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HYPERVALENT IODINE INDUCED OXIDATIVE CROSS COUPLING *VIA* THIOPHENE CATION RADICAL INTERMEDIATE

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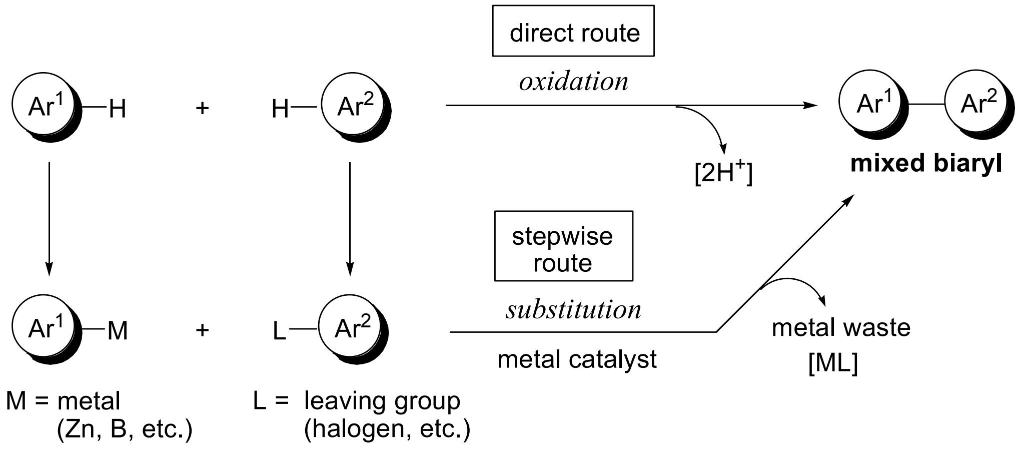
Abstract – The hypervalent iodine-induced arene cross coupling *via* a single-electron-transfer (SET) oxidation process could proceed in some extent even in heteroaromatic compounds, that is, several types thiophenes **1**, using alkyl benzenes **2** as coupling partners. The structure of the obtainable heteroaromatic biaryl products could be elaborated by utilizing the known metal-catalyzed coupling technology, *i.e.*, Negishi cross coupling, for the synthesis of multiple arylated (bi)thiophenes.

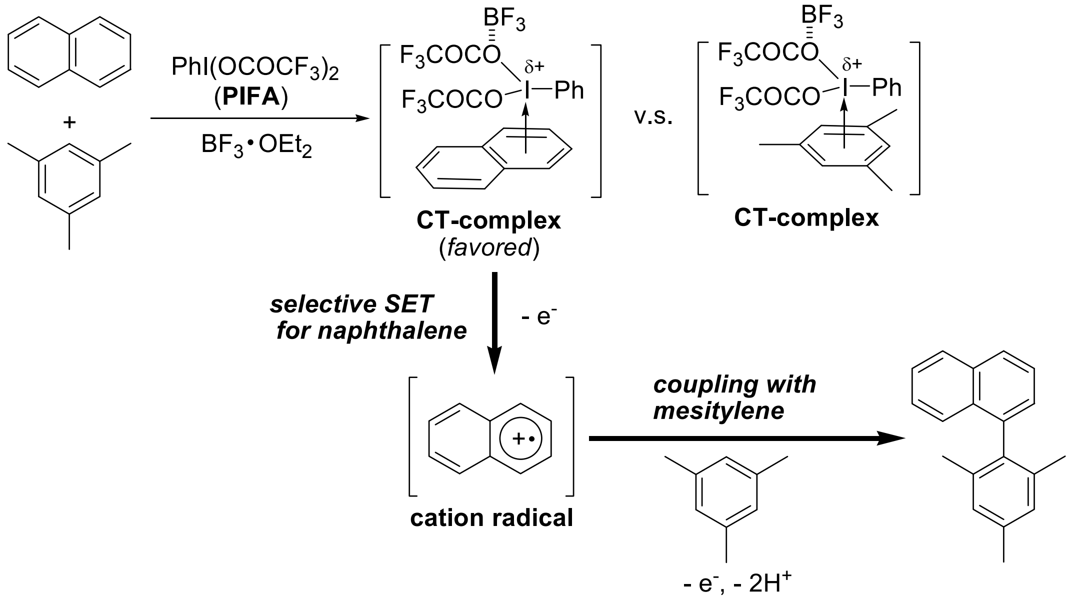
Dedicated to the Honor of Professor Ei-ichi Negishi.

The well-established cross coupling technologies using transition metal catalysts, such as the so-called Negishi coupling and Suzuki coupling,[1] are the most promising strategies to form new aryl carbon-carbon bonds of required biary structures.[2] The 1st generation cross couplings typically deal with extensive organic halides and organometallic compounds (*e.g.*, metal = [Zn]; Negishi, [B]; Suzuki) as pre-functionalized and activated aryl substrates (Scheme 1, stepwise route). Recently, rapid evolution of this area has opened a new opportunity of cross couplings with non-functionalized substrates.[3] One of them, the oxidative coupling between some unactivated aryl molecules, which only causes the loss of two protons from two coupling substrates, has become possible using transition metal catalysts with suitable stoichiometric terminal oxidants (Scheme 1, direct route).[4] This method can avoid the stepwise route, and decreases the steps and amount of released metal wastes classically observed in the 1st generation couplings. Needless to say, transition metal catalysts, such as palladium, persists for aiding the reaction progress in the latter oxidative cross coupling method, while a metal catalyst-free system, that only uses an oxidant, providing a direct route to biaryls, is quite limited and still remains as an important challenge in modern biaryl synthesis.



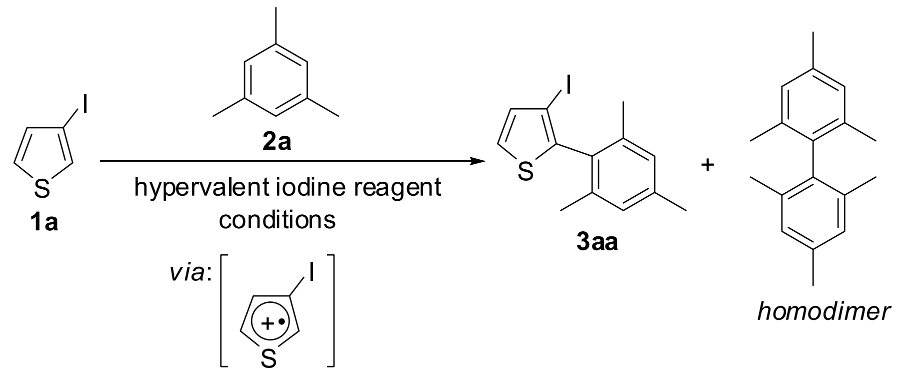
Scheme 1. Arene Cross Coupling: Direct and Stepwise Routes to Biaryls. (Ar^1, Ar^2 = aryl)

Over the past decades, we have continually tackled the development of a new metal-catalyst-free strategy utilizing an unique oxidation ability of hypervalent iodine reagents for the direct coupling route to biaryls.[5] Under suitable activation conditions, hypervalent iodine reagents show single-electron- transfer (SET) oxidation abilities toward various electron-rich aromatic rings.[6,7] It was also revealed that oxidative couplings of electron-rich aromatic hydrocarbons, *i.e.*, alkylbenzenes and phenyl ethers, smoothly proceed *via* their reactive aromatic cation radicals generated *in situ* by the action of $PhI(OCOCF_3)_2$ [phenyliodine(III) bis(trifluoroacetate), PIFA] with Lewis acids.[8] Recently, we extended the strategy for the first time to the corresponding intermolecular cross coupling versions.[9] The unprecedented formation of the cross coupling products of naphthalenes and alkylbenzenes would well explain the exclusive charge-transfer (CT) complexion of the naphthalene rings toward the suitably activated hypervalent iodine reagent (Scheme 2), from which subsequent generation of the naphthalene cation radicals should occur by the hypervalent iodine-induced SET oxidations. The nucleophilic alkylbenzenes, *e.g.*, mesitylene,[10] on the other hand, could attack the cationic intermediates, effectively producing the cross coupling products. We believe that the naphthalenes and the alkylbenzenes are thus regarded as indispensable aromatic cation radical sources and nucleophiles, respectively, for the successful cross couplings. Based on these considerations, the possibility of the SET oxidation strategy for the cross coupling for heteroaromatic compounds has not yet been fully investigated,[11,12] though generation of heteroaromatic cation radicals has already been confirmed in the homocoupling studies.[13]



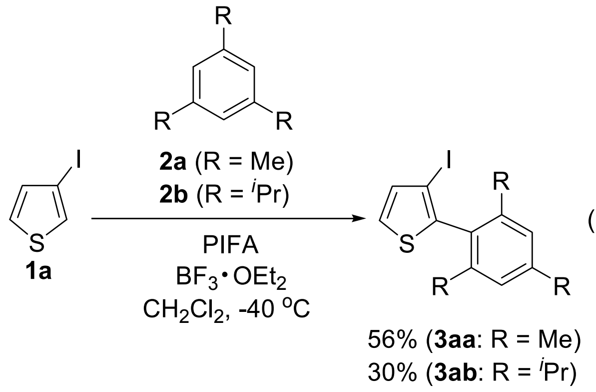
Scheme 2. Hypervalent Iodine Induced SET Strategy for Oxidative Arene Cross Coupling.

In this paper, we report the examinations and results of our cross coupling based on the SET oxidation strategy in heteroaromatic compounds, specifically, thiophenes **1**. Actually, halothiophene **1a** *via* its cation radical was first found to be a substrate for coupling with mesitylene **2a** (Eq. 1). Using 3 equiv. of mesitylene **2a** referred to the thiophene **1a**, the desired cross coupling thiophene biaryl **3aa** was formed in a moderate yield (56%) under the standard condition using PIFA (1 equiv.) and $BF_3·Et_2O$ (2 equiv.) in dichloromethane (0.1 M concentration for the substrate **1a**).[9a] However, we were also aware that the use of an excess amount of mesitylene **2a** produced a significant amount of its homocoupling dimer (ca. 20% formation). Thus, the reaction was re-tested using a lower amount of mesitylene **2a** (1.5 equiv.), but the yield of the coupling product **3aa** decreased to 40%. Unfortunately, screening of the concentration, temperature, and solvent for the reaction resulted in no considerable improvement in the ratio of the cross coupling product **3aa** versus the mesitylene homocoupling dimer. FPIFA (pentafluorophenyliodine(III) bis(trifluoroacetate), $C_6F_5I(OCOCF_3)_2$) was apparently an effective reagent for inducing the biaryl coupling reaction,[9b] and indeed could provide the two products, **3aa** (63%) and the mesitylene homodimer (33%), in a 96% total yield, while the selectivity decreased to 66 : 34 ratio (**3aa** : homodimer) similar to the previous study in mesitylene **2a**.[9a]

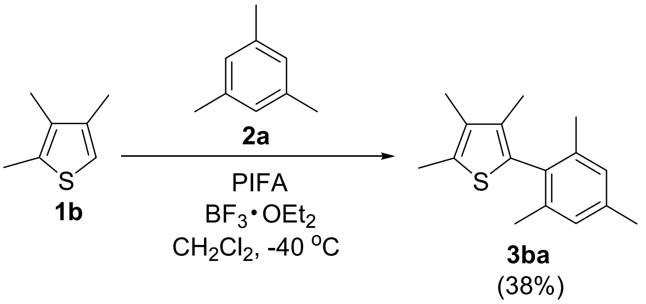


(1)

In spite of the low reaction yield, other alkylbenzene **2b** could partially produce the cross coupling product **3ab** by the reaction of the halothiophene **1a** under the standard conditions at -40 °C (Eq. 2). In comparison, the homocoupling problem was rather suppressed in the sterically hindered alkylbenzene **2b**. Indeed, the formation of very small amount (<5%) of homodimer was observed. Similarly, the alkylthiophene **1b** was coupled with mesitylene **2a**, albeit in a lower product yield than in the case of the halothiophene **1a** (Eq. 3).

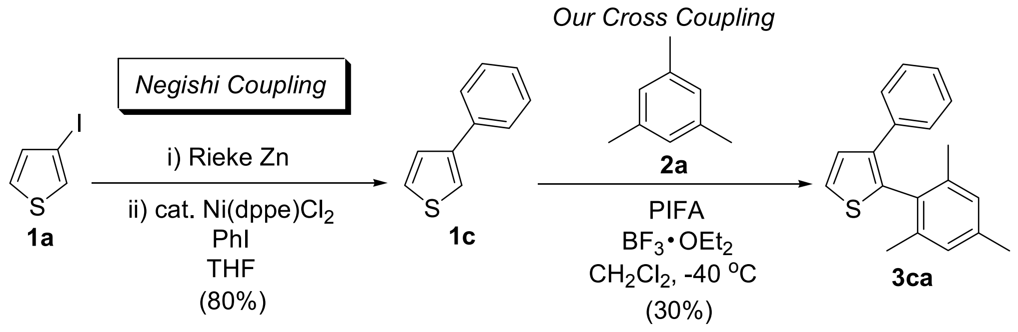


(2)



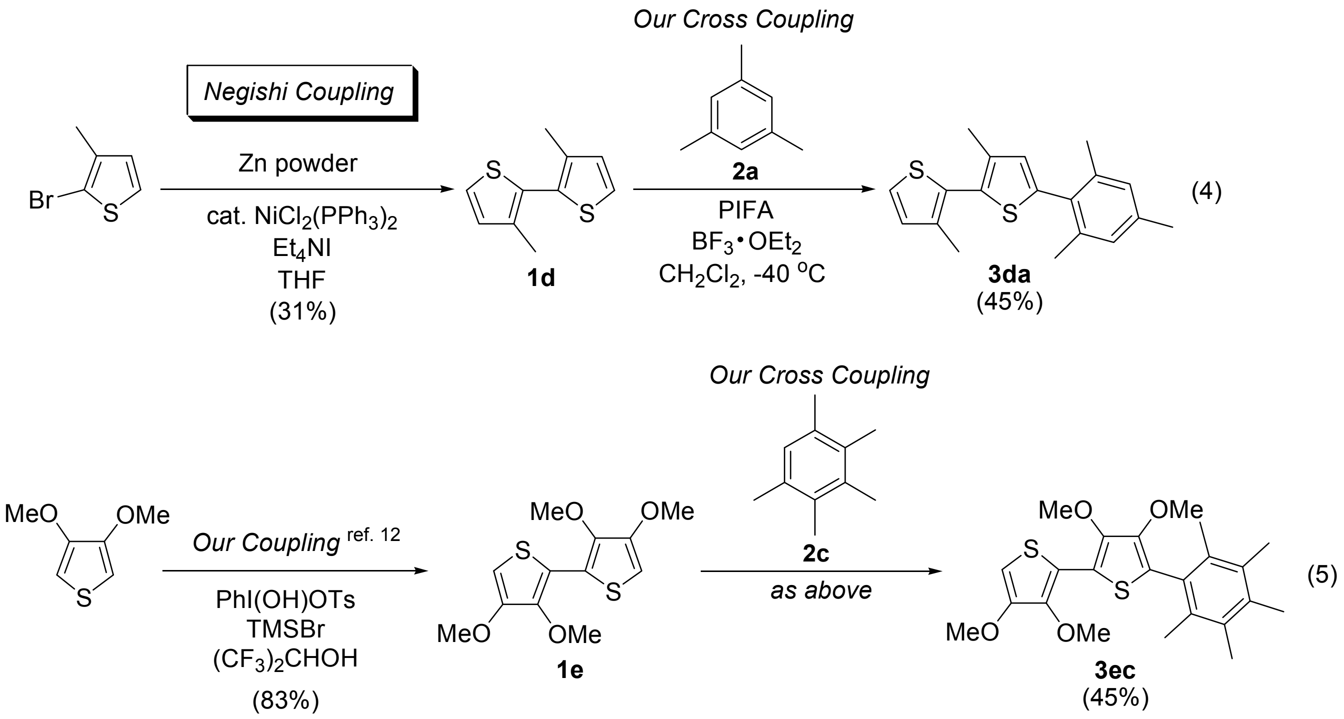
(3)

It is known that multiple arylated thiophenes are interesting synthetic targets being valuable in modern organic chemistry.[14] Inspired by this and expand the range of the obtainable thiophene biaryl products **3**, our coupling strategy should be utilized along with the well-known metal-catalyzed coupling technologies. Thus, we prepared 3-arylthiophene **1c** from the halothiphene **1a** by the standard Negishi coupling,[15a] and examined it for the hypervalent iodine-induced oxidative cross coupling in order to obtain a diarylated thiophene product (Scheme 3). Consequently, the thiophene **1c** containing a phenyl group has become a possible entry to our cross coupling strategy, and the two coupling sequences, *i.e.*, the Negishi coupling followed by our metal-free coupling, could provide the diarylthiophene **3ca** in only two steps from the halothiophene **1a**.



Scheme 3. Multiple Arylated Thiophene **3ca** by Collaboration of Our Method with Negishi Coupling. (dppe = 1,2-bis(diphenylphosphino)ethane)

Notably, bithiophenes have appeared as acceptable substrates, whose successes in oxidative coupling are very rare and quite specific in our method (Scheme 4). One example is that the metal-free coupling method was compatible with the alkylated bithiophene **1d**[15b] to give a linear teraryl compound **3da** (Eq. 4). The more electron-rich oxygenated bithiophene **1e**, prepared by our coupling method,[12] could also couple with pentamethylbenzene **2c** to give a linear teraryl compound **3ec** (Eq. 5). The oxygenated thiophene dimers and oligomers obtained in such a sequence have been found to be new applications as important structural units of several low band gap organic materials.[16] Due to the lower oxidation potential of bithiophenes compared to the corresponding thiophene monomers, the oxidation-sensitive bithiophene **1e** should be the most problematic substrate to control its reaction in other oxidative coupling methods. Thus, the hypervalent iodine-used case in Eq. 5 is, to our knowledge, the only successful example to date of the oxygenated bithiophene being supplied as a successful substrate in an oxidative cross coupling reaction.



Scheme 4. Cross Coupling of Bithiophenes **1d** and **1e**.

In summary, we have evaluated in this paper a series of halo-, alkyl-, aryl-, and bi-thiophenes **1a-e**, as useful heteroaromatic coupling substrates in the cross coupling with mesitylene **2a** and its analogues *via* the SET oxidation processes using hypervalent iodine reagents. The obtainable aryl-aryl linked systems in our coupling method should be further expanded when combined with the known Negishi cross coupling technology for the expeditious access to multiple arylated thiophenes.

EXPERIMENTAL

Melting points (mp) are uncorrected. All ^{1}H- and ^{13}C-NMR spectra of the products were measured in $CDCl_3$. Chemical shifts of ^{1}H-NMR were recorded in parts per million (ppm, δ) relative to tetramethyl silane (δ = 0.00 ppm) as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, sep = septet, m = multiplet), coupling constant (*J*) in Hz, and integration. Chemical shifts of ^{13}C-NMR were reported in ppm with the solvent as reference peak ($CDCl_3$: δ = 77.0 ppm). Infrared spectra (IR) were recorded by using a Hitachi 270-50 spectrometer; intensities of absorptions are reported in reciprocal centimeters (cm^{-1}). High resolution mass measurements and elemental analysis were performed by the Elemental Analysis Section of Osaka University and the Analysis Section of Osaka University of Pharmaceutical Sciences. Flash column chromatography was performed with Merck Silica Gel 60 (230-400 mesh) eluting with hexane and ethyl acetate. Thin-layer chromatography (TLC) was performed on Merk Silica Gel F_{254} plates (0.25 mm). The spots and bands were detected by UV light of irradiation (254, 365 nm).

Materials

Hypervalent iodine reagents, PhI$(OCOCF_3)_2$ (PIFA) and $C_6F_5I(OCOCF_3)_2$ (FPIFA), are commercially available. Trimethylthiophene **1b** was prepared according to literature.[17] All other chemicals and solvents for the experiments and chromatography were obtained from commercial suppliers, and used as received.

General procedure for the cross coupling reaction of thiophenes 1 using hypervalent iodine reagent

To a stirred solution of iodothiophene **1a** (1.04 g, 5 mmol) and alkylbenzene nucleophile **2a** (1.80 g, 15 mmol, 3 equiv.) in CH_2Cl_2 (0.1 M referred to **1a**) was successively added $BF_3 \cdot Et_2O$ (1.27 mL, 10 mmol, 2 equiv.) and PIFA (2.15 g, 5 mmol, 1 equiv.) under a nitrogen atmosphere at -40 °C. The reaction mixture was stirred for 3 h at the same temperature, then quenched with a saturated aqueous $NaHCO_3$ solution. After extraction using CH_2Cl_2, the obtained organic layer was dried over anhydrous Na_2SO_4. After filtration, removal of the solvent *in vacuo* followed by column chromatography of the residue gave the pure cross coupling product, the thiophene biaryl **3aa** (0.92 g, 2.8 mmol), in 56% yield.

3-Iodo-2-(2,4,6-trimethylphenyl)thiophene (3aa)

Colorless crystals; mp 120-122 °C; IR (KBr): 3101, 2914, 2729, 1735, 1608, 1473, 1440, 1373, 1334, 1224, 1136, 1031, 968, 910, 852, 790, 734, 715, 640, 553 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): 2.04 (s, 6H), 2.33 (s, 3H), 6.95 (s, 2H), 7.14 (d, J = 5.1 Hz, 1H), 7.33 (d, J = 5.1 Hz, 1H) ppm; ^{13}C-NMR (67.8 MHz, $CDCl_3$): 20.3, 21.2, 81.7, 127.4, 128.2, 130.5, 134.9, 138.2, 138.6, 142.1 ppm; HRMS (FAB): Calcd for $C_{13}H_{13}IS$ $(M)^+$: 327.9783, Found 327.9794.

3-Iodo-2-[2,4,6-tris(propan-2-yl)phenyl]thiophene (3ab)

Colorless crystals; mp 82-83 °C; IR (KBr): 2959, 1606, 1458, 1382, 1361, 911, 877, 856, 743, 706, 655 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): 1.09 (d, J = 6.8 Hz, 6H), 1.21 (d, J = 6.8 Hz, 6H), 1.29 (d, J = 6.8 Hz, 6H), 2.59 (sep, J = 6.8 Hz, 2H), 2.96 (sep, J = 6.8 Hz, 1H), 7.04 (s, 2H), 7.13 (d, J = 5.4 Hz, 1H), 7.31 (d, J = 5.4 Hz, 1H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): 24.1, 25.1, 30.7, 30.9, 34.5, 83.5, 121.2, 127.3, 128.2, 134.9, 142.4, 148.9, 150.0 ppm.

Trimethyl-2-(2,4,6-trimethylphenyl)thiophene (3ba)

Colorless crystals; mp 73-75 °C; IR (KBr): 2920, 2856, 1454, 1377, 912, 742, 711 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): 1.77 (s, 3H), 2.05 (s, 9H), 2.31 (s, 3H), 2.36 (s, 3H), 6.91 (s, 2H) ppm; ^{13}C-NMR (67.8 MHz, $CDCl_3$): 12.7, 13.1, 13.3, 20.4, 21.0, 127.9, 130.9, 131.0, 132.6, 133.9, 137.3, 138.6 ppm; Anal. Calcd for $C_{16}H_{20}S$: C, 78.63; H, 8.25; S, 13.12. Found C, 78.79; H, 8.28; S, 12.90.

3-Phenyl-2-(2,4,6-trimethylphenyl)thiophene (3ca)

Colorless crystals; mp 52-53 °C; IR (KBr): 2915, 2366, 1601, 1496, 1438, 1375, 1211, 1027, 877, 849, 769, 722, 694, 670, 658, 648 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): 2.08 (s, 6H), 2.36 (s, 3H), 6.94 (s, 2H), 7.21-7.25 (m, 5H), 7.37 (d, J = 4.0 Hz, 1H), 7.45 (d, J = 4.0 Hz, 1H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): 21.5, 22.1, 125.7, 127.5, 128.3, 129.2, 129.3, 129.4, 131.3, 137.4, 137.7, 138.8, 139.2, 139.3 ppm; HRMS (EI): Calcd for $C_{19}H_{18}S$ $(M)^+$: 278.1129, Found 278.1124.

3,3'-Dimethyl-5-(2,4,6-trimethylphenyl)-2,2'-bithiophene (3da)

Colorless oil; IR (KBr): 2920, 2856, 1446, 1377, 848, 833, 709 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): 2.19 (s, 9H), 2.22 (s, 3H), 2.31 (s, 3H), 6.60 (s, 1H), 6.91 (d, J = 4.8 Hz, 1H), 6.93 (s, 2H), 7.26 (d, J = 4.8 Hz, 1H) ppm; ^{13}C-NMR (67.8 MHz, $CDCl_3$): 14.9, 15.0, 20.7, 20.8, 21.1, 124.6, 127.9, 129.3, 129.9, 130.8, 136.0, 136.1, 137.6, 138.0, 140.8 ppm; Anal. Calcd for $C_{16}H_{20}S$: C, 73.03; H, 6.45. Found C, 73.20; H, 6.65.

3,3',4,4'-Tetramethoxy-5-pentamethylphenyl-2,2'-bithiophene (3ec)

Pale-yellow crystals; mp 115-120 °C; IR (KBr): 3111, 2933, 1556, 1520, 1477, 1388, 1308, 1276, 1255, 1204, 1156, 1127, 1088, 1066, 1037, 997, 961, 750, 695 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): 2.16 (s, 6H), 2.23 (s, 6H), 2.36 (s, 3H), 3.57 (s, 3H), 3.83 (s, 3H), 3.85 (s, 3H), 3.94 (s, 3H), 6.09 (s, 1H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): 16.7, 16.9, 18.5, 57.2, 59.1, 59.9, 60.1, 94.2, 116.3, 117.9, 120.6, 129.3, 132.4, 134.2, 135.5, 142.3, 144.6, 145.0, 150.4 ppm; HRMS (FAB): Calcd for $C_{23}H_{28}O_4S_2$ $(M)^+$: 432.1249, Found 432.1434.

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