CHEMISTRY
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Accepted Article

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To be cited as: *Chem. Eur. J.* 10.1002/chem.201800543

Link to VoR: http://dx.doi.org/10.1002/chem.201800543

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Nickel-Catalyzed Alkylarylation of Activated Alkenes with Benzylamines via C-N Bond Activation

Hui Yu, Bin Hu,* and Hanmin Huang*

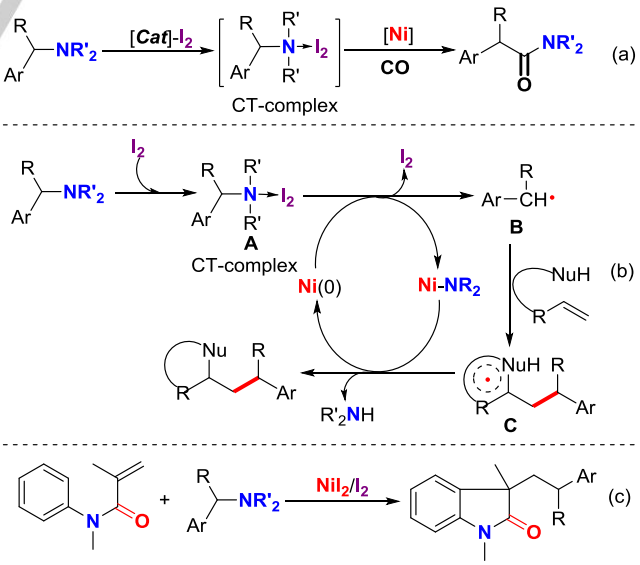
Abstract: A nickel-catalyzed alkylarylation of active alkenes with tertiary benzylamines was achieved via charge-transfer complex promoted C-N bond activation. The reaction proceeds through initial Ni-catalyzed C-N bond activation, followed by sequential radical addition, redox and proton-abstraction with cleaved amine-moiety in the absence of oxidant, which provides an efficient method to prepare various alkyl-substituted oxindoles and dihydroquinolinones in good yields.

Benzylic radicals are versatile intermediates that have been extensively utilized in synthetic organic chemistry.[1] In these processes, efficient methods for the generation of the reactive benzylic radicals are required. Among a variety of reactions initiated with benzylic radicals,[2] the oxidative activation of sp^3 C-H bonds of alkylarenes via hydrogen atom abstraction has been demonstrated as one of the most popular methods to access such kind of species. However, stoichiometric amounts of strong and expensive oxidants such as TBP and NSFI are general required. Moreover, almost in all of these reactions, a large excess of alkylarenes was required as the benzylic radical source, or even as a solvent. Therefore, the development of efficient alternative methods to generate benzylic radicals would be valuable.

The C-N bond is one of the most ample chemical bonds and widely exists in organic molecules and biomacromolecules.[3] The formation and transformation of C−N bonds are among the central topics in organic chemistry, organometallic chemistry, and biochemistry.[4,5] Although two kind of useful nucleophiles could be generated via the cleavage of one C-N bond of simple amines,[5] compared to the extensive studies on the activation of C−H bond,[6] the studies on the transition-metal-catalyzed C−N bond activation of simple amines is less explored because of the lack of suitable active frontier orbitals that could readily accept the d-electron from transition-metal center.[7] Our group has pursued the development of efficient strategies to cleave C-N bond of simple tertiary amines via transition-metal catalysis.[8] One promising strategy for activation of benzylic C-N bond by formation of amine-I_2 charge-transfer complex has been developed and successfully applied in the Ni-catalyzed direct insertion of CO into the C-N bond of simple benzylamines (Scheme-1a).[9] Our mechanistic experiments suggested that the C-N bond of the in-situ formed amine-I_2 complex is capable of extracting a single electron from Ni(0) in the absence of external oxidant to generate a benzylic radical. In this context, we questioned whether the method for generation of benzylic radicals via charge-transfer complex promoted C-N bond activation could be integrated with Ni-catalyzed alkene difunctionalization.[10] Such a manifold would offer a possibility of achieving coupling reactions via inert bond activation with even the strongest simple C-N bonds.

Successful realization of this goal, however, would require the identification of suitable alkene substrates to adopt the following reaction mechanism (Scheme-1b). Firstly, the radical **B** generated from the amine-I_2 charge-transfer complex could be reacted with the functionalized alkene via two sequential radical addition reaction to produce intermediates **C**. The intermediate **C** should be capable of reducing the Ni(I) to recycle the Ni(0)-catalyst via single-electron transfer (SET). Meanwhile, the proton contained in the oxidized intermediate **C** should be removed by the cleaved amine-moiety (R_2N^-) to produce the desired product. Herein, we report a novel Ni-catalyzed arylbenzylation of activated alkenes via C-N bond activation, in which the easily available and inexpensive benzylamines were utilized as benzyl source (Scheme-1c). The reaction can be carried out in the absence of strong oxidants and the cleaved

Scheme 1. Ni-catalyzed difunctionalization of activated alkenes via C-N bond activation



amine-moiety was used as a base to promote the reaction and avoids to use a large excess of starting materials. It is worth noting that this method represents one of efficient ways to synthesize a variety of alkylated oxindoles and dihydroquinolinones, which are important in natural products and biologically active compounds (Scheme-1c).[11,12]

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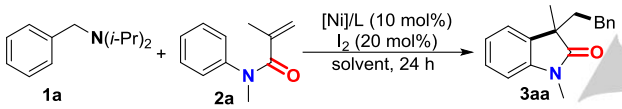
Initially, the cyclization of *N,N*-diisopropyl benzylamine (**1a**) and *N*-methyl-*N*-phenylmethacrylamide (**2a**) was chosen as a model reaction for the optimization investigation (Table 1, for more details see the SI). To our delight, when $NiCl_2$ was utilized as a catalyst precursor and **L1** as a ligand at 150 °C in the presence of catalytic amount of I_2, the desired oxindole **3aa** was obtained in 83% isolated yield (Table 1, entry 1). Further evaluation of the nickel source (Table 1, entries 2-4) demonstrated that both Ni(0) and Ni(II) could be utilized as the catalyst precursor and the NiI_2 stood out as the best one to deliver the desired product in 91% isolated yield (Table 1, entry 3). Furthermore, the impact of the ligands was carried out with NiI_2 as a catalyst precursor, revealing that the inexpensive and commercially available Xantphos was the most effective ligand for this reaction to give the desired product **3aa** in 92% isolated yield (Table 1, entry 5). Several representative solvents such as toluene, dioxane, DMSO and 2-PrOH were also screened, but they afforded lower yields of **3aa** (entries, 9–12). Control experiments demonstrated that no reaction occurred when the reaction was conducted in the absence of I_2 and only 14% yield of **3aa** was obtained in the absence of Ni catalyst, indicating the critical importance of the I_2 and Ni catalyst for activation of the C−N bond (entries, 13–14).

Table 1. Screening of reaction conditions [a]

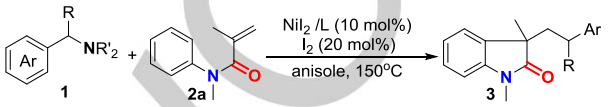


Entry	[Ni]	Ligand	Solvent	Yield (%)
1	$NiCl_2$	**L1**	anisole	87 (83)
2	$NiBr_2$	**L1**	anisole	88
3	NiI_2	**L1**	anisole	94 (91)
4	$Ni(cod)_2$	**L1**	anisole	74
5	NiI_2	Xantphos	anisole	94 (92)
6	NiI_2	BINAP	anisole	72
7	NiI_2	DPPF	anisole	39
8	NiI_2	PPh_3	anisole	50
9	NiI_2	Xantphos	toluene	46
10	NiI_2	Xantphos	dioxane	65
11	NiI_2	Xantphos	DMSO	0
12	NiI_2	Xantphos	2-PrOH	11
13[b]	$NiCl_2$	**L1**	anisole	0
14	-	**L1**	anisole	14

[a] Reaction conditions: **1a** (2.0 mmol), **2a** (0.5 mmol), [Ni] (0.05 mmol), **L1** (0.12 mmol, **L1** = 2-(Diphenylphosphino)benzoic acid), I_2 (0.1 mmol), anisole (2 mL), 150 °C, 24 h. Yield was determined by GC using *n*-hexadecane as an internal standard and isolated yields were given within parentheses; [b] without I_2.

Having established the optimized reaction conditions, the reactivity of benzylamines with different substituents on the nitrogen atom were firstly investigated under the standard conditions. As summarized in Table 2, tertiary benzylamines containing different groups on the nitrogen atom gave the desired product **3aa** in distinctly different yields (Table 2, entries 1-9). For the benzylamines with isopropyl (*i*-Pr), and benzyl (Bn) as substituents, the cyclization adduct **3aa** could be obtained in good yields in optimized reaction conditions (Table 2, entries 4 and 9). When other nitrogen groups, such as $N(CH_3)_2$, NEt_2, $N(n\text{-}Pr)_2$, $N(n\text{-}Bu)_2$, $N(allyl)_2$, NPh_2 and NCy_2 were installed in the benzyl skeleton, the conversion was dramatically decreased under other identical reaction conditions. The relatively lower activity of these substrates might be attributed to the difficult cleavage of the corresponding C-NR_2 bonds. Considering the distinct reactivity of different benzylamines, a variety of benzylamines with two isopropyl groups attached on the N-atom were subjected to the optimized conditions to investigate its

Table 2. Substrate scope of benzylamines [a]



Entry	Ar	R	R'	Product	Yield(%)[b]
1	Ph	H	Me	**3aa**	7
2	Ph	H	Et	**3aa**	23
3	Ph	H	*n*-Pr	**3aa**	34
4	Ph	H	*i*-Pr	**3aa**	92
5	Ph	H	*n*-Bu	**3aa**	41
6	Ph	H	allyl	**3aa**	41
7	Ph	H	Ph	**3aa**	11
8	Ph	H	Cy	**3aa**	49
9	Ph	H	Bn	**3aa**	75
10	2-$CH_3C_6H_4$	H	*i*-Pr	**3ba**	94
11	3-$CH_3C_6H_4$	H	*i*-Pr	**3ca**	75
12	4-$CH_3C_6H_4$	H	*i*-Pr	**3da**	75
13[c]	2-ClC_6H_4	H	*i*-Pr	**3ea**	76
14[c]	3-ClC_6H_4	H	*i*-Pr	**3fa**	72
15	4-ClC_6H_4	H	*i*-Pr	**3ga**	72
16	2,6-di-ClC_6H_4	H	*i*-Pr	**3ha**	94
17	4-FC_6H_4	H	*i*-Pr	**3ia**	73
18[c]	4-CNC_6H_4	H	*i*-Pr	**3ja**	76
19	4-$MeOC_6H_4$	H	*i*-Pr	**3ka**	92
20[c]	4-AcC_6H_4	H	*i*-Pr	**3la**	70
21[c]	4-$MeOC(O)C_6H_4$	H	*i*-Pr	**3ma**	91
22[c]	4-$NO_2C_6H_4$	H	*i*-Pr	**3na**	45
23	1-naphthyl	H	*i*-Pr	**3oa**	88
24	2-naphthyl	H	*i*-Pr	**3pa**	82
25	2-thienyl	H	*i*-Pr	**3qa**	70
26	2-furyl	H	*i*-Pr	**3ra**	54
27	Ph	CH_3	*i*-Pr	**3sa**	75(dr=1.5:1)
28[c]	Ph	Ph	*i*-Pr	**3ta**	39(dr=7:1)

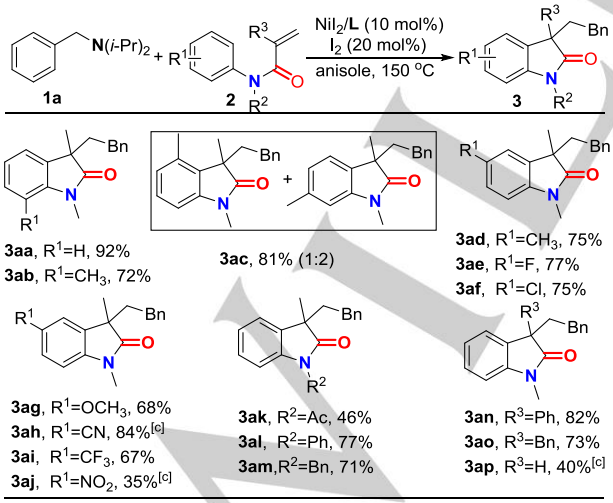
[a] Reaction conditions: **1** (2.0 mmol), **2a** (0.5 mmol), NiI_2 (0.05 mmol), L (0.06 mmol, L = 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene), I_2 (0.1 mmol), anisole (2 mL), 150 °C, 24 h. [b] Isolated yield. [c] 40 mol% I_2, the ratio of d.r. was determined by GC-MS analysis of the crude product.

substrate scope and generality. As shown in Table 2, the reaction is compatible with a wide range of benzylamines to

afford different oxindole **3ba−3ma** in good to excellent yields. Typical functional groups, such as alkyl, halides, ether, ester, ketone, and cyano were compatible with this method (Table 2, entries 10-21). However, strong electron-withdrawing substituent $–NO_2$ gave the corresponding product in moderate yield under the modified reaction conditions (Table 2, entry 22). In addition to phenyl-substituted amines, naphthyl-substituted amines were also compatible with this reaction, generating the corresponding adducts **3oa** and **3pa** in good yields (Table 2, entries 23 and 24). To our great delight, the hetero-aryl-substituted amines, such as *N*-isopropyl-*N*-(thiophen-2-ylmethyl)-propan-2-amine and *N*-(furan-2-ylmethyl)-*N*-isopropylpropan-2-amine, were also proceeded smoothly to provide the desired products in moderate to good yields (Table 2, entries 25 and 26). Furthermore, *α*-substituted benzylamines **1s** and **1t** were found to be compatible with these reaction conditions (Table 2, entries 27 and 28).

The scope of the reaction with respect to *N*-arylacrylamides **2** is summarized in Tables 3. A series of substituents regardless of electron-donating or -withdrawing properties other than strong electron-withdrawing nitro on the phenyl ring were well tolerated, providing the desired adducts **3ab**-**3ai** in moderate to good yields (67-84%).[13] Functional groups, such as alkyl, halides, ether, cyano, and nitro were compatible with this method, giving ample opportunities for further elaboration by transition-metal-catalyzed coupling or other reactions. Notably, *meta*-substituted substrates **2c** gave a mixture of two regioisomers. In addition to the methyl group, the acrylamides bearing a Ac, phenyl and benzyl protecting groups on the N–tether also afforded the corresponding oxindoles **3ak**, **3al**, **3am** in 46%-77% yields. Furthermore, the acrylamides bearing phenyl, benzyl and hydrogen groups at the *α*-position also gave the corresponding products **3an**-**3ap** in moderate to good yields (40-82% yields).

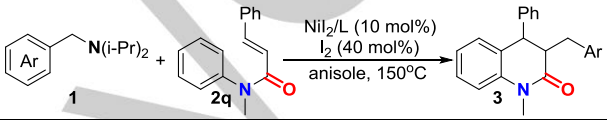
Table 3. Substrate scope of alkenes [a],[b]



[a] Reaction conditions: **1a** (2.0 mmol), **2** (0.5 mmol), NiI_2 (0.05 mmol), L (0.06 mmol, L = 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene), I_2 (0.1 mmol), anisole (2 mL), 150 °C, 24 h. [b] Isolated yield. [c] I_2 (40 mol%).

In addition to *α*-substituted acrylamide, we were pleased to find that *β*-substituted acrylamide **2q** can also be employed as substrates. Under the slightly modified reaction conditions, various benzylamines **1** containing different substituents on the phenyl ring reacted with acrylamide **2q** leading to the unexpected six-membered ring dihydroquinolinones **3** in good to excellent yields (Table 4, entries 1-8). Apart from phenyl-substituted amines, naphthyl-substituted amines were also compatible with this reaction, generating the corresponding adducts in good yields (Table 4, entries 9 and 10). Furthermore, the heteroaryl-substituted amine was also compatible with this transformation, providing the corresponding cycloaddition product **3qq** in 69% yield (Table 4, entry 11). Although two diastereoisomers were produced in these reactions, the two isomers could be isolated by simple chromatography (see SI).

Table 4. Cyclization reaction of benzylamine and acrylamide to dihydroquinolinones [a]



Entry	Ar	Product	Yield(%)[b]
1	C_6H_5	**3aq**	84 (dr=4.6:1)
2	4-$CH_3C_6H_4$	**3dq**	82 (dr=5.2:1)
3	4-ClC_6H_4	**3gq**	88 (dr=4.8:1)
4	4-FC_6H_4	**3iq**	87 (dr=4.9:1)
5	4-CNC_6H_4	**3jq**	70 (dr=4.4:1)
6	4-$MeOC_6H_4$	**3kq**	92 (dr=5.3:1)
7	4-AcC_6H_4	**3lq**	78 (dr=4.9:1)
8	4-$MeOC(O)C_6H_4$	**3mq**	76 (dr=5.6:1)
9	1-naphthyl	**3oq**	77 (dr=3.6:1)
10	2-naphthyl	**3pq**	77 (dr=5.0:1)
11	2-thienyl	**3qq**	69 (dr=4.9:1)

[a] Reaction conditions: **1** (2.0 mmol), **2q** (0.5 mmol), NiI_2 (0.05 mmol), L (0.06 mmol, L = 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene), I_2 (0.2 mmol), anisole (2 mL), 150 °C, 24 h. [b] Isolated yield, the ratio of d.r. was determined by GC-MS analysis of the crude product.

In conclusion, we have developed a novel nickel-catalyzed arylbenzylation of activated alkenes with tertiary benzylamines via charge-transfer complex promoted C-N bond activation. The reaction proceeds through initial Ni-catalyzed C-N bond activation, followed by sequential radical addition, redox via single-electron transfer and proton-abstraction with cleaved amine-moiety in the absence of oxidant to provide the products in good yields. This reaction creates a new method to construct a variety of bioactive molecules containing benzylated oxindole and dihydroquinolinone moieties. Further investigation of this transformation is in progress.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (21672199 and 21790333), the CAS Interdisciplinary Innovation Team, the Anhui provincial Natural

Science Foundation (1708085MB28), and the Fundamental Research Funds for the Central Universities.

Keywords: nickel • alkylarylation • charge-transfer complex • C-N bond activation

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[13] CCDC 1816850 (**3ah**), 1816851 (**3gq'**) and 1816852 (**3gq**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

10.1002/chem.201800543

Synthetic method

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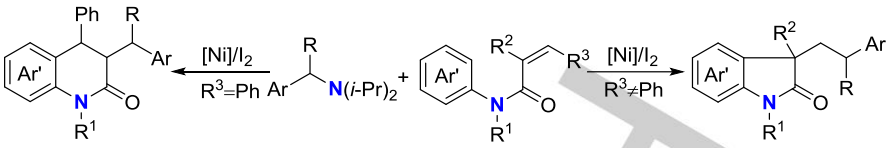
Nickel-Catalyzed Alkylarylation of Activated Alkenes with Benzylamines via C-N Bond Activation



Charge-transfer complex: A nickel-catalyzed alkylarylation of active alkenes with tertiary benzylamines was achieved via charge-transfer complex promoted C-N bond activation. The reaction proceeds through initial Ni-catalyzed C-N bond activation, followed by sequential radical addition, redox and proton-abstraction with cleaved amine-moiety in the absence of oxidant, which provides an efficient method to prepare various alkyl-substituted oxindoles and dihydroquinolinones in good yields.