JOC Article
pubs.acs.org/joc

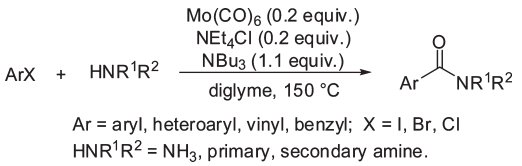
$Mo(CO)_6$-Mediated Carbamoylation of Aryl Halides

Wei Ren and Motoki Yamane*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore

yamane@ntu.edu.sg

Received August 19, 2010



A simple method for the synthesis of amides has been developed by molybdenum-mediated carbamoylation of aryl halides. Whereas the conventional palladium-catalyzed three-component coupling reaction requires a large excess of gaseous carbon monoxide, the incorporation of carbon monoxide in this Mo-mediated carbamoylation reaction is so efficient that it requires only a slight excess amount of carbon monoxide in the form of its molybdenum complex, $Mo(CO)_6$. The reaction is applicable for the synthesis of a wide variety of not only secondary and tertiary amides but also primary amides by using aqueous ammonia.

Introduction

It is well known that the palladium-catalyzed three-component coupling reaction between aryl halides, carbon monoxide, and amines is a very powerful synthetic method to prepare amides.[1] Various secondary and tertiary amides are prepared from aryl halides with one-carbon elongation by this method. However, it is necessary to use a large excess amount of carbon monoxide because the reaction takes place under gaseous carbon monoxide and sometimes high pressure is required. Recently, it was reported that group VI metal carbonyl complexes such as $Mo(CO)_6$ could be used as the sources of carbon monoxide in the reaction under microwave irradiation.[2] Nevertheless, it still requires a large excess of metal carbonyl complexes calculated on the basis of the stoichiometric amount of carbon monoxide.[3,4] In 1969, Corey and Hegedus reported the synthesis of amides in the reaction between aryl halides, $Ni(CO)_4$, and amines.[3h] Although it required 6 molar amounts of $Ni(CO)_4$, it is noteworthy that nickel carbonyl complex can also serve as a mediator to form carbon−carbon and carbon−nitrogen bonds, apart from being the source of carbon monoxide. Recently, our group reported the carbamoylation of aryl halides by using group VI metal amine carbonyl complexes (Scheme 1).[5] The results indicated that group VI metal carbonyl complexes as expected

(1) For selected reviews, see: (a) Schoenberg, A.; Bartoletti, I.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3318. (b) Schoenberg, A.; Heck, R. F. *J. Org. Chem.* **1974**, *39*, 3327. (c) Schoenberg, A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 7761. (d) Barnard, C. F. J. *Organometallics* **2008**, *27*, 5402. (e) Yasui, Y.; Takemoto, Y. *Chem. Rec.* **2008**, *8*, 386. (f) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318.

(2) (a) Wannberg, J.; Larhed, M. *J. Org. Chem.* **2003**, *68*, 5750. (b) Georgsson, J.; Hallberg, A.; Larhed, M. *J. Comb. Chem.* **2003**, *5*, 350. (c) Wu, X.; Mahalingam, A. K.; Wan, Y. Q.; Alterman, M. *Tetrahedron Lett.* **2004**, *45*, 4635. (d) Herrero, M. A.; Wannberg, J.; Larhed, M. *Synlett* **2004**, 2335. (e) Yamazaki, K.; Kondo, Y. *J. Comb. Chem.* **2004**, *6*, 121. (f) Wu, X.; Rönn, R.; Gossas, T.; Larhed, M. *J. Org. Chem.* **2005**, *70*, 3094. (g) Cao, H.; Xiao, W. J. *Can. J. Chem.* **2005**, *83*, 826. (h) Wannberg, J.; Dallinger, D.; Kappe, C. O.; Larhed, M. *J. Comb. Chem.* **2005**, *7*, 574. (i) Wannberg, J.; Kaiser, N.-F. K.; Vrang, L.; Samuelsson, B.; Larhed, M.; Hallberg, A. *J. Comb. Chem.* **2005**, *7*, 611. (j) Wu, X.; Larhed, M. *Org. Lett.* **2005**, *7*, 3327. (k) Lagerlund, O.; Larhed M. *J. Comb. Chem.* **2006**, *8*, 4. (l) Wu, X.; Ekegren, J. K.; Larhed, M. *Organometallics* **2006**, *25*, 1434. (m) Wu, X.; Wannberg, J.; Larhed, M. *Tetrahedron* **2006**, *62*, 4665. (n) Gold, H.; Ax, A.; Vrang, L.; Samuelsson, B.; Karlén, A.; Hallberg, A.; Larhed, M. *Tetrahedron* **2006**, *62*, 4671. (o) Letavic, M. A.; Ly, K. S. *Tetrahedron Lett.* **2007**, *48*, 2339.

(3) For using aldehyde as the substitute for CO gas, see: (a) Morimoto, T.; Fujioka, M.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. *Chem. Lett.* **2003**, *32*, 154. (b) Morimoto, T.; Fujioka, M.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. *J. Organomet. Chem.* **2007**, *692*, 625. For using formamide, see: (c) Wan, Y. Q.; Alterman, M.; Larhed, M.; Hallberg, A. *J. Comb. Chem.* **2003**, *5*, 82. For using dimethylformamide, see: (d) Hosoi, K.; Nozaki, K.; Hiyama, T. *Org. Lett.* **2002**, *4*, 2849. (e) Wan, Y. Q.; Alterman, M.; Larhed, M.; Hallberg, A. *J. Org. Chem.* **2002**, *67*, 6232. (f) Ju, J.; Jeong, M.; Moon, J.; Jung, H. M.; Lee, S. *Org. Lett.* **2007**, *9*, 4615. (g) Tambade, P. J.; Patil, Y. P.; Bhanushali, M. J.; Bhanage, B. M. *Tetrahedron Lett.* **2008**, *49*, 2221. For using $Ni(CO)_4$, see: (h) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 1233. For using group VI metal carbonyl complexes, see ref 2.

(4) Just after the submission of our manuscript, Roberts and co-workers reported molybdenum-mediated carbonylation of aryl halides using microwave irradiation. See: Roberts, B.; Liptrot, D.; Alcaraz, L.; Luker, T.; Stocks, M. J. *Org. Lett.* **2010**, *12*, 4280.

(5) Ren, W.; Yamane, M. *J. Org. Chem.* **2010**, *75*, 3017.

Published on Web 11/18/2010 DOI: 10.1021/jo101611g

SCHEME 1. Carbamoylation of Aryl Halides by Molybdenum Carbonyl Amine Complexes

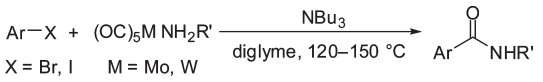
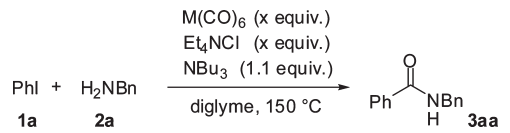


TABLE 1. Group VI Metal Carbonyl Complex-Mediated Carbamoylation of Phenyl Iodide[a]



entry	M	*x* (equiv)	time (h)	yield (%)
1	W	1.0	12	90
2[b]	W	1.0	20	13
3	Mo	1.0	3	97
4	Mo	0.2	3	97
5	Mo	0.167	3	85

[a]The reactions were carried out in the molar ratio of H_2NBn/PhI/NBu_3 = 1.0:1.2:1.1. [b]Reaction without Et_4NCl.

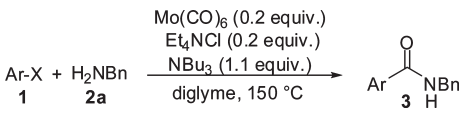
can used as both carbon monoxide source and the catalyst as well in the mechanistic cycle.[6] We considered that the amount of metal carbonyl complex could be reduced if the metal carbonyl amine complex was generated *in situ* in the reaction conditions. Herein, we present a simple and efficient amide synthesis with a low loading of $Mo(CO)_6$, which is used as both the catalyst and the carbon monoxide source.

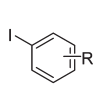
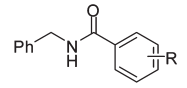
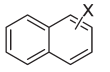
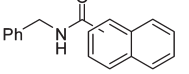
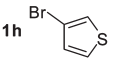
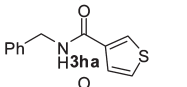
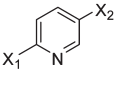
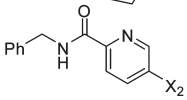
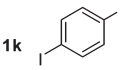
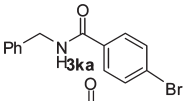
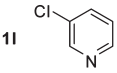
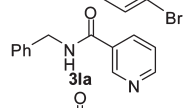
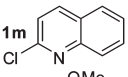
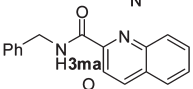
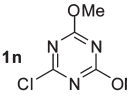
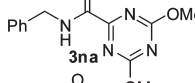
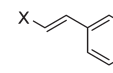
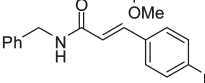
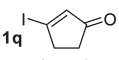
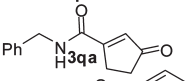
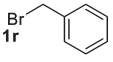
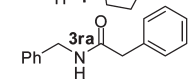
Group VI metal amine carbonyl complexes are known to be prepared from amine and $(CO)_5MClNEt_4$ (M = Cr, Mo, W),[7] which is readily obtained by subjecting $M(CO)_6$ to Et_4NCl. Thus, we first examined carbamoylation of phenyl iodide with $M(CO)_6$ and amine (Table 1). When $W(CO)_6$ (1 equiv) was treated with phenyl iodide and benzylamine in the presence of Et_4NCl and NBu_3, 90% yield of amide **3aa** was obtained (entry 1). The yield of the amide was decreased to 13% in the absence of Et_4NCl (entry 2). The reaction with $Mo(CO)_6$ showed an efficient conversion and **3aa** was obtained in 97% yield (entry 3). Interestingly, the yield of **3aa** was not affected even when the amount of $Mo(CO)_6$ was decreased to 0.2 equiv (entry 4). It is noteworthy that 0.167 equiv of $Mo(CO)_6$, which involves a stoichiometric amount of CO, gave 85% yield of amide **3aa** (entry 5). These results explain the high efficiency of the catalyst to incorporate its CO ligand into the amide product.

Results and Discussion

As we found that the carbamoylation of phenyl iodide with 0.2 equiv of $Mo(CO)_6$ sufficiently proceeded, we then investigated the scope of aryl halides for this reaction (Table 2). Regardless of the electronic property of the substituents and

TABLE 2. Scope of Aryl Halides for $Mo(CO)_6$-Mediated Carbamoylation Reaction[a]



entry	Ar-X	product	Time/h	yield/%
				
1	**1a**: R = H	**3aa**	3	97
2	**1b**: R = 4-OMe	**3ba**	4	96
3	**1c**: R = 3-OMe	**3ca**	2	99
4	**1d**: R = 2-OMe	**3da**	4	91
5	**1e**: R = 4-Ac	**3ea**	4	95
				
6	**1f**: X = 1-I	**3fa**	1	93
7	**1g**: X = 2-Br	**3ga**	2	97
8	 **1h**	 **3ha**	2	94
				
9[b]	**1i**: X_1 = Br, X_2 = H	**3ia**	0.5	45
10[c]	**1i'**: X_1 = Cl, X_2 = H	**3ia**	1	35
11[d]	**1j**: X_1 = Cl, X_2 = I	**3ja**	2	53
12	 **1k**	 **3ka**	1	76
13	 **1l**	 **3la**	7	trace
14[b]	 **1m**	 **3ma**	0.5	61
15	 **1n**	 **3na**	2	77
				
16[e]	**1o**: X = Br, R = H	**3oa**	0.5	85
17[b]	**1p**: X = Br, R = CF_3	**3pa**	0.5	77
18[f]	 **1q**	 **3qa**	0.5	72
19	 **1r**	 **3ra**	4	52

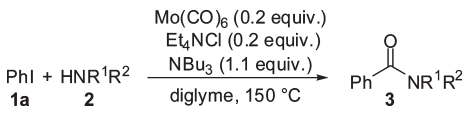
[a]The reactions were carried out with **1** (0.60 mmol), **2a** (0.50 mmol), and NBu_3 (0.55 mmol) in diglyme at 150 °C unless otherwise stated. [b]The reaction temperature is 90 °C. [c]The reaction temperature is 140 °C. [d]The reaction temperature is 120 °C. [e]The reaction temperature is 80 °C. [f]The reaction temperature is 100 °C.

substitution positions on the phenyl ring, the corresponding amides were obtained in excellent yields (entries 1−5). The naphthalenyl halides and heteroaromatic halides were also applicable for this reaction, and the corresponding amides were obtained (entries 6−11, 14, and 15). When 1-bromo-4-iodobenzene was used, selective carbamoylation proceeded to give *p*-bromobenzamide **3ka** (entry 12). Interestingly, when 2-chloro-5-iodopyridine was used, *N*-benzyl-5-iodopicolinamide **3ja** was obtained as the product in 53% yield instead of the expected

(6) For oxidative addition of sp^2-carbon halogen bond to molybdenum or tungsten carbonyl complexes, see: (a) Richmond, T. G.; King, M. A.; Kelson, E. P.; Arif, A. M. *Organometallics* **1987**, *6*, 1995. (b) Buffin, B. P.; Arif, A. M.; Richmond, T. G. *J. Chem. Soc., Chem. Commun.* **1993**, 1432. (c) Kiplinger, J. L.; Richmond, T. G. *Polyhedron* **1997**, *16*, 409. (d) Sangu, K.; Watanabe, T.; Takaya, J.; Iwasawa, N. *Synlett* **2007**, *6*, 929. (e) Takaya, J.; Sangu, K.; Iwasawa, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 7090.

(7) Schenk, W. A. *J. Organomet. Chem.* **1979**, *179*, 253.

TABLE 3. Scope of Amines for $Mo(CO)_6$-Mediated Carbamoylation Reaction[a]



entry	R^1R^2NH	product	time/h	yield/%
1	**2a**: R = H	**3aa**	3	97
2	**2b**: R = OMe	**3ab**	2	92
3	**2c**: R = H	**3ac**	4	79
4	**2d**: R = CO_2Me	**3ad**	7	64
5	**2e**: R = OMe	**3ae**	4	85
6[b]	**2f**: R = *n*-butyl	**3af**	2	97
7[b]	**2g**: R = *tert*-butyl	**3ag**	2	90
8[b]	**2h**: R = cyclopropyl	**3ah**	3	75
9[b]	**2i**: R = cyclohexyl	**3ai**	5	89
10[b]	**2j**: n = 1	**3aj**	7	83
11[b]	**2k**: n = 2	**3ak**	6	90
12[c]	**2l**: R^1 = Me, R^2 = benzyl	**3al**	3	91
13[b]	**2m**: R^1, R^2 = ethyl	**3am**	4	53
14[b]	**2n**	**3an**	3	63
15	**2o**	**3ao**	6	60
16	**2p**	**3ap**	6	64

[a]The reactions were carried out in diglyme at 150 °C with **1a** (0.60 mmol), **2** (0.50 mmol), and NBu_3 (0.55 mmol) unless otherwise mentioned. [b]The reaction was carried out with a 1:5 ratio of **1a** (0.5 mmol) and **2** (2.5 mmol). [c]The reaction was carried out with a 1:2 ratio of **1a** (0.5 mmol) and **2** (1.0 mmol).

product, *N*-benzyl-6-chloronicotinamide (entry 11).[8] 3-Chloropyridine, on the contrary, gave only a trace amount of amide **3la** despite longer reaction time (entry 13). These results suggest that the chelation-assisted oxidative addition of 2-chloropyridine to the molybdenum intermediate enhanced the reaction and gave higher yield.[9] The reaction with alkenyl halides **1o** and **1p** proceeded at lower temperatures (80−100 °C), to give the corresponding α,β-unsaturated amides **3oa** and **3pa** in good yields (entries 16−18). Although the yield was not so good, benzyl bromide was also applicable for this reaction (entry 19).

Next, the scope of this reaction was examined with respect to the amines (Table 3). *N*-Arylbenzamides **3ac**, **3ad**, and **3ae** were obtained in moderate to good yields when aniline derivatives **2c**−**e** were used (entries 3−5). Electron-rich aniline **2e** gave a better yield indicating that the nucleophilicity of anilines may affect the reaction. Not only the aryl amines but also the alkyl amines can be applied to give the corresponding amide in good yields (entries 6−9). Cyclic secondary amines such as pyrrolidine and piperidine as well as the acyclic secondary amines such as methylbenzylamine and diethylamine can be used in this reaction to provide good to excellent yields (entries 10−13). Heteroaromatic amines gave the corresponding amides in good yields (entries 14−16).

We applied this $Mo(CO)_6$-mediated carbamoylation reaction for the lactam synthesis via intramolecular aminocarbonylation. Primary amines **2q** and **2r** that contain a 2-iodoaryl moiety were prepared and subjected to the reaction conditions to give five- and six-membered ring lactams **3q** and **3r** in good yields (Scheme 2).

SCHEME 2. $Mo(CO)_6$-Mediated Intramolecular Aminocarbonylations

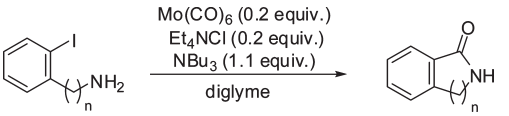
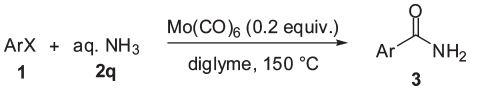


TABLE 4. Using Aqueous Ammonia To Synthesize the Primary Amide[a]



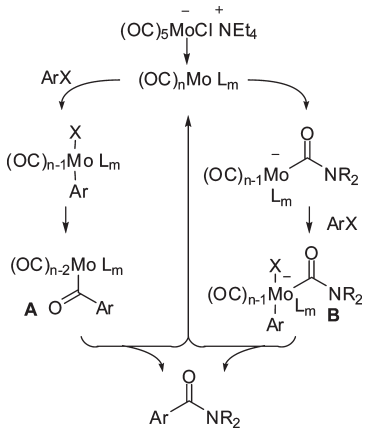
entry	ArX	product	time/h	yield/%
1	**1a**: R = H	**3aq**	4	91
2	**1b**: R = OMe	**3bq**	4	75
3	**1e**: R = Ac	**3eq**	1	50
4	**1h**	**3hq**	4	54
5	**1o**	**3oq**	1	76

[a]The reactions were carried out with ArX (0.5 mmol) and aq. NH_3 (ca. 1.5 mmol, 25−28% w/w) at 150 °C.

(8) For a review about palladium-catalyzed coupling reactions of aryl chlorides, see: (a) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176. (b) Blaser, H.-U.; Indolese, A.; Naud, F.; Nettekoven, U.; Schnyder, A. *Adv. Synth. Catal.* **2004**, *346*, 1583. For palladium-catalyzed aminocarbonylation of aryl chlorides, see: (c) Ben-David, Y.; Portnoy, M.; Milstein, D. *J. Am. Chem. Soc.* **1989**, *111*, 8742. (d) Takeuchi, R.; Suzuki, K.; Sato, N. *J. Mol. Catal.* **1991**, *66*, 277. (e) Carpentier, J. F.; Petit, F.; Mortreux, A.; Dufaud, V.; Basset, J. M.; Thivolle-Cazat, J. *J. Mol. Catal.* **1993**, *81*, 1. (f) Perry, R. J.; Wilson, B. D. *J. Org. Chem.* **1996**, *61*, 7482. (g) Kim, J. S.; Sen, A. *J. Mol. Catal. A* **1999**, *143*, 197. (h) Mägerlein, W.; Indolese, A. F.; Beller, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2856. (i) Calo, V.; Giannoccaro, P.; Nacci, A.; Monopoli, A. *J. Organomet. Chem.* **2002**, *645*, 152. (j) Lagerlund, O.; Larhed, M. *J. Comb. Chem.* **2006**, *8*, 4. (k) Martinelli, J. R.; Clark, T. P.; Watson, D. A.; Munday, R. H.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 8460.

(9) For references related to chelation assisted oxidative addition of Ar-X to tungsten or molybdenum carbonyl complexes, see refs 6a, 6b, 6c, and 6e.

SCHEME 3. Proposed Mechanism[a]



[a] n = 5, 4, 3, and 2 for the first, second, third, and fourth cycles, respectively. L = X^-, Cl^-, HNR_2, $^-NR_2$, 1,4-diglyme, or CO.

Finally, we also applied this $Mo(CO)_6$-mediated carbamoylation to the synthesis of primary amides. To the best of our knowledge, there is no example reported on the synthesis of primary amides by the conventional palladium-catalyzed three-component coupling reaction by means of aqueous ammonia, which is the most readily available ammonia source.[10,11] This is because the palladium catalysts may be deactivated in the reaction conditions with aqueous ammonia.

We attempted $Mo(CO)_6$-mediated carbamoylation of organic halides with aqueous ammonia as summarized in Table 4. When phenyl iodide was treated with aqueous ammonia in the presence of 0.2 equiv of $Mo(CO)_6$, benzamide was obtained in 91% yield (entry 1).[12] The reaction proceeded at ambient pressure, and hence special apparatus such as a sealed tube or autoclave is not necessary. Both electron-rich and -deficient aryl iodides **1b** and **1e** afforded the corresponding primary amides **3bq** and **3eq** in moderate yields (entries 2 and 3). 3-Bromothiophene was also used in this reaction to afford amide **3hq** in 54% yield (entry 4). Cinnamamide (**3oq**) was obtained in good yield when β-bromostyrene (**1o**) was used (entry 5).

Two possible mechanisms are depicted in Scheme 3. One of the plausible pathways involves oxidative addition of aryl halide and a subsequent insertion of carbon monoxide to generate acylmolybdenum intermediate **A**. Alternatively, carbamoylmolybdenum intermediate **B** would be generated by nucleophilic attack of amine to the carbonyl ligand followed by oxidative addition of aryl halide. Although the mechanism has yet to be elucidated, it is noteworthy that molybdenum carbonyl species acts as the catalyst and most of the carbonyl ligands on the molybdenum center are incorporated into the product.

Conclusions

In conclusion, we have established an efficient molybdenum-mediated carbamoylation of aryl halides. The procedure is simple and requires only slight excess of carbon monoxide in the form of $Mo(CO)_6$. This reaction provides a method for synthesis of a variety of amides. Primary amides are also prepared in the reaction with aqueous ammonia.

Experimental Section

General Procedure for $Mo(CO)_6$-Mediated Carbamoylation of Aryl Halides. A mixture of aryl halide **1** (0.60 mmol), amnie complex **2** (0.50 mmol), $Mo(CO)_6$ (0.10 mmol), NEt_4Cl (0.1 mmol), and NBu_3 (0.55 mmol) in diglyme (5 mL) was heated at 150 °C under N_2 atmosphere. The reaction was monitored by thin-layer chromatography. The volatile materials were removed under the reduced pressure, and the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate = 8:1) to afford the pure amide products.

***N*-Benzylbenzamide (3aa).**[13] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.65 (d, J = 6.0 Hz, 2H), 6.42 (br s, 1H), 7.28−7.37 (m, 5H), 7.41−7.45 (dd, J = 7.6 Hz, 7.2 Hz, 2H), 7.48−7.52 (t, J = 7.2 Hz, 1H), 7.79 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.1, 126.9, 127.6, 127.9, 128.6, 128.8, 131.5, 134.4, 138.1, 167.3.

***N*-Benzyl-4-methoxybenzamide (3ba).**[14] White solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.74 (s, 3H), 4.51 (d, J = 5.5 Hz, 2H), 6.50 (br s, 1H), 6.80 (d, J = 8.5 Hz, 2H), 7.18−7.27 (m, 5H), 7.68 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 44.0, 55.3, 113.7, 126.6, 127.4, 127.8, 128.7, 128.8, 138.4, 162.1, 166.9.

***N*-Benzyl-3-methoxybenzamide (3ca).**[15] Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.80 (s, 3H), 4.59 (d, J = 6.0 Hz, 2H), 6.70 (br s, 1H), 6.99−7.02 (m, 1H), 7.25−7.39 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 44.0, 55.3, 112.3, 117.7, 118.7, 127.5, 127.8, 128.7, 129.5, 135.8, 138.1, 159.7, 167.2.

***N*-Benzyl-2-methoxybenzamide (3da).**[16] Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.89 (s, 3H), 4.68 (d, J = 5.6 Hz, 2H), 6.95 (d, J = 8.4 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 7.25−7.37 (m, 5H), 7.41−7.46 (m, 1H), 8.21 (br s, 1H), 8.25 (dd, J = 7.6, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 43.6, 55.8, 111.2, 121.2, 121.3, 127.1, 127.4, 128.5, 132.3, 132.7, 138.7, 157.4, 165.2.

4-Acetyl-*N*-benzylbenzamide (3ea).[17] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.60 (s, 3H), 4.63 (d, J = 5.6 Hz, 2H), 6.75 (br s, 1H), 7.28−7.35 (m, 5H), 7.86 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 26.7, 44.2, 127.3, 127.7, 127.9, 128.5, 128.8, 137.8, 138.2, 139.1, 166.4, 197.4.

***N*-Benzylnaphthalene-1-carboxamide (3fa).**[18] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.70 (d, J = 5.6 Hz, 2H), 6.39 (br s, 1H), 7.28−7.43 (m, 6H), 7.49−7.60 (m, 3H), 7.85−7.91 (m, 2H), 8.33−8.35 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.1, 124.6, 124.9, 125.4, 126.4, 127.1, 127.6, 127.8, 128.3, 128.8, 130.1, 130.6, 133.6, 134.2, 138.1, 169.4.

***N*-Benzylnaphthalene-2-carboxamide (3ga).**[18] White solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.67 (d, J = 6.0 Hz, 2H), 6.90

(10) For palladium-catalyzed aminocarbonylation reactions by using water as the solvent, see: (a) Wu, X.; Larhed, M. *Org. Lett.* **2005**, *7*, 3327. (b) Wu, X.; Ekegren, J. K.; Larhed, M. *Organometallics* **2006**, *25*, 1434. (c) Tambade, P. J.; Patil, Y. P.; Bhanushali, M. J.; Bhanage, B. M. *Synthesis* **2008**, *15*, 2347.

(11) For Pd-catalyzed primary amides preparation, see: (a) Morera, E.; Ortar, G. *Tetrahedron Lett.* **1998**, *39*, 2835. (b) Schnyder, A.; Beller, M.; Mehltretter, G.; Nsenda, T.; Studer, M.; Indolese, A. F. *J. Org. Chem.* **2001**, *66*, 4311. (c) Shen, Q.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 10028. (d) Takács, E.; Varga, C.; Skoda-Földes, R.; Kollár, L. *Tetrahedron Lett.* **2007**, *48*, 2453. (e) Balogh, J.; Mahó, S.; Háda, V.; Kollár, L.; Skoda-Földes, R. *Synthesis* **2008**, *19*, 3040.

(12) The absence of Et_4NCl did not lower the yield of primary amide. Although we are not sure the role of Et_4NCl in the reaction of primary and secondary amine, chloride anion may coordinate to the molybdenum center and stabilize the intermediates. In the reaction with aqueous ammonia, ammonia or water molecule may coordinate and stabilize the molybdenum intermediate instead of chloride anion.

(13) Katritzky, A. R.; Cai, C.-M.; Singh, S. K. *J. Org. Chem.* **2006**, *71*, 3375.

(14) Yamazaki, K.; Kondo, Y. *J. Comb. Chem.* **2004**, *6*, 121.

(15) Agwada, V. C. *J. Chem. Eng. Data* **1982**, *27*, 479.

(16) Martinelli, J. R.; Watson, D. A.; Freckmann, D. M. M.; Barder, T. E.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 7102.

(17) Ren, W.; Yamane, M. *J. Org. Chem.* **2009**, *74*, 8332.

(18) Ragnarsson, U.; Grehn, L.; Maia, H. L. S.; Monteiro, L. S. *J. Chem. Soc., Perkin Trans. 1.* **2002**, 97.

(br s, 1H), 7.28−7.38 (m, 5H), 7.49−7.56 (m, 2H), 7.84−7.87 (m, 4H), 8.31 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 44.1, 123.6, 126.6, 127.4, 127.5, 127.6, 127.7, 127.8, 128.4, 128.69, 128.8, 131.5, 132.5, 134.7, 138.2, 167.5.

***N*-Benzylthiophene-3-carboxamide (3ha).**[17] White solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.57 (d, J = 5.5 Hz, 2H), 6.61 (br s, 1H), 7.26−7.35 (m, 6H), 7.39−7.41 (m, 1H), 7.87−7.88 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 43.7, 126.1, 126.4, 127.5, 127.8, 128.3, 128.7, 137.2, 138.2, 163.0.

***N*-Benzylpyridine-2-carboxamide (3ia).**[18] White solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.68 (d, J = 6.0 Hz, 2H), 7.27−7.30 (m, 1H), 7.33−7.39 (m, 4H), 7.41−7.44 (m, 1H), 7.84−7.87 (m, 1H), 8.23−8.25 (m, 1H), 8.39 (br, s, 1H), 8.52−8.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 43.5, 122.3, 126.2, 127.5, 127.8, 128.7, 137.4, 138.2, 148.1, 149.8, 164.2.

***N*-Benzyl-5-iodopyridine-2-carboxamide (3ja).** White solid; mp 76−77 °C (AcOEt); IR (NaCl, $CHCl_3$) 3392, 3018, 2399, 1670, 1523, 1456, 1215, 759, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.65 (d, J = 6.0 Hz, 2H), 7.27−7.35 (m, 5H), 7.99 (d, J = 8.0 Hz, 1H), 8.17 (dd, J = 2.0, 8.0 Hz, 1H), 8.26 (br s, 1H), 8.72 (d, J = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 43.5, 97.0, 124.0, 127.5, 127.8, 128.7, 137.9, 145.7, 148.6, 154.1, 163.7. ESIHRMS found: m/z 338.9981. Calcd for $C_{13}H_{12}IN_2O$: $(M + H)^+$ 338.9994.

***N*-Benzyl-4-bromobenzamide (3ka).**[19] White solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.61 (d, J = 5.7 Hz, 2H), 6.50 (br s, 1H), 7.29−7.38 (m, 5H), 7.55 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 44.2, 126.2, 127.7, 127.9, 128.6, 128.8, 131.8, 133.2, 137.9, 166.4.

***N*-Benzylquinoline-2-carboxamide (3ma).** White solid; mp 124−125 °C (AcOEt); IR (NaCl, $CHCl_3$) 3388, 3014, 1670, 1529, 1500, 1427, 1217, 846, 771, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.73 (d, J = 6.4 Hz, 2H), 7.24−7.40 (m, 5H), 7.57 (t, J = 7.6 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 8.64 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 43.5, 118.8, 127.4, 127.6, 127.77, 127.79, 128.6, 129.2, 129.5, 130.0, 137.4, 138.2, 146.4, 149.6, 164.4. ESIHRMS found: m/z 263.1176. Calcd for $C_{17}H_{15}N_2O$: $(M + H)^+$ 263.1184.

***N*-Benzyl-4,6-dimethoxy-1,3,5-triazine-2-carboxamide (3na).** White solid; mp 112−114 °C (AcOEt); IR (NaCl, $CHCl_3$) 3437, 3265, 3016, 2399, 1570, 1467, 1377, 1219, 1143, 1111, 819, 781, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.89 (s, 3H), 3.95 (s, 3H), 4.64 (d, J = 6.12 Hz, 2H), 6.89 (br s, 1H), 7.25−7.32 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 44.7, 54.4, 54.6, 127.2, 127.5, 128.4, 138.4, 168.1, 171.9, 172.4. ESIHRMS found: m/z 275.1140. Calcd for $C_{13}H_{15}N_4O_3$: $(M + H)^+$ 275.1144.

(*E*)-*N*-Benzylcinnamamide (3oa).[20] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.53 (d, J = 4.0 Hz, 2H), 6.49 (br s, 1H), 6.49 (d, J = 15.6 Hz, 1H), 7.27−7.47 (m, 10H), 7.668 (d, J = 15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 43.7, 120.5, 127.4, 127.7, 127.8, 128.6, 128.7, 129.6, 134.7, 138.2, 141.2, 165.9.

(*E*)-*N*-Benzyl-3-[4-(trifluoromethyl)phenyl]acrylamide (3pa). White solid; mp 163−165 °C (AcOEt); IR (NaCl, $CHCl_3$) 3263, 3018, 1666, 1627, 1512, 1415, 1323, 1215, 1168, 1130, 1068, 756, 669 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.56 (d, J = 5.8 Hz, 2H), 6.20 (br s, 1H), 6.50 (d, J = 15.6 Hz, 1H), 7.27−7.36 (m, 5H), 7.57 (dd, J = 8.4, 16.0 Hz, 4H), 7.67 (d, J = 15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 43.9, 122.5, 122.9, 125.2, 125.76 (q, J = 3.7 Hz), 127.7, 127.9, 128.8, 131.3 (q, J = 32.4 Hz), 137.9, 138.2, 139.7, 165.1. ESIHRMS found: m/z 306.1110. Calcd for $C_{17}H_{15}N_3OF_3$: $(M + H)^+$ 306.1106.

***N*-Benzyl-3-oxocyclopent-1-ene-1-carboxamide (3qa).** Colorless oil, IR (NaCl, $CHCl_3$) 3321, 3016, 1712, 1653, 1602, 1521, 1215, 771, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42−2.45 (m, 2H), 2.82−2.84 (m, 2H), 4.51 (d, J = 5.8 Hz, 2H), 6.46 (s, 1H), 7.03 (br s, 1H), 7.25−7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 27.7, 35.2, 43.7, 127.7, 127.8, 128.7, 133.4, 137.3, 163.9, 168.3, 209.3. ESIHRMS found: m/z 216.1025. Calcd for $C_{13}H_{14}NO_2$: $(M + H)^+$ 216.1025.

***N*-Benzyl-2-phenylacetamide (3ra).**[21] White solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.59 (s, 2H), 4.38 (d, J = 5.5 Hz, 2H), 5.90 (br s, 1H), 7.16 (d, J = 7.0 Hz, 2H), 7.22−7.34 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm) 43.5, 43.7, 127.28, 127.33, 127.4, 128.6, 128.9, 129.4, 134.8, 138.1, 170.9.

***N*-(4-Methoxybenzyl)benzamide (3ab).**[22] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.77 (s, 3H), 4.52 (d, J = 5.6 Hz, 2H), 6.69 (br s, 1H), 6.85 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.38−7.48 (m, 3H), 7.77 (d, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 43.5, 55.2, 114.0, 126.9, 128.4, 129.2, 130.3, 131.4, 134.4, 158.9, 167.3.

***N*-Phenylbenzamide (3ac).**[23] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.15 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.45−7.56 (m, 3H), 7.65 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 7.6 Hz, 2H), 7.95 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 120.2, 124.5, 127.0, 128.7, 129.0, 131.8, 135.0, 137.9, 165.8.

Methyl 4-Benzamidobenzoate (3ad).[24] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.92 (s, 3H), 7.49−7.60 (m, 3H), 7.75 (d, J = 8.2 Hz, 2H), 7.88 (d, J = 7.2 Hz, 2H), 7.99 (br s, 1H), 8.06 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 52.1, 119.2, 125.9, 127.1, 128.9, 130.9, 132.2, 134.5, 142.1, 165.8, 166.6.

***N*-(4-Methoxyphenyl)benzamide (3ae).**[25] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.82 (s, 3H), 6.91 (d, J = 9.2 Hz, 2H), 7.47−7.56 (m, 5H), 7.73 (br s, 1H), 7.86 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 55.5, 114.2, 122.1, 127.0, 128.7, 131.0, 131.7, 135.0, 156.6, 165.6.

***N*-Butylbenzamide (3af).**[26] Light yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.90 (t, J = 7.6 Hz, 3H), 1.35 (qt, J = 7.2, 7.6 Hz, 2H), 1.55 (tt, J = 7.2 Hz, 2H), 3.39 (dt, J = 6.8, 6.4 Hz, 2H), 6.65 (br s, 1H), 7.33−7.45 (m, 3H), 7.75 (d, J = 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 13.7, 20.0, 31.6, 39.7, 126.8, 128.3, 131.1, 134.7, 167.6.

***N*-*tert*-Butylbenzamide (3ag).**[27] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.46 (s, 9H), 5.99 (br s, 1H), 7.38−7.45 (m, 3H), 7.70 (d, J = 7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 28.8, 51.5, 126.6, 128.4, 131.0, 135.9, 166.9.

***N*-Cyclopropylbenzamide (3ah).**[28] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.59−0.63 (m, 2H), 0.81−0.86 (m, 2H), 2.85−2.91 (m, 1H), 6.49 (br s, 1H), 7.36−7.48 (m, 3H), 7.73 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 6.6, 23.1, 126.8, 128.4, 131.3, 134.3, 168.9.

***N*-Cyclohexylbenzamide (3ai).**[29] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.10−1.43 (m, 5H), 1.59−1.75 (m, 3H), 1.97−2.00 (m, 2H), 3.89−3.98 (m, 1H), 6.23 (br s, 1H), 7.35−7.46 (m, 3H), 7.74 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 24.9, 25.4, 33.1, 48.6, 126.8, 128.3, 131.1, 135.0, 166.6.

(19) Petricci, E.; Mugnaini, C.; Radi, M.; Corelli, F.; Botta, M. *J. Org. Chem.* **2004**, *69*, 7880.
(20) Knowles, H. S.; Parsons, A. F.; Pettifer, R. M.; Rickling, S. *Tetrahedron* **2000**, *56*, 979.
(21) Lee, H.-L.; Aubé, J. *Tetrahedron* **2007**, *63*, 9007.
(22) Thomas, G. L.; Böehner, C.; Ladlow, M.; Spring, D. R. *Tetrahedron* **2005**, *61*, 12153.
(23) Zhang, Z. H.; Yu, Y.; Liebeskind, L. S. *Org. Lett.* **2008**, *10*, 3005.
(24) Gould, S.; Laufer, D. A. *J. Magn. Reson.* **1979**, *34*, 37.
(25) Jammi, S.; Sakthivel, S.; Rout, L.; Mukherjee, T.; Mandal, S.; Mitra, R.; Saha, P.; Punniyamurthy, T. *J. Org. Chem.* **2009**, *74*, 1971.
(26) Zhang, M.; Vedantham, P.; Flynn, D. L.; Hanson, P. R. *J. Org. Chem.* **2004**, *69*, 8340.
(27) Baum, J. C.; Milne, J. E.; Murry, J. A.; Thiel, O. R. *J. Org. Chem.* **2009**, *74*, 2207.
(28) Tsuritani, T.; Strotman, N. A.; Yamamoto, Y.; Kawasaki, M.; Yasuda, N.; Mase, T. *Org. Lett.* **2008**, *10*, 1653.
(29) Jo, Y.; Ju, J.; Choe, J.; Song, K. H.; Lee, S. *J. Org. Chem.* **2009**, *74*, 6358.

1-Benzoylpyrrolidine (3aj).[30] Light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.83−1.99 (m, 4H), 3.42 (t, J = 6.4 Hz, 2H), 3.64 (t, J = 6.8 Hz, 2H), 7.38−7.51 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 24.4, 26.4, 46.1, 49.6, 127.0, 128.2, 129.7, 137.2, 169.7.

1-Benzoylpiperidine (3ak).[31] Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.48 (br s, 2H), 1.65 (br s, 4H), 3.31 (br s, 2H), 3.68 (br s, 2H), 7.36 (br s, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 24.5, 25.5, 26.4, 43.0, 48.7, 126.7, 128.3, 129.2, 136.4, 170.2.

***N*-Benzyl-*N*-methylbenzamide (3al).**[32] Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.86 (br s, 1.5H), 3.03 (br s, 1.5H), 4.51 (br s, 1H), 4.76 (br s, 1H), 7.17−7.47 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 33.1, 36.9, 50.7, 55.1, 126.7, 126.9, 127.4, 128.1, 128.4, 128.6, 128.7, 129.5, 136.2, 136,5, 136.9, 171.5, 172.2.

***N*,*N*-Diethylbenzamide (3am).**[33] Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.09 (br s, 3H), 1.23 (br s, 3H), 3.23 (br s, 2H), 3.53 (br s, 2H), 7.36 (br s, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 12.8, 14.2, 39.2, 43.2, 126.2, 128.3, 129.0, 137.2, 171.3.

1-Benzoyl-1*H*-pyrrole (3an).[34] Colorless oil, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.35 (m, 2H), 7.29 (m, 2H), 7.49−7.63 (m, 3H), 7.75 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 113.1, 121.3, 128.5, 129.5, 132.3, 133.2, 167.7.

***N*-Benzoyl-1*H*-indole (3ao).**[35] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.62 (d, J = 7.6 Hz, 1H), 7.29−7.39 (m, 3H), 7.41−7.62 (m, 4H), 7.74 (d, J = 7.6 Hz, 2H), 8.40 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 108.5, 116.4, 120.9, 123.9, 124.9, 127.6, 128.6, 129.2, 130.8, 131.9, 134.6, 136.0, 168.7.

***N*-Benzoyl-9*H*-carbazole (3ap).**[36] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32−7.38 (m, 4H), 7.52−7.55 (m, 4H), 7.66 (t, J = 7.2 Hz, 1H), 7.74 (d, J = 7.6 Hz, 2H), 8.02 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 115.7, 119.8, 123.4, 126.0, 126.7, 128.9, 129.0, 132.3, 135.7, 139.1, 169.6.

2,3-Dihydro-1*H*-isoindol-1-one (3q).[37] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.47 (s, 2H), 7.45−7.58 (m, 3H), 7.86 (d, J = 7.8 Hz, 1H), 8.23 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 45.8, 123.1, 123.6, 127.9, 131.6, 132.2, 143.7, 172.3.

1,2,3,4-Tetrahydroisoquinolin-1-one (3r).[38] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.93 (t, J = 6.4 Hz, 2H), 3.49−3.53 (m, 2H), 6.65 (br s, 1H), 7.14−7.19 (m, 1H), 7.26−7.30 (m, 1H), 7.36−7.40 (m, 1H), 7.99 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 28.3, 40.2, 127.0, 127.2, 127.9, 128.9, 132.1, 138.8, 166.4.

Benzamide (3aq).[39] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.21 (br s, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.81 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 127.3, 128.6, 132.0, 133.3, 169.6.

4-Methoxybenzamide (3bq).[40] White solid; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.79 (s, 3H), 6.97 (d, J = 8.8 Hz, 2H), 7.86 (d, J = 8.8 Hz, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 55.3, 113.4, 126.5, 129.4, 161.6, 167.5.

4-Acetylbenzamide (3eq).[41] White solid; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.61 (s, 3H), 7.57 (br s, 1H), 8.00 (s, 4H), 8.18 (br s, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 27.0, 127.8, 128.1, 138.1, 138.7, 167.2, 197.8.

Thiophene-3-carboxamide (3hq).[42] White solid; ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.25 (br s, 1H), 7.48−7.56 (m, 2H), 7.79 (br s, 1H), 8.13 (d, J = 1.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm) 126.6, 127.2, 129.1, 138.0, 163.8.

Cinnamamide (3oq).[43] White solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.65 (br s, 2H), 6.46 (d, J = 15.6 Hz, 1H), 7.37−7.38 (m, 3H), 7.51−7.53 (m, 2H), 7.65 (d, J = 15.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 119.5, 127.9, 128.8, 130.0, 134.5, 142.5, 167.9.

Acknowledgment. We thank Nanyang Technological University for the generous financial support.

Supporting Information Available: General experimental procedures for the synthesis of compounds **3** and spectral data for the amide products. This material is available free of charge via the Internet at http://pubs.acs.org.

(30) Li, J.; Xu, F.; Zhang, Y.; Shen, Q. *J. Org. Chem.* **2009**, *74*, 2575.
(31) Ghosh, S. C.; Muthaiah, S.; Zhang, Y.; Xu, X.; Honga, S. H. *Adv. Synth. Catal.* **2009**, *351*, 2643.
(32) Wang, J.; Li, J.; Xu, F.; Shen, Q. *Adv. Synth. Catal.* **2009**, *351*, 1363.
(33) Hans, J. J.; Driver, R. W.; Burke, S. D. *J. Org. Chem.* **2000**, *65*, 2114.
(34) D'Silva, C.; Iqbal, R. *Synthesis* **1996**, *4*, 457.
(35) Liégault, B.; Lee, D.; Huestis, M. P.; Stuart, D. R.; Fagnou, K. *J. Org. Chem.* **2008**, *73*, 5022.
(36) Bonesi, S. M.; Ponce, M. A.; Erra-Balsells, R. *J. Heterocycl. Chem.* **2004**, *41*, 161.
(37) Motherwell, W. B. *Tetrahedron* **2007**, *63*, 6462.
(38) Dohi, T.; Takenaga, N.; Goto, A.; Fujioka, H.; Kita, Y. *J. Org. Chem.* **2008**, *73*, 7365.
(39) Zweifel, T.; Naubron, J.-V.; Gruetzmacher, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 559.
(40) Ramón, R. S.; Marion, N.; Nolan, S. P. *Chem.—Eur. J.* **2009**, *15*, 8695.
(41) Schnyder, A.; Beller, M.; Mehltretter, G.; Nsenda, T.; Studer, M.; Indolese, A. F. *J. Org. Chem.* **2001**, *66*, 4311.
(42) Cao, L.; Ding, J.; Gao, M.; Wang, Z.; Li, J.; Wu, A. *Org. Lett.* **2009**, *11*, 3810.
(43) Owston, N. A.; Parker, A. J.; Williams, J. M. J. *Org. Lett.* **2007**, *9*, 73.