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Nickel-Catalyzed Reductive Cross-Coupling of Aryl Bromides with Alkyl Bromides: Et_3N as the Terminal Reductant

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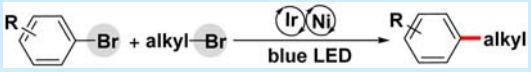
Supporting Information

ABSTRACT: Reductive cross-coupling has emerged as a direct method for the construction of carbon−carbon bonds. Most cobalt-, nickel-, and palladium-catalyzed reductive cross-coupling reactions to date are limited to stoichiometric Mn(0) or Zn(0) as the reductant. One nickel-catalyzed cross-coupling paradigm using Et_3N as the terminal reductant is reported. By using this photoredox catalysis and nickel catalysis approach, a direct Csp^2-Csp^3 reductive cross-coupling of aryl bromides with alkyl bromides is achieved under mild conditions without stoichiometric metal reductants.



Reductive cross-coupling, the coupling of two different electrophiles, recently has emerged as direct methods for the construction of C−C bonds, which has experienced a surge of development.[1] Compared with the conventional cross-coupling, such a strategy streamlines the preparation of electrophiles with air- and moisture-sensitive organometallics from the corresponding organic halides and avoids the formation of stoichiometric organometallic species. Recently, nickel-catalyzed reductive cross-coupling has attained significant attention, as one relatively electropositive late transition metal, the oxidative addition of electrophiles with which tends to occur quite readily; thus, the reaction conditions could be mild in accordance with good functional group tolerance. The Weix,[2] Gong,[3] and Molander[4] groups have achieved considerable progress in this field, and a variety of cross-electrophile coupling reactions have been developed. In fact, most cobalt-, nickel-, and palladium-catalyzed reductive cross-coupling reactions extensively require stoichiometric metal reductants and have been largely limited to Mn(0) or Zn(0) to complete the catalytic cycle (eq 1).[5] Few efforts have been devoted to

$$R^1\text{-}X + R^2\text{-}Y \xrightarrow[\text{Zn or Mn}]{\text{[Co], [Ni], [Pd]}} R^1\text{-}R^2 \qquad (1)$$

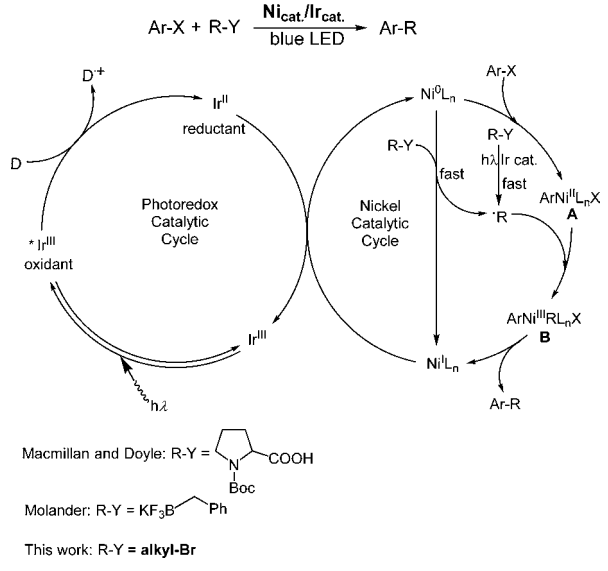
X, Y = Cl, Br, I, OTf, OTs, OMs, etc.

developing alternative reductants for sustaining the catalytic cycle. Searching for new reductants would be highly desirable, and great challenges still remain.

Visible-light-photoredox catalysis has been established as a powerful technique to facilitate activation of organic molecules, enabling achievement of a wide variety of new chemical reactions.[6] Extensive efforts have been made since the seminal studies from the groups of MacMillan,[7] Yoon,[8] and Stephenson.[9] Visible-light-photoredox catalysis has emerged as one of the most active research topics in organic synthesis and made tremendous advances in the past decade.[10] The application of photoredox/nickel dual catalysis via single electron transfer provides new opportunities for nickel catalysis.[7a,11] Crucially, the reduction of Ni(I) to Ni(0) using an iridium photocatalyst is thermodynamically favorable.

We envision that combining nickel catalysis and photoredox catalysis could achieve the cross-coupling of two different electrophiles. We propose a mechanistic cycle for a photoredox-nickel cocatalyzed reductive cross-coupling approach in Scheme 1. We speculate that an alkyl radical is generated from alkyl halides reacting with the nickel catalyst or via a single electron transfer process initiated by visible light irradiation. In fact, the allylic radical could be generated through single-electron transfer using $Ru(bpy)_3(PF_6)_2$ as the catalyst.[12] The generated alkyl radical reacts further with the arylnickel(II) halide (**A**) as

Scheme 1. Proposed Mechanism for Photoredox-Nickel Cocatalyzed Reductive Cross-Coupling Approach



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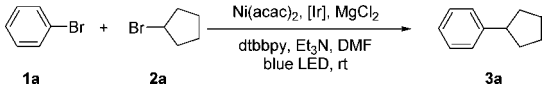
the result of the Ni(0) catalyst oxidative addition to aryl halides, forming the intermediate Ni(III) (**B**). The organometallic (**B**) species reductive elimination would forge the new C−C bond simultaneously delivering the reductive cross-coupling product. Finally, the expelled Ni(I) species was reduced by the Ir(II) reductant, completing the nickel catalytic cycles. By using photoredox/nickel dual catalysis, the research groups of Molander and MacMillan and Doyle have described carbon−carbon formation with an organoboron and amino acid as coupling reagents (Scheme 1).[7d,11b] Herein, we report one nickel/photoredox catalyzed reductive cross-coupling of aryl bromides with *alkyl bromides*, using Et_3N as the terminal reductant (Scheme 1, D = Et_3N).[13]

Our initial optimization for the synthesis cyclopentylbenzene (**3a**) from the reductive cross-coupling of bromobenzene (**1a**) and bromocyclopentane (**2a**) is summarized in Table 1. The

Table 1. Effects of Reaction Parameters[a]



1a 2a 3a

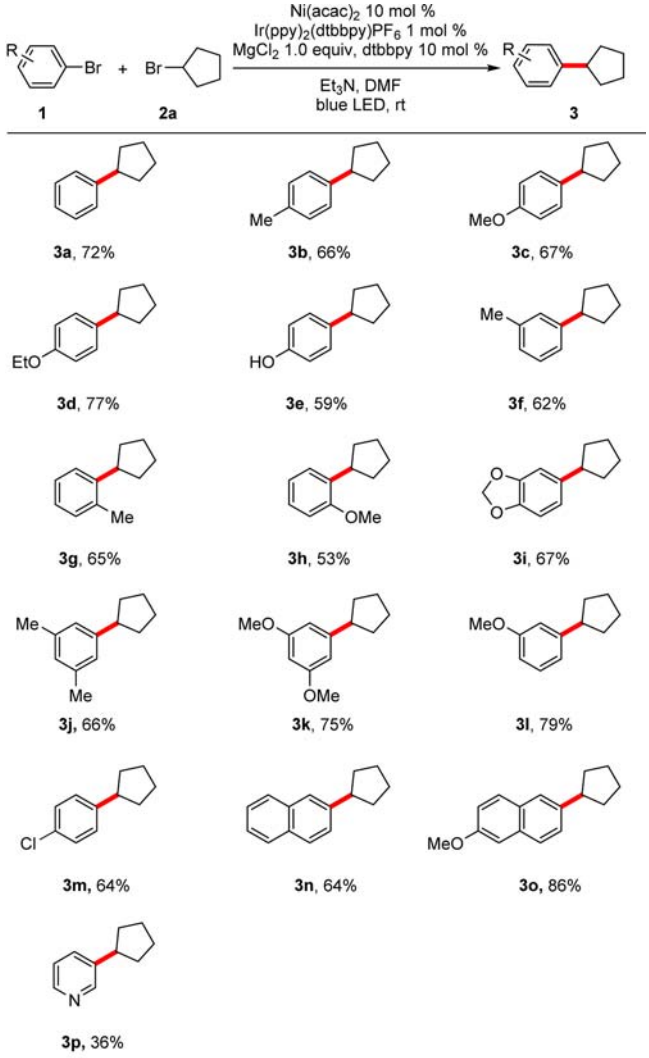
entry	deviation from "standard conditions"	yield (%)[b]
1	none	72 (72)[c]
2	$NiBr_2$ instead of $Ni(acac)_2$	60
3	$Ni(cod)_2$ instead of $Ni(acac)_2$	69
4	DMA instead of DMF	52
5	MeCN instead of DMF	54
6	toluene instead of DMF	34
7	THF instead of DMF	trace
8	$Ru(bpy)_3(PF_6)_2$ instead of [Ir]	0
9	$Ir[CF_3(df)ppy](dtbbpy)PF_6$ instead of $Ir(ppy)_2(dtbbpy)PF_6$	68
10	no $MgCl_2$	13
11	no dtbbpy	trace
12	no $Ni(acac)_2$	0
13	no [Ir]	0
14	no light	0

[a]Standard reaction conditions: **1a** (0.2 mmol), **2a** (1.0 mmol), $Ni(acac)_2$ (0.02 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (0.002 mmol), $MgCl_2$ (0.2 mmol), Et_3N (0.6 mmol), dtbbpy (0.02 mmol), DMF (2 mL), rt for 24 h. [b]Yields were determined by GC using diphenyl as an internal standard. [c]Yield of isolated product.

combination of $Ni(acac)_2$ (acac = acetylacetonate), $Ir(ppy)_2(dtbbpy)PF_6$, (ppy = 2-phenylpyridine, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), $MgCl_2$, and Et_3N in DMF (*N*,*N*-dimethylformamide) at room temperature, and then irradiated with the blue LEDs for 24 h, achieved the best result for the desired coupling in 72% yield. When $Ni(acac)_2$ was replaced by $NiBr_2$ or $Ni(cod)_2$ (cod = 1,5-cyclooctadiene), the yield of the desired product decreased (entries 2 and 3). As to solvent, DMA (dimethylacetamide), MeCN, and toluene led to a decreased yield respectively (entries 4, 5, and 6), while THF (tetrahydrofuran) proved to be ineffective (entry 7). Under equivalent conditions, $Ru(bpy)_3(PF_6)_2$ showed no efficiency in terms of the desired product yield (entry 8). A slightly decreased yield was obtained when another common iridium photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ ($dF(CF_3)ppy$ = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine) was used (entry 9). Notably, the additive was crucial for the reaction; the yield decreased dramatically without $MgCl_2$ (entry 10). The dtbbpy was also indispensable, as only a trace amount of desired product was detected without the ligand (entry 9). No desired product was obtained without the catalyst $Ni(acac)_2$ and $Ir(ppy)_2(dtbbpy)PF_6$ (entries 12 and 13). Without light irradiation, no product could be produced (entry 14).

With the optimized conditions, we focused our attention on the scope of the substrates and a range of aryl bromides were tested first (Scheme 2). Overall, all of the substrates studied

Scheme 2. Scope of Aryl Bromides[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.0 mmol), $Ni(acac)_2$ (0.02 mmol), [Ir] (0.002 mmol), $MgCl_2$ (0.2 mmol), Et_3N (0.6 mmol), dtbbpy (0.02 mmol), solvent (2 mL), rt for 24 h.

were conveniently converted into the corresponding reductive cross-coupled **2a**−**2m**, and most of the products were isolated in good yields, indicating the high versatility of this catalyst system. Substitution at the para position of the aryl bromide was well tolerated with both electron-donating and -withdrawing (**3b**−**3d**, **3l**, and **3m**) substituents. Importantly, the free proton containing substrates, such as phenol, underwent the reaction smoothly and provided **3e** in moderate yields. Substitution at the *meta*-position of aryl bromide had been explored, and efficient coupling occurred affording products in moderate yield. Several bifunctional substrates were tested and gave moderate to good yields (**3i**−**3k**). Similarly, 2-

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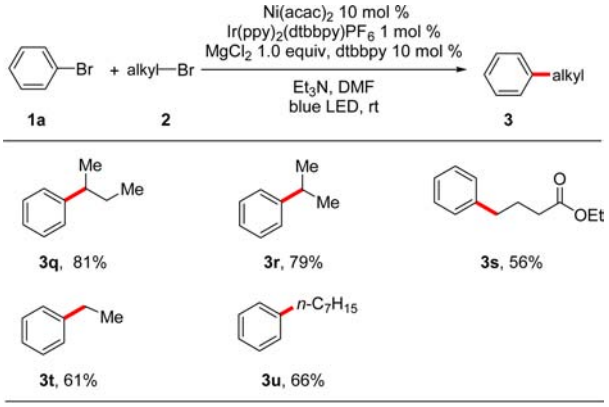
bromonaphthalene and substituted 2-naphthyl bromide could be coupled efficiently to afford the desired products in moderate to good yields (**3n** and **3o**).

In addition to demonstrating the scope of this reaction, the substrate scope of an alkyl bromide was also tested (Scheme 3).

Scheme 3. Scope of Alkyl Bromides[a]

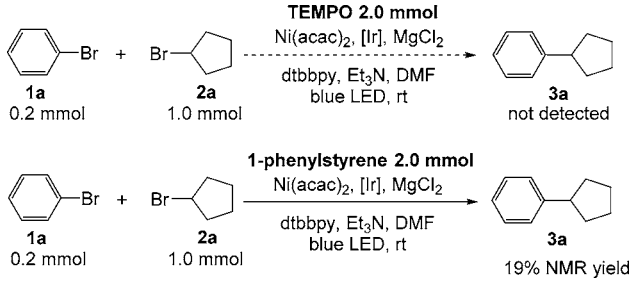


[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.0 mmol), $Ni(acac)_2$ (0.02 mmol), [Ir] (0.002 mmol), $MgCl_2$ (0.2 mmol), Et_3N (0.6 mmol), dtbbpy (0.02 mmol), solvent (2 mL), rt for 24 h.

Generally, moderate to high yields of the desired coupling products were obtained. Alkyl bromides with branching couple well with bromobenzene and gave high yields of the coupling products (**3q** and **3r**). In addition, ethyl 4-bromobutanoate successfully coupled with bromobenzene and gave a moderate yield (**3s**). Remarkably, bromoethane and 1-bromooctane also coupled efficiently to afford products in 61% and 66% isolated yields (**3t** and **3u**), independently.

Radical trapping experiments were subsequently performed in order to understand the mechanism of this nickel/photoredox catalyzed reductive cross-coupling (Scheme 4).

Scheme 4. Mechanistic Studies



The desired product **3a** was not detected when the 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added, implying that a radical pathway might be possible in this reaction. Furthermore, when 1-phenylstyrene was added to the mixture under the standards conditions, only 19% of desired reductive cross-coupling product **3a** was detected. This result further confirmed the involvement of a free radical pathway in this transformation.

In conclusion, we have developed a nickel-catalyzed reductive cross-coupling, without stoichiometric metal Mn(0) or Zn(0) as the reductant. By combining the photoredox catalysis and nickel catalysis, we have achieved a direct C_{sp^2}–C_{sp^3} reductive cross-coupling. In this single-electron transfer process, Et_3N acts as the terminal reductant. A deep understanding of the exact role of $MgCl_2$ and the final products of bromine in the current process would be the subject for future work. Finally, although the reaction mechanism is still under investigation, these results demonstrate the potential of combining nickel and visible-light-photoredox catalysis for reductive cross-coupling. We envision this dual catalytic system could be applied in other reactions using cobalt, nickel, or palladium as the catalyst and Mn(0) or Zn(0) as the reductant.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01837.

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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