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Direct C−H Arylation of Thiophenes at Low Catalyst Loading of a Phosphine-Free Bis(alkoxo)palladium Complex

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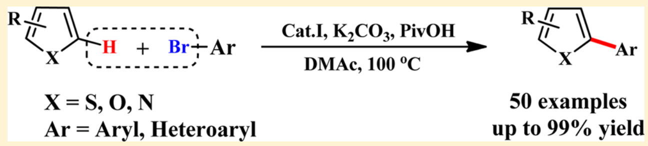
Supporting Information

ABSTRACT: An efficient phosphine-free direct C−H arylation of thiophenes at the α-position has been developed at low catalyst loading of bis(alkoxo)palladium complex (**Cat.I**, 0.1−0.2 mol %). The developed synthetic method can be applied to the synthesis of α-aryl/heteroaryl thiophenes from aryl or heteroaryl bromides in good to excellent yields and is compatible with the substrates bearing electron-donating or electron-withdrawing groups. The reactivities of the 2- and 5-positions of thiophenes are equivalent and not dependent on steric hindrance under optimal conditions. This condition can also be applied to other heterocyclic moieties such as benzothiophene, benzofuran, and pyrrole with high conversion yields.



INTRODUCTION

In recent years, much attention has been given to the synthesis of thiophene derivatives due to their biological or physical properties.[1] Aryl/heteroaryl thiophenes as important building blocks have been widely used in organic field-effect transistors (OFETs),[2] organic light emitting diodes (OLEDs),[3] and organic solar cells (OSC).[4] Traditionally, arylthiophenes have been prepared by palladium-catalyzed Suzuki, Stille, or Negishi cross-coupling reactions which required the appropriate functionalization of one or both coupling partners that may not be readily available.[5] In order to avoid these cumbersome operations, in 1990, Ohta and co-workers developed a palladium-catalyzed method of direct C−H arylation of heteroaromatics.[6] Recently, more successful improvements of direct C−H activation of thiophenes have been achieved by Doucet,[7] Fagnou,[8] Itami,[9] and others.[10] However, most of these catalytic systems require high loadings of palladium salts (1−10 mol %) or the complexes associated with phosphine ligands and other expensive additives.[7b,e−h,8a,b,10] Doucet et al. reported a ligand-free direct arylation of thiophenes using 0.01−0.5 mol % $Pd(OAc)_2$. However, the product yields were low in many cases. Additionally their reaction could only proceed at 130−150 °C.[7c,d,i] Furthermore, examples of five- or six-membered heteroaryl bromides having the regioselective arylation with thiophenes bearing multiple reactive centers are still rare. Therefore, an effective phosphine-free method for direct C−H arylation of thiophenes with aryl or heteroaryl bromides using low catalyst loading at relatively low temperature is still need.

More recently, our research interest has been focused on the catalytic application of *N,O*-ligand palladacycle catalysts: bis(alkoxo)palladium(II) complexes which have been successfully applied to Sonogashira,[11] Suzuki,[12] and oxidative Heck-type[13] reactions as effective catalysts. Herein, we report an effective and practical protocol that (1) could tolerate a wide range of aryl bromides and five- or six-membered heteroaryl bromides, (2) could adapt well for thiophenes bearing multiple reactive centers, and (3) could use low catalyst loadings of bis(alkoxo)palladium(II) complex (**Cat.I**, 0.1−0.2 mol %) in the absence of phosphine ligands at 100 °C (Figure 1).

RESULTS AND DISCUSSION

The reaction conditions were investigated using the coupling between 2-methylthiophene (**1a**) and 4-bromoanisole (**2a**) in PivOH/DMF with Na_2CO_3, and a low yield 42% of product **3a** was observed as a model study (Table 1, entry 1). Using K_2CO_3 as the base resulted in a high yield of **3a**, and other bases such as Cs_2CO_3, K_3PO_4, and KOAc gave slightly lower yields (Table 1, entries 1−5). When DMF was replaced with DMAc, the yield of **3a** was increased from 82% to 86% (Table 1, entries 6−9). It was found that most of the acids evaluated in this catalytic system were less effective except PivOH (Table 1, entries 6, 10−13). Subsequently, the catalytic activity of bis(alkoxo)palladium complexes **Cat.II** and **Cat.III** was studied but did not show better catalytic activity (Table 1, entries 14 and 15). Although the product yield was reduced with lower reaction temperature, it is worth reporting that the conversion yield could be up to 69% at 80 °C (Table 1, entries 16−19). Moreover, the catalytic activity was not obviously changed even when the catalyst loading was decreased to 0.1 mol % (Table 1, entries 20 and 21).

The substrates of direct C−H activation for the preparation of α-arylthiophenes were investigated under the discovered reaction conditions. The coupling reaction of 2-methylthiophene with aryl bromides could take place efficiently to afford the desired products in good to excellent yields (Table 2). Accordingly, aryl bromides having electron-withdrawing or electron-donating groups were well tolerated in this reaction,

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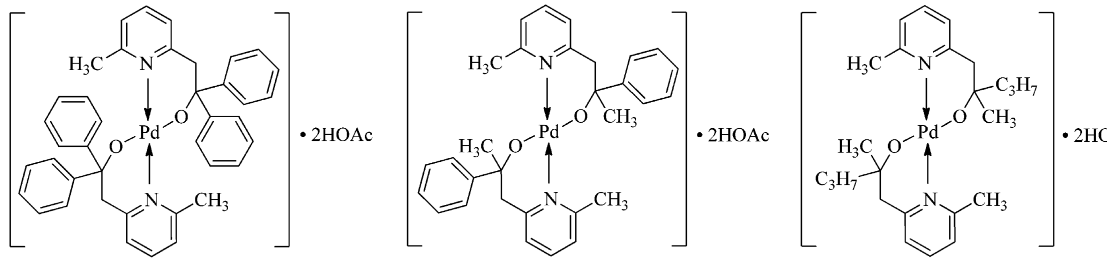
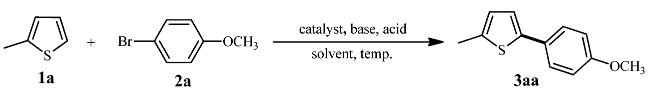


Cat.**I** Cat.**II** Cat.**III**

Figure 1. Structure of bis(alkoxo)palladium(II) complexes **Cat.I**, **Cat.II**, and **Cat.III**.

Table 1. Screening of the Influence of Reaction Conditions for Palladium-Catalyzed Coupling of 2-Methylthiophene with 4-Bromoanisole[a]



entry	base	solvent	acid	temp (°C)	cat.	yield (%)
1	Na_2CO_3	DMF	PivOH	120	I	42
2	K_2CO_3	DMF	PivOH	120	I	82
3	Cs_2CO_3	DMF	PivOH	120	I	50
4	K_3PO_4	DMF	PivOH	120	I	70
5	KOAc	DMF	PivOH	120	I	43
6	K_2CO_3	DMAc	PivOH	120	I	86
7	K_2CO_3	dioxane	PivOH	120	I	26
8	K_2CO_3	toluene	PivOH	120	I	17
9	K_2CO_3	DMAc/EtOH (7/1)	PivOH	120	I	31
10	K_2CO_3	DMAc	*p*-toluenesulfonic acid	120	I	21
11	K_2CO_3	DMAc	PhCOOH	120	I	44
12	K_2CO_3	DMAc	CF_3SO_3H	120	I	18
13	K_2CO_3	DMAc		120	I	45
14	K_2CO_3	DMAc	PivOH	120	II	56
15	K_2CO_3	DMAc	PivOH	120	III	65
16	K_2CO_3	DMAc	PivOH	110	I	86
17	K_2CO_3	DMAc	PivOH	100	I	85
19	K_2CO_3	DMAc	PivOH	80	I	69
20[b]	K_2CO_3	DMAc	PivOH	100	I	85
20[c]	K_2CO_3	DMAc	PivOH	100	I	85
21[d]	**K_2CO_3**	**DMAc**	**PivOH**	**100**	**I**	**84**

[a]Reaction conditions: 2-methylthiophene (0.75 mmol), 4-bromoanisole (0.5 mmol), base (0.75 mmol), solvent (1.5 mL), catalyst (2.0 mol %), and acid (30 mol %) under a nitrogen atmosphere for 24 h. [b]Catalyst (1.0 mol %). [c]Catalyst (0.5 mol %). [d]Catalyst (0.1 mol %).

affording more than 80% yields of the arylated thiophenes **3aa−at** (Table 2, **3aa−at**). An *ortho* steric effect was found to have no significant influence on this coupling reaction, and high yields (80−91%) were obtained with sterically hindered substrates **3ar−at**. An explanation for this phenomenon is that *ortho*-substituents on the molecule of aryl halides may have coordination properties with palladium, which may affect their reaction rates and yields.[7b] Subsequently, the reactivity of several thiophene derivatives has been examined (Table 2, **3bb−eb**). It was found that thiophenes containing electron-deficient groups tended to show higher reactivity compared from those having electron-donor groups except thiophene-2-carbonitrile **1e** (73%). Moreover, in an excess amount of 4-bromotoluene, the thiophenes substituted with aryl or heteroaryl groups on the C-2, C-3, and C-4 positions generally have high enough reactivity to give mono- or diarylated products in good to excellent yields (Table 2, **3fb−qb**).

The regioselectivity of some thiophenes with two or more active sites (**1m−p**) has been examined (Table 3). It was found that there are more than two different products formed depending on the concentration of 4-bromotoluene. In all of these examples, the conversion yield of 4-bromotoluene was more than 85%. Even with equimolar amounts of thiophenes and 4-bromobenzene, diarylated products **3mb−ob** were found more than monosubstituted compounds $\mathbf{3mb_1}$−$\mathbf{ob_1}$ (Table 3, entries 1−3). The unsymmetrical substrate 3-phenylthiophene (**1p**) was transformed into diarylated thiophene **3pb** and two monosubstituted products $\mathbf{3pb_1}$ and $\mathbf{3pb_2}$ (Table 3, entry 4). These results indicated that the reactivities of these thiophene analogues are the same and independent of the steric hindrance in this reaction.

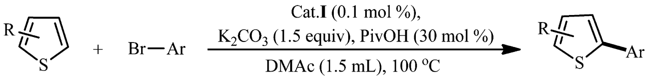
Heteroaryl bromides such as pyridine, pyrimidine, quinoline, thiophene, and furan derivatives were also investigated (Table 4). These heteroaryl bromides have higher reactivity in the presence of 0.2 mol % catalyst to give the desired products in good to excellent yields (Table 4, **3au−aac**). However, 2-bromo-5-methylthiophene showed lower activity, and the isolated product **3aab** was obtained in 51% yield (Table 4, **3aab**). In one example, the *ortho* steric hindrance had significant influence on this coupling reaction, where only a trace amount of 2-bromo-3-methylpyridine was transformed as determined by GC analysis. Under the optimized conditions, 2-hexylthiophene and benzo[*b*]thiophene were reacted with 3-bromopyridine to afford the desired products in 80% and 61%, respectively (Table 4, **3bw** and **3rw**). To characterize the structure of the obtained products, the crystal structures of **3ib**, **3mb**, and **3ax** were analyzed by X-ray (see the Supporting Information).

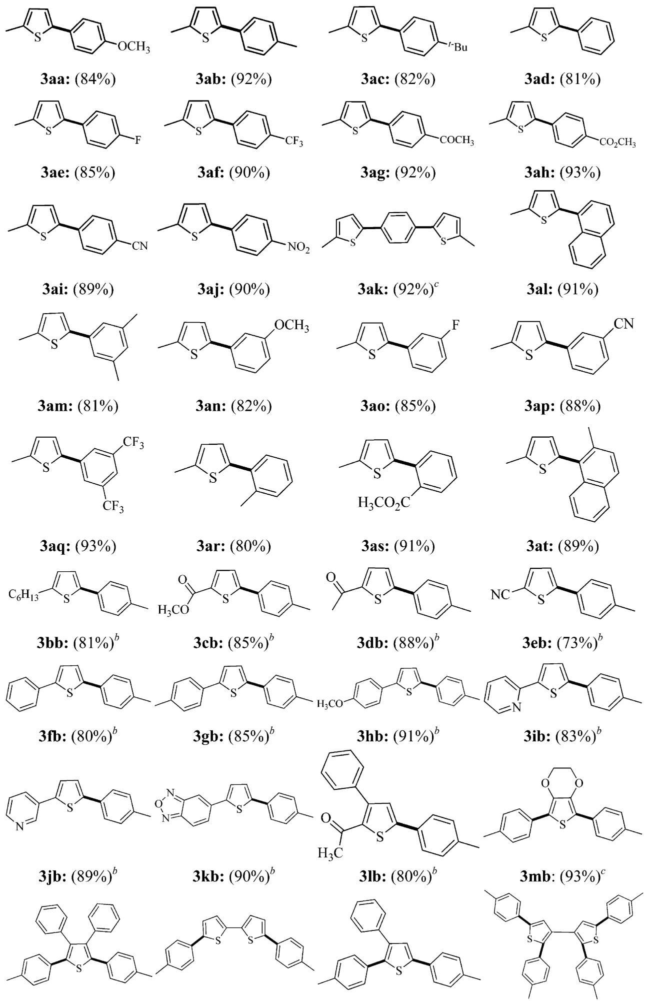
Finally, these reaction conditions could also be applied to benzofuran and pyrrole derivatives (Scheme 1). To our delight, high conversion yields for all of these investigated heterocyclic compounds were obtained. With an excess of 4-bromotoluene, benzofuran could be transformed into mono- and disubstituted products in an approximately 3:2 ratio.

■ CONCLUSION

In summary, we have developed an efficient and regioselective phosphine-free direct C−H arylation of thiophenes with aryl or heteroaryl bromides using a low catalyst loading of bis(alkoxo) palladium complex (**Cat.I**, 0.1−0.2 mol %) at 100 °C. This optimal reaction protocol exhibits a wide range of applications for various aryl, heteroaryl bromides and thiophene derivatives to give the corresponding products in good to excellent yields. In this catalytic reaction system, the reactivity of two or more

Table 2. Palladium-Catalyzed Reaction of Aryl Bromides with Thiophene Derivatives[a]





3aa: (84%); **3ab**: (92%); **3ac**: (82%); **3ad**: (81%); **3ae**: (85%); **3af**: (90%); **3ag**: (92%); **3ah**: (93%); **3ai**: (89%); **3aj**: (90%); **3ak**: (92%)[c]; **3al**: (91%); **3am**: (81%); **3an**: (82%); **3ao**: (85%); **3ap**: (88%); **3aq**: (93%); **3ar**: (80%); **3as**: (91%); **3at**: (89%); **3bb**: (81%)[b]; **3cb**: (85%)[b]; **3db**: (88%)[b]; **3eb**: (73%)[b]; **3fb**: (80%)[b]; **3gb**: (85%)[b]; **3hb**: (91%)[b]; **3ib**: (83%)[b]; **3jb**: (89%)[b]; **3kb**: (90%)[b]; **3lb**: (80%)[b]; **3mb**: (93%)[c]; **3nb**: (95%)[c]; **3ob**: (90%)[c]; **3pb**: (82%)[c]; **3qb**: (88%)[d]

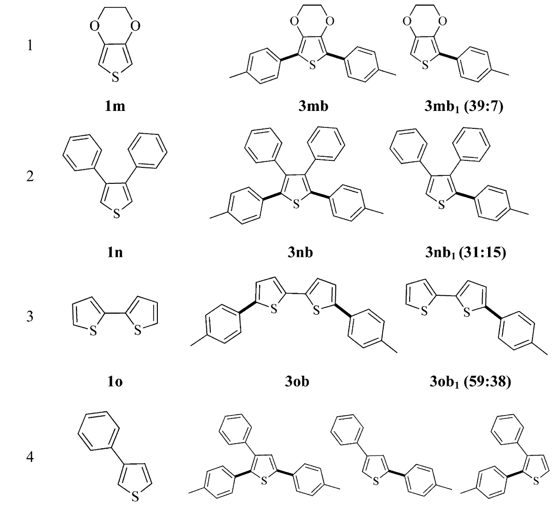
[a]Reaction conditions: thiophene derivative (0.75 mmol), aryl bromide (0.5 mmol), K_2CO_3 (0.75 mmol), DMAc (1.5 mL), **Cat.I** (0.1 mol %), and PivOH (30 mol %), 100 °C, under a nitrogen atmoshphere for 24 h. [b]Thiophene derivative (0.5 mmol), 4-bromotoluene (0.75 mmol), K_2CO_3 (0.75 mmol), DMAc (1.5 mL), **Cat.I** (0.1 mol %), PivOH (30 mol %), 100 °C, under a nitrogen atmoshphere for 24 h. [c]Thiophene derivative (0.5 mmol), 4-bromotoluene (1.5 mmol), K_2CO_3 (1.5 mmol), DMAc (2.0 mL), **Cat.I** (0.5 mol %), PivOH (60 mol %). [d]4-Bromotoluene (3.0 mmol), 28 h.

active sites of thiophenes are the same and independent of the steric hindrance. In addition, high conversion yields were obtained for benzothiophene, benzofuran, and pyrrole derivatives.

■ EXPERIMENTAL SECTION

General Methods. All reactions were run under nitrogen in Schlenk tubes using vacuum lines. DMAc analytical grade was not distilled before use. Chemical reagents were purchased from commercial suppliers and used without further purification. Complexes **Cat.I**, $PyCH_3[CH_2CPh_2OH]$ (**L$_1$**), and some thiophene derivatives (**1f–l** and **1n–p**) were prepared according to the literature procedure.[13,14] ^1H NMR and ^{13}C NMR spectra were recorded on 400 and 100 MHz NMR instruments using $CDCl_3$ as the solvent and TMS as the internal standard. High-resolution mass spectrometry data of the products were collected on an Q-TOF LC/MS instrument. Melting points are uncorrected. Flash chromatographies were performed on silica gel (200–300 mesh).

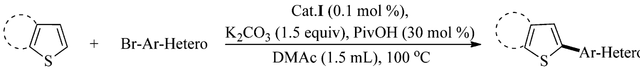
Table 3. Reaction of Multiple C–H Bond Arylation[a]

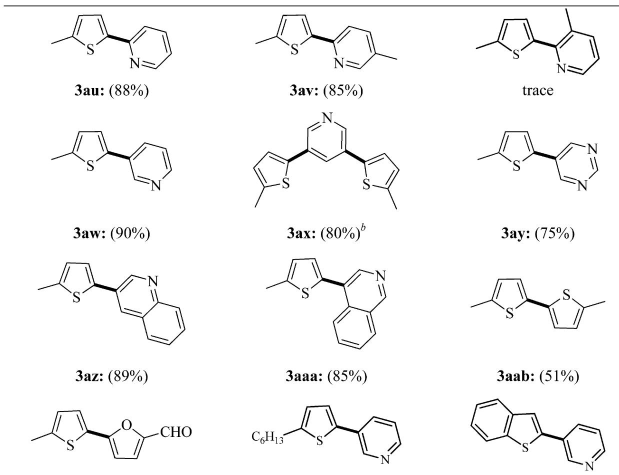


Entry	Thiophenes	Product			Yield [%]
1	**1m**	**3mb**	**3mb$_1$ (39:7)**		92
2	**1n**	**3nb**	**3nb$_1$ (31:15)**		93
3	**1o**	**3ob**	**3ob$_1$ (59:38)**		87
4	**1p**	**3pb**	**3pb$_1$**	**3pb$_2$ (70:9:9)**	88

[a]Reaction conditions: thiophene derivative (0.5 mmol), 4-bromotoluene (0.5 mmol), K_2CO_3 (0.6 mmol), DMAc (1.5 mL), catalyst (0.1 mol %), PivOH (30 mol %), 100 °C, 24 h.

Table 4. Palladium-Catalyzed Reaction of Heteroaryl Bromides with Thiophene Derivatives[a]



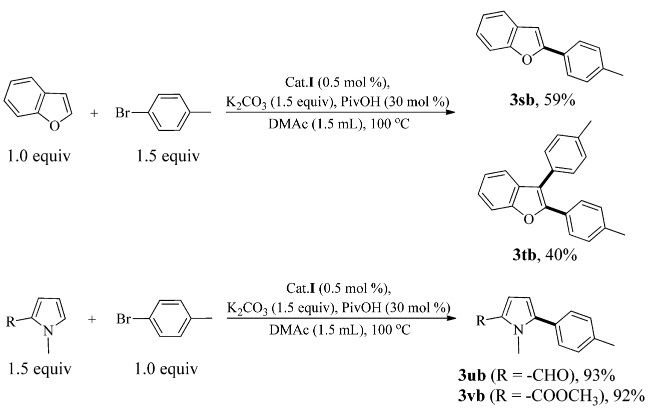


3au: (88%); **3av**: (85%); trace; **3aw**: (90%); **3ax**: (80%)[b]; **3ay**: (75%); **3az**: (89%); **3aaa**: (85%); **3aab**: (51%); **3aac**: (81%); **3bw**: (80%)[b]; **3rw**: (61%)[b]

[a]Reaction conditions: thiophene derivative (0.75 mmol), heteroaryl bromide (0.50 mmol), K_2CO_3 (0.75 mmol), DMAc (1.5 mL), **Cat.I** (0.2 mol %), PivOH (30 mol %), 100 °C, under a nitrogen atmoshphere for 24 h. [b]**Cat.I** (0.5 mol %).

Preparation of $PyCH_3[CH_2C(CH_3)PhOH]$ (L$_2$). To a stirred solution of 2,6-lutidine (5.00 g, 5.4 mL, 46.7 mmol) in 100 mL of THF was added 19.5 mL of a 2.4 M *n*-BuLi solution (46.7 mmol) in

Scheme 1. Direct Arylation of Other Heteroaromatics with 4-Bromotoluene



hexane dropwise at −60 °C and stirred for 1 h, and then acetophenone (5.61 g, 5.5 mL, 46.7 mmol) in 20 mL of THF was added. After additional stirring within 12 h at room temperature a yellow solution was formed, and then the reaction mixture was acidified to pH = 1 with 2 N HCl. After being stirred for 1 h, the mixture was neutralized with 2 N NaOH. The aqueous layer was extracted twice with ethyl acetate, and the organic layers were dried with Na_2SO_4. After evaporation of the solvents *in vacuo*, the product was purified by column chromatography (hexane/ethyl acetate = 10:1, R_f = 0.2) as a colorless oil: yield 10.12 g (95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54−7.44 (m, 2H), 7.39 (t, J = 7.7 Hz, 1H), 7.32−7.22 (m, 2H), 7.22−7.10 (m, 2H), 6.94 (t, J = 7.7 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 3.19 (m, 2H), 2.49 (s, 3H), 1.53 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 158.5, 156.9, 148.4, 137.0, 127.8, 126.0, 124.8, 121.2, 121.0, 74.5, 48.7, 30.5, 24.2; HRMS (ESI) calcd for $C_{15}H_{18}NO$ [M + H]$^+$ 228.1383, found 228.1392.

Preparation of $PyCH_3[CH_2C(CH_3)C_3H_7OH]$ (L_3). Analogously to L_2, L_3 was prepared from 2,6-lutidine (5.00 g, 5.4 mL, 46.7 mmol) and 19.5 mL of *n*-BuLi solution (2.4 M, 46.7 mmol) in hexane and pentan-2-one (4.02 g, 5.0 mL, 46.7 mmol). The product was purified by column chromatography (hexane/ethyl acetate = 10:1, R_f = 0.2) as a pale yellow oil: yield 7.76 g (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51 (t, J = 7.7 Hz, 1H), 7.01 (d, J = 7.7 Hz, 1H), 6.91 (d, J = 7.6 Hz, 1H), 6.27 (s, 1H), 2.93−2.74 (m, 2H), 2.51 (s, 3H), 1.47−1.35 (m, 4H), 1.13 (s, 3H), 0.96−0.82 (m, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 159.3, 157.2, 137.0, 121.2, 120.9, 72.5, 46.6, 45.0, 26.9, 24.3, 17.4, 14.7; HRMS (ESI) calcd for $C_{12}H_{20}NO$ [M + H]$^+$ 194.1539, found 194.1556.

Preparation of $\{PyCH_3[CH_2C(CH_3)PhO]\}_2Pd\cdot2AcOH$ (Cat.II). A solution of L_2 (466 mg, 2.05 mmol) in toluene (8 mL) was added to a stirred solution of $Pd(OAc)_2$ (224 mg, 1.0 mmol) in toluene (12 mL). The mixture was stirred at room temperature. After 3 days, the product was isolated by filtration to give **Cat.II** as a white solid: yield 618 mg (91%); NMR spectra were not recorded due to its poor solubility; HRMS (ESI) calcd for $C_{30}H_{33}N_2O_2Pd$ [M + H]$^+$ 559.1499, found 559.1582. Anal. Calcd for $C_{30}H_{32}N_2O_2Pd\cdot2AcOH$ (679.11): C, 60.13; H, 5.94; N, 4.13. Found: C, 60.25; H, 5.93; N, 4.02.

Preparation of $\{PyCH_3[CH_2C(CH_3)C_3H_7O]\}_2Pd\cdot2AcOH$ (Cat.III). Analogously to **Cat.II**, **Cat.III** was prepared from L_3 (396 mg, 2.05 mmol) and $Pd(OAc)_2$ (224 mg, 1.0 mmol) in 20 mL of toluene. The product was isolated by filtration to give **Cat.III** as a white solid: yield 550 mg (90%); NMR spectra were not recorded due to its poor solubility; HRMS (ESI) calcd for $C_{24}H_{37}N_2O_2Pd$ [M + H]$^+$ 491.1884, found 491.1901. Anal. Calcd for $C_{24}H_{36}N_2O_2Pd\cdot2AcOH$ (611.08): C, 55.03; H, 7.26; N, 4.58. Found: C, 55.03; H, 7.17; N, 4.56.

Typical Procedure for the Synthesis of Initial Thiophene Derivatives (1f−l and 1n−p). To a flask were added **Cat.I** (0.8 mg, 0.1 mol %), phenylboronic acid (185 mg, 1.5 mmol), KOH (112 mg, 2.0 mmol), aryl bromide (1.0 mmol), and C_2H_5OH (3 mL). The reaction mixture was stirred at 78 °C. After the reaction was completed, it was cooled to room temperature. The reaction mixture was dissolved in H_2O and extracted with ethyl acetate (3 × 15 mL). The organic layer was collected and dried by Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the desired product.

5-(Thiophene-2-yl)benzo[*c*][1,2,5]oxadiazole (1k): R_f = 0.2 (hexane/ethyl acetate = 20:1); yellow solid; mp 118−119 °C; yield 174 mg, (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (s, 1H), 7.87 (d, J = 9.4 Hz, 1H), 7.79−7.71 (m, 1H), 7.51 (d, J = 3.4 Hz, 1H), 7.45 (d, J = 4.9 Hz, 1H), 7.21−7.13 (m, 1H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 149.6, 148.5, 141.7, 137.1, 131.7, 128.6, 127.5, 126.0, 116.9, 110.1; HRMS (ESI) calcd for $C_{10}H_7N_2OS$ [M + H]$^+$ 203.0274, found 203.0279.

Typical Procedure for Palladium-Catalyzed Reaction of Aryl Bromides with Thiophenes and Other Heteroaromatics (3aa−aac,bb−lb,3sb−vb,bw,rw). In a typical experiment, aryl or heteroaryl bromide (0.5−0.75 mmol), thiophene derivative (0.5−0.75 mmol), **Cat.I** (0.4−2.0 mg, 0.1−0.5 mol %), PivOH (15 mg, 30 mol %), and K_2CO_3 (104 mg, 1.5 mmol) were dissolved in DMAc (1.5 mL) under a nitrogen atmosphere. Unless otherwise noted, the mixture was heated at 100 °C for 24 h. The suspension was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried with Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel column chromatography to afford the desired product.

2-Methyl-5-(*p*-methylphenyl)thiophene (3ab):[9a] R_f = 0.5 (100% hexane); white solid; mp 42−44 °C; yield 86 mg (92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 3.4 Hz, 1H), 6.76−6.68 (m, 1H), 2.51 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 142.1, 138.9, 136.8, 131.9, 129.4, 126.1, 125.4, 122.3, 21.1, 15.4; HRMS (ESI) calcd for $C_{12}H_{13}S$ [M + H]$^+$ 189.0732, found 189.0730.

2-(4-*tert*-Butylphenyl)-5-methylthiophene (3ac):[15] R_f = 0.6 (100% hexane); white solid; mp 48−50 °C; yield 94 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51−7.46 (m, 2H), 7.41−7.35 (m, 2H), 7.07 (d, J = 3.5 Hz, 1H), 6.74−6.68 (m, 1H), 2.53−2.48 (m, 3H), 1.34 (s, 9H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 150.1, 142.1, 139.0, 132.0, 126.1, 125.7, 125.3, 122.5, 34.5, 31.3, 15.4; MS (EI) calcd for $C_{15}H_{18}S$ [M]$^+$ 230.4, found 230.1.

2-Methyl-5-phenylthiophene (3ad):[9a] R_f = 0.6 (100% hexane); white solid; mp 44−46 °C; yield 71 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.62−7.53 (m, 2H), 7.41−7.34 (m, 2H), 7.31−7.22 (m, 1H), 7.16−7.10 (m, 1H), 6.78−6.72 (m, 1H), 2.53 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 142.0, 139.5, 134.7, 128.8, 127.0, 126.2, 125.5, 122.9, 15.4; MS (EI) calcd for $C_{11}H_{10}S$ [M]$^+$ 174.3, found 174.1.

2-(4-Fluorophenyl)-5-methylthiophene (3ae):[16] R_f = 0.5 (100% hexane); white solid; mp 87−89 °C; yield 82 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54−7.45 (m, 2H), 7.09−6.98 (m, 4H), 6.75−6.68 (m, 1H), 2.50 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 162.0 (d), 140.9, 139.5, 131.0, 127.1 (d), 126.2, 122.9, 115.7 (d), 15.4; MS (EI) calcd for $C_{11}H_9FS$ [M]$^+$ 192.3, found 192.1.

2-Methyl-5-(*p*-trifluoromethylphenyl)thiophene (3af):[9a] R_f = 0.7 (100% hexane); white solid; mp 117−119 °C; yield 109 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.67−7.56 (m, 4H), 7.19 (d, J = 3.5 Hz, 1H), 6.80−6.73 (m, 1H), 2.53 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 141.2, 140.2, 138.1, 128.7 (q), 126.5, 125.82, 125.78, 125.4, 124.4, 124.2 (q), 15.5; MS (EI) calcd for $C_{12}H_9F_3S$ [M]$^+$ 242.3, found 242.1.

2-(*p*-Acetylphenyl)-5-methylthiophene (3ag):[9a] R_f = 0.3 (hexane/ethyl acetate = 20:1); white solid; mp 140−142 °C; yield 99 mg (92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 3.5 Hz, 1H), 6.80−6.72 (m, 1H), 2.60 (s, 3H), 2.53 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 197.3, 141.5, 140.5, 139.1, 135.3, 129.1, 126.7, 125.1, 124.6, 26.5, 15.5; HRMS (ESI) calcd for $C_{13}H_{13}OS$ [M + H]$^+$ 217.0682, found 217.0682.

Methyl 4-(5-methylthiophene-2-yl)benzoate (3ah):[10f] R_f = 0.3 (hexane/ethyl acetate = 20:1); white solid; mp 149−150 °C; yield 108 mg (93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01 (d, J = 8.4

Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 3.6 Hz, 1H), 6.76−6.74 (m, 1H), 3.92 (s, 3H), 2.52 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 166.8, 141.3, 140.6, 138.9, 130.2, 128.2, 126.6, 125.0, 124.4, 52.1, 15.5; HRMS (ESI) calcd for $C_{13}H_{13}O_2S$ [M + H]$^+$ 233.0631, found 233.0631.

4-(5-Methylthiophene-2-yl)benzonitrile (3ai):[10f] R_f = 0.3 (hexane/ethyl acetate =30:1); white solid; mp 140−141 °C; yield 89 mg (89%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.61 (s, 4H), 7.22 (d, J = 3.6 Hz, 1H), 6.80−6.75 (m, 1H), 2.53 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 142.2, 139.6, 138.9, 132.7, 126.8, 125.5, 125.1, 119., 109.9, 15.5; MS (EI) calcd for $C_{12}H_9NS$ [M]$^+$ 199.3, found 199.1.

2-Methyl-5-(*p*-nitrophenyl)thiophene (3aj):[9a] R_f = 0.3 (hexane/ethyl acetate = 40:1); yellow solid; mp 129−130 °C; yield 99 mg (90%); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.21 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 3.6 Hz, 1H), 6.80 (d, J = 3.5 Hz, 1H), 2.54 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 146.2, 143.0, 140.9, 139.1, 127.0, 125.8, 125.4, 124.4, 15.6; HRMS (ESI) calcd for $C_{11}H_{10}NO_2S$ [M + H]$^+$ 220.0427, found 220.0427.

1,4-Bis(5-methylthiophene-2-yl)benzene (3ak).[9a] Following the general procedure, 2-methylthiophene (**1a**) (185 μL, 1.5 mmol), 1,4-dibromobenzene (**1k**) (119 mg, 0.5 mmol), **Cat.I** (2.0 mg, 0.5 mol %), PivOH (31 mg, 60 mol %), and K_2CO_3 (208 mg, 1.5 mmol) were dissolved in DMAc (2 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 100 °C for 24 h. The suspension was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried with Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel column chromatography (R_f = 0.4, hexane/CH_2Cl_2 = 5:1) to give the desired product as a white solid: mp 179−181 °C; yield 124 mg (92%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.53 (s, 4H), 7.11 (d, J = 3.5 Hz, 2H), 6.77−6.70 (m, 2H), 2.51 (s, 6H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 141.6, 139.5, 133.3, 126.3, 125.8, 122.8, 15.5; HRMS (ESI) calcd for $C_{16}H_{14}S_2$ [M]$^+$ 270.0531, found 270.0532.

2-Methyl-5-(naphthalen-1-yl)thiophene (3al):[7k] R_f = 0.4 (100% hexane); light yellow oil; yield 102 mg (91%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.33−8.26 (m, 1H), 7.93−7.80 (m, 2H), 7.59−7.44 (m, 4H), 7.08−7.01 (m, 1H), 6.88−6.81 (m, 1H), 2.59 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 140.2, 139.4, 133.9, 132.8, 131.8, 128.3, 128.1, 127.9, 127.2, 126.3, 125.9, 125.9, 125.5, 125.2, 15.3; MS (EI) calcd for $C_{15}H_{12}S$ [M]$^+$ 224.3, found 224.0.

2-(3,5-Dimethylphenyl)-5-methylthiophene (3am): R_f = 0.5 (100% hexane); light yellow oil; yield 82 mg (81%); ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.18 (s, 2H), 7.08 (d, J = 3.2 Hz, 1H), 6.90 (s, 1H), 6.78−6.66 (m, 1H), 2.51 (s, 3H), 2.34 (s, 6H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 142.2, 139.1, 138.3, 134.5, 128.7, 126.0, 123.4, 122.6, 21.3, 15.4. Anal. Calcd for $C_{13}H_{14}S$ (202.31): C, 77.18; H, 6.97. Found: C, 77.12; H, 6.99%.

2-(*m*-Methoxyphenyl)-5-methylthiophene (3an):[9a] R_f = 0.3 (100% hexane); light yellow oil; yield 84 mg (82%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27 (t, J = 7.9 Hz, 1H), 7.15 (d, J = 7.7 Hz, 1H), 7.13−7.06 (m, 2H), 6.84−6.76 (m, 1H), 6.76−6.69 (m, 1H), 3.85 (s, 3H), 2.51 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 159.9, 141.8, 139.6, 136.1, 129.8, 126.1, 123.1, 118.1, 112.5, 111.2, 55.3, 15.4; MS (EI) calcd for $C_{12}H_{12}OS$ [M]$^+$ 204.3, found 204.0.

2-(*m*-Fluorophenyl)-5-methylthiophene (3ao): R_f = 0.5 (100% hexane); white solid; mp 44−45 °C; yield 82 mg (85%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35−7.28 (m, 2H), 7.28−7.20 (m, 1H), 7.15−7.09 (d, J = 3.5 Hz, 1H), 6.98−6.89 (m, 1H), 6.77−6.70 (m, 1H), 2.51 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 163.1 (d), 140.5 (d), 140.3, 136.9 (d), 130.3 (d), 126.3, 123.7, 122.0 (d), 113.7 (d), 112.2 (d), 15.4; MS (EI) calcd for $C_{11}H_9FS$ [M]$^+$ 192.3, found 192.0. Anal. Calcd for $C_{11}H_9FS$ (192.04): C, 68.72; H, 4.72. Found: C, 68.69; H, 4.73.

3-(5-Methylthiophene-2-yl)benzonitrile (3ap):[7e] R_f = 0.6 (hexane/ethyl acetate =30:1); white solid; mp 74−75 °C; yield 88 mg (88%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (s, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.53−7.40 (m, 2H), 7.15 (d, J = 3.6 Hz, 1H), 6.79−6.73 (m, 1H), 2.52 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 141.3, 139.1, 135.9, 130.0, 129.6, 129.4, 128.6, 126.6, 124.3, 118.6, 113.0, 15.5; MS (EI) calcd for $C_{12}H_9NS$ [M]$^+$ 199.3, found 199.0.

2-(3,5-Bis(trifluoromethyl)phenyl)-5-methylthiophene (3aq):[16] R_f = 0.6 (100% hexane); white solid; mp 35−36 °C; yield 144 mg (93%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (s, 2H), 7.72 (s, 1H), 7.24 (d, J = 3.6 Hz, 1H), 6.82−6.76 (m, 1H), 2.54 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 142.1, 138.4, 136.7, 132.2 (q), 131.7, 126.8, 125.2, 125.1−125.0 (m), 123.3 (q), 120.1 (p), 15.5; MS (EI) calcd for $C_{13}H_8F_6S$ [M]$^+$ 310.3, found 310.1.

2-Methyl-5-(*o*-methylphenyl)thiophene (3ar):[9a] R_f = 0.6 (100% hexane); colorless oil; yield 75 mg (80%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42−7.35 (m, 1H), 7.29−7.23 (m, 1H), 7.23−7.16 (m, 2H), 6.88−6.83 (m, 1H), 6.77−6.71 (m, 1H), 2.53 (s, 3H), 2.44 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 140.8, 139.6, 135.9, 134.5, 130.7, 130.3, 127.4, 126.2, 125.8, 125.3, 21.2, 15.2; MS (EI) calcd for $C_{12}H_{12}S$ [M]$^+$ 188.3, found 188.0.

Methyl 2-(5-Methylthiophene-2-yl)benzoate (3as):[17] R_f = 0.3 (hexane/ethyl acetate = 20:1); yellow oil; yield 106 mg (91%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71−7.64 (m, 1H), 7.50−7.42 (m, 2H), 7.40−7.31 (m, 1H), 6.85−6.79 (m, 1H), 6.74−6.67 (m, 1H), 3.77 (s, 3H), 2.51 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 169.4, 140.6, 139.6, 134.4, 131.5, 130.9, 129.3, 127.3, 126.2, 125.6, 52.2, 15.3; HRMS (ESI) calcd for $C_{13}H_{12}NaO_2S$ [M]$^+$ 255.0450, found 255.0451.

2-Methyl-5-(2-methylnaphthalen-1-yl)thiophene (3at): R_f = 0.6 (100% hexane); light yellow oil; yield 106 mg (89%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86−7.76 (m, 2H), 7.74−7.67 (m, 1H), 7.45−7.37 (m, 3H), 6.88−6.81 (m, 1H), 6.79−6.72 (m, 1H), 2.59 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 140.3, 137.6, 135.9, 134.2, 131.8, 130.8, 128.4, 128.2, 127.7, 127.6, 126.1, 126.0, 125.2, 124.9, 21.0, 15.4. Anal. Calcd for $C_{16}H_{14}S$ (238.35): C, 80.63; H, 5.92. Found: C, 80.58; H, 5.93.

2-(5-Methylthiophene-2-yl)pyridine (3au):[10f] R_f = 0.3 (hexane/ethyl acetate = 20:1); pale yellow solid; mp 75−76 °C; yield 77 mg (88%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.56−8.49 (m, 1H), 7.67−7.60 (m, 1H), 7.60−7.54 (m, 1H), 7.38 (d, J = 3.6 Hz, 1H), 7.12−7.05 (m, 1H), 6.78−6.73 (m, 1H), 2.54−2.50 (m, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 152.8, 149.4, 142.4, 136.5, 126.3, 124.6, 121.3, 118.3, 15.6; MS (EI): calcd for $C_{10}H_9NS$ [M]$^+$ 175.3; found 175.0.

5-Methyl-2-(5-methylthiophen-2-yl)pyridine (3av):[18] R_f = 0.3 (hexane/ethyl acetate = 20:1); pale yellow solid; mp 70−72 °C; yield 80 mg (85%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.36 (s, 1H), 7.52−7.40 (m, 2H), 7.31 (d, J = 3.5 Hz, 1H), 6.79−6.69 (m, 1H), 2.51 (s, 3H), 2.32 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 150.3, 149.7, 142.4, 141.7, 137.1, 130.9, 126.2, 123.9, 117.9, 18.2, 15.6; MS (EI) calcd for $C_{11}H_{11}NS$ [M]$^+$ 189.3, found 189.0.

3-(5-Methylthiophene-2-yl)pyridine (3aw):[15] R_f = 0.3 (hexane/ethyl acetate = 30:1); pale yellow solid; mp 78−79 °C; yield 79 mg (90%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.82 (d, J = 2.3 Hz, 1H), 8.46 (dd, J = 4.8, 1.4 Hz, 1H), 7.82−7.75 (m, 1H), 7.30−7.23 (m, 1H), 7.15 (d, J = 3.6 Hz, 1H), 6.79−6.73 (m, 1H), 2.55−2.49 (m, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 148.0, 146.6, 140.9, 137.9, 132.4, 130.7, 126.5, 124.1, 123.5, 15.4; HRMS (ESI) calcd for $C_{10}H_{10}NS$ [M + H]$^+$ 176.0528, found 176.0530.

3,5-Bis(5-methylthiophene-2-yl)pyridine (3ax): R_f = 0.2 (hexane/ethyl acetate = 30:1); pale yellow solid, mp 68−69 °C; yield 108 mg (80%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.66 (d, J = 2.1 Hz, 2H), 7.87 (t, J = 2.1 Hz, 1H), 7.19 (d, J = 3.6 Hz, 2H), 6.80−6.75 (m, 2H), 2.53 (s, 6H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 144.8, 141.1, 137.6, 130.6, 128.8, 126.5, 124.4, 15.4; HRMS (ESI) calcd for $C_{15}H_{14}NS_2$ [M + H]$^+$ 272.0562, found 272.0567.

5-(5-Methylthiophene-2-yl)pyrimidine (3ay):[19] R_f = 0.1 (hexane/ethyl acetate =10:1); white solid; mp 59−60 °C; yield 66 mg (75%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.08 (s, 1H), 8.89 (s, 2H), 7.22 (d, J = 3.5 Hz, 1H), 6.82 (d, J = 2.7 Hz, 1H), 2.55 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 156.7, 152.9, 142.4, 133.7, 128.9, 126.8, 125.2, 15.5; HRMS (ESI) calcd for $C_9H_9N_2S$ [M + H]$^+$ 177.0481, found 177.0482.

3-(5-Methylthiophene-2-yl)quinoline (3az):[10d] R_f = 0.1 (hexane/ethyl acetate = 20:1); pale yellow solid; mp 91−93 °C; yield 100 mg (89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.18−9.13 (m, 1H), 8.21−8.15 (m, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.70−7.63 (m, 1H), 7.58−7.50 (m, 1H), 7.32−7.27 (m, 1H), 6.83−6.78 (m, 1H), 2.56 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 148.5, 147.1, 141.1, 138.3, 130.6, 129.3, 129.0, 128.0, 127.9, 127.7, 127.1, 126.6, 124.3, 15.5; HRMS (ESI) calcd for $C_{14}H_{12}NS$ $[M + H]^+$ 226.0685, found 226.0687.

4-(5-Methylthiophene-2-yl)isoquinoline (3aaa): R_f = 0.1 (hexane/ethyl acetate = 20:1); light yellow oil; yield 96 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.19 (s, 1H), 8.58 (s, 1H), 8.27 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 8.1 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 3.4 Hz, 1H), 6.86 (d, J = 2.7 Hz, 1H), 2.57 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 152.0, 143.3, 141.2, 135.3, 134.1, 130.7, 128.3, 127.9, 127.8, 127.2, 126.5, 125.8, 124.6, 15.3; HRMS (ESI) calcd for $C_{14}H_{12}NS$ $[M + H]^+$ 226.0685, found 226.0689.

5,5′-Dimethyl-2,2′-bithiophene (3aab):[7b] R_f = 0.5 (100% hexane); white solid; mp 59−61 °C; yield 50 mg (51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.86 (d, J = 3.4 Hz, 2H), 6.62 (d, J = 3.0 Hz, 2H), 2.45 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 138.4, 135.5, 125.7, 122.8, 15.3; MS (EI) calcd for $C_{10}H_{10}S_2$ $[M]^+$ 194.3; found 194.0.

5-(5-Methylthiophene-2-yl)furan-2-carbaldehyde (3aac):[7b] R_f = 0.3 (hexane/ethyl acetate = 30:1); orange oil; yield 78 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.58 (s, 1H), 7.33 (d, J = 3.6 Hz, 1H), 7.28−7.24 (m, 2H), 6.79−6.73 (m, 1H), 6.57 (d, J = 3.7 Hz, 1H), 2.53 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 176.7, 155.2, 151.3, 142.9, 129.3, 126.6, 126.5, 106.8, 15.4; MS (EI) calcd for $C_{10}H_8O_2S$ $[M]^+$ 192.2, found 192.0.

5-(1-Hexyl)-2-(*p*-methylphenyl)thiophene (3bb):[20] R_f = 0.5 (100% hexane); white solid; mp 49−50 °C; yield 105 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 7.07 (d, J = 3.5 Hz, 1H), 6.73 (d, J = 3.3 Hz, 1H), 2.89−2.74 (m, 2H), 2.35 (s, 3H), 1.77−1.62 (m, 2H), 1.45−1.28 (m, 6H), 0.94−0.85 (m, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 145.2, 141.8, 136.7, 132.0, 129.4, 125.4, 124.8, 122.1, 31.6, 31.6, 30.3, 28.8, 22.6, 21.1, 14.1; HRMS (ESI) calcd for $C_{17}H_{23}S$ $[M + H]^+$ 259.1515, found 259.1512.

Methyl 5-(*p*-tolyl)thiophene-2-carboxylate (3cb):[17] R_f = 0.2 (hexane/ethyl acetate = 40:1); white solid; mp 95−97 °C; yield 99 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J = 3.9 Hz, 1H), 7.56−7.50 (m, 2H), 7.25 (d, J = 3.9 Hz, 1H), 7.24−7.19 (m, 2H), 3.90 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 162.7, 151.5, 138.9, 134.4, 131.4, 130.7, 129.8, 126.1, 123.1, 52.1, 21.2; MS (EI) calcd for $C_{13}H_{12}O_2S$ $[M]^+$ 232.3, found 232.0.

1-(5-(*p*-Tolyl)thiophene-2-yl)ethanone (3db):[21] R_f = 0.2 (hexane/ethyl acetate = 40:1); pale yellow solid; mp 111−113 °C; yield 95 mg (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.65 (d, J = 3.9 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 3.9 Hz, 1H), 7.22 (d, J = 7.9 Hz, 2H), 2.56 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 190.5, 153.1, 142.6, 139.2, 133.5, 130.6, 129.8, 126.2, 123.4, 26.5, 21.3; HRMS (ESI) calcd for $C_{13}H_{13}OS$ $[M + H]^+$ 217.0682, found 217.0682.

5-(*p*-Tolyl)thiophene-2-carbonitrile (3eb): R_f = 0.4 (hexane/ethyl acetate = 30:1); yellow solid; mp 107−108 °C; yield 73 mg (73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56 (d, J = 4.0 Hz, 1H), 7.51−7.46 (m, 2H), 7.25−7.19 (m, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 152.0, 139.7, 138.3, 129.9, 129.5, 126.2, 122.7, 114.5, 107.6, 21.3; MS (EI) calcd for $C_{12}H_9NS$ $[M]^+$ 199.3, found 199.0. Anal. Calcd for $C_{12}H_9NS$ (199.05): C, 72.33; H, 4.55; N, 7.03. Found: C, 72.30; H, 4.57; N, 7.02.

2-Phenyl-5-(*p*-tolyl)thiophene (3fb):[22] R_f = 0.4 (hexane/CH_2Cl_2 = 6:1); white solid; mp 141−143 °C; yield 100 mg (80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63 (d, J = 7.4 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.44−7.35 (m, 2H), 7.32−7.27 (m, 2H), 7.26−7.23 (m, 1H), 7.20 (d, J = 7.9 Hz, 2H), 2.38 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 143.8, 143.1, 137.4, 134.4, 131.6, 129.6, 128.9, 127.4, 125.6, 125.6, 123.9, 123.5, 21.2; MS (EI) calcd for $C_{17}H_{14}S$ $[M]^+$ 250.4, found 250.1.

2,5-Di-*p*-tolylthiophene (3gb):[23] R_f = 0.5 (hexane/ethyl acetate =20:1); white solid; mp 170−172 °C; yield 112 mg (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.54−7.48 (m, 4H), 7.22 (s, 2H), 7.20−7.14 (m, 4H), 2.36 (s, 6H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 143.2, 137.3, 131.6, 129.5, 125.5, 123.4, 21.2; MS (EI) calcd for $C_{18}H_{16}S$ $[M]^+$ 264.4, found 264.1.

2-(4-Methoxyphenyl)-5-(4-methylphenyl)thiophene (3hb):[24] R_f = 0.4 (hexane/CH_2Cl_2 = 6:1); white solid; mp 172−174 °C; yield 128 mg (91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63−7.44 (m, 4H), 7.24−7.10 (m, 4H), 6.92 (d, J = 8.2 Hz, 2H), 3.84 (s, 3H), 2.37 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 159.2, 143.0, 142.8, 137.2, 131.7, 129.5, 127.3, 126.9, 125.5, 123.4, 122.9, 114.3, 55.4, 21.2; MS (EI) calcd for $C_{18}H_{16}OS$ $[M]^+$ 280.4, found 280.1.

2-(5-(*p*-Tolyl)thiophene-2-yl)pyridine (3ib): R_f = 0.1 (hexane/ethyl acetate = 10:1); yellow solid; mp 124−126 °C; yield 104 mg (83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.57 (d, J = 4.7 Hz, 1H), 7.71−7.63 (m, 2H), 7.60−7.50 (m, 3H), 7.28 (d, J = 3.9 Hz, 1H), 7.21 (d, J = 7.9 Hz, 2H), 7.16−7.11 (m, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 152.6, 149.6, 146.4, 143.3, 137.8, 136.6, 131.5, 129.6, 125.7, 125.4, 123.5, 121.7, 118.5, 21.2; HRMS (ESI) calcd for $C_{16}H_{14}NS$ $[M + H]^+$ 252.0841, found 252.0845.

3-(5-(*p*-Tolyl)thiophen-2-yl)pyridine (3jb): R_f = 0.1 (hexane/ethyl acetate = 10:1); white solid; mp 158−160 °C; yield 112 mg (89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.90 (d, J = 2.0 Hz, 1H), 8.51 (dd, J = 4.8, 1.4 Hz, 1H), 7.91−7.81 (m, 1H), 7.53 (d, J = 8.1 Hz, 2H), 7.34−7.26 (m, 3H), 7.21 (d, J = 8.1 Hz, 2H), 2.38 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 148.3, 146.7, 145.2, 138.9, 137.9, 132.5, 131.1, 130.4, 129.7, 125.7, 125.1, 123.6, 123.6, 21.2; HRMS $C_{16}H_{14}NS$ $[M + H]^+$ 252.0841, found 252.0849.

5-(5-(*p*-Tolyl)thiophene-2-yl)benzo[*c*][1,2,5]oxadiazole (3kb): R_f = 0.3 (hexane/CH_2Cl_2 = 10:1); yellow solid; mp 188−190 °C; yield 132 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (s, 1H), 7.87−7.82 (m, 1H), 7.79−7.72 (m, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 3.9 Hz, 1H), 7.31 (d, J = 3.9 Hz, 1H), 7.23 (d, J = 7.9 Hz, 2H), 2.39 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 149.7, 148.5, 146.9, 140.0, 138.5, 137.0, 131.3, 130.8, 129.8, 127.0, 125.8, 123.9, 116.8, 109.3, 21.3; HRMS $C_{17}H_{13}N_2OS$ $[M + H]^+$ 293.0743, found 293.0749.

1-(3-ZPhenyl-5-(*p*-tolyl)thiophene-2-yl)ethanone (3lb): R_f = 0.1 (hexane/ethyl acetate = 10:1); white solid; mp 74−76 °C; yield 117 mg (80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56 (d, J = 8.1 Hz, 2H), 7.45−7.43(m, 5H), 7.25−7.19 (m, 3H), 2.39 (s, 3H), 2.13 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 191.9, 149.7, 147.8, 139.2, 138.2, 136.7, 130.3, 129.8, 129.0, 128.4, 128.3, 127.4, 126.0, 29.1, 21.3; HRMS (ESI) calcd for $C_{19}H_{17}OS$ $[M + H]^+$ 293.0995, found 293.0998.

3-(5-Hexylthiophene-2-yl)pyridine (3bw): R_f = 0.1 (hexane/ethyl acetate = 20:1); pale yellow solid; mp 26−27 °C; yield 98 mg (80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.83 (d, J = 2.1 Hz, 1H), 8.46 (dd, J = 4.8, 1.3 Hz, 1H), 7.84−7.76 (m, 1H), 7.30−7.24 (m, 1H), 7.18 (d, J = 3.6 Hz, 1H), 6.78 (d, J = 3.5 Hz, 1H), 2.83 (t, J = 7.6 Hz, 2H), 1.76−1.63 (m, 2H), 1.46−1.26 (m, 6H), 0.90 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 146.9, 146.2, 145.6, 136.5, 131.4, 129.7, 124.3, 122.9, 122.6, 30.6, 30.6, 29.2, 27.8, 21.6, 13.1; HRMS (ESI) calcd for $C_{15}H_{20}NS$ $[M + H]^+$ 246.1311, found 246.1314.

3-(Benzo[*b*]thiophene-2-yl)pyridine (3rw):[10f] R_f = 0.2 (hexane/ethyl acetate = 5:1); pale yellow solid; mp 127−129 °C; yield 64 mg (61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.99 (d, J = 1.5 Hz, 1H), 8.57 (d, J = 4.0 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.83 (dd, J = 18.3, 7.4 Hz, 2H), 7.61 (s, 1H), 7.42−7.31 (m, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 149.1, 147.4, 140.3, 140.2, 139.7, 133.5, 130.3, 124.9, 124.8, 123.8, 123.7, 122.3, 120.7; HRMS (ESI) calcd for $C_{13}H_{10}NS$ $[M + H]^+$ 212.0528, found 212.0530.

2-(*p*-Tolyl)benzofuran (3sb):[10c] R_f = 0.4 (100% hexane); white solid; mp 131−133 °C; yield 61 mg (59%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.75 (d, J = 8.2 Hz, 2H), 7.59−7.54 (m, 1H), 7.53−

7.48 (m, 1H), 7.30–7.18 (m, 4H), 6.96 (d, J = 0.7 Hz, 1H), 2.39 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 156.2, 154.7, 138.6, 129.5, 129.3, 127.7, 124.9, 124.0, 122.8, 120.7, 111.1, 100.5, 21.4; HRMS (ESI) calcd for $C_{15}H_{13}O$ $[M + H]^+$ 209.0961, found 209.0960.

2,3-Di-*p*-tolylbenzofuran (3tb):[25] R_f = 0.3 (100% hexane); white solid; mp 89–90 °C; yield 60 mg (40%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.56 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.1 Hz, 1H), 7.50–7.46 (m, 1H), 7.41–7.35 (m, 2H), 7.33–7.27 (m, 1H), 7.27–7.18 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 153.9, 150.6, 138.2, 137.2, 130.4, 129.9, 129.6, 129.6, 129.1, 127.9, 126.9, 124.4, 122.7, 119.9, 116.7, 111.1, 21.3; HRMS (ESI) calcd for $C_{22}H_{18}O$ $[M]^+$ 298.1352, found 298.1354.

1-Methyl-5-(*p*-tolyl)-1*H*-pyrrole-2-carbaldehyde (3ub):[26] R_f = 0.2 (hexane/ethyl acetate = 20:1); colorless oil; yield 92 mg (93%); ^{11}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.56 (s, 1H), 7.33–7.26 (m, 4H), 6.97 (d, J = 4.1 Hz, 1H), 6.28 (d, J = 4.1 Hz, 1H), 3.92 (s, 3H), 2.41 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 179.4, 144.4, 138.6, 132.8, 129.3, 129.1, 128.1, 124.5, 110.5, 34.3, 21.3; HRMS (ESI) calcd for $C_{13}H_{14}NS$ $[M + H]^+$ 200.1070, found 200.1071.

Methyl 1-methyl-5-(*p*-tolyl)-1*H*-pyrrole-2-carboxylate (3vb):[26] R_f = 0.3 (hexane/ethyl acetate = 20:1); white solid; mp 38–40 °C; yield 105 mg (92%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32–7.21 (m, 4H), 7.01 (d, J = 4.0 Hz, 1H), 6.17 (d, J = 4.0 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 2.40 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 161.9, 141.8, 138.0, 129.22, 129.19, 129.17, 123.1, 117.6, 108.9, 51.0, 34.3, 21.2; HRMS (ESI) calcd for $C_{14}H_{16}NO_2$ $[M + H]^+$ 230.1176, found 230.1176.

Typical Procedure for the Reaction of Multiple C–H Bond Arylation (3mb–qb,mb$_1$–pb$_2$,qb). In a typical experiment, the 4-bromotoluene (61–185 μL, 0.5–1.5 mmol), thiophene derivative (0.5 mmol), **Cat.I** (0.4–2.0 mg, 0.1–0.5 mol %), PivOH (15–30 mg, 30–60 mol %), and K_2CO_3 (83–208 mg, 0.6–1.5 mmol) were dissolved in DMAc (1.5–2 mL) under a nitrogen atmosphere. Unless the otherwise noted, the mixture was heated at 100 °C for 24 h. The suspension was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried with Na_2SO_4. After evaporation of the solvents the residue was purified by silica gel column chromatography to give the desired product.

2,3-Dihydro-5,7-bis(4-methylphenyl)thieno[3,4-*b*][1,4]-dioxine (3mb): R_f = 0.3 (hexane/CH_2Cl_2 = 5:1); pale yellow solid; mp 152–153 °C; yield 150 mg (93%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63 (d, J = 8.2 Hz, 4H), 7.17 (d, J = 8.1 Hz, 4H), 4.33 (s, 4H), 2.35 (s, 6H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 138.2, 136.3, 130.2, 129.3, 126.0, 114.9, 64.5, 21.2; HRMS (ESI) calcd for $C_{20}H_{18}O_2S$ $[M]^+$ 322.1022, found 322.1025.

5-(*p*-Tolyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine (3mb$_1$):[27] R_f = 0.3 (hexane/CH_2Cl_2 = 5:1); pale yellow solid; mp 50–51 °C; yield 16 mg (7%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.0 Hz, 1H), 6.26 (s, 1H), 4.34–4.19 (m, 4H), 2.35 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 142.2, 137.7, 136.4, 130.3, 129.3, 126.0, 117.6, 97.0, 64.9, 64.6, 21.2; MS (EI) calcd for $C_{13}H_{12}O_2S$ $[M]^+$ 232.3, found 232.0.

3,4-Diphenyl-2,5-di-*p*-tolylthiophene (3nb):[28] R_f = 0.6 (hexane/ethyl acetate = 20:1); white solid; mp 179–181 °C; yield 198 mg (95%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.16–7.07 (m, 10H), 7.01 (d, J = 8.0 Hz, 4H), 6.99–6.94 (m, 4H), 2.29 (s, 6H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 139.1, 138.3, 136.9, 136.7, 131.4, 130.9, 129.0, 127.8, 126.5, 109.6, 21.2; MS (EI) calcd for $C_{30}H_{24}S$ $[M]^+$ 416.6, found 416.3.

3,4-Diphenyl-2-(*p*-tolyl)thiophene (3nb$_1$): R_f = 0.3 (100% hexane); white solid; mp 185–186 °C; yield 51 mg (31%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28 (s, 1H), 7.23–7.13 (m, 6H), 7.13–7.06 (m, 4H), 7.05–6.97 (m, 4H), 2.30 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 143.7, 140.7, 137.0, 137.0, 136.2, 131.6, 130.9, 129.2, 129.0, 128.9, 128.1, 127.9, 126.7, 126.6, 121.7, 21.2; HRMS (ESI) calcd for $C_{23}H_{18}S$ $[M]^+$ 326.1124, found 326.1125.

5,5′-Di-*p*-tolyl-2,2′-bithiophene (3ob):[29] R_f = 0.4 (hexane/CH_2Cl_2 = 10:1); yellow solid; mp 179–181 °C; yield 156 mg (90%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (d, J = 8.1 Hz, 4H), 7.22–7.17 (m, 6H), 7.14 (d, J = 3.8 Hz, 2H), 2.37 (s, 6H). Anal. Calcd for $C_{22}H_{18}S_2$ (346.51): C, 76.26; H, 5.24. Found: C, 76.30; H, 5.27%. ^{13}C NMR spectra were not recorded due to its poor solubility.

5-(*p*-Tolyl)-2,2′-bithiophene (3ob$_1$): R_f = 0.5 (hexane/CH_2Cl_2 = 10:1); yellow solid; mp 126–128 °C; yield 49 mg (38%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (d, J = 8.1 Hz, 2H), 7.23–7.16 (m, 5H), 7.16–7.11 (m, 1H), 7.05–7.00 (m, 1H), 2.38(s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 143.3, 137.5, 131.3, 129.6, 127.8, 125.5, 124.5, 124.2, 123.5, 123.2, 21.2; HRMS (ESI) calcd for $C_{15}H_{12}S_2$ $[M]^+$ 256.0375, found 256.0377.

3-Phenyl-2,5-di-*p*-tolylthiophene (3pb): R_f = 0.2 (100% hexane); white solid; mp 103–104 °C; yield 140 mg (82%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.53 (d, J = 8.0 Hz, 2H), 7.36–7.25 (m, 6H), 7.23–7.17 (m, 4H), 7.07 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 142.3, 138.5, 137.6, 137.4, 137.2, 136.8, 131.4, 131.4, 129.6, 129.2, 129.1, 129.0, 128.4, 126.9, 126.0, 125.5, 21.2; HRMS (ESI) calcd for $C_{24}H_{20}S$ $[M]^+$ 340.1280; Fonud 340.1284.

4-Phenyl-2-(*p*-tolyl)thiophene (3pb$_1$): R_f = 0.3 (100% hexane); colorless oil; yield 11 mg (9%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37–7.26 (m, 5H), 7.25–7.22 (m, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 5.2 Hz, 1H), 7.06 (d, J = 7.9 Hz, 2H), 2.23 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 138.8, 137.7, 137.2, 136.7, 131.4, 130.4, 129.2, 129.1, 128.3, 126.7, 123.8, 21.2; HRMS (ESI) calcd for $C_{17}H_{14}S$ $[M + H]^+$ 250.0811, found 250.0813.

3-Phenyl-2-(*p*-tolyl)thiophene (3pb$_2$): R_f = 0.3 (100% hexane); white solid; mp 97–98 °C; yield 11 mg (9%); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.65–7.59 (m, 2H), 7.57–7.51 (m, 3H), 7.44–7.37 (m, 2H), 7.35 (d, J = 1.4 Hz, 1H), 7.33–7.27 (m, 1H), 7.20 (d, J = 8.1 Hz, 2H), 2.37 (s, 3H); $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$) δ (ppm) 145.2, 143.0, 137.6, 135.9, 131.6, 129.6, 128.8, 127.2, 126.3, 125.7, 121.8, 119.2, 21.2; HRMS (ESI) calcd for $C_{17}H_{14}S$ $[M + H]^+$ 250.0811, found 250.0813.

2,2′,5,5′-Tetra-*p*-tolyl-3,3′-bithiophene (3qb). 4-Bromotoluene (370 μL, 3.0 mmol), 3,3′-bithiophene (0.5 mmol), **Cat.I** (2.0 mg, 0.5 mol %), PivOH (62 mg, 120 mol %), and K_2CO_3 (416 mg, 3 mmol) were dissolved in DMAc (3 mL) under a nitrogen atmosphere. The mixture was heated at 100 °C for 28 h. The suspension was cooled to room temperature and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried with Na_2SO_4. After evaporation of the solvents, the residue was purified by recrystallization (toluene) to afford the desired product: pale yellow solid; mp 292–293 °C; R_f = 0.5 (hexane/CH_2Cl_2 = 5:1); yield 232 mg (88%); ^1H NMR (400 MHz, C_6D_6) δ (ppm) 7.51–7.43 (m, 8H), 7.23 (s, 2H), 6.90 (d, J = 7.9 Hz, 4H), 6.79 (d, J = 8.0 Hz, 4H), 2.06 (s, 6H), 1.97 (s, 6H). Anal. Calcd for $C_{36}H_{30}S_2$ (526.75): C, 82.08; H, 5.74. Found: C, 82.04; H, 5.76%. ^{13}C NMR spectra were not recorded due to its poor solubility.

■ ASSOCIATED CONTENT

Supporting Information

All spectral data (^1H and ^{13}C) and data of X-ray analysis were indicated by figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For reviews, see: (a) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359−1469. (b) Perepichaka, I. F.; Perepichaka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281−2305. (c) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066−1096. (d) Mishra, A.; Ma, C.-Q.; Bäuerle, P. *Chem. Rev.* **2009**, *109*, 1141−1276. (e) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. *Chem. Rev.* **2009**, *109*, 5868−5923.

(2) (a) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070−4098. (b) Letizia, J. a.; Rivnay, J.; Facchetti, A.; Ratner, M. a.; Marks, T. J. *Adv. Funct. Mater.* **2010**, *20*, 50−58.

(3) (a) Gigli, G.; Anni, M.; Theander, M.; Cingolani, R.; Barbarella, G.; Favaretto, L.; Inganas, O. *Synth. Met.* **2001**, *119*, 581−582. (b) Mazzeo, M.; Pisignano, D.; Favaretto, L.; Barbarella, G.; Cingolani, R.; Gigli, G. *Synth. Met.* **2003**, *139*, 671−673. (c) Markham, J. P. J.; Namdas, E. B.; Anthopoulos, T. D.; Samuel, I. D. W.; Richards, G. J.; Burn, P. L. *Appl. Phys. Lett.* **2004**, *85*, 1463−1465.

(4) (a) Koumura, N.; Wang, Z.-S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256−14257. (b) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474−2499.

(5) For reviews, see: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483. (b) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442−4489. (c) Suzuki, A. *Chem. Commun.* **2005**, *38*, 4759−4763. (d) Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011**, *111*, 1417−1492. (e) Magano, J.; Dunetz, J. R. *Chem. Rev.* **2011**, *111*, 2177−2250.

(6) Ohta, A.; Akita, Y.; Ohkuwa, T.; Chiba, M.; Fukunaga, R.; Miyafuji, A.; Nakata, T.; Tani, N.; Aoyagi, Y. *Heterocycles* **1990**, *31*, 1951−1958.

(7) (a) Battace, A.; Lemhadri, M.; Zair, T.; Doucet, H.; Santelli, M. *Adv. Synth. Catal.* **2007**, *349*, 2507−2516. (b) Derridj, F.; Gottumukkala, A. L.; Djebbar, S.; Doucet, H. *Eur. J. Inorg. Chem.* **2008**, 2550−2559. (c) Roger, J.; Požgan, F.; Doucet, H. *Green Chem.* **2009**, *11*, 425−432. (d) Roger, J.; Požgan, F.; Doucet, H. *Adv. Synth. Catal.* **2010**, *352*, 696−710. (e) Roy, D.; Mom, S.; Beaupérin, M.; Doucet, H.; Hierso, J.-C. *Angew. Chem., Int. Ed.* **2010**, *49*, 6650−6654. (f) Roger, J.; Doucet, H. *Eur. J. Org. Chem.* **2010**, 4412−4425. (g) Derridj, F.; Roger, J.; Djebbar, S.; Doucet, H. *Org. Lett.* **2010**, *12*, 4320−4323. (h) Chen, L.; Roger, J.; Bruneau, C.; Dixneuf, P. H.; Doucet, H. *Chem. Commun.* **2011**, *47*, 1872−1874. (i) Bheeter, C. B.; Bera, J. K.; Doucet, H. *J. Org. Chem.* **2011**, *76*, 6407−6413. (j) Chen, L.; Roger, J.; Bruneau, C.; Dixneuf, P. H.; Doucet, H. *Adv. Synth. Catal.* **2011**, *353*, 2749−2760. (k) Bensaid, S.; Doucet, H. *ChemSusChem* **2012**, *5*, 1559−1567.

(8) (a) Liégault, B.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, K. *J. Org. Chem.* **2009**, *74*, 1826−1834. (b) Liégault, B.; Petrov, I.; Gorelsky, S. I.; Fagnou, K. *J. Org. Chem.* **2010**, *75*, 1047−1060. (c) René, O.; Fagnou, K. *Org. Lett.* **2010**, *12*, 2116−2119. (d) Schipper, D. J.; Fagnou, K. *Chem. Mater.* **2011**, *23*, 1594−1600. (e) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Org. Chem.* **2012**, *77*, 658−668.

(9) (a) Join, B.; Yamamoto, T.; Itami, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 3644−3647. (b) Yanagisawa, S.; Ueda, K.; Sekizawa, H.; Itami, K. *J. Am. Chem. Soc.* **2009**, *131*, 14622−14623. (c) Ueda, K.; Yanagisawa, S.; Yamaguchi, J.; Itami, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 8946−8949. (d) Kamiya, H.; Yanagisawa, S.; Hiroto, S.; Itami, K.; Shinokubo, H. *Org. Lett.* **2011**, *13*, 6394−6397.

(10) (a) Nakano, M.; Tsurugi, H.; Satoh, T.; Miura, M. *Org. Lett.* **2008**, *10*, 1851−1854. (b) Bellina, F.; Rossi, R. *Tetrahedron* **2009**, *65*, 10269−10310. (c) Tamba, S.; Okubo, Y.; Tanaka, S.; Monguchi, D.; Mori, A. *J. Org. Chem.* **2010**, *75*, 6998−7001. (d) Baghbanzadeh, M.; Pilger, C.; Kappe, C. O. *J. Org. Chem.* **2011**, *76*, 8138−8142. (e) Takita, R.; Fujita, D.; Ozawa, F. *Synlett* **2011**, *7*, 959−963. (f) Ghosh, D.; Lee, H. M. *Org. Lett.* **2012**, *14*, 5534−5537. (g) Hu, P.; Zhang, M.; Jie, X.; Su, W. *Angew. Chem., Int. Ed.* **2012**, *51*, 227−231. (h) Mercier, L. G.; Leclerc, M. *Acc. Chem. Res.* **2013**, *46*, 1597−1605.

(11) Mi, X.; Huang, M.; Feng, Y.; Wu, Y. *Synlett* **2012**, *23*, 1257−1261.

(12) Li, Y.; Mi, X.; Huang, M.; Cai, R.; Wu, Y. *Tetrahedron* **2012**, *68*, 8502−8508.

(13) Mi, X.; Huang, M.; Guo, H.; Wu, Y. *Tetrahedron* **2013**, *69*, 5123−5128.

(14) Koning, B.; Buter, J.; Hulst, R.; Stroetinga, R.; Kellogg, R. M. *Eur. J. Org. Chem.* **2000**, *15*, 2735−2743.

(15) Chow, W. K.; So, C. M.; Lau, C. P.; Kwong, F. Y. *J. Org. Chem.* **2010**, *75*, 5109−5112.

(16) Urban, S.; Beiring, B.; Ortega, N.; Paul, D.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 15241−15244.

(17) Salimbeni, A.; Canevotti, R.; Paleari, F.; Bonaccorsi, F.; Renzetti, A. R.; Belvisi, L.; Bravi, G.; Scolastico, C. *J. Med. Chem.* **1994**, *37*, 3928−3938.

(18) Lai, L.-L.; Shih, L.-H.; Lin, P.-Y.; Wang, J.-S.; Shiao, M.-J. *J. Chin. Chem. Soc.* **1994**, *41*, 75−79.

(19) Robbins, D. W.; Hartwig, J. F. *Org. Lett.* **2012**, *14*, 4266−4269.

(20) Nambo, M.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2011**, *133*, 2402−2405.

(21) Rao, M. L. N.; Banerjee, D.; Dhanorkar, R. J. *Synlett* **2011**, *9*, 1324−1330.

(22) Petr, V.; Toth, L. M. *Tetrahedron Lett.* **2004**, *45*, 7157−7161.

(23) Dong, C.-G.; Hu, Q.-S. *J. Am. Chem. Soc.* **2005**, *127*, 10006−10007.

(24) Tanaka, S.; Tanaka, D.; Sugie, A.; Mori, A. *Tetrahedron Lett.* **2012**, *53*, 1173−1176.

(25) Zeng, W.; Wu, W.; Jiang, H.; Huang, L.; Sun, Y.; Chen, Z.; Li, X. *Chem. Commun.* **2013**, *49*, 6611−6613.

(26) Roger, J.; Doucet, H. *Adv. Synth. Catal.* **2009**, *351*, 1977−1990.

(27) Amaladass, P.; Clement, J. A.; Mohanakrishnan, A. K. *Tetrahedron* **2007**, *63*, 10363−10371.

(28) Tùng, Đ. T.; Tuân, Đ. T.; Rasool, N.; Villinger, A.; Reinke, H.; Fischer, C.; Langer, P. *Adv. Synth. Catal.* **2009**, *351*, 1595−1609.

(29) Masui, K.; Ikegami, H.; Mori, A. *J. Am. Chem. Soc.* **2004**, *126*, 5074−5075.