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Chemo- and regioselective nucleophilic hydrofunctionalization of unactivated aliphatic alkenes under transition-metal-free catalysts†

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Transition-metal-free-catalyzed nucleophilic hydrofunctionalization of both terminal and internal unactivated aliphatic alkenes has been described for the first time. Most topical classes of carbon, nitrogen and oxygen nucleophiles are well-compatible. The highly chemoselective unprotected dinucleophiles are also presented in the atom-economical approach. More than 80 structurally complex β-hetero-substituted aliphatic amides were rapidly synthesized in good yield with exclusive Markovnikov selectivity, which are difficult to be achieved efficiently by the traditional Michael addition of conjugated amides due to their poor intrinsic electrophilicity.

Introduction

Nucleophilic hydrofunctionalization of alkenes represents one of the most atom-economical and fundamental strategies that has been widespread application in organic chemistry.[1] Despite numerous transformations being devoted to this strategy,[2] the nucleometalation approach has been mainly exploited to realize the intermolecular nucleophilic addition of unactivated aliphatic alkenes.[3] Hegedus *et al.* initially applied nucleopalladation to realize the alkylation of unactivated olefins with stabilized carbanions as active nucleophiles.[4] Recently, by introducing a removable directing group into unactivated aliphatic alkenes, both the hydroamination and hydrocarbonation of amide-tethered unactivated aliphatic alkenes have been well-developed in *anti*-Markovnikov selectivity; however, no relative Markovnikov selectivity was realized (Fig. 1).[5] Although significant progresses in the nucleophilic hydrofunctionalization of unactivated aliphatic alkenes have been achieved, the requirement of precious, eco-unfriendly transition-metal catalysts, poor compatibility of diverse nucleophiles in each method, and less success in divergent regioselectivity have severely hampered the potential industrial application. Thereby, the development of a more general and practical transition-metal-free-catalyzed nucleophilic hydrofunctionalization of unactivated aliphatic alkenes with diverse nucleophiles remains challenging but highly desirable from both academic and industrial viewpoints.

Base-catalyzed intermolecular nucleophilic hydrofunctionalization of olefins is in principle an ideal atom-economical methodology for both academia and industry;[6] however, only a few examples concerning the unactivated aliphatic alkenes have been exploited,[7] which are mostly restricted to the hydroamination and required strong bases such as ^{n}BuLi. The challenges in developing a general base-catalyzed nucleophilic addition to unactivated alkenes may be attributed to unfavorable pairing between the electrophilicity of alkenes and nucleophilicity of numerous nucleophiles and the reversibility between addition and elimination under basic conditions.[6,7] In our continuous effort on the regioselective functionalization of unactivated alkenes,[8] herein, we report a general Markovnikov selective hydrofunctionalization of unactivated

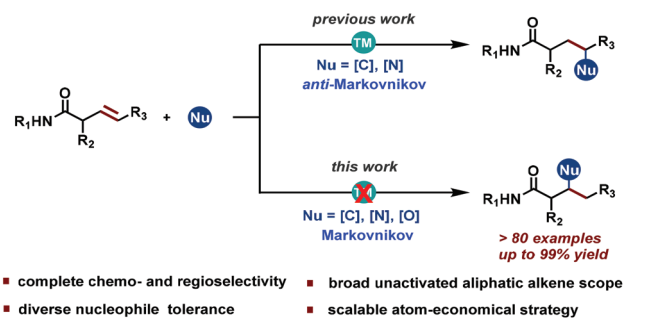

Fig. 1 Development of regiodivergent nucleophilic hydrofunctionalization of unactivated aliphatic alkenes (TM = transition metal).

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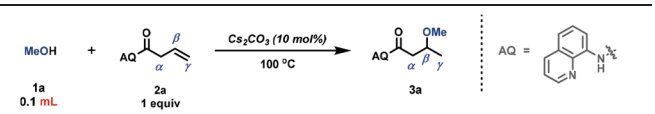
alkenes with a broad nucleophile scope under minimal solvent conditions[9] (Fig. 1). Most topical classes of carbon, nitrogen and oxygen nucleophiles could efficiently add to numerous unactivated terminal and internal aliphatic alkenes with complete Markovnikov selectivity. Notably, the chemo- and regioselective additions of diverse unprotected dinucleophiles to unactivated aliphatic alkenes were also achieved. Several features of this concise approach can be highlighted as follows: (a) transition-metal-free reaction: the simple approach avoids the fundamental restriction of using toxic and expensive metal catalysts in previous strategies. (b) Catalytic amount of inorganic bases, which are commercially available, inexpensive and easily quenchable to eco-friendly sources. (c) Minimal solvent conditions: most of the reactions are under neat condition and avoid the usage of additional organic solvents, which would lead to more environmental issues. (d) Operational simplicity and atom-economical process, which could afford more than 80 structurally complex amides under concise and eco-friendly reaction system.

Results and discussion

Initially, methanol (**1a**) and 3-butenamide (**2a**) were chosen as the model substrates. Through extensive screening of reaction conditions, a catalytic amount of Cs_2CO_3 was found to promote the reaction at 100 °C, affording 3-methoxy-*N*-(quinolin-8-yl) butanamide (**3a**) in 99% yield with exclusive Markovnikov selectivity (Table 1, entry 1). Remarkably, no additional solvent was needed for the nucleophilic hydromethoxylation. A decrease in the basicity of inorganic bases led to a lower yield (Table 1, entries 2–4). The organic base such as Et_3N was catalytically inactive (Table 1, entry 5). Besides, the amount of Cs_2CO_3 could be reduced to 5 mol%, while diminished reactivity was detected using 1 mol% of Cs_2CO_3 (Table 1, entries 6–8). Notably, the outcome of the nucleophilic addition was also dependent on the reaction temperature; temperature that was lower than 60 °C would significantly reduce the reactivity (Table 1, entries 9–11). For other reaction condition optimizations, see the ESI.†

Under the optimal reaction conditions, we first investigated the nucleophile scope in the intermolecular hydrofunctionalization of unactivated alkene (**2a**). As expected, numerous primary and secondary alcohols afforded the corresponding alkyoxylated products in good to excellent yields with complete Markovnikov selectivity (Table 2, **3a–i**). Sterically hindered alcohol (**3j**) also provided the product, albeit in a decreased yield. Alcohols featuring olefin and alkyne functional groups too were well compatible in this protocol (Table 2, **3k–l**). Next, in line with the alcoholic nucleophile studies, a range of diverse functionalized primary and secondary amines were well-tolerated, including olefin, alkyne, Bn, thiophene, Ts, pyrrolidine, morpholine, pyrrolidine-2,5-dione and imidazole group (Table 2, **3m–y**). Moreover, an array of carbonyl deriva-

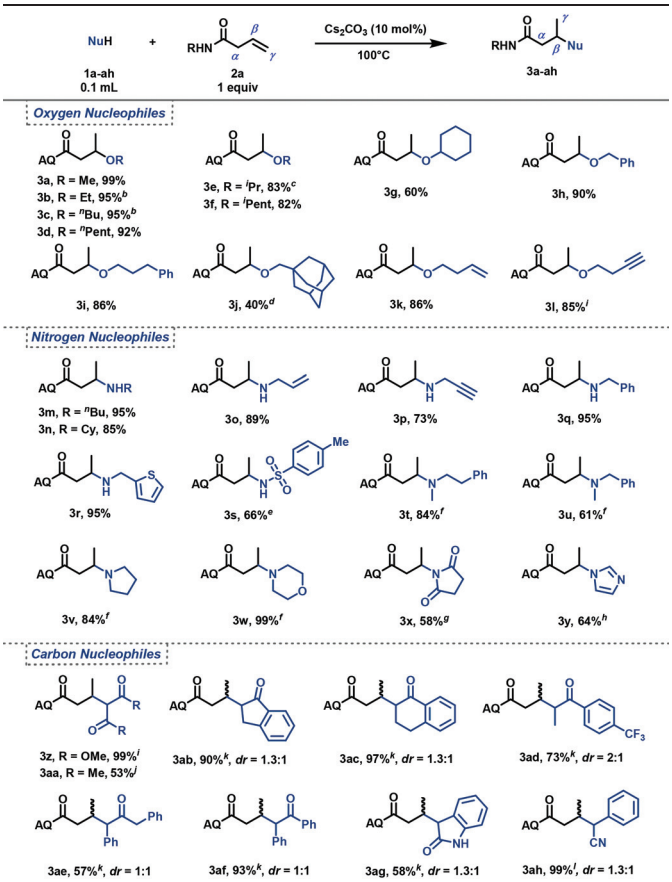
Table 1 Variation of parameters in model nucleophilic hydroalkyoxylation[a]



Entry	Deviation from standard conditions	Yield[b] (%)
1	**None**	**99**
2	K_2CO_3 instead of Cs_2CO_3	93
3	Na_2CO_3 instead of Cs_2CO_3	72
4	Li_2CO_3 instead of Cs_2CO_3	0
5	Et_3N instead of Cs_2CO_3	0
6	5 mol% Cs_2CO_3	99
7	3 mol% Cs_2CO_3	92
8	1 mol% Cs_2CO_3	84
9	80 °C instead of 100 °C	93
10	70 °C instead of 100 °C	85
11	60 °C instead of 100 °C	76

[a] Reactions were run on a 0.1 mmol scale. [b] Determined by GC analysis.

Table 2 Nucleophile scope in hydrofunctionalization[a]



[a] Reactions were run on a 0.1 mmol scale. Percentages represent isolated yields. [b] 80 °C. [c] 60 °C. [d] 2 equiv. NuH and 0.1 mL THF. [e] 2 equiv. NuH and 0.1 mL MeCN. [f] 20 mol% CsOAc. [g] 2 equiv. NuH, 50 mol% CsOAc, 0.1 mL MeCN. [h] 2 equiv. NuH, 20 mol% CsOAc, 0.1 mL MeCN. [i] 20 mol% Cs_2CO_3. [j] 50 mol% Cs_2CO_3. [k] 2 equiv. NuH, 50 mol% KOH, 0.1 mL THF. [l] 0.1 mL NuH and 50 mol% KOH.

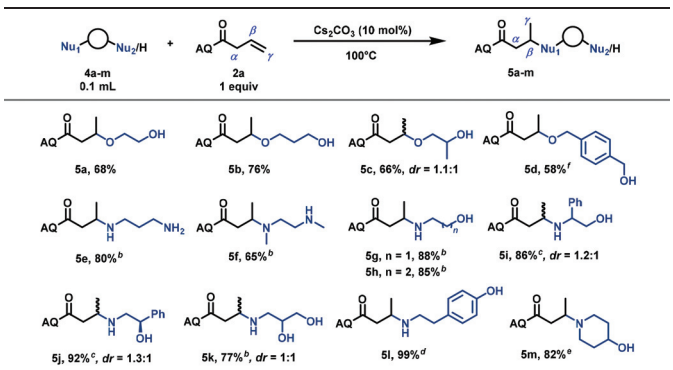
tives was explored due to the easy formation of nucleophilic carbanion under the base catalyst. Diverse carbon nucleophiles including dimethyl malonate, cyclic or aliphatic ketones, indolin-2-one and nitrile were generally well-tolerated as carbanion precursors (Table 2, **3z–3ah**). Collectively, this atom-economical and practical protocol has significantly extended the nucleophile scope in the base-catalyzed branched selective addition of unactivated alkenes.

To further demonstrate the generality of this reaction, we next evaluated the scope of unprotected dinucleophiles in the chemo- and regioselective hydrofunctionalization reactions of unactivated alkene (**2a**). Numerous diols and diamines were tested; the corresponding mono-adducts were afforded in good yields with exclusive Markovnikov selectivity (Table 3, **5a–f**). Secondary free nucleophilic group (OH or NH) could be well-tolerated in the standard basic condition. Furthermore, reaction involving an array of ambident N/O dinucleophiles including amino alcohols, amino diol, amino phenol and piperidinol proceeded well too (Table 3, **5g–m**). Only the relevant amino-adducts were afforded in complete chemo- and regioselectivity. The length of an aliphatic chain and the steric difference in N/O dinucleophiles have no obvious effect on the reactivity and selectivity. In summary, the addition of inherently more nucleophilic amino group of unprotected dinucleophiles has been achieved in our base-catalyzed protocol. The reason being exclusive chemoselectivity was favored by the innate nucleophilic ability of dinucleophiles.

Encouraged by the aforementioned extensive nucleophile scopes of this concise protocol, we next attempted to assess the potential tolerance of unactivated alkene. By using allyl amine as a representative nucleophile, an array of internal unactivated alkenes were examined, and moderate to good yield of the exclusive branched adduct was afforded in consistence with the relative steric hindrance (Table 4, **7a–7f**). Sterically hindered α-alkyl substituted terminal alkenes too could be compatible well (Table 4, **7g–7h**). Notably, the modification of amide groups has no effect on the reactivity of *N*-nucleophilic hydrofunctionalization (Table 4, **7i–7k**). Gratifyingly, while the amine was changed to the dinucleophile such as aminoethanol, dense functionalized *N*-adducts were produced in the reactions of both terminal and internal unactivated alkenes (Table 4, **7l–7v**). Encouraged by the results, less reactive 1,2-diphenylethanone was chosen as the model carbon nucleophile, and various sterically different terminal and internal alkenes also performed well in our atom-economic approach (Table 4, **7w–7af**).

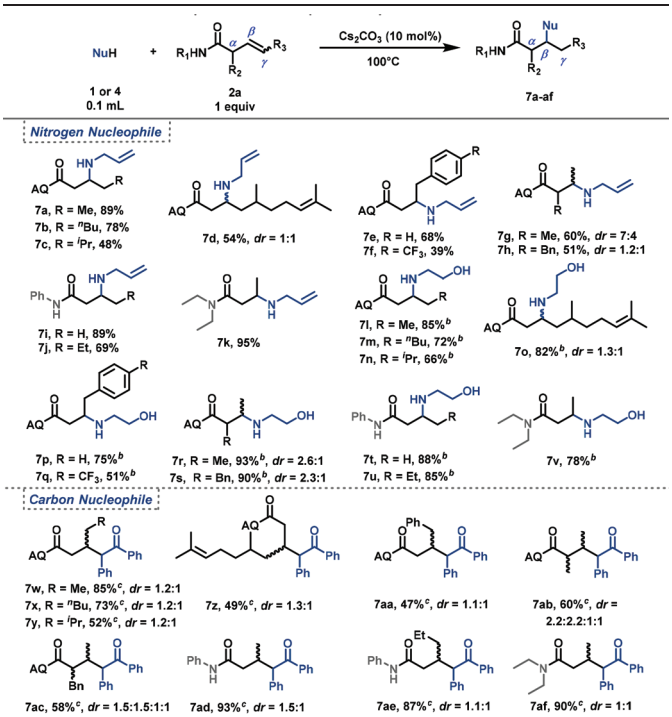
To showcase further synthetic practicality of this strategy, a multigram scale reaction was conducted to afford the branched product (**3a**) in 99% yield, while the catalyst loading was reduced to 2 mol%, 84% yield of the adduct could also be obtained (Scheme 1, eqn (1)). Furthermore, high yield of β-aminobutyric acid (**8a**) could be synthesized under this step-

Table 3 Chemo- and regioselective addition of unprotected dinucleophiles[a]

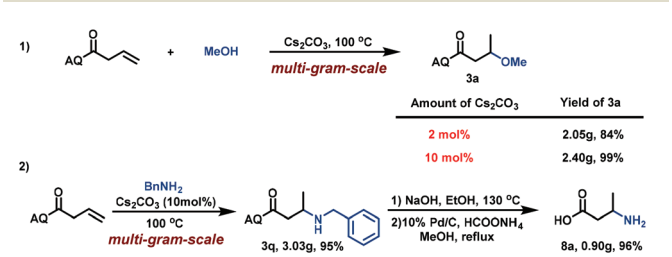


[a] Reactions were run on a 0.1 mmol scale. Percentages represent isolated yields. [b] 10 mol% CsOAc. [c] 2 equiv. NuH, 10 mol% CsOAc, neat condition. [d] 2 equiv. NuH, 10 mol% $CsOH{\cdot}H_2O$, 0.1 mL THF. [e] 2 equiv. NuH, 20 mol% CsOAc, 0.1 mL MeCN. [f] 2 equiv. NuH and 0.1 mL THF.

Table 4 Alkene scope in nucleophilic hydrofunctionalization[a]



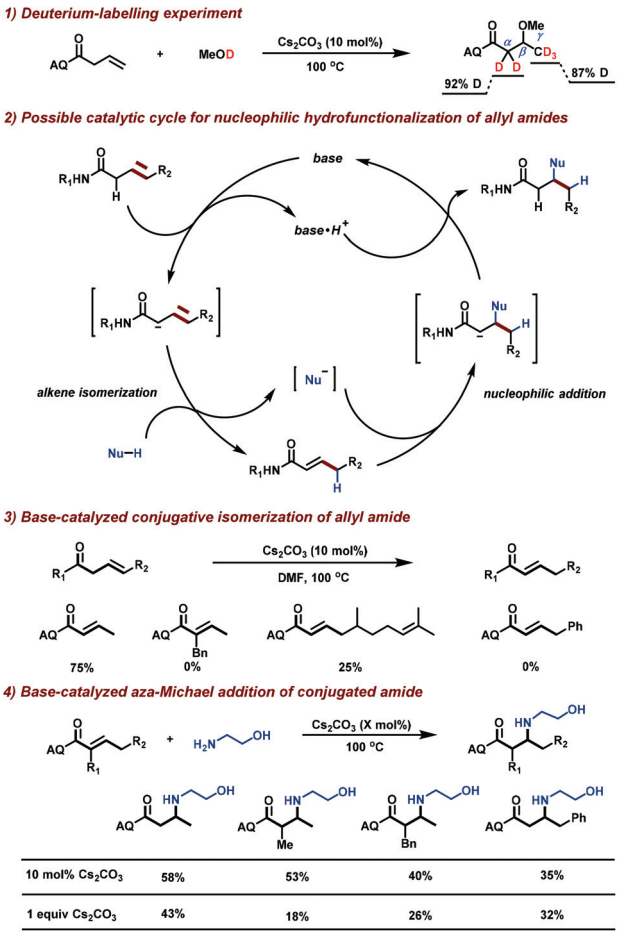
[a] Reactions were run on a 0.1 mmol scale. Percentages represent isolated yields. [b] 10 mol% CsOAc. [c] 2 equiv. NuH, 50 mol% KOH, 0.1 mL THF.



Scheme 1 Synthetic practicality and drug synthesis.

economic protocol too (Scheme 1, eqn (2)), which is an important plant resistance inducer.[10]

In order to gain possible mechanistic insight, the deuterium-labelling experiment was conducted first. The reaction using MeOD produced the desired adduct (**3a**) with the D-incorporation ratio of 92% and 87% at the α- and γ-positions, respectively (Scheme 2, eqn (1)). Based on the preliminary result and literature studies,[11] we proposed that a possible mechanism might involve the base-catalyzed tandem allylic isomerization and nucleophilic addition of the resulting conjugative amides (Scheme 2, eqn (2)). Subsequently, a series of control experiments were conducted to explore the possibility of our hypothesis. Initially, a variety of allylic amides were tested for the proposed conjugative isomerization of unactivated double bonds under the base catalyst (Scheme 2, eqn (3)); however, only allyl amide (**2a**) was converted to the conjugated amide in 75% yield, and neither steric hindered terminal nor internal alkenes could isomerize efficiently, despite the fact that they were well-tolerated substrates in our approach. Furthermore, the aza-Michael addition of the corresponding conjugated amides was tested under either catalytic or stoichiometric amount of base, where most of the reactions exhibited quite poor reactivity (Scheme 2, eqn (4)) due to the intrinsic poor electrophilicity of conjugated amides. Collectively, although preliminary studies partially supported the elementary steps of our proposed pathway, we still cannot exclude the above-mentioned reaction pathway. We reasoned that the complex allyl amides might be more reactive in our *in situ* occurring tandem equilibrium than in two separated elementary steps. Remarkably, despite well exploiting the Michael reaction,[12] the general application of the Michael addition to conjugated amides is still challenging and mainly limited to acrylamide,[13] which is consistent with the results of our control experiments (Scheme 2, eqn (4)). Thereby, our approach has provided a powerful complementary and environmental-friendly approach for the synthesis of structurally diverse β-hetero-substituted aliphatic amides, which are difficult to be achieved by the traditional Michael addition of conjugated amides owing to their intrinsic poor electrophilicity.



Scheme 2 Study on the possible reaction pathway.

Conclusions

In conclusion, a general and efficient transition-metal-free-catalyzed nucleophilic hydrofunctionalization of unactivated aliphatic alkenes under the minimal solvent conditions was developed. Most topical classes of carbon, nitrogen and oxygen nucleophiles proceeded efficiently with both terminal and internal unactivated aliphatic alkenes. The highly chemoselective unprotected dinucleophiles could also be presented in the concise approach. More than 80 structurally complex β-hetero-substituted aliphatic amides were rapidly synthesized in good yield with exclusive Markovnikov selectivity, which are difficult to be achieved efficiently by the traditional Michael addition of conjugated amides due to their intrinsic poor electrophilicity. The gram scale reaction and drug molecule synthesis have further demonstrated the potential synthetic utility of this scalable strategy. In contrast to previous transition-metal-catalyzed nucleophilic additions, this base-catalyzed protocol has made a comprehensive contribution to hydrofunctionalization of unactivated alkenes.

Author contributions

Xiaojin Wu: conceptualization, funding acquisition, investigation, project administration, resources, supervision, writing – original draft, writing – review & editing; Ying Zhan: data curation, formal analysis, investigation, methodology, software; Yao Zhao: data curation, formal analysis, investigation, methodology, software; Rizhi Chen: investigation, methodology, validation; Qian Du: investigation, methodology, validation; Jiacheng Rui: investigation, methodology, validation; Xintao Zheng: investigation, methodology, validation; all authors approve the current version of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

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