DMF-Promoted Redox-Neutral Ni–Catalyzed Intramolecular Hydroarylation of Alkene with Simple Arene

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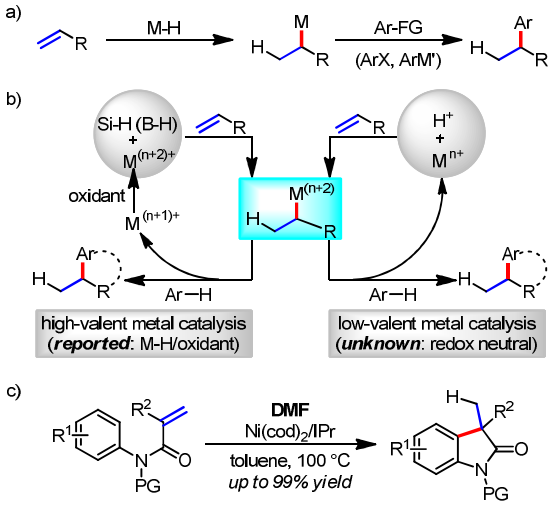
ABSTRACT: A redox-neutral Ni-catalyzed intramolecular hydroarylation of alkene with simple arene has been developed, in which DMF played a proton shuttle role in facilitating the intramolecular coupling, avoiding the use of additional reductants and oxidants. A series of oxindoles with a quaternary center were obtained in up to 99% yield.

INTRODUCTION

Transition metal-catalyzed hydroarylation of alkene has proved to a versatile synthetic method for construction of alkylated (hetero)arenes.[1] However, in contrast with well-established C–H alkylations of (hetero)arene with alkene,[2-5] this process mainly relies on the use of activated arenes such as aryl halides, aryl boronic acid and other aryl metallic reagents (Scheme 1a).[6] Although several examples have been reported to apply simple arenes in intra- or intermolecular reactions,[7] all of them have to employ a high-valent metal-catalyzed radical process (Scheme 1b), in which metallic hydride (silane or borane) is used as a hydride source for the hydrometallation step and additional oxidant (^{t}BuOO^{t}Bu, O_2, *etc*) is used for the regeneration of catalyst. This requirement of reductant and oxidant leads to not only stoichiometric amounts of undesired waste but also a challenging reaction system that is tolerant of both the metallic hydride and the oxidant. Considering that an appropriate proton source and a low-valent transition metal can form a M–H species,[8] we envisioned that this M–H species may participate into an alkene hydrometallation and a subsequent arylation with a simple arene through C–H activation (Scheme 1b). Moreover, the C–H activation step could regenerate the proton source and the low-valent metal, thus avoiding the use of additional oxidant for regeneration of the catalyst. All these steps would result into a more atom-economical and byproduct-free hydroarylation of alkene with simple arene. Herein we report the first alkene hydrometallation-initiated C–H alkylation under reductant- and oxidant-free conditions, in which only *N,N*-dimethylformamide (DMF) is needed to promote the Ni(0)-catalyzed C–H alkylation of *N*-arylacrylamide (Scheme 1c), providing a series of oxindoles with a quaternary center in up to 99% yield.[9]

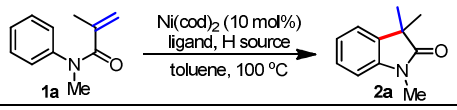


Scheme 1. Transition metal-catalyzed C–H alkylation of (hetero)arenes with alkenes. a) Traditional hydroarylation of alkene with activated arenes (Ar–FG). b) Hydroarylation of alkene with simple arenes (Ar–H). c) This work: Ni–DMF system (M–H and oxidant-free).

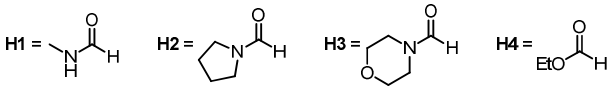
We commenced our studies by investigating the Ni-catalyzed intramolecular coupling reation of *N*-arylacrylamide **1a** in the presence of methanol as the proton source (Table 1).[10] Various mono- and bidentate phosphine ligands proved to be ineffective, whereas carbene ligands led to a trace amount of the desired product with complete 5-*exo* selectivity (entries 1–4). Encouraged by this result, we next examined various other proton sources, including other alcohols (entries 5–7), phenol (entry 8), and amides (entries 9–15). Results showed

that 1 equivalent of ^{t}BuOH greatly improved the yield to 22% (entry 7), whereas other alcohols and phenol were not good. To our surprise, *N,N*-dimethylforamide (DMF) provided a better yield than ^{t}BuOH (entry 9). Further increasing the loading of DMF to 2 equivalents led to 96% yield (entry 10). More than 2 equivalents of DMF gave the same results, but 0.5 equivalents of DMF significantly decreased the yield (14%, entry 11).

Table 1. Reaction Optimization.



entry	ligand (mol%)	base (mol%)	H source (equiv.)	yield (%)[a,b]
1	IMes·HCl (20)	^{t}BuOK (20)	MeOH (1)	<1
2	SIMes·HCl (20)	^{t}BuOK (20)	MeOH (1)	0
3	IPr·HCl (20)	^{t}BuOK (20)	MeOH (1)	1
4	SIPr·HCl (20)	^{t}BuOK (20)	MeOH (1)	<1
5	IPr·HCl (20)	^{t}BuOK (20)	EtOH (1)	2
6	IPr·HCl (20)	^{t}BuOK (20)	^{i}PrOH (1)	4
7	IPr·HCl (20)	^{t}BuOK (20)	^{t}BuOH (1)	22
8	IPr·HCl (20)	^{t}BuOK (20)	PhOH (1)	0
9	IPr·HCl (20)	^{t}BuOK (20)	DMF (1)	31
10	IPr·HCl (20)	^{t}BuOK (20)	DMF (2)	96
11	IPr·HCl (20)	^{t}BuOK (20)	DMF (0.5)	14
12	IPr·HCl (20)	^{t}BuOK (20)	**H1** (2)	0
13	IPr·HCl (20)	^{t}BuOK (20)	**H2** (2)	75
14	IPr·HCl (20)	^{t}BuOK (20)	**H3** (2)	92
15	IPr·HCl (20)	^{t}BuOK (20)	**H4** (2)	0
16	IPr·HCl (10)	^{t}BuOK (10)	DMF (2)	51
17	IPr·HCl (30)	^{t}BuOK (30)	DMF (2)	99
18	IPr·HCl (30)	^{t}BuONa (30)	DMF (2)	0
19	IPr·HCl (30)	^{t}BuONa (30)+KCl (30)	DMF (2)	99
20	IPr (30)	0	DMF (2)	0

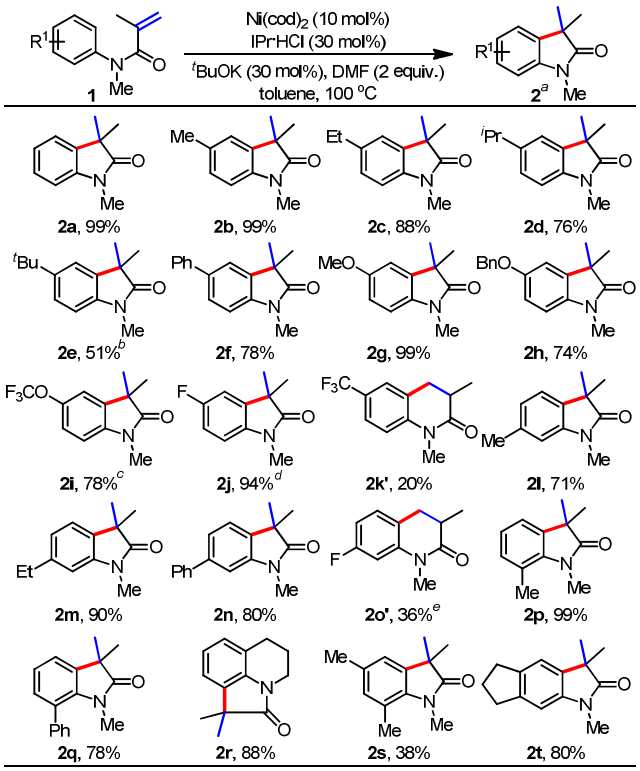


[a]Reaction Conditions: **1a** (0.2 mmol) in toluene (2 mL) at 100 °C under N_2 for 24 h. [b]Determined by ^{1}H NMR using CH_2Br_2 as the internal stand.

The structure of formamide had a big influence on the reaction (entries 12–15). For example, *N*-methylformamide **H1** did not promote this reaction at all (entry 12), whereas morpholine-derived foramide **H3** gave a high yield (entry 14). In addition, the ligand loading proved to be important (entries 16–17), and 30 mol% of ligand provided the optimal result in the presence of 2 equivalents of DMF (entry 17). Notably, potassium salt played another critical role in the reaction (entries 18–20). Replacing ^{t}BuOK with ^{t}BuONa gave no reaction (entry 18), but additional KCl enabled the reaction to be complete again (entry 19). We reasoned that both ^{t}BuO anion and K cation could assist the C–H bond cleavage.[11]

With the above optimized reaction conditions in hand, we first explored substituent effect on the aryl moiety of *N*-methyl-*N*-arylacrylamide (Table 2). Substitution at the *para* position of the aryl ring with various alkyls (**2b**–**2e**), phenyl (**2f**) and alkoxys (**2g**–**2i**) were well tolerated in the current reaction, leading to good to high yields of the corresponding oxindoles. However, the reaction was highly sensitive to steric hindrance of the substituents, for example, bulky *tert*-butyl group provided 5-*exo* and 6-*endo* cyclized products in 51% total yield (**2e**, *exo*:*endo* = 4.6:1). In addition, more electron-deficient group such as CF_3O (**2i**) and F (**2j**) also provided a mixture of 5-*exo* and 6-*endo* cyclized products. However, tuning the loading of DMF can change their ratio (see the Supporting Information). This result suggested that DMF could participate into the reductive elimination step in the arylation. However, no matter how many loadings of DMF were used, strong electron-withdrawing CF_3 preferred the 6-*endo* cyclization (**2k′**). These results meant steric and electronic nature of the substituted group on the aryl ring would have a big influence on the regioselectivity of alkene hydrometallation, suggesting that the hydrometallation could be an initial and reversible step. This result was quite different from those reported radical addition reactions,[9] wherein 5-*exo* cyclizations are generally preferred. Various substituents at the *meta*- or *ortho*-position such as alkyls and phenyl provided cyclized products in good to excellent yields (**2l**–**2r**). And again, *meta*-F led to a mixed 5-*exo* and 6-*endo* cyclized products, but 0.3 equivalents of DMF can provide nearly single 6-*endo* product in 36% yield (*endo*:*exo* = 45.1:1, **2o′**). In addition, aryl ring bearing two substituents also worked well to give 38% and 80% yield, respectively (**2s** and **2t**). A gram scale reaction was conducted for the model substrate **1a** and the yield reached as high as 91% when using 5 mol% of catalyst (see the Supporting Information).

Table 2. Substituted Group Effects on Aryl Moiety.

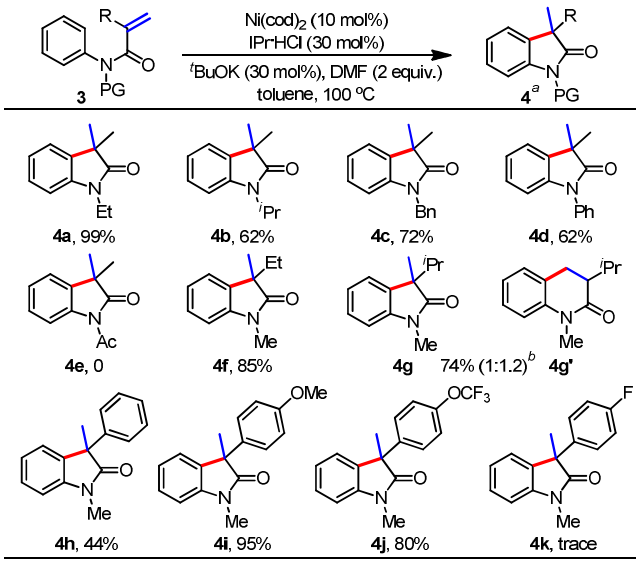


[a]Reaction Conditions: acrylamide **1** (0.2 mmol) in toluene (2 mL) under N_2 for 24 h; isolated yields and all ratios were determinined by ^{1}H NMR. [b]*exo*:*endo* = 4.6:1, total yield for two isomers. [c]DMF (1 equiv.), *exo*:*endo* = 15.0:1 [d]DMF (0.6 equiv.), *exo*:*endo* = 73.0:1. [e]DMF (0.3 equiv.), *exo*:*endo* = 1:45.1.

Next, we examined the substituent effect on the acrylamide moiety (Table 3). Substituents at the *N1* position of the substrate proved to be critical (**4a**–**4e**). Electron-rich group such as alkyls and phenyl was well compatible with the current reaction and provided the corresponding oxindoles in good to excellent yields (**4a**–**4d**), whereas electron-deficient group like

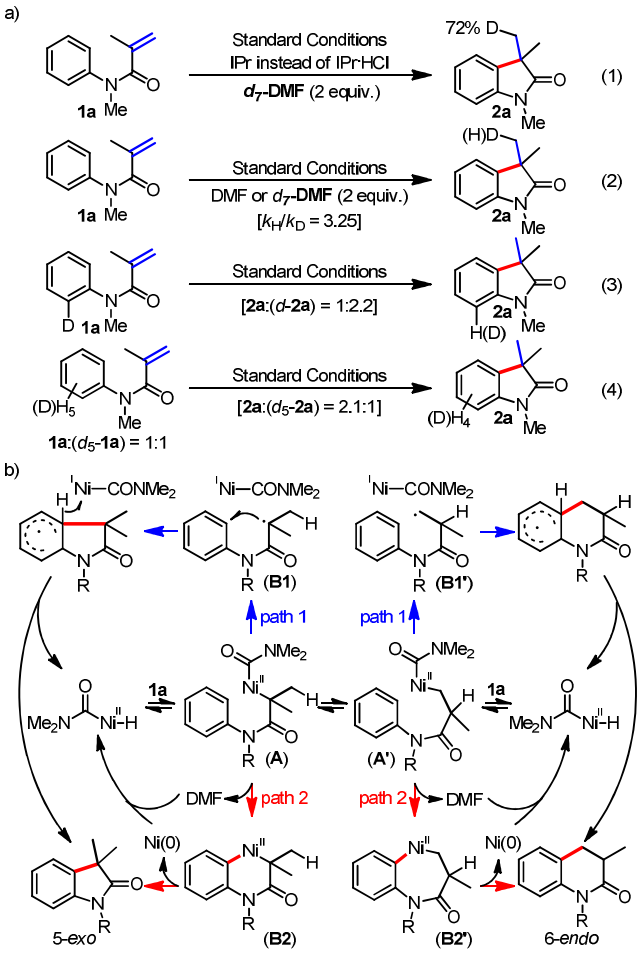
acetyl was ineffective (**4e**). The hydroarylation reaction was also tolerant of diverse acrylamides, but α-substitution and terminal alkene proved to be requisite. No α-substitution led to an alkene dimerization, suggesting alkene hydrometallation could be the initial step once again. Acrylamides with ethyl and aryl at the α-position reacted well to provide products **4f**–**4k** in 44% to 95% yield. However, sterically hindered isopropyl resulted into a mixture of 5-*exo* and 6-*endo* cyclized products (**4g** and **4g′**), and herein the loading of DMF cannot change the ratio. This result indicated that the bulky isopropyl preferred the less-hindered 6-*endo* cyclization. In addition, the reaction is sensitive to the electronic nature of aryl ring at the α-position, for example, electron-rich aryl elevated the yield to 95% (**4i** and **4j**), whereas electron-deficient aryl completely inhibited this reaction (**4k**).

Table 3. Substituted Group Effects on Acrylamide Moiety.



[a]Reaction Conditions: acrylamide **3** (0.2 mmol) in toluene (2 mL) under N_2 for 24 h; isolated yields. [b]Total isolated yield for two isomers and isomer ratio shown in parentheses was determined by ^{1}H NMR.

To better understand the mechanism of this reaction, some control experiments were conducted. Radical trapping experiments showed that BQ and TEMPO inhibited this reaction (see the Supporting Information), whereas butylated hydoxytoluene (BHT) and 1,1-diphenylethylene did not have big influence on the reaction. When 2 equivalents of d_7-DMF were used instead of DMF, a 72% D-incorporation at the terminal position of alkene was observed (Scheme 2a, eq (1)). Further reducing the loadings of d_7-DMF to 1 equivalent led to 10% of D-incorporation. In addition, parallel experiments disclosed a significant kinetic isotope effect for the C–H cleavage of DMF (k_H/k_D = 3.25, eq (2)). These results suggested the Ni–H species for the alkene hydrometallation should come from the oxidative addition of nickel with DMF. Next, NMR-tracing experiments of the reaction showed that 95% of DMF can be recovered after the reaction (see the Supporting Information), suggesting that proton source could regenerate itself after the initial hydrometallation and the subsequent arylation. A significant kinetic isotope effect was observed in intra- ((k_H/k_D = 2.2:1, eq (3)) and intermolecular ((k_H/k_D = 2.1:1, eq (4)) competitive reactions.



Scheme 2. Mechanistic Experiments and Proposed Mechanism. a) Deuterium-labeling experiments. b) Proposed mechanism.

Based on these experiments, we proposed two possible mechanistic pathways for this reaction. One is the typical radical process (Scheme 2b, path 1).[9] Hydrometallation of substrate **1a** with Ni–H species gave the intermediate (**A**) or (**A′**), which generates the corresponding α-amido radical (**B**) or (**B′**). Subsequent radical addition to the aromatic ring, followed by a hydride transfer, affords the final 5-*exo* or 6-*endo* cyclized product. However, considering that the selectivity of 5-*exo* and 6-*endo* is highly sensitive to steric (*t*Bu) and electronic (F, CF_3) factor of the substituent of the aromatic ring, we speculated that electrophilic C–H activation of arene is also possible (path 2). And thus, the intermediate (**A**) or (**A′**) delivers primary alkylnickel (**B2**) or tertiary alkylnickel (**C2**) species through direct C–H cleavage. Further reductive elimination of them affords the final products. Considering that DMF loadings could affect the ratio of 5-*exo* or 6-*endo* product, we proposed that the hydrometallation step could be fast and reversible, and the intermediate (**A**) and (**A′**) could be converted to one another. Further evidence is still required to clarify this mechanism.

In summary, we have successfully developed a Ni-catalyzed intramolecular hydroarylation of alkene with simple arene to synthesize a series of oxindoles with a quaternary center. Different from the reported methods that require stoichiometric amount of metallic hydride and oxidant, our reaction uses only DMF as a proton shuttle to achieve a redox-neutral and by-product-free coupling. This use of Ni(0) and proton source

provides a promising strategy for future development of hydrometallation-initiated C–H functionalization in our lab.

ASSOCIATED CONTENT

Supporting Information.
The Supporting Information is available free of charge on the ACS Publications websites at DOI.

Procedures, characterization, and spectra data (PDF)

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Notes

The authors declare no competing financial interests.

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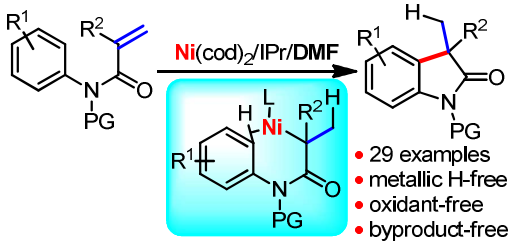
Ni(cod)2/IPr/DMF
29 examples
metallic H-free
oxidant-free
byproduct-free