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Cesium Carbonate Catalyzed Esterification of *N*-Benzyl-*N*-Boc-amides under Ambient Conditions

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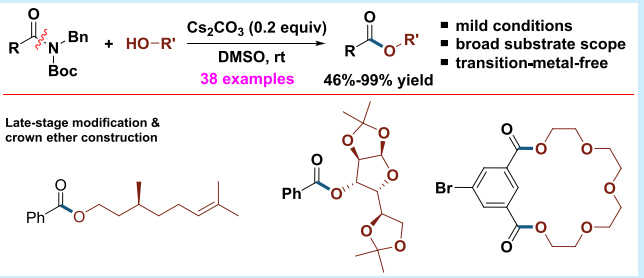
Supporting Information

ABSTRACT: We report a general activated amide to ester transformation catalyzed by Cs_2CO_3. Using this approach, esterification proceeds under relatively mild conditions and without the need for a transition metal catalyst. This method exhibits broad substrate scope and represents a practical alternative to existing esterification strategies. The synthetic utility of this protocol is demonstrated via the facile synthesis of crown ether derivatives and the late-stage modification of a representative natural product and several sugars in reasonable yields.



Amides are a fundamental functional group in organic chemistry.[1] They are an integral part of numerous complex molecular architectures and present in a broad range of molecules, including bioactive natural products,[2] pharmaceutical agents,[3] and fine chemicals.[4] Amide linkages are also present in numerous polymers, both natural and synthetic, and are found in a host of other functional materials.[5] The ubiquity of amides makes them attractive as feedstocks, and they continue to play important roles in the late-stage modification of drugs and other materials.[6] However, the amide bond is relatively strong. This strength is ascribed to resonance stabilization and is reflected in part in C−N rotation barriers on the order of 15−20 kcal/mol.[7] It also means that the conversion of amides to other functional groups usually requires harsh experimental conditions and a long reaction time. In particular, the direct esterification of amides requires strong acidic or basic conditions,[8] which are incompatible with sensitive functional groups. Efforts to overcome these classic limitations are attracting increasing attention.

In this context, the pioneering work by Garg and co-workers is of particular interest.[9] In 2015, they reported a revolutionary protocol for the esterification of amides based on a catalytic transition metal-based *N*-heterocyclic carbene (NHC) system (Figure 1a).[9a] The key step of this reaction involves the formation of a versatile acyl−nickel intermediate,[10] enabled by the facile oxidative addition of nickel(0) to *N*-alkyl-*N*-phenylamides. The success of the reaction is thought to be due to the unique conformation of the amide involved, which is slightly twisted from a *cis*-configuration due to both steric hindrance created by alkyl group and favorable electronic effects (weak $\pi-\pi$ interactions between the aryl and phenyl groups).[11] Nearly contemporaneously, Szostak[12,13] and others[14] developed a series of activated "twisted amides" in the form of either *N*-acyl-*N*-Boc-carbamates or *N*-acyl-*N*-tosylamides, which could be converted to esters by means of transition-metal-catalyzed[15] cross-coupling reactions (Figure 1a).

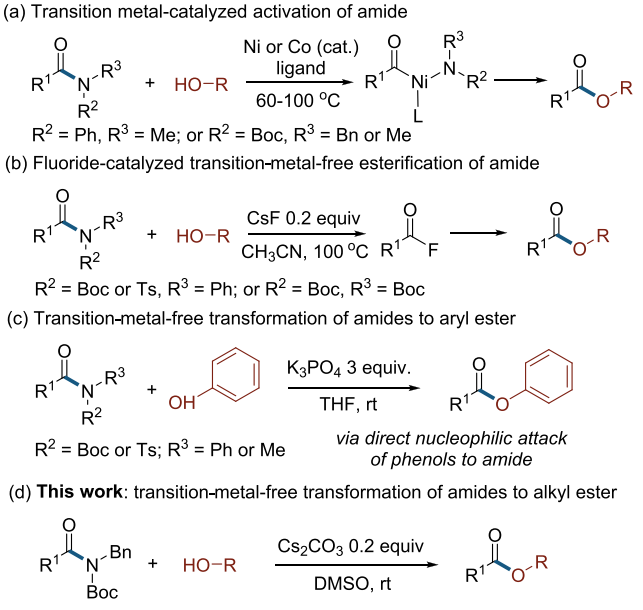


Figure 1. Methods for esterification reactions of amides.

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Recently, the *N*-activation strategy was further expanded to the transition-metal-free[16] esterification of twisted amides. For instance, Zeng et al. reported the fluoride-catalyzed esterification of amides via an acyl fluoride intermediate that proceeds at relatively high temperatures (Figure 1b).[17] Separately, Szostak et al. reported the esterification of amides using phenol and benzyl alcohol as nucleophiles promoted by an excess of K_3PO_4 (Figure 1c).[18] By using this method, a broad array of aromatic esters could be obtained that previously proved elusive in the context of transition metal-catalyzed amide bond activation, and under mild conditions. Despite these important advances, there remains a need for a general and operationally straightforward synthetic method that allows amides to be converted to the corresponding alkyl esters under mild conditions. As an extension of Szostak's transition-metal-free transformation of amides to aryl/benzyl ester, we report here progress toward achieving such a goal. Specifically, we show that *N*-Boc-*N*-benzyl amides may be converted to the corresponding esters by treatment with a range of alcohols in the presence of substoichiometric quantities of Cs_2CO_3 (Figure 1d). The reaction appears general and proceeds in good yields at room temperature.

The starting point for the present study was the consideration that the acyl fluoride intermediate that presumably permits Zeng's procedure to proceed in the absence of a metal catalyst might be replaceable by a lower energy species. Recently, we succeeded in trapping a carbonate monoester within a supramolecular host.[19] Carbonate monoesters are elusive species that are unstable under ambient conditions.[20] They decompose to produce (bi)carbonate and the constituent alcohol. As such, we hypothesized that they might act as viable intermediates in the conversion of appropriately chosen *N*-activated amides into esters, perhaps under readily accessible and mild laboratory conditions. Cesium carbonate was thus chosen as a potential catalyst to test this hypothesis.

Initially, we performed a number of test reactions using *N*-benzyl-*N*-Boc-carbamate (**1a**) as the amide electrophile and *n*-hexanol (**2a**) as the nucleophilic partner. (This choice of amide was also the result of more detailed screening studies as detailed below.) Through experimentation, we found that the reaction between **1a** and **2a** could be carried out in the presence of 20 mol % of Cs_2CO_3 at 23 °C in DMSO to give 89% isolated yield of the esterified product **3a** (Figure 2). Reducing the Cs_2CO_3 loading to 10 mol % did not affect the overall efficiency of the esterification reaction, although it did reduce the apparent rate. A solvent screening study revealed that DMSO constitutes the most effective medium for this reaction at least among other readily available solvents analyzed under identical conditions. For example, yields for **3a** of 71%, 62%, and 52% were obtained when the reaction was performed in CH_3CN, DMF, and DMA, respectively (Table 1). Other common organic solvents (e.g., toluene, diethyl ether, THF, DCM, and diglyme) gave little or no product (see Supporting Information).

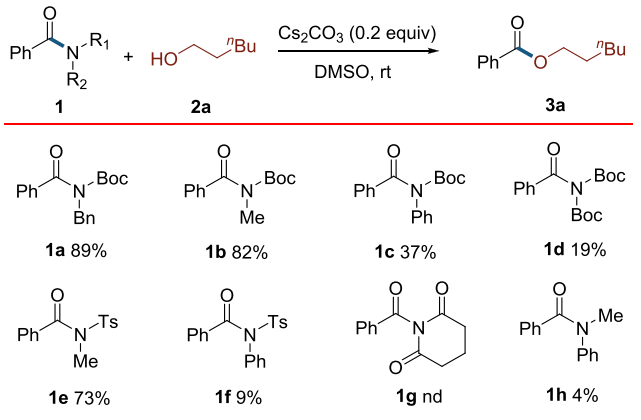

Figure 2. Evaluation of *N*,*N*-disubstituted benzamides. nd indicates not determined.

Table 1. Optimization for the Esterification of Amides 1a[a]

entry	variation from the standard conditions	yield (%)[b]
1	none	89
2	0.1 equiv of Cs_2CO_3	85
3	CsF instead of Cs_2CO_3	23
4	CsBr instead of Cs_2CO_3	nd[c]
5	CsOAc instead of Cs_2CO_3	nd
6	without adding of base	nd
7	CH_3CN instead of DMSO	71
8	DMF instead of DMSO	62
9	DMA instead of DMSO	52
10	DCM instead of DMSO	8

[a]Conditions: **1a** (1.0 equiv), **2a** (1.5 equiv), base (0.2 equiv), solvent (0.2 M), 23 °C, 12 h. [b]Calibrated GC yield. [c]nd indicates not determined.

By applying these optimized reaction conditions, a number of electronically and sterically crowded benzamides (imides) including Boc amides, tosyl amides, glutarimide, and *N*-methyl-*N*-phenylamide were tested. As summarized in Figure 2, it is evident that the esterification reaction is sensitive to the choice of *N*-substituents. Notably, *N*-benzyl-*N*-Boc-carbamate **1a** proved to be the most suitable electrophile for this esterification reaction, under these specific reaction conditions. Amide **1b** bearing an *N*-methyl group gives rise to a slightly reduced yield. However, when either the benzyl or methyl group is replaced by the phenyl group, the yield of the reaction dramatically decreases to 37% (**1a** and **1b** vs **1c**). The yield decreased significantly with the introduction of a phenyl group in the case of *N*-tosyl amides (**1e** vs **1f**). Additionally, it was observed that *N*-glutarimide, **1g**, and *N*-methyl-*N*-phenyl benzamide, **1h**, were completely unreactive when the same experimental conditions were employed. In fact, essentially none of the desired ester product could be detected as evidenced by GC analyses.

Next, the reaction scope was evaluated with respect to the acyl component (Figure 3). It was found that a diverse array of *N*-Boc-*N*-benzyl amides reacted smoothly to give the corresponding ester. However, studies of benzoic acid derivatives revealed that the reaction rate (as opposed to yield per se) was influenced by the substituents attached to the benzene ring. The presence of an electron-withdrawing group on the phenyl moiety led to higher reactivity. For example, in the case of the cyano-substituted amide (product **3l**), the reaction was deemed complete within 1 h. In contrast, a reaction time of 12 h was required for the corresponding 4-

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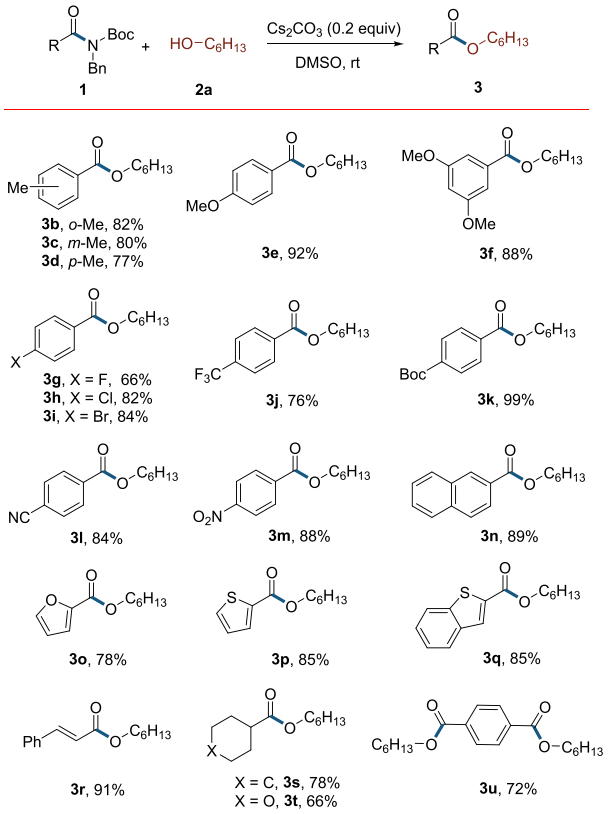

Figure 3. Substrate scope of the amides. Yields are isolated yields.

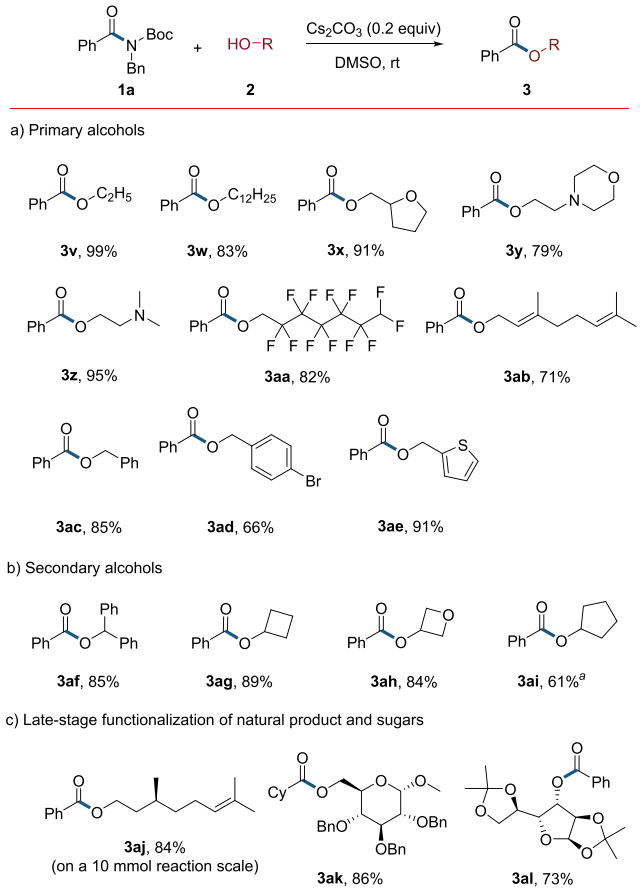

Figure 4. Substrate scope of the alcohol nucleophiles. Yield refers to isolated yield. [a] Cs_2CO_3 (2.0 equiv) was used.

methylphenyl-substituted amide (see Supporting Information). Substrates carrying aryl C−F, C−Cl, and C−Br bonds were found to be compatible with this transformation (giving products **3g**−**3i**). Both *ortho*- and *meta*-substituted aromatic amides showed comparable reactivity (products **3b** and **3c**). This leads us to infer that the reaction was not particularly sensitive to steric effects on the acyl moiety. Several substrates with functional groups that are not compatible with Garg's Ni-catalyzed system, e.g., *tert*-butyloxylcarbonyl, cyano, and nitro groups (products **3k**−**3m**),[9] could be converted to esters readily using our methodology. The present method also proved amenable to heteroaryl-derived amides, including those containing furan, thiophene, and benzothiophene (giving products **3o**−**3q**), as well as cinnamyl amide (product **3r**). It also accommodates alkyl amides (e.g., products **3s** and **3t**). Unfortunately, sterically hindered *tert*-butyl substituted substrates failed to give the corresponding esters.

The scope of the amide-to-ester transformation was further evaluated using a library of alcohols (Figure 4). Primary alcohols with different carbon chain lengths (giving products **3v** and **3w**) and heteroatom-containing moieties give the corresponding esters (e.g., products **3x**−**3z**) in excellent yields. An alcohol bearing a polyfluorinated alkyl chain (making the substrate comparatively less nucleophilic than **2a**) also performed well, giving rise to the corresponding ester (product **3aa**) in 82% yield. In addition, allylic alcohol can also be used without modification of the reaction conditions. Similarly, benzylic and heterobenzylic alcohols could be successfully converted to the corresponding products (**3ac**−**3ae**) in moderate to good yields. The present esterification procedure could also be applied successfully to secondary alcohols. For instance when benzhydryl alcohol was tested, the desired product (**3af**) was obtained in 85% yield. Cyclobutanol and 3-oxetanol also worked well, giving the desired ester in 89% and 84% yield, respectively. In contrast, in the case of cyclopentanol we found that 2.0 equiv of Cs_2CO_3 were required to promote the esterification reaction.

Using the original substoichiometric Cs_2CO_3 procedure, the natural product citronellol was found to give the corresponding product (**3aj**) in good yield. In this case, the chemistry could be carried out readily on the gram scale (10 mmol of substrate), illustrating its utility for the potential late-stage functionalization of a representative natural product. Sugar-containing complex alcohols were also tolerated. For instance, as shown in Figure 4, the use of α-D-allofuranose containing a sterically hindered secondary alcohol gave ester **3al** in 73% isolated yield using 0.2 equiv of Cs_2CO_3. This finding leads us to propose that the present strategy could prove useful in the modification of bioactive substrates.

However, an attempt at carrying out the esterification reaction using a tertiary alcohol (e.g., *t*-BuOH) using our standard reaction protocol failed to give an isolable quantities of the desired ester product. In this case, only the starting material was recovered, even when high temperatures (100 °C) were tested.

To demonstrate the synthetic utility of the present Cs_2CO_3-based method, a series of crown ether derivatives, **5a**−**c** (Figure 5),[21] were synthesized by treating *N*-activated amides with polyethylene glycols (**4a**−**c**). Consistent with early reports in the literature, the cesium cation acts as a template to promote ring closure in lieu of linear condensation (thus reducing polymerization).[22] There is a clear ring size

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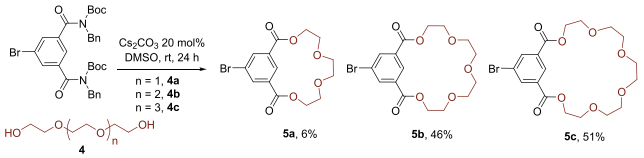
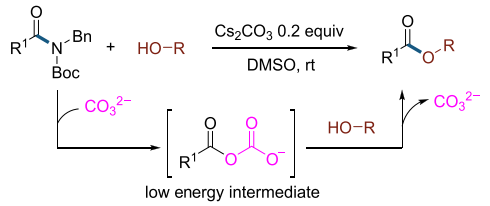


Figure 5. Synthesis of crown ether derivatives.

dependence on the yield. This dependence is reflected in the lower yield of **5a** (6%), a cyclic polyether-based product wherein the ring size does not match well the ionic radius of the Cs^+ cation (r_{Cs+} = 1.69 Å).[23] However, in the case of the polyether-diol, **5c**, a better size complementarity between the Cs^+-template and the incipient ring is expected; in this case, the overall yield for the formation of **5c** is 51%. While beyond the scope of the present study, the diester crown products produced by the present methodology are expected to endow unique molecular recognition features as compared to more classic crown ethers containing only ethylene bridges between the oxygen atoms.[24]

Detailed mechanistic studies are ongoing. However, two findings discussed above are noteworthy. First, the best results were obtained in the highly polar medium DMSO. Second, higher reaction rates were seen for the 4-cyanophenyl amide as compared to the corresponding 4-methylphenyl benzamide (vide supra). This leads us to propose a mechanistic pathway that involves initial nucleophilic attack of the carbonate anion on the amide carbonyl group; this is a first reaction step that is expected to be made more facile in the case of amides bearing strongly electron-withdrawing groups. Once formed, attack by the alcohol nucleophile and breakdown of the carbonate ester (CO_3^{2-} as the leaving group or HCO_3^- in the event the intermediate is protonated) as the second reaction step would then generate the observed ester products (Scheme 1).[20] An

Scheme 1. Proposed Reaction Mechanism



alternate reaction pathway involving direct nucleophilic addition of the alcohol to the amide is also possible wherein the cesium cation may act as a Lewis acid to activate the amide.[16f]

In summary, we describe here the esterification of amides using activated *N*-benzyl-*N*-Boc-carbamate and a variety of alcohols substrates, with Cs_2CO_3 as the catalyst. The effectiveness of this method and its wide tolerance for a variety of functional groups lead us to propose it may have a role to play in a range of practical synthetic applications. Initial demonstrations of this potential have been made via the esterification of citronellol and sugars, as well as the synthesis of several crown ether derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02513.

Experimental procedures, characterization of compounds, mechanistic studies (PDF)

NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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