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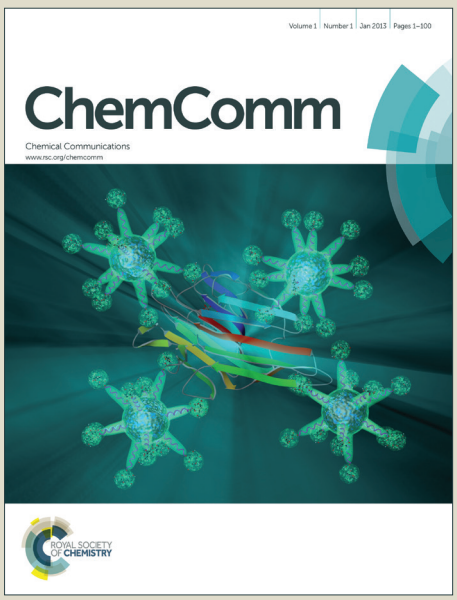

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COMMUNICATION

Ruthenium- and palladium-catalyzed consecutive coupling and cyclization of aromatic sulfoximines with phenylboronic acids: an efficient route to dibenzothiazines

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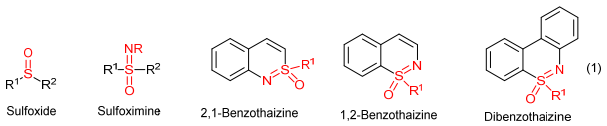
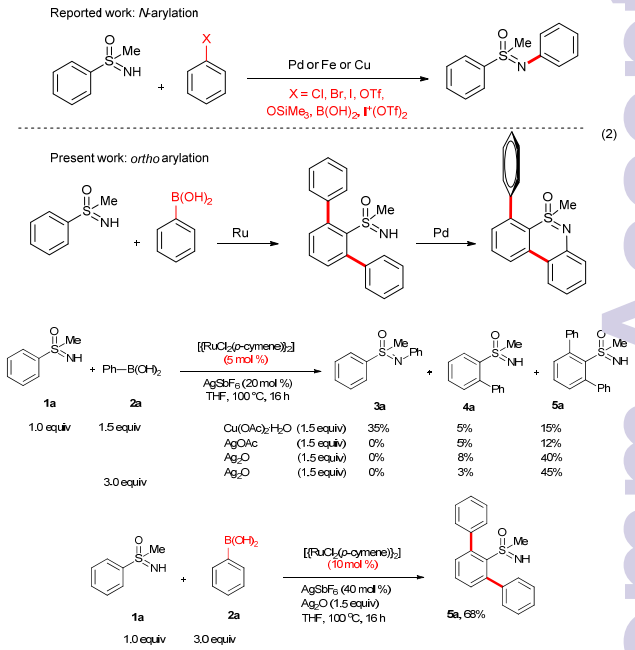
A ruthenium-catalyzed *ortho* arylation of aromatic sulfoximines with aromatic boronic acids followed by intramolecular cyclization in the presence of palladium catalyst, providing dibenzothiazine derivatives in two consecutive steps is described. By employing the present protocol, chiral tricyclic dibenzothiazines were synthesized in good yields by using chiral phenyl sulfoximines.

The sulfoximine is a pivotal structural motif which presents in various biologically active molecules, pharmaceuticals and agrochemicals (eq. 1).[1] The sulfoximine derivatives are also successfully used as chiral auxiliaries and ligands in asymmetric synthesis of various chiral organic molecules.[2] Several methods are available in the literature to synthesize linear sulfoximine derivatives.[3] But, the synthesis of cyclic sulfoximines is limited in the literature.[4] Recently, the synthesis of cyclic sulfoximines has gained much attention in organic synthesis despite their usefulness as scaffolds in drug development and acts as chiral ligands in enantioselective reactions.[5] Meanwhile, the sulfoximine derivatives are also served as key synthetic intermediates in various organic transformations.[5-7]



Harmata's group reported the synthesis of bicyclic sulfoximine derivatives such as 1,2-benzothiazine and 2,1-benzothiazine by a palladium-catalyzed cyclization of 2-bromo benzaldehydes or 2-alkenylated aromatic bromides with sulfoximines, $AlCl_3$-mediated cyclization of sulfonimidoyl chlorides with alkynes or alkenes and electrophilic cyclization of 2-bromophenyl substituted sulfoximines with terminal alkynes in the presence of palladium and copper catalysts.[6] Very recently, Bolm's group reported the synthesis of bicyclic 1,2-benzothiazine derivatives via a rhodium-catalyzed oxidative cyclization[7a] of phenyl sulfoximines with alkynes via chelation-assisted C-H bond activation reaction.[8-10] Subsequently, sulfoximine directed *ortho* alkenylation of phenyl sulfoximines with alkenes in the presence of a metal catalyst was also disclosed.[7b-e] In all these reports, sulfoximine containing bicyclic benzothiazine derivatives were synthesized efficiently.

Herein, we report the synthesis of tricyclic dibenzothiazines b a ruthenium-catalyzed *ortho* arylation of phenyl sulfoximines with aromatic boronic acids followed by intramolecu cyclization in the presence of palladium catalyst in the consecutive two steps (eq. 2). The present reaction compatible with various sensitive and useful functional group substituted phenyl sulfoximines and aromatic boronic acids. An enantioselective version of *ortho* arylation of phenyl sulfoximine with phenylboronic acids followed by cyclization, and this transformation leads to chiral dibenzothiazines in excellent 99% ee ratio was also disclosed.

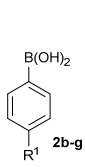
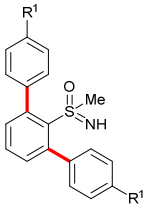
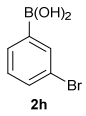
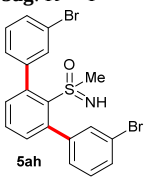
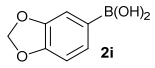
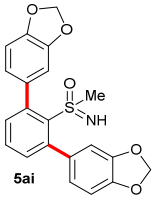
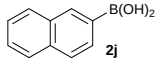
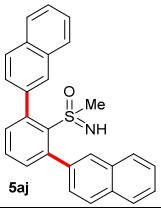


Scheme 1 *ortho* Arylation of sulfoximine **1a** with **2a**.

Initially, the *ortho* arylation of phenyl sulfoximine (**1a**) with phenylboronic acid (**2a**) (1.5 equiv) in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (5 mol %), $AgSbF_6$ (20 mol %) and $Cu(OAc)_2·H_2O$ (1.5 equiv) in THF at 100 °C for 16 h was examined (Scheme 1). In the reaction, *N*-arylated phenyl sulfoximine **3a** in 35% yield mono *ortho* arylated phenyl sulfoximine **4a** in 5% yield and *bis ortho* arylated phenyl sulfoximine **5a** in 15% yield were observed, respectively (Scheme 1). It is known that the free N-H

group of **1a** is acidic in nature and smoothly undergoes *N*-arylation with aromatic electrophiles or organometallic reagents providing *N*-arylated sulfoximines **3** in the presence of metal catalysts (eq. 2).[11] To success the *ortho* arylation reaction, the suppression of product **3** is highly important. Next, the reaction was examined with other oxidant and acetate sources such as AgOAc, NaOAc, K_2CO_3, CsOAc and Ag_2O. Among them, silver salts such AgOAc and Ag_2O were active for the reaction and no *N*-arylated product **3a** was observed. In AgOAc, product **4a** in 5% and **5a** in 12% yields were observed, respectively. In Ag_2O, product **4a** in 8% and **5a** in 40% yields were observed, respectively. Other acetate sources were not active for the reaction. Next, the coupling reaction was examined with an excess amount of phenylboronic acid **2a** (3.0 equiv). In the reaction also, a mixture of products **4a** and **5a** were observed in 3% and 45% yields, respectively. To increase the yield of **5a**, the coupling reaction was done in the presence of 10 mol % of catalyst and 40 mol % of $AgSbF_6$. Interestingly, in the reaction, only *bis ortho* arylated product **5a** was observed in 68% isolated yield and no *mono* arylated product **4a** was observed.

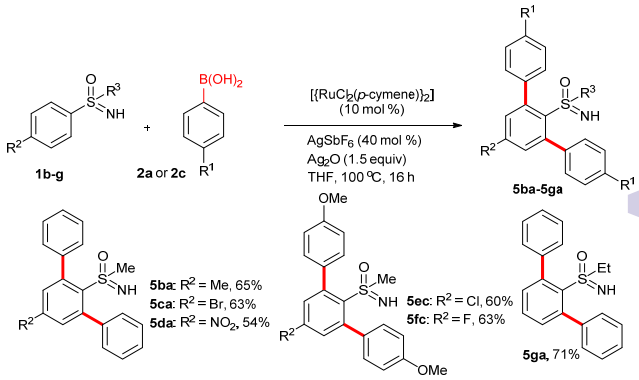
Table 1. Ruthenium-catalyzed *ortho* arylation of 1a with aromatic boronic acids 2b-j[a]

Entry	2b-j	Product 5	Yield (%)[b]
	 **2b-g**		
1	**2b**: R^1 = Ph	**5ab**: R^1 = Ph	72
2	**2c**: R^1 = OMe	**5ac**: R^1 = OMe	66
3	**2d**: R^1 = I	**5ad**: R^1 = I	65
4	**2e**: R^1 = Br	**5ae**: R^1 = Br	62
5	**2f**: R^1 = Cl	**5af**: R^1 = Cl	64
6	**2g**: R^1 = F	**5ag**: R^1 = F	60
7	 **2h**	 **5ah**	19
8	 **2i**	 **5ai**	61
9	 **2j**	 **5aj**	64

[a] All reactions were carried out using **1a** (100 mg), aromatic boronic acids (**2b-j**) (3.0 equiv), [{$RuCl_2$(*p*-cymene)}$_2$] (10 mol %), $AgSbF_6$ (40 mol %), Ag_2O (1.5 equiv) in THF (3.0 mL) at 100 °C for 16 h. [b] Isolated yield.

Further, the coupling reaction was examined with solvents such as toluene, MeOH, 1,4-dioxane and DMF apart from THF. However, in all these solvents, a mixture of **4a** and **5a** were observed in moderate yields (see ESI). THF solvent was effective solvent for the reaction. Further, the reaction was tested with other additives such as AgOTf, $AgBF_4$ and KPF_6 apart from $AgSbF_6$. $AgBF_4$ and AgOTf were partially active, providing product **5a** in 55% and 40% yields, respectively. KPF_6 was not active for the reaction. The optimization studies clearly revealed that [{$RuCl_2$(*p*-cymene)}$_2$] (10 mol %), $AgSbF_6$ (40 mol %) and Ag_2O (1.5 equiv) in THF at 100 °C for 16 h is the best conditions for the reaction. It is important to note that the C-H bond activation of both *ortho* carbons of phenyl sulfoximines were very facile and cannot be controlled. Due to the facile *bis* arylation, an excess amount of catalyst is required.

In addition to phenylboronic acid (**2a**), a wide range of aromatic boronic acids **2b-j** also readily participates in the reaction with **1a**. Table 1 summarizes the results of these reactions. Treatment of 4-phenyl substituted phenylboronic acid (**2b**) with **1a** provided *ortho bis* arylated product **5ab** in 72% yield (entry 1). Electron rich 4-methoxyphenyl boronic acid (**2c**) reacts smoothly with **1a**, yielding the corresponding product **5ac** in 66% yield (entry 2). Aromatic boronic acids having halogen groups I, Br, Cl and F **2d-g** also undergo *ortho* arylation reaction with **1a** efficiently, giving products **5ad-ag** in 65%, 62%, 64% and 60% yields, respectively (entries 3-6). However, 3-bromo phenylboronic acid (**2h**) yielded product **5ah** only in 19% yield (entry 7). Benzo[*d*][1,3]dioxol-5-ylboronic acid (**2i**) and 2-naphthylboronic acid (**2j**) also efficiently participated in the reaction, affording coupling products **5ai** and **5aj** in 61% and 64% yields, respectively (entries 8 and 9).

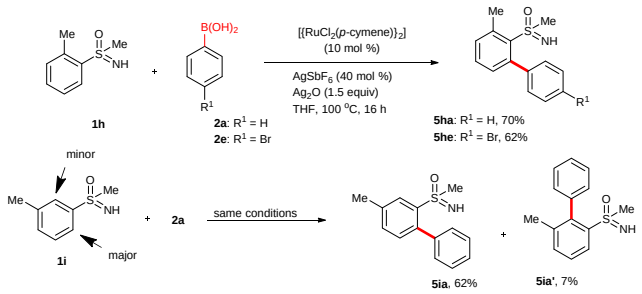


Scheme 2 Scope of aromatic sulfoximines.

The arylation reaction was examined with substituted aromatic sulfoximines **1b-g** (Scheme 2). Electron-rich, halogen and electron-deficient group substituted sulfoximines were compatible for the reaction. Methyl, Br and NO_2 substituted sulfoximines **1b-d** reacted with **2a,** yielding products **5ba-da** in 65%, 63% and 54% yields, respectively. Similarly, Cl and F substituted aromatic sulfoximines **1e-f** reacted with **2c**, providing products **5ec-fc** in 60% and 63% yields, respectively. Likewise, (ethylsulfonimidoyl)benzene (**1g**) yielded **5ga** in 71% yield.

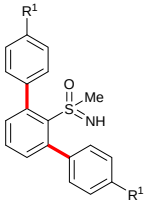
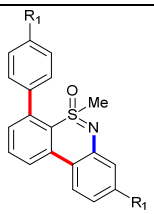
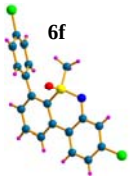
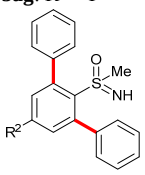
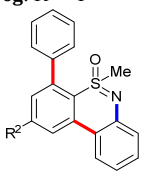
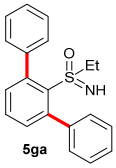
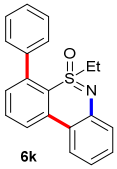
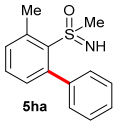
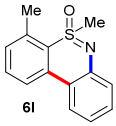
Apart from the *bis* arylation, *mono* arylation of phenyl sulfoximines was also disclosed (Scheme 3). Treatment of 2-methyl phenylsulfoximine (**1h**) with **2a** or **2f** gave *mono* arylated sulfoximine derivatives **5ha** and **5he** in 70% and 62% yields,

respectively. However, 3-methyl phenylsulfoximine (**1i**) afforded regioisomeric *mono* arylated products **5ia** and **5ia'** in 62% and 7% yields, respectively.



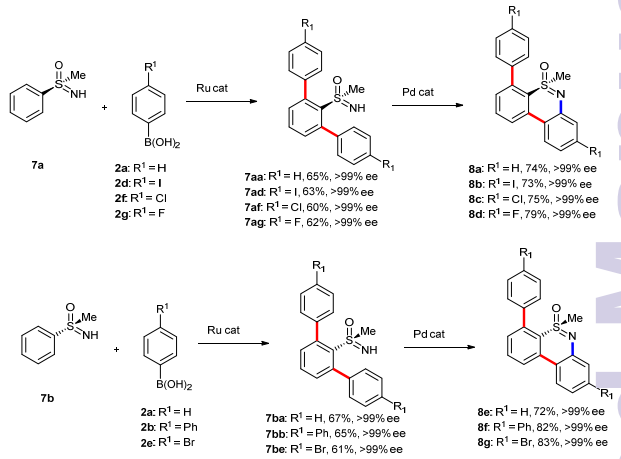
Scheme 3 *mono* Arylation of aromatic sulfoximines **1h-i**

Table 2. Synthesis of dibenzothiazines[a]

Entry	5	Product 6	Yield (%)[b]
			 6f
1	**5aa**: R^1 = H	**6a**: R^1 = H	76
2	**5ab**: R^1 = Ph	**6b**: R^1 = Ph	85
3	**5ac**: R^1 = OMe	**6c**: R^1 = OMe	65
4	**5ad**: R^1 = I	**6d**: R^1 = I	77
5	**5ae**: R^1 = Br	**6e**: R^1 = Br	85
6	**5af**: R^1 = Cl	**6f**: R^1 = Cl	79
7	**5ag**: R^1 = F	**6g**: R^1 = F	81
			
8	**5ba**: R^2 = Me	**6h**: R^2 = Me	80
9	**5ca**: R^2 = Br	**6i**: R^2 = Br	84
10	**5da**: R^2 = NO_2	**6j**: R^2 = NO_2	79
11	 5ga	 6k	83
12	 5ha	 6l	41

[a] All reactions were carried out using **5** (100 mg), $Pd(OAc)_2$ (10 mol %) and $PhI(OAc)_2$ (2.0 equiv) in toluene at 120 °C for 10 h. [b] Isolated yield.

Next, we have tried to couple the N-H bond of sulfoximine with one of the C-H bond of phenyl groups of compound **5** via chelation-assisted remote C-H activation in order to prepare tricyclic dibenzothiazine derivatives. $Pd(OAc)_2$ catalyst along with an oxidant is the suitable conditions for this type of cyclization.[12] The intramolecular cyclization of compound **5aa** proceeded smoothly in the presence of $Pd(OAc)_2$ (10 mol %) and $PhI(OAc)_2$ (2.0 equiv) in toluene at 120 °C for 10 h giving a tricyclic dibenzothiazine derivative **6a** in 76% yield (Table 2, entry 1). The cyclization reaction also proceeded in the presence of $PhI(OAc)_2$ without palladium catalyst. However, product **6** was observed in a less amount of 25% yield. Under similar reaction conditions, products **5ab**, **5ac**, **5ad**, **5ae**, **5af** and **5ag** also efficiently participated in the reaction, providing cyclization products **6b-g** in good to excellent yields (entries 2-7). Similarly products **5ba**, **5ca**, **5da**, **5ga** and **5ha** afforded dibenzothiazine **6h-l** in 80%, 84%, 79%, 83% and 41% yields, respectively (entries 8-12). The structure of compound **6f** was further confirmed by a single crystal X-ray analysis (see ESI).

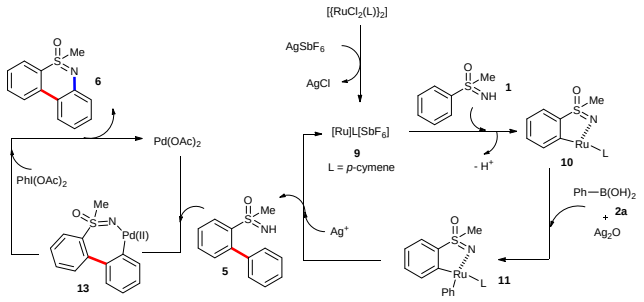


Scheme 4 Synthesis of chiral dibenzothiazines.

This result prompted us to explore the possibility of synthesis of chiral tricyclic dibenzothiazines by using chiral phenyl sulfoximines **7a-b** (Scheme 4). Treatment of chiral (*R*)-(-)-*S*-methyl-*S*-phenylsulfoximine (**7a**) with substituted phenyl boronic acids **2a**, **2d**, **2f** and **2g** in the presence of $[\{RuCl_2(p\text{-cymene})\}_2]$, $AgSbF_6$ and Ag_2O in THF at 100 °C for 16 h gave chiral *ortho* arylated phenyl sulfoximines **7aa-ag** in 65%, 63%, 60% and 62% yields, respectively (Scheme 3). Interestingly, the enantiomeric excess (ee) of products **7aa-ag** were not dropped and in all cases >99% ee ratios were observed. Later, compounds **7aa-ag** were cyclized into chiral dibenzothiazines **8a-d** in excellent 74%, 73%, 75% and 79% yields, respectively, in the presence of palladium catalyst. In all these reactions, >99% ee ratios were observed. Further, (*S*)-(-)- *S*-methyl-*S*-phenylsulfoximine (**7b**) underwent *ortho* arylation with aromatic boronic acids **2a**, **2b** and **2e** in the presence of ruthenium catalyst, providing chiral *ortho* arylated phenyl sulfoximines **7ba-be** in 67%, 65% and 61% yields, respectively, with >99% ee ratios. Further, **7ba-be** were converted into chiral dibenzothiazines **8e-g** in the presence of $Pd(OAc)_2$ in 72%, 82% and 83% yields, respectively.

A possible reaction mechanism is proposed to account for the present reaction in Scheme 5. Two different catalytic reactions were involved in the reaction. In the first catalytic cycle, $AgSbF_6$ likely removes all Cl^- ligands from the ruthenium complex providing a cationic ruthenium complex **9**.[13] Coordination of the nitrogen atom of sulfoximine **1** into catalyst **9** followed by *ortho*-metalation provides a ruthenacycle intermediate **10**. Transmetallation of phenyl boronic acid **2** into intermediate **10** in the presence of Ag_2O affords intermediate **11**. Subsequent reductive elimination of intermediate **11** in the presence of Ag source provides product **5** and regenerates the active ruthenium

species **9** for the next catalytic cycle. Another *ortho* arylation is also taken place in a similar fashion. In the second catalytic cycle, compound **5** reacts with $Pd(OAc)_2$ giving palladacycle **12**. Reductive elimination of intermediate **12** in the presence of $PhI(OAc)_2$ provides cyclic product **6** and regenerates the active $Pd(OAc)_2$ catalyst for the next catalytic cycle. The exact role of Ag_2O is not clear to us, it could be possible that the AgO^- anion acts as a base to accelerate the transmetallation of boronic acid **2** into intermediate **12** and the Ag^+ ion acts as an oxidant to oxidize Ru(0) to Ru(II).



Scheme 5 Proposed mechanism.

In conclusion, we have described a two-step synthesis of dibenzothiazines via a ruthenium-catalyzed *ortho* arylation of phenyl sulfoximines with phenyl boronic acids followed by intramolecular cyclization in the presence of $Pd(OAc)_2$. Chiral dibenzothiazines were prepared efficiently by using chiral phenyl sulfoximine in a similar protocol. A possible reaction mechanism was proposed to account for the present arylation followed by cyclization reaction.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures and spectroscopic data. See DOI: 10.1039/b000000x/

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