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International Edition: DOI: 10.1002/anie.201605162
German Edition: DOI: 10.1002/ange.201605162

Nickel-Catalyzed Reductive Amidation of Unactivated Alkyl Bromides

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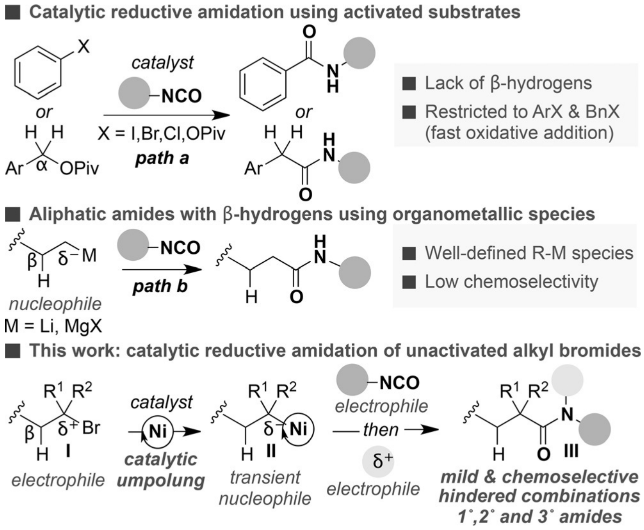
Abstract: *A user-friendly, nickel-catalyzed reductive amidation of unactivated primary, secondary, and tertiary alkyl bromides with isocyanates is described. This catalytic strategy offers an efficient synthesis of a wide range of aliphatic amides under mild conditions and with an excellent chemoselectivity profile while avoiding the use of stoichiometric and sensitive organometallic reagents.*

Although unactivated alkyl halides are inherently disposed towards destructive β-hydride elimination and homodimerization pathways, these molecules have successfully been employed in a myriad of metal-catalyzed cross-coupling reactions.[1] At present, the vast majority of these processes are based on stoichiometric, well-defined, and in many instances, air-sensitive organometallic species. Challenged by these drawbacks, recent years have witnessed the development of cross-electrophile coupling processes,[2] becoming powerful and practical synthetic alternatives to classical cross-coupling reactions, achieving an otherwise similar molecular complexity under milder reaction conditions while avoiding the need for organometallic reagents.

Despite the advances realized, the palette of electrophilic partners in cross-electrophile processes remains rather limited when compared with classical nucleophile/electrophile regimes. It comes as a surprise that isocyanates, privileged synthons in industrial settings,[3] have been virtually unexplored in cross-electrophile events with organic (pseudo)halides.[4,5] This is likely due to the strong binding properties of isocyanates to low-valent transition-metal complexes, leading to unproductive dimerization or trimerization pathways.[6] At present, cross-electrophile coupling reactions with isocyanates as coupling partners remain confined to substrates that rapidly undergo oxidative addition, such as aryl or benzyl halides lacking β-hydrogen atoms, thus preventing undesired pathways (Scheme 1, path a).[7] Ideally, this field of expertise should include the use of unactivated alkyl halides possessing β-hydrogen atoms,[1] thus resulting in a new synthetic route for rapidly preparing aliphatic amides, ubiquitous motifs in pharmaceuticals, agrochemicals, peptides, and polymers.[8] Indeed, a close look into the literature data indicates that there is a paucity of highly chemoselective catalytic C–C bond-forming processes[9] with improved flexibility, practicality, and generality that would give access to primary, secondary, or even tertiary amides at will, including hindered substrate combinations, while avoiding the handling of carbon monoxide (CO) at high pressures[10] or well-defined and stoichiometric organometallic species,[11] among others (Scheme 1, path b).[12]



Scheme 1. Amide synthesis through C–C bond formation using isocyanates. 1° = primary; 2° = secondary; 3° = tertiary.

As part of our interest in reductive coupling reactions,[13] we questioned whether a unified catalytic umpolung strategy through the in situ generation of carbogenic nucleophiles (**II**) from unactivated alkyl halides (**I**) and their coupling with isocyanates would constitute a generic platform for preparing aliphatic amides (**III**; Scheme 1, bottom). However, at the outset of our investigations it was unclear whether it would be possible to balance the high reactivity of isocyanates and the commonly observed parasitic β-hydride elimination or homodimerization pathways when using unactivated alkyl halides. Herein, we describe the successful realization of this concept, providing access to primary, secondary, and even tertiary alkyl amides by exploiting a previously unrecognized opportunity through sequential cross-coupling reactions of three different electrophiles.

We began our investigations by studying the reaction of **1a** with isocyanate **2a** (Scheme 2). The choice of **2a** was not arbitrary, as primary amides can be prepared by simple deprotection of the *tert*-butyl group.[14] After judicious

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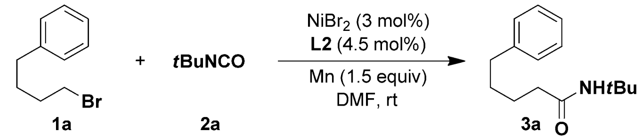
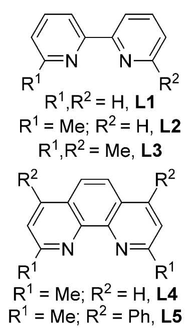


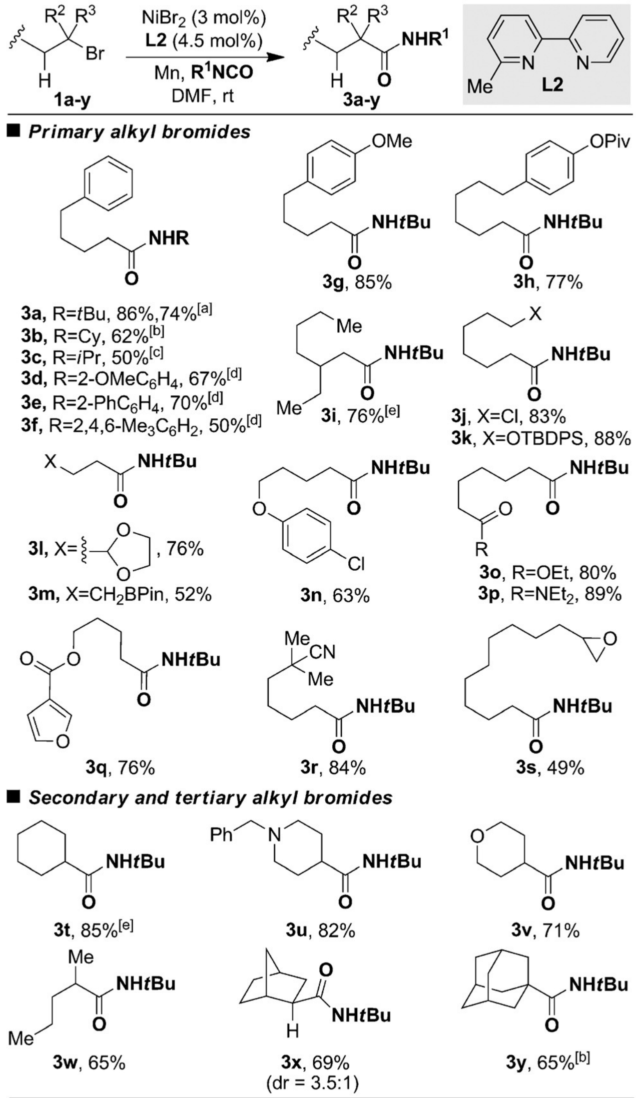
Entry	Devation from standard conditions	**3a** (%)[a],[b]
1	none	95 (86)[c]
2	**L1** instead of **L2**	39
3	**L3** instead of **L2**	55
4	**L4** instead of **L2**	33
5	**L5** instead of **L2**	30
6	$NiCl_2$·glyme instead of $NiBr_2$	80
7	$Ni(COD)_2$ instead of $NiBr_2$	45
8	MeCN instead of DMF	0
9	DMSO instead of DMF	0
10	Zn instead of Mn	0
11	Using **1a-I** instead of **1a**	0
12	Using **1a-OTs** instead of **1a**	40



Scheme 2. Optimization of the Ni-catalyzed reductive amidation of **1a** with **2a**. [a] Reaction conditions: **1a** (0.50 mmol), **2a** (0.75 mmol), $NiBr_2$ (3 mol%), ligand (4.5 mol%), Mn (0.75 mmol), DMF (1 mL) at RT, 16 h. [b] GC yield using *n*-decane as the internal standard. [c] Yield of isolated product. **1a-I** = 1-iodo-4-phenylbutane; **1a-OTs** = 4-phenylbutyl-4-methylbenzenesulfonate.

evaluation of the reaction parameters,[15] we found that a combination of inexpensive $NiBr_2$ (3 mol%), **L2** (4.5 mol%),[16] and Mn as the reducing agent in DMF at RT, delivered **3a**, which was isolated in 86% yield. Importantly, only traces of β-hydride elimination and homodimerization products were detected in the crude mixtures. Notably, ligand optimization revealed a crucial influence of the substitution pattern on the aromatic ring, with bipyridine ligands lacking *ortho* substituents (entry 2) or structurally similar phenanthroline ligands **L4** and **L5** providing inferior results (entries 4 and 5).[17,18] Strikingly, the utilization of **L3** had a deleterious impact on yield when using **2a** as substrate (entry 3),[19] revealing an interesting effect of the substituents located at the *ortho* position. As shown in entries 6–12, the use of other solvents, precatalysts, reducing agents, or **1a-I**/**1a-OTs** analogues resulted in diminished yields of **3a**,[20] thus showing the subtleties of our procedure. As expected, control experiments revealed that all of the reaction parameters were critical for success.[15]

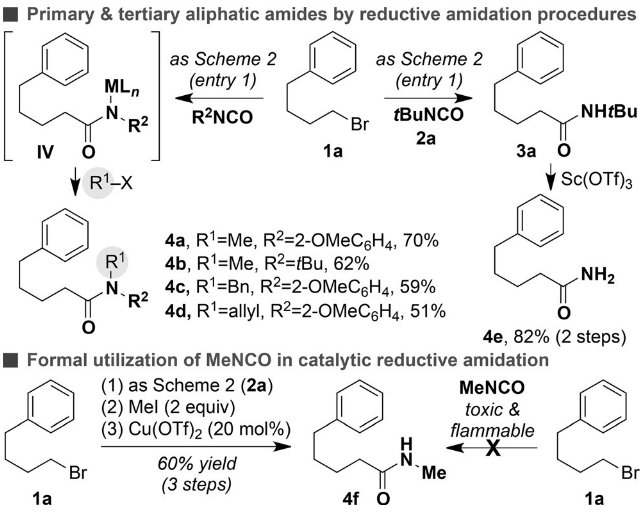
Encouraged by these results, we turned our attention to study the preparative scope of our Ni-catalyzed reductive amidation of unactivated alkyl bromides with isocyanates (Scheme 3). As shown for **3a**–**3f**, the procedure allowed for the coupling of either aromatic or aliphatic isocyanates with equal ease. Intriguingly, a procedure employing **L3** was particularly efficient when dealing with aromatic isocyanates.[21,22] At present, we do not have any rational explanation for this behavior. Particularly illustrative was the chemoselectivity profile of the procedure, as substrates containing silyl ethers (**3k**), acetals (**3l**), esters (**3h**, **3o**, **3q**), amides (**3p**), nitriles (**3r**), heterocycles (**3q**), or chlorides (**3j**, **3n**) could all be perfectly accommodated. As shown for **3h** and **3n**, aryl pivalates and chlorides, substrates commonly employed in Ni-catalyzed cross-electrophile couplings, do not



Scheme 3. Scope of alkyl bromides and isocyanates. Reaction conditions: as for Scheme 2, entry 1; Yields of isolated products, average of at least two independent runs. [a] **1a** (4.69 mmol). [b] $NiBr_2$ (10 mol%), **L2** (15 mol%). [c] [(TMEDA)Ni(*o*-tolyl)Cl] (15 mol%), **L2** (30 mol%). [d] $NiBr_2$ (10 mol%), **L3** (20 mol%), RNCO (0.5 mmol). [e] $NiBr_2$ (5 mol%), **L2** (7.5 mol%). TMEDA = tetramethylethylenediamine; cy = cyclohexyl; TBDPS = *tert*-butyldiphenylsilyl.

compete with the efficacy of this method. Boronic esters (**3m**) were tolerated as well, leaving an additional handle for further functionalization. Although in lower yields, we found that terminal epoxides could also participate in the targeted reaction (**3s**). Importantly, the reaction could be easily scaled up, obtaining **3a** in similar yields. On the basis of these results, we wondered whether our procedure could accommodate unactivated secondary or tertiary alkyl halides. Despite the higher statistical propensity for β-hydride elimination pathways and increased steric hindrance around the C–Br bond, a host of cyclic and acyclic secondary alkyl bromides could be equally accommodated under otherwise identical reaction conditions (**3t**–**3x**). A noteworthy observation concerns the preferential formation of **3x** from *exo*-**1x**, reinforcing the idea that radical species might come into play.[23] The successful preparation of **3y** showcases the generality of our approach as unactivated tertiary alkyl halides have rarely been employed in metal-catalyzed cross-electrophile coupling reactions.[24,25]

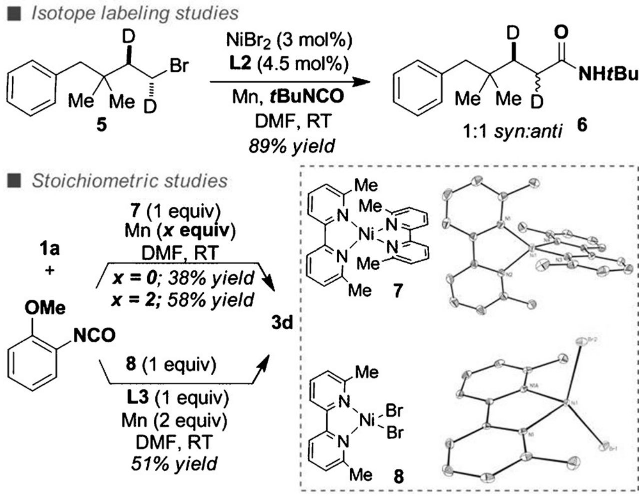
A close survey of the literature data reveals that a unified metal-catalyzed strategy for accessing primary, secondary, and tertiary amides remains elusive. In a final venture to unlock the full potential of our procedure, we sought to intercept the in situ generated **IV** upon subsequent addition of a proper electrophile, thus accessing tertiary aliphatic amides in a one-pot fashion (Scheme 4, top left). Although



Scheme 4. Sequential C–C bond-forming scenarios.

counterintuitive at first sight, the preparation of **4a–4d** demonstrates the feasibility of this approach, constituting a formal cross-coupling reaction of three different electrophiles. On the other hand, primary amides could easily be obtained by deprotection of the *tert*-butyl group with $Sc(OTf)_3$ (**4e**).[26] Importantly, such a design principle allowed us to rapidly convert **1a** into **4f**, thus constituting a powerful alternative platform for handling flammable and toxic MeNCO in amidation technologies (Scheme 4, bottom).[27] Taken together, the results in Scheme 3 and Scheme 4 demonstrate the prospective impact of our catalytic amidation procedure for accessing a wide variety of amides from simple starting materials in a straightforward manner.

Although a comprehensive mechanistic study should await further investigations, deuterium labelling experiments were performed to study the stereochemical course of the reaction (Scheme 5, top). Interestingly, we found a statistical mixture of diastereoisomers in **6** when exposing **5** to our optimized reaction conditions, suggesting the intermediacy of single-electron-transfer (SET) processes.[23] In line with this notion, a complete racemization was detected when using (*R*)-(3-bromo-butyl)benzene (97% *ee*) as substrate. We then turned our attention to study the reactivity of the putative $Ni^0(\mathbf{L3})_2$ (**7**) and $NiBr_2(\mathbf{L3})$ (**8**) species (Scheme 5, bottom).[28,29] These compounds were easily prepared from either $Ni(COD)_2$ or $NiBr_2$ and were characterized by X-ray crystallography.[15] As expected, both **7** and **8** were found to be



Scheme 5. Preliminary mechanistic studies.

catalytically competent as reaction intermediates, delivering **3d** in slightly lower yield to that observed in Scheme 3 (57% yield).[30] More importantly, we found that **3d** could be obtained regardless of whether Mn was present or not with stoichiometric amounts of **7**. As expected, **8** delivers **3d** with similar yields to those shown for **7**. Although we cannot rigorously rule out other conceivable pathways,[31] we propose a mechanistic scenario involving alkyl–Ni^I species generated by comproportionation of in situ generated alkyl–Ni^{II} intermediates and $Ni^0(L)_2$, followed by insertion of the isocyanate motif, and a final SET mediated by Mn.[32,33]

In summary, we have described the first Ni-catalyzed reductive amidation of unactivated alkyl halides with isocyanates for accessing primary, secondary, or even tertiary amides through iterative techniques. The reaction proceeds under mild conditions, thus minimizing unproductive β-hydride elimination or dimerization/trimerization events, while accommodating a wide range of substrates with an excellent chemoselectivity profile. Further investigations on the mechanism and the elaboration of an asymmetric version of the reaction are currently being pursued in our laboratories.

Acknowledgements

We thank ICIQ, the European Research Council (ERC-277883), MINECO (CTQ2015-65496-R and Severo Ochoa Excellence Accreditation 2014–2018, SEV-2013-0319), FEDER, and the Cellex Foundation for support. Johnson Matthey, Umicore, and Nippon Chemical Industrial are acknowledged for a gift of metal and ligand sources. E.S. thanks MINECO for a FPI fellowship. We sincerely thank E. Escudero and E. Martin for all X-ray data.

Keywords: cross-coupling · nickel · reductive coupling · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 11207–11211
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[19] Note, however, that **L3** turned out to be particularly efficient for aryl isocianates (see Scheme 3).

[20] Full conversion to β-hydride elimination products was observed for **1a-I**. The observed reactivity of **1a-OTs** is in line with the ability of these substrates to couple with other heterocumulenes (see Ref. [13a]).

[21] Unlike the utilization of aliphatic isocyanates, equimolar amounts of aromatic isocyanates were critical to prevent the formation of considerable amounts of *N*-acylureas.

[22] [(TMEDA)Ni(*o*-tolyl)Cl] turned out to be particularly suited for the coupling of *i*PrNCO, avoiding dimerization or trimerization pathways.

[23] This hypothesis is reinforced by the significant inhibition observed when reacting **1a** with **2a** in the presence of radical scavengers such as TEMPO or BHT. The intermediacy of radical-type intermediates gains credence from the observation that the Ni-catalyzed reductive amidation of 6-bromohex-1-ene results in a linear relationship between acyclic and 5-*exo-trig* cyclization products at different Ni/**L2** loadings.

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Received: May 26, 2016
Published online: June 30, 2016

