C–N Bond Formation

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Cobalt- and Manganese-Catalyzed Direct Amination of Azoles under Mild Reaction Conditions and the Mechanistic Details**

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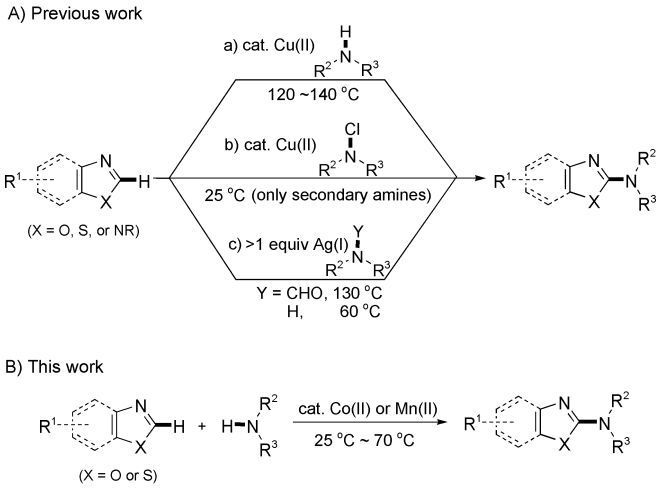
Transition metal catalyzed C–N bond formation is highly important in synthetic chemistry since it can lead to nitrogen-containing molecules that are of great interest in biological, pharmaceutical, and materials science.[1] A range of C–N bond-forming reactions have been reported utilizing organic (pseudo)halides such as aryl iodides, bromides, chlorides, triflates, and sulfonates reacting with amines or their precursors. In particular, since Ullmann and Goldberg pioneered the copper-mediated N-arylation of aryl halides,[2] Pd-, Cu-, and Rh-catalyzed C–N bond formation has been developed with suitable ligands.[3,4] Organometallic compounds including aryl boronic acids, stannanes, or siloxanes were also employed in the metal-mediated cross-couplings of amines.[2a,5] Despite the significant progress, only limited examples of direct C–N bond formation of unfunctionalized arenes or heterocyclic compounds with amines have been reported.[6] For instance, oxidative nitrenoid insertion of amido groups into double bonds or saturated C–H bonds were recently developed.[7] In addition, Pd- and Cu-catalyzed site-selective amination of directing-group-containing arenes has also been actively investigated.[8,9]

Since the elegant example of copper-catalyzed amidation of alkynes with amides by Stahl and co-workers,[10a] direct oxidative C–H amination of heteroarenes has been particularly scrutinized in recent years.[10b,11] For instance, Mori et al.,[12a] and Wang and Schreiber[12b] independently developed a copper-catalyzed amination and amidation of azoles, respectively, and they proceed under rather harsh reaction conditions (Scheme 1 A, a). More recently, Miura et al. successfully developed a new and milder catalytic protocol for azole amination using chloroamines instead of the parent amines albeit with a rather limited substrate scope with respect to the amine (Scheme 1 A, b).[13]

During the course of our studies on the metal-catalyzed C–H bond functionalization,[14] we found that C–N bond formation of azoles could be achieved with the use of either formamides or parent amines when a silver salt was employed in the presence of certain Brønsted acids (Scheme 1 A, c).[15]



Scheme 1. Transition-metal-mediated amination.

Although the substrate scope of the reaction turned out to be broad under relatively moderate conditions, the most critical disadvantage of our amination procedure was the use of stoichiometric amounts of a silver species; such amounts were required to "noncatalytically" oxidize the 2-aminoazolidine intermediates. This aspect has led us to search for a new catalytic amination reaction of azoles that employs amines under mild reaction conditions and has a broad substrate scope. Herein, we describe our efforts on the development of the new catalyst systems, and their mechanistic details are also presented (Scheme 1 B).

On the basis of the proposed mechanism of the silver-mediated amination of benzoxazoles,[15] we envisioned that stoichiometric amounts of a silver species could be replaced by other catalytic systems in either of two ways. Although regeneration of the +1 oxidation state of the silver species, probably by using an external oxidant, from Ag^0 [16] after the amination reaction would be the most straightforward route, our extensive efforts for this approach were unsuccessful (Table 1, entries 1–3).

This led us to search for another procedure wherein transition metals other than Ag salts were employed as a catalyst in combination with suitable oxidants. We were pleased to find that certain transition-metal species can catalyze the azole amination when they are used in combination with proper oxidants and Brønsted acids. For example, cobalt(II) acetate (2 mol%) efficiently catalyzed the amination reaction of benzoxazole to afford the desired 2-aminated product in high yield when aqueous *tert*-butyl hydroperoxide solution (T-HYDRO) was employed in the presence of a benzoic acid additive (1.2 equiv of each relative to morpho-

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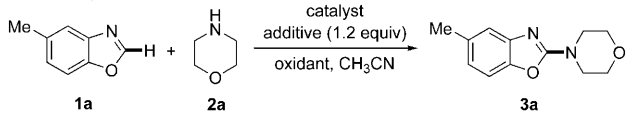
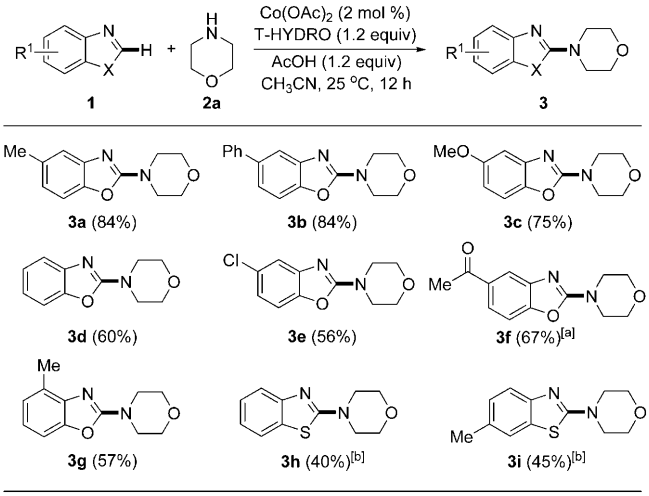
Table 1: Optimization of reaction conditions.[a]



1a 2a 3a

Entry	Catalyst (mol%)	Oxidant	Additive	T [°C]	Yield [%][b]
1	Ag_2CO_3 (120)	–	$PhCO_2H$	60	92
2	Ag_2CO_3 (10)	–	$PhCO_2H$	60	6
3	Ag_2CO_3 (10)	T-HYDRO[d]	$PhCO_2H$	60	8
4	$Co(OAc)_2$ (2)	T-HYDRO	$PhCO_2H$	60	85
5	$Co(OAc)_2$ (2)	–	$PhCO_2H$	60	4
6	$Co(OAc)_2$ (2)	T-HYDRO	–	60	19
7	–	T-HYDRO	$PhCO_2H$	60	12
8	$Co(acac)_3$ (10)	T-HYDRO	$PhCO_2H$	60	44
9	$Co(OAc)_2$ (2)	*t*BuOOH	$PhCO_2H$	60	70
10	$Co(OAc)_2$ (2)	BzOO*t*Bu	$PhCO_2H$	60	10
11	$Co(OAc)_2$ (2)	H_2O_2	$PhCO_2H$	60	13
12	$Co(OAc)_2$ (2)	T-HYDRO	$PhCO_2H$	25	68
13[c]	**$Co(OAc)_2$ (2)**	**T-HYDRO**	**AcOH**	**25**	**84**
14	$Mn(OAc)_2$ (10)	T-HYDRO	$PhCO_2H$	25	43
15	$Fe(OAc)_2$ (10)	T-HYDRO	$PhCO_2H$	25	47

[a] Reaction conditions: **1a** (1.2 equiv), **2a** (0.5 mmol), acid (1.2 equiv), peroxide (1.2 equiv), catalyst in CH_3CN (1 mL) for 12 h. [b] Yield based on NMR spectroscopy. [c] The reaction was carried out with 0.5 mmol of **1a** and 1.2 equiv of **2a**. [d] T-HYDRO is the trademark name for 70 wt% *t*BuOOH in H_2O. acac = acetylacetonate.



Scheme 2. Direct amination of azoles. Reaction conditions: **1** (0.5 mmol), **2a** (1.2 equiv), $Co(OAc)_2$ (2 mol%), T-HYDRO (1.2 equiv), AcOH (1.2 equiv) in CH_3CN (1 mL) at 25°C for 12 h under air (yield of isolated products). [a] Used 5 mol% of $Co(OAc)_2$ and 2.0 equiv of AcOH relative to **1**. [b] **1** (2 equiv), **2a** (0.5 mmol), $Co(OAc)_2$ (10 mol%), BzOO*t*Bu (1.1 equiv), $Zn(OAc)_2$ (5 mol%) in CH_3CN (1 mL) at 70°C for 12 h under O_2. Bz = benzoyl.

line; Table 1, entry 4). In fact, it was previously known that some cobalt, manganese, and iron complexes readily react with alkyl peroxides to generate organic radical species which exhibit high activity as an oxidizing agent.[17,18]

Importantly, in the absence of either of the reagents, metal species, oxidant, or Brønsted acid, the reaction efficiency was significantly decreased (Table 1, entries 5–7). Cobalt species other than $Co(OAc)_2$ exhibited reduced catalytic activity (Table 1, entry 8). The choice of oxidants and acid additives turned out to be crucial for the reaction efficiency, and T-HYDRO was the most effective among various oxidants investigated (Table 1, entries 9–11). The amination reaction could even be carried out at room temperature (Table 1, entry 12), thus affording an excellent product yield especially when acetic acid was employed as an additive (Table 1, entry 13). Although manganese or iron species can also facilitate this transformation, the reaction efficiency was slightly lower compared to that of cobalt catalyst (Table 1, entries 14 and 15).

To explore the substrate scope, we examined a range of azole derivatives in the coupling reaction with morpholine (**2a**) under the optimized reaction conditions (Scheme 2). It was observed that electronic variation of the substituents at the 5-position of benzoxazole did not significantly affect the reaction efficiency. In fact, 2-aminated products of benzoxazoles substituted with a 5-methyl (**3a**), 5-phenyl (**3b**), and 5-methoxy (**3c**) group were obtained in satisfactory yields at room temperature. Unsubstituted benzoxazole smoothly reacted with morpholine to provide the desired product **3d**. Benzoxazoles bearing electron-withdrawing groups such as chloride or acetyl could also be employed as facile substrates that provided the corresponding products (**3e** and **3f**, respectively) in acceptable yields at ambient temperature.

Not only 2-aminobenzoxazoles bearing substituents at the 5-position but also one substituted at the 4-position was readily obtained (**3g**). In the case of benzothiazole, the desired aminated product **3h** was obtained in moderate yield when *tert*-butyl peroxybenzoate was employed instead of T-HYDRO in the presence of catalytic amounts of zinc(II) acetate as an additive at higher temperatures under an O_2 atmosphere.[19] Likewise, a reaction of 6-methylbenzothiazole afforded the 2-aminated product **3i** in a slightly higher yield under the same reaction conditions.

We next examined the scope of the amine reactant in the cobalt-catalyzed amination of benzoxazoles (Scheme 3). Cyclic amines were readily employed for this reaction. For instance, benzoxazoles bearing cyclic amino groups such as morpholinyl (Scheme 2) and piperidinyl (**4a**), as well as piperazinyl (**4b**) could be isolated in good yields. It should be mentioned that important functional groups such as *N*-Boc (**4b**) were completely tolerated under the present reaction conditions. Acyclic secondary amines such as diallyl amine or benzylmethyl amine were smoothly reacted to give the corresponding products in high yields (**4c** and **4d**, respectively). Notably, the amination reaction can be easily carried out in a gram scale without difficulty, thereby delivering **4d** in excellent yield. Interestingly, an amine bearing a propargylic moiety was tolerated under the present reaction conditions (**4e**). Dialkylamine was readily employed in the coupling reaction with 5-chlorobenzoxazole albeit at a slightly higher temperature (**4f**).

In sharp contrast to the above results with secondary amines, no desired products were obtained when primary amines or ammonia were employed under the cobalt-catalyzed reaction conditions (e.g., **4g** or **4h**). Thus, we turned our attention to other catalytic systems especially those based on manganese or iron species as they were also

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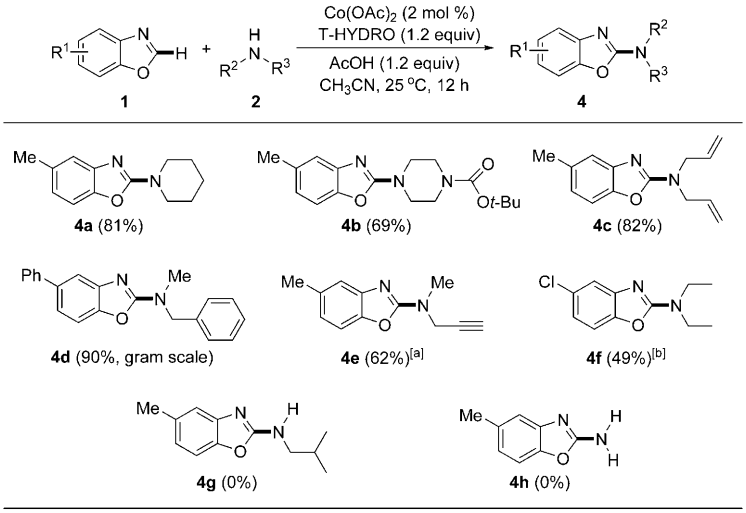
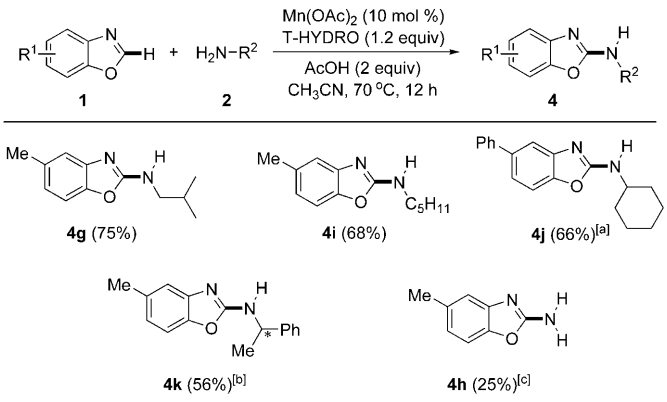


Scheme 3. Amination of benzoxazoles with various amines. Reaction conditions: **1** (0.5 mmol), **2** (1.2 equiv), $Co(OAc)_2$ (2 mol%), T-HYDRO (1.2 equiv), AcOH (1.2 equiv) in CH_3CN (1 mL) at 25°C for 12 h (isolated yields). [a] Used 5 mol% of $Co(OAc)_2$. [b] Carried out at 40°C.

effective in the preliminary screening albeit with lower efficiency (Table 1, entries 14–15) when compared to the cobalt catalyst system.

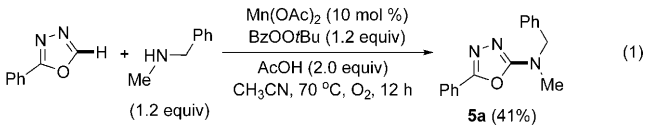
To our delight, we found that the amination efficiency in the reaction with primary amines was significantly improved upon the replacement of cobalt(II) acetate catalyst with manganese(II) acetate (Scheme 4). Although a higher reaction temperature (70°C) was required to achieve satisfactory product yields, the manganese catalyst system was efficient enough to include various types of amine reactants. For instance, 2-aminobenzoxazole derivatives substituted with *N*-isobutyl (**4g**), *n*-pentyl (**4i**), and cyclohexyl (**4j**) groups were easily obtained. Notably, an optically active primary amine was directly introduced at the 2-position of benzoxazoles without racemization (**4k**). Notably, aqueous ammonia can undergo the amination to afford the 2-aminobenzoxazole derivative **4h** albeit in low yield at the present stage.

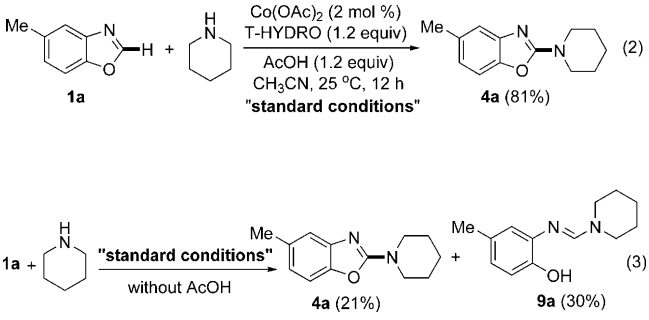


Scheme 4. Manganese-catalyzed amination of benzoxazoles with primary amines. Reaction conditions: **1** (1.2 equiv), **2** (0.5 mmol), Mn(OAc)$_2$ (10 mol%), T-HYDRO (1.2 equiv), AcOH (2.0 equiv) in CH_3CN (1 mL) at 70°C for 12 h (yield of isolated products). [a] Used 2 mol% of $Mn(OAc)_2$. [b] The enantiomeric excess (*ee*) of both the amine and product were determined to be 96%. [c] Aqueous ammonia solution (28%, 0.5 mmol) was used in the presence of anisic acid (1.2 equiv) instead of AcOH.

In addition, the amination reaction took place smoothly with oxadiazoles under the manganese catalyst system using *tert*-butyl peroxybenzoate [Eq. (1)].[20] This result is significant in that the substrate scope can be extended to not only fused heteroarenes but also to a monomeric heterocycle to give the corresponding aminated product **5a**, which is an important pharmacophore exhibiting a broad spectrum of biological activity.[21]

During the course of the present study, it was observed that the ring-opened amidine species **9a** was also generated along with the desired amination product **4a** when the reaction was carried out in the absence of an acid additive [Eq. (2) versus Eq. (3)]. Under the standard reaction conditions applied for the optimized amination, no trace of the amidine **9a** was detected in the crude reaction mixture, and only **4a** was obtained in high yield [Eq. (2)]. This result suggests the possibility that the ring-opening process might be involved during the course of the amination reaction, thus giving a "nonproductive" intermediate amidine species.





In fact, when the ring-opened amidine **9a** was subjected to our standard amination conditions, a full conversion was attained within 1 hour at room temperature to afford a similar mixture of benzoxazole **1a** and its 2-aminated product **4a** [Eq. (4)]. Interestingly, when the same transformation was tried in the absence of cobalt catalyst, lower conversion was observed leading to only 38% yield of the benzoxazole **1a**, but no aminated compound **4a** was produced [Eq. (5)]. In addition, the absence of an external oxidant (T-HYDRO) resulted in no formation of **4a** [Eq. (6)].

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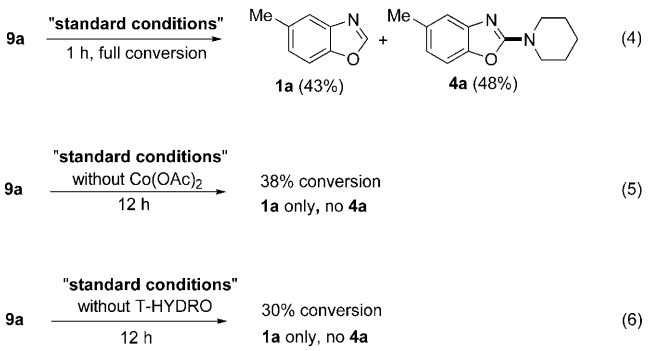
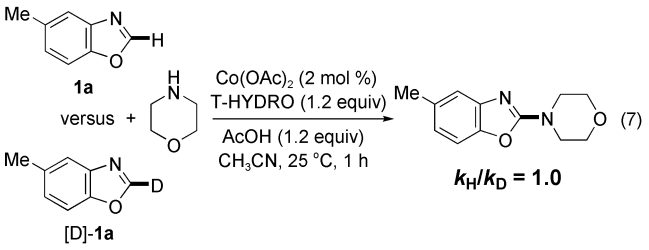
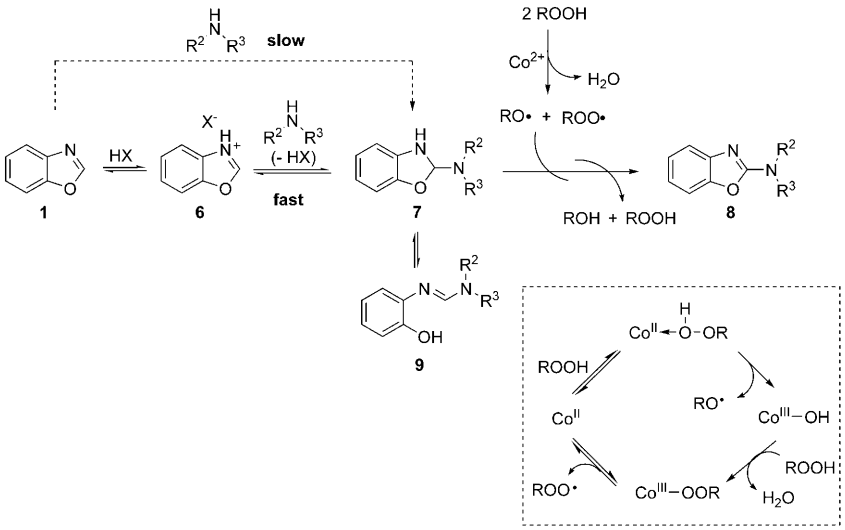


These experiments suggest that 2-aminoazole products are generated most efficiently by the combined action of the cobalt catalyst, oxidant, and acid additive. In addition, poor product yields obtained from the reaction of certain azoles and amines can be attributed to the formation of stable ring-opened amidine compounds.

A competition experiment between **1a** and its deuterated derivative at the 2-position ([D]-**1a**) was next performed to identify any kinetic isotope effects [Eq. (7)].[22] It was observed that the amination reaction does not exhibit kinetic isotope effects ($k_H/k_D = 1.0$), which may imply that the C–H bond cleavage at the C2 position of benzoxazoles is not involved in the rate-determining step in the overall catalytic processes.



On the basis of the above mechanistic clues and data, a plausible pathway of the cobalt-catalyzed amination reaction is proposed in Scheme 5. It is believed that an acid additive initially protonates the heteroarene **1** to provide the salt **6** which is more electrophilic than **1**, thus enabling the subsequent nucleophilic attack of amine to be more facile. In contrast, direct amine addition to the neutral benzoxazole **1** rather than its protonated species **6** can also be possible albeit at a slower rate. It is now presumed that the adduct **7** is in equilibrium with its ring-opened amidine species **9**, and the extent of which is dependent upon the type of heteroarenes and amine reactants. In this context, it is assumed that 2-aminobenzoxazolidine **7** derived from the addition of primary amines or ammonia is more prone to open leading to its amidines, thus resulting in lower product yields compared to the amination reaction with secondary amines.



Scheme 5. A proposed pathways of the cobalt-catalyzed amination of azoles.

It is postulated that a metal catalysis is operative in the rearomatization step of the putative 2-aminobenzoxazolidine intermediate **7**. Indeed, it is known that two radical species, alkoxy RO• and alkylperoxy ROO•, are generated, in addition to water, from two molecules of alkylhydroperoxides upon the action of cobalt or manganese species.[17,18] As a result, it is reasonable to propose that the in situ formed alkoxy and alkylperoxy radicals abstract two hydrogen atoms, one each, from the putative intermediate **7** to produce 2-aminobenzoxazole **8**.[23,24]

In summary, we have developed a new catalytic system for the direct amination of azoles with amines by using cobalt or manganese catalyst in the presence of peroxide and acid additive. The reaction is highly attractive from the synthetic point of view in that the catalyst loadings are low, optimal reaction conditions are mild, and substrate scope is broad. In addition, a mechanistic proposal is made on the basis of the kinetic isotope effects and isolation of amidine compounds. The present reaction, therefore, is anticipated to be a powerful tool for the synthesis of 2-aminoazoles which are an important pharmacophore of high biological activity.

Experimental Section

Representative procedure: A test tube equipped with a magnetic stir bar was charged with 5-methylbenzoxazole (0.5 mmol, 1.0 equiv), $Co(OAc)_2$ (0.01 mmol, 2 mol%), T-HYDRO (0.6 mmol, 1.2 equiv), acetic acid (0.6 mmol, 1.2 equiv), and morpholine (0.6 mmol, 1.2 equiv) in acetonitrile (1.0 mL) under air. The test tube was sealed with a rubber septum and stirred for 12 h at 25 °C under air. The crude mixture was filtered through a plug of celite and washed with dichloromethane (15 mL). The filtrate was washed with a saturated solution of $NaHCO_3$ (3×15 mL) and the aqueous layer was extracted again with dichloromethane (3×15 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by column

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chromatography on silica gel (*n*-hexane/EtOAc = 1:1) to afford 2-(4-morpholinyl)-5-methylbenzoxazole (**3a**, 84%)

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[22] See the Supporting Information for details.

[23] Analogous to the putative 2-aminobenzoxazolidine intermediate **7**, oxidation of carbinolamine or hemiacetal species by metal/peroxide oxidant systems has been invoked for the oxidative amidation or esterification of aldehydes with amines or alcohols: a) R. Gopinath, B. K. Patel, *Org. Lett.* **2000**, *2*, 577; b) W.-J. Yoo, C.-J. Li, *J. Am. Chem. Soc.* **2006**, *128*, 13064; c) K. Ekoue-Kovi, C. Wolf, *Org. Lett.* **2007**, *9*, 3429.

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