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Palladium-Catalyzed Oxidative Annulation of Sulfoximines and Arynes by C−H Functionalization as an Approach to Dibenzothiazines

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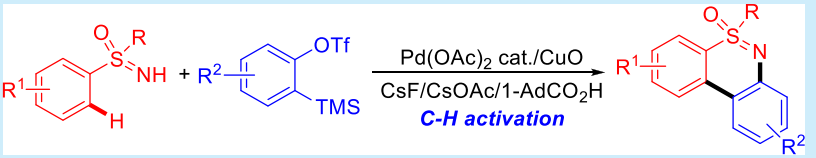

ABSTRACT: This work reports a novel and efficient palladium-catalyzed synthesis of tricyclic dibenzothiazines using easily prepared aryl sulfoximines and aryne precursors via C−H functionalization and cyclization. A mechanistic investigation indicated that the C−H bond cleavage at the position *ortho* to the sulfoximine group is the rate-determining step.

Sulfoximines are an important class of structural units prevalent in various natural products that exhibit remarkable biological and pharmaceutical properties.[1] Moreover, sulfoximine derivatives have also been widely utilized in the area of asymmetric syntheses[2] and as directing groups C−H bond functionalization.[3] Likewise, cyclic sulfoximines are an important class of heterocycles that exist in many bioactive molecules and play important roles in pharmaceutical chemistry.[4] Therefore, many unprecedented transformations have been reported toward the synthesis of this class of compounds and its derivatives.[5,6]

Among all of the synthetic methods for cyclic sulfoximines, transition-metal-catalyzed activation and annulation reactions through C−H bond functionalization have proved to be the most versatile and powerful synthetic strategies because of their high efficiency.[7] The groups of Bolm,[8] Lee,[9] and others[10] have employed sulfoximines as an *ortho*-directing groups to construct cyclic sulfoximines using alkynes, diazo compounds, allyl methyl carbonates, ketones, sulfoxonium ylides, and pyridotriazoles as coupling partners. However, it is important to note that only bicyclic sulfoximine derivatives were synthesized in all of those reports. There have been no reports on the synthesis of polycyclic sulfoximine derivatives such as tricyclic dibenzothiazines through C−H activation and cyclization of easily available aryl sulfoximines.

Synthetic procedures to construct tricyclic dibenzothiazine derivatives are very limited. In 2015, Jeganmohan and co-workers described a two-step procedure to synthesize dibenzothiazine derivatives through *ortho* arylation of sulfoximines with aromatic boronic acids and subsequent intramolecular cyclization.[11] Later on, a cascade *ortho* halogenation/Suzuki coupling/oxidative annulation procedure to synthesize dibenzothiazines from *N*-acylsulfoximines was investigated by the group of Bolm.[12] In 2018, Chen et al. reported a Pd/NBE cocatalyzed tandem C−H activation/annulation reaction of sulfoximines with aryl iodides for the synthesis of tricyclic dibenzothiazines in one pot and one step (Scheme 1a).[13] Recently, Zhang, Chen, and co-workers also obtained dibenzothiazines through sulfoximination of sulfides and intramolecular C−H amidation (Scheme 1b).[14] More recently, the research groups of Ma and Chen independently described a metal-free radical synthetic protocol for bromobenzothiazines through tandem C−H amination and bromination, respectively (Scheme 1c).[15] Although these are efficient strategies, multistep strategies or elaborated starting materials are necessary for these transformations. To overcome these problems, we envisioned a simplified and step-economical strategy toward the synthesis of tricyclic dibenzothiazines.

Arynes are highly reactive chemical intermediates.[16] Transition-metal-catalyzed annulation of arynes with sulfoximines would generate dibenzothiazines in one step, which would avoid the prefunctionalization of precursors. However, arynes have not been well-explored in the area of C−H activation because of their high reactivity, making this strategy very interesting but also very challenging.[17] Stimulated by our recent findings on the palladium-catalyzed C−H functionalization/annulation reaction of *N*-alkoxybenzsulfonamides with arynes to produce tricyclic dibenzosultams[18] and our continued interest in the synthesis of polycyclic aromatic

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Scheme 1. Strategies to Prepare Dibenzothiazines

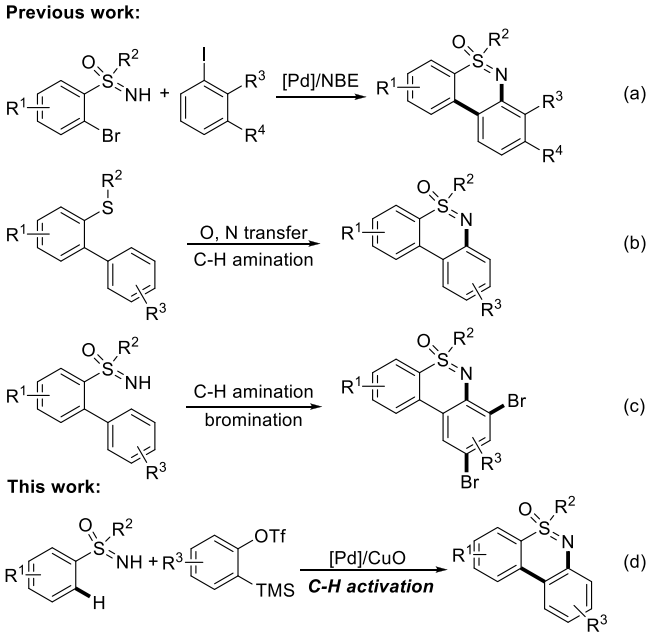
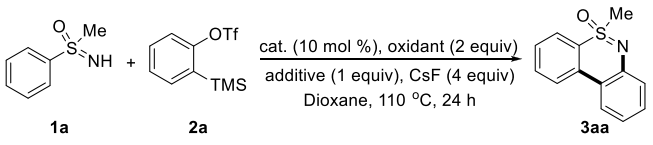


Table 1. Optimization of the Oxidative Annulation of Sulfoximine 1a and Benzyne Precursor 2a[a]



1a 2a 3aa

entry	catalyst	oxidant	additive	yield (%)[e]
1	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$		trace
2	$[RuCl_2(p\text{-cymene})]_2$	$Cu(OAc)_2$		0
3	$PdCl_2(NCPh)_2$	$Cu(OAc)_2$		22
4	$PdCl_2(NCMe)_2$	$Cu(OAc)_2$		25
5	$Pd(TFA)_2$	$Cu(OAc)_2$		30
6	$Pd(OAc)_2$	$Cu(OAc)_2$		37
7	$Pd(OAc)_2$	AgOAc		24
8	$Pd(OAc)_2$	Ag_2O		11
9	$Pd(OAc)_2$	$K_2S_2O_8$		18
10	$Pd(OAc)_2$	$PhI(OAc)_2$		13
11	$Pd(OAc)_2$	$Mn(OAc)_2$		24
12	$Pd(OAc)_2$	CuO		43
13	$Pd(OAc)_2$	CuO	1-AdCO_2H	49
14[b]	$Pd(OAc)_2$	CuO	1-AdCO_2H	62
15[c]	$Pd(OAc)_2$	CuO	1-AdCO_2H	58
16[d]	$Pd(OAc)_2$	CuO	1-AdCO_2H	79 (72[f])
17		CuO	1-AdCO_2H	0
18	$Pd(OAc)_2$		1-AdCO_2H	0

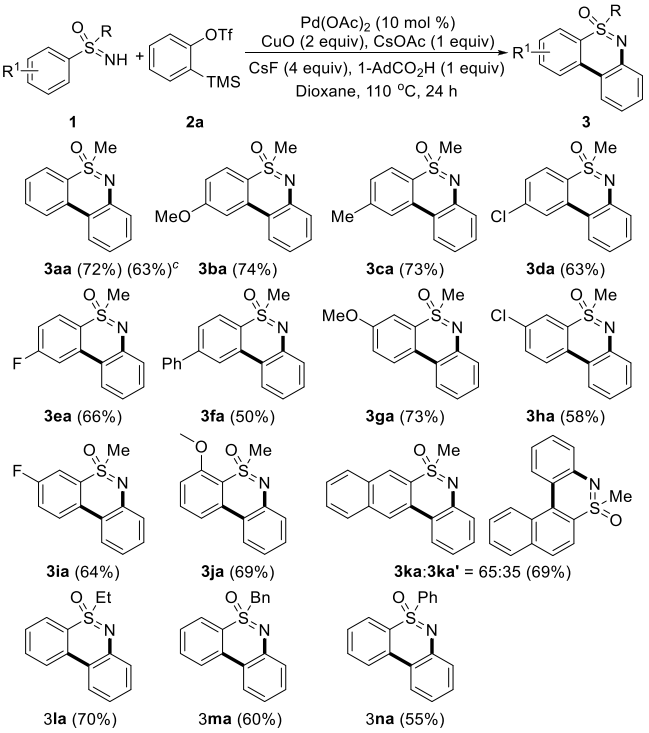
[a]The reaction was carried out using sulfoximine **1a** (0.1 mmol), benzyne precursor **2a** (0.2 mmol), catalyst (10 mol %), oxidant (0.2 mmol), CsF (0.4 mmol), and an additive (0.1 mmol) in dioxane (1 mL) at 110 °C under N_2 for 24 h. Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl. [b]NaOAc (0.1 mmol) was added. [c]KOAc (0.1 mmol) was added. [d]CsOAc (0.1 mmol) was added. [e]Yields are based on **1a** and were determined by ^1H NMR analysis of the crude reaction mixtures using 1,3,5-trimethoxybenzene as the internal standard. [f]The value in parentheses is the isolated yield.

hydrocarbons (PAHs),[19] we envisaged that tricyclic dibenzothiazines could be prepared from sulfoximines and aryne precursors through a C−H/N−H functionalization and cyclization strategy (Scheme 1d).

With this concept, we optimized the reaction conditions by employing sulfoximine **1a** and Kobayashi benzyne precursor **2a** as model substrates. Unfortunately, $[Cp^*RhCl_2]_2$ and $[RuCl_2(p\text{-cymene})]_2$ were not effective when $Cu(OAc)_2$ was used as the oxidant in dioxane solution, and sulfoximine **1a** was recovered (Table 1, entries 1 and 2). Pleasingly, when a catalytic amount of $PdCl_2(NCPh)_2$ was utilized, the formation of product **3aa** was observed in 22% ^1H NMR yield (Table 1, entry 3). Initial screening for prospective catalysts revealed that various palladium catalysts could also catalyze this reaction to some extent, among which $Pd(OAc)_2$ performed best, giving a 37% NMR yield of **3aa** (Table 1, entries 4−6). We investigated other oxidants, but lower yields were generally observed (Table 1, entries 7−11). In contrast, the use of CuO as the oxidant afforded **3aa** in 43% yield (Table 1, entry 12). When this transformation was carried out with 1 equiv of 1-AdCO_2H as an additive in the presence of 10 mol % $Pd(OAc)_2$ at 110 °C in dioxane, the yield of dibenzothiazine **3aa** improved to 49% (Table 1, entry 13). To our delight, the use of 1 equiv of acetate salt improved the yield of the target product **3aa** (Table 1, entries 14 and 15). CsOAc gave the best result, affording **3aa** in 79% yield (Table 1, entry 16). Control experiments indicated that no desired product **3aa** was observed without palladium catalyst or oxidant (Table 1, entries 17 and 18).

On the basis of the above investigation, the scope and generality of the present procedure was shown first by using sulfoximines **1** with benzyne precursor **2a** under the optimized

Scheme 2. Scope of Pd-Catalyzed Oxidative Annulation of Sulfoximines 1 and Benzyne Precursor 2a[a,b]



[a]The reaction was carried out using sulfoximines **1** (0.1 mmol), benzyne precursor **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), CuO (0.2 mmol), CsF (0.4 mmol), 1-AdCO_2H (0.1 mmol), and CsOAc (0.1 mmol) in dioxane (1 mL) at 110 °C under N_2 for 24 h. [b]Isolated yields are shown. [c]1.0 mmol scale based on sulfoximine **1a**.

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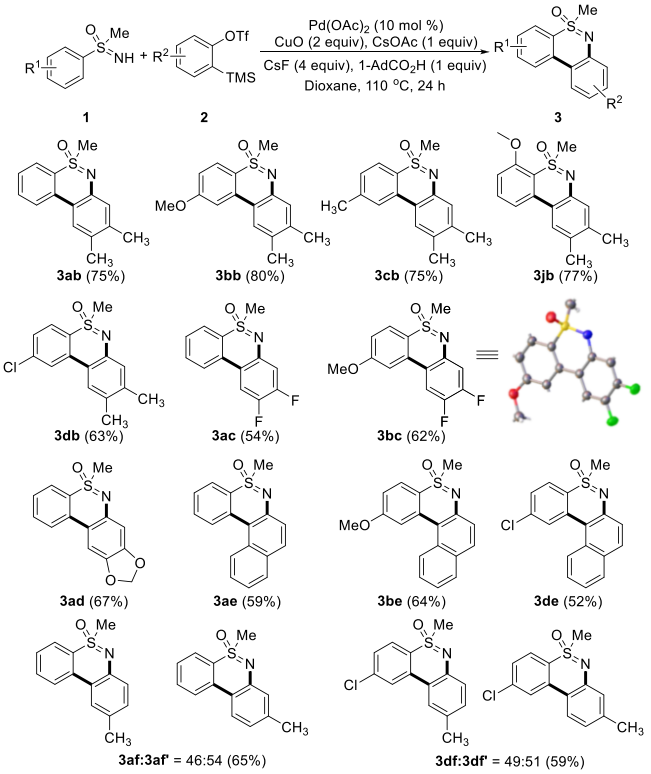
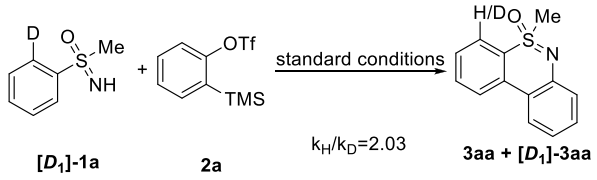
Scheme 3. Oxidative Annulation with Various Substituted Aryne Precursors[a,b]



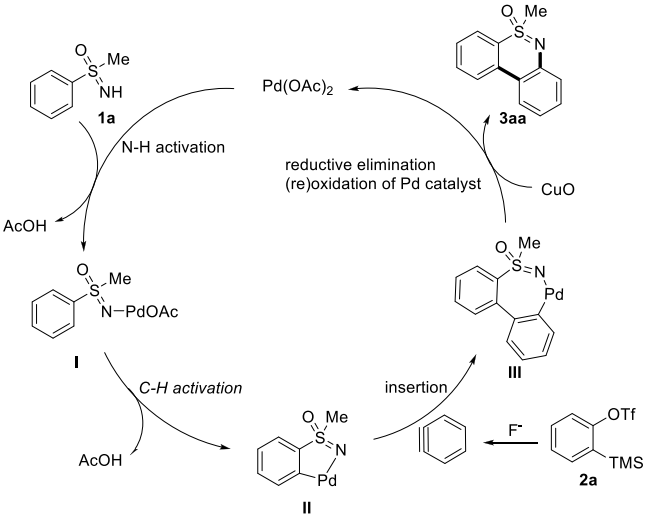
[a]The reaction was carried out using sulfoximines **1** (0.1 mmol), benzyne precursors **2** (0.2 mmol), $Pd(OAc)_2$ (10 mol %), CuO (0.2 mmol), CsF (0.4 mmol), 1-$AdCO_2H$ (0.1 mmol), and CsOAc (0.1 mmol) in dioxane (1 mL) at 110 °C under N_2 for 24 h. [b]Isolated yields are shown.

Scheme 4. Intramolecular Kinetic Isotope Effect



reaction conditions. As summarized in Scheme 2, a range of sulfoximines containing various substituents reacted smoothly to form the corresponding dibenzothiazines **3aa**–**na** in moderate to good yields. Introducing an electron-donating group such as methyl or methoxy at the *para* position of the sulfoximine led to efficient reactions, producing the target products **3aa** and **3ab** in good yields. In contrast, the reaction of benzyne with sulfoximines bearing electron-withdrawing substituents such as −Cl and −F proceeded smoothly but afforded **3da** and **3ea** in decreased yields. Sulfoximine **1f** was also applicable to the present reaction to afford dibenzothiazine **3fa** in 50% yield. The formation of **3ga**–**ia** revealed that this approach has high regioselectivity, and the C−H activation preferably occurred at the less sterically hindered position of the *meta*-substituted substrates **1g**–**i.** A moderate yield of the product **3ja** was obtained when sulfoximine **1j** was employed. Naphthyl-substituted sulfoximine **1k** reacted well to provide regioisomers **3ka** and **3ka′** in a 65:35 ratio in 69% combined yield. The reaction was also found to be applicable to

Scheme 5. Plausible Catalytic Cycle for Oxidative Annulation of Sulfoximines and Arynes



sulfoximines bearing *S*-ethyl, *S*-benzyl, and *S*-phenyl substituents, providing **3la**–**na** in yields of 55–70%. To demonstrate the synthetic utility, a 1.0 mmol scale experiment based on sulfoximine **1a** was performed, and dibenzothiazine **3aa** was isolated in 63% yield.

We next investigated the scope of this oxidative annulation with other substituted aryne precursors and sulfoximines, and the results are listed in Scheme 3. As we expected, aryne precursors bearing both electron-donating groups and electron-withdrawing groups were tolerated in the transformation. The reaction of **1** with symmetrical aryne precursors **2b**–**d** also proceeded well to afford the corresponding products **3ab**–**ad** in 63–80% yield. The structure of **3bc** was unambiguously characterized by single-crystal X-ray diffraction analysis. Particularly, we found that the unsymmetrical aryne generated from **2e** reacted with **1a**–**d** efficiently to generate **3ae**–**de** as sole products. Furthermore, the unsymmetrical aryne generated from **2f** underwent this transformation efficiently to give the regioisomeric mixtures **3af**/**3af′** (46:54) and **3df**/**3df′** (49:51) in combined yields of 65% and 59%, respectively.

An intramolecular kinetic isotope effect (KIE) experiment was performed to explore the reaction mechanism of this transformation (Scheme 4). A KIE of 2.03 was determined using [D_1]-**1a** as a model substrate for the oxidative annulation reaction, revealing that the C−H bond cleavage at the position *ortho* to the sulfoximine group is the rate-determining step.

On the basis of previous studies and our present experimental results, a plausible catalytic cycle for this oxidative annulation reaction is proposed (Scheme 5). Initially, sulfoximine **1a** reacts with $Pd(OAc)_2$ to afford intermediate **I**. The resulting palladium species with the sulfoximine subsequently undergoes intramolecular C−H activation to afford five-membered cyclic palladium intermediate **II**. Subsequent benzyne insertion leads to the formation of seven-membered palladacycle **III**. Reductive elimination of **III** affords dibenzothiazine **3aa**, and CuO can (re)oxidize Pd(0) to the Pd(II) species, which enters the next catalytic cycle.

In summary, we have demonstrated a novel protocol for the preparation of various dibenzothiazines by palladium-catalyzed strain-releasing oxidative annulation between easily prepared

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NH-sulfoximines and arynes. This transformation involves C−H functionalization and cyclization of aryl sulfoximines, and wide scopes of aryl sulfoximines and arynes were demonstrated. In addition, this work may provide a useful way to access a variety of biologically active heterocycles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02615.

Experimental procedures and full characterization for all new compounds (PDF)

Accession Codes

CCDC 1971000 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Author Contributions

[§]S.L. and L.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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