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Enantioselective Intermolecular Heck and Reductive Heck Reactions of Aryl Triflates, Mesylates and Tosylates Catalyzed by Nickel

Xiaolei Huang, Shenghan Teng,[#] Yonggui Robin Chi, Wenqiang Xu, Maoping Pu,[#] Yun-Dong Wu and Jianrong Steve Zhou*

Abstract: Nickel-catalyzed intermolecular Heck reaction of cycloalkenes proceeds well with aryl triflates, mesylates and tosylates in excellent enantiomeric ratios. The asymmetric reductive Heck reaction also works with a 2-cyclopentenone ketal, which is equivalent to conjugate arylation of the enone itself.

Asymmetric Heck reaction^[1] and reductive Heck reaction^[2] allow arylation of alkenes using readily available aryl halides and sulfonates (see examples in Scheme 1). To this end, many palladium-catalyzed methods have been developed and some have been successfully utilized in stereoselective synthesis of bioactive complex compounds. Unlike palladium, which is an expensive, rare noble metal, nickel is an earth-abundant, extremely cheap 3d metal. The latter is being produced over two million tons a year. Nickel is more electropositive than palladium, so oxidative addition of Ni(0) to aryl C-O bonds of mesylates, tosylates and pivalates is exergonic and has lower barriers of oxidative addition than that of Pd(0). In Heck reaction, β-insertion of aryl nickel(II) species to alkenes has low barriers than Pd(II), but β-hydride elimination from alkyl nickel(II) species is more difficult than palladium(II).^[3] To date, the mesylates and tosylates in palladium-catalyzed Heck reaction have been limited to alkenyl and electron-deficient heteroaryl ones. In contrast, nickelcatalyzed Heck reaction occurred smoothly with mesylates, tosylates and pivalates.^[4] Until now, asymmetric variants of nickel-catalyzed Heck and reductive Heck reactions still remain under-developed and are limited to intramolecular cyclization. For instance, in 2017, Desrosiers and Kozlowski et al. reported a nickel chloride complex of QuinoxP* for enantioselective Heck

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cyclization of aryl halides to form oxindoles with quaternary stereocenters (Scheme 1a),^[5] but only a few examples with over 90% *ee* was reported. Lately, our group disclosed nickel/semicorrin catalysts for asymmetric reductive Heck cyclization of aryl halides, which afforded substituted indolines (see Scheme 1b) and indanones.^[6] More recently, Wang *et al.* applied nickel/PyrOx catalysts to enantioselective reductive cyclization of unactivated alkenes.^[7] Notably, recent years also witnessed a surge of interest in Ni-catalyzed asymmetric bifunctionalization of alkenes.^[8]

Herein, we disclose our finding on first examples of asymmetric *intermolecular* Heck reaction using nickel catalysts. Cheap aryl mesylates and tosylates, which are readily prepared from phenols, coupled efficiently, as well as more reactive aryl triflates. The nickel catalysts were also successfully applied to asymmetric intermolecular reductive Heck reaction of a ketal made from 2-cyclopentenone (Scheme 1c).



c) Asymmetric Intermolecular (reductive) Heck reaction of aryl sulfonates (this work)



Scheme 1. Nickel-catalyzed asymmetric Heck and reductive Heck reactions (OTf = trifluoromethanesulfonyl, Ts = *p*-toluenesulfonyl, OMs = methanesulfonyl, Cbz = benzyloxycarbamate)

For a model asymmetric Heck reaction, we initially chose 4-*t*butylphenyl mesylate **1a** and 2,3-dihydrofuran **3a** (Fig 1). After extensive screening of nickel catalysts, we were gratified to find that a complex of NiCl₂[(R, R)-QuinoxP*] efficiently catalyzed the model reaction to give desired product **4a** in 85% yield and 99%

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ee in DMSO at 100 °C. The ratio of three isomers of Heck products was 95/3/2 by GC and GCMS. The dominant isomer 4a was formed via extensive double bond migration of initial Heck adduct 4a' in situ. Aryl triflate and aryl tosylate also coupled as well to give 4a in good yield and excellent ee values, although about 10% of isomer 4a" was produced. However, when p-tolyl halides (CI, Br, and I) were tested under the same conditions, the desired isomer 4a decreased to about 70% among three isomers, unfortunately (Fig 1). A stoichiometric amount of zinc dust (particle size <10 µm; purchased from Aldrich) was also needed to generate the active Ni(0) catalyst and to reduce nickel hydride species back to nickel(0) at the end of each catalytic cycle, with co-production of hydrogen gas.[4f] Without zinc dust, no desired Heck adduct was detected. Notably, replacement by zinc powder, manganese powder or indium powder significantly reduced the yield of 4a. Moreover, addition of inorganic bases or alkylamines did not improve the process. We noticed that no Heck adduct was produced from the aryl mesylate in solvents other than DMSO (see Table 1). In the reaction of the aryl triflate, Heck adduct 4a was also formed in good yield in DMSO, but less than 10% in DMF or DMA.



Figure 1. Effect of aryl electrophiles on nickel-catalyzed Heck reaction with 2,3-dihydrofuran. 2.5 and 10 mol% nickel used for ArOTf and ArOTs.

With the optimal protocol in hand, we examined the scope of aryl triflates and mesylates with 2,3-dihydrofuran **3a**. As summarized in Scheme 2a, various aryl triflates and mesylates with alkyl groups on aryl rings smoothly reacted to afford the Heck products in good yield with excellent *ee* values (**4a-4g**). The configuration of the major Heck adducts was determined to be (*R*), by comparison with optical rotation data of known compounds.^[9] The methoxy ethers (**4h**, **4i** and **4k**), diaryl ether (**4j**), aryl fluoride (**4l** –**m**), benzotrifluoride (**4n**) and ester (**4o**) were all well tolerated. In the case of *p*-cyanophenyl triflate (**4p**), the formation of benzonitrile and biaryl accounted for the moderate yield of product **4p**. Additionally, a hindered dihydrobenzofur-7-yl mesylate provided adduct **4q** in 60% yield.

In the investigation of 2-naphthyl sulfonates and other aryl sulfonates carrying extended π rings under "standard" conditions described in Scheme 2a, 2-naphthyl triflate unfortunately afforded <30% yield of product **4r**, while 2-naphthyl mesylate and tosylate led to little products. The main side reaction was reduction to arenes. Later, we switched the pre-catalyst to a mixture of Ni(cod)₂ and (*R*,*R*)-Quinoxp*, and added diisopropylethylamine to convert nickel hydride species back to nickel(0) in the catalytic cycle. The reaction of 2-naphthyl triflate delivered products **4r** in

50% yield in DMSO, which was increased to 67% in DMF. 1-Naphthyl triflate also delivered products **4s** in a reasonable yield (Scheme 2b). Moreover, several quinolyl triflates also became suitable substrates (**4t**–**v**), but pyridyl triflates did not. To our delight, the modified procedure was also applicable to alkenyl triflates (**4w**–**z**), which were readily prepared from cyclic ketones.



Scheme 2. (a) Intermolecular Heck reaction of 2,3-dihydrofuran of (hetero)aryl triflates and mesylates; (b) Intermolecular Heck reaction of (hetero)aryl and alkenyl triflates with extended π systems (cod = 1,5-cyclooctadiene. DIPEA = *N*,*N*,*N*-di-isopropylethylamine)

Aryl tosylates are more stable towards bases than triflates during reactions and storage. The former are also much cheaper to prepare, but they need palladium catalysts ligated by strongly donating phosphines or *N*-heterocyclic carbenes for oxidative addition. We found that the nickel catalyst of QuinoxP* allowed aryl tosylates to react efficiently (Scheme 3). The aryl rings of tosylates can carry electron-withdrawing esters (4e, 6k), electrondonating groups of methoxy (4d) and dimethylamino (6l). In particular, *ortho* substituents can be present on aryl rings (6g–j). In those reactions, reduction to arenes were the main side reactions, which accounted for most of the rest material.

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Scheme 3. Examples of intermolecular Heck reaction of aryl tosylates and of 2,3-dihydrofuran.

The nickel chloride complex of QuinoxP* also catalyzed the arylation of *N*-Cbz-2,3-dihydropyrrole **3b** as well; in comparison, the more congested *N*-Boc derivative reacted very sluggishly. As shown in Scheme 4, aryl triflates bearing alkyl groups smoothly coupled to generate Heck products (**7a**–c) in reasonably good yields and excellent enantioselectivities. 2-Naphthyl triflate successfully coupled to afford **7d** in 67% yields and 91% ee. While electron-rich aryl triflates reacted efficiently, most electron-poor aryl electrophiles gave poor yields with an exception of 4-fluorophenyl triflate (**7e-g**). In cases that gave moderate yields, significant reduction to arenes was observed. Reactions with cyclopentene and cyclohexene, however, led to the formation of conjugated Heck isomers as major products, however. Both aryl mesylates and tosylates were also tested, but only low conversion was detected.



Scheme 4. Examples of intermolecular Heck of aryl triflates with *N*-Cbz-2,3-dihydropyrrole.

We also successfully applied nickel chloride complex of (*R*)-DuanPhos to asymmetric reductive Heck reaction of 2cyclopentenone ketal **3c** in dry DMSO. 1 equiv water was added to provide the proton to the final product, which improved reproducibility of the results (Scheme 5a). After ketal hydrolysis,

the reaction is equivalent to asymmetric conjugate arylation of cyclic enones using aryl electrophiles, which still remains an elusive process at present. We found that a nickel chloride complex of (R)-DuanPhos provided better yields and ee values of the products than that of (R,R)-QuinoxP*. Electron-rich aryl triflates reacted well (8a-d), as well as naphthyl and biphenyl derivatives (8e-f). Unfortunately, electron-deficient aryl triflates carrying trifluoromethyl and ester groups only afforded a trace amount of products. Cyclohexenone ketals did not react, either. We hypothesized that after aryl insertion, the nickel-carbon bond in the key intermediate was protonated by water to release the final products. When 2 equiv of D₂O was added to a catalytic reaction of 4-biphenyl triflate and 3c in DMSO, the β-hydrogen syn to the aryl ring in isolated product 8d contained 32% deuterium (33% deuterium before purification as estimated by GCMS). The low extent of deuteration is attributed to trace amounts of water in DMSO solvent. Consistent with this, no trace amount of deuterium was incorporated to the product from DMSO-d₆.



Scheme 5. Asymmetric reductive Heck reaction of aryl triflates and a 2-cyclopentenone ketal.

In our preliminary mechanistic studies, we found that $[NiCl_2(QuinoxP^*)]$ was quickly reduced by zinc dust at RT in DMSO to give a dark blue solution of $[NiCl(QuinoxP^*)]_2$ (³¹P singlet at 23.3 ppm). It didn't react with 4-methoxyphenyl mesylate at RT, while it reacted with the aryl triflate gave a complex, unidentifiable mixture unfortunately. Treatment of the above mixtures of aryl mesylate or triflate with 5 equiv dihydrofuran didn't afford any Heck adduct at RT. After heating at 100 °C for 10 h, Heck isomer **4a** was detected by GC in 30-60% yields and 93% *ee*. Additionally, $[Ni(cod)(QuinoxP^*)]$ (³¹P singlet at 34.0 ppm) was prepared from Ni(cod)₂ and QuinoxP*, but it didn't react with aryl mesylate or triflate at RT.

Next, we resorted to DFT calculations to examine insertion of of 2,3-dihydrofuran, in order to differentiate if a cationic phenylnickel(II) complex^[10] or a neutral phenylnikcel(I) complex^[4s,11] is the actual species for olefin insertion, at M06L/Def2TZVP, SMD(DMSO)//M06L/6-31g*,SDD(Ni) level. Some conclusions are drawn as follows. (a) Both Ni(II) and Ni(I) complexes leads to the (*R*)-isomer **4b** as the major (90% *ee* observed at 100 °C), with insertion barriers of 10.2 and 9.2 kcalmol⁻¹, respectively. (b) On the Ni(II) and Ni(I) pathways, the energy gap between diastereomeric transition states of insertion is 1.6 and 2.3 kcalmol⁻¹, respectively. (c) Both favored transition

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states of Ni(II) and Ni(I) leading to the (R)-isomer share very similar square planar geometry with some distortion (Figure 2). The bound alkene is accommodated in the quadrant defined by a P-methyl group of DuPhos, while the Ni-phenyl group is tilted towards the diagonal quadrant of the other P-methyl group. (d) The barrier of subsequent hydrogen elimination is larger on the Ni(II) pathway than Ni(I), in 11.2 and 4.1 kcalmol⁻¹, respectively. Thus, olefin isomerization along the nickel(I) pathway should be much more facile than that of nickel(II). (e) Experimentally, alkene insertion of 4-t-butylphenyl sulfonates gave adduct 4a in 99% ee (see Scheme 2). In calculations, energy gap between diastereomeric TSs for insertion of 4-t-butylphenyl nickel(II) and nickel(I) also increases to 2.3 and 2.7 kcalmol-1, respectively. In disfavored transition states of insertion of both pathways, a large P-t-butyl group pushes 2,3-dihydrofuran away from itself so that the alkene fragment is positioned well above the coordination plane; the other P-t-butyl group forces the Ni-aryl group to tilt in the guadrant of P-methyl group. No close contact between quinoxP* and the distal *t*-butyl group on the inserting aryl ring is identified, so we conclude excellent stereoselectivity of 4a is electronic in origin.

Overall, both nickel(I) and nickel(II) pathways seem to be plausible based on the calculations. Experimentally, Ni(cod)₂ and QuninoxP* cleanly formed a precatalyst [Ni(cod)(QuinoxP*)], which promoted Heck insertion of some aryl triflates at 100 °C, without adding a reductant such as zinc dust (see Scheme 2b). This led us to tentatively lean toward a classical nickel(0)/(II) shuttle.



Figure 2. Insertion transition states of a cationic phenylnickel(II) complex of (R)-DuPhos (right) and a neutral phenylnickel(I) complex (left), both leading to the major (R)-enantiomer.

In conclusion, we identified that nickel complexes ligated by strongly donating diphosphines were effective for intermolecular asymmetric Heck reaction of aryl triflates, mesylates and tosylates. The nickel complexes also promoted asymmetric reductive Heck arylation of a ketal of 2-cyclopentenone.

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Nickel catalysts efficiently promote enantioselective Heck reaction of aryl triflates, mesylates and tosylates in excellent *ee* values. Asymmetric reductive Heck reaction with a ketal of 2-cyclopentenone also proceeds well.

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