

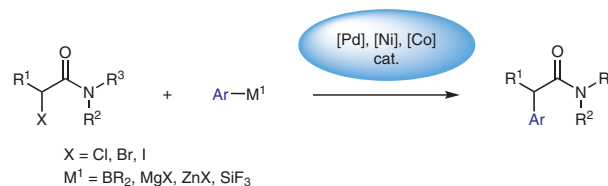
α -Arylation of Amides from α -Halo Amides Using Metal-Catalyzed Cross-Coupling Reactions

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Published as part of the 50 Years SYNTHESIS – Golden Anniversary Issue



Received: 06.11.2018

Accepted: 09.11.2018

Published online: 07.12.2018

DOI: 10.1055/s-0037-1611358; Art ID: st-z0745-sr

License terms: 

Abstract Metal-catalyzed α -arylation of amides from α -halo amides with organometallic reagents is reviewed. The article includes Suzuki–Miyaura, Kumada–Corriu, Negishi, and Hiyama cross-coupling reactions.

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Key words amide, arylation, cross-coupling, metal catalysis

1 Introduction

Aside from constituting the backbone of peptides, amides are ubiquitous moieties in natural products, pharmaceuticals, agrochemicals, and synthetic polymers.¹ More particularly, α -aryl amides are present in numerous biologically active molecules. For example, almoxerant² is used against insomnia while atenolol³ is involved in the treatment of cardiovascular diseases (Figure 1). In addition, α -aryl amides are one of the precursors of β -aryl amines, which are also important pharmacophores.⁴

One of the most widespread methods used to access α -aryl amides is the metal-catalyzed arylation of amide enolates.⁵ Extensive studies related to the α -arylation of carbonyl compounds have been reported, most of them concerning the functionalization of ketones and esters.⁶

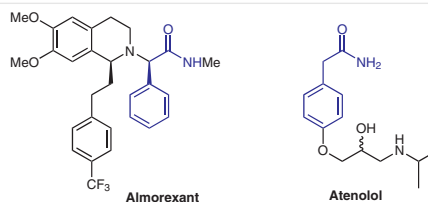
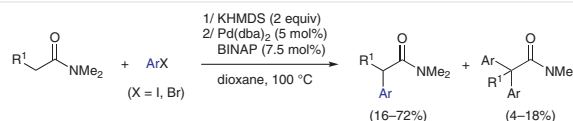


Figure 1 Bioactive molecules incorporating an α -aryl amide scaffolds

Due to the low acidity of the protons α to the carbonyl moiety,⁷ the arylation of amide enolates is scarcely reported in the literature. In 1998, Hartwig and co-workers developed a protocol enabling the palladium-catalyzed arylation of amide enolates with aryl halides.^{8–10} However, under these conditions, a significant amount of diarylated compound was formed as a mixture with the desired monoarylated product. This lack of selectivity is due to the higher acidity of the proton α to the carbonyl in the monoarylated compound compared to the acidity of protons of the starting amide. Furthermore, the presence of a strong base induced partial decomposition of the catalyst and high catalytic loadings are required (Scheme 1).¹¹



Scheme 1 Pd-catalyzed arylation of amide enolates

To circumvent these difficulties, the palladium-catalyzed arylation of pre-formed amide zinc enolates was developed. Zinc enolates were formed either by transmetalation of lithium, potassium or sodium enolates with ZnCl₂,¹² by direct insertion of activated zinc in the C–Br bond¹³ of α -bromo amides, or by deprotonation with Zn(tmp)₂ (tmp = 2,2,6,6-tetramethylpiperidinide).¹⁴ In comparison with the arylation of amide enolates, this two-step procedure allows



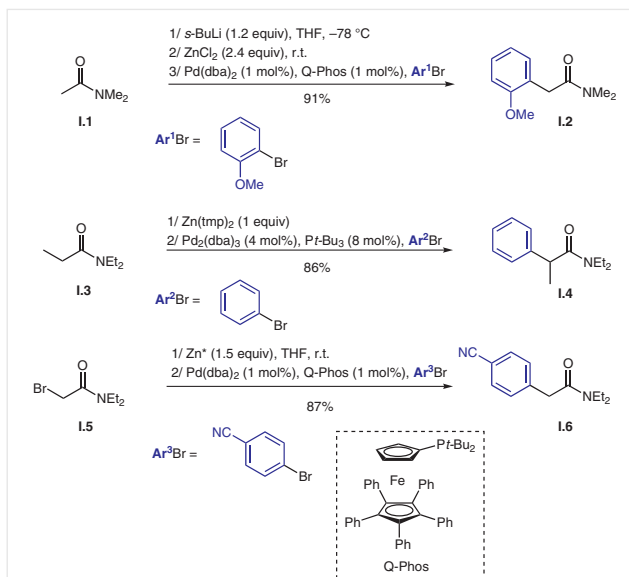
Janine Cossy's (Professor of Organic Chemistry, ESPCI Paris, Paris) early career was spent in Reims, where she did her undergraduate and graduate studies at the University of Champagne-Ardenne, working on photochemistry under the supervision of Pr. Jean Pierre Pête. After a postdoctoral stay with Pr. Barry M. Trost, for two years at the University of Wisconsin (USA), she returned to Reims where she became, in 1990, Director of Research at the CNRS. In the same year, she moved to Paris and, since 1990, she is Professor of Organic Chemistry at the ESPCI Paris. Janine Cossy's research interests focus on the synthesis of natural products and biologically active molecules and on the development of synthetic methods. Her research efforts have resulted in more than 500 publications and 15 patents. Among the awards, she received the CNRS Bronze Medal (1987), the CNRS Silver Medal (1996), UK Royal Society Rosalyn Franklin International Lecturership awarded to internationally recognized women scientists (UK) (2005), Le Bel Award from the French Chemical Society (France) (2009). In 2013, she was nominated Chevalier de la Légion d'Honneur and in 2015, she obtained the E. C. Taylor Senior Award (USA). She was elected at the French Academy of Sciences in 2017. She is Organic Letters Associate Editor since 2005.

Amandine Guérinot (Assistant professor in Organic Chemistry, ESPCI Paris, Paris) was born in 1983 in Troyes, France. She received her engineer's diploma from ESPCI ParisTech in 2007 and her Ph. D. in 2010 from the University Pierre et Marie Curie under the supervision of Dr. Sébastien Reymond and Pr. Janine Cossy. She joined the the group of Pr. Sylvain Canesi at UQAM, Montreal as a postdoctoral associate and then moved to ICMMO, Orsay, France for a one-year postdoctoral stay with Pr. Vincent Gandon. After a six months postdoctoral fellowship with Dr. Laurent Micouin (Paris Descartes University), she was appointed associate professor in 2013 at ESPCI Paris in the group of Pr. Janine Cossy. Her research interests include organometallic cross-couplings, iron catalysis and synthesis of biologically active compounds.

Etienne Barde (PhD student in Organic Chemistry, ESPCI Paris, Paris (France) was born in 1989 in Pau, France. He received his engineer's diploma from ENSCCF (now Sigma Clermont) in 2014 and then joined the organic chemistry laboratory at ESPCI Paris to prepare his Ph. D under the supervision of Dr. Amandine Guérinot and Pr. Janine Cossy.

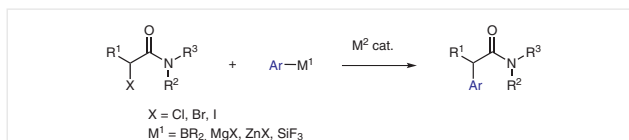
better yields to be reached yields in α -aryl amides and exhibits higher substrate scope. It could be applied to the synthesis of an array of α -arylated amides and lactams (Scheme 2).¹⁵

However, the preparation of zinc enolates is not straightforward and synthetic chemists have looked for more practical alternatives. In this context, a polarity reversal by using a metal-catalyzed cross-coupling between α -halo amides and aryl organometallics appeared as an attractive strategy. Indeed, metal-catalyzed cross-coupling reactions have emerged as powerful tools for the creation of C–C bonds.¹⁶ The purpose of this review is to give a short overview of the existing metal-catalyzed cross-coupling implying α -halo amides to produce α -aryl amides. A classi-



Scheme 2 Selected examples of Pd-catalyzed arylation of amide zinc enolates

fication according to the nature of the cross-coupling (i.e. Suzuki–Miyaura, Kumada–Corriu, Negishi, or Hiyama cross-coupling) is proposed (Scheme 3).

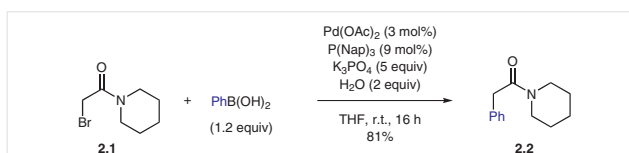


Scheme 3 Metal-catalyzed α -arylation of α -halo amides

2 Suzuki–Miyaura Cross-Coupling

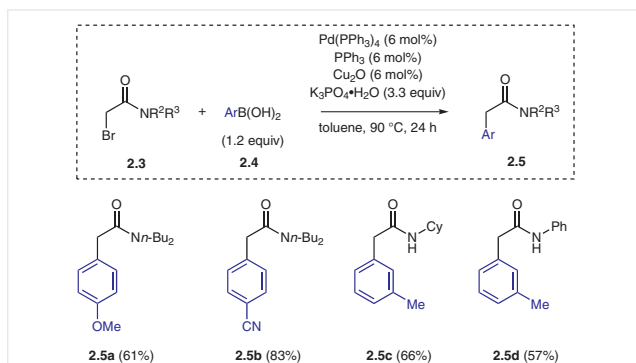
2.1 Palladium Catalysis

The first arylation of an α -halo amide using a Suzuki–Miyaura cross-coupling was reported in 2001.¹⁷ When the tertiary amide **2.1** featuring a primary bromide was reacted with phenylboronic acid in the presence of Pd(OAc)₂, tri(1-naphthyl)phosphine [P(Nap)₃], K₃PO₄ as the base, and water, the α -phenyl amide **2.2** was isolated in good yield (81%) (Scheme 4).



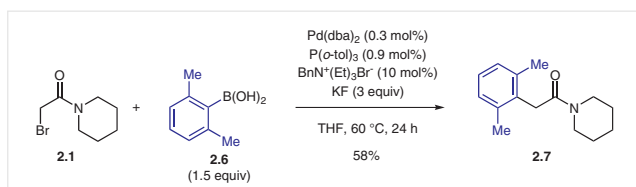
Scheme 4 Suzuki–Miyaura coupling on an α -bromo tertiary amide with phenylboronic acid

In 2003, a modification of the catalytic system [Pd(PPh₃)₄, PPh₃, Cu₂O] enabled the generalization of the arylation to a larger scope of α -bromo amides including tertiary and secondary amides.¹⁸ A variety of *meta*- and *para*-substituted arylboronic acids were successfully used in the transformation illustrating its functional group tolerance. However, primary bromides were exclusively employed (Scheme 5).



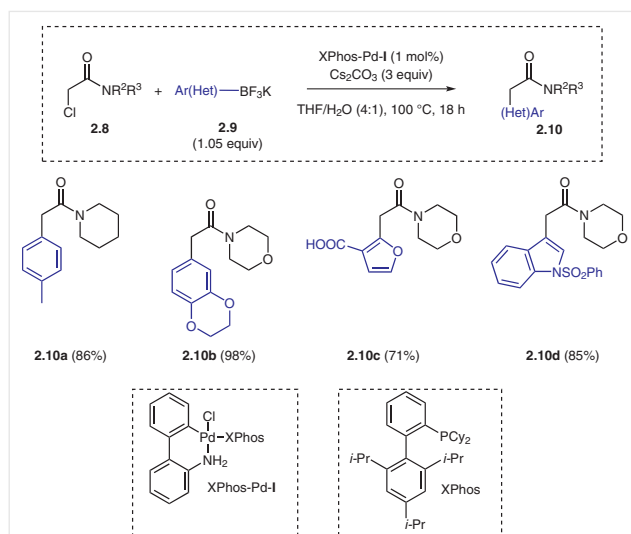
Scheme 5 α -Arylation of secondary and tertiary amides from α -bromo amides using Suzuki–Miyaura coupling

After optimization of the catalytic system, the reaction was extended to sterically demanding *ortho*-substituted boronic acids.¹⁹ With these coupling partners, the use of a catalytic amount of Pd(dba)₂ (0.3 mol%) together with P(*o*-tol)₃ (0.9 mol%) in the presence of a phase transfer agent BnN⁺(Et)₃Br[−] and a base (KF) exhibited the best performance, allowing the isolation of **2.7** in a good yield (58%) (Scheme 6).



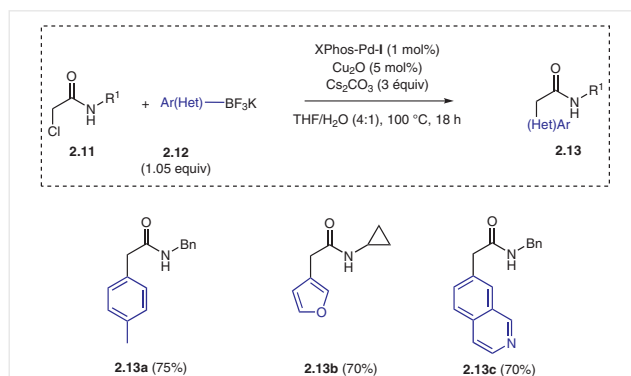
Scheme 6 Use of sterically demanding boronic acids

Due to the moderate stability of boronic acids under the coupling conditions, excess of the aryl partner is usually required and phase transfer agents are often added to accelerate the transmetalation step. To alleviate these problems, Molander and co-workers developed a cross-coupling between α -chloro amides and crystalline, moisture- and air-stable potassium aryltrifluoroborate salts.²⁰ The pre-catalyst XPhos–Pd–I, which is able to evolve into a monoligated Pd(0) species, was selected and Cs₂CO₃ was used as a base in a THF/H₂O mixture. Several α -chloro tertiary amides were efficiently coupled to an array of potassium aryltrifluoroborates including heteroaromatic partners (Scheme 7).



Scheme 7 Suzuki–Miyaura cross-coupling between α -chloro tertiary amides and potassium (het)aryltrifluoroborates

The reaction was then extended to secondary amides providing that Cu₂O was added. However, once again the reaction seems to be restricted to primary chlorides lacking β -H hydrogens. This limitation may come from the high propensity of organopalladium intermediates to achieve β -H elimination (Scheme 8).



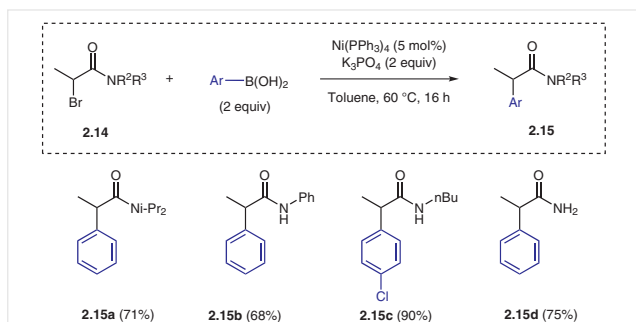
Scheme 8 Suzuki–Miyaura cross-coupling between α -chloro secondary amides and potassium (het)aryltrifluoroborates

To broaden the scope of the α -arylation of amides using the Suzuki–Miyaura coupling, nickel-based catalysts, which are less prone to β -H elimination, were selected.²¹

2.2 Nickel Catalysis

Lei and co-workers were the first to report nickel-catalyzed Suzuki–Miyaura cross-couplings between α -bromo amides and arylboronic acids.²² The use of Ni(PPh₃)₄ as a catalyst and K₃PO₄ as a base allowed the arylation of secondary bromides in good yields. Tertiary, secondary, and

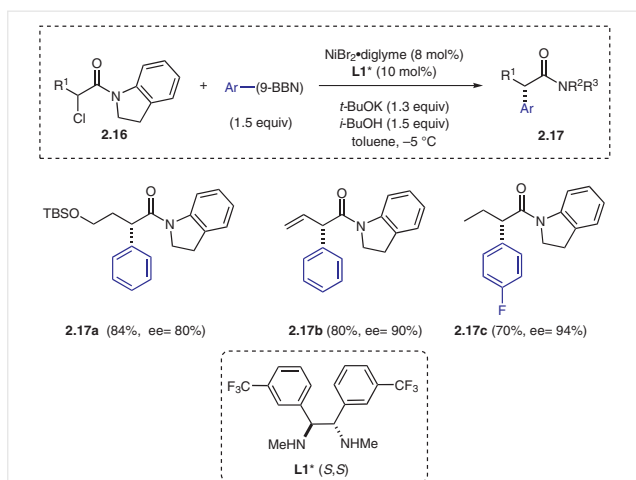
even primary amides were tolerated under these reaction conditions (Scheme 9).



Scheme 9 Nickel-catalyzed Suzuki–Miyaura coupling between α -bromo amides and boronic acids

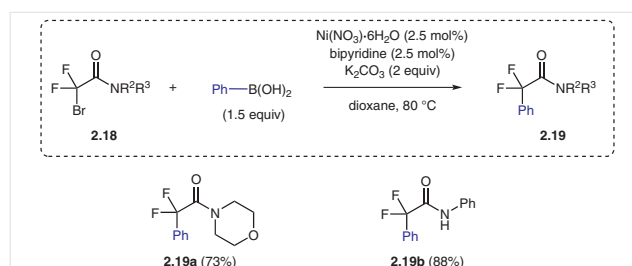
The compatibility of secondary halides with the coupling conditions offers the opportunity to develop an asymmetric arylation. In 2010, an enantio-convergent arylation of racemic α -chloro amides with aromatic boranes was reported.²³ The catalytic system was composed of NiBr_2 -diglyme and of the enantio-enriched chiral diamine **L1***, and the reaction was conducted in toluene in the presence of *i*-BuOH and *t*-BuOK. The use of an indolinylamide was found to be critical to reach high enantiomeric excesses. The reaction tolerates functional groups on the amide partner such as a silyl ether or an olefin and is not sensitive to the electronic nature of the borane (Scheme 10). The enantio-enriched arylated products could be transformed into the corresponding alcohols or carboxylic acids.

A nickel-catalyzed Suzuki–Miyaura cross-coupling was then developed to realize the α -arylation of amides incorporating a bromodifluoromethyl moiety.²⁴ The resulting product encompasses a difluoromethylene group (CF_2), which can play an important role in biologically active mol-



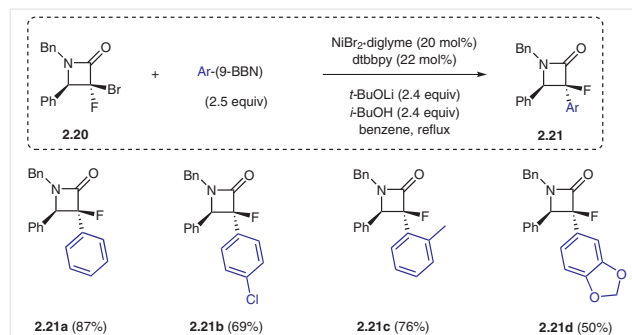
Scheme 10 Asymmetric nickel-catalyzed Suzuki–Miyaura coupling involving α -chloro amides

ecules as a bioisoster of an oxygen atom or carbonyl group.²⁵ Tertiary as well as secondary amides were successfully involved in this reaction using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and bipyridine as the catalytic system (Scheme 11).



Scheme 11 Nickel-catalyzed Suzuki–Miyaura coupling involving α -bromo- α,α -difluoro amides

The attractivity of organofluorine compounds was further illustrated by the efficient arylation of α -bromo- α -fluoro β -lactams with aromatic boranes.²⁶ The use of 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbbpy) as a ligand of NiBr_2 -diglyme gave the best results and a variety of *para*-, *meta*-, and *ortho*-substituted aromatics were introduced. The coupling exhibited complete diastereoselectivity and when an enantio-enriched lactam was used, no erosion of its optical purity was observed (Scheme 12).



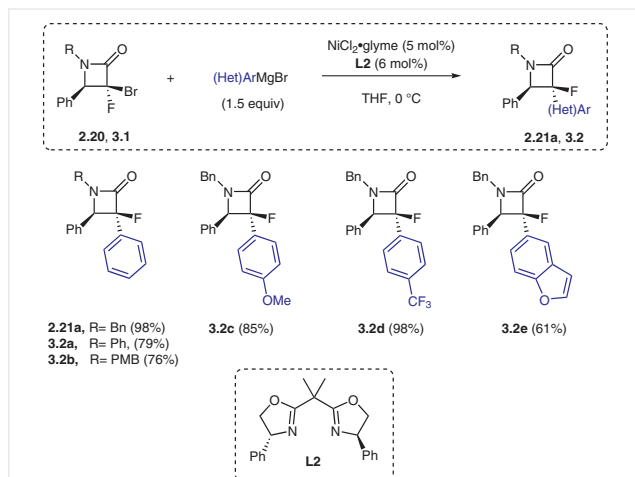
Scheme 12 Nickel-catalyzed Suzuki–Miyaura coupling on α -bromo- α -fluoro β -lactams

3 Kumada–Corriu Cross-Coupling

3.1 Nickel Catalysis

From a preparative and industrial point of view, Grignard reagents are useful organometallics. They are not expensive, several of them are commercially available or easy to prepare and they can be stored in solution. These advantages over other organometallic reagents make the Kumada–Corriu coupling particularly attractive. This area is still dominated by nickel catalysis. In 2013, Ando and co-workers developed a nickel-catalyzed α -arylation of α -bromo- α -fluoro β -lactams using aryl Grignard reagents.²⁷ Diverse protecting groups were tolerated on the nitrogen atom and

no influence of the electronic nature of the Grignard reagent was noticed. Interestingly, a benzofuran ring was successfully introduced on the β -lactam. The reaction was highly diastereoselective delivering exclusively the *trans*-product (Scheme 13).

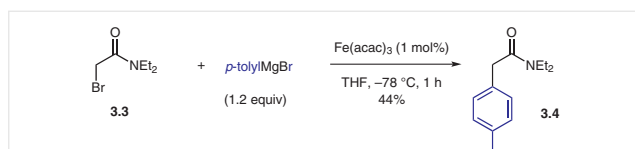


Scheme 13 Nickel-catalyzed Kumada–Corriu coupling involving α -bromo- α -fluoro β -lactams

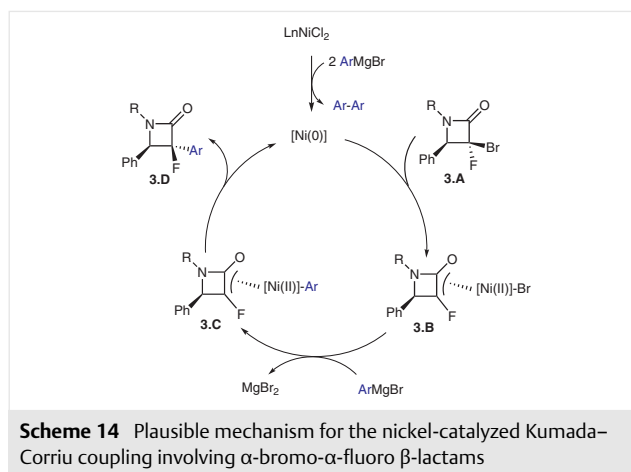
A plausible mechanism for the coupling is proposed. After reduction of the Ni(II) pre-catalyst into a Ni(0) species with the Grignard reagent, oxidative addition leads to the nickel enolate **3.B**. Transmetalation with the Grignard reagent followed by a reductive elimination furnishes the coupling product and regenerates the catalyst to complete the catalytic cycle (Scheme 14).

3.2 Iron Catalysis

The toxicity of nickel catalysts encouraged chemists to find alternatives and there has been a growing interest in iron-catalyzed cross-coupling reactions over the last 20 years.²⁸ However, to the best of our knowledge, only one example of the iron-catalyzed arylation of an amide from an α -bromo amide has been reported in the literature.²⁹ In the presence of a catalytic amount of Fe(acac)₃, the primary bromide **3.3** was transformed into the arylated product **3.4** albeit with a moderate yield of 44% (Scheme 15).



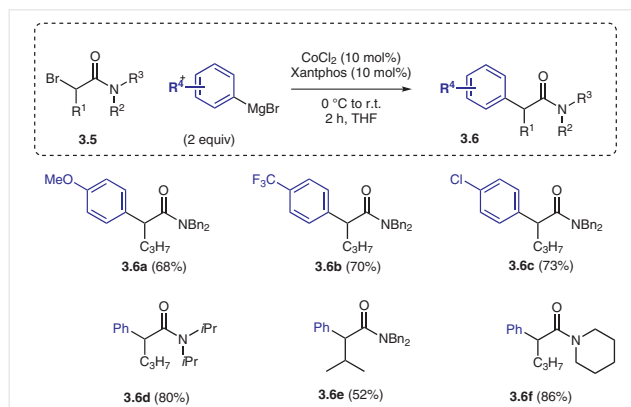
Scheme 15 Iron-catalyzed Kumada–Corriu cross-coupling involving an α -bromo amide



Scheme 14 Plausible mechanism for the nickel-catalyzed Kumada–Corriu coupling involving α -bromo- α -fluoro β -lactams

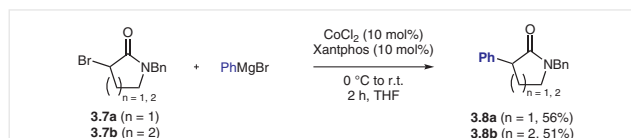
3.3 Cobalt Catalysis

With the objective of developing a general, efficient, and cost-effective α -arylation of amides from α -bromo amides with Grignard reagents, our group recently reported a cobalt-catalyzed Kumada–Corriu cross-coupling.³⁰ An array of aromatic Grignard reagents, displaying different electronic properties, were tolerated and a variety of tertiary amides could be arylated (Scheme 16).



Scheme 16 Cobalt-catalyzed α -arylation of amide from α -bromo amides with Grignard reagents

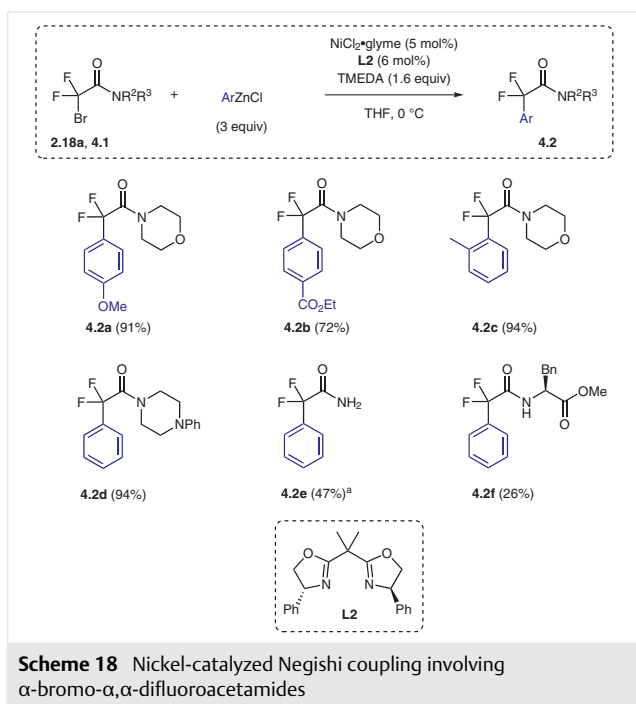
Interestingly, α -bromo lactams were also suitable substrates in this transformation (Scheme 17).



Scheme 17 Cobalt-catalyzed Kumada–Corriu coupling between α -bromo lactams and phenylmagnesium bromide

4 Negishi Cross-Coupling

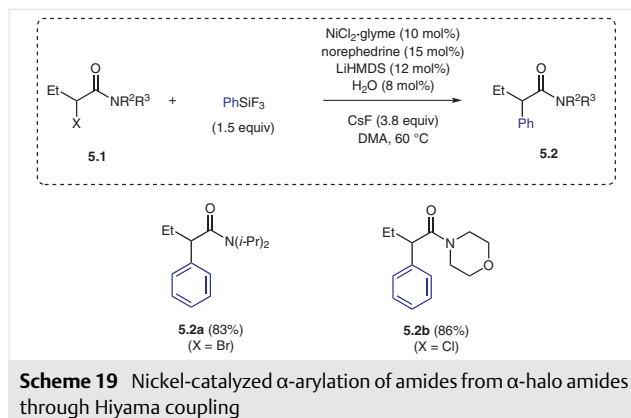
One drawback associated with the use of Grignard reagents is their high basicity and nucleophilicity that can pose functional group tolerance issues. In some cases, Negishi cross-coupling reactions using organozinc reagents that are less reactive than Grignard reagents can be more appropriated. In 2016, a nickel-catalyzed Negishi cross-coupling between α -bromo- α,α -difluoroacetamides and arylzinc chlorides was described.³¹ The mild conditions allowed the presence of electrophilic functional groups such as esters, nitriles, and even aldehydes. Until now, these substrates are the only α -bromo amides that have been involved in a Negishi cross-coupling (Scheme 18).



Scheme 18 Nickel-catalyzed Negishi coupling involving α -bromo- α,α -difluoroacetamides

5 Hiyama Cross-Coupling

Trifluoro(organo)silanes are also very mild reagents that can be used in metal-catalyzed cross-coupling. In 2007, a nickel-catalyzed Hiyama coupling involving activated and unactivated secondary alkyl halides was reported by Fu and co-workers.³² A complex catalytic system composed of $\text{NiCl}_2\cdot\text{glyme}$, norephedrine, LiHMDS, and water was identified and the reaction was performed in the presence of CsF to generate an active pentavalent organosilane. Under these conditions, α -bromo and α -chloro amides **5.1a** and **5.1b** were efficiently transformed to α -arylated amides **5.2a** and **5.2b** (83% and 86% yield, respectively) (Scheme 19).



Scheme 19 Nickel-catalyzed α -arylation of amides from α -halo amides through Hiyama coupling

6 Conclusion

In summary, several cross-couplings have been developed to perform the α -arylation of amides from α -halo amides. Palladium- and nickel-catalyzed Suzuki–Miyaura cross-couplings rule the field. A wide array of (hetero)aromatic substituents can be introduced thanks to a palladium-catalyzed arylation with potassium (het)aryltrifluoroborates, however, the reaction is restricted to primary halides. Due to their low propensity to afford β -H elimination, nickel catalysts offer the opportunity to extend the cross-couplings to secondary halides, and an asymmetric version of the reaction has been developed. Kumada–Corriu cross-couplings using easily available and inexpensive Grignard reagents are an attractive alternative to Suzuki–Miyaura couplings; a nickel catalyst was used to perform the arylation of α -bromo- α -fluoro β -lactams with Grignard reagents. A general method for the arylation of amides from both acyclic α -bromo amides and α -bromo lactams involves a cobalt salt as the metal catalyst. The use of less basic and nucleophilic organozinc and organosilane reagents compared to Grignard reagents is also possible increasing the functional group tolerance of the cross-coupling. All of the reported methods well illustrate the power of metal-catalyzed cross-couplings in the synthesis of attractive α -arylamide scaffolds.

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