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Ruthenium-Catalyzed Synthesis of Benzoxazoles Using Acceptorless Dehydrogenative Coupling Reaction of Primary Alcohols with 2-Aminophenol under Heterogeneous Conditions

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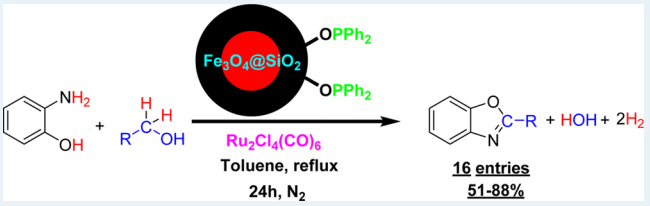
Supporting Information

ABSTRACT: An efficient ruthenium-catalyzed acceptorless dehydrogenative coupling reaction of primary alcohols with 2-aminophenol for one-pot synthesis of benzoxazoles is introduced. The phosphine-functionalized magnetic nanoparticles (PFMNPs; Fe_3O_4@SiO_2@PPh_2) as a magnetic recyclable phosphorus ligand in the presence of $Ru_2Cl_4(CO)_6$ was found to be an efficient heterogeneous catalytic system for promotion of the designed protocol. The reaction was carried out efficiently with a variety of substrates to give the corresponding products in moderate to good yields.



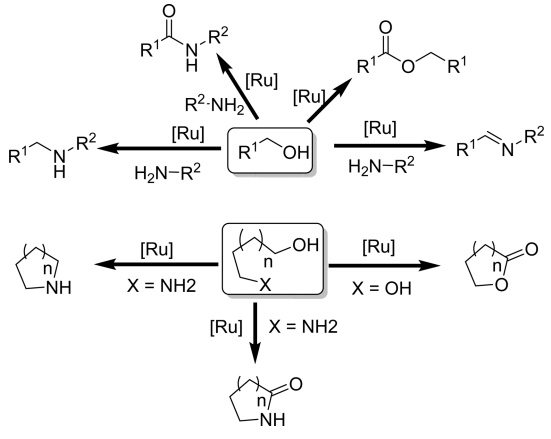
KEYWORDS: *ruthenium, benzoxazoles, acceptorless dehydrogenative coupling (ADC) reaction, alcohols, 2-aminophenol*

INTRODUCTION

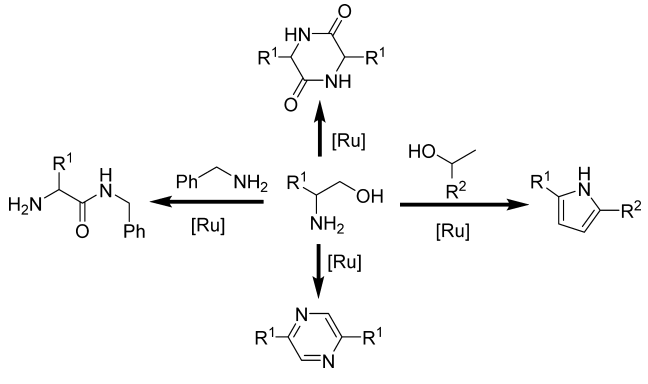
Ruthenium-catalyzed protocols play an important role in the organic synthesis, due to the scope of the reactions.[1−5] Among the used Ru-catalyzed processes, acceptorless dehydrogenative coupling (ADC) reactions have gained major interest because of their widespread applications in the organic synthesis.[6] These reactions allow the synthesis of valuable compounds from primary alcohols such as esters,[7−14] imines,[15,16] amides,[17,18] acetals,[19] amines,[20] formamides,[21] lactams,[22] lactones,[23−25] and ethers[26] (Scheme 1). In all of these transformations, the alcohol source is oxidized in the presence of Ru catalyst with the leaving of hydrogen to form a more reactive carbonyl group. Subsequently, the carbonyl group undergoes a subsequent transformation(s) to generate the final product.[27]

In the recent years, ADC reactions have been considered as an efficient strategy for the synthesis of new compounds using appropriate substrates. For example, Beller and co-workers reported an efficient dehydrogenative coupling reaction for synthesis of pyrroles from 1,4-diols and amines.[28] Milstein et al. reported an ADC sequence for synthesis of peptides and pyrazines from β-amino alcohols.[29] Very recently, the Milstein group developed a new one-pot synthesis of pyrroles using the ADC reaction of amino alcohols with secondary alcohols (Scheme 2).[30]

Scheme 1. Synthesis of Various Compounds Using ADC Approach



Scheme 2. Synthesis of Pyrrole, Peptide, and Pyrazine from β-Amino Alcohols Using ACD Reactions



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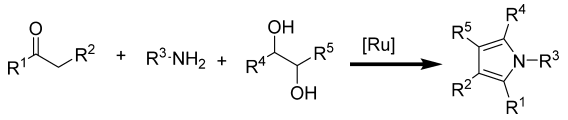
A general and regioselective method for one-pot synthesis of pyrroles via a ruthenium-catalyzed multicomponent reaction has been introduced by the Beller research group (Scheme 3).[31]

Scheme 3. One-Pot Synthesis of Pyrroles via a Ruthenium-Catalyzed Multicomponent Reaction



The ADC reactions have been also used for the synthesis of indoles,[32,33] quinolines,[34] and benzoazoles.[35,36] Benzoxazoles are important structural motifs in many biologically active compounds, pharmaceuticals, and natural products.[37,38] Accordingly, the development of efficient protocols to synthesize such compounds are of enormous importance.[39−45] Because of several synthetic problems associated with reported transformation, there is still an urgent need to develop a more efficient synthetic route for the synthesis of benzoxazoles under green conditions or using different substrates.[46−48] One of the interesting strategies for the synthesis of benzoxazoles is ADC reactions in the presence of a Ru catalyst system. What is highlighted in this strategy is the use of primary alcohol as a versatile precursor for the synthesis of benzoxazoles. The first Ru-catalyzed synthesis of benzoxazoles from primary alcohols has been reported by Kondo et al. (Scheme 4).[35] They used $RuCl_2(PPh_3)_3$ as a catalyst for the synthesis of benzoxazoles from 2-aminophenol and alcohols in toluene at 215 °C (a harsh condition). Then, Huh and Shim used this catalyst system for the synthesis of benzoxazoles under milder conditions (dioxane, 180 °C) (Scheme 4).[49] In the recent years, Blacker et al. reported the synthesis of benzoxazoles from amines in the presence of $\{[(\eta^5\text{-}Ph_4C_4CO)]_2H\}Ru_2(CO)_4(\mu\text{-}H)\}$ catalyst (cat. **1**) (Scheme 4).[50] In light of the recent developments in ADC methodology, herein, we report a novel synthetic method for one-pot synthesis of benzoxazoles, using reaction of alcohols and 2-aminophenol via a Ru-catalyzed ADC reaction (Scheme 4). Due to the scope of primary alcohol compounds, our convenient procedure for the synthesis of new benzoxazoles may have clinical significance.

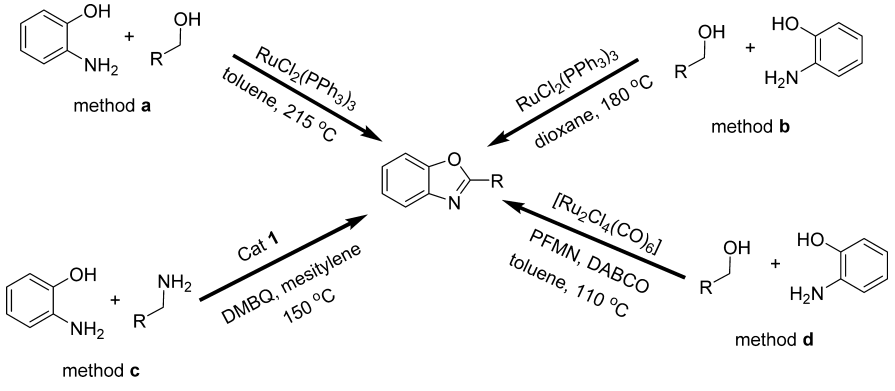
In this study, a magnetic recyclable phosphorus ligand (PFMN) was used in the presence of a Ru precursor to generate a heterogeneous catalyst system for the efficient synthesis of benzoxazoles using ADC reactions. The PFMN ligand has been previously reported by our research group and has been used as a magnetic recyclable phosphorus ligand in the Pd-catalyzed Heck reaction of chloroarenes with the excellent results.[51] It should be mentioned that the magnetic recyclable catalyst systems can be separated from reaction conditions using an external magnetic field, and this improved the applicability of this heterogeneous catalyst in organic transformations.[52] Thus, by using PFMN in the presence of a suitable Ru precursor, it is possible to prepare a highly efficient Ru-based catalyst for application in Ru-catalyzed organic reactions.

RESULTS AND DISCUSSION

In order to obtain the most appropriate conditions for the designed protocol, we set out to evaluate various experiments using 2-aminophenol (**1**) and benzyl alcohol (**2a**) as simple model substrates. Considering the work of Gelman et al., on ADC reaction of alcohols and amines using bifunctional Ru(II) PCP pincer complexes, we decided to use the ruthenium carbonyl chloride $[Ru_2Cl_4(CO)_6]$ as the Ru precursor.[15] The results of optimization study are summarized in Table 1.

First, when the $Ru_2Cl_4(CO)_6$ catalyst was used as catalyst, trace amounts of product were detected after 24 h (Table 1, entry 1). The yield of product (**3a**) was improved to 15% after addition of triphenylphosphine (PPh_3) as ligand to the reaction (Table 1, entry 2). These experiments suggest a significant role of the ligand in the reaction progress. The yield of desired product increased to 45% when 1,2-bis(diphenylphosphino)-ethane ($PPh_2CH_2CH_2PPh_2$, dppe)[53] was used (Table 1, entry 3). Furthermore, the yield was enhanced to 57% when bis(diphenylphosphanyl)amine (PPh_2NHPPh_2, dppa)[54] was added to the reaction media (Table 1, entry 4). However, the yield was decreased to 41% when 1,1-bis(diphenylphosphino)-methane ($PPh_2CH_2PPh_2$, dppm)[55] was used as ligand (Table 1, entry 5). In continuation of the optimization study, our recently reported ligand (Fe_3O_4@SiO_2@PPh_2, PFMN) was used in the reaction.[51] Interestingly, in the presence of the PFMN ligand, the product yield was increased to 78%. It is noteworthy to mention that in this ligand, P atom is directly linked to the magnetic nanoparticle via a surface O atom. This ligand can be well-dispersed in solution to produce a pseudohomogeneous system, generating highly reactive catalyst sites. Reusability and easy workup (using external magnetic attraction) were two other advantages of this ligand (Figure 1).

Scheme 4. Ruthenium-Catalyzed Synthesis of Benzoxazoles Using ADC Reaction of Primary Alcohols with 2-Aminophenol[a]



[a]Method **a**: from Kondo et. al.[35] Method **b**: from Huh and Shim.[49] Method **c**: from Blacker et. al.[50] Method **d**: our reported method in this study.

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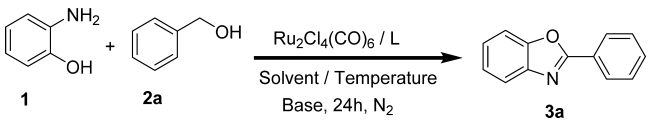
Table 1. Study of Various Conditions for the ADC Reaction of Benzyl Alcohol and 2-Aminophenol[a]



entry	ligand	solvent (temp in °C)	base	yield (%)[b]
1		toluene (110)	DABCO	trace
2	PPh_3	toluene (110)	DABCO	15
3	dppe	toluene (110)	DABCO	45
4	dppa	toluene (110)	DABCO	57
5	dppm	toluene (110)	DABCO	41
6	PFMN	toluene (110)	DABCO	78
7	PFMN	xylene (120)	DABCO	75
8	PFMN	THF (70)	DABCO	55
9	PFMN	$CHCl_3$ (70)	DABCO	62
10	PFMN	toluene (110)	DBU	76
11	PFMN	toluene (110)	$(i\text{-}Pr)_2EtN$	64
12	PFMN	toluene (110)	Cs_2CO_3	45
13	PFMN	toluene (110)	DABCO	75[c]
14	PFMN	toluene (110)	DABCO	77[d]

[a]Reaction conditions: 2-aminophenol (1 mmol), benzyl alcohol (1 mmol), $Ru_2Cl_4(CO)_6$ (4 mol % Ru, 10 mg), ligand [(0.02 mmol for organic ligands, for PFMN (50 mg, 4 mol % PPh_2)], base (0.5 mmol), solvent (2 mL). [b]Isolated yield. [c]Amount of base used is 0.3 mmol. [d]Amount of base used is 1 mmol.

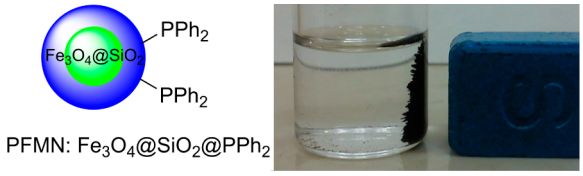


Figure 1. Schematic representation of PFMN ligand and its magnetic recyclable capability.

These interesting results encouraged us to continue the optimization study using PFMN as the best-tested ligand. As the reaction was examined with different type of solvents, toluene was demonstrated to be the best solvent. Also, among different bases applied in this study, DABCO (1,4-diazabicyclo[2.2.2]octane) was selected as the best base. To optimize the amount of PFMN ligand and $Ru_2Cl_4(CO)_6$, different experiments were completed, and the obtained results are shown in Table 2.

As shown in Table 2, reducing the amount of ligand and $Ru_2Cl_4(CO)_6$ led to a reduction in yield. Similar results were obtained by increasing the amount of catalyst to 5.0 mol %, indicating that a 4.0 mol % loading of catalyst for this reaction

Table 2. Optimization of Amount of Catalyst and Ligand[a]

entry	PFMN (mg)	$Ru_2Cl_4(CO)_6$ (mg)	yield (%)[b]
1	50 (~4.45 mol % PPh_2)	10 (4.0 mol % Ru)	78
2	50 (~4.45 mol % PPh_2)	8 (3 mol % Ru)	65
3	50 (~4.45 mol % PPh_2)	12.8 (5 mol % Ru)	79
4	40 (~3.56 mol % PPh_2)	10 (4 mol % Ru)	75
5	60 (~5.35 mol % PPh_2)	10 (4 mol % Ru)	79

[a]Reaction conditions: 2-aminophenol (1.0 mmol), benzyl alcohol (1.0 mmol), DABCO (0.5 mmol), toluene (2 mL), 110 °C and pH = 8.2. [b]Isolated yield.

was optimal. The EDX analysis of PFMN ligand showed that there is about 0.89 mmol of PPh_2 per 1 g of ligand, thus 50 mg of PFMN ligand is equal to about 4.45 mol % of PPh_2 (Figure 2).

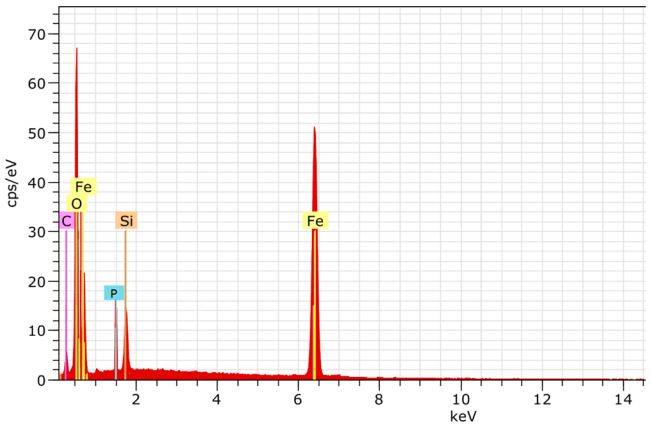


Figure 2. EDX spectrum of PFMN ligand.

According to the data which were obtained from the optimizing study (Table 1), the optimum reaction was carried out at the refluxing temperature of toluene in the presence of $Ru_2Cl_4(CO)_6$ (10 mg, 4.0 mol % Ru), PFMN (50 mg, 4.0 mol % PPh_2), using DABCO (0.5 mmol) as base, under N_2 gas without addition of any promoting additives.

In one experiment, the reused catalyst from the reaction mixture was applied in the subsequent reaction (**1** + **2a** = **3a**) without addition of Ru precursor. In this reaction, the obtained yield of the product was as much as 75%. This test revealed that the ligand has a good combination with $Ru_2Cl_4(CO)_6$ for generation of an efficient heterogeneous catalyst. For the next runs, the yield was decreased to 73, 71, 69, and 68%, respectively (Figure 3). The recycled catalyst could be reused

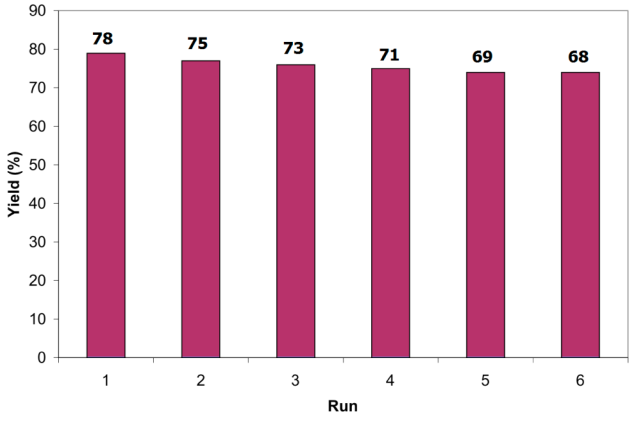


Figure 3. Reusability of catalyst system in the acceptorless dehydrogenative coupling reaction of primary alcohols with 2-aminophenol.

six times with almost consistent efficiency. The ICP analysis of the catalyst after five cycles of reusability has shown that only a very small amount (about 1.4%) of the Ru metal was removed from the substrate. The results confirmed that the supported Ru on the PFMN ligand provides the high catalytic activity without leaching of a significant quantity of Ru.

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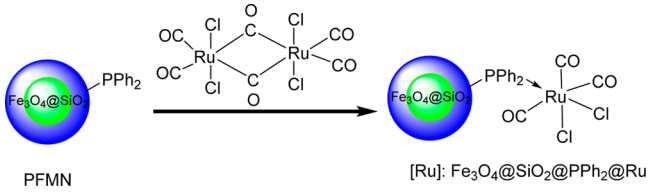
The following structure was proposed for the formed complex between PFMN and $Ru_2Cl_4(CO)_6$ during the reaction progress (Scheme 5).

Scheme 5. Proposed Structure for the Ru Catalyst Based on the PFMN Ligand and $Ru_2Cl_4(CO)_6$

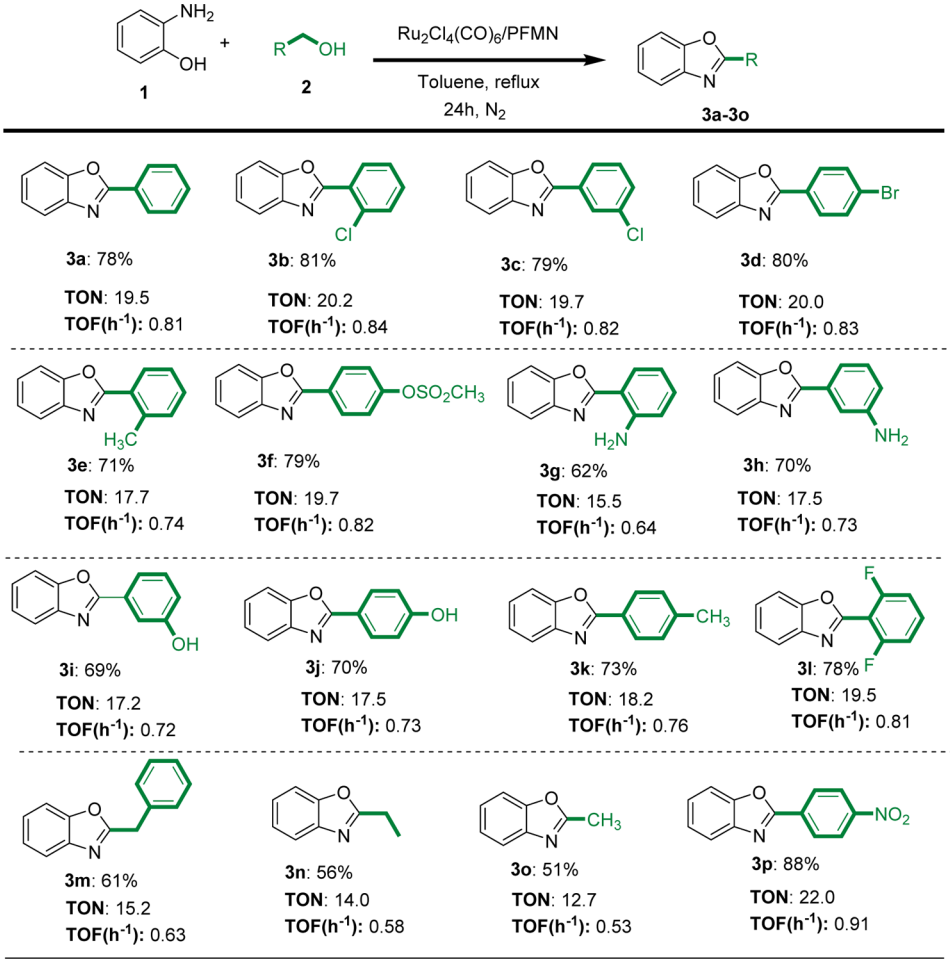


To determine the scope of the designed protocol, a number of primary alcohols were condensed with 2-aminophenol under optimized reaction conditions, and the results are shown in Scheme 6. As shown in Scheme 6, the reaction was satisfactorily accomplished for *ortho*-substituents (**3b**, **3e**, **3g**, **3l**), electron-withdrawing groups (**3c**, **3d**, **3f**, **3p**), electron-donating groups (**3i**, **3j**, **3k**), and alkyl groups (**3m**, **3n**, **3o**). Fortunately, ADC proceeded with the NH_2-functionalized substrate to furnish the amino-containing benzoxazole products **3g** and **3h** in 62 and 70% isolated yields, respectively. Also, (2,6-difluorophenyl)-methanol, as a sterically hindered alcohol, afforded **3l** in 78% isolated yield. The practical synthetic efficiency of the procedure was highlighted by the reaction of EtOH and *n*-PrOH, yielding the 2-methyl and 2-ethyl benzoxazole (**3o** and **3n**) in 51 and 56%, respectively. In addition to low reactivity of these alcohols, their low boiling point may affect the yield of product. The diversity of this process was further established with 2-phenyl-ethanol, leading to the formation of 2-benzyl-benzoxazole (**3m**) in 61% yield.

We proposed a plausible reaction mechanism for this protocol according to the literature, as shown in Scheme 7.[6,56] In all likelihood, alcohol is added to the catalyst in the first step to produce aldehyde by dehydrogenation. Then, 2-aminophenol reacts with the aldehyde to form the corresponding imine (**I**) via a condensation reaction. Subsequently, the hydroxyl group adds to activated imine to produce the 2,3-dihydro-benzooxazole intermediate (**II**). The latter can undergo a dehydrogenation reaction catalyzed by Ru to produce the benzoxazole product.

Some experiments were conducted to obtain a deeper insight into the reaction pathway. The reaction of benzyl alcohol (**2a**) and the catalysts in the absence of the aminophenol resulted in the production of benzaldehyde and benzoic acid in 82 and 5%, respectively. Also, the scope with regard to the aldehydes was

Scheme 6. Products of ADC Reaction between Alcohols and 2-Aminophenol under Optimized Conditions[a]



[a]Reagents and conditions: alcohol (1 mmol), 2-aminophenol (1 mmol), DABCO (0.5 mmol), PFMN (50 mg, 4.0 mol % PPh_2), $Ru_2Cl_4(CO)_6$ (10 mg, 4.0 mol % Ru), toluene (2 mL), and reflux. All yields are isolated yields. TON: mol product/mol cat. TOF: mol product/mol cat. h^{-1}.

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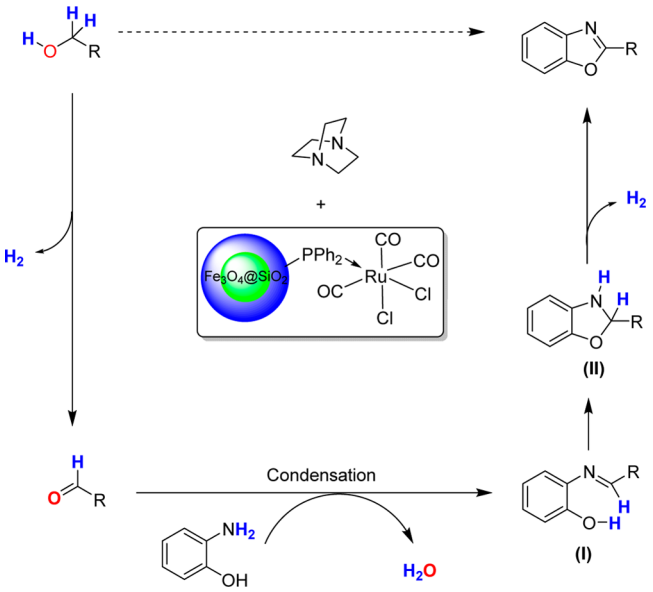
Scheme 7. Proposed Mechanism for the Acceptorless Dehydrogenative Coupling of Alcohols with 2-Aminophenol in the Presence of a Ru Catalyst System



studied. In case of benzaldehyde, 2-phenylbenzo[d]oxazole (**3a**) was obtained in 81% yield after 12 h. This protocol is strongly dependent on the strength of the group on the aldehyde. For example, 4-nitrobenzaldehyde yielded the corresponding benzoxazole in 92%, whereas for 4-hydroxybenzaldehyde, the product was obtained in 79% isolated yield. These experiments (Scheme 8b) clarify that our catalytic system efficiently catalyzed the reaction of aldehydes with 2-aminophenols for the synthesis of benzoxazoles under mild conditions. Furthermore, these two experiments revealed that the generation of aldehyde in the presence of catalyst is the key step in the reaction progress (Scheme 8a,b).

It should be mentioned that in the absence of $Ru_2Cl_4(CO)_6$ under optimized conditions, the composition of isolated products from the reaction mixture was the following: about 10% benzoxazole (**3a**), 30% imine (**3a′**), and 35% dihydrobenzoxazole (**3a″**). This experiment revealed that the optimized condition is suitable for conversion of produced aldehyde from the Ru-catalyzed dehydrogenative step to the corresponding benzoxazole product. The small amount of produced benzoxazole in this experiment can be attributed to the oxidizing power of phosphine ligand for conversion of dihydrobenzoxazole to benzoxazole.

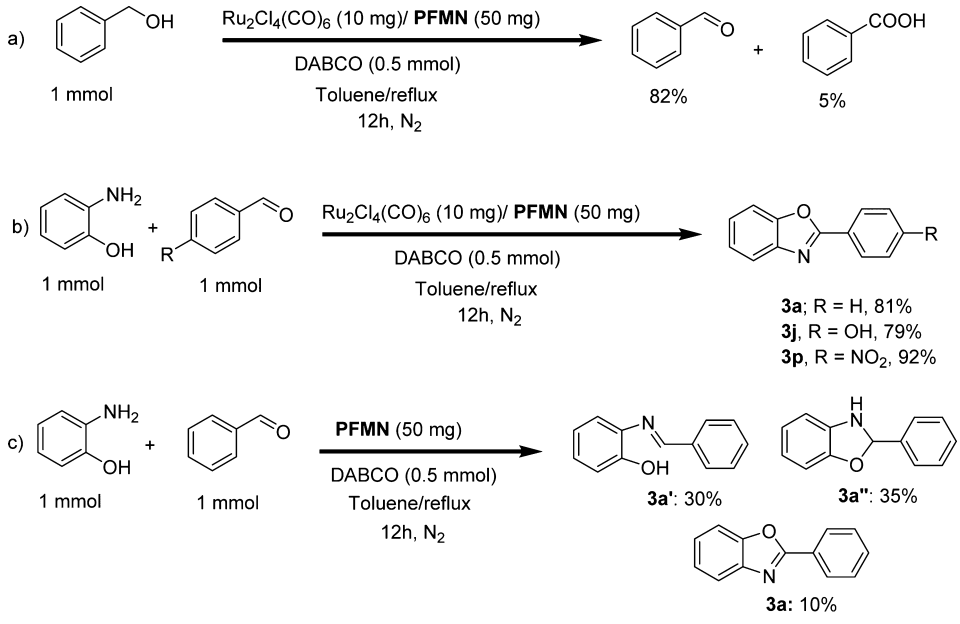
When 2-aminophenol and (ethoxymethyl)benzene (**4**) was used in the reaction, no product was obtained, suggesting that the oxidation of alcohol via H_2 extrusion is the main step for this process (Scheme 9).

Moreover, in the absence of the base (DABCO), the reaction yield is decreased to 31%, demonstrating that the removal of base from the reaction mixture has a remarkable effect on the reaction progress. Also, with increasing the temperature to 150 and 180 °C (in the absence of base), the yield was increased to 44 and 55%, respectively, confirming that in the presence of base the reaction can be performed under milder conditions.

CONCLUSION

In conclusion, we developed an efficient approach for the preparation of benzoxazole derivatives, via acceptorless dehydrogenative coupling of alcohols with 2-aminophenol, using a Ru catalytic system. In this process, phosphine-functionalized magnetic nanoparticles (PFMN) as a magnetic recyclable phosphorus ligand were found to be an efficient ligand. Moreover, $Ru_2Cl_4(CO)_6$ was suggested to function as a Ru precursor in this reaction. We believe that this protocol is

Scheme 8[a]



[a](a) Ru-catalyzed oxidation of benzyl alcohol to benzaldehyde and benzoic acid in the presence of $Ru_2Cl_4(CO)_6$/PFMN catalyst system. (b) Ru-catalyzed synthesis of benzoxazoles using aldehydes under optimized conditions. (c) A control experiment which show the generation of benzoxazole and its intermediates in the absence of Ru under optimized conditions.

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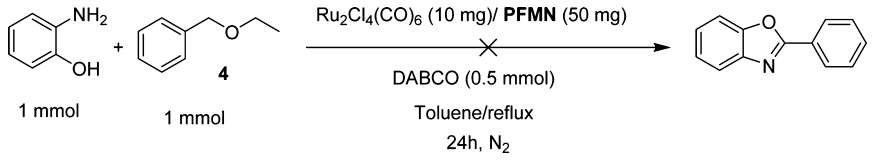
Scheme 9. Reaction of 2-Aminophenol and (Ethoxymethyl)benzene for Synthesis of Benzoxazole under Optimized Conditions



attractive for the preparation of a variety of benzoxazoles, using primary alcohols under heterogeneous conditions.

EXPERIMENTAL SECTION

General. Chemicals were purchased from Fluka and Aldrich chemical companies and used as received. Magnetic nanoparticles were prepared via the coprecipitation of Fe (III) and Fe (II) ions in the presence of sodium hydroxide based on a previous report.[57] Fe_3O_4@SiO_2 nanoparticles were also prepared based on the literature procedure.[58] FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer) was employed for characterization of the catalyst and synthesized compounds. For recorded ^1H and ^{13}C NMR spectra, we used a Bruker (250 MHz) Avance DRX in pure deuterated DMSO-d_6 and $CDCl_3$ solvents with tetramethylsilane (TMS) as the internal standard. Melting points were determined in open capillary tubes in a Barnstead Electrothermal 9100 BZ circulating-oil melting-point apparatus. The reaction monitoring was accomplished by TLC on silica gel PolyGram SILG/UV254 plates. Column chromatography was carried out on columns of silica gel 60 (70−230 mesh).

Synthesis of Phosphine-Functionalized Magnetic Nanoparticles (Fe_3O_4@SiO_2@PPh_2, PFMN).[51] To a mechanically stirred vessel mixture of Fe_3O_4@SiO_2 (5.0 g) in dry CH_2Cl_2 (80 mL), $ClPPh_2$ (4.2 mmol, 0.76 mL) and triethyl amine (1.0 mL) were added and refluxed under nitrogen gas for 12 h. Then, the mixture was filtered and washed with dichloromethane (3 × 10 mL) and deionized water (3 × 10 mL). After drying under reduced pressure for 6 h, PFMN ligand was obtained as dark powder (5.91 g).

General Producer for the Synthesis of Benzoxazoles Using ADC Reaction of Primary Alcohols with 2-Aminophenol. To a mixture of primary alcohol (1 mmol) and 2-aminophenol (1 mmol) in toluene (2 mL), DABCO (0.5 mmol), PFMN (50 mg), and $Ru_2Cl_4(CO)_6$ (10 mg) were added, and the resulting mixture was heated to the refluxing temperature of toluene for 24 h under N_2 gas. After completion of the reaction, the mixture was cooled to room temperature, and the PFMN ligand was magnetically separated from the reaction mixture. The reaction mixture was quenched with water and extracted with diethyl ether (10 mL, 3 times), and the organic phase was dried over Na_2SO_4. The benzoxazole product was purified by column chromatography (hexane/ethyl acetate) to obtain the desired purity.

ASSOCIATED CONTENT

Supporting Information

Spectral data for synthesized compounds along with the copy of ^1H and ^{13}C NMR of synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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