

Transamidation for the Synthesis of Primary Amides at Room Temperature

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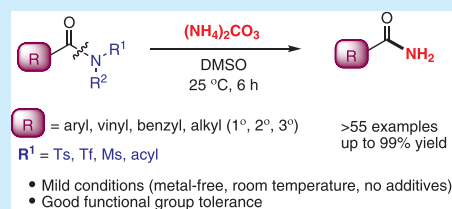
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ABSTRACT: Various primary amides have been synthesized using the transamidation of various tertiary amides under metal-free and mild reaction conditions. When $(\text{NH}_4)_2\text{CO}_3$ reacts with a tertiary amide bearing an *N*-electron-withdrawing substituent, such as sulfonyl and diacyl, in DMSO at 25 °C, the desired primary amide product is formed in good yield with good functional group tolerance. In addition, *N*-tosylated lactam derivatives afforded their corresponding *N*-tosylamido alkyl amide products via a ring opening reaction.



Amides are one of the most important functional groups in chemistry, biology, and materials science. They are widely employed as a core structural unit during the preparation of engineering plastics, lubricants, fertilizers, detergents, natural products, proteins, peptides, and pharmaceuticals.¹ Among them, primary amides have received significant research attention as useful building blocks because they are not only readily transformed into other amides, nitriles, primary amines, and oxazoles² but also found in many pharmaceuticals. In particular, primary benzamides are found in various drugs, such as salicylamide, frovatriptan, niraparib, lenvatinib, and labetalol (Figure 1).³ Therefore, tremendous efforts have been carried out to develop synthetic methods used for the preparation of primary amides.

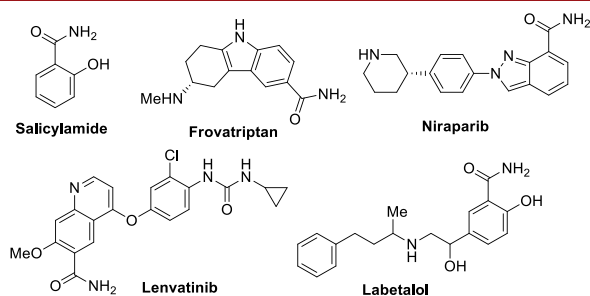
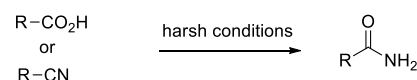


Figure 1. Examples of drugs containing a primary benzamide moiety.

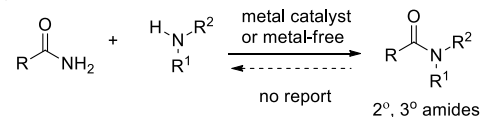
The amidation reaction of carboxylic acid derivatives (halides, esters, and anhydrides) with ammonia⁴ and the hydration of nitriles⁵ have been widely used for the preparation of primary amides in academia as well as industry (Scheme 1a). However, they have some drawbacks. The former requires toxic and corrosive starting materials, whereas the latter needs a strong acid or base, which may give rise to over hydrolysis of the desired primary amide product. To address these issues, more practical and efficient methods have been developed. For

Scheme 1. Synthesis of Primary Amides

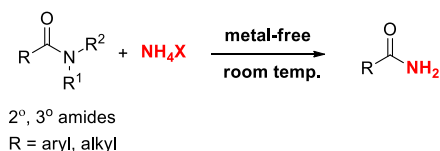
a) classical methods



b) transamidation



c) This work



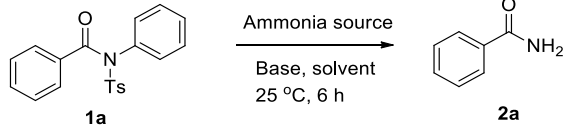
example, the employment of activators for the conversion of carboxylic acids into amides,⁶ metal-catalyzed hydration of nitriles,⁷ the rearrangement of aldoximes,⁸ Pd-catalyzed aminocarbonylation of aryl halides,⁹ C–C bond cleavage of ethylarenes,¹⁰ decarboxylative amoxidation of phenylacetic acid,¹¹ oxidation of primary benzyl amines,¹² and oxidative amidation of aldehydes, benzyl alcohols, methyl ketone, or methylarenes.¹³ However, there are no reports that secondary or tertiary amides have been employed as a starting material toward the synthesis of primary amides with the exception of those using a deprotection process.

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Transamidation involves the conversion of one amide into another and has gained considerable attention from several research groups.¹⁴ A number of catalytic systems using transition metals have been developed and employed in the transformation of a variety of amides.¹⁵ Recently, a metal-free system has also been reported to provide the desired transamidation products in good yield.¹⁶ A number of transamidation reactions are available to convert primary amides, which are free or protected, into secondary or tertiary amides,¹⁷ but no example of achieving the opposite transamidation process has been reported to date (Scheme 1b). Herein, we present the results obtained for a transamidation reaction used for the synthesis of primary amides (Scheme 1c).

To obtain the optimal reaction conditions, *N*-phenyl-*N*-tosylbenzamide was chosen as a model substrate and a variety of ammonium sources were investigated. No product was formed when NH₄Cl and NH₄BF₄ were used in DMSO at 25 °C (Table 1, entries 1 and 2). The use of NH₄OAc provided

Table 1. Optimal Conditions Used for the Synthesis of Primary Benzamides^a



entry	ammonia source	base ^b	solvent	yield (%) ^c
1	NH ₄ Cl	–	DMSO	0
2	NH ₄ BF ₄	–	DMSO	0
3	NH ₄ OAc	–	DMSO	66
4	NH ₄ OAc	DBU	DMSO	73
5	NH ₄ OAc	Na ₃ PO ₄	DMSO	90
6	NH ₄ OAc	Na ₂ CO ₃	DMSO	94
7	HCO ₂ NH ₄	–	DMSO	77
8	(NH ₄) ₂ CO ₃	–	DMSO	99
9	(NH ₄) ₂ CO ₃	–	DMF	83
10	(NH ₄) ₂ CO ₃	–	THF	27
11	(NH ₄) ₂ CO ₃	–	EtOH	23
12	(NH ₄) ₂ CO ₃	–	Toluene	0
13	(NH ₄) ₂ CO ₃	–	DCM	0
14	(NH ₄) ₂ CO ₃ ^d	–	DMSO	99 (92) ^e

^aReaction conditions: **1a** (0.2 mmol), ammonia source (0.4 mmol), solvent (1.0 mL), 25 °C, 6 h. ^b0.2 mmol was used. ^cDetermined using GCMS in the presence of an internal standard. ^d0.12 mmol was used. ^eIsolated yield.

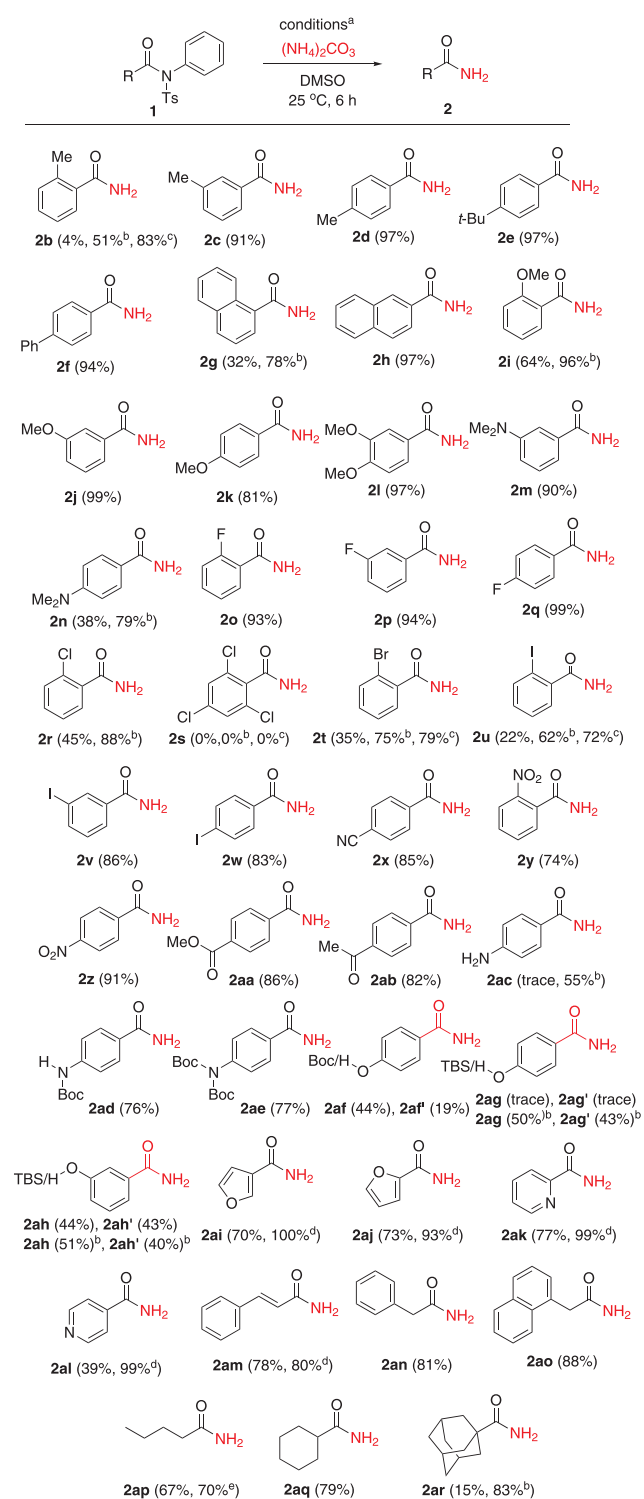
benzamide (**2a**) in 66% yield (entry 3). Additional bases were added to the reaction with NH₄OAc. DBU, Na₃PO₄, and Na₂CO₃ afforded the desired product in 73%, 90%, and 94% yield, respectively (entries 4–6). The fact that carbonate-type bases showed good results led us to employ carbonate-type ammonia sources. The reactions carried out using HCO₂NH₄ and (NH₄)₂CO₃ afforded the desired product in 77% and 99% yield, respectively (entries 7 and 8). When the reaction was performed in other solvents such as DMF, THF, EtOH, toluene, and CH₂Cl₂, the desired product was formed in low yield or not observed (entries 9–13). When the amount of (NH₄)₂CO₃ was decreased to 0.6 equiv, the product was still obtained in 99% yield (entry 14). The optimal conditions were as follows: *N*-phenyl-*N*-tosylbenzamide (1.0 equiv), (NH₄)₂CO₃ (0.6 equiv), DMSO, 25 °C, 6 h.

With the optimal conditions in hand, a variety of substituted *N*-phenyl-*N*-tosylbenzamides were investigated toward the synthesis of their corresponding primary benzamides (Scheme 2). When 2-methyl-*N*-phenyl-*N*-tosylbenzamide was reacted at 25 °C under the optimal conditions, the desired product **2b** was formed in 4% yield. The yield of product was increased to 51% upon heating at 40 °C. 3-Methyl-, 4-methyl-, 4-*tert*-butyl-, and 4-phenyl-substituted benzamides (**2c**, **2d**, **2e**, and **2f**) were formed in excellent yield. 1-Naphthyl benzamide was formed in 78% yield, but required the reaction to be heated at 40 °C. However, 2-naphthyl benzamide was formed in 97% yield at 25 °C. Methoxy-substituted benzamides were formed in good yield, although the 2-methoxy-substituted benzamide was formed at 40 °C. 3- and 4-Dimethylaminobenzamides **2m** and **2n** were formed at 25 °C in 90% and 38% yield, respectively. However, heating the reaction at 40 °C to form **2n** gave an increased yield (79%). Fluoro-, chloro-, bromo-, and iodo-substituted benzamides were formed in good yield, except in the case of **2r**, **2s**, **2t**, and **2u**. Although benzamides bearing a halide at the *ortho*-position were formed at 25 °C in low yields because of the steric hindrance of the substituent, heating the reaction at 40 °C gave the desired products in improved yields. However, the trichloro-substituted product (**2s**) was not formed even upon heating the reaction at 40 °C for 5 days. It was found that starting material **1s** was fully recovered.

Cyano- and nitro-substituted benzamides were formed in good yield. Benzamides **2aa** and **2ab** having an ester and a ketone group, respectively, were also formed in good yields. Unprotected amino-substituted product **2ac** was formed in 55% yield at 40 °C for 16 h. *N*-Boc protected benzamides **2ad** and **2ae** were formed in 76% and 77% yield, respectively. *O*-Boc and *O*-TBS protected benzamides **2af**, **2ag**, and **2ah** were formed with slightly low yields because the corresponding deprotected products such as **2af'**, **2g'**, and **2ah'** were also formed. Heteroaromatic compounds such as furancarboxamides, picolinamide, and isonicotinamide were formed in 93–99% yield; however, their isolated yields were lower due to their good solubility in water. Cinnamide, phenylacetamide, and naphthylacetamide were formed in good yield. In addition, primary, secondary, and tertiary alkyl carboxamides (**2ap**, **2aq**, and **2ar**) were formed in good yields, although product **2ar** required heating the reaction at 40 °C.

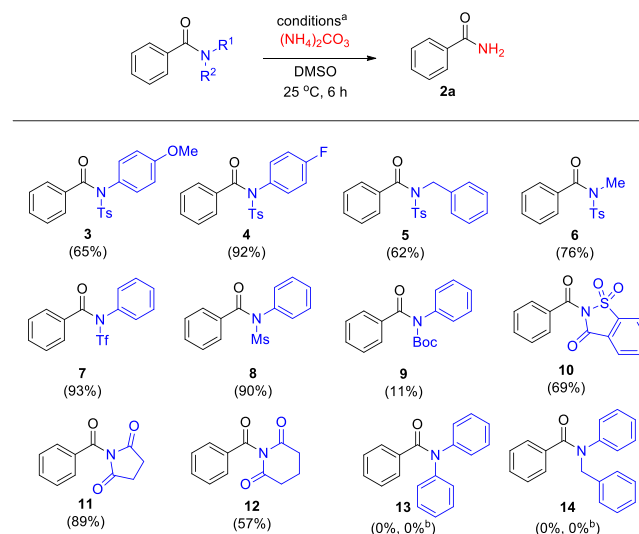
Subsequently, we studied the effect of the substituents on the nitrogen atom of the amide starting material (Scheme 3). All *N*-tosylbenzamides bearing *N*-4-methoxyphenyl, *N*-4-fluorophenyl, *N*-benzyl, and *N*-methyl groups provided the desired benzamide (**2a**) in good yield. *N*-Trifluoromethylsulfonyl and *N*-mesityl *N*-phenylbenzamides (**7** and **8**) gave **2a** in 93% and 90% yield, respectively. However, *N*-Boc protected *N*-phenylbenzamide **9** did not give **2a** in good yield because the deprotection of the Boc group predominantly occurred under the reaction conditions. It was found that *N*-benzoyl saccharin (**10**) gave **2a** in good yield. In addition, *N*-benzoyl succinimide and *N*-benzoyl glutarimide (**11** and **12**) gave **2a** in good and moderate yield. However, *N*-methyl-*N*-phenyl and *N,N*-diphenylbenzamides **13** and **14** were not formed in the reaction, even upon heating at 40 °C.

We found that *N*-tosylated benzamides showed higher reactivity than other benzamides. These results led us to evaluate this system for the transamidation reaction of *N*-tosyl lactams (Scheme 4). We used *N*-tosyl pyrrolidinone, piperidinone, and azepanone in the reaction with

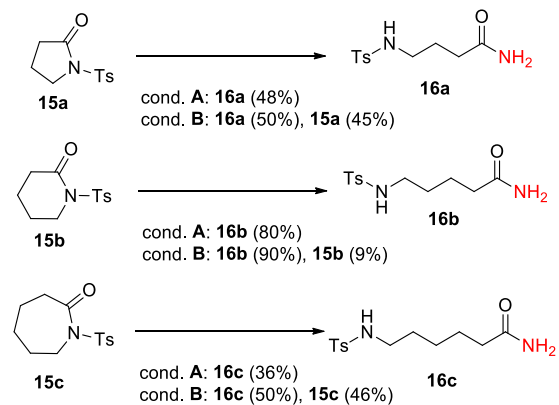
Scheme 2. Synthesis of Primary Amides from *N*-Tosyl Amides

^aReaction conditions: **1** (1.0 mmol), $(\text{NH}_4)_2\text{CO}_3$ (0.6 mmol), 25 °C, 6 h. The isolated yields were given in the parentheses. ^bThe reaction at 40 °C for 16 h. ^cThe reaction at 40 °C for 5 days. ^dThe yields were obtained using ¹H NMR spectroscopy in the presence of an internal standard. **2af'**, **2ag'**, and **2ah'** are deprotected products.

$(\text{NH}_4)_2\text{CO}_3$ at 40 °C (conditions A). *N*-Tosyl lactams **15a**, **15b**, and **15c** gave their corresponding *N*-tosylamide alkylamides (**16a**, **16b**, and **16c**) in 48%, 80%, and 36%

Scheme 3. Synthesis of **2a** from a Variety of Benzamides

^aReaction conditions: Benzamide (1.0 mmol), $(\text{NH}_4)_2\text{CO}_3$ (0.6 mmol), 25 °C for 6 h. The isolated yield for **2a** is reported in the parentheses. ^bThe yield obtained for the reaction heated at 40 °C for 16 h.

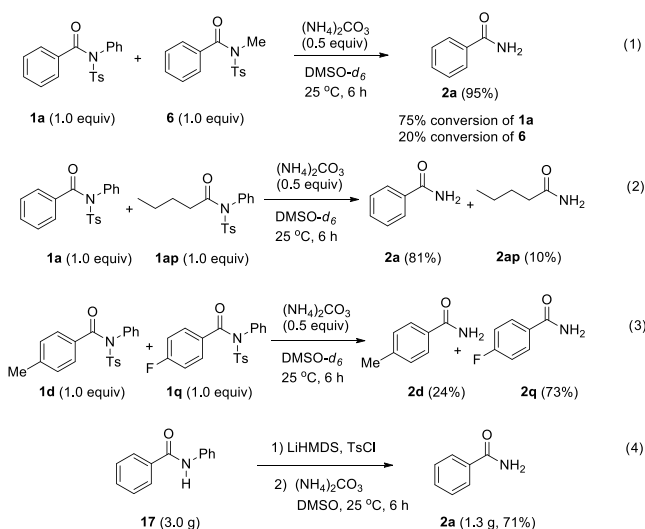
Scheme 4. Transamidation Reaction of *N*-Tosyl Lactams

conditions A : $(\text{NH}_4)_2\text{CO}_3$ (0.5 equiv), DMSO, 40 °C, 16 h
conditions B : $(\text{NH}_4)_2\text{CO}_3$ (1.0 equiv), DMSO, 40 °C, 36 h

yield, respectively. When the amount of $(\text{NH}_4)_2\text{CO}_3$ was increased to 1.0 equiv and the reaction time was longer, up to 36 h, in order to increase yields of products (conditions B), the yields of **16a**, **16b**, and **16c** increased; however, **15a**, **15b**, and **15c** were recovered with 45%, 9%, and 46%, respectively.

To understand this methodology in detail, several control experiments were carried out (Scheme 5). When the same amounts of **1a** and **6** were reacted under the optimal reaction conditions, **1a** was converted into the desired product in a higher yield than **6** (eq 1). When a similar reaction was conducted using **1a** and **1ap**, product **2a** was formed in a higher yield than **2ap** (eq 2). The competitive reaction between **1d** and **1q** showed that **2d** was formed in lower yield than **2q** (eq 3). From these results, the reactivity observed for the *N*-tosylated amides was found to have the following trends: (1) The *N*-phenyl group was more reactive than the *N*-methyl group, (2) aromatic amides were more reactive than aliphatic amides, and (3) electron-withdrawing substituents were more

Scheme 5. Control Experiments



reactive than electron-donating substituents. It is noteworthy that a gram-scale **2a** was obtained in 71% yield from nonprotected *N*-phenylbenzamide (**17**) through a sequential reaction (eq 4); however, **2a** was not formed from the direct reaction of **17** and $(\text{NH}_4)_2\text{CO}_3$. This result supported that this methodology can be a useful tool to convert a secondary amide to a primary amide by applying an *N*-tosyl group to the secondary amide.¹⁸

In summary, we have developed a direct transamidation reaction of tertiary amides used to prepare primary amides. The employment of $(\text{NH}_4)_2\text{CO}_3$ provided the primary amide products in good yields. This methodology has the following conceptual advances: (1) It is the first example of transamidation used for the synthesis of primary amides; (2) the reaction uses metal-free conditions; (3) the reaction does not require the use of any additives; (4) the reaction is conducted under mild conditions (25 °C), even though some substrates require heating at 40 °C; (5) the reaction works well for both aromatic and aliphatic tertiary amides; and (6) the reaction tolerates a wide range of functional groups. Finally, we found that the tertiary amides bearing an *N*-sulfonyl or *N,N*-diacyl group showed good activity in the transamidation reaction with $(\text{NH}_4)_2\text{CO}_3$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.0c00958>.

Experimental procedures and spectral data for the products (PDF)

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Notes

The authors declare no competing financial interest.

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