL) was added a hot solution of DDQ (363 mg, 1.6 mmol) in chloroform (45 mL). The mixture was stirred at 60−65 °C for 10 h. The cooled reaction mixture was washed with aqueous sodium carbonate (10%, 3 × 10 mL) and water (10 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (30 g, hexanes) to afford **1a** (173 mg, 76%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 18H) and 7.61 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 1.09, 134.73, and 145.43; MS m/z 228 (M^+, 19). Anal. Calcd for $C_{10}H_{20}SSi_2$: C, 52.56; H, 8.82. Found: C, 52.36; H, 8.82. The spectrometric data are identical to those reported in the literature.[18]

3,4-Bis(trimethylsilyl)thiophene (1a). Method B. 3,4-Dibromothiophene (**11**)[19] (3.87 g, 16 mmol), dry THF (16 mL), chlorotrimethylsilane (4.56 mL, 3.91 g, 36 mmol), and magnesium powder (0.86 g, 36 mmol) were placed in a sealed tube (15 cm length, 2.5 cm diameter). The tube was located in the middle of an ultrasonic bath (Branson 1210, power supply 143 W, output power 35 W) so that the bottom of the tube was 1 cm above the bottom of the bath. The reaction mixture was kept under ultrasonication for 4 days. The reaction course was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with hexanes (160 mL) and ice−water (40 mL), and the solids were filtered. The filtrate was separated, and the water layer was extracted with hexanes (3 × 30 mL). The combined hexanes solution was dried over $MgSO_4$, and the solvent was evaporated. The residue was chromatographed on silica gel (150 g, hexanes) to give an inseparable mixture of 3,4-bis(trimethylsilyl)thiophene (**1a**) and 3-bromo-4-(trimethylsilyl)thiophene.

To this mixture in a sealed tube (15 cm length, 2.5 cm diameter) were added dry THF (16 mL), chlorotrimethylsilane (2.28 mL, 1.95 g, 18 mmol), and magnesium powder (0.43 g, 18 mmol). The reaction was carried out under ultrasonication as described above for 3 days. After the same workup, a pure sample of **1a** (1.09 g, 30%) was obtained as a colorless oil, which was identical spectrometrically to an authentic sample prepared by method A.

General Procedure for Preparation of 1a−e. (a) 3,4-Bis(trimethylsilyl)thiophene (1a). A mixture of 4-phenylthiazole (**12b**)[34b] (9.7 g, 60 mmol), bis(trimethylsilyl)acetylene (**13a**) (11.1 g, 65 mmol), and DBU (1.5 mL) was placed in a tube (15 × 2.5 cm^2) that was then attached to a vacuum manifold (0.05 mmHg) and subjected to three freeze−thaw cycles (liquid nitrogen). The tube was then sealed and heated at 325 °C for 6 days. The resulting dark mixture was chromatographed on a silica gel column (250 g, hexanes; then hexanes−EtOAc 10:1 to 5:1) to give the recovered **12b** (3.4 g) and **1a** (8.2 g, 92% based on reacted **12b**) as a colorless oil. Compound **1a** was identical spectrometrically to an authentic sample prepared by method A.

(b) 3,4-Bis(trimethylsilyl)thiophene (1a). A mixture of 4-methylthiazole (**12a**) (300 mg, 3.0 mmol), **13a** (500 mg, 2.9 mmol), and triethylamine (0.1 mL) in a sealed tube (14 × 1.25 cm^2) was heated at 360 °C for 2.5 days to give **1a** (128 mg, 19%) that was identical spectrometrically to an authentic sample prepared previously.

(c) 3-Methyl-4-(trimethylsilyl)thiophene (1b). A mixture of **12a** (3.0 g, 30 mmol), 1-(trimethylsilyl)propyne (3.4 g, 30 mmol), and DBU (0.75 mL) in a sealed tube (14.5 × 2 cm^2) was heated at 340 °C for 4 days. Chromatography on silica gel (300 g, *n*-pentane; then *n*-pentane−ether 4:1) gave the recovered **12a** (1.7 g) and **1b** (716 mg, 32% based on reacted **12a**) as a colorless oil. For thiophene **1b**: ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9H), 2.37 (d, J = 1.0 Hz, 3H), 6.98 (dq, J = 2.8, 1.0, 1.0, 1.0 Hz, 1H), 7.36 (d, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.52, 16.78, 121.92, 132.92, 141.17, 142.20; MS m/z 170 (M^+, 20). Anal. Calcd for $C_8H_{14}SSi$: C, 56.41; H, 8.28. Found: C, 56.34; H, 8.17.

(d) 3-(Trimethylsilyl)thiophene (1c). A mixture of **12b** (4.83 g, 30 mmol), ethynyltrimethylsilane (3.30 g, 33.6 mmol), and DBU (0.75 mL) in a sealed tube (14.5 × 2 cm^2) was heated at 340 °C for 2 days. Chromatography on silica gel (300 g, *n*-pentane; then hexanes−EtOAc 10:1−5:1) gave the recovered **12b** (2.67 g) and **1c** (1.36 g, 65% based on reacted **12b**) as a

colorless oil. For thiophene **1c**: ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9H), 7.20 (dd, J = 4.8, 1.1 Hz, 1H), 7.40 (dd, J = 4.8, 2.6 Hz, 1H), 7.45 (dd, J = 2.6, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.57, 125.58, 131.37, 134.73, 141.27; MS m/z 156 (M^+, 7). The spectroscopic data coincide with the previous report.[27c]

(e) 3-*n*-Butyl-4-(trimethylsilyl)thiophene (1d). A mixture of **12b** (4.83 g, 30 mmol), 1-(trimethylsilyl)-1-hexyne (4.62 g, 30 mmol), and DBU (0.75 mL) in a sealed tube (14.5 × 2 cm^2) was heated at 330 °C for 7 days. Chromatography on silica gel (300 g, hexanes containing 1% Et_3N; then hexanes−EtOAc 10:1 to 5:1) gave the recovered **12b** (2.85 g) and **1d** (1.90 g, 73% based on reacted **12b**) as a colorless oil. For thiophene **1d**: ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9H), 0.95 (t, J = 7.2, 7.2 Hz, 3H), 1.38−1.68 (m, 4H), 2.69 (dt, J = 0.8, 7.8, 7.8 Hz, 2H), 6.99 (dt, J = 2.8, 0.8, 0.8 Hz, 1H), 7.35 (d, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.16, 13.97, 22.70, 30.63, 32.75, 120.66, 132.66, 140.98, 147.83; MS m/z 212 (M^+, 28). Anal. Calcd for $C_{11}H_{20}SSi$: C, 62.20; H, 9.49. Found: C, 62.10; H, 9.57.

(f) 3,4-Diphenylthiophene (1e). A mixture of **12b** (322 mg, 2 mmol) and diphenylacetylene (356 mg, 2 mmol) in a sealed tube (14 × 1.25 cm^2) was heated at 340 °C for 2.5 days to give the recovered **12b** (280 mg) and **1e** (51 mg, 83% based on reacted **12b**) as colorless crystals. For thiophene **1e**: mp 115−116 °C (lit.[10a] 112−113 °C; lit.[71] mp 114 °C); ^{1}H NMR ($CDCl_3$) δ 7.16−7.26 (m, 10H), 7.29 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 123.98, 126.87, 128.13, 129.05, 136.65, 141.86; MS m/z 236 (M^+, 100).

4-Iodo-3-(trimethylsilyl)thiophene (14). Thiophene **1a** (1.82 g, 8 mmol) in THF (120 mL) under nitrogen was cooled in a dry ice−acetone bath to −78 °C. Silver trifluoroacetate (3.54 g, 16 mmol) was added, and the mixture was stirred for 5 min to ensure complete dissolution. Then iodine (4.06 g, 16 mmol) in THF (60 mL) was added dropwise, and the reaction mixture was stirred at −78 °C for 8 h after the addition was finished. The reaction mixture was diluted with ether (150 mL) and filtered through Celite. The filter cake was washed with ether (50 mL). The filtrates were washed with 50% sodium thiosulfate solution (2 × 80 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (150 g, hexanes) to give **14** (2.16 g, 96%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9H), 7.31 (d, J = 2.9 Hz, 1H), 7.51 (d, J = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.65, 83.18, 130.39, 133.87, 144.69; MS m/z 282 (M^+, 32); high-resolution MS calcd for $C_7H_{11}SISi$ m/z 281.9392, found 281.9381.

General Procedure for Preparation of 15 and 16 by the Stille Coupling Reaction. (a) 3-(Trimethylsilyl)-4-ethynylthiophene (15). To a mixture of **14** (705 mg, 2.5 mmol) and ethynyltri-*n*-butyltin[72] (788 mg, 2.5 mmol) in dioxane (30 mL) was added $Pd(PPh_3)_4$ (290 mg, 0.25 mmol). The resulting mixture was heated at 90 °C for 6 h under a nitrogen atmosphere. The cooled reaction mixture was diluted with ether (150 mL), washed with water (2 × 25 mL), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel (150 g, *n*-pentane) to give **15** (406 mg, 90%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 9H), 3.12 (s, 1H), 7.32 (d, J = 2.8 Hz, 1H), 7.59 (d, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.08, 78.13, 80.37, 125.69, 131.67, 131.92, 143.35; MS m/z 180 (M^+, 22). Anal. Calcd for $C_9H_{12}SSi$: C, 59.94; H, 6.71. Found: C, 60.17; H, 6.84.

(b) Bis[4-(trimethylsilyl)thien-3-yl]acetylene (16). A mixture of **14** (70.5 mg, 0.25 mmol), bis(tri-*n*-butylstannyl)-acetylene (75.5 mg, 0.125 mmol), and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) in dioxane (3 mL) and triethylamine (1 mL) was heated at 90 °C for 8 h under nitrogen. Chromatography on silica gel (20 g, hexanes containing 2% Et_3N) afforded **16** (23.5 mg, 56%) as pale yellowish crystals: mp 69−71 °C; ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 18H), 7.37 (d, J = 2.9 Hz, 2H), 7.52 (d, J = 2.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −0.92, 86.76, 127.07, 129.41, 131.98, 143.08; MS m/z 334 (M^+, 100). Anal. Calcd for $C_{16}H_{22}S_2Si_2$: C, 57.43; H, 6.63. Found: C, 57.48; H, 6.75.

General Procedure for Preparation of Thiophenes 17a−j by the Sonogashira Coupling Reaction. (a) 3-(Trimethylsilyl)-4-(heptyn-1′-yl)thiophene (17a). A mixture consisting of **14** (141 mg, 0.5 mmol), 1-heptyne (96 mg, 1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), copper(I) iodide (19 mg, 0.1 mmol), dry acetonitrile (2 mL), and dry triethylamine (5 mL) was stirred at reflux temperature (nitrogen atmosphere) for 18 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel (20 g, hexanes) to give **17a** (110 mg, 88%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 9H), 0.91 (t, J = 7.0, 7.0 Hz, 3H), 1.33−1.45 (m, 4H), 1.55−1.60 (m, 2H), 2.40 (t, J = 7.1, 6.9 Hz, 2H), 7.29 (d, J = 2.8 Hz, 1H), 7.40 (d, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.07, 13.92, 19.40, 22.22, 28.40, 31.21, 90.97, 127.55, 128.84, 131.61, 142.93; MS m/z 250 (M^+, 41). Anal. Calcd for $C_{14}H_{22}SSi$: C, 67.13; H, 8.85. Found: C, 66.61; H, 8.86.

(b) 3-(Trimethylsilyl)-4-(nonyn-1′-yl)thiophene (17b). This was prepared from **14** (141 mg, 0.5 mmol) and 1-nonyne (93 mg, 0.75 mmol) in the same manner as described for **17a**, yielding **17b** (124 mg, 89%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 9H), 0.89 (t, J = 6.8, 6.6 Hz, 3H), 1.30−1.35 (m, 6H), 1.38−1.47 (m, 2H), 1.55−1.63 (m, 2H), 2.40 (t, J = 7.1, 6.9 Hz, 2H), 7.30 (d, J = 2.9 Hz, 1H), 7.40 (d, J = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.06, 14.06, 19.45, 22.64, 28.75, 28.86, 29.03, 31.79, 91.00, 127.54, 128.85, 131.64, 142.93; MS m/z 278 (M^+, 28). Anal. Calcd for $C_{16}H_{26}SSi$: C, 69.00; H, 9.41. Found: C, 69.25; H, 9.73.

(c) 3-(Trimethylsilyl)-4-(phenylethynyl)thiophene (17c). This was prepared from **14** (141 mg, 0.5 mmol) and phenylacetylene (76 mg, 0.75 mmol) in the same manner as described for **17a**, yielding **17c** (109 mg, 85%) as a colorless thick oil: ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9H), 7.30−7.35 (m, 4H), 7.48−7.52 (m, 2H), 7.57 (d, J = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −7.99, 79.17, 82.99, 116.56, 119.72, 121.07, 121.38, 122.99, 124.21, 124.99, 136.09; MS m/z 256 (M^+, 37). Anal. Calcd for $C_{15}H_{16}SSi$: C, 70.26; H, 6.29. Found: C, 70.51; H, 6.26.

(d) 3-(Trimethylsilyl)-4-(cyclohexen-1′-yl)thiophene (17d). This was prepared from **14** (141 mg, 0.5 mmol) and 1-ethynylcyclohexene (80 mg, 0.75 mmol) in the same manner as described for **17a**, yielding **17d** (114 mg, 88%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.34 (s, 9H), 1.59−1.69 (m, 4H), 2.10−2.22 (m, 4H), 6.14−6.18 (m, 1H), 7.31 (d, J = 2.8 Hz, 1H), 7.44 (d, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.06, 21.55, 22.35, 25.74, 29.04, 83.38, 91.85, 120.86, 127.21, 129.03, 131.73, 134.32, 142.94; MS m/z 260 (M^+, 42). Anal. Calcd for $C_{15}H_{20}SSi$: C, 69.17; H, 7.74. Found: C, 69.31; H, 7.66.

(e) 3-(Trimethylsilyl)-4-[(1′-hydroxycyclopentyl)ethynyl]thiophene (17e). This was prepared from **14** (141 mg, 0.5 mmol) and 1-ethynylcyclopentanol (82.5 mg, 0.75 mmol) in the same manner as described for **17a**. Chromatography on silica gel (20 g, hexanes−EtOAc 6:1) gave **17e** (123 mg, 93%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 9H), 1.76−1.91 (m, 4H), 2.01−2.06 (m, 5H), 7.31 (d, J = 2.9 Hz, 1H), 7.48 (d, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.10, 23.39, 42.26, 74.88, 79.74, 93.43, 126.23, 130.01, 131.84, 142.84; MS m/z 264 (M^+, 13). Anal. Calcd for $C_{14}H_{20}OSSi$: C, 63.58; H, 7.62. Found: C, 63.46; H, 7.64.

(f) 3-(Trimethylsilyl)-4-(4′-hydroxybutyn-1′-yl)thiophene (17f). This was prepared from **14** (141 mg, 0.5 mmol) and 3-butyn-1-ol (52.5 mg, 0.75 mmol) in the same manner as described for **17a**. Chromatography on silica gel (20 g, hexanes−EtOAc 3.5:1) gave **17f** (103 mg, 92%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.31 (s, 9H), 2.12 (br. s, 1H), 2.67 (t, J = 6.4, 6.4 Hz, 2H), 3.80 (t, J = 6.4, 6.4 Hz, 2H), 7.30 (d, J = 2.9 Hz, 1H), 7.44 (d, J = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.09, 23.78, 61.11, 78.92, 86.97, 126.69, 129.64, 131.81, 142.87; MS m/z 224 (M^+, 82). Anal. Calcd for $C_{11}H_{16}OSSi$: C, 58.88; H, 7.19. Found: C, 58.37; H, 7.34.

(g) 3-(Trimethylsilyl)-4-(6′-hydroxyhexyn-1′-yl)thiophene (17g). This was prepared from **14** (141 mg, 0.5 mmol) and 5-hexyn-1-ol (73.5 mg, 0.75 mmol) in the same manner as described for **17a**. Chromatography on silica gel (20 g, hexanes−EtOAc 4:1) gave **17g** (115 mg, 91%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.32 (s, 9H), 1.66−1.73 (m, 4H), 2.17 (br. s, 1H), 2.44 (t, J = 6.6, 6.5 Hz, 2H), 3.67 (t, J = 6.1, 6.0 Hz, 2H), 7.29 (d, J = 2.9 Hz, 1H), 7.40 (d, J = 2.8 Hz, 1H); ^{13}C NMR

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($CDCl_3$) δ −1.08, 19.18, 24.96, 31.95, 62.27, 77.36, 90.38, 127.28, 129.01, 131.66, 142.81; MS *m*/*z* 252 (M^+, 22). Anal. Calcd for $C_{13}H_{20}OSSi$: C, 61.85; H, 7.99. Found: C, 61.82; H, 8.03.

(h) 3-(Trimethylsilyl)-4-[3′-(benzylmethylamino)prop-yn-1′-yl]thiophene (17h). This was prepared from **14** (141 mg, 0.5 mmol) and *N*-benzyl-*N*-methylpropargylamine (119 mg, 0.75 mmol) in the same manner as described for **17a**. Chromatography on silica gel (20 g, hexanes−EtOAc 6:1) gave **17h** (143 mg, 91%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9H), 2.39 (s, 3H), 3.54 (s, 2H), 3.64 (s, 2H), 7.28−7.35 (m, 6H), 7.52 (d, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.95, 41.94, 46.00, 60.32, 81.94, 85.47, 126.67, 127.11, 128.25, 129.10, 130.26, 131.84, 138.62, 142.76; MS *m*/*z* 313 (M^+, 44). Anal. Calcd for $C_{18}H_{23}NSSi$: C, 68.95; H, 7.39; N, 4.47. Found: C, 68.98; H, 7.70; N, 4.00.

(i) 3-(Trimethylsilyl)-4-(*cis*-5′-hydroxy-3′-methyl-3′-penten-1′-ynyl)thiophene (17i). This was prepared from **14** (141 mg, 0.5 mmol) and *cis*-3-methyl-2-penten-4-yn-1-ol (72 mg, 0.75 mmol) in the same manner as described for **17a**. Chromatography on silica gel (20 g, hexanes−EtOAc 5:1) gave **17i** (92 mg, 74%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 9H), 1.91 (br s, 1H), 1.97 (q, J = 1.2, 1.2, 1.2 Hz, 3H), 4.40 (d, J = 6.7 Hz, 2H), 5.90 (tq, J = 6.8, 6.8, 1.5, 1.5, 1.5 Hz, 1H), 7.34 (d, J = 2.9 Hz, 1H), 7.51 (d, J = 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.08, 23.00, 61.41, 88.04, 91.05, 120.78, 126.41, 130.26, 132.04, 135.22, 142.75; MS (CI) *m*/*z* 250 (M^+, 20), 249 (M^+ − 1, 100). Anal. Calcd for $C_{13}H_{18}OSSi$: C, 62.35; H, 7.24. Found: C, 62.50; H, 7.37.

(j) 3-(Trimethylsilyl)-4-(*trans*-5′-hydroxy-3′-methyl-3′-penten-1′-ynyl)thiophene (17j). This was prepared from **14** (141 mg, 0.5 mmol) and *trans*-3-methyl-2-penten-4-yn-1-ol (72 mg, 0.75 mmol) in the same manner as described for **17a**. Chromatography on silica gel (20 g, hexanes−EtOAc 5:1) gave **17j** (85 mg, 68%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 9H), 1.62 (br. s, 1H), 1.92 (m, 3H), 4.28 (d, J = 6.8 Hz, 2H), 6.05 (tq, J = 6.8, 6.8, 1.4, 1.4, 1.4 Hz, 1H), 7.33 (d, J = 2.8 Hz, 1H), 7.49 (d, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.07, 17.36, 59.18, 84.44, 92.04, 121.08, 126.68, 129.86, 131.91, 134.82, 143.00; MS (CI) *m*/*z* 250 (M^+, 22), 249 (M^+ − 1, 100). Anal. Calcd for $C_{13}H_{18}OSSi$: C, 62.35; H, 7.24. Found: C, 62.02; H, 7.09.

3-Iodo-4-(phenylethynyl)thiophene (18). Thiophene **17c** (220 mg, 0.86 mmol) in THF−MeOH (3:1, 25 mL) under nitrogen was cooled to 0 °C. Silver trifluoroacetate (380 mg, 1.72 mmol) was added, and the mixture was stirred for 5 min to ensure complete dissolution. Then iodine (436 mg, 1.72 mmol) in THF−MeOH (3:1, 12 mL) was added dropwise, and the reaction mixture was stirred at 0 °C for 4 h after the addition was finished. The usual workup as described for **14** gave **18** (80 mg, 30%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.36−7.41 (m, 3H), 7.44 (d, J = 3.2 Hz, 1H), 7.48 (d, J = 3.2 Hz, 1H), 7.59−7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 84.62, 84.70, 92.06, 122.87, 128.08, 128.32, 128.49, 128.58, 128.72, 131.64; MS *m*/*z* 310 (M^+, 100); high-resolution MS Calcd for $C_{12}H_7SI$ *m*/*z* 309.9311, found 309.9264.

3-(Nonyn-1′-yl)-4-(phenylethynyl)thiophene (19a). This was prepared by the reaction of **18** (62.0 mg, 0.2 mmol) and 1-nonyne (37.2 mg, 0.3 mmol) in acetonitrile (0.8 mL) and triethylamine (2 mL) in the presence of $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) and CuI (7.6 mg, 0.04 mmol) in the same manner as described for **17a**, yielding **19a** (55.0 mg, 90%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.5, 7.0 Hz, 3H), 1.21−1.35 (m, 6H), 1.42−1.54 (m, 2H), 1.58−1.67 (m, 2H), 2.47 (t, J = 6.9, 7.0 Hz, 2H), 7.33−7.39 (m, 4H), 7.54 (d, J = 3.1 Hz, 1H), 7.52−7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.97, 19.54, 22.60, 28.84, 31.66, 74.38, 83.60, 91.19, 92.88, 123.40, 125.09, 125.82, 126.95, 127.73, 128.22, 131.64; MS *m*/*z* 306 (M^+, 19). Anal. Calcd for $C_{21}H_{22}S$: C, 82.30; H, 7.24. Found: C, 82.61; H, 7.63.

3-(4′-Hydroxybutyn-1′-yl)-4-(phenylethynyl)thiophene (19b). This was prepared by the reaction of **18** (37.0 mg, 0.12 mmol) and 3-butyn-1-ol (12.6 mg, 0.18 mmol) in acetonitrile (0.5 mL) and triethylamine (1.25 mL) in the presence of $Pd(PPh_3)_4$ (13.9 mg, 0.012 mmol) and CuI (4.6 mg, 0.024 mmol) in the same manner as described for **17a**, yielding **19b** (25.0 mg, 83%) as solids: mp 57−58 °C; ^{1}H NMR ($CDCl_3$) δ 2.12 (br s, 1H), 2.73 (t, J = 6.1, 6.1 Hz, 2H), 3.81 (t, J = 5.4, 5.4 Hz, 2H), 7.33−7.37 (m, 4H), 7.46 (d, J = 3.2 Hz, 1H), 7.52−7.56 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.00, 61.07, 83.35, 88.91, 91.45, 123.05, 124.96, 125.11, 127.62, 128.04, 128.39, 131.64; MS *m*/*z* 252 (M^+, 71). Anal. Calcd for $C_{16}H_{12}OS$: C, 76.16; H, 4.79. Found: C, 76.33; H, 4.63.

4-Phenyl-3-(trimethylsilyl)thiophene (20). To a stirred solution containing **14** (1.41 g, 5 mmol), phenylboronic acid (0.61 g, 5 mmol), and $Pd(PPh_3)_4$ (288 mg, 0.25 mmol) in methanol−toluene (1:1, 160 mL) was added a 2 M Na_2CO_3 aqueous solution (20 mL). The reaction mixture was heated at reflux for 5 h under nitrogen and was then poured into ice−water (200 mL). The resulting mixture was extracted with ether (3 × 250 mL). The combined ether extracts were dried over $MgSO_4$, and the solvent was removed. The residue was purified by chromatography on silica gel (150 g, hexanes) to give **20** (0.89 g, 77%) as colorless crystals: mp 59−62 °C; ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 9H), 7.36 (d, J = 2.9 Hz, 1H), 7.49−7.53 (m, 5H), 7.63 (d, J = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.14, 123.51, 127.15, 127.85, 129.29, 133.33, 139.10, 141.13, 148.78; MS *m*/*z* 232 (M^+, 44). Anal. Calcd for $C_{13}H_{16}SSi$: C, 67.18; H, 6.94. Found: C, 67.16; H, 6.94.

3-Iodo-4-phenylthiophene (21). Thiophene **20** (58 mg, 0.25 mmol) in THF−MeOH (5:1, 8 mL) under nitrogen was cooled to −78 °C. Silver trifluoroacetate (111 mg, 0.5 mmol) was added, and the mixture was stirred for 5 min to ensure complete dissolution. Then iodine (127 mg, 0.5 mmol) in THF−MeOH (5:1, 6 mL) was added dropwise. The reaction mixture was stirred at −78 °C for 4 h after the addition was finished and then warmed to room temperature for 20 h. The usual workup as described for **14** gave **21** (48 mg, 67%) as colorless crystals: mp 50−52 °C; ^{1}H NMR ($CDCl_3$) δ 7.20 (d, J = 3.4 Hz, 1H), 7.39−7.49 (m, 5H), 7.54 (d, J = 3.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 81.77, 122.46, 127.81, 128.10, 129.35, 129.89, 136.63, 145.49; MS *m*/*z* 286 (M^+, 100); high-resolution MS calcd for $C_{10}H_7SI$ *m*/*z* 285.9314, found 285.9355.

3-Phenyl-4-[*trans*-2′-(ethylcarbonyl)vinyl]thiophene (22a). A mixture of **21** (28.6 mg, 0.1 mmol), ethyl vinyl ketone (33.6 mg, 0.4 mmol), $Pd(OAc)_2$ (0.5 mg, 0.002 mmol), K_2CO_3 (34.5 mg, 0.25 mmol), and ^{n}Bu_4NI (36.9 mg, 0.1 mmol) in DMF (3 mL) was stirred at 90 °C for 8 h under nitrogen. The reaction mixture was diluted with ether (10 mL) and water (10 mL). The ether layer was separated, and the aqueous layer was extracted with ether (2 × 10 mL). The combined ether solution was dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel (10 g, hexanes−EtOAc 4:1) to give **22a** (12.1 mg, 50%) as a solid: mp 80−82 °C; ^{1}H NMR ($CDCl_3$) δ 1.03 (t, J = 7.3, 7.3 Hz, 3H), 2.51 (q, J = 7.3, 7.3, 7.3 Hz, 2H), 6.50 (d, J = 16.2 Hz, 1H), 7.20 (d, J = 3.2 Hz, 1H), 7.22−7.43 (m, 6H), 7.62 (dd, J = 3.3, 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.22, 33.63, 124.08, 125.58, 127.17, 127.72, 128.62, 129.10, 135.49, 135.64, 135.81, 143.33, 200.83; MS *m*/*z* 242 (M^+, 2). Anal. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82. Found: C, 73.90; H, 5.67.

3-Phenyl-4-[*trans*-2′-(methoxycarbonyl)vinyl]thiophene (22b). This was prepared from **21** (28.6 mg, 0.1 mmol) and methyl acrylate (34.4 mg, 0.4 mmol) in the same manner as described for **22a**, yielding **22b** (15 mg, 62%) as an oil: ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 3H), 6.27 (d, J = 16.0 Hz, 1H), 7.26 (d, J = 3.2 Hz, 1H), 7.33−7.47 (m, 5H), 7.60 (d, J = 16.0 Hz, 1H), 7.67 (d, J = 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 51.48, 118.70, 124.03, 125.61, 127.67, 128.60, 129.08, 135.63, 138.02, 143.19, 167.28; MS *m*/*z* 244 (M^+, 21). Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.83; H, 4.95. Found: C, 68.48; H, 4.99.

3-Phenyl-4-[*trans*-2′-(*m*-nitrophenyl)vinyl]thiophene (22c). A mixture of **21** (28.6 mg, 0.1 mmol), 3-nitrostyrene (22.4 mg, 0.15 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), and Ph_3P (5.2 mg, 0.02 mmol) in triethylamine (3 mL) and acetonitrile (0.5 mL) was refluxed overnight under nitrogen. After removal of the solvent, the residue was purified by chromatography on silica gel (10 g, hexanes−EtOAc 8:1) to give **22c** (20.0 mg, 65%) as an oil: ^{1}H NMR ($CDCl_3$) δ 6.97 (d, J = 16.3 Hz, 1H), 7.12 (dd, J = 16.3, 0.5 Hz, 1H), 7.28 (d, J = 3.2 Hz, 1H), 7.39−7.49 (m, 6H), 7.57 (dd, J = 3.3, 0.5 Hz, 1H), 7.66−7.70 (m, 1H), 8.04−8.08 (m, 1H), 8.20−8.21 (t, J = 2.0, 1.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 121.02, 121.89, 122.34, 123.82, 125.62, 127.35, 127.58, 128.61, 129.11, 129.47, 131.79, 136.23, 137.38, 139.43, 142.63, 148.93; MS *m*/*z* 307 (M^+, 58). Anal. Calcd for

$C_{18}H_{13}O_2NS$: C, 70.34; H, 4.26; N, 4.56. Found: C, 70.32; H, 4.42; N, 4.29.

3-Phenyl-4-(nonyn-1′-yl)thiophene (23a). This was prepared by the reaction of **21** (33.0 mg, 0.12 mmol) and 1-nonyne (21.5 mg, 0.17 mmol) in triethylamine (1.25 mL) and acetonitrile (0.5 mL) in the presence of $Pd(PPh_3)_4$ (13.3 mg, 0.012 mmol) and CuI (4.4 mg, 0.023 mmol) in the same manner as described for **17a**, yielding **23a** (23.5 mg, 73%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.5, 6.8 Hz, 3H), 1.25−1.40 (m, 8H), 1.51−1.56 (m, 2H), 2.34 (t, J = 6.9, 7.0 Hz, 2H), 7.24 (d, J = 3.3 Hz, 1H), 7.32−7.43 (m, 3H), 7.44 (d, J = 3.3 Hz, 1H), 7.67−7.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.01, 19.48, 22.60, 28.60, 28.85, 31.74, 75.77, 92.17, 121.82, 122.60, 127.29, 128.11, 128.20, 129.05, 135.72, 143.39; MS m/z 282 (M^+, 4). Anal. Calcd for $C_{19}H_{22}S$: C, 80.80; H, 7.85. Found: C, 80.69; H, 8.10.

3-Phenyl-4-(4′-hydroxybutyn-1′-yl)thiophene (23b). This was prepared by the reaction of **21** (28.6 mg, 0.1 mmol) and 3-butyn-1-ol (10.5 mg, 0.15 mmol) in triethylamine (1.25 mL) and acetonitrile (0.5 mL) in the presence of $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol) and CuI (3.8 mg, 0.02 mmol) in the same manner as described for **17a**, yielding **23b** (22.8 mg, 100%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.78 (br s, 1H), 2.61 (t, J = 6.1, 6.1 Hz, 2H), 3.71 (t, J = 6.1, 6.1 Hz, 2H), 7.25 (d, J = 3.3 Hz, 1H), 7.34−7.45 (m, 3H), 7.49 (d, J = 3.3 Hz, 1H), 7.63−7.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 23.95, 61.06, 77.85, 88.20, 122.05, 127.55, 128.19, 128.25, 129.61, 135.69, 143.58; MS m/z 228 (M^+, 50). Anal. Calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30. Found: C, 73.21; H, 5.39.

3-Phenyl-4-(*p*-tolyl)thiophene (24a). This was prepared by the reaction of **21** (28.6 mg, 0.1 mmol) and *p*-tolylboronic acid[73] (13.6 mg, 0.1 mmol) in methanol−toluene (1:1, 4 mL) in the presence of $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and 2 M Na_2CO_3 (0.5 mL) in the same manner as described for **20**, yielding **24a** (19 mg, 76%) as colorless crystals: mp 56−58 °C; ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3H), 7.06−7.07 (m, 4H), 7.17−7.30 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 21.11, 123.58, 123.90, 126.81, 128.10, 128.87, 129.03, 133.70, 136.52, 136.77, 141.80; MS m/z 250 (M^+, 100). Anal. Calcd for $C_{17}H_{14}S$: C, 81.56; H, 5.64. Found: C, 81.12; H, 5.73.

3-Phenyl-4-(4′-methoxyphenyl)thiophene (24b). This was prepared by the reaction of **21** (28.6 mg, 0.1 mmol) and 4-methoxyphenylboronic acid[73] (15.2 mg, 0.1 mmol) in methanol−toluene (1:1, 4 mL) in the presence of $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and 2 M Na_2CO_3 (0.5 mL) in the same manner as described for **20**, yielding **24b** (24.0 mg, 90%) as an oil: ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3H), 6.77−7.13 (ABq, J = 8.8 Hz, 4H), 7.17−7.27 (m, 6H), 7.29 (d, J = 3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.21, 113.65, 123.16, 123.87, 126.82, 128.14, 129.05, 130.11, 136.81, 141.47, 141.79, 158.74; MS m/z 266 (M^+, 100). Anal. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30. Found: C, 76.46; H, 5.32.

3-Phenyl-4-(naphth-1′-yl)thiophene (24c). This was prepared by the reaction of **21** (28.6 mg, 0.1 mmol) and 1-naphthylboronic acid[74] (17.2 mg, 0.1 mmol) in methanol−toluene (1:1, 4 mL) in the presence of $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and 2 M Na_2CO_3 (0.5 mL) in the same manner as described for **20**, yielding **24c** (22.2 mg, 78%) as colorless crystals: mp 104−106 °C; ^{1}H NMR ($CDCl_3$) δ 7.06−7.08 (m, 5H), 7.25−7.43 (m, 5H), 7.46 (d, J = 3.3 Hz, 1H), 7.73−7.84 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 122.99, 125.19, 125.66, 125.88, 126.22, 126.68, 127.73, 127.99, 128.05, 128.15, 132.55, 133.68, 134.84, 136.40, 139.90, 143.15; MS m/z 286 (M^+, 46). Anal. Calcd for $C_{20}H_{14}S$: C, 83.88; H, 4.93. Found: C, 83.66; H, 4.92.

3-Phenyl-4-mesitylthiophene (24d). This was prepared by the reaction of **21** (28.6 mg, 0.1 mmol) and mesitylboronic acid[75] (18.0 mg, 0.11 mmol) in ^{t}BuOH (4 mL) in the presence of $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and ^{t}BuOK (22.4 mg, 0.2 mmol) in a similar manner as described for **20**, yielding **24d** (15.6 mg, 56%) as white crystals: mp 59−61 °C; ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 6H), 2.31 (s, 3H), 6.88 (s, 2H), 7.09 (d, J = 3.3 Hz, 1H), 7.13−7.21 (m, 5H), 7.45 (d, J = 3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.56, 21.05, 122.75, 123.68, 126.70, 127.43, 128.12, 133.52, 136.58, 136.82, 137.07, 139.96, 142.08; MS m/z 278 (M^+, 100). Anal. Calcd for $C_{19}H_{18}S$: C, 81.97; H, 6.52. Found: C, 82.10; H, 6.52.

3-(Trimethylsilyl)-4-heptylthiophene (25a). To a solution of thiophene **17a** (500 mg, 2 mmol) in hexanes (20 mL) and triethylamine (4 mL) was added 10% Pd−C (0.11g, 0.1 mmol). The mixture was then stirred under a hydrogen atmosphere for 24 h. The reaction mixture was filtered, and the filtrate was collected. Removal of the solvent gave **25a** (507 mg, 100%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.29 (s, 9H), 0.89 (t, J = 6.9, 6.5 Hz, 3H), 1.25−1.38 (m, 8H), 1.57−1.69 (m, 2H), 2.68 (dt, J = 0.8, 8.1, 7.6 Hz, 2H), 7.00 (dt, J = 2.8, 0.8, 0.8 Hz, 1H), 7.36 (d, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.15, 14.01, 22.63, 29.21, 29.63, 30.65, 31.00, 31.83, 120.68, 132.67, 141.02, 147.93; MS m/z 254 (M^+, 77). Anal. Calcd for $C_{14}H_{26}SSi$: C, 66.07; H, 10.30. Found: C, 66.37; H, 10.40.

3-(Trimethylsilyl)-4-nonylthiophene (25b). This was prepared from **17b** (556 mg, 2 mmol) in the same manner as described for **25a**, yielding **25b** (562 mg, 100%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 9H), 0.90 (t, J = 6.8, 6.4 Hz, 3H), 1.23−1.43 (m, 12H), 1.61−1.73 (m, 2H), 2.69 (dt, J = 0.6, 8.2, 7.6 Hz, 2H), 7.01 (dt, J = 2.8, 0.7, 0.7 Hz, 1H), 7.37 (d, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.15, 14.07, 22.66, 29.31, 29.57, 29.66, 30.63, 31.00, 31.91, 120.67, 132.67, 141.01, 147.92; MS m/z 282 (M^+, 63). Anal. Calcd for $C_{16}H_{30}SSi$: C, 68.01; H, 10.70. Found: C, 68.26; H, 11.01.

3-(Trimethylsilyl)-4-(phenylethyl)thiophene (25c). This was prepared from **17c** (1.28 g, 5 mmol) in the same manner as described for **25a**, yielding **25c** (1.30 g, 100%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.29 (s, 9H), 3.00 (m, 4H), 7.04 (d, J = 2.7 Hz, 1H), 7.19−7.35 (m, 5H), 7.39 (d, J = 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.14, 32.67, 36.91, 121.32, 125.98, 128.34, 128.40, 132.86, 140.83, 141.77, 146.72; MS m/z 260 (M^+, 73). Anal. Calcd for $C_{15}H_{20}SSi$: C, 69.17; H, 7.74. Found: C, 69.19; H, 7.76.

General Procedure for Preparation of Boroxines 26a−c. (a) Tris(4-heptylthien-3-yl)boroxine (26a). To a solution of **25a** (50.8 mg, 0.2 mmol) in CH_2Cl_2 (8 mL) was added a solution of BCl_3 (1.0M) in CH_2Cl_2 (0.3 mL) under a nitrogen atmosphere at −78 °C. The mixture was stirred for 2 h and was allowed to slowly warm to 0 °C for 8 h. The reaction was quenched with 0.5 M Na_2CO_3 solution (10 mL), and the mixture was extracted with ether (3 × 15 mL). The organic layer was dried ($MgSO_4$), and the solvent was evaporated. The crude product was chromatographed on silica gel (10 g, hexanes−ether 1:1) to give **26a** (26.5 mg, 64%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.6, 6.3 Hz, 9H), 1.27−1.44 (m, 24H), 1.69−1.77 (m, 6H), 3.08 (t, J = 7.6, 7.4 Hz, 6H), 7.04 (d, J = 3.0 Hz, 3H), 8.27 (d, J = 3.0 Hz, 3H); MS m/z 624 (M^+, 14); high-resolution MS Calcd for $C_{33}H_{51}O_3B_3S_3$ m/z 624.3279, found 624.3326.

(b) Tris(4-nonylthien-3-yl)boroxine (26b). This was prepared from **25b** (67.5 mg, 0.24 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (0.3 mL) to give **26b** (38.0 mg, 67%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.8, 6.4 Hz, 9H), 1.27−1.45 (m, 36H), 1.69−1.77 (m, 6H), 3.08 (t, J = 7.6, 7.4 Hz, 6H), 7.04 (d, J = 3.0 Hz, 3H), 8.27 (d, J = 3.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 14.04, 22.66, 29.34, 29.68, 30.65, 31.02, 31.92, 121.41, 141.28, 148.85; MS m/z 708 (M^+, 13). Anal. Calcd for $C_{39}H_{63}O_3B_3S_3$: C, 66.11; H, 8.96. Found: C, 65.53; H, 8.84.

(c) Tris[4-(phenylethyl)thien-3-yl]boroxine (26c). This was prepared from **25c** (1.80 g, 6.92 mmol) and a solution of BCl_3 (1.0 M) in CH_2Cl_2 (10.5 mL) to give **26c** (1.26 g, 85%) as white solids: mp 119.5−120 °C; ^{1}H NMR ($CDCl_3$) δ 2.94−3.37 (AA′XX′, J = 7.3, 7.3 Hz, 12H), 6.96 (d, J = 3.0 Hz, 3H), 7.11−7.26 (m, 15H), 8.08 (d, J = 3.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 32.24, 37.51, 122.01, 125.94, 128.29, 128.64, 141.56, 141.77, 147.55; MS m/z 642 (M^+, 8). Anal. Calcd for $C_{36}H_{33}O_3B_3S_3$: C, 67.32; H, 5.18. Found: C, 67.42; H, 5.04.

Preparation of Thiophenes 27a−j by the Suzuki Coupling Reaction. (a) 3-Heptyl-4-(phenanthr-9′-yl)thiophene (27a). A mixture of **26a** (41.6 mg, 0.067 mmol), 9-bromophenanthrene (51.4 mg, 0.2 mmol), and $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) in methanol−toluene (1:1, 6 mL) was stirred under nitrogen. After 5 min, a 2 M Na_2CO_3 solution (1 mL) was

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added. The reaction mixture was then stirred while being heated at reflux for 2 h at 110 °C. After addition of water (6 mL) and cooling to room temperature, the mixture was extracted with ether (3 × 8 mL). The combined organic solution was washed with water (6 mL), dried ($MgSO_4$), and concentrated. Purification by column chromatography on silica gel (10 g, hexanes) yielded **27a** (62.3 mg, 87%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.76 (t, J = 7.0, 6.5 Hz, 3H), 1.06 (m, 8H), 1.40−1.45 (m, 2H), 2.29−2.39 (m, 2H), 7.13 (d, J = 3.2 Hz, 1H), 7.26 (d, J = 3.3 Hz, 1H), 7.48−7.55 (m, 1H), 7.58−7.71 (m, 5H), 7.88 (dd, J = 7.7, 1.7 Hz, 1H), 8.74 (t, J = 7.2, 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.93, 22.51, 28.89, 29.14, 29.83, 31.62, 120.43, 122.61, 122.79, 124.11, 126.49, 126.55, 126.63, 126.78, 127.02, 128.14, 128.61, 130.25, 130.49, 131.64, 132.07, 133.91, 141.25, 143.22; MS m/z 358 (M^+, 100). Anal. Calcd for $C_{25}H_{26}S$: C, 83.75; H, 7.31. Found: C, 83.86; H, 7.51.

(b) 1,4-Bis(4′-heptylthien-3′-yl)benzene (27b) and 3-Heptyl-4-(4′-bromophenyl)thiophene (27c). These were prepared from boroxine **26a** (41.6 mg, 0.067 mmol) and 1,4-dibromobenzene (23.6 mg, 0.1 mmol) in the same manner as described for **27a**. Chromatography on silica gel (10 g, hexanes) afforded **27b** (9.0 mg, 21%) and **27c** (16.5 mg, 49%). **27b**: white solid; mp 44−45 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 6.9, 6.4 Hz, 6H), 1.24−1.25 (m, 16H), 1.53−1.59 (m, 4H), 2.65 (t, J = 8.0, 7.4 Hz, 4H), 7.05 (d, J = 3.3 Hz, 2H), 7.21 (d, J = 3.2 Hz, 2H), 7.39 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 14.04, 22.60, 29.04, 29.31, 29.36, 30.07, 31.74, 121.05, 122.96, 128.61, 136.05, 141.54, 142.72; MS m/z 438 (M^+, 100). Anal. Calcd for $C_{28}H_{38}S_2$: C, 76.65; H, 8.73. Found: C, 76.93; H, 8.52.

27c: oil; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 7.0, 6.4 Hz, 3H), 1.22 (m, 8H), 1.45−1.56 (m, 2H), 2.57 (dt, J = 0.5, 8.0, 7.4 Hz, 2H), 7.03 (dt, J = 3.3, 0.8, 0.8 Hz, 1H), 7.15 (d, J = 3.2 Hz, 1H), 7.20−7.55 (AA′BB′, J = 8.2, 4.5, 0.4 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.61, 29.01, 29.20, 29.32, 30.04, 31.74, 121.16, 121.35, 123.28, 130.40, 131.43, 136.35, 141.32, 141.76; MS m/z 336 (M^+, 22), 338 (M^+ + 2, 18). Anal. Calcd for $C_{17}H_{21}SBr$: C, 60.53; H, 6.27. Found: C, 60.10; H, 6.43.

(c) 1,3,5-Tris[(4′-heptylthien-3′-yl)methyl]benzene (27d). This was prepared from boroxine **26a** (62.4 mg, 0.1 mmol) and 1,3,5-tris(bromomethyl)benzene[76] (35.7 mg, 0.1 mmol) to afford **27d** (55.0 mg, 83%) as an oil: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.8, 6.4 Hz, 9H), 1.27 (m, 24H), 1.51−1.56 (m, 6H), 2.41 (t, J = 8.0, 7.3 Hz, 6H), 3.80 (s, 6H), 6.71 (d, J = 3.1 Hz, 3H), 6.84 (s, 3H), 6.90 (d, J = 3.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.65, 28.86, 29.17, 29.54, 31.83, 35.22, 120.41, 122.01, 127.26, 140.34, 140.40, 141.96; MS m/z 661 (M^+ + 1, 9). Anal. Calcd for $C_{42}H_{60}S_3$: C, 76.30; H, 9.15. Found: C, 76.33; H, 9.28.

(d) 4-Bromo-4′-heptyl-3,3′-bithiophene (27e) and 3-heptylthiophene (27f). These were prepared from boroxine **26a** (41.6 mg, 0.067 mmol) and 3,4-dibromothiophene (24.2 mg, 0.1 mmol) in the same manner as described for **27a**. Chromatography on silica gel (10 g, hexanes) afforded **27e** (23.5 mg, 69%) and **27f** (22.5 mg, 94%). **27e**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, J = 6.9, 6.4 Hz, 3H), 1.22−1.25 (m, 8H), 1.43−1.55 (m, 2H), 2.48 (t, J = 8.0, 7.4 Hz, 2H), 7.01 (d, J = 3.2 Hz, 1H), 7.16 (d, J = 3.4 Hz, 1H), 7.20 (d, J = 3.2 Hz, 1H), 7.32 (d, J = 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.61, 29.00, 29.12, 29.23, 29.77, 31.71, 112.90, 120.29, 123.00, 123.95, 124.99, 135.47, 137.52, 142.50; MS m/z 342 (M^+, 26), 344 (M^+ + 2, 23). Anal. Calcd for $C_{15}H_{19}S_2Br$: C, 52.47; H, 5.58. Found: C, 52.98; H, 5.71.

27f:[77] colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.9, 6.5 Hz, 3H), 1.28−1.35 (m, 8H), 1.54−1.64 (m, 2H), 2.62 (t, J = 7.9, 7.4 Hz, 2H), 6.90−6.94 (m, 2H), 7.23 (dd, J = 4.8, 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.64, 29.13, 29.29, 30.28, 30.56, 31.81, 119.72, 124.97, 128.26, 143.23; MS m/z 182 (M^+, 11). Anal. Calcd for $C_{11}H_{18}S$: C, 72.47; H, 9.95. Found: C, 72.68; H, 10.24.

(e) 4-(Trimethylsilyl)-4′-heptyl-3,3′-bithiophene (27g). This was prepared from boroxine **26a** (62.4 mg, 0.1 mmol) and 4-iodo-3-(trimethylsilyl)thiophene (**14**) (84.6 mg, 0.3 mmol) to afford **27g** (99.0 mg, 98%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9H), 0.86 (t, J = 7.0, 6.4 Hz, 3H), 1.22−1.30 (m, 8H), 1.46−1.51 (m, 2H), 2.34 (t, J = 8.1, 7.3 Hz, 2H), 6.97 (dt, J = 3.2, 0.8, 0.8 Hz, 1H), 7.08 (d, J = 3.2 Hz, 1H), 7.15 (d, J = 2.8 Hz, 1H), 7.47 (d, J = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.26, 14.01, 22.60, 29.04, 29.28, 29.38, 29.90, 31.73, 119.64, 123.72, 124.27, 132.54, 138.96, 142.10, 143.08; MS m/z 336 (M^+, 63). Anal. Calcd for $C_{18}H_{28}S_2Si$: C, 64.23; H, 8.38. Found: C, 64.10; H, 8.52.

(f) 3-Nonyl-4-[4′-(methoxycarbonyl)benzyl]thiophene (27h). This was prepared from boroxine **26b** (94.4 mg, 0.133 mmol) and methyl 4-(bromomethyl)benzoate (91.6 mg, 0.4 mmol) to afford **27h** (135.5 mg, 95%) as white crystals: mp 28−29 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.9, 6.3 Hz, 3H), 1.25 (m, 12H), 1.51−1.59 (m, 2H), 2.42 (t, J = 7.9, 7.5 Hz, 2H), 3.90 (s, 3H), 3.94 (s, 2H), 6.80 (d, J = 3.1 Hz, 1H), 6.94 (d, J = 3.1 Hz, 1H), 7.22−7.98 (ABq, J = 8.5 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.01, 22.64, 28.85, 29.28, 29.48, 29.60, 31.87, 35.32, 51.89, 120.88, 122.59, 128.31, 128.76, 129.79, 139.22, 141.97, 145.72, 167.04; MS m/z 358 (M^+, 26). Anal. Calcd for $C_{22}H_{30}O_2S$: C, 73.70; H, 8.43. Found: C, 73.62; H, 8.50.

(g) 3-Nonyl-4-(*trans*-2′-phenylvinyl)thiophene (27i). This was prepared from boroxine **26b** (47.2 mg, 0.067 mmol) and (*E*)-β-bromostyrene (36.6 mg, 0.2 mmol) to afford **27i** (31.4 mg, 50%) as white crystals: mp 36.5−37 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 6.9, 6.3 Hz, 3H), 1.27−1.41 (m, 12H), 1.56−1.70 (m, 2H), 2.67 (t, J = 8.0, 7.5 Hz, 2H), 6.94 (d, J = 3.1 Hz, 1H), 6.95 (d, J = 16.2 Hz, 1H), 7.05 (d, J = 16.2 Hz, 1H), 7.21−7.51 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.66, 29.30, 29.47, 29.56, 29.98, 31.89, 120.40, 120.87, 121.88, 126.37, 127.43, 128.67, 129.52, 137.78, 138.84, 141.78; MS m/z 312 (M^+, 100). Anal. Calcd for $C_{21}H_{28}S$: C, 80.71; H, 9.03. Found: C, 80.99; H, 9.07.

(h) 3-(Phenylethyl)-4-(2′-methylpropenyl)thiophene (27j). This was prepared from boroxine **26c** (128.4 mg, 0.2 mmol) and 1-bromo-2-methylpropene (81.0 mg, 0.6 mmol) to afford **27j** (131.0 mg, 90%) as an oil: ^{1}H NMR ($CDCl_3$) δ 1.83 (d, J = 1.2 Hz, 3H), 1.89 (d, J = 1.4 Hz, 3H), 2.81−2.94 (m, 4H), 6.03−6.05 (m, 1H), 6.89 (d, J = 3.2 Hz, 1H), 7.01 (d, J = 3.0 Hz, 1H), 7.16−7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.63, 26.37, 31.29, 36.24, 118.67, 119.98, 121.89, 125.93, 128.35, 128.44, 136.40, 138.60, 141.44, 141.99; MS m/z 242 (M^+, 74). Anal. Calcd for $C_{16}H_{18}S$: C, 79.29; H, 7.49. Found: C, 79.42; H, 7.57.

4,4′-Bis(phenylethyl)-3,3′-bithiophene (28). A mixture of **26c** (107 mg, 0.167 mmol), 9,10-bis(bromomethyl)phenanthrene[78] (182 mg, 0.5 mmol), and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) in methanol-toluene (1:1, 50 mL) was stirred for 5 min. After that, 2 M Na_2CO_3 solution (5 mL) was added, and the reaction mixture was further stirred and refluxed for 4 h. After addition of water (40 mL) and cooling to room temperature, the mixture was extracted with ether (3 × 30 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. Purification by silica gel chromatography (15 g, hexanes) yielded **28** (42 mg, 44%) as colorless crystals: mp 59−61 °C; ^{1}H NMR ($CDCl_3$) δ 2.70−2.76 (m, 8H), 7.01−7.06 (m, 8H), 7.15−7.26 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 31.26, 36.44, 120.81, 123.70, 125.88, 128.29, 128.34, 137.12, 141.46, 141.66; MS m/z 374 (M^+, 24). Anal. Calcd for $C_{24}H_{22}S_2$: C, 76.96; H, 5.92. Found: C, 76.87; H, 6.06.

4,4‴-Diheptyl-3,3′:4′,3″:4″,3‴-quaterthiophene (29) and 4-Heptyl-3,3′-bithiophene (30). To a solution of **27g** (454 mg, 1.35 mmol) in CH_2Cl_2 (120 mL) was added a solution of BCl_3 (1.0 M) in CH_2Cl_2 (3 mL) under a nitrogen atmosphere at −78 °C. Then the mixture was allowed to slowly warm to room temperature and stirred for 24 h. The reaction was quenched with 0.5M Na_2CO_3 solution (60 mL), and the mixture was extracted with ether (3 × 100 mL). The combined ethereal solution was dried ($MgSO_4$), and the solvent was evaporated. The residue was chromatographed on silica gel (25 g, hexanes−ether 1:1) to give the corresponding boroxine intermediate, which was reacted under self-coupling conditions as stated above to afford **29** (73 mg, 21%) and **30** (39 mg, 11%). **29**: colorless needle crystals; mp 62.5−64 °C; ^{1}H NMR ($CDCl_3$) δ

(76) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921−1923.

(77) This is a known compound. See: Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706−6714.

(78) Cheng, S. K. T.; Wong, H. N. C. *Synth. Commun.* **1990**, *20*, 3053−3061.

0.86 (t, J = 6.8, 5.6 Hz, 6H), 1.26−1.29 (m, 16H), 1.56−1.63 (m, 4H), 2.68 (t, J = 8.0, 7.5 Hz, 4H), 7.02 (d, J = 3.2 Hz, 2H), 7.12 (d, J = 1.3 Hz, 2H), 7.26 (d, J = 3.2 Hz, 2H), 7.27 (d, J = 0.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.12, 22.63, 29.10, 29.42, 29.55, 29.93, 31.77, 120.64, 121.15, 123.02, 124.91, 137.05, 138.11, 141.43; MS m/z 526 (M^+, 2). Anal. Calcd for $C_{30}H_{38}S_4$: C, 68.39; H, 7.27. Found: C, 68.44; H, 7.47.

30: colorless crystals; mp 36.5−37 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.9, 6.4 Hz, 3H), 1.25−1.27 (m, 8H), 1.55−1.60 (m, 2H), 2.65 (t, J = 8.2, 7.2 Hz, 2H), 7.01 (d, J = 3.2 Hz, 1H), 7.18 (dd, J = 5.0, 1.3 Hz, 1H), 7.22 (d, J = 3.4 Hz, 1H), 7.24 (dd, J = 3.0, 1.3 Hz, 1H), 7.35 (dd, J = 5.0, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.12, 22.62, 29.07, 29.42, 29.57, 29.84, 31.75, 120.96, 121.55, 122.74, 125.17, 128.22, 137.39, 141.52; MS m/z 264 (M^+, 61). Anal. Calcd for $C_{15}H_{20}S_2$: C, 68.13; H, 7.62. Found: C, 68.31; H, 7.46.

3-(Phenylethyl)-4-(tri-*n*-butylstannyl)thiophene (31). To a stirred solution of tri-*n*-butylstannyl chloride (1.3 g, 4 mmol) and $Pd(PPh_3)_4$ (231 mg, 0.2 mmol) in methanol−toluene (1:1, 80 mL) was added **26c** (428 mg, 0.67 mmol) and solid sodium methoxide (216 mg, 4 mmol) under nitrogen. The reaction mixture was refluxed for 24 h, cooled, and poured into ice−water (50 mL). The resulting mixture was extracted with ether (3 × 50 mL). The combined ethereal extract was dried over $MgSO_4$, and the solvent was removed. The residue was purified by flash column chromatography on silica gel (40 g, hexanes containing 1% Et_3N) to give **31** (595 mg, 62%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.2, 7.2 Hz, 9H), 1.07 (t, J = 8.0, 8.3 Hz, 6H), 1.32 (sextet, J = 7.1, 7.1, 7.1, 7.1, 7.1 Hz, 6H), 1.45−1.55 (m, 6H), 2.94−2.97 (m, 4H), 7.05 (d, J = 2.6 Hz, 1H), 7.24 (d, J = 2.6 Hz, 1H), 7.19−7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 10.20, 13.61, 27.31, 29.14, 33.88, 37.08, 120.16, 125.93, 128.36, 131.72, 140.02, 141.76, 147.67; MS (CI) m/z 421 ($M^+ - C_4H_9$, 100). Anal. Calcd for $C_{24}H_{38}SSn$: C, 60.39; H, 8.02. Found: C, 60.33; H, 8.16.

3-(Phenylethyl)thiophene (32).[79] Compound **31** (47.7 mg, 0.1 mmol) was destannylated by passing slowly through a silica gel column (20 g, hexanes) to give **32** (18.5 mg, 98%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.92−2.94 (m, 4H), 6.91−6.94 (m, 2H), 7.17−7.32 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 32.16, 36.92, 120.31, 125.23, 125.95, 128.35, 128.40, 141.70, 142.11; MS m/z 188 (M^+, 65). Anal. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42. Found: C, 76.73; H, 6.48.

3-(Phenylethyl)-4-(benzylcarbonyl)thiophene (33) and Bis[4-(phenylethyl)thien-3-yl]ketone (34). A mixture of **31** (143.0 mg, 0.3 mmol), benzyl bromide (51.3 mg, 0.3 mmol), and $Pd(PPh_3)_4$ (35.0 mg, 0.03 mmol) in THF (2 mL) was placed in a sealed tube (14 × 1.25 cm^2) under a carbon monoxide atmosphere and then pressurized to 25−30 psi. The mixture was stirred and heated at 50−60 °C for 2 days. The remaining carbon monoxide was released, and the mixture was diluted with ether (20 mL) and water (6 mL). The organic layer was separated, and the water layer was extracted with ether (2 × 6 mL). The combined organic layer was dried ($MgSO_4$) and evaporated. The residue was chromatographed on silica gel (15 g, hexanes−EtOAc 15:1) to give **33** (46.0 mg, 50%) and **34** (16.0 mg, 13%). **33**: colorless crystals; mp 57−58 °C; ^{1}H NMR ($CDCl_3$) δ 2.81−3.21 (AA′XX′, J = 7.3, 7.3 Hz, 4H), 4.17 (s, 2H), 6.83 (d, J = 3.1 Hz, 1H), 7.14−7.35 (m, 10H), 8.07 (d, J = 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 32.16, 36.27, 47.60, 122.83, 125.73, 126.85, 127.79, 128.16, 128.53, 128.63, 129.38, 134.71, 138.96, 141.79, 143.49, 193.10; MS m/z 306 (M^+, 6). Anal. Calcd for $C_{20}H_{18}OS$: C, 78.40; H, 5.92. Found: C, 77.92; H, 6.13.

34: colorless crystals; mp 69−71 °C; ^{1}H NMR ($CDCl_3$) δ 2.90−3.24 (AA′XX′, J = 7.3, 7.3 Hz, 8H), 6.95 (d, J = 3.1 Hz, 2H), 7.15−7.32 (m, 10H), 7.65 (d, J = 3.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 31.41, 36.63, 122.70, 125.82, 128.23, 128.52, 134.45, 140.97, 141.65, 143.05, 186.81; MS (CI) m/z 403 ($M^+ + 1$, 100). Anal. Calcd for $C_{25}H_{22}OS_2$: C, 74.59; H, 5.51. Found: C, 74.75; H, 5.49.

General Procedure for Preparation of 36a−c. (a) 3-(Phenylethyl)-4-(1′-hydroxy-1′-methylethyl)thiophene (36a). To a solution of **31** (286 mg, 0.6 mmol) in dry THF (5 mL) was added *n*-butyllithium (1.6 M in hexane, 0.8 mL, 1.28 mmol) at −78 °C under nitrogen. After the solution was stirred for 0.5 h, a mixture of acetone (0.3 mL, 4.2 mmol) and DMPU (0.12 mL) was added. After 1 h at −78 °C, it was warmed to room temperature and quenched with saturated aqueous ammonium chloride (5 mL). The resulting mixture was extracted with ether (3 × 15 mL), and the ethereal solution was dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography on silica gel (20 g, hexanes−EtOAc 7:1) to give **36a** (76 mg, 51%) as a colorless solids: mp 65−66 °C; ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 6H), 1.76 (br s, 1H), 2.94−3.17 (m, 4H), 7.00 (d, J = 3.3 Hz, 1H), 7.08 (d, J = 3.3 Hz, 1H), 7.16−7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 30.97, 31.56, 36.92, 71.71, 120.11, 122.54, 125.90, 128.34, 128.41, 140.90, 141.94, 147.90; MS m/z 246 (M^+, 1), 228 ($M^+ - H_2O$, 66). Anal. Calcd for $C_{15}H_{18}OS$: C, 73.13; H, 7.36. Found: C, 73.33; H, 7.63.

(b) 3-(Phenylethyl)-4-formylthiophene (36b). Reaction of **31** (286 mg, 0.6 mmol) in THF (5 mL) with *n*-butyllithium (0.8 mL, 1.28 mmol), followed by addition of DMF (0.12 mL, 1.6 mmol) and DMPU (0.12 mL), gave, after chromatography on silica gel (20 g, hexanes−EtOAc 10:1), **36b** (76.5 mg, 59%) as a white solid: mp 52−53 °C; ^{1}H NMR ($CDCl_3$) δ 2.88−3.24 (AA′XX′, J = 7.3, 7.3 Hz, 4H), 6.92 (dd, J = 3.0, 0.7 Hz, 1H), 7.16−7.31 (m, 5H), 8.08 (d, J = 3.2 Hz, 1H), 9.97 (d, J = 0.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 31.25, 36.31, 123.55, 125.94, 128.29, 128.50, 139.93, 140.28, 141.42, 141.75, 185.57; MS m/z 216 (M^+, 76). Anal. Calcd for $C_{13}H_{12}OS$: C, 72.19; H, 5.59. Found: C, 72.30; H, 5.42.

(c) 3-(Phenylethyl)-4-(phenylselenenyl)thiophene (36c). Reaction of **31** (143 mg, 0.3 mmol) in THF (2.5 mL) with *n*-butyllithium (0.2 mL, 0.32 mmol), followed by addition of phenylselenenyl bromide (70.8 mg, 0.3 mmol) and DMPU (0.06 mL), gave, after chromatography on silica gel (15 g, hexanes), **36c** (55.6 mg, 54%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.78−2.94 (m, 4H), 7.00 (d, J = 3.2 Hz, 1H), 7.08−7.28 (m, 10H), 7.48 (d, J = 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 31.98, 36.39, 121.78, 123.88, 125.91, 126.43, 128.29, 128.43, 129.22, 130.18, 131.36, 132.49, 141.54, 144.03; MS m/z 344 (M^+, 76). Anal. Calcd for $C_{18}H_{16}SSe$: C, 62.97; H, 4.70. Found: C, 63.16; H, 4.81.

Phenyl[4-(trimethylsilyl)thien-3-yl]iodonium Triflate (38).[80] To a stirred suspension of $PhI(OAc)_2$ (3.3 g, 10.2 mmol) in dry CH_2Cl_2 (50 mL) was added trifluoromethanesulfonic acid (1.8 mL, 20.3 mmol) slowly at 0 °C with a syringe. The mixture was stirred for 1 h at room temperature, during which time the mixture became a clear yellowish solution. The solution was then cooled to 0 °C, and 3,4-bis(trimethylsilyl)-thiophene (**1a**) (2.5 g, 11.0 mmol) in CH_2Cl_2 (25 mL) was added dropwise with a syringe. After addition, the reaction mixture was stirred at room temperature for 20 min. After evaporation of the solvent, Et_2O was added to crystallize the residue. The solids formed were filtered, washed with Et_2O, and dried *in vacuo* to yield **38** (2.7 g, 53%): mp 169−172 °C ($CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9H), 7.43 (t, J = 6.5, 6.5 Hz, 2H), 7.52 (dd, J = 6.7, 1.1 Hz, 1H), 7.55 (d, J = 2.9 Hz, 1H), 7.80 (d, J = 6.4 Hz, 2H), 8.51 (d, J = 2.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.41, 100.82, 115.19, 131.99, 132.27, 132.98, 137.09, 140.86, 144.14; MS (CI) m/z 359 (M^+ − OTf, 100). Anal. Calcd for $C_{14}H_{16}O_3S_2SiF_3I$: C, 33.08; H, 3.17. Found: C, 33.03; H, 2.90.

General Procedure for Trapping Reactions of 3,4-Didehydrothiophene (2). (a) 4,9-Dihydro-4,9-*o*-benzenonaphtho[2,3-*c*]thiophene (39a) and 4,11-Dihydro-4,11-ethenoanthra[2,3-*c*]thiophene (39b). To a mixture of **38** (254 mg, 0.5 mmol), 18-crown-6 (79 mg, 0.3 mmol), and anthracene (89 mg, 0.5 mmol) in dry CH_2Cl_2 (6 mL) under N_2 was added KF (87 mg, 1.5 mmol). The reaction mixture was stirred for 30 min at room temperature. The resulting precipitate was removed by filtration. The filtrate was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column (8 g, hexanes) to give a mixture of **39a** and **39b** (13 mg, 10%; **39a**:**39b** = 2.7:1 from ^{1}H NMR) as white solids: MS m/z 260 (M^+, 100); high-resolution MS

(79) This is a known compound. See: Gronowitz, S.; Stenhammar, K.; Svensson, L. *Heterocycles* **1981**, *15*, 947−959.

(80) Kitamura, T.; Matsuyuki, J.; Taniguchi, H. *Synthesis* **1994**, 147−148.

calcd for $C_{18}H_{12}S$ *m/z* 260.0654, found 260.0658. Anal. Calcd for $C_{18}H_{12}S$: C, 83.04; H, 4.65. Found: C, 82.94; H, 4.92.

Careful partial recrystallization of the above mixture of **39a** and **39b** from methanol provided a pure sample of **39a**: mp 267−268 °C (lit.[68] mp 268 °C); ^{1}H NMR ($CDCl_3$) δ 5.34 (s, 2H), 6.90 (s, 2H), 7.01−7.39 (AA′BB′, J = 5.3, 3.3 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ 50.15, 114.38, 123.72, 125.46, 145.22, 147.02; MS *m/z* 260 (M^+, 100).

39b: ^{1}H NMR ($CDCl_3$) δ 5.11(t, J = 3.3, 3.3 Hz, 2H), 6.84 (s, 2H), 7.01 (2H), 7.66 (s, 2H), 7.39−7.75 (AA′BB′, J = 6.2, 3.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 46.34, 113.57, 121.20, 125.60, 127.45, 131.72, 138.93, 142.65, 147.31.

(b) 4,9-Dihydro-4,9-ethenonaphtho[2,3-*c*]thiophene (40). This was prepared by the reaction of **38** (1.02 g, 2 mmol), naphthalene (256 mg, 2 mmol), 18-crown-6 (317 mg, 1.2 mmol), and KF (348 mg, 6 mmol) in CH_2Cl_2 (20 mL), yielding **40** (26 mg, 6%) as colorless crystals: mp 151−153 °C; ^{1}H NMR ($CDCl_3$) δ 4.98 (dd, J = 4.1, 3.1 Hz, 2H), 6.74 (s, 2H), 6.98 (dd, J = 4.3, 2.9 Hz, 2H), 6.97−7.27 (AA′BB′, J = 5.2, 3.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 46.65, 113.00, 123.20, 124.84, 139.44, 145.87, 148.22; MS *m/z* 210 (M^+, 78). Anal. Calcd for $C_{14}H_{10}S$: C, 79.96; H, 4.79. Found: C, 79.69; H, 4.63.

(c) Thieno[*c*]bicyclo[2.2.2]octatriene (41). This was prepared by the reaction of **38** (1.02 g, 2 mmol), benzene (8 mL), 18-crown-6 (317 mg, 1.2 mmol), and KF (348 mg, 6 mmol) in CH_2Cl_2 (20 mL), yielding **41** (21 mg, 7%) as colorless crystals: mp 65−66 °C; ^{1}H NMR ($CDCl_3$) δ 4.69 (tt, J = 4.0, 4.0, 3.3, 3.3 Hz, 2H), 6.58 (s, 2H), 6.87 (dd, J = 4.0, 3.3 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 43.94, 111.16, 139.40, 149.84; MS *m/z* 160 (M^+, 100). Anal. Calcd for $C_{10}H_8S$: C, 74.96; H, 5.03. Found: C, 74.91; H, 4.98.

(d) 3-Methyl-3-(1′-methylvinyl)cyclobuteno[*c*]thiophene (42a) and 2-Methyl-3-(3′-thienylmethyl)-1,3-butadiene (42b). These were prepared by the reaction of **38** (254 mg, 0.5 mmol), 2,3-dimethyl-1,3-butadiene (1.5 mL), 18-crown-6 (79 mg, 0.3 mmol), and KF (87 mg, 1.5 mmol) in CH_2Cl_2 (5 mL). Chromatography on silica gel (8 g, *n*-pentane) gave a mixture of **42a** and **42b** (22 mg, 27%; **42a**:**42b** = 1:1 from ^{1}H NMR). Careful chromatography on silica gel (*n*-pentane as eluent) provided pure **42a** and **42b**.

42a: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 3H), 1.83 (s, 3H), 2.66 and 3.09 (ABq, J = 13.8 Hz, 2H), 4.79 (s, 1H), 4.88 (s, 1H), 6.85 (s, 1H), 6.89 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 19.16, 25.45, 40.13, 52.19, 109.96, 113.94, 115.59, 138.19, 148.35, 149.84; MS *m/z* 164 (M^+, 18); high-resolution MS calcd for $C_{10}H_{12}S$ *m/z* 164.0654, found 164.0615.

42b: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 3H), 3.62 (s, 2H), 4.95 (s, 1H), 4.99 (s, 1H), 5.11 (s, 1H), 5.23 (s, 1H), 6.91−6.95 (m, 2H), 7.22−7.25 (dd, J = 5.1, 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.07, 34.83, 113.48, 114.18, 121.00, 125.02, 128.52, 140.73, 142.38, 146.49; MS *m/z* 164 (M^+, 27); high-resolution MS calcd for $C_{10}H_{12}S$ *m/z* 164.0654, found 164.0662.

(e) 3-Cyanocyclobuteno[*c*]thiophene (43). This was prepared by the reaction of **38** (1.02 g, 2 mmol), acrylonitrile (10 mL), 18-crown-6 (317 mg, 1.2 mmol), and KF (348 mg, 6 mmol) in CH_2Cl_2 (20 mL). Chromatography on silica gel (20 g, hexanes-EtOAc 5:1) yielded **43** (34 mg, 13%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 3.42−3.50 (ddd, J = 14.0, 3.6, 1.0 Hz, 1H), 3.56−3.64 (ddd, J = 14.0, 6.0, 1.0 Hz, 1H), 4.11−4.15 (ddd, J = 6.0, 3.6, 1.0 Hz, 1H), 6.94−6.96 (dt, J = 1.2, 1.0, 1.0 Hz, 1H), 7.11−7.13 (dd, J = 1.2, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.60, 34.10, 116.98, 117.49, 118.93, 134.37, 138.11; MS *m/z* 135 (M^+, 100). Anal. Calcd for C_7H_5NS: C, 62.19; H, 3.73; N, 10.36. Found: C, 62.18; H, 3.58; N, 10.33.

(f) 7-Oxabicyclo[2.2.1]hept-5-eno-2,3-[*c*]thiophene (44a). This was prepared by the reaction of **38** (254 mg, 0.5 mmol), furan (1 mL), 18-crown-6 (79 mg, 0.3 mmol), and KF (87 mg, 1.5 mmol) in CH_2Cl_2 (5 mL). Chromatography on silica gel (8 g, hexanes−EtOAc 6:1) gave **44a** (23 mg, 31%) as colorless crystals: mp 70−72 °C; ^{1}H NMR ($CDCl_3$) δ 5.55 (t, J = 0.9, 0.9 Hz, 2H), 6.73 (s, 2H), 6.92 (t, J = 0.9, 0.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 79.77, 112.08, 141.34, 151.38; MS *m/z* 150 (M^+, 32). Anal. Calcd for C_8H_6OS: C, 63.98; H, 4.03. Found: C, 64.15; H, 4.14.

(g) 1-Methyl-7-oxabicyclo[2.2.1]hept-5-eno-2,3-[*c*]thiophene (44b). This was prepared by the reaction of **38** (508 mg, 1 mmol), 2-methylfuran (3 mL), 18-crown-6 (159 mg, 0.6 mmol), and KF (174 mg, 3 mmol) in CH_2Cl_2 (10 mL). Chromatography on silica gel (10 g, hexanes−EtOAc 5:1) gave **44b** (27.5 mg, 17%) as an oil: ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 3H), 5.47 (d, J = 1.7 Hz, 1H), 6.64 (dd, J = 1.8, 0.7 Hz, 1H), 6.69 (d, J = 1.8 Hz, 1H), 6.71 (d, J = 5.5 Hz, 1H), 6.92 (dd, J = 5.5, 1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.77, 79.64, 87.82, 111.10, 111.93, 142.35, 144.30, 153.19, 154.48; MS *m/z* 164 (M^+, 36). Anal. Calcd for C_9H_8OS: C, 65.82; H, 4.91. Found: C, 65.63; H, 4.90.

(h) 1,4-Dimethyl-7-oxabicyclo[2.2.1]hept-5-eno-2,3-[*c*]-thiophene (44c). This was prepared by the reaction of **38** (254 mg, 0.5 mmol), 2,5-dimethylfuran (1 mL), 18-crown-6 (79 mg, 0.3 mmol), and KF (87 mg, 1.5 mmol) in CH_2Cl_2 (5 mL). Chromatography on silica gel (8 g, hexanes−EtOAc 6:1) gave **44c** (11.5 mg, 13%) as an oil: ^{1}H NMR ($CDCl_3$) δ 1.82 (s, 6H), 6.61 (s, 2H), 6.72 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 15.93, 87.56, 111.01, 145.31, 156.25; MS *m/z* 178 (M^+, 11). Anal. Calcd for $C_{10}H_{10}OS$: C, 67.38; H, 5.65. Found: C, 66.93; H, 5.76.

(i) 4-(3′-Thienoxy)butanol (46). This was prepared by the reaction of **38** (508 mg, 1 mmol) and tetrabutylammonium fluoride (1.0 M solution in THF, water content ∼5 wt %, 1.8 mL) in CH_2Cl_2 (10 mL). Chromatography on silica gel (10 g, hexanes−EtOAc 3:1) gave **46** (10.0 mg, 6%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.66 (br. s, 1H), 1.69−1.78 (m, 2H), 1.79−1.91 (m, 2H), 3.72 (t, J = 6.3, 6.1 Hz, 2H), 3.99 (t, J = 6.1, 6.0 Hz, 2H), 6.24 (dd, J = 3.2, 1.5 Hz, 1H), 6.74 (dd, J = 5.2, 1.5 Hz, 1H), 7.17 (dd, J = 5.2, 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.83, 29.51, 62.54, 70.07, 97.48, 119.43, 124.58, 157.84; MS *m/z* 172 (M^+, 9); high-resolution MS calcd for $C_8H_{12}O_2S$ *m/z* 172.0559, found 172.0557.

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Supporting Information Available: Listing of ^{1}H- and ^{13}C-NMR spectra for compounds prepared (72 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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