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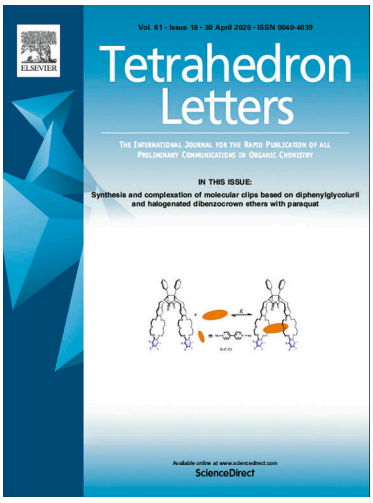

Bidentate geometry-constrained iminopyridyl nickel-catalyzed synthesis of amines or imines *via* borrowing hydrogen or dehydrogenative condensation

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Bidentate geometry-constrained iminopyridyl nickel-catalyzed synthesis of amines or imines *via* borrowing hydrogen or dehydrogenative condensation

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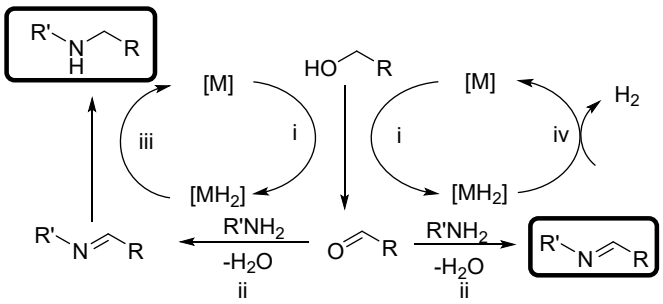
Abstract:

The efficient Ni-catalyzed *N*-alkylation of various anilines with alcohols *via* borrowing hydrogen is reported using a bidentate geometry-constrained iminopyridyl nickel complex as the catalyst. Substituted benzylic alcohols and short/long chain aliphatic alcohols could be applied as the alkylation sources to couple with aromatic and heteroaromatic amines to give a diverse set of *N*-alkylation outcomes in moderate to excellent yields. The nickel catalytic system was also suitable for aliphatic amines, selectively delivering the corresponding imines *via* an acceptorless dehydrogenative condensation strategy.

Keywords: *N*-Alkylation; Amines; Imines; Iminopyridyl Nickel; Borrowing Hydrogen; Dehydrogenative Condensation

Amines and imines are valuable organic compounds in synthetic chemistry. As versatile intermediates or precursors, they are widely applied in the synthesis of natural products, pharmaceuticals, pesticides, materials, and dyes [1]. Thus, developing efficient methods for constructing C-N bonds to prepare amines and imines is an important goal. The *N*-alkylation of amines is commonly utilized as an important tool for the synthesis of substituted amines [2]. The nucleophilic substitution of an amine with an alkyl halide is a typical method for *N*-alkylation [3], although over-alkylation limits its applications [4]. Alternatively, other catalytic approaches for the *N*-alkylation of amines have received great interest, such as Buchwald−Hartwig amination [5], hydroamination of alkenes [6], reductive amination of carbonyl compounds [7] and Fukuyama amine synthesis [8]. Since the pioneering work reported independently by the groups of Grigg [9] and Watanabe [10], significant progress has been achieved in applying alcohols as the alkyl source due to their intrinsic advantages, such as ready availability, inexpensiveness, and low toxicity, *via* homogeneous borrowing hydrogen (BH) catalysis [11]. The overall process is generally recognized as consisting of the following three steps (Scheme 1): (i) alcohol oxidation *via* acceptorless dehydrogenation by the metal catalyst to generate [MH_2]; (ii) imine formation *via* condensation between the amine and carbonyl species; (iii) hydrogenation of the imine by [MH_2] to release the target *N*-alkylated product [12]. From the mechanistic cycle, it can be clearly seen that a direct synthesis of imines could be realized *via* H_2 liberation (iv) instead of imine hydrogenation, which has been widely accepted as the concept of acceptorless dehydrogenative condensation (ADC) [13]. In view of its potential versatility and environmentally benign properties, imine synthesis through ADC catalysis from amines and alcohols has received considerable attention [14].



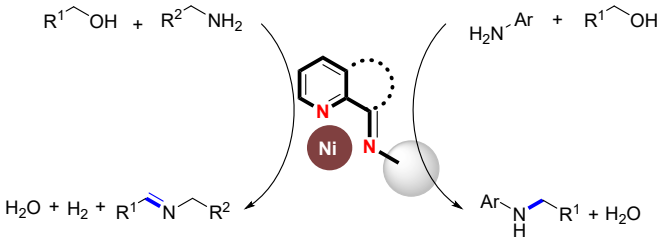
Scheme 1. Synthesis of amines and imines *via* the BH and ADC concepts.

In the field of *N*-alkylation, noble metal complexes, mainly Ru[15] and Ir [16], have been predominantly applied as the catalysts of choice when using amines and alcohols. In recent years, replacing these noble metal with nonprecious and/or earth-abundant transition metals, such as Fe [17], Co [14g, 18], and Mn [14k, 19], has received considerable interest by developing well-defined complexes [20]. Among 3d metals, Ni has been relatively less applied in BH catalysis, especially in *N*-alkylation reactions. To the best of our knowledge, only isolated examples of nickel-based homogeneously catalyzed *N*-alkylation reactions have been reported by Banerjee [21], Zhou [22], Adhikari [23], and Tang [24] in recent years. Although these reported nickel catalytic systems are rather impressive, they have also suffered from some obvious limitations. For example, a large excess of the alcohol (4 equiv. to amine) needed to be utilized and long reaction times were necessary. These phenomena strongly implied that the efficiency of these nickel catalyst systems could be improved. Moreover, although aryl and heteroaryl amines were suitable substrates in the reported examples, aliphatic amines were not discussed.

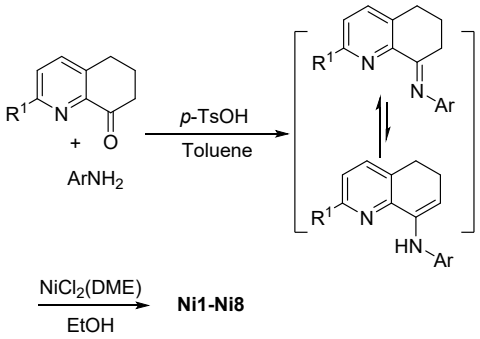
As previously mentioned, imines are commonly proposed as intermediates for the *N*-alkylation of amines. The synthesis of imines directly from amines and alcohols *via* ADC has also received significant attention. Recently, Fe [13i], Co [13f-h], and Mn-catalyzed [13j-n] imine formation with amines and alcohols has been reported, while nickel catalysis is less studied [25]. To this end, developing novel nickel

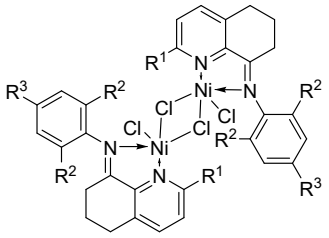
catalytic systems for the selective synthesis of *N*-alkyl amines or imines through BH or ADC catalysis is still appealing.

Adhikari and co-workers revealed that the redox-active azo moiety present on the ligand backbone played a crucial role in Ni-catalyzed *N*-alkylation [23]. Inspired by their work, we envisioned that ligands with appropriate redox-active properties should be investigated. The redox non-innocent iminopyridine scaffolds have been applied as the preferable platform in 3d-metal catalysis due to their facile electronic tunability that can result in unusual structures and reactivity [26]. In the past years, we have developed a series of geometry-constrained iminopyridyl (CImPy) compounds [27], which showed excellent catalytic efficiency and selectivity for hydride transfer reactions, such as the hydroarylation of alkynes [28] and alkenes [29] as well as the Markovnikov-selective hydrosilylation of alkynes [30]. Encouraged by these results, we decided to examine CImPy compounds in this transformation due to its high steric and electronic tunability and rigid environment, which can suppress the deactivation of the catalyst to improve the catalyst efficiency [31]. Herein, we reported an efficient Ni-catalyzed *N*-alkylation of aromatic amines with a wide substrate scope of alcohols using the bidentate CImPy ligand. Meanwhile, a selective ADC of aliphatic amines with alcohols affording imines is also established (Scheme 2).



Scheme 2. CImPy-Ni-catalyzed selective synthesis of amine and imine derivatives from amines and alcohols.





Ni1-Ni8

	R^1	R^2	R^3	Yield (%)
Ni1	H	H	H	73
Ni2	H	H	Me	74
Ni3	H	H	methoxy	71
Ni4	H	H	*N,N*-dimethyl	78
Ni5	H	Me	Me	73
Ni6	H	Ph_2CH	Me	83
Ni7	Ph	H	*N,N*-dimethyl	77
Ni8	Me	H	*N,N*-dimethyl	74

Scheme 3. Preparation of the ICmPy ligated nickel complexes.

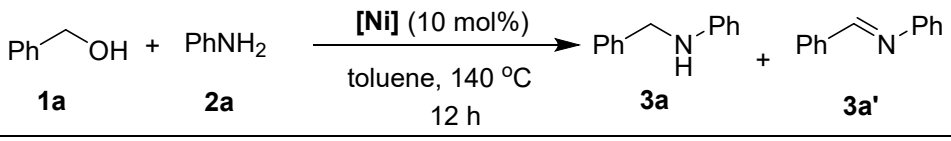
Following the reported procedure, a series of CImPy ligated nickel complexes were prepared [32]. Starting from tetrahydroquinolin-8-one, condensation reactions were carried out with the substituted anilines in the presence of *p*-TsOH in toluene to afford the target 8-aryl-imino-tetrahydroquinoline derivatives as yellowish oils in moderate yields. The obtained imino compounds were then reacted with $NiCl_2$(DME) to afford their corresponding nickel complexes **Ni1**-**Ni8** as green precipitates. These nickel complexes were characterized using FT-IR spectroscopy, which indicated effective coordination of the cationic nickel with the ligands as evidenced by the shift of the $\upsilon_{C=N}$ stretching vibrations (1570-1610 cm^{-1}). All efforts aimed at growing single crystals of **Ni1**-**Ni8** failed. However, analogous nickel complexes have been utilized as homogeneous catalysts in ethylene polymerization by Sun's group, for which structural analysis showed that they were centrosymmetric dimers with two Cl atoms as the bridges [32]. Therefore, we proposed that **Ni1-Ni8** possessed the similar dimeric structure as shown in Scheme 2 [33].

With these CImPy ligated nickel complexes in hand, we initially focused on applying them in the Ni-catalyzed *N*-alkylation of amines with alcohols. The reactions

catalyzed by **Ni1**-**Ni8** employing benzyl alcohol (**1a**, 2.0 mmol), aniline (**2a**, 1.0 mmol), base (1.5 mmol) and 5 mol% nickel complex in toluene were independently conducted. As shown in Table 1, all tested CImPy ligated nickel complexes exhibited different catalytic performance for aniline benzylation. When applying the ligand without any substituents on the pyridine ring and phenyl imine, *N*-benzyl aniline (**3a**) was obtained in 43% yield (Table 1, entry 1). Gratifyingly, an electron-donating group on the aryl imine site markedly improved the transformation (Table 1, entries 2-4). Remarkably, the ligand with an *N,N*-dimethyl group on the aryl imine gave the desired product in 94% yield (Table 1, entry 4). Nevertheless, changing the steric properties of the aryl imine site did not improve the reaction and lower conversion was observed (Table 1, entry 2 vs entries 5 and 6). Meanwhile, we also compared the ligands with various substituents on the *ortho*-position of the pyridine ring, which indicated that incorporating a phenyl or methyl group gave slightly lower yields of **3a** (Table 1, entry 4 vs entries 7 and 8). It was noted that most CImPy ligated nickel complexes tested, except **Ni1** and **Ni5**, exhibited high conversions but with varying yields of **3a** under identical reaction conditions. In these reactions, the imines were detected using GC and GC-MS analysis. These results revealed that although benzyl alcohol oxidation catalyzed by these nickel complexes occurred successfully, hydrogenation of the imine to deliver the amine was greatly influenced by the various CImPy ligands. Electron-rich ligands with a less hindered aryl imine site possibly favour the imine hydrogenation step. Furthermore, 1,10-phenthroline, an efficient ligand reported by Banerjee, was also examined under the same conditions [21],

which showed much lower conversion and yield (Table 1, entry 9). For activation of the nickel precatalyst and *β*-hydride elimination to generate nickel hydride, the base also played a very important role [21]. Thus other bases were also screened and found to be much less efficient than *t*-AmOK for the alkylation of aniline (Table 1, entries 10 and 11). In addition, reducing the catalyst loading or shortening the reaction time had little effect on the conversion of aniline, but supressed the alkylation product significantly (Table 1, entries 12 and 13). A lower amount of **1a** resulted in good conversion but only a moderate yield of **3a** (Table 1, entry 14). To this end, the optimal conditions for the *N*-alkylation of an amine was determined as amine (1 equiv.), alcohol (2 equiv.), *t*-AmOK (1.5 equiv.) and 5 mol% **Ni4**, at 140 ^{o}C in toluene for 12 h.

Table 1. Performance of **Ni1**-**Ni8** in the Ni-catalyzed *N*-alkylation of aniline with benzyl alcohol.[a]



1a **2a** **3a** **3a'**

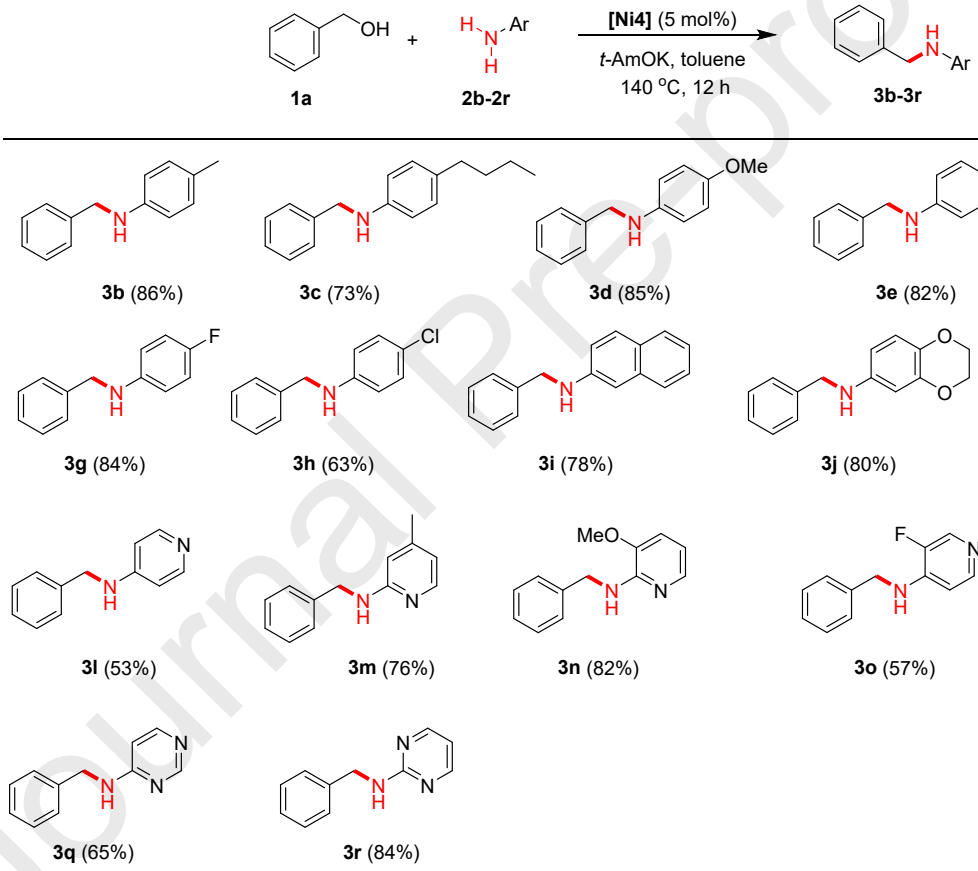
Entry	Cat. (mol%)	Base (1.5 eq.)	Conv. (%)[b]	Yield (%)[b]	
				3a	**3a'**
1	**Ni1**	*t*-AmOK	70	43	27
2	**Ni2**	*t*-AmOK	94	76	18
3	**Ni3**	*t*-AmOK	90	66	24
4	**Ni4**	*t*-AmOK	98	94 (90[c])	4
5	**Ni5**	*t*-AmOK	78	48	30
6	**Ni6**	*t*-AmOK	92	70	22
7	**Ni7**	*t*-AmOK	95	84	11
8	**Ni8**	*t*-AmOK	96	88	8
9	$NiCl_2$(DME)/ 1.10-phenthroline	*t*-AmOK	64	41	23
10	**Ni4**	*t*-AmONa	81	20	61
11	**Ni4**	*t*-BuOK	54	25	29
12[d]	**Ni4**	*t*-AmOK	91	72	19
13[e]	**Ni4**	*t*-AmOK	93	68	25
14[f]	**Ni4**	*t*-AmOK	81	58	23

[a] Reagents and conditions: **1a** (2.0 mmol), **2a** (1.0 mmol), **[Ni]** (0.05 mmol, 10 mol% of Ni), base (1.5 mmol), 140 °C, toluene (4.0 mL), 12 h. [b] Conversions and yields were determined by GC with area normalization. [c] Isolated yield in parenthesis. [d] 2.5 mol% **Ni4** was utilized. [e] 6 h. [f] 1.4 equiv. of **1a** was utilized.

With the aforementioned optimal reaction conditions, we then investigated the substrate tolerance of this Ni-catalyzed *N*-alkylation between benzyl alcohol and various anilines. As shown in Table 2, aromatic amines with electron-donating substituents reacted with benzyl alcohol to give their corresponding monoalkylated amines in good to excellent isolated yields (**3b**–**f**). It was noted that sterically hindered *o*-methoxyl aniline also proceeded efficiently (**3f**). Anilines with a weakly electron-withdrawing group, such as F, resulted in an excellent yield of the alkylated product (**3g**), however strongly electron-withdrawing groups, such as CN, NO_2 and the carbonyl group, were not well tolerated due to their reductive properties. 4-Chloroaniline gave the targeted product (**3h**) in 63% yield, in which the partially

dechlorinated product or reactant was also observed. Meanwhile, to illustrate the synthetic utility, heteroaromatic amines were also examined. Gratifyingly, *ortho*- and *para*-amino pyridines gave their corresponding alkylated amines in 85% (**3k**) and 53% (**3l**) yield, respectively; substituted amino pyridines either with electron-donating or electron-withdrawing groups were converted to the respective product in moderate to good yields (**3m**-**3p**). Additionally, the *N*-alkylation protocol was also suitable for amino pyrimidines (**3q** and **3r**).

Table 2. Alkylation of various anilines with benzyl alcohol.[a]

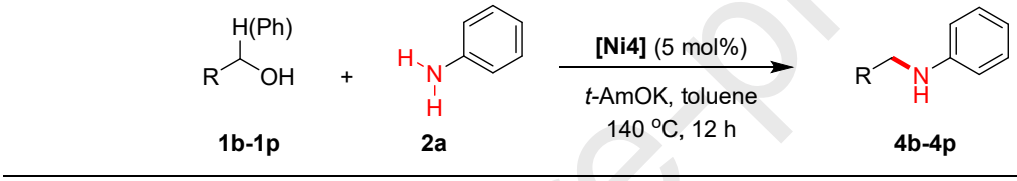


[a] Reagents and conditions: **1a** (2.0 mmol), **2** (1.0 mmol), **Ni4** (0.05 mmol), *t*-AmOK (1.5 mmol), 140 °C, toluene (4.0 mL), 12 h. Isolated yields in parentheses.

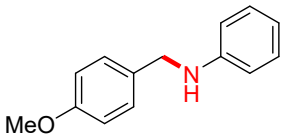
Next, we turned our attention to examining the scope of the alcohols under the optimized conditions (Table 3). We found that benzyl alcohols bearing electron-rich functional groups, naphthalene, and nitrogen-containing heterocycles smoothly

reacted with aniline to afford the corresponding *N*-alkylated products (**4b**-**4h**) in moderate to excellent yields. The application of a sterically hindered substrate resulted in a lower yield of the alkylated product (**4e**). Notably, the secondary alcohols also delivered the desired *N*-alkylated product in 81% yield (**4i**). Furthermore, to demonstrate the general applicability of the catalytic system, more challenging aliphatic alcohols were also evaluated. To our delight, both short-chain and long-chain aliphatic alcohols successfully afforded the desired *N*-alkylated aniline products in moderate to good yields (**4j**-**4o**).

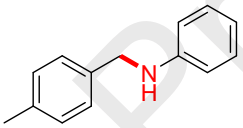
Table 3. Alkylation of aniline with various alcohols.[a]



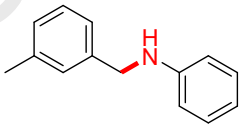
1b-1p **2a** **4b-4p**



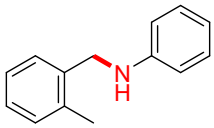
4b (78%)



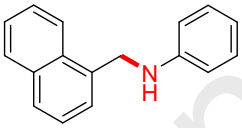
4c (74%)



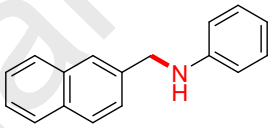
4d (56%)



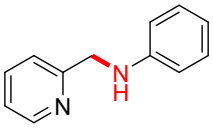
4e (58%)



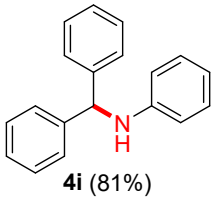
4f (92%)



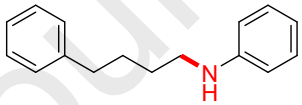
4g (84%)



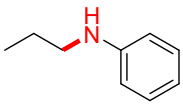
4h (56%)



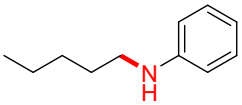
4i (81%)



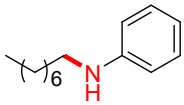
4j (53%)



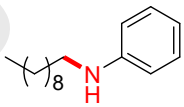
4k (48%)



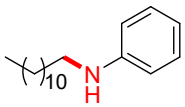
4l (55%)



4m (55%)



4n (71%)



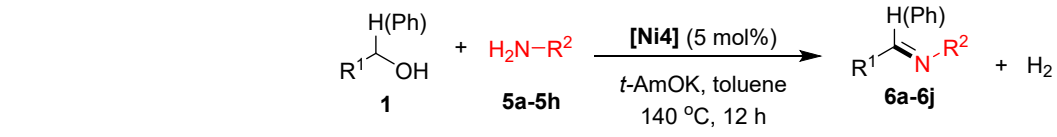
4o (57%)

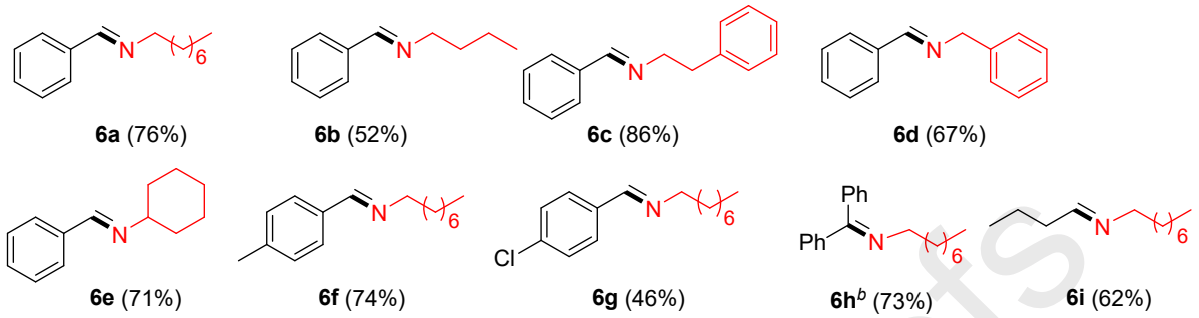
[a] Reagent and conditions: **1** (2.0 mmol), **2a** (1.0 mmol), **Ni4** (0.05 mmol), *t*-AmOK (1.5 mmol), 140 °C, toluene (4.0 mL), 12 h. Isolated yields in parentheses.

After exploring the scope of the aromatic amines and alcohols, we then tested

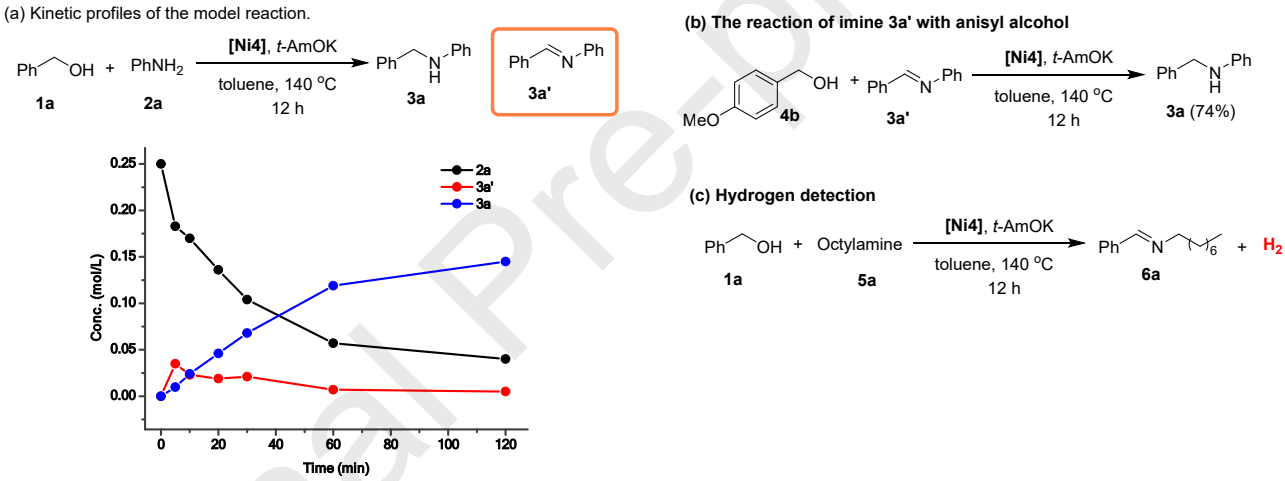
aliphatic amines. To the best of our knowledge, aliphatic amines have not been discussed in previous reported homogeneous Ni-catalyzed *N*-alkylations [21-23]. Under identical conditions for the above *N*-alkylation of anilines with alcohols, the dehydrogenative coupling of benzyl alcohol and octylamine was carried out. To our surprise, imine compound **6a** was isolated in 76% yield as the major product rather than the expected amine. In fact, selective imine formation *via* the ADC of alcohols and amines has been well demonstrated.[13] However, no example has been reported with a nickel catalyst, although imines are generally accepted as key intermediates in the Ni-catalyzed *N*-alkylation of amines. Therefore, a variety of aliphatic amines were screened under the optimal conditions. As shown in Table 4, linear and non-linear aliphatic primary amines, including benzyl amine, underwent dehydrogenative coupling with primary and secondary benzyl alcohols containing either electron-donating or electron-withdrawing substituents to give the corresponding imines in moderate to excellent yields (**6a**-**6h**). The synthesis of aliphatic imines is intrinsically more challenging due to their relative instability. Encouragingly, aliphatic alcohols reacted with aliphatic amines to form the corresponding imines in moderate yields (**6i**), further demonstrating the practicality of our developed CImPy nickel catalytic system.

Table 4. Dehydrogenative coupling of various alkyl amines with alcohols.[a]





[a] Reagents and conditions: **1** (2.0 mmol), **5** (1.0 mmol), **Ni4** (0.05 mmol), *t*-AmOK (1.5 mmol), 140 °C, toluene (4.0 mL), 12 h. Isolated yields in parentheses. [b] **Ni4** (0.1 mmol), other conditions were identical.



Scheme 4. Mechanistic experiments.

To gain insights into the mechanism of this Ni-catalyzed *N*-alkylation of amines with alcohols, a series of experiments were performed. First, the reaction employing **1a** and **2a** was monitored by GC under the optimal conditions (Scheme 4a). It can be observed that along with the consumption of **2a**, the target *N*-alkylated product **3a** was accumulated. Meanwhile, imine **3a'** was detected during the whole process. Moreover, the reaction utilizing imine **3a'** and benzyl alcohol was carried out under the optimal reaction conditions, in which the *N*-alkylation product **3a** was obtained in 76% yield

and 4-methoxybenzaldehyde was detected (Scheme 4b). These results indicated that the imine is generated and quickly hydrogenated to the amine, and that the alcohol is the hydride source. Furthermore, the reaction of benzyl alcohol and octylamine was also performed, in which the Schlenk tube was connected to another one, which contained diphenylacetylene and Pd/C in methanol. Reduction of diphenylacetylene to (*Z*)-stilbene confirmed the evolution of hydrogen gas during imine formation (see ESI). Based on these results, we believe that this nickel-catalyzed *N*-alkylation of amine proceeds through a BH pathway.

In summary, we have successfully developed an efficient Ni-catalyzed dehydrogenative coupling of amines and alcohols. The geometry-constrained iminopyridyl ligand played an important role to improve the efficiency of this transformation. The *N*-alkylation of various aromatic and heteroaromatic amines with alcohols, including substituted benzyl alcohols and aliphatic alcohols, was established in moderate to excellent yields. Under identical conditions, the dehydrogenative coupling of various aliphatic amines with alcohols to selectively form imines was demonstrated. Future work is ongoing in our laboratory towards obtaining additional mechanistic insights and developing more efficient reaction systems using modified ligands.

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Supplementary material

Supplementary data to this article can be found online at

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[33] When the CImPy ligand contains a sterically hindered 2,6-disubstituted aryl imine moiety, a monomeric nickel complex was obtained (ref 32a). For the tested ligand in this work, the dimeric nickel structure is more likely. For **Ni4**, XAFS analysis indicated a dinuclear structure as shown in Scheme 3 (see ESI for details).

Highlights

1. *N*-alkylaiton of various anilines with alcohols via borrowing hydrogen；
2. Acquiring imines via an acceptorless dehydrogenative condensation strategy

3. Bidentate geometry-constrained iminopyridyl nickel complex as the catalyst；

4. A diverse set of *N*-alkylation outcomes in moderate to excellent yields