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ARTICLE

Dual Nickel and Lewis Acid Catalysis for Cross-Electrophile Coupling: Allylation of Aryl Halides with Allylic Alcohols

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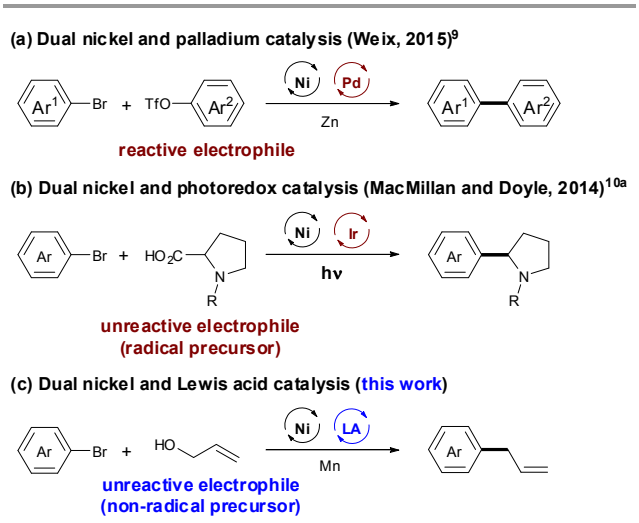
Controlling of the selectivity in cross-electrophile coupling reactions is a significant challenge, particularly when one electrophile is much more reactive. We report a general and practical strategy to address this problem in the reaction between reactive and unreactive electrophiles by a combination of nickel and Lewis acid catalysis. This strategy is used for the coupling of aryl halides with allylic alcohols to form linear allylarenes selectively. The reaction tolerates a wide range of functional groups (e.g. silanes, boronates, anilines, esters, alcohols, and various heterocycles) and works with various allylic alcohols. Complementary to most current routes for C3 allylation of unprotected indole, this method provides an access to C2 and C4-C7 allylated indoles. Preliminary mechanistic experiments reveal that the reaction might start with an arylnickel intermediate, which then reacts with Lewis acid activated allylic alcohols in the presence of Mn.

Introduction

Selective cross-electrophile coupling has recently emerged as an increasingly popular approach for constructing C-C bonds.[1] The reaction achieves the union of two different bench-stable electrophiles (aryl/alkyl halides etc.), avoiding using air and/or moisture sensitive organometallic reagents (RMgX, RZnX, $RSnR'_3$, $RB(OH)_2$ etc.).[2] Unlike in conventional cross-coupling, where the selectivity is controlled by oxidative addition of electrophile and transmetallation of nucleophile, generally both electrophiles will compete for the oxidative addition at the catalyst in cross-electrophile coupling. Thus the control of the selectivity for cross-product over symmetric dimer is of particular challenge, especially when one electrophile is much more reactive than the other. Indeed, such a reaction has been realized very recently[3] and significant progress is achieved in nickel catalysis with a metal reductant[4]. The substrate, however, remains to be confined to reactive electrophiles (R-I, Br, Cl, OTf etc.). Given that inert O-electrophiles (alcohol, phenol, ether etc.) are more readily available and their coupling reactions typically require organometallic reagents,[5] the development of a strategy to couple these compounds with electrophiles will be highly attractive but remains extremely challenge.[6]

Integration of multiple catalytic systems to enhance reactivity and/or selectivity is a concept often employed by biological catalysts[7] and is an emerging strategy in molecular catalysis.[8] The cooperative effects offer an opportunity to overcome the selectivity challenge in cross-electrophile coupling reactions. Recently, Weix has reported a dual nickel and palladium catalysis, achieving cross-coupling of two reactive electrophiles (Ar-Br + Ar-OTf).[9] MacMillan and Doyle demonstrated that the coorperative nickel and photoredox catalysis enabled the coupling between reactive and unreactive electrophiles (aryl/alkyl halides + carboxylic acids).[10] This strategy, while powerful, is less effective when non-radical precursor is used. We considered that the use of LA (Lewis acid) will lower the activation energy of inert C-O bond,[11] offering an opportunity for cross-electrophile coupling of unreactive O-electrophiles. We report here a general and practical strategy for cross-electrophile coupling between reactive and unreactive electrophiles by a combination of



Scheme 1 Dual catalysis to address the selectivity challenge in cross-electrophile coupling.

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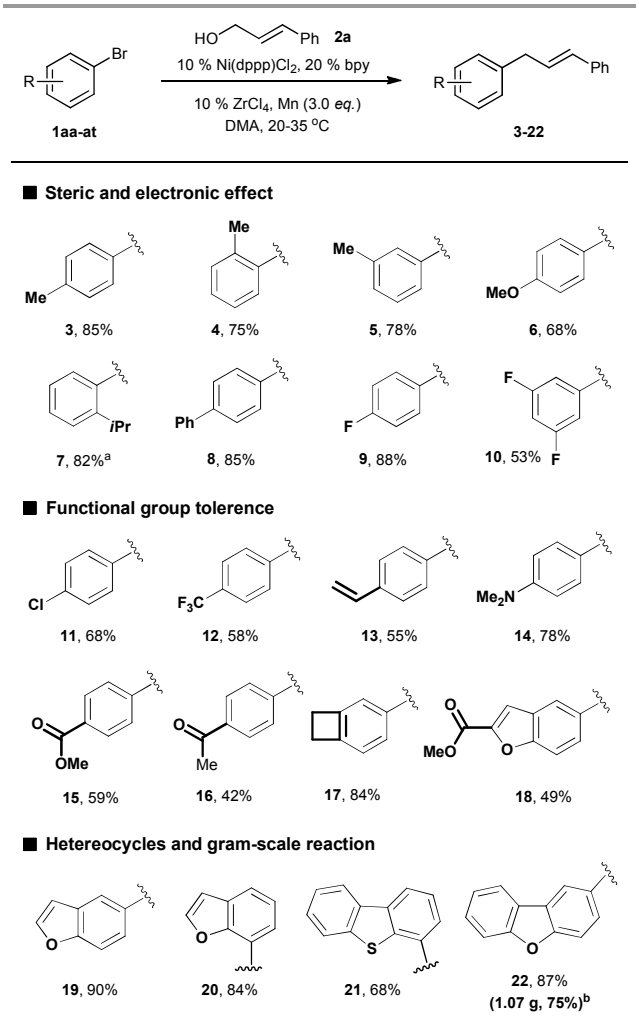
nickel and LA catalysis. The strategy was applied for the allylation of aryl halides with allylic alcohols to afford allylarenes.

Allylarenes are ubiquitous motifs in various biologically active natural products.[12] The precise synthesis of these compounds has been achieved by the coupling reaction of aryl halides with allyl metals,[13] the allylation reaction of aryl metals with allylic substrates,[14] and the reductive allylation reaction of Ar-Br with allylic acetate.[15] These reactions, while are powerful, the pre-activation of at least one reactant is required. In terms of atom- and step-economy, the synthesis of allylarenes directly from non-activated precursors will be much more attractive, but remains particular challenge, including: (1) the selectivity for the allylation of electrophiles (Ar-Br) over nucleophiles (C-OH),[16] (2) the selectivity for the reaction of Ar-Br with C-OH over C=C bonds. [17] In this article, we demonstrated such a convenient synthetic route for selective synthesis of allylarenes from Ar-Br and allylic alcohols.



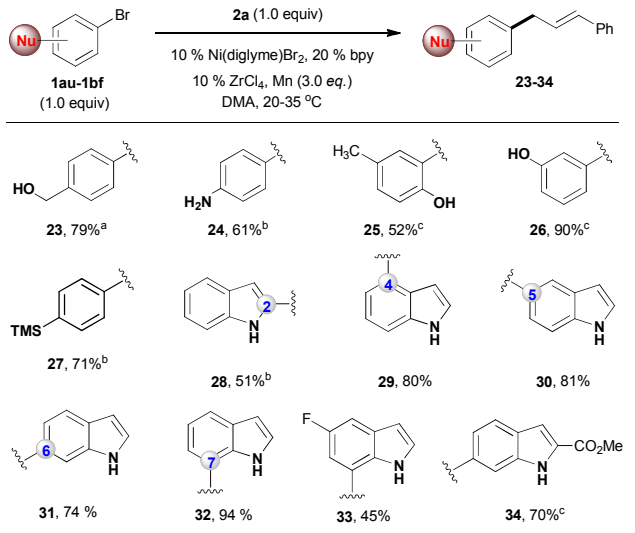
Scheme 2 Scope of aryl bromides. All data are the average of two experiments. **1aa**-**at** (1.5 equiv.) and **2a** (1 equiv.) were used. Reactions for 32-48 h. Yields are isolated yields. [a] Catalyst: 10% Ni(diglyme)Br_2. [b] 95 h.

Results and discussion

We began our investigations by exploring the reaction of 4-bromotolune **1aa** with cinnamyl alcohol **2a**.[18] The Mizoroki-Heck reaction product was not observed under reductive conditions. In the absence of a LA, significant amount of biaryl dimer was obtained, but no or trace of cross-product **3** was observed (Table S1). Addition of catalytic amount of LA significantly improved the selectivity for **3** (Table S2). Further optimization of reaction conditions revealed that the use of Ni(dppp)Cl_2 (10 mol %), bpy (20 mol %), $ZrCl_4$ (10 mol %) and Mn (3.0 equiv) in DMA afforded **3** in 85% yield.[19]

With optimized conditions in hand, we then investigated the reaction scope of aryl bromides. Both electron-rich and electron-poor aryl bromides gave cross-coupling products in moderate to good yields (Scheme 2, **3**-**10**). Substitution around the aromatic ring was tolerated (**3**-**5**). A steric hindered substitution was tolerated when Ni(diglyme)Br_2 was used as a catalyst (**7**). The reaction was selective for functionalization of C–Br bond over C-Cl, C-F bonds and styrenyl group, thus enabling the later available for additional transformation (**9**-**13**). Functional groups such as tertiary amine, ester, ketone, as well as a strained ring were accommodated and remained intact (**14**-**18**). Heteroarenes and polyarenes, which are prevalent in pharmaceuticals, could be precisely allylated (**18**-**22**). The reaction could be scaled up to gram scale and gave **22** in a 75% yield.

While the existing allylation reactions of allylic alcohols are efficient for allylating nucleophiles,[14] this reaction is highly selective for electrophiles. A broad range of nucleophilic aryl bromides were then selectively allylated, leaving alcohol,[20] amine,[21] phenol,[22] indole[23] and silane intact (Scheme 3). The utility of this method was illustrated by regiodivergent synthesis of allylated indoles, which are important structure



Scheme 3 Reactions of **2a** with nucleophilic aryl bromides. All data are the average of two experiments. Yields are isolated yields. Reactions for 32-48 h. [a] Conditions in Scheme 2, reaction for 60 h. [b] Conditions in Scheme 2, amount of ArBr: 1.0 equiv. [c] Amount of ArBr: 1.5 equiv.

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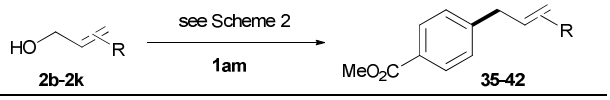
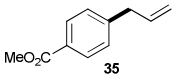
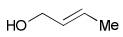
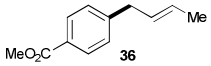
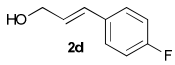
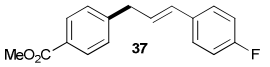
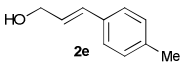
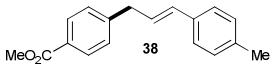
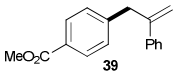
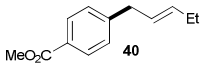
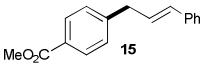
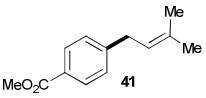
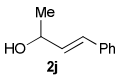
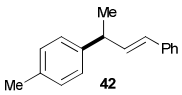
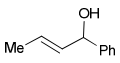
motif in many bioactive natural products and drugs.[24] Being complementary to conventional methods for the allylation of indoles at the C3 position,[23] our approach provides a direct access to C2-, C4-, C5-, C6- and C7-allylated indoles (**28**-**34**). Of note, the desired products were obtained in high yields even when an equal amount of two electrophiles was used.

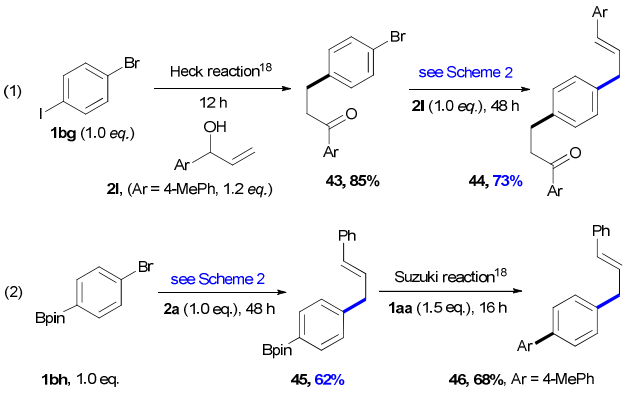
The reaction proceeded efficiently with a variety of allylic alcohols and in most cases gave linear (*E*)-products selectively (Table 1). In addition to cinnamyl alcohols, unsubstituted and alkyl-substituted allylic alcohols also coupled with a functionalized aryl group (entries 1-5). Although the reaction with α-ethyl substituted alcohol is less selective, substrate with phenyl substitution gave only linear (*E*)-product (entries 6-7).

Table 1 Scope of allylic alcohols.



entry	allylic alcohol	product	yield
1			80%
2			62%[a, b]
3			75%
4			73%
5			58%
6			63%[a, c]
7			76%
8			66%[a, d]
9			56%[e]
10		42	60%

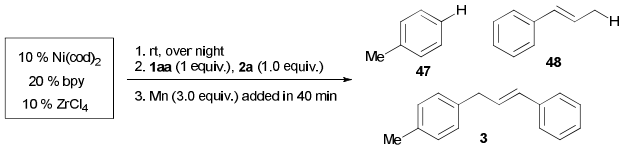
All data are the average of two experiments. Yields are isolated yields. Reactions for 48-50 h. Amount of **1am**: 2.0 equiv. **1aa** were used for **2j** and **2k** [a] Catalyst: 10% Ni(dppf)Cl_2, 20% 3,4,7,8-tetramethyl-1,10-phenanthroline, 20% $AlCl_3$, **1am** (1.5 equiv). [b] [l/b] (linear/branched ratio) = 4:1, linear product is a 3:1 *E*/*Z* isomers. [c] [l/b] = 11:1, linear product is a 5:1 *E*/*Z* isomers. [d] [l/b] = 180:1. [e] 15 % catalysts were used.



Prenylated arenes have been found in many bioactive compounds, and their synthesis has been extensively studied but requires prenyl-metal species (allylfluorosilanes, allylstannanes, allylboron derivatives *etc.*).[13] Such a structure, however, could be efficiently constructed here from isoprenyl alcohol with a linear/branched ratio of 180:1 (entry 8). Both nonsymmetrical substrates **2j** and **2k** gave the same product **42** in useful yields, suggesting the reaction goes through a π-allyl nickel intermediate.

The cross-electrophile coupling reaction is well complementary to the Pd-catalyzed reactions, enabling 1-bromo-4-iodobenzene to be sequentially functionalized with allylic alcohol **2l** to ketone **43** and allylated product **44** (eq. 1). Our reaction conditions were also compatible with aryl borates and a sequence of C-Br bond allylation and C-B bond coupling is possible for the conversion of substrate **1bh** to product **46** (eq. 2).

LA was expected to lower the activation energy of C-OH bond. To confirm this assumption and understand the mechanistic details of this process, we monitored the reaction of **1aa** with **2j** by GC analysis. In the absence of a LA, no cross-coupling product **42** and side products from **2j** was observed in 40 min, but aryl dimer **51** was steadily increasing (Figure S1a). This result indicates that aryl bromide is reactive towards Ni catalyst, while allylic alcohol is inert. The use of 15 mol % of



Percent of contents (%) \ time (min)	10	20	30	↓ Mn added 40	50	60
Ar-H (47)	4.6	4.5	4.6	4.6	6.2	8.3
Allyl-H (48)	0	0	0	0	0	0
Ar-Allyl (3)	0	0	0	0	4.3	12.5

Scheme 4 Selectivity of Ar-Br and allylic alcohol in initial oxidative addition to Ni(0). A mixture of **1aa**/**2a** (1:1) was added to an in situ generated Ni(0) catalytic system. Samples were collected in each 10 min and analysed by GC. Mn was added in 40 min.

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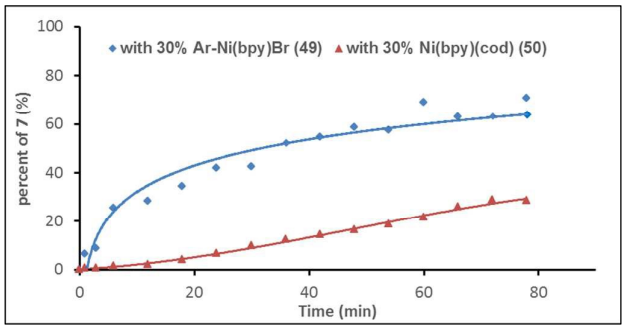


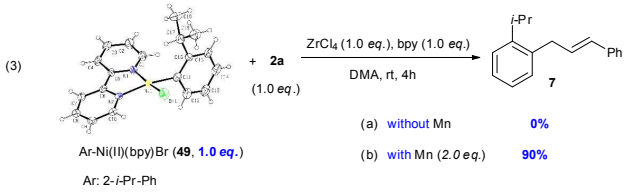
Figure 1 Relative reactivity of Ar-Ni^{II}(bpy)Br (**49**) and (bpy)Ni^{0}(cod) (**50**) capable of catalysing the reaction of **1ae** with **2a**. Complex **49** or **50** (30 mol %) was added to a solution of **1ae** (1.2 or 1.5 equiv.), **2a** (1.0 equiv.), bpy (30 mol %), $ZrCl_4$ (10 mol %) and Mn (3.0 equiv.) in DMA. Samples were collected, quenched with H_2O and analysed by GC.

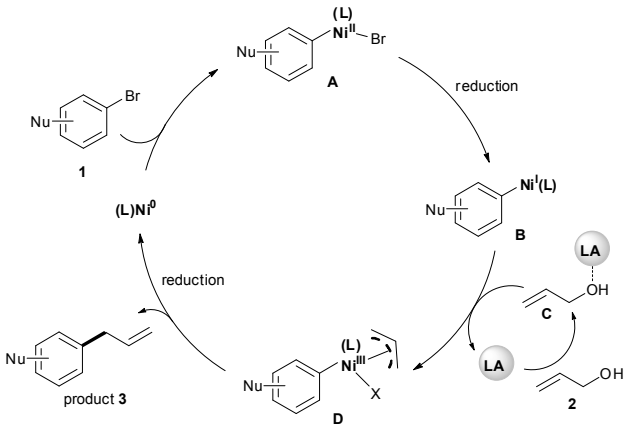
$ZrCl_4$ significantly promoted the cross-coupling process, indicating the crucial role of LA in the activation of allylic alcohols (Figure S1b).

Both aryl bromide and allylic alcohol will undergo oxidative addition to Ni(0), generating Ar-Ni^{II}(L)Br and allyl-Ni^{II}(L)X[16a,b,21b]. In order to determine which intermediate is formed firstly, we studied the relative reactivity of **1aa** and **2a** with in situ generated (bpy)Ni^{0}(cod).[25] We would expect, by quenching the reaction, a Ni(II) intermediate would afford Ar-H (**47**) or Allyl-H (**48**).[26] Scheme 4 shows that, in every 10 min before addition of Mn, 4.6% of Ar-H is obtained in each sample but no Allyl-H is observed, consistent with Ar-Ni^{II}(L)Br forming firstly. While both cross-product **3** and Ar-Ar dimer were steadily increasing after addition of Mn (3 equiv.), Allyl-H or Allyl-Allyl was still not observed (Scheme S1), suggesting a mechanism in which Ar-Ni^{II}(L)Br serves as an intermediate.

To take more insight into the mechanism of this process, complex Ar-Ni^{II}(bpy)Br (**49**)[27] was synthesized from the reaction of (bpy)Ni^{0}(cod) (**50**) with aryl bromide **1ae**. We would expect that, if Ar-Ni^{II}(bpy)Br (**49**) is an intermediate, the initial rate of reaction with complex **49** would be faster than that of reaction with pre-catalyst **50**. Figure 1 shows that, in 6 min, the use of complex **49** (30 mol %) give product **7** in almost 30% yield, while only trace of **7** is formed when pre-catalyst **50** (30 mol %) is used (Figure 1). This result further indicates that Ar-Ni^{II}(L)Br is likely the key intermediate in this reaction.

Reduction of Ni(II) complex to Ni(I) by Mn has been extensively reported.[4a-b] The stoichiometric reactions of **49** with alcohol **2a** gave product **7** in 0% yield (without Mn) and 90% yield (with Mn), suggesting that Ni(II) complex **49** might be reduced to more nucleophilic ArNi(I) firstly, then reacts with allylic alcohols (eq. 3). The use of electron-poor aryl bromides (e.g. **18** *vs* **19**, **32** *vs* **33**) generally gave inferior results, which is consistent with this process. While the use of





Scheme 5 Proposed mechanism for allylation of aryl bromides with allylic alcohols by dual catalysis.

radical scavenger such as butylated hydroxytoluene (BHT), hydroquinone and 1,1-diphenylethylene did not inhibit the reaction of **1aa** and **2a**, no product **3** was obtained when 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO, 1.5 equiv.) was employed (Table S8), consistent with the presence of a single-electron process capable of reducing oxidized Ni catalyst.

Although a detailed mechanistic picture for this reaction requires further investigation, based on above results, we tentatively proposed a catalytic cycle as shown in Scheme 5.[28] The oxidative addition of Ar-Br to Ni(0) gives an arylnickel(II) intermediate **A**. Reduction of **A** to arylnickel(I) **B**[4a-b] followed by oxidative addition of LA-activated allylic alcohol will give π-allylnickel(III) intermediate **D**.[29] Reductive elimination of this complex will afford the desired product and recycle the catalyst with Mn. At present, we cannot rule out a radical mechanism as shown in the reaction of aryl halides with alkyl halides.[30]

Conclusions

In summary, we have reported a dual nickel and Lewis acid-catalyzed allylation of aryl halides with allylic alcohols. This approach represents a new strategy for cross-electrophile coupling between reactive and unreactive electrophiles. The reaction tolerated a wide range of functional groups including alcohols, phenols, anilines, silanes, and even borates. In most cases, the reaction gave linear (*E*)-allylarenes highly selectively. The utility of this method is clearly illustrated by facile access to C2 and C4-C7 allylated indoles. Preliminary mechanistic studies revealed that the reaction might start with an arylnickel intermediate, which then reacted with allylic alcohols in the presence of Lewis acid and reductant. The application of this strategy for cross-electrophile coupling of other unreactive electrophiles is ongoing in our laboratory.

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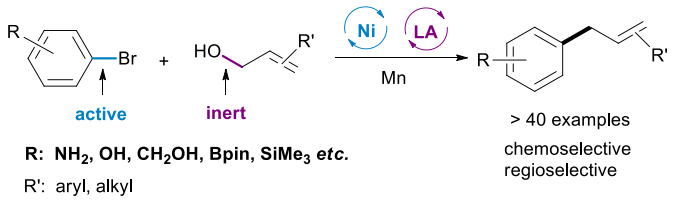

A dual nickel and Lewis acid catalysis has been developed for the coupling reaction between reactive and unreactive electrophiles.