Synthesis of Unsymmetrical 2,3-Diaryl- and 2,4-Diarylthiophenes Starting from 2,5-Dichlorothiophene[1)]

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Unsymmetrically substituted 2,4-diaryl- and 2,3-diarylthiophenes were synthesized from 2,5-dichlorothiophene via 4-aryl-2-chlorothiophenes in two and four steps including Ni-mediated cross-coupling, respectively. Aluminum chloride-catalyzed reaction of 3-aryl-2-chlorothiophenes with some aromatic ethers unexpectedly led to the formation of the corresponding 2,4-isomers.

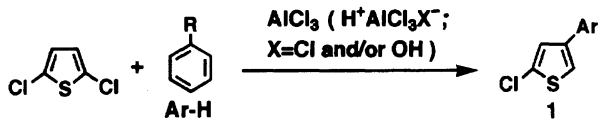
Although the chemistry of oligophenylenes has been systematically investigated, that of thiophene containing analogs has not yet been fully explored. The mixed thiophene–arene oligomers containing 2,4-, 2,3-, or 3,4-thienylene unit are rather limited in number in particular.

During the course of studies on the acid-catalyzed reactions of thiophene nuclei, we found that chlorothiophenes easily reacted with some aromatic compounds in the presence of $AlCl_3$; 2-chlorothiophene[2)] gave the corresponding 2-arylthiophenes, while 2,5-dichlorothiophene[3)] unexpectedly yielded 4-aryl-2-chlorothiophenes (**1**) (Scheme 1). Further, we demonstrated that **1** were versatile starting substances for the synthesis of mixed thiophene-arene oligomers containing 3-aryl-2-thienyl or 4-aryl-2-thienyl unit.[4,5)] These findings suggest a new route from 2,5-dichlorothiophene to 2,4-diaryl- (**2**) and 2,3-diarylthiophenes (**6**), one of the simplest mixed thiophene–arene oligomers corresponding to terphenyls. Only a very few of hitherto known 2,4- (**2**) and 2,3-diarylthiophenes (**6**) contain two different aryl substituents.[6)] They have been synthesized principally by several types of ring closure consisting of high-temperature sulfuration of appropriate olefins or ketones. Most of these methods, however, are not practical enough, because of the difficulty in obtaining starting substances and the severe reaction conditions. As an extension of our previous studies, we investigated the synthesis of **2** and **6** using **1** as the intermediates.

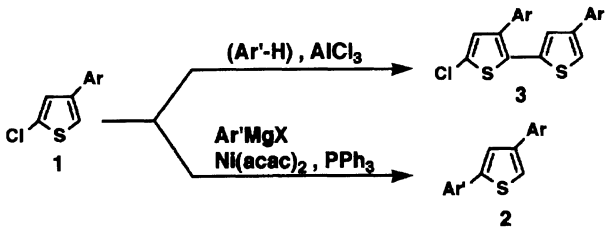
Results and Discussion

The $AlCl_3$-catalyzed reaction of **1** with aromatic compounds failed to afford **2**, the self-condensation of **1** being predominant.[4)] The unsymmetrical 2,4-diarylthiophenes (**2**) were prepared in 50—70% yields by cross-coupling of **1** with arylmagnesium iodide (ArMgI; 3 molar equiv) in the presence of bis(acetylacetonato)nickel-(II) ($Ni(acac)_2$; 0.05 molar equiv) and PPh_3 (0.1 molar equiv) (Scheme 2). The results are summarized in Table 1.

In the hope of obtaining 2,3-diarylthiophenes (**6**), we next investigated the Friedel–Crafts type reaction of 3-aryl-2-chlorothiophenes (**5**) with aromatic compounds. 3-Aryl-2-chlorothiophenes (**5**) were easily prepared from **1** by catalytic dechlorination, followed by chlorination of the resulting 3-arylthiophenes (**4**) with SO_2Cl_2. The structures of the chlorinated 3-arylthiophenes were confirmed by the ^1H NMR spectra, which clearly showed the presence of 2,3-disubstituted thiophene ring[7)] in their molecules. The $AlCl_3$-catalyzed reaction gave, however, the 2,4-diaryl isomers **2** or self-condensation product **7** (Scheme 3) depending upon the reactivity of the substrate. Namely, with benzene or toluene, the reaction of 2-chloro-3-phenylthiophene (**5a**) gave the same product, 5-chloro-4,4′-diphenyl-2,2′-bithiophene (**7**; Ar=Ph) in low yields (23 and 28%, respectively). The structure was identified by dechlorination of the product, which gave symmetrical 4,4′-diphenyl-2,2′-bithiophene. On the other hand, the reaction with much more reactive compounds such as anisole and 1-methoxynaphthalene led to the formation of **2** in reasonable yields (Table 2). It should be pointed out that, in these reactions, an aryl group is introduced into the vacant α-position accompanied by the elimination of the chlorine atom on the other α-position. The structures of **2** were established on the basis of their elemental analyses, and spectral data. The ^1H NMR spectra showed, in addition to the absorptions ascribable to the aromatic protons, an AB quartet with a coupling of 1.2—1.7 Hz, characteristic for 2,4-disubstituted thiophenes[7)] in the ring proton region. Further support for the structural



Scheme 1.



Scheme 2.

Table 1. Ni(acac)$_2$-Mediated Coupling of 4-Aryl-2-chlorothiophenes (**1**) with Aryl Grignard Reagents

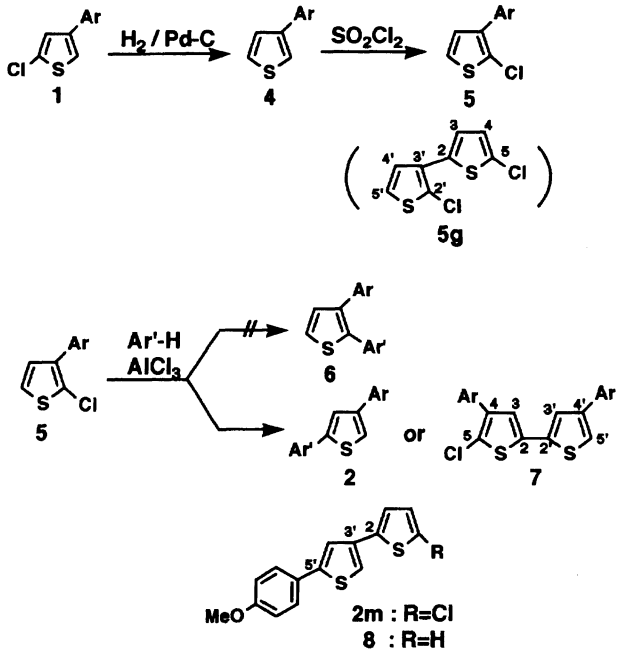
1	Ar′MgX	**2**				
Ar		Ar	Ar′	Yield[a]	Mp (θ_m/°C)	
a: Ph	PhMgI	**a**: Ph	Ph	63	120—121[c]	(hex)[d]
Ph	2-ThMgBr[b]	**b**: Ph	2-Th	53	74—76	(hex)
b: 4-MeC$_6$H$_4$	PhMgI	**c**: 4-MeC$_6$H$_4$	Ph	61	116—117	(hex)
c: 4-EtC$_6$H$_4$	PhMgI	**d**: 4-EtC$_6$H$_4$	Ph	61	94—96	(hex)
d: 4-MeOC$_6$H$_4$	PhMgI	**e**: 4-MeOC$_6$H$_4$	Ph	57	159—161[e]	(hex+ben)
e: 2,4-Me$_2$C$_6$H$_3$	PhMgI	**f**: 2,4-Me$_2$C$_6$H$_3$	Ph	70	Oil[f]	
f: 2-Naph[b]	PhMgI	**g**: 2-Naph	Ph	50	129—130	(hex+ben)

a) Isolated yields based on **1** used. b) Naph=naphthyl; Th=thienyl. c) lit, 124—125 °C,[8a] 120.6—121.5 °C,[11a] 121.0—121.5 °C.[11b] d) Solvent for recrystallization: hex=hexane, ben=benzene. e) lit,[6a] 161.5—163.5 °C. f) Bp 105 °C (bath temp)/1×10^{-4} mmHg.

Table 2. Friedel–Crafts Type Reaction of 3-Aryl-2-chlorothiophenes (**5**) with Aromatic Ethers

5	Ar′-H	**2**				
Ar		Ar	Ar′	% Yield[a]	Mp (θ_m/°C)	
a: Ph	PhH			(23)[b]		
Ph	PhMe			(28)[b]		
Ph	PhOMe	**h**: Ph	4-MeOC$_6$H$_4$	56	143—144[d]	(ben)[e]
Ph	1-NaphOMe	**i**: Ph	4-MeO-1-Naph[c]	66	93—94	(hex)
b: 4-MeC$_6$H$_4$	PhOMe	**j**: 4-MeC$_6$H$_4$	4-MeOC$_6$H$_4$	43	164—166	(hex)
c: 4-EtC$_6$H$_4$	PhOMe	**k**: 4-EtC$_6$H$_4$	4-MeOC$_6$H$_4$	46	139—140	(hex+chl)
d: 4-MeOC$_6$H$_4$	PhOMe	**l**: 4-MeOC$_6$H$_4$	4-MeOC$_6$H$_4$	45	223—224[f]	(ben+EtOH)
g: 5-Cl-2-Th	PhOMe	**m**: 5-Cl-2-Th[c]	4-MeOC$_6$H$_4$	41	117—118	(hex)

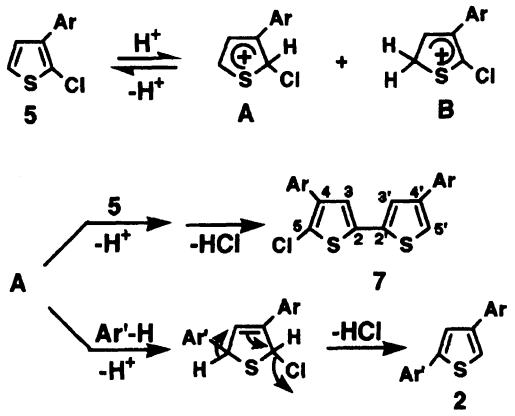
a) Isolated yield based on **5** used. b) 5-Chloro-4,4′-diphenyl-2,2′-bithiophene (**7**), mp 144—145 °C. c) Naph=naphthyl; Th=thienyl. d) lit,[6a] 144.5—145.5 °C. e) Solvent for recrystallization: hex=hexane, ben=benzene, chl=chlororform. f) lit, 219—221 °C,[2] 204—205 °C,[8a] 218—219 °C.[8b]



Scheme 3.

assignment was provided by the comparison of some products with their authentic samples; 2-(*p*-methoxyphenyl)-4-phenylthiophene (**2h**)[6a] and 2,4-bis(*p*-methoxyphenyl)thiophene (**2l**).[2,8]

A plausible pathway of the unusual formation of the 2,4-diarylthiophenes (**2**) is shown in Scheme 4. This apparently involves 3-aryl-2-chloro-2*H*-thiophenium ion **A** with the positive charge on the 5-position, although a molecular orbital calculation (MNDO method; Chart 1) predicts the formation of 3-aryl-2-chloro-5*H*-thiophenium ion **B** (Ar=Ph) in preference to the cation **A** (Ar=Ph) in the protonation of 2-chloro-3-phenylthiophene (**5a**). The chlorothiophenium ion **A** reacts



Scheme 4.

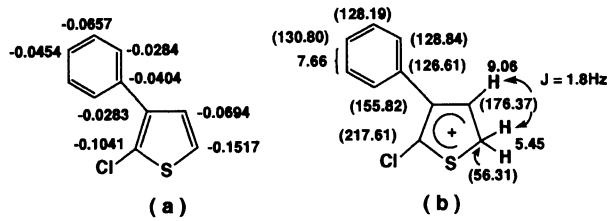
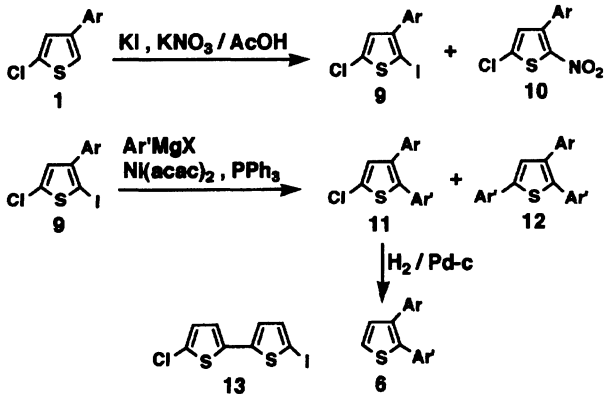


Chart 1. Atomic charges for carbons in **5a** (a) and ^{1}H and ^{13}C NMR data for protonated **5a** (b).

with an aromatic molecule, followed by the loss of a proton and a HCl molecule to give **2**. With the substrates much less reactive than **5**, the cation **A** attacks parent molecule **5** at the 5-position to produce the self-condensation product **7**. The cation **B** is not reactive enough to form 2,3-diarylthiophenes (**6**) under the conditions; steric effect of the 3-positioned aryl group in the cation may be responsible for the decrease in reactivity.

^{1}H and ^{13}C NMR spectra[9] of the protonated species, which was produced from **5a** in HSO_3F at low temperature in an attempt to confirm the existence of the cation **A**, indicated, however, that the species was the cation **B** (Chart 1). This suggests the rearrangement of the cation **A** to the thermodynamically stable cation **B** through a hydrogen shift; the conversion occurs too fast on the NMR time scale to observe the initially formed ion **A**. Such an irreversible 2,5-hydrogen shift has been observed by NMR spectroscopy in the protonation of 2-chloro-5-methylthiophene.[10]

Finally, 2,3-diarylthiophenes (**6**) were synthesized by the $Ni(acac)_2$-mediated cross-coupling of 3-aryl-5-chloro-2-iodothiophenes (**9**) with ArMgX, followed by the catalytic dechlorination of the resultant 2,3-diaryl-5-chlorothiophenes (**11**) (Scheme 5; Tables 3 and 4). The iodides **9** were obtained by the reaction of **1** with KI and KNO_3 in acetic acid together with the nitro derivatives **10**. The cross-coupling afforded the diarylthiophenes **11** in 40—50% yields. The reaction under the conditions used for the synthesis of 2,4-diarylthiophenes (**2**) was accompanied by the formation of the corresponding 2,3,5-triarylthiophenes (**12**; 20—30%). The structures



Scheme 5.

of **6** were confirmed by their spectral data and elemental analyses.

2,4-Diaryl- (**2**) and 2,3-diarylthiophenes (**6**) (Ar= *p*-substituted phenyl) show characteristic UV absorptions; **2** have an intense absorption band at 258—268 nm with an inflection at 302—310 nm, while **6** have two distinctive bands at 237—240 nm and 275—279 nm. The 2,3-diaryl isomers **6** generally absorb at shorter wavelengths with reduced intensity compared to **2**, as is true for *o*-terphenyl against *m*-terphenyl.[17] This tendency is apparently ascribed to steric inhibition of resonance caused by the two neighboring aryl groups. The steric effect is also seen in the spectrum of 4-(2,4-dimethylphenyl)-2-phenylthiophene (**2f**), which absorbs at shorter wavelengths compared to the parent **2a**.

In conclusion: 1) A series of unsymmetrically substituted 2,3-diaryl- and 2,4-diarylthiophenes was synthesized from 2,5-dichlorothiophene via 4-aryl-2-chlorothiophenes (**1**). The result demonstrates the usefulness of **1**, namely, 2,5-dichlorothiophene as a precursor of the thiophene oligomers containing 2,3- and 2,4-thienylene unit. 2) 3-Aryl-2-chlorothiophenes were found to yield the corresponding 2,4-diarylthiophenes in the $AlCl_3$-catalyzed reaction with aromatic ethers. This makes a sharp contrast with the similar reactions of other chlorothiophenes, in which α-chlorine atom is directly replaced by an aryl group or removed with the introduction of an aryl group into the neighboring β-position.

Experimental

All the melting and boiling points are uncorrected. The UV (in MeOH otherwise noted) and MS spectra (70 eV) were obtained on a Hitachi 228A and a Hitachi RMU-6M, respectively. The ^{1}H NMR spectra (in $CDCl_3$ otherwise noted) were recorded on a Hitachi R-600 (60 MHz), Hitachi R-90H (90 MHz), or Varian XL-200 (200 MHz) spectrometer using TMS as an internal reference, while ^{13}C NMR measurement was made on a Varian XL-200 spectrometer at 50.31 MHz. The protonated **5** was prepared in HSO_3F at −78 °C and its NMR spectra were taken with a similar manner as described previously.[10,14]

4-Aryl-2-chlorothiophenes[3] (**1**) and 2′,5-dichloro-2,3′-bithiophene[15] (**5g**) were prepared by the method described previously. Commercial $AlCl_3$ was used without special precautions against moisture.

The MNDO MO calculations were done using a HITAC M680 and a library program (MOPAC) at the Computer Center, Institute for Molecular Science in Okazaki.

Coupling of 4-Aryl-2-chlorothiophenes (1) with Arylmagnesium Halides. A Grignard reagent which was prepared from iodobenzene or 2-bromothiophene (15 mmol) and Mg (0.4 g, 16.5 mmol) in dry ether (20 ml) was added dropwise over a period of 1 h to a stirred solution of **1** (5 mmol), bis(acetylacetonato)nickel(II) ($Ni(acac)_2$; 64 mg, 0.25 mmol), and PPh_3 (130 mg, 0.5 mmol) in dry ether (15 ml). The resulting brown-black solution was stirred for 3 h at room temperature, and then poured into 5% HCl solution (20 ml). The ether layer was separated and the

Table 3. Ni(acac)$_2$-Mediated Coupling of 4-Aryl-2-chloro-5-iodothiophenes (**9**) with Aryl Grignard Reagents

9	Ar′MgX	Coupling product **11** and **12**			
Ar		Ar	Ar′	% Yield[a]	Mp (θ_m/°C)[b]
a: Ph	PhMgI	**11a**: Ph	Ph	46 (33)	73—74
		12a: Ph	Ph	19	142—143[d]
Ph	2-ThMgI	**11b**: Ph	2-Th[c]	(51)	61—62
Ph	3-Me-2-ThMgI	**11c**: Ph	3-Me-2-Th	(58)	Oil[e]
Ph	5′-ClThThMgI	**11d**: Ph	5′-ClThTh[c]	(41)	76—77
b: 4-MeC$_6$H$_4$	PhMgI	**11e**: 4-MeC$_6$H$_4$	Ph	40	71—72
		12b: 4-MeC$_6$H$_4$	Ph	28	98—99
c: 4-EtC$_6$H$_4$	PhMgI	**11f**: 4-EtC$_6$H$_4$	Ph	41	Oil[f]
		12c: 4-EtC$_6$H$_4$	Ph	21	84—86
d: 4-MeOC$_6$H$_4$	PhMgI	**11g**: 4-MeOC$_6$H$_4$	Ph	47	73—74
		12d: 4-MeOC$_6$H$_4$	Ph	20	86—88

a) Isolated yields based on **9** used. Figures in parentheses indicate the yields in the absence of PPh_3. b) Recrystallized from hexane. c) Naph=naphthyl; Th=thienyl; 5′-ClThTh=5′-chloro-2,2′-bithiophen-5-yl. d) lit, 142—143 °C,[12a] 141—142 °C,[12b] 139—140 °C,[12c] 132—134 °C.[12d] e) Bp 135 °C (bath temp)/1 mmHg. f) Bp 105 °C (bath temp)/2 mmHg.

Table 4. Catalytic Dechlorination of the Coupling Products **11**

Coupling product	Dechlorination product **6**			
11	Ar	Ar′	% Yield[a]	Mp (θ_m/°C)[b]
a	**a**: Ph	Ph	76	82—84[d]
b	**b**: Ph	2-Th[c]	77	75—76
c	**c**: Ph	3-Me-2-Th	83	61—62
d	**d**: Ph	ThTh[c]	80	104—106
e	**e**: 4-MeC$_6$H$_4$	Ph	86	Oil[e]
f	**f**: 4-EtC$_6$H$_4$	Ph	85	Oil[f]
g	**g**: 4-MeOC$_6$H$_4$	Ph	83	67—68

a) Isolated yields based on **11** used. b) Recrystallized from hexane. c) Naph=naphthyl; Th=thienyl; ThTh=2,2′-bithiophen-5-yl. d) lit,[11b,13] 82.5—83 °C. e) Bp 125 °C (bath temp)/2 mmHg. f) Bp 135 °C (bath temp)/2 mmHg.

aqueous layer was extracted with $CHCl_3$ (10 ml). The combined organic layers were washed with H_2O (20 ml×2) and dried. The residual mass after removal of the solvent was chromatographed (silica gel/hexane or hexane–$CHCl_3$ (3 : 1; for **2f**)) to give 2,4-diarylthiophene (**2**) along with a small amount of biphenyl (about 0.3 g).

2,4-Diphenylthiophene (2a). UV 221 (sh, log ε 4.20), 258 (4.56) and 302 nm (sh, 3.94) (lit,[11b] (96% EtOH) 221 (sh, 4.21), 258 (4.52), and 305 nm (sh, 3.97)); ^{1}H NMR (60 MHz) δ=7.85—7.2 (m, 3-H, 5-H, and Ph (phenyl)); MS *m/z* (rel intensity) 236 (M^+, 100).

4-Phenyl-2,2′-bithiophene (2b). UV 224 (sh, log ε 4.12), 262 (4.40), 286 (sh, 4.04), and 314 nm (4.03); ^{1}H NMR (60 MHz) δ=7.75—6.85 (m, 3-H, 5-H, Th (thienyl) and Ph); MS *m/z* 242 (M^+, 100). Found: C, 69.27; H, 3.92%. Calcd for $C_{14}H_{10}S$: C, 69.38; H, 4.16%.

2-Phenyl-4-(*p*-tolyl)thiophene (2c). UV 223 (sh, log ε 4.21), 260 (4.60), and 305 nm (sh, 3.87); ^{1}H NMR (60 MHz) δ=8.1—6.9 (11H, m, 3-H, 5-H, ph, and *p*-Ph (*p*-substituted phenyl)) and 2.37 (3H, s, CH_3); MS *m/z* 250 (M^+, 100). Found: C, 81.56; H, 5.53%. Calcd for $C_{17}H_{14}S$: C, 81.56; H, 5.64%.

4-(*p*-Ethylphenyl)-2-phenylthiophene (2d). UV 223 (sh, log ε 4.22), 261 (4.61), and 306 nm (sh, 3.87); ^{1}H NMR (60 MHz) δ=8.15—6.5 (11H, m, 3-H, 5-H, ph, and *p*-Ph), 2.68 (2H, q, J=7.7 Hz, $\underline{CH_2}CH_3$), and 1.25 (3H, t, J=7.7 Hz, $CH_2\underline{CH_3}$); MS *m/z* 264 (M^+, 100). Found: C, 82.06; H, 6.02%. Calcd for $C_{18}H_{16}S$: C, 81.77; H, 6.10%.

4-(*p*-Methoxyphenyl)-2-phenylthiophene (2e). UV 265 (log ε 4.59) and 317 nm (sh, 3.67); ^{1}H NMR (60 MHz) δ=8.05—7.1 (9H, m, including a AA′BB′m at 7.63 and 7.49; 3-H, 5-H, ph, and *p*-Ph), 7.02 and 6.87 (2H, AA′BB′m, *p*-PH), and 3.84 (3H, s, OCH_3); MS *m/z* 266 (M^+, 100). Found: C, 76.65; H, 5.25%. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30%.

4-(2,4-Dimethylphenyl)-2-phenylthiophene (2f). UV 254 (log ε 4.42) and 292 nm (sh, 4.10); ^{1}H NMR (60 MHz) δ=7.85—6.75 (10H, m, 3-H, 5-H, Ph, and three benzene ring protons), and 2.35 (6H, s, CH_3); MS *m/z* 264 (M^+, 100). Found: C, 81.91; H, 6.10%. Calcd for $C_{18}H_{16}S$: C, 81.77; H, 6.10%.

4-(2-Naphthyl)-2-phenylthiophene (2g). UV 231 (log ε 4.45), 259 (4.78), 279 (sh, 4.45), 289 (sh, 4.43), 304 nm (sh, 4.26); ^{1}H NMR (60 MHz) δ=8.2—7.0 (m, 3-H, 5-H, Ph, and 2-Naph (Naph=naphthyl)); MS *m/z* 286 (M^+, 100). Found: C, 84.08; H, 4.79%. Calcd for $C_{20}H_{14}S$: C,

83.88; H, 4.93%.

Preparation of 3-Aryl-2-chlorothiophenes (5). A solution of 3-arylthiophene[3] (**4**; 10 mmol) and SO_2Cl_2 (1.35 g, 10 mmol) in CCl_4 (15 ml) was refluxed for 8 h. The reaction mixture was poured into ice-water (about 30 ml) and the organic layer was separated from the aqueous layer and the aqueous layer was extracted with CCl_4 (10 ml×2). The combined extracts were washed successively with H_2O, 5% $NaHCO_3$ solution, and again H_2O, and dried. After removal of the solvent the residue was chromatographed (silica gel/hexane or hexane–$CHCl_3$ (2:1)), yielding **5** along with small amounts of **4** and the isomeric 4-aryl-2-chlorothiophene (less than 5% of the monochlorinated derivatives of **4**).

2-Chloro-3-phenylthiophene (5a). 51% Yield. Colorless oil, bp 60 °C (bath temp; 2 mmHg; 1 mmHg=133.322 Pa). UV 227 ($\log\varepsilon$ 4.23) and 256 nm (4.06); ^{1}H NMR (60 MHz) δ=7.8—7.25 (5H, m, Ph) and 7.15 and 7.03 (1H, d, J=5.4 Hz each, 4-H and 5-H); MS m/z 194 (M^+, 100) and 196 (M^++2, 39). Found: C, 61.48; H, 3.48%. Calcd for $C_{10}H_7ClS$: C, 61.70; H, 3.62%.

2-Chloro-3-(*p*-tolyl)thiophene (5b). 48% Yield. Colorless oil, bp 75 °C (bath temp; 2 mmHg). UV 230 ($\log\varepsilon$ 4.26) and 259 nm (4.08); ^{1}H NMR (60 MHz) δ=7.55 and 7.41 (2H, AA′BB′m, *p*-Ph), 7.29 and 7.16 (2H, AA′BB′m, *p*-Ph), 7.12 and 7.03 (1H, d, J=5.4 Hz each, 4-H and 5-H), and 2.38 (3H, s, CH_3); MS m/z 208 (M^+, 100) and 210 (M^++2, 36). Found: C, 63.57; H, 4.27%. Calcd for $C_{11}H_9ClS$: C, 63.30; H, 4.35%.

2-Chloro-3-(*p*-ethylphenyl)thiophene (5c). 77% Yield. Colorless oil, bp 90 °C (bath temp; 2 mmHg). UV 230 ($\log\varepsilon$ 4.26) and 259 nm (4.09); ^{1}H NMR (60 MHz) δ= 7.59 and 7.44 (2H, AA′BB′m, *p*-Ph), 7.33 and 7.19 (2H, AA′BB′m, *p*-Ph), 7.13 and 7.04 (1H, d, J=5.9 Hz each, 4-H and 5-H), and 2.70 (2H, q, J=7.7 Hz, $\underline{CH_2}CH_3$), 1.27 (3H, t, J=7.7 Hz, $CH_2\underline{CH_3}$); MS m/z 222 (M^+, 97) and 224 (M^++2, 35). Found: C, 64.93; H, 4.98%. Calcd for $C_{12}H_{11}ClS$: C, 64.71; H, 4.98%.

2-Chloro-3-(*p*-methoxyphenyl)thiophene (5d). 57% Yield. Pale yellow oil, bp 125—130 °C (bath temp; 5×10^{-3} mmHg). UV 235 ($\log\varepsilon$ 4.23) and 267 nm (4.10); ^{1}H NMR (60 MHz) δ=7.58 and 7.43 (2H, AA′BB′m, *p*-Ph), 7.25—6.8 (4H, m including a pair of doublets, J=5.5 Hz, at 7.11 and 6.99 and a AA′BB′m at 7.03 and 6.87; 4-H, and 5-H, and *p*-Ph), and 3.81 (3H, s, OCH_3); MS m/z 224 (M^+, 100) and 226 (M^++2, 37%). Found: C, 58.52; H, 3.91%. Calcd for $C_{11}H_9ClOS$: C, 58.80; H, 4.04%.

$AlCl_3$-Catalyzed Reaction of 3-Aryl-2-chlorothiophenes (5) with Aromatic Compounds. Pulverized $AlCl_3$ (0.68 g, 5 mmol) was added to a mixture of **5** (5 mmol) and aromatic compound (40 mmol) in CH_2Cl_2 (4 ml) under ice-cooling, and the mixture was stirred at about 5 °C for 30 min, then at room temperature for 1 h, and at about 40 °C for additional 30 min. The reaction mixture was poured into ice-water and extracted with $CHCl_3$ (10 ml×2). After usual work-up the solvent and excess aromatic compound were distilled off and the residual mass was chromatographed (silica gel/hexane–$CHCl_3$) to give 2,4-diarylthiophenes (**2**) together with a small amount of unreacted **5**.

The product is less soluble in $CHCl_3$ in the reaction of 2-chloro-3-(*p*-methoxyphenyl)thiophene (**5d**) with anisole. In this case, $CHCl_3$ (about 15 ml) was added to the reaction mixture, and resulting suspension was poured onto ice-water. The precipitates thus separated out were filtered, washed with a small amount of MeOH, and recrystallized to give 2,4-bis(*p*-methoxyphenyl)thiophene (**2l**). Work-up and evaporation of the organic filtrate left a residual mass, which was chromatographed (silica gel/hexane–benzene) to afford another crop of **2l** in small quantity.

5-Chloro-4,4′-diphenyl-2,2′-bithiophene (7). UV (MeOH) 255 ($\log\varepsilon$ 4.62) and 328 nm (4.10); ^{1}H NMR (200 MHz; acetone-*d*) δ=7.9—7.3 (m including a pair of doublets at 7.79 and 7.75, J=1.5 Hz; 3-H, 3′-H, 5′-H, and Ph); MS m/z 352 (M^+, 100) and 354 (M^++2, 44). Found: C, 67.93; H, 3.64%. Calcd for $C_{20}H_{13}S_2Cl$: C, 68.07; H, 3.71%.

Catalytic dechlorination of **7** by the procedure described below for 2,3-diaryl-5-chlorothiophene (**11**) yielded 4,4′-diphenyl-2,2′-bithiophene, mp 225—226.5 °C (lit,[4] 224—225 °C).

2-(*p*-Methoxyphenyl)-4-phenylthiophene (2h). UV (EtOH) 261 ($\log\varepsilon$ 4.55) and 302 nm (sh, 4.11); ^{1}H NMR (200 MHz) δ=7.95—7.2 (9H, m including a AA′BB′m at 7.64 and 7.60, and a pair of doublets at 7.48 and 7.32, J=1.5 Hz; 3-H, 5-H, Ph, and *p*-Ph), 6.95 and 6.91 (2H, AA′BB′m, *p*-Ph), and 3.83 (3H, s, OCH_3); MS m/z 266 (M^+, 100). Found: C, 76.64; H, 5.26%. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30%.

2-(4-Methoxy-1-naphthyl)-4-phenylthiophene (2i). UV (EtOH) 239 (sh, $\log\varepsilon$ 4.49), 248 (sh, 4.44), 314 (4.04), and 323 nm (4.01); ^{1}H NMR (200 MHz) δ=8.5—8.2 (4H, m, 1,4-Naph (1,4-disubstituted naphthalene), 7.65 and 6.83 (1H, d, J=7.5 Hz each, 1,4-Naph), 7.65—7.2 (7H, m, 3-H, 5-H, and Ph), and 4.02 (3H, s, OCH_3); MS m/z 316 (M^+, 100). Found: C, 79.96; H, 5.03%. Calcd for $C_{21}H_{16}OS$: C, 79.71; H, 5.10%.

2-(*p*-Methoxyphenyl)-4-(*p*-tolyl)thiophene (2j). UV (EtOH) 264 ($\log\varepsilon$ 4.60) and 308 nm (sh, 4.05); ^{1}H NMR (200 MHz) δ=7.59 and 7.55 (2H, AA′BB′m, *p*-Ph), 7.53 and 7.49 (2H, AA′BB′m, *p*-Ph), 7.46 and 7.28 (1H, d, J=1.4 Hz each, 3-H and 5-H), 7.23 and 7.19 (2H, AA′BB′m, *p*-Ph), 6.95 and 6.91 (2H, AA′BB′m, *p*-Ph), and 3.83 (3H, s, OCH_3), and 2.37 (3H, s, CH_3); MS m/z 280 (M^+, 100). Found: C, 77.05; H, 5.65%. Calcd for $C_{18}H_{16}OS$: C, 77.11; H, 5.75%.

4-(*p*-Ethylphenyl)-2-(*p*-methoxyphenyl)thiophene (2k). UV (EtOH) 264 ($\log\varepsilon$ 4.61) and 307 nm (sh, 4.07); ^{1}H NMR (200 MHz) δ=7.7—7.5 (4H, m including two AA′BB′m at 7.59 and 7.55 and at 7.56 and 7.52, *p*-Ph), 7.46 (1H, d, J=1.5 Hz, 5-H), 7.35—7.2 (3H, m including a doublet at 7.28, J=1.5 Hz, and a AA′BB′m at 7.26 and 7.22; 3-H, and *p*-Ph), 6.95 and 6.91 (2H, AA′BB′m, *p*-Ph), 3.83 (3H, s, OCH_3), 2.75 (2H, q, J=7.6 Hz, $\underline{CH_2}CH_3$), and 1.26 (3H, t, J=7.6 Hz, $CH_2\underline{CH_3}$); MS m/z 294 (M^+, 100). Found: C, 77.46; H, 6.08%. Calcd for $C_{19}H_{18}OS$: C, 77.51; H, 6.16%.

5-Chloro-5′-(*p*-methoxyphenyl)-2,3′-bithiophene (2m). UV (EtOH) 285 ($\log\varepsilon$ 4.57) and 321 nm (sh, 4.06); ^{1}H NMR (60 MHz) δ=7.61 and 7.47 (2H, AA′BB′m, *p*-Ph), 7.28 and 7.17 (1H, d, J=1.4 Hz each, 2′-H and 4′-H), 7.1—6.8 (4H, m including a AA′BB′m at 6.99 and 6.87 and a pair of doublets, J=3.7 Hz, at 6.96 and 6.84; 3-H, 4-H and *p*-Ph), and 3.84 (3H, s, OCH_3); MS m/z 306 (M^+, 100) and 308 (M^++2, 42). Found: C, 59.01; H, 3.53%. Calcd for $C_{15}H_{11}OClS_2$: C, 58.72; H, 3.61%.

The catalytic dechlorination **2m** as described below for the preparation of **6** from **11** gave 5′-(*p*-methoxyphenyl)-2,3′-bithiophene (**8**; 81%), mp 129—131 °C (hexane–$CHCl_3$). UV (EtOH) 278 ($\log\varepsilon$ 4.56) and 308 nm (sh, 4.13); ^{1}H NMR (200 MHz) δ=7.57 and 7.53 (2H, AA′BB′m, *p*-Ph), 7.38 (1H, d, J=1.4 Hz, 2′-H or 4′-H), 7.35—7.2 (3H, m including a doublet at 7.24, J=1.4 Hz; 2′-H or 4′-H, 3-H, and 5-H), 7.15—7.0 (1H, m, 4-H), 6.94 and 6.90 (2H, AA′BB′m, *p*-Ph), and 3.82 (3H, s, OCH_3); MS m/z 272 (M^+, 100). Found: C, 65.90; H, 4.39%. Calcd for $C_{15}H_{12}OS_2$: C, 66.14; H, 4.44%.

Preparation of 3-Aryl-5-chloro-2-iodothiophenes (9). To a solution of 2-chloro-4-arylthiophene (**1**; 10 mmol) in acetic acid (50 ml) was added ground crystals of KI (10 mmol) and then KNO_3 (15 mmol) with stirring. The reaction mixture was carefully heated to reflux. The color of the mixture turned purple with the evolution of brown nitrogen oxides gas. After being refluxed for 30 min, the reaction mixture was poured into H_2O (50 ml) and extracted with $CHCl_3$ (20 ml×3). The $CHCl_3$ extracts were combined, washed with 10% $Na_2S_2O_3$ (30 ml), and then H_2O (20 ml×2), and dried. The solvent was removed and the residual oil was chromatographed (silica gel/hexane) to give the iodides **9** and 3-aryl-5-chloro-2-nitrothiophene (**10**).

5-Chloro-2-iodo-3-phenylthiophene (9a). 78% Yield. Yellow viscous oil, bp 70 °C (bath temp; 1×10^{-3} mmHg). UV 236 ($\log\varepsilon$ 4.28) and 267 nm (3.96); ^{1}H NMR (60 MHz) δ=7.42 (5H, s, Ph) and 6.80 (1H, s, 4-H); MS m/z 320 (M^+, 100) and 322 (M^++2, 37%). Found: C, 37.64; H, 1.83%. Calcd for $C_{10}H_6ClIS$: C, 37.47; H, 1.83%.

5-Chloro-2-nitro-3-phenylthiophene (10a). 17% Yield. Yellow needles, mp 97—98 °C (hexane). UV 221 (sh, $\log\varepsilon$ 4.06), 252 (sh, 3.58), and 328 nm (4.03); ^{1}H NMR (60 MHz) δ=7.44 (5H, s, Ph) and 6.91 (1H, s, 4-H); MS m/z 239 (M^+, 100) and 241 (M^++2, 37). Found: C, 50.14; H, 2.39; N, 5.91%. Calcd for $C_{10}H_6ClNO_2S$: C, 50.11; H, 2.52; N, 5.84%.

5-Chloro-2-iodo-3-(*p*-tolyl)thiophene (9b). 72% Yield. Yellow viscous oil, bp 95 °C (bath temp; 1×10^{-3} mmHg). UV 239 ($\log\varepsilon$ 4.32) and 268 nm (3.99); ^{1}H NMR (60 MHz) δ=7.44 and 7.29 (2H, AA′BB′m, *p*-Ph), 7.26 and 7.11 (2H, AA′BB′m, *p*-Ph), 6.78 (1H, s, 4-H), and 2.38 (3H, s, CH_3); MS m/z 334 (M^+, 100) and 336 (M^++2, 39). Found: C, 39.77; H, 2.24%. Calcd for $C_{11}H_8ClIS$: C, 39.48; H, 2.41%.

5-Chloro-2-nitro-3-(*p*-tolyl)thiophene (10b). 20% Yield. Yellow needles, mp 99—100 °C (hexane). UV 222 ($\log\varepsilon$ 4.14), 258 (sh, 3.62), and 329 nm (4.02); ^{1}H NMR (60 MHz) δ=7.29 (4H, s, *p*-Ph), 6.88 (1H, s, 4-H), and 2.40 (3H, s, CH_3); MS m/z 253 (M^+, 100) and 255 (M^++2, 38). Found: C, 52.15; H, 3.01; N, 5.57%. Calcd for $C_{11}H_8ClNO_2S$: C, 52.08; H, 3.18; N, 5.52%.

5-Chloro-3-(*p*-ethylphenyl)-2-iodothiophene (9c). 78% Yield. Yellow viscous oil, bp 100 °C (bath temp; 1×10^{-3} mmHg). UV 240 ($\log\varepsilon$ 4.34) and 269 nm (4.01); ^{1}H NMR (60 MHz) δ=7.46 and 7.33 (2H, AA′BB′m, *p*-Ph), 7.29 and 7.15 (2H, AA′BB′m, *p*-Ph), 6.79 (1H, s, 4-H), 2.69 (2H, q, J=7.6 Hz, $\underline{CH_2}CH_3$), and 1.26 (3H, t, J=7.6 Hz, $CH_2\underline{CH_3}$); MS m/z 348 (M^+, 100) and 350 (M^++2, 36). Found: C, 41.35; H, 2.69%. Calcd for $C_{12}H_{10}ClIS$: C, 41.33; H, 2.89%.

5-Chloro-3-(*p*-ethylphenyl)-2-nitrothiophene (10c). 17% Yield. Yellow needles, mp 71—72 °C (hexane). UV 222 ($\log\varepsilon$ 4.17), 258 (sh, 3.63), and 329 nm (4.02); ^{1}H NMR (60 MHz) δ=7.52 and 7.33 (2H, AA′BB′m, *p*-Ph), 7.33 and 7.14 (2H, AA′BB′m, *p*-Ph), 6.90 (1H, s, 4-H), 2.73 (2H, q, J=7.3 Hz, $\underline{CH_2}CH_3$), and 1.28 (3H, t, J=7.3 Hz, $CH_2\underline{CH_3}$); MS m/z 267 (M^+, 100) and 269 (M^++2, 37). Found: C, 53.94; H, 3.63; N, 5.27%. Calcd for $C_{12}H_{10}ClNO_2S$: C, 53.83; H, 3.76; N, 5.23%.

5-Chloro-2-iodo-3-(*p*-methoxyphenyl)thiophene (9d). 66% Yield. Yellow viscous oil, bp 110 °C (bath temp; 1×10^{-3}). UV 245 ($\log\varepsilon$ 4.34) and 271 nm (4.05); ^{1}H NMR (60 MHz) δ=7.46 and 7.31 (2H, AA′BB′m, *p*-Ph), 6.86 and 7.00 (2H, AA′BB′m, *p*-Ph), 6.77 (1H, s, 4-H), and 3.83 (3H, s, OCH_3); MS m/z 350 (M^+, 100) and 352 (M^++2, 38). Found: C, 37.80; H, 2.15%. Calcd for $C_{11}H_8ClIS$: C, 37.68; H, 2.30%.

5-Chloro-3-(*p*-methoxyphenyl)-2-nitrothiophene (10d). 28% Yield. Yellow needles, mp 112—113 °C (hexane). UV 231 ($\log\varepsilon$ 4.21), 264 (sh, 3.75), 330 (3.97), and 383 nm (sh, 3.74); ^{1}H NMR (60 MHz) δ=7.50 and 7.35 (2H, AA′BB′m, *p*-Ph), 7.03 and 6.89 (2H, AA′BB′m, *p*-Ph), 6.89 (1H, s, 4-H), and 3.86 (3H, s, OCH_3); MS m/z 269 (M^+, 100) and 271 (M^++2, 36). Found: C, 49.05; H, 2.82; N, 5.23%. Calcd for $C_{11}H_8ClNO_3S$: C, 48.99; H, 2.99; N, 5.19%.

5-Chloro-5′-iodo-2,2′-bithiophene (13). To a ice-cooled and vigorously stirred solution of 5-chloro-2,2′-bithiophene[15] (4.0 g, 20 mmol) in benzene (50 ml), HgO (yellow, 4.3 g, 20 mmol) and I_2 (5.1 g, 20 mmol) were added alternately in small amounts during a period of 10 min. The reaction mixture was stirred for 2 h under ice-cooling. The mixture was filtered and the residue (HgI_2) was washed with benzene (50 ml×2). The combined benzene filtrates were shaken with 10% $Na_2S_2O_3$ (50 ml×2) to remove excess I_2 and then with H_2O (50 ml×2) and dried. After removal of the solvent, the residue was recrystallized from hexane to give **13** (3.4 g, 52%), mp 125—126 °C. UV 243 ($\log\varepsilon$ 3.78), 257 (sh, 3.64), 320 (4.26), 335 (sh, 4.21), and 354 nm (3.84); ^{1}H NMR (60 MHz) δ=7.15 (1H, d, J=3.9 Hz, 4′-H) and 6.95—6.65 (3H, m including three doublets at 6.89, J=3.9, 6.80, J=3.9 and 6.76, J=3.9 Hz; 4-H, 3-H, and 3′-H); MS m/z 326 (M^+, 100) and 328 (M^++2, 40). Found: C, 29.32; H, 1.10%. Calcd for $C_8H_4ClS_2$: C, 29.42; H, 1.23%.

Coupling of 3-Aryl-5-chloro-2-iodothiophenes (9) with Arylmagnesium Halides. a) In the Presence of PPh_3: Grignard reagent which was prepared from iodobenzene (3.05 g, 15 mmol) and Mg (0.4 g, 16.5 mmol) was reacted with **9** (5 mmol) in the presence of $Ni(acac)_2$ (64 mg, 0.25 mmol) and PPh_3 (130 mg, 0.5 mmol) for 1 h in a similar manner as described for the coupling of 4-aryl-2-chlorothiophenes (**1**) with PhMgI. After removal of the solvent from $CHCl_3$ extract of the products, the residual mass was chromatographed (silica gel/hexane); two main fractions consisting of a mixture of 2,3-diaryl-5-chlorothiophene (**11**) and biphenyl, and 2,3,5-triarylthiophene (**12**) were obtained in order of decreasing R_f. Elimination of biphenyl (about 0.3 g) from the mixture by sublimation under reduced pressure (60—70 °C (bath temp)/2 mmHg) afforded **11**, while evaporation of the second fraction gave **12**. The crude products were recrystallized from hexane.

b) In the Absence of PPh_3: Dry benzene (10 ml) was added to a Grignard reagent which was prepared from an

aryl iodide (15 mmol) and Mg (0.4 g, 16.5 mmol) in dry ether (20 ml). To the Grignard solution was added under reflux a mixture of 5-chloro-2-iodo-3-phenylthiophene **9a** (5 mmol) and $Ni(acac)_2$ (15 mg; 0.06 mmol) in dry benzene (20 ml). The resulting brown black solution was refluxed with stirring for 1 h. The reaction mixture was poured into 20% NH_4Cl solution (50 ml), worked up, and evaporated. The residue contained, besides desired **11**, biaryl which was produced by homocoupling of Ar'MgI and, in addition to them, unreacted iodide **9** and deiodination products **1** in some cases which were removed by column chromatography (silica gel/hexane). The diarylthiophenes, **11b** and **11d**, were obtained by the repeated chromatography of the residue in each case. After removal of **9** and/or **1**, the diarylthiophene **11a** (90—110 °C (bath temp)/2 mmHg) were isolated from biphenyl (60—80 °C (bath temp)/2 mmHg; mp 69—70 °C) by sublimation under reduced pressure of the residue originated from the reactions with 2-thienylmagnesium iodide. Likewise, distillation under reduced pressure of the residue resulted from 3-methyl-2-thienylmagnesium iodide yielded **11c** as viscous yellow oil together with 3,3'-dimethyl-2,2'-bithiophene (100—120 °C (bath temp)/1 mmHg; lit,[16] 131°C/11 mmHg) ^{1}H NMR (60 MHz) δ=6.93 and 7.26 (2H, d, J=5.1 Hz each, 4-, 4'-, 5-, and 5'-H), and 2.18 (6H, s, CH_3). The solid products were purified by recrystallization from hexane.

2-Chloro-4,5-diphenylthiophene (11a). UV 240 ($\log\varepsilon$ 4.31) and 292 nm (4.00); ^{1}H NMR (60 MHz) δ=7.25 (10H, s, Ph) and 6.99 (1H, s, 3-H); MS m/z 270 (M^+, 100) and 272 (M^++2, 42). Found: C, 70.93; H, 3.91%. Calcd for $C_{16}H_{11}ClS$: C, 70.97; H, 4.09%.

2,3,5-Triphenylthiophene (12a). UV 262 ($\log\varepsilon$ 4.36) and 319 nm (4.10); ^{1}H NMR (60 MHz) δ=8.0—7.0 (m, 4-H and Ph); MS m/z 312 (M^+, 100). Found: C, 84.72; H, 5.10%. Calcd for $C_{22}H_{16}S$: C, 84.58; H, 5.16%.

5-Chloro-3-phenyl-2,2'-bithiophene (11b). UV 245 ($\log\varepsilon$ 4.23) and 313 nm (3.96); ^{1}H NMR (60 MHz) δ=7.32 (5H, s, Ph) and 7.25—6.8 (4H, m, 4-H and Th); MS m/z 276 (M^+, 100) and 278 (M^++2, 43). Found: C, 61.01; H, 3.05%. Calcd for $C_{14}H_9ClS_2$: C, 60.75; H, 3.28%.

5-Chloro-3'-methyl-3-phenyl-2,2'-bithiophene (11c). UV 239 ($\log\varepsilon$ 4.33) and 295 nm (3.87); ^{1}H NMR (60 MHz) δ=7.3—6.8 (8H, m including a singlet at 7.05 ascribable to 4-H, a doublet at 6.79, J=4.9 Hz; 4'-H, 5'-H, and Ph) and 1.85 (3H, s, CH_3); MS m/z 290 (M^+, 100) and 292 (M^++2, 41). Found: C, 61.88; H, 3.67%. Calcd for $C_{15}H_{11}ClS_2$: C, 61.95; H, 3.81%.

5',5''-Dichloro-3'-phenyl-2,2':5,2''-terthiophene (11d). UV 240 ($\log\varepsilon$ 4.20) and 360 nm (4.31); ^{1}H NMR (60 MHz) δ=7.35 (5H, s, Ph) and 7.0—6.7 (5H, m including a pair of doublet, J=3.8 Hz, at 6.94 and 6.77; 3-H, 4-H, 3''-H, 4''-H, and 4'-H); MS m/z 392 (M^+, 100) and 394 (M^++2, 82). Found: C, 55.07; H, 2.39%. Calcd for $C_{18}H_{10}Cl_2S_3$: C, 54.96; H, 2.56%.

2-Chloro-5-phenyl-4-(*p*-tolyl)thiophene (11e). UV 242 ($\log\varepsilon$ 4.37) and 293 nm (4.04); ^{1}H NMR (60 MHz) δ=7.23 (5H, s, Ph), 7.08 (4H, s, *p*-Ph), 6.95 (1H, s, 3-H), and 2.31 (3H, s, CH_3); MS m/z 284 (M^+, 100) and 286 (M^++2, 39). Found: C, 71.83; H, 4.54%. Calcd for $C_{17}H_{13}ClS$: C, 71.69; H, 4.60%.

2,5-Diphenyl-3-(*p*-tolyl)thiophene (12b). UV 265 ($\log\varepsilon$ 4.39) and 320 nm (4.27); ^{1}H NMR (60 MHz) δ=7.8—6.75 (15H, m, 4-H, Ph, and *p*-Ph) and 2.33 (3H, s, CH_3); MS m/z 326 (M^+, 100). Found: C, 84.80; H, 5.49%. Calcd for $C_{23}H_{18}S$: C, 84.62; H, 5.56%.

2-Chloro-4-(*p*-ethylphenyl)-5-phenylthiophene (11f). UV 243 ($\log\varepsilon$ 4.38) and 292 nm (4.03); ^{1}H NMR (60 MHz) δ=7.25 (5H, s, Ph), 7.12 (4H, s, *p*-Ph), 6.97 (1H, s, 3-H), 2.64 (2H, q, $\underline{CH_2}CH_3$), and 1.23 (3H, t, $CH_2\underline{CH_3}$); MS m/z 298 (M^+, 100) and 300 (M^++2, 36). Found: C, 72.54; H, 5.04%. Calcd for $C_{18}H_{15}ClS$: C, 72.25; H, 5.06%.

3-(*p*-Ethylphenyl)-2,5-diphenylthiophene (12c). UV 265 ($\log\varepsilon$ 4.41) and 320 nm (4.27); ^{1}H NMR (60 MHz) δ=6.85—7.8 (15H, m, 4-H, Ph, and *p*-Ph), 2.66 (2H, q, $\underline{CH_2}CH_3$), and 1.24 (3H, t, $CH_2\underline{CH_3}$); MS m/z 340 (M^+, 100). Found: C, 84.91; H, 5.87%. Calcd for $C_{24}H_{20}S$: C, 84.66; H, 5.92%.

2-Chloro-4-(*p*-methoxyphenyl)-5-phenylthiophene (11g). UV 245 ($\log\varepsilon$ 4.36) and 294 nm (4.06); ^{1}H NMR (60 MHz) δ=7.23 (5H, s, Ph), 7.2—6.65 (5H, m including a singlet at 7.07 and AA'BB'm at 7.07 and 6.94, and at 6.84 and 6.70; 3-H, and *p*-Ph), and 3.76 (3H, s, OCH_3); MS m/z 300 (M^+, 100), 302 (M^++2, 38). Found: C, 68.09; H, 4.28%. Calcd for $C_{17}H_{13}ClOS$: C, 67.88; H, 4.36%.

3-(*p*-Methoxyphenyl)-2,5-diphenylthiophene (12d). UV 271 ($\log\varepsilon$ 4.40) and 322 nm (4.24); ^{1}H NMR (60 MHz) δ=7.85—7.0 (13H, m, 4-H, Ph, and *p*-Ph), 6.90 and 6.75 (2H, AA'BB'm, *p*-Ph), and 3.80 (3H, s, OCH_3); MS m/z 342 (M^+, 100). Found: C, 80.93; H, 5.20%. Calcd for $C_{23}H_{18}OS$: C, 80.67; H, 5.30%.

Catalytic Dechlorination of 2,3-Diaryl-5-chlorothiophene (11). The reaction was done by stirring a mixture of **11** (1.5 mmol), 10% Pd–C (0.3 g), KOH (0.6 g), and MeOH (30 ml) at about 40 °C in an atmospheric pressure hydrogenation apparatus filled with H_2. After hydrogenation was complete (within 1.5 h), the catalyst was removed by filtration and washed with $CHCl_3$ (30 ml) and the filtrate was concentrated. The residue was dissolved in the $CHCl_3$ washing and the solution was washed successfully with H_2O (20 ml), 10% HCl (20 ml), and H_2O (20 ml) and dried. The solvent was removed by distillation, and the residue was chromatographed (silica gel/hexane) and recrystallized from hexane to give diarylthiophenes **6**.

2,3-Diphenylthiophene (6a). UV 237 ($\log\varepsilon$ 4.27) and 275 nm (4.01) (lit,[11b] (96% EtOH) 238 (4.30) and 278 nm (4.05)); ^{1}H NMR (60 MHz) δ=7.4—7.05 (m including a doublet, J=5.0 Hz, at 7.15; 4-H, 5-H, and Ph); MS m/z 236 (M^+, 100).

3-Phenyl-2,2'-bithiophene (6b). UV 246 ($\log\varepsilon$ 4.17) and 304 nm (3.91); ^{1}H NMR (60 MHz) δ=7.35 (5H, s, Ph) and 7.3—6.85 (5H, m, 4-H, 5-H, and Th); MS m/z 242 (M^+, 100). Found: C, 69.24; H, 3.91%. Calcd for $C_{14}H_{10}S_2$: C, 69.38; H, 4.16%.

3'-Methyl-3-phenyl-2,2'-bithiophene (6c). UV 227 ($\log\varepsilon$ 4.19), 246 (4.23), 270 (sh, 3.97), and 296 nm (sh, 3.80); ^{1}H NMR (60 MHz) δ=7.55—7.15 (8H, m including a doublet, J=5.4 Hz at 7.40 and a prominent peak at 7.27; three thiophene ring protons and Ph), 6.80 (1H, d, J=5.0 Hz, a thiophene ring proton), and 1.84 (3H, s, CH_3); MS m/z 256 (M^+, 100). Found: C, 70.23; H, 4.58%. Calcd for $C_{15}H_{12}S_2$: C, 70.27; H, 4.72%.

3'-Phenyl-2,2':5,2''-terthiophene (6d). UV 248 ($\log\varepsilon$ 4.15) and 350 nm (4.27); ^{1}H NMR (60 MHz) δ=7.45—6.8 (m, 3-H, 4-H, 4'-H, 5'-H, Th, and Ph); MS m/z 324

(M^+, 100). Found: C, 66.43; H, 3.55%. Calcd for $C_{18}H_{12}S_3$: C, 66.63; H, 3.73%.

2-Phenyl-3-(*p*-tolyl)thiophene (6e). UV 239 ($\log\varepsilon$ 4.31) and 277 nm (4.15); ^{1}H NMR (60 MHz) δ=7.5—7.05 (11H, m, 4-H, 5-H, Ph, and *p*-Ph) and 2.33 (3H, s, CH_3); MS *m/z* 250 (M^+, 100). Found: C, 81.50; H, 5.55%. Calcd for $C_{17}H_{14}S$: C, 81.56; H, 5.64%.

3-(*p*-Ethylphenyl)-2-phenylthiophene (6f). UV 239 ($\log\varepsilon$ 4.32) and 275 nm (4.06); ^{1}H NMR (60 MHz) δ= 7.5—7.0 (11H, m, 4-H, 5-H, Ph, and *p*-Ph), 2.64 (2H, q, $\underline{CH_2}CH_3$) and 1.23 (3H, t, $CH_2\underline{CH_3}$); MS *m/z* 264 (M^+, 100). Found: C, 81.96; H, 6.00%. Calcd for $C_{18}H_{16}S$: C, 81.77; H, 6.10%.

2-(*p*-Methoxyphenyl)-3-phenylthiophene (6g). UV 240 ($\log\varepsilon$ 4.34) and 279 nm (4.10); ^{1}H NMR (60 MHz) δ=7.5—7.0 (9H, m including a pair of doublets, J=5.1 Hz, at 7.30 and 7.11; 4-H, 5-H, Ph, and *p*-Ph), 6.88 and 6.73 (2H, AA′BB′m, *p*-Ph), and 3.78 (3H, s, OCH_3); MS *m/z* 266 (M^+, 100). Found: C, 76.83; H, 5.27%. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30%.

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