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# Highly Efficient Copper-Catalyzed Amidation of Aldehydes by C–H Activation

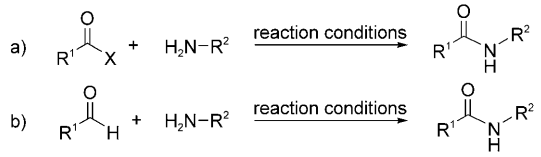
**Long Wang,[a] Hua Fu,*[a] Yuyang Jiang,[a, b] and Yufen Zhao[a]**

**Abstract:** We have developed a highly efficient method for the copper-catalyzed amidation of aldehydes in the presence of *N*-bromosuccinimide (NBS). This method is simple, economical, and has practical advantages for synthesis of imides.

**Keywords:** aldehydes · amide bond formation · C–H activation · copper · homogeneous catalysis

## Introduction

Construction of amide bonds is of great interest in organic, biological, medicinal, and materials chemistry because the amide functional group is ubiquitous in natural products, pharmaceuticals, and polymers.[1] Traditional methods for the synthesis of amides are highly concentrated on the coupling of activated carboxylic acid derivatives and amines. Although these methods have been shown to be exceptionally efficient for the synthesis of small peptides (Scheme 1a), there are limitations, such as the lability of the activated acid derivatives and tedious procedures.[2]




Scheme 1. a) The coupling of activated carboxylic acid derivatives and amines to form amides; b) the direct reactions of the acyl C–H bond in aldehydes with amines to form amides.

In view of the shortcomings above, alternative amide bond formation strategies have been actively pursued. The direct reactions of the acyl C–H bond in aldehydes with amines has attracted attention (Scheme 1b).[3–8] For example, the radical-mediated oxidative amidation with radical initiators,[3] the amidation by means of Cannizzaro reactions with lithium diisopropylamide (LDA)[4] or lanthanide reagents,[5] and the *N*-heterocyclic carbene (NHC)-catalyzed amidation[6] were reported. Most catalytic amidation processes have utilized transition-metal complexes[7] (such as copper,[7a] rhodium,[7b] ruthenium,[7c] and palladium[7d]) in the presence of an oxidant. In addition, metal-free oxidative amidation of aldehydes has also been reported.[8] Very recently, Milstein and co-workers developed a direct, endothermic ruthenium-catalyzed amidation from alcohols and amines with the liberation of $H_2$ via aldehyde intermediates.[9] The previous methods for the amidation of aldehydes used amines (strong nucleophilic reagents) as the partners; however, coupling of various amides, such as sulfonamides and carboxamides (weak nucleophilic reagents), with aldehydes is still limited. The direct functionalization of carbon–hydrogen bonds has recently received increasing attention,[10] and great progress on the intramolecular and intermolecular amidation of C–H bonds has been achieved in the past two decades.[11–14] Recently, rhodium and ruthenium-catalyzed sulfamidation of aldehydes has been developed via metal–nitrene intermediates.[15]

To the best of our knowledge, amidation of aldehydes to form imides by using free amides as the partners has not been reported, although the imide motif often appears as a key component in a variety of reactions[16] and in certain natural products, such as fumaramidmycin,[17] coniothyriomycin,[18] and SB-253514.[19] Very recently, we have devel-

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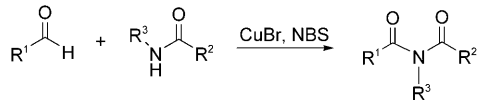
oped the iron or copper catalyst/*N*-halosuccinimide (NXS)-mediated direct functionalization of carbon–hydrogen bonds to form C–N and C–C bonds.[20] Herein, we report a novel, simple, and highly efficient copper-catalyzed coupling of aldehydes with free amides in the presence of *N*-bromosuccinimide (NBS) to give imides (Scheme 2).

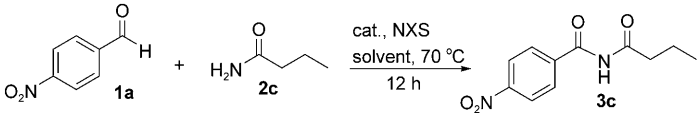



Scheme 2. Our strategy: direct reactions of the acyl C–H bond in aldehydes with amides to form imides.

## Results and Discussion

To achieve the amidation of 4-nitrobenzaldehyde, we examined a variety of conditions including *N*-halosuccimides, copper salts, and solvents at 70 °C under a nitrogen atmosphere (Table 1). Several solvents were tested by using

Table 1. Copper-catalyzed coupling of 4-nitrobenzaldehyde with butyramide in the presence of *N*-halosuccinimide: Optimization of conditions.[a]




| Entry | Cat. | NXS | Solvent | Yield [%][b] |
|---|---|---|---|---|
| 1 | CuBr | NBS | THF | trace |
| 2 | CuBr | NBS | $CH_3COOCH_3$ | 25 |
| 3 | CuBr | NBS | $CH_3CN$ | 69 |
| 4 | CuBr | NBS | $CH_3CN/CCl_4$[c] | 87 |
| 5 | CuI | NBS | $CH_3CN/CCl_4$[c] | 72 |
| 6 | $CuCl_2$ | NBS | $CH_3CN/CCl_4$[c] | 68 |
| 7 | $Cu(OAc)_2$ | NBS | $CH_3CN/CCl_4$[c] | 70 |
| 8 | CuBr | NCS | $CH_3CN/CCl_4$[c] | trace |

[a] Reaction conditions: nitrogen atmosphere, 4-nitrobenzaldehyde (1 mmol), butyramide (1.2 mmol), catalyst (0.05 mmol), *N*-halosuccinimide (1.5 mmol), solvent (3 mL). [b] Yield of isolated product. [c] $CH_3CN/CCl_4$ (v/v 1:5).

5 mol% CuBr as the catalyst and NBS as the oxidant (Table 1, entries 1–4), and the mixed solvent, $CH_3CN/CCl_4$ (volume ratio 1:5), proved to be the best medium for this reaction (Table 1, entry 4). We attempted to use various copper salts, including CuBr, CuI, $CuCl_2$, and $Cu(OAc)_2$ (Table 1, entries 4–7), and CuBr showed the highest catalytic activity. Only a trace amount of imide **3c** was observed when *N*-chlorosuccinimide (NCS) replaced NBS as the oxidant (Table 1, entry 8). After the optimization process, couplings of various aldehydes and amides were carried out under our standard conditions: 5 mol% CuBr as the catalyst, 1.5 equivalents of NBS as the oxidant (relative to aldehydes), and $CH_3CN/CCl_4$ (volume ratio 1:5) as the solvent.

As shown in Table 2, all the substrates examined provided good to excellent yields. Aromatic aldehydes containing electron-withdrawing groups showed higher activity. Nitrogen-containing heterocyclic compound, 2-pyridinecarboxaldehyde, also provided the target products in good yields (Table 2, entries 14 and 15). Couplings of secondary amides with aldehydes gave good results (Table 2, entries 16–18). We attempted copper-catalyzed intramolecular cyclization of **4** containing an aldehyde and a secondary amide group under our standard conditions and the cyclic compound **3s** was obtained in 85% yield (Table 2, entry 19). To the best of my knowledge, there are no examples for couplings of secondary amides with aldehydes. Remarkable functional-group tolerability was observed with coupling occurring in the presence of nitro, carbon–halogen bonds on aryl ring, and nitrogen-containing heterocycles.

## Conclusion

We have developed a highly efficient copper-catalyzed amidation of aldehydes in the presence of NBS, the corresponding target products were obtained in good to excellent yields, and an array of functional groups are tolerated under the mild conditions with respect to both amides and aldehydes. The protocol uses inexpensive and low loading CuBr as the catalyst. No additional ligand and additive were required, so the method is simple, economical, and has practical advantages for synthesis of imides. Further investigations in this direction are in progress.

## Experimental Section

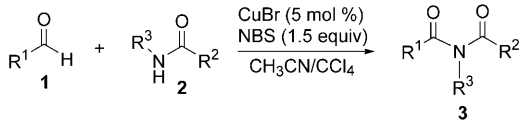
**General methods**: All reactions were carried out under a nitrogen atmosphere. Unless stated otherwise, all reagents were purchased commercially without further purification. All reagents were weighed and handled in air at room temperature. $^1H$ and $^{13}C$ NMR spectra were recorded by using tetramethylsilane (TMS) in $CDCl_3$ ($^1H$ NMR: TMS at $\delta=0.00$ ppm, $CHCl_3$ at $\delta=7.24$ ppm; $^{13}C$ NMR: $CDCl_3$ at $\delta=77.0$ ppm) or $[D_6]$DMSO as the internal standard ($^1H$ NMR: TMS at $\delta=0.00$ ppm, DMSO at $\delta=2.50$ ppm; $^{13}C$ NMR: DMSO at $\delta=40.0$ ppm).

**General procedure for the synthesis of compounds 3a–s**: A round-bottomed flask (10 mL) was charged with a magnetic stirrer, and $CH_3CN/CCl_4$ (volume ratio 1:5, 3 mL), aldehyde (**1**) (1 mmol), amide (**2**) (1.2 mmol), and CuBr (0.05 mmol, 7 mg) were added to the flask at room temperature under a nitrogen atmosphere (for Table 2, entries 14 and 15, 1.5 mmol of MgO was used to neutralize HBr freed from the reaction). After stirring for 15 min, NBS (1.5 mmol, 267 mg) was added to the solution. The mixture was stirred for a time and at a temperature as shown in Tables 1 and 2. The resulting solution was cooled to room temperature and filtered. The solid was washed with ethyl acetate (2×5 mL) and the combined filtrate was concentrated by a rotary evaporator. The residue was purified by column chromatography on silica gel by using petroleum ether/ethyl acetate as eluent to give the desired product.

**4-Nitrodibenzamide (3a)**:[21] Eluent: petroleum ether/ethyl acetate 1:1; white solid; yield: 242.8 mg, 90%; m.p. 167–169 °C; $^1H$ NMR ($[D_6]$DMSO, 300 MHz): $\delta=11.63$ (s, 1H), 8.33 (d, $^3J=8.6$ Hz, 2H), 8.10 (d, $^3J=8.6$ Hz, 2H), 7.95 (d, $^3J=7.6$ Hz, 2H), 7.66 (t, $^3J=7.8$ Hz, 1H), 7.54 ppm (t, $^3J=8.0$ Hz, 2H); $^{13}C$ NMR ($[D_6]$DMSO, 75 MHz): $\delta=167.9$, 167.6, 150.0, 140.4, 133.8, 133.5, 130.4, 129.3, 129.0, 123.9 ppm; ESI-MS: $m/z$: 292.9 $[M+Na]^+$.

Table 2. Copper-catalyzed amidation of aldehydes in the presence of NBS.[a]




1 + 2 → 3

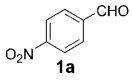
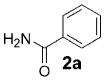
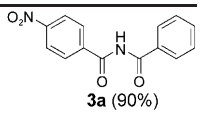
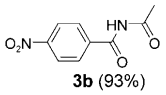
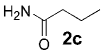
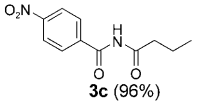
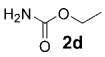
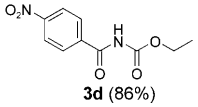
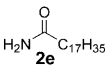
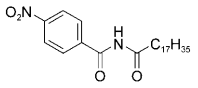
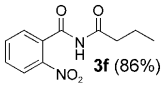
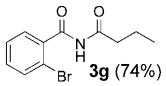
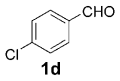
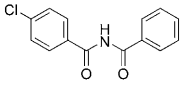
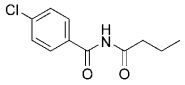
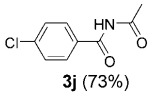
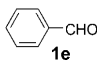
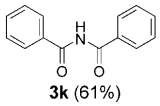
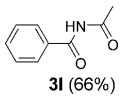
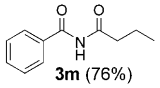
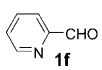
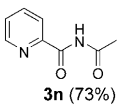
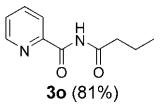
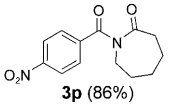
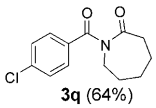
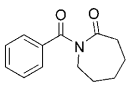
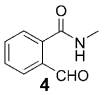
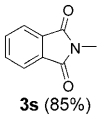
| Entry | Aldehyde | Amide | $T$ [°C]/$t$ [h] | Product [Yield][b] |
|---|---|---|---|---|
| 1 |  **1a** |  **2a** | 90/15 |  **3a** (90%) |
| 2 | **1a** |  **2b** | 90/15 |  **3b** (93%) |
| 3 | **1a** |  **2c** | 90/15 |  **3c** (96%) |
| 4 | **1a** |  **2d** | 90/15 |  **3d** (86%) |
| 5 | **1a** |  **2e** | 90/15 |  **3e** (80%) |
| 6 |  **1b** | **2c** | 90/15 |  **3f** (86%) |
| 7 |  **1c** | **2c** | 75/28 |  **3g** (74%) |
| 8 |  **1d** | **2a** | 90/15 |  **3h** (64%) |
| 9 | **1d** | **2c** | 90/15 |  **3i** (92%) |
| 10 | **1d** | **2b** | 90/15 |  **3j** (73%) |
| 11 |  **1e** | **2a** | 75/28 |  **3k** (61%) |
| 12 | **1e** | **2b** | 75/28 |  **3l** (66%) |
| 13 | **1e** | **2c** | 75/28 |  **3m** (76%) |
| 14[c] |  **1f** | **2b** | RT/15 |  **3n** (73%) |
| 15[c] | **1f** | **2c** | RT/15 |  **3o** (81%) |

Table 2. (Continued)

| Entry | Aldehyde | Amide | $T$ [°C]/$t$ [h] | Product [Yield][b] |
|---|---|---|---|---|
| 16 | **1a** |  **2f** | 90/15 |  **3p** (86%) |
| 17 | **1d** | **2f** | 90/15 |  **3q** (64%) |
| 18 | **1e** | **2f** | 75/28 |  **3r** (70%) |
| 19 |  **4** | | 75/12 |  **3s** (85%) |

[a] Reaction conditions: nitrogen atmosphere, aldehyde (1 mmol), amide (1.2 mmol), CuBr (0.05 mmol), NBS (1.5 mmol), $CH_3CN$ (0.5 mL), $CCl_4$ (2.5 mL). [b] Yield of isolated product. [c] 1.5 mmol of MgO was used to neutralize HBr freed from the reaction.

***N*-Acetyl-4-nitrobenzamide (3b)**:[21] Eluent: petroleum ether/ethyl acetate 1:1; white solid; yield: 193.2 mg, 93%; m.p. 236–238°C; $^1$H NMR ([D$_6$]DMSO, 300 MHz): $\delta$=11.3 (s, 1H), 8.33 (d, $^3J$=8.9 Hz, 2H), 8.11 (d, $^3J$=8.9 Hz, 2H), 2.35 ppm (s, 3H); $^{13}$C NMR ([D$_6$]DMSO, 75 MHz): $\delta$=172.5, 165.9, 150.2, 139.6, 130.4, 124.0, 26.0 ppm; ESI-MS: $m/z$: 230.7 [$M$+Na]$^+$.

***N*-Butyryl-4-nitrobenzamide (3c)**: Eluent: petroleum ether/ethyl acetate 3:1; white solid; yield: 226.6 mg, 96%; m.p. 142–144°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.63 (s, 1H), 8.35 (d, $^3J$=8.6 Hz, 2H), 8.14 (d, $^3J$=8.6 Hz, 2H), 3.00 (t, $^3J$=7.2 Hz, 2H), 1.76 (m, 2H), 1.04 ppm (t, $^3J$=7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=177.1, 164.3, 150.5, 138.3, 129.3, 124.1, 39.7, 17.5, 13.8 ppm; ESI-MS: $m/z$: 258.7 [$M$+Na]$^+$.

**Ethyl *N*-(4-nitrobenzoyl)carbamate (3d)**:[22] Eluent: petroleum ether/ethyl acetate 3:1; white solid; yield: 204.6 mg, 86%; m.p. 123–126°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=8.61 (s, 1H), 8.33 (d, $^3J$=8.6 Hz, 2H), 8.04 (d, $^3J$=8.6 Hz, 2H), 4.30 (q, $^3J$=7.2 Hz, 2H), 1.33 ppm (t, $^3J$=7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=164.2, 151.2, 150.3, 138.6, 129.2, 124.0, 63.0, 14.3 ppm; ESI-MS: $m/z$: 260.8 [$M$+Na]$^+$.

***N*-(4-Nitrobenzoyl)stearamide (3e)**: Eluent: petroleum ether/ethyl acetate 5:1; white solid; yield: 345.5 mg, 80%; m.p. 88–90°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.24 (s, 1H), 8.35 (d, $^3J$=8.9 Hz, 2H), 8.07 (d, $^3J$=8.9 Hz, 2H), 2.99 (t, $^3J$=7.56 Hz, 2H), 1.70 (m, 2H), 1.32 (s, 28H), 0.88 ppm (t, $^3J$=6.6 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=176.7, 164.1, 150.5, 138.4, 129.2, 124.1, 37.8, 32.0, 29.8, 29.7, 29.6, 29.5, 29.2, 24.1, 22.8, 14.2 ppm; ESI-MS: $m/z$: 455.4 [$M$+Na]$^+$.

***N*-Butyryl-2-nitrobenzamide (3f)**: Eluent: petroleum ether/ethyl acetate 3:1; white solid; yield: 203.0 mg, 86%; m.p. 108–110°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.26 (s, 1H), 8.20 (d, $^3J$=8.3 Hz, 1H), 7.74 (m, 1H), 7.62 (m, 1H), 7.44 (m, 1H), 2.56 (t, $^3J$=7.5 Hz, 2H), 1.64 (m, 2H), 0.95 ppm (t, $^3J$=7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=173.4, 167.9, 145.4, 134.4, 132.6, 130.7, 127.8, 124.4, 39.0, 17.7, 13.6 ppm; ESI-MS: $m/z$: 258.7 [$M$+Na]$^+$.

***N*-Butyryl-2-bromobenzamide (3g)**: Eluent: petroleum ether/ethyl acetate 3:1; white solid; yield: 198.9 mg, 74%; m.p. 98–102°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=8.58 (s, 1H), 7.60 (m, 1H), 7.50 (m, 1H), 7.38 (m, 2H), 1.91 (t, $^3J$=7.2 Hz, 2H), 1.73 (m, 2H), 1.02 ppm (t, $^3J$=7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=174.9, 166.4, 136.6, 133.8, 132.4, 129.3, 127.8, 119.2, 39.6, 17.3, 13.8 ppm; ESI-MS: $m/z$: 292.0, 293.9 [$M$+Na]$^+$.

***N*-(4-Chlorobenzoyl)benzamide (3h)**:[21] Eluent: petroleum ether/ethyl acetate 3:1; white solid; yield: 165.6 mg, 64%; m.p. 132–134°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.36 (s, 1H), 7.85 (d, $^3J$=7.6 Hz, 2H), 7.79 (d,

$^3J$=8.6 Hz, 1H), 7.55 (t, 3H), 7.44 ppm (m, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=166.9, 166.5, 139.5, 133.3, 133.2, 131.8, 129.8, 129.1, 128.2 ppm; ESI-MS: $m/z$: 281.9 $[M+Na]^+$.

**4-Chloro-*N*-(1-oxobutyl)benzamide (3i)**: Eluent: petroleum ether/ethyl acetate 5:1; white solid; yield: 206.8 mg, 92%; m.p. 151–153°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.41 (s, 1H), 7.90 (d, $^3J$=8.6 Hz, 2H), 7.47 (d, $^3J$=8.6 Hz, 2H), 2.99 (t, $^3J$=7.2 Hz, 2H), 1.74 (m, 2H), 1.03 ppm (t, $^3J$=7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=177.2, 164.9, 139.7, 131.2, 129.5, 129.3, 39.7, 37.6, 13.8 ppm; ESI-MS: $m/z$: 247.7 $[M+Na]^+$.

***N*-Acetyl-4-chlorobenzamide (3j)**:[23] Eluent: petroleum ether/ethylacetate 3:1; white solid; yield: 143.6 mg, 73%; m.p. 145–146°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.31 (s, 1H), 7.87 (d, $^3J$=8.6 Hz, 2H), 7.48 (d, $^3J$=8.3 Hz, 2H), 2.61 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=174.2, 165.0, 139.9, 131.1, 129.4, 129.3, 25.8 ppm; ESI-MS: $m/z$: 219.7 $[M+Na]^+$.

***N*-Benzoylbenzamide (3k)**:[21] Eluent: petroleum ether/ethylacetate 3:1; white solid; yield: 137.1 mg, 61%; m.p. 149–150°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.12 (s, 1H), 7.86 (d, $^3J$=7.6 Hz, 4H), 7.59 (t, $^3J$=7.2 Hz, 2H), 7.49 ppm (t, $^3J$=7.2 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=166.7, 133.2, 128.9, 128.1 ppm; ESI-MS: $m/z$: 247.7 $[M+Na]^+$.

***N*-Acetylbenzamide (3l)**:[21] Eluent: petroleum ether/ethylacetate 3:1; white solid; yield: 107.3 mg, 66%; m.p. 97–99°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.10 (s, 1H), 7.88 (d, $^3J$=8.3 Hz, 2H), 7.59 (t, $^3J$=6.9 Hz, 1H), 7.49 ppm (t, $^3J$=7.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=173.9, 165.9, 133.3, 132.8, 129.0, 127.9, 25.7 ppm; ESI-MS: $m/z$: 185.2 $[M+Na]^+$.

***N*-Butyrylbenamide (3m)**:[16a] Eluent: petroleum ether/ethylacetate 5:1; white solid; yield: 145.0 mg, 76%; m.p. 104–106°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.24 (s, 1H), 7.92 (d, $^3J$=7.2 Hz, 2H), 7.58 (t, $^3J$=7.2 Hz, 1H), 7.49 (t, $^3J$=7.9 Hz, 2H), 2.99 (t, $^3J$=7.2 Hz, 2H), 1.76 (m, 2H), 1.02 ppm (t, $^3J$=7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=176.8, 165.9, 133.2, 132.9, 129.0, 127.9, 39.6, 17.6, 13.8 ppm; ESI-MS: $m/z$: 213.4 $[M+Na]^+$.

***N*-Acetyl-2-pyridinecarboxamide (3n)**: Eluent: petroleum ether/ethylacetate 3:1; white solid; yield: 119.6 mg, 73%; m.p. 73–75°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=10.48 (s, 1H), 8.63 (d, $^3J$=4.8 Hz, 1H), 8.26 (d, $^3J$=7.9 Hz, 1H), 7.94 (m, 1H), 7.56 (m, 1H), 2.62 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=172.1, 163.0, 148.5, 148.2, 137.9, 127.7, 123.2, 25.5 ppm; ESI-MS: $m/z$: 186.2 $[M+Na]^+$.

***N*-Butyryl-2-pyridinecarboxamide (3o)**: Eluent: petroleum ether/ethylacetate 3:1; white solid; yield: 155.5 mg, 81%; m.p. 42–43°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=10.47 (s, 1H), 8.62 (d, 1H, $^3J$=4.5 Hz), 8.26 (d, $^3J$=7.9 Hz, 1H), 7.94 (t, $^3J$=7.2 Hz, 1H), 7.55 (m, 1H), 2.96 (t, $^3J$=7.2 Hz, 2H), 1.76 (m, 2H), 1.04 ppm (t, $^3J$=7.2 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=174.8, 162.6, 148.4, 148.3, 138.1, 127.7, 123.3, 39.6, 17.7, 13.8 ppm; ESI-MS: $m/z$: 214.4 $[M+Na]^+$.

***N*-(4-Nitrobenzoyl)caprolactam (3p)**: Eluent: petroleum ether/ethyl acetate 3:1; white solid; yield: 225.2 mg, 86%; m.p. 100–102°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=8.24 (d, $^3J$=8.9 Hz, 2H), 7.60 (d, $^3J$=8.8 Hz, 2H), 4.03 (s, 2H), 2.71 (m, 2H), 1.86 ppm (s, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=177.7, 171.9, 148.8, 143.0, 128.0, 123.6, 44.9, 38.8, 29.5, 29.2, 23.8 ppm; ESI-MS: $m/z$: 285.0 $[M+Na]^+$.

***N*-(4-Chlorobenzoyl)caprolactam (3q)**: Eluent: petroleum ether/ethyl acetate 5:1; liquid; yield: 160.5 mg, 64%; colorless oil; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.47 (d, $^3J$=8.6 Hz, 2H), 7.35 (d, $^3J$=8.6 Hz, 2H), 3.96 (t, 2H), 2.69 (t, 2H), 1.83 ppm (m, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=177.7, 173.2, 137.6, 135.1, 129.3, 128.5, 45.3, 38.9, 29.6, 29.3, 23.8 ppm; ESI-MS: $m/z$: 273.8 $[M+Na]^+$.

***N*-Benzoyl caprolactam (3r)**:[24] Eluent: petroleum ether/ethylacetate 8:1; liquid; yield: 151.6 mg, 70%; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.54 (d, $^3J$=6.8 Hz, 2H), 7.46 (m, 1H), 7.38 (m, 2H), 3.97 (s, 2H), 2.69 (m, 2H), 1.84 ppm (s, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=177.7, 174.3, 136.7, 131.4, 128.2, 127.8, 45.3, 39.0, 29.7, 29.3, 23.8 ppm; ESI-MS: $m/z$: 239.8 $[M+Na]^+$.

***N*-Methylphthalimide (3s)**:[25] Eluent: petroleum ether/ethylacetate 3:1; white solid; yield: 136.9 mg, 85%; m.p. 130–132°C; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.84 (m, 2H), 7.72 (m, 2H), 3.18 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=168.5, 133.9, 132.3, 123.2, 24.0 ppm; ESI-MS: $m/z$: 200.4 $[M+K]^+$.

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