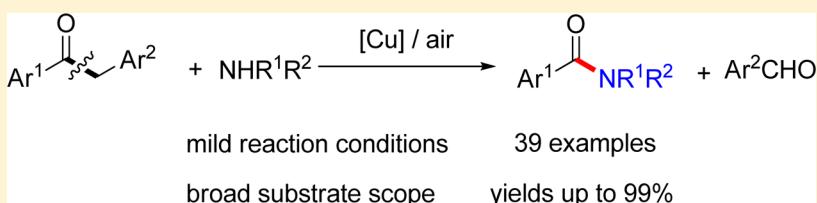


Copper-Catalyzed N-Benzoylation of Amines via Aerobic C–C Bond Cleavage

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Supporting Information



ABSTRACT: A general copper/air catalytic system for selectively oxidative C–C bond cleavage of 1,2-diarylethan-1-one has been developed, giving aromatic aldehydes and *N*-benzoylation products of various amines in moderate to excellent yields. This research provides an alternative approach for the *N*-benzoylation of amine in mild and neutral conditions.

INTRODUCTION

Carbon–carbon bond cleavage as an emerging research topic has attracted considerable attention in recent years,¹ in which unstrained carbon–carbon bond cleavage is still challenging due to its inert reactivity.² Aerobic C–C bond cleavage is a kind of transformation with unique features that include (1) the use of oxygen as a terminal oxidant, (2) the incorporation of an oxygen atom into the final product, and (3) the compatibility of converting an unstrained carbon–carbon bond, which enables the assembly of a multifunctionalized product by one-step manipulation in an environmentally benign manner.^{3,4}

Benzamide is a ubiquitous motif in the skeleton of natural products, drugs, pesticides, and functional materials.⁵ On the other hand, *N*-benzoylation is commonly applied to the protection of an amine group in a multistep synthesis.⁶ Conventionally, benzoylation of an amine is realized by the reaction of amines with benzoyl chloride, benzoic anhydride, or other benzoylating reagents (Scheme 1a).⁷ These benzoylating reagents such as benzoyl chloride and benzoic anhydride are commonly susceptible to moisture. As a result, their storage and the process of the related *N*-benzoylation become complicated. Additionally, oxidative amidation of an aromatic

aldehyde or benzylic alcohol with amines, *N*-chloroamines, azobenzenes, or even nitro benzenes is a type of strategy recently developed (Scheme 1b).^{8,9} Recently, we reported a copper-catalyzed aerobic oxidative C–C bond cleavage of unstrained ketones with air and amines.¹⁰ In continuation of this work, we disclose herein a general approach for the *N*-benzoylation of amine via selective aerobic C–C bond cleavage of 1,2-diarylethan-1-one (Scheme 1c).

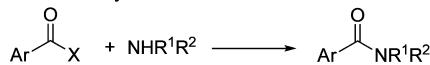
RESULTS AND DISCUSSION

Initially, we tried to carry out the reaction of 1,2-diphenylethan-1-one (**1a**) and aniline (**2a**) under the reaction conditions that we previously reported (Table 1, entries 1 and 2). The desired *N*-benzoylation product was only obtained in trace or moderate yield. In order to improve the yield, some adjustments to the reaction conditions were made. Gratifyingly, slightly switching the solvent from a mixed solvent (CH_3CN /dioxane) to a single solvent (acetonitrile) made a great improvement in the product yield (entry 8).

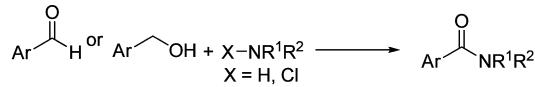
With the optimized conditions in hand, the substrate scope of amines was examined. The results are summarized in Scheme 2. Except for aniline with 2,4,6-trimethyl substitution that causes considerable steric hindrance, anilines with a mono-methyl substituent at the *ortho*-, *meta*-, or *para*-position all gave the desired amides in nearly quantitative yield (**3ab**–**3ae**). Notably, the transformation afforded the product with a methoxy substituent in moderate yield that may result from the instability of the electron-enriching aniline under the reaction conditions (**3af**). As for aniline with an electron-withdrawing group, 4-cyano aniline gave the corresponding amide (**3an**) in excellent yield, while no product was obtained when 4-nitro aniline was used. Substrates containing different

Scheme 1. Strategies for *N*-Benzoylation

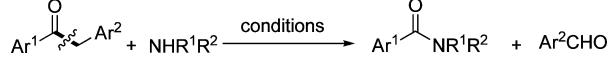
(a) Conventional *N*-benzoylation



(b) Oxidative amidation



(c) *This work*



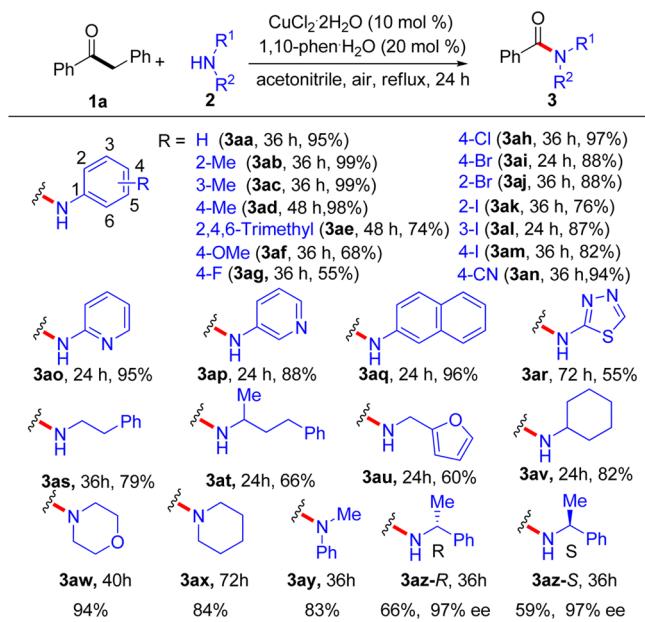
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Table 1. Optimization of Reaction Conditions^a

| entry | cat. (10 mol %) | ligand (mol %) | temp (°C) | solvent | yield | 1a | 2a | 3aa |
|-----------------|--|------------------------------------|--------------|-------------------------------|-------|------------------------------|--------------------|----------------|
| | | | | | | Ph-C(=O)-CH ₂ -Ph | Ph-NH ₂ | Ph-C(=O)-NH-Ph |
| 1 | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (20) | 40 | MeCN/ dioxane ^b | trace | | | |
| 2 | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (20) | 100 | MeCN/ dioxane ^b | 55 | | | |
| 3 | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (20) | 100 | DMA | 52 | | | |
| 4 | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (20) | 100 | DMSO | 29 | | | |
| 5 | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (20) | 100 | toluene | 74 | | | |
| 6 | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (20) | reflux | DCE | 61 | | | |
| 7 | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (20) | reflux | dioxane | 81 | | | |
| 8 | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (20) | reflux | MeCN | 95 | | | |
| 9 ^c | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (20) | reflux | MeCN | 37 | | | |
| 10 | none | 1,10-phen-H ₂ O (20) | reflux | MeCN | 0 | | | |
| 11 | CuCl ₂ · 2H ₂ O | none | reflux | MeCN | trace | | | |
| 12 | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (10) | reflux | MeCN | 24 | | | |
| 13 ^d | CuCl ₂ · 2H ₂ O | 1,10-phen-H ₂ O (20) | reflux | MeCN | 83 | | | |

^aReaction conditions: 1a (0.5 mmol), 2a (0.25 mmol), CuCl₂·2H₂O (10 mol %), 1,10-phenanthroline monohydrate (20 mol %), solvent (2.0 mL), 100 °C, 24 h, air (1 atm). ^bThe volume ratio of mixed solvents is 3:1. ^c1a (0.25 mmol) was used. ^dUnder an oxygen atmosphere.

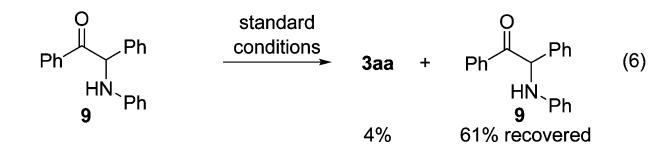
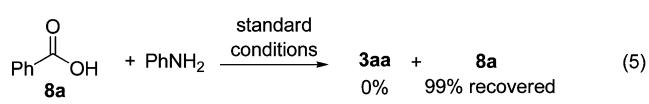
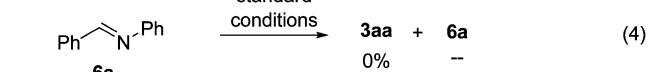
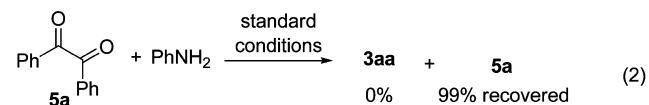
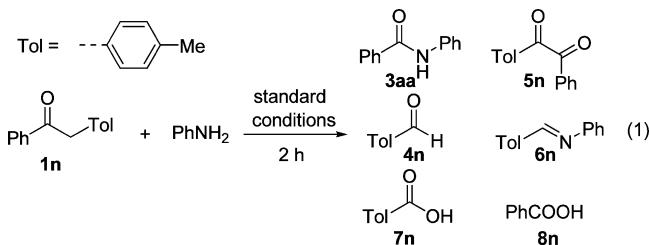
Scheme 2. Substrate Scope of Amine^a

^aReaction conditions: 1a (0.5 mmol), 2 (0.25 mmol), CuCl₂·2H₂O (10 mol %), 1,10-phenanthroline monohydrate (20 mol %), acetonitrile (2.0 mL), reflux, 24 h, air (1 atm).

halo groups were well-tolerated (3ah–3am), whereas 4-fluoroaniline afforded product 3ag in decreased yield. In particular, heterocyclic amines, such as pyridyl amines and 2-amino-1,3,4-thiadiazole or naphthyl amine, were smoothly transformed into the corresponding amides (3ao–3ar). As for alkyl primary and secondary amines, this transformation gave the desired N-benzoylation product in moderate to excellent yields (3as–3ay). In addition, enantiopure amines were also compatible, delivering an amide (3az-R and 3az-S) without deterioration in the enantiopurity, which enables its application in asymmetric synthesis.

Subsequently, the substrate scope of this transformation with respect to the ketones was investigated (Table 2). Different 1,2-diarylethan-1-ones were subjected to the standard conditions, giving rise to the corresponding amides in moderate to excellent yield. It is worth mentioning that, owing to the fact that an excessive amount of 1,2-diarylethan-1-one was used (2 equiv), and oxidative cleavage of 1,2-diarylethan-1-one via an enolate was an inevitable side reaction, this transformation commonly afforded aromatic aldehydes in higher yield than amides, even more than quantitative yield.^{10,11}

To gain insight into the reaction mechanism, control experiments were carried out. First, when ketone 1n was used as the substrate under the standard conditions for 2 h, many compounds could be detected in the reaction solution by GC-MS (eq 1). Second, the results of reaction eqs 2–5



indicated that these compounds were not the intermediates that led to the amide. Finally, compound 9 was discarded as an intermediate in the reaction (eq 6).

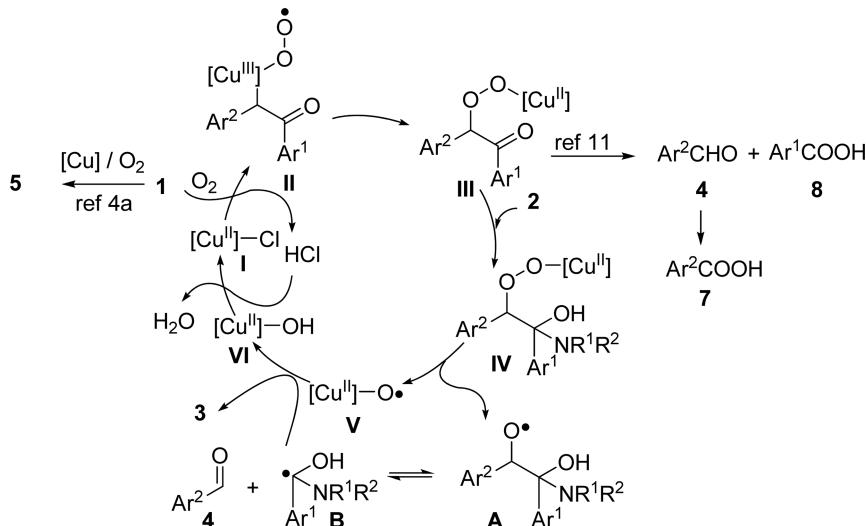
Based on these preliminary results, a plausible mechanism that is similar to our previous report is depicted in Scheme 3. Initially, copper complex I reacts with ketone 1 and dioxygen to give peroxide III via peroxy-copper(III) species II, followed by

Table 2. Substrate Scope of Ketone^a

| Entry | Ketone | Product ^b | | |
|-------|--------|----------------------|----------|-----------|
| | | Amide | Aldehyde | |
| 1 | | | | |
| 2 | | | | 89% |
| 3 | | | | 103% |
| 4 | | | | 67% |
| 5 | | | | 71% |
| 6 | | | | 70% |
| 7 | | | | 93% |
| 8 | | | | 96% |
| 9 | | | | 52% |
| 10 | | | | 99% |
| 11 | | | | 102% |
| 12 | | | | 49%, 105% |

^aReaction conditions: **1** (0.5 mmol), **2a** (0.25 mmol), CuCl₂·2H₂O (10 mol %), 1,10-phenanthroline monohydrate (20 mol %), acetonitrile (2.0 mL), reflux, 24 h, air (1 atm). ^bGC-yield for aldehyde.

Scheme 3. A Plausible Mechanism



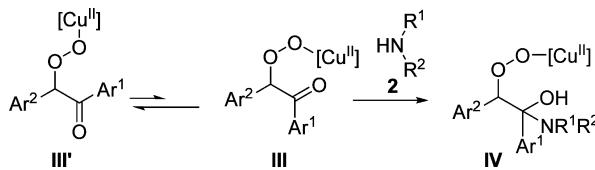
the formation of intermediate **IV** through the nucleophilic attack of amine **2** to species **III**. Radical **A** that formed by the homolytic O–O bond cleavage of intermediate **IV** undergoes β -fragmentation to afford radical species **B** and aromatic aldehyde **4**. Intermediate **B** would be further in turn oxidized by species **V** to furnish the desired amide **3** and liberate [Cu(II)–OH] species **VI**, which gives rise to the active catalyst with the aid of hydrochloride to initiate a new catalytic cycle. Two undesirable side reactions inevitably take place in the reaction

system: (1) ketone **1** could be oxidized to diketone **5**; (2) species **III** could be alternatively transformed into aldehydye **4** and acid **8**, which explains why an excessive amount of ketone must be used to ensure the high yield of the amide, as well as why this transformation commonly afforded aromatic aldehydes in higher yield than amides. Aldehydye **4** could also be further oxidized to acid **7** under standard conditions that supports the formation of **7n** when ketone **1n** was employed as the substrate. Moreover, in a proposed mechanism, the nucleo-

philicity of an aniline would affect the formation of intermediate **IV** that is consistent with the result when 4-nitro aniline was used.

When the reaction was carried out at 40 °C, only a trace of amide was detected (**Table 1**, entry 1). While the reaction was carried out under reflux (**Table 1**, entry 2), a moderate yield of amide was obtained, which is in accord with the result we previously reported when benzyl alkylketones were used. We deem that the reaction tends to take place when intermediate **III** is in a specific conformation as shown in **Scheme 4**. In this

Scheme 4. Preferred Conformation for the Reaction



conformation, copper(II) could activate the carbonyl group and facilitate the nucleophilic attack of amine **2**. For the cycloketone, this conformation is readily reached. So, the reaction occurs at a lower temperature (40 °C). However, for an open-chain ketone, this conformation is unfavorable from the aspect of energy. Thus, a higher reaction temperature (reflux) is needed for the intermediate to obtain this conformation.

In conclusion, we have developed a copper/air catalytic system for the efficient and selective oxidative C–C bond cleavage of 1,2-diarylethan-1-one derivatives with amines. This research provides an alternative approach for the *N*-benzoylation of amines in mild and neutral conditions.

EXPERIMENT SECTION

General Remarks. ¹H NMR spectra were recorded on a 400 or 500 MHz NMR spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in CDCl₃ or DMSO-d₆ as an internal standard. ¹³C NMR spectra were obtained by using the same NMR spectrometers and calibrated with CDCl₃ (δ = 77.00 ppm) or DMSO-d₆ (δ = 39.60 ppm). Mass spectra were recorded using a GC-MS and Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Enantiomeric excesses (ee) of the products of enantiopure amines were determined using an HPLC with an AD-H column (25 cm in length × 0.46 cm in internal diameter). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Typical Procedure. To a tube equipped with a condenser were added ketone **1** (0.5 mmol), amine **2** (0.25 mmol), CuCl₂·2H₂O (4.3 mg, 0.025 mmol, 10 mol %), 1,10-phenanthroline monohydrate (9.9 mg, 0.05 mmol, 20 mol %), and acetonitrile (2.0 mL). The mixture was stirred under reflux in an air atmosphere and monitored by TLC. The reaction mixture was cooled down to room temperature (the yield of aldehyde **4** was determined by GC using *n*-dodecane as the internal standard at this stage), dried under vacuum and purified by column chromatography on silica gel (petroleum ether/acetone = 8:1) to obtain the desired products **3**.

N-Phenylbenzamide (3aa).¹² The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), aniline (**2a**, 0.25 mmol, 23 mg, 22 μ L), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the typical procedure, afforded 94 mg (95%) of **3aa** as a solid; mp: 160–161 °C; ¹H NMR (DMSO-d₆, 400 MHz): δ = 10.22 (s, 1H), 7.95 (d, J = 7.4 Hz, 2H), 7.78 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H); ¹³C NMR (DMSO-d₆, 100 MHz): δ = 165.6, 139.2, 135.0,

131.5, 128.6, 128.4, 127.6, 123.7, 120.4 ppm; MS (70 eV): *m/z* (%) 197 (M⁺, 30), 105 (100).

N-o-Tolylbenzamide (3ab).¹³ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 2-methylaniline (**2b**, 0.25 mmol, 27 mg, 27 μ L), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the typical procedure, afforded 105 mg (99%) of **3ab** as a solid; mp: 136–137 °C; ¹H NMR (DMSO-d₆, 400 MHz): δ = 9.87 (s, 1H), 7.98 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 7.2 Hz, 2H), 7.34 (d, J = 7.9 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.24–7.14 (m, 2H), 2.24 (s, 3H); ¹³C NMR (DMSO-d₆, 125 MHz): δ = 165.4, 136.5, 134.6, 133.8, 131.6, 130.4, 128.5, 127.7, 126.7, 126.1, 18.0 ppm; MS (70 eV): *m/z* (%) 211 (M⁺, 30), 105 (100).

N-m-Tolylbenzamide (3ac).¹⁴ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 3-methylaniline (**2c**, 0.25 mmol, 27 mg, 27 μ L), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the typical procedure, afforded 105 mg (99%) of **3ac** as a solid; mp: 124–125 °C; ¹H NMR (DMSO-d₆, 400 MHz): δ = 10.15 (s, 1H), 7.95 (d, J = 7.2 Hz, 2H), 7.65–7.49 (m, 5H), 7.23 (t, J = 7.7 Hz, 1H), 6.92 (d, J = 7.7 Hz, 1H), 2.31 (s, 3H); ¹³C NMR (DMSO-d₆, 100 MHz): δ = 165.5, 139.1, 137.8, 135.1, 131.5, 128.43, 128.37, 127.6, 124.4, 121.0, 117.6, 21.2 ppm; MS (70 eV): *m/z* (%) 211 (M⁺, 30), 105 (100).

N-p-Tolylbenzamide (3ad).¹³ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 4-methylaniline (**2d**, 0.25 mmol, 27 mg, 27 μ L), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 48 h using the typical procedure, afforded 103 mg (98%) of **3ad** as a solid; mp: 155–156 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.90–7.70 (m, 3H), 7.60–7.43 (m, 5H), 7.21–7.14 (m, 2H), 2.34 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 165.7, 135.3, 135.0, 134.2, 131.7, 129.5, 128.7, 127.0, 120.3, 118.0, 20.9 ppm; MS (70 eV): *m/z* (%) 211 (M⁺, 30), 105 (100).

N-Mesitylbenzamide (3ae).¹⁵ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 2,4,6-trimethylaniline (**2e**, 0.25 mmol, 34 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 48 h using the typical procedure, afforded 89 mg (79%) of **3ae** as a solid; mp: 205–206 °C; ¹H NMR (DMSO-d₆, 400 MHz): δ = 9.68 (s, 1H), 7.99 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.3 Hz, 2H), 6.93 (s, 2H), 2.25 (s, 3H), 2.13 (s, 6H); ¹³C NMR (DMSO-d₆, 100 MHz): δ = 165.1, 135.7, 135.4, 134.6, 132.8, 131.4, 128.5, 128.4, 127.6, 20.6, 18.0 ppm; MS (70 eV): *m/z* (%) 239 (M⁺, 30), 105 (100).

N-(4-Methoxyphenyl)benzamide (3af).¹³ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 4-methoxyaniline (**2f**, 0.25 mmol, 31 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 48 h using the typical procedure, afforded 89 mg (79%) of **3af** as a solid; mp: 145–146 °C; ¹H NMR (DMSO-d₆, 400 MHz): δ = 10.12 (s, 1H), 7.94 (d, J = 7.3 Hz, 2H), 7.67 (d, J = 9.0 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.3 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 3.75 (s, 3H); ¹³C NMR (DMSO-d₆, 125 MHz): δ = 165.5, 155.9, 135.2, 132.4, 131.7, 128.6, 127.8, 122.4, 114.0, 55.4 ppm; MS (70 eV): *m/z* (%) 227 (M⁺, 30), 105 (100).

N-(4-Fluorophenyl)benzamide (3ag).¹⁶ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 4-fluoroaniline (**2g**, 0.25 mmol, 28 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the typical procedure, afforded 59 mg (55%) of **3ag** as a solid; mp: 140–141 °C; ¹H NMR (DMSO-d₆, 400 MHz): δ = 10.30 (s, 1H), 7.95 (d, J = 7.2 Hz, 2H), 7.82–7.76 (m, 2H), 7.63–7.50 (m, 3H), 7.23–7.16 (m, 2H); ¹³C NMR (DMSO-d₆, 125 MHz): δ = 165.6, 158.4 (d, J_{C-F} = 238.4 Hz), 135.6 (d, J_{C-F} = 2.1 Hz), 134.9, 131.7, 128.5, 127.7, 122.3 (d, J_{C-F} = 7.1 Hz), 115.3 (d, J_{C-F} = 21.6 Hz) ppm; MS (70 eV): *m/z* (%) 215 (M⁺, 40), 123 (100).

N-(4-Chlorophenyl)benzamide (3ah).¹³ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 4-chloroaniline (**2h**, 0.25 mmol, 32 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile

(2.0 mL) for 36 h using the **typical procedure**, afforded 113 mg (97%) of **3ah** as a solid; mp: 208–209 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.37 (s, 1H), 7.95 (d, *J* = 7.36 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ = 165.8, 138.3, 134.8, 131.8, 128.6, 128.5, 127.8, 127.4, 121.9 ppm; MS (70 eV): *m/z* (%) 231 (M⁺, 35Cl, 40), 233 (M⁺, ³⁷Cl, 36), 105 (100).

N-(4-Bromophenyl)benzamide (3ai).¹⁴ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 4-bromoaniline (**2i**, 0.25 mmol, 43 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.05 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 24 h using the **typical procedure**, afforded 122 mg (88%) of **3ai** as a solid; mp: 208–209 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.37 (s, 1H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.63–7.50 (m, 5H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 165.7, 138.7, 134.8, 131.8, 131.5, 128.5, 127.8, 122.3, 115.4 ppm; MS (70 eV): *m/z* (%) 275 (M⁺, ⁷⁸Br, 40), 277 (M⁺, ⁸⁰Br, 36), 105 (100).

N-(2-Bromophenyl)benzamide (3aj).¹⁵ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 2-bromoaniline (**2j**, 0.25 mmol, 43 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.05 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the **typical procedure**, afforded 121 mg (88%) of **3aj** as a solid; mp: 96–97 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.04 (s, 1H), 7.99 (d, *J* = 6.4 Hz, 2H), 7.72 (d, *J* = 7.0 Hz, 1H), 7.63–7.51 (m, 4H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.23 (t, *J* = 7.0 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 165.7, 138.7, 134.8, 131.8, 131.5, 128.5, 127.8, 122.3, 115.4 ppm; MS (70 eV); *m/z* (%) 275 (M⁺, ⁷⁸Br, 40), 277 (M⁺, ⁸⁰Br, 36), 105 (100).

N-(2-Iodophenyl)benzamide (3ak).¹⁸ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 2-iodoaniline (**2k**, 0.25 mmol, 55 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the **typical procedure**, afforded 123 mg (76%) of **3ak** as a solid; mp: 139–140 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.03 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.65–7.42 (m, 5H), 7.10–7.04 (m, 1H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ = 165.3, 149.9, 138.9, 134.3, 131.9, 128.9, 128.6, 128.3, 127.7, 98.8 ppm; MS (70 eV): *m/z* (%) 323 (M⁺, 30), 105 (100).

N-(3-Iodophenyl)benzamide (3al).¹⁹ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 3-iodoaniline (**2l**, 0.25 mmol, 55 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 24 h using the **typical procedure**, afforded 140 mg (87%) of **3al** as a solid; mp: 163–164 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.31 (s, 1H), 8.26 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.64–7.42 (m, 4H), 7.16 (t, *J* = 7.7 Hz, 1H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 165.8, 140.7, 134.7, 132.2, 131.8, 130.7, 128.52, 128.50, 127.8, 119.6, 94.5 ppm; MS (70 eV): *m/z* (%) 323 (M⁺, 30), 105 (100).

N-(4-Iodophenyl)benzamide (3am).²⁰ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 4-iodoaniline (**2m**, 0.25 mmol, 55 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the **typical procedure**, afforded 132 mg (82%) of **3am** as a solid; mp: 228–229 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.35 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.71–7.50 (m, 7H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 165.7, 139.2, 137.4, 134.8, 131.8, 128.5, 127.8, 122.6, 87.4 ppm; MS (70 eV): *m/z* (%) 323 (M⁺, 30), 105 (100).

N-(4-Cyanophenyl)benzamide (3an).²¹ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 4-aminobenzonitrile (**2n**, 0.25 mmol, 30 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the **typical procedure**, afforded 104 mg (94%) of **3an** as a solid; mp: 150–151 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.64 (s, 1H), 8.02–7.93 (m, 4H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.66–7.50 (m, 3H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ = 166.3, 143.6, 134.5, 133.2, 132.1, 128.6, 128.0, 120.3, 119.2, 105.5 ppm; MS (70 eV): *m/z* (%) 323 (M⁺, 30), 105 (100).

N-(Pyridin-2-yl)benzamide (3ao).²² The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 2-aminopyridine (**2o**, 0.25 mmol, 24 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 24 h using the **typical procedure**, afforded 94 mg (95%) of **3ao** as a solid; mp: 89–90 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 8.72 (s, 1H), 8.41 (d, *J* = 7.0 Hz, 1H), 8.28 (s, 1H), 7.94 (d, *J* = 7.4 Hz, 2H), 7.77 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ = 165.9, 151.6, 147.7, 138.5, 134.3, 132.2, 128.8, 127.3, 119.9, 114.3 ppm; MS (70 eV): *m/z* (%) 198 (M⁺, 35), 105 (100).

N-(Pyridin-3-yl)benzamide (3ap).²² The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 3-aminopyridine (**2p**, 0.25 mmol, 24 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 24 h using the **typical procedure**, afforded 87 mg (88%) of **3ap** as a solid; mp: 116–117 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.46 (s, 1H), 8.93 (s, 1H), 8.34–8.29 (m, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 6.8 Hz, 2H), 7.65–7.52 (m, 3H), 7.43–7.36 (m, 1H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 166.0, 144.6, 142.1, 135.9, 134.5, 131.9, 128.5, 127.8, 127.4, 123.6 ppm; MS (70 eV): *m/z* (%) 198 (M⁺, 35), 105 (M⁺).

N-(Naphthalen-2-yl)benzamide (3aq).²³ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), β-aminonaphthalene (**2q**, 0.25 mmol, 36 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 24 h using the **typical procedure**, afforded 119 mg (97%) of **3aq** as a solid; mp: 160–161 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.45 (s, 1H), 8.47 (s, 1H), 8.04–7.98 (m, 2H), 7.93–7.81 (m, 4H), 7.65–7.40 (m, 5H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 165.9, 136.9, 135.0, 133.4, 131.6, 130.1, 128.5, 128.2, 127.8, 127.5, 127.4, 126.4, 124.8, 121.1, 116.7 ppm; MS (70 eV): *m/z* (%) 247 (M⁺, 35), 105 (100).

N-(1,3,4-Thiadiazol-2-yl)benzamide (3ar).²⁴ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 2-amino-1,3,4-thiadiazole (**2r**, 0.25 mmol, 25 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 72 h using the **typical procedure**, afforded 56 mg (57%) of **3ar** as a solid; mp: 210–211 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 13.07 (s, 1H), 9.24 (s, 1H), 8.12 (d, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ = 165.4, 159.6, 149.1, 133.1, 131.7, 128.8, 128.5 ppm; MS (70 eV): *m/z* (%) 205 (M⁺, 30), 105 (100).

N-Phenethylbenzamide (3as).²⁵ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 2-phenylethanamine (**2s**, 0.25 mmol, 30 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the **typical procedure**, afforded 89 mg (79%) of **3as** as a solid; mp: 110–111 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 77.72–7.66 (m, 2H), 7.52–7.30 (m, 5H), 7.27–7.22 (m, 3H), 6.14 (bs, 1H), 3.78–3.68 (m, 2H), 2.98–2.91 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 167.5, 138.9, 134.7, 131.2, 128.7, 128.6, 128.4, 126.8, 126.5, 41.1, 35.6 ppm; MS (70 eV): *m/z* (%) 225 (M⁺, 40), 105 (100).

N-(4-Phenylbutan-2-yl)benzamide (3at).²⁶ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), 1-methyl-3-phenylpropyl amine (**2t**, 0.25 mmol, 37 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the **typical procedure**, afforded 84 mg (66%) of **3at** as a solid; mp: 110–111 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 8.27–8.21 (m, 1H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.30–7.13 (m, 5H), 4.10–3.95 (m, 1H), 2.68–2.54 (m, 2H), 1.92–1.68 (m, 2H), 1.19–1.13 (m, 3H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ = 165.9, 142.1, 135.1, 131.0, 128.4, 128.34, 128.26, 127.4, 125.7, 44.7, 37.9, 32.2, 20.9 ppm; MS (70 eV): *m/z* (%) 253 (M⁺, 40), 105 (100).

N-((Furan-2-yl)methyl)benzamide (3au).²⁷ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), furfurylamine (**2u**, 0.25 mmol, 24 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 24 h using the **typical procedure**, afforded 60 mg (60%)

of **3au** as a solid; mp: 100–101 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 9.0–8.93 (m, 1H), 7.90–7.84 (m, 2H), 7.60–7.42 (m, 4H), 6.42–6.37 (m, 1H), 6.30–6.25 (m, 1H), 4.47 (d, *J* = 5.6 Hz, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ = 166.2, 152.5, 142.1, 134.2, 131.4, 128.4, 127.4, 110.6, 106.9, 36.1 ppm; MS (70 eV): *m/z* (%) 201 (M⁺, 40), 105 (100).

N-Cyclohexylbenzamide (3av).²⁵ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), cyclohexylamine (**2v**, 0.25 mmol, 24 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 24 h using the typical procedure, afforded 83 mg (82%) of **3av** as a solid; mp: 153–154 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 8.21–8.14 (m, 1H), 7.83 (d, *J* = 7.1 Hz, 2H), 7.50 (t, *J* = 7.1 Hz, 1H), 7.44 (t, *J* = 7.1 Hz, 2H), 3.81–3.69 (m, 1H), 1.85–1.69 (m, 4H), 1.65–1.56 (m, 1H), 1.38–1.22 (m, 4H), 1.18–1.07 (m, 1H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 165.5, 135.0, 131.0, 128.2, 127.4, 48.4, 32.5, 25.4, 25.1 ppm; MS (70 eV): *m/z* (%) 203 (M⁺, 30), 105 (100).

Morpholino(phenyl)methanone (3aw).²⁶ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), morpholine (**2w**, 0.25 mmol, 21.8 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 40 h using the typical procedure, afforded 90 mg (94%) of **3aw** as a solid; mp: 70–71 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 7.50–7.36 (m, 5H), 3.75–3.48 (m, 8H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ = 169.2, 135.7, 129.7, 128.5, 127.1, 66.2, 47.8, 42.1 ppm; MS (70 eV): *m/z* (%) 191 (M⁺, 35), 105 (100).

Phenyl(piperidin-1-yl)methanone (3ax).²⁸ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), piperidine (**2x**, 0.25 mmol, 21 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.05 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 40 h using the typical procedure, afforded 79 mg (84%) of **3ax** as an oil; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 7.46–7.41 (m, 3H), 7.37–7.32 (m, 2H), 3.62–3.52 (m, 1H), 3.29–3.20 (m, 1H), 1.64–1.58 (m, 3H), 1.55–1.40 (m, 5H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 168.9, 136.6, 129.3, 128.5, 126.6, 48.0, 42.3, 26.0, 25.4, 24.1 ppm; MS (70 eV): *m/z* (%) 188 (M⁺, 30), 105 (100).

N-Methyl-N-phenylbenzamide (3ay).²⁹ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), *N*-methylaniline (**2y**, 0.25 mmol, 27 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 40 h using the typical procedure, afforded 88 mg (83%) of **3ay** as a solid; mp: 60–61 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 7.30–7.10 (m, 10H), 3.37 (s, 3H); ¹³C NMR (DMSO-*d*₆, 125 MHz): δ = 169.6, 144.6, 136.4, 129.4, 129.1, 128.3, 127.8, 127.1, 126.5, 37.9 ppm; MS (70 eV): *m/z* (%) 211 (M⁺, 30), 105 (100).

N-((R)-1-Phenylethyl)benzamide (3az-R).²⁹ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), (R)-1-phenylethylamine (**2z-R**, 0.25 mmol, 30 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 40 h using the typical procedure, afforded 74 mg (66%) of **3az-R** as a solid; mp: 118–119 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 8.79 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 5.22–5.12 (m, 1H), 1.48 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 165.7, 145.0, 134.7, 131.2, 128.32, 128.30, 127.5, 126.7, 126.2, 48.5, 22.3 ppm; MS (70 eV): *m/z* (%) 225 (M⁺, 40), 105 (100).

N-((S)-1-Phenylethyl)benzamide (3az-S).³⁰ The reaction of 1,2-diphenylethan-1-one (**1a**, 0.50 mmol, 98 mg), (S)-1-phenylethylamine (**2z-S**, 0.25 mmol, 30 mg), CuCl₂·2H₂O (0.025 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.0 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 40 h using the typical procedure, afforded 66 mg (59%) of **3az-S** as a solid; mp: 124–125 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 8.79 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.55–7.50 (m, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 6.93 Hz, 2H), 7.32 (t, *J* = 6.9 Hz, 2H), 7.22 (t, *J* = 6.9 Hz, 1H), 5.22–5.12 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 165.7, 145.1, 134.7, 131.2, 128.32, 128.30, 127.5, 126.7, 126.2, 48.5, 22.3 ppm; MS (70 eV): *m/z* (%) 225 (M⁺, 40), 105 (100).

4-Fluoro-N-phenylbenzamide (3ea).³¹ The reaction of 1-(4-fluorophenyl)-2-phenylethanone (**1e**, 0.50 mmol, 107 mg), aniline (**2a**, 0.25 mmol, 23 mg, 22 μL), CuCl₂·2H₂O (0.25 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the typical procedure, afforded 36 mg (67%) of **3ea** as a solid; mp: 185–186 °C; ¹H NMR (DMSO-*d*₆, 400 MHz): δ = 10.26 (bs, 1H), 8.06–8.01 (m, 2H), 7.80–7.72 (m, 2H), 7.40–7.32 (m, 4H), 7.15–7.07 (m, 1H) ppm; ¹³C NMR (DMSO-*d*₆, 100 MHz): δ = 164.6, 164.2 (d, *J*_{C-F} = 248 Hz), 139.2, 131.5, 130.5 (d, *J*_{C-F} = 9.0 Hz), 128.7, 123.8, 120.5, 115.4 (d, *J*_{C-F} = 22.0 Hz) ppm; MS (70 eV): *m/z* (%) 215 (M⁺, 30), 123 (100).

N-Phenyl-4-(trifluoromethyl)benzamide (3fa).³² The reaction of 2-phenyl-1-(4-(trifluoromethyl)phenyl)ethanone (**1f**, 0.50 mmol, 132 mg), aniline (**2a**, 0.25 mmol, 23 mg, 22 μL), CuCl₂·2H₂O (0.25 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the typical procedure, afforded 47 mg (71%) of **3ea** as a solid; mp: 189–190 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.92 (d, *J* = 8.0 Hz, 2H), 7.82 (bs, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.17 (t, *J* = 7.9 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ = 164.5, 151.7 (d, *J*_{C-F} = 1.8 Hz), 137.6, 133.4, 129.2, 129.0, 124.9, 120.8, 120.3, 119.1 ppm; MS (70 eV): *m/z* (%) 265 (M⁺, 30), 105 (100).

N-Phenyl-4-(trifluoromethoxy)benzamide (3ga).³² The reaction of 2-phenyl-1-(4-(trifluoromethoxy)phenyl)ethanone (**1g**, 0.50 mmol, 140 mg), aniline (**2a**, 0.25 mmol, 23 mg, 22 μL), CuCl₂·2H₂O (0.25 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the typical procedure, afforded 49 mg (70%) of **3ga** as a solid; mp: 179–180 °C; ¹H NMR (CDCl₃, 400 MHz, 400 MHz): δ = 7.92 (d, *J* = 8.2 Hz, 2H), 7.82 (bs, 1H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.7 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ = 164.5, 151.7, 137.6, 133.4, 129.2, 129.0, 124.9, 120.8, 120.3, 110.0 ppm; MS (70 eV): *m/z* (%) 281 (M⁺, 30), 189 (100).

4-Methoxy-N-phenylbenzamide (3ha).³³ The reaction of 1-(4-methoxyphenyl)-2-phenylethanone (**1h**, 0.50 mmol, 113 mg), aniline (**2a**, 0.25 mmol, 23 mg, 22 μL), CuCl₂·2H₂O (0.25 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.05 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the typical procedure, afforded 53 mg (93%) of **3ha** as a solid; mp: 177–178 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.84 (d, *J* = 8.4 Hz, 2H), 7.80 (bs, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 2H), 3.87 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 162.5, 138.1, 129.0, 128.9, 124.3, 120.2, 114.0, 99.4, 55.4 ppm; MS (70 eV): *m/z* (%) 227 (M⁺, 20), 135 (100).

4-Bromo-N-phenylbenzamide (3ja).³⁴ The reaction of 1-(4-bromophenyl)-2-phenylethanone (**1j**, 0.50 mmol, 138 mg), aniline (**2a**, 0.25 mmol, 23 mg, 22 μL), CuCl₂·2H₂O (0.25 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the typical procedure, afforded 36 mg (52%) of **3ja** as a solid; mp: 190–191 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.86–7.80 (m, 1H), 7.78–7.71 (m, 3H), 7.65–7.58 (m, 3H), 7.42–7.32 (m, 2H), 7.20–7.12 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ = 164.7, 137.7, 133.9, 132.1, 129.2, 128.6, 126.6, 124.8, 120.3 ppm; MS (70 eV): *m/z* (%) 275 (M⁺, ⁷⁸Br, 35), 277 (M⁺, ⁸⁰Br, 33), 183 (100).

4-Methyl-N-phenylbenzamide (3ka).³⁵ The reaction of 2-phenyl-1-(*p*-tolyl)ethanone (**1k**, 0.50 mmol, 106 mg), aniline (**2a**, 0.25 mmol, 23 mg, 22 μL), CuCl₂·2H₂O (0.25 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile (2.0 mL) for 36 h using the typical procedure, afforded 52 mg (99%) of **3ka** as a solid; mp: 144–145 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.82–7.72 (m, 3H), 7.66–7.60 (m, 2H), 7.40–7.32 (m, 2H), 7.31–7.26 (m, 2H), 7.17–7.10 (m, 1H), 2.42 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 165.8, 142.3, 138.1, 132.1, 129.4, 129.0, 127.0, 124.4, 120.2, 21.4 ppm; MS (70 eV): *m/z* (%) 211 (M⁺, 30), 119 (100).

N-Phenyl-2-naphthamide (3la).³⁴ The reaction of 1-(naphthalen-2-yl)-2-phenylethanone (**1l**, 0.50 mmol, 123 mg), aniline (**2a**, 0.25 mmol, 23 mg, 22 μL), CuCl₂·2H₂O (0.25 mmol, 4.3 mg), and 1,10-phenanthroline monohydrate (0.050 mmol, 9.9 mg), in acetonitrile

(2.0 mL) for 36 h using the typical procedure, afforded 44 mg (71%) of 3la as a solid; mp: 168–169 °C; ^1H NMR (CDCl_3 , 400 MHz): δ = 8.38 (bs, 1H), 8.01–7.87 (m, 5H), 7.70 (d, J = 7.5 Hz, 2H), 7.63–7.54 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.18 (t, J = 7.5 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ = 165.8, 138.0, 134.8, 132.6, 132.2, 129.1, 128.9, 128.7, 127.9, 127.8, 127.5, 126.9, 124.6, 123.5, 120.3 ppm; MS (70 eV): m/z (%) 247 (M^+ , 30), 105 (100).

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.joc.5b01670](https://doi.org/10.1021/acs.joc.5b01670).

^1H NMR and ^{13}C NMR spectra for products and HPLC charts for enantiopure amides ([PDF](#))

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Notes

The authors declare no competing financial interest.

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