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Ir-Catalyzed Intermolecular Branch-Selective Allylic C−H Amidation of Unactivated Terminal Olefins

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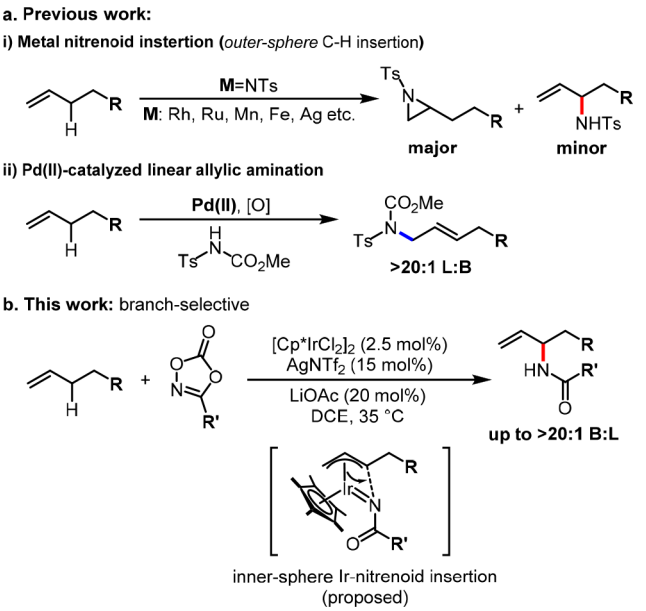
Supporting Information

ABSTRACT: An efficient method for intermolecular branch-selective allylic C−H amidation has been accomplished via Ir(III) catalysis. The reaction proceeds through initial allylic C−H activation, supported by the isolation and crystallographic characterization of an allyl-Ir(III) intermediate, followed by a subsequent oxidative amidation with readily available dioxazolones as nitrenoid precursors. A diverse range of amides are successfully installed at the branched position of terminal alkenes in good yields and regioselectivities. Importantly, the reaction allows the use of amide-derived nitrenoid precursors avoiding problematic Curtius-type rearrangements.

Due to the ubiquity of nitrogen-containing functionalities in both natural and synthetic bioactive molecules,[1] C−N bond formation reactions are some of the most frequently used transformations in medicinal chemistry.[2] In addition to classic strategies which usually require prefunctionalization, direct amination of C−H bonds could dramatically simplify synthetic routes, providing more straightforward disconnections for amine synthesis.[3] A number of reports have recently demonstrated chelate-assisted C−H amination; however, these methods usually employ preinstalled coordinating directing groups that limit their general application.[4] In contrast, allylic C−H amination only involves a simple alkene as the "directing group" which is not only prevalent in a variety of compounds but is also easily manipulated with a diverse range of robust methods.

Current strategies in allylic C−H amination utilize either C−H insertion by a metal nitrenoid[5] or nucleophilic amination of allyl-metal species generated via C−H activation.[6] Despite these advances, controlling chemoselectivity and regioselectivity remains challenging in intermolecular allylic C−H amination reactions. For instance, terminal olefins that react with a metal-nitrenoid species suffer from poor chemoselectivity between aziridination of the alkene and desired C−H amination.[5h,7] (Scheme 1a(i)). An alternative strategy was independently reported by the White[6d] and Liu[6e] groups in 2008, demonstrating that linear amination could be achieved under Pd(II) catalysis (Scheme 1a(ii)). The reaction is proposed to proceed through an allyl-Pd(II) intermediate that is generated via allylic C−H activation, followed by reductive quenching with a nitrogen nucleophile at the less hindered terminal position. Based on these initial reports, many modifications and improvements have been developed in recent years,[8] offering various choices for the synthesis of linear allylic amines. On the other hand, the branch-selective allylic C−H amination of terminal olefins has been achieved through an intramolecular manner.[5c,e,g,i,6b,g,9] Two important exceptions are Tambar's work employing a sulfurdiimide reagent followed by a Pd-catalyzed asymmetric [2,3]-rearrangement, and Hartwig's Pd-catalyzed oxidation followed by asymmetric Ir-catalyzed amination to deliver the branched amination product.[10] Moreover, the majority of these examples involve the use of a nitrogen bearing a sulfonyl or carbamate group; amide-derived nitrenoids are more challenging due to the potential intervention of a Curtius-type rearrangement.[11] Herein, we report an intermolecular Ir(III)-catalyzed branch-selective allylic C−H amidation of unactivated terminal olefins.

Scheme 1. Catalytic Allylic C−H Amidation



We have recently reported the intramolecular Ir-catalyzed diamination of alkenyl hydroxamate esters wherein the transformation was proposed to partially proceed via Ir-nitrenoid species.[12] We wondered whether Ir nitrenoids might have sufficient lifetime to allow intermolecular aziridination or amination of feedstock α-olefins. Inspired by previous reports of group 9 metal-catalyzed C−H amidations,[3f] together with our long-term interests in C−H functionalizations,[13] the

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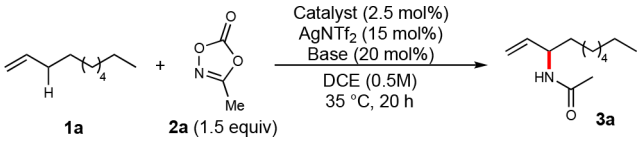
hypothesis was initially tested with $[Cp^*MCl_2]_2$ as the precatalysts (M = Rh, Co, Ir), and either sulfonyl azides[14] or dioxazolones[15] as nitrene precursors. Cossy and co-workers have reported that Cp*Rh(III) promotes an intramolecular allylic C−H amidation reaction proceeding through an allyl-Rh(III) intermediate.[6g] We previously demonstrated that the allylic activation chemistry could be coupled with a C−C bond formation.[16] More recently, Blakey and co-workers reported an intermolecular allylic C−H amidation of β-substituted styrenes that exhibits exclusive linear selectivity with allylbenzene.[6i] In sharp contrast, the allylic C−H amidation of **1a** with $[Cp^*RhCl_2]_2$ in combination with methyl dioxazolone **2a** gives the branched amidation product **3a** as the major isomer, albeit with a moderate yield and regioselectivity (Table 1, entry 1). We speculated that this was due to the oxidative nitrene formation and insertion process which favors the more electron-rich position. Both yield and regioselectivity were found to be significantly improved with $[Cp^*IrCl_2]_2$ while $[Cp^*CoCl_2]_2$ failed to produce any amidation products (entries 2 and 3).

Table 1. Reaction Development[a]



1a **2a** (1.5 equiv) **3a**

entry	catalyst	base	yield[b]	B:L[c]
1	$[Cp^*RhCl_2]_2$	LiOAc	40%	2.9:1
2	$[Cp^*CoCl_2]_2$	LiOAc	N.D.	–
3	$[Cp^*IrCl_2]_2$	LiOAc	75% (73%)[d]	>20:1
4[e]	$[Cp^*IrCl_2]_2$	LiOAc	24%	>20:1
5[f]	$Cp^*Ir(OAc)_2$	–	75%	>20:1
6[f,g]	$Cp^*Ir(OAc)_2$	–	N.R.	–
7	$[Cp^*IrCl_2]_2$	CsOAc	8%	–
8	–	LiOAc	N.R.	–
9	$[Cp^*IrCl_2]_2$	–	15%	–
10[g]	$[Cp^*IrCl_2]_2$	LiOAc	N.R.	–
11[h]	$[Cp^*IrCl_2]_2$	LiOAc	39%[i]	>20:1

[a]Reactions were conducted on a 0.1 mmol scale using **1a** (1.0 equiv), **2a** (1.5 equiv), $[Cp^*IrCl_2]_2$ (2.5 mol %), $AgNTf_2$ (15 mol %) and LiOAc (20 mol %). [b]Yield of dominant isomer as determined by ^1H NMR. [c]Determined by analysis of ^1H NMR of the unpurified reaction mixture. [d]Isolated yield. [e]$AgNTf_2$ (10 mol %) was used. [f]$Cp^*Ir(OAc)_2$ (5 mol %) was used. [g]Without $AgNTf_2$. [h]TsN_3 instead of **2a** was applied at 80 °C. [i]Yield of the corresponding allylic tosyl amide.

The higher reactivity of Cp*Ir(III) is consistent with the observations and computational arguments advanced by Baik and Chang.[17] Additionally, the optimized conditions include a catalytic amount of $AgNTf_2$ and LiOAc. We also found that the use of Li_2CO_3 instead of LiOAc produces **3a** in 62% yield with only 10 mol % of $AgNTf_2$ (see the Supporting Information). $Cp^*Ir(OAc)_2$, which was postulated to be the reactive catalyst generated in situ, was ineffective without adding additional $AgNTf_2$ (entries 5 and 6). Taken together with the above observations, we suggest that $AgNTf_2$ probably helps the dissociation of the acetate ligand (or the amide product) from iridium, which promotes the alkene coordination and further activation. It is also worth noting that the yield is dramatically reduced when CsOAc is used instead of LiOAc (entry 7). Given that CsOAc is much more soluble than LiOAc in DCE, this further suggests that excess acetate inhibits the reaction, supporting our assertion that a monoacetato-Ir is required. Moreover, tosyl azide was also tested. It was found to afford moderate yield of branched amidation product with excellent regioselectivity, when the reaction was heated to 80 °C (entry 11).

Having established the optimal conditions for branch-selective allylic amidation, we next sought to examine the scope of this transformation with various terminal alkenes. The reaction tolerates a broad range of functional groups, giving rise to various branched amidation products. As shown in Scheme 2, several commonly used oxygen, nitrogen or arene containing functional groups are compatible, affording corresponding amidation products in good yields and regioselectivities (**3b**−**3h**). Even substrates with susceptible functionalities, like −Br, −CN and $-CO_2H$, participated smoothly with the standard condition to provide the desired products (**3i**−**3k**). Although a lower yield was observed with the alkene bearing a carboxylic acid group, the regioselectivity remains unaffected, giving the branched product **3k** predominately. Despite precedent for Ir-catalyzed dehydrogenation of alkenes bearing homoallylic carbonyl groups under oxidative conditions,[18] exclusive amidation of 4-phenyl-1-butene and ethyl 4-pentenoate was observed with no evidence of diene formation (**3l**, **3m**). Although yield and regioselectivity are moderate with ethyl 4-pentenoate, the alternative conditions with TsN_3 as the nitrene precursor leads to moderate yield and excellent regioselectivity (**3m**). Furthermore, substrates with homoallylic heteroatoms were found to decrease the reactivity. Moderate conversions and yields were obtained even with elevated temperature(**3n**, **3o**). Additionally, sterically hindered allyl-cyclohexane was remarkably well-tolerated (**3p**). Allylarenes with electron-rich (−OMe) and electron-poor ($-CF_3$) substituents were also examined. It was found that the regioselectivity decreased from >20:1 to 2.6:1 by changing the para- substituent from −OMe to $-CF_3$ (**3q**−**3s**). Excellent regioselectivity could be restored with TsN_3 as the nitrene precursor.

The generality of dioxazolone coupling partners were next explored. Primary, secondary and tertiary alkyl groups on the dioxazolone are tolerated with no significant decrease in reactivity (Scheme 3, **4b**−**4f**). Additionally, the cyclopropane dioxazolone could also be utilized without detectable ring-opening (**4d**). Moreover, electron-donating and electron-withdrawing substituted phenyl dioxazolones are well tolerated (**4g**−**4j**). Even an alkenyl substituted dioxazolone can participate to afford **4k** in moderated yield. In general, these aryl and alkenyl dioxazolones are slightly less reactive and require elevated temperature for full conversion. Under all these reaction conditions, the Curtius/Lossen-type rearrangement is not competitive[5i,19] presumably because of a change in mechanism (vide infra).

Further mechanistic insight was gained from isotopic labeling studies and stoichiometric reactions (Scheme 4). When subjecting **1aa**-d_2 to the optimized reaction conditions using acetic acid as the proton source, no deuterium leaching was observed at the allylic position of the amidation product. This indicates that the allylic C−H activation is irreversible under the standard reaction condition. Furthermore, a smaller kinetic isotopic effect from intermolecular competition reaction compared to the one from intramolecular reaction was observed (KIE = 1.9 vs 2.6). We speculate that the allylic C−H bond activation is probably not the sole rate-determining

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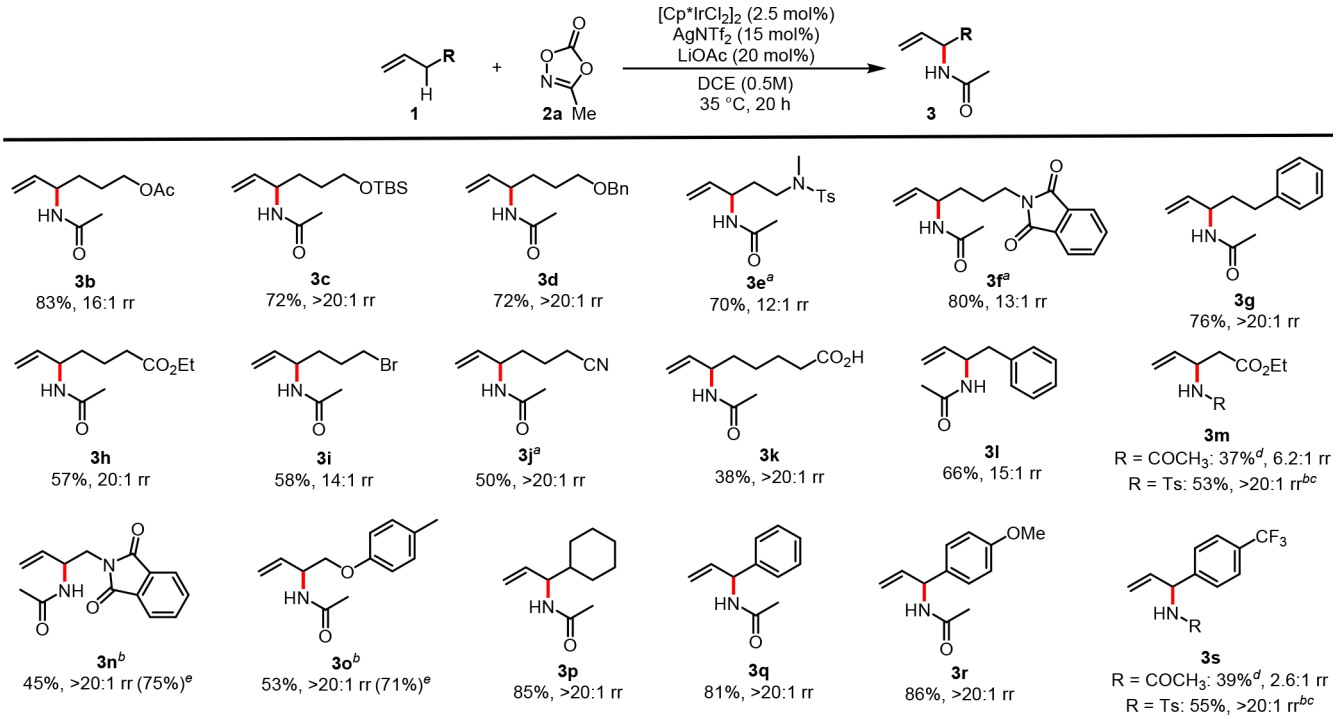
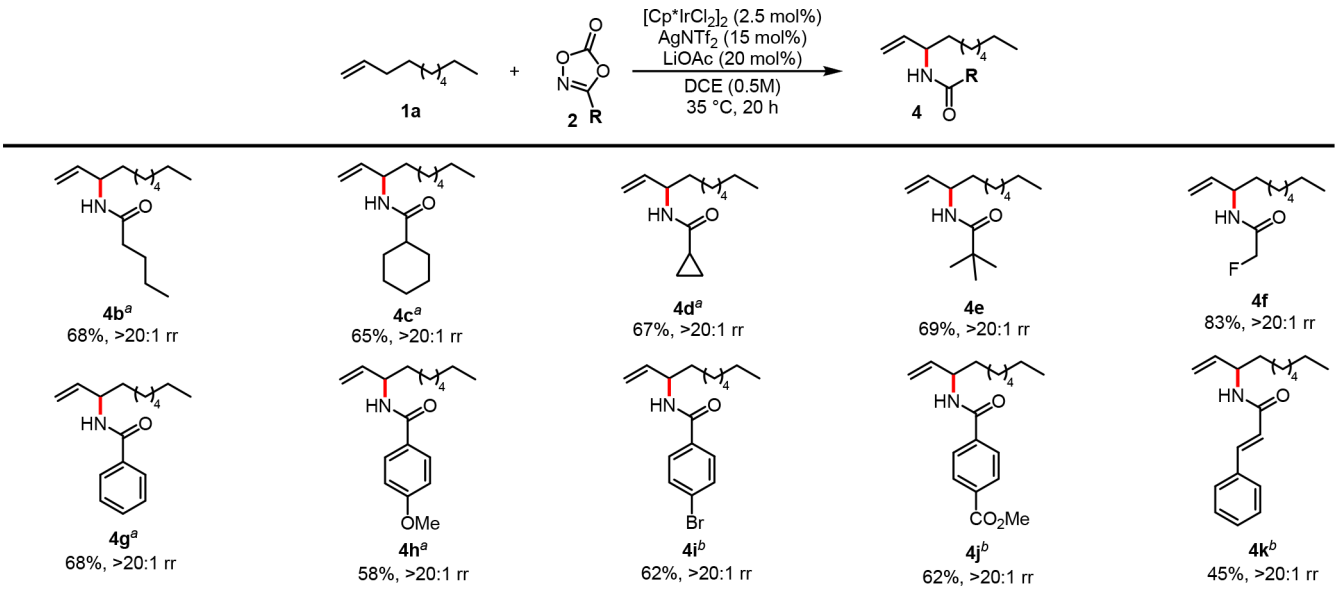
Scheme 2. Alkene Scope



[a]60 °C was used. [b]80 °C was used. [c]TsN_3 was used instead of **2a**. [d]NMR yield. [e]Yield based on recovered starting material.

Scheme 3. Dioxazolone Scope



[a]60 °C was used. [b]80 °C was used.

step.[20] Stoichiometric studies were also performed. An allyl-Ir(III) complex **5** was trapped by an additional *p*-toluenesulfonamide ligand which stabilizes the intermediate for isolation. Interestingly, the subsequent amidation is only achieved with the assistance of $AgNTf_2$, which delivers the desired product in high yield and regioselectivity. In this case, $AgNTf_2$ might also act as a Lewis acid promoting the dissociation of the *p*-toluenesulfonamide ligand to regenerate the active species with an empty coordination site. Finally, stoichiometric reactions with **1ab-d_1** were also conducted, leading to the same distribution between deuterated and protonated products of either the allyl-Ir(III) complex (P_D/P_H = 2.6) or the amidation product (P_D/P_H = 2.7) (see Supporting Information).

On the basis of the above observations, we hypothesize the following catalytic cycle (Scheme 5). The active catalyst is presumably the coordinatively unsaturated cationic mono-acetato Cp*Ir(III) I that is generated from $[Cp^*IrCl_2]_2$, $AgNTf_2$, and LiOAc. Alkene coordination and irreversible metalation form allyl-Ir(III) species III. The oxidation of

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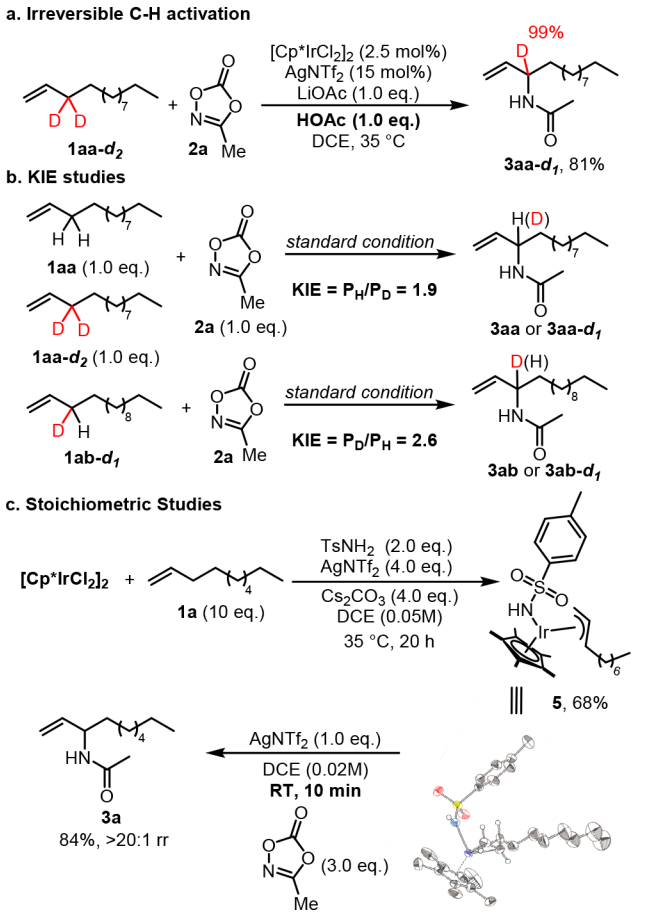
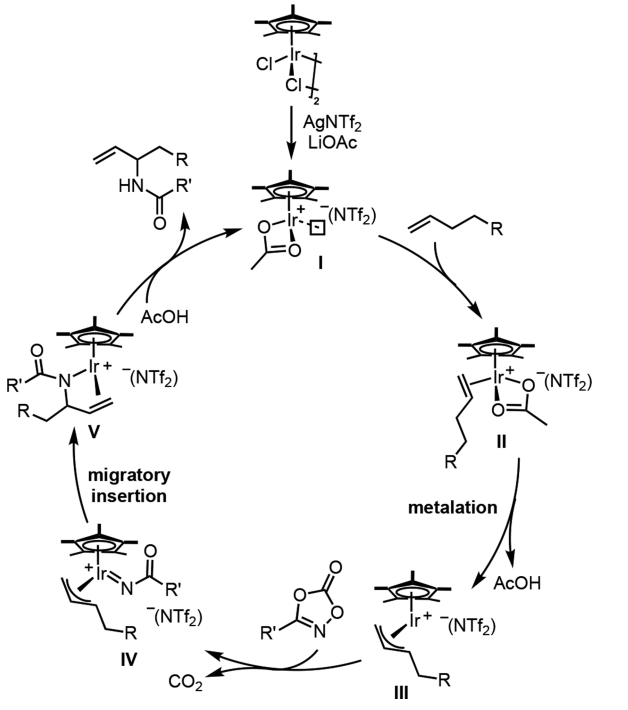
Scheme 4. Mechanistic Studies



Scheme 5. Proposed Mechanism



Ir(III) via N−O bond cleavage and CO_2 extrusion produces the key allyl-Ir-nitrenoid species **IV**. Subsequent migratory insertion would install the desired amide bond at the internal position. Finally proto-demetalation regenerates the active catalyst and produces the amide product. Importantly, the allyl Ir intermediate **III** is more oxidizable than **I** or **II** and only undergoes oxidation/nitrene formation once the allyl moiety is in place. Thus, the Ir nitrenoid undergoes reductive elimination to form product faster than Curtius/Lossen-type rearrangement. This is consistent with Chang's observations in intramolecular C−H insertion with related Ir nitrenoids.[5i]

In summary, we have developed an intermolecular branch-selective allylic C−H amidation reaction via Ir(III) catalysis. The inner-sphere Ir-nitrenoid insertion after allylic C−H activation is key for prevention of undesired aziridination and achieving branched-selectivity. This opens a new pathway for branched functionalizations of terminal olefins. Further efforts at elucidating the mechanism and extending this chemistry are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b00237.

Detailed experimental procedures, characterization data, copies of ^{1}H NMR and ^{13}C NMR spectra for all isolated compounds (PDF)

Data for $C_{27}H_{42}IrNO_2S$ (CIF)

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Notes

The authors declare no competing financial interest.

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