Cu(Ⅱ)-promoted oxidative C-N bond cleavage of N-benzoylamino acids to primary aryl amides

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DOI: https://doi.org/10.24820/ark.5550190.p009.726

Abstract

A novel protocol for $CuCl_2$-promoted oxidative C-N bond cleavage of N-benzoyl amino acids was developed. It is the first example of using accessible amino acid as an ammonia synthetic equivalent for the synthesis of primary aryl amides *via* $CuCl_2$-promoted oxidative C-N bond cleavage reaction. The present protocol shows excellent functional group tolerance and provides an alternative method for the synthetic of primary aryl amides in 84-96% yields.

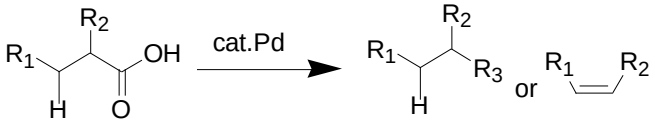
Keywords: C-N bond cleavage, amino acid, aryl amide

Introduction

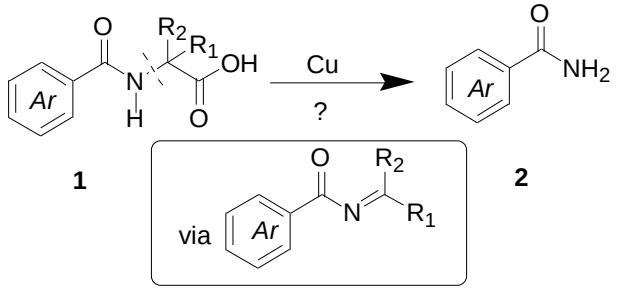
Amide bond forming reactions are among the most important and widely studied transformations in organic chemistry,[1] because they are widely present in detergents, lubricants, biologically active molecules, agrochemicals, pharmaceuticals and polymers.[2] Amide is the most important functional group necessary to maintain biological systems,[3] as well as the importance intermediates in organic syntheses.[4] Therefore, various approaches to the construction of the amide have been developed. The traditional methods for the synthesis of primary amides rely on the treatment of acyl halides, acid anhydrides, esters or acids with ammonia.[5] However, the use of ammonia can often be hampered by handling issues, importantly, since ammonia can react with carboxylic acids, esters and other functional groups, these methods are sometimes not suitable for selective amide generation. Other methods for amide synthesis include the Beckmann rearrangement[6,7] and the Schmidt reaction.[8] However, both of them involve hazardous reagents and produce stoichiometric quantities of noxious by-products. Recently, metal complexes have been used to access amides through the dehydrogenative reaction between amines and alcohols or aldehydes.[9,10] Furthermore, the hydration of nitriles[11] and the rearrangement of aldoximes[12,13] can also provide alternative synthetic routes to amides. Very recently, Sekar and coworkers developed an efficient process for

the direct synthesis of amides from methylarenes and amines using an iron catalyst.[14] In this new catalytic reaction, the methyl group of the methylarene is oxidized to the corresponding aldehyde through non-directed C(sp3)-H oxidation followed by its oxidative amidation with *N*-chloroamine, yielding the carboxylic amide. However, these above-mentioned methods suffer several drawbacks, such as low functional group tolerance, undesired hydrolysis of the amides into carboxylic acids. Therefore, development of a general, practical and efficient method for the construction of primary aryl amides is still a challenge, and such a method is highly desirable.

The C−N bond is one of the most abundant chemical bonds and widely exists in many organic molecules and biomacromolecules. The formation and transformation of C−N bond are among the central topics in organic chemistry, organometallic chemistry, and biochemistry.[15] The C–N bond is strong in organic molecules, thus, the transformations via C–N bond cleavage are usually difficult.[16] Recently, transition-metal-catalyzed decarboxylative coupling reactions have generated much interest because of its efficiency, selectivity, as well as convenience (Scheme 1),[17] Very recently, decarbonylation/dehydration reactions also have been studied and constitute a useful tool in synthesis of olefins[18] Despite the significant advances in decarbonylation reactions, questions concerning decarbonylation/dehydration of amino acids was less explored. [19-22] Based on the previous work, we reasoned that the C-N bond cleavage of N-benzoyl amino acids **1** can also be realized *via* oxidative decarbonylation/dehydration reaction, followed by hydrolysis to afford the corresponding primary amides **2** (Scheme 2). Herein, we describe the first example of the use of amino acids as an ammonia synthetic equivalent for the synthesis of primary aryl amides *via* Cu(Ⅱ)-promoted oxidative C-N bond cleavage of N-benzoyl amino acids.



Scheme 1. Transition metal catalyzed decarbonylation/dehydration reactions.

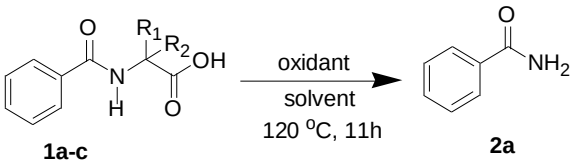


Scheme 2. Cu(Ⅱ)-promoted oxidative C-N bond cleavage of N-benzoylamino acids.

Results and Discussion

In our initial study, **1a** containing a 2-aminoisobutyric acid was chosen as a model substrate and selected results from our screening experiments are summarized (Table 1). Only trace amount of product **2a** was detected by using 1 equivalent of CuO as oxidant in DMSO at 120 °C for 11 h (Table 1, entry 1).

Table 1. Examination of reaction conditions



1a-c **2a**

1a R_1 = Me; R_2= Me
1b R_1 = Me; R_2 = H
1c R_1 = H; R_2 = H

Entry[a]	Cu	Solvent	Yield of **2a**/%[b]
1	CuO	DMSO	trace
2	$CuSO_4$	DMSO	12
3	$Cu(OAc)_2$	DMSO	17
4	$CuCl_2$	DMSO	96
5	AgOAc	DMSO	32
6	MnO_2	DMSO	74
7	$CuCl_2$	DMF	56
8	$CuCl_2$	DMA	86
9	$CuCl_2$	Xylene	trace
10	$CuCl_2$	TFA	trace
11	$CuCl_2$	^{t}BuOH	trace
12	$CuCl_2$	AcOH	trace
15	$CuCl_2$	Dioxane	trace
16[c]	$CuCl_2$	DMSO	56
17[d]	$CuCl_2$	DMSO	93
18[e]	$CuCl_2$	DMSO	trace

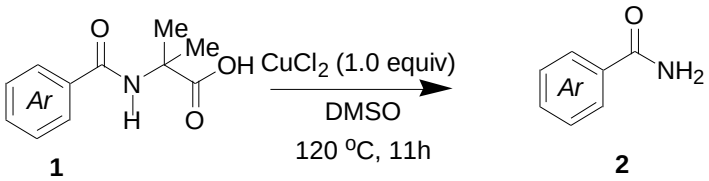
[a] Reaction conditions: benzoyl amino acid (0.5 mmol), oxidant (0.5 mmol), solvent (0.5 mL), at 120 °C for 11 h. [b] Isolated yield. [c] Reaction at 100 °C. [d] **1b** was used substrate. [e] **1c** was used substrate.

Then, other copper precursors were tested, only 12% and 17% yields of **2a** were obtained with $CuSO_4$ and $Cu(OAc)_2$ as oxidants, respectively (Table 1, entries 2,3). Surprisingly, the yield was dramatically improved to 96% by using $CuCl_2$ as oxidant, (Table 1, entry 4). In addition, we found that 34 % yield of **2a** was obtained by using AgOAc as oxidant (Table 1, entry 5). To our delight, we found that MnO_2 can afford the desired product **2a** in good yield (Table 1, entry 6). To further optimize the reaction, an extensive screening of various solvents was conducted by using $CuCl_2$

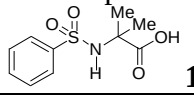
as the oxidant; we found that DMF as solvent gave a 56% yield (Table 1, entry 7). Notably, DMA showed similar reactivity compared to that of DMSO and 86% yield was obtained (Table 1, entry 4 *vs* 8). However, we found that nonpolar solvents and protic solvents were ineffective in the present protocol (Table 1, entries 9-15). Then, the effect of variation of reaction temperature was studied; when the reaction temperature was decreased to 100 ^{o}C, only 56% yield of **2a** was obtained (Table 1, entry 16). Finally, the substrates employing other amino acids were tested, for example, **1b** containing 2-amino-propionic acid showed almost the same reaction efficiency compared to that of **1a** (Table 1, entry 17). Interestingly, substrate **1c** containing an aminoacetic acid, only less than 5% yield of **2a** was detected (Table 1, entry 18). Therefore, by a systematic variation of the reaction parameters, the optimtimal reaction conditions were found to be: $CuCl_2$ (1 equiv) as oxidant in DMSO at 120 °C for 11 h (Table 1, entry 4).

With the optimized conditions in hand, we investigated the scope of substrates (Table 2).

Table 2. $CuCl_2$-promoted oxidative C-N bond cleavage of N-benzoylamino acids



1 **2**

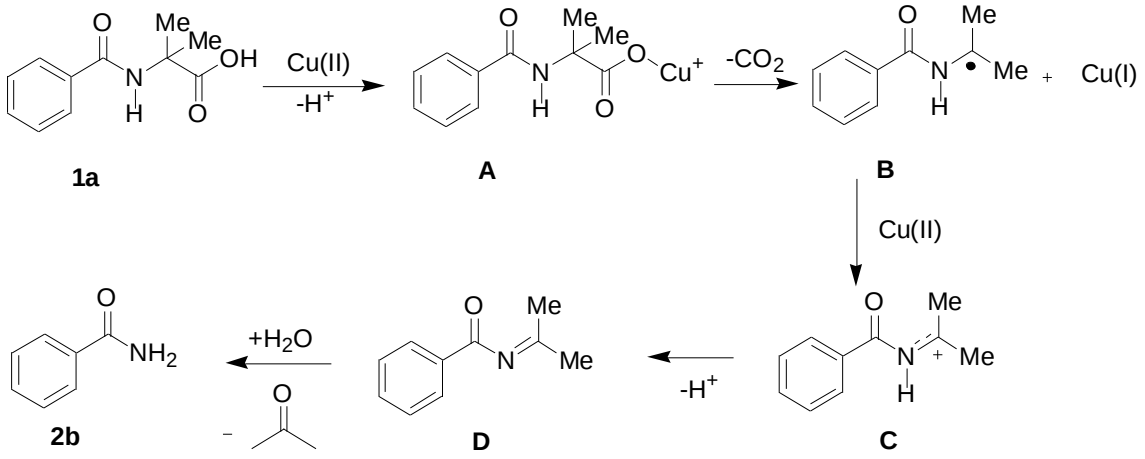
Entry[a]	Ar	Product	Yield/%[b]
1	Ph **1a**	**2a**	96
2	*p*-MeC_6H_4 **1d**	**2b**	91
3	*P*-MeOC_6H_4 **1e**	**2c**	93
4	*p*-ClC_6H_4 **1f**	**2d**	92
5	*p*-FC6H4 **1g**	**2e**	91
6	*p*-$CF_3C_6H_4$ **1h**	**2f**	95
7	*m*-MeC_6H_4 **1i**	**2g**	86
8	*o*-ClC_6H_4 **1j**	**2h**	88
9	2-naphthalene **1k**	**2i**	84
10	2- thiophene **1l**	**2j**	89
11	 **1m**	**2k**	trace

[a] Reaction conditions: benzoyl amino acid **1** (0.5 mmol), $CuCl_2$ (0.5 mmol), DMSO (0.5 mL), at 120 ^{o}C for 11 h. [b] Isolated yield.

We found that substrates **1** containing either electron-donating or electron-withdrawing group smoothly reacted to afford the corresponding products **2** in 84-96% yields. For example, the substrates **1d-h** containing a substituent group at the para position such as *p*-Me, *p*-MeO, *p*-Cl, *p*-F, and *p*-CF_3 gave the corresponding aryl primary amides in excellent yield (Table 2, entries 2-6). As for different substitution patterns in the arene ring, meta- and ortho- substituted substrates**1i-j**

all worked well in this reaction to afford the desired products **2g-2h**. For example, substrates **1i** bearing a meta-substituent such as *m*-Me gave an 86% isolated yield (Table 2, entry 7); substrate **1j** bearing ortho-substituent such as *o*-Cl afforded the corresponding products in 88% isolated yield (Table 2, entry 8). Substrate derived from 2-Naphthalene such as **1k** was suitable, giving the corresponding product **2i** in 84% yield (Table 2, entry 9). Notably, a substrate **1l**, bearing a thiophenyl ring underwent reaction smoothly to afford the desired product **1j** in 89% yield (Table 2, entry 10). Unfortunately, the present protocol does not appear to be applicable to the similar arylsulfonyl amino acid **1m**, only a trace amount of the primary sulfonamides product **2k** was obtained (Table 2, entry 11).

On the basis of these results and previous reports, a plausible reaction mechanism is proposed (Scheme 4). Initially, interaction of $CuCl_2$ and benzoylamino acid **1a** afford organocopper species **A**, The oxidative decarboxylation of **A** gives the radical intermediate **B** and simultaneously generates CO_2. Subsequently, **B** is further oxidized to afford the iminium intermediate **C**, which affords the imine **D** after deprotonation. Finally, the imine **D** is hydrolyzed to afford the primary arylamide **2a** and acetone.



Scheme 4. A plausible reaction mechanism.

Conclusions

In conclusion, a novel Cu(Ⅱ)-promoted oxidative C-N bond cleavage of N-benzoylamino acids has been developed. Readily available benzoylamino acids with broad substrate scope were fully compatible by employing $CuCl_2$ as the oxidant. The present protocol shows excellent functional group tolerance and provides an efficient method for the synthesis of aryl amides in excellent yields. Further applications to the synthesis of biologically important molecules are in progress.

Experimental Section

General. All reagents were obtained from commercial sources and used without further purification. The reactions were carried out in air; all products were purified by column chromatography on silica gel (200–300 mesh) using petroleum ether (60-90^{o}C) and ethyl acetate as eluate. Compounds described in the literature were characterized by HRMS and NMR. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-400 (400 MHz) spectrometer with TMS as an internal standard. High-resolution mass spectral (HRMS) data were recorded on Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionization (ESI). Melting points were determined on an XT-4 electrothermal micro-melting-point apparatus.

Synthesis of N-benzoylamino acids 1: typical procedure.[23] Amino acid (100 mmol) was dissolved in 10% sodium hydroxide solution (100 mL), and then benzoyl chloride or aryl sulfonly chloride (100 mmol) was added in portions to this solution, stirred vigorously after each addition. Crushed ice (100 g) was added to the solution and then concentrated HCl was added dropwise until the mixture was acidified (pH 2-3). The resulting compounds **1a-1m** were obtained as a white or yellow crystalline solid.

2-Benzoylamino-2-methyl-propionic acid[24] (1a). White solid, mp 199-201^{o}C (lit.[24] 199 °C). ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.45 (s, 6H), 7.52-7.44 (m, 2H), 7.54 (d, *J* 8.0 Hz, 1H), 7.85 (d, *J* 8.0 Hz, 2H), 8.47 (s, 1H).

2-Benzoylamino-propionic acid[25] (1b). White solid, mp 119-121 $^{\circ}$C (lit.[25] 119 °C). ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.13 (d, *J* 8.0 Hz, 3H), 3.73 (t, *J* 8.0 Hz, 1H), 7.37 (d, *J* 8.0 HZ, 2H), 7.67 (d, *J* 8.0 Hz, 2H), 8.05 (d, *J* 8.0 HZ, 1H).

Benzoylamino-acetic acid[26] (1c). White solid, mp 191-193 $^{\circ}$C (lit.[26] 191 °C). ^{1}H NMR (*d*-DMSO, 400 MHz): δ 3.54 (d, *J* 4.0 Hz, 2H), 7.37 (d, *J* 8.0 Hz, 2H), 7.67 (d, *J* 8.0 Hz, 2H), 7.94 (s, 1H).

2-Methyl-2-(4-methyl-benzoylamino)-propionic acid (1d). White solid, mp 217-219 $^{\circ}$C. ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.44 (s, 6H), 2.35 (s, 3H), 7.26 (d, *J* 8.0 Hz, 2H), 7.77 (d, *J* 8.0 Hz, 2H), 8.38 (s, 1H). ^{13}C NMR (*d*-DMSO, 100 MHz): δ 20.9, 25.0, 55.3, 127.4, 128.6, 131.5, 140.9, 166.7, 175.5. HRMS (Q-TOF): calcd. For $C_{12}H_{16}NO_3$ $[M+H]^+$ 222.1130; found 222.1134.

2-(4-Methoxy-benzoylamino)-2-methyl-propionic acid (1e). White solid, mp 234-236 $^{\circ}$C. ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.24 (s, 3H), 3.82 (d, *J* 4.0 Hz, 2H), 7.06 (d, *J* 8.0 Hz, 2H), 7.72 (d, *J* 8.0 Hz, 2H), 7.79 (s, 1H). ^{13}C NMR (*d*-DMSO, 100 MHz): δ 26.40, 55.07, 58.73, 124.71, 128.19, 149.62, 149.67, 175.19. HRMS (Q-TOF): calcd. For $C_{12}H_{16}NO_4$ $[M+H]^+$ 238.1079; found 238.1076.

2-(4-Chloro-benzoylamino)-2-methyl-propionic acid (1f): Yellow solid, mp 218-219 $^{\circ}$C. ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.46 (s, 3H), 7.53 (d, *J* 8.0 Hz, 2H), 7.87 (d, *J* 8.0 Hz, 2H), 8.50 (s, 1H). ^{13}C NMR (*d*-DMSO, 100 MHz): δ 24.9, 55.7, 128.2, 129.3, 133.22, 135.9, 164.7, 175.5. HRMS (Q-TOF): calcd. For $C_{11}H_{13}ClNO_3$ $[M+H]^+$ 242.0584; found 242.0581.

2-(4-Fluoro-benzoylamino)-2-methyl-propionic acid (1g): Yellow solid, mp 214-216 $^{\circ}$C. ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.46 (s, 3H), 7.28 (t, *J* 8.0 Hz, 2H), 7.92 (t, *J* 8.0 Hz, 2H), 8.42 (s,

1H). ^{13}C NMR (*d*-DMSO, 100 MHz): δ 24.9, 55.5, 114.8, 115.1, 130.0, 130.1, 130.8, 162.6, 164.8, 175.4. HRMS (Q-TOF): calcd. For $C_{11}H_{13}FNO_3$ $[M+H]^+$ 226.0879; found 226.0876.

2-Methyl-2-(4-trifluoromethyl-benzoylamino)-propionic acid (1h): White solid, mp 226-228 °C. ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.48 (s, 3H), 7.84 (d, *J* 8.0 Hz, 2H), 8.05 (d, *J* 8.0 Hz, 2H), 8.68 (s, 1H). ^{13}C NMR (*d*-DMSO, 100 MHz): δ 25.4, 56.2, 123.1, 125.6, 125.6, 128.9, 131.5, 131.2, 131.8, 132.1, 138.6, 165.3, 175.8. HRMS (Q-TOF): calcd. For $C_{12}H_{13}F_3NO_3$ $[M+H]^+$ 276.0847; found 278.0849.

2-Methyl-2-(3-methyl-benzoylamino)-propionic acid (1i): White solid, mp 200-202 °C. ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.45 (s, 6H), 2.36 (s, 3H), 7. 32 (s, 2H), 7.66-7.61 (m, 2H), 8.35 (s, 1H). ^{13}C NMR (*d*-DMSO, 100 MHz): δ 20.9, 24.9, 55.4, 124.6, 127.9, 127.9, 131.6, 134.4, 137.3, 165.9, 175.5. HRMS (Q-TOF): calcd. For $C_{12}H_{13}NO_3$ $[M+H]^+$ 222.1130; found 222.1136.

2-(2-Chloro-benzoylamino)-2-methyl-propionic acid (1j): White solid, mp 195-197 °C. ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.44 (s, 6H), 7.48-7.39 (m, 4H), 8.56 (s, 1H). ^{13}C NMR (*d*-DMSO, 100 MHz): δ 24.8, 55.5, 126.9, 128.9, 129.5, 130.0, 130.6, 136.7, 165.5, 175.2. HRMS (Q-TOF): calcd. For $C_{10}H_{13}N_2O_6S$ $[M+H]^+$ 242.0584; found 242.0587.

2-Methyl-2-[(naphthalene-2-carbonyl)-amino]-propionic acid (1k): White solid; mp 196-198 °C. ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.53 (s, 6H), 7.63-7.57 (m, 2H), 7.93-7.91 (m, 1H), 8.02-7.96 (m, 2H), 8.04 (d, *J* 8.0 Hz, 1H), 8.46 (s, 1H), 8.61 (s, 1H). ^{13}C NMR (*d*-DMSO, 100 MHz): δ 24.9, 55.8, 124.3, 126.6, 127.4, 127.5, 127.7, 128.6, 132.1, 165.7, 170.9, 175.9. HRMS (Q-TOF): calcd. For $C_{15}H_{16}NO_3$ $[M+H]^+$ 258.1130; found 258.1134.

2-Methyl-2-[(thiophene-2-carbonyl)-amino]-propionic acid (1l): White solid, mp 224-226 °C. ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.45 (s, 6H), 7.13 (t, *J* 4.0 Hz, 1H), 7.73 (d, *J* 4.0 Hz, 1H), 7.81 (d, *J* 8.0 Hz, 1H), 8.40 (s, 1H). ^{13}C NMR (*d*-DMSO, 100 MHz): δ 24.9, 55.8, 127.7, 128.4, 130.50, 140.1, 160.5, 175.7. HRMS (Q-TOF): calcd. For $C_9H_{12}NO_3S$ $[M+H]^+$ 214.0538; found 214.0535.

2-Benzenesulfonylamino-2-methyl-propionic acid[27] **(1m)**: White solid, mp 145-147 °C (lit. 145-146 °C). ^{1}H NMR (*d*-DMSO, 400 MHz): δ 1.23 (s, 6H), 7.56 (dd, *J* 8.0 Hz, *J* 12.0 Hz, 2H), 7.80 (d, *J* 4.0 Hz, 2H), 7.97 (s, 1H).

General procedure for **$CuCl_2$-promoted oxidative C-N bond cleavage of N-benzoyl amino acids for primary aryl amides 2.** A mixture of benzoyl amino acid **1** (0.5 mmol), $CuCl_2$ (85 mg, 0.5 mmol), and DMSO (0.5 mL) was placed in a 25 mL flask under air. The tube was heated at 120 ℃ for 11 h. The reaction mixture was cooled, diluted with ethyl acetate (10 mL), filtered through Celite, and concentrated in vacuo. The residue was purified by silica gel column chromatography with ethyl acetate/ petroleum ether (ethyl acetate/ petroleum ether = 1:3) to afford the desired product **2**.

Benzamide[28] **(2a). (table 2, entry 1).** White solid, yield 96%, 58 mg, mp 124-126 °C (lit.[28] 127 °C). ^{1}H NMR (400 MHz, DMSO-*d*6 /TMS): δ 7.93 (s, 1H), 7.87 (d, *J* 8.0 Hz, 2H), 7.35 (s, 1H), 7.31 (d, *J* 8.0 Hz, 2H).

4-Methylbenzamide[28] **(2b). (table 2, entry 2).** White solid, yield 91%, 62 mg, mp 163-165 °C (lit.[28] 163 °C). ^{1}H NMR (400 MHz, DMSO-*d*6 /TMS): δ 7.97 (s, 1H), 7.83 (d, *J* 8.0 Hz, 2H), 7.35 (s, 1H), 7.31 (d, *J* 8.0 Hz, 2H), 2.40 (s, 3H).
4-Methoxylbenzamide[28] **(2c). (table 2, entry 3).** White solid, yield 93%, 70 mg, mp 165-167 °C (lit.[28] 166 °C). ^{1}H NMR (400 MHz, DMSO-*d*6 /TMS): δ 7.75 (2 H, *d* = 8.0 Hz) 7.17 (s, 2H), 7.08 (2 H, d, *J* 8.0 Hz), 3.80 (s, 3H).
4-Chlorobenzamide[29] **(2d). (table 2, entry 3).** White solid, yield 92%, 72 mg, mp 178-180 °C (lit.[29] 180 °C). ^{1}H NMR (400 MHz, DMSO-*d*6 /TMS): δ 8.08 (s, 1H), δ 7.89 (d, *J* 8.0 Hz, 2H), 7.54-7.52 (m, 3H).
4-Fluorobenzamide[30] **(2e). (table 2, entry 4).** White solid, yield 91%, 63 mg, mp 124-126 °C (lit.[30] 123 °C). ^{1}H NMR (400 MHz, DMSO-*d*6 /TMS): δ 8.03 (s, 1H), 7.97-7.93 (m, 2H), 7.45 (s, 1H).7.31-7.26 (m, 2H).
4-Trifluoromethylbenzamide[31] **(2f). (table 2, entry 5).** White solid, yield 95%, 90 mg, mp 183-185 °C (lit.[31] 185-188 °C). ^{1}H NMR (400 MHz, DMSO-*d*6 /TMS): δ 8.16 (s, 1H), 8.07 (d, *J* 8.0 Hz, 2H), 7.83 (d, *J* 8.0 Hz, 2H), 7.58 (s, 1H).
3-Methylbenzamide[32] **(2g). (table 2, entry 6)** White solid, yield 86%, 58 mg, mp 93-95 °C (lit.[32] 93-94 °C). ^{1}H NMR (400 MHz, DMSO-*d*6 /TMS): δ 7.88 (s, 1H), 7.70-7.66 (m, 2H), 7.33 (m, 2H), 7.26 (s, 1H).
2-Chlorobenzamide[33] **(2h). (table 2, entry 7).** White solid, yield 88%, 68 mg, mp 139-141 °C (lit.[33] 141 °C). ^{1}H NMR (400 MHz, DMSO-*d*6 /TMS): δ 7.90 (s, 1H), δ 7.61 (s, 1H), 7.50-7.36 (m, 4H).
Naphthalene-2-carboxylic acid amide[34] **(2i). (table 2, entry 8).** White solid, yield 84%, 72 mg, mp 194-196 °C (lit.[34] 195 °C). ^{1}H NMR (400 MHz, DMSO-*d*6 /TMS): δ 8.48 (s, 1H), 7.97 (m, 5H), 7.60 (m, 2H), 7.42 (s, 1H).
Thiophene-2-carboxylic acid amide[35] **(2j). (table 2, entry 9).** White solid, yield 96%, 32 mg, mp 147-149 °C (lit.[35] 147°C). ^{1}H NMR (400 MHz, DMSO /TMS): δ 7.92 (s, 1H), 7.73 (d, *J* 8.0 Hz, 2H), 7.33 (m, 1H), 7.13 (s, 1H).

Acknowledgements

We are grateful for the financial support of Science and Technology Planning Project of Jiangxi Province, China (20142BAB203007).

References

1. Zabicky, J. *The Chemistry of Amides, ed.* Wiley-Interscience, New York, 1970.
2. Loudon, M. G. *Organic Chemistry*; Oxford University Press: New York, NY, 2002; p982,

3. Carey, J. S.; Laffan, D.; Thomson, C.; Williams, M. T. *Org. Biomol. Chem.* **2006**, *4*, 2337. http://dx.doi.org/10.1039/B602413K
4. Mebermann, C. E. *Encyclopedia of Chemical Technology*, Wiley: New York, 1991, Vol. 1; p 251.
5. Chen, S. T.; Wu, S. H.; Wang, K. T. *Synthesis* **1989**, 37. http://dx.doi.org/10.1055/s-1989-27139
6. Gawley, R. E. *Org. React.* **1988**, *35*, 1. http://dx.doi.org/10.1002/0471264180
7. De Luca, L.; Giacomelli, G.; Porcheddu, A. *J. Org. Chem.* **2002**, *67*, 6272. http://dx.doi.org/10.1021/jo025960d
8. Schuerch, C.; Huntress, E. H. *J. Am. Chem. Soc.* **1949**, *71*, 2233. http://dx.doi.org/10.1021/ja01174a087
9. Gunanathan, C.; Ben-David, Y.; Milstein, D. *Science* **2007**, *317*, 790. http://dx.doi.org/10.1126/science.1145295
10. Wang, Y.; Zhu, D.; Tang, L.; Wang, S.; Wang, Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 8917. http://dx.doi.org/10.1002/anie.201102374
11. Yamaguchi, K.; Matsushita, M.; Mizuno, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 1576. http://dx.doi.org/10.1002/anie.200353461
12. Fujiwara, H.; Ogasawara, Y.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 5202. http://dx.doi.org/10.1002/anie.200701273
13. Fujiwara, H.; Ogasawara, Y.; Kotani, M.; Yamaguchi, K; Mizuno, N. *Chem. Asian J.* **2008**, *3*, 1715.
14. Kotha, S. S.; Badigenchala, S.; Sekar, G. *Adv. Synth. Catal.* **2015**, *357*, 1437. http://dx.doi.org/10.1002/adsc.201401086
15. Ouyang, K.; Hao, W.; Zhang, W.; Xi, Z. *Chem. Rev.* **2015**, *115*, 12045. http://dx.doi.org/10.1021/acs.chemrev.5b00386
16. Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255. http://dx.doi.org/10.1021/ar020230d
17. Gooßen, L. J.; Rudolphi, F.; Oppel, C.; Rodríguez, N. *Angew. Chem., Int. Ed.*, **2008**, *47*, 3043. http://dx.doi.org/10.1002/anie.200705127
18. Huang, H.; Jia, K.; Chen, Y. *Angew. Chem., Int. Ed.*, **2015**, *54*, 1881. http://dx.doi.org/10.1002/anie.201410176
19. Ranganathan, D.; Vaish, N. K.; Shah, K. *J. Am. Chem. Soc.* **1994**, *116*, 6545. http://dx.doi.org/10.1021/ja00094a008
20. Hellwig, M.; Löbmann, K.; Orywol, T. *J. Pept. Sci.* **2015**, *21*, 17. http://dx.doi.org/10.1002/psc.2713
21. Kuang, L.; Zhou, J.; Chen, S.; Ding, K. *Synthesis*, **2007**, *20*, 3129. http://dx.doi.org/10.1055/s-2007-990795

22. Easton, C. J.; Eichinger, S. K.; Pitt, M. J. *Tetrahedron*, *1997*, 53, 5609. http://dx.doi.org/10.1016/S0040-4020(97)00216-0
23. 23 Lucchesi, C.; Arboré, A.; Pascual, S.; Fontaine, L.; Maignan, C.; Dujardin, G. *Carbohydr. Res.*, **2010**, *345*, 844. http://dx.doi.org/10.1016/j.carres.2010.01.017
24. Jiang, W.; Costa, S. P. G.; Maia, H. L. S. *Org. Biomol. Chem.*, **2003**, *1*, 3804. http://dx.doi.org/10.1039/B307111C
25. Chattopadhyay, G.; Chakraborty, S.; Saha C. *Syn. Commun.*, **2008**, *38*, 4068. http://dx.doi.org/10.1080/00397910802250929
26. Muhammad, A. M.; Shagufta, R.; Khalid, M. K.; Ullah, Z.; Muhammad, I. C.; Shahnaz, M.; Zakiah, I.; Rahman, A.; Aqeel, A. *Bioorg. Med. Chem.*, **2004**, *12*, 2049. http://dx.doi.org/10.1016/j.bmc.2004.02.034
27. Schröder, J.; Henke, A.; Wenzel,H.; Brandstetter, H.; Stammler, H. G.; Stammler, A.; Pfeiffer, W. D.; Tschesche, H. *J. Med. Chem.*, **2001**, *44*, 3231. http://dx.doi.org/10.1021/jm010887p
28. Sharghi, H.; Sarvari, M. H. *Tetrahedron* **2002**, *58*, 10323. http://dx.doi.org/10.1016/S0040-4020(02)01417-5
29. Bhagwat, V. K.; Moore, D. K.; Pyman, F. L.; Kao, C. H.; Ma, S.; Simonsen, J. L.; Hewitt, J. T.; Lewcock, W. *J. Chem. Soc.*, **1931**, 443.
30. Quan, M. L.; Ellis, C. D.; He, M. Y.; Liauw, A. Y.; Woerner, F. J.; Alexander, R. S.; Knab, R. M.; Lam, P. Y. S.; Luettgen, J. M.; Wong, P. C.; Wright, M. R.; Wexler, R. R. *Bioorg. Med. Chem. Lett.*, **2003**, *13*, 369. http://dx.doi.org/10.1016/S0960-894X(02)00951-4
31. Christensen, J. J.; Rytting, J. H.; Izatt, R. M., *J. Chem. Soc.*, **1969**, 861. http://dx.doi.org/10.1039/J39690000861
32. Sansone, M. F.; Koyanagi, T.; Przybyla, D. E.; Nagorski, R. W. *Tetrahedron Lett.*, **2010**, *51*, 6031. http://dx.doi.org/10.1016/j.tetlet.2010.09.043
33. Poeschl, A.; Mountford, D. M. *Org. Biomol. Chem.*, *2014*, *12*, 7150. http://dx.doi.org/10.1039/C4OB01166J
34. Hanada, S.; Motoyama, Y.; Nagashima, H. *Eur. J. Org. Chem.*, **2008**, 4097. http://dx.doi.org/10.1002/ejoc.200800523
35. Maurin, P.; Ibrahim-Ouali, M.; Santelli, M. *Tetrahedron Lett.*, **2001**, *42*, 847. http://dx.doi.org/10.1016/S0040-4039(00)02119-5

