JOC The Journal of Organic Chemistry

Note

Copper-Catalyzed Synthesis of Benzo[b]thiophenes and Benzothiazoles Using Thiocarboxylic acids as a Coupling Partner

Hui Yu, Meishu Zhang, and Yuzhe Li

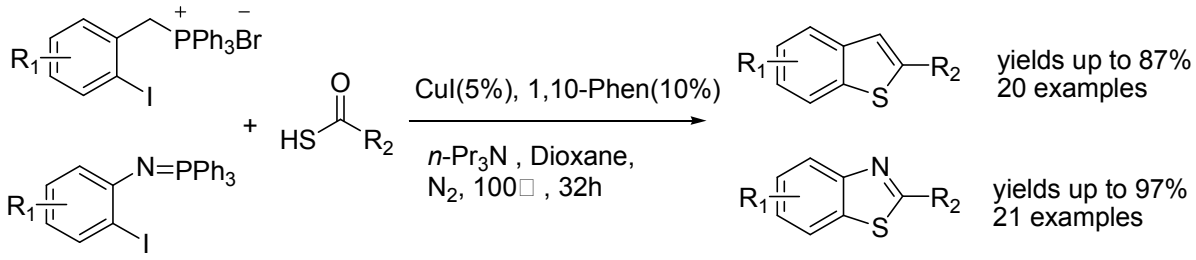
J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo401353w • Publication Date (Web): 19 Aug 2013

Copper-Catalyzed Synthesis of Benzo[*b*]thiophenes and Benzothiazoles Using Thiocarboxylic Acids as a Coupling Partner

Hui Yu, Meishu Zhang, and Yuzhe Li*

Department of Chemistry, Tongji University, 1239 Siping Road, Shanghai, 200092 (P. R. China).

yuhui@tongji.edu.cn



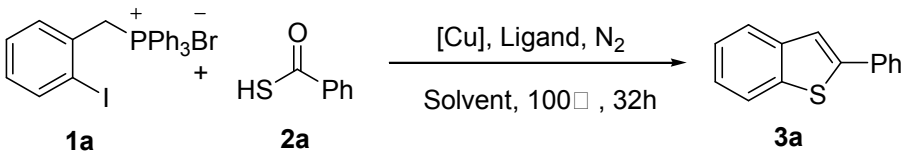
Abstract: An efficient copper-catalyzed approach to benzo[*b*]thiophene and benzothiazole derivatives using thiocarboxylic acids as a sulfur source has been developed. In the presence of CuI and 1,10-Phen, *n*-Pr_3N as the base, (2-iodobenzyl)triphenylphosphonium bromide and (2-iodophenylimino) triphenylphosphorane reacted smoothly with thiocarboxylic acids to give benzo[*b*]thiophene and benzothiazole derivatives in good yields via sequential Ullmann-type C–S bond coupling and Wittig condensation.

Benzo[*b*]thiophene and benzothiazole derivatives are important heterocyclic compounds because of their broad applications in the biological and pharmaceutical areas.[1] These heterocycles exist in numerous bioactive molecules and natural products, and they are also found in clinically important drugs such as arzoxifene, zileuton, and zopolrestat. Thus, development of general methods for the synthesis of these compounds is valuable in drug discovery. Conventional methods for the construction of benzo[*b*]thiophene and benzothiazole framework commonly start from thiophenol derivatives.[2, 3] However, these methods are limited by the difficulties in the preparation of readily oxidized thiophenol precursors. Benzo[*b*]thiophene and benzothiazole can also be synthesized by cyclization reactions of thioenols or thiocarbonyl compounds. For example, benzo[*b*]thiophene was synthesized from thioamide through a nucleophlic displacement procedure, [4] or from thioenol, using a simple palladium catalyst. [5]

Benzothiazoles were synthesized from 2-halophenylthiobenzamides using Pd or Cu as a catalyst, [6] or from phenylthiobenzamides via C–H functionalization under oxidative condition.[7] Generally, the preparation of thioamides and thioenols requires P_4S_{10} or Lawesson's reagent, which is not feasible for substrates comprised of ketone, ester, and amides. In recent years, the development of transition metal-catalyzed intermolecular C–S bonds formation has provided a new efficient route to benzo[*b*]thiophene and benzothiazole moieties.[8] By a Cu- or Pd-catalyzed thiolation annulation strategy, benzo[*b*]thiophenes and benzothiazoles have been synthesized successfully from 2-bromoalkynylbenzene and 2-haloaniline derivatives using a dihydrosulfide surrogate as a coupling partner, [9, 10] such as metal sulfides, thiourea, and HSTIPS. In most cases, these dihydrosulfide surrogates only contribute one sulfur atom to the structure of the product, and all the functional groups have to be preassembled on the substrates for the synthesis of a multi-substituted target molecule. Obviously, using functionalized dihydrosulfide as coupling partner will make this method more flexible and convienent for organic syntheses. For example, using benzyl thiols as coupling partners, Liu and co-workers reported an efficient synthesis of a variety of benzo[*b*]thiophene and benzothiazole derivatives via a cross-coupling/intramolecular cyclization process. [11] Here, as another example of this methodology, we report a new one-pot copper-catalyzed approach to benzo[*b*]thiophenes and benzothiazoles using thiocarboxylic acids as the coupling partner. [12]

Initially, the coupling of (2-iodobenzyl)triphenylphosphonium bromide **1a** with thiobenzoic acid **2a** was examined in DMF with CuI (5 mol%), 1,10-phenthroline (10 mol%) as the catalyst, and DIPEA (3.0 equiv) as the base at 100°C under N_2. The desired product 2-phenylbenzo[*b*]thiophenes **3a** was isolated in 67% yield (Table 1, entry 1). Then, reaction conditions, including solvents, bases, and ligands, were screened and the results are listed in Table 1. Various solvents were screened and dioxane was found to be the best one (Table 1, entries 1–4). Different bases were evaluated and all the tertiary amine gave good results; in the case of Pr_3N, the yield increased to 87%. In contrast, no product could be found when inorganic bases, such as Cs_2CO_3 and K_3PO_4, were introduced in the reaction (Table 1, entries 5–9). No product could be obtained without a ligand, and other ligands including TMEDA, L-proline gave lower yield than 1,10-Phen (Table 1, entries 10–12). Some other copper salts were also tested and CuI remained the best one (Table 1, entries 13, 14). (2-Bromobenzyl) triphenylphosphonium bromide was also examined instead of **1a** in the present of 0.5 eq KI as an additive to afford **3a** in 47% yield, and no product could be isolated without KI (Table 1, entry 15). [13] Finally, a mixture of benzoic acid and Lawesson's reagent was used to generate thiobenzoic acid *in situ*， and **3a** was obtain in about 53% yield but was difficult to separate from the complex reaction mixture (Table 1, entry 16). On the basis of these results, entry 6 represented the best conditions.

Table 1. **Screening conditions**



1a **2a** **3a**

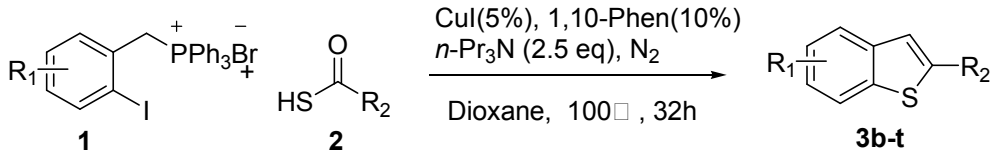
Entry[a]	Cat.	Ligand	Base	Solvent	Yield (%)[b]
1	CuI	1,10-Phen	DIPEA	DMF	67
2	CuI	1,10-Phen	DIPEA	Toluene	40
3	CuI	1,10-Phen	DIPEA	DMSO	53
4	CuI	1,10-Phen	DIPEA	Dioxane	75
5	CuI	1,10-Phen	Et_3N	Dioxane	48
6	**CuI**	**1,10-Phen**	***n*-Pr_3N**	**Dioxane**	**87**
7	CuI	1,10-Phen	*n*-Bu_3N	Dioxane	78
8	CuI	1,10-Phen	Cs_2CO_3	Dioxane	Trace
9	CuI	1,10-Phen	K_3PO_4	Dioxane	Trace
10	CuI	—	*n*-Pr_3N	Dioxane	0
11	CuI	TMEDA	*n*-Pr_3N	Dioxane	56
12	CuI	L-Proline	*n*-Pr_3N	Dioxane	35
13	CuBr	1,10-Phen	*n*-Pr_3N	Dioxane	67
14	Cu_2O	1,10-Phen	*n*-Pr_3N	Dioxane	79
15	CuI	1,10-Phen	*n*-Pr_3N	Dioxane	47[c]
16	CuI	1,10-Phen	*n*-Pr_3N	Dioxane	55[d]

[a]At 0.10 mmol, [b]isolated yield, [c](2-bromobenzyl) triphenylphosphonium bromide was used instead of **1a** with 0.5 eq KI as an additive, [d]mixture of benzoic acid and Lawesson's reagent was used instead of thiobenzoic acid.

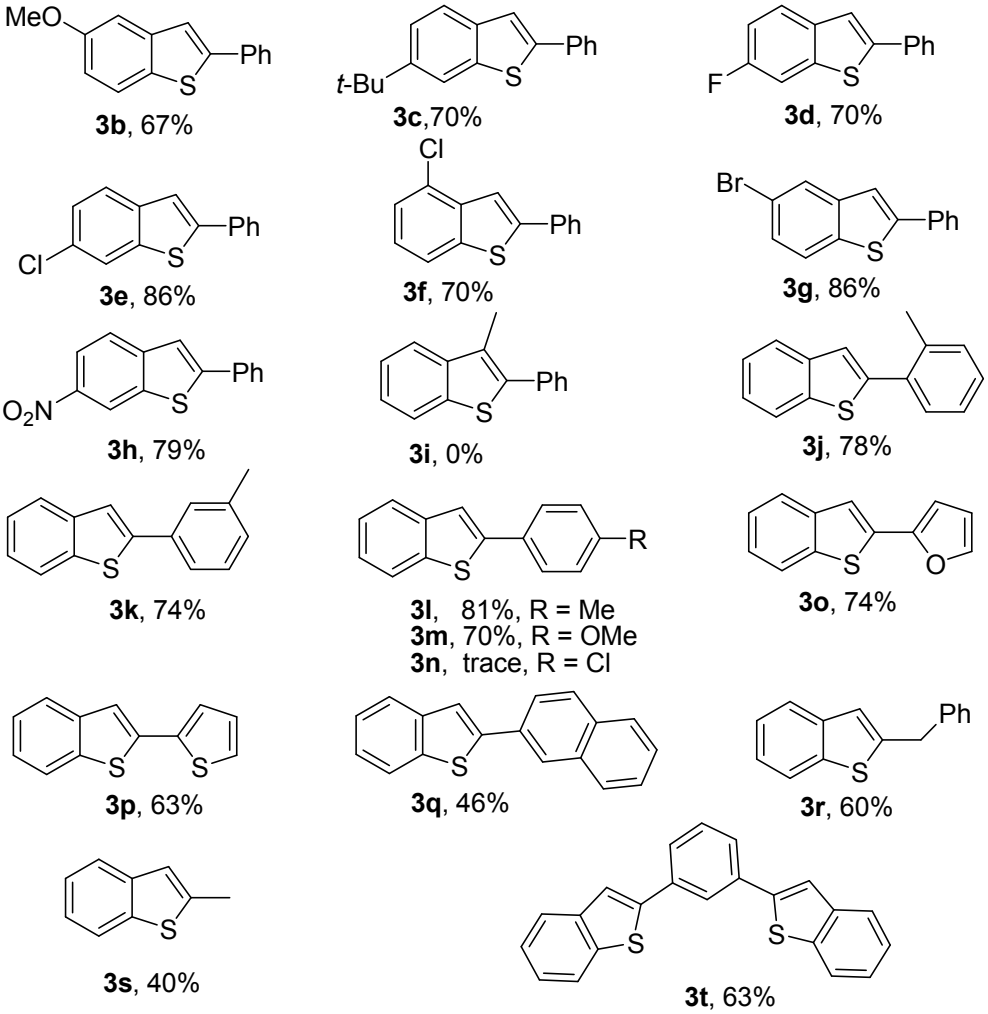
With the optimized reaction conditions established, the substrate scope was examined, and the results are summarized in Table 2. Different (2-iodobenzyl)triphenylphosphonium bromides with electron-donating or electron-withdrawing groups on the benzene ring reacted smoothly with thiobenzoic acid **2a** to give the corresponding 2-phenylbenzo[*b*]thiophenes in moderate-to-good yields (Table 2, **3b**–**3h**). However, substrates with a methyl group in the α-position were not active to the reaction, and no desired product 2-phenyl-3-methyl benzo[*b*]thiophene was isolated (Table 2, **3i**). Next, a variety of substituted thiobenzoic acids was employed to react with **1a**. Thiobenzoic acids with electron-donating groups displayed high reactivity under the present reaction conditions to afford the corresponding products, regardless of the substituent position on the phenyl ring (Table 2, **3j**–**3m**). In contrast, electron-deficient

thiobenzoic acids were less reactive under these reaction conditions and only traces of the expected product were detected (Table 2, **3n**). Heteroaryl thiocarboxylic acids were also found to be favored in the reaction and benzo[*b*]thiophenes with heteroaryl substituent on C-2 position were synthesized in moderate yields, showing the potential of our methodology (Table 2, **3o**–**3q**). This reaction was not limited to aromatic acids. Aliphatic acids, such as thiophenylacetic acid and thioacetic acid, were also investigated which provided the desired products in 60% and 40% yields, respectively (Table 2, **3r**, **3s**). Finally, thioisophthalic acid was used in the optimized conditions, leading to product **3t** in 63% yield.

Table 2. Copper-Catalyzed Synthesis of Benzo[*b*]thiophene Derivatives[a,b]



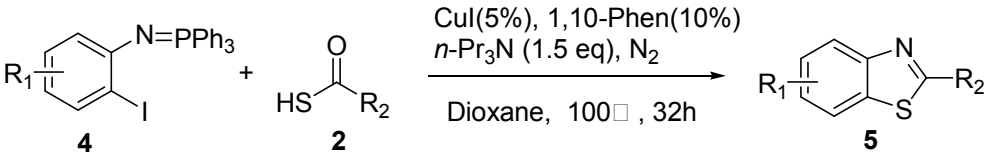
1 **2** **3b-t**



[a] On a 0.3 mmol scale; [b] Isolated yield.

Subsequently, a Cu-catalyzed annulation reaction between (2-iodophenylimino) triphenylphosphorane and thiobenzoic acid **2a** was examined under the optimized reaction conditions. In this case, the amount of *n*-Pr_3N was decreased to 1.5 equiv. The expected product 2-phenyl benzothiazole was isolated in high yield, up to 95%. Then, the scope of copper-catalyzed coupling reaction of substituted (2-iodophenylimino)triphenylphosphorane with thiocarboxylic acids were examined under the optimized conditions. As shown in Table 3, (2-iodophenylimino) triphenylphosphoranes with electron-donating group on the phenyl ring gave the products in excellent yields (Table 3, **5a**–**5d**). The existence of other halides, such as F, Cl, and Br, had no significant effect on the reaction, and the desired products were obtained in good yields (Table 3, **5e**–**5g**). Notably, ketones and esters were tolerated in the reaction, and the products were obtained in good yields (Table 3, **5h**–**5j**). Next, a series of substituted thiobenzoic acids was also examined. It is found that substitution at the 2-position resulted in lower yields than substitution at the 3-position or 4-position, indicating a steric effect in this reaction (Table 3, **5k**–**5m**). Furthermore, thiobenzoic acids bearing electron-donating groups on the phenyl ring gave the desired products in higher yields than those with electron-withdrawing groups (Table 3, **5m**–**5o**). Several heteroaryl thiocarboxylic acids were also tested and the corresponding products were obtained in good yields (Table 3, **5p**–**5r**). Aliphatic acid, such as thiophenylacetic acid, gave excellent yields, but thioacetic acid was not suitable for this reaction (Table 3, **5s**, **5t**). Finally, thiocinnamic acid also underwent this reaction smoothly, generating the corresponding product in 68% yield (Table 3, **5u**). Finally, (2-bromophenylimino)triphenylphosphorane was also used to react with thiobenzoic acid under optimized conditions, but only trace product could be isolated for its less reactivity.

Table 3. Copper-Catalyzed Synthesis of Benzothiazole Derivatives[a,b]



4 **2** **5**

5a, 95%, R = H
5b, 96%, R = Me
5c, 90%, R = *i*-Pr
5d, 85%, R = *t*-Bu

5e, 94%, X = F
5f, 90%, X = Cl
5g, 80%, X = Br

5h, 77%, EWG = NO_2
5i, 87%, EWG = Ac
5j, 70%, EWG = COOEt

5k, 72%

5l, 97%

5m, 85%, R = Me
5n, 87%, R = OMe
5o, 67%, R = Cl

5p, 85%

5q, 75%

5r, 91%

5s, 90%

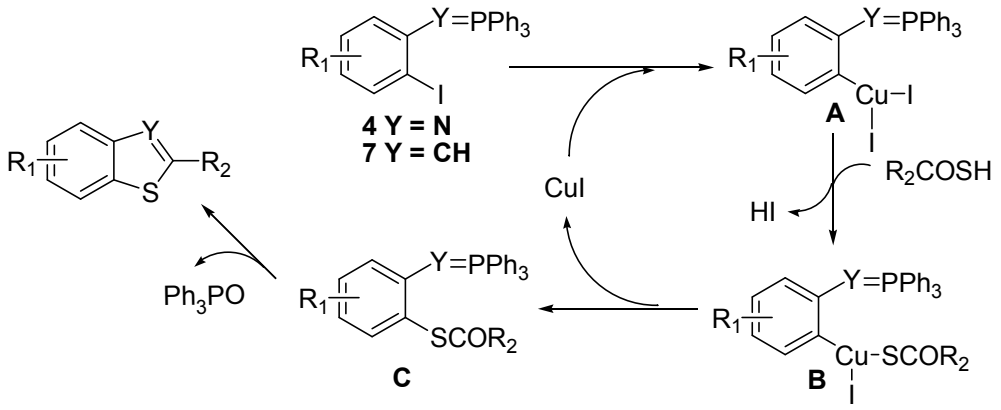
5t, trace

5u, 68%

[a] On a 0.3 mmol scale; [b] Isolated yield.

Based on the present results and a previously reported mechanism, [9a, 10b] a proposed mechanism is outlined below (Scheme 1). Oxidative addition of CuI to substrate **4** or **7** (generated from **1** in the present of base) afforded intermediate **A**, which was converted to intermediate **B** by ligand exchange. Reductive elimination of **B** would regenerate CuI and provide **C**, then **C** underwent an intramolecular (aza-)Witttig condensation to give the products spontaneously. Further investigation of the details of the mechanism is still in progress in our lab.

Scheme 1. Proposed Reaction mechanism



In conclusion, we have developed a practical method for the synthesis of benzo[*b*]thiophenes and benzothiazoles by a combination of copper-catalyzed C–S bond formation and a Wittig condensation. This may be the first example of copper-catalyzed construction of S-heterocycles using thiocarboxylic acid as a coupling partner. In most cases, the corresponding benzo[*b*]thiophenes and benzothiazoles were obtained in good-to-excellent yields. This method provides a new alternative route for preparing benzo[*b*]thiophenes and benzothiazoles derivatives for use in organic and medicinal chemistry.

Experimental Section

General Methods

Commercially available reagents were used as received without further purification unless otherwise indicated. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) using Silica Gel 60 F254 plates and were visualized by fluorescence quenching at 254 nm. For chromatographic purifications, analytically pure solvents were used and the silica gel 300-400 mesh was used as the solid support. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^{1}H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77.0 ppm, respectively.

Typical experimental procedure for the synthesis of Benzo[b]thiophene

In a 15 mL two-necked flask, a mixture of (2-Iodobenzyl)triphenylphosphonium Bromide (168mg, 0.3 mmol), thiobenzoic acid (53 mg, 0.33 mmol), CuI (2.8 mg, 5% mol), and 1,10-phenthroline (5.2 mg, 10 mol%) in Dioxane (3 mL) were stirred at room temperature under N2 atmosphere for 5 min. Then the solution was stirred at 100℃ for 32 h until complete consumption of starting material as monitored by TLC. After the reaction was finished, the mixture was washed with brine, extracted with EtOAc, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 8/1) to give the product **3a**.

2-phenylbenzo[b]thiophene[9a] (**3a**): White solid; 54.9 mg (87% yield); mp 172-173 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 7.3 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.59 (s, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.42 – 7.32 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 140.7, 139.5, 134.3, 128.9, 128.3, 126.5, 124.5, 124.3, 123.6, 122.3, 119.4.

5-Methoxy-2-phenylbenzo[*b*]thiophene[14] (**3b**): White solid; 48.6 mg (67% yield); mp 143-144℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 7.8, 6.2 Hz, 3H), 7.50 (s, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 2.4 Hz, 1H), 6.99 (dd, J = 8.8, 2.4 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 145.4, 141.6, 134.5, 132.1,128.9, 128.2, 126.4, 122.9, 119.3, 114.5, 105.7, 55.5.

6-*tert*-Butyl-2-phenylbenzo[*b*]thiophene (**3c**): White solid; 55.9 mg (70% yield); mp 165-168 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 0.6 Hz, 1H), 7.63 (d, J = 7.0 Hz, 3H), 7.42 (s, 1H), 7.38 -7.30 (m, 3H), 7.26 (d, J = 7.3 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 143.5, 139.7, 138.4, 134.5, 128.9, 128.0, 126.4, 123.0, 122.8, 119.1, 118.3, 34.9, 31.5. HRMS (ESI) m / z $[M + H]^+$ calcd for $C_{18}H_{19}S$ 267.1207, found 267.1241.

6-Fluoro-2-phenylbenzo[*b*]thiophene[9a] (**3d**): White solid; 47.9 mg (70% yield); mp 164-165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 13.3, 6.2 Hz, 3H), 7.58 – 7.50 (m, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.13 (td, J = 8.9, 2.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7 (d, J_{C-F} = 245.0 Hz), 144.1 (d, J_{C-F} = 4.0 Hz), 140.5 , 137.2 , 134.5 , 129.1, 128.6, 126.4 , 124.8 (d, J_{C-F} = 9.0 Hz), 118.8, 113.5 (d, J_{C-F} = 24.2 Hz), 108.4 (d, J_{C-F} = 25.5 Hz).

6-Chloro-2-phenylbenzo[*b*]thiophene[9a] (**3e**):White solid; 63.1 mg (86% yield); mp 193-195 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.71 (dd, J = 7.6, 6.2 Hz, 3H), 7.53 (s, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.41 – 7.31 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 140.4, 139.1, 133.8, 130.3, 129.0, 128.5, 126.4, 125.3, 124.3, 121.8, 118.9.

4-Chloro-2-phenylbenzo[*b*]thiophene[15] (**3f**):White solid; 51.3 mg (70% yield); mp 110-111 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.63 (m, 4H), 7.56 – 7.34 (m, 4H), 7.26 (t, J = 7.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 140.5, 138.9, 133.8, 129.0, 128.7, 128.5, 126.6, 124.9, 124.5, 120.8, 117.6. 4-chloro-2-phenylbenzo[b]thiophene

5-Bromo-2-phenylbenzo[*b*]thiophene[16] (**3g**): White solid; 74.6 mg (86% yield); mp 186-187℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 1.7 Hz, 1H), 7.71 (t, J = 7.6 Hz, 3H), 7.53 – 7.38 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.2, 142.2, 138.0, 133.8, 129.0, 128.7, 127.3, 126.5, 126.1, 123.6, 118.5, 118.5.

6-Nitro-2-phenylbenzo[*b*]thiophene (**3h**): Brown solid; 60.4 mg (79% yield); mp 196-197 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.25 (dd, J = 8.8, 1.9 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 7.1 Hz, 2H), 7.66 (s, 1H), 7.49 (dt, J = 14.2, 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 145.1, 139.0, 133.2, 129.5, 129.2, 126.8, 123.6, 119.9, 119.0, 118.7. HRMS (EI) m / z [M^+] calcd for $C_{14}H_9NO_2S$ 255.0354, found 255.0362.

2-*o*-Tolylbenzo[*b*]thiophene[9d] (**3j**): White solid; 52.2 mg (78% yield); mp 68-70 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.9 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.56 (d, J = 6.8 Hz, 1H), 7.48 – 7.30 (m, 6H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 140.2, 140.1, 136.5, 134.3, 130.8, 130.7, 128.3, 126.4, 126.1, 124.4, 124.1, 123.5, 123.0, 122.0, 21.1.

2-*m*-Tolylbenzo[*b*]thiophene[9a] (**3k**): White solid; 49.5 mg (74% yield); mp 117-118℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.3 Hz, 1H), 7.56 (d, J = 8.5 Hz, 3H), 7.41 – 7.30 (m, 3H), 7.19 (d, J = 7.7 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 140.7, 139.4, 138.6, 134.2, 129.0, 128.8, 127.2, 124.4, 124.2, 123.6, 123.5, 122.2, 119.3, 21.4.

2-*p*-Tolylbenzo[*b*]thiophene[9a] (**3l**): White solid; 54.2 mg (81% yield); mp 166-168 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.54 (s, 1H), 7.34-7.38 (m, 2H), 7.27 (d, J = 8.2 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 140.8, 139.3, 138.3, 131.5, 129.6, 126.4, 124.4, 124.1, 123.4, 122.2, 118.8, 21.2.

2-(4-Methoxyphenyl)benzo[*b*]thiophene[9a] (**3m**): White solid; 50.8 mg (70% yield); mp 188-190℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.67 (d, J = 8.6 Hz, 2H), 7.45 (s, 1H), 7.40 - 7.30 (m, 2H), 6.99 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 144.1, 140.9, 139.2, 127.7, 127.0, 124.4, 123.9, 123.2, 122.1, 118.2, 114.3, 55.4.

2-(Fruan-2-yl)benzo[*b*]thiophene[11] (**3o**): White solid; 44.4 mg (74% yield); mp 113-114 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 20.2, 7.8 Hz, 2H), 7.51 (s, 2H), 7.35 (dt, J = 15.1, 7.2 Hz, 2H), 6.60 (dd, J = 60.0, 2.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 142.5, 140.2, 138.9, 133.3, 124.6, 124.4, 123.5, 122.2, 118.5, 111.9, 107.0.

2-(Thiophen-2-yl)benzo[*b*]thiophene[9a] (**3p**): White solid;40.8 mg (63% yield); mp 119-120 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 7.4 Hz, 1H), 7.43 (s, 1H), 7.40 - 7.30 (m, 4H), 7.13 – 7.04 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 139.1, 137.4, 137.2, 127.9, 125.4, 125.0, 124.6, 124.4, 123.4, 122.1, 119.7.

2-(Naphthalen-2-yl)benzo[*b*]thiophene[17] (**3q**): White solid; 35.9 mg (46% yield); mp 221-222 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.85—7.91 (m, 6H), 7.71 (s, 1H), 7.58 – 7.48 (m, 2H), 7.44 –- 7.33 (m, 2H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 140.7, 139.5, 133.5, 133.1, 132.6, 131.6, 128.6, 128.2, 127.7, 126.7, 126.3, 125.3, 124.6, 124.3, 123.6, 122.3, 119.9.

2-Benzylbenzo[*b*]thiophene[18] (**3r**): White solid; 40.3 mg (60% yield); mp 76-78 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.41 – 7.22 (m, 8H), 4.25 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 140.0, 139.8, 139.5, 128.7, 128.6, 126.7, 124.1, 123.6, 122.9, 122.1, 121.6, 37.0.

2-Methylbenzo[*b*]thiophene[19] (**3s**):White solid; 17.8 mg (40% yield); mp 47-52 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.9 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.38 – 7.25 (m, 2H), 7.02 (s, 1H), 2.63 (d, J = 1.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 140.5, 139.7, 124.0, 123.3, 122.5, 122.0, 121.6, 16.1.

1,3-Di(benzo[*b*]thiophen-2-yl)benzene (**3t**): White solid; 64.6 mg (63% yield); mp 169-171 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.89 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 7.2 Hz, 2H), 7.72 (dd, J = 7.8, 1.6 Hz, 2H), 7.66 (s, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.45-7.33 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 140.6, 139.5, 135.1, 129.5, 126.3, 124.6, 124.5, 123.7, 122.3, 120.0. HRMS (ESI) m / z $[M+H]^+$ calcd for $C_{22}H_{15}S_2$ 343.0615, found 343.0627.

Typical experimental procedure for the synthesis of Benzothiazole

In a 15 mL two-necked flask, a mixture of (2-Iodophenylimino)triphenylphosphorane (168mg, 0.3 mmol), thiobenzoic acid (53 mg, 0.33 mmol), CuI (2.8 mg, 5% mol), and 1,10-phenthroline (5.2 mg, 10 mol%) in Dioxane (3 mL) were stirred at room temperature under N2 atmosphere for 5 min. Then the solution was stirred at 100℃ for 32 h until complete consumption of starting material as monitored by TLC. After the reaction was finished, the mixture was washed with brine, extracted with EtOAc, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 4/1) to give the product **5a**.

2-phenylbenzo[d]thiazole[10a] (**5a**): White solid; 60.1mg (95% yield) M.p. 107-110 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 3H), 7.94 (d, J = 7.6 Hz, 1H), 7.55 – 7.50 (m, 4H), 7.42 (t, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.8, 168.0, 154.1, 135.1, 133.6, 130.9, 129.0, 127.5, 125.2, 123.2, 121.6.

6-Methyl-2-phenylbenzothiazole[10a] (**5b**): white solid; 67.4 mg (96% yield); mp 149-150 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H), 7.98 (d, J = 8.3 Hz, 1H), 7.72 (s, 1H), 7.54 – 7.48 (m, 3H),

7.33 (dd, J = 8.3, 1.0 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 152.3, 135.3, 135.2, 133.7, 130.7, 128.9, 127.9, 127.4, 122.7, 121.3, 21.5.

6-*iso*-Propyl-2-phenylbenzothiazole (**5c**): White solid; 68.3 mg (90% yield); mp 137-139℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 2H), 8.03 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 1.6 Hz, 1H), 7.54-7.49 (m, 3H), 7.40 (dd, J = 8.4, 1.6 Hz, 1H), 3.09 (dt, J = 13.8, 6.9 Hz, 1H), 1.36 (d, J = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 152.5, 146.4, 135.3, 133.8, 130.7, 129.0, 127.4, 125.5, 122.9, 118.7, 34.3, 24.2. HRMS (ESI) m / z $[M+H]^+$ calcd for $C_{16}H_{16}NS$ 254.1003, found 254.1005.

6-*tert*-Butyl-2-phenylbenzothiazole (**5d**): White solid; 68.1 mg (85% yield); mp 125-128℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.08 (m, 2H), 8.03 (d, J = 8.6 Hz, 1H), 7.92 (d, J = 1.8 Hz, 1H), 7.58 (dd, J = 8.7, 1.9 Hz, 1H), 7.54 – 7.49 (m, 3H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 152.1, 148.7, 135.1, 133.8, 130.7, 129.0, 127.4, 124.5, 122.5, 117.7, 35.1, 31.5. HRMS (ESI) m / z $[M+H]^+$ calcd for $C_{17}H_{18}NS$ 268.1160, found 268.1170.

6-Fluoro-2-phenylbenzothiazole[10a] (**5e**): White solid; 64.6 mg (94% yield); mp 152-153℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.06 (m, 2H), 8.04 (dd, J = 9.0, 4.8 Hz, 1H), 7.61 (dd, J = 8.1, 2.6 Hz, 1H), 7.52 (dd, J = 6.8, 3.6 Hz, 3H), 7.25 (td, J = 9.0, 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 160.5 (d, J_{C-F} = 245.8 Hz), 150.8, 136.0 (d, J_{C-F} = 11.3 Hz), 133.3, 131.0, 129.1, 127.4, 124.1 (d, J_{C-F} = 9.4 Hz), 114.9 (d, J_{C-F} = 24.7 Hz), 107.8 (d, J_{C-F} = 26.8 Hz).

6-Chloro-2-phenylbenzothiazole[10a] (**5f**):White solid; 66.3 mg (90% yield); mp 156-157 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.05 (m, 2H), 7.99 (d, J = 8.7 Hz, 1H), 7.89 (d, J = 2.0 Hz, 1H), 7.55 – 7.50 (m, 3H), 7.47 (dd, J = 8.7, 2.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 152.7, 136.2, 133.2, 131.2, 131.1, 129.1, 127.5, 127.1, 123.9, 121.3.

6-Bromo-2-phenylbenzothiazole[7d] (**5g**): White solid; 62.4 mg (80% yield); mp 150-151 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H), 8.06 (d, J = 1.7 Hz, 1H), 7.94 (d, J = 8.7 Hz, 1H), 7.61 (dd, J = 8.7, 1.7 Hz, 1H), 7.56 – 7.48 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 153.0, 136.7, 133.2, 131.3, 129.8, 129.1, 127.5, 124.3, 124.1, 118.7.

6-Nitro-2-phenylbenzothiazole[7d] (**5h**): Yellow solid; 59.1 mg (77% yield); mp 189-190 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 2.1 Hz, 1H), 8.39 (dd, J = 9.0, 2.2 Hz, 1H), 8.15 (m, 3H), 7.64 – 7.52 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 157.8, 144.9, 135.3, 132.7, 132.2, 129.3, 127.9, 123.3, 121.9, 118.2.

1-(2-Phenylbenzothiazol-6-yl)ethanone[10a] (**5i**):Yellow solid; 66.0 mg (87% yield); mp 185-188℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.12 (d, J = 8.9 Hz, 4H), 7.54 (d, J = 6.1 Hz, 3H), 2.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 171.8, 157.0, 135.3, 133.9, 133.2, 131.6, 129.1, 127.8, 126.5, 123.0, 122.5, 26.8. HRMS (ESI) m / z $[M+H]^+$ calcd for $C_{15}H_{12}NOS$ 254.0640, found 254.0653.

Ethyl 2-phenylbenzothiazole-6-carboxylate[10a] (**5j**[l]: White solid; 59.4 mg (70% yield); mp 196-197 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 1.1 Hz, 1H), 8.20 (dd, J = 8.6, 1.6 Hz, 1H), 8.17 – 8.09 (m, 3H), 7.55 (d, J = 1.7 Hz, 2H), 7.54 (d, J = 1.7 Hz, 1H), 4.46 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 166.1, 157.0, 134.9, 133.2, 131.5, 129.1, 127.7, 127.5, 127.3, 123.7, 122.8, 61.2, 14.3.

2-*o*-Tolylbenzothiazole[20] (**5k**): White solid; 48.4 mg (72% yield); mp 53-54 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 7.4 Hz, 1H), 7.55 – 7.47 (m, 1H), 7.43 – 7.28 (m, 4H), 2.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 153.8, 137.2, 135.6, 133.1, 131.5, 130.5, 130.1, 126.1, 125.1, 123.4, 121.3, 21.4.

2-*m*-Tolylbenzothiazole[10a] (**5l**): White solid; 65.2 mg (97% yield); mp 69-70 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.2 Hz, 1H), 7.97 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 7.7 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 7.6 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 154.1, 138.8, 135.0, 133.6, 131.8, 128.9, 128.0, 126.2, 125.1, 124.8, 123.2, 121.6, 21.3.

2-*p*-Tolylbenzothiazole[10a] (**5m**): White solid; 57.1 mg (85% yield);mp 85-86 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.01 (d, J = 8.1 Hz, 2H), 7.92 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 7.9 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 154.2, 141.4, 134.9, 130.9, 129.7, 127.5, 126.2, 125.1, 123.0, 121.5, 21.5.

2-(4-Methoxyphenyl)benzothiazole[10a] (**5n**): White solid; 62.9 mg (87% yield); mp 121-122 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (m, 3H), 7.90 (d, J = 7.9 Hz, 1H), 7.50 (t, J = 8.1 Hz, 1H), 7.38 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 161.9, 154.2, 134.8, 129.1, 126.4, 126.2, 124.8, 122.8, 121.5, 114.4, 55.4.

2-(4-Chlorophenyl)benzothiazole[10a] (**5o**): Straw yellow solid; 49.3 mg (67% yield); mp 118-120 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.04 (m, 3H), 7.94 (d, J = 8.0 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.45 – 7.40 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 154.1, 137.0, 135.0, 132.1, 129.2, 128.7, 126.4, 125.4, 123.3, 121.6.

2-(Furan-2-yl)benzothiazole[10a] (**5p**): White solid; 51.5 mg (85% yield); mp 106-107 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 1.0 Hz, 1H), 7.57 – 7.47 (m, 1H), 7.46 – 7.36 (m, 1H), 7.22 (d, J = 3.1 Hz, 1H), 6.63 (dd, J = 3.5, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 153.7, 148.8, 144.7, 134.3, 126.4, 125.2, 123.1, 121.5, 112.5, 111.4.

2-(Thiophen-2-yl)benzothiazole[21] (**5q**): Yellow solid; 48.8 mg (75% yield); mp 99-100 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.9 Hz, 1H), 7.68 (dd, J = 3.7, 0.9 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.49 (dd, J = 11.3, 4.2 Hz, 1H), 7.40 (dd, J = 11.1, 4.1 Hz, 1H), 7.16 (dd, J = 5.0, 3.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 153.7, 137.3, 134.7, 129.2, 128.6, 128.0, 126.4, 125.2, 123.0, 121.4.

2-(Naphthalen-2-yl)benzothiazole[22] (**5r**): White solid; 71.2 mg (91% yield); mp 125-127 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.25 (dd, J = 8.6, 1.7 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 8.03 – 7.88 (m, 4H), 7.61 – 7.52 (m, 3H), 7.48 – 7.40 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 154.2, 135.1, 134.6, 133.2, 131.0, 128.8, 127.9, 127.6, 127.4, 126.9, 126.4, 125.3, 124.4, 123.2, 121.6.

2-Benzylbenzothiazole[7a] (**5s**): White solid; 60.8 mg (90% yield); mp 158-160 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.44 – 7.30 (m, 6H), 4.47 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 153.3, 137.2, 135.7, 129.2, 128.9, 127.3, 125.9, 124.8, 122.8, 121.5, 40.6.

2-Styrylbenzothiazole[23] (**5u**): White solid;48.3 mg (67% yield); mp 106-108 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.61 (t, J = 9.0 Hz, 2H), 7.55 – 7.36 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 153.9, 137.6, 135.4, 134.3, 129.4, 128.9, 127.40, 126.3, 125.4, 122.9, 122.1, 121.5.

Acknowledgement The financial support from NSFC (20802053) is highly appreciated.

Supporting Information Available: Copies of ^{1}H NMR and ^{13}C NMR of all the products. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Horton, D. A.; Bourne, G. T.; Smythe, M. L. *Chem. Rev.* **2003**, *103*, 893. (b) Guo, H. F.; Shao, H. Y.; Yang, Z. Y.; Xue, S. T.; Li, X.; Liu, Z. Y.; He, X. B.; Jiang, J. D.; Zhang, Y. Q.; Si, S. Y.; Li, Z. R. *J. Med. Chem.* **2010**, *53*, 1819. (c) Berrade, L.; Aisa, B.; Ramirez, M.; Galiano,S.;

Guccione, S.; Moltzau,L.R.; Levy, F. O.; Nicoletti, F.; Battaglia, G.; Molinaro, G.; Aldana, I.; Monge, A.; Perez-Silandes, S. *J. Med. Chem*. **2011**, *54*, 3086.

(2) For synthesis of benzo[*b*]thiophenes, see: (a) Liu, K.; Jia, F.; Xi, H.; Li, Y.; Zheng, X.; Guo, Q.; Shen, B.; Li, Z. *Org. Lett.* **2013**, *15,* 2026. (b) Topolski, M. *J. Org. Chem.* **1995**, *60*, 5588. (c) Christopher S.; Bryan, J. A.; Lautens, M. *Angew. Chem. Int. Ed*. **2009**, *48*, 7064.

(3) For synthesis of benzothiazoles, see: (a) Bochatay, V. N.; Boissarie, P. J.; Murphy, J. A.; Suckling, C. J.; Lang, S. *J. Org. Chem.* **2013**, *78*, 1471.(b) Siddappa, C.; Kambappa, V.; Umashankara, M.; Rangappa, K. S. *Tetrahedron Lett.* **2011**, *52*, 5474. (c) Yoo, W.; Yuan, H.; Miyamura, H.; Kobayashi, S. *Adv. Synth. Catal.* **2011**, *353*, 3085. (d) Sun, Y.; Jiang, H.; Wu, W.; Zeng, W.; Wu, X. *Org. Lett.* **2013**, *15*, 1598. (e) Yu, C.; Lee, K.; You, Y.; Cho, E. J. *Adv. Synth. Catal.* **2013**, *355*, 1471.

(4) Harris, T. W.; Smith, H. E.; Mobley, P. L.; Manier, D. H.; Sulser, F. *J. Med. Chem*. **1982**, *25*, 855.

(5) Inamoto, K.; Arai, Y.; Hiroya, K.; Doi, T. *Chem. Commun.* **2008**, 5529.

(6) (a) Saha, P.; Ramana, T.; Purkait, N.; Ali, M. A.; Paul, R.; Punniyamurthy, T. *J. Org. Chem.* **2009**, *74,* 8719. (b) Evindar, G.; Batey, R. A. *J. Org. Chem.* **2006**, *71*, 1802. (c) Feng, E.; Huang, H.; Zhou, Y.; Ye, D.; Jiang, H.; Liu, H. *J. Comb. Chem.* **2010**, *12*, 422.

(7) (a) Wang, H.; Wang, Lu.; Shang, J.; Li, X.; Wang, H.; Gui, J.; Lei, A. *Chem. Commun.* **2012**, *48*, 76. (b) Cheng, Y.; Yang, J.; Qu, Y.; Li, P. *Org. Lett.* **2012**, *14*, 98. (c) Bose, D. S.; Idrees, M. *J. Org. Chem.* **2006**, *71*, 8261. (d) Inamoto, K.; Hasegawa, C.; Hiroya, K.; Doi, T. *Org. Lett.* **2008**, *10*, 5147.

(8) For Pd or Cu catalyzed C-S bond formation, see: (a) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596. (b) Ma, D.; Xie, S.; Xue, P.; Zhang, X.; Dong, J.; Jiang, Y. *Angew. Chem. Int. Ed.* **2009,** *48*, 4222. (c) Ma, D.; Cai, Q. *Acc. Chem. Res.* **2008**, *41*, 1450. (d) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400. (e) Li, Y.; Nie, C.; Wang, H.; Li, X.; Verpoort, F.; Duan, C. *Eur. J. Org. Chem.* **2011**, 7331. (f) Prasad, D. J.; Sekar, G. *Org. Lett.* **2011**, *13*, 1008. (g) F. Ke, Y. Y. Qu, Z. Q.Jiang, Z. K. Li, D. Wu, X. G. Zhou, *Org. Lett.* **2011**, *13*, 454. (h) Park, N.; Park, K.; Jang, M.; Lee, S. *J. Org. Chem.* **2011**, *76*, 4371. (i) Qiao, Z.; Liu, H.; Xiao, X.; Fu, Y.; Wei, J.; Li, Y.; Jiang, X. *Org. Lett.* **2013**, *15*, 2594.

(9) (a) Sun, L.; Deng, C.; Tang, R.; Zhang, X. *J. Org. Chem.* **2011**, *76*, 7546. (b) Li, C.; Zhang, X.; Tang R.; Zhong, P.; Li, J. *J. Org. Chem.* **2010**, *75*, 7037. (c) Guilarte, V.; Fern, M. A.; Patricia G.; Hernando, E.; Sanz, R. *Org. Lett.* **2011**, *13*, 5100. (d) Kuhn, M.; Falk, F. C.; Paradies, J. *Org. Lett.* **2011**, *13*, 4100,

(10) (a) Deng, H.; Li, Z.; Ke, F.; Zhou, X. *Chem. Eur. J.* **2012**, *18*, 4840. (b) Ma, D.; Xie, S.; Xue, P.; Zhang, X.; Dong, J.; Jiang, Y. *Angew. Chem. Int. Ed*. **2009**, *48*, 4222. (c) Itoh, T.; Mase, T. *Org. Lett.* **2007**, *9*, 3687.

(11) Duan, Z.; Ranjit, S.; Liu, X. *Org. Lett.* **2010**, *12*, 2430.

(12) Sawada, N.; Itoha, T.; Yasuda, N. *Tetrahedron Lett.* **2006**, *47*, 6595.

(13) Cristau, H. J.; Ouali, A.; Spindler, J. F.; Taillefer, M. *Chem. Eur. J.* **2005**, *11*, 2483.

(14) Leardini, R.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *Chem. Comm.* **1985**, *20*, 1390.

(15) Liu, J.; Chen, W.; Ji, Y.; Wang, L. *Adv. Synth. Catal.* **2012**, *354*, 1585.

(16) Matsuki, Y.; Shoji, F. *Nippon Kagaku Zasshi.* **1965,** *86*, 1067.

(17) Liegault, B.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, Keith. *J. Org. Chem* .**2009**, *74*, 1826.

(18) Lapointe, D.; Fagnou, Keith. *Org. Lett,* **2009**, *11*, 4160.

(19) Slawomir, U.; Bernhard, B.; Nuria, O.; Daniel P.; Frank G. *J. Am. Chem. Soc.,* **2012**, *134*, 15241.

(20) Hitoshi, H.; Koji, H.; Tetsuya, S.; Masahiro, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 2202.

(21) Takuya Y.; Kei, M.; Masato, K.; Junichiro, Y.; Kenichiro, I. *Chem. Eur. J.* **2011**, *17*, 10113.

(22) Sukanta, K.; Benjamin, K.; Edward, R. B. *J. Hetero. Chem.* **2006**, *43*, 1609.

(23) Alphonse, F.A.; Suzenet, F.;Keromnes, A.; Lebret, B.; Guillaumet, G. *Org. Lett.* **2003**, *5*, 803.