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Asymmetric Three-Component Heck Arylation/Amination of Nonconjugated Cyclodienes

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Abstract: *Substituted cyclohexylamines are becoming increasingly important in drug discovery. Asymmetric Heck insertion/amination of nonconjugated cyclodienes proceeds to give 5-aryl cyclohexenylamines with good enantioselectivity and exclusive trans configurations. Primary and secondary anilines, indoline, and benzylamines are suitable amines. The weakly donating diphosphite Kelliphite forms a deep unsymmetrical pocket, which is essential for stereoselective anti attack of amines.*

In the early 1990s, Larock et al. reported that Heck arylation of nonconjugated dienes produces π-allyl Pd species, which can be trapped by external amines and malonates (Figure 1 a).[1] The reaction involved palladium migration after an insertion step, via sequential β-hydrogen elimination and reinsertion.[2,3] For many years, an asymmetric variant with nonconjugated dienes has remained elusive. In comparison, asymmetric Heck insertion of conjugated dienes followed by nucleophilic attack has met with more success.[4] For example, in 1993 Shibasaki et al. reported intramolecular cyclization of alkenyl triflates on a pendent conjugated diene (cyclopentadiene), which was quenched by nucleophilic attack by acetate ion or benzylamine in 80% *ee*.[4a] Finally, in 2019, Wu et al. disclosed asymmetric Heck cyclization on a tethered 1,4-cyclohexadiene, which was successfully trapped by malonates, phenols, and a special aniline (Figure 1 b).[5] In this reaction, alkene insertion was the stereodetermining step. Moreover, tethering of the two reaction partners made asymmetric alkene insertion much easier to achieve than that in intermolecular reactions.

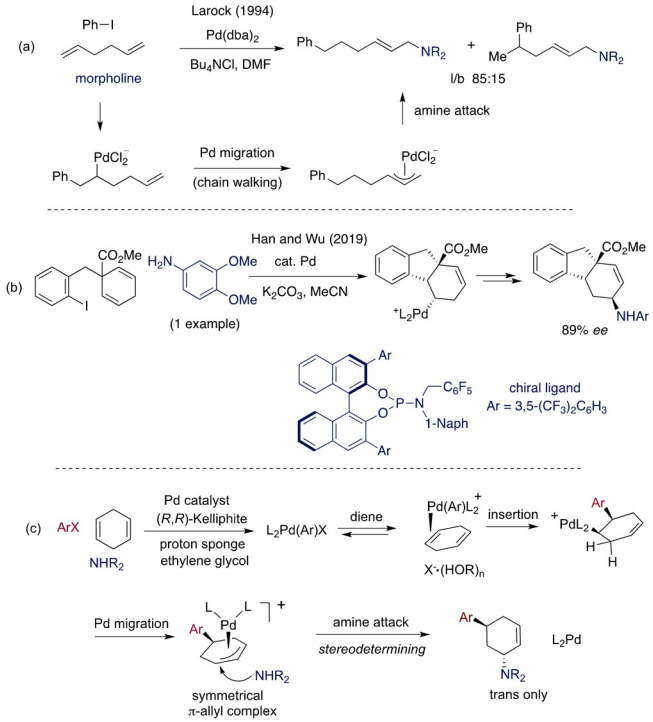

Figure 1. Examples of asymmetric Heck arylation/amination of nonconjugated dienes.

Herein, we report the first asymmetric examples of a 3-component Heck arylation/amination of nonconjugated cyclic dienes (Figure 1 c). This domino reaction combines two major classes of organometallic reactions, alkene insertion and allylic substitution, and uses easily available reagents to add an aryl ring and an amine onto cyclic dienes with excellent stereocontrol of two new stereogenic centers. This reaction is thus ideally suited for the preparation of chiral arylated cyclohexylamines.

Substituted cyclohexylamines are becoming increasingly important as core motifs in drug candidates. The amine functionalities not only help to quickly assemble fragments of drugs, but also provide hydrogen-bonding sites with target receptors. Saturated azacycles, including those carrying stereogenic centers, confer unique three-dimensional shape and help to reduce promiscuous binding, thus increasing the chance of success through clinical trials.[6] Examples of drugs containing cyclohexylamine fragments include cariprazine for the treatment of bipolar depression (see Figure 2) and glimepiride, which stimulates insulin secretion.[7] Some drug candidates carrying 3-substituted cyclohexylamines are also shown in Figure 2, along with the diseases that they target,[8]

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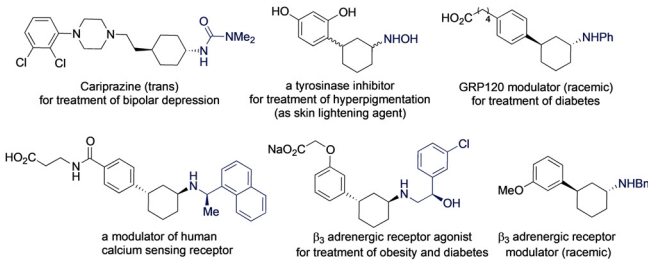


Figure 2. Examples of drugs and drug candidates containing cyclohexylamines.

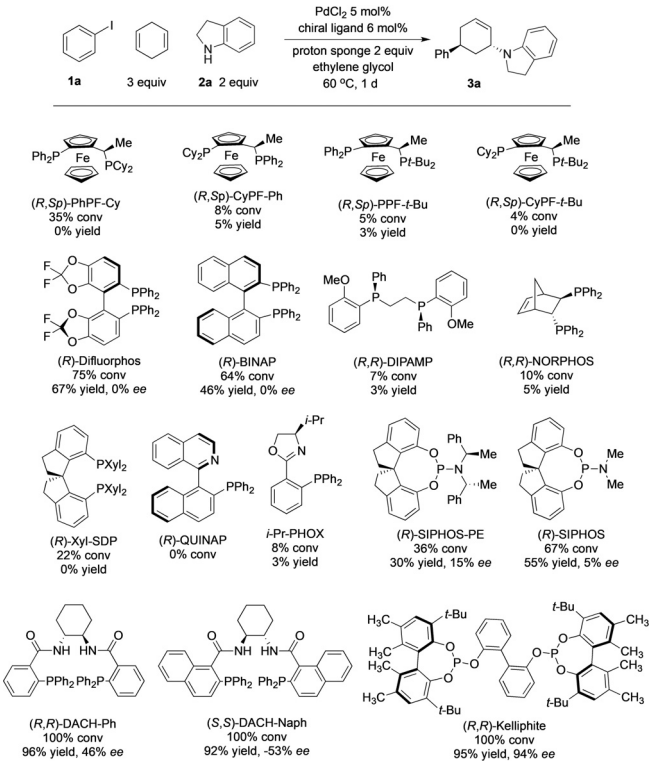
but efficient stereoselective methods for these chiral amines are still lacking.[9]

We foresaw several obstacles in developing such an asymmetric transformation as in Figure 1c: 1) a weakly donating ligand must be used to activate the π-allylic complex for external nucleophilic attack, but it may be easily displaced by alkylamines in the reaction mixture. 2) Asymmetric amination on substituted π-cycloallylic complexes of Pd is nontrivial, and only a limited number of examples of this kind have been reported.[10] 3) The last step of amine attack may be reversible,[11] especially in alcoholic solvents, which can racemize the products. We did indeed encounter *ee* erosion over time in glycol, for example, while using Et_3N and *i*-Pr_2NEt as bases. The problem disappeared when a stronger base was employed.

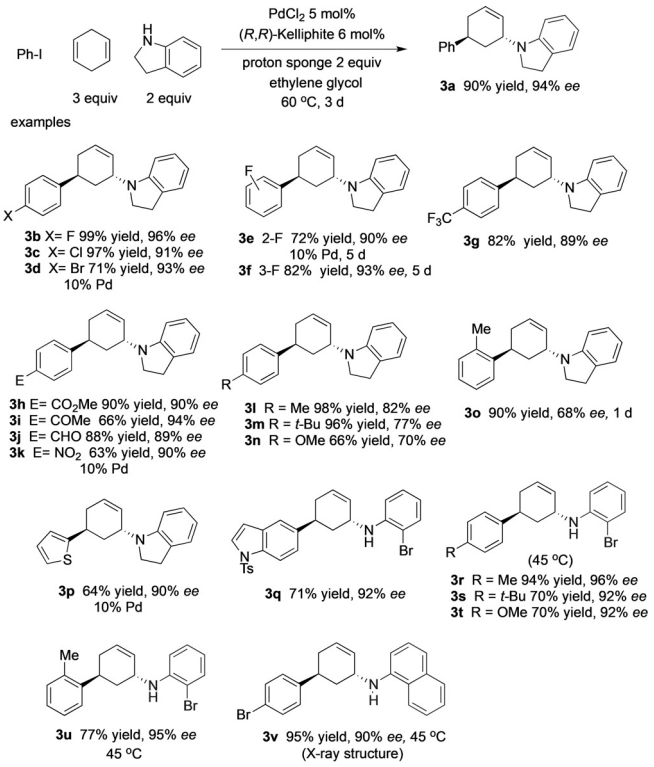
We initially attempted to use aryl triflates in a model Heck arylation/amination, but they underwent partial hydrolysis and reduction under basic conditions. Later, we switched to aryl iodides and used ethylene glycol as a solvent. The alcohol was known to promote reversible ionization of arylpalladium halides in Heck reactions.[12] The ionization creates a vacant site, which is crucial for subsequent alkene insertion, palladium migration, and formation of cationic π-cycloallyl species (see Figure 1c).

In a model reaction with phenyl iodide, 1,4-cyclohexadiene, and indoline, we screened an extensive list of chiral ligands for the Pd catalyst (Scheme 1 and see the Supporting Information for details). For example, BINAP and Difluorphos delivered desired adduct **3a** in good yields, but the *ee* value was unfortunately zero. Other chiral phosphines formed catalysts with very low activity, including Josiphos ligands, DIPAMP, Norphos, PHOX, and QUINAP. The Pd catalysts of two chiral phosphoramidites only showed moderate activity and gave less than 20% *ee*. Trost ligands on a backbone of *trans*-1,2-diaminocyclohexane are usually considered to be the first choice of chiral ligands for Pd-catalyzed asymmetric amination of cycloallylic electrophiles,[13] but they only provided around 50% *ee* in our model reaction. Luckily, we finally identified that Kelliphite affords excellent results, providing adduct **3a** in good yield, exclusive *trans*-selectivity, and 94% *ee*. This highly electron-deficient diphosphite was previously developed for rhodium-catalyzed asymmetric olefin hydroformylation.[14]

With the optimal catalyst in hand, we examined the scope with respect to the aryl iodides in reactions with indoline (Scheme 2). Aryl fluorides, chlorides, and bromides were well



Scheme 1. The effect of ancillary ligands on model arylation/amination (yields and ees of **3a** are indicated).

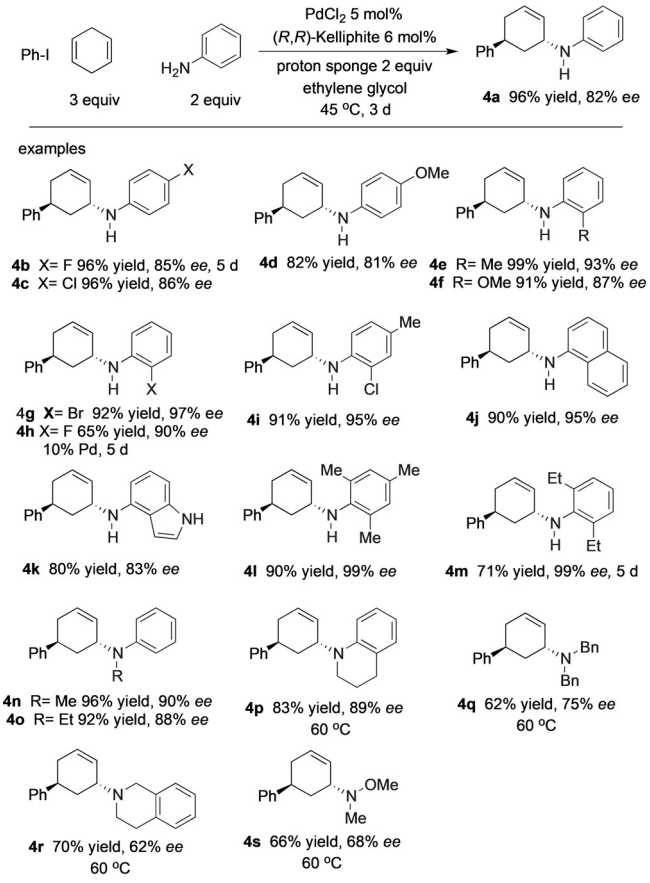


Scheme 2. Scope with respect to aryl iodides in the asymmetric arylation/amination.

preserved during Pd catalysis (**3b–f**). Ester, ketone, aldehyde, and nitro substituents on the aryl ring were also tolerated

(**3h–k**). Electron-rich aryl iodides, including *p*-tolyl and *p*-anisyl aryle iodides, provided adducts with indoline with *ee* values in the range of 70–80% (**3l–o**), but greater than 90% *ee* was obtained in similar reactions using the larger amine *o*-bromoaniline (**3r–u**). These brominated adducts can be readily converted into useful tetrahydrocarbazoles through Heck cyclization (see Scheme 5b). Adduct **3v** was subjected to single-crystal X-ray diffraction, which established its configuration as (3*R*,5*S*).[15] Furthermore, we found both thiophene and indole rings were tolerated in this reaction (**3p–q**), while 3-pyridyl iodide was fully consumed but did not afford any desired product.

Next, we examined the scope with respect to amines (Scheme 3). Typical primary anilines provided the adducts with *ee* values of around 80%. Both electron-donating and -withdrawing groups can be present on the anilines (**4b–d**). Notably, anilines carrying *ortho* substituents produced adducts with greater than 90% *ee* (**4e–i**). Aryl fluorides, bromides, and chlorides were well tolerated, as well as an unprotected N-H indole (**4k**). Furthermore, nearly perfect *ee* was obtained when very bulky *o*,*o*′-alkylated anilines were used (**4l–m**). This trend can be explained on the grounds of steric factors, namely that the disfavored transition state is further destabilized by larger anilines (see Figure 3). Secondary anilines were also suitable substrates and delivered products in around 90% *ee* (**4n–p**). Furthermore, dibenzylamine, tetrahydroisoquinoline, and a methoxylamine reacted to give adducts (**4q–s**) with moderate *ee* values. Unfortunately, smaller amines such as diethylamine and pyrrolidine can bind to cationic palladium species and inhibit the catalytic process. For the same reason, heteroaryl amines like pyridine, pyrimidine, and benzoxazole did not afford the desired adducts.



Scheme 3. Scope with respect to arylamines and an alkoxyamine in the asymmetric arylation/amination.

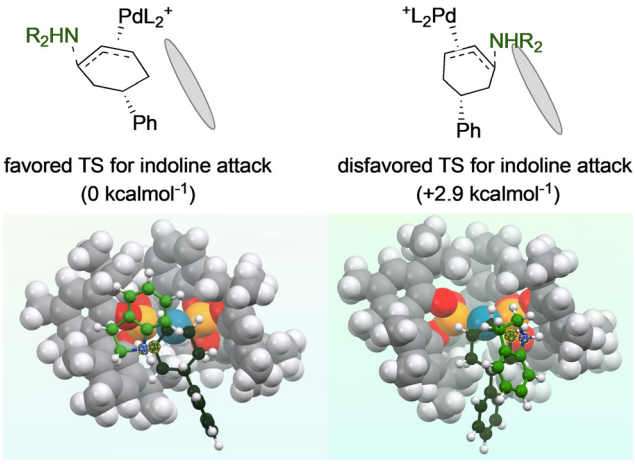
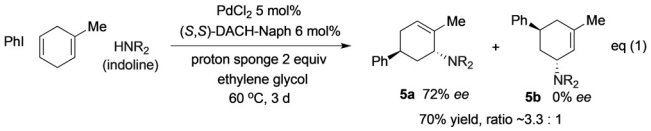


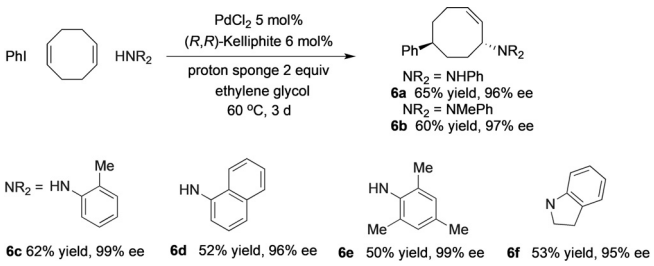
Figure 3. Favored and disfavored transitions states (left and right) for indoline attack on η^3-5-phenylcyclohexenyl complex of (*R*,*S*,*R*)-Kelliphite. The Kelliphite-Pd fragment is shown in space-filling representation, while indoline (in green) and η^3-phenylcyclohexyl (in black) are shown as ball-and-stick models.

We later discovered that the Heck arylation/amination of 1,5-cyclooctadiene also afforded adducts **6** with excellent *ee* values (Scheme 4). Both primary and secondary anilines reacted smoothly and the reaction tolerated steric elements next to the nitrogen atom of anilines (**6b–d**). Simple Heck byproducts accounted for most of the rest of the material.

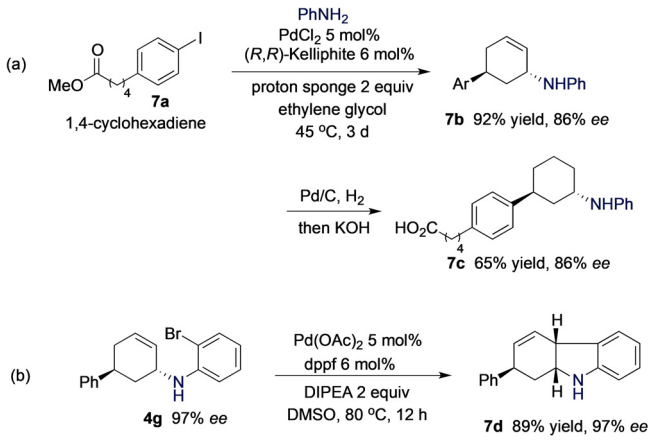
To demonstrate synthetic usefulness of the Heck arylation/amination, adduct **7b** was hydrogenated to afford *trans* isomer **7c**, which was patented for the treatment of diabetes (Scheme 5a).[8e] In another example, brominated adduct **4g** readily underwent Pd/dppf-catalyzed Heck cyclization to provide all-*syn* tetrahydrocarbazole **7d** (Scheme 5b). Partially hydrogenated carbazoles are core motifs in many drug

Unfortunately, reactions of other substituted 1,4-cyclohexadienes catalyzed by Pd/Kelliphite afforded several isomers in low stereoselectivity. It should be pointed out that the diene-insertion step became stereodetermining in these reactions, instead. After switching to the Trost ligand (*S*,*S*)-DACH-Naph, we found that 1-methyl-1,4-cyclohexadiene gave two isomers in a ratio of approximately 3:1, with the major isomer **5a** in 72% *ee* whereas the minor **5b** as a racemate [Eq. (1)].





Scheme 4. Asymmetric arylation/amination of 1,5-octadiene.



Scheme 5. Application in the synthesis of medicinally active compounds.

candidates targeting diseases such as cancers and neurodegenerative diseases,[16] but only racemic samples have so far been used in biological testing owing to a shortage of enantioselective methods.[17]

To understand the origin of the enantioselectivity in the model reaction (Figure 3), we performed DFT calculations for the reaction pathway at the wB97X-D/6-31G(d)/SDD level. The central biphenol ring of (*R*,*R*)-Kelliphite is known to be flexible. Based on calculation, the (*R*,*S*,*R*) conformer formed a much more stable complex with $PdCl_2$ than the (*R*,*R*,*R*) form, which is consistent with previous observations made with rhodium complexes by others.[14] In the key step of indoline attack at the π-allyl palladium species, two dominant transition states were 3.1 kcal mol^{-1} apart in energy, which is in good agreement with observed 94% *ee* in product **3a** at 60 °C. Close examination of the chiral pocket of the η^3-cyclohexenyl complex formed by (*R*,*S*,*R*)-Kelliphite reveals that two peripheral xylyl rings of Kelliphite form deep crevice, which partially buries the π-cyclohexenyl fragment. Moreover, the left xylyl ring is relatively open to accommodate the incoming indoline leading to the major enantiomer. In contrast, the right peripheral xylyl ring forms a rigid steep wall, which obstructs the alternative approach of indoline that forms the minor enantiomer.

In summary, we report a three-component arylation/amination of nonconjugated cyclic dienes with complete *trans* selectivity and excellent enantioselectivity. After aryl insertion, palladium migration leads to the formation of electrophilic π-allyl complexes. These are activated by a weakly donating Kelliphite for external attack of amines. Kelliphite also forms a deep chiral pocket that allows enantioselective attack of the π-allyl fragment by external amines from the opposite side of the palladium center.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: allylic amination · phosphites · Heck reaction · palladium · metal migration

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