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Selective Mono- to Perarylations of Tetrabromothiophene by a Cyclobutene-1,2-diylbisimidazolium Preligand

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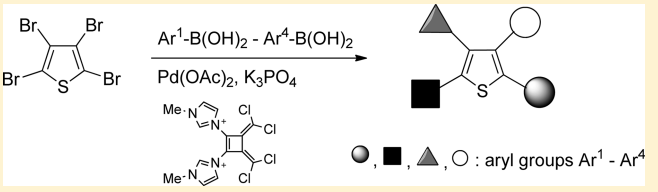
Supporting Information

ABSTRACT: (Cyclobut-1-ene-1,2-diyl)bis(1-methylimidazolium)tetrafluoroborate is applied as preligand in palladium-catalyzed cross-coupling reactions starting from tetrabromothiophene for the synthesis of mono-, bi-, tri-, and tetraaryl-substituted thiophenes bearing up to four different aryl rings. A synthetic kit for preparations of nine different substitution patterns of arylated thiophenes is presented by application of only one single catalyst system. In agreement with DFT calculations, which predict energetically low rotational barriers in triaryl-3-bromothiophenes and tetraarylthiophenes, no NOE effects between adjacent aryl rings are detectable. The regioselectivity of their syntheses has therefore been elucidated by reduction of triaryl-3-bromothiophene to 2,3,5-triarylthiophene followed by HMBC, HSQC, and NOESY NMR measurements. Additionally, results of an X-ray single structure analysis are presented.



INTRODUCTION

Due to their optoelectronic and biological activities, arylated thiophenes are of great interest in materials chemistry as well as medicinal chemistry. They have been described as photoluminescent compounds,[1] semiconductors,[2] liquid crystals,[3] light-emitting materials,[4] partial structures of light-emitting oligomers,[5] organic field-effect transistors,[6] and materials displaying aggregation-induced emission.[7] During the last years, arylated thiophene derivatives have also been reported as potassium channel blocking,[8] antitumor,[9] antiparasitic,[10] as well as antileishmanial[11] agents and as inhibitors of the NorA multidrug transporter of *Staphylococcus aureus*[12] and 17β-hydroxysteroid dehydrogenase type 1.[13] Moreover, they were identified as agonists of the sphingosine-1-phosphate 1 receptor[14] and as compounds for β-amyloid plaque imaging.[15] As a consequence, much effort is currently being devoted to the development of reliable and high-yielding preparative procedures for this interesting class of compounds. Undoubtedly, the palladium-catalyzed cross-coupling reaction[16] proved to be one of the most powerful methods for the preparation of arylated thiophenes.[17] Thus, Stille,[18] Negishi,[19] and Suzuki−Miyaura[20] reactions as well as direct arylations via C−H bond activation[21] and combinatorial syntheses[22] leading to this class of compounds have been described. Tetraarylthiophenes possessing four identical aryl substituents with modest functional group tolerance have been prepared by Suzuki−Miyaura reactions starting from tetrabromothiophene employing tetrakis(triphenylphosphate)palladium(0) as catalyst and potassium phosphate[23a] or potassium carbonate[7] as bases, respectively. The syntheses of symmetric as well as nonsymmetric 2,5-diaryl-3,4-dibromothiophenes have been accomplished by a catalyst system consisting of $Pd(OAc)_2$ and dicyclohexyl(2′,3′-dimethoxy[1,1′-biphenyl]-2-yl)-phosphine[24] by a one-pot procedure or a sequence of two cross-couplings via the monoarylated thiophenes.[23] The bromine atoms in the positions 3,4 of thiophene were then subsequently replaced by aryl rings to a symmetric aryl-substituted thiophene. Moreover, a programmed synthesis of tetraarylthiophenes through sequential C−H activation was developed recently (Scheme 1).[25] Thus, ligand-controlled regiodivergent arylation of 3-methoxy-2-phenylthiophene was followed by a Pd/bipy/Ag_2CO_3-catalyzed arylation to afford thiophenes possessing two different aryl rings in positions 2, 4, and 5. Tetraarylthiophenes were finally obtained by converting the methoxy group into a triflate which underwent cross-coupling with arylboronic acids. In summary, this procedure subsequently employs four different catalyst systems for the synthesis of tetraaryl-substituted thiophenes.

An alternative approach to tetraaryl-substituted thiophenes possessing four identical aryl rings starts from 3-thiophenecarboxylic acid, which was reacted with various aryl bromides in the presence of $Pd(OAc)_2$, PCy_3, cesium carbonate, and molecular sieves in xylene or mesitylene. This approach requires temperatures between 150 and 170 °C, whereupon C−H bond cleavage and decarboxylation occurred[26] (Scheme 2).

In addition, Suzuki couplings of 3,4-diaryl-2,5-dibromothiophenes, prepared by bromination of 3,4-diaryl-2,5-dihydrothiophene, to tetraaryl-substituted thiophenes having two different aryl groups in the 2,5- and 3,4-positions were reported.[27]

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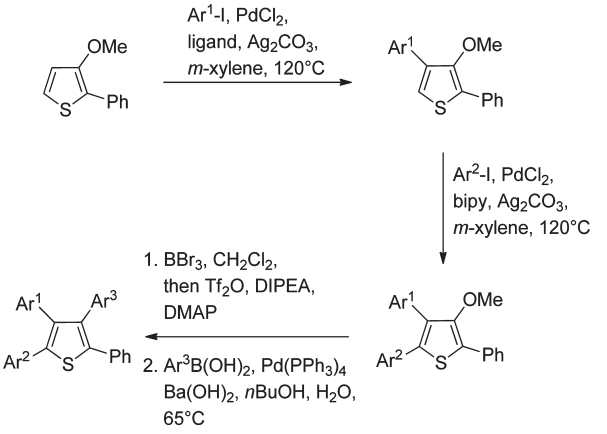
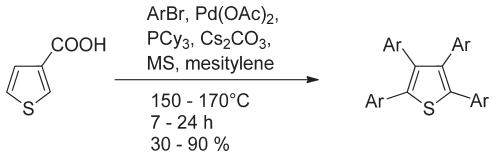
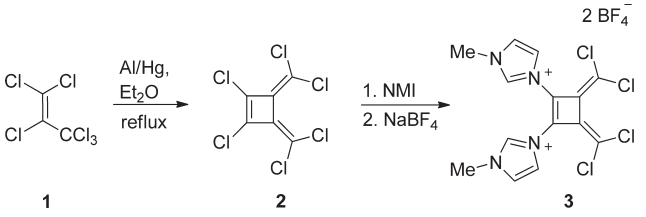
Scheme 1. Sequential CH Activation for the Synthesis of Tetraaryl-Substituted Thiophenes Employing Subsequently Four Different Catalyst Systems



Scheme 2. Synthesis of Tetraaryl-Substituted Thiophenes Possessing Four Identical Aryl Groups



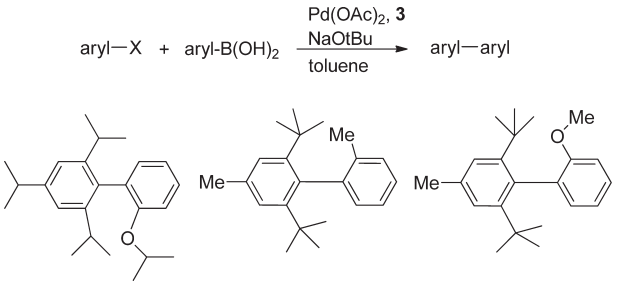
Scheme 3. Synthesis of the Preligand



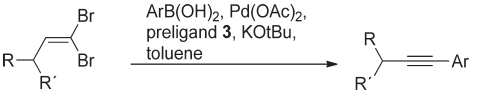
In the course of our studies directed toward the chemistry of heterocyclic mesomeric betaines[28] as well as heteroaromatic salts[29] and their conversion into N-heterocyclic carbenes,[30] we prepared (cyclobut-1-ene-1,2-diyl)bis(1-methylimidazolium)chloride from perchloropropene **1**, which we treated with Al/Hg to give 1,2-dichloro-3,4-bis(dichloromethylene)cyclobut-1-ene **2**. Reaction of cyclobutene **2** with 1-methylimidazole (NMI) resulted in the formation of (cyclobut-1-ene-1,2-diyl)bis(1-methylimidazolium)chloride. This was subjected to anion exchange with sodium tetrafluoroborate, and **3** was finally obtained in 73% yield from **2** (Scheme 3).[31] On deprotonation, the N-heterocyclic carbene of this compound is formed. Depending on the base strength, a monocarbene or biscarbene is obtained.

We found that the catalytic system consisting of this new ligand, palladium(II) acetate, and sodium *tert*-butanolate in toluene is highly efficient for room temperature Suzuki−Miyaura cross-coupling reactions.[32] At elevated temperatures, syntheses of sterically extremely hindered biaryls were possible for the first time (Scheme 4).[31]

Scheme 4. Suzuki−Miyaura Reactions for the Synthesis of Sterically Extremely Hindered Biphenyls Employing Preligand 3



Scheme 5. Acetylene Synthesis Employing Preligand 3



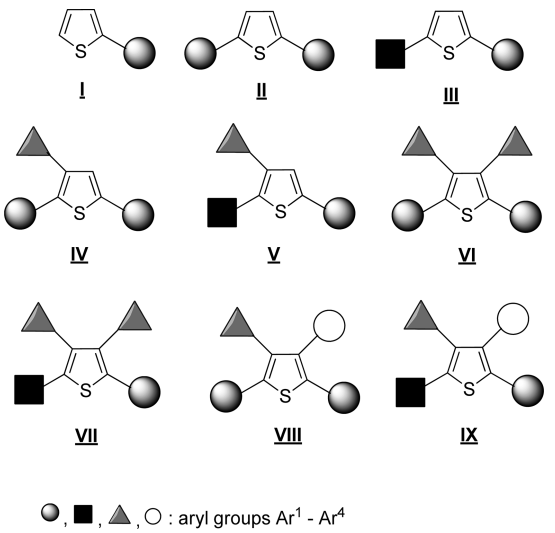


Figure 1. Substitution patterns of mono-, di-, tri-, and tetraaryl thiophenes described in this work.

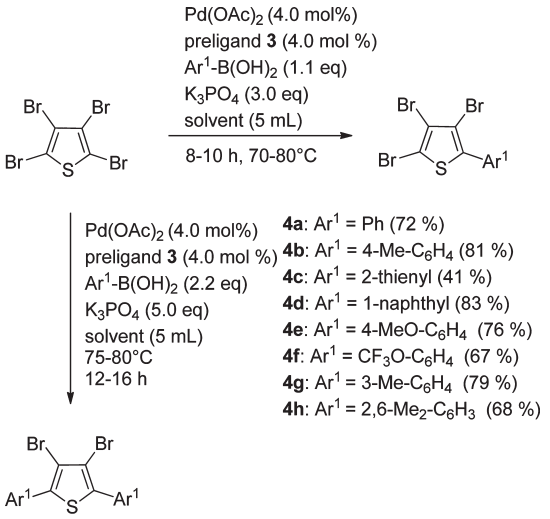
We also showed that Corey−Fuchs reactions starting from aldehydes gave geminal dibromides which underwent tandem Suzuki−Miyaura/dehydrobromination reactions to alkynes in the presence of the new preligand **3** in high yields (Scheme 5).[33]

We report here that preligand **3** is highly efficient for simple syntheses of arylated thiophenes possessing up to four different aryl substituents without the necessity to change the catalyst system. Figure 1 shows combinations of aryl rings (symbolized) attached to a thiophene which have been prepared in this work, that is, monoaryl (**I**), symmetric and nonsymmetric diaryl (**II**, **III**), triaryl (**IV**, **V**), and tetraaryl-substituted thiophenes (**VI**−**IX**).

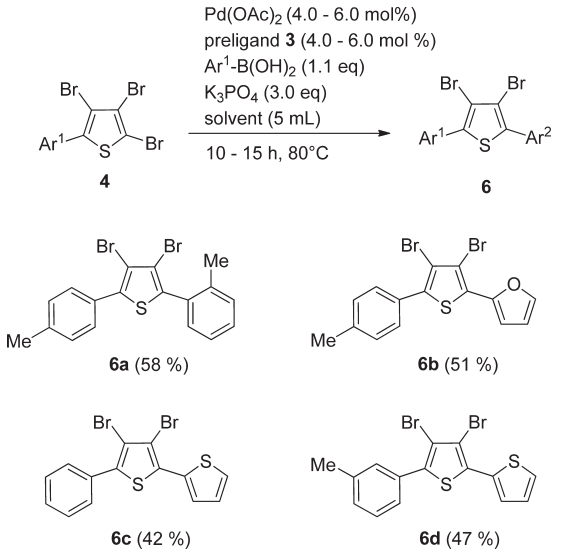
RESULTS AND DISCUSSION

We first optimized the reaction conditions for monoarylations and diarylations of tetrabromothiophene with different aromatic

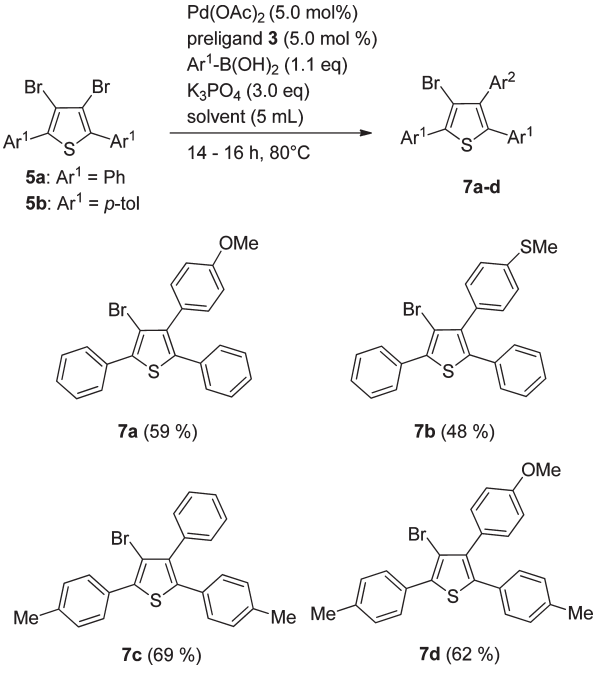
Scheme 6. Syntheses of Monoarylated and 2,5-Diarylated Thiophenes



Scheme 7. Syntheses of Thiophenes Possessing Two Different Aryl Groups in Positions 2,5



Scheme 8. Syntheses of Triarylthiophenes of General Type IV



and heteroaromatic boronic acids to obtain thiophenes of the general types **I** and **II** (cf. Figure 1). As a model system, we studied the reaction of phenylboronic acid and tetrabromothiophene. Details are presented in the Supporting Information. Best results for the synthesis of the monoarylated thiophenes **4a**−**h** were obtained when 4.0 mol % of $Pd(OAc)_2$ and 4.0 mol % of the preligand **3** in toluene were used. Thus, **4a** was obtained in 72% yield (Scheme 6), whereas usage of 6 mol % of $Pd(PPh_3)_4$ gave 61% yield.[23a] The synthesis of 3,4,5-tribromo-2,2′-bithiophene **4c** and 2,3,4-tribromo-5-(4-methoxyphenyl)thiophene **4e** gave best results when reactions were conducted in a mixture of toluene and dioxane. Under analogous reaction conditions, pyridine-3-boronic acid resulted in a mixture of yet unidentified decomposition products. Addition of 2.2 equiv of aryl boronic acid yielded the 2,5-diarylthiophenes **5a**−**h** under analogous reaction conditions, except for **5c** which required 6 mol % of catalyst. Conducting the reaction of tetrabromothiophene with 5.0 mol % of $Pd(OAc)_2$ and preligand **3** improved the yield of **5b** to 92%. This compound is literature-known. It was prepared before in 77% yield with 6 mol % of $Pd(PPh_3)_4$ at 90 °C within 12 h.[23] We also tested alternative procedures for the synthesis of these thiophenes, which are presented in the Supporting Information. In our hands, $PdCl_2(PPh_3)_2$ converted phenylboronic acid almost quantitatively into biphenyl without attacking the tetrabromothiophene. $Pd(PPh_3)_4$ as catalyst (6 mol %) gave a 42:55 ratio of mono- and bisphenylated 3,4-dibromothiophene, and only 55% of **5a** was isolated. The usage of Xphos (10 mol %) gave small yields in our experiments. Thus, our catalyst system competes with a catalyst system consisting of $Pd(OAc)_2$ (5 mol %) and Buchwalds biarylmonophoshine ligand (10 mol %), which gave slightly better yields of **5a** (88%)[23a] and **5c** (71%)[23a] but smaller yields of **4a** (61%).[23a] Thiophene **5e** was obtained in considerably better yield and in shorter time (82%/12 h vs 43%/24 h)[23b] than reported earlier using 6 mol % of $Pd(PPh_3)_4$ and almost identical yields applying $Pd(OAc)_2$ (5 mol %) and SPhos (10 mol %).[23a]

We then applied these reaction conditions to prepare hitherto unknown 2,5-diarylated thiophenes **6** possessing two different aryl or heteroaryl substituents corresponding to the general type

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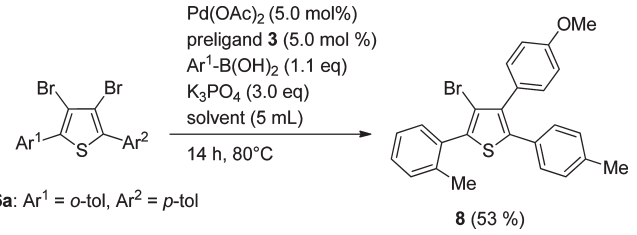
Scheme 9. Syntheses of a Triarylthiophene of General Type V



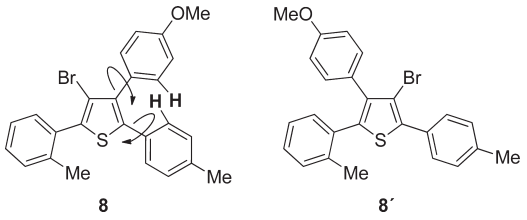


Figure 2. Two possible regioisomers of **8**. Arrows indicate the calculated rotational barriers. No NOE effects between the *ortho* protons have been detected.

III shown in Figure 1. Again, a solvent mixture of toluene and dioxane gave the best yields, except for the synthesis of **6a** which was performed in pure toluene (Scheme 7). Thus, the thiophen-2-yl-furane **6b** and the 2,2′-bithiophenes **6c,d** were prepared in reasonable yields.

The syntheses of new triarylated thiophenes having identical aryl rings in positions 2,5 (general type **IV**, Figure 1) was then accomplished starting from the thiophenes **5a,b** in the presence of 5 mol % of $Pd(OAc)_2$ and preligand **3** at 80 °C (Scheme 8). As expected, the use of toluene and dioxane proved to be advantageous with respect to yield and purity.

Choosing the nonsymmetrically substituted thiophene **6a** as starting material for the coupling with 4-methoxyphenyl boronic acid resulted in the formation of the hitherto unknown 3-bromo-4-(4-methoxyphenyl)-2-(*o*-tolyl)-5-(*p*-tolyl)thiophene **8** with three different aryl rings (Scheme 9). This compound is a representative of the general type **V**.

Elucidation of the regiochemistry of the Suzuki−Miyaura reaction to **8** proved to be challenging, as no NOE effects were determined between adjacent aryl rings, regardless of solvent (C_6D_6, $CDCl_3$, CD_2Cl_2) and temperature (−35 to 50 °C). This is in accordance to DFT calculations, which predict low energetic barriers for rotation of the aryl rings of the two possible regioisomers **8** and **8′**. In their most stable conformations, they are nonplanar and show long distances between the *ortho*-hydrogen atoms (Figure 2).

The distances of the *ortho*-hydrogen atoms of the *p*-methoxyphenyl and *p*-tolyl ring of **8** have been calculated to adopt values between 320 and 431 pm on rotation around the arylthiophene bonds. In the most stable conformation (Figure 3), the *p*-tolyl ring, *p*-methoxyphenyl ring, and the *o*-tolyl ring in **8** adopt torsion angles of 38.8, 59.1, and 76.5°, respectively, in relation to the thiophene ring. The distance between the *ortho*-hydrogen atoms is then 338 pm. The energetic barrier for rotation of the *o*-tolyl ring was calculated to be as small as 39 kJ/mol, so that there is no steric repulsion caused by the van der Waals radius of

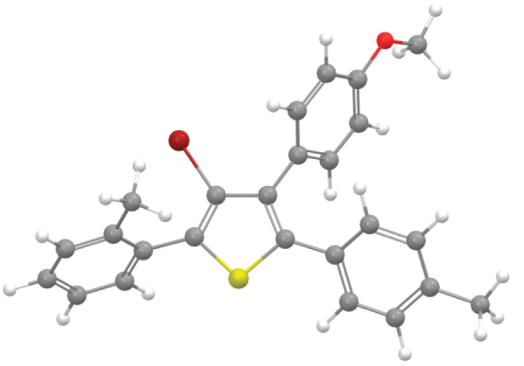
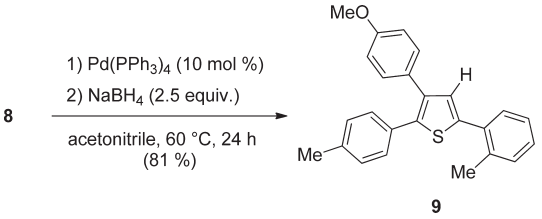


Figure 3. Most stable conformation of **8** according to DFT calculations.

Scheme 10. Reduction of 8 to 9



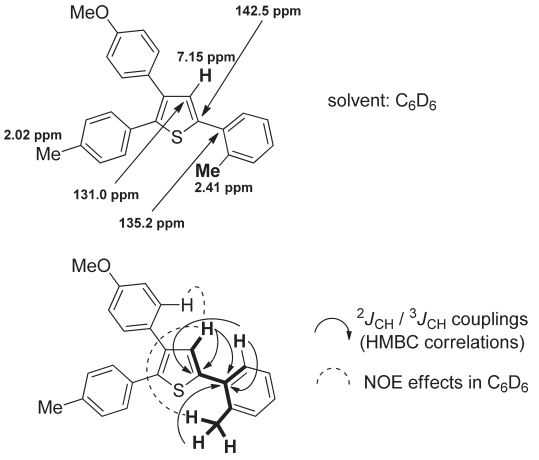


Figure 4. Selected peak assignments according to HMBC and HSQC correlations (CD_2Cl_2) as well as NOESY effects in C_6D_6 and measured $^2J_{CH}$ and $^3J_{CH}$ couplings in thiophene **9**.

the bromine substituent. Analogous results were obtained for the regioisomer of **8′** (31.1 kJ/mol).

Due to the lack of information available from the NMR spectra to prove the regiochemistry of the Suzuki−Miyaura coupling, we reduced the bromine atom of **8** by palladium-catalyzed hydrodebromination and obtained **9** in 81% yield (Scheme 10).

The hydrogen atom of **9** is clearly detectable at δ = 7.12 ppm in CD_2Cl_2 and 7.15 ppm in C_6D_6. The ^{13}C NMR data displayed all expected 21 carbon signals. Analysis of the HH COSY and HSQC spectra of **9** enabled us to assign all protons to their bonding carbons, and HMBC experiments confirmed the structural fragments by long-range C−H couplings. In accordance with structure **9**, 3-*H* displays HMBC correlations to the

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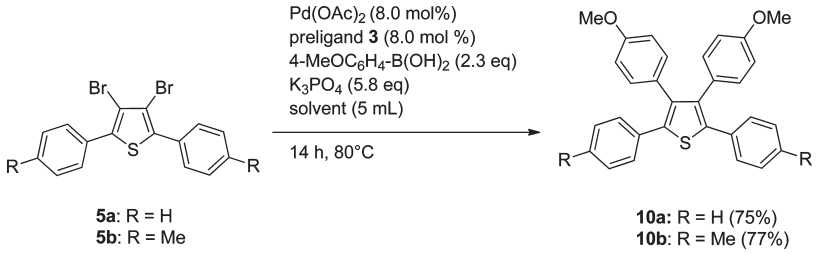
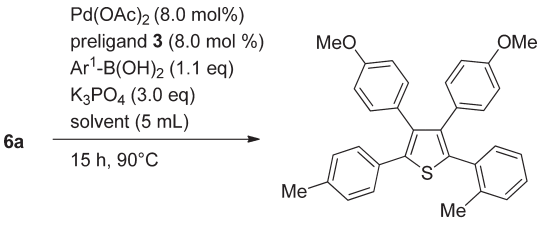
Scheme 11. Synthesis of a Tetraaryl-Substituted Thiophenes of General Type VI



5a: R = H
5b: R = Me

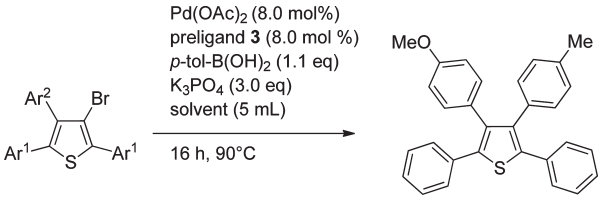
10a: R = H (75%)
10b: R = Me (77%)

Scheme 12. Synthesis of a Tetraaryl-Substituted Thiophene of General Type VII



11 (63 %)

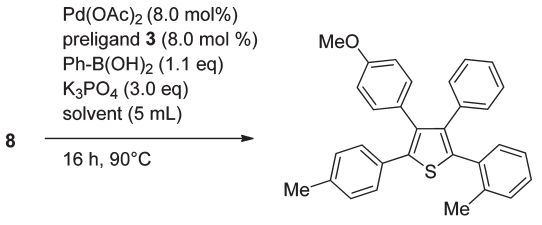
Scheme 13. Synthesis of a Thiophene of General Type VIII



7a: Ar^1 = Ph, Ar^2 = 4-MeOPh

12 (57 %)

Scheme 14. Selective Arylations to a Tetraarylated Thiophene of Type IX



13 (51 %)

expected carbon atoms by $^2J_{C-H}$ and $^3J_{C-H}$ couplings, respectively, as shown in Figure 4. Furthermore, the HMBC correlation of 6-*H* of the *o*-tolyl ring with the thiophene ring was detectable. Finally, applying deuterobenzene, a mixing time of 0.75 s, and a pulse repetition delay of 5 s, we were able to detect NOE effects between the *ortho* proton of the *p*-methoxyphenyl ring as well as of the 2-methyl group and each with 3-*H* of the thiophene, respectively. With these results in hand, we can unambiguously conclude that regioisomer **8** was formed.

Finally, encouraged by the promising results of this investigation, we subjected selected examples of di- and trisubstituted thiophenes to additional Suzuki−Miyaura couplings to obtain tetra-substituted thiophenes of the general types **VI**−**IX** shown in Figure 1. We used 8 mol % of the catalyst system at 90 °C, which resulted in the formation of tetraarylthiophenes in good to very good yields (Schemes 11−14). Thiophenes **5a** and **5b** reacted with *p*-methoxyphenylboronic acid and 8 mol % of the catalyst system at 80 °C to the symmetric tetraarylthiophenes **10a** and **10b** in 75 and 77% yield (Scheme 11). These molecules belong to general type **VI** and have been described before, so that we were able to compare our method to literature-known procedures. Thiophene **10a** gives a considerably better yield under milder conditions and lower catalyst loadings than reported.[26] Thiophene **10b** was synthesized in a similar yield when 10 mol % of $Pd(PPh_3)_4$ at 100 °C for 24 h were used for the cross-coupling.[23]

Treatment of **6a** with *p*-methoxyphenylboronic acid and our catalyst system gave **11** possessing two different types of aryl groups in the α positions and identical groups in positions 3,4, that is, a new structure according to general type **VII** (Scheme 12).

Fortunately, we were able to obtain suitable single crystals of **11** by slow evaporation in *n*-hexane, which we subjected to an X-ray crystallographic examination. The molecular drawing displays the tetra-fold substitution. The compound crystallized monoclinic. The *p*-tolyl ring adopts a torsion angle of −37.5(2)°, whereas its neighboring 4-methoxyphenyl ring has a torsion angle of −70.2(2)°. The *o*-tolyl ring is twisted by −71.4(2)° from the planar thiophene ring, and its neighboring 4-methoxyphenyl ring adopts a dihedral angle of −55.9(2)°. A molecular drawing is shown in the Supporting Information.

Starting from **7a** the thiophene **12** was formed in 57% yield (Scheme 13). This new arylated thiophene represents the substitution pattern **VIII**.

Finally, in a smooth reaction, **8** gave **13** in 51% yield, which has four different aryl groups (Scheme 14).

Similar to the bromo derivative **8** described above, the thiophene **13** bearing four different aryl rings displayed no NOE effects between neighboring aryl substituents. This is in accordance with calculations which hint at a most stable conformation with twisted *p*-tolyl-, 4-methoxy-, phenyl-, and *o*-tolyl rings (41.3, 54.7, 53.7, and 62.2°, respectively). The distances between hydrogen atoms of the neighboring *o*-tolyl and the phenyl ring were calculated to be between 222 and 791 pm depending on the torsion angles. In the most stable conformation, the distance is 282 pm. The rotational barrier of the *o*-tolyl

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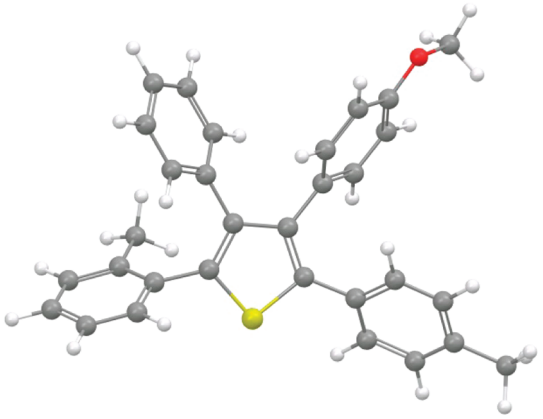

Figure 5. Most stable conformation of **13** according to DFT calculations.

ring was determined to be only 32 kJ/mol, which means the absence of steric hindrance (Figure 5).

CONCLUSIONS

We showed that a catalytic system of preligand **3**, palladium(II) acetate, and potassium phosphate can be employed for the sequential synthesis of arylated thiophenes bearing up to four different aryl rings. Representatives of nine different substitution patterns have been prepared.

EXPERIMENTAL SECTION

General Considerations. Tetrabromothiophene and all boronic acids were purchased and used without further purification. The solvents toluene and dioxane were dried over sodium according to standard procedures. Acetonitrile was dried over CaH_2. The ligand was synthesized as described earlier.[31] For weighing small amounts of catalyst (palladium source + ligand) easily and precisely, $Pd(OAc)_2$ (1 mmol, 224.5 mg) and preligand **3** (1.1 mmol, 604.9 mg) were weighed and mixed in a mortar (ratio = 1:1.1). The resulting fine powder was kept in a capped vial in a desiccator. Flash chromatography was performed with silica gel 60 (0.040−0.063 mm). ^{1}H NMR spectra were recorded at 400 or 600 MHz and ^{13}C NMR spectra at 100 or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, and m = multiplet. FT-IR spectra were obtained in the range of 400 to 4000 cm^{-1}. Solids were measured as pellets (2.5%) in KBr, and oils were measured as films in NaCl plates. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). Accurate masses are listed employing the ^{79}Br isotope. All yields are isolated yields. All density functional theory (DFT) calculations were carried out by using the Jaguar 7.7.107 software running on Linux 2.6.18-238.el5 SMP (x86_64) on two AMD Phenom II X6 1090T processor workstations (Beowulf cluster) parallelized with OpenMPI 1.3.4. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented LACVP* (Hay−Wadt effective core potential (ECP) basis on heavy atoms, N31G6* for all other atoms) basis set and with the B3LYP density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies. Plots were obtained using Maestro 9.1.207, the graphical interface of Jaguar. Rotational barriers have been calculated fully relaxed, fixating one torsion angle around the rotated bond, and optimizing all remaining degrees of freedom. Torsion angles were modified in steps of 10°.

General Procedure for Suzuki−Miyaura Coupling Reactions of Tetrabromothiophene with Aryl Boronic Acids: A 10 mL flame-dried flask was charged with tetrabromothiophene (0.5 mmol), boronic acid (0.55 mmol for one substitution and 1.1 mmol for two substitutions), mixture of palladium source and preligand **3** (4 mol %), and potassium phosphate (1.5 mmol), and then evacuated and backfilled with nitrogen three times. Five milliliters of solvent was added, and the mixture was stirred at the temperatures given below for the indicated periods of time. Then, 5 mL of water was added, and the product was extracted with dichloromethane, dried over $MgSO_4$ and concentrated in vacuo. Purification was accomplished by flash column chromatography.

2,3,4-Tribromo-5-phenylthiophene (4a): A mixture of tetrabromothiophene (0.5 mmol, 199.8 mg), phenylboronic acid (0.55 mmol, 67.1 mg), K_3PO_4 (1.5 mmol, 318.4 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) in toluene (5 mL) was stirred at 75 °C for 8 h. Column chromatography (petroleum ether) provided 142.8 mg (72%) of the title compound as colorless solid: mp 80−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57−7.55 (m, 2H), 7.46−7.41 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.9, 132.2, 129.1, 128.8, 128.7, 125.4, 118.4, 110.4 ppm; IR (KBr) 3072, 3022, 1480, 1443, 1285, 1266, 1073, 998, 741, 689 cm^{-1}; HRMS (70 eV) calcd for $C_{10}H_5Br_3S$ 393.76621, found 393.76609.

2,3,4-Tribromo-5-*p*-tolylthiophene (4b): To a mixture of tetrabromothiophene (0.5 mmol, 199.8 mg), 4-methylphenylboronic acid (0.55 mmol, 74.8 mg), K_3PO_4 (1.5 mmol, 318.4 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) was added 5 mL of toluene and stirred at 70 °C for 8 h. Column chromatography (petroleum ether) gave 166.4 mg (81%) of title compound as colorless solid: mp 88−90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 2.4 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 139.3, 129.4, 128.7, 125.3, 118.3, 110.0, 109.6, 21.3 ppm; IR (KBr) 3068, 3022, 2917, 1636, 1489, 1437, 1286, 1272, 859, 797, 746 cm^{-1}; HRMS (70 eV) calcd for $C_{11}H_7Br_3S$ 407.78186, found 407.78205.

3,4,5-Tribromo-2,2′-bithiophene (4c): A mixture of polybromothiophene (0.5 mmol, 199.8 mg), 2-thiopheneboronic acid (0.55 mmol, 70.4 mg), K_3PO_4 (1.5 mmol, 318.4 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) in 3 mL of toluene plus 2 mL of dioxane was stirred at 80 °C for 12 h. Column chromatography (petroleum ether) provided 82.6 mg (41%) of the title compound as light yellow solid: mp 83−84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4 (dd, J = 5.1, 1.1 Hz, 1H), 7.38 (dd, J = 3.8, 1.1 Hz, 1H), 7.09 (dd, J = 5.1, 3.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9, 133.5, 127.4, 127.3, 127.1, 118.7, 110.4, 109.4 ppm; IR (KBr) 3096, 2918, 1544, 1484, 1412, 1282, 1077, 840, 700 cm^{-1}; m/z (70 ev) 403.1 [M$^+$]. Anal. Calcd for $C_8H_3Br_3S_2$: C, 23.85; H, 0.75. Found: C, 23.77; H, 0.75.

2,3,4-Tribromo-5-(naphthalen-1-yl)thiophene (4d): To a mixture of tetrabromothiophene (0.5 mmol, 199.8 mg), 1-naphthaleneboronic acid (0.55 mmol, 94.6 mg), K_3PO_4 (1.5 mmol, 318.4 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) was added 5 mL of toluene. The reaction mixture was then heated and stirred at 70 °C for 10 h. Column chromatography (petroleum ether) gave 185.5 mg (83%) of **4d** as colorless solid: mp 101−102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.9 (m, 2H), 7.73−7.71 (m, 1H), 7.55−7.46 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 133.6, 131.6, 130.3, 129.6, 129.4, 128.5, 127.0, 126.5, 125.6, 125.0, 117.6, 113.7, 110.9 ppm; IR (KBr) 3045, 2922, 1592, 1504, 1436, 1338, 1280, 1231, 865, 816, 796 cm^{-1}; HRMS (70 eV) calcd for $C_{14}H_7Br_3S$ 443.78186, found 443.78212.

2,3,4-Tribromo-5-(4-methoxyphenyl)thiophene (4e): Into a 10 mL oven-dried flask were placed tetrabromothiophene (0.5 mmol, 199.8 mg), 4-methoxybenzeneboronic acid (0.55 mmol, 83.65 mg), K_3PO_4 (1.5 mmol, 318.4 mg), 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg), 3 mL of toluene plus 2 mL of dioxane. The reaction

mixture was then heated and stirred at 80 °C for 10 h. Column chromatography (petroleum ether/ethyl acetate 50:1) provided 162.2 mg (76%) of **4e** as colorless solid: mp 119−120 °C (mp[23] 124−125 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8, 2H), 3.85 (s, 3H) ppm; spectroscopic data are identical to those reported; HRMS (70 eV) calcd for $C_{11}H_7Br_3OS$ 423.77677, found 423.77681.

2,3,4-Tribromo-5-(4-(trifluoromethoxy)phenyl)thiophene (4f): A mixture of tetrabromothiophene (0.5 mmol, 199.8 mg), 4-trifluoromethoxyphenylboronic acid (0.55 mmol, 74.8 mg), K_3PO_4 (1.5 mmol, 318.4 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) in toluene (5 mL) was stirred at 80 °C for 8 h. After extraction and column chromatography, a colorless solid was obtained in 67% yield (161.2 mg): mp 48−49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7 (d, J = 1.6 Hz), 138.3, 130.8, 130.5, 121.1, 120.3 (q, J = 256 Hz), 118.8, 111.1, 110.7 ppm; IR (KBr) 2963, 2924, 1609, 1530, 1467, 1299, 1208, 1156, 835, 805 cm^{-1}; HRMS (70 eV) calcd for $C_{11}H_4Br_3F_3OS$ 477.74851, found 477.74823.

2,3,4-Tribromo-5-(*m*-tolyl)thiophene (4g): A mixture of polybromothiophene (0.5 mmol, 199.8 mg), 3-methylphenylboronic acid (0.55 mmol, 70.4 mg), K_3PO_4 (1.5 mmol, 318.4 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) in 5 mL of toluene was stirred at 80 °C for 8 h. Column chromatography (petroleum ether) resulted 162.3 mg (79%) of the title compound as light yellow solid: mp 72−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.28 (m, 3H), 7.24−7.21 (m, 1H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.6, 132.2, 130.0, 129.6, 128.7, 126.1, 118.5, 110.3, 110.0, 21.5 ppm; IR (KBr) 3031, 2920, 2853, 1603, 1582, 1471, 1271, 1091, 862, 781, 749 cm^{-1}; m/z (70 ev) 411.8 [M$^+$]. Anal. Calcd for $C_{11}H_7Br_3S$: C, 32.15; H, 1.72. Found: C, 32.23; H, 1.73.

2,3,4-Tribromo-5-(2,6-dimethylphenyl)thiophene (4h): To a mixture of tetrabromothiophene (0.5 mmol, 199.8 mg), 2,6-dimethylphenylboronic acid (0.55 mmol, 82.5 mg), K_3PO_4 (1.5 mmol, 318.4 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) was added 5 mL of toluene. The reaction mixture was then heated and stirred at 80 °C for 10 h. Column chromatography (petroleum ether) gave 144.5 mg (68%) of **4h** as colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 7.5 Hz, 2H), 2.14 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.5, 131.1, 129.6, 127.6, 117.2, 112.8, 110.7, 20.3 ppm; IR (NaCl) 3064, 3023, 2921, 2855, 1595, 1465, 1275, 892, 818, 771 cm^{-1}; m/z (70 ev) 425.9 [M$^+$]. Anal. Calcd for $C_{12}H_9Br_3S$: C, 33.91; H, 2.13. Found: C, 33.84; H, 2.14.

3,4-Dibromo-2,5-diphenylthiophene (5a): A mixture of tetrabromothiophene (0.5 mmol, 199.8 mg), phenylboronic acid (1.20 mmol, 146.5 mg), K_3PO_4 (2.5 mmol, 530.6 mg), and 5 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) in toluene (5 mL) was stirred at 75 °C for 10 h. After extraction and column chromatography a colorless solid was obtained in 69% yield (136 mg): mp 103−104 °C (mp[35] 101.5−102.5 °C, mp[36] 95−96 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67−7.64 (m, 4H), 7.47−7.40 (m, 6H) ppm; spectroscopic data are identical to those reported;[23] HRMS (70 eV) calcd for $C_{16}H_{10}Br_2S$ 391.88700, found 391.88717.

3,4-Dibromo-2,5-di-*p*-tolylthiophene (5b): A mixture of tetrabromothiophene (0.5 mmol, 199.8 mg), 4-methylphenylboronic acid (1.20 mmol, 163.2 mg), K_3PO_4 (2.5 mmol, 530.6 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) in toluene (5 mL) was stirred at 75 °C for 12 h. After extraction and column chromatography (petroleum ether), a colorless solid was obtained in 82% yield (173 mg): mp 146−147 °C (mp[23] 152−155 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.0 Hz, 4H), 7.26 (d, J = 8.0 Hz, 4H), 2.4 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.9, 130.1, 129.4, 128.9, 111.8, 21.4 ppm; IR (KBr) 3020, 2917, 1636, 1489, 1265, 863, 797 cm^{-1}; HRMS (70 eV) calcd for $C_{18}H_{14}Br_2S$ 419.91830, found 419.91843.

3,4-Dibromo-2,5-di(thien-2-yl)thiophene (5c): A mixture of polybromothiophene (0.5 mmol, 199.8 mg), 2-thiopheneboronic acid (1.1 mmol, 140.8 mg), K_3PO_4 (2.5 mmol, 530.6 mg), and 6 mol % of [$Pd(OAc)_2$ + ligand] (0.03 mmol, 24.9 mg) in 3 mL of toluene plus 2 mL of dioxane was stirred at 80 °C for 16 h. Column chromatography (petroleum ether/ethyl acetate/100:1) provided 99.5 mg (49%) of a the title compound as light yellow solid: mp 97−98 °C, mp[23] 89−91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 3.8, 1.1 Hz, 2H), 7.41 (dd, J = 3.8, 1.1 Hz, 2H), 7.11 (dd, J = 5.2, 3.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 131.0, 127.3, 127.1, 126.8, 112.3 ppm; IR (KBr) 3095, 3064, 1483, 1417, 1231, 1219, 1059, 843, 685 cm^{-1}; HRMS (70 eV) calcd for $C_{12}H_6Br_2S_3$ 403.79984, found 403.80005.

3,4-Dibromo-2,5-di(naphthalen-1-yl)thiophene (5d): To a mixture of tetrabromothiophene (0.5 mmol, 199.8 mg), 1-naphthaleneboronic acid (1.2 mmol, 189.2 mg), K_3PO_4 (2.5 mmol, 530.6 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) was added 5 mL of toluene. The reaction mixture was then heated and stirred at 75 °C for 14 h. Column chromatography (petroleum ether) gave 192.7 mg (78%) of **5d** as yellow solid: mp 136−138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.2 Hz, 2H), 7.85 (d, J = 8.2 Hz, 2H), 7.50 (dd, J = 8.2, 7.1 Hz, 2H), 7.41 (dd, J = 7.1, 1.2 Hz, 2H) 7.38 (ddd, J = 8.2, 7.1, 1.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.20 (ddd, J = 8.2, 7.1, 1.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 133.5, 132.8, 128.1 (2C), 127.9, 127.8, 126.5, 125.9 (2C), 125.8, 125.4 ppm; IR (KBr) 3042, 2922, 1588, 1504, 1379, 1135, 804, 769 cm^{-1}; m/z (70 ev) 491.8 [M$^+$]. Anal. Calcd for $C_{24}H_{14}Br_2S$: C, 58.32; H, 2.86. Found: C, 58.48; H, 2.87.

3,4-Dibromo-2,5-bis(4-methoxyphenyl)thiophene (5e): Into a 10 mL oven-dried flask were placed tetrabromothiophene (0.5 mmol, 199.8 mg), 4-methoxybenzeneboronic acid (1.2 mmol, 182.5 mg), K_3PO_4 (2.5 mmol, 530.6 mg), 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg), 3 mL of toluene plus 2 mL of dioxane. The reaction mixture was then heated and stirred at 80 °C for 12 h. Column chromatography (petroleum ether/ethyl acetate 40:1) resulted 188.4 mg (83%) of the title compound as yellow solid: mp 163−164 °C, mp[23] 171−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.8 Hz, 4H), 6.97 (d, J = 8.8, 4H), 3.85(s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 137.4, 130.3, 125.3, 114.0, 111.5, 55.4 ppm; IR (KBr) 3029, 2996, 2961, 2835, 1607, 1535, 1491, 1439, 1299, 1253, 1031, 828, 803, 755 cm^{-1}; m/z (70 ev) 453.9 [M$^+$]. Anal. Calcd for $C_{18}H_{14}Br_2O_2S$: C, 47.60; H, 3.11. Found: C, 47.51; H, 3.12.

3,4-Dibromo-2,5-bis(4-(trifluoromethoxy)phenyl)thiophene (5f): A mixture of tetrabromothiophene (0.5 mmol, 199.8 mg), 4-trifluoromethoxyphenylboronic acid (1.2 mmol, 163.2 mg), K_3PO_4 (2.5 mmol, 530.6 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) in toluene (5 mL) was stirred at 80 °C for 12 h. After extraction and column chromatography, a colorless solid was obtained in 62% yield (174.2 mg): mp 92−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.8 Hz, 4H), 7.32 (d, J = 8.8 Hz, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0 (d, J = 1.6 Hz), 137.7, 129.9, 120.5, 119.7 (q, J = 256 Hz), 110.5, 110.0 ppm; IR (KBr) 2973, 2931, 1601, 1525, 1471, 1289, 1201, 1147, 837 cm^{-1}; m/z (70 ev) 561.7 [M$^+$]. Anal. Calcd for $C_{18}H_8Br_2F_6O_2S$: C, 38.46; H, 1.43. Found: C, 38.38; H, 1.43.

3,4-Dibromo-2,5-di-*m*-tolylthiophene (5g): A mixture of polybromothiophene (0.5 mmol, 199.8 mg), 3-methylphenylboronic acid (1.2 mmol, 153.6 mg), K_3PO_4 (2.5 mmol, 530.6 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) in 5 mL of toluene was stirred at 75 °C for 12 h. Column chromatography (petroleum ether) provided 162.5 mg (77%) of the title compound as colorless solid: mp 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.46 (m, 4H), 7.36−7.33 (m, 2H),7.25−7.21 (m, 2H), 2.41 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.2, 132.8, 129.7, 129.6, 128.6, 126.1, 112.1, 21.5 ppm; IR (KBr) 3015, 2918, 2854, 1602, 1581, 1406, 1271, 1020, 889, 785, 742 cm^{-1}; m/z (70 ev) 422.0 [M$^+$]. Anal. Calcd for $C_{18}H_{14}Br_2S$: C, 51.21; H, 3.34. Found: C, 51.31; H, 3.35.

3,4-Dibromo-2,5-bis(2,6-dimethylphenyl)thiophene (5h): To a mixture of tetrabromothiophene (0.5 mmol, 199.8 mg), 2,6-dimethylphenylboronic acid (1.2 mmol, 180 mg), K_3PO_4 (2.5 mmol, 530.6 mg), 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg) was added 5 mL of toluene. The reaction mixture was then heated and stirred at 80 °C for 14 h. Column chromatography (petroleum ether) resulted 139.5 mg (62%) of **5h** as colorless solid: mp 181−182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 7.5 Hz, 2H), 7.13 (d, J = 7.5 Hz, 4H), 2.14 (s, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.5, 131.1, 129.6, 127.6, 117.2, 112.8, 110.7, 20.3 ppm; IR (KBr) 3061, 3022, 2918, 2854, 1462, 1377, 1281, 1094, 855, 768 cm^{-1}; m/z (70 ev) 450.0 [M^+]. Anal. Calcd for $C_{20}H_{18}Br_2S$: C, 53.35; H, 4.03. Found: C, 53.44; H, 4.04.

3,4-Dibromo-2-*o*-tolyl-5-*p*-tolylthiophene (6a): Five milliliters of toluene was added to a mixture of 2,3,4-tribromo-5-*p*-tolylthiophene (0.5 mmol, 205.5 mg), 2-methylphenylboronic aicd (0.55 mmol, 74.8 mg), K_3PO_4 (1.5 mmol, 318.4 mg), and 4 mol % of [$Pd(OAc)_2$ + ligand] (0.02 mmol, 16.6 mg). The mixture was heated at 80 °C for 10 h. Column chromatography (petroleum ether) gave **6a** as colorless oil in 58% (122.4 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.27−7.21 (m, 4H), 2.4 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.9, 138.3, 137.9, 136.7, 130.0, 129.5 (2C), 129.4 (2C), 128.9 (2C), 126.8 (2C), 111.8, 21.4, 21.1 ppm; IR (NaCl) 3061, 3023, 2921, 2864, 1638, 1515, 1482, 1265, 1115, 860, 810, 705 cm^{-1}; HRMS (70 eV) calcd for $C_{18}H_{14}Br_2S$ 419.91830, found 419.91863.

2-(3,4-Dibromo-5-(*p*-tolyl)thiophen-2-yl)furane (6b): To a mixture of 2,3,4-tribromo-5-(*p*-tolyl)thiophene (0.4 mmol, 164.4 mg), 2-furanylboronic acid (0.45 mmol, 50.4 mg), K_3PO_4 (1.2 mmol, 254.7 mg), and 6 mol % of [$Pd(OAc)_2$ + ligand] (0.024 mmol, 19.92 mg) was added a mixture of 2 mL of toluene plus 3 mL of dioxane. The reaction mixture was then heated and stirred at 80 °C for 16 h. Column chromatography (petroleum ether/EtOAc = 60: 1) gave 81.2 mg (51%) of a light brown solid: mp 58−59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, J = 7.8 Hz, 2H), 7.47 (dd, J = 3.5, 1.8 Hz, 1H), 7.27 (d, J = 7.8 Hz, 2H), 7.15 (dd, J = 3.5, 0.8 Hz, 1H), 6.54 (dd, J = 3.5, 1.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.2, 142.2, 139.0, 137.1, 129.8, 129.4, 128.8, 128.5, 112.1, 111.9, 110.1, 108.6, 21.4 ppm; IR (KBr) 3022, 2918, 1647, 1509, 1483, 1273, 1019, 811, 735 cm^{-1}; HRMS (70 eV) calcd for $C_{15}H_{10}Br_2OS$ 395.88191, found 395.88209.

3,4-Dibromo-5-phenyl-2,2′-bithiophene (6c): To a mixture of 2,3,4-tribromo-5-phenylthiophene (0.4 mmol, 158.8 mg), 2-thiopheneboronic acid (0.45 mmol, 57.6 mg), K_3PO_4 (1.2 mmol, 254.7 mg), and 6 mol % of [$Pd(OAc)_2$ + ligand] (0.024 mmol, 19.92 mg) was added 3 mL of toluene plus 2 mL of dioxane. The reaction mixture was then heated and stirred at 80 °C for 16 h. Column chromatography (petroleum ether) gave 67.2 mg (42%) of title compound as yellow solid: mp 73−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 8.1, 1.6 Hz, 2H), 7.47−7.38 (m, 5H), 7.10 (dd, J = 5.1, 1.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 137.2, 134.3, 132.6, 132.1, 129.0, 128.9, 128.7, 127.4, 127.0, 126.7, 112.5,112.4 ppm; IR (KBr) 3108, 3058, 3023, 1598, 1480, 1279, 1242, 860, 747 cm^{-1}; HRMS (70 eV) calcd for $C_{14}H_8Br_2S_2$ 397.84342, found 397.84323.

3,4-Dibromo-5-(*m*-tolyl)-2,2′-bithiophene (6d): To a mixture of 2,3,4-tribromo-5-(*m*-tolyl)thiophene (0.4 mmol, 164.4 mg), 2-thiopheneboronic acid (0.45 mmol, 57.6 mg), K_3PO_4 (1.2 mmol, 254.7 mg), and 6 mol % of [$Pd(OAc)_2$ + ligand] (0.024 mmol, 19.92 mg) were added 3 mL of toluene and 2 mL of dioxane. The reaction mixture was then heated and stirred at 80 °C for 16 h. Column chromatography (petroleum ether) provided 77.8 mg (47%) of **6d** as green solid: mp 46−47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.44 (m, 3H), 7.40 (dd, J = 5.1, 1.2 Hz, 1H), 7.36−7.21 (m, 2H), 7.11 (dd, J = 5.1, 3.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 138.5, 137.4, 134.3, 132.5, 131.9, 129.7, 129.6, 128.0, 127.7, 127.4, 127.0, 126.7, 126.1, 112.3, 21.5 ppm; IR (KBr) 3097, 3008, 2957, 1578, 1257, 1186, 874, 747 cm^{-1}; m/z (70 ev) 413.9 [M^+]. Anal. Calcd for $C_{15}H_{10}Br_2S_2$: C, 43.50; H, 2.43. Found: C, 43.42; H, 2.44.

3-Bromo-4-(4-methoxyphenyl)-2,5-diphenylthiophene (7a): To a mixture of 3,4-dibromo-2,5-diphenylthiophene (0.3 mmol, 118.2 mg), 4-methoxybenzeneboronic acid (0.35 mmol, 53.2 mg), K_3PO_4 (1.2 mmol, 254.7 mg), and 5 mol % of [$Pd(OAc)_2$ + ligand] (0.015 mmol, 12.44 mg) was added 5 mL of toluene. The reaction mixture was then heated and stirred at 80 °C for 12 h. Column chromatography (petroleum ether/ethyl acetate = 60:1) gave 89 mg (71%) of **7a** as yellow solid: mp 162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, J = 7.9 Hz, 2H), 7.48−7.39 (m, 3H), 7.22−7.19 (m, 7H), 6.90 (d, J = 7.9 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.1, 139.0, 138.6, 136.9, 133.8, 133.4, 131.9, 129.4, 128.8, 128.6, 128.5, 128.3, 128.2, 127.6, 113.7, 111.6, 55.2 ppm; IR (KBr) 3055, 3018, 2953, 2833, 1597, 1540, 1483, 1287, 1245, 1147, 1027, 754, 693 cm^{-1}; HRMS (70 eV) calcd for $C_{23}H_{17}BrOS$ 420.01835, found 420.01822.

3-Bromo-4-(4-(methylthio)phenyl)-2,5-diphenylthiophene (7b): A mixture of 3,4-dibromo-2,5-diphenylthiophene (0.3 mmol, 118.2 mg), 4-(methylthio)phenylboronic acid (0.35 mmol, 58.8 mg), K_3PO_4 (1.2 mmol, 254.7 mg), and 6 mol % of [$Pd(OAc)_2$ + ligand] (0.018 mmol, 14.93 mg) in toluene (5 mL) was stirred at 90 °C for 14 h. Column chromatography (petroleum ether/ethyl acetate 100:1) afforded the title compound as yellow solid in 53.8 mg (41%): mp 120−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0, 2H), 7.25−7.19 (m, 10H), 2.50 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.3, 138.2, 137.2, 133.6, 133.3, 132.4, 131.2, 129.4, 128.8, 128.6, 128.5, 128.4, 127.8, 125.9, 111.1, 15.4 ppm; IR (KBr) 3062, 3020, 2923, 2851, 1597, 1480, 1419, 1238, 1089, 969, 880, 755, 648 cm^{-1}; HRMS (70 eV) calcd for $C_{23}H_{17}BrS_2$ 435.99550, found 435.99561.

3-Bromo-4-phenyl-2,5-di-p-tolylthiophene (7c): To a mixture of 3,4-dibromo-2,5-di-*p*-tolylthiophene (0.3 mmol, 126.65 mg), phenylboronic acid (0.35 mmol, 42.7 mg), K_3PO_4 (1.2 mmol, 254.7 mg), and 5 mol % of [$Pd(OAc)_2$ + ligand] (0.015 mmol, 12.44 mg) was added 5 mL of toluene. The reaction mixture was then heated and stirred at 80 °C for 14 h. Column chromatography (petroleum ether/ethyl acetate 60:1) gave 86.8 mg (69%) of title compound as light yellow solid: mp 128−129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.33−7.23 (m, 5H), 7.08 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 138.5, 138.3, 137.6, 136.8, 136.2, 130.8, 130.5, 129.4, 129.3, 129.2, 128.6, 128.3, 127.7, 125.5, 110.8, 21.4, 21.2 ppm; IR (KBr) 3061, 3023, 2918, 2859, 1692, 1603, 1506, 1486, 1281, 1247, 1021, 818, 764 cm^{-1}; m/z (70 ev) 418.1 [M^+]. Anal. Calcd for $C_{24}H_{19}BrS$: C, 68.73; H, 4.57. Found: C, 68.58; H, 4.59.

3-Bromo-4-(4-methoxyphenyl)-2,5-di-*p*-tolylthiophene (7d): To a mixture of 3,4-dibromo-2,5-di-*p*-tolylthiophene (0.3 mmol, 126.65 mg), 4-methoxyphenylboronic acid (0.35 mmol, 53.2 mg), K_3PO_4 (1.2 mmol, 254.7 mg), 5 mol % of [$Pd(OAc)_2$ + ligand] (0.015 mmol, 12.44 mg) were added 3 mL of toluene and 2 mL of dioxane. The reaction mixture was then heated and stirred at 80 °C for 13 h. Column chromatography (petroleum ether/ethyl acetate 45:1) resulted 83.6 mg (62%) of title compound as yellow solid: mp 121−122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.8, 2H), 7.09 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 138.8, 138.3, 138.1, 137.5, 136.6, 131.9, 131.0, 130.6, 129.3, 129.2, 129.1, 128.6, 128.4, 113.7, 111.2, 55.2, 21.4, 21.2 ppm; IR (KBr) 3022, 2956, 2930, 2855, 1609, 1514, 1492, 1452, 1287, 1246, 1176, 1034, 880, 802, 756 cm^{-1}; HRMS (70 eV) calcd for $C_{25}H_{21}BrOS$ 448.04965, found 448.04939.

3-Bromo-4-(4-methoxyphenyl)-2-(*o*-tolyl)-5-(*p*-tolyl)thiophene (8): A mixture of 3,4-dibromo-2-(*o*-tolyl)-5-(*p*-tolyl)thiophene (0.3 mmol, 118.2 mg), 4-methoxyphenylboronic acid (0.35 mmol, 58.8 mg), K_3PO_4 (1.2 mmol, 254.7 mg), 5 mol % of [$Pd(OAc)_2$ + ligand] (0.015 mmol, 12.44 mg) in 3 mL of toluene plus 2 mL of dioxane was

stirred at 80 °C for 14 h. Flash chromatography (petroleum ether/EtOAc 45:1) to provide the title compound as a colorless solid in 71.5 mg (53%): mp 165−166 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.42−7.37 (m, 3H), 7.33−7.31 (m, 1H), 7.28 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.3, 138.7, 137.9, 137.3, 136.2, 135.7, 132.4, 131.6, 131.0, 130.4, 130.0, 129.1, 128.9, 128.3, 127.5, 125.4, 113.3, 113.2, 55.0, 21.2, 20.4 ppm; IR (KBr) 3005, 2954, 2835, 1610, 1514, 1485, 1288, 1249, 1175, 1033, 799, 719 cm^{-1}; HRMS (70 eV) calcd for $C_{25}H_{21}BrOS$ 448.04965, found 448.04957.

3,4-Bis(4-methoxyphenyl)-2,5-diphenylthiophene (10a): Five milliliters of solvent (toluene 2 mL + dioxane 3 mL) was added to a mixture of 3,4-dibromo-2,5-diphenylthiophene (0.3 mmol, 118.2 mg), 4-methoxybenzeneboronic acid (0.7 mmol, 106.4 mg), K_3PO_4 (1.75 mmol, 371.5 mg), and 8 mol % of [$Pd(OAc)_2$ + ligand] (0.024 mmol, 19.90 mg). The mixture was heated at 80 °C for 14 h. Column chromatography (petroleum ether/ethyl acetate 60:1) afforded 101 mg (75%) of **10a** as yellow solid: mp 207−208 °C, mp[26] 210−211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.18 (m, 10H), 6.87 (d, J = 8.6 Hz, 4H), 6.66 (d, J = 8.6, 4 Hz), 3.74 (s, 6H) ppm; spectroscopic data are identical to those reported; HRMS (70 eV) calcd for $C_{30}H_{24}O_2S$ 448.14970, found 448.14953.

3,4-Bis(4-methoxyphenyl)-2,5-di-*p*-tolylthiophene (10b): A mixture of 3,4-dibromo-2,5-di-*p*-tolylthiophene (0.3 mmol, 126.65 mg), 4-methoxyphenylboronic acid (0.7 mmol, 106.4 mg), K_3PO_4 (1.75 mmol, 371.5 mg), and 8 mol % of [$Pd(OAc)_2$ + ligand] (0.024 mmol, 19.90 mg) in 3 mL of toluene plus 2 mL of dioxane was stirred at 80 °C for 14 h. Column chromatography (petroleum ether/ethyl acetate 40:1) provided the title compound as colorless solid in 110.1 mg (77%): mp 203−204 °C, mp[23] 230−231 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.0 Hz, 4H), 7.02 (d, J = 8.0 Hz, 4H), 6.87 (d, J = 8.8 Hz, 4H), 6.66 (d, J = 8.8 Hz, 4H), 3.74 (s, 6H), 2.30 (s, 6H) ppm; spectroscopic data are identical to those reported. Anal. Calcd for $C_{32}H_{28}O_2S$: C, 80.64; H, 5.92. Found: C, 80.48; H, 5.94.

3,4-Bis(4-methoxyphenyl)-2-(*o*-tolyl)-5-(*p*-tolyl)thiophene (11): A mixture of 2 mL of toluene plus 3 mL of dioxane was added to a mixture of 3,4-dibromo-2-(*o*-tolyl)-5-(*p*-tolyl)thiophene (0.3 mmol, 126.65 mg), 4-methoxybenzeneboronic acid (0.7 mmol, 106.4 mg), K_3PO_4 (1.75 mmol, 371.5 mg), and 8 mol % of [$Pd(OAc)_2$ + ligand] (0.024 mmol, 19.90 mg). The mixture was heated at 90 °C for 15 h. Chromatography (petroleum ether/EtOAc 40:1) gave the title compound as colorless solid: yield 90.2 mg (63%); mp 144−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34−7.32 (m, 1H),7.23−7.08 (m, 3H), 7.12 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 8.6, 2 Hz), 6.54 (d, J = 8.6 Hz, 2H), 3.74 (s, 3H), 3.66 (s, 3H), 2.29 (s, 3H), 2.02 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 157.8, 140.2, 138.3, 137.6, 137.3, 137.0, 136.8, 134.0, 132.1, 132.0, 131.8, 131.5, 130.1, 129.2, 129.16, 129.11, 129.0, 128.0, 125.4, 113.4, 113.0, 55.1, 55.0, 21.2, 20.5 ppm; IR (KBr) 3008, 2954, 2923, 2835, 1609, 1524, 1506, 1303, 1287, 1246, 1110, 889, 869, 769 cm^{-1}; m/z (70 eV) 476.3 [M^+]. Anal. Calcd for $C_{32}H_{28}O_2S$: C, 80.64; H, 5.92. Found: C, 80.81; H, 5.94.

3-(4-Methoxyphenyl)-2,5-diphenyl-4-*p*-tolylthiophene (12): To a mixture of 3-bromo-4-(4-methoxyphenyl)-2,5-diphenylthiophene (0.2 mmol, 84.26 mg), 4-methylbenzeneboronic acid (0.24 mmol, 32.6 mg), K_3PO_4 (0.6 mmol, 127.36 mg), 8 mol % of [$Pd(OAc)_2$ + ligand] (0.016 mmol, 13.27 mg) was added 5 mL of toluene. The reaction mixture was then heated and stirred at 90 °C for 16 h. Column chromatography (petroleum ether/ethyl acetate 50:1) gave 39.8 mg (46%) of a yellow solid: mp 177−179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26−7.18 (m, 10H), 6.92 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 8.8, 2 Hz), 3.73 (s, 6H), 2.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.1, 139.5, 139.1, 138.1, 138.0, 136.0, 134.4, 133.4, 131.9, 130.6, 129.1 (2C), 128.8, 128.5, 128.3 (2C), 128.2, 127.0, 126.9, 113.2, 55.0, 21.2 ppm; IR (KBr) 3055, 3025, 3001, 2950, 2932, 2833, 1607, 1597, 1524, 1504, 1482, 1285, 1244, 1173, 1031, 833, 764, 753 cm^{-1}; HRMS (70 eV) calcd for $C_{30}H_{24}OS$ 432.15479, found 432.15482.

3-(4-Methoxyphenyl)-4-phenyl-5-(*o*-tolyl)-2-(*p*-tolyl)thiophene (13): A mixture of 3-bromo-4-(4-methoxyphenyl)-2-(*o*-tolyl)-5-(*p*-tolyl)thiophene (0.3 mmol, 134.8 mg), phenylboronic acid (0.4 mmol, 49 mg), K_3PO_4 (1.2 mmol, 254.7 mg), and 8 mol % of [$Pd(OAc)_2$ + ligand] (0.024 mmol, 19.9 mg) in a mixture of 3 mL of toluene plus 2 mL of dioxane was stirred at 90 °C for 16 h. Chromatography (petroleum ether/ethyl acetate 45:1) provided **13** as colorless solid in 68.3 mg (51%): mp 161−163 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.37−7.35 (m, 1H), 7.21−7.20 (m, 1H), 7.17−7.14 (m, 3H), 7.13−7.12 (m, 1H), 7.08−7.06 (m, 2H), 7.05−7.02 (m, 3H), 6.94 (d, J = 8.8 Hz, 2H), 6.85 (dd, J = 8.1, 1.6 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.34 (s, 3H), 2.06 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.2, 140.6, 138.4, 137.6, 137.5, 137.3, 136.8, 136.6, 133.8, 132.0, 131.9, 131.6, 131.0, 130.4, 130.0, 129.1, 129.0, 128.0, 127.4, 126.0, 125.3, 113.4, 55.0, 21.2, 20.4 ppm; IR (KBr) 3057, 2993, 2923, 1609, 1575, 1486, 1246, 1176, 1100, 1033, 815, 727 cm^{-1}; m/z (70 eV) 446.2 [M^+]. Anal. Calcd for $C_{31}H_{26}OS$: C, 83.37; H, 5.87. Found: C, 83.22; H, 5.89.

Debromination[34] Procedure of 3-Bromo-4-(4-methoxyphenyl)-2-(*o*-tolyl)-5-(*p*-tolyl)thiophene (9): Five milliliters of dry CH_3CN was added to an oxygen-free mixture of bromothiophene (022 mmol, 100 mg) and $Pd(PPh_3)_4$ (0.022 mmol,25.7 mg) and stirred for about 20 min. After that, $NaBH_4$ (0.55 mmol, 21.2 mg) was added. The mixture was stirred at 75 °C under inert atmosphere for 24 h. Then, the solvent was evaporated, and the residue was extracted by dichloromethane (3 × 30 mL). Organic phase was combined and dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified via flash chromatography on silica gel (petroleum ether/ethyl acetate 40:1) to provide the title compound as colorless viscous oil in 66 mg (81%): ^{1}H NMR (600 MHz, C_6D_6) δ 7.58−7.53 (m, 1H), 7.41 (d, J = 7.9 Hz,2H), 7.33 (d, J = 8.7 Hz, 2H), 7.15 (s, 1H), 7.09−7.08 (m, 3H), 6.87 (d, J = 7.9 Hz, 2H), 6.71 (d, J = 8.7 Hz, 2H), 3.27 (s, 3H), 2.41 (s, 3H), 2.02 (s, 3H) ppm; ^{13}C NMR (150 MHz, C_6D_6) δ 159.9, 142.5, 138.9, 138.8, 137.9, 136.8, 135.2, 132.9, 131.9, 131.3, 131.0, 130.33, 130.30, 130.2, 129.0, 128.8, 127.1, 115.0, 55.4, 22.0, 21.7 ppm; IR (NaCl) 3049, 2955, 2925, 1610, 1488, 1462, 1442, 1291, 1247, 1177, 1035, 835, 738 cm^{-1}; m/z (70 ev) 370.2 [M^+]. Anal. Calcd for $C_{25}H_{22}OS$: C, 81.04; H, 5.98. Found: C, 81.20; H, 6.00.

■ ASSOCIATED CONTENT

Supporting Information. Reaction optimization conditions, X-ray data, results of calculations, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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