ChemPubSoc Europe

DOI: 10.1002/chem.201504179

CHEMISTRY
A European Journal
Communication

Homogeneous Catalysis |*Hot Paper*|

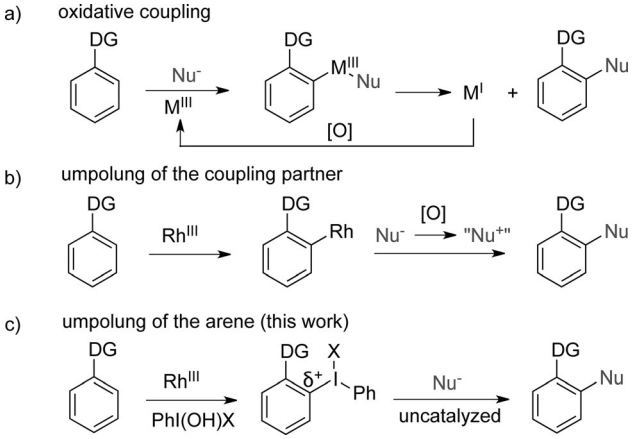
Rhodium-Catalyzed C–S and C–N Functionalization of Arenes: Combination of C–H Activation and Hypervalent Iodine Chemistry

Fen Wang, Xinzhang Yu, Zisong Qi, and Xingwei Li*[a]

Abstract: Rhodium-catalyzed sulfonylation, thioetherification, thiocyanation, and other heterofunctionalizations of arenes bearing a heterocyclic directing group have been realized. The reaction proceeds by initial Rh^{III}-catalyzed C–H hyperiodination of arene at room temperature followed by uncatalyzed nucleophilic functionalization. A diaryliodonium salt is isolated as an intermediate, which represents umpolung of the arene substrate, in contrast to previous studies that suggested umpolung of the coupling partner.

C–H activation has been extensively explored and numerous efficient catalytic systems have been developed.[1] The C–H activation of arenes has also allowed the development of valuable synthetic methods in the synthesis of natural products and materials.[2] In the case of C–H activation of arenes that are not electronically activated, installation of a directing group on the arene is typically required to offer chelation assistance.[3] Thus, generation of the reactive M–C bond offers ample opportunities for further manipulation and eventual functionalization of the arene substrate.

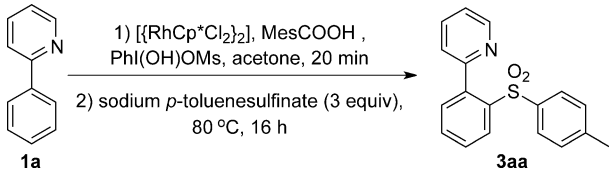
Despite the significant and diverse reactivity of M–C(aryl) species as a key intermediate in C–H activation, the aryl group is nucleophilic and is only compatible with an electrophile. However, although incompatible nucleophiles are arguably more abundant in nature, they are not directly applicable. To address this limitation, two approaches have been adopted (Scheme 1). In an oxidative coupling strategy,[4] reductive elimination of an aryl and an anionic ligand (nucleophile) constitutes a product-forming step that proceeds via a low-valent metal intermediate (Scheme 1 a). Catalytic turnover can be fulfilled when the low-valent metal is re-oxidized. In this strategy the oxidant interacts directly with the metal. Alternatively, our group[5] and others[6] have proposed an umpolung strategy whereby a nucleophilic coupling partner is converted into an electrophilic one (Scheme 1 b). This strategy was rendered possible by the versatility of Rh^{III} catalysts; Rh^{III} complexes were employed to effect the successful combination of C–H activation and umpolung, given that Rh^{III} catalysis is well known in



Scheme 1. Coupling of arenes with nucleophiles.

effecting the C–H activation of arenes and subsequent functionalization with electrophiles.[7] As a continuation of our interest in Rh^{III}-catalyzed C–H activation of arenes,[1l] we pondered the possibility of umpolung of arenes. This can be executed by rhodium-catalyzed activation of an arene to afford an Ar–Rh species that further interacts with an oxidant, generating an oxidized form of the arene. This process can be regarded as in situ umpolung of the arene, provided that the oxidized arene is highly electrophilic and can react in situ with a nucleophile. Recently, we reported the formation, isolation,

Table 1. Optimization studies[a]



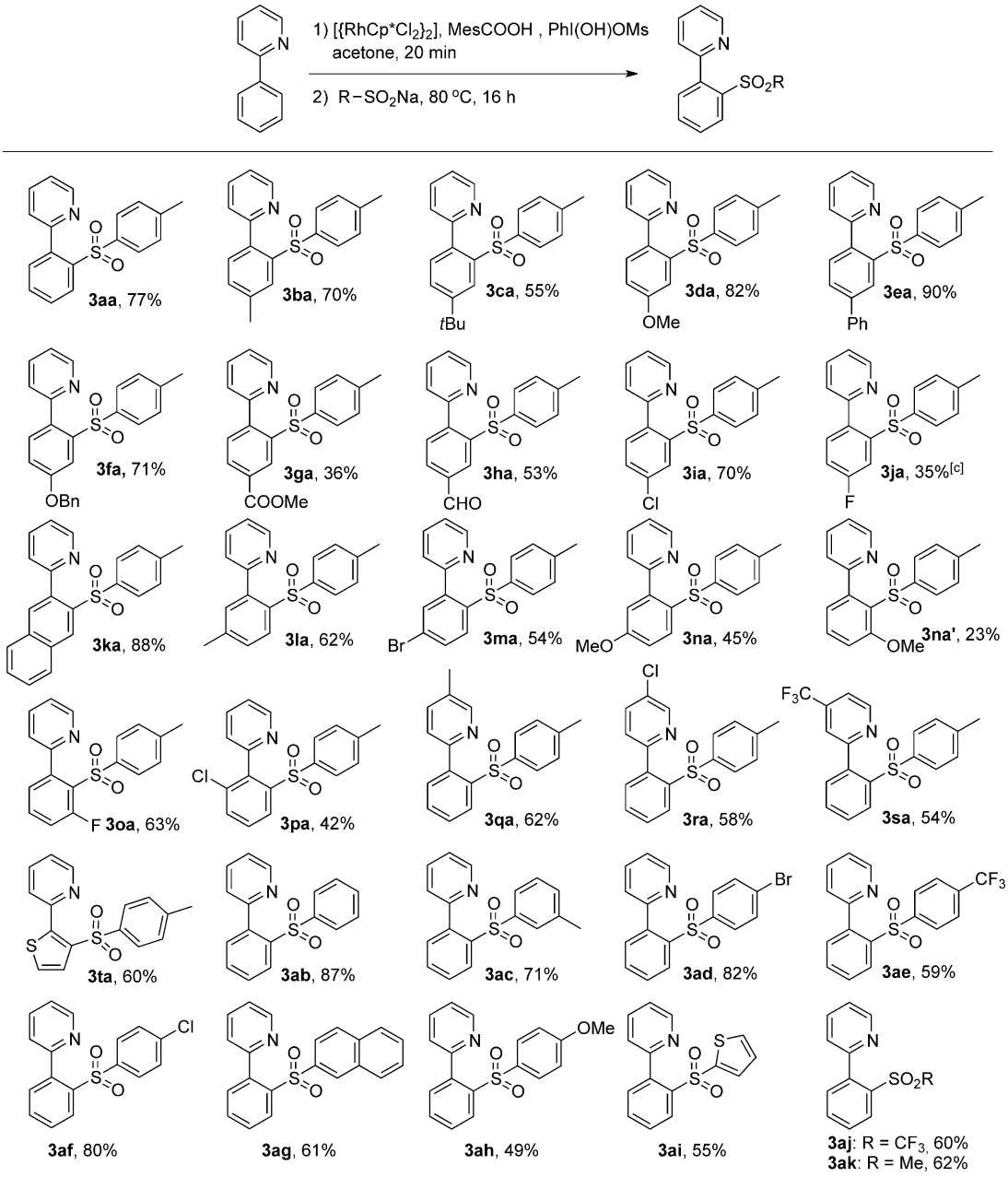
1a **3aa**

Entry	Changes to the optimized conditions	Yield [%][b]
1	none	77
2	single-step procedure	10
3	MesCOOH was omitted.	65
4	PhI(OH)OTs was used.	70
5	acetonitrile was used as the solvent	29

[a] Optimized conditions: A mixture of the arene (0.3 mol), [{RhCp*Cl_2}$_2$] (5 mol%), PhI(OH)OMs (1.6 equiv), and MesCOOH (20 mol%) were stirred in acetone (3 mL) at room temperature for 20 min. Sodium sulfinate (0.9 mmol) was then added, and the mixture was stirred at 80 °C for 16 h. [b] Yield of product isolated by chromatography.

[a] *F. Wang, X. Yu, Z. Qi, Prof. Dr. X. Li*
Dalian Institute of Chemical Physics, Chinese Academy of Sciences
Dalian 116023 (China)
E-mail: xwli@dicp.ac.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504179.



Scheme 2. Substrate scope.

and subsequent catalytic transformation of diaryliodonium salts through rhodium-catalyzed C–H activation of arenes.[5d] We report herein that diaryliodonium salts can act as an activated form of arene as a result of C–H umpolung (Scheme 1c), thus enabling sulfonylation,[8] thiolation, and other heterofunctionalization.

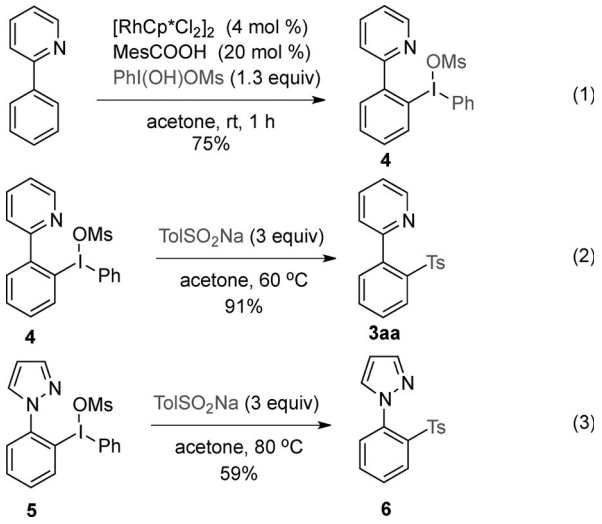
We initiated our studies with the coupling of 2-phenylpyridine (**1a**) and sodium *p*-toluenesulfinate (**2a**) in the presence of [{RhCp*Cl_2}$_2$] catalyst with PhI(OH)OMs as oxidant[9] at 80 °C (Table 1). The reaction was found to proceed with poor efficiency when all reagents and the catalyst were premixed prior to the addition of acetone solvent. In contrast, a two-stage process with pre-stirring of a mixture of **1a**, the hypervalent iodine reagent, and the Rh^{III} catalyst in acetone at RT followed by introduction of **2a** afforded the desired sulfonylated product **3aa** in 70% yield (isolated product; 80 °C, see ref. [5d]). The requirement of a two-stage reaction is in contrast to our previously reported nitration reaction of the same arene substrate.[7a] Further improvement of the efficiency (to 77% yield) was realized when a catalytic amount of 2,4,6-trimethylbenzoic acid[8b,10] (0.2 equiv) was introduced. However, acetic acid or PivOH (2 equiv) additives proved to be less efficient. The reaction occurred in slightly lower yield when the hypervalent iodine reagent was changed to its tosylate analogue (PhI(OH)OTs). The reaction performed in other solvents [MeCN, 1,2-dichloroethane (DCE), and dichloromethane] afforded the

product in poor yields. Control experiments also confirmed that the rhodium catalyst is necessary.

The scope and limitations of this coupling system were next explored by using the optimized conditions. Installation of various electron-donating, -withdrawing, and halogen groups at the *para* position of the phenyl ring had limited effects on the outcome of the coupling system (**3ba**–**ia**; Scheme 2), and there was no direct correlation between the electronic effect of the substituent and the reaction yield. The compatibility of halogen (**3ia**), ester (**3ga**), and aldehyde (**3ha**) groups should allow further manipulation of the coupled product. An exception was found for the coupling of 2-(4-fluorophenyl)pyridine, from which essentially no desired product was detected under the standard conditions. However, prolonging the pre-stirring in the first stage to 15 h increased the yield of product **3ja** to 35%. Introduction of electron-withdrawing and -donating substituents into the pyridine ring of 2-phenylpyridines was well tolerated and the sulfonylated product was isolated in moderate yields (**3qa**–**sa**). Discrepancies in site selectivity of different *meta*-substituted substrates were observed. The coupling occurred at the less hindered site for *m*-methyl and -bromo substituted arenes (**3ka**–**ma**). Decreasing the substituent size to a *m*-OMe group caused formation of a mixture of two regioisomers (**3na** and **3na**′). In contrast, only sulfonylation at the more hindered *ortho* position was detected for *m*-fluoro-substituted arene **3oa**, a trend that was also observed in our previous studies.[5a] In addition, an *o*-chloro-substituted substrate exhibited comparable activity (**3pa**). The arene scope was not limited to phenyl rings and the reaction of a thiophene substrate afforded product **3ta** in moderate yield.

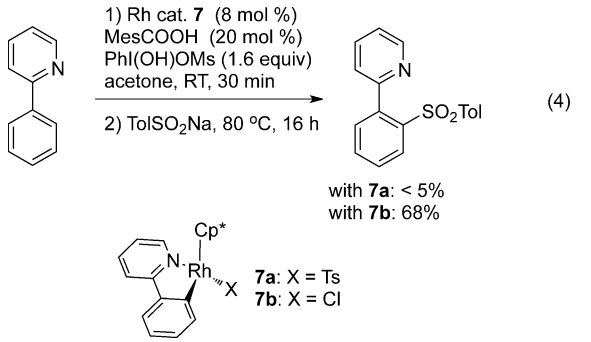
Variation of the sulfinate coupling partner was also well tolerated. Introduction of (hetero)arenesulfinate bearing different electron-donating and -withdrawing substituents at different positions were viable, and the coupled products were isolated in consistently moderate to high yields (**3ac**–**ai**; Scheme 2). Furthermore, the sulfinate scope could be extended to (trifluoro)methanesulfinate with no obvious deterioration of the reaction efficiency (**3aj**, **3ak**).

During pre-stirring of a mixture of 2-phenylpyridine, the Rh^{III} catalyst, the 2-mesitylenecarboxylic acid (MesCOOH), and PhI(OH)OTs in acetone, a white precipitate was formed [Eq. (1)], which may indicate formation of a reactive intermediate. Indeed, this intermediate (**4**) was isolated in 75% yield after simple filtration and was identified as an unsymmetrical diaryliodonium salt on the basis of NMR spectroscopy and HRMS analyses. The NMR spectra of **4** are in close agreement with those of its tosylate analogue.[5d] To probe the intermediacy of this hypervalent iodine species, a mixture of **4** (recrystallized) and **2a** (recrystallized) was stirred in acetone. Interestingly, the sulfonylated product **3aa** was isolated in 91% yield from a reaction at 60 °C, even in the absence of any catalyst [Eq. (2)].[11,12] Thus, the overall catalytic reaction comprises a Rh^{III}-catalyzed hyperiodination of the arene followed by an uncatalyzed nucleophilic sulfonylation reaction. Furthermore, the intermediacy of a hypervalent iodine species seems in agreement with the poor efficiency of the coupling of 2-(4-fluorophenyl)pyridine, because essentially no hyperiodination was detected (by TLC and HPLC) when it was allowed to react for 30 min, which is line with the failure of the catalytic reaction under our standard conditions.[13]



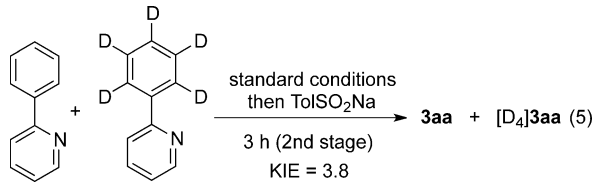
Although most 2-phenylpyridines reacted efficiently under the standard conditions, essentially no desired reaction occurred for 1-phenylpyrazole. To address this limitation, 1-phenylpyrazole was hyperiodinated to afford **5** by following our previously reported protocol.[5d] Treatment of **5** with **2a** afforded the corresponding product **6** in 59% yield [Eq. (3)].

In addition to identification of the intermediate hypervalent iodine species, the mechanism of the sulfonylation reaction was explored. Cyclometalated Rh^{III} sulfinate complex **7a** was prepared and tested as a catalyst [Eq. (4)]. However, no desired catalytic reaction occurred. This suggests that it is not an active catalyst, which stands in stark contrast to the efficacy of the previously reported cyclometalated Rh^{III} nitrate complex in the nitration of 2-phenylpyridines with $NaNO_2$.[5a] Thus, reductive C–S bond formation from **7a** is likely irrelevant and an oxidative coupling process that involves the oxidation of a low-valent Rh^{I} species to Rh^{III} is not plausible (Scheme 1a). This result also suggests that the sulfinate anion exhibits an inhibitive effect at the hyperiodination stage.

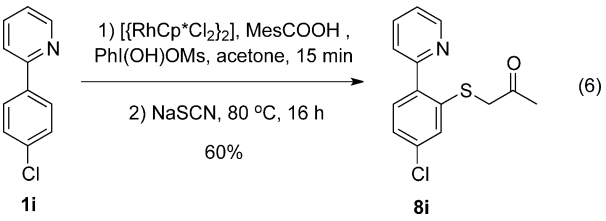


To probe the C–H activation process, rhodacyclic complex **7b** was also applied as a catalyst [Eq. (4)]. It follows that complex **7b** exhibited comparable activity to the real catalyst

system. Thus, a C–H activation mechanism is followed and the chloride ligand seems necessary for an active catalyst system. To further investigate the details of the C–H activation process, a kinetic isotope effect (KIE) experiment was performed on equimolar amounts of **1a** and [D_5]**1a** in a competitive reaction with sodium *p*-toulenesulfinate at low conversion [Eq. (5)]. ^{1}H NMR spectroscopy of the product mixture gave a KIE value of 3.8, indicating that C–H activation is likely turnover-limiting in the catalytic cycle. This value should reflect the KIE of the hyperiodination stage.



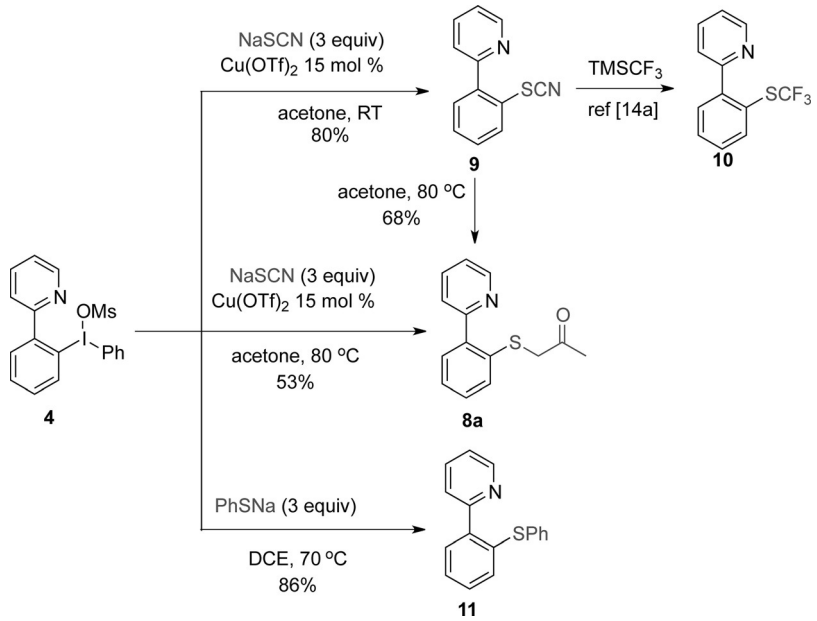
Inspired by the sulfonylation system, C–H thiocyanation[14] was next explored by using sodium thiocyanate. Interestingly, the two-stage coupling between **1i** and NaSCN afforded thioether **8i**, in which an acetone molecule was incorporated, in moderate yield [Eq. (6)].



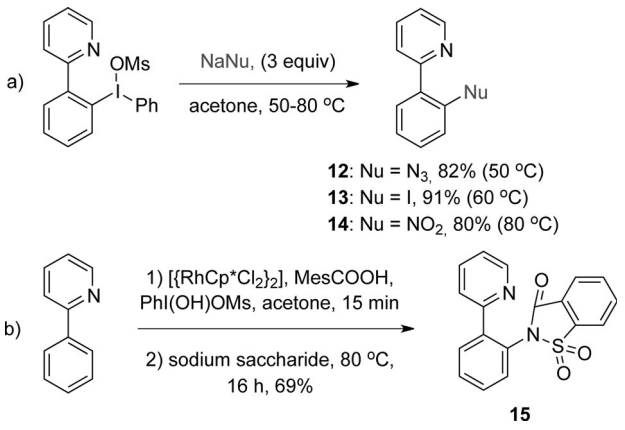
Several experiments were performed to understand the mechanism. The copper-catalyzed reaction of hypervalent iodine reagent **4** and NaSCN afforded the thiocyanation product **9** in good yield (room temperature, Scheme 3).[15] Further reaction of **9** with acetone at 80 °C generated the corresponding thioether **8a** in 68% yield. In addition, thiocyanate **9a** could be readily transformed into the corresponding trifluomethylthioether **10** in good yield by following a previously reported protocol.[14a] Thus, the formation of **8i** proceeded by initial thiocyanation followed by nucleophilic functionalization with acetone and the thioether could be prepared in one pot starting from either the arene or the hypervalent iodine reagent. In addition to this thioetherification reaction via a thiocyanate intermediate, uncatalyzed nucleophilic thioetherification of **4** with sodium thiophenolate readily occurred to afford diarylthioether **11** in high yield.[16]

In addition to the C–S bond formation reactions, the nucleophilic functionalization of a hypervalent iodine was extended to amidation, azidation, nitration, and iodination reactions (products **12**–**15**; Scheme 4). In the previous studies of Rh^{III}-catalyzed one-pot nitration, azidation, and halogenation of 2-arylpyridines with the corresponding sodium salts as the coupling partner in combination with phenyliodine(III) diacetate (PIDA)/TsOH as an oxidant, our group[5a] and others[6d] postulated that the coupling occurred through umpolung of the coupling partner so that the nucleophilic Rh–Ar bond might interact with an electrophilic nitro, azido, or halogen species. On the basis of the results of our diversified C–H functionalizations via an established I^{III} intermediate, the previously proposed mechanism warrants correction. These reactions most likely proceed by initial hyperiodination followed by nucleophilic functionalization and, in most cases, this nucleophilic functionalization is uncatalyzed.

In summary, we have developed an efficient heterofunctionalization of arenes using sodium salts as the coupling partners. The reactions proceeded by C–H activation under relatively mild conditions and tolerated a broad scope of substrates. Mechanistic studies, particularly isolation of the hypervalent



Scheme 3. Thiocyanation and thioetherification of arenes.



Scheme 4. Other heterofunctionalzation reactions using iodine(III) reagents.

iodine intermediate, revealed that the reaction proceeded by initial rhodium-catalyzed C–H hyperiodination followed by an uncatalyzed and highly chemoselective nucleophilic sulfonylation, thiocyanation, thioetherification, azidation, nitration, or amidation. With the assistance of the rhodium catalyst and a hypervalent iodine oxidant, the formation of a diaryliodonium salt offers an important strategy to convert the nucleophilic aryl group in Ar–H or Ar–Rh into an electrophilic one in Ar–I^{III}. This umpolung of the arene substrate is complementary to our previous report on the umpolung of the coupling partner. Functionalization of other arenes by using this strategy is currently underway in our laboratory and will be reported in due course.

Acknowledgements

Financial support from the NSFC (Grant Nos. 21272231, 21402190, 21472186, and 21525208) and the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, is gratefully acknowledged.

Keywords: C–H activation · homogeneous catalysis · hypervalent iodine · rhodium · umpolung

[1] For reviews on C–H activation, see: a) K. Godula, D. Sames, *Science* **2006**, *312*, 67; b) I. A. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890; c) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315; d) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068; e) L. McMurray, F. O'Hara, M. J. Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885; f) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; g) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879; h) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 10236; *Angew. Chem.* **2012**, *124*, 10382; i) J. Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2012**, *51*, 8960; *Angew. Chem.* **2012**, *124*, 9092; j) K. M. Engle, J.-Q. Yu, *J. Org. Chem.* **2013**, *78*, 8927; k) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651; l) G. Song, X. Li, *Acc. Chem. Res.* **2015**, *48*, 1007.

[2] a) S. Allard, M. Forster, B. Souharce, H. Thiem, U. Scherf, *Angew. Chem. Int. Ed.* **2008**, *47*, 4070; *Angew. Chem.* **2008**, *120*, 4138; b) A. Facchetti, *Chem. Mater.* **2011**, *23*, 733; c) C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.* **2012**, *112*, 2208; d) P. S. Baran, E. J. Corey, *J. Am. Chem. Soc.* **2002**, *124*, 7904; e) E. M. Beck, R. Hatley, M. J. Gaunt, *Angew. Chem. Int. Ed.* **2008**, *47*, 3004; *Angew. Chem.* **2008**, *120*, 3046; f) N. K. Garg, D. Caspi, B. M. Stoltz, *J. Am. Chem. Soc.* **2004**, *126*, 9552.

[3] a) T. Satoh, M. Miura, *Synthesis* **2010**, 3395; b) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; c) T. Satoh, K. Ueura, M. Miura, *Pure Appl. Chem.* **2008**, *80*, 1127; d) D. A. Colby, A. S. Tsai, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2012**, *45*, 814; e) Q.-Z. Zheng, N. Jiao, *Tetrahedron Lett.* **2014**, *55*, 1121.

[4] For well-established oxidative coupling systems using Rh^{III} catalysts, see: a) G. Zhang, L. Yang, Y. Wang, Y. Xie, H. Huang, *J. Am. Chem. Soc.* **2013**, *135*, 8850; b) N. Wang, B. Li, H. Song, S. Xu, B. Wang, *Chem. Eur. J.* **2013**, *19*, 358; for other related systems, see: c) L. Jin, Z. Huang, J. He, A. Lei, *J. Am. Chem. Soc.* **2010**, *132*, 9607; d) M. Chen, X. Zheng, W. Li, J. He, A. Lei, *J. Am. Chem. Soc.* **2010**, *132*, 4101; e) L. Jin, H. Zhang, P. Li, J. Sowa, R. Ji, A. Lei, *J. Am. Chem. Soc.* **2009**, *131*, 9892.

[5] a) F. Xie, Z. Qi, X. Li, *Angew. Chem. Int. Ed.* **2013**, *52*, 11862; *Angew. Chem.* **2013**, *125*, 12078; b) S. Yu, B. Wan, X. Li, *Org. Lett.* **2013**, *15*, 3706; c) F. Xie, Z. Qi, S. Yu, X. Li, *J. Am. Chem. Soc.* **2014**, *136*, 4780; d) F. Xie, Z. Zhang, X. Yu, G. Tang, X. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 7405; *Angew. Chem.* **2015**, *127*, 7513.

[6] For selected examples on C–H activation/coupling with nucleophiles by proposed umpolung, see: a) H. Zhao, Y. Shang, W. Su, *Org. Lett.* **2013**, *15*, 5106; b) C. Feng, T.-P. Loh, *Angew. Chem. Int. Ed.* **2014**, *53*, 2722; *Angew. Chem.* **2014**, *126*, 2760; c) K. D. Collins, F. Lied, F. Glorious, *Chem. Commun.* **2014**, *50*, 4459; d) P. Zhang, L. Hong, G. Li, R. Wang, *Adv. Synth. Catal.* **2015**, *357*, 345; e) X. Huang, Y. Wang, J. Lan, J. You, *Angew. Chem. Int. Ed.* **2015**, *54*, 9404; *Angew. Chem.* **2015**, *127*, 9536.

[7] a) K. D. Hesp, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2011**, *133*, 11430; b) J. Kim, S. Park, J. Ryu, S. Cho, S. Kim, S. Chang, *J. Am. Chem. Soc.* **2012**, *134*, 9110; c) D. G. Yu, M. Suri, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 8802; d) L. Yang, C. A. Correia, C.-J Li, *Adv. Synth. Catal.* **2011**, *353*, 1269; e) Y. Li, X.-S. Zhang, K. Chen, K.-H. He, F. Pan, B.-J. Li, Z.-J. Shi, *Org. Lett.* **2012**, *14*, 636; f) Y. Li, B.-J. Li, W.-H. Wang, W.-P. Huang, X.-S. Zhang, K. Chen, Z.-J. Shi, *Angew. Chem. Int. Ed.* **2011**, *50*, 2115; *Angew. Chem.* **2011**, *123*, 2163; g) W.-W. Chan, S.-F. Lo, Z. Zhou, W.-Y. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 13565; h) T. K. Hyster, K. E. Ruhl, T. Rovis, *J. Am. Chem. Soc.* **2013**, *135*, 5364; i) S. Cui, Y. Zhang, Q. Wu, *Chem. Sci.* **2013**, *4*, 3421; j) B. Zhou, J. Du, Y. Yang, H. Feng, Y. Li, *Org. Lett.* **2014**, *16*, 592.

[8] For selected examples on sulfonylation by C–H activation, see a) X. Zhao, E. Dimitrijevic, V. M. Dong, *J. Am. Chem. Soc.* **2009**, *131*, 3466; b) W.-H. Rao, B.-B. Zhan, K. Chen, P.-X. Ling, Z.-Z. Zhang, B.-F. Shi, *Org. Lett.* **2015**, *17*, 3552; c) W.-H. Rao, B.-F. Shi, *Org. Lett.* **2015**, *17*, 2784; d) X. Tang, L. Huang, Y. Xu, J. Yang, W. Wu, H. Jiang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4205; *Angew. Chem.* **2014**, *126*, 4289; e) X.-S. Wu, Y. Chen, M.-B. Li, M.-G. Zhou, S.-K. Tian, *J. Am. Chem. Soc.* **2012**, *134*, 14694; f) Z. Wu, H. Song, X. Cui, C. Pi, W. Du, Y. Wu, *Org. Lett.* **2013**, *15*, 1270; g) K. Sun, X.-L. Chen, X. Li, L.-B. Qu, W.-Z. Bi, X. Chen, H.-L. Ma, S.-T. Zhang, B.-W. Han, Y.-F. Zhao, C.-J. Li, *Chem. Commun.* **2015**, *51*, 12111; h) D. Zhang, X. Cui, Q. Zhang, Y. Wu, *J. Org. Chem.* **2015**, *80*, 1517; i) J. Liu, L. Yu, S. Zhuang, Q. Gui, X. Chen, W. Wang, Z. Tan, *Chem. Commun.* **2015**, *51*, 6418; j) Y. Xu, P. Liu, S.-L. Li, P. Sun, *J. Org. Chem.* **2015**, *80*, 1269; k) F. Xiao, H. Chen, H. Xie, S. Chen, L. Yang, G. Deng, *Org.Lett.* **2014**, *16*, 50.

[9] a) E. A. Merritt, B. Olofsson, *Angew. Chem. Int. Ed.* **2009**, *48*, 9052; *Angew. Chem.* **2009**, *121*, 9214; b) M. Bielawski, B. Olofsson, *Chem. Commun.* **2007**, 2521.

[10] a) L. Ackermann, E, Diers, A. Manvar, *Org. Lett.* **2012**, *14*, 1154; b) B. Zhao, *Syn. Commun.* **2013**, *43*, 2110; c) Y. Aihara, N. Chatani, *J. Am. Chem. Soc.* **2014**, *136*, 898; for the original report on the use of MesCOOH, see: d) L. Ackermann, R. Vicente, A. Althammer, *Org. Lett.* **2008**, *10*, 2299.

[11] For a recent report on uncatalyzed nucleophlic functionalization of diaryliodoniums, see: N. Margraf, G. Manolikakes, *J. Org. Chem.* **2015**, *80*, 2582.

[12] For selected arylation reactions using diaryliodoniums, see: a) R. Phipps, M. J. Gaunt, *Science* **2009**, *323*, 1593; b) A. Bigot, A. E. Williamson, M. J. Gaunt, *J. Am. Chem. Soc.* **2011**, *133*, 13778; c) B. S. L. Collins, M. G. Suero, M. J. Gaunt, *Angew. Chem. Int. Ed.* **2013**, *52*, 5799; *Angew. Chem.* **2013**, *125*, 5911; d) F. Zhang, S. Das, A. J. Walkinshaw, A. Casitas, M. Taylor, M. G. Suero, M. J. Gaunt, *J. Am. Chem. Soc.* **2014**, *136*, 8851; e) N. Ichiishi, A. J. Canty, B. F. Yates, M. S. Sanford, *Org. Lett.* **2013**, *15*, 5134.

[13] The hyperiodination product was detected in an appreciable amount after 15 h.

[14] For selected reports on C–H thiocynation, see: a) K. Jouvin, C. Matheis, L. J. Goossen, *Chem. Eur. J.* **2015**, *21*, 14324; b) S. Mitra, M. Ghosh, S. Mishra, A. Hajra, *J. Org. Chem.* **2015**, *80*, 8275; c) D. Yang, K. Han, W. Wei, G. Li, S. Li, C. Zhao, L. Tian, H. Wang, *J. Org. Chem.* **2015**, *80*, 11073 – 11079.

[15] The uncatalyzed nucleophilic thiocyanation of **4** with NaSCN could occur at a higher temperature (60 °C), but a mixture of **9** and **8a** was obtained.

[16] For selected reports on electrophilic C–H thioetherification, see: a) C. Li, W. Yu, J. Yao, B. Wang, Z. Liu, Y. Zhang, *Org. Lett.* **2015**, *17*, 1340; b) S.-Y. Yan, Y.-J. Liu, B. Liu, Y.-H. Liu, Z.-Z. Zhang, B.-F. Shi, *Chem. Commun.* **2015**, *51*, 7341; c) Y. Yang, W. Hou, L. Qin, J. Du, H. Feng, B. Zhou, Y. Li, *Chem. Eur. J.* **2014**, *20*, 416.

Received: October 16, 2015
Published online on December 3, 2015