Research Article

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Synergistic promoting effect of ball milling and Fe(II) catalysis for cross-dehydrogenative-coupling of 1,4-benzoxazinones with indoles

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Abstract: In this work, a novel C(sp^3)–C(sp^2) cross-dehydrogenative-coupling method is developed to react benzoxazin-2-one derivatives with various indoles. As a result, combined use of ball milling and Fe(II) catalysis leads to rapid coupling of 1,4-benzoxazinones with derivatives of indole. Under the conditions, derivatives of **1** couple with various indoles at room temperature to produce good yields of the desired compounds within 0.5–2 h time period. Thus, derivatives of both starting materials couple smoothly under relatively mild conditions to give good yields of **3**.

Keywords: ball mill, benzoxazinones, CDC reactions, heterocycles

1 Introduction

Implementation of environmentally compatible protocols has received tremendous attention from organic chemists in recent decades [1]. This policy has been mainly involved with the use of fewer chemicals [2] and safer sources of energy [3], leading to overwhelming growth in the development of sustainable chemistry [4]. An outstanding approach in designing green synthetic procedures has been connected with the use of non-conventional methods for the activation of functional groups employing microwave [5–7], ultrasound [8,9], and ball milling [10], resulting in numerous interesting clean synthetic procedures with increased activities and selectivities [11]. Among these new techniques, ball milling, causing mechanical grinding of solid reactants, has witnessed a rapid growth in developing new procedures for diverse synthetic transformations [12].

One important approach for rapid and selective combination of smaller molecules into complex target products is direct cross-dehydrogenative-coupling (CDC) reaction [13,14]. The approach is applicable to both carbon–carbon (C–C) [15–19] and carbon–heteroatom (C–X) [20–26] bond formation reactions and has found many applications in organic synthesis [13]. An interesting point about CDC reactions is that they can be conveniently used for the oxidation of amines [27–29]. Moreover, in CDC reactions preliminary operations to prepare starting materials with appropriate carbon–metal bonds and carbon-leaving groups are unnecessary [30–35]. These privileges have led to many practical applications of CDC reactions in the synthesis of natural products [14,36–40] and compounds with interesting biochemical properties [41].

An important structural motif that occurred in the skeleton of bioactive molecules is 1,4-benzoxazinone [42]. These compounds can also be used as reactive intermediates for the preparation of other molecules of choice with biomedical applications through derivatization of the carbon atom adjacent to the amine group of the benzoxazinone moiety [43]. A few synthetic and natural examples of such molecules are shown in Figure 1 [43–46]. Although the method is very convenient, scattered investigations are performed till now. Separate CDC-based studies by Huo et al. [47], Zhang et al. [41], and Sharifi et al. [48] groups can serve as the examples. Despite that these methods introduce working procedures to access new 4-benzoxazin-2-one derivatives, there is still a need to develop a more environmentally safe benign methods.

We have previously carried out investigations to design environmentally friendly synthetic methods [49,50]. Following that, we would like to report a new procedure exposing the synergistic effect rising from the combined use of ball milling and Lewis acid. This combination promotes convenient synthesis of a diverse series of 1,4-benzoxazinone

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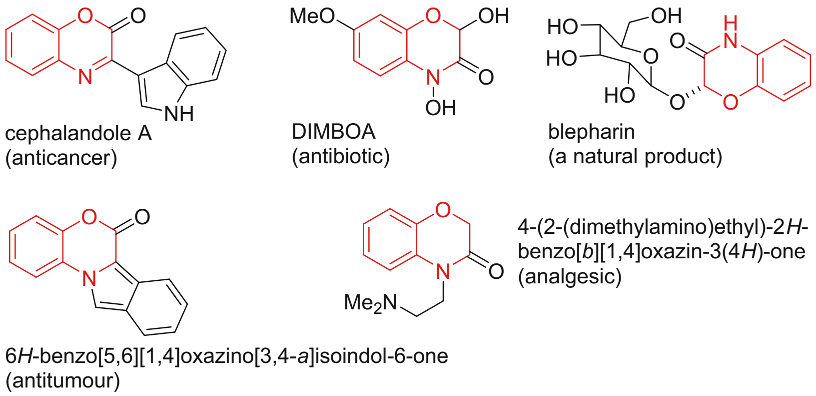


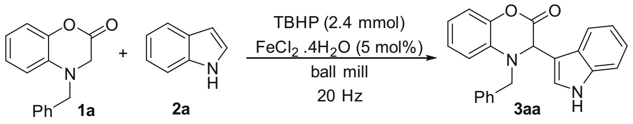
Figure 1: Some important 1,4-benzoxazinone structures.

structures at ambient temperature, as illustrated in Scheme 1 for the reaction between benzoxazinones and 1*H*-indole derivatives.

2 Results and discussion

We first optimized the reaction for the synthesis of **3aa** by evaluating the coupling of **1a** with parent 2*H*-indole **2a** under various sets of conditions (Table 1). The best results were obtained when a solvent-free mixture of the two reactants (1.0:1.2) and *tert*-butyl hydroperoxide (TBHP) was shaken at 20 Hz in an oscillatory ball mill apparatus in the presence of catalytic amounts (5 mol%) of $FeCl_2{\cdot}4H_2O$, leading to 91% formation of **3aa** after 3 h (entry 1). When the reaction was conducted under the conditions reported by Huo et al. [47], only 55% formation of **3aa** was noticed after 1 h (entry 2), and even longer reaction times up to 3 h did not improve the yield. Use of other amounts of the catalyst did not lead to better outcomes (entries 3–6). Variation in the oxidant quantity could not improve the results as well (entries 7 and 8). Similarly, the results with other catalysts (entries 9–17) were in favor of using $FeCl_2{\cdot}4H_2O$ as the best catalyst.

With the optimization results in hand, we then evaluated the scope of the reaction by allowing various derivatives of **1** to couple with 2*H*-indoles **2** (Scheme 2). As a result, reaction of **1a** with the parent 1*H*-indole **2a** or its various *N*-substituted derivatives gave high yields of **3aa**–**3ad** products within 3–6 h. Similarly, reactions with **2e**–**f**, having methyl or phenyl substitutions at position 2, behaved equally well and produced **3ae**–**af**. This was also the case for the reactions of **1a** with other indoles (**2g**–**i**) possessing various substitutions at other positions. Alternatively, when **1a** was reacted with double substituted indoles (**2j**–**l**), the respective products were obtained within 3–6 h. Finally, reactions of **1b**–**d** with **2a** were successful to further show the generality of the method.



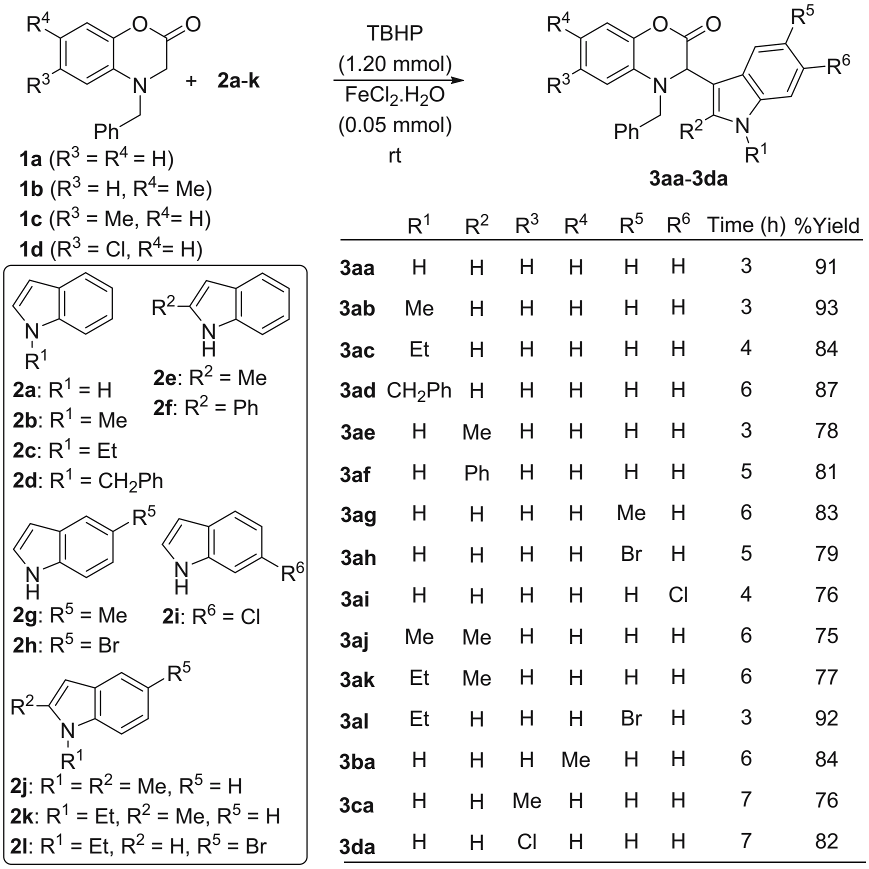
Scheme 1: Typical synthesis of **3aa**.

Based on the results, an iron catalyzed mechanism can be proposed for the reaction, as is shown in Scheme 3 for the formation of **3aa**. TBHP is initially reduced by Fe(II)

Table 1: Optimization of the conditions for the synthesis of **3aa**

Entry	TBHP (equiv.)	Catalyst (mol%)	Yield (%)[a]
1	2.4	$FeCl_2{\cdot}4H_2O$ (5)[b]	91
2	2.4	$FeCl_2{\cdot}4H_2O$ (5)[c]	55
3	2.4	$FeCl_2{\cdot}4H_2O$ (1)[b]	57
4	2.4	$FeCl_2{\cdot}4H_2O$ (3)[b]	65
5	2.4	$FeCl_2{\cdot}4H_2O$ (7)[b]	91
6	2.4	$FeCl_2{\cdot}4H_2O$ (10)[b]	91
7	1.2	$FeCl_2{\cdot}4H_2O$ (5)[b]	70
8	3.6	$FeCl_2{\cdot}4H_2O$ (5)[b]	30
9	2.4	$CuBr_2$ (5)[b]	75
10	2.4	CuBr (5)[b]	50
11	2.4	CuCl (5)[b]	50
12	2.4	$CuCl_2$ (5)[b]	20
13	2.4	$FeCl_3$ (5)[b]	25
14	2.4	$ZnCl_2$ (5)[b]	50
15	2.4	$Cu(NO_3)_2{\cdot}3H_2O$ (5)[b]	65
16	2.4	$Cu(OAc)_2{\cdot}H_2O$ (5)[b]	40
17	2.4	$CoCl_2{\cdot}6H_2O$ (5)[b]	65

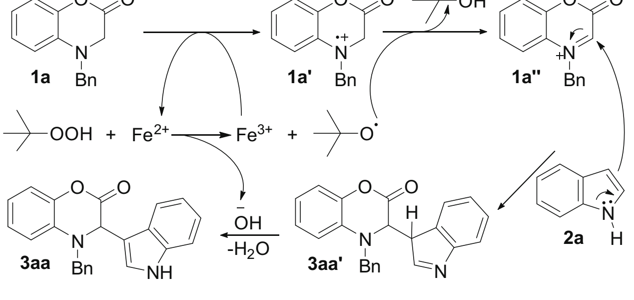
[a] Isolated yields. [b] Ball mill, 20 Hz. [c] MeCN (10 mL), mixing at room temperature.



	R^1	R^2	R^3	R^4	R^5	R^6	Time (h)	%Yield
3aa	H	H	H	H	H	H	3	91
3ab	Me	H	H	H	H	H	3	93
3ac	Et	H	H	H	H	H	4	84
3ad	CH_2Ph	H	H	H	H	H	6	87
3ae	H	Me	H	H	H	H	3	78
3af	H	Ph	H	H	H	H	5	81
3ag	H	H	H	H	Me	H	6	83
3ah	H	H	H	H	Br	H	5	79
3ai	H	H	H	H	H	Cl	4	76
3aj	Me	Me	H	H	H	H	6	75
3ak	Et	Me	H	H	H	H	6	77
3al	Et	H	H	H	Br	H	3	92
3ba	H	H	H	Me	H	H	6	84
3ca	H	H	Me	H	H	H	7	76
3da	H	H	Cl	H	H	H	7	82

Scheme 2: One-pot synthesis of various derivatives of **3**.

ions to produce *tert*-butoxide radicals and Fe(III) ions. Fe (II) ions are regenerated by oxidizing **1a** to its respective cation-radical **1a′**. This cation-radical is further oxidized by *tert*-butoxide radicals to the intermediate imminium **1a″**. Finally, nucleophilic attack of **2a** on **1a″** and rearomatization of the indole ring (in **3aa′**) give the target product **3aa**. This mechanism was supported by showing that the reaction is halted when a radical scavenger is used. In the presence of (2,2,6,6-tetramethylpiperidin-1-yl)-oxyl, no **3aa** was detected and the staring materials were recovered. This suggests that the process might go via a radical pathway.



Scheme 3: Plausible mechanism for the reaction.

3 Conclusion

In summary, we have developed an efficient method to couple indoles with 1,4-benzoxazinone derivatives at ambient temperature. As a result, high yield synthesis of indolyl-benzoxazin-2-one derivatives was achieved, where chemoselective formation of the target products was observed within 3–7 h. The reaction was solvent-free, the catalyst is inexpensive and was used in minimum quantities, and a diverse array of reactants could be used under the conditions.

4 Experimental

Reactions were monitored by thin layer chromatography using silica gel-coated plates and hexane/EtOAc solutions as the eluent. Melting points (MPs) are uncorrected. Fourier-transform infrared spectroscopy spectra are recorded using KBr disks on a Bruker Vector-22 infrared spectrometer and absorptions are reported as wave numbers (cm^{-1}). ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra are obtained on an FT-NMR Bruker Ultra Shield™ instrument as $CDCl_3$ solutions and the chemical shifts are expressed as δ units using Me_4Si as the internal standard. Mass spectra are obtained on a Finnigan Mat 8430 apparatus at an ionization potential of 70 eV. Elemental analyses are performed using a Thermo Finnigan Flash EA 1112 instrument. Reagents and starting materials are purchased from commercial sources and are freshly used after being purified by standard procedures. For ball milling conditions, reactions were carried out in a Retsch® Mixer Mills MM 200. The identities of the known products (**3aa**, **3ab**, **3ad**–**j**, and **3ba**–**3da**) are confirmed by the comparison of their MPs and their ^1H NMR data with those reported in the literature [47,48]. New products (**3ac**, **3al**, and **3ak**) are characterized by their ^1H NMR, ^{13}C NMR, IR, and mass spectra, and their purity are confirmed by elemental analyses.

4.1 Typical procedure for the synthesis of 3aa

A 5.0 mL of stainless steel vial was charged with **1a** (0.24 g, 1.0 mmol), 1*H*-indole (**2a**, 0.15 g, 1.2 mmol), $FeCl_2{\cdot}4H_2O$ (0.01 g, 5 mol%), TBHP (0.3 g, 2.4 mmol), and a 10 mm stainless steel ball. The mixture was capped and shaken at 20 Hz in an oscillatory ball mill apparatus for 3 h. The mixture was extracted with EtOAc (10 mL), the extract was washed with water (15 mL) and dried over Na_2SO_4, and the volatile portion was removed under reduced pressure. The residue was fractionated by column chromatography using hexane/EtOAc (10:1) as the eluent to obtain **3aa** (0.33 g, 91%).

4.2 Spectral data of new products

4.2.1 4-Benzyl-3-(1-ethyl-1*H*-indol-3-yl)-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-one (3ac)

MP: 158–160°C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 1H), 7.41–7.31 (m, 6H), 7.29–7.24 (m, 1H), 7.20–7.08 (m, 3H), 6.95 (t, J = 8.0 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 6.68 (s, 1H), 5.44 (s, 1H), 4.64 (d, J = 15.0 Hz, 1H), 4.19 (d, J = 15.0 Hz, 1H), 4.08 (q, J = 7.0 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 141.9, 136.3, 135.7, 134.2, 128.8, 127.8, 127.7, 126.9, 125.6, 125.3, 122.2, 120.0, 119.8, 119.3, 116.5, 113.9, 109.5, 107.2, 55.9, 51.5, 41.1, 15.2; IR (KBr, cm^{-1}) 2,977, 1,765, 1,501, 741; MS (70 eV) *m*/*z* (%) 382, 354, 263, 185, 157, 91, 65; anal. calcd for $C_{25}H_{22}N_2O_2$: C, 78.51; H, 5.80; N, 7.32. Found: C, 78.40; H, 5.89; N, 7.58.

4.2.2 4-Benzyl-3-(5-bromo-1-ethyl-1*H*-indol-3-yl)-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-one (3al)

MP: 162–164°C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.33–7.43 (m, 3H), 7.33–7.26 (m, 3H), 7.19–7.10 (m, 3H), 6.97 (t, J = 8.0 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.65 (s, 1H), 5.32 (s, 1H), 4.63 (d, J = 14.5 Hz, 1H), 4.08 (d, J = 14.5 Hz, 1H), 3.99 (q, J = 7.5 Hz, 2H), 1.33 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 141.9, 135.9, 134.4, 134.1, 128.9, 128.5, 128.0, 127.9, 126.6, 125.5, 125.1, 122.0, 120.1, 116.6, 114.1, 113.4, 111.0, 106.9, 55.4, 51.5, 41.3, 15.2; IR (KBr, cm^{-1}) 2,923, 1,763, 1,500, 1,198; MS (70 eV) *m*/*z* (%) 461, 462, 463, 432, 341, 247, 128, 91, 65; anal. calcd for $C_{25}H_{21}BrN_2O_2$: C, 65.08; H, 4.59; N, 6.07. Found: C, 65.15; H, 4.66; N, 5.90.

4.2.3 4-Benzyl-3-(1-ethyl-2-methyl-1*H*-indol-3-yl)-3,4-dihydro-2*H*-benzo[b][1,4]oxazin-2-one (3ak)

MP: 81–100°C; ^1H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, J = 7.2 Hz, 3H), 2.07 (s, 3H), 3.99 (d, J = 16.2 Hz, 1H), 4.03–4.18 (m, 2H), 4.60 (d, J = 16.2 Hz, 1H), 5.39 (s, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.9 (t, J = 7.7 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.8 Hz, 1H), 7.11–7.15 (m, 3H), 7.15–7.21 (m, 2H), 7.24–7.31 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 140.6, 136.8, 136.2, 135.7, 134.7, 128.6, 127.2, 127.1, 126.0, 125.5, 121.2, 119.8, 119.0, 118.7, 116.9, 113.1, 109.0, 105.3, 56.0, 49.9, 37.9, 15.1, 9.9; IR (KBr, cm^{-1}) 2,979, 1,763, 1,499, 1,281; MS (70 eV) *m*/*z* (%); 398, 397, 278, 330, 278, 199, 143, 91, 65; anal. calcd for $C_{26}H_{24}N_2O_2$: C, 78.76; H, 6.10; N, 7.07. Found: C, 78.85; H, 6.15; N, 7.01.

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Conflict of interest: Authors state no conflict of interest.

Data availability statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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