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Palladium(II)-Catalyzed Synthesis of Dibenzothiophenes from 2-Biphenyl Disulfides via C-H functionalization

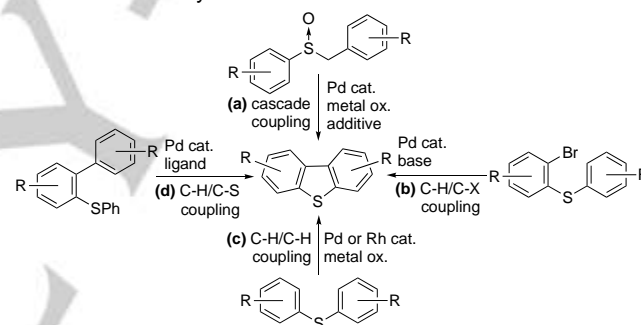
Kota Nishino^[a] Yohei Ogiwara^[a] and Norio Sakai*^[a]

Abstract: Described herein is the palladium-catalyzed oxidative preparation of dibenzothiophene derivatives from 2-biphenyl disulfides via C-H functionalization. This procedure shows a high tolerance toward various functional groups and does not require the further addition of a metal oxidant, a base, or a ligand. Also, the present method was applied to the facile preparation of dibenzoselenophene.

Dibenzothiophene derivatives constitute a core framework in many highly valuable molecules, such as pharmaceuticals, organic conductors, and dyes.^[1] Therefore, the development of facile and efficient access to various dibenzothiophene derivatives would make a significant contribution to the fields of medicinal chemistry and materials science. Fundamental procedures for the construction of dibenzothiophene derivatives have been reported since the 1930's.^[2] The Pleixats group established a palladium-catalyzed intramolecular Heck-type cyclization of allyl *o*-iodophenyl sulfides leading to dibenzothiophenes.^[3] Other reports have included the syntheses of dibenzothiophenes with a ring-closure procedure via either an aromatic nucleophilic substitution (S_NAr) reaction of halogen-substituted biaryl sulfide or an aromatic electrophilic substitution (S_EAr) reaction of 2-biphenyl methyl sulfoxides in the presence of a strong acid.^[4,5] Recently, *S*-arylation of a diaryliodonium salt with a sulfur reagent such as AcSK or S₈ was independently described by the Shimizu and Jiang groups.^[6] In this context, various dibenzothiophene derivatives and analogues such as dibenzoselenophene, thioxanthene, and dihydrodibenzothiepine, have been produced via the chalcogen-iodine exchange reaction of a diaryliodonium salt with a sulfur source.

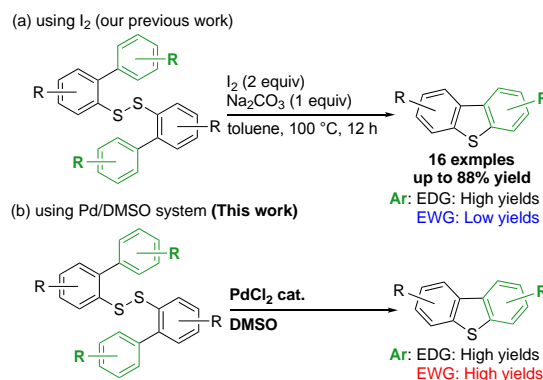
On the other hand, transition metal-catalyzed C-H functionalization is a powerful synthetic tool for the preparation of tricyclic hetero compounds such as dibenzofurans,^[7] carbazoles,^[8] dibenzophospholes,^[9] and dibenzosiloles.^[10] However, there have been few reports on the synthesis of dibenzothiophene skeletons via C-H functionalization with a metal catalyst, because sulfur atoms generally act as a catalytic poison, which leads to the deactivation of subsequent reactions. In 2011,

Antonchick *et al.* reported the synthesis of dibenzothiophenes through a unique process of double C-H functionalization of aryl benzyl sulfoxides (path a in Scheme 1).^[11] Also, cyclization of *ortho*-monohalogenated diaryl sulfides through an intramolecular C-H/C-X coupling reaction is known to produce dibenzothiophenes (path b in Scheme 1).^[12] Moreover, Zhao and Liu described the transition metal-catalyzed preparation of dibenzothiophene derivatives via the intramolecular dehydrogenative C-H/C-H coupling of diaryl sulfides (path c in Scheme 1).^[13] On the other hand, Tobisu, Chatani and co-workers have described a palladium-catalyzed C-H/C-S coupling of biphenyl sulfides leading to dibenzothiophene derivatives (path d in Scheme 1).^[14] These synthetic methods have enabled the provision of dibenzothiophenes bearing versatile functional groups. However, these synthetic methods generally require essential additives, such as a metal oxidant, a ligand or a base to drive the desired cyclization.



Scheme 1. Divergent approaches to dibenzothiophene via C-H functionalization.

In this context, our group developed I₂-mediated synthesis of dibenzothiophenes using 2-biphenyl disulfides, which can easily cleave a S-S bond with either an oxidant or a metal (Scheme 2a).^[15]



Scheme 2. Novel approach to dibenzothiophene from 2-biphenyl disulfide.

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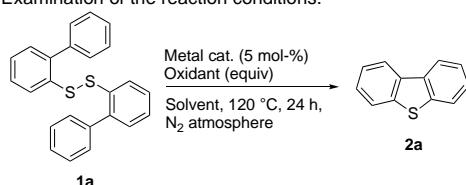
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However, this protocol was unsuccessful for the efficient production of dibenzothiophene derivatives with an electron-withdrawing group. Thus, after several examinations of transition metals, a palladium(II) catalyst without extra additives was effective in the cyclization of 2-biphenyl disulfide involving an electron-withdrawing group, which was a novel approach to sulfur-containing heterocycles (Scheme 2b). Herein, we describe the palladium(II)-catalyzed synthesis of various dibenzothiophene derivatives. This protocol represents an unconventional approach to the preparation of dibenzothiophenes via C-H/S-S coupling.

Initially, we focused on optimizing the reaction conditions. When disulfide **1a** was treated with palladium dichloride and 2 equiv of either AgOAc or CuCl₂ as an oxidant, the corresponding dibenzothiophene **2a** was afforded in excellent yields (entries 1 and 2). However, when the reaction was examined in the absence of an oxidant, such as AgOAc or CuCl₂, the yield of product **2a** was remarkably decreased (entry 3).

Table 1. Examination of the reaction conditions.^[a]



Entry	Metal catalyst	Oxidant (equiv)	Solvent	Conversion	Yield [%] ^[b]
1	PdCl ₂	AgOAc (2)	AcOH	>99	97
2	PdCl ₂	CuCl ₂ (2)	AcOH	>99	82
3	PdCl ₂	----	AcOH	4	2
4 ^[c]	PdCl ₂	CuCl ₂ (0.1)	AcOH	>99	87
5	PdCl ₂	CuCl ₂ (0.1)	AcOH	31	12
6 ^[d]	PdCl ₂	CuCl ₂ (0.1)	AcOH	53	27
7 ^[e]	PdCl ₂	----	DMSO	>99	92
8 ^[f]	PdCl ₂	----	DMSO	98	67
9	Pd(PPh ₃) ₄	----	DMSO	49	5
10	NiCl ₂	----	DMSO	21	3
11	----	----	DMSO	<1	0

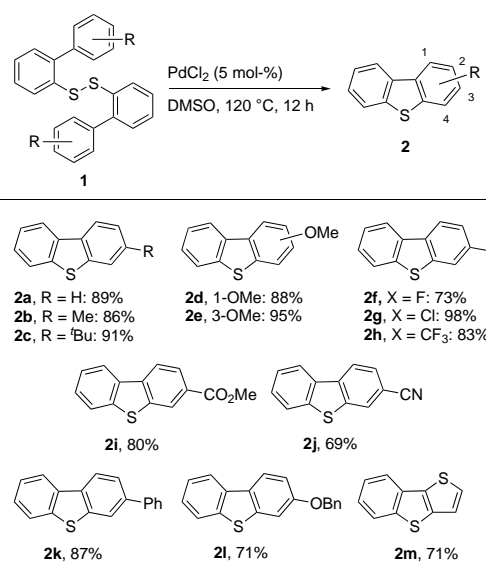
[a] Reaction conditions: 2-biphenyl disulfide (**1**: 0.1 mmol), metal cat. (0.005 mmol), DMSO, (0.2 mL), under a N₂ atmosphere, 120 °C, 12 h. [b] GC yield. [c] O₂ atmosphere (balloon). [d] Ambient atmosphere. [e] For 12 h. [f] At 100 °C.

Next, while carrying out a Wacker process involving a catalytic amount (0.1 equiv) of CuCl₂ and a protonic solvent, such as HCl aq. or AcOH, under an O₂ atmosphere,^[16] the cyclization efficiently proceeded to give dibenzothiophene (entry 4). On the other hand, this procedure under either an ambient or a N₂ atmosphere in the presence of CuCl₂ (0.1 equiv) led to a low production of **2a** (entries 5 and 6). Noteworthy, because the use of DMSO as a solvent instead of acetic acid produced **2a** in an

excellent yield, it was found that DMSO also has a role as an oxidant (entry 7).^[17] Lowering the reaction temperature resulted in a slight decrease in the product yield (entry 8). Also, when attempting the use of other transition metal catalysts such as Pd(PPh₃)₄ or NiCl₂, the expected cyclization did not proceed and nor are there any by-products, except for **2a** (entries 9 and 10). Particularly, at this stage, we have no reasonable explanation for the result that the initial use of palladium (0) catalyst led to a remarkable decrease in the product yield. Consequently, these results showed a higher adaptability of PdCl₂ toward cyclization containing a sulfur moiety that was preferable to Pd(0) and Ni(II) catalysts. When the cyclization was conducted in the absence of a palladium catalyst, the formation of **2a** was not observed (entry 11).

With the optimal conditions in hand, the synthesis of various dibenzothiophenes was then examined (Table 2). The present cyclization system isolated dibenzothiophene **2a** in an 89% yield. 2-Biphenyl disulfides bearing an electron-donating group such as a methyl, a *tert*-butyl, or a methoxy substituent produced the corresponding products **2b-2e** in excellent yields. Interestingly, in contrast with our previous study using I₂ as a promoter, the present palladium-catalyzed cyclization showed a high catalytic effect toward the starting disulfide derivatives bearing an electron-withdrawing group such as a fluoro, a chloro, or a trifluoromethyl substituent, and afforded dibenzothiophene derivatives **2f-h** in excellent yields. Gratifyingly, a methoxycarbonyl or a cyano-substituted dibenzothiophenes **2i** and **2j**, which have a strong electron-deficient substituent, were obtained in good yields. Also, each of the phenyl or benzyloxy-substituted dibenzothiophenes **2k** and **2l** were given in high yields. Moreover, the smooth formation of an interesting sulfur-containing framework, benzo[*b*]thieno[3,2-*d*]thiophene (**2m**), was achieved in a good yield.

Table 2. Scope and limitations of dibenzothiophene derivatives.

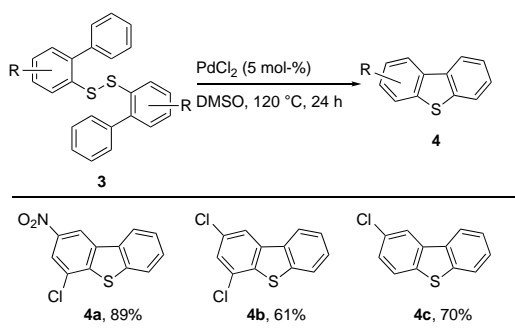


[a] Reaction conditions: 2-biphenyl disulfide (0.2 mmol), metal cat. (0.01 mmol), DMSO (0.4 mL), under a N₂ atmosphere, 120 °C, 12 h.

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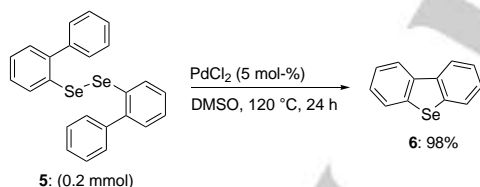
The synthesis of unsymmetrical dibenzothiophenes was then examined (Table 3). For example, with the present cyclization, 2-nitro-4-chloro-dibenzothiophene (**4a**) bearing two different electron-deficient groups was given in a good yield. We speculated that even the sulfur moiety bonding to a remarkable electron-deficient benzene ring would readily achieve cyclization with a vicinal benzene ring. Similarly, dibenzothiophene derivatives **4b** and **4c** with a chlorine substituent were efficiently obtained.

Table 3. Synthesis of unsymmetrical dibenzothiophene derivatives.



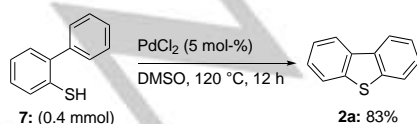
[a] Reaction conditions: 2-biphenyl disulfide (**1**: 0.2 mmol), metal cat. (0.01 mmol), DMSO, (0.4 mL), under a N₂ atmosphere, 120 °C, 24 h.

Interestingly, the present cyclization could be applied to the synthesis of a dibenzoselenophene framework. For instance, when 2-biphenyl diselenide (**5**) was processed with 5 mol-% of PdCl₂ in DMSO, dibenzoselenophene (**6**) was obtained in an almost quantitative yield (Scheme 3). Thus, the oxidizing catalytic system showed high tolerance toward a selenium moiety that generally is poison to a metal catalyst.



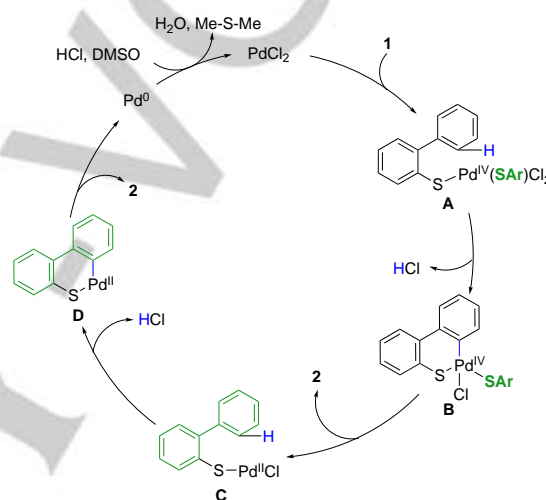
Scheme 3. Application to the synthesis of dibenzoselenophene.

To establish the present reaction mechanism, the cyclization of 2-phenylbenzenethiol (**7**), instead of 2-biphenyl disulfide, was thus examined (Scheme 4). The cyclization proceeded to produce **2a** in a high yield. This result implied that the cyclization path involves a 2-phenylbenzenethiolate intermediate via the cleavage of an S-S bond by the oxidative insertion of a palladium(II) catalyst.^[17]



Scheme 4. Examination of the synthesis of dibenzothiophene from 2-phenylbenzenethiol.

A plausible reaction mechanism is shown in Scheme 5. Initially, palladium dichloride oxidatively inserts to a S-S bond of 2-biphenyl disulfide **1**, producing Pd(IV) species **A**.^[18] Then, intermediate **A** generates a six-membered palladacycle **B** via C-H functionalization. Next, reductive elimination from complex **B** affords a dibenzothiophene **2** and palladium(II) complex **C** with a 2-phenylbenzenethiolate anion. Again, the cyclization of species **C** via C-H functionalization leads to six-membered palladacycle **D**. Finally, reductive elimination from complex **D** occurs to form another dibenzothiophene and a Pd(0) catalyst. Afterward, the Pd(0) catalyst is oxidized with DMSO and HCl to regenerate a Pd(II) catalyst.^[19,20] It is assumed that the formation of dibenzoselenophene proceeds through the same reaction path.



Scheme 5. Plausible reaction mechanism.

We demonstrated the palladium-catalyzed cyclization of 2-biphenyl disulfides bearing various substituents leading to the preparation of dibenzothiophene derivatives via C-H functionalization. A remarkable feature of the synthetic process is the lack of additives such as metal oxidants, ligands, or a base. Also, with a palladium(II) catalyst, versatile dibenzothiophene derivatives, unlike our previous work with I₂, were provided in relatively high yields. When applied, this process was successful in the preparation of dibenzoselenophene. Further studies towards the synthesis of other heterocycles and the reaction mechanisms are ongoing in this laboratory.

Experimental Section

To a freshly distilled DMSO solution (0.4 mL) in a screw-capped test tube under a nitrogen atmosphere were successively added a magnetic stirrer bar, 2-biphenyl disulfide **1** (0.2 mmol), and palladium dichloride (0.01 mmol, 1.8 mg). The test tube was sealed with a cap that contained a PTFE septum and was heated to 120 °C for 12 h. After the reaction, the resultant reaction mixture was diluted with ethyl acetate (3 mL). The solution was then filtered through a celite pad. The filtered solution was dried over anhydrous Na₂SO₄, filtered, and then evaporated under reduced pressure. The crude material was purified by silica gel column chromatography (hexane as an eluent) to give dibenzothiophene derivative **2**.

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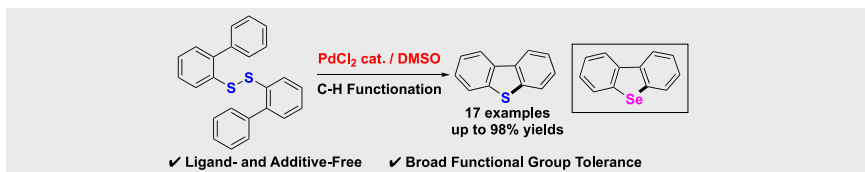
This work was partially supported by the Sasagawa Scientific Research Grant from The Japan Science Society.

Keywords: Dibenzothiophene • Palladium • C-H activation • Disulfide • Cyclization

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Palladium(II)-Catalyzed Synthesis of Dibenzothiophenes from 2-Biphenyl Disulfides via C-H Functionalization

Synthesis of dibenzothiophenes via C-H functionalization. Dibenzothiophenes can be prepared from 2-biphenyl disulfides via a PdCl₂-DMSO system. No additives, such as a metal oxidant, a ligand, or a base, are required in this protocol. Also, this method effectively provides dibenzoselenophene.

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