Synthesis Y. Ou et al. Special Topic

An Iron-Catalyzed Direct Approach to Amides from Benzyl Azides via C–C Bond Cleavage

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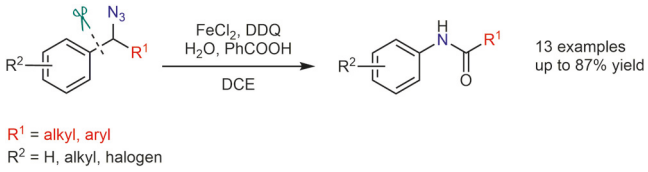

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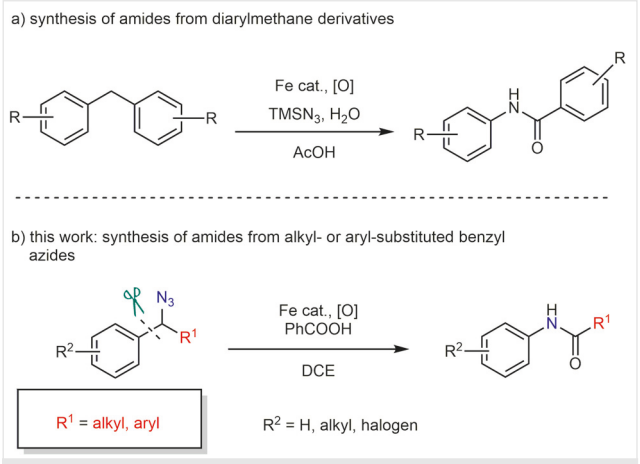
Abstract A novel iron-catalyzed transformation of benzyl azides to give the corresponding amides via C–C bond cleavage under mild reaction conditions is developed. This method provides a new synthetic tool for the construction of amides and the opportunity to accomplish C–C functionalization under mild conditions.

Key words C–C bond cleavage, azides, amides, rearrangement

Amides are versatile building blocks in synthetic organic chemistry, and are found in a wide number of biologically active molecules and natural products.[1] They are commonly formed via reactions of carboxylic acids with amines. However, the unification of these two functional groups does not occur spontaneously at ambient temperature. For the most part, these reactions require the activation of the carboxylic acid partner by coupling agents such as acid chlorides, anhydrides, carbonic anhydrides or active esters. Although these methods are easily performed and highly efficient, the conditions are usually harsh involving the use of toxic, corrosive and/or expensive coupling reagents, with poor atom economy.[2] Hence, the development of new methods for the synthesis of amides is still attractive.

Significant progress has been made on the direct approach to nitrogen-containing compounds proceeding through transition-metal-catalyzed selective C–H[3] and C–C[4] bond cleavage. Among the various nitrogen sources utilized for amide synthesis, organic azides have attracted considerable attention for reasons of high atom economy. Aubé et al. have developed Lewis acid mediated Schmidt reactions of ketones with 2-azidoethanols or 3-azidopropanols for the synthesis of amides.[5] Chang has reported copper-catalyzed hydrative amide synthesis by employing sulfonyl azides.[6] In addition, our group has realized the gold-catalyzed nitrogenation of alkynes to give amides, promoted by Brønsted acids.[7] Hong and co-workers have developed a ruthenium N-heterocyclic carbene (NHC) catalyzed synthesis of amides from organic azides and alcohols.[8] Furthermore, an elegant synthesis of amides from vinyl azides and imines was reported by Chiba.[9] Recently, our group demonstrated iron-catalyzed C–H and C–C bond cleavage of benzyl hydrocarbons for the synthesis of amides (Scheme 1, a).[10] However, despite the novelty of this transformation, only diarylmethane and 1,3-diphenylpropene substrates were tolerated. In order to prepare an *N*-acylaniline via this strategy, and further, to prove the mechanism of the nitrogenation reaction,[10] we envisioned that alkyl-substituted azides would show potential as precursors for the synthesis of amides. Herein, we describe an iron-catalyzed oxidative rearrangement of alkyl-substituted benzyl azides for the direct preparation of *N*-acylanilines (Scheme 1, b).



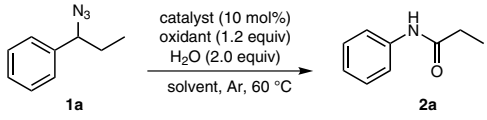
Scheme 1 Synthesis of amides from: (a) benzyl hydrocarbons, and (b) organic azides

We commenced our studies by employing (1-azidopropyl)benzene (**1a**) as a model substrate in order to optimize the reaction conditions (Table 1). Treatment of (1-azidopropyl)benzene (**1a**) with water (2.0 equiv), iron(II) chloride ($FeCl_2$) (10 mol%) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.2 equiv) in acetic acid[10] at 60 °C resulted in a 15% yield of the desired product, *N*-phenylpropionamide (**2a**) (Table 1, entry 1). Solvent screening showed that 1,2-dichloroethane (DCE) was the most efficient for this transformation (Table 1, entries 2–6). Next, we examined the effects of different catalysts on this reaction. Iron(II) bromide ($FeBr_2$), iron(III) bromide ($FeBr_3$) and copper(II) triflate [$Cu(OTf)_2$] led to low yields of **2a** (Table 1, entries 7–9). Several common oxidants, including *tert*-butyl hydroperoxide (TBHP), cerium(IV) ammonium nitrate (CAN) and phenyliodonium diacetate (PIDA), showed low efficiencies in this reaction (Table 1, entries 10–12).

In our previous studies, we found that the addition of an appropriate Brønsted acid usually played an important role in the reaction system.[4e,7,10] Hence, Brønsted acids such as acetic acid (AcOH), trifluoroacetic acid (TFA) and benzoic acid (PhCOOH) were employed to test their activity. Gratifyingly, it was found that the reaction could be performed in good yield when benzoic acid was employed as an additive (Table 1, entry 15). After extensive screening of other parameters, the optimum reaction conditions were determined as follows: benzyl azide (0.5 mmol, 1.0 equiv), iron(II) chloride (10 mol%), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.2 equiv), water (2.0 equiv), benzoic acid (5.0 equiv), 60 °C, argon atmosphere.

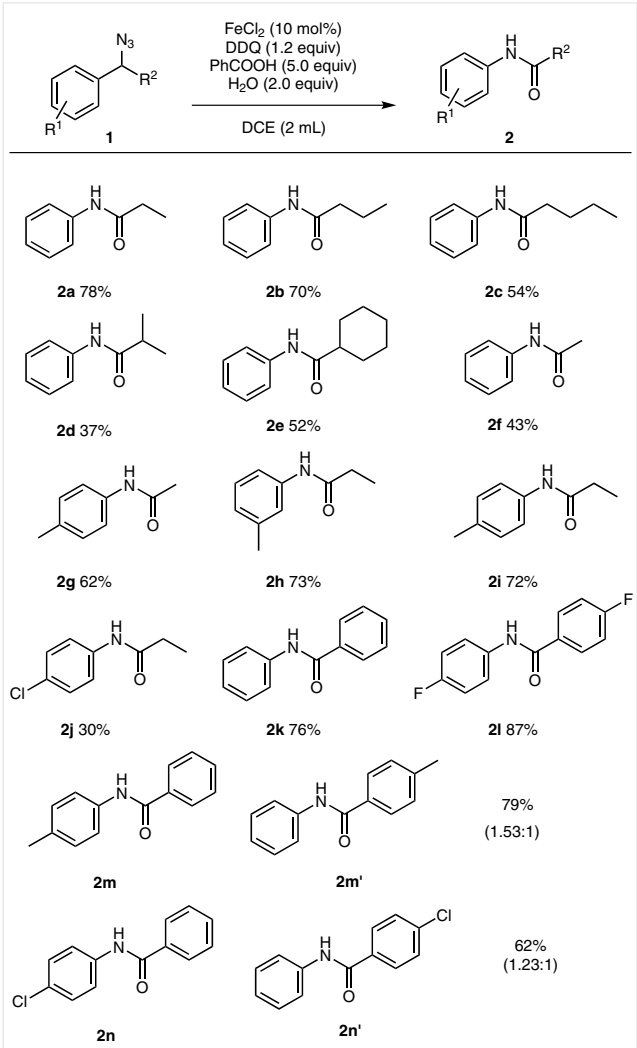
With optimized reaction conditions in hand, we next explored the scope of this reaction using various alkyl- and aryl-substituted benzyl azides (Scheme 2). Benzyl azides with different alkyl groups (ethyl, propyl, butyl, isopropyl, cyclohexyl and methyl) were transformed into the corresponding amides (**2a**–**j**) in moderate to good yields. In our previous study,[10] only benzanilides were accessible via the

Table 1 Optimization of the Reaction Conditions[a]

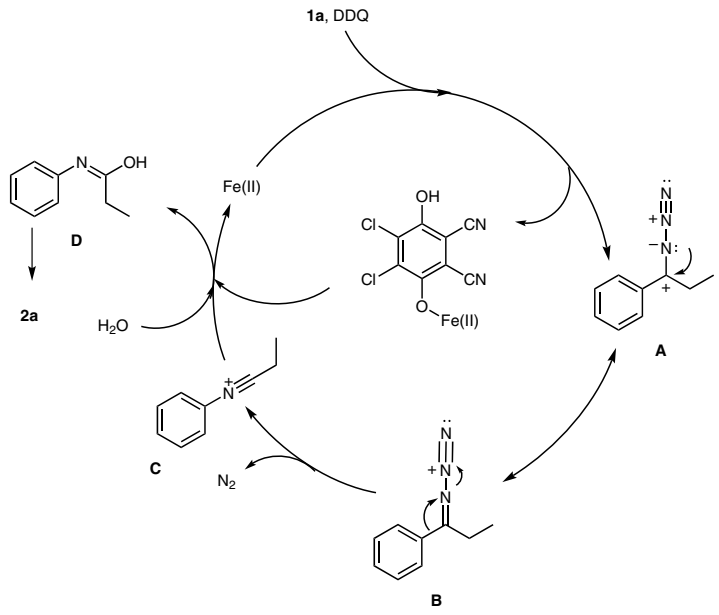


Entry	Catalyst	Oxidant	Solvent	Acid	Yield (%)[b]
1	$FeCl_2$	DDQ	AcOH	–	15
2	$FeCl_2$	DDQ	MeCN	–	<5
3	$FeCl_2$	DDQ	toluene	–	<5
4	$FeCl_2$	DDQ	DCE	–	51
5	$FeCl_2$	DDQ	DMF	–	0
6	$FeCl_2$	DDQ	DMSO	–	0
7	$FeBr_2$	DDQ	DCE	–	35
8	$FeBr_3$	DDQ	DCE	–	32
9	$Cu(OTf)_2$	DDQ	DCE	–	32
10	$FeCl_2$	TBHP	DCE	–	0
11	$FeCl_2$	CAN	DCE	–	0
12	$FeCl_2$	PIDA	DCE	–	0
13	$FeCl_2$	DDQ	DCE	AcOH	50
14	$FeCl_2$	DDQ	DCE	TFA	18
15	**$FeCl_2$**	**DDQ**	**DCE**	**PhCOOH**	**78**
16	$FeCl_2$	DDQ	DCE	4-$MeOC_6H_4COOH$	71
17	$FeCl_2$	DDQ	DCE	4-$O_2NC_6H_4COOH$	52

[a] Reaction conditions: **1a** (0.5 mmol), H_2O (1.0 mmol, 2.0 equiv), catalyst (0.05 mmol, 10 mol%), oxidant (0.6 mmol, 1.2 equiv), solvent (2 mL), 60 °C, Ar, 12 h.
[b] Yield of isolated product.



Scheme 2 Substrate scope of the $FeCl_2$-catalyzed synthesis of amides from benzyl azides. *Reaction conditions*: benzyl azide **1** (0.5 mmol), H_2O (1.0 mmol, 2.0 equiv), $FeCl_2$ (0.05 mmol, 10 mol%), DDQ (0.6 mmol, 1.2 equiv), PhCOOH (5.0 equiv), DCE (2 mL), 60 °C, Ar, 12 h.



Scheme 3 Proposed mechanism for the $FeCl_2$-catalyzed synthesis of amides

nitrogenation of diarylmethenes; however, the present strategy has expanded the scope to alkyl-substituted amides. The efficiency of this process was influenced by the nature of the substituents on the aromatic ring. An electron-withdrawing group resulted in a slightly decreased yield, while an electron-donating group increased the yields (see products **2g**–**j**). Satisfactory results were obtained in the reaction of diarylmethyl azides **2k** and **2l**. When unsymmetrical diphenylmethyl azides, such as 1-[azido(phenyl)methyl]-4-methylbenzene (**1m**) and 1-[azido(phenyl)methyl]-4-chlorobenzene (**1n**) were employed, two regioisomeric products (**2m**,**m′** and **2n**,**n′**) were obtained in ratios of 1.53:1 and 1.23:1, respectively.

On the basis of our previous work, a tentative reaction mechanism is shown in Scheme 3. Initially, the oxidation of **1a** by the iron/2,3-dichloro-5,6-dicyano-1,4-benzoquinone oxidative system, assisted by the azido group,[11] affords the corresponding benzylic azide cation **A**. Subsequent isomerization of this benzylic azide cation leads to intermediate **B**. Next, a Beckmann rearrangement occurs with migration of the phenyl group from carbon to the adjacent nitrogen to generate nitrile cation **C**. Subsequent nucleophilic attack of water leads to the intermediate **D**, isomerization of which gives the final product **2a**.[12]

In summary, we have reported a novel iron-catalyzed transformation of benzyl azides into the corresponding amides via C–C bond cleavage under mild reaction conditions. The inclusion of benzoic acid in the reaction is very important to improve the efficiency of this transformation. Compared to our previous work, this method expands the product scope to benzanilides and *N*-phenylalkylamides. Nitrogen is the only by-product of this transformation, which demonstrates good atom economy. This procedure not only provides a new synthetic tool for amide construction, but also permits C–C functionalization under mild conditions.

All reactions were carried out under an inert atmosphere with anhydrous solvents under anhydrous conditions unless otherwise stated. Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. Chemicals obtained from commercial suppliers were used without further purification unless otherwise noted. All manipulations were conducted in Schlenk tubes. Column chromatography was performed using Qingdao Ocean brand silica gel (200–300 mesh). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) are referenced to $CDCl_3$ or DMSO-d_6. Low-resolution mass spectra were obtained using an Agilent PE SCLEX QSTAR GC-MS instrument.

N-Phenylpropionamide (2a);[13] Typical Procedure

To a Schlenk tube (25 mL) were added sequentially $FeCl_2$ (6.3 mg, 0.05 mmol), DDQ (136 mg, 0.6 mmol), PhCOOH (305 mg, 2.5 mmol), (1-azidopropyl)benzene (**1a**) (80.5 mg, 0.5 mmol), H_2O (18 μL, 1.0 mmol) and dry DCE (2 mL). The resulting mixture was stirred at 60 °C under an argon atmosphere for 24 h. The mixture was filtered, concentrated and purified by flash chromatography on silica gel (PE–EtOAc, 10:1) to afford amide **2a**.

Yield: 58.1 mg (78%); white solid; mp 106–108 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.84 (s, 1 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 7.28 (t, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 7.6 Hz, 1 H), 2.39–2.27 (m, 2 H), 1.10 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.5, 139.9, 129.1, 123.3, 119.5, 30.0, 10.1.

MS (EI, 70 eV): *m*/*z* (%) = 149.0 (100) $[M]^+$.

***N*-Phenylbutyramide (2b)**[7]

Yield: 57.1 mg (70%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.83 (s, 1 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 7.27 (t, *J* = 8.0 Hz, 2 H), 7.01 (t, *J* = 7.6 Hz, 1 H), 2.28 (t, *J* = 7.6 Hz, 2 H), 1.67–1.53 (m, 2 H), 0.91 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.5, 139.7, 129.7, 123.4, 119.5, 38.8, 19.0, 14.1.

MS (EI, 70 eV): *m*/*z* (%) = 163.0 (100) [M]$^+$.

***N*-Phenylpentanamide (2c)**[14]

Yield: 47.8 mg (54%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.83 (br s, 1 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.27 (t, *J* = 8.0 Hz, 2 H), 7.01 (t, *J* = 7.6 Hz, 1 H), 2.30 (t, *J* = 7.6 Hz, 2 H), 1.61–1.52 (m, 2 H), 1.38–1.25 (m, 2 H), 0.90 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 171.2, 139.2, 128.6, 122.9, 119.0, 36.1, 27.2, 21.8, 13.7.

MS (EI, 70 eV): *m*/*z* (%) = 177.0 (100) [M]$^+$.

***N*-Phenylisobutyramide (2d)**[14]

Yield: 30.2 mg (37%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.81 (br s, 1 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 7.29 (t, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 7.6 Hz, 1 H), 2.60 (t, *J* = 7.6 Hz, 1 H), 1.10 (d, *J* = 7.2 Hz, 6 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 175.2, 139.4, 128.6, 122.9, 119.1, 34.9, 19.5.

MS (EI, 70 eV): *m*/*z* (%) = 163.0 (100) [M]$^+$.

***N*-Phenylcyclohexanecarboxamide (2e)**[15]

Yield: 52.9 mg (52%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.77 (s, 1 H), 7.61 (d, *J* = 7.6 Hz, 2 H), 7.28 (t, *J* = 7.6 Hz, 2 H), 7.01 (t, *J* = 7.6 Hz, 1 H), 2.36–2.29 (m, 1 H), 1.81–1.75 (m, 4 H), 1.67–1.64 (m, 1 H), 1.46–1.38 (m, 2 H), 1.32–1.17 (m, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 174.8, 140.0, 129.0, 123.3, 119.5, 45.3, 29.6, 25.9, 25.7.

MS (EI, 70 eV): *m*/*z* (%) = 203.1 (100) [M]$^+$.

***N*-Phenylacetamide (2f)**[7]

Yield: 29.0 mg (43%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.27 (br s, 1 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.27 (t, *J* = 7.6 Hz, 2 H), 7.08 (t, *J* = 7.6 Hz, 1 H), 2.13 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.9, 138.0, 128.8, 124.2, 120.0, 24.3.

MS (EI, 70 eV): *m*/*z* (%) = 135.0 (100) [M]$^+$.

***N*-(*p*-Tolyl)acetamide (2g)**[14]

Yield: 46.2 mg (62%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.77 (br s, 1 H), 7.37 (d, *J* = 7.6 Hz, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 2.30 (s, 3 H), 2.13 (s, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.6, 135.3, 133.8, 129.3, 120.1, 24.3, 20.8.

MS (EI, 70 eV): *m*/*z* (%) = 149.1 (100) [M]$^+$.

***N*-(*m*-Tolyl)propionamide (2h)**[14]

Yield: 59.1 mg (73%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.73 (br s, 1 H), 7.44 (s, 1 H), 7.38 (d, *J* = 7.6 Hz, 1 H), 7.15 (t, *J* = 8.0 Hz, 1 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 2.35–2.25 (m, 2 H), 2.26 (s, 3 H), 1.08 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.4, 139.7, 138.2, 128.9, 124.1, 120.0, 116.7, 30.0, 21.6, 10.1.

MS (EI, 70 eV): *m*/*z* (%) = 163.0 (100) [M]$^+$.

***N*-(*p*-Tolyl)propionamide (2i)**[14]

Yield: 58.9 mg (72%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.76 (br s, 1 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 2.35–2.23 (m, 2 H), 2.24 (s, 3 H), 1.09 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.2, 137.4, 132.2, 129.5, 119.5, 29.9, 20.8, 10.2.

MS (EI, 70 eV): *m*/*z* (%) = 163.0 (100) [M]$^+$.

***N*-(4-Chlorophenyl)propionamide (2j)**[14]

Yield: 27.3 mg (30%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.98 (br s, 1 H), 7.63 (d, *J* = 8.8 Hz, 2 H), 7.31 (d, *J* = 8.8 Hz, 2 H), 2.39–2.29 (m, 2 H), 1.09 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 172.6, 138.8, 129.0, 126.9, 121.0, 30.0, 10.0.

MS (EI, 70 eV): *m*/*z* (%) = 183.0 (100) [M]$^+$.

***N*-Phenylbenzamide (2k)**[14]

Yield: 74.8 mg (76%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.25 (s, 1 H), 7.96 (d, *J* = 7.6 Hz, 2 H), 7.79 (d, *J* = 8.0 Hz, 2 H), 7.61–7.51 (m, 3 H), 7.36 (t, *J* = 7.6 Hz, 2 H), 7.10 (t, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.0, 139.5, 135.4, 132.0, 129.1, 128.9, 124.1, 120.8.

MS (EI, 70 eV): *m*/*z* (%) = 197.1 (100) [M]$^+$.

4-Fluoro-*N*-(4-fluorophenyl)benzamide (2l)[16]

Yield: 101.3 mg (87%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.31 (br s, 1 H), 8.05–8.02 (m, 2 H), 7.79–7.77 (m, 2 H), 7.40–7.36 (m, 2 H), 7.23–7.19 (m, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.8, 164.6 (d, *J* = 250.0 Hz), 158.8 (d, *J* = 237.5 Hz), 135.9, 131.7, 130.8, 122.7, 115.8 (d, *J* = 25.0 Hz), 115.6 (d, *J* = 12.5 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 233.1 (100) [M]$^+$.

N-(*p*-Tolyl)benzamide (2m) and 4-Methyl-*N*-phenylbenzamide (2m′)[14]

Yield: 83.0 mg (79%); ratio **2m**/**2m′** = 1.53:1; white solid.

2m

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.18 (br s, 1 H), 7.95 (d, *J* = 7.6 Hz, 2 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 7.60–7.48 (m, 3 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 2.28 (s, 3 H).

2m′

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.17 (br s, 1 H), 7.88 (d, *J* = 8.2 Hz, 2 H), 7.79 (d, *J* = 8.2 Hz, 2 H), 7.39–7.30 (m, 4 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 2.39 (s, 3 H).

***N*-(4-Chlorophenyl)benzamide (2n) and 4-Chloro-*N*-phenylbenzamide (2n′)**[14]

Yield: 71.6 mg (62%); ratio **2n**/**2n′** = 1.23:1; white solid.

2n

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.38 (br s, 1 H), 7.96 (d, *J* = 7.6 Hz, 2 H), 7.84 (d, *J* = 8.0 Hz, 2 H), 7.62–7.56 (m, 1 H), 7.56–7.45 (m, 2 H), 7.41 (d, *J* = 8.8 Hz, 2 H).

2n′

^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.32 (br s, 1 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 7.78 (d, *J* = 8.0 Hz, 2 H), 7.60 (d, *J* = 7.2 Hz, 2 H), 7.35 (t, *J* = 7.8 Hz, 2 H), 7.11 (t, *J* = 7.2 Hz, 1 H).

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Supporting Information

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References

(1) (a) Crochet, P.; Cadierno, V. *Chem. Commun.* **2015**, *51*, 2495. (b) Horie, M.; Yamaguchi, I.; Yamamoto, T. *Macromolecules* **2006**, *39*, 7493. (c) Dingledine, R.; Borges, K.; Bowie, D.; Traynelis, S. F. *Pharmacol. Rev.* **1999**, *51*, 7. (d) Wallace, O. B.; Lauwers, K. S.; Jones, S. A.; Dodge, J. A. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 1907. (e) Aramaki, Y.; Seto, M.; Okawa, T.; Kansaki, N.; Shiraishi, M. *Chem. Pharm. Bull.* **2004**, *52*, 254.

(2) (a) Valeur, E.; Bradley, M. *Chem. Soc. Rev.* **2009**, *38*, 606. (b) Han, S.-Y.; Kim, Y.-A. *Tetrahedron* **2004**, *60*, 2447. (c) Montalbetti, C. A. G. N.; Falque, V. *Tetrahedron* **2005**, *61*, 10827. (d) Bode, J. W. *Curr. Opin. Drug Discovery Dev.* **2006**, *9*, 765. (e) Allen, C. L.; Williams, J. M. J. *Chem. Soc. Rev.* **2011**, *40*, 3405. (f) Watson, A. J. A.; Williams, J. M. J. *Science* **2010**, *329*, 635. (g) Ekoue-Kovi, K.; Wolf, C. *Chem. Eur. J.* **2008**, *14*, 6302.

(3) For some recent examples with azides, see: (a) Sharma, A.; Hartwig, J. F. *Nature* **2015**, *517*, 600. (b) Telvekar, V. N.; Sasane, K. A. *Synth. Commun.* **2012**, *42*, 1085. (c) Lubriks, D.; Sokolovs, I.; Suna, E. *J. Am. Chem. Soc.* **2012**, *134*, 15436. (d) Tang, C.; Jiao, N. *J. Am. Chem. Soc.* **2012**, *134*, 18924. (e) Xie, F.; Qi, Z.; Li, X. *Angew. Chem. Int. Ed.* **2013**, *52*, 11862. (f) Fan, Y.; Wan, W.; Ma, G.; Gao, W.; Jiang, H.; Zhu, S.; Hao, J. *Chem. Commun.* **2014**, *50*, 5733. (g) Deng, Q.-H.; Bleith, T.; Wadepohl, H.; Gade, L. H. *J. Am. Chem. Soc.* **2013**, *135*, 5356. (h) Chen, H.; Yang, W.; Wu, W.; Jiang, H. *Org. Biomol. Chem.* **2014**, *12*, 3340. (i) Shin, K.; Baek, Y.; Chang, S. *Angew. Chem. Int. Ed.* **2013**, *52*, 8031. (j) Kim, J. Y.; Park, S. H.; Ryu, J.; Cho, S. H.; Kim, S. H.; Chang, S. *J. Am. Chem. Soc.* **2012**, *134*, 9110. (k) Qin, C.; Jiao, N. *J. Am. Chem. Soc.* **2010**, *132*, 15893. (l) Zheng, Q.-Z.; Feng, P.; Liang, Y.-F.; Jiao, N. *Org. Lett.* **2013**, *15*, 4262. (m) Zhou, W.; Zhang, L.; Jiao, N. *Angew. Chem. Int. Ed.* **2009**, *48*, 7094. (n) Chen, F.; Huang, X.; Cui, Y.; Jiao, N. *Chem. Eur. J.* **2013**, *19*, 11199. (o) Ou, Y.; Jiao, N. *Chem. Commun.* **2013**, *49*, 3473. (p) Li, Z.; Huang, X.; Chen, F.; Zhang, C.; Wang, X.; Jiao, N. *Org. Lett.* **2015**, *17*, 584. (q) Yan, Y.; Yuan, Y.; Jiao, N. *Org. Chem. Front.* **2014**, *1*, 1176. (r) Tang, C.; Jiao, N. *Angew. Chem. Int. Ed.* **2014**, *53*, 6528. (s) Tang, C.; Yuan, Y.; Jiao, N. *Org. Lett.* **2015**, *17*, 2206.

(4) For some recent examples with azides, see: (a) Chen, F.; Qin, C.; Cui, Y.; Jiao, N. *Angew. Chem. Int. Ed.* **2011**, *50*, 11487. (b) Shen, T.; Wang, T.; Qin, C.; Jiao, N. *Angew. Chem. Int. Ed.* **2013**, *52*, 6677. (c) Wang, T.; Jiao, N. *J. Am. Chem. Soc.* **2013**, *135*, 11692. (d) Tang, C.; Jiao, N. *Angew. Chem. Int. Ed.* **2014**, *53*, 6528. (e) Qin, C.; Shen, T.; Tang, C.; Jiao, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 6971.

(5) (a) Katz, C. E.; Aubé, J. *J. Am. Chem. Soc.* **2003**, *125*, 13948. (b) Sahasrabudhe, K.; Gracias, V.; Furness, K.; Smith, B. T.; Katz, C. R.; Reddy, D. S.; Aubé, J. *J. Am. Chem. Soc.* **2003**, *125*, 7914. (c) Desai, P.; Schildknegt, K.; Agrios, K. A.; Mossman, C.; Milligan, G. L.; Aubé, J. *J. Am. Chem. Soc.* **2000**, *122*, 7226. (d) Gracias, V.; Frank, K. E.; Milligan, G. L.; Aubé, J. *Tetrahedron* **1997**, *53*, 16241.

(6) (a) Cho, S. H.; Chang, S. *Angew. Chem. Int. Ed.* **2007**, *46*, 1897. (b) Cho, S. H.; Yoo, E. J.; Bae, I.; Chang, S. *J. Am. Chem. Soc.* **2005**, *127*, 16046.

(7) Qin, C.; Feng, P.; Ou, Y.; Shen, T.; Wang, T.; Jiao, N. *Angew. Chem. Int. Ed.* **2013**, *52*, 7850.

(8) Fu, Z.; Lee, J.; Kang, B.; Hong, S. H. *Org. Lett.* **2012**, *14*, 6028.

(9) Zhang, F.; Wang, Y.; Lonca, G. H.; Zhu, X.; Chiba, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 4390.

(10) Qin, C.; Zhou, W.; Chen, F.; Ou, Y. *Angew. Chem. Int. Ed.* **2011**, *50*, 12595.

(11) Wang, T.; Zhou, W.; Yin, H.; Ma, J.-A.; Jiao, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 10823.

(12) Bach, R. D.; Wolber, G. J. *J. Org. Chem.* **1982**, *47*, 239.

(13) Funder, E. D.; Trads, J. B.; Gothelf, K. V. *Org. Biomol. Chem.* **2015**, *13*, 185.

(14) Xiang, S.-K.; Zhang, D.-X.; Hu, H.; Shi, J.-L.; Liao, L.-G.; Feng, C.; Wang, B.-Q.; Zhao, K.-Q.; Hu, P.; Yang, H.; Yu, W.-H. *Adv. Synth. Catal.* **2013**, *355*, 1495.

(15) Ueda, S.; Nagasawa, H. *J. Org. Chem.* **2009**, *74*, 4272.

(16) Xu, M.; Zhang, X.-H.; Shao, Y.-L.; Han, J.-S.; Zhong, P. *Adv. Synth. Catal.* **2012**, *354*, 2665.