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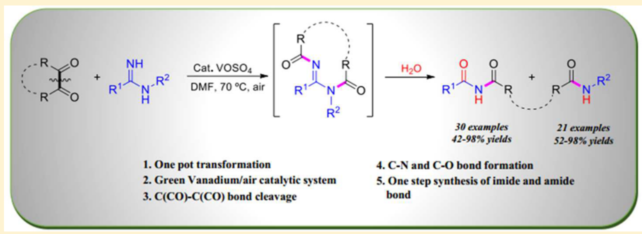
Vanadium-Catalyzed Oxidative C(CO)−C(CO) Bond Cleavage for C−N Bond Formation: One-Pot Domino Transformation of 1,2-Diketones and Amidines into Imides and Amides

Chander Singh Digwal, Upasana Yadav, P. V. Sri Ramya, Sravani Sana, Baijayantimala Swain, and Ahmed Kamal*

Department of Medicinal Chemistry, National Institute of Pharmaceutical Education and Research (NIPER), Balanagar, Hyderabad 500037, India

S *Supporting Information*

ABSTRACT: A novel vanadium-catalyzed one-pot domino reaction of 1,2-diketones with amidines has been identified that enables their transformation into imides and amides. The reaction proceeds by dual acylation of amidines via oxidative C(CO)−C(CO) bond cleavage of 1,2-diketones to afford *N*,*N*′-diaroyl-*N*-arylbenzamidine intermediates. In the reaction, these intermediates are easily hydrolyzed into imides and amides through vanadium catalysis. This method provides a practical, simple, and mild synthetic approach to access a variety of imides as well as amides in high yields. Moreover, one-step construction of imide and amide bonds with a long-chain alkyl group is an attractive feature of this protocol.



■ INTRODUCTION

Imides are the key structural motifs in many natural products as well as pharmaceutical agents[1] and also appear as important precursors in a variety of reactions.[2] Accordingly, imide synthesis was explored extensively and many improved methods were developed in the past few decades.[3] However, the use of sophisticated reagents, low yield of imides, limited substrate availability, and product diversity are some limitations for most of them. The efficient routes for the synthesis of imides rely on direct oxidation of *N*-alkylbenzamides[4] (Figure 1a) and cerric ammonium nitrate (CAN)-promoted oxidation of 4,5-diphenyloxazoles (Figure 1b).[5] In addition, Fe/Cu-catalyzed direct coupling of amides with thioesters[6] and aldehydes[7] also provided access to a variety of imides. Moreover, Guan and co-workers reported the Pd-catalyzed aminocarbonylation of aryl iodides with amides for the rapid synthesis of imides (Figure 1c).[8] It is noteworthy that, in most of these methods, a stoichiometric or excess amount of oxidants, sometimes additives, or special preparation of the substrates is required for the synthesis of imides. Hence, the development of simple, inexpensive, greener, and high-yielding methods for the preparation of imides from easily accessible starting materials is of considerable importance, especially one which could be operative under oxidant- and additive-free conditions.

Over the past several years, the prominence of C−C bond cleavage has grown increasingly, because these reactions provide multifarious molecular transformations that are otherwise hard to achieve.[9,10] Among them, the C(CO)−C(α) bond cleavage of ketones has evolved as a powerful tool for the construction of many organic functional groups such as acids,[11] aldehydes,[12] esters,[13] and α-ketoesters[14] etc. Moreover, some remarkable approaches to Cu-catalyzed direct aerobic oxidative C−N bond formation utilizing C(CO)−C(α) bond cleavage of ketones have also been reported.[15]

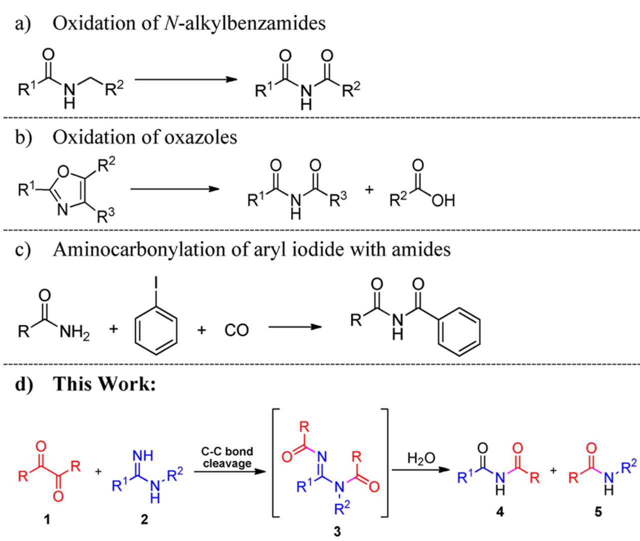


Figure 1. Comparison of previous approaches with the present method developed for the synthesis of imides.

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Vanadium is nontoxic, inexpensive, readily available, and also present in various bacterial enzymes.[16] Several research groups have explored the potential utility of vanadium-based catalysts to afford oxidative C−C bond cleavage of ditertiary glycols,[17] α-hydroxyketones or ketones,[18] and catechols[19] etc. Although the synthetic utility of C(CO)−C(CO) bond cleavage of 1,2-diketones for their transformation into acids and/or esters is also well documented in the literature,[20] a metal catalytic system for direct C−N bond formation through C(CO)−C(CO) bond cleavage has not been realized to date. Herein, we report a novel vanadium-catalyzed oxidative C(CO)−C(CO) bond cleavage reaction of 1,2-diketones **1** with *N*-arylamidines **2** for C−N bond formation, which allows their transformation into imides **4** and amides **5** through hydrolysis of in situ generated *N*,*N*′-diaroyl-*N*-arylbenzamidines **3** in a one-pot manner (Figure 1d).

RESULTS AND DISCUSSION

In 1952, Peak reported that the acidic hydrolysis of *N*,*N*′-dibenzoyl-*N*-phenylbenzamidine (**3a**) provided *N*-benzoylbenzamide (**4aa**) and benzanilide (**5a**) by the reaction at the amidino carbon center (Figure 2a).[21] Moreover, a photo-

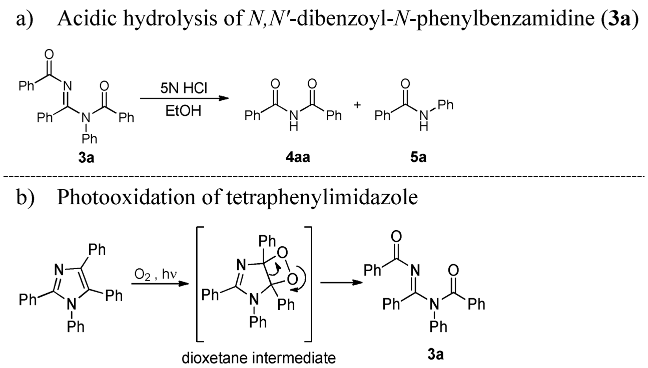

Figure 2. Previously reported acid hydrolysis of *N*,*N*′-dibenzoyl-*N*′-phenylbenzamidine (**3a**) and photosensitized autoxidation of tetraphenylimidazole to **3a**.

sensitized autoxidation of tetraphenylimidazole to **3a,** probably via ring opening of the dioxetane intermediate, was described by the group of Wasserman (Figure 2b).[22] These investigations led us to question whether (1) the C(CO)−C(CO) bond of 1,2-diketones could be activated with *N*-arylamidines in the presence of an appropriate metal catalyst to provide the corresponding *N*,*N*′-diaroyl-*N*-arylbenzamidines **3** and (2) the hydrolysis of **3** could be secured under mild conditions by employing a Lewis acid metal catalyst to activate the *N*′-carbonyl group, as it might promote electron deficiency at the amidino carbon atom due to keto−imine conjugation.

To test this concept, we commenced our research with the screening of a 20 mol % concentration of various metal catalysts for the model reaction of benzil (**1a**), *N*-phenylbenzimidamide (**2aa**), and H_2O using dry *N*,*N*-dimethylformamide (DMF) as the solvent under an air atmosphere (Supporting Information, Table S1). These experiments disclosed that the frequently used copper sources $Cu(OAc)_2$, $CuCl_2$, CuBr, CuI, and $Cu(OTf)_2$ could activate the C(CO)−C(CO) bond to afford **3a** in 26−55% yields after 48 h at room temperature. Interestingly, in the presence of more acidic $Cu(OTf)_2$, the hydrolyzed products **4aa** and **5a** were also obtained in 21% and 22% yields, respectively. However, further modification of the reaction conditions using $Cu(OTf)_2$ did not give satisfying results, and other tested metal catalysts such as silver-based catalysts, $In(OTf)_3$, $Zn(OTf)_2$, $Sc(OTf)_3$, and $FeCl_3$ were found ineffective for this transformation.

Very recently, we reported that an inexpensive and less toxic vanadium salt, vanadyl sulfate ($VOSO_4$), is a highly efficient catalyst for the transformation of **1a** and *o*-phenylenediamines into quinaoxalines.[23] With this knowledge base, the model reaction was carried out in the presence of 20 mol % $VOSO_4$ at room temperature. Gratifyingly, **3a** was obtained in 96% yield after 8 h (entry 1, Table 1). The reaction did not show improvements with varying amounts of water (entries 2 and 3, Table 1). The hydrolysis of **3a** was very slow at room temperature, and **3a** remain unreacted even after a week (entry 4, Table 1). However, heating the reaction mixture at 70 °C for a period of 20 h afforded **4aa** and **5a** in 97% and 96% yields, respectively, with complete consumption of **3a** (entry 5, Table 1). Furthermore, the variation in the reaction temperature did not give superior results in terms of reaction time or yield of the products (entries 6 and 7, Table 1). The subsequent exploration of the effect of the catalyst loading proved that 20 mol % $VOSO_4$ was optimal for the reaction (entries 8 and 9, Table 1). Among various tested common solvents, DMF appeared to be the best solvent in terms of yield and reaction time (Supporting Information, Table S2). Thus, 20 mol % $VOSO_4$, 70 °C, and DMF are the optimal conditions to obtain **4aa** and **5a** in excellent yields (entry 5, Table 1).

To investigate the role of $VOSO_4$ on the hydrolysis of **3a**, two control experiments with and without $VOSO_4$ were carried out. The results revealed that the hydrolysis of **3a** did certainly occur only in the presence of $VOSO_4$ (Supporting Information, control experiments, eqs S1 and S2). Next, to shed light on the role of dioxygen in this one-pot process, the reaction was performed under a nitrogen atmosphere. After 20 h, **4aa** and **5a** were obtained with lower conversion of **3a** (entry 10, Table 1). Likewise, the hydrolysis of **3a** was also slow under anaerobic conditions (Supporting Information, control experiments, eq S3). These results indicate that oxygen is not required for C(CO)−C(CO) bond cleavage as well as catalyst turnover, although it does increase the rate of reaction (entry 11, Table 1). Furthermore, when the model reaction was performed in anhydrous conditions under an O_2 atmosphere, 74% **1a**, 19% **3a**, and traces of **4aa** and **5a** were obtained (entry 12, Table 1). These results strongly suggest that water is the crucial component for this one-pot transformation.

After adoption of the optimal reaction conditions, various amidines **2** were investigated with **1a** for the synthesis of imides considering *N*-phenylbenzamide (**5a**) as a byproduct (Table 2). To our delight, both electron-rich (**2ab** and **2ah**) and electron-deficient (**2ac−2ag**) substituents arylamidines provided excellent yields of the corresponding imide products (**4ab−4ah,** Table 2). Notably, halo substituents at *meta*- and *ortho*-positions on the aryl ring affected only the reaction times but not the yields (**4ad, 4ae,** and **4ag,** Table 2). It was observed that electron-donating substituents arylamidines react faster with **1a** than electron-deficient ones and favor formation of the corresponding intermediates **3**. On the other hand, hydrolysis of the intermediates to their corresponding imides and **5a** was faster with electron-deficient substituents arylamidines than electron-donating ones. This could be due to the fact that an electron-deficient group decreases the nucleophilicity of the nitrogen atom to attack carbonyl groups but increases the electron deficiency at the amidino carbon atom for water attack.

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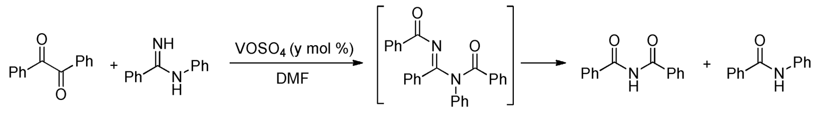
Table 1. Optimization of the Reaction Conditions Using $VOSO_4$ in DMF[a]



entry	[$VOSO_4 \cdot xH_2O$] (mol %)	amt of H_2O (equiv)	T (°C)	time (h)	yield of products[b] (%) 3a	4aa	5a
1[c]	20	5	rt	8	96	trace	trace
2[c]	20	10	rt	8	94	trace	trace
3[c]	20	2.5	rt	8	85	trace	trace
4[c]	20	5	rt	168	nd	nd	nd
5	20	5	70	20	0	97	96
6	20	5	60	32	0	92	91
7	20	5	80	18	0	87	92
8	30	5	70	20	0	94	95
9	10	5	70	30	0	89	92
10[d]	20	5	70	20	47	50	52
11[e]	20	5	70	17	0	87	90
12[f]	20	5	70	17	19	trace	trace

[a]Reaction conditions: 0.5 mmol of **1a** and 0.6 mmol of **2a** in the presence of $VOSO_4 \cdot xH_2O$ in dry DMF (3 mL) under air. [b]Isolated yields of pure products based on **1a**. nd = not determined. [c]The reaction was run at room temperature. [d]The reaction was run under a N_2 balloon. [e]The reaction was run under an O_2 balloon. [f]The reaction was run in dry DMF under an O_2 balloon with 4 Å molecular sieves; 74% **1a** was recovered.

Steric effects could be observed in the case of 2-methyl-*N*-phenylbenzmidamide (**2ai**), and the reaction afforded imide product **4ai** (Table 2) in 42% yield. In addition, *ortho*- and *meta*-disubstituted arylamidines **2aj** and **2ak** also provided good yields of the corresponding imide products **4aj** and **4ak** (Table 2). Heterocycle-derived amidines such as *N*-phenylthiophene-2-carboximidamide (**2al**), *N*-phenylfuran-2-carboximidamide (**2am**), 2-chloro-*N*-phenylnicotinimidamide (**2an**), and *N*-phenylisonicotinimidamide (**2ao**) reacted smoothly to yield the corresponding imide products **4al**−**4ao** (Table 2) in 84−94% yields. Moreover, the reaction of amidines bearing cyclopropyl (**2ap**) and 1-propyl (**2aq**) groups do not affect the efficiency of the method, and the corresponding imides **4ap** and **4aq** (Table 2) were obtained in 88% and 80% yields, respectively.

Next, the reactivity of symmetrical 1,2-diketones **1b** and **1c** toward various amidines was studied (Table 3). Comparable results with regard to the yields were obtained, when 1,2-bis(4-chlorophenyl)ethane-1,2-dione (**1b**) was reacted with amidines containing aromatic (**2aa**, **2ad**, and **2af**), heterocyclic (**2al**−**2an**), and aliphatic (**2ap** and **2aq**) partners, affording the corresponding imides **4ac** and **4ar**−**4ay** (Table 3) in 82−96% yields within 24 h. Notably, **2ai** also underwent smooth conversion to furnish imide product **4at** (Table 3) in 91% yield. This effect can be allied to the increased reactivity of carbonyl groups of **1b** due to chloro substituents, and thereby, amidines react faster with **1b** than **1a**. Moreover, chloro substituents on the aryl ring of **1b** also facilitate the hydrolysis of the corresponding intermediate. As expected, 1,2-bis(4-methoxyphenyl)ethane-1,2-dione (**1c**) reacted very slowly with amidines due to the decreased electrophilicity of the carbonyl groups and required much longer reaction times (72−96 h) to obtain good yields (77−86%) of the corresponding imide products **4ab** and **4az**−**4bb** (Table 3). The effect of electron-withdrawing groups on the aryl ring of amidines for the hydrolysis of intermediates is more obvious when we compare the reactions of **1c** with **2ac** and **2ah** in the generation of imides **4az** and **4ba** (Table 3). In the case of 4-chloro-*N*-phenylbenzimidamide (**2ac**), the corresponding intermediate was not obtained after 72 h, whereas a 10% yield of the corresponding intermediate was observed with 4-methyl-*N*-phenylbenzimidamide (**2ah**) even after 96 h.

In the present protocol, it could be expected that an unsymmetrical 1,2-diketone can give two corresponding intermediates with amidine, and as a result of their hydrolysis, four products (two imides and two amides) will exist in the reaction mixture. As evident from Table 4, the reaction of 1-(4-nitrophenyl)-2-phenylethane-1,2-dione (**1d**) with **2aa** certainly provided two imides (42% **4aa** and 44% **4bc**, Table 4) and two amides (45% **5a** and 42% **5d**, Table 4); however, it was somewhat disappointing as no selectivity was observed in the formation of these products. A comparable result was also obtained with **1e**, and the products **4bc**, **4ab**, **5b**, and **5d** (Table 4) were isolated in 38−41% yields. It is noteworthy that, in all the above reactions, the amide derivatives were also obtained in high yields.

Amides, as one of the most important classes of N-containing organic compounds, are known to be present in proteins, natural products, bioactive compounds, and agrochemicals.[24] In recent years, constant efforts have targeted efficient catalytic methods for the construction of the omnipresent amide bond.[25] Despite significant advancement in this area, there is still a continuing need for development of new synthetic methods for amide bond synthesis. Therefore, we turned to explore the scope and limitation of the present protocol for the amide synthesis (Table 5). In general, amidines containing electron-donating groups such as methoxy (**2ar**), trimethoxy (**2as**), methyl (**2aw**), and isopropyl (**2ax**) as well as halogen substituents (**2at**−**2av**) reacted efficiently with **1a** and afforded the corresponding amide derivatives **5e**−**5k** (Table 5) in 92−98% yields. However, the position of the chloro substituent (*para* and *meta*) has an obvious effect on the reaction time (8 h for **5g** and 6 h for **5h**, Table 5). This effect of chloro substituents present on the amidines is probably due to the reduction of the electron donor capacity of the nitrogen atom and thereby promotion of electron deficiency at the amidino

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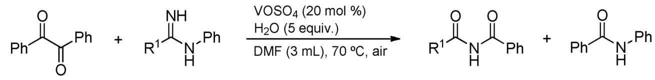
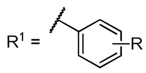
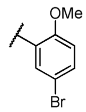
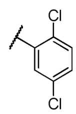
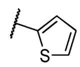
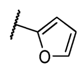
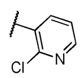
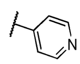
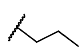
Table 2. One-Pot Synthesis of Imides: Substrate Scope of Amidines[a]



1a **2** **4** **5a**

Entry	Amidine (**2**)	Time (h)	Yield of products (%)[b]	
			Imide (**4**)	Amide (**5a**)
1	R = H **(2aa)**	20	97 **(4aa)**	96
2	4-OMe **(2ab)**	18	91 **(4ab)**	96
3	4-Cl **(2ac)**	18	98 **(4ac)**	95
4	3-Cl **(2ad)**	24	96 **(4ad)**	98
5	R¹ =  2-Cl **(2ae)**	36	96 **(4ae)**	94
6	4-Br **(2af)**	18	92 **(4af)**	96
7	3-Br **(2ag)**	22	92 **(4ag)**	91
8	4-Me **(2ah)**	22	95 **(4ah)**	98
9[c]	2-Me **(2ai)**	96	42 **(4ai)**	45
10	 **(2aj)**	24	82 **(4aj)**	78
11	 **(2ak)**	32	90 **(4ak)**	92
12	 **(2al)**	24	89 **(4al)**	93
13	 **(2am)**	18	94 **(4am)**	98
14	 **(2an)**	36	92 **(4an)**	91
15	 **(2ao)**	24	84 **(4ao)**	92
16	 **(2ap)**	18	88 **(4ap)**	93
17	 **(2aq)**	28	80 **(4aq)**	84

[a]Standard reaction conditions: **1a** (0.5 mmol), **2** (0.6 mmol), H_2O (2.5 mmol, 45 μL), and $VOSO_4{\cdot}xH_2O$ (0.1 mmol) in dry DMF (3 mL), at 70 °C, under air. [b]Isolated yields. [c]Accompanied by 35% unreacted corresponding intermediate.

carbon atom for facilitating attack by a water molecule. Moreover, this method becomes valuable for *N*-benzoylation of heat-sensitive electron-rich anilines **5e** and **5f** and electron-deficient anilines **5g**–**5i**. In the case of *N*- mesitylbenzamide (**2ay**), only a 76% yield of amide product **5l** (Table 5) was obtained due to considerable steric hindrance of the methyl groups. Aliphatic partners such as cyclopropyl (**2az**) and 2-pentyl (**2ba**) groups of amidines provided moderate yields of the corresponding amide products **5m** and **5n** (Table 5). Disappointingly, the reaction did not proceed when *N*-(*tert*-butyl)benzimidamide (**2bb**) was employed in the reaction. Furthermore, pyridine-derived amidines **2bc** and **2bd** transformed smoothly under optimal conditions and provided amides **5o** and **5p** (Table 5) in 95% and 97% yields, respectively. Although the reaction of *N*-(pyridin-2-yl)-benzimidamide (**2be**) and *N*-(5-bromopyridin-2- yl)-benzimidamide (**2bf**) also afforded good yields of the corresponding amide products **5q** and **5r** (Table 5), surprisingly their corresponding imide product **4aa** was obtained in 28% and 15% yields, respectively, with some unidentified products. These results indicate that an alternative reactivity of these amidines (**2be** and **2bf**) is involved in the generation of the corresponding amide products. These reactions are our focus for future development of new synthetic methods. Furthermore, a similar scope was observed for the synthesis of amides **5s** and **5t** (Table 5) when the reaction of **1b** and **1c** was carried out with **2aw** and **2ar**, respectively.

Overall, the present method displayed high functional group tolerance and the synthesis of the two most important N-containing classes of compounds, i.e., imides and amides, in moderate to high yields. Moreover, the scope of 1,2-diketones could also be extended to cyclohexane-1,2-dione (**1f**), but we ended up with low yields (33–41%) of the target products **6a**–**6c** (Table 6) and many byproducts. However, the reaction of biacetyl (**1g**) with **2ar** provided the corresponding imide (**4bd**, Table 6) and amide (**5u**) products in 74% and 78% yields,

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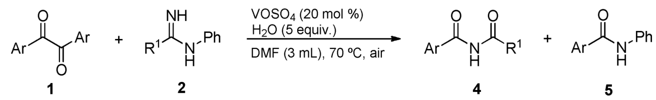
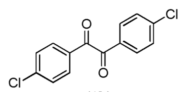
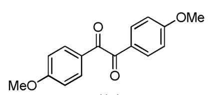
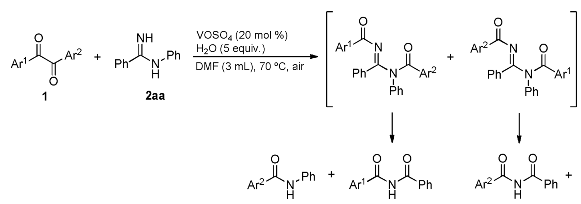
Table 3. One-Pot Synthesis of Imides: Substrate Scope of 1,2-Diketones[a]

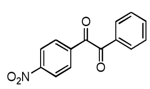
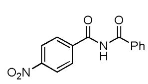
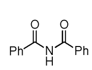
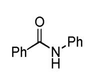
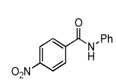
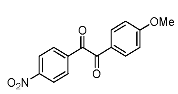
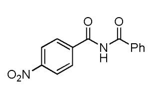
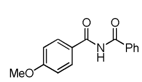
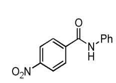
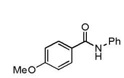


Entry	1,2-Diketone (**1**)	Amidine (**2**)	Time (h)	Yield of products (%)[b]	
				Imide (**4**)	Amide (**5**)
1		**2aa**	16	96 (**4ac**)	97 (**5b**)
2		**2ad**	18	95 (**4ar**)	97 (**5b**)
3		**2af**	16	89 (**4as**)	93 (**5b**)
4		**2ai**	16	91 (**4at**)	94 (**5b**)
5	 (**1b**)	**2al**	18	90 (**4au**)	93 (**5b**)
6		**2am**	18	91 (**4av**)	94 (**5b**)
7		**2an**	24	90 (**4aw**)	92 (**5b**)
8		**2ap**	18	84 (**4ax**)	88 (**5b**)
9		**2aq**	18	82 (**4ay**)	85 (**5b**)
10[c]		**2aa**	72	85 (**4ab**)	88 (**5c**)
11[c]	 (**1c**)	**2ac**	72	82 (**4az**)	83 (**5c**)
12[c,d]		**2ah**	96	77 (**4ba**)	80 (**5c**)
13[c]		**2ap**	72	86 (**4bb**)	87 (**5c**)

[a]Standard reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), H_2O (2.5 mmol, 45 μL), and $VOSO_4 \cdot xH_2O$ (0.1 mmol) in dry DMF (3 mL), at 70 °C, under air. [b]Isolated yields. [c]Accompanied by unreacted **1c**: 5% with **2aa**, 10% with **2ac**, 8% with **2ah**, 6% with **2ap**. [d]Accompanied by a 10% yield of the corresponding intermediate.

Table 4. One-Pot Reaction of Unsymmetrical 1,2-Diketones with 2aa[a]



Entry	1,2-Diketones (**1**)	Yield of the products[b]			
		Imides (**4**)		Amides (**5**)	
1	 (**1d**)	 44% (**4bc**)	 42% (**4aa**)	 45% (**5a**)	 42% (**5d**)
2	 (**1e**)	 40% (**4bc**)	 41% (**4ab**)	 38% (**5d**)	 40% (**5b**)

[a]Standard reaction conditions: **1** (0.5 mmol), **2aa** (0.6 mmol), H_2O (2.5 mmol, 45 μL), and $VOSO_4 \cdot xH_2O$ (0.1 mmol) in dry DMF (3 mL), at 70 °C, under air for 12 h.

respectively. It may be noted that, in the case of **1f**, the corresponding intermediates were not observed during the reaction by TLC analysis, which could be attributed to the rapid hydrolysis of the intermediates into **6a**–**6c**. The lower yields of these products might be correlated with increased side reactions due to the enolic form of **1f** or by the decomposition of the product formed. In spite of the low yield of these products, this approach represents an interesting research area for future catalyst development, by which imide and amide bond construction with a long-chain alkyl group can be achieved in one step.

Next, to elucidate the reaction mechanism of C(CO)–C(CO) bond cleavage of 1,2-diketones, some control experiments were carried out. It was found that benzil (**1a**) does not

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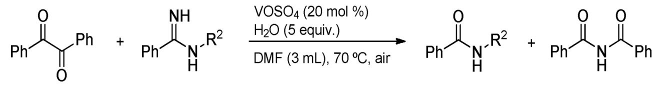
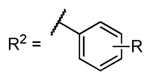
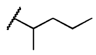
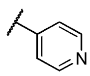
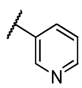
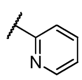
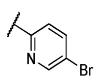
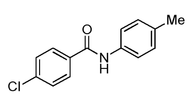
Table 5. Substrate Scope for One-Pot Synthesis of Amides[a]

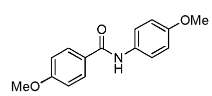


1a 2 5 4aa

Entry	Amidine (2)		Time (h)	Yield of products (%)[b]	
				Amide (5)	Imide (4aa)
1		R= 4-OMe (**2ar**)	18	97 (**5e**)	96
2		3,4,5-OMe (**2as**)	24	95 (**5f**)	93
3		4-Cl (**2at**)	8	98 (**5g**)	96
4		3-Cl (**2au**)	6	98 (**5h**)	95
5		4-F (**2av**)	24	94 (**5i**)	92
6		4-Me (**2aw**)	18	97 (**5j**)	94
7		4-*i*-propyl (**2ax**)	24	92 (**5k**)	89
8		2,4,6-Me (**2ay**)	96	76 (**5l**)	74
9	 (**2az**)		48	74 (**5m**)	76
10	 (**2ba**)		96	52 (**5n**)	58
11	 (**2bb**)		12	nr	nr
12	 (**2bc**)		24	95 (**5o**)	95
13	 (**2bd**)		18	97 (**5p**)	94
14	 (**2be**)		24	86 (**5q**)	28
15	 (**2bf**)		18	83 (**5r**)	15



5s: 18 h, 93 %
4ac: 91 %



5t: 96 h, 80 %
4ab: 74 %

[a]Standard reaction conditions: **1a** (0.5 mmol), **2** (0.6 mmol), H_2O (2.5 mmol, 45 μL), and $VOSO_4{\cdot}xH_2O$ (0.1 mmol) in dry DMF (3 mL), at 70 °C, under air. [b]Isolated yields. nr = no reaction.

undergo C(CO)−C(CO) bond cleavage to afford benzoic acid under standard conditions at room temperature (Supporting Information, control experiments, eq S4). In addition, the reaction of benzaldehyde and 1,2-diphenylethanone with *N*-phenylbenzimidamide (**2aa**) excludes the possibility of imine formation (Supporting Information, control experiments, eqs S5 and S6). The reaction proceeds through direct nucleophilic addition of amidine to 1,2-diketone to produce a tertiary vicinal diol intermediate which rapidly undergoes C−C bond cleavage in the presence of $VOSO_4$. The vanadium catalyst is not likely to produce the cyclic intermediates as in the case of C−C bond cleavage of 1,2-diols with higher valence inorganic oxidants, such as periodates and lead tetracarboxylates. In the case of lead tetracarboxylate oxidation, *cis*-glycols react much faster than *trans*-glycols,[26] whereas cyclic *trans*-glycols are usually inactive in the case of oxidation by periodates, probably due to difficulty in the formation of cyclic intermediates.[27] It was reported that both cyclic *cis*- and *trans*-ditertiary glycols similarly undergo oxidative cleavage in the presence of vanadium oxytrichloride ($VOCl_3$).[17]

Furthermore, in the absence of **1a** and **2aa**, a mixture of 16 mg of $VOSO_4$ and H_2O (45 μL) in dry DMF (3 mL) was stirred at room temperature under air. A dark violet homogeneous reaction mixture was observed after 2 h (Supporting Information, p S6). The dark violet color has been proven for vanadium(V) species for the aerobic oxidation of alcohols with the $VOSO_4$/TEMPO catalytic system.[28] The dark violet color turned black on addition of **1a** and **2aa**, which then turned green after the reaction mixture was stirred for 8 h at room temperature. The green color of the reaction mixture suggests the presence of vanadium(IV) species.[29] A similar color change was also observed when **3a** was added to the dark violet mixture of $VOSO_4$ in DMF. Interestingly, the reaction mixture did not produce a dark violet color when a mixture of

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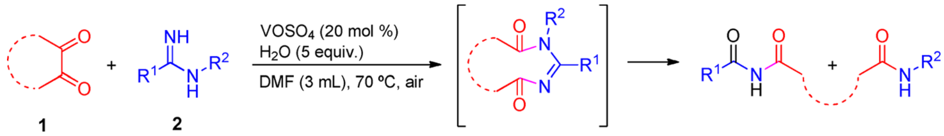
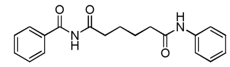
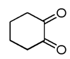
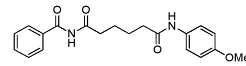
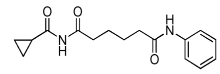
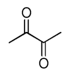
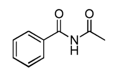
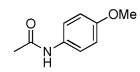
Table 6. Reaction of Aliphatic 1,2-Diketones with Amidines[a]



Entry	1,2-Diketone (1)	Amidine (2)	Time (h)	Yield of products[b]	
1[c]		**2aa**	8	 **6a**: 33 %	
2[c]	 **(1f)**	**2ar**	6	 **6b**: 38 %	
3[c]		**2ap**	8	 **6c**: 41 %	
4	 **(1g)**	**2ar**	24	 **4bd**: 74%	 **5u**: 78 %

[a]Standard reaction conditions: **1** (1 mmol), **2** (1.2 mmol), H_2O (5 mmol, 90 μL), and $VOSO_4 \cdot xH_2O$ (0.2 mmol) in dry DMF (3 mL), at 70 °C, under air. [b]Isolated yield. [c]The reaction was monitored until complete consumption of **1f**.

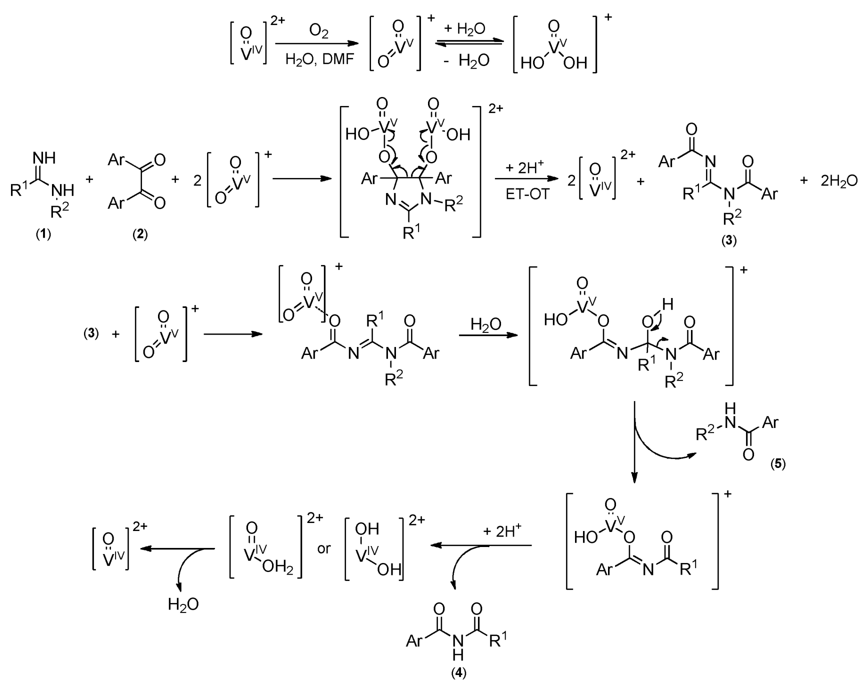


Figure 3. Mechanistic proposal for the C−C bond cleavage of 1,2-diketones following the redox conversion of VO_2^+/VO^{2+}.

$VOSO_4$ and H_2O in dry DMF was stirred for 2 h under a nitrogen atmosphere. These results indicate that a V^V−V^{IV} catalytic cycle in water may participate in the present one-pot process. Molecular oxygen probably shows its effect by accelerating the oxidation of V^{IV} species to V^V species. However, the role of DMF in the oxidation of vanadium is not clear at this stage. Recently, Wang and co-workers demonstrated the $VOSO_4$ catalyzed the transformation of cellulose and its derived carbohydrates into formic and lactic acids in water.[30] The redox conversion between VO_2^+ and VO^{2+} species participated in the transformation of glucose into formic acid under an oxygen atmosphere. An electron-transfer and oxygen-transfer (ET−OT) mechanism was proposed for oxidative C−C bond cleavage of the intermediary glyceraldehyde to produce formic acid on the basis of the polyoxometalate $H_5PV_2Mo_{10}O_{40}$-catalyzed transformation.[31] In this mechanism, two V^V species are required to accept two electrons from the substrate at the same time to be reduced to V^{IV} and donate one O atom at the same time.

On the basis of the aforementioned results and the literature reports, we speculate that the C−C bond cleavage of 1,2-diketones may also follow the ET−OT mechanism. A plausible mechanism following the redox conversion of VO_2^+/VO^{2+} is proposed in Figure 3. The reaction is initiated by the activation of 1,2-diketone by two VO_2^+ species or its hydrolyzed form ($H_2VO_3^+$) in water;[32] in the next step, the nucleophilic addition of amidines produces a binuclear V^V intermediate coordinated by a tetrasubstituted imidazolyl ring. Each V^V center is reduced

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to V^{IV} by accepting one electron from the V−O bond connected to the C−O bond. This leads to the formation of two C=O bonds and the simultaneous cleavage of the C−C bond to produce **3**. The reduced VO^{2+} is reoxidized into VO_2^+ in our aerobic reaction conditions. The VO_2^+ cation may act as a Lewis acid[33] to catalyze the hydrolysis of **3**. The VO_2^+ cation activates the carbonyl group of **3** and promotes electron deficiency at the amidino carbon atom. The water attacks at the amidino carbon atom to afford **5** and the V^V intermediate coordinated by **4**. This V^V intermediate produces **4** and the hydrolyzed form of the vanadium(IV) species ($H_2VO_2^{2+}$) in the presence of water.[34] The $H_2VO_2^{2+}$ form is converted to VO^{2+} cation after elimination of water.

In conclusion, a new facile and efficient one -pot domino route for the synthesis of imides and amides from easily accessible 1,2-diketones and amidines via oxidative C(CO)−C(CO) bond cleavage has been developed. The reaction employs an inexpensive, less toxic, and water-soluble vanadium catalyst. A series of imide as well as amide derivatives could be easily synthesized under oxidant- and additive-free conditions. One-step construction of imide and amide bonds with a long-chain alkyl group is another important feature of this protocol. This transformation is proposed to proceed through redox conversion between the VO_2^+ and VO^{2+} cations, and further mechanistic investigations, including the interaction of $VOSO_4$ with 1,2-diketones, amidines, and DMF at the molecular level, are under way.

■ EXPERIMENTAL SECTION

General Information. Unless otherwise specified, all reagents and solvents were purchased from commercial sources and were used as received. Vanadium(IV) sulfate oxide hydrate ($VOSO_4 \cdot xH_2O$,; 99.9%) was purchased from Alfa-Aesar. Merck precoated silica gel $60_{F\text{-}254}$ (0.5 mm) aluminum plates were used for thin-layer chromatography (TLC), and visualization of the spots on the TLC plates was achieved by UV light. Melting points were measured on a Stuart SMP3 melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz instrument using tetramethylsilane (TMS) as the internal standard. Chemical shifts for ^{1}H and ^{13}C are expressed in parts per million (ppm) relative to the resonance for TMS at δ 0.00 or DMSO-d_6 at δ 2.50 for ^{1}H NMR and δ 39.9 for ^{13}C NMR. Coupling constant (J) values are reported in hertz. HRMS spectra were determined with an Agilent QTOF mass spectrometer 6540 series instrument.

General Procedures for the Synthesis of 1,2-Diketones 1b−1e. *General Procedure for the Preparation of Deoxybenzoins.*[35] To a solution of substituted phenylacetic acid (50 mmol) in dichloromethane (50 mL) were added thionyl chloride (75.0 mmol) and dimethylformamide (0.05 mmol), and the reaction mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum to provide arylacetyl chlorides in quantitative yield, which were used without further purification. The arylacetyl chlorides were stirred with the appropriate benzene derivatives (500 mmol) at 0 °C. Anhydrous aluminum chloride (62.5 mmol) was added slowly portionwise, maintaining the internal temperature below 5 °C. The solution was allowed to warm to room temperature and stirred until the acid chloride was completely consumed as indicated by TLC. The reaction mixture was then poured onto ice−water. The organic layer was separated, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified over silica gel (60−120 mesh) using hexane/ethyl acetate (19:1) as the eluent to give the corresponding deoxybenzoin derivatives.

General Procedure for the Oxidation of Deoxybenzoins.[36] To a solution of deoxybenzoin derivatives (5 mmol) in DMSO (50 mL) was added selenium dioxide (7.5 mmol), and the reaction mixture was irradiated in the microwave oven (domestic household oven, 650 W) for 5 min at 40 °C. The reaction mixture was filtered while hot to remove the selenium metal and was poured onto ice−water mixture to precipitate the crude product. The crude product was collected, dried, and purified over silica gel using hexane/ethyl acetate (19:1) as the eluent to provide the corresponding 1,2-diketones **1b−1e**.

General Procedures for the Synthesis of Amidines 2.[37] *Method A.* A round-bottom flask (100 mL volume) was charged with NaH (60% in mineral oil) (15 mmol, 1.5 equiv), sealed with a rubber septum, evacuated, and backfilled with nitrogen using a balloon. DMSO (5 mL) was added and the resulting suspension cooled with an ice−water bath prior to the addition of carbonitrile (10.0 mmol) and aniline (12.0 mmol, 1.2 equiv). The mixture was kept at 0 °C for 30 min and stirred at room temperature until the starting material was consumed as indicated by TLC analysis. After completion of the reaction, ice−water (50 mL) was added to quench the reaction mixture while maintaining vigorous stirring. In the cases when the amidine precipitated upon addition of water, the solid was filtered off and dissolved in EtOAc. In all other cases, the aqueous layer was extracted with EtOAc (3 × 50 mL). The extracts were combined and washed with water (2 × 50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified either by silica gel chromatography or upon recrystallization (solvent DCM/hexane) to provide the corresponding amidine derivatives **2aa−2ac**, **2ae**, **2af**, **2ah**, **2ai**, **2al**, **2am**, **2ao**, **2ar−2at**, **2av**, **2aw**, and **2bc−2bf**.

Method B. A sealed tube (15 mL in volume) equipped with a stir bar was charged with the carbonitrile (10.0 mmol) and the aniline (11.0 mmol, 1.1 equiv) under air. $AlCl_3$ (10.0 mmol, 1.0 equiv) was added portionwise. The tube was tightly sealed with a cap and lowered into a preheated oil bath at 140 °C. The reaction mixture was stirred for about 1 h. The hot mixture was poured into a concentrated NaOH solution (40 mL) in mixed water and ice (100 mL) and the resulting mixture stirred for about 15 min. Then the mixture was extracted with EtOAc or DCM (50 mL × 3). The combined organic layers were washed with brine (30 mL × 3), dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified either by silica gel chromatography or upon recrystallization (solvent DCM/hexane) to provide the corresponding amidine derivatives **2ad**, **2ag**, **2aj**, **2ak**, **2an**, **2ap**, **2aq**, and **2ax−2bb**.

General Procedure for the Synthesis of Imides 4 and Amides 5. To an oven-dried test tube (27 mL volume) equipped with a stir bar were added the 1,2-diketone **1** (0.5 mmol, 1 equiv), amidine **2** (1.2 equiv), H_2O (5 equiv), 20 mol % $VOSO_4 \cdot xH_2O$, and dry DMF (3 mL). The reaction mixture was lowered into a preheated oil bath at 70 °C and stirred for the specified time under air. After completion of the reaction, the reaction mixture was allowed to cool to room temperature. The reaction mixture was added to water (50 mL), and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuum. The residue was purified by column chromatography on silica gel (60−120 mesh). The amide products **5** were purified using hexane/ethyl acetate (9:1) as the eluent. The imide products **4** were purified using hexane/ethyl acetate (7:3) as the eluent.

***N,N′*-Dibenzoyl-*N*-phenylbenzamidine (3a).**[21] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2aa** (117 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) at room temperature afforded **3a** (194 mg, 96%) as a white solid (eluent hexane:ethyl acetate = 9:1): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 7.76−7.70 (m, 2H), 7.68−7.61 (m, 4H), 7.57−7.51 (m, 1H), 7.45−7.29 (m, 10H), 7.28−7.23 (m, 2H), 7.15−7.10 (m, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 176.4, 171.6, 158.2, 140.7, 135.1, 134.6, 133.6, 133.1, 132.2, 132.1, 129.7, 129.4, 129.3, 129.2, 129.0, 128.9, 128.8, 128.7, 127.9; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{27}H_{21}N_2O_2$ 405.1603, found 405.1603.

***N*-Benzoylbenzamide (4aa).**[4c] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2aa** (117 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4aa** (109 mg, 97%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.34 (s, 1H), 7.94−7.90 (m, 4H), 7.68−7.60 (m, 2H), 7.56−7.51 (m, 4H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.2, 134.3, 133.1, 129.1, 128.9; HRMS

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(ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{11}NNaO_2$ 248.0687, found 248.0691.

***N*-Benzoyl-4-methoxybenzamide (4ab).**[4a] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ab** (136 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4ab** (116 mg, 91%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.18 (s, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 7.9 Hz, 2H), 7.65−7.61 (m, 1H), 7.54−7.50 (m, 2H), 7.07−7.04 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.4, 167.2, 163.3, 134.6, 132.9, 131.4, 129.0, 128.8, 126.21, 114.1, 56.0; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{13}NNaO_3$ 278.0793, found 278.0796.

***N*-Benzoyl-4-chlorobenzamide (4ac).**[4c] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ac** (139 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4ac** (127 mg, 98%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.40 (s, 1H), 7.95−7.89 (m, 4H), 7.67−7.62 (m, 1H), 7.60 (d, J = 8.6 Hz, 2H), 7.53 (t, J = 7.7 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.1, 167.3, 137.8, 134.1, 133.16, 133.13, 131.0, 129.1, 128.9, 128.8; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{10}ClNNaO_2$ 282.0298, found 282.0299.

***N*-Benzoyl-3-chlorobenzamide (4ad).**[7a] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ad** (139 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4ad** (124 mg, 96%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.42 (s, 1H), 7.99−7.95 (m, 1H), 7.95−7.90 (m, 2H), 7.87−7.84 (m, 1H), 7.72−7.69 (m, 1H), 7.67−7.62 (m, 1H), 7.58−7.51 (m, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.0, 166.8, 136.3, 134.1, 133.5, 133.1, 132.7, 130.8, 129.1, 128.8, 128.7, 127.7; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{10}ClNNaO_2$ 282.0298, found 282.0299.

***N*-Benzoyl-2-chlorobenzamide (4ae).** According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ae** (139 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4ae** (124 mg, 96%) as a white solid: mp 139−141 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.74 (s, 1H), 7.93 (d, J = 7.4 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.58−7.47 (m, 5H), 7.43 (td, J = 7.3, 1.4 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.4, 166.7, 136.8, 133.5, 133.1, 131.6, 129.83, 129.81, 129.1, 129.0, 128.9, 127.6; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{10}ClNNaO_2$ 282.0298, found 282.0299.

***N*-Benzoyl-4-bromobenzamide (4af).**[7a] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2af** (165 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4af** (140 mg, 92%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.40 (s, 1H), 7.94−7.90 (m, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.74 (d, J = 8.6 Hz, 2H), 7.67−7.62 (m, 1H), 7.53 (t, J = 7.7 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.0, 167.5, 134.1, 133.5, 133.1, 131.8, 131.1, 129.1, 128.8, 126.9; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{10}BrNNaO_2$ 325.9793, found 325.9794.

***N*-Benzoyl-3-bromobenzamide (4ag).** According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ag** (165 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4ag** (140 mg, 92%) as a white solid: mp 122−124 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.43 (s, 1H), 8.12−8.10 (m, 1H), 7.94−7.98 (m, 3H), 7.84 (d, J = 8.0 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.57−7.47 (m, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.0, 166.7, 136.5, 135.6, 134.1, 133.1, 131.5, 131.0, 129.1, 128.8, 128.1, 122.0; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_{10}BrNNaO_2$ 325.9793, found 325.9793.

***N*-Benzoyl-4-methylbenzamide (4ah).**[4c] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ah** (126 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4ah** (112 mg, 95%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.25 (s, 1H), 7.90 (d, J = 7.5 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.2, 167.8, 143.4, 134.4, 133.0, 131.4, 129.4, 129.3, 129.0, 128.8, 21.5; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{13}NNaO_2$ 262.0844, found 262.0844.

***N*-Benzoyl-2-methylbenzamide (4ai).**[7a] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ai** (126 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4ai** (50 mg, 42%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.50 (s, 1H), 8.00−7.96 (m, 2H), 7.71−7.66 (m, 1H), 7.57 (t, J = 7.8 Hz, 2H), 7.54−7.51 (m, 1H), 7.45 (td, J = 7.5, 1.3 Hz, 1H), 7.37−7.30 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 170.7, 167.2, 136.4, 135.9, 133.6, 133.2, 130.9, 130.6, 129.0, 128.8, 127.9, 126.0, 19.8; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{13}NNaO_2$ 262.0844, found 262.0846.

***N*-Benzoyl-5-bromo-2-methoxybenzamide (4aj).** According to the general procedure, **1a** (105 mg, 0.5 mmol), **2aj** (183 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4aj** (137 mg, 82%) as a white solid: mp 168−170 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.42 (s, 1H), 7.93−7.88 (m, 2H), 7.71−7.63 (m, 3H), 7.56 (t, J = 7.7 Hz, 2H), 7.16−7.10 (m, 1H), 3.82 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.3, 165.8, 156.3, 135.3, 133.5, 133.4, 132.1, 129.1, 128.7, 127.0, 114.9, 112.3, 56.9; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{15}H_{12}BrNNaO_3$ 355.9898, found 355.9901.

***N*-Benzoyl-2,5-dichlorobenzamide (4ak).** According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ak** (160 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4ak** (132 mg, 90%) as a white solid using silica gel (100−200 mesh) and hexane/ethyl acetate (19:1) as the eluent: mp 153−155 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.84 (s, 1H), 7.94 (d, J = 7.6 Hz, 2H), 7.72 (s, 1H), 7.66 (t, J = 7.4 Hz, 1H), 7.57−7.51 (m, 4H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.1, 166.7, 138.4, 133.6, 132.8, 132.2, 131.5, 131.2, 129.1, 129.0, 128.5, 128.4; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{14}H_9Cl_2NNaO_2$ 315.9908, found 315.9912.

***N*-Benzoylthiophene-2-carboxamide (4al).**[8] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2al** (122 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4al** (103 mg, 89%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.28 (s, 1H), 8.16 (dd, J = 3.8, 1.1 Hz, 1H), 8.00 (dd, J = 5.0, 1.1 Hz, 1H), 7.90−7.84 (m, 2H), 7.68−7.60 (m, 1H), 7.57−7.50 (m, 2H), 7.25 (dd, J = 5.0, 3.8 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.1, 161.3, 138.8, 134.8, 134.5, 133.0, 132.6, 129.1, 128.9, 128.8; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{12}H_9NNaO_2S$ 254.0252, found 254.0259.

***N*-Benzoylfuran-2-carboxamide (4am).**[8] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2am** (114 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4am** (101 mg, 94%) as a light yellow solid (eluent hexane:ethyl acetate = 1:1): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.11 (s, 1H), 8.03−8.00 (m, 1H), 7.89−7.84 (m, 2H), 7.67−7.62 (m, 1H), 7.60 (d, J = 3.6 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 6.74 (dd, J = 3.6, 1.7 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.7, 157.2, 147.9, 146.7, 134.3, 133.1, 129.0, 128.8, 118.2, 112.8; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{12}H_9NNaO_3$ 238.0480, found 238.0485.

***N*-Benzoyl-2-chloronicotinamide (4an).** According to the general procedure, **1a** (105 mg, 0.5 mmol), **2an** (139 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4an** (120 mg, 92%) as a white solid: mp 148−150 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.91 (s, 1H), 8.52 (dd, J = 4.8, 1.9 Hz, 1H), 8.05 (dd, J = 7.6, 1.9 Hz, 1H), 7.97−7.92 (m, 2H), 7.69−7.64 (m, 1H), 7.57−7.52 (m, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.4, 166.7, 150.7, 145.9, 138.1, 133.7, 133.5, 132.7, 129.1, 129.0, 123.5; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{13}H_9ClN_2NaO_2$ 283.0250, found 283.0251.

***N*-Benzoylisonicotinamide (4ao).** According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ao** (118 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4ao** (83 mg, 84%) as a light yellow solid (eluent hexane:ethyl acetate = 3:7): mp 188−190 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.60 (s, 1H), 8.81−8.74 (m, 2H), 7.98−7.90 (m, 2H), 7.78 (d, J = 5.8 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.8, 167.5, 150.6, 141.8, 133.7, 133.4, 129.2, 128.9, 122.4; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{13}H_{10}N_2NaO_2$ 249.0640, found 249.0644.

***N*-(Cyclopropylcarbonyl)benzamide (4ap).**[4c] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ap** (96 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **4ap** (83 mg, 88%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.15 (s, 1H), 7.93−7.88 (m, 2H), 7.66−7.60 (m, 1H), 7.55−7.49 (m, 2H), 2.50−2.44 (m, 1H), 1.03−0.79 (m, 4H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 175.3, 166.7, 134.0, 133.0, 128.9, 128.8, 15.0, 9.8; HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for $C_{11}H_{11}NNaO_2$ 212.0687, found 212.0690.

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***N*-Butyrylbenzamide (4aq).**[4b] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2aq** (97 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4aq** (76 mg, 80%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.93 (s, 1H), 7.91−7.88 (m, 2H), 7.65−7.58 (m, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.3 Hz, 2H), 1.64−1.55 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 174.9, 166.8, 133.8, 133.0, 128.8, 128.7, 39.4, 17.9, 14.0; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{13}NNaO_2$ 214.0844, found 214.0850.

3-Chloro-*N*-(4-chlorobenzoyl)benzamide (4ar). According to the general procedure, **1b** (139 mg, 0.5 mmol), **2ad** (139 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4ar** (140 mg, 95%) as a white solid: mp 155−157 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.53 (s, 1H), 8.04−8.01 (m, 1H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.61 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.1, 166.8, 138.0, 136.2, 133.6, 132.9, 132.8, 131.1, 130.8, 128.9, 128.7, 127.8; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_9Cl_2NNaO_2$ 315.9908, found 315.9910.

4-Bromo-*N*-(4-chlorobenzoyl)benzamide (4as). According to the general procedure, **1b** (139 mg, 0.5 mmol), **2af** (165 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4as** (151 mg, 89%) as a white solid: mp 190−192 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.45 (s, 1H), 7.95−7.91 (m, 2H), 7.87−7.83 (m, 2H), 7.77−7.73 (m, 2H), 7.63−7.59 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.4, 167.2, 138.0, 133.3, 132.9, 131.8, 131.1, 131.0, 128.9, 127.0; HRMS (ESI-TOF) *m*/*z* [M + Na,^{81}Br]$^+$ calcd for $C_{14}H_9BrClNNaO_2$ 361.9383, found 361.9384.

***N*-(4-Chlorobenzoyl)-2-methylbenzamide (4at).** According to the general procedure, **1b** (139 mg, 0.5 mmol), **2ai** (126 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4at** (125 mg, 91%) as a white solid: mp 167−169 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.50 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.31−7.24 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 170.4, 166.3, 138.0, 136.2, 136.0, 132.5, 131.0, 130.7, 128.9, 128.0, 126.0, 19.82; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{12}ClNNaO_2$ 296.0454, found 296.0455.

***N*-(4-Chlorobenzoyl)thiophene-2-carboxamide (4au).** According to the general procedure, **1b** (139 mg, 0.5 mmol), **2al** (122 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4au** (119 mg, 90%) as a white solid: mp 162−164 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.35 (s, 1H), 8.16−8.12 (m, 1H), 8.01 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.25 (dd, *J* = 4.9, 3.9 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.3, 161.2, 138.6, 137.7, 135.0, 133.3, 132.8, 131.0, 128.9, 128.8; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_8ClNNaO_2S$ 287.9862, found 287.9863.

***N*-(4-Chlorobenzoyl)furan-2-carboxamide (4av).** According to the general procedure, **1b** (139 mg, 0.5 mmol), **2am** (114 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4av** (113 mg, 91%) as a yellow solid (eluent hexane:ethyl acetate = 1:1): mp 126−128 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.20 (s, 1H), 8.02 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.91−7.85 (m, 2H), 7.64−7.53 (m, 3H), 6.74 (dd, *J* = 3.6, 1.7 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.9, 157.1, 148.0, 146.6, 137.8, 133.1, 130.9, 128.9, 118.4, 112.8; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_8ClNNaO_3$ 272.0090, found 272.0094.

2-Chloro-*N*-(4-chlorobenzoyl)nicotinamide (4aw). According to the general procedure, **1b** (139 mg, 0.5 mmol), **2an** (139 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4aw** (132 mg, 90%) as a white solid: mp 166−168 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.97 (s, 1H), 8.52 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.06 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.7 Hz, 2H), 7.55 (dd, *J* = 7.6, 4.9 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.3, 165.8, 150.8, 146.0, 138.6, 138.2, 133.3, 131.5, 131.0, 129.2, 123.5; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_8Cl_2N_2NaO_2$ 316.9861, found 316.9862.

4-Chloro-*N*-(cyclopropylcarbonyl)benzamide (4ax). According to the general procedure, **1b** (139 mg, 0.5 mmol), **2ap** (96 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4ax** (94 mg, 84%) as a white solid: mp 173−175 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.19 (s, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.60 (d, *J* = 8.7 Hz, 1H), 2.47−2.41 (m, 1H), 1.11−0.43 (m, 4H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 175.2, 165.8, 137.9, 132.8, 130.8, 129.0, 15.0, 9.9; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{10}ClNNaO_2$ 246.0298, found 246.0298.

***N*-Butyryl-4-chlorobenzamide (4ay).**[7c] According to the general procedure, **1b** (139 mg, 0.5 mmol), **2aq** (97 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4ay** (92 mg, 82%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.00 (s, 1H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 1.66−1.49 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 174.9, 165.9, 137.9, 132.6, 130.7, 128.9, 39.3, 17.8, 14.0; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{12}ClNNaO_2$ 248.0454, found 248.0455.

4-Chloro-*N*-(4-methoxybenzoyl)benzamide (4az).[4a] According to the general procedure, **1c** (135 mg, 0.5 mmol), **2ac** (115 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4az** (119 mg, 82%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.24 (s, 1H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.5, 167.1, 163.4, 137.6, 133.3, 131.4, 130.9, 128.8, 126.0, 114.1, 56.0; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{12}ClNNaO_3$ 312.0403, found 312.0405.

4-Methoxy-*N*-(4-methylbenzoyl)benzamide (4ba).[4a] According to the general procedure, **1c** (135 mg, 0.5 mmol), **2ah** (126 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4ba** (104 mg, 77%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.08 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 168.6, 167.8, 163.7, 143.3, 131.6, 131.8, 129.6, 129.6, 126.2, 114.2, 56.0, 21.7; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{15}NNaO_3$ 292.0950, found 292.0953.

***N*-(Cyclopropylcarbonyl)-4-methoxybenzamide (4bb).** According to the general procedure, **1c** (135 mg, 0.5 mmol), **2ap** (96 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4bb** (94 mg, 86%) as a white solid: mp 148−150 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.99 (s, 1H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 2.80−2.25 (m, 1H, merged with DMSO), 0.93−0.88 (m, 4H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 175.4, 165.9, 163.2, 131.0, 125.9, 114.1, 55.9, 14.9, 9.7; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{13}NNaO_3$ 242.0793, found 242.0798.

***N*-Benzoyl-4-nitrobenzamide (4bc).**[7c] According to the general procedure, **1d** (128 mg, 0.5 mmol), **2aa** (118 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **4bc** (60 mg, 44%) as a white solid using silica gel (100−200 mesh) and hexane/ethyl acetate (9:1) as the eluent: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.65 (s, 1H), 8.34 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.9 Hz, 2H), 7.97−7.91 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.8, 167.5, 149.9, 140.3, 133.7, 133.4, 130.3, 129.2, 128.9, 123.8; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{10}N_2NaO_4$ 293.0538, found 293.0539.

***N*-Acetylbenzamide (4bd).**[4c] According to the general procedure, **1g** (86 mg, 1 mmol), **2ar** (271 mg, 1.2 mmol), and $VOSO_4 \cdot xH_2O$ (32 mg, 0.2 mmol) afforded **4bd** (121 mg, 74%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 11.01 (s, 1H), 7.93−7.89 (m, 2H), 7.65−7.59 (m, 1H), 7.54−7.49 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 172.6, 167.0, 133.6, 133.1, 128.9, 128.8, 26.0; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_9H_9NNaO_2$ 186.0531, found 186.0528.

***N*-Phenylbenzamide (5a).**[17] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2aa** (117 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5a** (95 mg, 96%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.25 (s, 1H), 7.99−7.94 (m, 2H), 7.79 (d, *J* = 7.7 Hz, 2H), 7.62−7.56 (m, 1H), 7.56−7.50 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.0, 139.6, 135.4, 132.0, 129.0, 128.8, 128.1, 124.1, 120.8; HRMS (ESI-TOF) *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{11}NNaO$ 220.0738, found 220.0738.

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4-Chloro-*N*-phenylbenzamide (5b).[17] According to the general procedure, **1b** (139 mg, 0.5 mmol), **2aa** (117 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5b** (111 mg, 97%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.32 (s, 1H), 7.99 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 7.9 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 7.36 (t, J = 7.8 Hz, 2H), 7.12 (t, J = 7.3 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 164.9, 139.4, 136.8, 134.1, 130.0, 129.1, 128.9, 124.2, 120.8; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{13}H_{10}ClNO$ 232.0529, found 232.0527.

4-Methoxy-*N*-phenylbenzamide (5c).[17] According to the general procedure, **1c** (135 mg, 0.5 mmol), **2aa** (117 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5c** (100 mg, 88%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.09 (s, 1H), 7.97 (d, J = 8.8 Hz, 2H), 7.79−7.74 (m, 2H), 7.37−7.31 (m, 2H), 7.11−7.03 (m, 3H), 3.84 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 165.3, 162.3, 139.8, 130.0, 129.0, 127.4, 123.8, 120.8, 114.0, 55.8; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{14}H_{13}NNaO_2$ 250.0844, found 250.0845.

4-Nitro-*N*-phenylbenzamide (5d).[38] According to the general procedure, **1e** (142 mg, 0.5 mmol), **2aa** (117 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5d** (46 mg, 38%) as a light yellow solid using silica gel (100−200 mesh) and hexane:ethyacetate (19:1) as the eluent: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.57 (s, 1H), 8.38 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.9 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 164.3, 149.6, 141.0, 139.1, 129.6, 129.1, 124.6, 123.9, 120.9; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{13}H_{11}N_2O_3$ 243.0770, found 243.0766.

***N*-(4-Methoxyphenyl)benzamide (5e).**[17] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ar** (136 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5e** (110 mg, 97%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.13 (s, 1H), 7.95 (d, J = 7.4 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 165.5, 156.0, 135.5, 132.7, 131.8, 128.8, 128.0, 122.4, 114.2, 55.6. HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{14}H_{14}NO_2$ 228.1025, found 228.1024.

***N*-(3,4,5-Trimethoxyphenyl)benzamide (5f).**[39] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2as** (172 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5f** (136 mg, 95%) as a white solid (eluent hexane:ethyl acetate = 4:1): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.15 (s, 1H), 7.98−7.93 (m, 2H), 7.62−7.57 (m, 1H), 7.56−7.50 (m, 2H), 7.25 (s, 2H), 3.77 (s, 6H), 3.64 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 165.7, 153.0, 135.7, 135.3, 134.1, 132.0, 128.8, 128.0, 98.5, 60.5, 56.2; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{16}H_{18}NO_4$ 288.1236, found 288.1241.

***N*-(4-Chlorophenyl)benzamide (5g).**[17] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2at** (138 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5g** (113 mg, 98%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.39 (s, 1H), 8.04−7.93 (m, 2H), 7.84 (d, J = 8.9 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.4 Hz, 2H), 7.42 (d, J = 8.9 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.1, 138.6, 135.2, 132.1, 128.9, 128.8, 128.1, 127.7, 122.3; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{13}H_{11}ClNO$ 232.0529, found 232.0527.

***N*-(3-Chlorophenyl)benzamide (5h).**[40] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2au** (138 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5h** (114 mg, 98%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.42 (s, 1H), 7.99 (t, J = 2.0 Hz, 1H), 7.98−7.94 (m, 2H), 7.73 (ddd, J = 8.2, 1.9, 0.8 Hz, 1H), 7.65−7.59 (m, 1H), 7.58−7.52 (m, 2H), 7.39 (t, J = 8.1 Hz, 1H), 7.17 (ddd, J = 8.0, 2.1, 0.9 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.2, 141.1, 135.0, 133.4, 132.2, 130.7, 128.9, 128.1, 123.7, 120.1, 119.0; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{13}H_{11}ClNO$ 232.0529, found 232.0527.

***N*-(4-Fluorophenyl)benzamide (5i).**[17] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2av** (128 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5i** (101 mg, 94%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.31 (s, 1H), 7.99−7.90 (m, 2H), 7.83−7.77 (m, 2H), 7.63−7.57 (m, 1H), 7.54 (t, J = 7.4 Hz, 2H), 7.23−7.16 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 165.9, 159.7 (d, J_{C-F} = 240.2 Hz), 136.0 (d, J_{C-F} = 2.5 Hz), 135.2, 132.0, 128.8, 128.0, 122.67 (d, J_{C-F} = 7.8 Hz), 115.7 (d, J_{C-F} = 22.2 Hz); HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{13}H_{11}FNO$ 216.0825, found 216.0824.

***N*-(*p*-Tolyl)benzamide (5j).**[17] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2aw** (126 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5j** (102 mg, 97%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.17 (s, 1H), 7.95 (d, J = 7.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.60−7.56 (m, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 165.8, 137.0, 135.2, 133.0, 131.9, 129.4, 128.8, 128.0, 120.8, 20.9; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{14}H_{14}NO$ 212.1075, found 212.1074.

***N*-(4-Isopropylphenyl)benzamide (5k).**[25i] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ax** (143 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5k** (110 mg, 92%) as a light yellow solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.18 (s, 1H), 7.98−7.89 (m, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.61−7.56 (m, 1H), 7.55−7.50 (m, 2H), 7.22 (d, J = 8.5 Hz, 2H), 2.91−2.81 (m, 1H), 1.21 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 165.7, 144.2, 137.3, 135.5, 131.9, 128.8, 128.0, 126.7, 120.9, 33.3, 24.4; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{16}H_{18}NO$ 240.1388, found 240.1389.

***N*-Mesitylbenzamide (5l).**[17] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ay** (142 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5l** (110 mg, 76%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.68 (s, 1H), 7.99 (d, J = 7.3 Hz, 2H), 7.63−7.55 (m, 1H), 7.52 (t, J = 7.3 Hz, 2H), 6.93 (s, 2H), 2.26 (s, 3H), 2.14 (s, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 165.5, 136.0, 135.7, 134.9, 133.1, 131.8, 128.8, 128.7, 127.9, 40.50, 21.01, 18.4; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{16}H_{18}NO$ 240.1388, found 240.1395.

***N*-Cyclopropylbenzamide (5m).**[25a] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2az** (96 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5m** (60 mg, 74%) as a white solid (eluent hexane:ethyl acetate = 4:1): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.44 (s, 1H), 7.84−7.76 (m, 2H), 7.53−7.48 (m, 1H), 7.46−7.41 (m, 2H), 2.89−2.77 (m, 1H), 0.71−0.66 (m, 2H), 0.62−0.52 (m, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 167.9, 134.9, 131.5, 128.6, 127.6, 23.5, 6.2; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{10}H_{11}NNaO$ 184.0738, found 184.0736.

***N*-(Pentan-2-yl)benzamide (5n).** According to the general procedure, **1a** (105 mg, 0.5 mmol), **2ba** (114 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5n** (50 mg, 52%) as a white solid: mp 78−80 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 8.16−8.09 (m, 1H), 7.87−7.79 (m, 2H), 7.53−7.48 (m, 1H), 7.47−7.41 (m, 2H), 4.07−3.94 (m, 1H), 1.60−1.49 (m, 1H), 1.46−1.37 (m, 1H), 1.35−1.27 (m, 2H), 1.13 (d, J = 6.6 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.0, 135.4, 131.3, 128.5, 127.6, 44.9, 38.6, 21.2, 19.5, 14.3; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{12}H_{18}NO$ 192.1388, found 192.1387.

***N*-(Pyridin-4-yl)benzamide (5o).**[25j] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2bc** (118 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5o** (94 mg, 95%) as a white crystalline solid (eluent hexane:ethyl acetate = 1:1): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.61 (s, 1H), 8.49 (d, J = 5.8 Hz, 2H), 7.97 (d, J = 7.5 Hz, 2H), 7.80 (d, J = 5.1 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.56 (t, J = 7.5 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.9, 150.7, 146.4, 134.7, 132.5, 128.9, 128.3, 114.4; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{12}H_{11}N_2O$ 199.0871, found 199.0873.

***N*-(Pyridin-3-yl)benzamide (5p).**[25j] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2bd** (118 mg, 0.6 mmol), and $VOSO_4 \cdot xH_2O$ (16 mg, 0.1 mmol) afforded **5p** (96 mg, 97%) as a brown solid (eluent hexane:ethyl acetate = 1:1): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.48 (s, 1H), 8.95 (d, J = 2.2 Hz, 1H), 8.32 (d, J = 4.5 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 7.3 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.56 (t, J = 7.5 Hz, 2H), 7.41 (dd, J = 8.3, 4.7 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.4, 145.0, 142.4, 136.3, 134.8,

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132.3, 128.9, 128.2, 127.8, 124.0; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{12}H_{11}N_2O$ 199.0871, found 199.0892.

***N*-(Pyridin-2-yl)benzamide (5q).**[25j] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2be** (118 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **5q** (85 mg, 86%) as a white solid (eluent hexane:ethyl acetate = 19:1): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.79 (s, 1H), 8.42–8.37 (m, 1H), 8.24–8.18 (m, 1H), 8.08–8.00 (m, 2H), 7.89–7.81 (m, 1H), 7.64–7.57 (m, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.21–7.15 (m, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.4, 152.6, 148.4, 138.5, 134.5, 132.4, 128.8, 128.4, 120.2, 115.2; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{12}H_{11}N_2O$ 199.0871, found 199.0876.

***N*-(5-Bromopyridin-2-yl)benzamide (5r).**[25j] According to the general procedure, **1a** (105 mg, 0.5 mmol), **2bf** (166 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **5r** (115 mg, 83%) as a white solid (eluent hexane:ethyl acetate = 19:1): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.99 (s, 1H), 8.52 (d, J = 2.2 Hz, 1H), 8.20 (d, J = 8.9 Hz, 1H), 8.08 (dd, J = 8.9, 2.4 Hz, 1H), 8.02 (d, J = 7.4 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 166.5, 151.6, 148.9, 141.0, 134.3, 132.5, 128.8, 128.5, 116.7, 114.4; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{12}H_{10}BrN_2O$ 276.9977, found 276.9976.

4-Chloro-*N*-(*p*-tolyl)benzamide (5s).[25i] According to the general procedure, **1b** (139 mg, 0.5 mmol), **2bw** (126 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **5s** (113 mg, 93%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.23 (s, 1H), 7.98 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 164.6, 136.9, 136.7, 134.1, 133.2, 130.0, 129.4, 128.8, 120.9, 20.9; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{14}H_{13}ClNO$ 246.0686, found 246.0685.

4-Methoxy-*N*-(4-methoxyphenyl)benzamide (5t).[40] According to the general procedure, **1c** (135 mg, 0.5 mmol), **2ar** (136 mg, 0.6 mmol), and $VOSO_4{\cdot}xH_2O$ (16 mg, 0.1 mmol) afforded **5t** (102 mg, 80%) as a white solid: ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.97 (s, 1H), 7.95 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.9 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 3.83 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 164.9, 162.2, 155.8, 132.8, 129.9, 127.5, 122.4, 114.1, 114.0, 55.8, 55.6; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_{15}H_{16}NO_3$ 258.1130, found 258.1130.

***N*-(4-Methoxyphenyl)acetamide (5u).**[41] According to the general procedure, **1g** (86 mg, 1 mmol), **2ar** (271 mg, 1.2 mmol), and $VOSO_4{\cdot}xH_2O$ (32 mg, 0.2 mmol) afforded **5u** (129 mg, 78%) as a light yellow solid (eluent hexane:ethyl acetate = 1:1): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 9.77 (s, 1H), 7.48 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 3.71 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): 168.2, 155.4, 132.9, 121.0, 114.2, 55.5, 24.2; HRMS (ESI-TOF) m/z [M + H]$^+$ calcd for $C_9H_{12}NO_2$ 166.0868, found 166.0864.

***N*^{1}-Benzoyl-*N*^{6}-phenyladipamide (6a).** According to the general procedure, **1f** (112 mg, 1 mmol), **2aa** (235 mg, 1.2 mmol), and $VOSO_4{\cdot}xH_2O$ (33 mg, 0.2 mmol) afforded **6a** (107 mg, 33%) as a white solid (eluent hexane:ethyl acetate = 3:7): mp 155–157 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.96 (s, 1H), 9.89 (s, 1H), 7.93–7.83 (m, 2H), 7.65–7.57 (m, 3H), 7.51 (t, J = 7.7 Hz, 2H), 7.28 (t, J = 7.9 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 2.74 (t, J = 6.8 Hz, 2H), 2.34 (t, J = 6.9 Hz, 2H), 1.71–1.55 (m, 4H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 174.9, 171.5, 166.8, 139.7, 133.8, 133.1, 129.1, 128.89, 128.81, 123.4, 119.5, 37.3, 36.7, 25.1, 24.1; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{19}H_{20}N_2NaO_3$ 347.1372, found 347.1377.

***N*^{1}-Benzoyl-*N*^{6}-(4-methoxyphenyl)adipamide (6b).** According to the general procedure, **1f** (112 mg, 1 mmol), **2ar** (272 mg, 1.2 mmol), and $VOSO_4{\cdot}xH_2O$ (33 mg, 0.2 mmol) afforded **6b** (135 mg, 38%) as a white solid (eluent hexane:ethyl acetate = 1:1): mp 160–162 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.95 (s, 1H), 9.75 (s, 1H), 7.90 (d, J = 7.4 Hz, 2H), 7.62 (t, J = 7.4 Hz, 2H), 7.56–7.38 (m, 4H), 6.86 (d, J = 9.0 Hz, 2H), 3.71 (s, 3H), 2.73 (t, J = 6.6 Hz, 2H), 2.30 (t, J = 6.6 Hz, 2H), 1.80–1.40 (m, 4H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 174.9, 170.9, 166.8, 155.4, 133.8, 133.1, 132.9, 128.9, 128.8, 121.0, 114.2, 55.5, 37.3, 36.5, 25.2, 24.2; HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{20}H_{22}N_2NaO_4$ 377.1477, found 377.1480.

***N*^{1}-(Cyclopropylcarbonyl)-*N*^{6}-phenyladipamide (6c).** According to the general procedure, **1f** (112 mg, 1 mmol), **2ap** (192 mg, 1.2 mmol), and $VOSO_4{\cdot}xH_2O$ (33 mg, 0.2 mmol) afforded **6c** (118 mg, 41%) as a white solid (eluent hexane:ethyl acetate = 1:1): mp 192–194 °C; ^{1}H NMR (DMSO-d_6, 500 MHz) δ 10.83 (s, 1H), 9.88 (s, 1H), 7.59 (d, J = 7.9 Hz, 2H), 7.28 (t, J = 7.8 Hz, 2H), 7.02 (t, J = 7.3 Hz, 1H), 2.57 (t, J = 6.7 Hz, 2H), 2.31 (t, J = 6.8 Hz, 2H), 2.16–2.09 (m, 1H), 1.65–1.50 (m, 4H), 0.89–0.79 (m, 4H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 174.4, 174.1, 171.5, 139.7, 129.1, 123.4, 119.5, 36.9, 36.6, 25.1, 24.1, 14.6, 9.3. HRMS (ESI-TOF) m/z [M + Na]$^+$ calcd for $C_{16}H_{20}N_2NaO_3$ 311.1372, found 311.1375.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00950.

Screening of the metal catalysts and solvents, control experiments, color change during the reaction of **1a** with **2aa**, and ^{1}H and ^{13}C NMR spectra of all compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ahmedkamal@iict.res.in.

ORCID

Ahmed Kamal: 0000-0002-4107-1775

Notes

The authors declare no competing financial interest.

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