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Catalytic Thiolation Hot Paper

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Heterogeneously Catalyzed Direct C–H Thiolation of Heteroarenes**

*Suhelen Vásquez-Céspedes, Angélique Ferry, Lisa Candish, and Frank Glorius**

Abstract: *The first general methodology for the direct thiolation of electron-rich heteroarenes was developed by employing Pd/Al_2O_3, a recoverable and commercially available heterogeneous catalyst, and $CuCl_2$. This method represents an operationally simple approach for the synthesis of these valuable compounds. Preliminary mechanistic studies indicate a heterogeneous catalytic system, in which both metals play a complementary role in the formation of the thiolated products.*

The formation of C–S bonds is important because of their prevalence in many biologically active compounds and organic materials.[1] Sulfenylated heteroarenes can be found in molecules such as AZD4407, a 5-lipoxygenase inhibitor,[2] and thienoacene-based materials (Figure 1).[3]

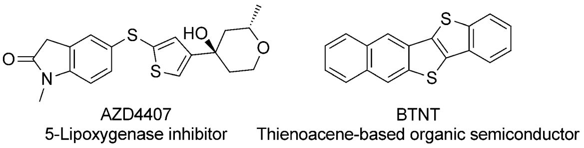

Figure 1. Examples of sulfenylated heterocycles used in pharmaceutical and materials chemistry.

The thiolation of heteroarenes usually involves a transition-metal-catalyzed cross-coupling reaction between an organic halide or boronic acid and thiols or disulfides.[4] These methods have the disadvantage of employing prefunctionalized substrates and usually require ligands and numerous additives for efficient reaction. While numerous approaches to C–N or C–C bond formation through direct C–H functionalization have been reported in recent years,[5] reports of analogous C–S bond formation through direct C–H thiolation remain scarce. This is presumably due to the poisoning effect on some reagents and transition metals by sulfur compounds.[6] Pioneering work by the group of Inamoto in 2008 utilized palladium to synthesize heterocycles through homogeneous C–H thiolation in an intramolecular fashion.[7] Cu, Rh, and Ru catalysts have also proven to be successful at promoting this transformation.[5t] Nevertheless, a directing group free[8] general method for the direct C–H functionalization of electron-rich heteroarenes, such as thiophene, benzo[*b*]thiophene, or benzofuran, remains elusive.[9] Indeed, only few examples of non-directed C–H thiolation exist in the literature and they usually require very specific sulfenylating agents that are not commercially available. In 2001, Kita and co-workers reported the first sulfenylation of electron-rich (hetero)arenes through the use of a quinone-derived thiolation reagent (Figure 2).[10] In 2011, Yamaguchi and co-workers reported a rhodium-catalyzed C–H thiolation of heteroaromatic compounds that makes use of α-(phenylthio)ketones as the thiol source, however, only single examples of an electron-poor benzo[*b*]thiophene and thiophene were described.[11] The Prabhu group developed the direct benzoxazolethiolation of hetero(arenes) by utilizing a benzoxazolethione under strongly oxidizing conditions.[12] Some reports in the literature refer to the undirected C–H functionalization of electron-rich arenes from disulfides,[13] however these methods suffer from limited scope and

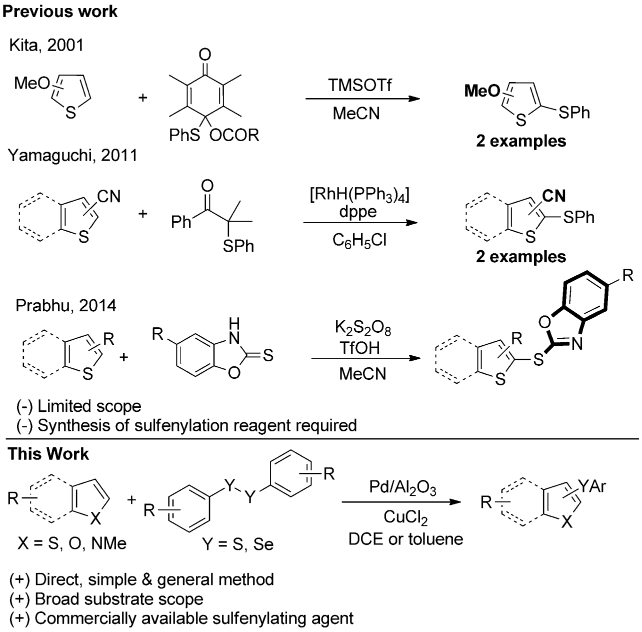

Figure 2. Conversion of heteroarene C–H bonds into C–S/C–Se bonds. dppe = 1,2-bis(diphenylphosphanyl)ethane, Tf = trifluoromethanesulfonyl, TMSOTf = trimethylsilyl trifluoromethanesulfonate.

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[*] S. Vásquez-Céspedes,[+] Dr. A. Ferry,[+] Dr. L. Candish, Prof. Dr. F. Glorius
Westfälische Wilhelms-Universität Münster
Organisch-Chemisches Institut
Corrensstraße 40, 48149 Münster (Germany)
E-mail: glorius@uni-muenster.de

[+] These authors contributed equally to this work.

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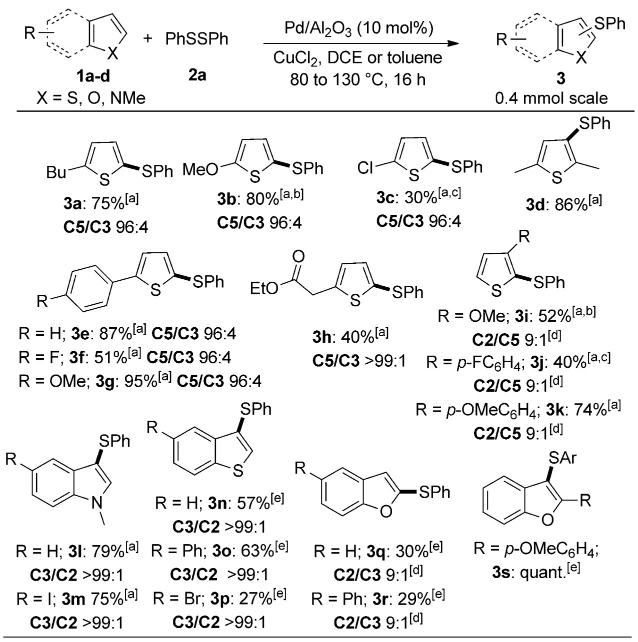
selectivity and have not been applied to electron-rich heteroarenes.[14] Therefore, the development of general conditions for the direct C–H thiolation of electron-rich heteroarenes with high selectivity, from ubiquitous thiol or disulfide precursors, is desirable.

Heterogeneous catalysis has potential advantages including the easy removal of transition metals from reaction mixtures and the possibility to recycle the catalyst. Our group recently reported the Pd/C-catalyzed regioselective arylation of (hetero)arenes.[15] Following these results, we decided to focus on the formation of more challenging C–heteroatom bonds through C–H functionalization. Indeed, to the best of our knowledge, no heterogeneously catalyzed methodology exists for direct C–H thiolation on electron-rich heteroarenes.[16] Herein, we present a general method involving palladium/copper(II) catalysis for the direct thiolation of different heteroarenes through the use of disulfides, and the extension of this method to the synthesis of selenated compounds through the use of diselenides.

Following our previous results based on the activation of heteroarenes by heterogeneous catalysts,[15a,b] we expected to be able to perform the more challenging C–H thiolation by using easily available diphenyldisulfide (**2a**) as the sulfur source. After extensive screening (see the Supporting Information), we successfully realized a highly selective C5-thiolation of 2-*n*-butylthiophene (**1a**) to afford **3a** by using Pd/Al_2O_3 (Acros Organics: 5 wt% Pd/Al_2O_3, dry) in the presence of $CuCl_2$ (Scheme 1).

With the optimized conditions in hand, we explored the scope of the reaction (Scheme 1). Satisfyingly, we found a broad range of thiophenes substituted with electron-donating and electron-withdrawing groups to be suitable substrates for the reaction, although it was apparent that the reaction was enhanced by electron-donating substituents on the thiophene (see **3b** versus **3c**).

Pleasingly, the high selectivity was maintained with all of the 2-substitued thiophenes (**3a**–**3h**). High yield and selectivity for monosulfenylation on the 3-position was also obtained when a 2,5-disubstituted thiophene was employed (**3d**). Halogens and a carboxyl ester were also tolerated, which would allow for further derivatization (**3c**, **3h**, **3p**). Notably, the 3-substituted thiophenes proved to be more challenging compared to the 2-substituted ones (**3b** versus **3i**). In the case of bulkier substituents in the 3-position, decreased selectivity was also observed (**3j**, **3k**). We next explored different heteroarenes and were pleased to find that *N*-methylindole and 5-iodo-*N*-methylindole reacted with high selectivity and gave good yields (**3l**, **3m**). The reactivity of benzo[*b*]thiophene and benzofuran were also investigated, however only low yields of the products were obtained under the optimized reaction conditions. Increasing the amount of $CuCl_2$ and using toluene as the solvent resulted in the formation of the thiolated products in modest to good yields and with high selectivity in the case of benzo[*b*]thiophenes (**3n**–**3p**). Interestingly, employing a benzofuran substituted at the 2-position led to the formation of the sulfenylated product **3s** in quantitative yield.



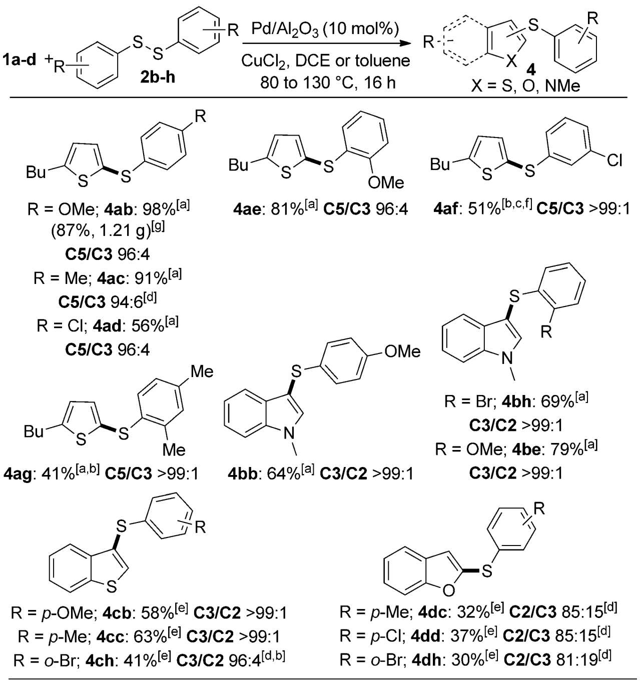
Scheme 1. Phenylthiolation of different heteroarenes. Ratios determined by GC–MS analysis of the crude mixture and yields of isolated product are given. [a] General procedure A: heteroarene (2.5 equiv), diphenyldisulfide (0.5 equiv = 1 equiv of thiol), Pd/Al_2O_3 (10 mol%), and $CuCl_2$ (1 equiv) in 1,2-dichloroethane (DCE) at 80 °C. [b] 0.5 equiv of $CuCl_2$. [c] 100 °C in DCE. [d] Isolated as a mixture of isomers. [e] General procedure B: heteroarene (2.5 equiv), diphenyldisulfide (0.5 equiv), Pd/Al_2O_3 (10 mol%) and $CuCl_2$ (2 equiv) in toluene at 130 °C. Ar = *p*-$OMeC_6H_4$.

Next, we explored the scope in terms of the disulfide **2** (Scheme 2). Electronically diverse disulfides were found to be efficient coupling partners, although a preference for electron-rich disulfides was observed for coupling with **1a** (**4ab**, **4ac**, **4ae**). Disulfides containing *ortho* and *para* substitution on the arene were well tolerated (**4ag**), as were aryl disulfides with electron-withdrawing groups such as Cl and Br (**4ad**, **4af**, **4ch**, **4dd**).[17] Moreover, the high selectivity for the sulfenylation of *N*-methylindole, benzo[*b*]thiophene, and benzofuran was not affected when we changed the electronic properties of the disulfides (Scheme 2). Furthermore, we applied a robustness screen (see the Supporting Information) to further explore the functional-group tolerance of this reaction.[18]

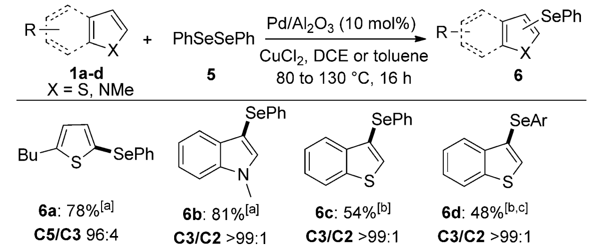
We extended the scope of the reaction to include the formation of C–Se bonds (Scheme 3). Organoselenium compounds are relevant in medicinal chemistry owing to their biological activity, specifically their antitumor and anticancer properties.[19] The selenated heteroarenes (**6a**–**6d**) were obtained in moderate to good yields and with high selectivity. This seems to represent the first C–H selenation of the benzo[*b*]thiophene core.

To demonstrate the utility of our transformation, we prepared an extended sulfur based heterocycle, a common motif of organic semiconductors.[1d,3] We subjected the benzo[*b*]thiophene thiolated product **4ch** to a palladium-catalyzed intramolecular arylation to obtain BTBT in 79% yield (Scheme 4).[1d]

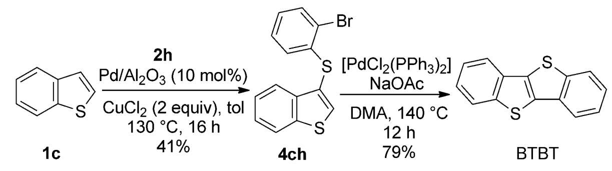
Given that the palladium source utilized in the thiolation reaction was heterogeneous in nature, we were interested to understand whether the catalytic system was also heteroge-



Scheme 2. Arylthiolation with different disulfides. Ratios determined by GC–MS analysis of the crude mixture and yields of isolated product are given. [a] General procedure A: See Scheme 1. [b] 1:1 ratio of starting materials. [c] 100 °C in DCE. [d] Isolated as a mixture of isomers. [e] General procedure B: See Scheme 1. [f] Isolated by preparative HPLC. [g] 5.0 mmol scale.



Scheme 3. Phenylselenation of heteroarenes. Ratios determined by GC–MS analysis of the crude mixture. [a] General procedure A: heteroarene (2.5 equiv), diphenyldiselenide (0.5 equiv), Pd/Al_2O_3 (10 mol%), and $CuCl_2$ (1 equiv) in DCE at 80 °C. [b] General procedure B: heteroarene (2.5 equiv), diphenyldiselenide (0.5 equiv), Pd/Al_2O_3 (10 mol%), and $CuCl_2$ (0.5 equiv) in toluene at 130 °C. [c] 1:1 ratio of starting materials. Ar = o-BrC_6H_4.



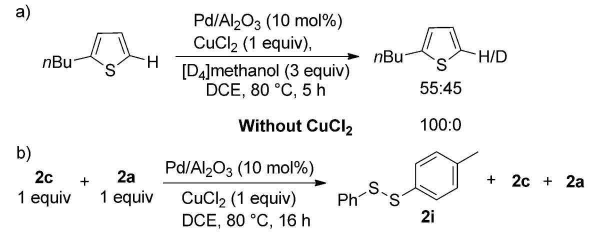
Scheme 4. Application of the synthetic methodology to the synthesis of [1]benzothieno[3,2-*b*][1]benzothiophene (BTBT).

neous. Therefore, we employed two common procedures to explore the heterogeneity of the reaction.[20] The hot-filtration test indicated no further increase in product formation after filtration and the three-phase test suggested that no active homogeneous palladium species were formed (see the Supporting Information).

The presence of metals in the solution was measured by Total reflection X-Ray Fluorescence (TXRF)[21] for both catalytic systems (DCE and toluene). Copper was found to be insoluble and palladium was detected in solution in different amounts depending on the reaction time (see the Supporting Information). However, heterogeneity tests (see above) indicated that this leached Pd is not the active catalytic species.

These results, along with the observation of the dependence of the reaction on rapid stirring rates, suggest that the catalytically active system is heterogeneous in nature. The recycling of Pd/Al_2O_3 was also investigated, however a decrease in yield was found for the second (63 %) and third (42 %) cycles.

To investigate the role of the metals in the activation of the heteroarene, a series of experiments were performed. H/D exchange was observed when the standard substrate **1a** was treated with the catalytic system in presence of an excess of CD_3OD (Scheme 5 a). A lesser degree of deuteration was also observed when using only $CuCl_2$. However, no deuteration of **1a** was found when employing only Pd/Al_2O_3 (Scheme 5 a). No kinetic isotope effect (KIE) was observed when 2-*n*-butylthiophene and 2-*n*-butyl-4-deuterothiophene were employed under the reaction conditions in parallel and competition experiments (KIE = 0.95 and 1.2, respectively), thus suggesting that C–H bond cleavage is not rate determining.[22] Moreover, a sigmoidal reaction profile indicates the formation of an active catalytic species from the precursors.



Scheme 5. Deuteration and scrambling experiments.

The importance of the metals for the activation of the S–S bond was investigated through scrambling and competition experiments (see the Supporting Information). In the reaction of two disulfides (**2a** and **2c**), we observed significant formation of the mixed disulfide **2i** when employing either our catalytic system or only an equivalent amount of Cu (Scheme 5 b). The use of only Pd/Al_2O_3 did not result in formation of the mixed disulfide. In a competition experiment, **1a** was reacted with an equivalent mixture of two electronically different disulfides (**2c** and 1,2-bis(4-bromophenyl)disulfane) under the optimized reaction conditions. After 2 h, we detected the formation of the sulfenylated thiophene **4ac** and the mixed disulfide as the major product. In addition, a Hammett plot for the reactionbetween **1a** and different disulfides gave a ρ value of −2.5, thus suggesting the buildup of a positively charged transition state in the rate-determining step of the catalytic cycle.[23]

At this stage, it would be speculative to provide a reaction mechanism for this transformation. Nevertheless, we consider the formation of a highly electrophilic species from the disulfide or an oxidative addition of the active catalytic species to the S–S bond to be key steps in the reaction. The data obtained enable the preliminary proposal of two alternative reaction pathways (see the Supporting Information).

In summary, a new C–H functionalization of heteroarenes to synthesize different sulfenylated and selenated compounds was developed by using a recoverable heterogeneous catalyst and readily available materials. This strategy provides a method for the direct selective C–H thiolation/selenation of electron-rich heteroarenes with disulfides or diselenides in an operationally simple approach for the preparation of these valuable molecules.

Keywords: C–H functionalization · disulfides · heteroarenes · heterogeneous catalysis · thiolation

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