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Ni-catalyzed enantioselective three-component reductive alkylacylation of alkenes: modular access to structurally complex α -amino ketones†

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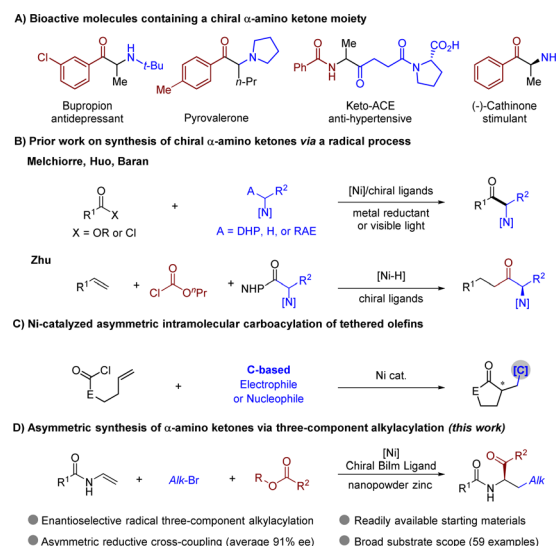
Chiral α -amino ketones have found extensive applications as functional molecules. A nickel-catalyzed, enantioselective, and fully intermolecular three-component 1,2-alkylacylation of *N*-acyl enamides has been realized with tertiary alkyl bromides and carboxylic acid-derived electrophiles as the coupling reagents. This reductive coupling strategy is operationally simple, exhibiting broad substrate scope and excellent functional group tolerance using readily available starting materials and allowing rapid access to structurally complex α -amino ketone derivatives in high enantioselectivity. A suitable chiral biimidazole ligand together with additional chelation of the amide carbonyl group in a Ni alkyl intermediate facilitates the enantioselective control by suppressing the background reaction, accounting for the excellent enantioselectivity. Mechanistic studies indicated intermediacy of radical species.

Introduction

Chiral α -amino ketones are a key structural motif in various bioactive molecules and pharmaceuticals, and they are also valuable building blocks in synthetic chemistry (Scheme 1A).^{1–4} Accordingly, the development of efficient asymmetric approaches for synthesis of chiral α -amino ketones has been a long-lasting pursuit in organic chemistry.^{5–8} Reported classic synthetic routes typically involve nucleophilic amination of α -halogenated ketones, electrophilic amination of suitable enolates, and homologation of chiral α -amino acids.^{9–19} Nevertheless, these two-electron-based strategies often suffer from limitations, such as poor availability of the nitrogen source, racemic synthesis or racemization of product, requirement of multiple steps, and/or harsh reaction conditions. Owing to the unique properties of nickel catalysts, recently, the groups of Melchiorre,²⁰ Huo,²¹ and Baran²² elegantly developed nickel-catalyzed asymmetric synthesis of enantio-enriched α -amino ketones *via* the coupling of an amine-containing reagent and an electrophilic acyl source (Scheme 1B). Meanwhile, the Zhu group reported synthesis of α -amino ketones *via* reductive coupling of olefins with a carbonyl source and a redox-active ester.²³ Despite the advances, there remains an increasing demand for the development of efficient and concise protocols

that permit a rapid assembly of α -amino ketones with high levels of complexity, modularity, and diversity from readily available commodities.

On the other hand, nickel-catalyzed asymmetric functionalization of olefins stands out as a prominent strategy toward facile construction of chiral complex molecules owing to the unique roles of Ni catalysts that readily participate in single electron transfer (SET) and reductive elimination.^{24–26} Consequently, catalytic three-component radical difunctionalizations of alkenes represent a powerful strategy for rapid enhancement



Scheme 1 Chiral α -amino ketones and enantioselective carboacylation of olefins.

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of molecular complexity by simultaneously forging two functionalities in one single operation, thus enriching the synthetic toolbox to access synthetic building blocks, medicines, and bioactive molecules.^{27–41} However, enantioselective control of the target stereogenic center remains a formidable challenge. Impressive progress has been made in nickel-catalyzed asymmetric radical three-component difunctionalizations of alkenes. These coupling systems include diarylation,⁴² alkyl-arylation,^{43–49} alkyl-alkenylation,^{50,51} aryl-alkylation,⁵² and sulfonyl-carbonylation^{53,54} under redox-neutral or reductive conditions, where organohalides serve as the terminal (the 3rd) component.^{55,56} However, as an important class of dicarbofunctionalization, asymmetric carboacylation reactions have received less attention and are restricted to two categories of intramolecular couplings. A carbamoyl halide-tethered olefin may react with a carbon terminating reagent *via* cyclization and C–C coupling under redox-neutral or reductive conditions (Scheme 1C).^{57–66} Alternatively, an aryl iodide-tethered olefin may react with an acylating reagent to fulfil the similar type of reaction.^{67,68} More recently, the groups of Chu,⁶⁹ Stanley,⁷⁰ Wang,⁷¹ Yuan⁷² and other^{73–77} have developed various methods for fully three-component racemic carboacylation of olefins. In most cases, a nickel acyl species captured a secondary radical species to deliver the final product through reductive elimination. However, the exceptionally high instability and reactivity of open-shell radical intermediates poses significant challenges in enantioselective control in these three-component reactions in general.^{78–82} In addition, the carbon radical intermediate may also undergo uncatalyzed C–C coupling with a reactive acylating reagent, leading to a background reaction. To the best of our knowledge, enantioselective fully three-component 1,2-alkylacylation of alkenes remains unknown. Therefore, the development of 1,2-alkylacylation reactions toward asymmetric synthesis of α -amino ketones will be an intriguing but challenging task.

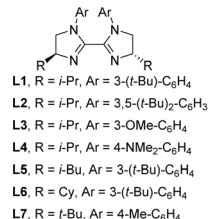
Herein, we now describe modular synthesis of enantio-enriched α -amino ketones *via* an efficient nickel-catalyzed enantioselective 1,2-alkylacylation of enamides with an alkyl bromide and an acylating reagent, which demonstrates an example of the integration of fully three-component carboacylation of alkenes with a high level of enantioselectivity for the first time (Scheme 1D).

Results and discussion

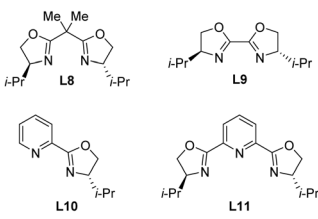
By taking advantage of the chelating effect during the formation of an organonickel intermediate, our initial investigation of asymmetric carboacylation was conducted using *N*-vinylbenzamide (**1a**) as the olefin and 2-bromo-2-methylpropane (**2a**) and 4-chlorobenzoic anhydride (**3a**) as the coupling components (Table 1). Through systematic investigation of the reaction parameters, the final optimal conditions were found to comprise a chiral biimidazoline (BiIm) ligand **L1**, NiBr₂·diglyme as a precatalyst, nanopowder zinc (40–60 nm) as a reductant, and MgCl₂ and 2-picoline as additives in THF/DMAc (5 : 1, 0.1 M) at room temperature for 48 h, from which conditions the α -amino ketone **4** was isolated in 81% yield and

Table 1 Optimization of reaction conditions^a

Entry	Deviation from standard conditions	Yield ^b (%)	ee ^c (%)
1	None	82	92
2	L2 instead of L1	81	91
3	L3 instead of L1	75	87
4	L4 instead of L1	77	87
5	L5 instead of L1	65	77
6	L6 instead of L1	70	79
7	L7 instead of L1	23	21
8	L8 instead of L1	43	12
9	L9 instead of L1	67	31
10	L10 instead of L1	32	15
11	L11 instead of L1	13	45
12	Zinc instead of nanopowder zinc	53	91
13	No L1	26	0
14	No NiBr ₂ ·diglyme	21	0
15	No nanopowder zinc	0	—
16	No MgCl ₂	18	93
17	No 2-picoline	44	92
18	THF only	38	72
19	DMAC only	85	89



L1, R = *i*-Pr, Ar = 3-(*t*-Bu)-C₆H₄
L2, R = *i*-Pr, Ar = 3,5-(*t*-Bu)₂-C₆H₃
L3, R = *i*-Pr, Ar = 3-OMe-C₆H₄
L4, R = *i*-Pr, Ar = 4-NMe₂-C₆H₄
L5, R = *i*-Bu, Ar = 3-(*t*-Bu)-C₆H₄
L6, R = Cy, Ar = 3-(*t*-Bu)-C₆H₄
L7, R = *t*-Bu, Ar = 4-Me-C₆H₄



L8, **L9**, **L10**, **L11**

^a Optimal reaction conditions: enamide (**1a**, 0.1 mmol), alkyl bromide (**2a**, 0.2 mmol), acid anhydride (**3a**, 0.15 mmol), NiBr₂·diglyme (10 mol%), **L1** (15 mol%), picoline, MgCl₂, nanopowder Zn (4.0 equiv.), and DMAc/THF was stirred at 25 °C for 48 h. ^b Isolated yield. ^c The ee was determined using HPLC with a chiral stationary phase.

92% ee (entry 1). A ligand screen revealed that chiral BiIm ligands (**L1**–**L7**, entries 1–7) were consistently superior to other oxazoline-based ligands (**L8**–**L11**, entries 8–11). BiIm skeletons with other alkyl chains or other aryl protecting groups (**L2**–**L7**) worked with comparable efficiency but with slightly decreased enantioselectivity, while Box ligand (**L8**), BiOx (**L9**), Pyrox (**L10**), and Pybox (**L11**) all gave sluggish reactions. Control experiments indicated that the nickel catalyst, ligand, nanopowder zinc, magnesium chloride, 2-picoline and the solvent (entries 13–19) each played a pivotal role in this transformation. The racemic α -amino ketone product can still be obtained in low yield in the absence of the ligand **L1** or nickel catalyst (entries 13 and 14), indicating a background reaction. Of note, the particle size of the Zn reductant is vital; nanopowder zinc can dramatically improve the efficiency when compared with other reductants (entry 12, see the ESI† for more information). Furthermore, omitting the MgCl₂ and 2-picoline additives led to



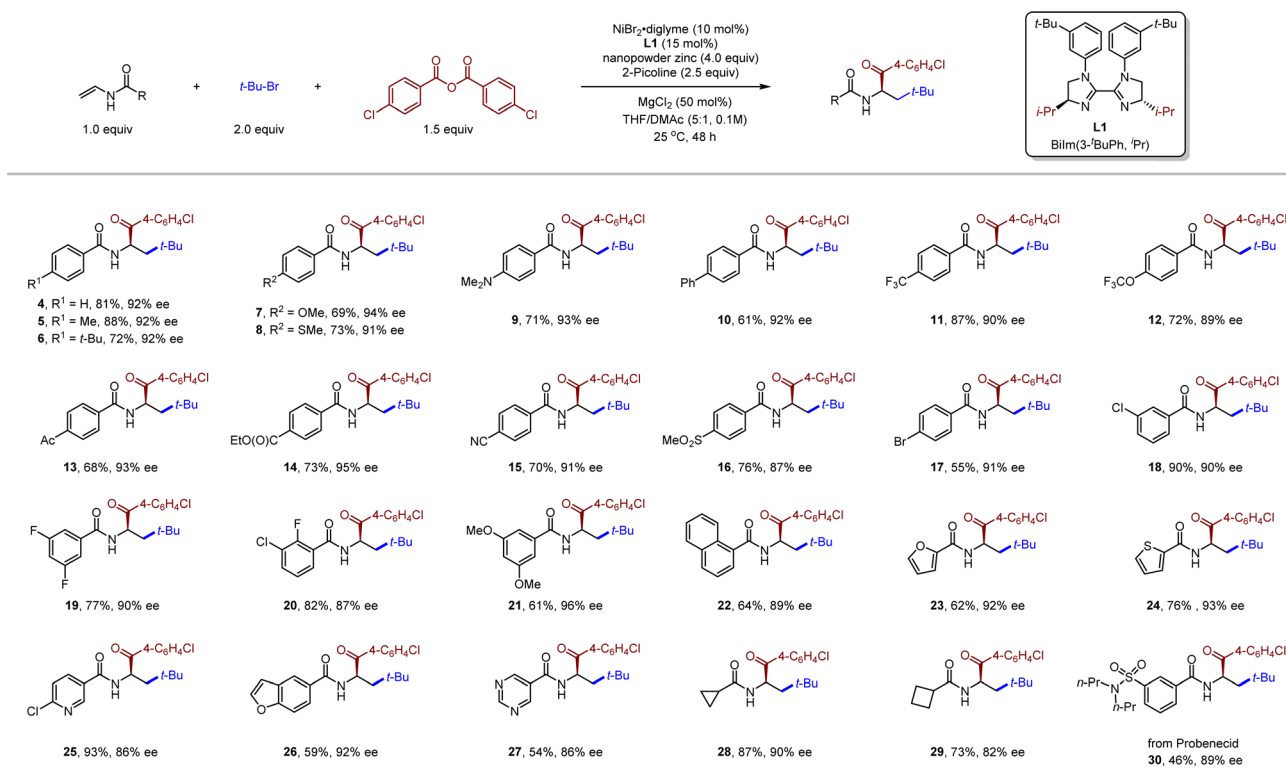
a substantial decrease of the reaction efficiency, albeit with no erosion of the enantioselectivity (entries 16 and 17). Screening of the solvent indicated that comparable results can be obtained in a single DMAc solvent, but introduction of THF further improved the enantioselectivity (entries 18 and 19, see the ESI† for more information).

With the optimized conditions in hand, we next investigated the generality of this three-component carboacylation. As illustrated in Table 2, vinyl amides bearing a wide variety of substituents delivered the desired products in good to excellent yields with good to excellent enantioselectivities. Enamides with an electron-donating (5–9 and 21) or -withdrawing (10–20 and 30) substituent at different positions of the benzene ring coupled efficiently, affording the α -amino ketones in 55–90% yields and 87–94% ee. Such mild reaction conditions allowed the use of a diverse spectrum of functional groups, including ether (7 and 12), thioether (8), amine (9), ketone (13), ester (14), nitrile (15), sulfone (16), and aminosulfonyl (30). Notably, some potentially reactive functionality such as aryl bromide (17) and chlorides (18, 20 and 25) were left intact, offering opportunities for further useful transformations. A series of heterocycles including furan (23), thiophene (24), pyridine (25), benzofuran (26), and pyrimidine (27), which are frequently found in pharmaceutically active molecules, were also compatible. To our delight, cycloalkyl-substituted amides were also viable (28 and 29), albeit with attenuated enantioselectivity (82–90% ee). In

contrast, 1,1- and 1,2-disubstituted internal olefins turned out to be inapplicable under the standard conditions (see the ESI† for unsuccessful olefins).

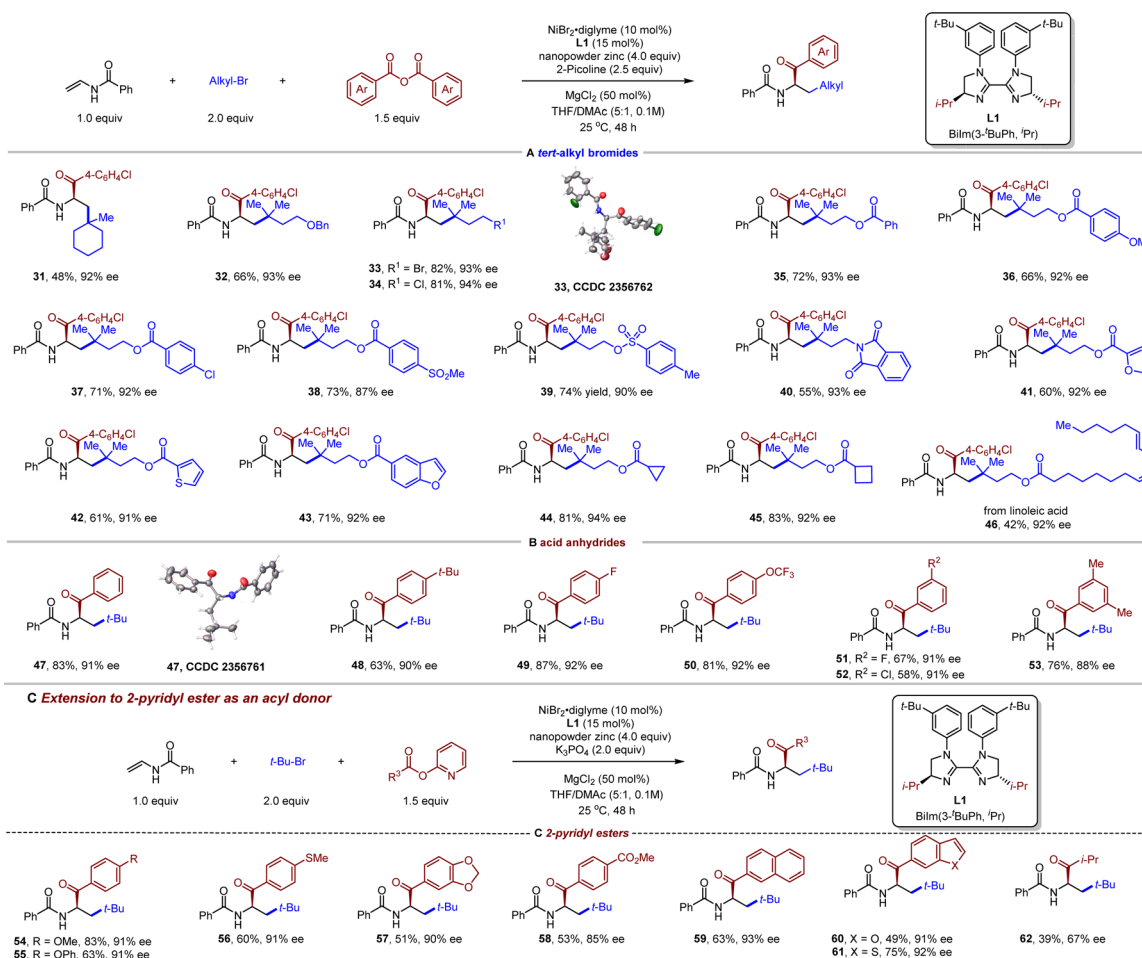
After defining the scope of vinyl amides, attention was then turned to the scope of the alkyl bromide component. Both cyclic tertiary bromide (31) and open-chained tertiary bromides (32–46) proved to be amenable to the coupling conditions (Table 3 (A)). We were pleased to find excellent functional group compatibility for the tertiary alkyl bromides component. Functional groups such as ether (32), primary alkyl bromide/chloride (33 and 34), aryl chloride (37), sulfone (38), tosylate (39), phthalimide (40), strained ring (44 and 45), and an internal alkene (46) were compatible, affording the corresponding products in moderate to good yields (58–82%) and excellent enantioselectivities (up to 94% ee). The absolute configuration for products 33 and 47 has been confirmed by X-ray crystallographic analyses. Interestingly, when the substrate contains both tertiary and primary alkyl bromide, the reaction is completely selective for the more sterically congested C–Br bond to give product 33 in 82% yield and 93% ee, leaving primary alkyl bromide unchanged, indicative of a stable radical species. Notably, heterocyclic substrates such as furan (41), thiophene (42), and benzofuran (43) were equally suitable for this chemistry. Unfortunately, primary and secondary alkyl bromides were found to be unreactive in our protocol, giving

Table 2 Scope of the enamide coupling component^a



^a Reaction conditions: enamide (0.1 mmol), alkyl bromide (0.2 mmol), acid anhydride (0.15 mmol), NiBr₂·diglyme (10 mol%), ligand L1 (15 mol%), picoline, MgCl₂, and nanopowder Zn (4.0 equiv.) in DMAc/THF was stirred at 25 °C for 48 h. Isolated yield. The ee was determined using HPLC with a chiral stationary phase.



Table 3 Scope of alkyl bromides and acylating reagents^a

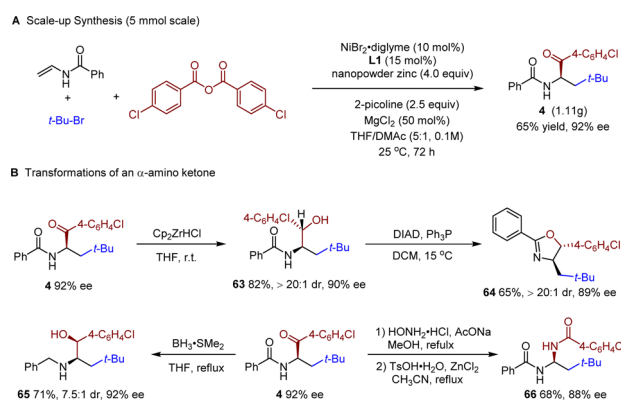
^a Reaction conditions: enamide (0.1 mmol), alkyl bromide (0.2 mmol), acid anhydride or 2-pyridyl ester (0.15 mmol), NiBr₂-diglyme (10 mol%), ligand L1 (15 mol%), picoline (or K₃PO₄), MgCl₂, and nanopowder Zn (4.0 equiv.) in DMAc/THF was stirred at 25 °C for 48 h. Isolated yield. The ee was determined using HPLC with a chiral stationary phase.

rise to only two-component coupling reaction with the benzoic acid anhydride.

We next demonstrated the substrate spectrum with respect to the acyl donors. Both electron-rich and -deficient groups on the different positions of the aromatic ring of the benzoic anhydrides were tolerated, furnishing the desired α -amino ketones 47–53 in moderate to good efficiency (Table 3 (B)). Additionally, we wondered whether other acyl precursors are suitable for this asymmetric three-component reductive alkylation. Gratifyingly, 2-pyridyl esters⁶⁶ were identified to be compatible with our protocol after subtle changes of the reaction conditions (K₃PO₄ instead of 2-picoline as a base, Table 3 (C)). Accordingly, a variety of 2-pyridyl esters were examined. A series of functional groups, including ether (54 and 55), thioether (56), ester (58), 2-naphthyl (59), benzofuran (60), and benzothiophene (61), were nicely accommodated. Besides aryl 2-pyridyl esters, an aliphatic acid-derived 2-pyridyl ester (62) also exhibited moderate reactivity.

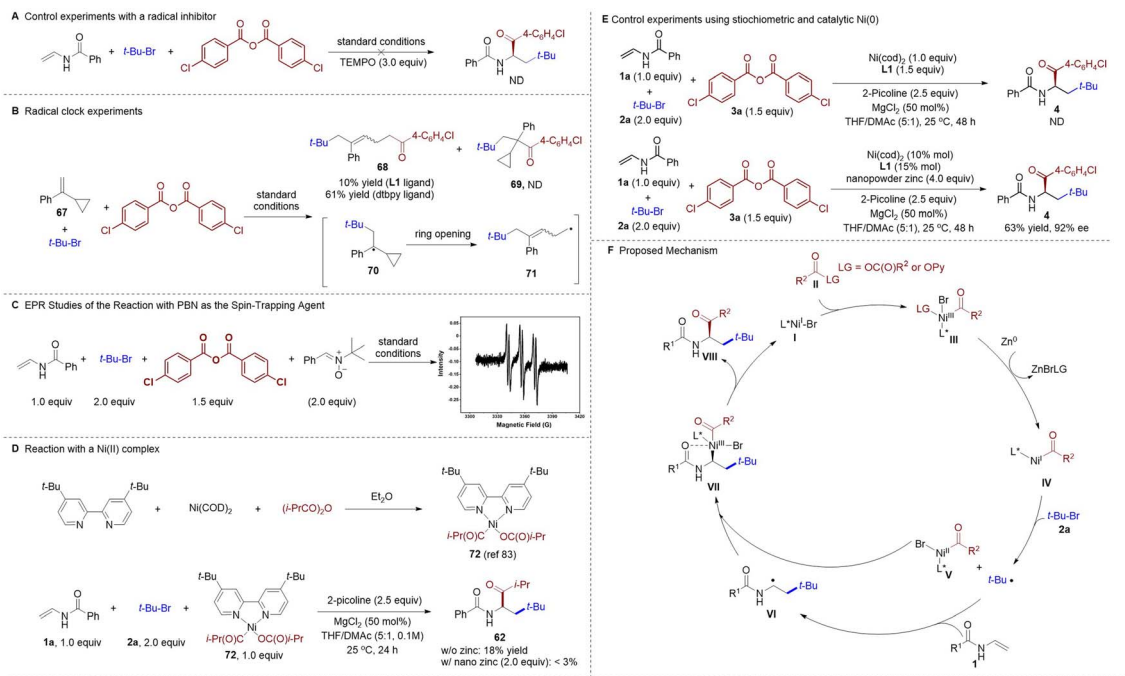
To further demonstrate the synthetic utility of our protocol, a gram-scale (5 mmol scale) reaction was carried out. Product 4

was isolated in a synthetically useful yield (1.11 g) with excellent enantioselectivity (92% ee, Scheme 2A). Chemoselective reduction of the ketone carbonyl group afforded product 63 in good yield and high diastereoselectivity (Scheme 2B). The reduction-



Scheme 2 Gram-scale experiment and synthetic transformations.





Scheme 3 Mechanistic studies.

Mitsunobu reaction of **4** afforded a chiral oxazoline **64** bearing two chiral centers in high dr, which could be a potential chiral ligand. Reduction of the carbonyls in both the ketone and the amide moieties afforded the amino alcohol **65** in 7.5 : 1 dr. Condensation between **4** and hydroxyamine followed by a Beckmann rearrangement afforded amide **66** in good yield. In all cases, only slight, if any, erosion of the enantiopurity was observed.

To shed light on the mechanism of this novel nickel-catalyzed asymmetric alkylacylation system, a series of experiments were conducted. The desired alkylacylation reaction was completely inhibited when a radical scavenger was added (Scheme 3A). Next, a radical-clock experiment using a α -cyclopropyl styrene **67** was conducted (Scheme 3B), and only the ring-opened product **68** was obtained through a sequential radical addition, ring opening, and acylation process, whereas the formation of the direct cross-coupled product **69** was not observed. This result indicated the formation of a *tert*-butyl radical which, upon addition to the alkene, delivers a new carbon radical that can be intercepted by the acyl-Ni species. The formation of radical species was further confirmed by an electron paramagnetic resonance (EPR) study using a spin-trapping agent phenyl *tert*-butyl nitron (PBN, Scheme 3C). Additionally, a nickel(II) acyl complex **72** (ref. 83) was prepared to elucidate the nature of the active nickel species in the catalytic cycle. The stoichiometric reaction of Ni(II)-complex **72**, *N*-vinylbenzamide **1a**, and 2-bromo-2-methylpropane **2a** in the absence of any zinc reductant gave the desired cross-coupled product **62** in 18% yield, whereas only traces of **62** were detected when a stoichiometric amount of nanopowder zinc was introduced (Scheme 3D). Taken together, these results suggest that the putative acyl-Ni(II) complex could be a productive

intermediate in this catalytic cycle. No corresponding product **4** could be observed when employing stoichiometric Ni(cod)₂ but lacking the zinc reductant, whereas catalytic amount Ni(cod)₂ with stoichiometric zinc resulted in the formation of product **4** in 63% yield (Scheme 3E). These outcome suggests that the reduction of Ni(III) acyl species **III** to Ni(I) acyl intermediate **IV** is likely required in the current protocol.

On the basis of our mechanistic investigations and insight from prior studies,^{71,72,83,84} a plausible mechanism of this asymmetric three-component alkylacylation reaction is proposed (Scheme 3F). Initially, Ni(I) species **I** may be formed *via* reduction of the Ni(II) precatalyst. Oxidative addition of the Ni(I) species **I** to the anhydrides or 2-pyridyl esters **II** generates a Ni(III) intermediate **III**, which reduced by nanopowder zinc as facilitated by MgCl₂ (ref. 83 and 84) to give Ni(I) intermediate **IV**. Then, the tertiary alkyl bromide **2a** is reduced by a Ni(I) complex **IV** to give a *tert*-butyl radical together with a Ni(II) species **V** (reduction of **2a** by nanopowder zinc to give the tertiary alkyl radical cannot be ruled out now). Subsequent addition of the *tert*-butyl radical to the vinyl amides **1** affords a secondary alkyl radical **VI**. At this juncture, oxidative addition of the radical **VI** to Ni(II) **V** delivers Ni(III) species **VII**, which then undergoes reductive elimination to release the chiral α -amino ketone product **VIII** and regenerates the Ni(I) species **I** to complete the catalytic cycle. We anticipate that the chelation of the carbonyl group to the BiIM-ligated nickel center would be beneficial to control the stereoselectivity in the radical capture step (**V** + **VI** \rightarrow **VII**).^{43–45,50,85}

Conclusions

In conclusion, we present herein the first enantioselective, fully intermolecular three-component 1,2-alkylacylation of alkenes



using tertiary alkyl bromides and an anhydride or a 2-pyridyl esters under reductive conditions. This mild and efficient protocol allows for the straightforward construction of structurally diverse enantioenriched α -amino ketones with good efficiency and excellent enantioselectivity from readily available electrophiles, avoiding the using of preformed air- or moisture-sensitive organometallic reagents. The amide group in the olefin substrate displays a vital role in enhancing regio- and enantioselectivity as well as the reactivity. Studies to further uncover the detailed mechanism of this transformation and expansion to other olefins and electrophiles are ongoing in our laboratory.

Data availability

The authors declare that all data supporting the findings of this study, including experimental procedures and compound characterization, NMR, HPLC, and X-ray analyses, are available within the article and its ESI† or from the corresponding author. The crystallographic data used in this study are available in the Cambridge Crystallographic Database under accession codes CCDC 2356762 (33) and 2356761 (47).

Author contributions

X. L. and J. X. conceived the concept and directed the project. J. X. and X. L. co-wrote the manuscript, analyzed the data, discussed the results, and commented on the manuscript. J. X., T. J., S. C., and M. P. conducted the experiments. All authors contributed to discussions.

Conflicts of interest

The authors declare no competing interests.

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