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ARTICLE

Nickel-Catalyzed C-H/N-H Annulation of Aromatic Amides with Alkynes in the Absence of a Specific Chelation System

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The Ni-catalyzed reaction of aromatic amides with alkynes in the presence of KOBu^t involves C-H/N-H oxidative annulation to give 1(2H)-isoquinolinones. A key to the success of the reaction is the use of a catalytic amount of a strong base, such as KOBu^t. The reaction shows a high functional group compatibility. The reaction with unsymmetrical alkynes, such as 1-arylalkynes gives the corresponding 1(2H)-isoquinolinones with a high level of regioselectivity. This discovery would lead to the development of Ni-catalyzed chelation-assisted C-H functionalization reactions without the need for a specific chelation.

Introduction

The direct functionalization of C-H bonds has emerged as an increasingly valuable tool for step-economical organic synthesis. A wide variety of transition metal complexes, including Pd, Ru, Rh, and Ir can be used as catalysts in a variety of catalytic functionalizations of C-H bonds.[1] Nickel-catalyzed C-H functionalizations have recently become a subject of great interest, owing to the low cost of the reaction, the use of readily available nickel, and the uniqueness of the reaction. However, the functionalization of C-H bonds catalyzed by Ni complexes was limited to C-H bonds in specific aromatic systems, such as pyridine or activated pyridine derivatives, perfluorinated benzene, azoles, and indoles, all of which contain an acidic C-H bond.[2] No general and reliable system for the nickel-catalyzed functionalization of non-acidic C-H bonds in benzene rings was available.[3] In 2011, we reported on the Ni(0)-catalyzed reaction of aromatic amides that contain a 2-pyridinylamine moiety as a directing group, with alkynes, leading to the production of isoquinolinones.[4] In 2013, we also reported on the Ni(II)-catalyzed C-H alkylation of aromatic amides that contain an 8-aminoquinoline moiety as a directing group, with alkyl halides.[5a] Since then, significant advances in Ni(II)-catalyzed C-H functionalization reactions that involve the use of a bidentate chelation system have been reported by many other groups, as well as our group.[5-7] A newly developed chelation system in which a bidentate directing group is used is now recognized as a powerful and reliable strategy for developing Ni-catalyzed C-H functionalizations. The presence of both N(sp^2) and NH groups is crucial for the reaction to proceed. The reactions reported to date can be classified into two types, depending on the oxidation state of the key catalytic species. In the case of a Ni(0)-catalyzed system, the coordination of an N(sp^2) atom to the nickel(0) center, followed by the oxidative addition of an N-H bond to give complex **A**,[8,9] where the cleavage of a C-H bond proceeds through σ-bond metathesis to generate the cyclometalated complex **B** with concomitant generation of the formal "H_2", which is then trapped by a hydrogen acceptor, such as an alkyne. In the Ni(II)-catalyzed system, the coordination of an N(sp^2) atom to a nickel(II) center followed by a ligand exchange gives complex **C**, which, after the cleavage of a C-H bond through a concerted metalation deprotonation mechanism (CMD), generates a cyclometalated complex **D**. After the metalacycle **B** or **D** is formed, various reagents can then be used in the remainder of the reaction. Irrespective of the mechanism, the role of the N(sp^2) atom is to bring the nickel catalyst into close proximity to the NH bond by coordination, followed by the formation of a covalent N-Ni bond via oxidative addition or ligand exchange. The nickel atom in the resulting intermediates **A** and **C** is now sufficiently close to activate *ortho* C-H bonds, which are then cleaved. Thus, the formation of a covalent N-Ni bond is a key step in the activation of C-H bonds in the Ni-catalyzed bidentate chelation system. In the case of Pd, Ru, Rh, and Ir-catalyzed reactions, a wide variety of chelating groups are known to function as directing groups that are capable of activating C-H bonds. Even the weak coordination of a heteroatom to these metals can promote the activation of C-H bonds. In sharp contrast, when the heteroatom is weakly coordinated to nickel, the C-H bonds are not activated. Because of this, the pre-coordination of an N(sp^2) atom to the nickel center is required to allow the nickel to come into close proximity to the N-H bonds to form an N-Ni bond.

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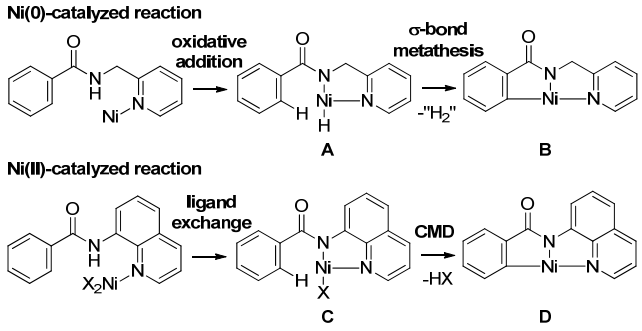
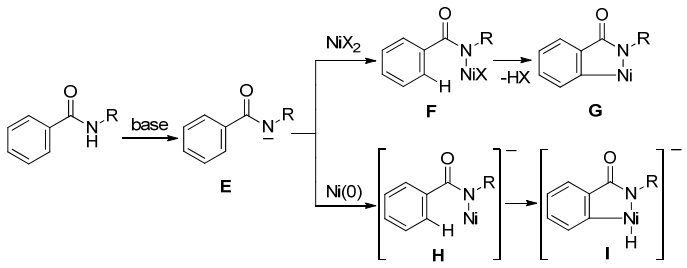


Scheme 1 Key steps for the activation of C-H bonds by nickel complexes in a bidentate-chelation system. For simplicity, groups that are not involved in the transformation, such as ligands and reagents, are omitted.

A bidentate chelation system using 2-pyridinylamine and 8-aminoquinoline as the directing group is recognized as a powerful and reliable strategy for developing new types of Ni-catalyzed C-H functionalizations. However, elaborating these directing groups into useful functional groups is not an easy task.[10] Our next target involves the use of a simpler directing group instead of strong and specific directing groups, such as 2-pyridinylamine and 8-aminoquinoline groups. Our working hypothesis is that if a strong base could be used, the anion generated by the deprotonation of an amide NH would easily react with the Ni(II) catalyst to produce a new bond between N and Ni, as in **F**, which would function as a key intermediate for C-H activation, as mentioned above, C-H bond cleavage would then take place, with the generation of the metalacycle **G**. In the case of a Ni(0) catalyst, the nickel complex **H** would be expected to participate in the oxidative addition of C-H bonds to generate complex **I**.[9,11] Thus, no pre-coordination of an N(sp^2) atom to a nickel center would be required.



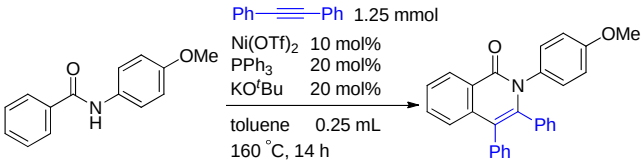
Scheme 2 Working hypothesis.

We recently realized such a reaction. Herein, we report on the Ni-catalyzed oxidative annulation of C-H bonds in aromatic amides with alkynes, leading to the production of 1(2H)-isoquinolinones. A specific directing group is not required for the success of the reaction. A key to the success of the reaction is the use of a catalytic amount of KOBut.[12]

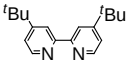
Results and Discussion

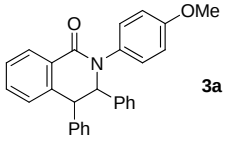
The reaction of the aromatic amide **1a** with 5 equivalents of diphenylacetylene in the presence of $Ni(OTf)_2$ (10 mol%) and PPh_3 (20 mol%) in toluene (0.25 mL) at 160 °C for 14 h gave 2-(4-methoxyphenyl)-3,4-diphenyl-1(2*H*)-isoquinolinone (**2a**) in 67% NMR yield (entry 1 in Table 1). It was found that the catalytic activity of $Ni(cod)_2$ is comparable to that for $Ni(OTf)_2$ (entry 2). Among the ligands examined (entries 3-5), PPh_3 was the ligand of choice. Although the use of 4,4'-di-tert-butyl-2,2'-bipyridine resulted in a higher yield of **2a** than phosphine ligands, a small amount of the saturated product **3a** was also formed (entry 6) The reaction proceeded efficiently in the presence of a strong base (entries 7 and 8). In sharp contrast, no reaction took place when weak bases were used (entries 9 and 10). Finally, the use of m-xylene (0.6 mL) as the solvent and an alkyne (10 equivalents) gave **2a** in 89% isolated yield (entry 14).

Table 1. Ni-catalyzed reaction of aromatic amide with diphenylacetylene.[a]



1a 0.25 mmol **2a**

Entry	Notes	NMR Yields: **2a**	recovered **1a**
1	-	67% (61%)	31%
2	$Ni(cod)_2$	63% + **3a** 8%	27%
3	PCy_3	55%	31%
4	PBu_3	56%	35%
5	$P(OPh)_3$	0%	71%
6		72% + **3a** 4%	4%
7	LiO^tBu	62%	37%
8	KOMe	71% + **3a** 5%	24%
9	KOAc	no reaction	
10	K_3PO_4	no reaction	
11	m-xylene	63%	33%
12	140 °C	69% + **3a** 6%	27%
13	m-xylene, alkyne 10 equiv	81%	17%
14	m-xylene 0.6 mL, alkyne 10 equiv	90% (89%; **2a**:**3a** = 39:1)	4%



3a

[a] The number in parenthesis refers to the isolated yield.

The effect of substituents on the amide nitrogen was examined under optimized reaction conditions (entry 14 in Table 1). Aryl groups containing both electron-donating and electron-withdrawing groups gave the corresponding isoquinolinones in high yields, while alkyl groups, such as methyl and tert-butyl groups gave the corresponding products in poor yields.

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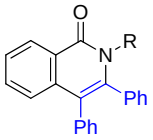


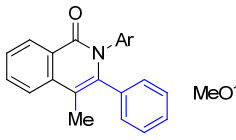
R = 4-MeOC$_6$H$_4$ (**2a**) 89%
R = Ph (**4a**) 87%
R = 4-CF$_3$C$_6$H$_4$ (**4b**) 78%

Scheme 3 Effect of substituents on the amide nitrogen

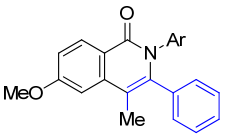
The scope of this oxidative annulation reaction was investigated with respect to the amide used (Table 2). The reaction shows a broad substrate scope and a high functional group tolerance. Various functional groups, including methoxy, dimethylamino, cyano, fluoride, and trifluoromethyl groups were tolerated. In the case of meta-trifluoromethyl-substituted aromatic amides **1l**, the less hindered C-H bond was exclusively activated to give **2l** in 91% isolated yield as a single isomer. On the other hand, in the case of the meta-methyl-substituted aromatic amide **1m**, a 2:1 mixture of regioisomers **2m** was obtained.

The scope of alkynes was also examined (Scheme 3). Although terminal alkynes did not give the corresponding isoquinolinones, various internal alkynes were applicable to the reaction. When 1-phenyl-1-propyne was used as the alkyne under the standard reaction conditions, the product yield of **2r** was moderate (26% yield) and a regioisomeric mixture (3:1) was produced. Gratifyingly, after screening various reaction parameters, the reaction was dramatically improved to give a 77% yield with a high degree of regioselectivity (>50:1) when 4,4'-di-tert-butyl-2,2'-bipyridine was used as the ligand instead of PPh_3. The regioselectivity was not affected by electronic effects of substituents on the aromatic ring of both amides and alkynes, as in **2r**, **2s**, **2t**, and **2u**. The use of 4,4'-di-tert-butyl-2,2'-bipyridine also dramatically improved the product yield of **2x** in the reaction of **1a** with 4-octyne. The use of the unsymmetrical dialkylacetylene gave nearly a 1:1 ratio of regioisomers of **2y**.

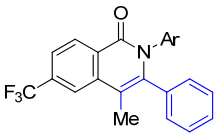
Table 3 Scope of alkynes.[a,b]



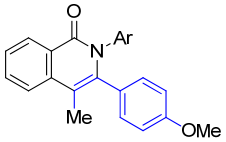
2r 26% (3:1)[c]
2r 77% (>50:1)



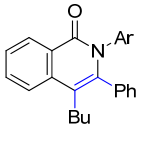
2s 51% (26:1)



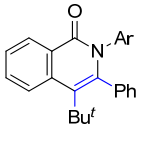
2t 76% (40:1)



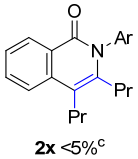
2u 60% (44:1)



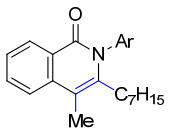
2v 77% (>50:1)



2w 71% (one isomer)



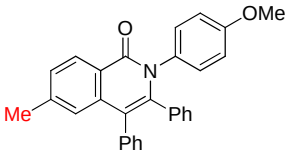
2x <5%[c]
2x 70%



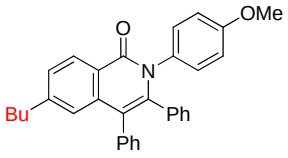
2y 39% (1:1)

[a] Reaction conditions: amide (0.25 mmol), alkyne (2.5 mmol), Ni(OTf)$_2$ (0.025 mmol), 4,4'-di-tert-butyl-2,2'-bipyridine (0.05 mmol), KO^{t}Bu (0.05 mmol) in *m*-xylene (0.6 mL) at 160 °C for 48 h. [b]Isolated yields. The number in parenthesis refers to regioselectivity. [c] The reaction was carried out under the conditions shown in entry 14 in Table 1.

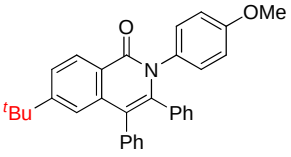
Table 2. Scope of amides[a,b]



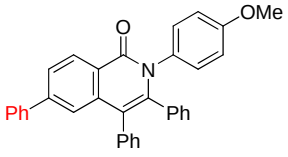
2b 67%



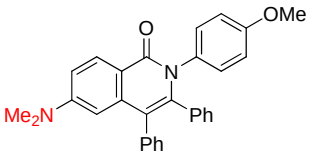
2c 68%



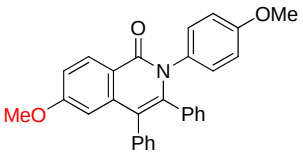
2d 88%



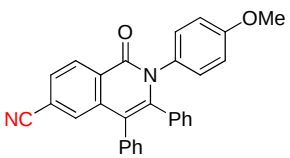
2e 60%



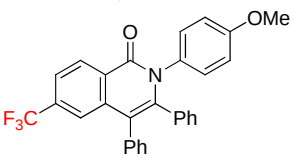
2f 80%



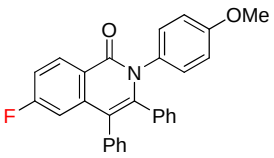
2g 83%



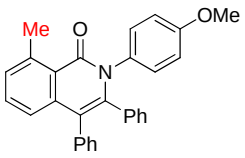
2h 71%[c]



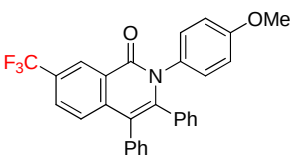
2i 68%



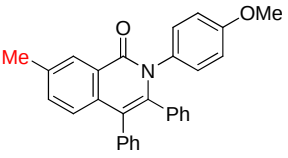
2j 69%



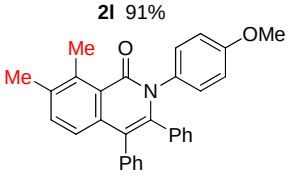
2k 81%



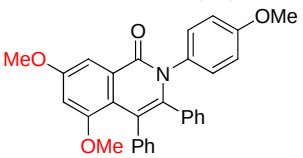
2l 91%



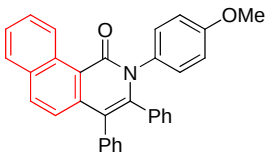
2m 81% (2:1)[d]



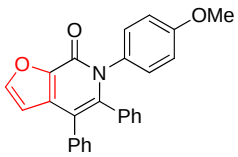
2n 76%



2o 56%



2p 74%[c]



2q 32%

[a] Reaction conditions: amide (0.25 mmol), diphenylacetylene (2.5 mmol), $Ni(OTf)_2$ (0.025 mmol), PPh_3 (0.05 mmol), $KOBu^t$ (0.05 mmol) in m-xylene (0.6 mL) at 160 °C for 14 h. [b] Isolated yields. [c] For 48 h. [d] The number in parenthesis refers to regioselectivity.

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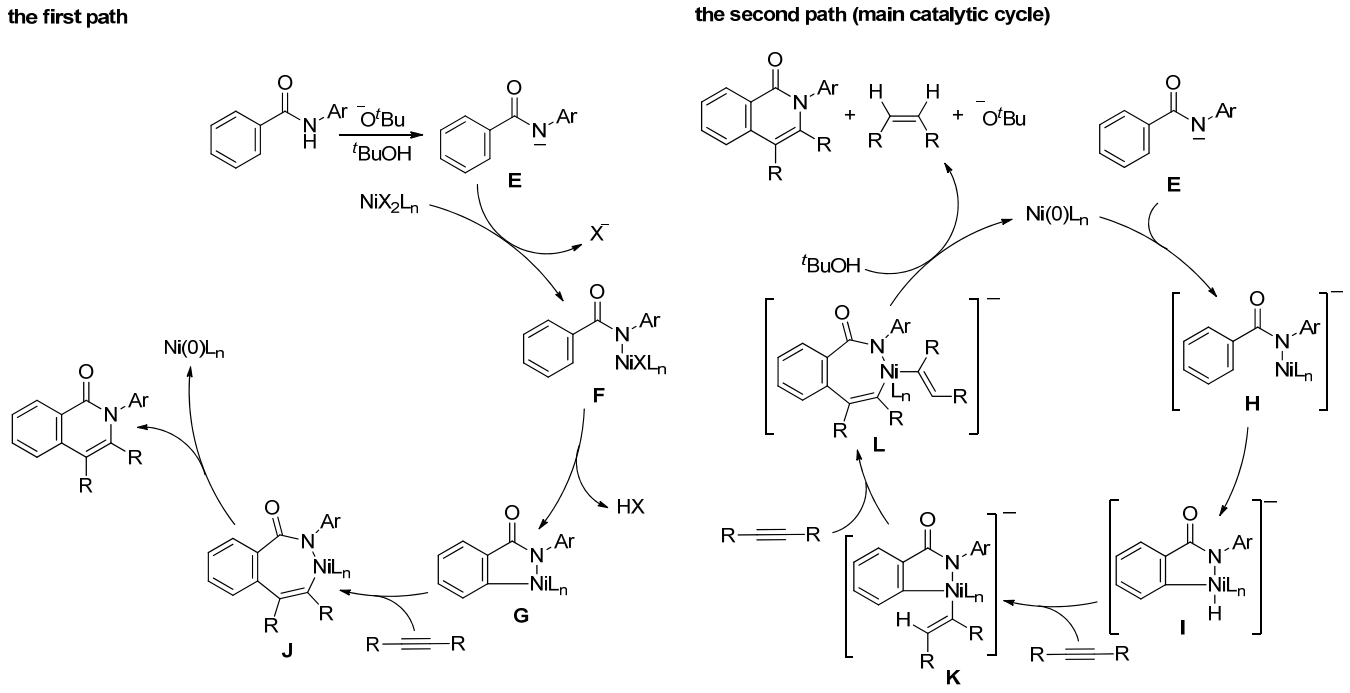
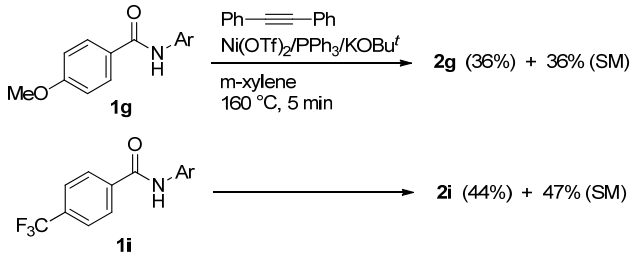
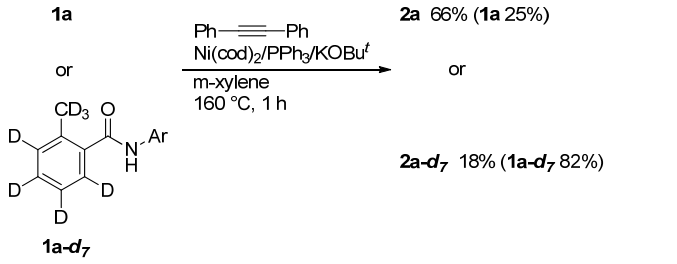


Scheme 8 Proposed mechanism.



Scheme 4 Competition experiments.

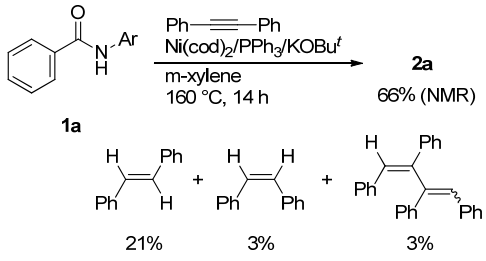


Scheme 5 Deuterium labeling experiments.

To gain mechanistic insights into the reaction, some additional experiments were conducted. We performed a competition experiment using 4-methoxy- and 4-trifluoromethyl-substituted aromatic amides (Scheme 4). However, no significant difference in electronic effects between the two substituents was observed.

Deuterium-labeling experiments were also carried out (Scheme 5). No H/D exchange was observed both in the product and the recovered amide, even at the *ortho*-position, indicating that the cleavage of C-H bonds is irreversible. These results are completely different from those obtained when an 8-aminoquinoline directing group was used.[5] In addition, a KIE of 3.7 was determined, suggesting that the cleavage of C-H bonds is the rate determining step.

Although the material balance was not high, it was found that an alkyne functions as, not only a two-component coupling partner, but also hydrogen acceptor (Scheme 6).



Scheme 6. Detection of alkenes.

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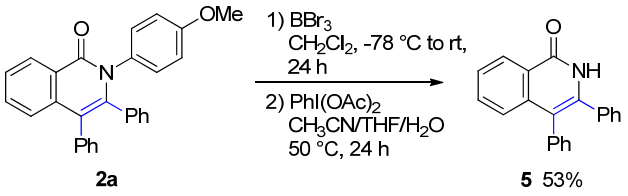
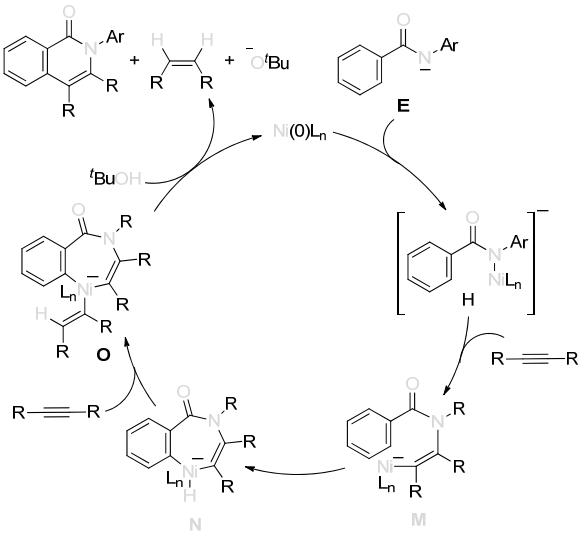
The para-methoxyphenyl group was successfully removed. The treatment of **2a** with BBr_3 followed by $PhI(OAc)_2$ in $CH_3CN/THF/H_2O$ gave the 3,4-diphenylisoquinolin-1(2H)-one (**5**).



Scheme 7. A removal of para-methoxyphenyl group.

A proposed mechanism for the above reaction is shown in Scheme 8. The mechanism involves two paths. The Ni(II) complex initiates the first path (left scheme). A proton is abstracted from an amide by $KOBu^t$ to generate the amidate anion **E**, which reacts with Ni(II) to give the complex **F**. The cleavage of the *ortho* C-H bonds gives the nickelacycle **G**, followed by the insertion of an alkyne into a N-Ni bond, which then undergoes reductive elimination to give the isoquinolinone and Ni(0). Ni(0) cannot be oxidized to Ni(II) under the reaction conditions employed. However, the main catalytic cycle in which Ni(0) is the key catalytic species initiates the reaction (right scheme). The amidate anion **E** reacts with Ni(0) to give a nickel complex **H**, which is sufficiently reactive to undergo oxidative addition to generate the nickel hydride species **I** because the complex is sufficiently electron rich.[11,13] The successive insertion of an alkyne into H-Ni and C-Ni bonds gives the complex **L**. Reductive elimination followed by protonation by ^{t}BuOH affords the isoquinolinone with the regeneration of Ni(0) and $KOBu^t$ with concomitant formation of an alkene.



Scheme 9 Alternative mechanism.

An alternative mechanism would involve the insertion of an alkyne from the N-Ni bond in **H** to generate the complex **M** (Scheme 8).[14] The oxidative addition of the *ortho* C-H bond gives a seven-membered nickelacycle **N**, which then permits the insertion of an alkyne to give the complex **O** (Scheme 9). Complex **O** undergoes reductive elimination and protonation by ^{t}BuOH to afford the isoquinolinone with the regeneration of Ni(0) and $KOBu^t$ with the concomitant formation of an alkene. Based on the above findings, this alternative mechanism cannot be excluded.

Conclusions

In summary, we report on the development of a new system for C-H functionalizations catalyzed by nickel complexes. In the past, an *N,N*-bidentate chelation system was the only reliable, general, and powerful system for developing Ni-catalyzed C-H functionalizations.[6a,b] The above findings show that aromatic amides with a simple directing group can also participate in the Ni-catalyzed C-H functionalization. The reaction displays a broad substrate scope and has a high functional group tolerance. A specific directing group, such as 2-pyridinylamine and 8-aminoquinoline is not required for the reaction to proceed. A key to the success of the reaction is the use of a catalytic amount of $KOBu^t$, which forms an N-Ni bond which permits the C-H bond to be activated. Nickel-catalyzed synthesis of isoquinolinones with the extraction of CO or N_2 or the cleavage of C-halogen bonds that are already present on the aromatic ring has been reported.[15] Our new system has the potential for applications to new types of Ni-catalyzed functionalization of C-H bonds, which continues to be a challenging issue

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