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Pd-catalyzed oxidative cross-coupling between two electron rich heteroarenes†

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The transition-metal-catalyzed oxidative cross-coupling between two coupling partners with similar structure and electronic characteristics remains a challenge owing to difficulty in suppressing undesired homo-couplings. We herein report a Pd-catalyzed oxidative cross-coupling between two thiophenes under mild reaction conditions. This approach can also be extended to furans. Some notable advantages of this reaction lie in its synthetic simplicity with the omission of the toxic stannanes coupling partner and excellent functional-group compatibility. The features of this protocol make it an ideal strategy for the construction of a 2,2′-thiophene–thiophene linkage of interest in electronic and optoelectronic materials.

Because bithiophenes can alternate π-conjugated oligomers or polymers with unique electrical and optical properties, such an important structural motif is a popular choice for the preparation of advanced materials in various electronic and optoelectronic devices, such as organic light-emitting diodes (OLEDs),[1] organic field-effect transistors (OFETs),[2] organic electrochromic devices (ECDs),[3] and organic solar cells (OSCs).[4] A common synthetic method toward bithiophenes is palladium-catalyzed cross-coupling of stannyl thiophenes with thienyl halides (Stille cross-coupling).[5] Despite its great reliability and versatility, this method involves drawbacks such as the use of toxic stannanes that are difficult to handle or require extra steps to prepare, and often generate stoichiometric amount of toxic and environmentally risky by-products. Moreover, the important functional groups such as halides are incompatible in these reactions. From the point of view of synthetic simplicity as well as a new practical and environmentally benign process, the construction of a thiophene–thiophene linkage structural motif *via* a transition-metal-catalyzed oxidative cross-coupling between two simple thiophenes would be an ideal strategy, since the use of the C–H bond as the functional group[6] avoids the prefunctionalization steps of both thiophenes. However, the formation of the bithiophene-structure *via* this strategy is still a great challenge, and has not been reported to date.[7] The reason is that thiophenes are π-electron rich heteroarenes, and are susceptible to homocoupling in the existing catalytic systems.[8] Furthermore, although important progress has been made in the transition-metal-catalyzed oxidative cross coupling between two (hetero)arenes during the past few years,[9,10] realizing such a strategy between two coupling partners with similar structure and electronic characteristics remains a hindrance owing to the difficulty in suppressing undesired homo-couplings.[11] Hence, it is highly desirable to develop a new catalytic system to overcome these limitations for widespread applications. Herein, we report a Pd-catalyzed oxidative cross-coupling between two thiophenes (π-electron rich *vs.* π-electron rich). The reaction proceeds smoothly under mild reaction conditions. The high reaction efficiency as well as the excellent functional group compatibility of this approach represent an ideal strategy for the construction of well-defined bithiophenes. Furthermore, this approach can also be extended to furans. To demonstrate the synthetic importance of the approach, the application of the reaction in functional materials has also been described in a highly efficient manner.

Considering that 3-hexylthiophene is an important unit in the development of high performance electronic and optoelectronic materials,[12] and bromide and amide could be further functionalized in the preparation of a thiophene-based structure, 2-bromo-3-hexylthiophene **2a** and *N*,*N*-dimethylthiophene-2-carboxamide **1a** were chosen as model substrates (Table 1). Initially, no desired product **3a** was observed when the reaction was carried out in DMF at 80 °C by using $Pd(OAc)_2$ (10 mol%) as a catalyst and AgOAc (3.0 equiv.) as an oxidant (Table 1, entry 1). After a survey of the reaction parameters, such as solvents, oxidants, and the additives, carboxylic acids previously demonstrated to have a beneficial effect on the C–H bond activation of simple arenes[13] (for details see ESI†), it turned out that DMSO,[14] Ag_2O and benzoic acid are critical to the reaction efficiency, providing **3a** in 67% yield (Table 1, entry 7).

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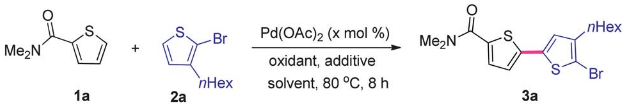
Table 1 Representative results for optimization of Pd-catalyzed oxidative cross-coupling of *N*,*N*-dimethylthiophene-2-carboxamide **1a** with 2-bromo-3-hexylthiophene **2a**[a]



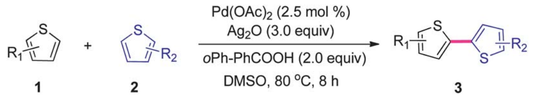
Entry	x	Oxidant (equiv.)	Solvent	Additive (equiv.)	Yield (%)[b]
1[c]	10	AgOAc (3)	DMF	—	NR
2[c]	10	AgOAc (3)	Dioxane	—	NR
3[c]	10	AgOAc (3)	DCE	—	NR
4[c]	10	AgOAc (3)	DMSO	—	28
5[c]	10	Ag_2CO_3 (3)	DMSO	—	24
6[c]	10	Ag_2O (1.5)	DMSO	—	29
7	10	Ag_2O (3)	DMSO	$PhCO_2H$ (3)	67
8	5	Ag_2O (3)	DMSO	$PhCO_2H$ (3)	72
9	2.5	Ag_2O (3)	DMSO	$PhCO_2H$ (3)	65
10	2.5	Ag_2O (3)	DMSO	*o*Me-$PhCO_2H$ (3)	70
11	2.5	Ag_2O (3)	DMSO	*p*Me-$PhCO_2H$ (3)	64
12	2.5	Ag_2O (3)	DMSO	*o*NO_2-$PhCO_2H$ (3)	52
13	2.5	Ag_2O (3)	DMSO	*o*Ph-$PhCO_2H$ (3)	71
14	2.5	Ag_2O (3)	DMSO	*o*Ph-$PhCO_2H$ (2)	71[d]
15	2.5	Ag_2O (3)	DMSO	HOAc (2)	61
16	2.5	Ag_2O (3)	DMSO	CF_3CO_2H (2)	26
17	2.5	Ag_2O (3)	DMSO	—	28
18	2.5	—	DMSO	*o*Ph-$PhCO_2H$ (2)	NR
19	—	Ag_2O (3)	DMSO	*o*Ph-$PhCO_2H$ (2)	NR

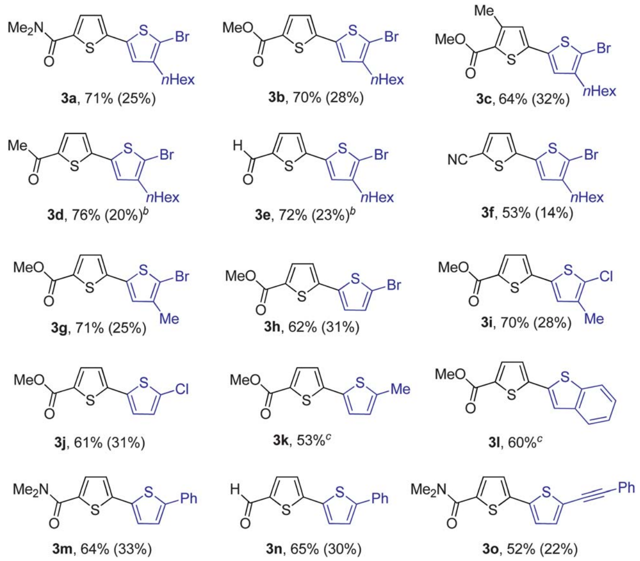
[a] Reaction conditions (unless otherwise specified): **1a** (0.9 mmol), **2a** (0.3 mmol), solvent (2 mL). [b] Isolated yield. [c] **1a**/**2a** = 1 : 1.5, 0.3 mmol scale. [d] 25% homocoupling of **2a** was isolated.

Decreasing the loading amount of $Pd(OAc)_2$ from 10 mol% to 5 mol% further improved the yield to 72% (Table 1, entry 8). However, when 2.5 mol% of $Pd(OAc)_2$ was used, a lower yield (65%) was observed (Table 1, entry 9). Considering that the steric and electronic effect of benzoic acid could be tuned by the substituents, which may influence the activity of the carboxylic acid and benefit formation of cross-coupling product **3a**, different substituted benzoic acids were then investigated to further optimize the catalytic system (Table 1, entries 10–13). Finally, the desired cross-coupling product **3a** was improved to 71% yield albeit with the formation of homocoupling by-products (25% yield of homocoupling of **2a** was obtained[15]) when 2.0 equiv. of *ortho*-phenyl benzoic acid (*o*Ph-$PhCO_2H$) and 2.5 mol% of $Pd(OAc)_2$ were used (Table 1, entry 14). It is worth noting that benzoic acid with a bulky substituent at its *ortho* position benefits the reaction efficiency, while an electron-deficient substituent diminishes the yield. A control experiment using AcOH was also performed under the optimized reaction conditions (Table 1, entry 14), providing a slightly lower yield than *o*Ph-$PhCO_2H$ (Table 1, entry 15), while a dramatically decreased yield was observed when more acidic TFA or no acid was used (Table 1, entries 16–17). Thus, these findings demonstrate that the nature of carboxylic acids is critical for the reaction efficiency. We supposed that the *o*Ph-$PhCO_2^-$ generated by the reaction of *o*Ph-$PhCO_2H$ with Ag_2O may serve as a suitable base to assist the C–H cleavage for thiophenes as previously reported.[13] In addition, no reaction was observed in the absence of Ag_2O or $Pd(OAc)_2$, thus demonstrating that a palladium redox catalytic cycle is involved in the reaction (Table 1, entries 18–19).

Under the optimum reaction conditions (Table 1, entry 14), a wide range of 2,2′-bithiophenes were generated in moderate to good yields (Table 2).[16] Thiophenes bearing important functional groups, such as methyl ketone, ester, aldehyde, and nitrile, underwent the cross-coupling smoothly with 2-bromo-3-hexylthiophene **2a** (**3a–f**), thus providing a good opportunity for further transformation by using these functional groups. Importantly, compound **3e**, a useful building block in the development of organic solar cells,[17] can be easily prepared from simple thiophene in good yield (72%) *via* only one step, thus featuring the advantages of present strategy. Interestingly, thiophenes with bromide and chloride at C2-position showed similar reactivity (**3h** and **3j**), while providing slightly lower yields than their corresponding 2-halo-3-methylthiophenes (**3g** and **3i**). However, when 2-methyl-thiophene was investigated, only a moderate yield (53%) of **3k** was afforded. These results indicated that the efficient cross-coupling of thiophenes depends on their electronic-profiles. Benzothiophene and 2-phenylthiophene are also suitable substrates with good yields obtained (**3l–n**). It is worth noting that an alkyne can also tolerate the reaction conditions (**3o**), and as a result some alkyne containing thiophene-based functional materials can be efficiently prepared *via* this strategy[18] or an additional thiophene ring can be introduced from the alkyne.[19]

Table 2 Pd-catalyzed oxidative cross-coupling between two thiophenes[a]





3a, 71% (25%) **3b**, 70% (28%) **3c**, 64% (32%)

3d, 76% (20%)[b] **3e**, 72% (23%)[b] **3f**, 53% (14%)

3g, 71% (25%) **3h**, 62% (31%) **3i**, 70% (28%)

3j, 61% (31%) **3k**, 53%[c] **3l**, 60%[c]

3m, 64% (33%) **3n**, 65% (30%) **3o**, 52% (22%)

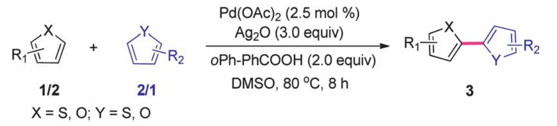
[a] Reaction conditions (unless otherwise specified): **1** (3 equiv.), **2** (0.3 mmol), DMSO (2 mL). All reported yields are isolated yields. The number in parentheses is the homocoupling yield of compound **2**. [b] 5 mol% of $Pd(OAc)_2$ was used. [c] No homocoupling of **2** was observed.

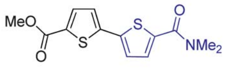
The construction of 2,2′-bithiophenes *via* the present strategy is not limited to the cross-coupling of two thiophenes bearing substituents with different electronic characteristics. Thiophenes with similar electron-deficient groups, such as ester and amide, also furnished the corresponding bithiophene **3p** in high efficiency (Table 3, **3p**). Importantly, the introduction of a highly electron-deficient pentafluorophenyl group at C2 position of thiophene did not affect the cross-coupling with **1a**, thus providing a new strategy for the preparation of a polyfluoroarylthiophene based structural motif of interest in functional materials[20] (**3q**). Furthermore, thiophenes bearing electron-donating groups are also suitable substrates, providing **3r**, **3t**, and **3u** in moderate to good yields. A reasonable yield of **3s** was obtained due to significant formation of homocoupling by-products. Extension to furans could also afford synthetically useful yields by using Pd(TFA)$_2$, AgOAc, and 1,10-phen catalytic systems (**3v** and **3w**). However, the cross-coupling between furans led to a low yield due to formation of some uncertain by-products (**3x**). It should be mentioned that an important monomer **3y** used for organic solar cell and other useful electronic devices[21] was easily prepared in only one step without the prerequirement of the preparation of thienyl bromides or organotin reagents.

The importance of the protocol can also be featured by the rapid access of π-conjugated oligomer **7** for dye-sensitized solar cell in only three steps[17a] (Scheme 1). Application of the present method, the key intermediate oligothiophene **5** was obtained in an efficient way, followed by the direct introduction of another thiophene ring with the use of the Pd(OAc)$_2$/PPh$_3$ catalytic system,[22] providing compound **6** in good yield. Finally, condensation of **6** with 2-cyanoacetic acid afforded **7** in 98% yield. Thus, compared with the traditional method,[17a] the present method features the following advantages: (1) high efficiency and synthetic simplicity without extra prefunctionalization steps, such as the preparation of stannyl thiophene and bromination of thiophene (3 steps *vs.* 6 steps); (2) environmental friendliness without the generation of toxic and environmentally risky by-products (H *vs.* Sn). To further demonstrate the usefulness of this protocol, bithiophene **9**, a key intermediate in the preparation of the *in vivo* optical imaging agent **11** for diagnosing Alzheimer's disease,[23] was also synthesized in high efficiency. Deprotection of a methyl group on compound **9** with BBr$_3$followed by condensation with malononitrile afforded **11** with even higher overall yield than the traditional method did using an organotin intermediate (45% overall yield, 3 steps *vs.* 37% overall yield, 5 steps).[23]

To gain some mechanistic insight into the present reaction, kinetic isotope effect (KIE) experiments for both coupling partners were conducted (Scheme 2). Initial rate measurements revealed KIEs of 2.6 and 4.1 for **1e** and **2h**, respectively (for details see ESI†). These findings imply that (1) the turnover-limiting

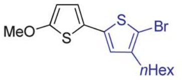
Table 3 Pd-catalyzed oxidative cross-coupling between two electron-rich heteroarenes[a]



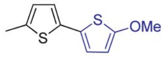


3p, 69% (27%)

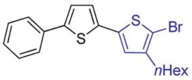
3q, 60%[e]



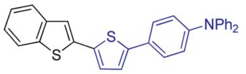
3r, 56% (18%)



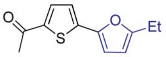
3s, 44% (37%)



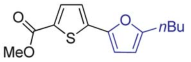
3t, 66% (27%)



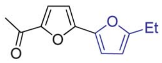
3u, 53% (27%)



3v, 50%[b,c]



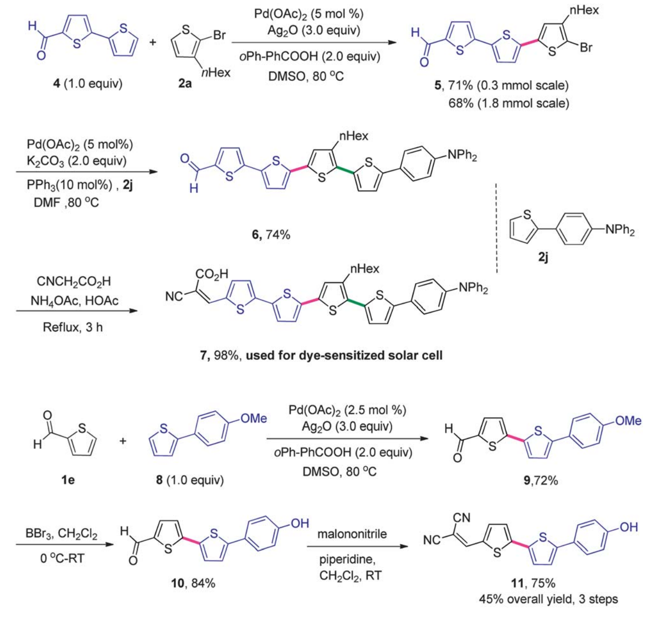
3w, 49%[b,c]



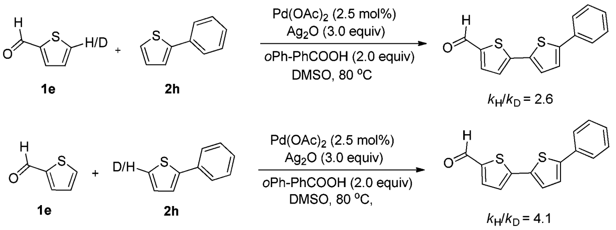
3x, 25%[c]

3y, 41%[d, e]

[a] Reaction conditions (unless otherwise specified): **1/2** (3 equiv.), **2/1** (0.3 mmol), DMSO (2 mL). All reported yields are isolated yields. The number in parentheses is the homocoupling yield of compound **2/1**. [b] Pd(TFA)$_2$ (10 mol%), AgOAc (3.0 equiv.), 1,10-phen (0.2 equiv.), DMSO/DMA (3 : 1, 2 mL) at 100 °C. [c] No homocoupling of **2** was observed. [d] 0.1 mmol scale, Pd(OAc)$_2$ (5% mmol), **2a** (6 equiv.), Ag$_2$O (6 equiv.), DMSO (3 mL), 14 h. [e] The homocoupling of **2/1** was not determined.



Scheme 1 Synthesis of functional materials π-conjugated oligomer **7** and optical imaging agent **11**.

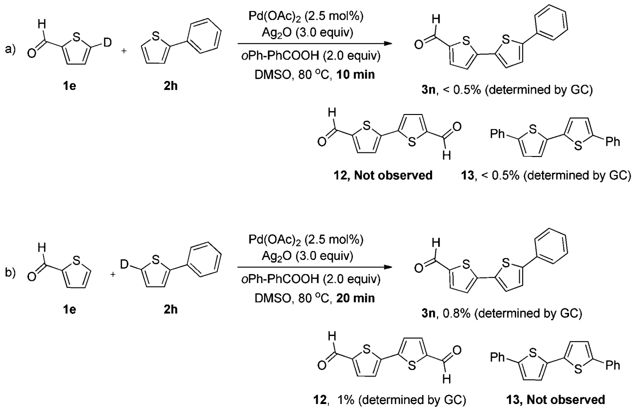


Scheme 2 Kinetic isotope effect studies.

step[24] of the catalytic cycle is the C–H cleavage of relatively electron-rich thiophene, and (2) the cleavage of the C–H bonds in both thiophenes depends on their electronic-profiles, and the C–H bond cleavage for thiophenes bearing electron-deficient substituents is relatively easier than that of electron-rich ones. Thus, the possibility of C–H bond cleavage for thiophenes under present reaction conditions *via* a typical electrophilic aromatic substitution (S_EAr) pathway can be ruled out, as the observed reactivity of substituted thiophenes **1e** and **2h** is not in agreement with S_EAr reactivity.

Additionally, when the reaction of *d*-**1e** with **2h** was conducted within 10 min, no homocoupling of **1e** was formed (Scheme 3a). A similar result was also observed in the treatment of **1e** with *d*-**2h**, in which the homocoupling of **2h** was not detected until the reaction lasted 20 min (Scheme 3b). However, both of these reactions provided the cross-coupling product **3n** and homocoupling by-products of non-deuterated coupling partners. Thus, these results implied that the present reaction could be initiated from both thiophenes.

On the basis of above results, we proposed that the present reaction could be initiated from both thiophenes to give a palladated thienyl complex, which then reacts with the other thiophene to form a dithienyl palladium complex. Finally, reductive elimination provides the final product, and the released Pd(0) species is reoxidized by silver salt to regenerate Pd(II). Among these two pathways, the reaction begins with relatively electron-deficient thiophene might be the major pathway. However, the formation of a dithienyl palladium complex through metal-exchange between two palladated thienyl complexes could not be ruled out. Previous studies showed that a concerted metalation-deprotonation (CMD)[25] pathway could be involved for a Pd(II)–acetate complex catalyzed C–H bond cleavage for thiophenes.[26] Since the typical S_EAr pathway was ruled out, on the basis of previous studies as well as the fact that the C–H bond cleavage of present reaction depends on the C–H bond acidity and the nature of carboxylate, we proposed that the present reaction may proceed *via* a CMD pathway. However, the detailed mechanism remains a point of discussion.



Scheme 3 Pd-catalyzed oxidative cross-coupling between H/*d*-**1e** and H/*d*-**2h**.

In conclusion, a Pd-catalyzed oxidative cross-coupling of thiophenes has been developed. The solvent effect and additive benzoic acid play critical roles in the reaction efficiency. Thiophenes bearing electron-withdrawing or electron-donating groups all furnished the cross-coupling products efficiently. Application of the method led to important and useful oligothiophene building blocks, which can be further applied in photovoltaics. Because of the high reaction efficiency under mild reaction conditions, operational simplicity with the omission of organotin reagents and prefunctionalization process, as well as excellent functional group compatibility, this protocol provides a straightforward and efficient access to 2,2′-bithiophenes. Furthermore, this approach can also be extended to furans. We believe that this protocol should be useful for the atom/step-economical synthesis of new thiophene-based electronic and optoelectronic materials. Mechanistic studies revealed that the cleavage of C–H bonds for both thiophenes depends on their electronic-profiles. Further studies to uncover the detailed mechanism and expand the substrate scope and their applications are now in progress.

Acknowledgements

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Notes and references

1 (*a*) J. Roncali, *Macromol. Rapid Commun.*, 2007, **28**, 1761; (*b*) S. Gunes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324; (*c*) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897; (*d*) P.-L. T. Boudreault, A. Najari and M. Leclerc, *Chem. Mater.*, 2011, **23**, 456.

2 (*a*) V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J.-L. Bredas, *Chem. Rev.*, 2007, **107**, 926; (*b*) M. Mas-Torrent and C. Rovira, *Chem. Soc. Rev.*, 2008, **37**, 827; (*c*) S. Allard, M. Forster, B. Souharce, H. Thiem and U. Scherf, *Angew. Chem., Int. Ed.*, 2008, **47**, 4070; (*d*) W. Wu, Y. Liu and D. Zhu, *Chem. Soc. Rev.*, 2010, **39**, 1489.

3 (*a*) A. A. Argun, P. H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid and J. R. Reynolds, *Chem. Mater.*, 2004, **16**, 4401; (*b*) P. M. Beaujuge and J. R. Reynolds, *Chem. Rev.*, 2010, **110**, 268.

4 (*a*) B. C. Thompson and J. M. J. Frechet, *Angew. Chem., Int. Ed.*, 2008, **47**, 58; (*b*) Z. Ning and H. Tian, *Chem. Commun.*,

2009, 5483; (*c*) Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868.

5 (*a*) A. de Meijere and F. Diederich, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, 2nd edn, 2004; (*b*) Y.-J. Cheng, S.-H. Yan and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868; (*c*) B. Carsten, F. He, H.-J. Son, T. Xu and L. Yu, *Chem. Rev.*, 2011, **111**, 1493.

6 For selected recent reviews related to C–H bonds activation, see: (*a*) L.-C. Campeau and K. Fagnou, *Chem. Commun.*, 2006, 1253; (*b*) O. Daugulis, V. G. Zaitzev, D. Shabashov, Q.-N. Pham and A. Lazareva, *Synlett*, 2006, 3382; (*c*) D. Alberico, M. E. Scott and M. Lautens, *Chem. Rev.*, 2007, **107**, 174; (*d*) R. Giri, B. F. Shi, K. M. Engle, N. Maugel and J.-Q. Yu, *Chem. Soc. Rev.*, 2009, **38**, 3242; (*e*) L. Ackermann, R. Vicente and A. R. Kapdi, *Angew. Chem., Int. Ed.*, 2009, **48**, 9792; (*f*) D. A. Colby, R. G. Bergman and J. A. Ellman, *Chem. Rev.*, 2010, **110**, 624; (*g*) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147; (*h*) C.-L. Sun, B.-J. Li and Z.-J. Shi, *Chem. Commun.*, 2010, **46**, 677.

7 Metal-free arylation of thiophenes, see: (*a*) Y. Kita, K. Morimoto, M. Ito, C. Ogawa, A. Goto and T. Dohi, *J. Am. Chem. Soc.*, 2009, **131**, 1668, For copper-catalyzed iodination/arylation sequence, see: (*b*) H.-Q. Do and O. Daugulis, *J. Am. Chem. Soc.*, 2011, **133**, 13577.

8 (*a*) K. Masui, H. Ikegami and A. Mori, *J. Am. Chem. Soc.*, 2004, **126**, 5074; (*b*) M. Takahashi, K. Masui, H. Sekiguchi, N. Kobayashi, A. Mori, M. Funahashi and N. Tamaok, *J. Am. Chem. Soc.*, 2006, **128**, 10930.

9 For selected recent reviews related to transition-metal catalyzed oxidative cross-coupling, see: (*a*) C. S. Yeung and V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215; (*b*) J. L. Bras and J. Muzart, *Chem. Rev.*, 2011, **111**, 1170; (*c*) C. Liu, H. Zhang, W. Shi and A. Lei, *Chem. Rev.*, 2011, **111**, 1780; (*d*) W. Han and A. R. Ofial, *Synlett*, 2011, 1951; (*e*) S. H. Cho, J. Y. Kim, J. Kwak and S. Chang, *Chem. Soc. Rev.*, 2011, **40**, 5068; (*f*) X. Bugaut and F. Glorius, *Angew. Chem., Int. Ed.*, 2011, **50**, 7479.

10 For selected examples related to transition-metal catalyzed oxidative di(hetero)arylation cross-coupling, see: (*a*) R. Li, L. Jiang and W. Lu, *Organometallics*, 2006, **25**, 5973; (*b*) D. R. Stuart and K. Fagnou, *Science*, 2007, **316**, 1172; (*c*) T. A. Dwight, N. R. Rue, D. Charyk, R. Josselyn and B. DeBoef, *Org. Lett.*, 2007, **9**, 3137; (*d*) D. R. Stuart, E. Villemure and K. Fagnou, *J. Am. Chem. Soc.*, 2007, **129**, 12072; (*e*) K. L. Hull and M. S. Sanford, *J. Am. Chem. Soc.*, 2007, **129**, 11904; (*f*) B.-J. Li, S.-L. Tian, Z. Fang and Z.-J. Shi, *Angew. Chem., Int. Ed.*, 2008, **47**, 1115; (*g*) G. Brasche, J. Garcia-Fortanet and S. L. Buchwald, *Org. Lett.*, 2008, **10**, 2207; (*h*) K. L. Hull and M. S. Sanford, *J. Am. Chem. Soc.*, 2009, **131**, 9651; (*i*) C.-Y. He, S. Fan and X. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 12850; (*j*) P. Xi, F. Yang, S. Qin, D. Zhao, J. Lan, G. Gao, C. Hu and J. You, *J. Am. Chem. Soc.*, 2010, **132**, 1822; (*k*) Y. Wei and W. Su, *J. Am. Chem. Soc.*, 2010, **132**, 16377; (*l*) H. Li, J. Liu, C.-L. Sun, B.-J. Li and Z.-J. Shi, *Org. Lett.*, 2011, **13**, 276; (*m*) X. Wang, D. Leow and J.-Q. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 13864; (*n*) Z. Wang, K. Li, D. Zhao, J. Lan and J. You, *Angew. Chem., Int. Ed.*, 2011, **50**, 5365; (*o*) D. Mandal, A. D. Yamaguchi, J. Yamaguchi and K. Itami, *J. Am. Chem. Soc.*, 2011, **133**, 19660; (*p*) A. D. Yamaguchi, D. Mandal, J. Yamaguchi and K. Itami, *Chem. Lett.*, 2011, **40**, 555; (*q*) J. Wencel-Delord, C. Nimphius, F. W. Patureau and F. Glorius, *Angew. Chem., Int. Ed.*, 2012, **51**, 2247; (*r*) L. Zhou and W. Lu, *Organometallics*, 2012, **31**, 2124; (*s*) C.-Y. He, Q.-Q. Min and X. Zhang, *Organometallics*, 2012, **31**, 1335; (*t*) J. Dong, Z. Long, F. Song, N. Wu, Q. Guo, J. Lan and J. You, *Angew. Chem., Int. Ed.*, 2013, **52**, 580.

11 For transition-metal-catalyzed oxidative cross-coupling between two similar structures, see: (*a*) W. Han, P. Mayer and A. R. Ofial, *Angew. Chem., Int. Ed.*, 2011, **50**, 2178; (*b*) J. Dong, Y. Huang, X. Qin, Y. Cheng, J. Hao, D. Wan, W. Li, X. Liu and J. You, *Chem.–Eur. J.*, 2012, **18**, 6158; (*c*) N. Kuhl, M. N. Hopkinson and F. Glorius, *Angew. Chem., Int. Ed.*, 2012, **51**, 8230; (*d*) X. Qin, B. Feng, J. Dong, X. Li, Y. Xue, J. Lan and J. You, *J. Org. Chem.*, 2012, **77**, 7677; (*e*) Z. Mao, Z. Wang, Z. Xu, F. Huang, Z. Yu and R. Wang, *Org. Lett.*, 2012, **14**, 3854; (*f*) S. Fan, Z. Chen and X. Zhang, *Org. Lett.*, 2012, **14**, 4950.

12 For review, see: (*a*) H. Klauk, *Chem. Soc. Rev.*, 2010, **39**, 2643. For selected examples, see: (*b*) M. Sevignon, J. Papillon, E. Schulz and M. Lemaire, *Tetrahedron Lett.*, 1999, **40**, 5873; (*c*) Q. Wang, R. Takita, Y. Kikuzaki and F. Ozawa, *J. Am. Chem. Soc.*, 2010, **132**, 11420; (*d*) S. Tamba, K. Shono, A. Sugie and A. Mori, *J. Am. Chem. Soc.*, 2011, **133**, 9700.

13 (*a*) D. L. Davies, S. M. A. Donald and S. A. Macgregor, *J. Am. Chem. Soc.*, 2005, **127**, 13754; (*b*) D. Garcia-Cuadrado, P. de Mendoza, A. A. C. Braga, F. Maseras and A. M. Echavarren, *J. Am. Chem. Soc.*, 2007, **129**, 6880; (*c*) M. Lafrance, S. I. Gorelsky and K. Fagnou, *J. Am. Chem. Soc.*, 2007, **129**, 14570; (*d*) S. I. Gorelsky, D. Lapointe and K. Fagnou, *J. Am. Chem. Soc.*, 2008, **130**, 10848.

14 DMSO benefits the palladium catalytic cycle, see: B. A. Steinhoff and S. S. Stahl, *J. Am. Chem. Soc.*, 2006, **128**, 4348 and ref. 10*i*.

15 29% yield (based on **1a**) of homocoupling of **1a** was also observed, because 3.0 equiv. of **1a** was used.

16 Both of homocoupling by products of **1** and **2** were observed. Since excessive amounts of compound **1** were used, the yields of homocoupling byproducts of **1** were not determined. For the homocoupling byproducts of **2**, see the numbers in parentheses in Tables 2 and 3.

17 For selected examples, see: (*a*) E. Kozma, I. Concina, A. Braga, L. Borgese, L. E. Depero, A. Vomiero, G. Sberveglieri and M. Catellani, *J. Mater. Chem.*, 2011, **21**, 13785; (*b*) H.-C. Chu, D. Sahu, Y.-C. Hsu, H. Padhy, D. Patra, J.-T. Lin, D. Bhattacharya, K.-L. Lu, K.-H. Wei and H.-C. Lin, *Dyes Pigm.*, 2012, **93**, 1488; (*c*) F. Fages, E. Shilova, C. Martini and J. Ackermann, WO 2012049167, 2012.

18 (*a*) C. Wang, H. Dong, W. Hu, Y. Liu and D. Zhu, *Chem. Rev.*, 2012, **112**, 2208; (*b*) S. C. Rasmussen, R. L. Schwiderski and M. E. Mulholland, *Chem. Commun.*, 2011, **47**, 11394.

19 K. T. Potta, S. A. Nye and K. A. Smith, *J. Org. Chem.*, 1992, **57**, 3895.

20 For a review, see: (*a*) F. Babudri, G. M. Farinola, F. Naso and R. Ragni, *Chem. Commun.*, 2007, 1003. For selected recent papers, see: (*b*) M. L. Tang, A. D. Reichardt, N. Miyaki, R. M. Stoltenberg and Z. Bao, *J. Am. Chem. Soc.*, 2008, **130**, 6064; (*c*) Y. Wang, S. R. Parkin and M. D. Watson, *Org. Lett.*, 2008, **10**, 4421; (*d*) Y. Wang and M. D. Watson, *J. Am. Chem. Soc.*, 2006, **128**, 2536; (*e*) M.-H. Yoon, A. Facchetti, C. E. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 2006, **128**, 5792; (*f*) J. A. Letizia, A. Facchetti, C. L. Stern, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 13476.

21 (*a*) W. Li, W. S. C. Roelofs, M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2012, **134**, 13787; (*b*) Y. Zou, D. Gendron, R. Neagu-Plesu and M. Leclerc, *Macromolecules*, 2009, **42**, 6361.

22 S. Fan, C.-Y. He and X. Zhang, *Chem. Commun.*, 2010, **46**, 4926.

23 (*a*) E. E. Nesterov, J. Skoch, B. T. Hyman, W. E. Klunk, B. J. Backai and T. M. Swager, *Angew. Chem., Int. Ed.*, 2005, **44**, 5452; (*b*) compound **9** can also be used for preparation of non-linear optical materials, see: C. Herbivo, A. Comel, G. Kirsch, A. M. C. Fonseca, M. Belsley and M. M. M. Raposo, *Dyes Pigm.*, 2010, **86**, 217.

24 E. M. Simmons and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 2012, **51**, 3066.

25 For a review, see: D. Lapointe and K. Fagnou, *Chem. Lett.*, 2010, **39**, 1118.

26 S. I. Gorelsky, D. Lapointe and K. Fagnou, *J. Org. Chem.*, 2012, **77**, 658.