Cross-Coupling

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Palladium-Catalyzed Oxidative C–H/C–H Cross-Coupling of Indoles and Pyrroles with Heteroarenes**

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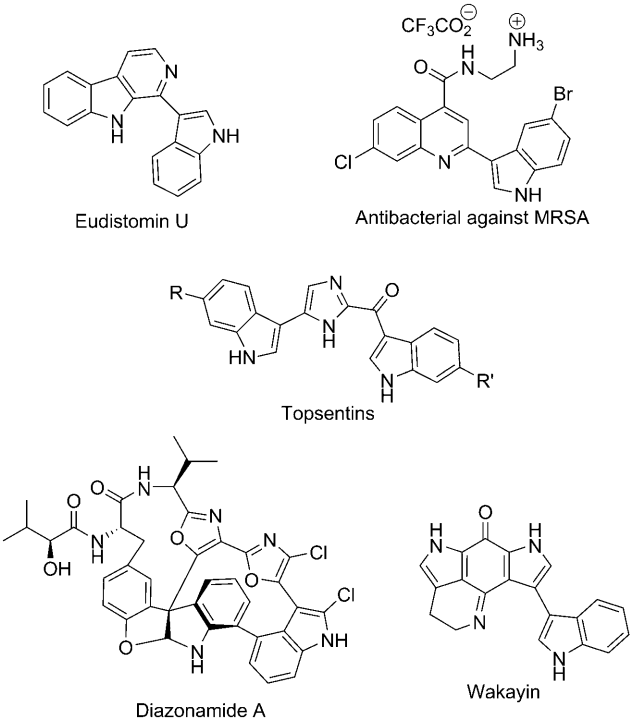
The bi-heteroaryl structural motif is prevalent in polymers, advanced materials, liquid crystals, ligands, molecules of medicinal interest, and natural products.[1] Transition-metal-catalyzed cross-coupling reactions of a heteroaryl halide or surrogate with a heteroaryl metal represents one of the most powerful and reliable methodologies for the preparation of bi-heteroaryl compounds.[2] However, from the viewpoint of synthetic simplicity, atom economy, and sustainable chemistry, direct oxidative coupling between heteroarenes through a double C–H activation would be the most ideal strategy for connecting two heteroarenes, thus avoiding prefunctionalization of both of substrates prior to the coupling reaction.[3] In recent years, a few groups disclosed their pioneering work directed toward transition-metal-catalyzed oxidative C–H/C–H cross-coupling between a directing-group-containing arene and an arene,[4] between two simple arenes,[5] and between a heteroarene and an arene.[6,7] In sharp contrast, metal-catalyzed direct oxidative C–C couplings between two heteroarenes have a limited substrate scope. Arguably the remaining challenge in this area is to develop a compatible method for a variety of heteroarenes since such species have often been documented to undergo homocoupling, and have inadequate stability for participating in the coupling process. In addition, the presence of heteroarenes may lead to low reactivity and selectivity in coupling reactions because of the binding of the heteroatom in both the substrate and product to the metal complex. Recently, we reported the first Pd(OAc)$_2$-catalyzed copper-salt-activated oxidative C–H/C–H cross-coupling of xanthines, azoles, and pyridine *N*-oxides with thiophenes and furans.[8] Quite recently, Ofial and coworkers described the efficient palladium-catalyzed dehydrogenative cross-couplings of benzothiazole and benzimidazoles with N-, O-, and S-containing azoles.[9]

(Hetero)arylated indoles and pyrroles represent important structural elements for pharmaceuticals, fragrances, dyes, agrochemicals, materials, and natural products (Scheme 1). Transition-metal-catalyzed direct oxidative C–H/C–H coupling methods to form (hetero)arylated indoles and pyrroles pose a great synthetic challenge because the indole and pyrrole substrates and products are susceptible to oxidative decomposition under the oxidative reaction conditions and there are elements of C2/C3 regiocontrol.[6a–c,e,f,7b,10] The palladium-catalyzed regioselective oxidative arylation of indoles and pyrroles with simple benzenes through dual C–H functionalization was developed independently by the groups of Fagnou[6a,b] and DeBoef.[6c,e] Quite recently, Pintori and Greaney showed that the palladium-catalyzed intramolecular oxidative C–H coupling of an indole ring with an arene at the indole 2-position was an effective strategy for synthesizing medium-sized ring compounds.[7b] However, transition-metal-catalyzed direct oxidative intermolecular C–H/C–H cross-coupling of indoles and pyrroles with heteroarenes has not been reported to date. Herein we disclose the solutions to meet these challenges, including the



Scheme 1. Selected medicinal and natural molecules containing heteroarylated indoles and pyrroles.

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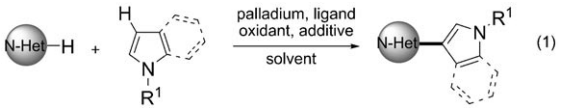
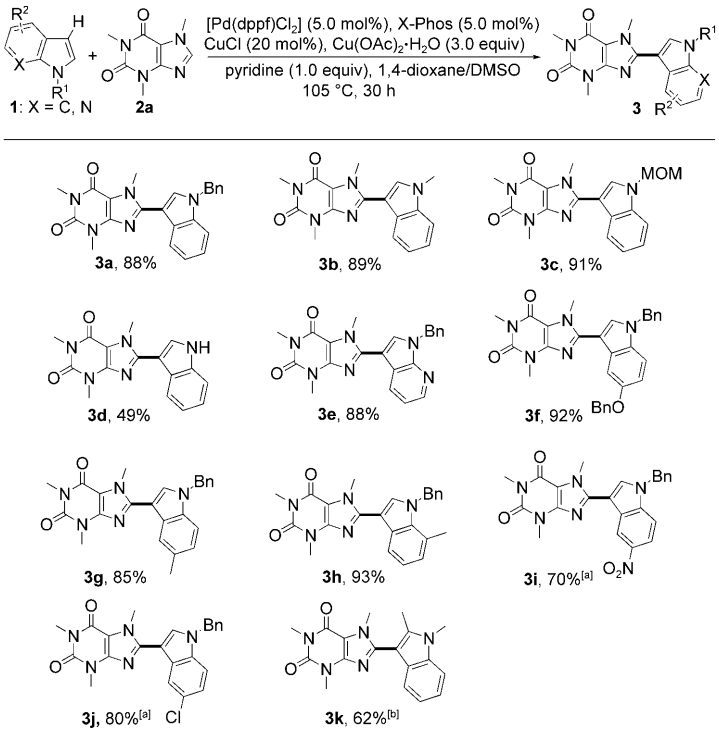
prevention of the oxidative decomposition of substrates and products, the complete inversion in reactivity/selectivity in the two metalation steps of the catalytic cycle to restrain the formation of intractable homocoupling, and the control of regioselectivity [Eq. (1)].



Xanthines (e.g., caffeine, theophylline, theobromine, etc.) are important biologically active alkaloids. 8-(Hetero)aryl-substituted xanthines are highly potent antagonists at human A_{2B} adenosine receptors.[11] As part of our ongoing effort to synthesize (hetero)aryl-substituted xanthines,[8,12] we initially focused on the cross-coupling of caffeine with 1-benzylindole to optimize the conditions (see Table S1 in the Supporting Information). After screening several parameters (e.g., palladium source, solvent, oxidant, ligand, additive, temperature, etc.), we found that the addition of extra X-Phos could greatly prevent the decomposition of *N*-alkylindoles, and dramatically improved the yield of the desired product **3a** to up to 70% (Table S1, entry 9). DMSO played a critical role in the reaction efficiency, and the absence of DMSO diminished the yield of **3a** (Table S1, entries 5 and 8). We supposed that DMSO might act as a ligand to prevent the formation of palladium black.[6f,13] Excitingly, a catalytic amount of CuCl further advanced the catalytic efficiency and C3/C2 regioselectivity. Finally, the cross-coupling reactions proceeded well when 5 mol% of [Pd(dppf)Cl_2] was employed in combination with X-Phos (5 mol%), CuCl (0.2 equiv), $Cu(OAc)_2{\cdot}H_2O$ (3.0 equiv), and pyridine (1.0 equiv) in 1,4-dioxane/DMSO (9:1; Table S1, entry 10). This transformation was highly regioselective by reacting at C3 of the indole, and other regioisomeric products were not observed. An X-ray analysis of single crystals of **3a** confirmed that a direct C–H/C–H cross-coupling took place between C3 on the 1-benzylindole and C8 on caffeine (see Figure S1 in the Supporting Information).[14]

With optimized conditions now in hand, we examined the scope of this methodology with respect to indoles as summarized in Scheme 2. Gratifyingly, we found that a relatively broad range of indole derivatives could couple with caffeine with complete C3 selectivity and good yields. Indoles having an N-protecting group such as methyl, benzyl, or MOM group all gave the corresponding N-protected xanthine-substituted indoles **3a–c**, whereas the protection of the indole with the TIPS (triisopropylsilyl) group afforded the N-unprotected indole derivative **3d**. Interestingly, the N-unprotected indole could also be oxidatively cross-coupled with caffeine, albeit in a diminished yield of 39%. A variety of substituents on the indole substrates (e.g., alkyl, chloride, nitro, benzyloxy groups, etc.) were tolerated. Indoles with the



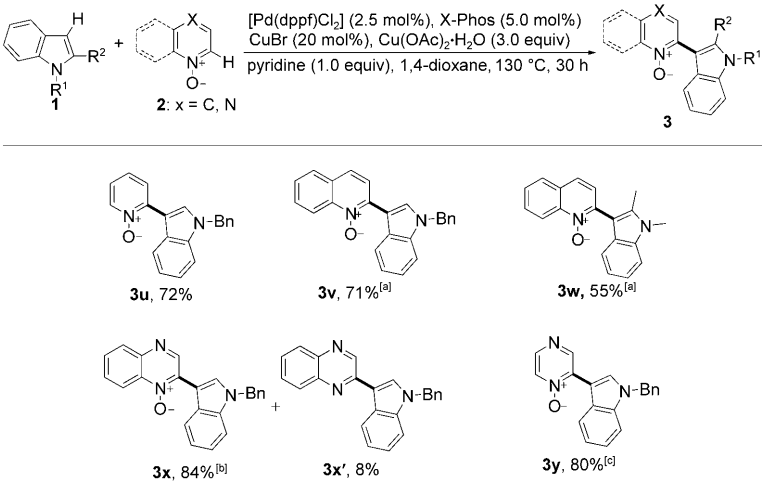
Scheme 2. Selective cross-coupling of indole derivatives with caffeine. For all reactions 0.5 mmol caffeine (**2a**) and 3.0 equiv indole **1** were used under an N_2 atmosphere. Yields of the isolated product are based on **2a**. [a] Carried out at 120°C. [b] Carried out at 140°C without X-Phos. DMSO = dimethyl sulfoxide, X-Phos = 2-(dicyclohexylphosphino)-2′,4′,6′-tri-*iso*-propyl-1,1′-biphenyl, Pd(dppf)Cl_2 = [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II).

electron-withdrawing or 2-substituted groups required relatively higher reaction temperatures (up to 120–140°C; **3i–k**). Notably, the reaction of 1-benzyl-7-aza-1*H*-indole proceeded well and result in an 88% yield (**3e**).

We subsequently applied this protocol to other xanthines (e.g., benzylic theobromine, benzylic theophylline, *n*-butyl theophylline, etc.) to synthesize xanthine-substituted indoles **3l–n** in good to excellent yields (Scheme 3). Simple purine heterocycles are attractive as "functional" π components in organic materials with biological relevance.[15] Recently, the C arylation of purines with aryl boronic acids and aryl halides has started to attract interest.[12c,16] Our methodology was suitable for the synthesis of the purine-substituted indoles **3o–p**. In addition to these important alkaloids with imidazole skeletons, the catalytic system could also effectively promote the cross-coupling of *N*-alkylindoles with other azoles (e.g., benzothiazoles, benzoxazoles, oxazoles, etc.) at the C2 site of azoles in synthetically useful yields (**3q–r, t**). Interestingly, the 2-substituted thiazole was amenable to the oxidative coupling reaction at the C5-position of the thiazole in 70% yield (**3s**). However, indolizines were limited under the standard reaction conditions, and gave only a trace amount of product.

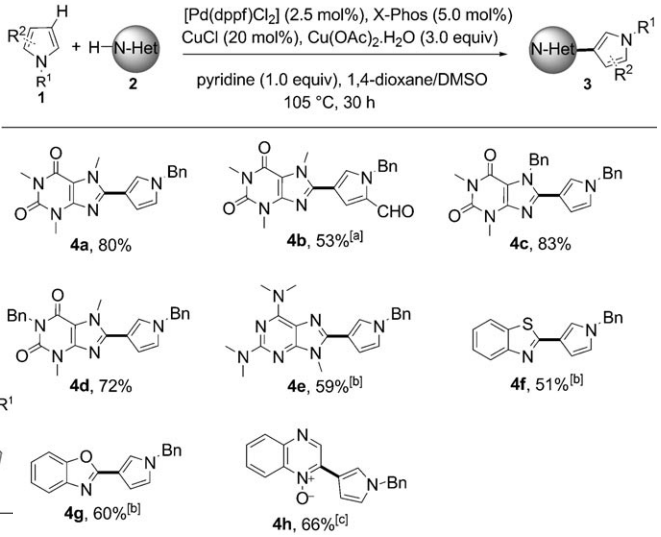
N-Heteroarene *N*-oxides are a key intermediate in many transformations that assemble functionality adjacent to the nitrogen atom. The *N*-oxides may also be converted into the deoxygenated products by hydrogenolysis with Pd/C/H_2. The

pyridinyl–indolyl linkage and its analogue are important structural motifs for pharmacophores, natural products, and synthetic building blocks (Scheme 1). Clearly, the most direct method for synthesizing these heteroaryl–heteroaryl linkages should be oxidative coupling of an indole with a six-membered N-heteroarene or the corresponding *N*-oxide.[17,18] To our delight, π-electron-poor N-heteroarene *N*-oxides (e.g., pyridine *N*-oxide, quinoline *N*-oxide, quinoxaline *N*-oxide, pyrazine *N*-oxide, etc.) smoothly underwent the dehydrogenative couplings with the N-alkylated indoles in good yields, thus affording a general and reliable method for forging the pyridinyl–indolyl bonds (Scheme 4; **3u–y**). Notably, the coupling of 1-benzylindole with quinoxaline *N*-oxide gave 2-(1-benzyl-indol-3-yl)-quinoxaline *N*-oxide (**3x**) as a major product (84% yield) with a concomitant of a small amount of the deoxygenated product **3x′** (8% yield). Inspired by the deoxygenation,[18] we investigated the reaction in the absence of added oxidants, but only 14% yield of **3x′** was obtained.

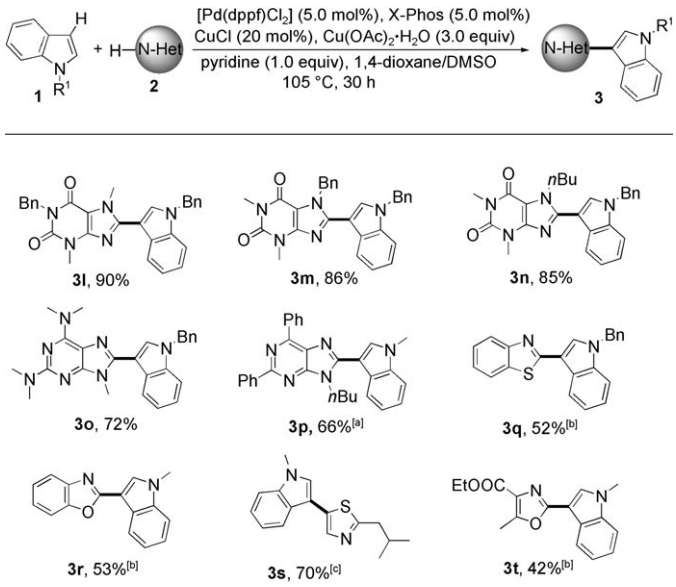


Scheme 4. Selective oxidative cross-coupling of indoles with a variety of N-heteroarene *N*-oxides. For all reactions 0.5 mmol indole **1** and 3.0 equiv N-heteroarene *N*-oxide **2** were used under an N_2 atmosphere. Yields of isolated product is based on indole **1**. [a] Carried out at 110°C, **2** (0.5 mmol), and indole **1**. [b] Pyridine (2 equiv), carried out at 140°C.

Fortunately, our method was suitable for more sensitive pyrroles. This palladium/copper bimetallic catalytic system could effectively avoid the decomposition of pyrrole substrates. Pyrroles coupled with a number of N-heteroarenes (e.g., xanthines, purines, benzothiazoles, benzoxazoles, N-heteroarene *N*-oxides, etc.) to afford the heteroarylated pyrroles in synthetically useful yields (Scheme 5; **4a–h**). Notably, the previously reported oxidative coupling reactions of pyrroles, except the sterically bulky N-TIPS pyrrole, occurred predominantly at the C2 position of pyrroles.[6b,10b–d,19] More interestingly, our catalytic system gave



Scheme 5. Selective oxidative cross-coupling of pyrroles with a variety of N-heteroarenes. For all reactions 0.5 mmol N-heteroarene **2** and 3.0 equiv of pyrrole **1** were used under an N_2 atmosphere. Yields of isolated product based on N-heteroarene **2**. [a] Carried out at 130°C. [b] $[Pd(dppf)Cl_2]$ (5.0 mol%). [c] CuBr (20 mol%), pyridine (2.0 equiv), and 1,4-dioxane (1.5 mL).



Scheme 3. Selective oxidative cross-coupling of indoles with a variety of azoles. For all reactions 0.5 mmol N-heteroarene **2** and 3.0 equiv indole were used under an N_2 atmosphere. Yields of isolated product are based on **2**. [a] Carried out at 120°C. [b] Carried out at 130°C. [c] Carried out at 140°C.

only the C3 product, which provided an efficient and complementary route to form 3-heteroarylated pyrroles. The structure of **4a** was confirmed by an X-ray analysis (Figure S2).[14]

In the previous examples, the oxidative C–H/C–H cross-couplings of (hetero)arenes with arenes usually employed a large amount of one of the coupling components in up to 100 equivalents.[4–6] In this study, these examples indeed used only up to 3.0 equivalents, and the reactions were reasonably selective for the cross-coupled products as opposed to the statistical distribution of

products. For example, the reactions of indoles (3.0 equiv) with azoles afforded the homocoupled of indoles in yields in a range of 5–10%, whereas the reactions arising from N-heteroarene *N*-oxides (3.0 equiv) gave a negligible amount of unwanted bis(*N*-oxide). In addition, this palladium/copper bimetallic catalytic system could also effectively preclude the dimerization of pyrrole substrates.

In conclusion, we have developed a palladium/copper co-catalytic double C–H activation that allows, for the first time, the highly regioselective C3 heteroarylation of indoles and pyrroles with an array of N heteroarenes. The homocoupling and decomposition of the starting material and product are suppressed successfully under the optimized oxidative reaction conditions. Additionally studies aimed at elucidating the mechanism of the reactions, and at extending this catalytic methods to other cross-coupling reactions are underway. We anticipate that this approach may represent a practical route to unsymmetrical bi-heteroaryl molecules in medical, material, and natural product chemistry.

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[1] For reviews, see: a) Y. Liu, S. Zhang, P. J. M. Abreu, *Nat. Prod. Rep.* **2006**, *23*, 630; b) R. A. Hughes, C. J. Moody, *Angew. Chem.* **2007**, *119*, 8076; *Angew. Chem. Int. Ed.* **2007**, *46*, 7930.

[2] a) *Metal-Catalyzed Cross-Coupling R eactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, New York, **1998**; b) S. P. Stanforth, *Tetrahedron* **1998**, *54*, 263; c) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359; d) M. Schnürch, R. Flasik, A. F. Khan, M. Spina, M. D. Mihovilovic, P. Stanetty, *Eur. J. Org. Chem.* **2006**, 3283; e) M. Hapke, L. Brandt, A. Lützen, *Chem. Soc. Rev.* **2008**, *37*, 2782.

[3] For recent selected reviews for direct C–H functionalization, see: a) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; b) I. V. Seregin, V. Gevorgyan, *Chem. Soc. Rev.* **2007**, *36*, 1173; c) L.-C. Campeau, D. R. Stuart, K. Fagnou, *Aldrichimica Acta* **2007**, *40*, 35; d) J. C. Lewis, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2008**, *41*, 1013; e) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; f) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; g) G. P. McGlacken, L. M. Bateman, *Chem. Soc. Rev.* **2009**, *38*, 2447; h) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624; i) G. P. Chiusoli, M. Catellani, M. Costa, E. Motti, N. Della Cá, G. Maestri, *Coord. Chem. Rev.* **2010**, *254*, 456.

[4] a) J.-B. Xia, S.-L. You, *Organometallics* **2007**, *26*, 4869; b) K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2007**, *129*, 11904; c) B.-J. Li, S.-L. Tian, Z. Fang, Z.-J. Shi, *Angew. Chem.* **2008**, *120*, 1131; *Angew. Chem. Int. Ed.* **2008**, *47*, 1115; d) G. Brasche, J. García-Fortanet, S. L. Buchwald, *Org. Lett.* **2008**, *10*, 2207; e) K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2009**, *131*, 9651; f) X. Zhao, C. S. Yeung, V. M. Dong, *J. Am. Chem. Soc.* **2010**, *132*, 5837.

[5] a) R. Li, L. Jiang, W. Lu, *Organometallics* **2006**, *25*, 5973; b) T. Dohi, M. Ito, K. Morimoto, M. Iwata, Y. Kita, *Angew. Chem.* **2008**, *120*, 1321; *Angew. Chem. Int. Ed.* **2008**, *47*, 1301; c) Y. Wei, W. Su, *J. Am. Chem. Soc.* **2010**, *132*, 16377; d) E. Faggi, R. M. Sebastián, R. Pleixats, A. Vallribera, A. Shafir, A. Rodríguez-Gimeno, C. R. de Arellano, *J. Am. Chem. Soc.* **2010**, *132*, 17980.

[6] For intermolecular dehydrogenative arylations, see: a) D. R. Stuart, K. Fagnou, *Science* **2007**, *316*, 1172; b) D. R. Stuart, E. Villemure, K. Fagnou, *J. Am. Chem. Soc.* **2007**, *129*, 12072; c) T. A. Dwight, N. R. Rue, D. Charyk, R. Josselyn, B. DeBoef, *Org. Lett.* **2007**, *9*, 3137; d) S. H. Cho, S. J. Hwang, S. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 9254; e) S. Potavathri, K. C. Pereira, S. I. Gorelsky, A. Pike, A. P. LeBris, B. DeBoef, *J. Am. Chem. Soc.* **2010**, *132*, 14676; f) C.-Y. He, S. Fan, X. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 12850; g) M. Kitahara, N. Umeda, K. Hirano, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2011**, *133*, 2160; h) C. C. Malakar, D. Schmidt, J. Conrad, U. Beifuss, *Org. Lett.* **2011**, *13*, 1378; i) S.-L. You, J.-B. Xia, *Top. Curr. Chem.* **2010**, *292*, 165.

[7] For intramolecular dehydrogenative arylations, see: a) L. Ackermann, R. Jeyachandran, H. K. Potukuchi, P. Novák, L. Büttner, *Org. Lett.* **2010**, *12*, 2056; b) D. G. Pintori, M. F. Greaney, *J. Am. Chem. Soc.* **2011**, *133*, 1209.

[8] P. Xi, F. Yang, S. Qin, D. Zhao, J. Lan, G. Gao, C. Hu, J. You, *J. Am. Chem. Soc.* **2010**, *132*, 1822.

[9] W. Han, P. Mayer, A. R. Ofial, *Angew. Chem.* **2011**, *123*, 2226; *Angew. Chem. Int. Ed.* **2011**, *50*, 2178.

[10] a) N. P. Grimster, C. Gauntlett, C. R. A. Godfrey, M. J. Gaunt, *Angew. Chem.* **2005**, *117*, 3185; *Angew. Chem. Int. Ed.* **2005**, *44*, 3125; b) E. M. Beck, N. P. Grimster, R. Hatley, M. J. Gaunt, *J. Am. Chem. Soc.* **2006**, *128*, 2528; c) E. M. Beck, R. Hatley, M. J. Gaunt, *Angew. Chem.* **2008**, *120*, 3046; *Angew. Chem. Int. Ed.* **2008**, *47*, 3004; d) A. García-Rubia, R. G. Arrayás, J. C. Carretero, *Angew. Chem.* **2009**, *121*, 6633; *Angew. Chem. Int. Ed.* **2009**, *48*, 6511.

[11] a) J. W. Daly, W. Padgett, M. T. Shamim, P. Butts-Lamb, J. Waters, *J. Med. Chem.* **1985**, *28*, 487; b) Y.-C. Kim, X.-D. Ji, N. Melman, J. Linden, K. A. Jacobson, *J. Med. Chem.* **2000**, *43*, 1165; c) R. V. Kalla, E. Elzein, T. Perry, X. Li, V. Palle, V. Varkhedkar, A. Gimbel, T. Maa, D. Zeng, J. Zablocki, *J. Med. Chem.* **2006**, *49*, 3682; d) L. Yan, C. E. Müller, *J. Med. Chem.* **2004**, *47*, 1031; e) A. M. Hayallah, J. S. Ramírez, U. Reith, U. Schobert, B. Preiss, B. Schumacher, J. W. Daly, C. E. Müller, *J. Med. Chem.* **2002**, *45*, 1500; f) P. G. Baraldi, M. A. Tabrizi, D. Preti, A. Bovero, R. Romagnoli, F. Fruttarolo, N. A. Zaid, A. R. Moorman, K. Varani, S. Gessi, S. Merighi, P. A. Borea, *J. Med. Chem.* **2004**, *47*, 1434.

[12] a) D. Zhao, W. Wang, F. Yang, J. Lan, L. Yang, G. Gao, J. You, *Angew. Chem.* **2009**, *121*, 3346; *Angew. Chem. Int. Ed.* **2009**, *48*, 3296; b) D. Zhao, W. Wang, S. Lian, F. Yang, J. Lan, J. You, *Chem. Eur. J.* **2009**, *15*, 1337; c) B. Liu, X. Qin, K. Li, X. Li, Q. Guo, J. Lan, J. You, *Chem. Eur. J.* **2010**, *16*, 11836.

[13] B. A. Steinhoff, S. S. Stahl, *J. Am. Chem. Soc.* **2006**, *128*, 4348.

[14] CCDC 814134 (**3a**) and 814135 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] a) S. Sivakova, S. J. Rowan, *Chem. Soc. Rev.* **2005**, *34*, 9; b) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491; c) J. T. Davis, G. P. Spada, *Chem. Soc. Rev.* **2007**, *36*, 296; d) J. L. Sessler, C. M. Lawrence, J. Jayawickramarajah, *Chem. Soc. Rev.* **2007**, *36*, 314; e) R. S. Butler, P. Cohn, P. Tenzel, K. A. Abboud, R. K. Castellano, *J. Am. Chem. Soc.* **2009**, *131*, 623.

[16] a) J. Liu, M. J. Robins, *Org. Lett.* **2005**, *7*, 1149; b) I. Čerňa, R. Pohl, B. Klepetářová, M. Hocek, *Org. Lett.* **2006**, *8*, 5389; c) L. Ackermann, A. Althammer, S. Fenner, *Angew. Chem.* **2009**, *121*, 207; *Angew. Chem. Int. Ed.* **2009**, *48*, 201; d) T. E. Storr, C. G. Baumann, R. J. Thatcher, S. D. Ornellas, A. C. Whitwood, I. J. S. Fairlamb, *J. Org. Chem.* **2009**, *74*, 5810; e) D. Kim, H. Jun, H. Lee, S.-S. Hong, S. Hong, *Org. Lett.* **2010**, *12*, 1212; f) I. Čerňa, R. Pohl, B. Klepetářová, M. Hocek, *J. Org. Chem.* **2010**, *75*, 2302.

[17] For direct C-arylation of N-heteroarene *N*-oxides with aryl halides, see: a) L.-C. Campeau, S. Rousseaux, K. Fagnou, *J. Am. Chem. Soc.* **2005**, *127*, 18020; b) J.-P. Leclerc, K. Fagnou, *Angew. Chem.* **2006**, *118*, 7945; *Angew. Chem. Int. Ed.* **2006**, *45*, 7781; c) L.-C. Campeau, D. R. Stuart, J.-P. Leclerc, M. Bertrand-Laperle, E. Villemure, H.-Y. Sun, S. Lasserre, N. Guimond, M. Lecavallier, K. Fagnou, *J. Am. Chem. Soc.* **2009**, *131*, 3291.

[18] For C–H/C–H oxidative alkenylation and arylation of N-heteroarene *N*-oxides, see: J. Wu, X. Cui, L. Chen, G. Jiang, Y. Wu, *J. Am. Chem. Soc.* **2009**, *131*, 13888. Also see Ref. [6d].

[19] For metal-free oxidative cross-coupling of pyrroles and thiophenes, see: Y. Kita, K. Morimoto, M. Ito, C. Ogawa, A. Goto, T. Dohi, *J. Am. Chem. Soc.* **2009**, *131*, 1668.

