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Ligand-Enabled Ni−Al Bimetallic Catalysis for Nonchelated Dual C−H Annulation of Arylformamides and Alkynes

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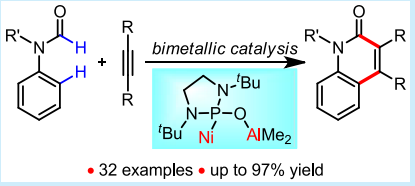
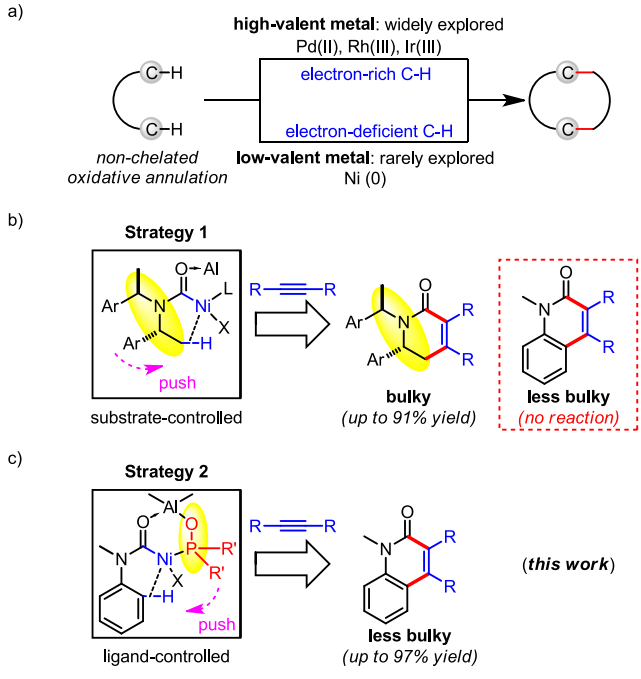
ABSTRACT: A bifunctional secondary phosphine oxide (SPO) ligand-controlled method was developed for Ni−Al-catalyzed nonchelated dual C−H annulation of arylformamides with alkynes, providing a series of substituted amide-containing heterocycles in ≤97% yield. The SPO-bound bimetallic catalysis proved to be critical to the reaction efficiency.



Transition metal-catalyzed nonchelated oxidative annulation of dual C−H bonds with π-unsaturated compounds has received an increasing amount of attention in recent years, because it provides an atom- and step-economical pathway to various cyclic compounds (Scheme 1a).[1−6] However, the absence of a chelating group causes difficulty for C−H bond activations. Most reported examples had to rely on electron-rich (hetero)arenes as substrates and high-valent precious metals as catalysts such as Pd(II),[2] Rh(III),[3] and Ir(III).[4] So far, only one example reported by Nakao, Hiyama, and co-workers used an inexpensive low-valent metal [Ni(0)] as a catalyst to activate the electron-deficient formyl C−H bond and alkyl C−H bond of amides (Scheme 1b).[6] Despite a substantial breakthrough, the reaction required the use of sterically hindered substrates to accelerate C−H activation, leading to the severe restriction of substrates. Only special *N*,*N*-bis(1-arylalkyl)formamides were compatible, whereas other formamides including less bulky but readily available arylformamides did not undergo the reaction at all (Scheme 1b). To address this challenge, the development of a general strategy instead of the substrate-controlled method is required. We reasoned that less bulky *N*-methyl and *N*-aryl group significantly decreased the steric hindrance between the carbonyl and the N substituent, so that the aromatic C−H bond could not be effectively pushed to the nickel center, rendering subsequent aromatic C−H bond activation more difficult. On the basis of our recent works on bimetallic catalysis,[7,8] we proposed to use a bifunctional SPO[9] (secondary phosphine oxide) ligand to solve this problem, because a SPO ligand would bind both Al and Ni to form a cyclic intermediate, which would force the nickel center to closely approach the aromatic C−H bond, thus accelerating C−H bond activation (Scheme 1c). Herein, we report our recent result: a bifunctional bulky SPO ligand significantly facilitated the reaction of arylformamides with alkynes for the first time, providing a series of amide-containing heterocycles[10] in ≤97% yield.

Scheme 1. Nonchelated Oxidative Annulation of Dual C−H Bonds



We selected *N*-phenylformamide (**1a**) and oct-4-yne (**2a**) as model substrates to commence our studies. The reported optimal $^{t}Bu_3P$[6] gave only side products from hydrocarbamoy-

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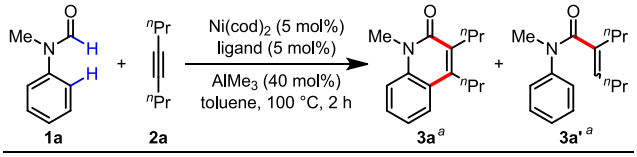
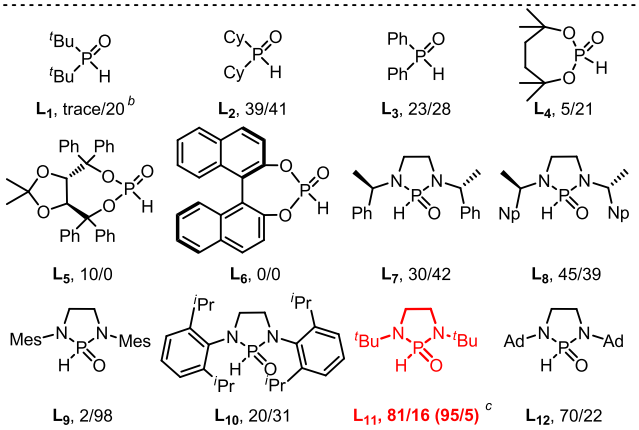
lation[11] and decarbonylation (Scheme 2, entries 1 and 2, respectively). Other traditional ligands such as phosphines and

Scheme 2. Ligand Optimization



entry	ligand	yield (**3a**, %)	yield (**3a'**, %)
1		0	0
2	^{t}Bu$_3$P	0	30
3	Ph$_3$P	0	8
4	Cy$_3$P	0	28
5	dcype	0	0
6	IPr	0	6
7	IMes	0	14
8	Ph$_2$P(O)Cl	0	4
9	Ph$_2$POPh	0	8

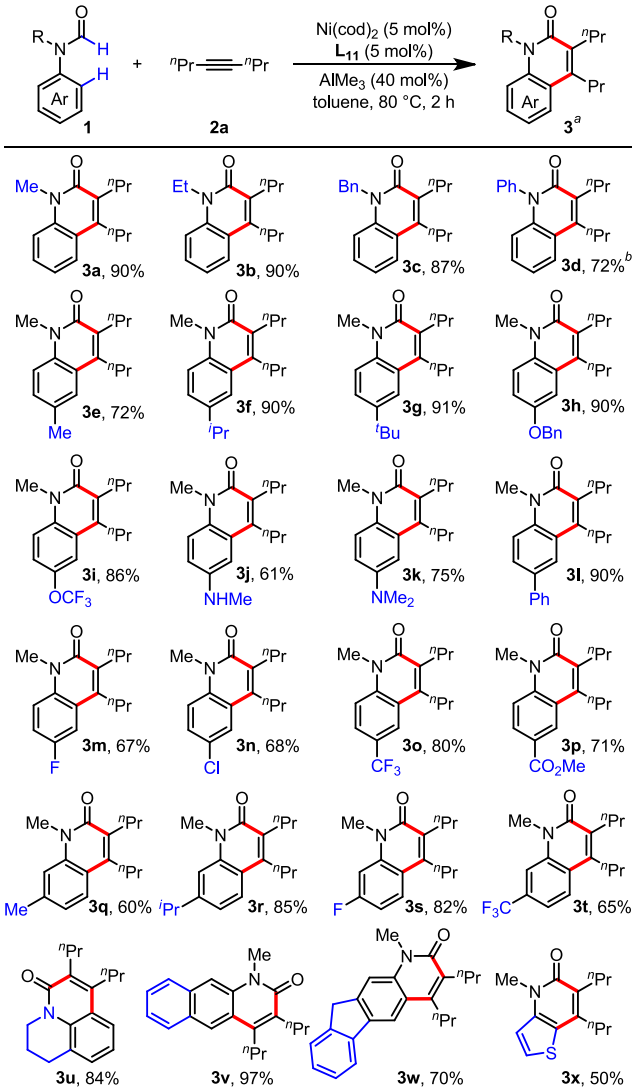


[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.1 mmol), and toluene (1.0 mL) under N_2. Yield determined by ^{1}H NMR using CH_2Br_2 as the internal standard. [b]All ratios refer to the ^{1}H NMR yield (%) of **3a**/**3a'**. [c]Toluene (0.2 mL) and **2a** (1.0 mmol) at 80 °C. Np = 1-naphthyl. Ad = 1-adamantyl.

carbenes also proved to be ineffective (entries 3−9). Pleasingly, bifunctional ^{t}Bu$_2$P(O)H (**L$_1$**) did afford trace amounts of desired product **3a**. Further tuning the steric hindrance of the SPO ligand led to a significantly improved yield of **3a** (**L$_2$** and **L$_3$**), albeit still with side product **3a'** from the hydrocarbamoylation. Encouraged by this result, we then examined a wide range of SPO ligands, including diol-derived (**L$_4$** and **L$_5$**), biphenol-derived (**L$_6$**), and diamine-derived SPOs (**L$_7$**−**L$_{12}$**). In the end, sterically hindered di-*tert*-butylethyldiamine-derived SPO (**L$_{11}$**) provided the best yield (81%). Decreasing the temperature and increasing the concentration gave the best yield (95%), and in this case, side reactions such as hydrocarbamoylation and decarbonylation were significantly suppressed. Notably, a lower efficiency of bulky ligands (**L$_{10}$** and **L$_{12}$**) could suggest that the reactivity of the current reaction may also be affected by other factors such as the cone angle and the electronic properties of the ligands.

With the optimized reaction conditions in hand, we first explored an array of arylformamides bearing various substituents on the nitrogen and the aryl ring to test the generality of the reaction (Scheme 3). Commonly used protecting groups of the nitrogen such as Et (**3b**), Bn (**3c**), and Ph (**3d**) were

Scheme 3. Scope of Arylformamides



[a]Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mmol), and toluene (0.2 mL) under N_2 for 2 h. Yield for isolated products. [b]DABCO (20 mol %) was added.

quite compatible with the current reaction, providing the corresponding products in 72−90% yields. Notably, in the case of the phenyl group, 20 mol % 1,4-diazabicyclo[2.2.2]octane (DABCO) was needed to improve the yield. We speculated that its coordination to Al could inhibit possible oligomerization of Al species, thus enhancing coordination of the substrate. However, electron-withdrawing protecting groups such as Ac, BOC, and Bz were not suitable, leading to significant decarbonylation. The reaction displayed a high tolerance to a series of *para* substituents on the phenyl ring, including either electron-donating alkyls (**3e**−**3g**), alkoxyls (**3h** and **3i**), aminos (**3j** and **3k**), phenyl (**3l**) or electron-withdrawing halos (**3m** and **3n**), CF_3 (**3o**), and carboxylate (**3p**), providing the corresponding products in yields varying from 61% to 91%. Various *meta* substituents also did not have a strong influence on the yield. For example, both electron-rich alkyl groups (**3q** and **3r**) and electron-deficient F (**3s**) and CF_3 (**3t**) gave moderate to good yields. In contrast, most *ortho* substituents resulted in significant hydrocarbamoylation of **2a**. We reasoned that *ortho* substituents could result in a twist of

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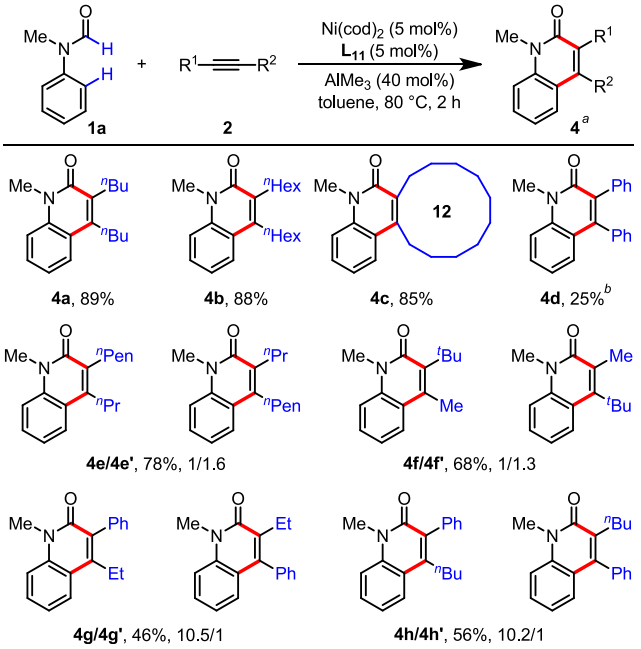
the aryl ring, rendering the following C−H bond cleavage more difficult. On the basis of this analysis, a cyclic formamide (**3u**) that could efficiently inhibit the twist of the aryl ring was tested and yields of ≤84% was achieved. Other aryls (**3v** and **3w**) and heteroaryls (**3x**) also worked well in the reactions, providing yields of ≤97% yield.

We then proceeded to investigate the substituent effect of alkynes (Scheme 4). Various alkyl substituents, including both

Scheme 4. Scope of Alkynes

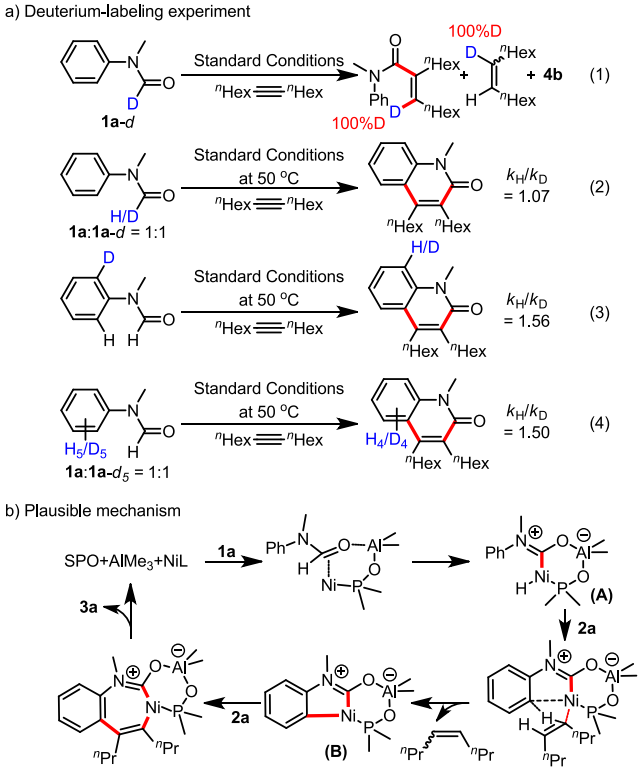


[a]Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), and toluene (0.2 mL) under N_2 for 2 h. Yield for isolated products. [b]$\mathbf{L_4}$ (5 mol %) was used instead of $\mathbf{L_{11}}$.

linear alkynes (**4a** and **4b**) and cyclic alkyne (**4c**), can be tolerated well, providing the corresponding product in yields of 85−89%, whereas diphenyl alkyne was not suitable for this annulation, leading to only undesired acrylamides. We speculated that the insertion of diphenyl alkyne would significantly increase the steric hindrance of the intermediate, thus inhibiting subsequent aryl C−H activation. Therefore, in this case, more flexible SPO ligands were then re-examined. To our delight, $\mathbf{L_4}$ can promote the reaction, albeit only in 25% yield in the current stage (**4d**). Although low regioselectivities were obtained for asymmetric dialkyl alkynes (**4e**/**4e′** and **4f**/**4f′**), asymmetric alkylphenyl alkynes (**4g**/**4g′** and **4h**/**4h′**) led to pretty good regioselectivities (>10:1). Moreover, the phenyl was exclusively proximate to the carbonyl group, which was confirmed by X-ray analysis (see the Supporting Information). These results suggested that the second alkyne insertion of the nickelacycle could start from the aryl−Ni bond, thus preferentially forming a more stable benzylic nickel species.

To understand the mechanism, some mechanistic experiments were performed. Tracking formyl H of the amide by the use of deuterated formamide **1a**-*d* under the standard conditions showed that D was completely transferred into the acrylamide and the alkene (Scheme 5a, eq 1). Parallel reactions disclosed no isotope effect for the formyl C−H bond (eq 2), excluding this C−H bond cleavage from the rate-determining step. Either oxidative addition of Ni to the C−H

Scheme 5. Mechanistic Experiments and a Plausible Mechanism



bond along with alkyne insertion or Ni-catalyzed direct H transfer into alkyne occurred in this step.[6,12] Intra- and intermolecular competitive experiments gave two similar k_H/k_D values, 1.56 and 1.50, respectively (eqs 3 and 4), suggesting that the second C−H activation may occur through a concerted pathway instead of the typical S_EAr mechanism.[6] ^{31}P NMR tracing experiments showed that small amounts of the SPO-bound Ni−Al complex could be formed (95.9 ppm) when equal numbers of equivalents of $\mathbf{L_{11}}$, $AlMe_3$, and $Ni(cod)_2$ were mixed at 80 °C (see the Supporting Information). However, the process can be accelerated by addition of the formamide, whereas the alkyne did not have the same influence. The result suggested that the formamide that coordinated to Ni promoted isomerization of SPO with $AlMe_3$. Notably, the resulting complex was found to be able to promote the annulation of alkyne **2a**, providing product **3a** in 60% yield. On the basis of these observations and previous discussions,[13] we proposed a plausible mechanism for this reaction (Scheme 5b). First, the formed SPO-bound Ni−Al bimetallic complex initiates formyl C−H bond cleavage through oxidative addition (or H transfer).[14] Subsequent alkyne insertion provides the key intermediate (**A**), which undergoes aryl C−H bond cleavage to produce the intermediate (**B**). Final alkyne insertion and reductive elimination led to the desired product **3a**.

In summary, we have developed a ligand-controlled method for nickel-catalyzed dual C−H annulation of arylformamides and alkynes, affording various quinolin-2(1*H*)-ones in yields of ≤97%. This SPO-enabled bimetallic catalysis demonstrates its unique ability to activate C−H activation and suppress decarbonylation of arylformamides, which will improve the future design of other types of C−H bond functionalization in our lab.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00432.

Experimental procedures and characterization of the substrates and products (PDF)

Accession Codes

CCDC 1887875 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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