PAPER

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Fe-mediated synthesis of N-aryl amides from nitroarenes and acyl chlorides†

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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.
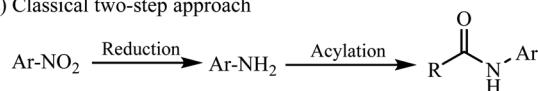
1. Introduction

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.[14,15] 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 ZrO_2 and acetic anhydride, molybdenum hexacarbonyl/acetic acid, and also anilides have been obtained either *via* nickel or rhodium or platinum catalyzed carbonylation of nitroarenes.[16–18] However, 50–100 atm CO is required in each case. In 2018, Hu and co-workers described Mn-catalyzed reductive transamidation of tertiary amides with nitroarenes (Scheme 1b).[19] 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
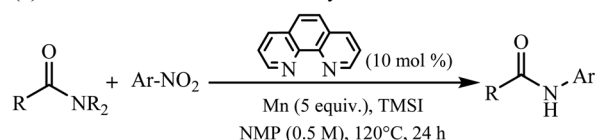
widely used in organic synthesis. In addition, Fe dust is a cheap and safe reducing agent and can be used in many organic reactions.[23,24] We are interested in Fe-promoted organic reactions performed in water. Therefore, we developed a mild Fe-promoted reaction of nitroarenes with acyl chloride (fluoride) 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).
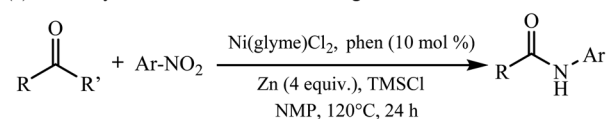
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Scheme 1 Different approaches for amidation using nitroarenes as amino sources.

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 Screening optimal conditions[a]

Entry	Variations from standard conditions	Yield[b]
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 of Fe	18
5	80 °C instead of 60 °C	68
6	40 °C instead of 60 °C	78
7	NMP instead of H_2O	30
8	DMF instead of H_2O	22
9	Toluene instead of H_2O	11
10	PhCl instead of H_2O	14
11	EtOH instead of H_2O	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	PhCOCl (2.5 equiv.) instead of (2 equiv.)	87
16	PhCOCl (1.5 equiv.) instead of (2 equiv.)	59
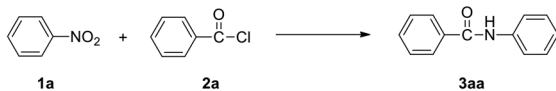
[a] All reactions were performed with nitrobenzene (**1a**, 0.25 mmol), acyl chloride (**2a**, 0.5 mmol), reductant (1 mmol) and solvent (1 mL), 36 h. [b] Isolated yield.

Table 2 Substrate scope with respect to acyl chloride [a,b]

[a] Conditions: **1a** (0.25 mmol), **2** (0.5 mmol), Fe (1 mmol) and H_2O (1 mL), 60 °C, 36 h. [b] After column chromatography. [c] 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**).
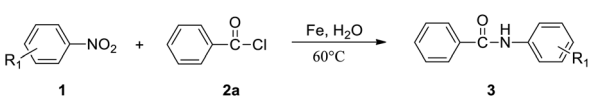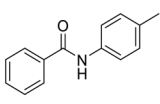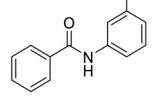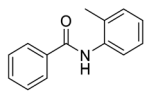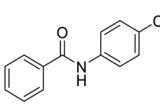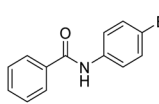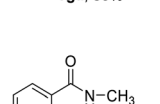
Subsequently, various nitroarenes were reacted with benzoyl chloride (**2a**) as shown in Table 3. The reaction of **2a** with 1-methyl-4-nitrobenzene, 1-methyl-3-nitrobenzene and 1-chloro-4-methyl-2-nitrobenzene gave the corresponding products, **3ba**, **3ca** and **3ga** in good yields. The 1-chloro-4-nitrobenzene and 1-bromo-4-nitrobenzene also participated well in this reaction (**3ea**, **3fa**). Meanwhile, this reaction is also tolerant of 1-chloro-4-methoxy-2-nitrobenzene and 1,4-dichloro-2-nitrobenzene, 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.
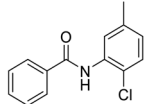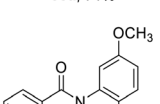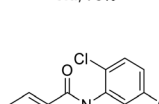
To verify the practicality of the reaction, a scale–up reaction were carried out. Nitrobenzene (**1a**, 10 mmol) reacted with benzoyl chloride and Fe under standard conditions, and the expected product **3aa** was obtained in 80% yield (Scheme 2).

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[a,b]


3ba, 95%   3ca, 85%   3da, 79%

3ea, 71%   3fa, 70%   3ga, 80%

3ha, 78%   3ia, 64%   3ja, N.D.

[a] Conditions: **1** (0.25 mmol), **2a** (0.5 mmol), Fe (1 mmol) and H_2O (1 mL), 60 °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 $PhNH_2$ generated (Scheme 3b). Then, we usedsd nitrosobenzene as the reactant under the standard conditions and the product **3aa** was obtained (Scheme
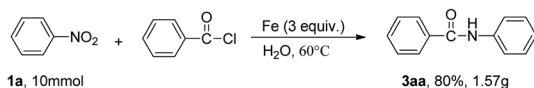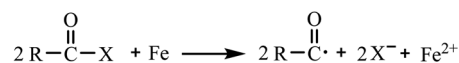

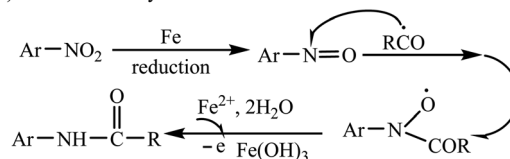
Scheme 2   Gram scale synthesis.
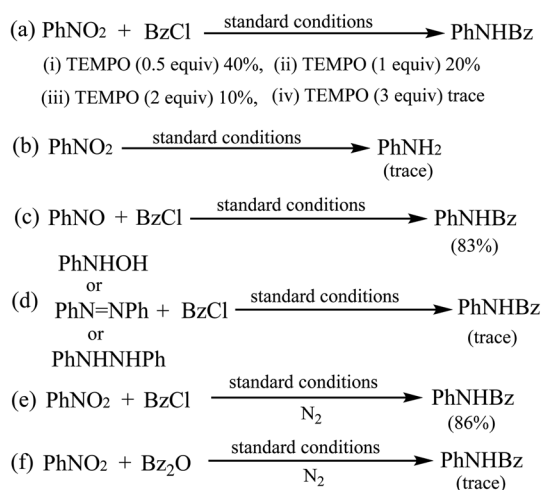
Scheme 3   Control experiments.

(a) Reduction of Formyl halide by Fe

(b) Reaction benzoyl halide with nitrosoarene and reduction

Scheme 4   Proposed reaction mechanism.

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_2O could not produce **3aa** under the standard conditions (Scheme 3f).

According to the aforementioned experimental results and literature reports,[25] 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 (^{1}H NMR) and 100 MHz (^{13}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 °C for 36 h

under air. After cooling to room temperature, water (10 mL) was added and the aqueous phase was extracted by EtOAc (3 × 10 mL). The combined organic phases were dried over Na_2SO_4, 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 °C (lit[12] 164–165 °C). Yield 45 mg (88%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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).

^{13}C NMR (100 MHz, DMSO-d_6) δ 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[12] 145–146 °C). Yield 39 mg (91%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) 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}C NMR (100 MHz, DMSO-d_6) δ 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[12] 125–126 °C). Yield 35 mg (67%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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).

^{13}C NMR (100 MHz, DMSO-d_6) 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[12] 125–126 °C). Yield 45 mg (86%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) 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}C NMR (100 MHz, DMSO-d_6) δ 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.

^{1}H NMR (400 MHz, DMSO-d_6) 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}C NMR (100 MHz, DMSO-d_6) δ 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 °C (lit[12] 102–103 °C). Yield 25 mg (62%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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}C NMR (100 MHz, DMSO-d_6) δ 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[12] 183–184 °C). Yield 33 mg (63%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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).

^{13}C NMR (100 MHz, DMSO-d_6) 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[12] 145–147 °C). Yield 44 mg (64%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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}C NMR (100 MHz, DMSO-d_6) δ 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[12] 199–200 °C). Yield 41 mg (71%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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}C NMR (100 MHz, DMSO-d_6) δ 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 °C (lit[12] 196–197 °C). Yield 41 mg (73%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) 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_6) δ 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 °C. Yield 36 mg (78%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 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).

^{13}C NMR (101 MHz, DMSO-d_6) δ 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.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 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}C NMR (101 MHz, DMSO-d_6) δ 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[12] 156–157 °C). Yield 50 mg (95%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) 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}C NMR (100 MHz, DMSO-d_6) δ 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[12] 124–125 °C). Yield 45 mg (85%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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}C NMR (100 MHz, DMSO-d_6) δ 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 °C (lit[12] 143–145 °C). Yield 42 mg (79%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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}C NMR (100 MHz, DMSO-d_6) δ 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[12] 199–200 °C). Yield 42 mg (71%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) 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}C NMR (100 MHz, DMSO-d_6) δ 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 °C (lit[12] 205–206 °C). Yield 48 mg (70%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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}C NMR (100 MHz, DMSO-d_6) δ 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 °C. Yield 49 mg (80%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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).

^{13}C NMR (100 MHz, DMSO-d_6) 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 $C_{14}H_{13}ClNO$ [M + H]$^+$: 246.0680, found 246.0682.

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

White solid. Mp: 124–125 °C. Yield 50 mg (78%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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).

^{13}C NMR (100 MHz, DMSO-d_6) 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[12] 123–124 °C). Yield 42 mg (64%) at 0.25 mmol scale.

^{1}H NMR (400 MHz, DMSO-d_6) δ 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}C NMR (100 MHz, DMSO-d_6) δ 165.9, 136.9, 134.1, 132.6, 131.9, 131.4, 129.0, 128.4, 128.2, 128.1, 127.6.

Author contributions

Conflicts of interest

The authors have declared that no conflicting interests exist.

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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.