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Copper(I)-Catalyzed N-O Bond Formation through Vinyl Nitrene-Mediated Pathway under Mild Conditions

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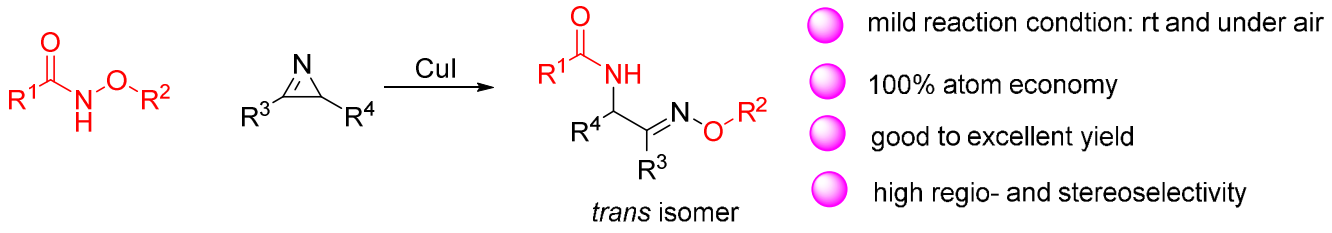
ABSTRACT: Copper(I)-catalyzed N-O bond formation reactions through vinyl nitrene-mediated pathway were described. The reactions of *N*-alkoxylbenzamides and 2*H*-azirines afforded *α*-amino oxime ethers in good to excellent yields at room temperature, which involved the cleavage of C-N and N-O bonds, and the construction of new N-O and C-N bonds. It offers an efficient, regio- and stereoselective synthetic route for *α*-amino oxime ethers.



INTRODUCTION

Nitrogen-oxygen single bonds have been found in many biologically active compounds.[1] They exist in both aromatic *N*-heterocycles such as isoxazoles, benzisoxazoles, furazans, 1,2-azines, 1,2-oxazines, and nonaromatic chain compounds like *N*-hydroxylamine, oximes, and *N*-oxides. These compounds show promising biological activities, such as antifungal, anti-inflammatory and analgesic, as well as anti-histamine effects.[2] For example, Orysastrobin is used to control the leaf and panicle blast (*Magnaporthe grisea*) and sheath blight (*Thanatephorus cucumeris*) in rice.[3] SCH 206272 is a potent and orally active tachykinin NK1, NK2, and NK3 receptor antagonist (Figure 1).[4]

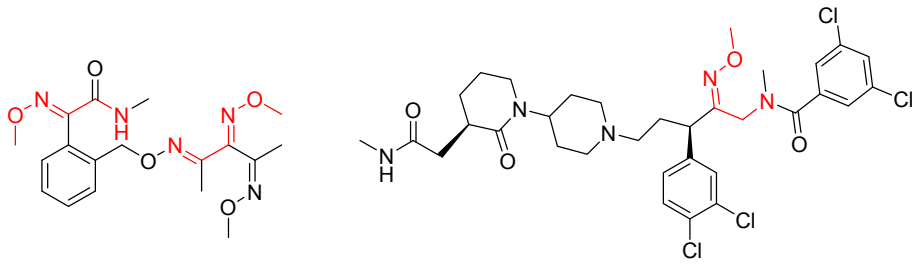


Figure 1. Representative examples of α-amino oxime ethers.

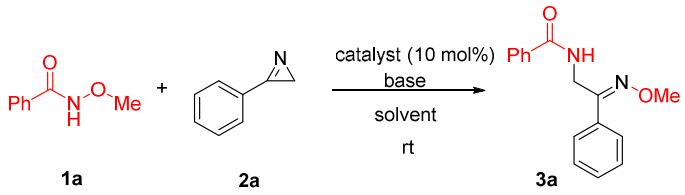
Typically, the N-O moieties are constructed from the derivation of the starting materials with pre-existing N-O bonds such as hydroxylamines and nitro compounds. Although amine *N*-oxides and pyridine *N*-oxides are easily accessible through direct oxidation with peroxides,[5] metal-catalyzed direct N-O coupling has been scarcely studied. Usually, the known N-O bond formation approaches involve oxidative N-O coupling. Oxidation of β-aminoketones by $PhI(OAc)_2$ could afford isoxazolo[3,4-d]primidine-4,6-dione derivatives due to N-O bond formation.[6] Cu-catalyzed oxidative N-O bond formation between amides and organic nitriles led to 1,2,4-oxadiazoles using O_2 as the oxidant.[7] $FeBr_2$ catalyzed reaction of aryl and vinyl azides with ketone resulted in 2,1-benzisoxazoles.[8] It was believed that azide was activated via coordination of the terminal N-atom to iron(II), then the activated azide was attacked by O-atom of ketone, and finally N_2 lost. Reactions of *ortho*-hydroxyaryl N–H ketimines with NCS or NaClO yielded 2- and 3-substituted

benzisoxazoles through N–Cl imine intermediate.[9] Reactions of aldehydes or ketones with $TMSN_3$ in the presence of $ZrCl_4$ or TfOH afforded benzisoxazoles after nitrogen extrusion via an intramolecular nucleophilic substitution of azido methanolate complex or imine diazonium ion.[10] The above described synthetic approaches are restricted to synthesize heterocyclic compounds containing N-O bonds. The construction of N-O bonds in chain compounds has seldom been studied.

Transition metal catalyzed reactions of 2*H*-azirines[11] have been used to synthesize indoles,[12] amides,[13] oxime ethers,[14] and 1,2,3-triazole derivatives[15]. These transformations usually involve nitrene intermediate. We envisioned that *N*-alkoxyl benzamide containing a fissionable N-O bond would react with vinyl nitrene to form a new N-O bond.[16] Herein we describe copper(I)-catalyzed difunctionalization of 2*H*-azirines offering *α*-amino oxime ethers through vinyl nitrene-mediated pathway under mild conditions in good to excellent yields.[17]

RESULTS AND DISCUSSION

Table 1. Optimization of Reaction Conditions[a]



1a 2a 3a

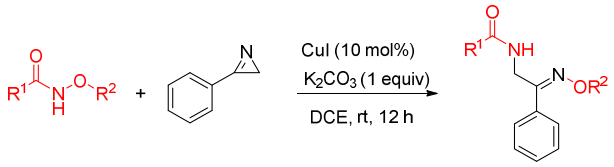
Entry	Catalyst (10 mol%)	Base (1 equiv.)	Solvent	Yield[b] (%)
1	$Pd(OAc)_2$	-	DCE	84
2	$Pd(OAc)_2$	K_2CO_3	DCE	99
3	$\{Cp^*RhCl_2\}_2$	K_2CO_3	DCE	75
4	$Pd(OAc)_2$	K_2CO_3	methanol	0
5	$MnBr(CO)_5$	K_2CO_3	DCE	54
6	CuI	K_2CO_3	DCE	99(97)
7	-	K_2CO_3	DCE	0
8[c]	CuI	K_2CO_3	DCE	93
9[d]	CuI	K_2CO_3	DCE	89
10	$Cu(OAc)_2$	K_2CO_3	DCE	87
11	$CuCl_2$	K_2CO_3	DCE	92
12	$Cu(OTf)_2$	K_2CO_3	DCE	68
13	CuI	K_2CO_3	DMF	7
14	CuI	K_2CO_3	Toluene	75

[a] Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), catalyst (0.02 mmol), base (0.2 mmol) in 2 mL of solvent at room temperature for 12 h; [b] Yields determined by ^1H NMR analysis using CH_2Br_2 as the internal standard and isolated yields shown in parentheses; [c] CuI (5 % mmol); [d] CuI (2 % mmol).

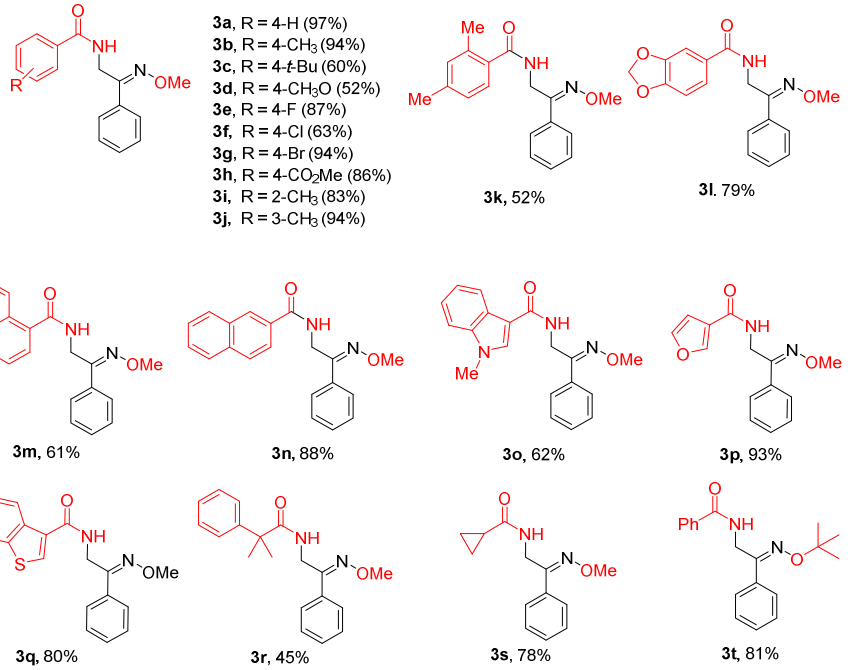
Initially, we started our work by taking *N*-methoxylbenzamide **1a** and 3-phenyl-2*H*-azirine **2a** as the model substrates using $Pd(OAc)_2$ catalyst to optimize the reaction conditions. The optimization results were shown in Table 1. At a loading of 10 mol% of the palladium catalyst, we were pleased to find that α-amino oxime ether **3a** was obtained in 84% yield in DCE at room temperature based on ^1H NMR analysis (Table 1, entry 1). Addition of K_2CO_3 could further promote the reaction, and **3a** could be almost quantitatively obtained (Table 1, entry 2). $\{Cp^*RhCl_2\}_2$ was also active, and **3a** was afforded in 75% yield under the same conditions (Table 1, entry 3). When protonic solvent methanol was used, the reaction was totally inhibited (Table 1,

entry 4). $MnBr(CO)_5$ could also catalyse the reaction, and **3a** was obtained in a moderate yield (Table 1, entry 5). To our surprise, the cheap copper(I) salt was quite efficient to give **3a** in a quantitative yield (Table 1, entry 6). Without metal catalysts the reaction did not proceed (Table 1, entry 7). When 2-5 mol% of CuI was used, the yield of **3** was slightly decreased (Table 1, entries 8 and 9). Other copper catalysts such as $Cu(OAc)_2$, $CuCl_2$, and $Cu(OTf)_2$ are less efficient than CuI (Table 1, entries 10-12). The ^1H NMR spectral analysis showed that in solution only the *anti* isomer was formed. The structures of **3a** and **3b** were further identified by X-ray crystallography, which were presented in Figure S1 in the Supporting Information.

Table 2. Scope of 2*H*-azirines[a,b]



1a **2a** **3a**

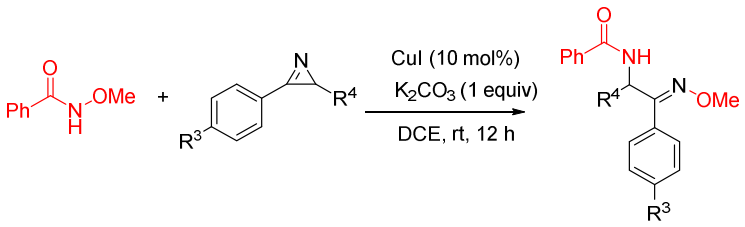


[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), CuI (0.02 mmol), K_2CO_3 (0.2 mmol) in 2 mL of DCE at room temperature for 12 h. [b] Isolated yields.

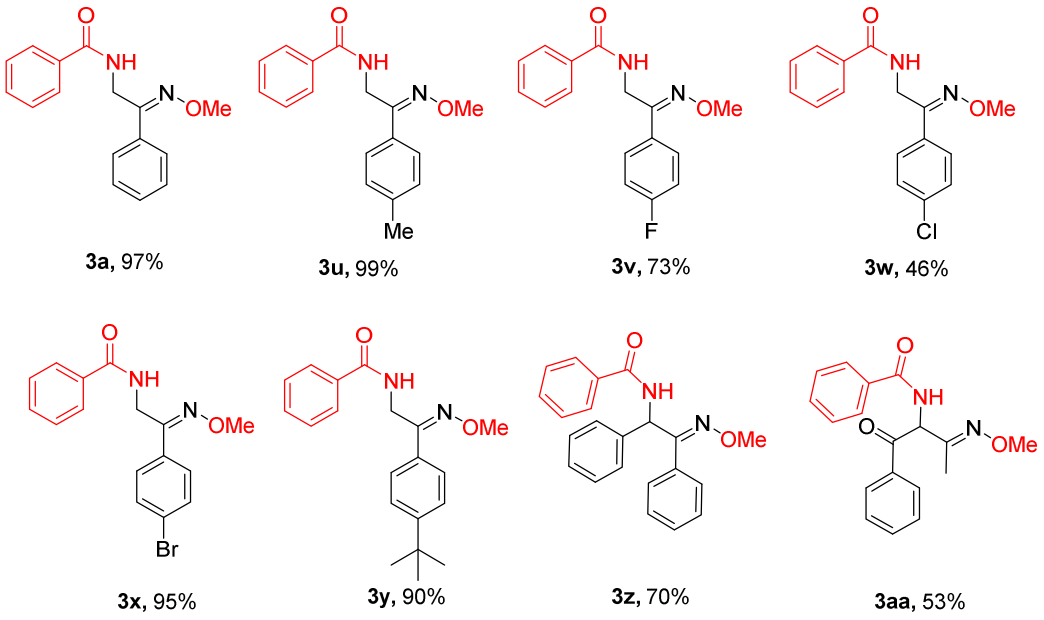
With optimized conditions in hand, we continued to explore the substrate scope of

the reaction. Various *N*-alkoxylamides containing both electron-donating and electron-withdrawing groups were examined (Table 2). The results showed that both electron-donating and electron-withdrawing groups at their aromatic rings were tolerated. *N*-Methoxylbenzamides bearing methyl groups at *o*-, *m*-, and *p*-positions were quite reactive, and in such cases **3** were obtained in more than 83% yields. *N*-Methoxylbenzamides containing halogen substituents are also good reaction partners giving *α*-amino oxime ethers **3e**, **3f**, and **3g** in good to excellent yields. Reactions of two *N*-methoxynaphthalenecarboxamides **1m** and **1n** with 2*H*-azirine afforded **3m** and **3n** in 61% and 88% yields, respectively. Unexpectedly, the substrates having 4-*t*-Bu and 4-OMe are less reactive, and the corresponding products **3c** and **3d** were produced in only 60% and 52% yields, respectively. Heterocyclic compounds containing N, O, and S did not show negative effect, and **3o**, **3p**, and **3q** were isolated in 62, 93, and 80% yields, respectively. Aliphatic amides *N*-methoxy-2-methyl-2-phenylpropanamide **1r** and *N*-methoxycyclopropanecarboxamide **1s** could participate in the reaction, and **3r** and **3s** were isolated in moderate yields. Bulkier *N*-*t*-butoxylbenzamide **1u** also showed good reactivity, and the reactivity was not affected by the steric hindrance.

Table 3. Scope of 2*H*-azirines[a,b]

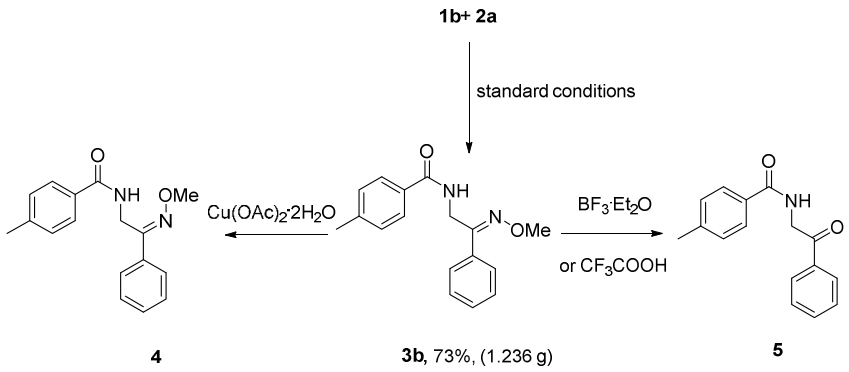


1a **2** **3a**



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), CuI (0.02 mmol), K_2CO_3 (0.2 mmol) in 2 mL of DCE at room temperature for 12 h. [b]Isolated yield.

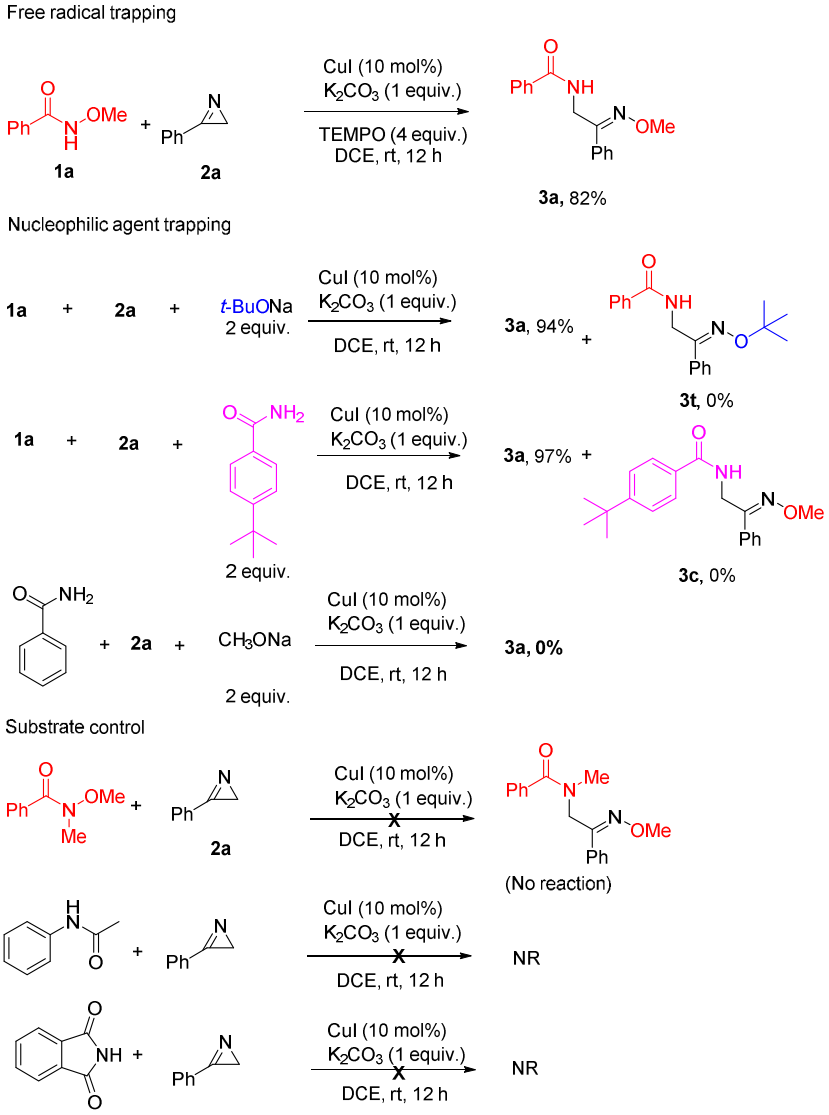
Subsequently, the reactions of various 2*H*-azirines **2** with *N*-methoxylbenzamide **1a** were further investigated (Table 3). Generally, 3-phenyl-2*H*-azirine derivatives having an alkyl, F, Br substituents proceeded smoothly to give the desired products in good to excellent yields. However, the chlorine-containing 2*H*-azirine showed relatively lower activity, and **3w** was isolated in only 46% yield. In addition, the disubstituted azirine, 2,3-diphenyl-2*H*-azirine **1z,** gave the corresponding products **3z** in 70% yield. In addtion, 3-alkyl-2*H*-azirine was also compatible, and **3aa** was afforded from (3-methyl-2*H*-azirin-2-yl)(phenyl)methanone in 53% yield.



Scheme 1. Gram scale and further transformation experiments

The optimized reaction conditions were suitable for gram-scale preparation. For

example, when 10 mol% CuI was used, the reaction of **2b** (0.990 g) and **1a** (0.702 g) was conducted at room temperature for twelve hours, the desired product **3b** (1.236 g) was isolated in 73% yield. We found that treatment of **3b** with $Cu(OAc)_2{\cdot}2H_2O$ at 100 ^oC resulted in *anti-syn* isomerization, and the *syn* isomer (*Z*)-*N*-(2-(methoxyimino)-2-phenylethyl)-4-methylbenzamide **4** was obtained in 28% yield, and **3b** was recovered in 68% yield (Scheme 1). Treatment of **3b** with CF_3COOH resulted in isomerization and partial hydrolysis to 4-methyl-*N*-(2-oxo-2-phenylethyl)benzamide **5**. In the presence of CF_3COOH or BF_3, only the hydrolysed product *α*-aminoketone **5** was isolated in 53% yield.



Scheme 2. Control experiments.

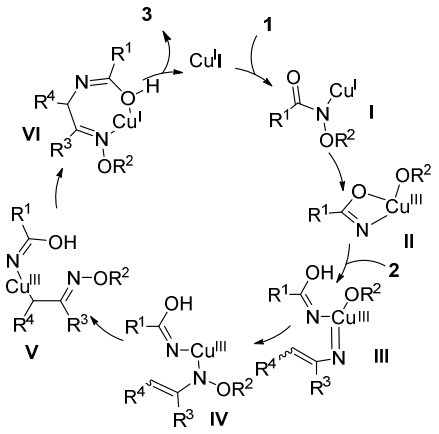


Figure 2. A possible reaction pathway

To explore the possible mechanism, a few control experiments were performed under the standard conditions (Scheme 2). In the presence of a radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), the reaction of **1a** and **2a** afforded **3a** in 82% yield, indicating that the radical pathway could be excluded. When 2 equiv. of *t*-BuONa was added, the reaction of **1a** and **2a** gave **3a** in 94% yield. The reaction of **1a** and **2a** in the presence of 2 equiv. of 4-(*tert*-butyl)benzamide did not give the mixtures of **3a** and **3c**. In addition, the reaction of benzamide and **2a** in the presence of 2 equiv. of CH_3ONa did not result in the formation of **3a**. These results illustrate that the reaction is not proceeded via substitution reaction. It was also found that when *N*-methoxy-*N*-methylbenzamide was used in the reaction, no product was generated. The reaction of *N*-phenylacetamide and phthalimide with azirine did not occur under the same reaction conditions, and the starting materials could be recovered, indicating that the reaction was not initiated by nucleophilic addition of amidate to C=N bond and subsequent ring-opening. Based on these observations, a possible reaction pathway was proposed and depicted in Figure 2. In the presence of a base, Cu(I) *N*-alkoxylamidate complex **I** would be expected upon deprotonation of *N*-alkoxylamide. Intramolecular oxidative addition of N-O bond toward Cu(I) would occur to give Cu(III) intermediate **II**.[18] The Cu(III) species was captured by 2*H*-azirine **2,** and subsequent rearrangement would result in the formation of Cu(nitrene) amidate intermediate **III**. Insertion of nitrene into the Cu-O bond gave

species **IV**. Intermediate **V** was afforded through 1,3-migration.[19,20] Reductive elimination would finally generate product **3**.

In conclusion, the reaction of *N*-methoxylbenzamides and 2*H*-azirines was developed leading to *α*-amino oxime ethers in good to excellent yields under mild conditions. It involved copper(I)-catalyzed N-O bond formation through vinyl nitrene-mediated pathway. The *α*-amino oxime ethers could be afforded at 100% atom economy with excellent regioselectivity and stereoselectivity. Further exploration of a detailed mechanism and relevant reactions involving 2*H*-azirines is currently underway.

EXPERIMENTAL SECTION

General remarks

Reagents were obtained from commercial sources and used without further purification. Solvents were dried and stored over 4 Å molecular sieves under nitrogen. Reactions were carried out under nitrogen using standard Schlenk technique unless otherwise noted. Flash column chromatography was performed on silca gel 300 and thin-layer chromatography on GF 254 plates. Melting points were determined with an Electrothermal apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 and 100 MHz, respectively, using the solvents as internal standard. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, br = broad. *J*-values are in Hz. Commercially obtained reagents were used without further purification. *N*-Methoxybenzamides **1** and 2*H*-azirines **2** were prepared according to literatures.[21, 22]

General procedure for synthesis of 3. To a flame-dried flask were added *N*-alkoxylamide **1** (0.2 mmol, 1.0 equiv), CuI (0.02 mmol, 0.1 equiv) and K_2CO_3 (0.2 mmol 1.0 equiv). Then, DCE (2.0 mL) and **2** (0.4 mmol, 2.0 equiv) were added subsequently. The reaction mixture was stirred for 12 hours at room temperature. The crude product was purified by silica gel chromatography (petroleum ether:ethyl acetate = 3:1) to afford the desired product **3**.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)benzamide (**3a**): White solid; mp: 129-130

ºC; yield: 52 mg, 97%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.78 (m, 2H), 7.55-7.37 (m, 8H), 7.07 (br, 1H), 4.51 (d, J = 4.8 Hz, 2H), 3.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 151.7, 134.3, 131.6, 131.5, 129.7, 128.6, 128.4, 128.0, 127.0, 62.5, 43.4; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{16}N_2O_2$ 268.1212; Found 268.1215.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)-4-methylbenzamide (**3b**): White solid; mp: 95-97 ºC; yield: 53 mg, 94%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, J = 7.6 Hz, 2H), 7.54-7.52 (m, 2H), 7.43-7.38 (m, 3H), 7.24 (d, J = 7.6 Hz, 2H), 7.00 (br, 1H), 4.51 (d, J = 4.8 Hz, 2H), 3.92 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 151.8, 142.0, 131.6, 131.5, 129.7, 129.3, 128.4, 128.0, 127.0, 62.4, 43.3, 21.5; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{18}N_2O_2$ 282.1368; Found 282.1371.

(*E*)-4-(*tert*-butyl)-*N*-(2-(methoxyimino)-2-phenylethyl)benzamide (**3c**): White solid; mp: 108-110 ºC; yield: 39 mg, 60%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.4 Hz, 2H), 7.55-7.52 (m, 2H), 7.47-7.38 (m, 2H), 7.03 (br, 1H), 4.51 (d, 4.8 Hz, 2H), 3.91 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 155.0, 151.8, 131.6, 131.5, 129.7, 128.4, 128.0, 126.9, 125.6, 62.4, 43.3, 34.9, 31.2; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{24}N_2O_2$ 324.1838; Found 324.1834.

(*E*)-4-methoxy-*N*-(2-(methoxyimino)-2-phenylethyl)benzamide (**3d**): White solid; mp: 106-108 ºC; yield: 31 mg, 52%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (m, 2H), 7.55-7.52 (m, 2H), 7.44-7.36 (m, 3H), 6.95-6.92 (m, 3H), 4.50 (d, J = 4.8 Hz, 2H), 3.92 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 162.3, 151.9, 131.6, 129.7, 128.8, 128.4, 128.0, 126.6, 113.8, 62.4, 55.4, 43.3; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{18}N_2O_3$ 298.1317; Found 298.1313.

(*E*)-4-fluoro-*N*-(2-(methoxyimino)-2-phenylethyl)benzamide (**3e**): White solid; mp: 111-113 ºC; yield: 50 mg, 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82-7.78 (m, 2H), 7.54-7.52 (m, 2H), 7.44- 7.32 (m, 3H), 7.11 (t, J = 8.4 Hz), 7.03 (b, 1H), 4.5 (d, J = 4.8 Hz, 2H), 3.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 164.8 (d, J_{CF} = 250.4 Hz), 151.6, 131.5, 130.5 (d, J_{CF} = 2.9 Hz), 129.7, 129.4 (d, J_{CF} = 9.0 Hz), 128.4, 128.0, 115.7 (d, J_{CF} = 21.9 Hz), 62.5, 43.4; ^{19}F NMR (376 MHz， $CDCl_3$): δ = -108.1; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{15}FN_2O_2$ 286.1118; Found 286.1118.

(*E*)-4-chloro-*N*-(2-(methoxyimino)-2-phenylethyl)benzamide (**3f**): White solid; mp:

114-115 ºC; yield: 38 mg, 63 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74-7.72 (m, 2H), 7.54-7.52 (m, 2H), 7.44-7.39 (m, 5H), 7.04 (br, 1H), 4.50 (d, J = 4.4 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 151.5, 137.8, 132.7, 131.4, 129.8, 128.9, 128.4, 128.0, 62.5, 43.4; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{15}ClN_2O_2$ 302.0822; Found 302.0818.

(*E*)-4-bromo-*N*-(2-(methoxyimino)-2-phenylethyl)benzamide (**3g**): White solid; mp: 138-140 ºC; yield: 65 mg, 94 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67-7.64 (m, 2H), 7.59-7.51 (m, 4H), 7.45-7.37 (m, 3H), 7.05 (s, 1H), 4.49 (d, J = 4.8 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 151.5, 133.1, 131.8, 131.4, 129.8, 128.6, 128.4, 128.0, 126.3, 62.5, 43.4; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{15}BrN_2O_2$ 346.0317; Found 346.0316.

methyl (*E*)-4-((2-(methoxyimino)-2-phenylethyl)carbamoyl)benzoate (**3h**): White solid; mp: 159-161 ºC; yield: 56 mg, 86 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 7.55-7.53 (m, 2H), 7.44-7.38 (m, 3H), 7.14 (br, 1H), 4.52 (d, J = 4.2 Hz, 2H), 3.94 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 166.2, 151.4, 138.2, 132.8, 131.4, 129.9, 129.8, 128.4, 128.0, 127.1, 62.5, 52.4, 43.4; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{18}N_2O_4$ 326.1267; Found 326.1274.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)-2-methylbenzamide (**3i**): White solid; mp: 109-110 ºC; yield: 47 mg, 83 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56-7.54 (m, 2H), 7.45-7.39 (m, 3H), 7.35-7.29 (m, 2H), 7.21-7.18 (m, 2H), 6.51 (br, 1H), 4.51 (d, J = 5.2 Hz, 2H) 3.88 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 151.9, 136.2, 136.1, 131.4, 131.0, 130.0, 129.7, 128.4, 128.1, 126.9, 125.8, 62.4, 43.1, 19.8; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{18}N_2O_2$ 282.1368; Found 282.1364.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)-3-methylbenzamide (**3j**): White solid; mp: 105-107 ºC; yield: 53 mg, 94 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (s, 1H), 7.55-7.52 (m, 3H), 7.42-7.30 (m, 5H), 7.03 (br, 1H), 4.50 (d, J = 4.4 Hz, 2H), 3.92 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 151.8, 138.5, 134.3, 132.3, 131.5, 129.7, 128.5, 128.4, 128.0, 127.9, 123.9, 62.4, 43.3, 21.4; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{18}N_2O_2$ 282.1368; Found 282.1364.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)-2,4-dimethylbenzamide (**3k**): White solid; mp: 94-96 ºC; yield: 31 mg, 52 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55-7.53 (m, 2H), 7.44-7.36 (m, 3H), 7.25 (d, J = 8.0 Hz, 1H), 7.02 (s, 1H), 7.00 (d, J = 8.4 Hz, 1H), 6.49 (br, 1H), 4.50 (d, J = 4.8 Hz, 2H), 3.88 (s, 3H), 2.37 (s, 3H), 2.32 (3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.7, 152.0, 140.1, 136.3, 133.2, 131.9, 131.4, 129.7, 128.4, 128.1, 127.1, 126.4, 62.4, 43.1, 21.3, 19.8; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{20}N_2O_2$ 296.1525; Found 296.1521.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)benzo[*d*][1,3]dioxole-5-carboxamide (**3l**): White solid; mp: 116-118 ºC; yield: 49 mg, 79 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54-7.51 (m, 2H), 7.44-7.38 (m, 3H), 7.33-7.26 (m, 2H), 6.94 (br, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.01 (s, 2H), 4.48 (d, J = 4.8 Hz, 2H) 3.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 151.8, 150.4, 148.0, 131.5, 129.7, 128.5, 128.4, 128.0, 121.7, 108.1, 107.6, 101.7, 62.4, 43.4; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{16}N_2O_4$ 312.1110; Found 312.1114.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)-1-naphthamide (**3m**): White solid; mp: 94-96 ºC; yield: 39 mg, 61%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20-8.18 (m, 1H), 7.91- 7.84 (m, 2H), 7.59-7.57 (m, 3H), 7.51-7.48 (m, 2H), 7.46-7.41 (m, 4H), 6.72 (b, 1H), 4.62 (d, J = 5.2 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.3, 152.0, 134.2, 133.7, 131.5, 130.7, 130.1, 129.7, 128.5, 128.3, 128.2, 127.1, 126.4, 125.4, 125.2, 124.8, 62.4, 43.3; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{18}N_2O_2$ 318.1368; Found 318.1365.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)-2-naphthamide (**3n**): White solid; mp: 133-135 ºC; yield: 56 mg, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 7.93-7.83 (m, 4H), 7.58-7.51 (m, 4H), 7.45-7.37 (3H), 7.19 (br, 1H), 4.58 (d, J = 4.8 Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 151.8, 134.8, 132.7, 131.6, 129.7, 129.0, 128.5, 128.4, 128.0, 127.8, 127.7, 127.6, 126.8, 123.6, 62.5, 43.5; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{18}N_2O_2$ 318.1368; Found 318.1370.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)-1-methyl-1*H*-indole-3-carboxamide (**3o**): Yellow solid; mp: 144-146 ºC; yield: 40 mg, 62%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00-7.98 (m, 1H), 7.69 (s, 1H), 7.58-7.56 (m, 2H), 7.45-7.35 (m, 4H), 7.32-7.24 (m,

2H), 6.94 (b, 1H), 4.58 (d, J = 4.8 Hz, 2H), 3.97 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 152.1, 137.3, 132.9, 131.7, 129.6, 128.4, 128.1, 125.2, 122.5, 121.4, 119.9, 110.7, 110.2, 62.5, 43.1, 33.3; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{19}N_3O_2$ 321.1477; Found 321.1480.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)furan-3-carboxamide (**3p**): White solid; mp: 102-103 ºC; yield: 48 mg, 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (s, 1H), 7.53-7.51 (m, 2H), 7.43-7.36 (m, 4H), 6.73 (b, 1H), 6.64 (d, J = 0.8 Hz, 1H), 4.56 (d, J = 4.8 Hz), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3, 151.6, 144.8, 143.8, 131.5, 129.7, 128.4, 128.0, 122.4, 108.3, 62.4, 42.8; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{14}H_{14}N_2O_3$ 258.1004; Found 258.1003.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)benzo[*b*]thiophene-3-carboxamide (**3q**): White solid; mp: 111-112 ºC; yield: 52 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, J = 7.6 Hz, 1H), 7.90 (s, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.57-7.54 (m, 2H), 7.46-7.37 (m, 5H), 6.95 (br, 1H), 4.56 (d, J = 4.8 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 151.7, 140.3, 136.6, 131.9, 131.5, 129.9, 129.8, 128.5, 128.1, 125.2, 125.1, 124.1, 122.7, 62.5, 43.1; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{16}N_2O_2S$ 324.0932; Found 324.0933.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)-2-methyl-2-phenylpropanamide (**3r**): Yellow liquid; yield: 28 mg, 45 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.36 (m, 5H), 7.33-7.23 (m, 5H), 5.83 (br, 1H), 4.24 (d, J = 5.2 Hz, 2H), 3.75 (s, 3H), 1.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.1, 152.2, 144.7, 131.3, 129.5, 128.6, 128.3, 128.1, 126.9, 126.6, 62.2, 47.0, 42.8, 26.9; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{22}N_2O_2$ 310.1681; Found 310.1682.

(*E*)-*N*-(2-(methoxyimino)-2-phenylethyl)cyclopropanecarboxamide (**3s**): Yellow solid; mp: 116-118 ºC; yield: 36 mg, 78 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.48 (m, 2H), 7.42-7.39 (m, 3H), 6.45 (b, 1H), 4.34 (d, J = 4.8 Hz, 2H), 3.90 (s, 3H), 1.46-1.40 (m, 1H), 0.99-0.95 (m, 2H), 0.77-0.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.4, 152.0, 131.6, 129.6, 128.3, 128.0, 62.3, 43.2, 14.7, 7.3; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{13}H_{16}N_2O_2$ 232.1212; Found 232.1210.

(*E*)-*N*-(2-(*tert*-butoxyimino)-2-phenylethyl)benzamide (**3t**): Yellow solid; mp: 93-95

ºC; yield: 50 mg, 81%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81-7.79 (m, 2H), 7.66-7.64 (m, 2H), 7.54-7.35 (m, 6H), 7.21 (br, 1H), 4.54 (d, J = 4.4 Hz, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 148.8, 134.5, 131.8, 131.5, 129.4, 128.7, 128.3, 128.2, 126.9, 79.4, 43.6, 27.5; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{22}N_2O_2$ 310.1681; Found 310.1681.

(*E*)-*N*-(2-(methoxyimino)-2-(*p*-tolyl)ethyl)benzamide (**3u**): White solid; mp: 92-94 ºC; yield: 56 mg, 99 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72-7.70 (m, 2H), 7.44-7.34 (m, 5H), 7.01 (br, 1H), 4.42 (d, J = 4.8 Hz, 2H), 3.84 (s, 1H), 2.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 151.5, 139.9, 131.6, 129.1, 128.6, 128.5, 128.0, 127.0, 62.4, 43.3, 21.5; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{18}N_2O_2$ 282.1368; Found 282.1369.

(*E*)-*N*-(2-(4-fluorophenyl)-2-(methoxyimino)ethyl)benzamide (**3v**): White solid; mp: 128-130 ºC; yield: 42 mg, 73 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80-7.77 (m, 2H), 7.62-7.57 (m, 2H), 7.54-7.50 (m, 1H), 7.47-7.43 (m, 2H), 7.14-7.08 (m, 2H), 6.98 (br, 1H), 4.52 (d, J = 4.8 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 163.1 (d, J_{CF} = 249.2 Hz), 150.6, 134.2, 131.7, 130.4 (d, J_{CF} = 8.3 Hz), 128.7, 127.3 (d, J_{CF} = 3.3 Hz), 127.0, 115.5 (d, J_{CF} = 21.5 Hz), 62.5, 43.2.; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.0; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{15}FN_2O_2$ 286.1118; Found 286.1115.

(*E*)-*N*-(2-(4-chlorophenyl)-2-(methoxyimino)ethyl)benzamide (**3w**): White solid; mp: 95-97 ºC; yield: 28 mg, 46 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 7.6 Hz, 2H), 7.55-7.52 (m, 3H), 7.46 (t, J = 7.2 Hz, 2H), 7.41 (d, J = 8.8 Hz), 7.03 (br, 1H), 4.52 (d, J = 4.8 Hz, 2H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 150.7, 135.7, 134.2, 131.7, 129.7, 129.6, 128.7, 128.6, 127.0, 62.5, 43.1; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{15}ClN_2O_2$ 302.0822; Found 302.0820.

(*E*)-*N*-(2-(4-bromophenyl)-2-(methoxyimino)ethyl)benzamide (**3x**): White solid; mp: 136-138 ºC; yield: 66 mg, 95 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79-7.77 (m, 2H), 7.55-7.49 (m, 3H), 7.46-7.42 (m, 4H), 4.50 (d, J = 4.8 Hz, 1H), 3.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 150.8, 134.2, 131.7, 131.6, 130.1, 129.8, 128.6, 127.0, 124.0, 62.5, 43.1; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{15}BrN_2O_2$

346.0317; Found 346.0320.

(*E*)-*N*-(2-(4-(*tert*-butyl)phenyl)-2-(methoxyimino)ethyl)benzamide (**3y**): Yellow oil; yield: 58 mg, 90 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.4 Hz, 2H), 7.54-7.43 (m, 7H), 7.08 (br, 1H), 4.52 (d, J = 4.4 Hz, 2H), 3.93 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 152.9, 151.2, 134.4, 131.5, 128.6, 128.4, 127.9, 127.0, 125.4, 62.5, 43.3, 34.8, 31.2; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{24}N_2O_2$ 324.1838; Found 324.1840.

(*E*)-*N*-(2-(methoxyimino)-1,2-diphenylethyl)benzamide (**3z**): White solid; mp: 150-152 ºC; yield: 48 mg, 70 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84-7.82 (m, 2H), 7.75 (br and d, J = 6.8 Hz, 1H), 7.53-7.37 (m, 5H), 7.32-7.19 (m, 8H), 6.12 (d, J = 7.6 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 155.1, 138.6, 134.4, 132.0, 131.6, 129.2, 128.7, 128.6, 128.2, 128.1, 128.0, 127.9, 127.1, 62.6, 57.1; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{22}H_{20}N_2O_2$ 344.1525; Found 344.1524.

(*E*)-*N*-(3-(methoxyimino)-1-oxo-1-phenylbutan-2-yl)benzamide (**3aa**): Yellow oil; yield: 33 mg, 53 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13-8.11 (m, 2H), 7.89-7.87 (m, 2H), 7.64-7.60 (m,1H), 7.56-7.45 (m, 6H), 6.36 (d, J = 7.2 Hz, 1H), 3.83 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.5, 153.0, 134.5, 134.1, 133.7, 132.0, 129.2, 128.7, 128.6, 127.2, 122.3, 62.0, 58.7, 11.9; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{18}H_{18}N_2O_3$ 310.1317; Found 310.1316.

General procedure for the synthesis of 4. To a seal tube were added **3b** (0.2 mmol, 1.0 equiv), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol, **2** equiv), and DCE (2.0 mL). The reaction mixture was stirred for 12 hours at 100 ^{o}C. The crude product was purified by silica gel chromatography (petroleum ether: ethyl acetate = 3:1) to afford the desired product **4**.

(*Z*)-*N*-(2-(methoxyimino)-2-phenylethyl)-4-methylbenzamide (**4**): White solid; mp: 135-137 ºC; yield: 16 mg, 28%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.82 (m, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.40-7.38 (m, 3H), 7.22 (d, J = 8.0 Hz, 2H), 6.75 (br, 1H), 4.69 (d, J = 6.0 Hz, 2H), 4.08 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 155.8, 142.0, 133.9, 131.4, 129.7, 129.3, 128.7, 127.0, 126.9, 62.6, 36.0, 21.5; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{17}H_{18}N_2O_2$ 282.1368; Found 282.1367.

General procedure for the synthesis of 5. Method 1: To a seal tube were added **3b** (0.2 mmol, 1.0 equiv), CF_3COOH (0.4 mmol, 2 equiv), and H_2O (20 equiv), and DCE (2.0 mL). The reaction mixture was stirred for 12 hours at 50 ^oC. The crude product was purified by silica gel chromatography (petroleum ether: ethyl acetate = 3:1) to afford the desired product **5** (24 mg, 47% yield). Method 2: To a seal tube were added **3b** (0.2 mmol, 1.0 equiv) and $BF_3{\cdot}Et_2O$ (0.4 mmol, 2 equiv). Subsequently, DCE (2.0 mL) was added to this tube. The reaction mixture was stirred for 12 hours at 50 ^oC. The crude product was purified by silica gel chromatography (petroleum ether: ethyl acetate = 3:1) to afford the desired product **5** (27 mg, 53% yield).

4-methyl-*N*-(2-oxo-2-phenylethyl)benzamide (**5**): White solid; mp: 115-117 ºC ; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.05-8.03 (m, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.28-7.26 (m, 3H), 4.96 (d, J = 4.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.4, 167.4, 142.3, 134.4, 134.3, 131.0, 129.3, 129.0, 128.0, 127.2, 46.9, 21.5; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{16}H_{15}NO_2$ 253.1103; Found 253.1099.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information. Spectra of ^1H and ^{13}C NMR for new products and crystallographic data for **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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