# **RSC** Advances



View Article Online

 $\mathbf{O}$ 

View Journal | View Issue

# PAPER

Check for updates

Cite this: RSC Adv., 2021, 11, 15290

Received 27th December 2020 Accepted 19th April 2021

DOI: 10.1039/d0ra10868e

rsc.li/rsc-advances

## 1. Introduction

Amides are synthetically important intermediates and usually serve as useful building blocks for drugs, fine chemicals, and bioactive molecules such as peptides and proteins.1-8 The amidation reaction with anilines or amines as amino sources is used to construct amide motifs.9-13 It is more efficient to start directly from the nitrocompounds which are readily available industrial chemicals rather than to start from the corresponding amines or isocyanates.<sup>14,15</sup> In general, the classical two-step approach should be often proposed when someone is asked to prepare an amide from a nitro compound, namely reduction to amine with subsequent acylation (Scheme 1a). More importantly, several methods for direct conversion of nitroarenes to acetanilides are carried out by Pt nanoparticle ZrO2 and acetic anhydride, molybdenum hexacarbonyl/acetic acid, and also anilides have been obtained either via nickel or rhodium or platinum catalyzed carbonylation of nitroarenes.<sup>16-18</sup> However, 50-100 atm CO is required in each case. In 2018, Hu and coworkers described Mn-catalyzed reductive transamidation of tertiary amides with nitroarenes (Scheme 1b).<sup>19</sup> Recently, the reductive amidation between esters and nitroarenes can be achieved by nickel catalysis by cleavage of acyl C-O bonds, wherein metallic zinc serves as efficient reductant (Scheme 1c).20-22 However, these methods have some obvious shortcomings such as the use of organic solvents and additives which are difficult to recover. To overcome the difficulties in the transformation of N-aryl amides, we need to find an efficient and improved synthesis route. Water, as a green solvent, is

# Fe-mediated synthesis of *N*-aryl amides from nitroarenes and acyl chlorides<sup>†</sup>

Yundong Wu,<sup>a</sup> Lei Guo, <sup>(1)</sup> \*<sup>a</sup> Yuxuan Liu,<sup>b</sup> Jiannan Xiang<sup>b</sup> and Jun Jiang<sup>\*c</sup>

Amides are prevalent in nature and valuable functional compounds in agrochemical, pharmaceutical, and materials industries. In this work, we developed a selective and mild method for the synthesis of *N*-aryl amides. Starting from commercially available nitroarenes and acyl halides, *N*-aryl amides with good yields can be obtained in water. Especially in the process of transformation, Fe dust is the only reductant and additive, and the reaction can be easily performed on a large scale.

widely used in organic synthesis. In addition, Fe dust is a cheap and safe reducing agent and can be used in many organic reactions.<sup>23,24</sup> We are interested in Fe-promoted organic reactions performed in water. Therefore, we developed a mild Fepromoted reaction of nitroarenes with acyl chloride (fluoride) using water as solvent in this work. Using the Fe-mediated synthetic method, a series of *N*-aryl amides can be produced in moderate to good yields, showing its fascinating application prospects (Scheme 1d).

#### Known methods

(a) Classical two-step approach

Ar-NO<sub>2</sub> 
$$\xrightarrow{\text{Reduction}}$$
 Ar-NH<sub>2</sub>  $\xrightarrow{\text{Acylation}}$  R  $\xrightarrow{\text{M}}$  Ar

(b) Mn-mediated amidation of tertiary amides with nitroarenes

$$\mathbb{R} \xrightarrow{\text{O}}_{\text{NR}_{2}} + \text{Ar-NO}_{2} \xrightarrow{\mathbb{R} \xrightarrow{\text{N}}_{\text{N}}} (10 \text{ mol } \%) \\ \frac{\text{Mn (5 equiv.), TMSI}}{\text{MMP (0.5 M), 120°C, 24 h}} \mathbb{R} \xrightarrow{\text{O}}_{\text{H}} \mathbb{A}^{\text{Ar}}$$

(c) Ni-catalyzed amidation of esters using nitroarenes as amino sources

$$R^{O} = R^{O} + Ar-NO_{2} \xrightarrow{Ni(glyme)Cl_{2}, phen (10 mol \%)}{Zn (4 equiv.), TMSCl} R^{O} + N^{Ar}_{H}$$

This work

(d) Fe-promoted amidation of acyl halide with nitroarenes

$$R \xrightarrow{X}_{X=Cl, F} + Ar-NO_2 \xrightarrow{Fe}_{Fe} \xrightarrow{Fe^{2^+}}_{Ar-N} Ar - N \xrightarrow{O}_{COR} \xrightarrow{Fe^{2^+}, H_2O}_{COR} \xrightarrow{O}_{H} \xrightarrow{Ar}_{H} Ar$$

-Direct, catalytic activation of Acyl halide

- -Cheaper & more stable nitroarenes in place of anilines
- -Broad scope of Acyl halide & nitroarenes
- -Water as solvent, No additives, Mild conditions

Scheme 1 Different approaches for amidation using nitroarenes as amino sources.

<sup>&</sup>quot;School of Material and Chemical Engineering, Tongren University, Tongren 554300, China. E-mail: cqglei@163.com

<sup>&</sup>lt;sup>b</sup>College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China

School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China. E-mail: jiangjunhust@163.com

 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available:  $^{11}{\rm H}$  NMR and  $^{13}{\rm C}$  NMR spectra of new compounds. See DOI: 10.1039/d0ra10868e

## 2. Results and discussion

We used the reaction of nitrobenzene (1a) with benzoyl chloride (2a, 2 equiv.) as test reaction (Table 1). Using the conditions of benzoyl chloride (0.5 mmol) with nitrobenzenes (0.25 mmol), iron dust (4 equiv.) as reductant, and water (1 mL) as solvent, the transamidation was actually successful, giving the desired amide product N-phenyl benzamide (3aa), in 88% yield (Table 1, entry1). We optimized the Fe-mediated transamidation of 1a with 2a. Other metal reductants such as zinc, aluminium, and magnesium were not effective (Table 1, entries 2-4). By changing the temperature to 80 °C or 40 °C, the yield of 3aa was reduced (Table 1, entries 5 and 6). We believe that weak hydrolysis reaction may occur for acyl chlorides at elevated temperature, resulting in diminished yield of target product. The use of other solvent instead of water all led to a great reduction of yields (Table 1, entries 7-11). More loading of Fe (5 equiv.) or PhCOCl (2.5 equiv.) have no effect on yield, but lower loading of Fe (3 equiv.) or PhCOCl (1.5 equiv.) led to a modest reduction of yields (Table 1, entries 12-16).

The optimized reaction conditions were employed for the transamidation of nitroarenes (1a) with acyl chloride (2) (shown in Table 2). The reaction of nitrobenzene (1a) and benzoyl chloride (2a) efficiently offered 88% yield of 3aa in 36 h at 60 °C. Various acyl chlorides reacted smoothly with nitrobenzene to give the *N*-aryl amide products in medium to excellent yields. It was observed that benzoyl chlorides with electron donating substituents afforded the higher yields of corresponding products (3ab–3ad, 3ak). However, the yield of anilides with electron withdrawing substituents were reduced (3ae, 3ag–3aj). Notably,

Table 1	e 1 Screening optimal conditions <sup>a</sup>			
Entry	Var	iations from stan	dard conditions	Yield <sup>z</sup>
1	No	variation		88
2	Zn (4 equiv.) instead of Fe			45
3	Al (	4 equiv.) instead	of Fe	17
4	Mg	(4 equiv.) instead	l of Fe	18
5	80	°C instead of 60 °	C	68
6	40	$^{\circ}$ C instead of 60 $^{\circ}$	С	78
7	NM	P instead of H <sub>2</sub> O	1	30
8	DM	F instead of H <sub>2</sub> O		22
9	Tol	uene instead of H	I <sub>2</sub> O	11
10	PhO	Cl instead of H <sub>2</sub> O		14
11	EtC	H instead of H <sub>2</sub> C	)	45
12	Fe (	(5 equiv.) instead	of (4 equiv.)	88
13	Fe (3 equiv.) instead of (4 equiv.)		55	
14	Absence of Fe		Trace	
15	PhO	COCl (2.5 equiv.)	instead of (2 equiv	.) 87
16	PhO	COCl (1.5 equiv.)	instead of (2 equiv	.) 59
			$\longrightarrow$	o -C-N
	1a	2a		3aa

<sup>*a*</sup> All reactions were performed with nitrobenzene (**1a**, 0.25 mmol), acyl chloride (**2a**, 0.5 mmol), reductant (1 mmol) and solvent (1 mL), 36 h. <sup>*b*</sup> Isolated yield.

RSC Advances

View Article Online



<sup>*a*</sup> Conditions: **1a** (0.25 mmol), **2** (0.5 mmol), Fe (1 mmol) and H<sub>2</sub>O (1 mL), 60  $^{\circ}$ C, 36 h. <sup>*b*</sup> After column chromatography. <sup>*c*</sup> Use BzF as 2.

both isobutyryl chloride and cyclohexanecarbonyl chloride were proven to be effective to produce the desired products in medium yield (**3af, 3al**). However, when we used 4-nitrobenzoyl chloride (**2n**) or 2-nitrobenzoyl chloride (**2m**), no obvious reactions were observed. Moreover, benzoyl fluoride reacted with nitrobenzene to give **3aa** in 56% yield (**3aa**).

Subsequently, various nitroarenes were reacted with benzoyl chloride (2a) as shown in Table 3. The reaction of 2a with 1methyl-4-nitrobenzene, 1-methyl-3-nitrobenzene and 1-chloro-4-methyl-2-nitrobenzene gave the corresponding products, **3ba**, **3ca** and **3ga** in good yields. The 1-chloro-4-nitrobenzene and 1-bromo-4-nitrobenzene also participated well in this reaction (**3ea**, **3fa**). Meanwhile, this reaction is also tolerant of 1chloro-4-methoxy-2-nitrobenzene and 1,4-dichloro-2nitrobenzene, and the desired products **3ha** and **3ia** were produced in 78% and 64% yields. However, it was observed that nitromethane (**1j**) failed to produce desired *N*-methylbenzamide in practical yields.

To verify the practicality of the reaction, a scale-up reaction were carried out. Nitrobenzene (1a, 10 mmol) reacted with benzoyl chloride and Fe under standard conditions, and the expected product 3aa was obtained in 80% yield (Scheme 2).

A series of control experiments were carried out to gain some insights into the possible mechanism. When radical trapping reagents (TEMPO) was added to the reaction mixture, the

 Table 3
 Substrate scope with respect to nitroarenes<sup>a,b</sup>



 $^a$  Conditions: 1 (0.25 mmol), 2a (0.5 mmol), Fe (1 mmol) and H\_2O (1 mL), 60  $^\circ C$ , 36 h.  $^b$  After column chromatography.

transformation was inhibited, implying that the transformation might proceed *via* radical process (Scheme 3a). Lacking of BzCl in the reaction, there was no PhNH<sub>2</sub> generated (Scheme 3b). Then, we usedsd nitrosobenzene as the reactant under the standard conditions and the product **3aa** was obtained (Scheme



Scheme 2 Gram scale synthesis.



Scheme 3 Control experiments.

(a) Reduction of Formyl halide by Fe

$$\begin{array}{c} O \\ B \\ 2 R - C - X \end{array} + Fe \longrightarrow 2 R - C + 2 X^{-} + Fe^{2+} \end{array}$$

(b) Reaction benzoyl halide with nitrosoarene and reduction

$$Ar - NO_{2} \xrightarrow{Fe} Ar - N = O \xrightarrow{RCO}$$

$$Ar - NH - C - R \xrightarrow{Fe^{2+}, 2H_{2}O} Ar - N \xrightarrow{O} COR$$



3c), but *N*-phenyl-hydroxylamine or azobenzene or N,N'-diphenylhydrazine could not react with benzoyl chloride to generate **3aa** (Scheme 3d) suggesting that nitrosobenzene might be involved as an intermediate in the transformation. Finally, when the reaction was conducted under a nitrogen atmosphere, we got the product **3aa** in 86% yield (Scheme 3e). We observed that the color of the mixtures changed from colourless to pale brown and some brown solid was generated. We added 1 mL HCl (1 M) to the reaction mixtures and the precipitation was disappeared followed by color changing from pale brown to pale yellow. So we speculated that ferric hydroxide was generated in the transformation. Finally, the reaction of 1a with carboxylic acid anhydride Bz<sub>2</sub>O could not produce **3aa** under the standard conditions (Scheme 3f).

According to the aforementioned experimental results and literature reports,<sup>25</sup> PhCOCl or PhCOF was activated by ferrous powder to produce a benzoyl radical (Scheme 4a). Then, the benzoyl radical reacted with nitrosoarene originating from the reduction of nitroarene by ferrous powder to form the N–C bond. Finally, the generated radical further transforms into the desired product 3 in the presence of Ferrous ion and water (Scheme 4b).

## 3. Conclusions

In conclusion, we have developed a step-economic amidation of PhCOX using nitroarenes as amino sources promoted by Fe. Broad scope and functional group compatibility have been demonstrated. The direct use of nitroarenes in place of anilines would provide potential advantages in cost and step economy.

## 4. Experimental details

NMR spectroscopy was performed on a Bruker advanced spectrometer operating at 400 MHz (<sup>1</sup>H NMR) and 100 MHz (<sup>13</sup>C NMR). Melting point was measured with a XRC-1 melting point apparatus. FT infrared (IR) spectra was recorded using FD-5DX spectrometer. Mass spectrometric analysis was performed on MAT 95 XP (Thermo Finnigan).

### General procedure for synthesis of N-phenylacetamides (3)

A mixture of nitroarenes (0.25 mmol) and acyl chloride (fluoride) (0.5 mmol) and  $H_2O$  (1 mL) was stirred at 60  $^\circ C$  for 36 h

#### Paper

under air. After cooling to room temperature, water (10 mL) was added and the aqueous phase was extracted by EtOAc (3  $\times$  10 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuum. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as eluent to afford the corresponding product.

#### N-Phenylbenzamide (3aa)

Pale brown solid. Mp: 162–163  $^{\circ}\mathrm{C}$  (lit^{12} 164–165  $^{\circ}\mathrm{C}$ ). Yield 45 mg (88%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.31 (s, 1H), 8.01 (d, J = 7.2 Hz, 2H), 7.84 (d, J = 7.8 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.56 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  166.1, 139.7, 135.5, 132.4, 129.1, 128.9, 128.1, 124.1, 120.9.

#### 4-Methyl-N-phenylbenzamide (3ab)

White solid. Mp: 142–143 °C (lit<sup>12</sup> 145–146 °C). Yield 39 mg (91%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.22 (s, 1H), 7.92 (d, J = 7.6 Hz, 2H), 7.83 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 8.0 Hz, 4H), 7.12 (t, J = 7.0 Hz, 1H), 2.41 (s, 3H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  165.8, 142.0, 139.7, 132.6, 129.4, 129.0, 128.2, 124.0, 120.8, 21.5.

#### 3-Methyl-N-phenylbenzamide (3ac)

White solid. Mp: 125–127 °C (lit<sup>12</sup> 125–126 °C). Yield 35 mg (67%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.28 (s, 1H), 7.86–7.78 (m, 4H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 2.43 (s, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 166.2, 139.7, 138.2, 135.5, 132.6, 129.1, 128.7, 128.6, 125.3, 124.1, 120.8, 21.4.

#### 2-Methyl-N-phenylbenzamide (3ad)

White solid. Mp: 125–126 °C (lit<sup>12</sup> 125–126 °C). Yield 45 mg (86%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.34 (s, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.48 (d, J = 7.4 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.38–7.31 (m, 4H), 7.12 (t, J = 7.2 Hz, 1H), 2.41 (s, 3H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  168.3, 139.8, 137.7, 135.6, 131.0, 130.1, 129.2, 127.7, 126.1, 124.0, 120.1, 19.8.

#### 3,5-Dichloro-N-phenylbenzamide (3ae)

White solid. Mp: 148–149 °C. Yield 47 mg (71%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.46 (s, 1H), 8.00 (s, 2H), 7.86 (s, 1H), 7.79 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.2 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  163.1, 139.1, 138.5, 134.7, 131.3, 129.1, 127.0, 124.6, 120.9.

HRMS (ESI) m/z calcd for  $C_{13}H_{10}Cl_2NO [M + H]^+$ : 266.0134, found 266.0135.

#### *N*-Phenylisobutyramide (3af)

Shallow brown solid. Mp: 101–102  $^{\circ}$ C (lit<sup>12</sup> 102–103  $^{\circ}$ C). Yield 25 mg (62%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  9.86 (s, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.04 (t, J = 7.2 Hz, 1H), 2.65–2.58 (m, 1H), 1.12 (d, J = 6.8 Hz, 6H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  175.7, 139.9, 129.1, 123.4, 119.5, 35.4, 20.0.

#### 4-Fluoro-N-phenylbenzamide (3ag)

Pale brown solid. Mp: 182–184 °C (lit<sup>12</sup> 183–184 °C). Yield 33 mg (63%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.31 (s, 1H), 8.07 (t, J = 6.6 Hz, 2H), 7.80 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 4H), 7.13 (t, J = 7.2 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 164.9, 164.5 (d,  $J_{C-F} = 247$  Hz), 139.5, 131.9 (d,  $J_{C-F} = 3$  Hz), 130.9 (d,  $J_{C-F} = 9$  Hz), 129.1, 124.2, 120.9, 115.8 (d,  $J_{C-F} = 22$  Hz).

#### 3-Bromo-N-phenylbenzamide (3ah)

White solid. Mp: 146–148 °C (lit<sup>12</sup> 145–147 °C). Yield 44 mg (64%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.39 (s, 1H), 8.18 (s, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.83–7.79 (m, 3H), 7.52 (t, J = 7.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  164.4, 139.4, 137.6, 134.7, 131.1, 130.7, 129.1, 127.3, 124.4, 122.2, 120.9.

#### 4-Chloro-N-phenylbenzamide (3ai)

White solid. Mp: 197–198 °C (lit<sup>12</sup> 199–200 °C). Yield 41 mg (71%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.36 (s, 1H), 8.02 (d, J = 7.8 Hz, 2H), 7.81 (d, J = 7.8 Hz, 2H), 7.63 (t, J = 7.8 Hz, 2H), 7.38 (t, J = 7.2 Hz, 2H), 7.14 (t, J = 7.0 Hz, 1H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  164.9, 139.4, 136.9, 134.1, 130.1, 129.1, 128.9, 124.3, 120.9.

#### N-Phenyl-4-(trifluoromethyl)benzamide (3aj)

Brown solid. Mp: 196–197  $^\circ C$  (lit  $^{12}$  196–197  $^\circ C$ ). Yield 41 mg (73%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.58 (s, 1H), 8.00 (d, J = 6.8 Hz, 2H), 7.92 (d, J = 7.8 Hz, 2H), 7.25 (t, J = 7.2 Hz, 2H), 7.15 (t, J = 7.8 Hz, 2H), 7.05 (t, J = 7.0 Hz, 1H).

13C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  160.0, 143.8, 137.6, 133.0 (q,  $J_{C-F} = 26$  Hz),129.7, 128.1, 126.9 (q,  $J_{C-F} = 3$  Hz), 125.0, 123.8 (q,  $J_{C-F} = 271$  Hz), 121.0.

#### N-Phenylfuran-2-carboxamide (3ak)

White solid. Mp: 178–179  $^{\circ}\text{C}.$  Yield 36 mg (78%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  = 10.17 (s, 1H), 7.93 (s, 1H), 7.75 (d, J = 7.6 Hz, 2H), 7.40–7.27 (m, 3H), 7.09 (t, J = 7.6 Hz, 1H), 6.70 (dd, J = 3.4, 1.8 Hz, 1H).

RSC Advances

 $^{13}\mathrm{C}$  NMR (101 MHz, DMSO- $d_6) \delta$  156.7, 148.0, 146.1, 139.0, 129.1, 124.2, 120.8, 115.2, 112.6.

HRMS (ESI) m/z calcd for  $C_{11}H_{10}NO_2 [M + H]^+$ : 188.0712, found 188.0716.

#### N-Phenylcyclohexanecarboxamide (3al)

White solid. Mp: 133–135 °C. Yield 34 mg (67%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  = 9.78 (s, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.27 (t, J = 7.8 Hz, 2H), 7.00 (t, J = 7.5 Hz, 1H), 2.32 (t, J = 11.6 Hz, 1H), 1.78–1.73 (m, 4H), 1.67–1.63 (m, 1H), 1.45–1.38 (m, 2H), 1.27–1.23 (m, 3H).

 $^{13}{\rm C}$  NMR (101 MHz, DMSO- $d_6) \delta$  174.7, 140.0, 129.0, 123.3, 119.5, 45.3, 29.6, 25.7.

HRMS (ESI) m/z calcd for  $C_{13}H_{18}NO [M + H]^+$ : 204.1388, found 204.1385.

#### *N*-(*p*-Tolyl)benzamide (3ba)

White solid. Mp: 158–159 °C (lit<sup>12</sup> 156–157 °C). Yield 50 mg (95%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ10.23 (s, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 7.0 Hz, 1H), 7.55 (t, J = 7.4 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 2.31 (s, 3H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  165.8, 137.1, 135.5, 133.1, 131.9, 129.5, 128.8, 128.1, 120.9, 21.0.

#### N-(m-Tolyl)benzamide (3ca)

White solid. Mp: 125–126 °C (lit<sup>12</sup> 124–125 °C). Yield 45 mg (85%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.23 (s, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.68 (s, 1H), 7.61 (t, J = 7.4 Hz, 2H), 7.55 (t, J = 7.4 Hz, 2H), 7.29–7.23 (m, 1H), 6.95 (d, J = 7.2 Hz, 1H), 2.34 (s, 3H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  166.0, 139.6, 138.2, 135.5, 132.0, 128.9, 128.8, 128.1, 124.8, 121.4, 118.0, 21.7.

#### N-(o-Tolyl)benzamide (3da)

White solid. Mp: 145–146  $^\circ C$  (lit<sup>12</sup> 143–145  $^\circ C$ ). Yield 42 mg (79%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  9.96 (s, 1H), 8.05 (d, J = 7.0 Hz, 2H), 7.64 (d, J = 6.8 Hz, 1H), 7.59 (d, J = 7.0 Hz, 2H), 7.41 (d, J = 6.8 Hz, 1H), 7.34 (t, J = 7.0 Hz, 1H), 7.28–7.23 (m, 2H), 2.30 (s, 3H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  165.8, 136.9, 135.0, 134.2, 132.0, 130.8, 128.9, 128.1, 127.1, 126.5, 18.4.

#### N-(4-Chlorophenyl)benzamide (3ea)

White solid. Mp: 195–196 °C (lit<sup>12</sup> 199–200 °C). Yield 42 mg (71%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 10.44 (s, 1H), 8.00 (d, J = 7.2 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 7.63–7.59 (m, 1H), 7.56 (t, J = 7.2 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  166.1, 138.7, 135.2, 132.2, 129.0, 128.9, 128.2, 127.8, 122.3.

#### N-(4-Bromophenyl)benzamide (3fa)

White solid. Mp: 205–207  $^\circ C$  (lit  $^{12}$  205–206  $^\circ C$ ). Yield 48 mg (70%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.46 (s, 1H), 8.03 (d, J = 7.2 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H), 7.65 (t, J = 7.2 Hz, 1H), 7.62–7.56 (m, 4H).

 $^{13}\mathrm{C}$  NMR (100 MHz, DMSO-d\_6)  $\delta$  166.1, 139.1, 135.2, 132.2, 131.9, 128.9, 128.2, 122.7, 115.8.

#### N-(2-Chloro-5-methylphenyl)benzamide (3ga)

White solid. Mp: 121–122  $^\circ C.$  Yield 49 mg (80%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.46 (s, 1H), 8.04 (d, J = 7.8 Hz, 2H), 7.67–7.62 (m, 1H), 7.57 (t, J = 6.8 Hz, 2H), 7.46 (t, J = 8.4 Hz, 2H), 7.14 (d, J = 8.2 Hz, 1H), 2.35 (s, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 165.8, 137.5, 135.2, 134.5, 132.3, 129.6, 129.4, 129.0, 128.6, 128.1, 126.9, 20.9.

HRMS (ESI) m/z calcd for  $C_{14}H_{13}CINO [M + H]^+$ : 246.0680, found 246.0682.

#### N-(2-Chloro-5-methoxyphenyl)benzamide (3ha)

White solid. Mp: 124–125  $^{\circ}\text{C}.$  Yield 50 mg (78%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.03 (s, 1H), 8.03 (d, J = 7.8 Hz, 2H), 7.64 (t, J = 7.0 Hz, 1H), 7.57 (t, J = 7.2 Hz, 2H), 7.48 (d, J = 8.8 Hz, 1H), 7.29 (s, 1H), 6.92 (d, J = 8.8 Hz, 1H),3.81 (s, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 165.8, 158.7, 136.3, 134.4, 132.4, 130.3, 129.0, 128.2, 120.9, 113.9, 113.5, 56.1.

HRMS (ESI) m/z calcd for  $C_{14}H_{13}ClNO_2 [M + H]^+$ : 262.0629, found 262.0626.

#### N-(2,5-Dichlorophenyl)benzamide (3ia)

White solid. Mp: 122–123 °C (lit<sup>12</sup> 123–124 °C). Yield 42 mg (64%) at 0.25 mmol scale.

<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  10.19 (s, 1H), 8.02 (d, J = 7.5 Hz, 2H), 7.80 (s, 1H), 7.67–7.62 (m, 2H), 7.58 (t, J = 7.2 Hz, 2H), 7.41 (d, J = 8.4 Hz, 1H).

 $^{13}{\rm C}$  NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  165.9, 136.9, 134.1, 132.6, 131.9, 131.4, 129.0, 128.4, 128.2, 128.1, 127.6.

## Author contributions

Conceptualization: J. N. Xiang; data curation: Y. X. Liu and Y. D. Wu; formal analysis: Y. D. Wu. and J. Jiang; investigation: Y. D. Wu and L. Guo; methodology: Y. X. Liu and L. Guo; resources: J. N. Xiang; visualization: Y. D. Wu and Y. X. Liu; writing – original draft preparation: Y. D. Wu and L. Guo; writing – review and editing: Y. D. Wu, L. Guo, Y. X. Liu, J. N. Xiang; supervision: J. Jiang; project administration: L. Guo and J. N. Xiang; funding acquisition: L. Guo. All authors have read and agreed to the published version of the manuscript.

# Conflicts of interest

The authors have declared that no conflicting interests exist.

## Acknowledgements

This work was supported by the Guizhou Provincial Department of Education Foundation (QJHKY2020-067), the National Natural Science Foundation of China (21502049, 22062022), and the Foundation of the Department of Education of Guizhou Province (KY[2018]030).

# References

- 1 C. W. Cheung, M. L. Ploeger and X. Hu, *Nat. Commun.*, 2017, **8**, 14878.
- 2 R. M. de Figueiredo, J. S. Suppo and J. M. Campagne, *Chem. Rev.*, 2016, **116**, 12029–12122.
- 3 U. Manna and G. Das, Coord. Chem. Rev., 2021, 427, 213547.
- 4 J. M. Humphrey and A. R. Chamberlin, *Chem. Rev.*, 1997, **97**, 2243–2266.
- 5 J. Jiang, S. Zeng, D. Chen, C. Cheng, W. Deng and J. Xiang, Org. Biomol. Chem., 2018, **16**, 5016–5020.
- 6 C. W. Cheung, M. L. Ploeger and X. Hu, *ACS Catal.*, 2017, 7, 7092–7096.
- 7 B. L. Korbad and S. H. Lee, *Chem. Commun.*, 2014, **50**, 8985-8988.
- 8 C. L. Allen, B. N. Atkinson and J. M. Williams, *Angew. Chem., Int. Ed. Engl.*, 2012, **51**, 1383–1386.
- 9 H. Lundberg, F. Tinnis, N. Selander and H. Adolfsson, *Chem. Soc. Rev.*, 2014, **43**, 2714–2742.

- 10 M. Sun, J. Jiang, J. Chen, Q. Yang and X. Yu, *Tetrahedron*, 2019, **75**, 130456.
- 11 C. L. Allen and J. M. Williams, *Chem. Soc. Rev.*, 2011, 40, 3405–3415.
- 12 R. Takise, K. Muto and J. Yamaguchi, *Chem. Soc. Rev.*, 2017, **46**, 5864–5888.
- 13 A. S. Santos, A. M. S. Silva and M. M. B. Marques, *Eur. J. Org. Chem.*, 2020, **2020**, 2501–2516.
- 14 E. M. Nahmed and G. Jenner, *Tetrahedron Lett.*, 1991, 32, 4917-4920.
- 15 B. N. Atkinson, A. R. Chhatwal, H. V. Lomax, J. W. Walton and J. M. Williams, *Chem. Commun.*, 2012, **48**, 11626–11628.
- 16 M. L. Kantam, R. S. Reddy, K. Srinivas, R. Chakravarti, B. Sreedhar, F. Figueras and C. Venkat Reddy, J. Mol. Catal. A: Chem., 2012, 355, 96–101.
- 17 T. L. Ho, J. Org. Chem., 1977, 42, 3755.
- 18 Y. Watanabe, Y. Tsuji, T. Kondo and R. Takeuchi, J. Org. Chem., 1984, 49, 4451–4455.
- 19 C. W. Cheung, J. A. Ma and X. Hu, J. Am. Chem. Soc., 2018, 140, 6789–6792.
- 20 C. W. Cheung, M. Leendert Ploeger and X. Hu, *Chem. Sci.*, 2018, **9**, 655–659.
- 21 L. Hie, N. F. Fine Nathel, T. K. Shah, E. L. Baker, X. Hong, Y. F. Yang, P. Liu, K. N. Houk and N. K. Garg, *Nature*, 2015, **524**, 79–83.
- 22 C. W. Cheung, N. Shen, S.-P. Wang, A. Ullah, X. Hu and J.-A. Ma, *Org. Chem. Front.*, 2019, **6**, 756–761.
- 23 L. N. de Paula, L. A. dos Reis Giusto, J. D. Ardisson and F. Magalhães, *Environ. Chem. Lett.*, 2015, **13**, 347–351.
- 24 M. Zhang, J. Li, Q. Zeng and Q. Mou, Appl. Sci., 2019, 9, 3604.
- 25 C. W. Cheung and X. Hu, Nat. Commun., 2016, 7, 13776.