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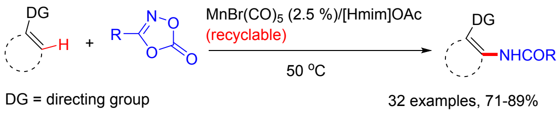

Base metal as the catalyst
Low catalyst loading
Recyclable solvent and catalyst
Good functional group tolerance

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Ortho-C-H Amidations Enabled by a Recyclable Manganese-Ionic liquid Catalytic System

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ABSTRACT

We described an environmentally benign, recyclable base metal catalyst system ($MnBr(CO)_5$/[Hmim]OAc) for ortho-C-H amidation. The readily available dioxazolones was used as the amidation agents. A broad substrate scope and high functional group tolerance were observed. The catalyst system ($MnBr(CO)_5$/[Hmim]OAc) could be easily reused by simple phase separations.

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C-H activation has become an atom- and step-economic tool for the synthesis of natural products, pharmaceuticals, and advanced materials, and late transition metals such as Rh, Ir, and Ru-based catalysts have played a major role. More sustainable base-metals such as iron,[1-3] cobalt,[4-13], and manganese[14-31] have shown great potential in C-H activation[32] in recent developments. Although base metals themselves are inexpensive, the complete catalytic systems (metal plus ligands, e.g. $[Cp^*Co(CO)I_2]/AgSbF_6$, $MnBr(CO)_5$) are still relatively expensive. From the viewpoint of green chemistry, it is highly desirable to develop recyclable or reusable base metal-based C-H activation catalyst systems.

The amide is among the most important functionalities in materials, pharmaceuticals, and other fine chemicals. Moreover, the site-selective C-H amidation using directing groups is an atom- and a step-economic way to make them. Among many amidation reagents, dioxazolones are readily available, redox-neutral and CO_2 is the only byproduct. Indeed, many efficient dioxazolones-based C-H amidation protocols have been developed (Scheme 1). There are many suitable directing groups which include heterocycles such as pyridine, triazole (Scheme 1a),[33-40] oxime (Scheme 1b),[41] nitrone (Scheme 1c),[42] azobenzene (Scheme 1d),[43, 44] anilide (Scheme 1e),[45, 46] benzamide (Scheme 1f),[47, 48] ketone/aldehyde (Scheme 1g),[44, 49, 50] enaminone (Scheme 1h),[51, 52] oxazoline (Scheme 1i)[53-55] and many other directing groups.[56-63] Depending on the direction groups, catalyst systems such as $[IrCp^*Cl_2]_2/AgNTf_2$, $Rh[Cp^*Cl_2]_2$ /$AgSbF_6$, $[Cp^*Co(CO)I_2]/AgSbF_6$ have been employed. However, most of these catalyst systems are relatively expensive and could not be easily reused or recycled.

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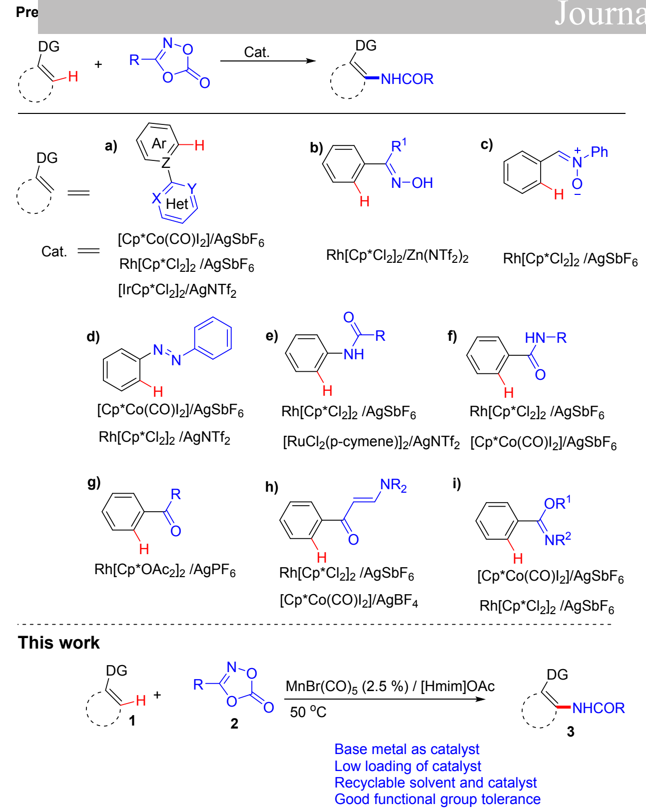
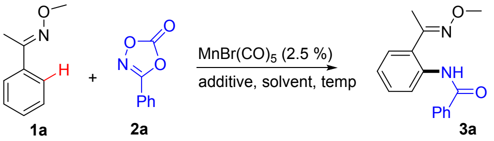


Scheme 1. Selected examples of C–H amidations using dioxazolones.

Ionic liquids[64-66] are recyclable solvent systems and have shown to be able to enable more efficient catalytic reactions in comparison with conventional solvents[67, 68], and they have been used successfully in C-H activations.[69, 70] And recently, we have used the ionic liquid in oxime-directed amidation.[71] We envisioned that the weakly coordinating counteranion in ionic liquids might interact with the halide in the base-metal catalyst (e.g., $MnBr(CO)_5$) and facilitate the metalation step in the catalytic cycle, which led to catalyst systems with superior activity. Moreover, their combination could be reused after simple phase separation. Herein, we are glad to report a highly efficient and recyclable manganese/ionic liquid-catalyzed *ortho*-C-H amidation protocol using the readily available dioxazolones as amidation reagents.

We used the amidation of oxime **1a** as our model reaction (Table 1) using a base metal catalyst - $MnBr(CO)_5$. First, we investigated the effect of conventional organic solvents (Table 1, entries 1-3). Among common organic solvents, diethyl ether gave the best results (for complete information on screening of solvents and other conditions, please see Table S-1 in the Supporting Information). The yield of product **3a** did not improve when we increased the reaction temperature from 30 °C to 50 °C (Table 1, entry 4). We then investigated the effects of Lewis acidic additives. Silver salts such as $AgSbF_6$, $AgNTf_2$, AgOAc did not improve the yields (Table 1, entries 5-7). One possible reason is the generated Mn species such as $Mn(CO)_5OAc$ is not stable. To our delight, an additive - $Zn(OAc)_2$ significantly improved the chemical yield of **3a** (Table 1, entry 8). Because of the significant effect of ionic salts such as $Zn(OAc)_2$, we then screened various ionic liquids containing various ions. To our delight, both [Hmim]OAc, [Hmim]OTf gave good results, and [Hmim]OAc is the optimal ionic liquid solvent (Table 1, entries 9-16). What is more, an increase of the reaction temperature from 30 °C to 50 °C and shortening of reaction time from 12 h to 4 h further improved the yield of **3a** (Table 1, entry 17). Commercial ionic liquid may contain water and water may have some effect on the reactivity. We investigated the effect of water by adding 1-40 equivalents of water to the reaction, we found water had little influence on the reaction (see Table S-2 in SI).

Table 1. Optimization of reaction conditions.[a]



No	Additive (%)	Solvent	Temp (℃)	Time (h)	3a (%)[b]
1	-	DMA	30	12	8
2	-	CH_3CN	30	12	0
3	-	Et_2O	30	12	66
4	-	Et_2O	50	12	20
5	$AgSbF_6$ (10)	Et_2O	30	12	60

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7	AgOAc (10)	Et_2O	30	12	10
8	$Zn(AcO)_2$ (100)	Et_2O	30	12	93(90[c])
9	-	[Emim]Br	30	12	13
10	-	[Bmim]Br	30	12	20
11	-	[Hmim]Br	30	12	23
12	-	[Omim]Br	30	12	28
13	-	[Hmim]Cl	30	12	25
14	-	[Hmim]OAc	30	12	79
15	-	[Hmim]OTf	30	12	75
16	-	[Hmim] BF_4	30	12	10
17	-	[Hmim]OAc	50	4	89

[a] Conditions: **1a** (0.2 mmol), **2a** (0.21 mmol, 1.05 equiv), $MnBr(CO)_5$ (2.5%), additive, solvent (1.0 mL). [b] GC yields. [c] Isolated yields. [Emim] = 1-ethyl-3-methylimidazolium; [Bmim] = 1-butyl-3-methylimidazolium; [Hmim] = 1-hexyl-3-methylimidazolium; [Omim] = 1-octyl-3-methylimidazolium.

With the optimized conditions in hand, we explored the substrate scope and functional group tolerance for the manganese/[Hmim]OAc-catalyzed aminations of oximes **1** (Table 2). First, we evaluated the reaction of **1** with various substitutions on the phenyl ring (Table 2, **3a** – **3j**). The substitution pattern (*meta*, *para*) and electronic properties of substituents (electron-deficient or rich) on the phenyl ring of **1** played a small role; good yields were obtained regardless (Table 2, **3a**-**3j**). We also evaluated the effect of the R group on the side chain of oxime **1**, **1** with both alkyl and aromatic side chains were all suitable substrates (Table 2, **3n-3o**). Even oximes **1** derived from cyclic ketones worked very well (Table 2, **3p-3r**). We also investigated the scope of dioxazolones **2**, both aromatic and aliphatic dioxazolones worked very well (Table 2, **3t-3v**).

Table 2. Scope for manganese-catalyzed amination of oximes **1**.[a]

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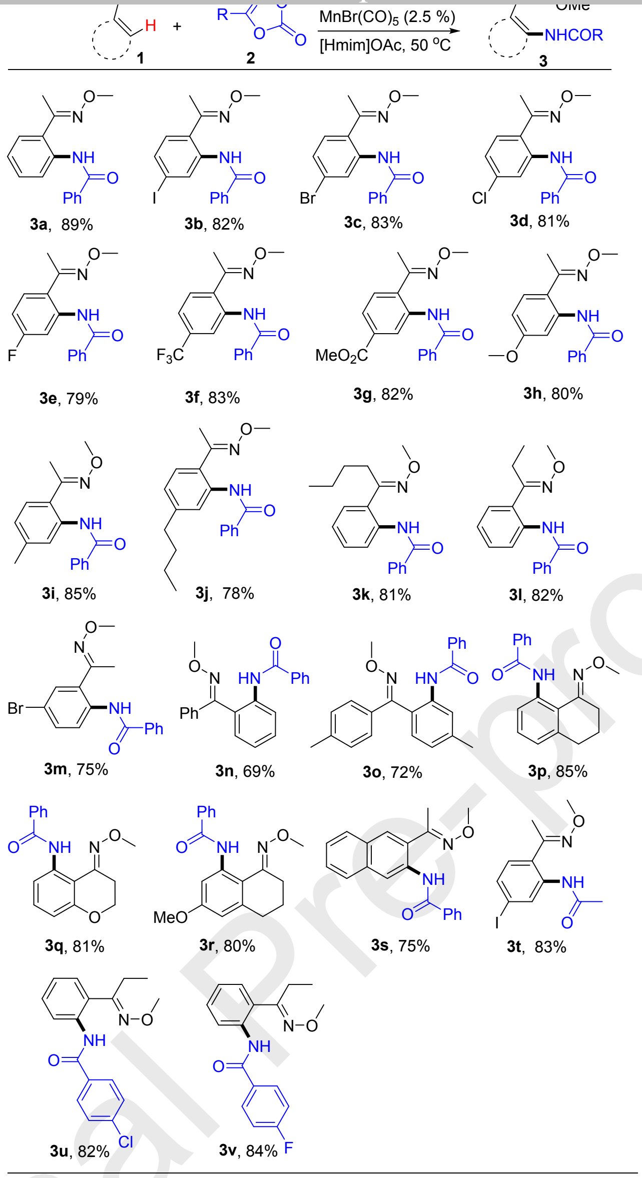

[a] Conditions: **1** (0.2 mmol), **2** (0.21 mmol), $MnBr(CO)_5$ (2.5 mol %), [Hmim]OAc (1 mL), 50 °C, 4 h. All yields are isolated yields.

Our protocol also worked well for pyridine directed amidations (Table 3). Similarly to the oxime directed amidations, pyridine-directed amidations (Table 3, **3w**-**3ae**) also worked very well using both aromatic and aliphatic dioxazolones **2** as amidation agents. Moreover, the substitution pattern (*meta*, *para*) and electronic properties of substitution (electron-deficient or rich) on the aromatic ring of **1** played a small role; good yields were obtained regardless. What is more, in addition to pyridine, pyrazole was also a suitable directing group (Table 3, **3af**).

Table 3. Scope for manganese-catalyzed aminations of heteroarenes.[a]

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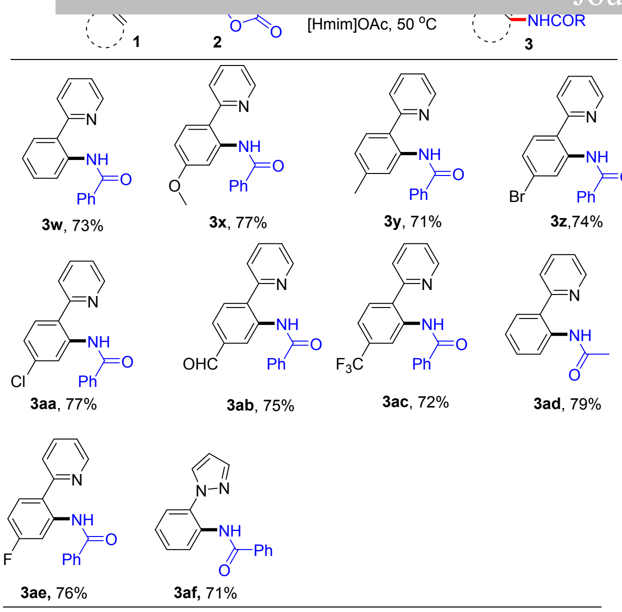
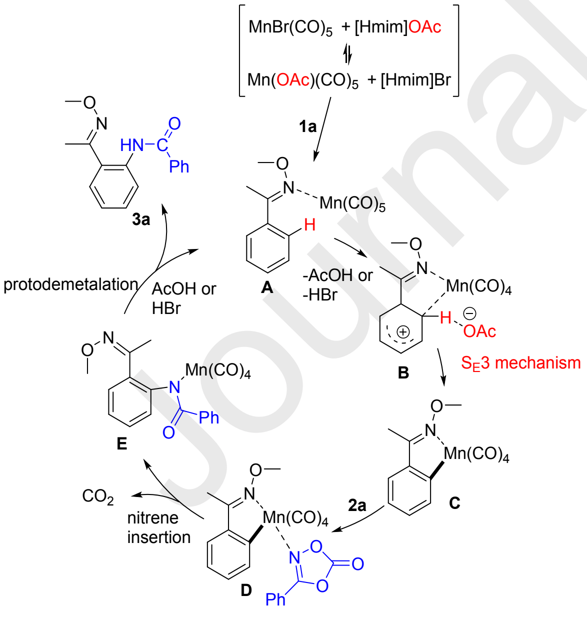


[a] Conditions: **1** (0.2 mmol), **2** (0.21 mmol), $MnBr(CO)_5$ (2.5 mol %), [Hmim]OAc (1 mL), 50 °C, 4 **h.** All yields are isolated yields.

The proposed mechanism is illustrated in Scheme 2. Because of the reaction rate enhancing effects of both $Zn(OAc)_2$ and [Hmim]OAc and the lower reactivity of [Hmim]Br, [Hmim]Cl, [Hmim]BF_4 systems (Table 1), we propose that the counterion (OAc) plays an important role. Due to the high concentration of acetate in the reaction system, a ligand or ion exchange may happen and $MnOAc(CO)_5$ might be generated, and it may have higher reactivity than $MnBr(CO)_5$. The catalytic cycle starts with the generation of manganese species **A** from **1a** and catalyst $MnOAc(CO)_5$ or $MnBr(CO)_5$. Then the key intermediate **B** is formed via a concerted-metalation-deprotonation (CMD) pathway,[72] and the acetate anion in the system may play a key role in proton abstraction. Reversible coordination of **2a** to the cationic Mn center in **C** gives Mn-intermediate **D**; then a nitrene insertion to C-Mn bond in **D** gives Mn-intermediate **E** by releasing a carbon dioxide molecule. In the last, the protodemetalation of **E** affords the final amidated product **3a** and regenerates the Mn catalyst.

Out attempt to synthesize the proposed Mn-intermediate $MnOAc(CO)_5$ was not successful (eq 1). After treatment of $MnBr(CO)_5$ with 1.0 equiv. of AgOAc, the reaction gave a complex mixture. This result indicated the MnOAc(CO)5 could be a highly reactive yet transitional species.



Scheme 2. Proposed mechanism.

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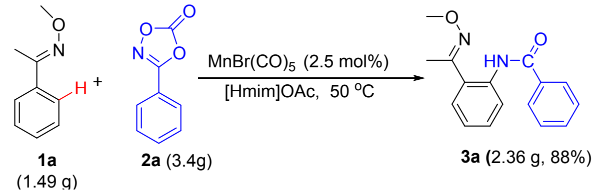
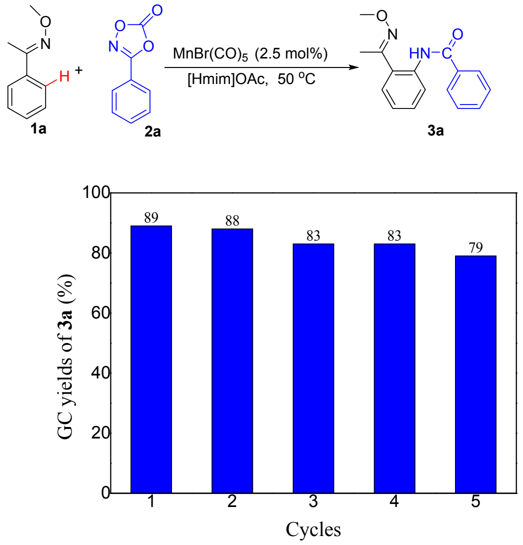


1a (1.49 g) **2a** (3.4g) **3a** (2.36 g, 88%)

(eq 2)

Figure 1. Reuse of Mn-ionic liquid catalyst system.



Our protocol could proceed in the gram scale without any implication (eq 2). We also investigated the reusability of our catalytic system (Figure 1). Five runs of amidations were carried; when the reaction was finished, it was easy to recycle the catalyst system by extraction of the reaction mixture using diethyl ether, the products **3** will be extracted to the ethyl phase, and most of the Mn catalyst will stay in the ionic liquid phase. After phase separation, the ionic liquid phase containing the Mn catalyst could be used in the next run directly. We were glad to find that the Mn-ionic liquid system could be reused for five times without a significant decrease in the catalytic activity (Figure 1). After 5 cycles, there was still 84.8% of Mn content left in the reaction mixture (determined by ICP-MS).

In summary, we have developed an efficient and recyclable base metal C-H amidation catalyst system (MnBr(CO)$_5$/[Hmim]OAc) using the readily available dioxazolones as the amidation agents. At present, base metal catalysts such as MnBr(CO)$_5$ are still relatively expensive, high efficiency and recyclability of (MnBr(CO)$_5$/[Hmim]OAc) system may become attractive in large scale C-H activations.

Acknowledgments

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1. Base metal (Mn) as the catalyst
2. Low catalyst loading
3. Recyclable solvent and catalyst
4. Readily available amidation agents

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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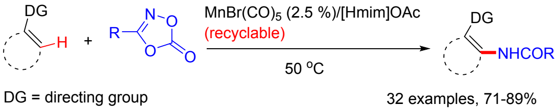

Base metal as the catalyst
Low catalyst loading
Recyclable solvent and catalyst
Good functional group tolerance

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