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Access to dialkylated allylic stereogenic centers by Ni-catalysed enantioselective hydrovinylation of unactivated alkenes†

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Tertiary dialkylated allylic stereogenic centers are widespread substructures in bioactive molecules and natural products. However, enantioselective access to dialkyl substituted allylic motifs remains a long-term challenge. Herein, a straightforward protocol to build allylic dialkylated stereogenic centers enabled by nickel-catalysed regio- and enantioselective hydrovinylation of isolated unactivated alkenes facilitated by a weakly coordinating group with vinyl bromides was developed, affording dialkylated allylic species in good yields with excellent enantioselectivities. The reaction distinguishes distinct alkenes and works for both terminal and internal aliphatic alkenes. The reaction proceeds under mild conditions and tolerates a wide range of functional groups.

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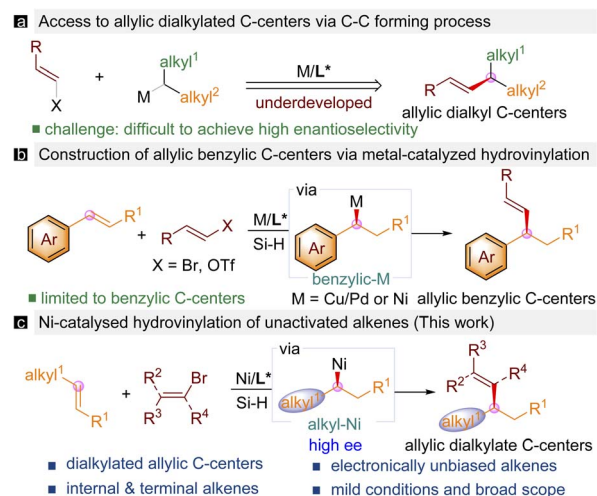
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Introduction

Tertiary allylic carbons bearing two alkyl substituents are widely found in natural products and other bioactive molecules.¹ Traditional methods to access substituted allylic carbon centers heavily rely on transition-metal-catalysed asymmetric allylic alkylation (AAA) reactions. However, it remains challenging to access dialkyl substituted allylic tertiary carbon centers due to the difficulties in differentiating two alkyl groups similar in steric and electronic properties. Over the past few decades, transition-metal catalysed asymmetric cross-coupling enabled C–C bond-forming processes have proved to be a powerful tool to construct saturated stereogenic carbon centers.² In particular, transition-metal catalysed asymmetric cross-couplings of vinyl electrophiles with alkyl electrophiles are a straightforward and complementary way to build allylic stereogenic carbon centers. While significant progress has been achieved regarding transition-metal-catalysed asymmetric synthesis of the C_{sp}²–C_{sp}³ bond, the available methods only allow access to only allylic structures next to aryl,³ nitrile,⁴ amides,⁵ or esters.⁶ No successful examples are known to construct dialkylated allylic motifs (Scheme 1a). Recently, alkenes have been employed as surrogates for alkyl nucleophiles in the presence of metal hydride species.^{7,8} Accordingly, metal-catalysed asymmetric C_{sp}²–C_{sp}³ coupling using alkenes as alkyl nucleophiles with

metal hydride *via* hydrofunctionalizations has been established. However, the use of this strategy to build allylic stereogenic centers is challenging due to the competitive reactivity between alkenes with vinyl electrophiles. In 2021, Buchwald reported the first example of Pd/Cu co-catalysed enantioselective hydrovinylation of styrenes with vinyl triflates to deliver allylic benzylic stereogenic centers (Scheme 1b).⁹ In the same year, Zhu and Gong developed the Ni-catalysed enantioselective hydrovinylation of styrenes to form the same type of stereogenic carbon center.¹⁰ However, enantioselective access to dialkyl substituted allylic stereogenic centers *via* hydrovinylation of unactivated alkenes remains underexplored partially due to the



Scheme 1 Impetus for the development of dialkylated allylic stereogenic centers.

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low reactivity of unactivated alkenes and associated poor selectivity issues. Recently, Giri disclosed a Ni-catalysed regio-selective alkenylation of γ,δ -alkenyl ketones *via* carbonyl coordination.¹¹ Engle reported a directed racemic hydroarylation and hydroalkenylation of unactivated alkenes bearing a remote coordination group.¹² Herein, we report a general protocol to construct tertiary allylic stereogenic centers with two alkyl substituents enabled by Ni-catalysed regio- and enantio-selective hydrovinylation of unactivated aliphatic alkenes with vinyl halides (Scheme 1c). The strategy allows for the chemo-selective hydrofunctionalizations between two alkenes facilitated by a weak coordinating group to furnish substituted tertiary carbon centers with good functional group tolerance.

Results and discussion

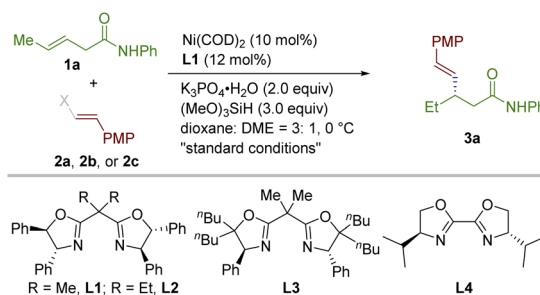
We started to test the feasibility of the transformation using internal aliphatic alkene **1a** and (*E*)-1-(2-bromovinyl)-4-methoxybenzene **2a** as the prototype substrates (Table 1). After evaluation of a wide range of reaction parameters, the reaction using Ni(COD)₂ (10 mol%) as a precatalyst, the bisoxazolidine-based ligand (**L1**, 12 mol%) as an anchoring ligand, (MeO)₃SiH (3.0 equiv.) as a hydride source, potassium

phosphate monohydrate (2 equiv.) as a base in the mixture of dioxane and DME (3 : 1, 0.05 M) at 0 °C delivered the desired product **3a** with optimal results (79% isolated yield and 92% ee, *rr* = 10 : 1, Table 1, entry 1).¹³

Other bidentate chiral ligands could catalyse the desired transformation, albeit in lower yields and levels of enantioselectivity (Table 1, entries 2–4). Replacing vinyl bromides with vinyl chlorides or iodides dramatically decreases the efficiency of the hydrovinylation reaction (Table 1, entries 5 and 6). The other nickel source could be used as a precatalyst for the reaction, delivering **3a** with good efficiency (Table 1, entries 7–9). The use of dioxane or dimethyl ether (DME) as the sole solvent substantially diminishes the yield and enantioselectivity of the product (Table 1, entries 10 and 11). Inorganic bases, such as cesium carbonate, potassium carbonate, and sodium carbonate, could mediate the reaction to give **3a** in 30–55% yields with comparable enantioselectivity (Table 1, entries 12–14). Carrying out the reaction at room temperature delivered the hydrovinylation product **3a** in 85% yield with 83% ee (Table 1, entry 15). In addition, decreasing the stoichiometry of **2a** diminished the efficiency of the reaction (Table 1, entry 16).

With the optimized conditions in hand, we turned to investigate the scope of this protocol to construct dialkylated

Table 1 Condition optimization of Ni-catalysed hydrovinylation of unactivated alkenes



Entry	Variation from "standard conditions"	Yield ^a [%]	ee ^b [%]	rr ^c
1	None, 2a (X = Br)	84 (79)	92	10 : 1
2	L2 instead of L1	65	87	10 : 1
3	L3 instead of L1	60	–60	10 : 1
4	L4 instead of L1	36	5	5 : 1
5	2b (X = Cl)	15	87	8 : 1
6	2c (X = I)	19	69	20 : 1
7	NiBr ₂ ·DME instead of Ni(COD) ₂	76	87	11 : 1
8	NiCl ₂ ·DME instead of Ni(COD) ₂	75	91	10 : 1
9	NiBr ₂ ·diglyme instead of Ni(COD) ₂	79	90	10 : 1
10	DME as the solvent	58	80	8 : 1
11 ^d	Dioxane as the solvent	81	83	11 : 1
12	Cs ₂ CO ₃ instead of K ₃ PO ₄ ·H ₂ O	55	90	11 : 1
13	K ₂ CO ₃ instead of K ₃ PO ₄ ·H ₂ O	32	87	10 : 1
14	Na ₂ CO ₃ instead of K ₃ PO ₄ ·H ₂ O	30	86	10 : 1
15	Room temperature	85	83	9 : 1
16	2a (2.0 equiv.)	75	91	10 : 1

^a The reaction was conducted using **1a** (0.1 mmol), **2** (0.25 mmol), [Ni] (10 mol%), ligand (12 mol%), K₃PO₄·H₂O (0.2 mmol), and (MeO)₃SiH (0.3 mmol) in solvent (0.05 M) under a N₂ atmosphere at 0 °C for 48 h unless otherwise stated. Yield was determined by GC using *n*-dodecane as the internal standard. Isolated yield is shown in parentheses. PMP = 4-methoxyphenyl. ^b Enantiomeric excess (ee) was determined by HPLC analysis using a stationary chiral phase. ^c Regio-isomeric ratio (rr) was determined by GC; rr = ratio of β -vs. γ -selective vinylation product. ^d The reaction was conducted at room temperature.

allylic stereogenic centers (Table 2). First, the scope of the unactivated aliphatic alkenes was tested. Various 1-mono-substituted and 1,2-disubstituted aliphatic alkenes with a range

of functional groups could be coupled with vinyl bromides to afford corresponding formal allylic alkylated products (3a–3o) in good to excellent yields with good levels of regio- and

Table 2 Substrate scope^a

<p>1 E & Z alkenes ● = amides, N-acyl amines</p>		<p>2 E & Z vinyl bromides aryl & alkyl vinyl bromides</p>	
Scope for unactivated alkenes			
<p>3a, R = Ph, 79%, 92% ee, rr = 10: 1 3b, R = 4-MeCOC₆H₄, 71%, 90% ee, rr = 12: 1 3c, R = 4-CF₃C₆H₄, 75%, 91% ee, rr = 10: 1 3d, R = 4-MeOC₆H₄, 73%, 90% ee, rr = 10: 1 3e, R = 3-thiophenyl, 70%, 92% ee, rr = 11: 1</p>		<p>3f, 54%, 88% ee, rr = 9: 1 Ar = 4-MeOC₆H₄ 3g, 78%, 88% ee, rr = 10: 1 Ar = 4-EtO₂CC₆H₄ 3h, 55%, 88% ee, rr = 12: 1^b From (Z)-alkene</p>	
<p>3i, 78%, 91% ee, rr = 9: 1 3j, 74%, 90% ee, rr = 9: 1</p>		<p>3k, 75%, 88% ee, rr = 11: 1 3l, 72%, rr = 18: 1 d.r. = 1.05: 1 (89% ee, 87% ee) 3m, 62%, 85% ee, rr = 5: 1</p>	
Scope for vinyl bromides			
<p>3n, 78%, 92% ee, rr = 7: 1 3o, 60%, 85% ee, rr = 6: 1</p>		<p>4a, 65%, 90% ee, rr = 13: 1 4b, 75%, 89% ee, rr = 12: 1 4c, 55%, 89% ee, rr = 12: 1</p>	
<p>4d, 50%, 86% ee, rr = 12: 1 4e, 60%, 97% ee, rr = 14: 1</p>		<p>4f, 55%, 87% ee, rr = 8: 1 4g, 60%, 85% ee, rr = 9: 1^b 4h, 55%, 88% ee, rr = 8: 1^b</p>	
<p>4i, 52%, 90% ee, rr = 8: 1 4j, 67%, 90% ee, rr = 10: 1</p>		<p>4k, 70%, 89% ee, rr = 12: 1 4l, 63%, 93% ee, rr = 9: 1 4m, 80%, 87% ee, rr = 9: 1</p>	
<p>4n, 78%, 85% ee, rr = 7: 1^b 4o, 74%, 87% ee, rr = 13: 1</p>		<p>4p, 63%, 91% ee, rr = 9: 1^b 4q, 56%, 89% ee, rr = 11: 1 CCDC 2131923</p>	
<p>4r, 65%, 89% ee, rr = 9: 1 4s, 51%, 93% ee, rr = 5: 1^b</p>		<p>4t, 41%, 93% ee, rr = 5: 1^c 4u, 46%, 94% ee, rr = 5: 1^c 4v, 42%, 87% ee, rr = 3: 1^d</p>	

^a For standard conditions, see Table 1. rr = ratio of β and γ selective product. rr was determined by GC. Enantiomeric excess was determined by chiral HPLC analysis using a chiral stationary phase. ^b NiBr₂·glyme (10 mol%), NaI (1.0 equiv.), and dioxane (0.05 M) were used. ^c 1 : 2 = 2.5 : 1, NiBr₂·glyme (10 mol%), NaI (0.2 equiv.), and dioxane (0.05 M) were used. ^d 1 : 2 = 2 : 1, NiBr₂·glyme (10 mol%), NaI (0.5 equiv.), KCl (0.5 equiv.), CsF (2.0 equiv.), HBpin (3.0 equiv.), and dioxane (0.05 M) were used.

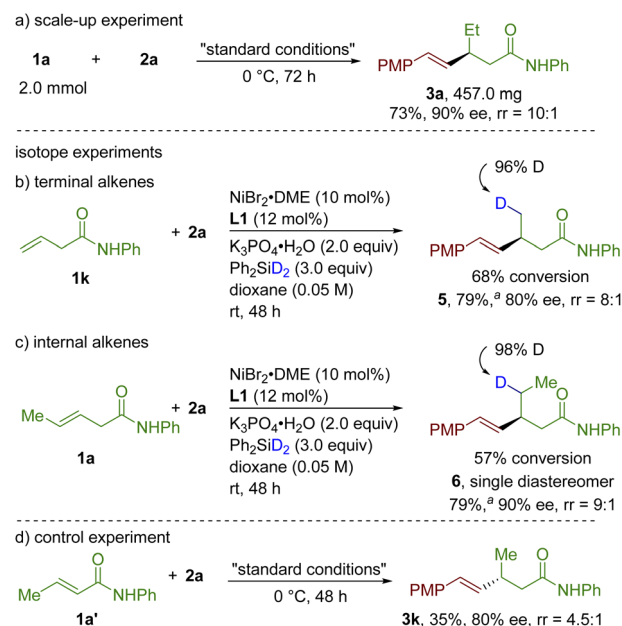


enantioselectivity. Electron-withdrawing and electron-donating group substituted aniline-derived amides were well-tolerated in the reaction, delivering dialkylated allylic stereogenic centers in 71–79% yields with 90–92% ee (**3a–3d**). Notably, ketone could be tolerated under the reductive conditions, delivering **3b** in 71% yield with 90% ee. Heteroaromatic amine-based alkene was transformed into **3e** in 70% yield with 92% ee. *E*-internal alkenes with different functional groups, such as aryls and esters, are compatible in the reaction (**3f–3j**), giving the desired products in 54–78% yields with 88–91% ee. Notably, *Z*-internal alkenes are also compatible in this reaction to furnish **3h** in 55% yield with 88% ee. Terminal aliphatic alkenes are also good substrates for this reaction (**3k** and **3l**). Interestingly, allylic branched alkene undergoes the desired transformation to afford dialkylated allylic product **3l** bearing two continuous saturated stereogenic centers in 72% yield (dr = 1.05 : 1) with 89% and 87% ee. Both terminal and internal allylic *N*-acyl amines could be involved in the reaction, giving β -vinyl chiral amines (**3m–3o**) in 60–78% yields with 85–92% ee.

Next, the scope of vinyl bromides was examined. *E*-styryl bromides are well-tolerated in the reaction, affording corresponding *E*-styryl dialkylated compounds (**4a–4r**) in good yields with good levels of regio- and enantioselectivity. Styrene derivatives with *para*-substitution patterns are all well compatible under the reaction conditions. Electron-donating group substituted aryl vinyl bromides were transformed into **4b–4e** in 50–75% yields with 86–97% ee. Meanwhile, electron-withdrawing group substituted aryl vinyl bromides were successfully involved in the reaction to give the desired products (**4f–4h**) in 55–60% yields with 85–88% ee. *meta*- and *ortho*-substituted aryl vinyl bromides with electron-donating and electron-withdrawing groups underwent the regio- and enantioselective hydrovinylation reaction to give **4i–4l** in 52–70% yields with 89–93% ee. It is noteworthy that chloro- (**4f**), -Bpin (**4g**), and bromo- (**4j**) were compatible under the reaction conditions, leaving chemical handles for further elaborations.

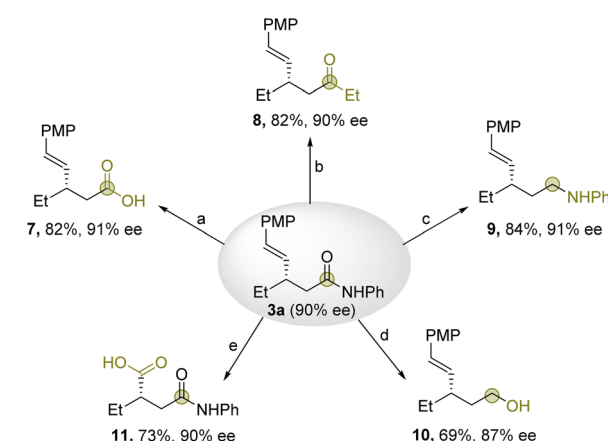
Moreover, multi-substituted styryl bromides could be converted to desired products (**4m–4o**) in 74–80% yields with 85–87% ee. Heteroaryl vinyl bromides, including carbazole, thiophene, and pyridine, were converted to **4p–4r** in 56–65% yields with 89–91% ee. The absolute configuration of the products is confirmed to be *S* unambiguously by X-ray diffraction analysis of **4q**. Moreover, *Z*-alkenyl bromide could be involved in the reaction, delivering the desired product **4s** in 51% yield with 93% ee. Impressively, 1,1-disubstituted and 1,1,2-trisubstituted vinyl bromides proved successful in the reaction, giving sterically demanding dialkylated allylic products (**4t** and **4u**) in synthetic useful yields with 93–94% ee, which are inaccessible otherwise. In addition, aliphatic vinyl bromides could be used in the reaction to form desired product **4v** in 42% yield with 87% ee.

Next, the reaction proceeded smoothly on the 2.0 mmol scale under standard conditions, giving **3a** in 73% yield with 90% ee, which showcased the potential of this protocol for the application of large-scale synthesis (Scheme 2a). To probe the reaction mechanism of this reaction, a series of control experiments were conducted. First, the reaction of 1-substituted aliphatic



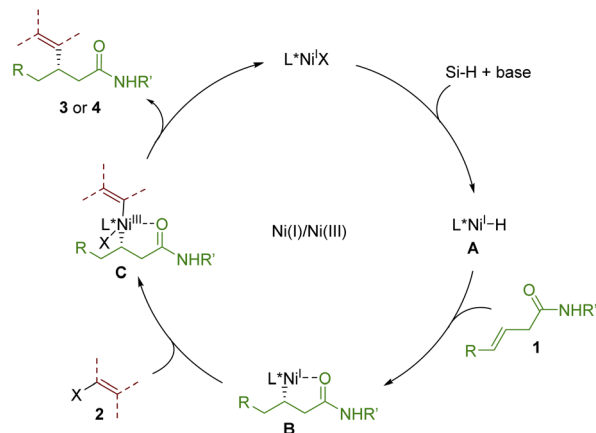
Scheme 2 Scale-up experiment and mechanistic experiments. ^a Yield was calculated based on the recovery of alkenes.

alkene **1k** with **2a** was carried out at room temperature using a deuterated silane (Ph_2SiD_2). Desired product **5** was obtained in 79% yield based on the conversion of **1k** with 80% ee (Scheme 2b). Under identical conditions, the reaction of 1,2-disubstituted aliphatic alkene **1a** with **2a** delivered the desired product **6** based on the conversion of **1a** with 90% ee (Scheme 2c). In both cases, deuterium was exclusively delivered to γ -position of the amide group, indicating that the hydrometalation of Ni–H with alkenes is irreversible or the following $\text{C}_{\text{sp}^3}\text{--}\text{C}_{\text{sp}^2}$ bond-forming step is much faster. Furthermore, the reaction of corresponding



Scheme 3 Synthetic applications of **3a**. Reaction conditions: (a) (1) $(\text{Boc})_2\text{O}$, Et_3N , DMAP, DCM, and 0 °C to room temperature; (2) LiOH , H_2O_2 , $\text{THF}/\text{H}_2\text{O}$ = 3 : 1, and 0 °C to room temperature. (b) (1) TiF_4 , 2-F-pyridine, DCM, and –78 °C to 0 °C; (2) EtMgBr and 0 °C. (c) LAH, THF, and 0 °C to 85 °C. (d) (1) NaH , BnBr , DMF, and 0 °C to room temperature; (2) LAH, THF, and 0 °C to 85 °C. (e) RuCl_3 , NaIO_4 , $\text{CCl}_4/\text{CH}_3\text{CN}$ = 1 : 1, and rt.





Scheme 4 Proposed mechanism for the reaction.

α,β -unsaturated amide **1a'** successfully led to desired hydrovinylation product **3k** in 35% yield with opposite absolute configuration (80% ee), excluding the isomerized alkene **1a'** as an intermediate for the reaction (Scheme 3d).

Furthermore, transformations of the allylic dialkylated products were examined using **3a** to further demonstrate the synthetic potential of this reaction (Scheme 3). First, the amide moiety could be transformed into diverse functional groups (**7–10**) without erasing the levels of enantioselectivity. Accordingly, β -vinyl acids and ketones as well as γ -vinyl amines and alcohols were obtained in good yields (69–84%) with good levels of enantioselectivity (87–91%). Moreover, α -alkylated carboxylic acid bearing acidic α -proton (**11**) was obtained in 73% yield with 90% ee by C=C cleavage.

Finally, a plausible mechanism for this reaction is proposed in Scheme 4.^{8–10} First, Ni(I)–H(**A**) was formed from the reaction of Ni(I)–X with silane with the assistance of the base. **A** coordinated with first alkenes **1** to undergo regioselective migratory insertion to generate secondary alkyl nickel species **B**, which could undergo oxidative addition with vinyl bromides **2** to form intermediate **C**. The final dialkylated allylic product was obtained *via* reductive elimination of **C** along the formation of Ni(I) to finish the catalytic cycle.

Conclusions

In summary, a straightforward protocol to access dialkylated allylic stereogenic centers has been developed by nickel catalysed enantioselective hydrovinylation of unactivated aliphatic alkenes with vinyl bromides facilitated by a directing group. The reaction proceeded under mild conditions with great chemo- and regioselectivities over two distinct alkenes to afford formal allylic dialkylated products with excellent levels of enantioselectivity for the first time. The reaction tolerates diverse substitution patterns and a wide range of functional groups.

Data availability

Experimental data have been provided in the ESI.†

Author contributions

J. X. Z. discovered the project. W. S. conceived and directed the project. J. X. Z. and P. F. Y. carried out the experiments and collected the data. WS wrote the manuscript with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

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