C–H Functionalization

DOI: 10.1002/anie.201100775

Palladium-Catalyzed Double C–H Activation Directed by Sulfoxides in the Synthesis of Dibenzothiophenes**

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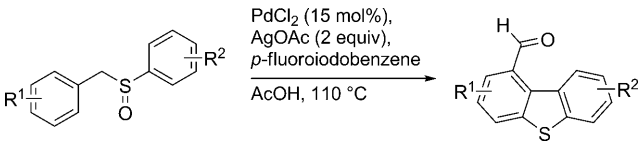
C–H functionalization is a sustainable and straightforward approach to complex substances.[1] Numerous practical methods for the formation of C–C, C–N, and C–O bonds through direct C–H activation have been developed using transition-metal catalysis. The activation of $C(sp^2)$–H bonds of aromatic compounds provides access to key scaffolds of natural products, drugs, and materials. Double C–H activation is a challenging, attractive, and highly economical method to create C–C biaryl bonds.[2,3] However, the previously developed methods often suffer from selectivity problems in the formation of substituted biaryls and require a great excess of one coupling partner. For the efficient solution to this problem a number of directing groups such as carbonyl-based or nitrogen-containing groups have been used. The development of efficient methods for the construction of complex molecules by multiple C–H functionalization poses a great challenge. Herein, we report our preliminary results on a palladium-catalyzed double C–H activation using sulfoxide as a new traceless directing group, and its application in a highly regioselective synthesis of polysubstituted dibenzothiophenes through a cascade reaction (Scheme 1).

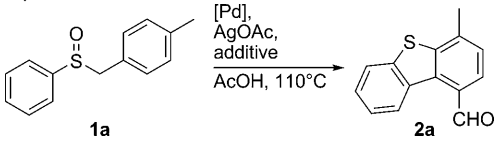


Scheme 1. Sulfoxide-directed synthesis of dibenzothiophenes.

Dibenzothiophene is a key scaffold for pharmaceutically active compounds. Besides, its derivatives have numerous applications as dyes, agrochemicals, liquid crystals, photoactive compounds, and conducting polymers.[4,5] Several straightforward methods for the synthesis have been reported.[6] These methods include multistep procedures, require halogenated or metalated compounds, and are neither atom- nor time-economical nor environmentally friendly. Application of transition-metal catalysts is limited because of the known poisoning effect of sulfur.[7,8] The development of an efficient method to these heterocyclic compounds using easily accessible chemicals is of great interest.

The reaction conditions were optimized based on the model transformation of sulfoxide **1a** (Table 1). Our initial attempts using $Pd(OAc)_2$ and AgOAc led to the stoichiometric formation of dibenzothiophene **2a**. However, no catalytic activity of Pd^{II} was observed (see the Supporting Information, Table S1). Therefore, we screened different additives in subsequent experiments. We found that the reaction can be promoted by using iodoarenes as additives (Table 1, entries 3–6). Application of *p*-fluoroiodobenzene led to the target product in 77% yield. We then screened various catalysts and oxidation reagents. We were able to reduce the loading of the Pd^{II} catalyst and showed that a variety of Ag^+ sources can be applied in the reaction (see Table S1).

Table 1: Optimization of reaction conditions.[a,b]



1a **2a**

Entry	Catalyst	Cat. [mol%]	Additive	*t* [h]	Yield [%]
1	$Pd(OAc)_2$	25	–	20	18
2	$Pd(OAc)_2$	25	NIS	16	<20
3	$Pd(OAc)_2$	25	$PhI(OAc)_2$[c]	20	46
4	$Pd(OAc)_2$	25	4-$MeOC_6H_4I$	20	55
5	$Pd(OAc)_2$	25	PhI	20	65
6	$Pd(OAc)_2$	25	4-FC_6H_4I	20	77
7	$[PdCl_2(CH_3CN)_2]$	25	4-FC_6H_4I	20	62
8	$[PdCl_2(PPh_3)_2]$	25	4-FC_6H_4I	20	45
9	$[Pd(PPh_3)_4]$	25	4-FC_6H_4I	20	<15
10	$PdCl_2$	25	4-FC_6H_4I	20	78
11	PdI_2	25	4-FC_6H_4I	16	67
12	**$PdCl_2$**	**15**	**4-FC_6H_4I**	**40**	**74**
13	$PdCl_2$	10	4-FC_6H_4I	90	66

[a] Conditions: **1a** (0.2 mmol), Pd catalyst (0.03 mmol), AgOAc (0.4 mmol), additive (0.4 mmol) in AcOH (1 mL) at 110°C. [b] Yield of isolated product. [c] 0.2 mmol additive. NIS = *N*-iodosuccinimide.

These optimized reaction conditions were applied to investigate the scope of the reaction (Table 2). A wide array of sulfoxides **1** were subjected to the reaction, and the corresponding products were isolated in moderate to good yields with excellent functional-group tolerance.

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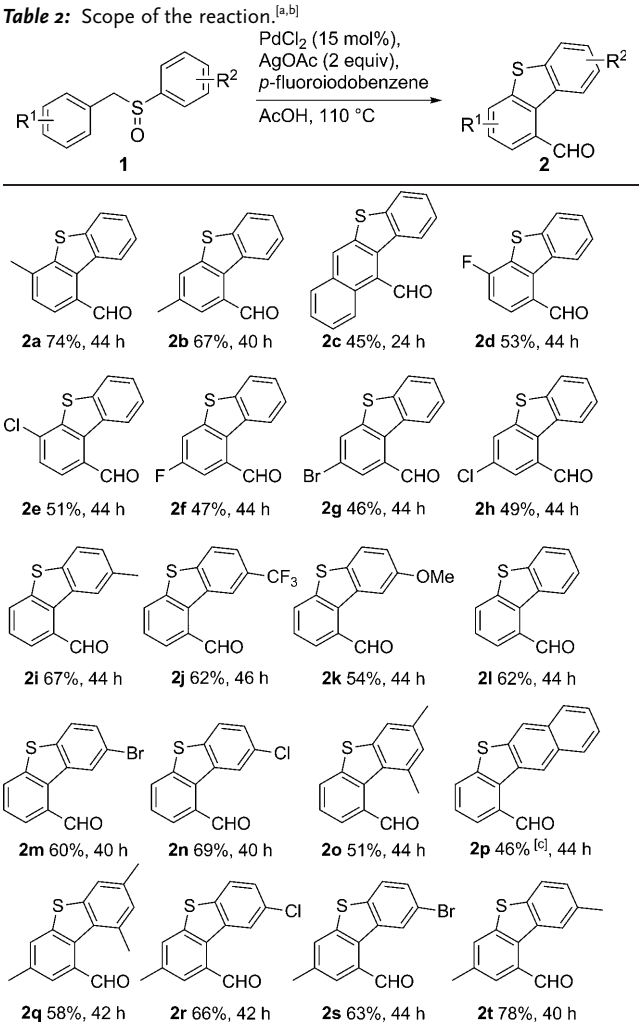
[**] We thank Prof. Dr. H. Waldmann for his generous support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201100775.

Table 2: Scope of the reaction.[a,b]

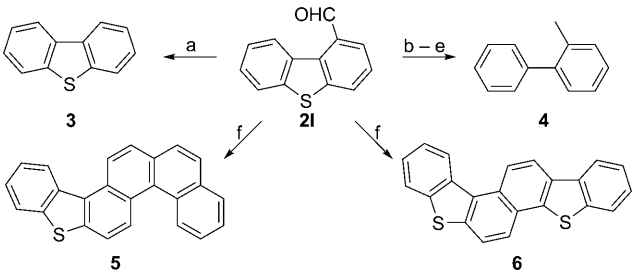


[a] Conditions: **2** (0.1 mmol), $PdCl_2$ (0.015 mmol), AgOAc (0.2 mmol), *para*-fluoroiodobenzene (0.2 mmol) in AcOH at 110°C for the given time. [b] Yields of isolated products. [c] Combined yield (mixture of two diastereomers in 10:1 ratio according to ^{1}H NMR analysis; the major isomer is shown).

In general, it was observed that sulfoxides in which the thiophenol part contains electron-withdrawing or -donating groups reacted smoothly to give the corresponding dibenzothiophene products in good yields (compounds **2i**–**p** in Table 2). These transformations occurred smoothly when the thiophenol part of the sulfoxide was substituted in *meta* and *para* position with a variety of substituents including halide, alkyl, trifluoromethyl, and methoxy groups. The *ortho*-substituted derivatives led to desired products only in trace amounts, owing to steric interactions between the sulfoxide group and the *ortho* substituent. Substrates with an alkyl substituent in the benzyl part of the sulfoxide afforded good yields. A number of other substituents in *meta*- and *para*- are tolerated giving products in yields of 45–74% (compounds **2a**–**h** in Table 2). We also found that *ortho* substitution in the benzylic part of the sulfoxide did not create problems for product formation (see example **2c** in Table 2). In general, phenyl benzyl sulfoxides having substituted electron-rich and -poor phenyl and benzyl groups provided access to the desired dibenzothiophenes.

In addition, when we extended the scope with substrates with substituents in both parts of the sulfoxide, the corresponding dibenzothiophene products were isolated in good yields (compounds **2q**–**t** in Table 2). Finally, we performed the reaction on a larger scale with 5 mmol of the sulfoxide. Dibenzothiophene **2l** was obtained in 67% yield.

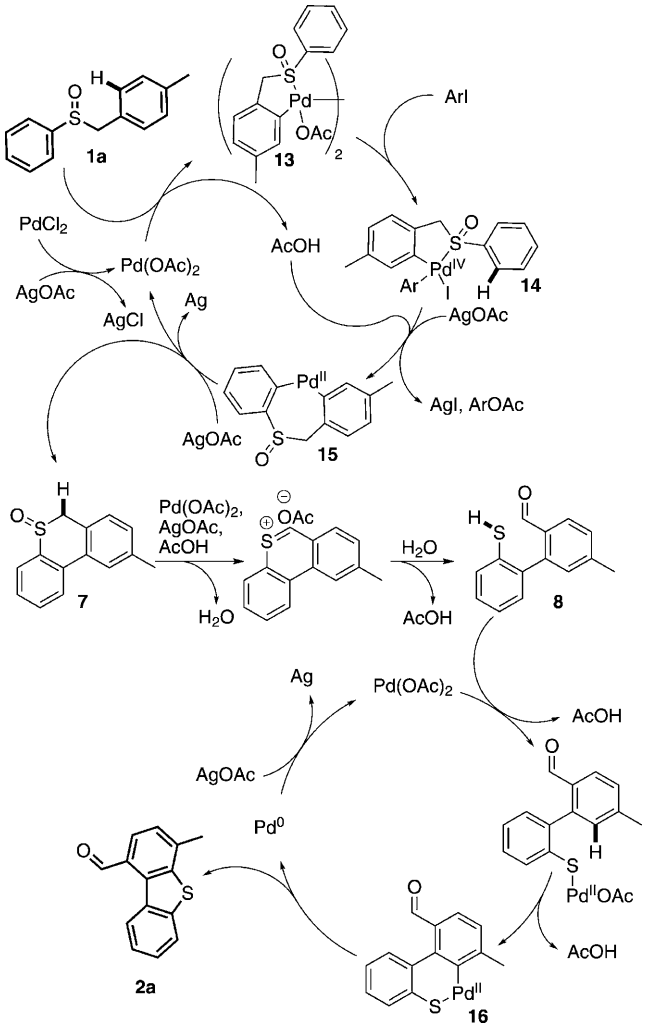
To further explore the applicability of the newly developed method we examined transformations of the obtained dibenzothiophene. The carbonyl group of **2l** was removed using Wilkinson's catalyst (Scheme 2). 2-Methylbiphenyl (**4**) was obtained by reduction of the carbonyl group to methyl group and desulfurization. In addition dibenzothiophene **2l** was converted in two steps to the polycyclic aromatic compounds **5** and **6**, which are used for preparation of organic transistors.[9c]



Scheme 2. Transformations of dibenzo[*b*,*d*]thiophene-1-carbaldehyde (**2l**). Reagents and conditions: a) $[RhCl(PPh_3)_3]$, toluene, reflux, 36 h, 68%; b) $NaBH_4$, MeOH, 0°C, 0.5 h, 90%; c) TsCl, Et_3N, DMAP, CH_2Cl_2, RT, 3 h; d) $LiAlH_4$, THF, RT, 3 h, 65% for two steps; e) $[Ni(cod)_2]$, bipy, $LiAlH_4$, THF, 48 h, reflux, 92%; f) see Ref. [9]. DMAP = 4-dimethylaminopyridine, bipy = 2,2′-bipyridine.

Mechanistically we assume that the first step in the cascade synthesis of dibenzothiophenes is the sulfoxide-group-directed double C–H activation of **1a** to give the cyclic sulfoxide **7** (Scheme 3). A subsequent Pummerer[10] reaction leads to mercaptoaldehyde **8**. S–H and C–H activation, followed by formation of a new C–S bond, provides the desired product **2a**.

To investigate the roles of the reagents, a number of control experiments were performed. Interestingly, under our reaction conditions only the cyclic sulfoxide **7** undergoes the Pummerer rearrangement, the starting sulfoxide **1a** does not. Addition of a known activator of the Pummerer rearrangement to the reaction mixture, such as acetic anhydride, led to selective formation of thiophenol and tolualdehyde and the desired dibenzothiophene **2a** formed in only trace amounts. Under thermal conditions and with added acid, sulfoxide **7l** reacted to provide a mixture of compounds **9** and **10** (see Scheme S1); however, the desired product **2l** was obtained from cyclic sulfoxide **7l** in the presence of Pd^{II} and AgOAc in acetic acid. This transformation proceeded smoothly and no intermediates were detected. Both $PdCl_2$ and AgOAc are required for the successful transformation, and in the absence of either the desired product **2l** was not obtained. In the reaction with AgOAc, in addition to products **9** and **10**,



Scheme 3. Possible mechanistic pathways.

disulfide was obtained as the result of the oxidation of the Pummerer rearrangement product. In addition, the application of $PdCl_2$ and AgOAc in DMF led to dramatically reduced yield of **21** from the cyclic sulfoxide **7l**. Addition of aryl iodides to the reaction mixture was not required for the catalytic activity of $PdCl_2$.

We then focused on the formation of the C–S bond through the activation of S–H and C–H bonds by using 2-mercaptobiphenyl (**11**) as a model substrate (see the Supporting Information, Scheme S1). Formation of dibenzothiophene (**12**) was not observed when Pd^{II} in acetic acid was used. However, in the presence of $[Pd(dba)_2]$ in acetic acid without added AgOAc, 2-mercaptobiphenyl (**11**) reacted for form product **12** in 15% yield. Addition of AgOAc improved the catalytic activity of Pd^0 and Pd^{II}. The best yield of dibenzothiophene (**12**) was obtained using $PdCl_2$ and AgOAc in acetic acid (see Scheme S1). Addition of aryl iodides to the reaction mixture resulted in decreasing yields of **12** and formation of by-products resulting from S-arylation of **11**. Interestingly, under these reaction conditions the disulfide obtained by oxidation of **11** reacted to give a trace amount of **12**.

Based on these results, we believe that the reaction proceeds as follows (Scheme 3): First, electrophilic attack of Pd^{II}, directed by the sulfoxide function, leads to the formation of bimetallic species **13**.[11] Subsequent oxidative addition of aryl iodide provides complex **14**, which undergoes first reductive elimination and then C–H activation to produce palladacycle **15** and aryl acetate. It is interesting that aryl iodides, which are common arylation reagents, promoted the formation of species **15**. The formation of arylated sulfoxides by reductive elimination of Pd^{II} from complex **14** with formation of a C–C bond was not observed. However, the desired dibenzothiophenes can be obtained without added aryl iodides through the use of stoichiometric amounts of Pd^{II} (see the Supporting Information). The ensuing reductive elimination leads to the formation of cyclic sulfoxide **7** and Pd^0, which is reoxidized to Pd^{II} by AgOAc. In the next cycle sulfoxide **7** undergoes a Pummerer rearrangement, which is promoted by AgOAc and acetic acid, to give mercaptoaldehyde **8**. Then, the coordination of Pd^{II} at the sulfur atom and subsequent C–H activation leads to palladacycle **16**. Reductive elimination of **16** produces the desired dibenzothiophene **2a** by formation of a C–S bond and Pd^0, which can be reoxidized by AgOAc.

In conclusion, we have developed a highly efficient double C–H activation directed by the sulfoxide group. The method was applied to the straightforward synthesis of dibenzothiophenes from simple benzyl phenyl sulfoxides. The products are formed in a cascade reaction by the abstraction of four hydrogen atoms. The method is highly regioselective as a result of the strictly defined sequence of reactions. An impressive role for aryl iodide additives has been proposed. Further work is currently underway.

Received: January 30, 2011
Published online: April 19, 2011

Keywords: arylation · C–H activation · dibenzothiophenes · palladium · Pummerer rearrangement

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