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Iron-catalyzed arylation of benzoazoles with aromatic aldehydes using oxygen as oxidant[†]

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An iron-catalyzed arylation of azoles with aromatic aldehydes using oxygen as oxidant has been discovered. The reaction proceeded well for a range of different substrates under oxidative conditions.

The biaryl motif is an important substructure of many bioactive and functional molecules and has been the focus of organic chemists for over a century.¹ Over the last few decades, transitionmetal-catalyzed cross-coupling reactions have proved to be effective synthetic tools for the formation of biaryls between aryl halides and organometallics.² A variety of other arylation methods using organic substrates instead of organometallics has also been successfully explored.³ Among them, the decarboxylative coupling reactions developed by Goossen et al. have emerged as powerful alternatives for selective biaryl formation using cheap arenecarboxylates as the coupling partners.⁴ In the meantime, the direct conversion of C-H bonds into C-C bonds can potentially lead to a more efficient synthesis with a reduced number of synthetic operations and thus has attracted great interest in recent years. Since the pioneering efforts of Murai et al.,⁵ great progress has been achieved in the transition-metal-catalyzed activation and subsequent reaction of C-H bonds especially for biaryl synthesis.⁶

Aryl-substituted benzoazoles are common building blocks for the synthesis of pharmaceuticals, natural products, functional materials, and many other biologically active molecules.⁷ The conventional methods for the synthesis of these important compounds typically involve either the metal-catalyzed intramolecular cyclization of thioformanilides or the cross-coupling of carboxylic acids or aldehydes with 2-aminophenol (or 2-aminothiophenol),^{8,9} but such methods suffer from difficulties in the preparation of readily oxidized 2-aminothiophenols. Alternatively, aryl-substituted benzoazoles have been successfully synthesized by direct C–H activation and subsequent C–C bond formation with aryl halides,¹⁰ arylsilanes,¹¹ aromatic carboxylic acids,¹² aryl boronic acids,¹³ sodium sulfinates¹⁴ and aryl triflates (or mesilates and sulfamates),¹⁵ and even with areen C– H bonds via double C-H activations.¹⁶ However, the direct arylation of benzoazoles using aromatic aldehydes as aryl sources remains a challenge. Aromatic aldehydes are cheap, commercially available and easy to handle and thus can be potentially used as the ideal arylation reagents. Very recently, we and others developed various catalytic systems for direct aryl ketone formation between arene C-H bonds and aromatic aldehydes.¹⁷ We also developed a rhodium-catalyzed oxidative C-H arylation of 2-arylpyridine derivatives via the decarbonylation of aromatic aldehydes using peroxides as oxidants.¹⁸ In this reaction, various aromatic aldehydes act as the aryl sources. It would be highly desirable to develop a process using inexpensive and non-toxic metal such as iron as catalyst for the preparation of aryl-substituted benzoazoles using benzoazoles and aromatic aldehydes as starting materials.^{19,20} Herein, we report an iron-catalyzed arylation of benzoazoles with aldehvdes in the presence of oxygen. affording the aryl-substituted benzothiazoles and benzoxazoles in high yields (Scheme 1).

We began our study by examining the reaction of benzothiazole (1a) with benzaldehyde (2a) in H₂O-diglyme by using oxygen (1 atm) as oxidant at 130 °C. When benzaldehyde reacted with 1.5 equivalents of benzothiazole in the absence of any catalyst, the desired product 3aa was obtained in 6% yield as determined by GC and ¹H NMR methods (Table 1, entry 1). Then various iron salts were investigated for this reaction under similar reaction conditions. Only a trace amount of product was observed when $Fe(acac)_2$ and Fe_2O_3 were used (entries 2 and 3). Fe(NO₃)₃ and ferrocene were also inefficient catalysts for this kind of transformation (entries 4 and 5). The use of $FeCl_3$ and FeCl₂ improved the reaction yield to 28% and 55%, respectively (entries 6 and 7). Among the various iron salts examined, FeSO₄ was the most effective, and its use resulted in the formation of 3aa in 77% yield (entry 8). The choice of solvents was crucial for this reaction. Moderate yields were obtained when reactions were carried out in pure organic solvents such as NMP, ethanol and diglyme (entries 9-11). Interestingly, 60% yield was achieved when water was used as the sole solvent and the reaction completed in 4 h, which is much faster than those in organic



Scheme 1 Iron-catalyzed arylation of benzoazoles with aldehydes.

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				solvent CLN	
	1a	2a		3aa	
			Т		Yield ^b
Entry	Catalyst	Oxidant	(°C)	Solvent	(%)
1		02	130	H_2O -diglyme (1 : 1)	6
2	$Fe(acac)_2(10)$	$\tilde{0_2}$	130	H_2O -diglyme (1:1)	Trace
3	$Fe_2O_3(10)$	$\tilde{O_2}$	130	H_2O -diglyme (1:1)	Trace
4	$Fe(NO_3)_3$ (10)	$\tilde{O_2}$	130	H_2O -diglyme (1:1)	11
5	ferrocene (10)	$\overline{O_2}$	130	H_2O -diglyme (1 : 1)	9
6	FeCl ₃ (10)	$\overline{O_2}$	130	H_2O -diglyme (1 : 1)	28
7	$\operatorname{FeCl}_2(10)$	O_2	130	H_2O -diglyme (1 : 1)	55
8	FeSO ₄ (10)	O_2	130	H_2O -diglyme (1 : 1)	77
9	$FeSO_4(10)$	O_2	130	NMP	56
10	FeSO ₄ (10)	O_2	130	C ₂ H ₅ OH	49
11	FeSO ₄ (10)	O_2	130	Diglyme	51
12	FeSO ₄ (10)	O_2	130	H ₂ O	60
13	FeSO ₄ (10)	O_2	130	$H_2O-DMA(1:1)$	36
14	FeSO ₄ (10)	O_2	130	$H_2O-DMF(1:1)$	28
15	FeSO ₄ (10)	O_2	130	$H_2O-1,4$ -dioxane	68
				(1:1)	
16	FeSO ₄ (10)	O_2	130	$H_2O-C_2H_5OH(1:1)$	64
17	FeSO ₄ (10)	O ₂	130	$H_2O-DMSO(1:1)$	70
18	FeSO ₄ (10)	O ₂	130	$H_2O-NMP(1:1)$	72
19	$FeSO_4(10)$	O_2	150	H_2O -diglyme (1 : 1)	84
20	FeSO ₄ (20)	O ₂	150	H_2O -diglyme (1 : 1)	94
21	FeSO ₄ (20)	Air	150	H_2O -diglyme (1:1)	45
^a Conditions: 1a (0.3 mmol), 2a (0.2 mmol), solvent (0.4 mL), 20 h					

^a Conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), solvent (0.4 mL), 20 h b GC yield based on **1a**.

solvents (entry 12). The combination of water with other organic solvents all resulted in lower yields (entries 13–18). The reaction temperature is another important factor for the yield of the product. The reaction yield could be improved to 84% when the reaction temperature was increased to 150 °C (entry 19). The use of 20 mol% FeSO₄ further improved the reaction yield to 94% in the absence of any ligand (entry 20).²¹ However, a much lower yield was obtained when the reaction was carried out under an atmosphere of air (entry 21).

Under the optimized reaction conditions, the scope and generality of the oxidative cross-coupling reaction was explored (Table 2). The reactions with aromatic aldehydes bearing electron-donating groups at the aromatic ring proceeded smoothly to give the desired products (3ab-3ae) in good to excellent yields. However, the reaction yield decreased significantly when 4-(dimethylamino)benzaldehyde was reacted with benzothiazole in water-diglyme solvent system. The yield of the desired product 3af could be improved to 52% when a mixture of DMSO-H₂O was used as the solvent. Aldehydes possessing electron-withdrawing groups on the phenyl ring also reacted smoothly with benzothiazole and afforded the desired arylated products (3ag-3aj) in good yields. The position of substituents on phenyl ring of aldehydes affected the reaction yield slightly (3ak-3am). A good yield was achieved when 3,4,5-trimethoxybenzaldehyde was used, and the desired product 3an was obtained in 83% yield. Functional groups such as fluoro, chloro, bromo were well tolerated under the optimized conditions. A free hydroxy group was also tolerated, and the reaction of 4-hydroxy-3-methoxybenzaldehyde reacted with 1a gave 3ao in good yield. Notably, the

coupling of heteroaromatic aldehydes such as picolinaldehyde and furan-2-carbaldehyde with **1a** afforded **3ap** and **3aq** in 78% and 53% yields, respectively. Aliphatic aldehydes such as octanal also coupled with **1a** and afforded the alkylated product **3ar** in 30% yield.

The reaction results of various azoles with benzaldehyde 2a are also investigated. Benzothiazoles bearing electron-donating substituents at the phenyl ring proved to be good substrates for this transformation, affording the corresponding products 3ba, 3ca, and 3da in good yields. Having an electron-withdrawing substituent at the phenyl ring, 6-nitro-2-phenylbenzothiazole gave a slightly lower yield of 3ea. Unfortunately, benzoxazoles are not good substrates for this transformation due to the hydrolysis side reaction in aqueous media. To find reaction conditions suitable for benzoxazoles, we reinvestigated the reaction conditions systematically. Fe₂(SO₄)₃·xH₂O-P(C₆F₅)₃ was found to be a good catalyst system and diglyme was a good solvent. When benzoxazole reacted with benzaldehyde at 110 °C with an extended reaction time to 36 h, the desired product 3fa was obtained in 70% yield. Various functional groups including methyl, chloro, and nitro at the phenyl ring were well tolerated under the optimal reaction conditions.

To get more information about the reaction mechanism, several control experiments were set up under the standard conditions. A ¹³C-labeled product was detected as the major product by GC-MS when ¹³C-labeled benzaldehyde was reacted with **1a** and 1f (Scheme 2, 1 and 4). This means for the arylation of benzoazoles with aldehydes, the reaction did not take a decarbonylative and C-H activation pathway. The reaction mainly took a ring-opening pathway and iron mainly acted as a Lewis acid catalyst. The reaction of 2-aminothiophenol with benzaldehyde (2a) also gave the desired product 3aa in 79% yield, which was slightly lower than the reaction yield of benzothiazole with benzaldehyde (Scheme 2, 2). However, the reaction of 2-aminophenol with benzaldehyde did not result in the desired product in aqueous or organic solvent systems (Scheme 2, 3). Although the exact reaction mechanism is not clear for the arylation of benzoazoles with aldehydes at this stage.²² This reaction is still an attractive method since cheap and non-toxic iron was used as the catalyst and oxygen was used as a green oxidant.²⁰

In summary, we have demonstrated a direct arylation of benzoazoles with aromatic aldehydes. The cheap and non-toxic iron catalyst efficiently catalyzed the coupling reactions in good to excellent yields using oxygen as oxidant under base-free conditions. Solvent played an important role in this transformation and better yields were obtained in a mixture of water-diglyme than in organic solvents when benzothiazoles were used as substrates. Functional groups such as methyl, methoxy, fluoro, chloro, bromo and nitro were all well tolerated under the optimized reaction conditions. This method affords a cheap and efficient alternative route for the synthesis of heteroaromatic biaryls. The scope, mechanism, and synthetic applications of this reaction are under investigation.

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Table 2 Arylation of benzoazoles with various aldehydes^a



^a Conditions: 1 (0.3 mmol), 2 (0.2 mmol), FeSO₄·7H₂O (0.04 mmol), H₂O-diglyme (0.4 mL, 1:1), 150 °C, 20 h under oxygen, isolated yield. ^b DMSO-H₂O (0.4 mL, 1:1). ^c Fe₂(SO₄)₃ xH₂O (0.04 mmol), P(C₆F₅)₃ (0.02 mmol), diglyme (0.4 mL), 110 °C, 36 h under air. ^d 2 equiv. of octanal was used.



Scheme 2 Control experiments.

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