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MnO_2 catalyzed formylation of amines and transamidation of amides under solvent-free condition

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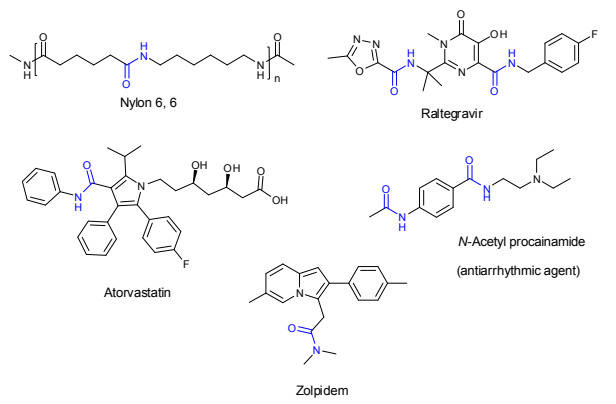
A facile and efficient MnO_2 catalyzed one-pot protocol for formylation of amine and transamidation of primary and secondary amides by amines has been developed. The present methodology is operationally simple, inexpensive and scalable under solvent free conditions. A series of formylated and transamidated products were synthesized in good to excellent yields.

Introduction

The amide linkage is one of the most prevalent bonds, being found in a wide variety of polymers, dyes, pharmaceuticals and biologically active compounds (Scheme 1).[1-4] It forms the primary backbone of all naturally occurring proteins and peptides (which is the basis of all life-forms), thus making it an ubiquitous functional group. By statistical figures, it is found that nearly one-fourth of all pharmaceuticals drugs contain amide bond linkages.[5]



Scheme 1. Examples of molecules containing an amide functional group

Traditionally, amides are synthesized by reaction of amines with activated carboxylic acids,[6] acid chlorides,[7] aldehydes,[8] esters,[9] oxidative coupling of alcohols with amines,[10] ketone (aldoxime rearrangement).[11] However, these methods are limited by utilization of stoichiometric amount of activating reagents/oxidizing agents/base/acids with poor atom economy.

The transamidation involves the cleavage of an existing C-N bond and formation of a new C-N bond in amide functional groups.[12] In past decade, transamidation has gained great attention of various research groups. Nevertheless, these methods have several disadvantages: (a) The use of expensive, specialized metal complexes and metal oxide catalysts such as $Zr(NMe_2)_4$,[13] CeO_2,[14] Cp_2ZrCl_2,[15] Nb_2O_5,[16] Fe (III)[17] and [Ru–NHC][18] (b) longer reaction time[19] (c) inert reaction conditions[20] and (d) the use of different polar and non polar solvents.[21] Moreover, most of these methods involve tedious workup procedures for the preparation of catalysts.[14,16] In 2014, Yu et al reported microwave-assisted heteropolyanion-based ionic liquids catalyzed transamidation.[22] However, the synthesis of ionic liquid require various organic solvents with inert condition. Williams and co-workers have carried out transamidation using hydroxylamine hydrochloride as an inorganic catalyst.[23] However; they used toluene as an organic solvent.

In the last few years, application of manganese oxide (MnO_2) has gained great attention not only as an oxidant but also as an excellent catalyst in organic transformations.[24] Recently, Singh and co-workers have reported a binuclear Mn (II) complex for the transamidation of caboxamides with amines.[25] However, this reported method is limited by the use of 2-benzoylpyridine and oxalic acid dihydrazide as ligand, tedious procedure for preparation of catalyst. Moreover, the substrate scope for formylation and transamidation is limited to acetamide. In addition, this protocol is not applicable for the gram-scale synthesis.

In continuation of our ongoing research on the development of facile and efficient protocols for C-N bond formation,[24] herein we report a simple and an inexpensive MnO_2 catalyzed formylation of aromatic amines and transamidation of primary and secondary amides with amines. The results of our studies are described herein.

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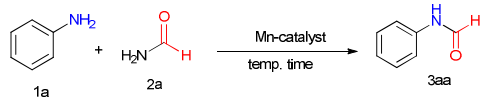
Results and Discussion

To optimize the reaction conditions, aniline **1a** and formamide **2a** were chosen as model substrates for the formylation reaction. A series of experiments were carried out to study the effect of various reaction parameters such as catalyst loading, temperature and time. Initially, various commercially available Mn based catalysts were screened such as $MnSO_4 \cdot H_2O$, $MnCl_2 \cdot 4H_2O$, $Mn(OAc)_2 \cdot 4H_2O$, MnO_2 and $KMnO_4$ (Table 1, entries 1–5). It was observed that all Mn based catalysts showed good catalytic activity for the formylation of **1a** with **2a** to give formanilide **3aa** and MnO_2 was found to be the best catalyst as it furnished maximum yield of **3aa** (Table 1, entry 4). In the absence of the catalyst, only trace amount of **3aa** was observed (Table 1, entry 6). To our delight, increase in temperature has significant effect on the yield of **3aa** and it was found that a maximum yield of 97 % of the desired product **3aa** was formed at 150 °C (Table 1, entry 7). Further increase in the reaction temperature has no effect on the yield of **3aa** (Table 1, entry 8). Next, the reaction time was studied (Table 1, entries 9-12), and it revealed that the reaction time could be reduced to 3 h from 12 h (Table 1, entry 11). However, decreasing the reaction time to 2 h resulted in a considerable decrease in the yield of **3aa** (Table 1, entry 12). In the next set of experiments, catalyst loading was studied (Table 1, entries 15 and 16). It was found that decreasing the catalyst loading from 10 mol% to 5 mol% resulted in the decrease of yield of **3aa** (Table 1, entry 15). However, increasing the catalyst loading from 10 mol% to 20 mol% did not affect the yield of **3aa**, even after carrying out the reaction for 12 h (Table 1, entry 16).

Table 1. Optimization of reaction conditions[a]

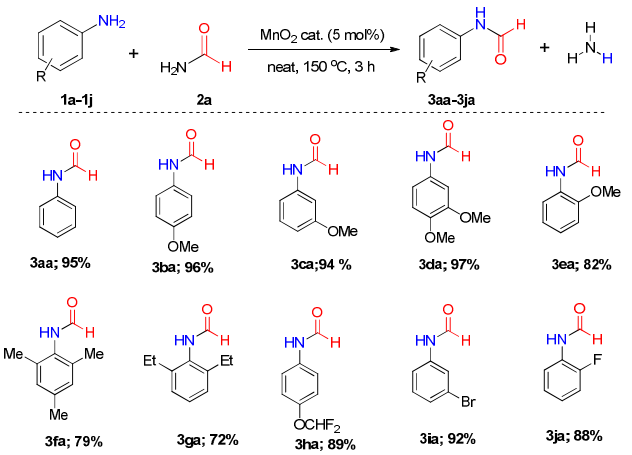


Entry	Catalyst (mol%)	Time (h)	Temp (°C)	Yield (%)[b]
Catalyst screening				
1	$MnSO_4 \cdot H_2O$ (10)	12	140	80
2	$MnCl_2 \cdot 4H_2O$ (10)	12	140	74
3	$Mn(OAc)_2 \cdot 4H_2O$ (10)	12	140	75
4	MnO_2 (10)	12	140	81
5	$KMnO_4$ (10)	12	140	72
6	-	12	140	trace
Effect of time and temperature				
7	MnO_2 (10)	12	150	97
8	MnO_2 (10)	12	160	97
9	MnO_2 (10)	6	150	97
10	MnO_2 (10)	4	150	97
11	MnO_2 (10)	3	150	97
12	MnO_2 (10)	2	150	54
Effect of catalyst loading				
15	MnO_2 (5)	3	150	82
16	MnO_2 (20)	3	150	97,97[c]

[a] Reaction conditions: aniline **1a** (2 mmol), formamide **2a** (4 mmol) under solvent-free conditions. [b] G. C. yields. [c] Reaction time 12 h.

With these optimized reaction conditions in hand, substrate scope of this protocol was studied for the formylation of a wide range of aromatic amines and these results are summarized in Table 2. In general, aniline **1a** reacts with formamide **2a** to give the corresponding formylated product **3aa** in 95% yield. Aniline derivatives with electron-donating groups such as –Me and –OMe at *para*- and *meta*- position were employed, and it was observed that, the formylation reaction with electron rich anilines offers excellent yields **3ba-3da**. Next, the steric effect was studied and it was found that *ortho*–methoxy aniline, 2,4,6-trimethyl aniline and 2,6-diethyl aniline provided low yield of **3ea-3ga** as compared to **3ba-3da**. The *para*-$OCHF_2$ substituted aniline also gave an excellent yield of 89% of **3ha**. Weakly electron withdrawing groups such as –Br and –F on the aniline, afforded corresponding products **3ia** and **3ja** in excellent yields.

Table 2. Substrate scope of formylation of aniline derivatives[a,b]

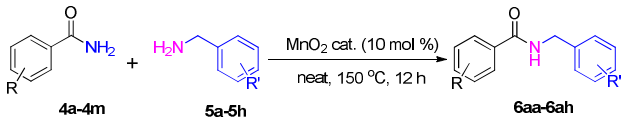


[a] Reaction conditions: aniline derivatives **1a-1j** (2 mmol), formamide **2a** (4 mmol), MnO_2 (10 mol%) in a sealed tube for 3 h at 150 °C, [b] Yield of isolated pure product.

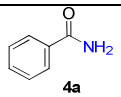
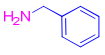
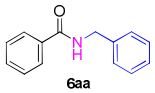
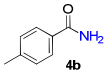
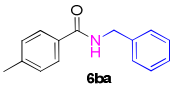
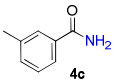
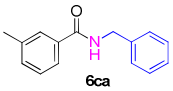
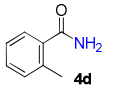
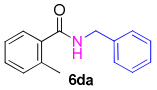
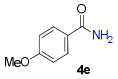
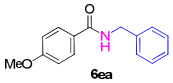
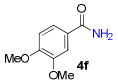
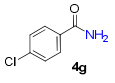
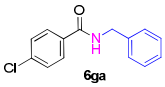
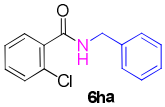
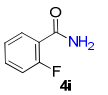
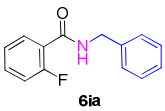
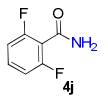
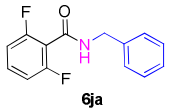
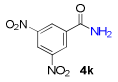
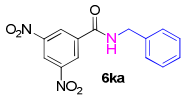
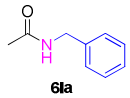
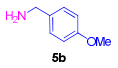
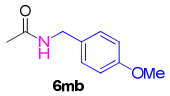
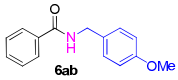
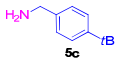
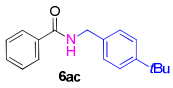
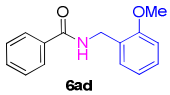
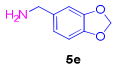
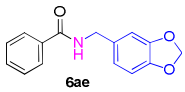
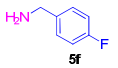
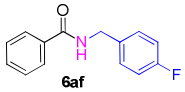
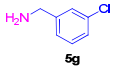
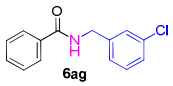
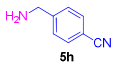
After the study of formylation reaction, the study of transamidation of primary amide with benzylamine was carried out and the corresponding results are shown in Table 3. Firstly, we initiated our work by choosing benzamide **4a** and benzylamine **5a** as model substrates under the same reaction parameters as that of formylation reaction. This resulted in a 56% yield of **6aa**. Encouraged by this result, we increased the catalyst loading and the reaction was run for a longer period of time. To our delight, the yield of **6aa** went up to 93% (Table 3, entry 1). Thus, the optimized reaction conditions of transamidation are: **4a** (2 mmol), **5a** (4 mmol), MnO_2 (20 mol%) at 150 °C for 12 h. Under the optimized reaction conditions, scope of this methodology was explored for various aromatic and aliphatic amides with different amines. As shown in Table 2, all the substrates examined provided excellent to good yields. Effects of electron donating and withdrawing groups were also studied. It was found that electron donating groups on benzamide **4a** produced corresponding products **6ba-6fa** in excellent yields (Table 3, entries 2-6). Subsequently, the reaction of **4a** bearing electron

weakly withdrawing groups also furnished corresponding amides **6ag-6aj** in good to moderate yields (Table 3, entries 7-10). However, the amide **4k** bearing two -NO_2 groups provided only 24% yield of **6ka** (Table 1, entry 11). Interestingly, the reaction could also tolerate aliphatic amide **4l** thus leading to the formation of products **6la** and **6lb** respectively (Table 3, entry 12 and 13). In the next set of experiments, we explored the substrate scope of benzylamines. The electron donating groups on benzylamine **5a** at *para*- and *ortho*- positions provided the products **6ab-6ae** in excellent yields (Table 3, entries 14-17). Benzyl amine containing weak electron withdrawing groups reacts smoothly with benzamide afforded

Table 3. Substrates cope of transamidation of amide by amine



4a-4m 5a-5h 6aa-6ah

Entry	Primary amides	Amines	Products	Yield (%)[b]
1	 4a	 5a	 6aa	93
2	 4b	5a	 6ba	91
3	 4c	5a	 6ca	90
4	 4d	5a	 6da	83
5	 4e	5a	 6ea	89
6	 4f	5a	 6fa	86
7	 4g	5a	 6ga	82
8	 4h	5a	 6ha	71
9	 4i	5a	 6ia	77
10	 4j	5a	 6ja	65
11	 4k	5a	 6ka	27
12	 4l	5a	 6la	81
13	4l	 5b	 6mb	83
14	4a	5b	 6ab	90
15	4a	 5c	 6ac	93
16	4a	 5d	 6ad	81
17	4a	 5e	 6ae	87
18	4a	 5f	 6af	82
19	4a	 5g	 6ag	83
20	4a	 5h	6ah	64

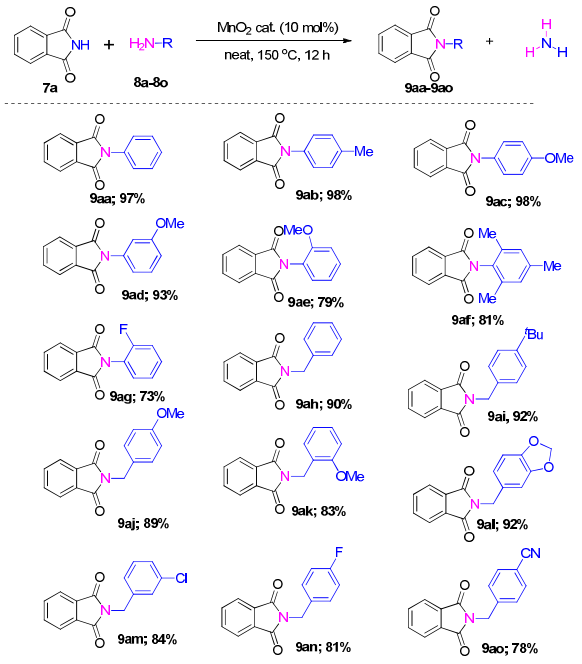
[a] Reaction conditions: primary amide derivatives **4a-4r** (2 mmol), amine **5a-5h** (4 mmol), MnO_2-catalyst (20 mol%) in a sealed tube for 12 h at 150 °C, [b] Isolated yields.

corresponding products with good yield **6af-6ag**. The benzyl amine containing –CN group at -*para* position furnishes moderate yield of product **6ah**.

Finally, we investigated transamidation of phthalimide (secondary amide) with various primary amines (Table 4). Phthalimides are widely used in organic transformations as a precursor for dyestuffs, drugs and in fine chemicals.[26] Initially, the reaction parameters were optimized by using phthalimide **7a** (2 mmol) and aniline **8a** (4 mmol) in the presence of 10 mol% of MnO_2 catalyst at 150 °C for 3 h. Unfortunately, a very low yield of 36% of the desired product **9aa** was obtained.

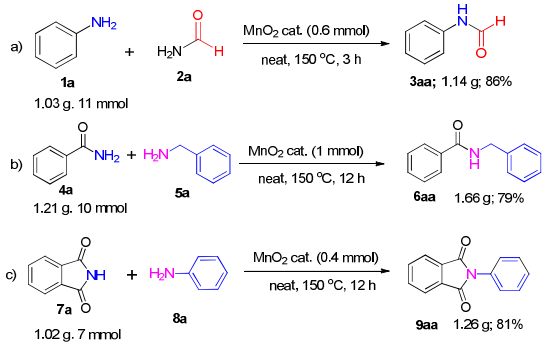
However, when the reaction was carried out for 12 h, an excellent yield of 98% of **9aa** was obtained. Thus, the optimized reaction conditions of transamidation of phthalimide are: **7a** (2 mmol), **8a** (4 mmol), MnO_2 (10 mol%), at 150 °C for 12 h.

Table 4. MnO_2 catalysed transamidation of phthalimide with primary amines [a,b]



[a] Reaction conditions: phthalimide **9a** (2 mmol), amine derivatives **8a-8o** (4 mmol), catalyst (10 mol%) in a sealed tube for 12 h at 150 °C, [b] Isolated yields.

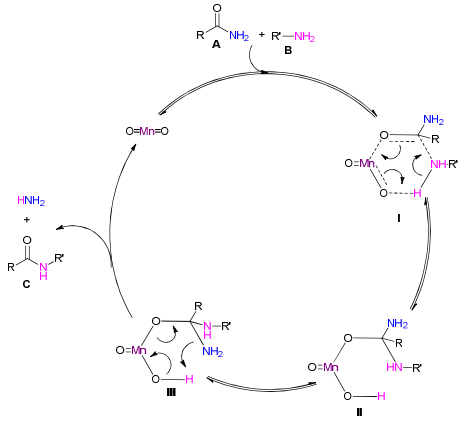
Various transamidated products of phthalimide with anilines and benzylamines were synthesised in good to excellent yields (78-98%). Aniline and benzylamine with electron donating substituents at *para*- and *meta*- position gave excellent yields whereas sterically hindered *ortho*- substituted aniline and benzylamine gave corresponding products **9ab-9al** in good yields. Benzylamine containing weakly electron withdrawing groups such as –Cl, –F and –CN gave good to excellent yields of products **9am-9ao**.



Scheme 2. Gram scale formylation and transamidation reaction

To demonstrate the synthetic utility of this developed protocol, gram scale reactions were carried out by employing 1.02 g (11 mmol) of aniline **1a** under the standard reaction condition (Scheme 2, eqn. a). This transformation proceeded smoothly to give 1.14 g (86%) of formanilide **3aa** (eqn. b, Scheme 2). Further, transamidation of both benzamide and phthalimide with benzylamine and aniline were also carried out successfully and provided corresponding products **6aa** and **9aa** in good isolated yields 1.66 g (79%) and 1.26 g (81%) respectively (Scheme 2, eqn. b and c).

A plausible reaction mechanism for the MnO_2 catalyzed transamidation reactions is proposed (Scheme 3). Manganese acts as a Lewis acid possessing strong adjacent basic sites. It is believed that the reaction first precedes with the formation of a six-member intermediate[15] **I** by addition of **A** and **B** to MnO_2. This is followed by a proton transfer which takes place from **B** to MnO_2 resulting in the formation of intermediate **II** which further isomerises to intermediate **III**. This intermediate collapses to afford the product along with expulsion of ammonia and simultaneous regeneration of MnO_2. The regenerated MnO_2 is available for the subsequent catalytic cycle.



Scheme 3. Plausible mechanism for MnO_2 catalyzed transamidation reaction.

Conclusions

In conclusion, we have developed a simple and synthetically efficient protocol for the synthesis of *N*-substituted amides by carrying out formylation and transamidation reactions catalyzed by MnO_2. The present methodology involves the use of relatively inexpensive Mn catalyst as compared to other expensive transition metals reported. Additionally, the protocols do not require inert atmosphere, take place in less reaction time, solvent free (neat) reaction conditions, are scalable and provide good to excellent yield of the products.

General procedure

All reactions were carried out in oven-dried glassware. All derivatives of amine, amide and MnO_2 were purchased from

Aldrich, Alfa Aesar, Spectrochem and Thomas Baker. Analytical TLC was performed with 60 F254 silica gel plates (0.25 mm thickness). Column chromatography was performed with silica gel (100-200 mesh). NMR spectra were recorded with an Agilent Technologies (^{1}H NMR at 500 MHz, ^{13}C NMR at 125 MHz) spectrometer. The chemical shifts are reported in ppm relative to tetramethylsilane as internal standard and the coupling constant in Hz. GC yields were obtained with a Perkin Elmer Clarus 400 instrument with an ELITE-1 column. The mass spectrometry was performed with a Shimadzu instrument in Electro Spray Ionization (ESI) mode.

I) Experimental procedure for MnO_2 catalyzed formylation of aniline using formamide

An oven dried 15 mL glass vial with a magnetic bar was charged with aniline (**1a**, 2 mmol, 186 mg), formamide (**2a**, 4 mmol, 180 mg) and MnO_2 (10 mol%, 8.7 mg), the reaction mixture was stirred for 3 h at 150 ^{o}C. After completion of reaction, the reaction mixture was cooled to room temperature. All volatiles were removed under vacuum. The product was extracted with 20 mL of ethyl acetate and the organic layer was washed with saturated aq. HCl (20 mL) and dried over Na_2SO_4 and the solvent was removed under vacuum. The formylated amide product was purified by column chromatography (silica gel, 100-200 mesh).

II) Experimental procedure for MnO_2 catalyzed transamidation of benzamide with benzylamine

An oven dried 15 mL glass vial with a magnetic bar was charged with MnO_2 (20 mol%, 17.4 mg), benzamide (**4a**, 2 mmol, 242 mg), benzylamine (**5a**, 4 mmol, 428 mg), the reaction mixture was stirred for 12 h at 150 ^{o}C in 15 mL. After completion of reaction, the reaction mixture was cooled to room temperature. All volatiles were removed under vacuum. The product was extracted with 20 mL of ethyl acetate and the organic layer was washed with saturated aq. HCl (20 mL) and dried over Na_2SO_4 and the solvent was then removed under vacuum. The *N*-benzylbenzamide product was purified by column chromatography (silica gel, 100-200 mesh).

III) Experimental procedure MnO_2 catalyzed transamidation of phthalimide with aniline

An oven dried 15 mL glass vial with a magnetic bar was charged with MnO_2 (10 mol%, 8.7 mg), phthalamide (**7a**, 2 mmol, 370 mg), aniline (**8a**, 4 mmol, 372 mg), the reaction mixture was stirred for 12 h at 150 ^{o}C. After completion of reaction, the reaction mixture was cooled to room temperature. All volatiles were removed under vacuum. The product was extracted with 20 mL of ethyl acetate and the organic layer was washed with saturated aq. HCl (20 mL) and dried over Na_2SO_4 and the solvent was then removed under vacuum. The transamidated amide product was purified by column chromatography (silica gel, 100-200 mesh).

Representative analytical data

***N*-phenylformamide (3aa)** [17]

pale brownish solid ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.91 (d, *J* = 11.0 Hz, 1H), 8.49 (d, *J* = 11.5 Hz, 1H), 8.43 (s, 1H), 8.23 (d, *J* = 1.8 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.08 – 6.96 (m, 2H), 6.89 – 6.74 (m, 4H), 3.77 (s, 3H), 3.74 (s, 3H).

***N*-(4-methoxyphenyl)formamide (3ba)**[18]

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.54 (d, *J* = 11.4 Hz, 1H), 8.47 (s, 1H), 8.30 (s, 1H), 7.80 (s, 1H), 7.31 (dd, *J* = 33.9, 3.5 Hz, 2H), 6.92 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.80 (dd, *J* = 19.0, 8.5 Hz, 2H), 6.66 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 3.85 (d, *J* = 10.1 Hz, 12H).

***N*-(3-methoxyphenyl)formamide (3ca)**[27a]

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.69 (s, 2H), 8.35 (d, *J* = 1.7 Hz, 1H), 7.82 (s, 1H), 7.34 – 7.16 (m, 3H), 7.09 – 6.98 (m, 1H), 6.78 – 6.57 (m, 4H), 4.01 – 3.67 (m, 6H).

***N*-(3,4-dimethoxyphenyl)formamide (3da)**[27b]

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.53 (d, *J* = 11.5 Hz, 1H), 8.33 (s, 1H), 7.89 (d, *J* = 10.0 Hz, 1H), 7.57 (ddd, *J* = 43.5, 22.4, 1.7 Hz, 1H), 7.39 – 7.25 (m, 3H), 7.03 – 6.88 (m, 2H), 6.82 (dd, *J* = 15.0, 8.5 Hz, 2H), 6.70 – 6.60 (m, 2H), 3.98 (d, *J* = 6.3 Hz, 2H), 3.89 – 3.86 (m, 11H).

***N*-(2-methoxyphenyl)formamide (3ea)**[27c]

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm 8.67–8.29 (m, 2H), 8.07 (d, *J* = 83.8 Hz, 1H), 7.13–6.94 (m, 1H), 6.93–6.75 (m, 2H), 3.77 (s, 3H); 13C NMR (101 MHz, $CDCl_3$) δ_C/ppm 161.89, 159.26, 148.90, 147.98, 126.75, 126.07, 125.34, 124.27, 120.98, 120.86, 120.41, 117.05, 111.31, 110.15, 55.66; GCMS (EI, 70 eV): m/z (%): 151 (72.3, M^+), 123 (35.3), 108 (100.0), 92 (5.9), 80 (62.6), 65 (16.8), 52 (15.8).

***N*-mesitylformamide (3fa)**[27d]

White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.40 – 8.03 (m, 1H), 6.92 (d, *J* = 15.2 Hz, 3H), 2.26 (dd, *J* = 22.2, 18.4 Hz, 9H).

***N*-(2,6-diethylphenyl)formamide (3ga)**[27d]

White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.31 (d, *J* = 1.5 Hz, 1H), 8.05 (d, *J* = 11.9 Hz, 1H), 7.82 (d, *J* = 10.8 Hz, 1H), 7.41 (s, 1H), 7.30 – 7.20 (m, 2H), 7.13 (dd, *J* = 19.7, 7.6 Hz, 4H), 2.62 (dd, *J* = 43.4, 7.6 Hz, 8H), 1.26 – 1.13 (m, 12H).

***N*-(4-(difluoromethoxy)phenyl)formamide (3ha)**

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.64 (t, *J* = 18.8 Hz, 1H), 8.34 (s, 1H), 7.87 (s, 1H), 7.54 (d, *J* = 8.9 Hz, 2H), 7.11 (dt, *J* = 17.4, 8.6 Hz, 5H), 6.48 (td, *J* = 73.7, 10.0 Hz, 2H).

***N*-(3-bromophenyl)formamide (3ia)** [27a]

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm 9.37–8.62 (m, 2H), 8.30 (s, 1H), 7.78 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.22–6.95 (m, 3H), 3.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C/ppm 162.99, 160.15, 138.24, 138.17, 131.03, 130.37, 128.19, 127.75, 123.22, 123.13, 122.53, 121.55, 118.71, 117.15; GCMS (EI, 70 eV): m/z (%): 201 (54.1, M^+), 199 (57.7), 173 (47.6), 171 (49.3), 143 (3.8), 145 (3.6), 92 (99.3), 65 (100.0), 50 (6.9).

***N*-(2-fluorophenyl)formamide (3ja)**[27d]

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.69 (d, *J* = 11.3 Hz, 1H), 8.47 (s, 2H), 8.32 (t, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 86.1 Hz, 3H), 7.25 (dd, *J* = 13.2, 3.6 Hz, 1H), 7.19 – 7.02 (m, 8H).

_N_-benzylbenzamide (6aa)[16]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.79 (dd, *J* = 5.0, 3.9 Hz, 2H), 7.52–7.41 (m, 3H), 7.35 (d, *J* = 4.4 Hz, 4H), 7.30 (dd, *J* = 8.8, 4.5 Hz, 1H), 6.61 (br s, 1H), 4.64 (d, *J* = 5.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C/ppm 167.43, 138.19, 134.33, 131.55, 128.76, 128.58, 127.89, 127.59, 126.99, 44.10; GCMS (EI, 70 eV): m/z (%): 211 (47.6, M^+), 105 (100.0), 91 (10.7), 77 (65.1), 51 (20.2).

_N_-benzyl-4-methylbenzamide (6ba)[16]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.70 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 4.3 Hz, 3H), 7.30 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.49 (s, 1H), 4.64 (d, *J* = 5.6 Hz, 2H), 2.39 (s, 3H).

_N_-benzyl-3-methylbenzamide (6ca)[28a]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.63 (s, 1H), 7.57 (dd, J = 4.2, 2.8 Hz, 1H), 7.43 – 7.21 (m, 7H), 4.63 (d, *J* = 5.7 Hz, 2H), 2.38 (s, 3H).

_N_-benzyl-4-methoxybenzamide (6ea)[21]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.77 (d, *J* = 8.7 Hz, 2H), 7.39 – 7.22 (m, 4H), 6.93 – 6.85 (m, 2H), 6.64 (s, 1H), 4.60 (d, *J* = 5.5 Hz, 2H), 3.83 (s, 3H).

_N_-benzyl-4-chlorobenzamide (6ga)[15]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.72 (dd, *J* = 8.8, 2.2 Hz, 2H), 7.48 – 7.24 (m, 7H), 6.61 (s, 1H), 4.61 (d, *J* = 5.7 Hz, 2H).

_N_-benzyl-2-chlorobenzamide (6ha)[28b]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.14 (t, *J* = 7.9 Hz, 1H), 7.54 – 7.43 (m, 1H), 7.39 – 7.27 (m, 5H), 7.11 (dd, *J* = 12.1, 8.3 Hz, 2H), 4.69 (d, *J* = 5.7 Hz, 2H).

_N_-benzyl-2-fluorobenzamide (6ia)[28c]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.14 (t, *J* = 8 Hz, 1H), 7.53 – 7.44 (m, 1H), 7.41 – 7.25 (m, 5H), 7.11 (dd, *J* = 12, 8 Hz, 2H), 4.69 (d, *J* = 5.7 Hz, 2H).

_N_-benzyl-3,5-dinitrobenzamide (6ka)[28d]
Yellow solid; ^{1}H NMR (500 MHz, DMSO) δ_H/ppm 9.08 – 8.59 (m, 2H), 7.39 (ddd, *J* = 34.2, 23.6, 7.3 Hz, 2H), 4.08 (s, 1H).

_N_-benzylacetamide (6la)[18]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.39 – 7.13 (m, 5H), 6.38 (s, 1H), 4.36 (t, *J* = 6.7 Hz, 2H), 2.00 – 1.91 (m, 3H).

_N_-(4-methoxybenzyl)benzamide (6ab)[16]
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm 7.76 (d, *J* = 6.7 Hz, 2H), 7.41 (dd, *J* = 26.0, 6.8 Hz, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.59 (br s, 1H), 4.52 (d, *J* = 4.9 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C/ppm 167.28, 159.05, 134.39, 131.45, 130.24, 129.25, 128.52, 126.93, 114.10, 55.28, 43.58; GCMS (EI, 70 eV): m/z (%): 241 (27.5, M^+), 221(7.3), 207 (42.9), 191(6.7), 121 (10.5), 105 (45.3), 91(20.0), 77 (70.3), 55 (40.2), 39 (100.0).

_N_-(4-*(tert*-butyl)benzyl)benzamide (6ac)[28d]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.80 (dd, *J* = 4.3, 3.9 Hz, 2H), 7.58 – 7.47 (m, 1H), 7.44 – 7.35 (m, 4H), 7.33 – 7.26 (m, 2H), 6.62 (s, 1H), 4.60 (d, *J* = 5.5 Hz, 2H), 1.33 (d, *J* = 1.3 Hz, 9H).

_N_-(2-methoxybenzyl)benzamide (6ad)[28e]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.93 – 7.69 (m, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.28 (dd, *J* = 13.0, 4.3 Hz, 1H), 7.05 – 6.86 (m, 2H), 6.76 (s, 1H), 4.64 (d, *J* = 5.8 Hz, 2H), 3.88 (s, 3H).

_N_-(benzo[d][1,3]dioxol-5-ylmethyl)benzamide (6ae)[28f]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.78 (d, *J* = 6.6 Hz, 2H), 7.54 – 7.45 (m, 1H), 7.39 (dd, *J* = 10.0, 5.1 Hz, 2H), 6.84 – 6.73 (m, 3H), 6.67 (s, 1H), 5.92 (d, *J* = 2.7 Hz, 2H), 4.51 (dd, *J* = 4.9, 2.9 Hz, 2H).

_N_-(3-chlorobenzyl)benzamide (6ag)[19b]
White solid; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm 7.76 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 5.5 Hz, 1H), 7.33 (s, 2H), 7.17 (t, *J* = 22.8 Hz, 4H), 4.47 (d, *J* = 3.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C/ppm 167.70, 140.46, 134.37, 133.99, 131.62, 129.88, 128.52, 127.64, 127.50, 127.09, 127.07, 125.75, 43.29; GCMS (EI, 70 eV): m/z (%): 245 (6.8, M^+), 135 (5.1), 105 (50.0), 103 (36.0), 91 (3.7), 77 (35.4), 76 (17.5), 51 (15.4), 32 (100.0).

_N_-(4-cyanobenzyl)benzamide (6ah)[28g]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.80 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.48 – 7.22 (m, 4H), 6.94 (s, 1H), 4.66 (d, *J* = 5.7 Hz, 2H).

2-phenylisoindoline-1,3-dione (9aa)[21b]
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm 7.94–7.92 (m, 2H), 7.78–7.77 (m, 2H), 7.45 (dt, *J* = 17.7, 8.1 Hz, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C/ppm 167.26, 134.37, 131.72, 131.62, 129.09, 128.09, 126.55, 123.73; GCMS (EI, 70 eV): m/z (%): 223 (100.0, M^+), 207 (18.2), 179 (60.4), 152 (7.5), 111 (6.9), 104 (26.8), 76 (58.6), 50 (15.6).

2-(*p*-tolyl)isoindoline-1,3-dione (9ab)[19b]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.96–7.94 (m, 2H), 7.80–7.78 (m, 2H), 7.32–7.27 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C/ppm 167.46, 138.21, 134.33, 131.80, 129.80, 128.67, 126.47, 123.70, 21.24; GCMS (EI, 70 eV): m/z (%):(100.0, M^+), 193 (41.9), 165 (8.1), 117 (10.2), 104 (18.2), 90 (9.5), 76 (43.1), 50 (12.9).

2-(4-methoxyphenyl)isoindoline-1,3-dione (9ac)[19b]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.95-7.93(m, 2H), 7.79–7.77 (m, 2H), 7.35–7.33 (m, 2H), 7.04–7.00 (m, 2H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C/ppm 167.61, 159.22,

134.33, 134.28, 131.77, 127.96, 124.21, 123.67, 123.54, 114.46, 55.51; GCMS (EI, 70 eV): m/z (%): 253 (100.0, M^+), 238 (54.8), 210 (17.7), 130 (15.3), 106 (13.8), 76 (25.6).

2-(3-methoxyphenyl)isoindoline-1,3-dione (9ad)[29a]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.01 – 7.91 (m, 2H), 7.85 – 7.73 (m, 2H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.07 – 6.90 (m, 3H), 3.84 (s, 3H).

2-(2-methoxyphenyl)isoindoline-1,3-dione (9ae)[29b]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.96-7.77 (m, 4H), 7.46–7.42 (m, 1H), 7.28–7.26 (m, 1H), 7.10–7.05 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ_C/ppm 167.42, 155.39, 134.29, 134.13, 132.23, 130.70, 129.98, 123.67, 123.56, 120.86, 120.20, 112.12, 55.82; GCMS (EI, 70 eV): m/z (%): 253 (100.0, M^+), 235 (38.7), 224 (16.3), 210 (10.4), 195 (7.3), 179 (32.0), 154 (5.8), 120 (17.9), 104 (43.3), 76 (60.2), 50 (15.2).

2-mesitylisoindoline-1,3-dione (9af)[29c]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.97 (dd, *J* = 4.4, 3.3 Hz, 2H), 7.80 (dd, *J* = 4.4, 3.2 Hz, 2H), 7.01 (s, 2H), 2.34 (s, 3H), 2.13 (s, 6H).

2-(2-fluorophenyl)isoindoline-1,3-dione (9ag)[29d]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 8.01 – 7.93 (m, 2H), 7.85 – 7.76 (m, 2H), 7.46 (ddd, *J* = 8.2, 7.1, 4.1 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.28 (ddd, *J* = 9.6, 8.7, 7.6 Hz, 2H).

2-benzylisoindoline-1,3-dione (9ah)[20]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.85 (dd, *J* = 5.2, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.24 (m, 3H), 4.85 (s, 2H).

2-(4-(*tert*-butyl)benzyl)isoindoline-1,3-dione (9ai)[29e]
White solid; ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.84 (dd, *J* = 5.2, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.36 (dd, *J* = 23.0, 8.3 Hz, 4H), 4.83 (s, 2H), 1.29 (s, 9H).

2-(4-methoxybenzyl)isoindoline-1,3-dione (9aj)[29f]
White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm 7.74 (d, *J* = 2.4 Hz, 2H), 7.60 (s, 2H), 7.36–7.26 (m, 2H), 6.78 (dd, *J* = 4.6, 3.3 Hz, 2H), 4.72 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ_C/ppm 167.99, 159.14, 133.87, 132.08, 130.09, 128.63, 123.20, 113.93, 55.19, 40.99; GCMS (EI, 70 eV): m/z (%): 241 (27.5, M^+), 221(7.3), 207 (42.9), 191(6.7), 121 (10.5), 105 (45.3), 91(20.0), 77 (70.3), 55 (40.2), 39 (100.0).

2-(2-methoxybenzyl)isoindoline-1,3-dione (9ak)[29g]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.92 – 7.81 (m, 2H), 7.76 – 7.67 (m, 2H), 7.30 – 7.13 (m, 2H), 6.88 (td, *J* = 8.6, 5.6 Hz, 2H), 4.92 (s, 2H), 3.85 (s, 3H).

2-(benzo[d][1,3]dioxol-5-ylmethyl)isoindoline-1,3-dione (9al)[29h]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.0 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 1H), 5.91 (s, 2H), 4.75 (s, 2H).

2-(4-fluorobenzyl)isoindoline-1,3-dione (9an)[29i]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm 7.95 – 7.82 (m, 2H), 7.78 – 7.70 (m, 2H), 7.64 – 7.57 (m, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 4.88 (s, 2H).

4-((1,3-dioxoisoindolin-2-yl)methyl)benzonitrile (9ao)[29d]
White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm δ 7.87 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.75 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 4.89 (s, 2H).

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Notes and references

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MnO_2 catalyzed formylation of amines and transamidation of amides under solvent-free condition

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Graphical abstract