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# Cobalt-Catalyzed Esterification of Amides

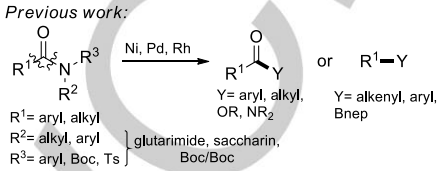
Yann Bourne-Branchu, Corinne Gosmini* and Grégory Danoun*

**Abstract:** The first cobalt-catalyzed amide activation of *N*-Boc-amides, and their conversion into esters, is reported herein. This new methodology presents a very practical process, that does not require an inert atmosphere, uses an inexpensive cobalt catalyst, and proceeds under mild reaction conditions. This catalytic system has a broad substrate scope and has been shown to be highly efficient, with catalyst loadings as low as 1 mol%.

Amides are versatile building blocks commonly found in natural organic molecules. They exhibit high stability and good coordination to metals due to the delocalization of the nitrogen lone pair into orbitals on the carbonyl moiety.[1] As such, this functional group has recently been used as metal-coordinating directing group to activate *ortho* C–H bonds.[2] The development of a palette of *ortho*-metalation reactions has shown the amide functional group to be one of the most powerful and versatile directing groups employed in C–H bond activation reactions.[3] Several transformations using amides as *O*- or *N*-chelating monodentate or bidentate directing groups have been developed and have shown high efficiency in C($sp^2$)–H or C($sp^3$)–H bond activation reactions with different metal catalysts. In comparison with its important utility in organometallic coordination chemistry, the metal-catalyzed activation of amides has not been extensively studied.[4]

Since the seminal reports by Hanessian and Charette of the transformation of amides into esters or nitriles using unstable and potent electrophiles such as trialkyloxonium or triflic anhydride,[5] the pursuit of developing new methodologies for the activation of amides has been dormant.[6] In 2015, Garg and co-workers described an elegant nickel(0)-catalyzed conversion of benzamides into esters using a Ni(0)/NHC catalyst system that involves the first direct oxidative addition into the amidic C–N bond.[7] Independently, Szostak and co-workers developed a sterically and electronically twisted amide derived from glutarimide which disfavored the delocalization of the nitrogen lone-pair. This particular configuration of the amide allowed oxidative addition of palladium catalytic system into the amidic C–N bond.[8] This peculiar strategy to twist amides notably *via* the introduction of a Boc or a Tosyl group proved to be highly efficient in various coupling reactions.[9] In particular, oxidative addition of palladium,[10] nickel[11] or rhodium[12] was greatly eased using these twisted amides that allowed the development of new methodologies to form C–X (X= O, N, B) or C–C bonds.[13]

However, these two esterification methodologies[7,11a] suffer from drawbacks such as significant catalyst loadings (typically 10-15 mol%) and the use of unstable (*i.e.* not easy-to-handle) catalytic systems.[14]




**Scheme 1:** Previous metal-catalyzed coupling reaction of amides.

Among the several metals that are active enough to insert into these unreactive bonds,[15] cobalt seems promising to avoid these drawbacks. Indeed, mixing a simple, cheap and easy-to-handle cobalt precursor in combination with the appropriate reductant form *in-situ* low-valent cobalt species. The latter has already demonstrated high activity in catalytic processes and possessed a remarkable robustness regarding oxygen or water contamination of the reaction media.[16] Moreover, to the best of our knowledge, no cobalt catalytic system has been previously reported in the activation of benzamides.

Based on Garg's mechanism, we envisaged the oxidative addition of a low-valent cobalt complex into the C–N bond. Then, an exchange of the *N*-Boc amine moiety for an alkoxide at the acyl-cobalt intermediate would occur, followed by reductive elimination (Figure 1).

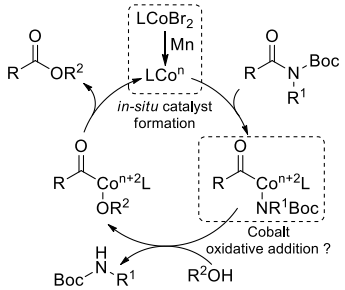



**Figure 1.** Possible mechanism of the cobalt-catalyzed esterification.

To probe our hypothesis, we began our study with *N*-Boc-benzanilide (**1**) as a test substrate and ethanol as coupling partner. The use of classical reaction conditions developed in our group – $CoBr_2$ as precursor, bipyridine as ligand, TMSCl activated manganese as reductant and a mixture of DMF/pyridine as the solvent – allowed the formation of a substantial amount of ethyl benzoate (**2**) in only 3 h with no precautions to exclude oxygen and water from the reaction mixture (Table 1, entry 1). Encouraged by this preliminary result, we decided to further optimize these reaction conditions.

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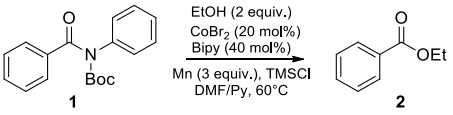
**Table 1.** Optimization of the coupling reaction between *N*-Boc-benzanilide and ethanol.[a] Bipy = 2,2'-bipyridine. TMSCl = trimethylsilylchloride. Py = pyridine. Boc = *tert*-butylcarbamate. Phen= 1,10-phenantroline.




1 2

| Entry | Deviation from standard conditions | Yield %[b] |
|---|---|---|
| 1 | None | 67 |
| 2 | No $CoBr_2$ / No Bipy / No Mn / No TMSCl | n.d. |
| 3 | No Mn | n.d. |
| 4 | No $CoBr_2$ | n.d. |
| 5 | No TMSCl | 24, 65[c] |
| 6 | $CoCl_2$ instead of $CoBr_2$ | 52 |
| 7 | $Co(OAc)_2$ instead of $CoBr_2$ | 63 |
| 8 | Phen instead of bipy | 65 |
| 9 | No bipy | 15 |
| 10 | No Py | 11 |
| 11 | Zn instead of Mn | 51 |
| 12 | In instead of Mn | 7 |
| 13[d] | none | 80 |
| 14[d] | 1 equiv. Mn | 84 |
| 15[d] | 20 mol% Mn | 2 |

[a] reaction conditions: *N*-Boc-benzanilide (0.5 mmol), $CoBr_2$ (20 mol%), bipy (40 mol%), Mn (3 equiv.), EtOH (2 equiv.) in DMF (2.3 mL) and pyridine (0.2 mL) was activated by TMSCl (traces) and stirred at 60 °C during 3 h. [b] GC yield using dodecane as internal standard. [c] during 20 h. [d] 5 mol% $CoBr_2$ / 10 mol% bipy.

First, a series of control experiments was examined. The blank reaction without any metal did not yield any ester (Table 1, entry 2). In order to identify any Lewis-acid assisted reactivity of the cobalt or manganese, reactions in the presence of only $CoBr_2$ and bipyridine without any reductant (Table 1, entry 3), and in the presence of only activated reductant (Mn(II) or Mn(III)) (Table 1, entry 4) were performed and none of the desired ester was detected. Only starting material was observed in all control experiments, consistent with the oxidative addition of a low-valent cobalt complex which is in turn consistent with the observation of traces of benzophenone and biphenyl in initial reactions. Finally, removal of TMSCl from the reaction mixture dramatically slowed down the catalysis process which only attained 24% conversion after 3h – albeit the reaction could be pushed to 65% yield after 20 h (Table 1, entry 5 vs entry1). This important difference in rate points out the specific role of TMSCl as a manganese activating agent.[17]

The catalytic system was next examined and different Co(II) sources were tested. Changing cobalt bromide for the chloride or acetate precursor had no influence on the process (Table 1, entries 6 and 7). The use of a ligand, and in particular *N*-heteroaromatics, was detrimental for the reaction to proceed (Table 1, entry 1 and 8 *vs* entry 9). Similarly, the use of pyridine as co-solvent greatly enhanced the reactivity (Table 1, entry 10). Replacing the manganese reductant with either zinc or indium led to a decrease of reactivity (Table 1, entries 11 and 12). Among all the solvents tested, polar and aprotic solvents such as DMF and NMP, gave the best yields (see supporting information). Decreasing the catalytic loading from 20 mol% to 5 mol% slightly enhanced the reaction yield (Table 1, entry 1 *vs* entry 13). In order to reduce waste, the amount of manganese was reduced to one equivalent which allowed to obtain **2** in 84% yield. Of note, a further decrease in the amount of reductant to a catalytic amount dramatically affected the yield which dropped to 2% (Table1, entries 14 and 15).

With these optimal reaction conditions in hand, we then explored the scope of *N,N*-disubstituted benzamides (Figure 2). Different benzanilides protected by methyl carbamate (**3**) or a *p*-toluenesulfonyl (**4**) groups were tested but only low to moderate yields were observed, even after 20 h. The lack of reactivity of amide **3** may arise from the scission of the methyl carbamate group that led to a deactivated benzanilide. No scission of the tosyl group was observed for amide **4** and only the starting material remained as observed by GC after 20 h. Interestingly, *N*-methylbenzanilide (**5**) used by Garg was completely unreactive under our reaction conditions. This result highlights the complementarity of those metal-catalyzed esterification methods. Some other *N*-Boc-benzamides bearing benzyl (**6**) or methyl (**7**) groups were also reacted and converted successfully into the corresponding ester with excellent yields. Two amides that are commonly used as C–H bond activation directing groups, *N*-methoxy- and *N*-quinolin-8-yl amides, were first activated by Boc protection (**8** and **9**) and transformed efficiently into ethyl benzoate **2**.[18] Of note, only the unprotected benzamide was observed by GC as side product when using Boc-protected benzamides substrates in reaction.

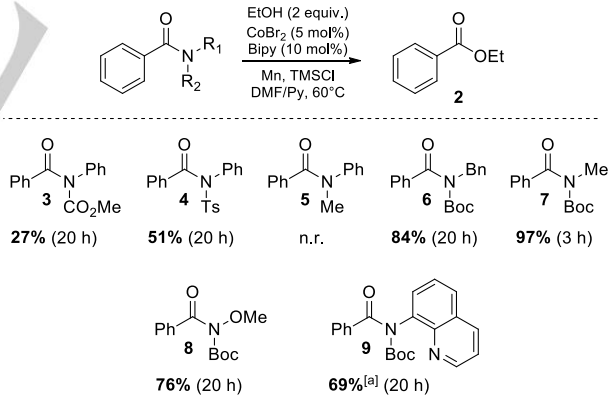



**Figure 2.** Scope of *N,N*-bis-substituted benzamide. GC yield using dodecane as internal standard are given. Reaction conditions: benzamide (0.5 mmol), $CoBr_2$ (5 mol%), bipy (10 mol%), Mn (1 equiv.), EtOH (2 equiv.) in DMF (2.3 mL) and pyridine (0.2 mL) was activated by TMSCl (traces) and stirred at 60 °C. [a] reaction was heated at 80 °C. Ts = *p*-toluenesulfonyl.

We then subjected *N*-methyl-*N*-Boc-benzamides to our methodology (Figure 3). Gratifyingly, the reaction tolerates a wide variety of functionalities, such as methyl (**10** to **12**), methoxy (**13**), dimethylamino (**14**), cyano (**15**), ester (**16**) and even aldehyde (**17**). In the case of the benzamide bearing methyl ester group (**16**), transesterification of the latter was also

observed. Iodo-, bromo- and even chlorobenzamides (**18**) were completely converted, with concomitant protodehalogenation, into ethyl benzoates (**2**) .The process could even be extended to the cinnamyl amide (**19**), as well as heteroaromatic compounds (**20** to **22**) and gave the desired esters in high yields. We were pleased to see that our methodology could also successfully be applied to aliphatic amides. In our reaction conditions, primary (**23**), neopentylic (**24**) and secondary (**25** and **26**) aliphatic amides were smoothly converted into esters. Gratifyingly, no epimerization of the chiral α-stereocenter of aminoacid **26** occurred during the process.[19]

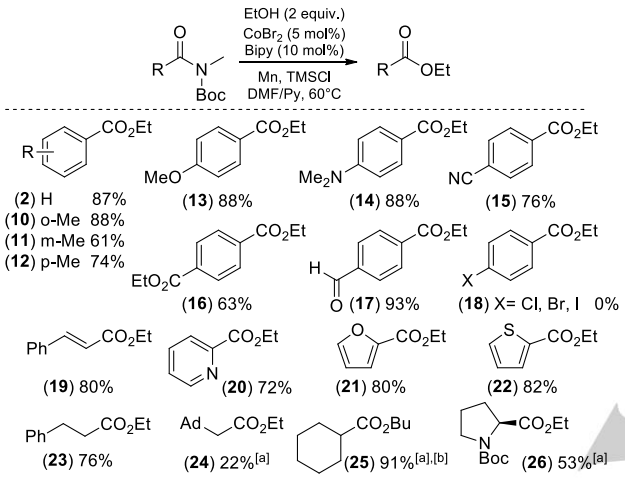



**Figure 3.** Scope of *N*-methyl-*N*-Boc-amides. Isolated yields are given. Reaction conditions: amide (0.5 mmol), $CoBr_2$ (5 mol%), bipy (10 mol%), Mn (1 equiv.), EtOH (2 equiv.) in DMF (2.3 mL) and pyridine (0.2 mL) was activated by TMSCl (traces) and stirred at 60 °C during 20 h. [a] reaction was heated at 80 °C. [b] 1-butanol instead of ethanol. Ad = adamantyl

Finally, we examined the reactivity of a variety of alcohol coupling partners which were used in only a slight excess (1.2 equiv.) (Figure 4). Numerous primary alcohols bearing various functional groups were reacted. Different chain lengths (**27** to **29**) as well as functional groups such as aryl (**30**), methoxy (**31**) and even dimethylamino (**32**) groups were smoothly activated. Interestingly, the presence of a secondary amino group (**33**) on the alcohol chain completely inhibited the catalysis. Nonetheless, we were delighted to observe the full conversion of the chlorinated alcohol into its corresponding ester (**34**) though the protodehalogenated side product was also observed (83:17 ratio of chlorinated to dechlorinated products). Surprisingly, while allylic alcohol (**35**) was completely unreactive, homoallylic alcohol (**36**) was successfully converted and the corresponding ester was isolated in good yield. Noteworthy, a small amount of *Z* to *E* isomerization of *ca*. 10% was observed for the latter. Benzylic (**37** and **38**) or heterobenzylic (**39**) alcohols also proved to be efficient coupling partners in the reaction. In contrast with previously used halogenated aryl partners (**38** vs **18**), chlorinated benzylic alcohol did not undergo any protodehalogenation side reactions yielding the corresponding ester **38** in 80% yield. Poor nucleophiles such as phenol (**40** and **41**) were converted into esters in moderate yields along with a substantial amount of unprotected benzamide. This methodology was next applied to various secondary alcohols. Interestingly, the reaction was significantly influenced by their steric hindrance. Indeed less sterically hindered secondary alcohols such as cyclobutanol (**43**) were esterified very efficiently while isopropanol (**42**), cyclopentanol (**44**) and cyclohexanol (**45**) led to around 65% yields of the corresponding esters. Hexafluoroisopropanol could also be used as a partner despite its poor nucleophilicity and the corresponding ester **46** was isolated in 26% yield.

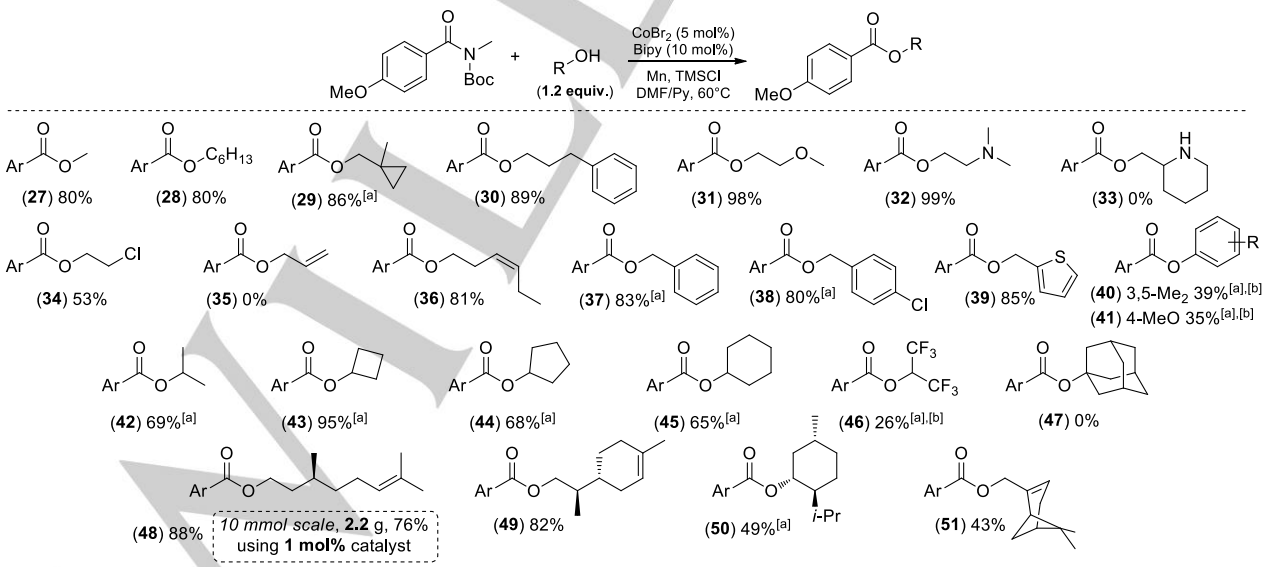



**Figure 4.** Scope of the alcohol coupling partner. Isolated yields are given. Reaction conditions: benzamide (1 mmol), $CoBr_2$ (5 mol%), bipy (10 mol%), Mn (1 equiv.), alcohol (1.2 equiv.) in DMF (4.6 mL) and pyridine (0.4 mL) was activated by TMSCl (traces) and stirred at 60 °C during 20 h. Ar = p-anisol [a] reaction was heated at 80 °C. [b] 2 equiv. of alcohol was used.

Tertiary alcohols such as 1-adamantanol (**47**) were completely inert under these reaction conditions and only the starting material was recovered.

As a proof of concept of our methodology for late-stage functionalization, we tackled the coupling of N-Boc-methoxybenzamide with structurally complex alcohols such as natural products or fragrances which would give access to advanced compounds. Under our reaction conditions, *L*-citronellol (**48**), (+)-*p*-Menth-1-en-9-ol (**49**), (+)-menthol (**50**) and (-)-myrtenol (**51**) were successfully acylated and gave access to the ester derivatives in moderate to excellent isolated yields. The scalability of this cobalt-catalyzed esterification of amides was evaluated. Thus, with a reduced catalyst loading of 1 mol%, we were pleased to isolate 76% yield of ester **48** on a 10 mmol scale. This result demonstrates the high activity of the cobalt catalytic system for the conversion of benzamide derivatives into esters.

Moreover this methodology can be directly carried out in a one-pot sequence starting from *N*-methylbenzamide. First, the latter is converted into *N*-Boc-benzamide and is subsequently reacted in the cobalt catalysis without any intermediary workup. Importantly, both the *t*-butanol, generated in the Boc introduction step, as well as the DMAP catalyst used, did not interfere at all with the catalytic process and the corresponding ester was obtained in 84% yield.

To conclude, we have developed a new cobalt-catalyzed esterification of *N*-Boc-benzamides allowing a straightforward route to access esters. The particular advantages of this newly discovered methodology include the use of an inexpensive, simple and low loading catalyst system, the direct and practical process which requires neither distilled solvents nor inert atmosphere, as well as mild reaction conditions. A broad scope of variously functionalized alcohols and amides were compatible with this methodology. Moreover, a one-pot process enables the direct synthesis of these esters from benzamides. Deeper mechanistic investigations are currently on-going as well as developing a second generation catalytic system that would be even more active.

## Experimental Section

**Typical procedure for amide conversion into ester:** a 20 mL reaction tube was charged with *N*-Boc-amide (1.0 mmol), bipyridine (0.10 mmol, 15.6 mg), manganese powder (1.0 mmol, 54.9 mg), $CoBr_2$ (0.050 mmol, 10.9 mg), alcohol (1.2 mmol), DMF (4.6 mL) and pyridine (0.4 mL). Then, TMSCl (0.32 mmol, 40 µL) was added to the reaction medium and the tube was sealed and placed into heated aluminium block. The tube was stirred at the indicated temperature for 20 h. After cooling to room temperature, the reaction medium was diluted with $Et_2O$ and filtered through a pad of silica gel. The resulting organic layer was washed with HCl (1N) and LiCl aqueous solution (5%) three times, and dried over $MgSO_4$, filtered and evaporated. The crude product was purified by flash chromatography and characterized by NMR spectroscopy ($^1H$, $^{13}C$).

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**Keywords:** Cobalt • Amides • Esterification • Cross-coupling • Homogeneous catalysis

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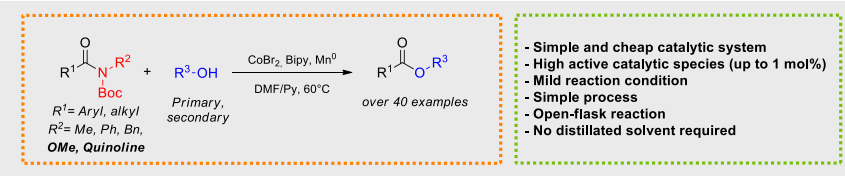


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**Cobalt-Catalyzed Esterification of Amides**

A practical mild and efficient cobalt-catalytic system is described that converts amides into esters. This methodology is complementary to previous nickel-catalyzed systems, affording new selectivity and a more diverse range of amide substrates, including common C–H bond activation directing groups. This new reaction requires neither inert atmosphere nor distilled solvents and even proceeds at low catalyst loading such as 1 mol% catalyst.