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Nickel-catalyzed asymmetric reductive aryl-allylation of unactivated alkenes†

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Herein we report a nickel-catalyzed asymmetric reductive aryl-allylation of aryl iodide-tethered unactivated alkenes, wherein both acyclic allyl carbonates and cyclic vinyl ethylene carbonates can serve as the coupling partners. Furthermore, the direct use of allylic alcohols as the electrophilic allyl source in this reaction is also viable in the presence of BOC anhydride. Remarkably, this reaction proceeds with high linear/branched-, *E*/*Z*- and enantio-selectivity, allowing the synthesis of various chiral indanes and dihydrobenzofurans (50 examples) containing a homoallyl-substituted quaternary stereocenter with high optical purity (90–98% *ee*). In this reductive reaction, the use of pregenerated organometallics can be circumvented, giving this process good functionality tolerance and high step-economy.

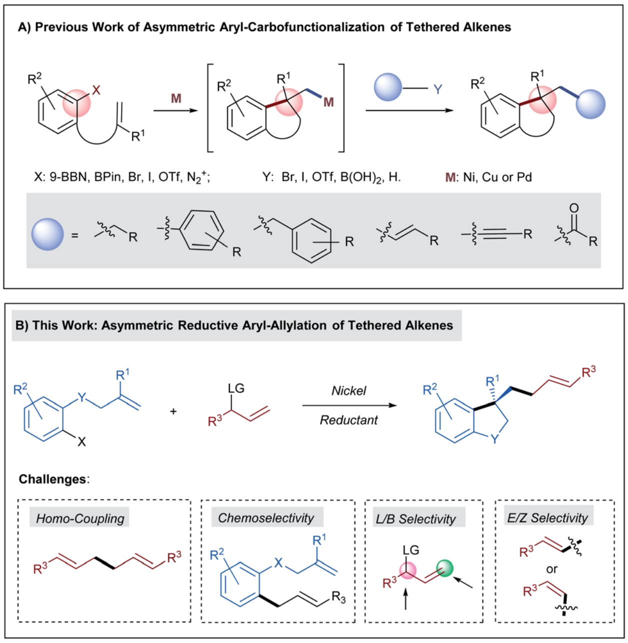
Introduction

In recent years, the rapid development of transition-metal catalyzed asymmetric aryl-carbofunctionalizations of aryl borane- or aryl (pseudo)halide-tethered alkenes allow the efficient synthesis of chiral benzene-annulated cyclic compounds in a highly enantioselective fashion (Scheme 1A).[1] The enantiodetermining step of these reactions relies on facially selective intramolecular Heck-type arylmetallation. After ring closure, the generated chiral alkyl metal species can be intercepted by a boronic acid, an organo(pseudo) halide, a terminal alkyne, or carbon monoxide to deliver the cross-coupling products in either a redox-neutral or a reductive pathway. Hitherto, the successfully installed carbo-moieties following this reaction sequence include alkyl,[2–4] aryl,[4–6] benzyl,[7] alkenyl,[4,8] alkynyl,[9] and carbonyl.[10] However, transition-metal catalyzed highly enantioselective olefin carbo-allylation still remains elusive mainly due to the issues in controlling chemo-, regio-, and stereo-selectivity.[11,12]

Herein we anticipated that a two-component enantioselective aryl-allylation of aryl-halide-tethered alkenes would be achieved through a reaction with an appropriate electrophilic allylating agent under reductive nickel catalysis[13] (Scheme 1B). The challenges of the target reaction lie in the following aspects: (1) allylic electrophiles are highly reactive and thus could easily outcompete aryl halides in the interaction with low-valent nickel, leading to undesired homo-coupling; (2) the direct coupling between aryl halides and allylic electrophiles is also a significant complicating factor; (3) difficulty in discriminating both ends of the generated π-allylic nickel intermediate could result in a mixture of linear and branched products; (4) the newly formed C–C double bond gives rise to a potential issue of controlling *E*/*Z*-selectivity.

Results and discussion

For the optimization of the reaction conditions, the aryl-iodide-tethered alkene **1a** and the allylic Boc carbonate **2a** (ref. 14) were



Scheme 1 (A) Previous work of asymmetric aryl-carbofunctionalizations of tethered alkenes; (B) asymmetric reductive aryl-allylation of tethered alkenes.

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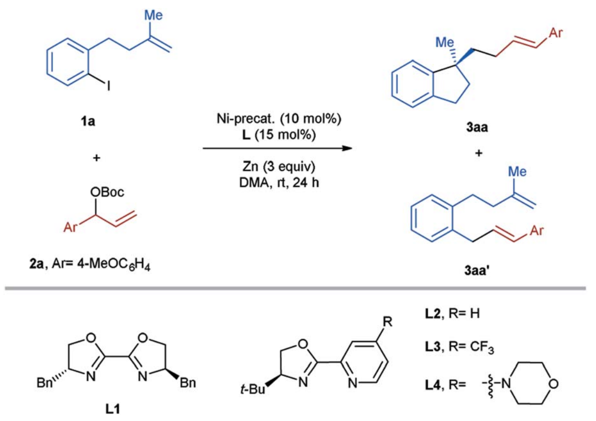
selected as the standard substrates (Table 1). In our previous work,[3,7,15] BiOX **L1** and pyrox **L2** have proved to be successful ligands for various asymmetric transformations with arylnickelation as the enantiodetermining step. Therefore, these two ligands were first tested for the studied reaction using $NiBr_2$(dme) (10 mol%) as a precatalyst and Zn as a reductant in DMA at room temperature for 24 h. In both cases, the desired aryl-allylation product **3aa** was formed in a mixture with the direct cross-coupling product **3aa′**, which could not be separated through column chromatography (entries 1 and 2). It is noteworthy that the issue of the competing direct coupling did not exist in our previously reported aryl-alkylation reaction.[3] Encouragingly, the cyclization/cross-coupling cascade reaction proceeded with complete regio- and *E*/*Z*-selectivity, affording only the linear product with an *E*-configured olefinic unit with high enantioselectivity. Since a better result concerning both efficiency and asymmetric induction was achieved in the reaction using **L2**, we continued the optimization sticking to the use of **L2** as the ligand. Next, the bromo analog of **1a** was employed as the substrate, but only the homo-coupling of **2a** occurred, indicating that the reactivity of the allylic carbonate **2a** outcompetes the aryl bromide completely (entry 3). We also examined the acetate analog of **2a** in the studied reaction. In this case, the formation of **3aa′** turned out to be the major reaction (entry 4). Replacing Zn by Mn as the reducing agent led to the complete shut-down of the desired reaction (entry 5). Performing the reaction in other polar aprotic solvents like DMF and NMP could also provide the aryl-allylation product **3aa**, but with less selectively (entries 6 and 7). Subsequently, several nickel salts were screened as the precatalysts (entries 8–11). To our delight, the formation of **3aa′** could be avoided in the case of $NiCl_2$ (entry 10). Raising the reaction temperature to 50 °C improved the yield to 67%, while the enantioselectivity remained excellent (entry 12). Further elevating the temperature to 70 °C showed a detrimental effect on the reaction efficiency (entry 13). When the catalyst loading was increased to 20 mol%, the target product **3aa** was obtained in 74% yield and 96%ee (entry 14). We also investigated the substitution effect on the pyridine ring of the pyrox **L2**. In the case of **L3** bearing an electron-withdrawing CF_3 group, the aryl-allylation reaction did not occur (entry 15). Moreover, the introduction of an electron-donating amine group also gave rise to a relatively low yield, although the enantiomeric ratio was slightly higher (entry 16). Finally, we tested cinnamyl bromide and chloride as the allylating agents for the studied reaction, but did not observe the formation of the desired product (entry 17).

Table 1 Optimization of the reaction conditions[a]

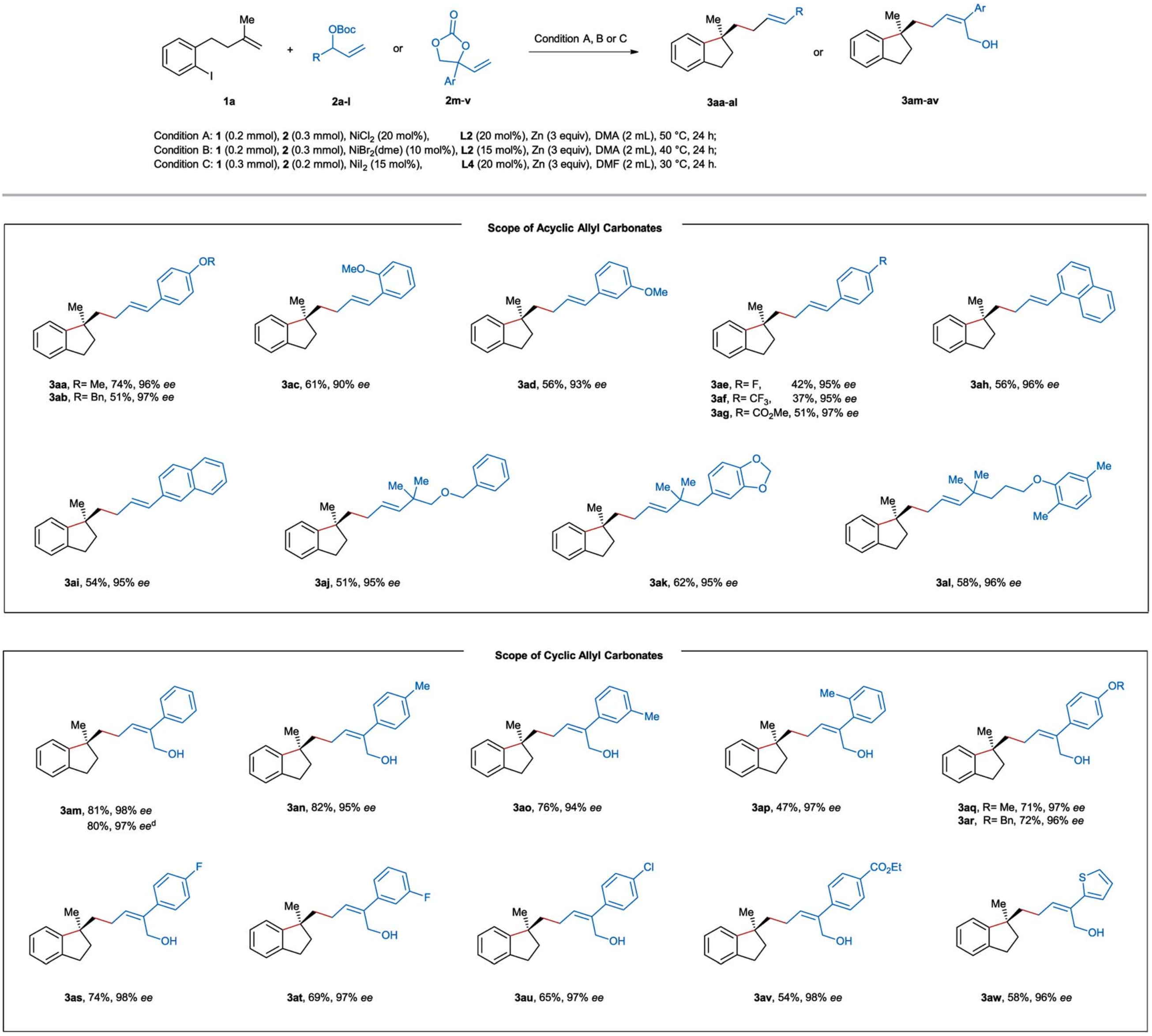


Entry	Ligand	Ni-precatalyst	Yield **3aa** (%)[b]	**3aa**/**3aa′**[c]	*ee* (%)[c]
1	**L1**	$NiBr_2$(dme)	43	96 : 4	−86
2	**L2**	$NiBr_2$(dme)	60	90 : 10	94
3[d]	**L2**	$NiBr_2$(dme)	0	—	—
4[e]	**L2**	$NiBr_2$(dme)	21	39 : 61	n.d.
5[f]	**L2**	$NiBr_2$(dme)	0	—	—
6[g]	**L2**	$NiBr_2$(dme)	42	58 : 42	92
7[h]	**L2**	$NiBr_2$(dme)	51	81 : 19	92
8	**L2**	NiI_2	24	52 : 48	90
9	**L2**	$NiBr_2$	46	91 : 9	94
10	**L2**	$NiCl_2$	61	98 : 2	96
11	**L2**	$Ni(acac)_2$	0	—	—
12[i]	**L2**	$NiCl_2$	67	>99 : 1	96
13[j]	**L2**	$NiCl_2$	50	>99 : 1	95
14[i,k]	**L2**	$NiCl_2$	74	>99 : 1	96
15[i,k]	**L3**	$NiCl_2$	0	—	—
16[i,k]	**L4**	$NiCl_2$	52	>99 : 1	97
17[l]	**L2**	$NiCl_2$	0	—	—

[a] Unless otherwise specified, reactions were performed on a 0.2 mmol scale of the aryl iodide-tethered alkene **1a** using 1.5 equiv of the allylic carbonate **2a**, 10 mol% Ni-precatalyst, 15 mol% ligand **L** and 3 equiv of Zn in 1.0 mL DMA at room temperature for 24 h. [b] Yields of the isolated product obtained through column chromatography. [c] Determined by HPLC-analysis on a chiral stationary phase. [d] The bromo analog of **1a** was used instead of **1a**. [e] The acetate analog of **2a** was used instead of **2a**. [f] Mn was used as the reductant instead of Zn. [g] Reaction was performed in DMF. [h] Reaction was performed in NMP. [i] Reaction was performed at 50 °C. [j] Reaction was performed at 70 °C. [k] Reaction was performed using a 20 mol% Ni-precatalyst and 20 mol% ligand. [l] Cinnamyl chloride or bromide was used instead of **2a**.

After establishing the optimal reaction conditions, we started to evaluate the substrate scope of this nickel-catalyzed aryl-allylation reaction. First, we turned our attention to the substrate spectrum of allylic carbonates (Table 2). Various acyclic aryl-substituted secondary allylic carbonates (**2b–g**) were reacted with the aryl iodide-tethered alkene **1a**. In the case of alkoxy-substituted phenyl (**2a–d**), the reactions proceeded smoothly under the optimized conditions, providing the products **3aa–ad** in moderate to good yields and excellent enantioselectivities. When the phenyl ring is substituted by an electron-withdrawing group (**2e–g**), modifications of the reaction conditions were needed. Under the amended conditions ($NiBr_2$(dme) instead of $NiCl_2$), the corresponding products **3ae–ag** were obtained in moderate efficiency with a high level of asymmetric induction. Furthermore, both α- and β-naphthyl substituted carbonates (**2h** and **2i**) also turned out to be competent precursors, affording the coupling products **3ah** and **3ai** in moderate yields and excellent enantiomeric excesses. When the allylic position of the carbonates is substituted by a tertiary alkyl group (**2j–l**), the aryl-allylation reaction still occurred, furnishing the products **3aj–al** in yields ranging from 51–58% with excellent enantioselectivities. Unfortunately, no desired products were formed in the case of primary or secondary alkyl-substituted allylic carbonates. Of note is that

Table 2 Evaluation of the substrate scope of allylic carbonates[a–c]



[a] Condition A: **3aa–ad**; condition B: **3ae–al**; condition C: **3am–aw**. [b] Yields of the isolated products after column chromatography. [c] Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase. [d] The reaction was performed on a 5 mmol scale of aryl iodide-tethered alkene **1a**.

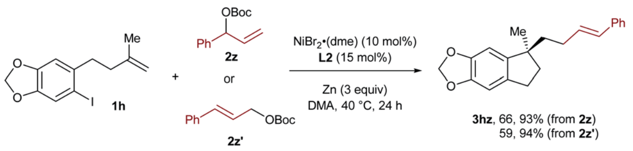
complete linear- and *E*-selectivities were achieved for all the isolated products mentioned above.

As a specific class of cyclic allyl carbonates, vinyl ethylene carbonates have been widely applied as a substrate with various coupling partners under the catalysis of Pd, Cu, Ir, or Rh.[16,17] However, the use of vinyl ethylene carbonates in nickel-catalyzed reductive cross-electrophile coupling is still unknown. After screening various reaction parameters, we reoptimized the reaction conditions for vinyl ethylene carbonates as follows: NiI_2 (15 mol%), **L4** (20 mol%), and Zn (3 equiv) in DMF at 30 °C for 24 h. Under these conditions, a series of vinyl-substituted 1,3-dioxolan-2-ones **2m–w** were successfully utilized as the allyl source in our reductive aryl-allylation, and the corresponding *Z*-configured chiral allylic alcohols **3am–av** and *E*-configured **3aw** were obtained as the only geometry isomer in moderate to good efficiency, complete linear-selectivity and excellent enantioselectivities (Table 2). Notably, the reported reaction could be simply scaled up to 5 mmol in the case of **3am** with a similar yield.

Next, diverse tethered alkenes **1b–l** were subjected to the reaction with different acyclic and cyclic carbonates under the optimal reaction conditions (Table 3). Generally, all the reactions provided the desired products with complete linear- and *E*/*Z*-selectivities as well as excellent enantioselectivities. Larger geminal substituents of the olefinic unit (**1b–e**) posed no problem, and moderate to good efficiency could be achieved in these cases. Substituted iodobenzene (**1f–i**) also turned out to be suitable precursors, producing chiral indanes in yields ranging from 41 to 83%. Moreover, our method is also applicable to the efficient construction of a chiral dihydrobenzofuran scaffold starting from the allyl phenyl ethers **1j–l**. In addition, we attempted to construct an indoline and isochroman framework by means of this nickel-catalyzed reaction. Unfortunately, no target cyclization products were formed in these cases.

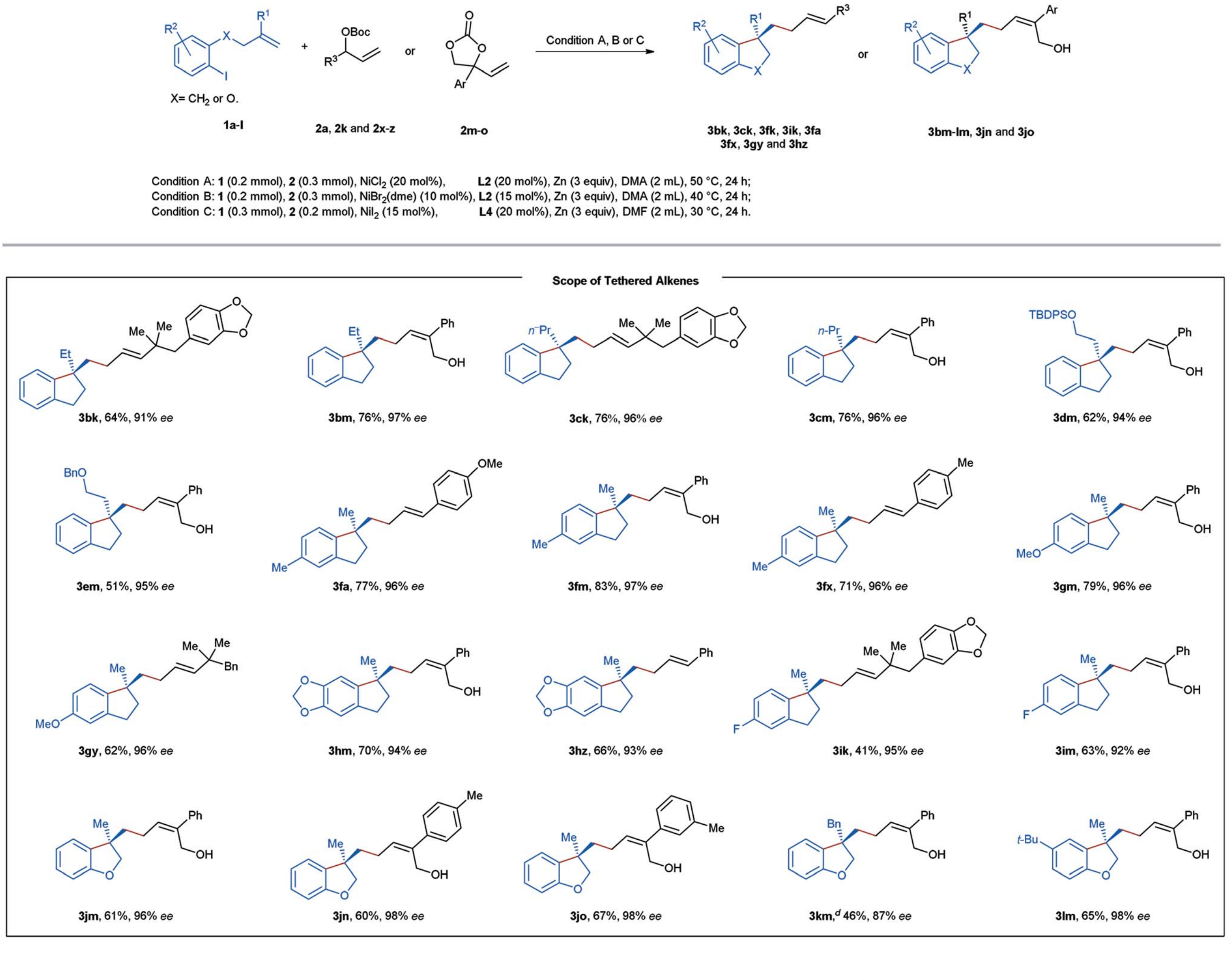
In the case of **3hz**, we utilized the linear cinnamyl acetate **2z′** as the coupling partner instead of its branched analog **2z**, and found that the same product was afforded with a similar outcome concerning both yields and selectivities (Scheme 2). This result suggests the presence of a π-allylic nickel intermediate in the reaction, and the linear selectivity could be attributed to a regioselective reductive elimination.

To improve the step economy of our method, we tested the reactions using directly allylic alcohols as the substrates, which were transformed into the corresponding carbonates *in situ via* a reaction with BOC anhydride (Table 4). Gratifyingly, the target products **3aa** and **3ak** were yielded with excellent enantioselectivities in the selected reactions, although the efficiency was somewhat lower than those obtained using the corresponding carbonates. During the process of scope evaluation of acyclic allyl carbonates, we noticed that some of them, particularly heteroaryl-substituted secondary allylic carbonates, could not be isolated through column chromatography due to rapid decomposition on silica gel. Therefore, this one-pot procedure



Scheme 2 Comparison of the reactions using linear and branched allylic carbonates.

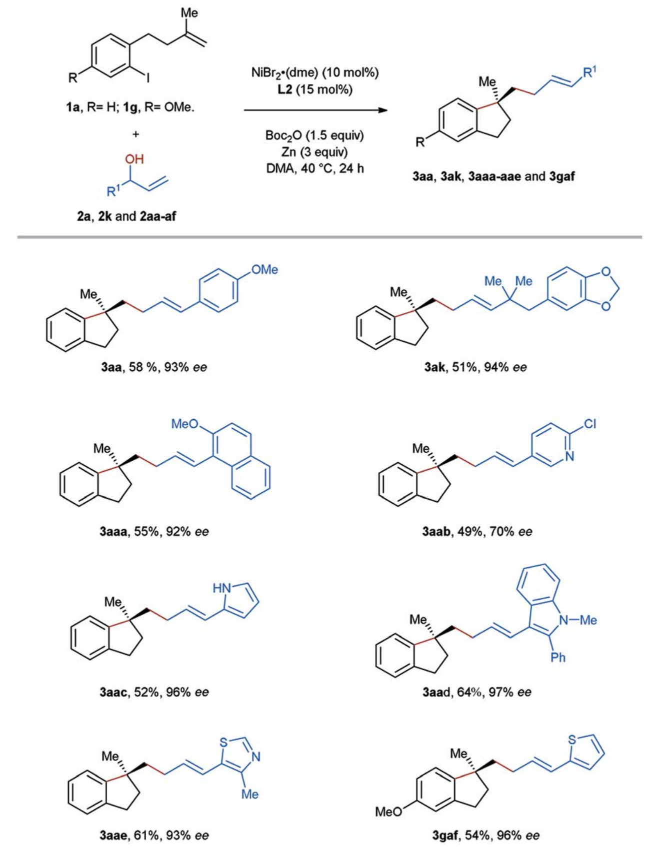
Table 3 Evaluation of the substrate scope of tethered alkenes[a–c]



Condition A: **1** (0.2 mmol), **2** (0.3 mmol), NiCl$_2$ (20 mol%), **L2** (20 mol%), Zn (3 equiv), DMA (2 mL), 50 °C, 24 h;
Condition B: **1** (0.2 mmol), **2** (0.3 mmol), NiBr$_2$(dme) (10 mol%), **L2** (15 mol%), Zn (3 equiv), DMA (2 mL), 40 °C, 24 h;
Condition C: **1** (0.3 mmol), **2** (0.2 mmol), NiI$_2$ (15 mol%), **L4** (20 mol%), Zn (3 equiv), DMF (2 mL), 30 °C, 24 h.

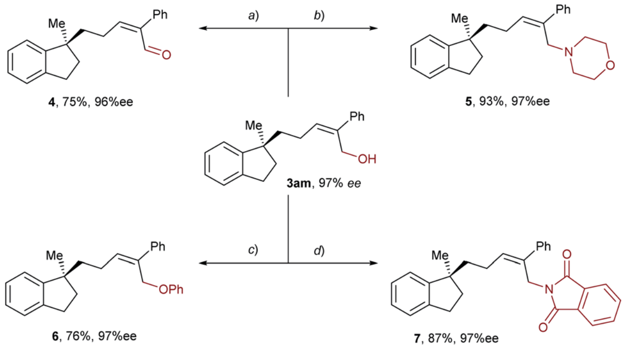
[a] Condition A: **3fa**; condition B: **3ck**, **3fk**, **3ik**, **3fa**, **3fx**, **3gy** and **3hz**; condition C: **3bm–lm**, **3jn** and **3jo**. [b] Yields of the isolated products after column chromatography. [c] Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase. [d] Reaction time: 48 h.

Table 4 Aryl-allylation reaction using allylic alcohols[a–c]

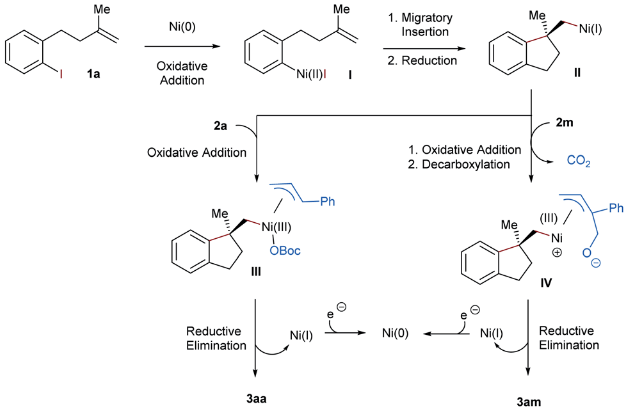


[a] Unless otherwise specified, reactions were performed on a 0.2 mmol scale of the aryl iodide-tethered alkene **1a** or **1g** using 2.0 equiv of allylic alcohols **2a**, **2k** and **2aa–af**, 10 mol% $NiBr_2$(dme), 15 mol% ligand **L2** and 3 equiv of Zn in 1.0 mL DMA at 40 °C for 24 h. [b] Yields of the isolated product obtained through column chromatography. [c] Enantiomeric Excesses were determined by HPLC analysis on a chiral stationary phase.

provides an entry to prepare aryl-allylation products, which are inaccessible following the reaction employing carbonates. A group of moieties including methoxy-substituted naphthalene (**3aaa**), pyridine (**3aab**), pyrrole (**3aac**), indole (**3aad**), thiazole (**3aae**), and thiophene (**3gaf**) were successfully incorporated into the framework of the aryl-allylation products according to the protocol of the reactions employing allylic alcohols.



Scheme 3 Derivatizations of the aryl-allylation product.



Scheme 4 Proposed mechanism.

Taking advantage of the attached hydroxyl group as a functional handle, various derivatizations of the aryl-allylation product **3am** were conducted, and the results are demonstrated in Scheme 3. First, compound **3am** was oxidized into an α,β-unsaturated aldehyde **4** in 75% yield by means of Dess–Martin oxidation. Next, PBr_3-mediated bromination of **3am** followed by nucleophilic substitution with morpholine furnished an allylic amine **5** in 83% yield over two steps. Moreover, **3am** was subjected to the Mitsunobu reaction using phenol or phthalimide as the nucleophile, delivering an allyl phenyl ether **6** and an allylic imide **7** in 76% and 87% yields, respectively. Notably, the enantioselectivities of all the derivatization products mentioned above remained high.

On the basis of previous reports, we proposed a plausible mechanism for this nickel-catalyzed aryl-allylation reaction in Scheme 4. Initially, Ni(0) is formed under reductive conditions and undergoes subsequently oxidative addition with the alkene-tethered aryl iodide **1a**. The resultant Ni(II) complex **I** performs a facially selective intramolecular migratory insertion into the pendant olefinic unit, to complete the construction of the chiral benzene-fused ring framework.[6–8] Alternatively, the enantiodiscriminating step could also be facially selective oxidative addition prior to the insertion.[18] The following zinc-mediated single-electron reduction affords the Ni(I) intermediate **II**, to which the allylic carbonates **2a** and **2m** are oxidatively added. In the case of the cyclic allyl carbonate **2m**, decarboxylation succeeds the oxidative addition. Next, terminal selective reductive elimination from the generated π-allylic nickel species **III** or **IV** yields the linear aryl-allylation product **3aa** or **3am**, respectively.[14,19] Finally, Zn-mediated reduction of Ni(I) regenerates Ni(0) for the next catalytic cycle.

Conclusions

In conclusion, we have developed a highly enantioselective nickel-catalyzed reductive aryl-allylation of aryl iodide-tethered unactivated alkenes with both acyclic and cyclic allyl carbonates as the allylating agent. Moreover, allylic alcohols can be employed directly as the electrophilic allyl source in the presence of BOC anhydride. The enantiodetermining step of the studied reaction relies on facially selective intramolecular Heck-type arylnickelation, while regioselective reductive elimination from the π-allylic nickel intermediates leads to the linear selectivity of the coupling product. Furthermore, the formation of a new C–C double bond proceeds with high *E*/*Z*-selectivity. The aforementioned high chemo-, regio- and stereo-control along with mild reductive reaction conditions allow the preparation of diverse highly enantioenriched indanes and dihydrobenzofurans bearing a homoallyl-substituted quaternary stereogenic center with a high tolerance of functionalities.

Author contributions

C. W. conceived and designed the experiments. Z. L., Y. J. and W. H. performed the experiments and prepared the Supporting Information. C. W. directed the project and wrote the manuscript.

Conflicts of interest

There are no conflicts to declare.

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