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Reductive coupling of azonaphthalenes for the synthesis of BINAMs *via* a diboron-enabled [5,5]-sigmatropic rearrangement†

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The [5,5]-sigmatropic rearrangement is a less-studied reaction and may be strategically utilized to devise unique synthetic processes. Herein, we document a diboron-enabled [5,5]-sigmatropic rearrangement for practical synthesis of BINAM derivatives. Mechanistically, a concerted activation of azonaphthalenes by diboron creates a unique ten-membered transition state, which subsequently triggers a [5,5]-sigmatropic rearrangement. The reaction occurs under mild conditions, and offers operational simplicity, remarkable chemo- and regioselectivities, and good scalability (>10 grams).

Sigmatropic rearrangements are common processes that find wide application in modern organic synthesis, representing an effective approach to reorganize organic molecules in an atom economic manner.[1] Typically, these rearrangements involve the movement of a sigma-bonded atom, flanked by one or more π-electron systems, to a new position with a corresponding rearrangement of the π-electrons.[2] A plethora of contributions from different research groups have shed light on this interesting research topic, leading to the development of a variety of sophisticated reactions such as [1,2], [1,5], [2,3], [3,3], [3,5] and [5,5]-sigmatropic rearrangements; many of them are classical named reactions such as Wittig rearrangement and Claisen rearrangements (Fig. 1a).[3] Among these reactions, [5,5]-sigmatropic rearrangements are studied to a very limited extent, possibly due to their specific substrate requirements and challenging selectivity issues.[4] The earliest reports of [5,5]-sigmatropic rearrangements can be traced back to acid-catalyzed benzidine rearrangement of 1,2-diarylhydrazine to access the *para*-benzidine, along with [1,3] and [3,3]-sigmatropic rearrangement by-products.[5] Similarly, a thermally induced rearrangement of *trans*-penta-2,4-dienyl-phenyl ether gave a mixture of [3,3] and [5,5]-sigmatropic rearrangement products.[6] Very recently, the groups of Hashmi and Li have successfully developed a selective [5,5]-sigmatropic rearrangement in gold catalysis and for the remote diastereoselective functionalization of arynes, respectively.[7] Moreover, Peng and co-workers have disclosed a highly robust assembly/deprotonation protocol of aryl sulfoxides with allyl nitriles whereby the chemo- and regioselectivity in the C–C bond formation was well-controlled *via* [5,5]-sigmatropic rearrangement.[8]

1,1′-Binaphthyl-2,2′-diamine (BINAM), a privileged atropisomeric biaryl motif,[9] has found wide applications in

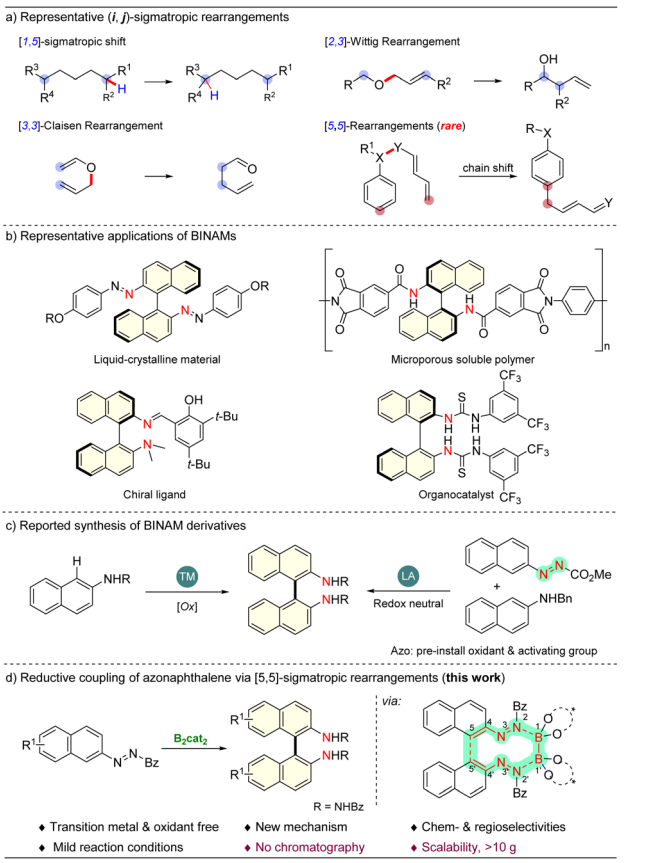

Fig. 1 BINAMs and their synthesis.

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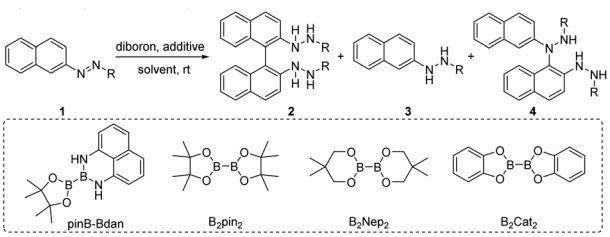
asymmetric catalysis and materials science (Fig. 1b).[10] Despite its significant synthetic utility, practical strategies to access this privileged scaffold remain limited. The oxidative coupling of aryl amines is a straightforward method for BINAM synthesis with good atom economy.[11] However, the intrinsic electronic nature of β-naphthylamine makes it susceptible to over-oxidation, leading to the formation of various oxidized intermediates, including hydroxylamine, nitroso, azo, and nitro compounds. Since Kocovsky's pioneering work,[12] a number of atroposelective strategies for the synthesis of BINAMs *via* transition metal-promoted oxidative coupling using Cu, Fe, or Rh appeared.[13] It is noteworthy that protective groups are often required, and subsequent removal of such groups may be problematic. An alternative approach for the synthesis of this privileged scaffold makes use of acid-catalyzed [3,3]-sigmatropic rearrangement of 1,2-dinaphthylhydrazine, which needs to be prepared by transition metal-promoted C–N coupling of the free arylhydrazine.[14,15] By pre-installing the azo as the internal oxidant and activating group and through chiral Lewis acid catalysis, Tan and co-workers developed a redox-neutral cross-coupling of azonaphthalene with β-naphthylamine for the synthesis of BINAM derivatives (Fig. 1c).[16] Given the broad applications of BINAM and its derivatives, there still exists a need for the development of an efficient approach for the synthesis of diverse BINAM scaffolds, ideally in a highly economical and sustainable manner.

In searching for a viable methodology for practical synthesis of BINAM, we turned our attention to diboron compounds,[17] which are tremendously useful in organic synthesis. By exploiting the Lewis acidity and oxidation potential of the diboron reagent, Westcott *et al.* synthesized racemic vicinal diamines through reductive coupling of imines.[18] Recently, Tang and co-workers accomplished enantioselective reductive coupling of isoquinolines[19] and imines[20] templated by chiral diborons. For the eventual creation of BINAM products, a suitable nitrogen-containing precursor needs to be chosen, and the exploitation of its Lewis base–Lewis acid interaction with diboron is critical for the reaction design. Azonaphthalene was thus selected for our studies. In our working hypothesis, we reasoned that the employment of a diboron reagent may trigger a [5,5]-sigmatropic rearrangement of azonaphthalene, providing a facile synthetic route to access BINAMs. In this reductive homocoupling strategy, the utilization of azonaphthalene as a substrate is crucial; the association of two molecules of azonaphthalenes with diboron is expected to create a ten-membered transition state, enabling the otherwise impossible [5,5]-sigmatropic rearrangement (Fig. 1d). An added advantage of the above design is that the oxidative potential of the substrate may be easily tuned through the installation of different electron-withdrawing groups on the azo moiety.[21] We indeed foresee a number of challenges in this design: (1) the direct reduction of unsaturated azo group may occur; (2) the complex regioselectivity issue resulting from other competing sigmatropic rearrangements. Herein, we document a reductive coupling of azonaphthalenes for the synthesis of BINAM derivatives *via* a diboron-enabled [5,5]-sigmatropic rearrangement.

To start our investigation, the reactions between β-azonaphthalene **1** and different diborons were examined (Table 1). In the presence of bis(catecholato)diboron (B_2cat_2), the effect of protective groups on the reaction was evaluated. The employment of an ester and a tosyl protecting group led to undesired [3,5]-sigmatropic rearrangement and direct reduction products, respectively (entries 1 and 2). When a benzoyl group was utilized, the desired [5,5]-sigmatropic rearrangement product and the undesired [3,5]-sigmatropic rearrangement product were obtained in a ratio of 1.2 to 1 (entry 3). Given the crucial role that a diboron has played as a template for the rearrangement, a number of other diboron reagents, *i.e.* B_2pin_2, B_2nep_2 and pinB-Bdan, were evaluated. However, none of these diborons provided sufficient activation for the desired [5,5]-sigmatropic rearrangement to take place (entries 4–6). We next conducted a solvent screening, which turned out to be a critical factor for the chemo-selectivity of the reaction (entries 7–10). Gratifyingly, by increasing the amount of B_2cat_2 to 1.1 equivalence, and running the reaction in 1,2-dimethoxyethane (DME), the desired [5,5]-sigmatropic rearrangement product was obtained in 73% yield, and the formation of other side products was not detected (entry 11). Subsequently, the effects of additives on the reaction were examined. Whereas water was found

Table 1 Optimization of the reaction conditions for the [5,5]-sigmatropic rearrangement[a]



Entry	R	Diboron	Solvent	Additive	Yield[b] (%) 2/3/4
1	CO_2Et	B_2cat_2	THF	—	0/0/87
2	Tosyl	B_2cat_2	THF	—	0/95/0
3	Bz	B_2cat_2	THF	—	40/0/34
4	Bz	B_2pin_2	THF	—	n.r.
5	Bz	B_2nep_2	THF	—	n.r.
6	Bz	pinB-Bdan	THF	—	n.r.
7	Bz	B_2cat_2	1,4-Dioxane	—	32/0/35
8	Bz	B_2cat_2	MTBE	—	44/0/32
9	Bz	B_2cat_2	DME	—	51/0/20
10	Bz	B_2cat_2	MeOH	—	0/70/30
11[c]	Bz	B_2cat_2	DME	—	73/0/0
12[c]	Bz	B_2cat_2	DME	H_2O	13/72/0
13[c]	Bz	B_2cat_2	DME	Cs_2CO_3	81/0/0
14[c]	Bz	B_2cat_2	DME	DMAP	81/0/0
15[c]	Bz	B_2cat_2	DME	2,6-diBrPy	89/0/0

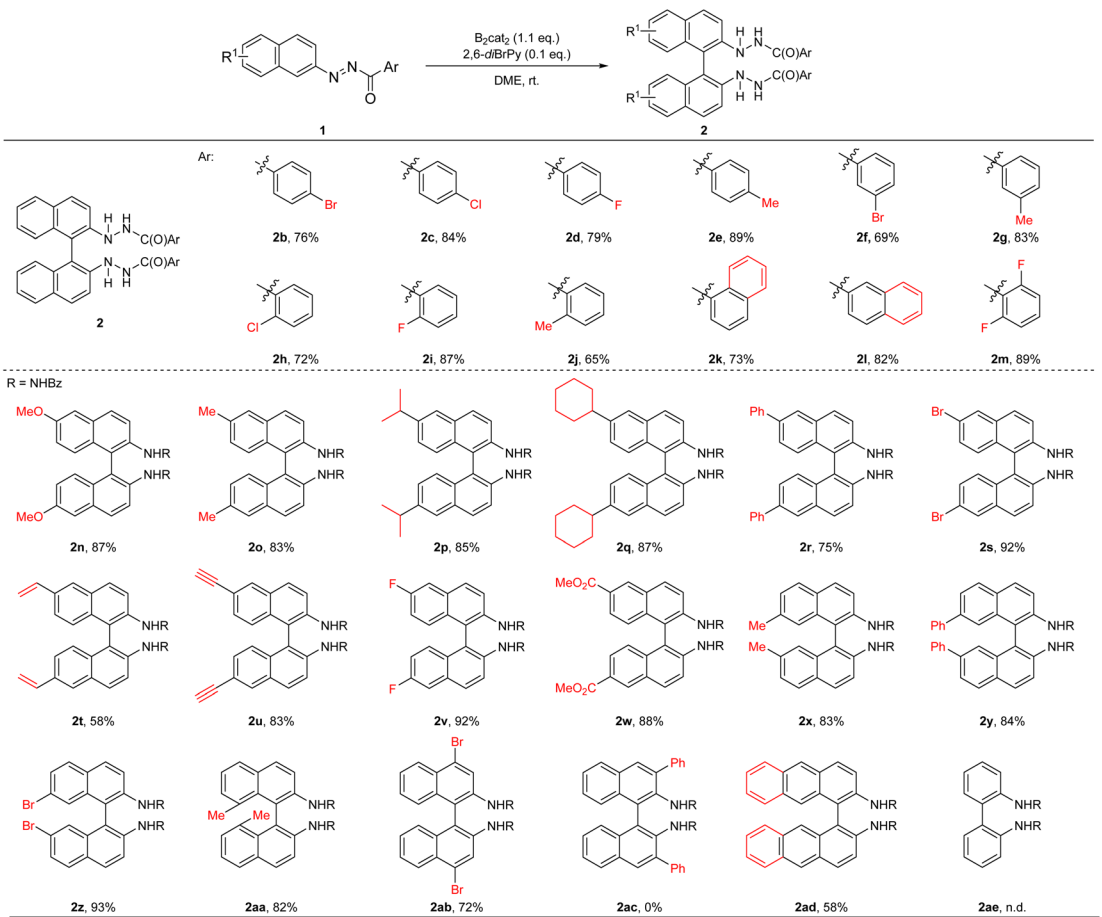
[a] Unless otherwise indicated, reactions were performed by employing azonaphthalene **1** (0.1 mmol), diboron (0.055 mmol), and additive (0.01 mmol) in the solvent specified (1.0 mL) at room temperature for 2 h. [b] Yields were determined by crude ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard, and the yield of **3** was calculated based on the use of 0.1 mmol azonaphthalene **1**. [c] 0.11 mmol of B_2cat_2 was used. n.r., no reaction.

to be detrimental (entry 12), the addition of Lewis bases such as Cs_2CO_3 or DMAP improved the reaction efficiency (entries 13 and 14). Finally, 2,6-dibromopyridine (2,6-diBrPy) was found to be best, and the sole [5,5]-sigmatropic rearrangement product was formed in an 89% yield (entry 15).

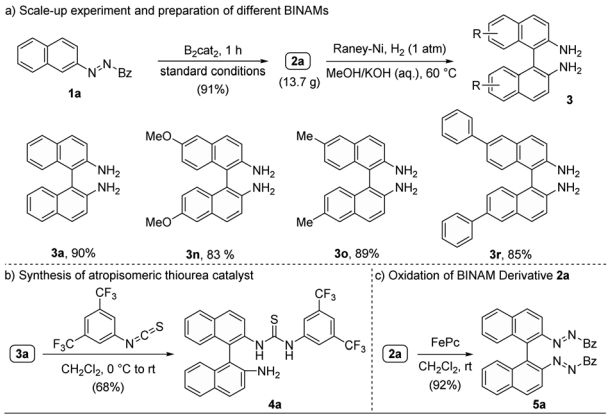
With the optimal conditions in hand, the reaction scope was next examined (Table 2). We first examined the flexibility of the aryl moieties in the benzoyl protective groups on the nitrogen atom of β-azonaphthalenes, and different halogen and methyl-substituted phenyl rings were all found to be suitable, regardless of the substitution patterns (**2b–2j**). Moreover, both α and β-naphthoyl groups, as well as the difluoro-substituted benzoyl group could be utilized (**2k–2m**). The reaction scope with regard to the β-azonaphthalenes was next evaluated. Electron-donating substituents such as methoxyl, methyl, isopropyl, and cyclohexyl at the 6-position of naphthalene were well tolerated (**2n–2q**). When 6-phenyl (**2r**), bromo (**2s**), or fluoro-(**2v**) substituted azonaphthalenes were utilized, the desired rearrangement products were obtained in high yields. Furthermore, naphthalene substrates bearing an alkenyl group (**2t**), an alkynyl substituent (**2u**), and an ester moiety (**2w**) at the 6-position were all found to be suitable. The substituents at the 7-position of azonaphthalenes could also be varied, including methyl (**2x**), phenyl (**2y**), and bromo (**2z**), and consistently high yields of the desired [5,5]-rearranged products were obtained. Azonaphthalene substrates containing a 4-, or 8-substituent were shown to be good substrates as well, forming the desired products in good yields. However, this [5,5]-sigmatropic rearrangement protocol is not applicable to C3-phenyl-substituted azonaphthalene (**2ac**). Despite extensive efforts, we were unable to obtain the desired product. We reasoned that the steric hindrance introduced by the bulky diboron and the substituent at the 3-position of naphthalene prevents the concerted [5,5]-sigmatropic rearrangement from taking place. Finally, azoanthracene and azobenzene were subjected to our standard reaction conditions; whereas the anthracene diamine was obtained in moderate yield (**2ad**), the formation of the biphenyl diamine derivative was not observed (**2ae**) as phenyl hydrazine was the dominant product. The structure of **2z** was unambiguously confirmed by X-ray crystallographic analysis.[22]

Synthetic applications of this [5,5]-sigmatropic rearrangement protocol are depicted in Scheme 1. A scale-up experiment

Table 2 Substrate scope[a]



[a] Reaction conditions: **1** (0.2 mmol), B_2cat_2 (0.22 mmol) and 2,6-dibromopyridine (0.02 mmol) in DME (2 mL) at room temperature for 2 h; n.d.: not detected.



Scheme 1 Gram-scale reaction and synthetic transformations. Reaction conditions: (a) **1a** (57.7 mmol), B_2cat_2 (63.5 mmol), 6-dibrPy (5.8 mmol) in DME (280 mL) at room temperature. (b) **2a** (0.1 mmol), 5 equiv. of KOH (2 M), Raney Ni (100 mg) in MeOH (1 mL), H_2 balloon (1 atm) at 60 °C. (c) **3a** (1 mmol), isothiocyanate (1 mmol) in CH_2Cl_2 (5 mL), 0 °C to room temperature. (d) **2a** (0.2 mmol), FePc (0.6 mmol) in CH_2Cl_2 (4 mL) at room temperature.

was carried out, and the desired rearranged product **2a** was obtained in 91% yield (13.7 g). The N–N bond was readily cleaved when treated with Raney-Ni, furnishing various BINAM structures in excellent yields (Scheme 1a). The operational simplicity of the protocol is worth highlighting; the reaction is typically completed within one hour, and purification requires only simple washing with methanol, and laborious chromatography is not needed. As an illustration, BINAM **3a** was readily converted to an atropisomeric primary amine thiourea catalyst **4a** (Scheme 1b).[10a] Given the importance of azo molecules in liquid crystal structures,[23] **2a** was oxidized to give azo-BINAM **5a** in excellent yield (Scheme 1c).

To gain insight into the reaction mechanism, we performed a number of control experiments for the reductive coupling of azonaphthalenes. The addition of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as a radical scavenger reduced both the rate and yield of the reaction. However, **2a** was isolated in a comparable yield when either diphenylethylene or BHT was introduced as a radical scavenger. These experiments suggested that the reaction does not proceed through a radical pathway. On the basis of the above experiments and related literature precedents on diboron-promoted reductive coupling,[19,20] a plausible mechanism is proposed. The concerted activation of two molecules of azonaphthalenes by B_2cat_2 *via* a Lewis base–Lewis acid interaction initiates a ten-membered transition state. Although the beneficial effects of adding 2,6-diBrPy is not entirely clear, we reason that it may serve as a base to facilitate the proton transfer during the rearomatization process. This proposal is similar to Tang's proposal on the concerted diboron activation of imines[19] and isoquinolines.[20] The subsequent [5,5]-sigmatropic rearrangement leads to the remote construction of the biaryl axis, forming a dearomatization intermediate. A rearomatization step then takes place to yield the desired thermodynamically stable BINAM derivative (Fig. 2).

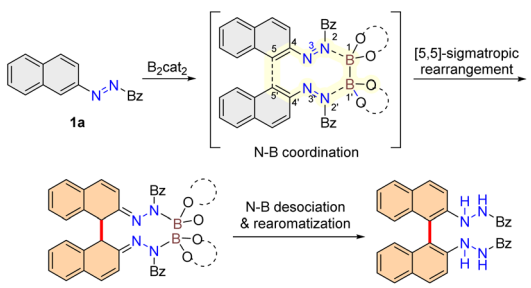


Fig. 2 Proposed reaction pathways.

Conclusion

In conclusion, we have successfully developed a reductive coupling of azonaphthalene for the synthesis of structurally diverse BINAMs. The key to the above process is the discovery of a diboron-enabled [5,5]-sigmatropic rearrangement, which concertedly activates two molecules of azonaphthalenes and creates the crucial axial bond of the BINAM derivatives in a single step reaction. The reported protocol is operationally simple, and offers practical synthesis of a class of important axial molecules. The novel [5,5]-sigmatropic rearrangement process we introduced offers new insight into the reaction development through structural reorganization of molecular architectures at remote sites.

Data availability

All experimental procedures, characterization, and copies of NMR spectra for all new compounds related to this article can be found in the ESI.†

Author contributions

L.-W. Q. and E. B. T. contributed equally to this work.

Conflicts of interest

There are no conflicts to declare.

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