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Manganese(III) Acetate Catalyzed Oxidative Amination of Benzylic C(sp^3)–H Bonds with Nitriles

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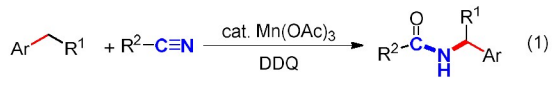
A Mn-catalyzed oxidative amination of benzylic C(sp^3)–H bonds with nitriles is disclosed, which enables the synthesis of a broad range of secondary amides in moderate to excellent yields under mild conditions. The interaction between Mn(III) and DDQ facilitates the oxidation and makes it highly efficient and selective.

Manganese is abundant in nature, and manganese salts are emerged as ideal catalysts or promotors in various oxidative free-radical reactions because of their inexpensiveness, appropriate reactivity and oxidation tendency,[1] in which they directly intervened single-electron transfer (SET) processes. However, with an exception,[2] manganese salts are not recognized as Lewis acid catalysts. Manganese(III) acetate is one of the most easily available manganese salts and is frequently used in radical initiated reactions. However, compared to extensive achievements in C–P bond,[3] C–O bond,[4] and C–C bond[5] formation reactions, $Mn(OAc)_3$ intervened C–N bond formation reaction is still an unfamiliar field of study.[1b,d] To the best of our knowledge, manganese(III) acetate catalyzed C–H bond amination has not been explored.

Herein, we report a Mn-catalyzed oxidative amination of benzylic C–H bonds with nitriles, which produces a broad range of secondary amides in good to excellent yields with high selectivity under mild conditions (eq 1). Other than direct participation in single-electron transfer, manganese(III) acetate acts as a Lewis acid catalyst, and the interaction between Mn(III) and DDQ significantly increases efficiency and selectivity.



(1)

Secondary amides are a basic and important class of nitrogen-containing compounds, which are prevalent in natural products, pharmaceutical agents, agrochemicals, fine chemicals, and functional materials.[6] Over the past decades, amination of C–H bonds proves as a powerful and straightforward tool to construct nitrogen-containing compounds.[7] In this regard, amination of the relatively less reactive C(sp^3)–H bonds is more challenging due to its inertness and poor selectivity, and thus transition-metals such as Pd,[8] Ru,[9] Rh,[10] Ag,[11] Cu,[12] and Ir,[13] etc., are generally required. Recently, the direct C(sp^3)–H bond amination with nitriles for the synthesis of secondary amides have been achieved, providing the corresponding products in overall good yields.[14] However, the substrate scope of nitriles that must be used as solvents is rather limited, and many functionally useful am ides cannot be obtained. Furthermore, ammonium hexanitratocerate(IV) (CAN) and Selectfluor are often employed, which are not preferred oxidants because of the drawbacks of tedious pretreatment and/or poor atom economy. Therefore, it still needs a breakthrough to establish facile C(sp^3)–H bonds amination with mild conditions, enhanced scope, high efficiency, and selectivity for the straightforward synthesis of amides.

We commenced our investigation with the treatment of diphenylmethane **1a** with acetonitrile **2a** in the presence of trifluoroacetic acid (TFA, 10.0 equiv.) and DDQ (2.0 equiv.) at 90 °C for 12 h, and Ritter-type product N-benzhydrylacetamide **3a** was observed in a 63% GC yield (Table 1, entry 1). When 1.0 equiv. DDQ was used, only a 51% yield of **3a** was observed (Table 1, entry 2). Greater DDQ loading or higher temperature gave much more yields of side product diphenyl ketone **4a** without any promotion of **3a** (Table 1, entries 3,4). It is reported that Lewis acid catalysts could interact with DDQ and accelerate the oxidation process.[15] Thus frequently used Lewis acids, such as $Cu(OAc)_2$, $FeCl_3$, $Zn(OTf)_2$, and $In(OTf)_3$, were investigated, which further improved the reaction performance, giving **3a** in 70–75% yields (Table 1, entries 5–8). Excitedly, addition of $Mn(OAc)_3{\cdot}2H_2O$ resulted in excellent yield of **3a** (95%, Table 1, entry 9) with successful suppression of the side product (2% yield of **4a**,). The result showed that

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Electronic Supplementary Information (ESI) available: General information, experimental procedures, copies of ^{1}H and ^{13}C NMR spectra for products. See DOI: 10.1039/x0xx00000x

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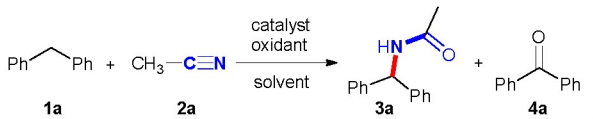
Table 1. Optimization of the reaction conditions[a]

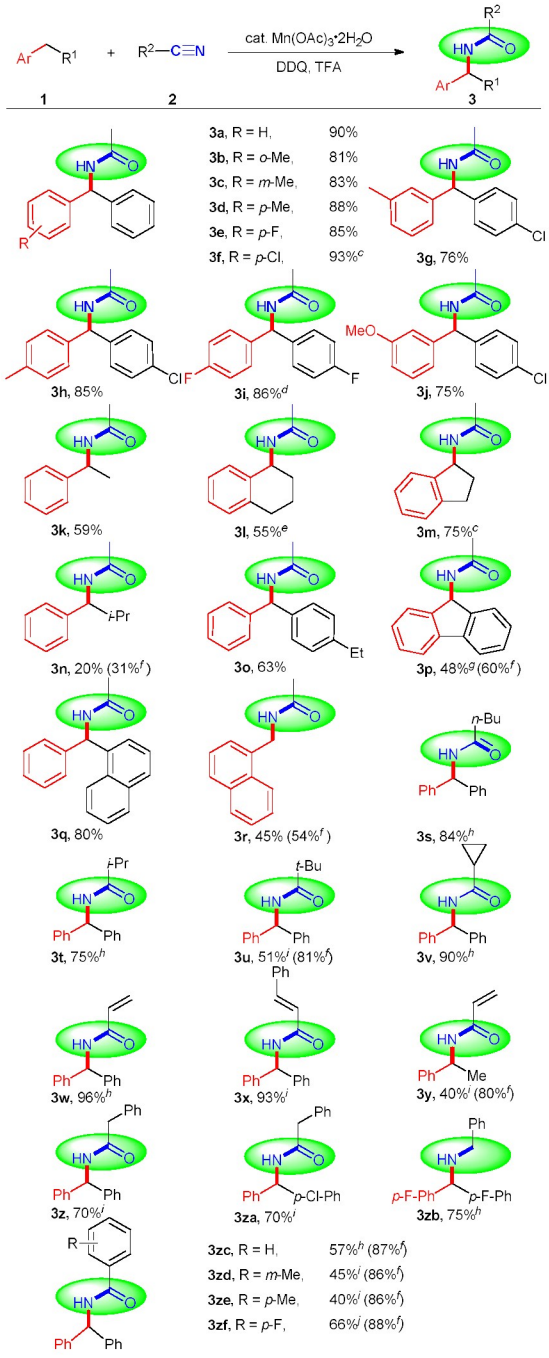


entry	catalyst	oxidant (eq)	solvent	yield[b] (%) 3a	4a
1	/	DDQ	CH_3CN	63	7
2[c]	/	DDQ	CH_3CN	51	7
3[d]	/	DDQ	CH_3CN	62	18
4[e]	/	DDQ	CH_3CN	42	23
5	$Cu(OAc)_2$	DDQ	CH_3CN	70	4
6	$FeCl_3 \cdot 6H_2O$	DDQ	CH_3CN	74	9
7	$Zn(OTf)_2$	DDQ	CH_3CN	75	9
8	$In(OTf)_3$	DDQ	CH_3CN	71	trace
9	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	CH_3CN	**95**	**2**
10[f]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	CH_3CN	80	3
11[g]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	CH_3CN	23	20
12[h]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	CH_3CN	52	7
13[i]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	CH_3CN	24	23
14[j]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	CH_3CN	6	n.d.
15	$Mn(OAc)_3 \cdot 2H_2O$	$Na_2S_2O_8$	CH_3CN	20	trace
16	$Mn(OAc)_3 \cdot 2H_2O$	$PhI(OAc)_2$	CH_3CN	28	34
17	$Mn(OAc)_3 \cdot 2H_2O$	$KHSO_5$	CH_3CN	trace	trace
18	$Mn(OAc)_3 \cdot 2H_2O$	$NaIO_4$	CH_3CN	trace	trace
19	$Mn(OAc)_3 \cdot 2H_2O$	BQ	CH_3CN	n.d.	n.d.
20	$Mn(OAc)_3 \cdot 2H_2O$	/	CH_3CN	n.d.	n.d.
21[k]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	DMF	n.d.	n.d.
22[k]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	DMAc	n.d.	n.d.
23[k]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	DMSO	n.d.	n.d.
24[k]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	EtOH	n.d.	n.d.
25[k]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	acetone	n.d.	n.d.
26[k]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	1,4-dioxane	trace	32
27[k]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	toluene	73	20
28[k]	$Mn(OAc)_3 \cdot 2H_2O$	DDQ	DCE	80	7

[a] Reaction conditions: diphenylmethane **1a** (0.2 mmol), CH_3CN **2a** (0.5 mL), catalyst (0.04 mmol, 20 mol%), oxidant (0.4 mmol, 2.0 equiv.), TFA (10.0 equiv.), N_2, 90 °C, 12 h. [b] GC yield using n-dodecane as an internal standard. [c] DDQ (0.2 mmol, 1.0 equiv.). [d] DDQ (0.6 mmol, 3.0 equiv.). [e] 110 °C. [f] $Mn(OAc)_3 \cdot 2H_2O$ (0.02 mmol, 10 mol%), DDQ (0.2 mmol, 1.0 equiv.). [g] TFA free. [h] CH_3COOH instead of TFA. [i] HCl instead of TFA. [j] H_2SO_4 instead of TFA. [k] CH_3CN **2a** (15.0 equiv.), solvent (0.35 mL).

manganese(III) acetate might act as a good Lewis acid catalyst for this transformation. Even if 1.0 equiv. DDQ was used, high yield of **3a** (80%) was also obtained only in the presence of 10 mol% $Mn(OAc)_3 \cdot 2H_2O$ (Table 1, entry 10). $Mn(OAc)_3 \cdot 2H_2O$ not only significantly improved the yield (80 vs 51%), but also decreased the amounts of the oxidant (1.0 vs 2.0 equiv.), which are probably due to the interaction between Mn(III) and HDDQ radical (*vide infra*). TFA was essential for the reaction, which could accelerat hydrolysis of nitrilium cation to yield amide (vide infra). In absence of it, low yield was obtained (23%, Table 1, entry 11). Acetic acid was also effective for the reaction, and the desired product **3a** was observed in a 52% yield. In contrast, other protic acids such as HCl and H_2SO_4, only gave low 24 and 6% yields, respectively (Table 1, entries 12–14). The choice of oxidants turned out to be crucial for the reaction efficiency. $Na_2S_2O_8$ and $PhI(OAc)_2$ were much inferior to DDQ, while other chemical oxidants such as $KHSO_5$, $NaIO_4$ and 1,4-benzoquinone (BQ) were ineffective for the reaction (Table 1, entries 15–19). In the absence of the oxidant, no desired product was observed at all (Table 1, entry 20). Finally, we attempted to seek a suitable solvent for extending the substrate scope of nitriles. It was found that solvent played a

Table 2. Substrate scope[a,b]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (CH_3CN, 0.5 mL), DDQ (0.4 mmol, 2.0 equiv.), $Mn(OAc)_3 \cdot 2H_2O$ (0.04 mmol, 20 mol%), TFA (10.0 equiv.), N_2, 90 °C, 12 h. [b] Isolated yield. [c] $Mn(OAc)_3 \cdot 2H_2O$ (0.02 mmol, 10 mol%), DDQ (0.24 mmol, 1.2 equiv.), **2a** (15.0 equiv.), DCE (0.35 mL), 70 °C. [d] **2a** (15.0 equiv.), DCE (0.35 mL). [e] 60 °C. [f] Yield based on conversion rate of **1**. [g] 120 °C. [h] **2** (25.0 equiv.), DCE (0.35 mL). [i] **2** (20.0 equiv.), DCE (0.35 mL). [j] **2** (1.5 equiv.), DCE (0.35 mL).

key role in the reaction. The reaction did not proceed in DMF, DMAc, DMSO, ethanol, and acetone (entries 21–25). Only side product **4a** was produced in 1,4-dioxane (32% yield, Table 1, entry 26). When toluene was used as the solvent, 73% yield of

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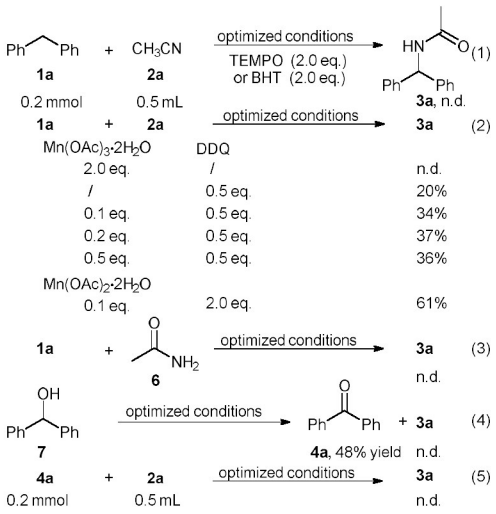
3a was observed with concomitant generation of 20% yield of **4a** (Table 1, entry 27). Fortunately, changing the solvent to DCE resulted in high yield of **3a** (80%, Table 1, entry 28).

With the optimal reaction conditions in hand, the substrate scope was surveyed (Table 2). For diphenylmethane derivatives, the reaction proceeded smoothly and produced the corresponding products in high yields (75–93%, Table 2, **3a–j**), regardless of electronic effect of substituted groups, which is attributed to their contradictory performance in the reaction. For example, the electron-donating groups facilitate the oxidation of the benzylic C–H bonds to carbon cations, but disfavor the subsequent electrophilic addition of carbon cations to nitriles (*vide infra*). The steric hindrance has a slightly detrimental effect on the reaction (Table 2, **3a–d**). Phenylmethane derivatives such as ethylbenzene, tetrahydronaphthalene, and indane also were good substrates for the transformation, giving the corresponding products in satisfactory yields (55–75%, Table 2, **3k–m**). Whereas, much lower yield was observed instead of ethylbenzene with isobutyl benzene (20%, Table 2, **3n**) because of the steric effect. Although ethylbenzene was reactive for the reaction, oxidative amination of *p*-ethyl diphenylmethane proceeded selectively with the ethyl remained, producing the corresponding product in a 63% yield (Table 2, **3o**). In addition, the reaction of larger steric benzylic compounds such as fluorene and 1-benzylnaphthalene also gave the corresponding products in 48 and 80% yields, respectively (Table 2, **3p**,**q**). Notably, amination of primary C–H bond could take place using 1-methylnaphthalene as substrate, albeit in a 45% yield (54% based on the conversion of 1-methylnaphthalene, Table 2, **3r**), but it did not occur with toluene.

The scope and generality with respect to various nitriles are next investigated. Alkyl nitriles including primary, secondary, and tertiary nitriles all worked smoothly, providing the corresponding products in good to excellent yields. Pentanenitrile and isobutyronitrile showed good reactivity, which gave the desired products in 84 and 75% yields respectively (Table 2, **3s**,**t**). Trimethylacetonitrile was less reactive probably due to its steric hindrance, and only 63% yield of **1a** was consumed, giving the desired product in a 51% yield (81% based on the conversion of **1a**, Table 2, **3u**). Cyclopropanecarbonitrile that contains strained C–C bonds was well tolerated, affording the corresponding product **3v** in a 90% yield (Table 2, **3v**). Notably, *α*,*β*-conjugated nitriles, such as acrylonitrile and cinnamonitrile underwent selective addition to C–N triple bond to produce the functional amides in excellent yields (96 and 93% yields, respectively, Table 2, **3w**,**x**). Ethylbenzene was also suited for the transformation, and *α*,*β*-conjugated amide **3y** was produced in a 40% yield (80% based on the conversion of ethylbenzene). It was noted that the molecule **3w** could actually has biological activity related to that of doxorubicin (anti-tumour drug).[16] In addition to alkyl nitriles, aryl nitriles could also act well as substrates, producing the corresponding products in 40–75% yields (86–88% yields based on the conversion of **1**, Table 2, **3zb–zf**).

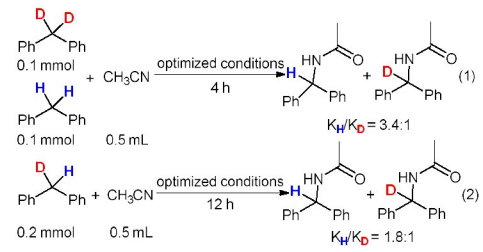
To gain insight into the mechanism of the reaction, control experiments were conducted. Radical scavengers such as BHT



Scheme 1. Control experiments

and TEMPO could thoroughly restrain the reaction, and the radical adduct of BHT with acetamide was observed, suggesting that free-radical was involved in the reaction (Scheme 1, eq 1; see SI for details). When the reaction was carried out using stoichiometric $Mn(OAc)_3{\cdot}2H_2O$ instead of DDQ, no desired product was observed (Scheme 1, eq 2). The result showed that $Mn(OAc)_3$ could not act as oxidant (Scheme 3, dash line). The reaction produced **3a** in a 20% yield (less than 25%) in the presence of 0.5 equiv. of DDQ, whereas, when 0.1 equiv. $Mn(OAc)_3{\cdot}2H_2O$ was added, 34% yield of the was observed. These observations suggested that **1a** could be oxidized to benzyl cation **9** by exact 1.0 equiv. DDQ with the aid of $Mn(OAc)_3{\cdot}2H_2O$. Greater amounts of $Mn(OAc)_3{\cdot}2H_2O$ (0.2 and 0.5 equiv.) did not increase the yield of the product (37 and 36%, respectively). When $Mn(OAc)_2$ was used as catalyst, 61% yield was observed, which is comparable to that of in absence of catalyst (63%, Table 1, entry 1). These results further confirm that $Mn(OAc)_3$ did not act as an oxidant but a Lewis acid catalyst (Scheme 1, eq 2). No desired product was observed during the reaction of **1a** with acetamide **6** suggesting that oxidative dehydrogenative coupling **1a** with primary amide from hydroxylation of nitrile was not involved (Scheme 1, eq 3). Only **4a** was obtained by the treatment of benzhydrol **7** with acetonitrile (Scheme 1, eq 4), and **4a** could not be transformed to **3a** under the standard conditions (Scheme 1, eq 5). These results indicated that the formation of side product **4a** is competitive to the amination reaction.

In addition, experiments focusing on the kinetic isotopic effect were also carried out. The intermolecular and intramolecular K_H/K_D ratios were 3.4:1 and 1.8:1, respectively,



Scheme 2. Kinetic isotopic effect experiments

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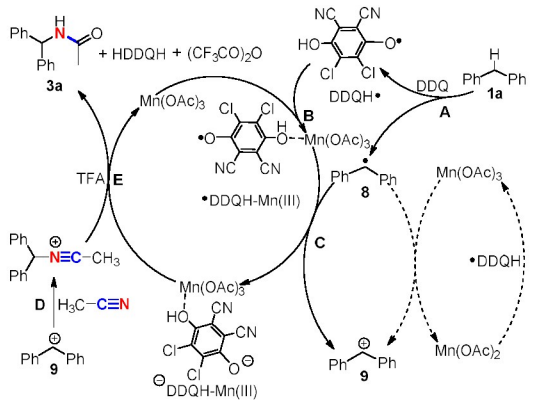

Scheme 3. Possible reaction mechanism

suggesting that C–H bond cleavage to form a benzyl radical could be the rate-determining step (Scheme 2, eqs 1,2).

On the basis of above results and literature reports,[14d,15b,17] a possible mechanism exemplified by the reaction of diphenylmethane **1a** with acetonitrile is proposed (Scheme 3). Initially, **1a** is oxidized by DDQ to form benzyl radical **8** (**A**), with concomitant generation of DDQH radical.[1b,d] The interaction of Lewis acid Mn(III) species with DDQH forms a DDQH–Mn(III) complex (**B**). Then a single electron transfer (SET) process proceeds to form benzyl cation **9** from benzyl radical **8** (**C**). Benzyl cation **9** undergoes an electrophilic addition to acetonitrile to generate a nitrilium cation (**D**), followed by acidic hydrolysis with TFA[6f,18] to give the desired product **3a**. Subsquently, the release of Mn(III) closes the catalytic cycle (**E**).

Conclusions

In conclusion, by using manganese(III) acetate as Lewis acid catalyst, we have developed a selective benzylic C(sp^3)–H bonds amination to prepare secondary amides under mild conditions. Various nitriles including primary, secondary, and tertiary alkyl, alkenyl, benzyl, and aryl nitriles are well applicable, providing a broad range of functional amides in satisfactory yields. The interaction between $Mn(OAc)_3$ and DDQ that accelerates the free-radical oxidation process and improves the selectivity, making it more efficient than the known methods. This finding not only provides a facile and efficient method for the synthesis functionally useful amides, but also expands the toolbox for the unreactive C(sp^3)–H bonds amination.

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