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Synthesis of Polysubstituted Benzothiophenes and Sulfur-Containing Polycyclic Aromatic Compounds via Samarium Diiodide Promoted Three-Component Coupling Reactions of Thiophene-2-carboxylate

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By the promotion of samarium diiodide, thiophene-2-carboxylate reacted with 2 equiv of ketones at the C-4 and C-5 positions to give diols such as **2** and **9**. Because the intermediary organosamarium species were oxophilic but not too basic, the double hydroxyalkylations with various ketone substrates, including alkyl aryl ketones, acetylthiophenes, cyclohexanone, α-tetralone, and α-phenylacetophenones, were realized without complication of side reactions. The diol products underwent an acid-catalyzed dehydration to give dienes such as **3** and **10**, which were treated with DDQ to give either polysubstituted thiophenes (e.g., **4** and **11**) or benzothiophenes (e.g., **5**, **13**, and **14**) depending on the reaction conditions. Oxidative annulations of 4,5-diarylthiophenes **11** and 4,5,6,7-tetraphenylbenzothiophenes **14** were carried out by photochemical or chemical methods to give the sulfur-containing polycyclic aromatic compounds, such as phenanthro[9,10-*b*]thiophene-2-carboxylate, piceno[13,14-*b*]thiophene-2-carboxylate, and tribenzo[*fg*,*ij*,*rst*]pentapheno[15,16-*b*]-thiophene-2-carboxylates. This method is applicable to the preparation of polysubstituted thiophenes, benzothiophenes, and the related compounds possessing liquid crystalline, photochromic, and other functional properties.

Introduction

Benzothiophenes and their related sulfur-containing polycyclic aromatic derivatives are of interest in many aspects.[1−3] A recent review[1c] evokes the aromaticity[1a] of these sulfur-containing compounds, reminiscent of polycyclic aromatic hydrocarbons (PAHs),[1b] according to the theoretical approach and experimental measurements. The polycyclic aromatic compounds provide the planar structure suitable to DNA intercalation. Phenanthro[*c*]-thiophenes with appropriate substituents have been shown to intercalate with calf thymus DNA specifically at the sites of A−T sequence.[2] Thiophenes and their polycyclic aromatic derivatives also exhibit remarkable electrochemical,[3a,b] optical,[3c] physical,[3d] and biological[3e,f] properties that render their applications in material and pharmaceutical sciences.

Benzothiophenes and the sulfur-containing polycyclic aromatic derivatives are generally prepared by two approaches,[4] either via construction of a thiophene ring onto an aromatic moiety[5] or via annulation of an aromatic ring onto a thiophene moiety.[6] The first approach can be exemplified by the acid-catalyzed cyclization of dimethoxyethyl phenyl sulfide to give benzothiophene.[5a,b] Condensation of 9-chlorophrenthrene-10-carboxaldehyde with mercaptoacetic acid affords phenanthro[9,10-*b*]thiophene.[5c] The reaction of cinnamic acid with thionyl chloride gives 3-chlorobenzothiophene-2-carboxyl chloride.[5d−f] The zirconocene complexes of benzyne generated from bromobenzenes are trapped by alkynes and sulfur dichloride to furnish the skeleton of benzothiophenes.[5g] Alternatively, the Lewis acid promoted Friedel−Crafts cyclization of 4-thienylalkenoic acid derivatives serves as an instance of the second approach for benzothiophene synthesis.[6a,b] The oxidative photocyclization of hexatriene systems (e.g., 1-phenyl-2-thienylethene and the related

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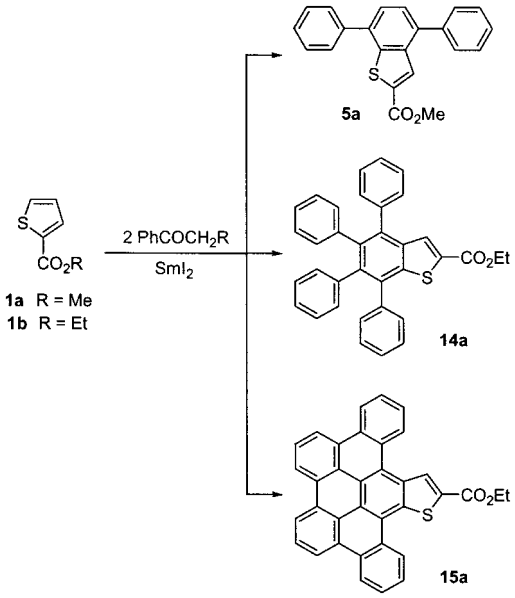
SCHEME 1. SmI_2-Promoted Three-Component Coupling Reaction as the Key Step for the Transformation of Thiophene-2-carboxylates 1a,b into Thieno-*p*-terphenyl 5a, Tetraphenylbenzothiophene 14a, and Sulfur-Containing Polycyclic Aromatic Compound 15a

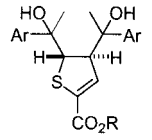


polycyclic analogues) provides a versatile method for aromatic annulation.[6c−e] The Michael reaction of 2-(sulfonylmethyl)thiophene-2-carboxaldehyde also affords a series of polysubstituted benzothiophenes.[6f] Benzothiophenes have been obtained by the Diels−Alder reactions of 2-vinylthiophenes[6g] and thiophene-2,3-quinodimethane equivalents[7] generated from thienoisofurans[6h] and thienopyranones.[6i] In one case,[6j] the copper-mediated coupling of 2,3,4,5-tetraethylzirconacyclopentadiene with 2-iodo-3-bromothiophene gives 4,5,6,7-tetraethylbenzo[*b*]thiophene in 32% yield. A palladium-catalyzed method for multiple arylation of thiophenes has recently been explored.[6k]

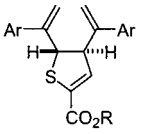
In addition to the above-mentioned elegant methods, we have devised an SmI_2-promoted coupling reaction[8] of thiophene-2-carboxylate in a one-pot procedure to introduce two substituents to the C-4 and C-5 positions.[9] SmI_2 promoted the double electrophilic reactions of thiophene-2-carboxylate with a variety of ketones, including phenyl methyl ketones, cyclic ketones, and even the enolizable ketones (e.g., α-phenylacetophenones). By comparison, metalations[10a] of thiophene-2-carboxylates and thiophene-2-carbamides can only introduce substituents to their C-3 or C-5 positions. Friedel−Crafts reactions of methyl thiophene-2-carboxylate with paraformaldehyde in the presence of $ZnCl_2$ give a mixture of 4-chlromethyl-, 5-chloromethyl-, and 4,5-bis(chloromethyl)thiophene-2-carboxylates in 19%, 38%, and 15% yields, respectively.[10b] Using the SmI_2-promoted coupling reaction appears to be a favorable and direct method for modification of thiophene-2-carboxylate at the C-4 and C-5 positions. We outlined in Scheme 1 an expedient synthesis of several specifically substituted benzothiophenes (e.g., thieno-*p*-terphenyl **5a** and 4,5,6,7-tetraphenylbenzothiophene **14a**) as well as the sulfur-containing polycyclic aromatics (e.g., **15a**), which are not easily obtained by other methods.

Results and Discussion

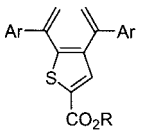
The SmI_2-promoted three-component coupling reactions of methyl thiophene-2-carboxylate (**1a**) with 2 equiv of acetophenones afforded diols **2a**−**n** in 60−67% yields (Table 1). The reaction was likely initiated by a hydroxyalkylation at the C-5 position of the thienyl ring (Scheme 2). The samarium dienolate intermediate **A** was readily trapped by the second ketone electrophile in a regio- and stereoselective manner. This one-pot procedure thus introduced two substituents to the C-4 and C-5 positions of the dihydrothiophene-2-carboxylate.



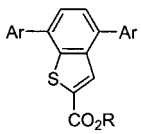
2a–e, g



3a–k

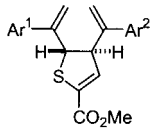


4a–e, g–k

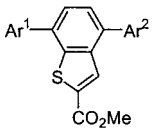


5a–e, g–k

compound	R =	Ar =
a series:	Me	C_6H_5
b series:	Me	4-ClC_6H_4
c series:	Me	4-MeC_6H_4
d series:	Me	4-$MeOC_6H_4$
e series:	Et	2-naphthyl
g series:	Me	4-$C_{17}H_{35}COOC_6H_4$
h series:	Et	4-$C_{10}H_{21}OC_6H_4COOC_6H_4$
i series:	Et	4-$C_{12}H_{25}OC_6H_4COOC_6H_4$
j series:	Et	4-$C_{14}H_{29}OC_6H_4COOC_6H_4$
k series:	Et	4-$C_{16}H_{33}OC_6H_4COOC_6H_4$



3f Ar^1 = 4-ClC_6H_4, Ar^2 = 4-$MeOC_6H_4$



5f

Even though each diol (**2a**−**d**) had four asymmetric carbon centers, the diol product usually existed as a mixture of two diastereomers. The diastereomers were separated by silica gel column chromatography. Both

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TABLE 1. Synthesis of 4,7-Diarylbenzothiophenes: (i) Coupling Reactions of Thiophene-2-carboxylate with Aryl Methyl Ketones[a] Giving Diols 2, (ii) Dehydration[b] Giving Dienes 3, and (iii) DDQ Oxidation[c] Giving Trienes 4 or Benzothiophenes 5

thiophene	ArCOMe, Ar =	diol (yield, %)	diene (yield, %)	triene (yield, %)	benzothiophene (yield, %)
1a	C_6H_5	**2a** (61)[d]	**3a** (90)		**5a** (90)[e]
1a	4-ClC_6H_4	**2b** (62)[d]	**3b** (97)	**4b** (89)[f]	**5b** (91)[e]
1a	4-MeC_6H_4	**2c** (60)[d]	**3c** (98)		**5c** (89)[e]
1a	4-$MeOC_6H_4$	**2d** (67)[d]	**3d** (95)		**5d** (72)[e]
1b	2-naphthyl	**2e** (50)	**3e** (92)	**4e** (82)	**5e** (84)[g]
1a[h]	4-ClC_6H_4/4-$MeOC_6H_4$				**5f** (43)[h]
1a	4-$C_{17}H_{35}COOC_6H_4$		**3g** (48)[i]		**5g** (89)[e]
1b	4-(4-$C_{10}H_{21}OC_6H_4COO$)C_6H_4		**3h** (46)[i]	**4h** (67)	**5h** (81)[g]
1b	4-(4-$C_{12}H_{25}OC_6H_4COO$)C_6H_4		**3i** (43)[i]	**4i** (78)	**5i** (75)[g]
1b	4-(4-$C_{14}H_{29}OC_6H_4COO$)C_6H_4		**3j** (38)[i]	**4j** (72)	**5j** (71)[g]
1b	4-(4-$C_{16}H_{33}OC_6H_4COO$)C_6H_4		**3k** (40)[i]	**4k** (70)	**5k** (68)[g]
1a	2-thienyl				**7a** (38)[j]
1a	5-Br-2-thienyl				**7b** (35)[j]
1a	3-Me-2-thienyl				**7c** (36)[j]
1a	3-thienyl				**8** (42)[j]

[a] Thiophene-2-carboxylate (**1a** or **1b**) and 2 equiv of aryl methyl ketone in THF/HMPA was treated with SmI_2 at 0−25 °C for 1−2 h. [b] The dehydration was achieved by the catalysis of *p*-TsOH in refluxing benzene. [c] The reaction with 1.2 equiv of DDQ at 60 °C gave trienes **4**, whereas the reaction with 2.2 equiv of DDQ in refluxing toluene gave benzothiophenes **5**. [d] A mixture of diastereomers. [e] The product was obtained by DDQ oxidation of dienes **3**, and the yield was calculated on the basis of dienes **3**. [f] Accompanied by 5% of **5b**. [g] The product was obtained by DDQ oxidation of trienes **4**. [h] The SmI_2-promoted coupling reaction of **1a** with 1 equiv of 4-chloroacetylphenone and then with 1 equiv of 4-methoxyacetylphenone. [i] The overall yield of two steps from **1b**. [j] The overall yield of three steps from **1a**.

diastereomers showed relatively small coupling constants (~3 Hz) for H-4 and H-5, indicating their trans orientations. The trans configuration could be established by an attack of the second electrophile on the less hindered face of the dienolate intermediate. Although the stereochemistry of diols **2a**−**d** was not rigorously determined, the more polar isomers consistently exhibited the H-5 signals at the lower fields than the less polar isomers ($\Delta\delta_H \approx$ 0.2 ppm). Under the reaction conditions (SmI_2/HMPA/THF, 25 °C, 2−10 h), the chlorophenyl groups in **2b** were not reduced. No apparent pinacolic coupling reactions of acetophenones were found to interfere with the SmI_2-promoted three-component coupling reactions. By a similar procedure, diol **2e** was prepared in 50% yield by coupling of ethyl thiophene-2-carboxylate (**1b**) with 2 equiv of 2-acetylnaphthalene.

On treatment with a catalytic amount of *p*-TsOH in refluxing benzene, diols **2a**−**e** underwent dehydrations to yield dienes **3a**−**e** with terminal double bonds. Dienes **3a**−**e** retained the 4,5-trans configuration. The characteristic C-5 protons appeared at lower fields ($\delta_H \approx 6.5$) as doublets with small coupling constants (~3 Hz). When dienes **3a**−**c** were treated with excess amounts of DDQ (2.2 equiv) in refluxing toluene for 7−18 h, the corresponding 4,7-diphenylbenzophenone-2-carboxylates **5a**−**c** were obtained as the exclusive products in high yields (~90%). As benzothiophenes **5a**−**c** were formed, the H-3 signals were shifted downfield ($\delta_H \approx 8.2$). The yield of **5d** (Ar = *p*-$MeOC_6H_5$) was somewhat lower (72%), presumably because the anisole moieties partly decomposed on DDQ oxidation.[11] Under mild reaction conditions, diene **3b** reacted with 1 equiv of DDQ at 60 °C in benzene to give the primary dehydrogenation product **4b** in 89% yield. Besides the quantity of DDQ, the reaction temperature was another key factor to manipulate the formation of triene **4b** or benzothiophene **5b**. The amount of **5b** increased (~15%) at an elevated reaction temperature (>70 °C), even utilizing only 1 equiv of DDQ. The similar phenomena were observed in the DDQ oxidation of **3e** (Ar = naphthyl). At an elevated temperature, electrocyclization[12a] of triene **4b** (or **4e**) might occur to give the intermediate **B**. Dehydrogenation of the intermediate could be effected by DDQ to afford benzothiophene **5b** (or **5e**). Indeed, the intermediate **B** generated from electrocyclization of **4e** exhibited the nature of *o*-thiophenequinodimethane,[7a] which was successfully trapped by a dienophile of *N*-phenylmaleimide to give the [4 + 2] cycloaddition product **6** (Scheme 2). The cycloaddition was consistent with a concerted mechanism to give adduct **6** in the endo configuration. The NOESY correlation of H-4a/H-7a (δ 4.34−4.33, m) with the ethylene-bridge protons (δ 2.15−2.11, m) supported the stereochemical assignment. Electrocyclization of triene **4e** was also achieved by irradiation with 300-nm light, and the cyclohexadiene intermediate **B** could be oxidized to **5e** in the presence of oxygen.[12a]

A photochromic system between the colorless trienes **4l**−**n** and their corresponding closed-ring species of yellow color was devised (Scheme 3).[12b] Trienes **4l**−**n** were similarly prepared from the SmI_2-promoted coupling reactions of **1b** with isobutyronaphthone, isobutyrophenone, and 4-methoxyisobutyrophenone, followed by acid-catalyzed dehydration and DDQ dehydrogenation. Unlike **4e**, trienes **4l**−**n** carried four methyl substituents to prevent their closed-ring isomers from oxidative aroma-

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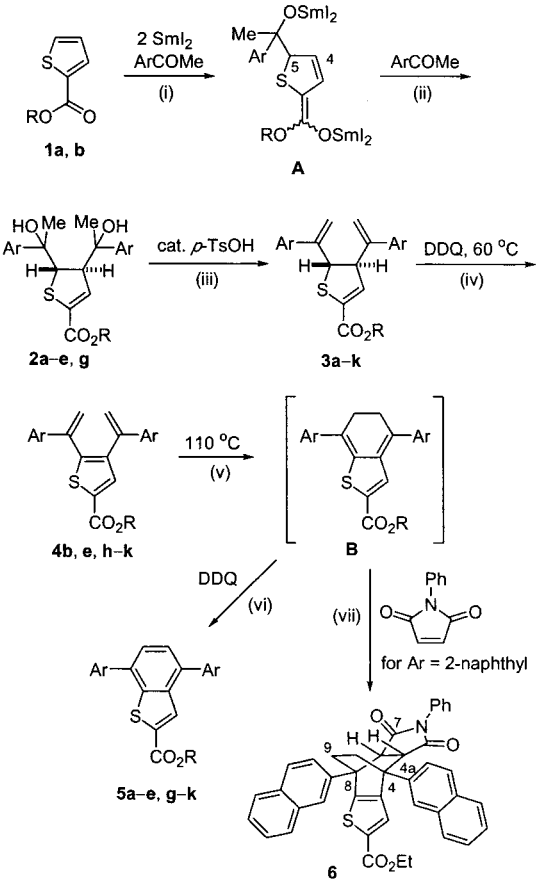
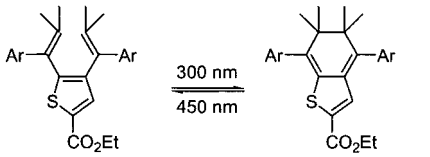
SCHEME 2. Reaction Pathways: (i) SmI_2-Promoted Coupling Reaction, (ii) Hydroxyalkylation of Dienolate Intermediate, (iii) Dehydration, (iv) Dehydrogenation, (v) Electrocylization, (vi) Oxidative Aromatization, and (vii) Trapping of the Proposed *o*-Thiophenequinodimethane Intermediate B by a Dienophile



SCHEME 3. Electrocyclization of Trienes 4l−n upon Irradiation with 300-nm Light in CH_3CN Solution To Give the Corresponding Closed-Ring Species with Absorption λ_{Max} ~425 nm[a]

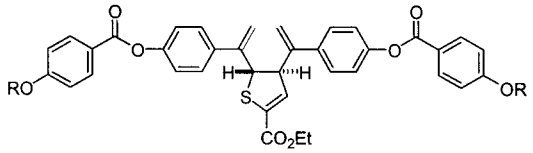


[a] The Interconversion between 4l−n and their corresponding closed-ring species constitutes an interesting photochromic system.

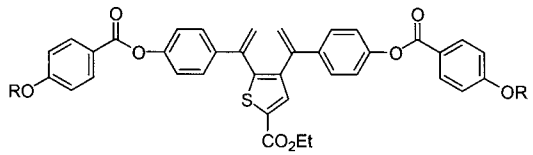
tization. The closed-ring isomers **C**−**E** returned to the open-ring isomers **4l**−**n** on irradiation with 450-nm light.[12b]

Diol **2f** bearing two different aryl substituents was prepared by treatment of thiophene-2-carboxylate **1a** consecutively with 1 equiv of 4-chloroacetophenone (stirring for 2 h at 25 °C) and 4-methoxyacetophenone. The acid-catalyzed dehydration of diol **2f** gave diene **3f**, which was treated with 2.2 equiv of DDQ in refluxing toluene to afford benzothiophene **5f** in 43% overall yield. Our present three-step procedure, via the coupling reaction of thiophenecarboxylate with ketones, acid-catalyzed dehydration and DDQ, oxidative cyclization, is thus applicable to the synthesis of various thieno-*p*-terphenyls[13] **5a**−**k** having the same or different aryl groups. Similar to common terphenyl compounds, the phenyl rings are not coplanar with the benzothiophene ring in these thieno-*p*-terphenyls. The crystal structure of **5c** showed that two tolyl rings had the dihedral angles of 54° and 133°, respectively, against the central benzothiophene ring (see the Supporting Information).

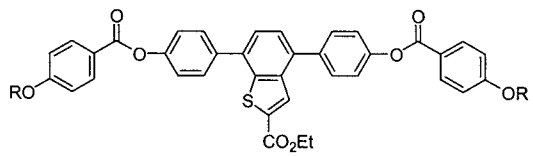
By a similar procedure, dienes **3g**−**k**, trienes **4g**−**k**, and benzothiophenes **5g**−**k** bearing long-chain substituents were prepared. These compounds could be considered to have a pseudo-C_2 symmetry dissected by the carboxylate group. Among them, dienes **3h**−**j** and trienes **4h**−**k** possess the liquid−crystalline properties[14] of smectic-A type. The phase transition temperatures occur in the ranges of 67−47 °C for **3h**−**j** and 72−52 °C for **4h**−**k**. Thieno-*p*-terphenyls **5h**−**k** exist as solids with rather high melting points (197−185 °C), even though they are equipped with soft long chains of decoxy, dodecoxy, tetradecoxy, and hexadecoxy groups. By comparison with the thienyl rings in **3h**−**j** and **4h**−**k**, the rigid core of benzothiophene is longer to disfavor the liquid−crystalline property.



3h, R = $C_{10}H_{21}$, K 67.3 °C, mp 112.0 °C.
3i, R = $C_{12}H_{25}$, K 55.4 °C, mp 97.5 °C.
3j, R = $C_{14}H_{29}$, K 47.4 °C, mp 83.2 °C.
3k, R = $C_{16}H_{33}$, mp 40 °C.



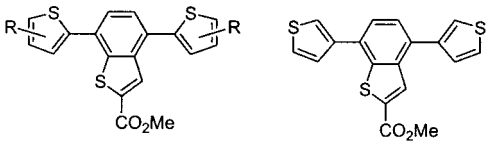
4h, R = $C_{10}H_{21}$, K 72.3 °C, mp 119.2 °C.
4i, R = $C_{12}H_{25}$, K 59.8 °C, mp 109.5 °C.
4j, R = $C_{14}H_{29}$, K 52.5 °C, mp 100.3 °C.
4k, R = $C_{16}H_{33}$, K 67.0 °C, mp 99.8 °C.



5h, R = $C_{10}H_{21}$, mp 195.6 °C.
5i, R = $C_{12}H_{25}$, mp 187.5 °C.
5j, R = $C_{14}H_{29}$, mp 184.7 °C.
5k, R = $C_{16}H_{33}$, mp 188.5 °C.

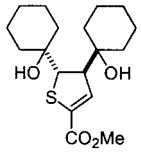
Benzothiophenes bearing two thienyl substituents at the C-4 and C-7 positions, e.g., **7a**−**c** and **8**, were also prepared by using appropriate acetylthiophenes as the starting materials for the similar three-step reaction

sequence. Compound **7b** having bromine atoms on the thienyl rings is especially versatile because it can be elaborated by coupling with arenes, heterocyclic arenes, alkenes, and alkynes, e.g., via Heck, Stille, Suzuki and Sonogashira reactions,[15] to construct various useful conjugated systems, including the oligo- and polymeric derivatives of **7b**.

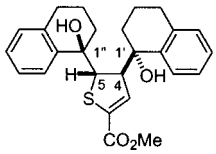


7a R = H
7b R = 5-Br
7c R = 3-Me

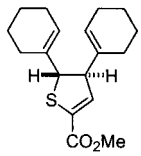
8



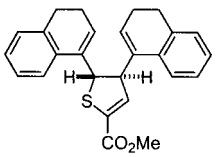
9a (91%)



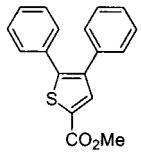
9b (68%)



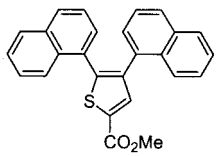
10a (88%)



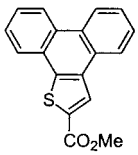
10b (97%)



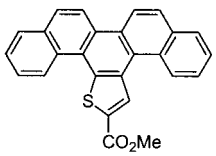
11a (89%)



11b (94%)

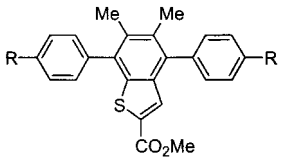


12a (86%)



12b (89%)

By the promotion of SmI_2, **1a** reacted with 2 equiv of cyclohexanone to give diol **9a** in 91% yield. The trans configuration of **9a** was confirmed by its crystal structure, and the two hydroxyl groups were shown to have the axial orientations. As lanthanoid ion (e.g., Sm^{3+}) is oxophilic and less basic than alkali and alkaline metal ions,[16] additions of organosamarium species (e.g., the samarium dienolate **A**) to the enolizable ketones (e.g., α-tetralone and α-phenylacetophenones) were realized. The SmI_2-promoted reaction of **1a** with tetralone gave diol **9b** as a single isomer. Its relative configuration was determined to be (4*R**,5*S**,1′*S**,1″*R*) by X-ray analysis. The acid-catalyzed dehydration of **9a** and **9b** gave the corresponding dienes **10a** and **10b**. Treatment of **10a** with excess amounts (6.5 equiv) of DDQ in refluxing xylene gave diphenylthiophene **11a** (89% yield), instead of the cyclization compound **12a**. Phenanthrothiophene **12a**[5b] was finally obtained by irradiation (300-nm light) of **11a** in the presence of iodine.[6c,d,h,17] By a similar procedure, dehydrogenation of **10b** with DDQ (4.5 equiv) in refluxing toluene gave dinaphthylthiophene **11b** (94% yield), and the subsequent photochemical reaction (300-nm light, 1 equiv I_2) gave picenothiophene **12b** (89% yield).



13a, R = H (42% for 3 steps)
13b, R = OMe (23% for 3 steps)

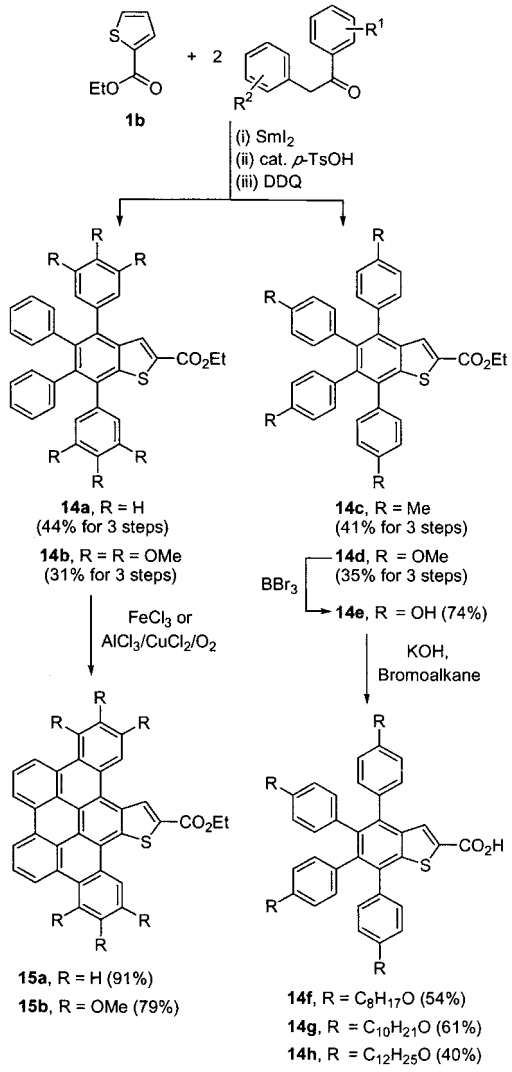
A variety of 4,5,6,7-tetrasubstituted benzothiophenes such as **13a**,**b** and **14a**−**c** were also synthesized via the following three-step reaction sequence: (i) using propiophenones or α-phenylacetophenones to couple with thiophene-2-carboxylate, (ii) using *p*-TsOH to catalyze dehydration, and (iii) using excess DDQ to mediate the consecutive processes of dehydrogenation, electrocyclization, and oxidative aromatization. In the case of **13a**, a photochemical oxidative aromatization was also applied. Tetraphenylbenzothiophenes **14a** and **14b** underwent the oxidative annulations by treatment with $AlCl_3/CuCl_2/O_2$[18a,b] or $FeCl_3$,[18c] giving tribenzopentaphenothiophenes **15a** and **15b** in 91% and 79% yields.

Tetraanisole **14d** was demethylated by BBr_3 to give tetraphenol **14e** in 74% yield. Alkylation of **14e** with 1-bromooctane, 1-bromodecane, and 1-bromododecane gave acids **14f**−**h** because of the concurrent saponification in the presence of KOH (Scheme 4). The long alkyl chains were introduced to the radial-type benzothiophenes as these acids might form dimeric assembly via hydrogen bondings to render a discotic liquid−crystalline property.[19] However, acids **14f**−**h** turn out to be crystalline compounds. None of them exhibit the desired liquid crystal properties.

In summary, we have developed a three-step procedure for the preparation of polysubstituted benzothiophenes (e.g., **5a**−**k**, **7a**−**c**, **13a**,**b**, and **14a**−**d**) and the related sulfur-containing polycyclic aromatic compounds (e.g., **12a**,**b** and **15a**,**b**). By the promotion of SmI_2, thiophene-2-carboxylate underwent a double-electrophilic reaction

(13) Schoning, A.; Debaerdemaeker, T.; Zander, M.; Friedrichsen, W. *Chem. Ber.* **1989**, *122*, 1119.
(14) (a) Miyake, S.; Kusabayashi, S.; Takenaka, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2404. (b) Brown, J. W.; Byron, D. J.; Harwood: D. J.; Wilson, R. C.; Tajbakhsh, A. R. *Mol. Cryst. Liq. Cryst.* **1989**, *173*, 121.
(15) (a) Kalinin, V. N. *Synthesis* **1992**, 413. (b) Zhang, F.-J.; Cortez, C.; Harvey, R. G. *J. Org. Chem.* **2000**, *65*, 3952.
(16) (a) Molander, G. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 1, pp 251−282. (b) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29. (c) Imamoto, T. *Lanthanides in Organic Synthesis*; Academic Press: London, 1994.
(17) (a) Baldwin, L. J.; Tedjamulia, M. L.; Stuart, J. G.; Castle, R. N.; Lee, M. L. *J. Heterocycl. Chem.* **1984**, *21*, 1775. (b) Fischer, E.; Larsen, J.; Christensen, J. B.; Fourmigue, M.; Madsen, H. G.; Harrit, N. *J. Org. Chem.* **1996**, *61*, 6997.
(18) (a) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357. (b) Muller, M.; Mauermann-Dull, H.; Wagner, M.; Enkelmann, V.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1583. (c) Dötz, F.; Brand, J. D.; Ito, S.; Gherghel, L.; Müllen, K. *J. Am. Chem. Soc.* **2000**, *122*, 7707.
(19) Kleppinger, R.; Lillya, C. P.; Yang, C. *J. Am. Chem. Soc.* **1997**, *119*, 4097.

SCHEME 4. Synthesis of 4,5,6,7-Tetraphenylbenzo[*b*]thiophenes 14a-h, and the Fan-Shaped Polycyclic Aromatics 15a,b



effectively with a variety of ketones, including the enolizable ketones (e.g., tetralone and α-phenylacetophenones), to give the desired diol products (e.g., **2a**−**e**). Dehydration of the diol products was accomplished by the catalysis of *p*-TsOH to afford a series of dialkenyldihydrothiophenes (e.g., **3a**−**k** and **10a**,**b**). For synthetic purposes, dialkenyldihydrothiophenes **3a**−**k** were directly converted to 4,7-diarylbenzothiophenes **5a**−**k** by treatment with excess amounts of DDQ in refluxing toluene. The intermediary dialkenylthiophenes (e.g., **4b** and **4f**−**k**) were obtained under mild reaction conditions (1 equiv of DDQ in benzene, 60 °C). Compounds **3h**−**j** and **4h**−**k** bearing long-chain alkoxyphenyl substituents are liquid crystals of smectic-A type. Phenanthrothiophene **12a**, picenothiophene **12b**, and tribenzopentaphenothiophenes **15a** and **15b** were obtained by chemical or photochemical oxidative annulations of diphenylthiophene **11a**, dinaphthylthiophene **11b**, and tetraphenylbenzothiophenes **14a** and **14b**. The polycyclic aromatic compounds **12a**,**b** and **15a**,**b** may be used as DNA intercalators as they exhibit characteristic planar structures similar to those of PAHs.[2] As **12a**,**b** and **15a**,**b** are fluorescent compounds, their interactions with DNA can be monitored by the change of fluorescence intensity. The ester groups in **12a**,**b** and **15a**,**b** can be modified, e.g., by transformation into carboxylic acids and other functional derivatives, to improve their chemical and physical properties, e.g., the water solubility and the sequence specificity in DNA recognition. Furthermore, incorporation of sulfur atom in these polycyclic aromatics can provide an opportunity for photochemical activation. We are currently exploring the interaction of picenothiophene **12b** with calf thymus DNA and the possible cleavage of DNA double helix by photochemical activation.

Heterosuperbenzenes such as the nitrogen-functionalized graphite molecules[20a] are interesting research subjects. As we have previously demonstrated that indolecarbonyl coupling reactions are feasible by the promotion of SmI_2,[20b] we plan to explore further the nitrogen-containing polyaromatic systems, such as those derived from pyrroles, by using an approach similar to that described in this paper.

Experimental Section

General Methods. All reactions requiring anhydrous conditions were conducted in a flame-dried apparatus under an atmosphere of nitrogen. Syringes and needles for the transfer of reagents were dried at 100 °C and allowed to cool in a desiccator over P_2O_5 before use. Ethers were distilled from sodium benzophenone ketyl; (chlorinated) hydrocarbons, and amines from CaH_2. Reactions were monitored by TLC using plates precoated with a 0.25 mm layer of silica gel containing a fluorescent indicator (Merck Art. 5544). Column chromatography was carried out on Kieselgel 60 (40−63 μm). The photochemical reactions were conducted in a Rayonet photochemical reactor using 300-nm lamps.

Melting points are uncorrected. Chemical shifts of ^1H and ^{13}C NMR spectra are reported relative to $CHCl_3$ [δ_H 7.24, δ_C (central line of t) 77.0]. Coupling constants (*J*) are given in Hz. Distortionless enhancement polarization transfer (DEPT) spectra were taken to determine the types of carbon signals.

Representative Procedure for the SmI_2-Promoted Coupling Reactions of Thiophene-2-carboxylate with 2 equiv of Aryl Ketones, Giving Diols 2. *Caution*: HMPA is suspected as a carcinogen. Handle HMPA with care. Under an atmosphere of argon, a deep blue SmI_2 solution (0.1 M) was prepared by treatment of Sm (661 mg, 4.4 mmol) with 1,2-diiodoethane (1.01 g, 3.6 mmol) in anhydrous HMPA (2.8 mL, 16 mmol) and THF (35 mL) for 1.5 h at room temperature (25 °C). To the SmI_2 solution (cooled in an ice bath) were added a THF solution (3 mL) of methyl thiophene-2-carboxylate (142 mg, 1.0 mmol) and acetophenone (252 mg, 2.1 mmol). The reaction mixture was stirred at 0 °C for 20 min and then at room temperature for 2−10 h. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (1 mL). The mixture was passed through a short silica gel column by rinsing with EtOAc/hexane (1:1). The filtrate was concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (2:8) to give the desired three-component coupling product **2a** (233 mg, 61%). Two diastereomers (42:58) were separable on the silica gel column. The less polar isomer corresponded to the minor isomer.

Representative Procedure for Dehydration of Diols 2, Giving Dienes 3. Diol **2a** (300 mg, 0.78 mmol) and *p*-TsOH (catalytic amount) in benzene (30 mL) were heated at reflux for 5−12 h, while a Dean−Stark apparatus removed the generated water azeotropically. The reaction mixture was concentrated under reduced pressure and chromatographed

(20) (a) Draper, S. M.; Gregg, D. J.; Madathil, R. *J. Am. Chem. Soc.* **2002**, *124*, 3486. (b) Lin, S.-C.; Yang, F.-D.; Shiue, J.-S.; Yang, S.-M.; Fang, J.-M. *J. Org. Chem.* **1998**, *63*, 2909.

on a silica gel column by elution with EtOAc/hexane (1:9) to afford the corresponding diene **3a** (245 mg, 90%).

Representative Procedure for DDQ Oxidation of Dienes 3, Giving 4,5-Dialkenylthiophenes 4 and 4,7-Diarylbenzothiophenes 5. A mixture of diene **3b** (140 mg, 0.34 mmol) and DDQ (92 mg, 0.40 mmol) in anhydrous benzene (10 mL) was heated at 60 °C for 10−12 h. The reaction mixture was concentrated under reduced pressure and chromatographed on a silica gel column by elution with EtOAc/hexane (2:8) to give thiophene **4b** (125 mg, 89%). On the other hand, diene **3a** (290 mg, 0.70 mmol) was reacted with excess amounts of DDQ (352 mg, 1.55 mmol) in refluxing toluene (15 mL) for 7−18 h to give benzothiophene **5b** (262 mg, 91%).

Representative Procedure for Oxidative Cyclization under Photochemical Conditions. Diarylthiophene **11a** (30 mg, 0.1 mmol) and iodine (26 mg, 0.1 mmol) in deoxygenated anhydrous benzene (20 mL) were placed in a quartz tube equipped with a cooling circulation of ice−water. The solution was irradiated by 300-nm light in a Rayonet photochemical reactor for 20 h. The mixture was concentrated, treated with aqueous $Na_2S_2O_3$ to remove the remaining iodine, and extracted with CH_2Cl_2 (3×). The organic phase was dried (Na_2SO_4) and concentrated. Pure polyaromatic product **12a** (86% yield) was obtained by crystallization from CH_2Cl_2/hexane or by chromatography on a silica gel column with elution of EtOAc/hexane (1:9).

Methyl 4,5-Bis(l-hydroxy-l-phenylethyl)-4,5-dihydrothiophene-2-carboxylate (2a). 2a, minor isomer: oil; TLC (EtOAc/hexane, 3:7) $R_f = 0.21$; IR (neat) 3452, 1710 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.47−7.18 (10 H, m), 6.21 (1 H, d, $J = 3.6$ Hz), 4.03 (1 H, d, $J = 3.1$ Hz), 3.71 (3 H, s), 3.61 (1 H, dd, $J = 3.6$, 3.1 Hz), 2.70 (1 H, br s, OH), 2.35 (1 H, br s, OH), 1.65 (3 H, s), 1.16 (3 H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.3, 145.2, 143.9, 135.1, 134,5, 128.2 (2×), 128.1 (2×), 127.4, 126.8, 125.9 (2×), 124.7 (2×), 76.4 (2×), 61.7, 60.7, 52.3, 27.7, 26.1; FAB-MS *m/z* 367.0 ($M^+ + 1 - H_2O$); HRMS calcd for $C_{22}H_{24}O_4S$ 384.1396, found 384.1391. **2a**, major isomer: oil; TLC (EtOAc/hexane, 3:7) $R_f = 0.18$; IR (neat) 3480 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.41−7.21 (10 H, m), 6.23 (1 H, d, $J = 3.5$ Hz), 4.23 (1 H, d, $J = 3.0$ Hz), 3.67 (3 H, s), 3.65 (1 H, dd, $J = 3.5$, 3.0 Hz), 2.86 (1 H, s, OH), 2.41 (1 H, s, OH), 1.45 (3 H, s), 1.31 (3 H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.2, 145.5, 145.4, 135.4, 134.6, 128.3 (2×), 128.2 (2×), 127.2 (2×), 125.3 (2×), 125.1 (2×), 76.8, 76.3, 61.3, 60.6, 52.3, 26.6, 25.0; FAB-MS *m/z* 367.0 ($M^+ + 1 - H_2O$); HRMS calcd for $C_{22}H_{24}O_4S$ 384.1396, found 384.1398.

Methyl 4,5-Bis[1-(4-octadecanoyloxy)phenylethenyl]-4,5-dihydrothiophene-2-carboxylate (3g). According to the representative procedure, the SmI_2-promoted coupling reaction of **1a** with 4-acetylphenyl stearate, followed by the acid-catalyzed dehydration, gave diene **3g** in 48% overall yield: solid; mp 84−85 °C; TLC (EtOAc/hexane, 1:9) $R_f = 0.34$; IR (KBr) 1754, 1727 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.22 (2 H, d, $J = 8.6$ Hz), 7.16 (2 H, d, $J = 8.6$ Hz), 6.96 (2 H, d, $J = 8.6$ Hz), 6.95 (2 H, d, $J = 8.6$ Hz), 6.51 (1 H, d, $J = 3.1$ Hz), 5.40 (1 H, s), 5.32 (1 H, s), 5.27 (1 H, s), 5.17 (1 H, s), 4.67 (1 H, d, $J = 6.7$ Hz), 4.30 (1 H, dd, $J = 6.7$, 3.1 Hz), 3.78 (3 H, s), 2.52 (4 H, t, $J = 7.3$ Hz), 1.71 (4 H, quint, $J = 7.3$ Hz), 1.33−1.24 (56 H, br s). 0.86 (6 H, t, $J = 6.7$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.1 (2×), 162.7, 150.4 (2×), 146.9, 145.8, 137.4, 137.3, 135.0, 134.9, 128.4 (2×), 127.7 (2×), 121.6 (2×), 121.4 (2×), 115.9, 115.2, 58.1 (2×), 52.4, 34.4 (2×), 31.9 (2×), 29.67 (12×), 29.64 (2×), 29.60 (2×), 29.4 (2×), 29.3 (2×), 29.2 (2×), 29.1 (2×), 24.9 (2×), 22.6 (2×), 14.1 (2×); FAB-MS *m/z* 913.6 ($M^+ + 1$). Anal. Calcd for $C_{58}H_{88}O_6S$: C, 76.26; H, 9.72. Found: C, 75.96; H, 9.74.

Ethyl 4,5-bis[1-(naphth-2-yl)-2-methylpropenyl]thiophene-2-carboxylate (4l): oil; TLC (EtOAc/hexane (1:19)) $R_f = 0.13$; IR (neat) 1705, 1617 cm^{-1}; UV ($CHCl_3$) λ_{max} (ϵ) 290 nm (35400), 364 nm (17100); FL ($CHCl_3$, $c = 2 \times 10^{-5}$ M) λ_{em} 415 nm by excitation at 364 nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.70 (2 H, dd, $J = 6.0$, 3.2 Hz), 7.57 (1 H, s), 7.54 (2 H, dd, $J = 6.0$, 3.2 Hz), 7.37−7.34 (6 H, m), 7.00−6.95 (4 H, m), 4.29 (2 H, q, $J = 6.2$ Hz), 1.69 (3 H, s), 1.67 (3 H, s), 1.60 (3 H, s), 1.57 (3 H, s), 1.33 (3 H, t, $J = 6.2$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.5, 148.1, 141.8, 139.5, 139.0, 137.9, 136.5, 134.3, 133.1, 132.0 (2×), 131.8, 131.1, 131.0, 128.8 (2×), 128.7 (2×), 128.1, 127.9, 127.8, 127.7, 127.4, 127.0, 126.8, 125.8, 125.7, 125.5, 125.4, 60.9, 22.8, 22.5, 22.3, 21.9, 14.4; FAB-MS 516.2 (M^+); HRMS calcd for $C_{35}H_{32}O_2S$ 516.2123, found 516.2122. Anal. Calcd for $C_{35}H_{32}O_2S$: C, 81.36; H, 6.24. Found: C, 81.62; H, 6.36.

Methyl 7-(4-Chlorophenyl)-4-(4-methoxyphenyl)benzo[*b*]thiophene-2-carboxylate (5f). A mixture of methyl thiophene-2-carboxylate (142 mg, 1.0 mmol) and 4-chloroacetophenone (155 mg, 1.0 mmol) in THF (2 mL) was treated with SmI_2/HMPA (3.6/16.0 mmol) at 0 °C for 10 min and at 25 °C for 2 h. The second electrophile of 4-methoxyacetophenone (180 mg, 1.2 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 14 h and then worked up to give the diol product **2f** according to the representative procedure. The subsequent acid-catalyzed dehydration gave diene **3f** in 51% overall yield. The reaction of diene **3k** with 2.2 equiv of DDQ in refluxing toluene gave benzothiophene **5f** in 85% yield: solid; mp 201−202 °C; TLC (EtOAc/hexane, 1:9) $R_f = 0.23$; IR (KBr) 1723 cm^{-1}; UV ($CHCl_3$) λ_{max} (ϵ) 282 nm (61600), 347 nm (24000); FL ($CHCl_3$, $c = 2 \times 10^{-4}$ M) λ_{em} 435 nm by excitation at 347 nm; ^1H NMR ($CDCl_3$, 200 MHz) δ 8.21 (1 H, s), 7.65 (2 H, dd, $J = 8.6$, 2.0 Hz), 7.50−7.40 (6 H, m), 7.04 (2 H, dd, $J = 8.6$, 2.0 Hz), 3.89 (3 H, s), 3.88 (3 H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.1, 159.5, 141.8, 138.9, 138.2, 137.9, 134.3, 134.2, 133.2, 132.2, 130.7, 130.2 (2×), 129.5 (2×), 129.4 (2×), 127.0, 125.9, 114.2 (2×), 55.4, 52.5; FAB-MS *m/z* 407.9 (M^+); HRMS calcd for $C_{23}H_{17}ClO_3S$ 408.0587, found 408.0583. Anal. Calcd for $C_{23}H_{17}ClO_3S$: C, 67.64; H, 4.20. Found: C, 67.21; H, 4.36.

Ethyl 6-Aza-4,8-di(naphth-2-yl)-5,7-dioxo-6-phenyl-1-thiatetracyclo[7.3.2.^{4,8}0.^{3a,8a}0^{4a,7a}]tetradeca-2,3a(8a)-diene-2-carboxylate (6). A mixture of triene **4e** (96 mg, 0.2 mmol) and *N*-phenylmaleimide (353 mg, 2.0 mmol) in deoxygenated anhydrous toluene (15 mL) was heated at reflux for 48 h. The mixture was concentrated and chromatographed on a silica gel column by elution with EtOAc/hexane (2:8) to give an oxidative aromatization product **5e** (73 mg, 80%) and a Diels−Alder addition product **6** (15 mg, 12%). **6**: oily solid; TLC (EtOAc/hexane (1:4)) $R_f = 0.10$; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.44 (1 H, s), 8.33 (1 H, s), 7.97−7.79 (7 H, m), 7.78 (1 H, s), 7.52−7.48 (5 H, m), 7.21−7.18 (3 H, m), 6.69−6.66 (2 H, m), 4.34−4.33 (2 H, m), 4.27 (2 H, q, $J = 7.2$ Hz), 2.15−2.11 (4 H, m), 1.28 (3 H, t, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.3, 173.8, 162.2, 147.9, 143.3, 138.1, 137.6, 133.1, 133.0, 132.7, 132.5, 131.9, 131.4, 131.3, 128.8, 128.5, 128.3, 128.2, 127.9, 127.7 (2×), 127.6, 127.5 (2×), 127.1, 126.6 (2×), 126.4, 126.3, 126.2, 126.17, 126.1, 125.3, 61.2, 49.9, 49.0, 48.3, 47.8, 38.7, 38.6, 14.4. FAB-MS *m/z* 633.2 (M^+); HRMS calcd for $C_{41}H_{31}NO_4S$ 633.1974, found 633.1968.

Methyl 4,7-Bis(5-bromo-2-thienyl)benzo[*b*]thiophene-2-carboxylate (7b). According to the representative procedure, the SmI_2-promoted coupling reaction of **1a** with 2-acetyl-5-bromothiophene, followed by the acid-catalyzed dehydration and DDQ oxidative cyclization, gave benzothiophene **7b** in 35% overall yield: solid; mp 145−147 °C; TLC (EtOAc/hexane, 1:19) $R_f = 0.21$; IR (KBr) 1724 cm^{-1}; UV ($CHCl_3$) λ_{max} (ϵ) 294 nm (14700), 333 nm (12300), 368 nm (11600); FL ($CHCl_3$, $c = 1 \times 10^{-5}$ M) λ_{em} 461 nm by excitation at 368 nm; ^1H NMR ($CDCl_3$, 200 MHz) δ 8.38 (1 H, s), 7.52 (1 H, d, $J = 7.7$ Hz), 7.43 (1 H, d, $J = 7.7$ Hz), 7.33 (1 H, d, $J = 3.9$ Hz), 7.12 (2 H, d, $J = 3.8$ Hz), 7.07 (1 H, d, $J = 3.9$ Hz), 3.94 (3 H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.8, 142.7, 142.6, 140.8, 137.4, 134.2, 130.8, 130.75, 130.73, 130.0, 128.6, 127.0, 126.23, 126.19, 126.0, 113.13, 113.09, 52.7; EI-MS *m/z* (rel intensity) 516 (13, $C_{18}H_{10}(^{81}Br)_2O_2S_3$), 514 (17), 512 (10, $C_{18}H_{10}(^{79}Br)_2O_2S_3$), 91 (100); HRMS calcd for $C_{18}H_{10}(^{81}Br)_2O_2S_3$ 515.8169, found 515.8168.

Methyl 4,5-Diphenylthiophene-2-carboxylate (11a). According to the representative procedure, the reaction of diene **10a** with 6.5 equiv of DDQ in refluxing xylene for 48 h gave diphenylthiophene **11a** in 89% yield: solid; mp 85−86 °C; TLC (EtOAc/hexane, 1:9) $R_f = 0.33$; IR (KBr) 1715 cm^{-1}; UV ($CHCl_3$) λ_{max} (ϵ) 317 nm (48000); FL ($CHCl_3$, $c = 1 \times 10^{-5}$ M) λ_{em} 410 nm by excitation at 317 nm; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.81 (1 H, s), 7.31−7.19 (10 H, m), 3.90 (3 H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 162.6, 145.6, 138.8, 136.2, 135.4 (2×), 133.3, 131.1, 129.2 (2×), 128.9 (2×), 128.6 (2×), 128.4 (2×), 128.3, 127.3; EI-MS *m*/*z* (rel intensity) 294 (100, M^+); HRMS calcd for $C_{18}H_{14}C_2S$ 294.0715, found 294.0721. Anal. Calcd for $C_{18}H_{14}O_2S$: C, 73.45; H, 4.80. Found: C, 73.29; H, 4.67.

Methyl Piceno[13,14-*b*]thiophene-2-carboxylate (12b). The photochemical reaction of dinaphthylthiophene **11b** in the presence of I_2, under conditions similar to that for **12a**, gave picenothiophene **12b** in 89% yield: solid; mp 218−219 °C; TLC (EtOAc/hexane, 1:9) $R_f = 0.22$; IR (KBr) 1712 cm^{-1}; UV ($CHCl_3$) λ_{max} (ϵ) 348 nm (25700), 365 nm (25200), 406 nm (8100); FL ($CHCl_3$, $c = 1 \times 10^{-5}$ M) λ_{em} 416 and 437 nm by excitation at 406 nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.24 (1 H, d, $J = 8.5$ Hz), 9.09 (1 H, s), 8.35 (1 H, d, $J = 8.2$ Hz), 8.56 (1 H, d, $J = 10$ Hz), 8.52 (1 H, d, $J = 10$ Hz), 7.98−7.92 (3 H, m), 7.89 (1 H, d, $J = 8.5$ Hz), 7.76 (1 H, td, $J = 8.0$, 1.2 Hz), 7.70−7.60 (3 H, m), 4.00 (3 H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.2, 139.4, 134.2, 133.1, 132.8, 132.5, 131.8, 129.6, 129.3, 129.0, 128.8, 128.4, 128.3, 127.5, 127.4, 127.3, 127.2, 126.8, 126.7, 126.6, 126.2, 125.6, 125.0, 121.7, 121.3, 52.5; MS *m*/*z* (rel intensity) 392 (14, M^+), 91 (100); HRMS calcd for $C_{26}H_{16}O_2S$ 392.0871, found 392.0873. Anal. Calcd for $C_{26}H_{16}O_2S$: C, 79.57; H 4.11. Found: C, 79.52, H 4.08.

Ethyl 4,5,6,7-Tetraphenylbenzo[*b*]thiophene-2-carboxylate (14a). According to the representative procedure, the SmI_2-promoted coupling reaction of ethyl thiophene-2-carboxylate (**1b**) with α-phenylacetophenone, followed by acid-catalyzed dehydration and DDQ oxidative cyclization, gave tetraphenylbenzothiophene **14a** in 44% overall yield: solid; mp >300 °C; TLC (EtOAc/hexane, 1:4) $R_f = 0.32$; IR (KBr) 1715 cm^{-1}; UV ($CHCl_3$) λ_{max} (ϵ) 309 nm (50600), 345 nm (18900); FL ($CHCl_3$, $c = 1 \times 10^{-5}$ M) λ_{em} 399 nm by excitation at 345 nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.86 (1 H, s), 7.28−7.16 (10 H, m), 6.89−6.80 (10 H, m), 4.31 (2 H, q, $J = 7.2$ Hz), 1.32 (3 H, t, $J = 7.2$ Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.8, 139.5 (2×), 139.4 (2×), 137.7 (2×), 135.2 (2×), 134.0 (2×), 131.5 (2×), 131.3 (2×), 131.2 (2×), 130.5 (2×), 129.8 (2×), 128.1 (2×), 127.7 (2×), 127.3 (2×), 126.8 (2×), 125.8 (2×), 125.6 (2×), 61.5, 14.3; FAB-MS *m*/*z* 510.2 (M^+); HRMS calcd for $C_{35}H_{26}O_2S$ 510.1653, found 510.1657.

Ethyl Tribenzo[*fg*,*ij*,*rst*]pentapheno[15,16-*b*]thiophene-2-carboxylate (15a). To a solution of tetraphenylbenzothiophene **14a** (228 mg, 0.45 mmol) in CH_2Cl_2 (10 mL) was added slowly a solution of $FeCl_3$ (320 mg, 3 mmol) in CH_3NO_2 (5 mL). The mixture was stirred at room temperature for 5 h, water (10 mL) was added, and and the mixture was extracted with CH_2Cl_2. The organic phase was dried (Na_2SO_4), concentrated, and recrystallized from CH_2Cl_2/hexane to give polycyclic aromatic compound **15a** (183 mg, 81%). Alternatively, treatment of **14a** with excess amounts of $AlCl_3$ and anhydrous $CuCl_2$ in CS_2 solution under the atmosphere of oxygen for 36 h afforded **15a** in 91% yield: solid; mp >300 °C; IR (KBr) 1715 cm^{-1}; UV ($CHCl_3$) λ_{max} (ϵ) 312 nm (19000), 325 nm (20300), 341 nm (21300), 380 nm (7700), 401 nm (9100), 412 nm (6900), 436 nm (5000); FL ($CHCl_3$, $c = 1 \times 10^{-5}$ M) λ_{em} 436 and 472 nm by excitation at 436 nm; ^1H NMR ($CDCl_3$, 200 MHz) δ 9.25 (1 H, dd, $J = 8.0$, 2.3 Hz), 9.06 (1 H, s), 8.74−8.59 (7 H, m), 7.85−7.76 (6 H, m), 4.48 (2 H, q, $J = 7.2$ Hz), 1.47 (3 H, t, $J = 7.2$ Hz); FAB-MS *m*/*z* 504.1 (M^+); HRMS calcd for $C_{35}H_{20}O_2S$ 504.1184, found 504.1180. Anal. Calcd for $C_{35}H_{20}O_2S$: C, 83.31; H, 4.00. Found: C, 83.18; H, 4.24.

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Supporting Information Available: Physical and spectral data, NMR spectra, and X-ray analyses of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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