

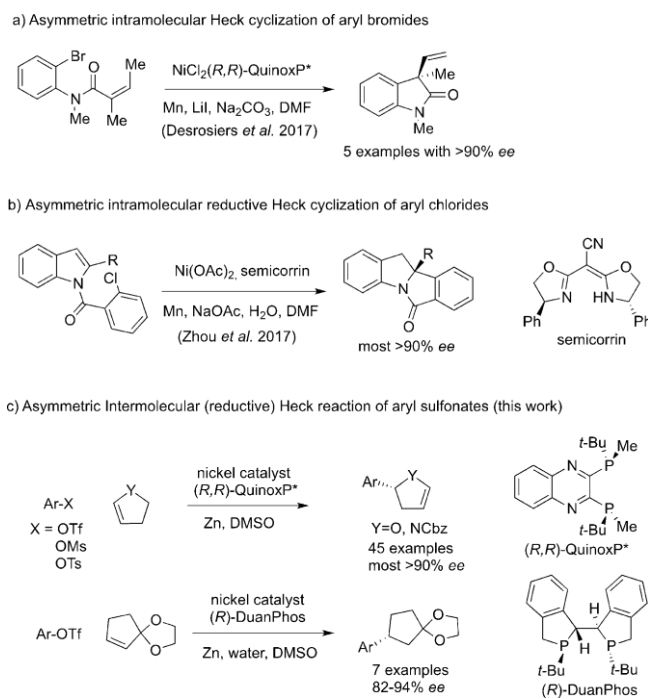
Heck Reactions

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<sup>[1]</sup> and reductive Heck reaction<sup>[2]</sup> allow arylation of alkenes with 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<sup>0</sup> to aryl C–O bonds of mesylates, tosylates and pivalates is exergonic and has lower barriers of oxidative addition than those of Pd<sup>0</sup>. In Heck reaction, *b*-insertion of aryl nickel(II) species to alkenes was calculated to have lower barriers than Pd<sup>II</sup>, but *b*-hydride elimination from alkyl nickel(II) species was more difficult than palladium(II).<sup>[3]</sup> To date, the mesylates and tosylates in palladium-catalyzed Heck reaction have been limited to alkenyl and electron-deficient heteroaryl ones.<sup>[4a]</sup> In contrast, nickel-catalyzed Heck reaction occurred smoothly with



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

[\*] Prof. Dr. J. S. Zhou

State Key Laboratory of Chemical Oncogenomics, Key Laboratory of Chemical Genomics, School of Chemical Biology and Biotechnology, Peking University Shenzhen Graduate School  
2199 Lishui Road, Room F312, Nanshan District, Shenzhen 518055 (China)

E-mail: jrzhou@pku.edu.cn

W. Xu, Prof. Dr. Y.-D. Wu

Lab of Computational Chemistry and Drug Design, State Key Laboratory of Chemical Oncogenomics, Peking University Shenzhen Graduate School  
Shenzhen (China)

Dr. M. Pu<sup>[+]</sup>

Shenzhen Bay Laboratory  
Shenzhen 518055 (China)

Dr. X. Huang, Dr. S. Teng,<sup>[+]</sup> Prof. Dr. Y. R. Chi

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University  
21 Nanyang Link, 637371, Singapore (Singapore)

[+] Co-first authors

Supporting information and the ORCID identification number(s) for



mesylates, tosylates and pivalates.<sup>[4]</sup> 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 Kozłowski et al. reported a nickel chloride complex of QuinoxP\* for enantioselective Heck cyclization of aryl halides which formed oxindoles with quaternary stereocenters (Scheme 1a),<sup>[5]</sup> 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.<sup>[6]</sup> More recently, Wang et al. applied nickel/PyrOx catalysts to enantioselective reductive cyclization of unactivated alkenes.<sup>[7]</sup> Notably, recent years also witnessed a surge of interest in Ni-catalyzed asymmetric bifunctionalization of alkenes with two different organohalides or sulfonates.<sup>[8]</sup>

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

# Communications



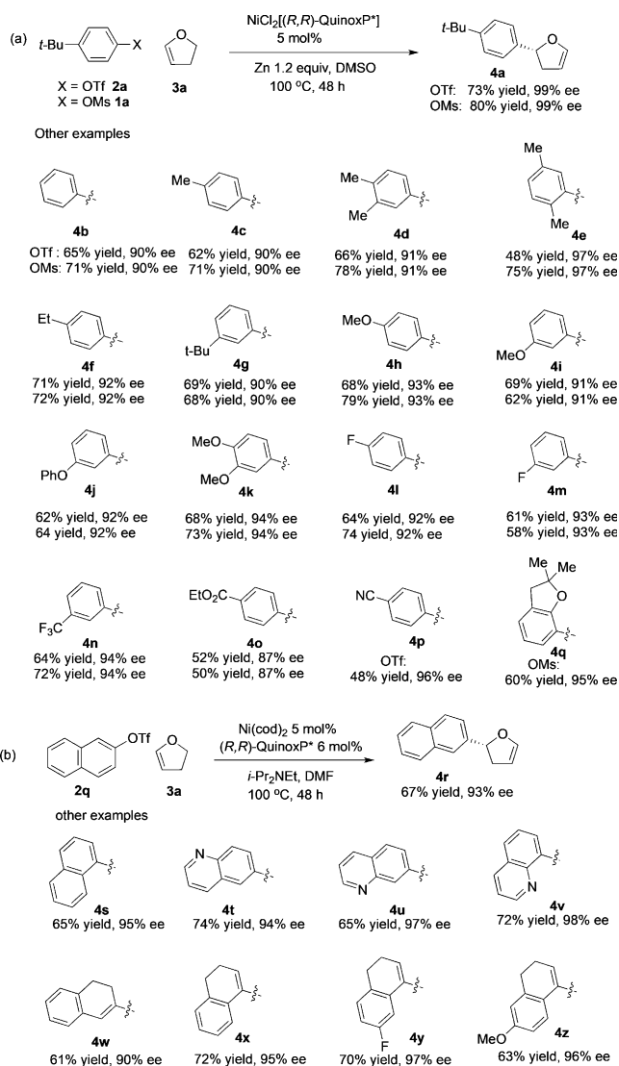
ArX	Yield of 4a (%)	Ee of 4a (%)	Ratio (4a/4a'/4a'')
<i>p</i> - <i>t</i> -BuC <sub>6</sub> H <sub>4</sub> OMs	85	99	95/3/2
<i>p</i> - <i>t</i> -BuC <sub>6</sub> H <sub>4</sub> OTf	77	99	86/1/13
<i>p</i> - <i>t</i> -BuC <sub>6</sub> H <sub>4</sub> OTs	70	99	86/2/12
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> Cl	34	92	70/14/16
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> Br	40	90	78/3/19
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> I	26	91	66/10/24

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, respectively.

reactive aryl triflates. The nickel catalysts were also successfully applied to asymmetric intermolecular reductive Heck reaction of a ketal made from 2-cyclopentenone (Scheme 1 c).

For a model asymmetric Heck reaction, we initially chose 4-*t*-butylphenyl mesylate 1a and 3 equiv of 2,3-dihydrofuran 3a (Figure 1). After extensive screening of nickel catalysts, we were gratified to find that a complex of NiCl<sub>2</sub>[(*R,R*)-QuinoxP\*] efficiently catalyzed the model reaction to give desired product 4a in 85 % yield and 99 % 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 (Cl, Br, and I) were tested under the same conditions, the desired isomer 4a decreased to about 70 % among three isomers, unfortunately (Figure 1). Stoichiometric amount of zinc dust (particle size < 10 μm; purchased from Aldrich) was also needed to generate the active Ni<sup>0</sup> catalyst and to reduce nickel hydride species back to nickel(0) at the end of each catalytic cycle, with co-production of hydrogen gas.<sup>[4f]</sup> 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 the Supporting Information). 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.

With the optimal protocol in hand, we examined the scope of aryl triflates and mesylates with 2,3-dihydrofuran 3a. As summarized in Scheme 2 a, 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.<sup>[9]</sup> 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

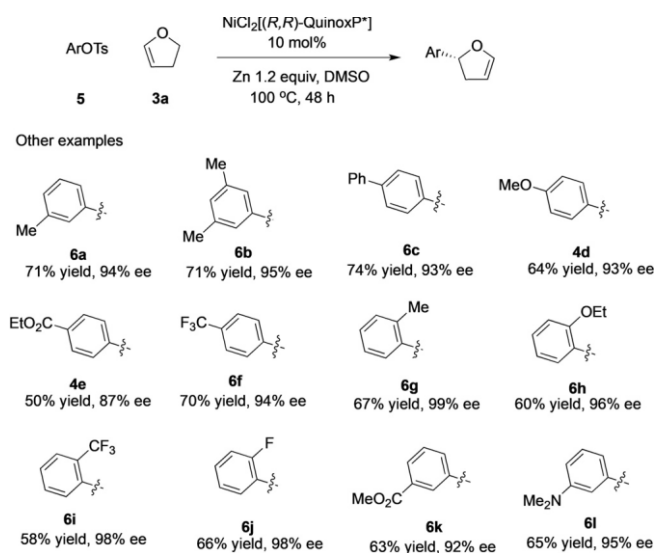


Scheme 2. a) Intermolecular Heck reaction of 2,3-dihydrofuran of (hetero)aryl triflates and mesylates; b) Intermolecular Heck reaction of (hetero)aryl and alkenyl triflates with extended *p* systems (cod = 1,5-cyclooctadiene). DIPEA = *N,N,N*-di-isopropylethylamine).

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 *p* rings under “standard” conditions described in Scheme 2 a, 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)<sub>2</sub> 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 2 b). 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.

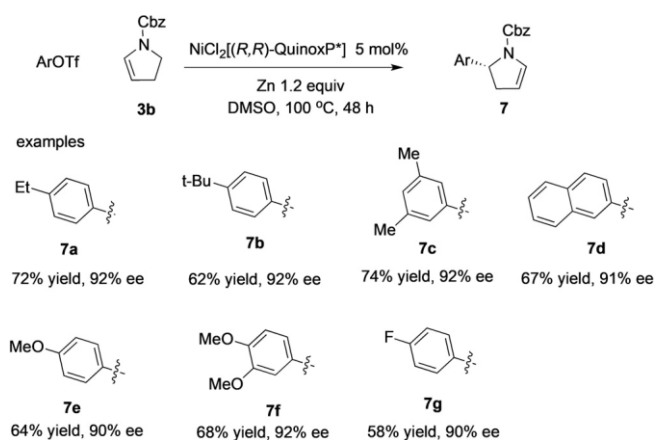
# Communications



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

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 (4 e, 6 k), electron-donating groups of methoxy (4 d) and dimethylamino (6 l). In particular, *ortho* substituents can be present on aryl rings (6 g–j). In those reactions, reduction to arenes were the main side reactions, which accounted for most of the rest material.

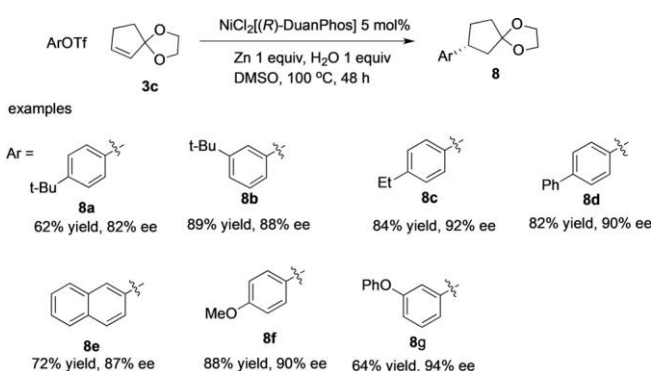
The nickel chloride complex of QuinoxP\* also catalyzed the arylation of *N*-Cbz-2,3-dihydropyrrole 3b as well; in comparison, the more congested *N*-Boc derivative reacted very sluggishly. As shown in Scheme 4, aryl triflates bearing alkyl groups smoothly coupled to generate Heck products (7 a–c) in reasonably good yields and excellent enantioselectivities. 2-Naphthyl triflate successfully coupled to afford 7d



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

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 (7 e–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.

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



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

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 (8 a–d), as well as naphthyl and biphenyl derivatives (8 e–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 D<sub>2</sub>O was added to a catalytic reaction of 4-biphenyl triflate and 3c in DMSO, the *b*-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 [D<sub>6</sub>]DMSO.

In our preliminary mechanistic studies, we found that [NiCl<sub>2</sub>(QuinoxP\*)] was quickly reduced by zinc dust at RT in DMSO to give a dark blue solution of [NiCl(QuinoxP\*)]<sub>2</sub> (<sup>31</sup>P singlet at 23.3 ppm). It didn't react with 4-methoxyphenyl mesylate at RT, while it reacted with the aryl triflate gave a quite complex 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\*)] (<sup>31</sup>P singlet at 34.0 ppm) was prepared from Ni(cod)<sub>2</sub> and QuinoxP\*, but it didn't react with aryl mesylate or triflate at RT.

Next, we resorted to DFT calculations to examine insertion of 2,3-dihydrofuran, in order to differentiate whether a cationic phenylnickel(II) complex<sup>[10]</sup> or a neutral phenylnickel(I) complex<sup>[45,11]</sup> 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<sup>II</sup> and Ni<sup>I</sup> 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 kcal mol<sup>-1</sup>, respectively. (b) On the Ni<sup>II</sup> and Ni<sup>I</sup> pathways, the energy gap between diastereomeric transition states of insertion is 1.6 and 2.3 kcal mol<sup>-1</sup>, respectively. (c) Both favored transition states of Ni<sup>II</sup> and Ni<sup>I</sup> leading to the (*R*)-isomer share very similar square planar geometry with some distortion (Figure 2). The bound alkene is accommo-

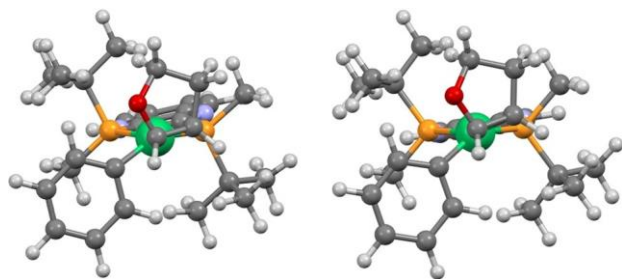


Figure 2. Calculated insertion transition states of a cationic phenylnickel(II) complex of (*R*)-DuPhos (right) and a neutral phenylnickel(I) complex (left), both leading to the major (*R*)-enantiomer.

dated in the top-right quadrant defined by a *P*-methyl group of DuPhos, while the Ni-phenyl group is *tilted* in the diagonal quadrant of the other *P*-methyl group. (d) The barrier of subsequent hydrogen elimination is larger on the Ni<sup>II</sup> pathway than Ni<sup>I</sup>, in 11.2 and 4.1 kcal mol<sup>-1</sup>, 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 kcal mol<sup>-1</sup>, respectively. In disfavored transition states of insertion of both pathways, a large *P*-*t*-butyl group in the bottom-right quadrant 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 bottom-left quadrant of *P*-methyl group. No close contact between quinoxP\* and the distal *t*-butyl group on the inserting Ni-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)<sub>2</sub> and QuinoxP\* 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 2 b). This led us to tentatively lean toward a classical nickel(0)/(II) shuttle at least under the aforementioned conditions in Scheme 2b.

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 in the presence of water as proton source.

## Acknowledgements

We acknowledge financial supports from Peking University Shenzhen Graduate School, Shenzhen Bay Laboratory Institute of Chemical Biology, Nanyang Technological University, GlaxoSmithKline and the Singapore Economic Development Board Trust Fund (2017 GSK-EDB Green and Sustainable Manufacturing Award) and A\*STAR Science and Engineering Research Council (A1783c0010).

## Conflict of interest

The authors declare no conflict of interest.

Keywords: aryl halides · aryl sulfonates · Heck reaction · nickel catalysis · reductive Heck reaction

- [1] Reviews and examples: a) O. Loiseleur, M. Hayashi, N. Schmees, A. Pfaltz, *Synthesis* 1997, 1338; b) O. Loiseleur, M. Hayashi, M. Keenan, N. Schmees, A. Pfaltz, *J. Organomet. Chem.* 1999, 576, 16; c) A. B. Dounay, L. E. Overman, *Chem. Rev.* 2003, 103, 2945; d) M. Shibasaki, E. M. Vogl, T. Ohshima, *Adv. Synth. Catal.* 2004, 346, 1533; e) L. F. Tietze, H. Ila, H. P. Bell, *Chem. Rev.* 2004, 104, 3453; f) D. Mc Cartney, P. J. Guiry, *Chem. Soc. Rev.* 2011, 40, 5122; g) E. W. Werner, T.-S. Mei, A. J. Burckle, M. S. Sigman, *Science* 2012, 338, 1455; h) Z. Yang, J. Zhou, *J. Am. Chem. Soc.* 2012, 134, 11833; i) J. Hu, H. Hirao, Y. Li, J. Zhou, *Angew. Chem. Int. Ed.* 2013, 52, 8676; *Angew. Chem.* 2013, 125, 8838; j) C. Wu, J. Zhou, *J. Am. Chem. Soc.* 2014, 136, 650; k) C. C. Oliveira, A. Pfaltz, C. R. D. Correia, *Angew. Chem. Int. Ed.* 2015, 54, 14036; *Angew. Chem.* 2015, 127, 14242; l) Z. Jiao, Q. Shi, J. S. Zhou, *Angew. Chem. Int. Ed.* 2017, 56, 14567; *Angew. Chem.* 2017, 129, 14759.
- [2] a) A. Minatti, X. Zheng, S. L. Buchwald, *J. Org. Chem.* 2007, 72, 9253; b) S. Liu, J. Zhou, *Chem. Commun.* 2013, 49, 11758; c) C. Shen, R.-R. Liu, R.-J. Fan, Y.-L. Li, T.-F. Xu, J.-R. Gao, Y.-X. Jia, *J. Am. Chem. Soc.* 2015, 137, 4936; d) W. Kong, Q. Wang, J. Zhu, *Angew. Chem. Int. Ed.* 2017, 56, 3987; *Angew. Chem.* 2017, 129, 4045; e) S. Mannathan, S. Raouf moghaddam, J. N. H. Reek, J. G. de Vries, A. J. Minnaard, *ChemCatChem* 2017, 9, 551; f) Z.-M. Zhang, B. Xu, Y. Qian, L. Wu, Y. Wu, L. Zhou, Y. Liu, J. Zhang, *Angew. Chem. Int. Ed.* 2018, 57, 10373; *Angew. Chem.* 2018, 130, 10530; g) T. Ghosh, *ChemistrySelect* 2019, 4, 4747; h) L. J. Oxtoby, J. A. Gurak, Jr., S. R. Wisniewski, M. D. Eastgate, K. M. Engle, *Trends Chem.* 2019, 1, 572; i) Z. Yuan, Z. Feng, Y. Zeng, X. Zhao, A. Lin, H. Yao, *Angew. Chem. Int. Ed.* 2019, 58, 2884; *Angew. Chem.* 2019, 131, 2910; j) X. Huang, M. H. Nguyen, M. Pu, L. Zhang, Y. R. Chi, Y.-D. Wu, J. S. Zhou,

- Angew. Chem. Int. Ed.* 2020, *59*, 10814; *Angew. Chem.* 2020, *132*, 10906.
- [3] Calculations and experiments on elementary steps catalyzed by nickel: a) B.-L. Lin, L. Liu, Y. Fu, S.-W. Luo, Q. Chen, Q.-X. Guo, *Organometallics* 2004, *23*, 2114; b) V.H. Menezes da Silva, A. A. C. Braga, T. R. Cundari, *Organometallics* 2016, *35*, 3170; c) A. B. Durr, G. Yin, I. Kalvet, F. Napoly, F. Schoenebeck, *Chem. Sci.* 2016, *7*, 1076; d) S. Bajo, G. Laidlaw, A. R. Kennedy, S. Sproules, D. J. Nelson, *Organometallics* 2017, *36*, 1662; e) X. Li, X. Hong, *J. Organomet. Chem.* 2018, *864*, 68; f) K. D. Vogiatzis, M. V. Polynski, J. K. Kirkland, J. Townsend, A. Hashemi, C. Liu, E. A. Pidko, *Chem. Rev.* 2019, *119*, 2453.
- [4] A review on Pd-catalyzed Heck reaction of mesylates and tosylates: a) B.-J. Li, D.-G. Yu, C.-L. Sun, Z.-J. Shi, *Chem. Eur. J.* 2011, *17*, 1728; reviews on nickel-catalyzed Heck reaction: b) S. Z. Tasker, E. A. Standley, T. F. Jamison, *Nature* 2014, *509*, 299; c) A. L. Clevenger, R. M. Stolley, J. Aderibigbe, J. Louie, *Chem. Rev.* 2020, *120*, 6124; d) S. Bhakta, T. Ghosh, *Adv. Synth. Catal.* 2020, <https://doi.org/10.1002/adsc.202000820>; Examples of nickel-catalyzed Heck reaction: e) G. P. Boldrini, D. Savoia, E. Tagliavini, C. Trombini, A. U. Ronchi, *J. Organomet. Chem.* 1986, *301*, C62; f) S. A. Lebedev, V. S. Lopatina, E. S. Petrov, I. P. Beletskaya, *J. Organomet. Chem.* 1988, *344*, 253; g) S. Iyer, C. Ramesh, A. Ramani, *Tetrahedron Lett.* 1997, *38*, 8533; h) T. M. Gøgsig, J. Kleimark, S. O. Nilsson Lill, S. Korsager, A. T. Lindhardt, P.-O. Norrby, T. Skrydstrup, *J. Am. Chem. Soc.* 2012, *134*, 443; i) R. Matsubara, A. C. Gutierrez, T. F. Jamison, *J. Am. Chem. Soc.* 2011, *133*, 19020; j) see Ref. [1h]; k) aryl pivalates: A. R. Ehle, Q. Zhou, M. P. Watson, *Org. Lett.* 2012, *14*, 1202; l) R. Lhermet, M. Durandetti, J. Maddaluno, *Beilstein J. Org. Chem.* 2013, *9*, 710; m) R. Shrestha, S. C. M. Dorn, D. J. Weix, *J. Am. Chem. Soc.* 2013, *135*, 751; n) benzylic ethers: M. R. Harris, M. O. Konev, E. R. Jarvo, *J. Am. Chem. Soc.* 2014, *136*, 7825; o) aryl mesylates, tosylates and sulfamates: S. Z. Tasker, A. C. Gutierrez, T. F. Jamison, *Angew. Chem. Int. Ed.* 2014, *53*, 1858; *Angew. Chem.* 2014, *126*, 1889; p) J.-N. Desrosiers, L. Hie, S. Biswas, O. V. Zatolochnaya, S. Rodriguez, H. Lee, N. Grinberg, N. Haddad, N. K. Yee, N. K. Garg, C. H. Senanayake, *Angew. Chem. Int. Ed.* 2016, *55*, 11921; *Angew. Chem.* 2016, *128*, 12100; q) K. M. M. Huihui, R. Shrestha, D. J. Weix, *Org. Lett.* 2017, *19*, 340; r) J. M. Medina, J. Moreno, S. Racine, S. Du, N. K. Garg, *Angew. Chem. Int. Ed.* 2017, *56*, 6567; *Angew. Chem.* 2017, *129*, 6667; s) B. R. Walker, C. S. Sevov, *ACS Catal.* 2019, *9*, 7197.
- [5] J.-N. Desrosiers, J. Wen, S. Tcyrulnikov, S. Biswas, B. Qu, L. Hie, D. Kuroski, L. Wu, N. Grinberg, N. Haddad, C. A. Busacca, N. K. Yee, J. J. Song, N. K. Garg, X. Zhang, M. C. Kozlowski, C. H. Senanayake, *Org. Lett.* 2017, *19*, 3338.
- [6] Examples: a) X. Qin, M. W. Y. Lee, J. S. Zhou, *Angew. Chem. Int. Ed.* 2017, *56*, 12723; *Angew. Chem.* 2017, *129*, 12897; b) X. Qin, M. W. Yao Lee, J. S. Zhou, *Org. Lett.* 2019, *21*, 5990.
- [7] F. Yang, Y. Jin, C. Wang, *Org. Lett.* 2019, *21*, 6989.
- [8] Examples: a) K. Wang, Z. Ding, Z. Zhou, W. Kong, *J. Am. Chem. Soc.* 2018, *140*, 12364; b) D. Anthony, Q. Lin, J. Baudet, T. Diao, *Angew. Chem. Int. Ed.* 2019, *58*, 3198; *Angew. Chem.* 2019, *131*, 3230; c) Y. Jin, C. Wang, *Angew. Chem. Int. Ed.* 2019, *58*, 6722; *Angew. Chem.* 2019, *131*, 6794; d) Y. Li, Z. Ding, A. Lei, W. Kong, *Org. Chem. Front.* 2019, *6*, 3305; e) T. Ma, Y. Chen, Y. Li, Y. Ping, W. Kong, *ACS Catal.* 2019, *9*, 9127; f) Z.-X. Tian, J.-B. Qiao, G.-L. Xu, X. Pang, L. Qi, W.-Y. Ma, Z.-Z. Zhao, J. Duan, Y.-F. Du, P. Su, X.-Y. Liu, X.-Z. Shu, *J. Am. Chem. Soc.* 2019, *141*, 7637; g) Y. Jin, H. Yang, C. Wang, *Org. Lett.* 2020, *22*, 2724; h) X. Qi, T. Diao, *ACS Catal.* 2020, *10*, 8542; i) K. E. Poremba, S. E. Dibrell, S. E. Reisman, *ACS Catal.* 2020, *10*, 8237; j) H.-Y. Tu, F. Wang, L. Huo, Y. Li, S. Zhu, X. Zhao, H. Li, F.-L. Qing, L. Chu, *J. Am. Chem. Soc.* 2020, *142*, 9604; k) X. Wei, W. Shu, A. Garcia-Dominguez, E. Merino, C. Nevado, *J. Am. Chem. Soc.* 2020, *142*, 13515.
- [9] F. Ozawa, A. Kubo, T. Hayashi, *J. Am. Chem. Soc.* 1991, *113*, 1417.
- [10] Examples of arylnickel(II) halide complexes of diphosphines: a) T. J. Bruncker, N. F. Blank, J. R. Moncarz, C. Scriban, B. J. Anderson, D. S. Glueck, L. N. Zakharov, J. A. Golen, R. D. Sommer, C. D. Incarvito, A. L. Rheingold, *Organometallics* 2005, *24*, 2730; b) E. A. Standley, S. J. Smith, P. Muller, T. F. Jamison, *Organometallics* 2014, *33*, 2012.
- [11] Arylnickel(I) complexes of diphosphines: a) M. Mohadjer Beromi, G. Banerjee, G. W. Brudvig, N. Hazari, B. Q. Mercado, *ACS Catal.* 2018, *8*, 2526; b) J. B. Diccianni, J. Katigbak, C. Hu, T. Diao, *J. Am. Chem. Soc.* 2019, *141*, 1788.