

Asymmetric Catalysis

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An Iridium(I) N-Heterocyclic Carbene Complex Catalyzes Asymmetric Intramolecular Allylic Amination Reactions

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Abstract: A chiral iridium(I) N-heterocyclic carbene complex was reported for the first time as the catalyst in the highly enantioselective intramolecular allylic amination reaction. The current method provides facile access to biologically important enantioenriched indolopiperazinones and piperazinones in good yields (74–91 %) and excellent enantioselectivities (92–99 % ee). Preliminary mechanistic investigations reveal that the C–H activation occurs at the position ortho to the N-aryl group of the ligand.

Iridium-catalyzed allylic substitution reactions featuring high regio- and enantioselective control for a broad scope of nucleophiles with disubstituted *E*-allylic substrates have witnessed significant progress during the past decade.^[1,2] Since the first asymmetric reaction enabled by an Ir/Phox complex, introduced by the group of Helmchen,^[3] the development of chiral ligands has been one of the most important tasks in this field. Among the many chiral ligands used, the bulk of work on iridium-catalyzed allylic substitution reactions mainly focused on catalysts derived from chiral phosphoramidite ligands, represented by the Feringa^[4]/Alexakis^[5] P,C ligands and Carreira P,olefin ligand^[6] (Figure 1). In

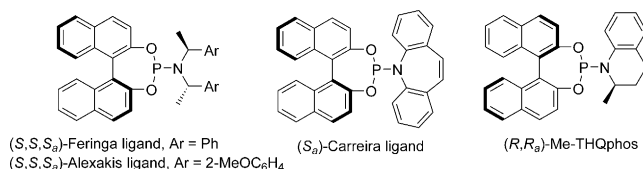


Figure 1. Phosphoramidite ligands in iridium-catalyzed allylic substitution reactions.

particular, the Feringa and Alexakis ligands have been proven to be privileged ones, thus affording excellent regio- and enantioselectivity. Mechanistic studies disclosed that the iridium complex formed by C–H activation, that is, addition

of iridium center into the C(sp³)–H bond in the methyl group of the amine part of the ligand, is the active catalytic species.^[7] Inspired by these findings, our group developed an N-aryl phosphoramidite (Me-THQphos; Figure 1) from which the active complex is formed by C(sp²)–H activation of the N-aryl group in the ligand.^[8] The same C(sp²)–H activation mode was also identified in the iridium complex derived from BHPphos.^[9] These findings suggest that C(sp²)–H activation is a useful strategy when designing new chiral ligands for iridium-catalyzed enantioselective allylic substitution reactions.

N-Heterocyclic carbenes (NHCs) have witnessed rapid development in the last decade both as ligands^[10] and organocatalysts.^[11] However, chiral NHCs have not been employed in the iridium-catalyzed asymmetric allylic substitution reactions,^[12] despite rare examples in palladium catalysis^[13] and extensive studies in copper catalysis.^[14] As part of our ongoing program towards iridium-catalyzed allylic substitution reactions,^[15] we envisaged that chiral NHCs would be promising ligands for iridium and the corresponding Ir/NHC complexes might be efficient catalysts in allylic substitution reactions. Herein, we report the first example of using an iridium(I) N-heterocyclic carbene complex as the catalyst for the highly enantioselective intramolecular allylic amination reaction of indoles and pyrroles.

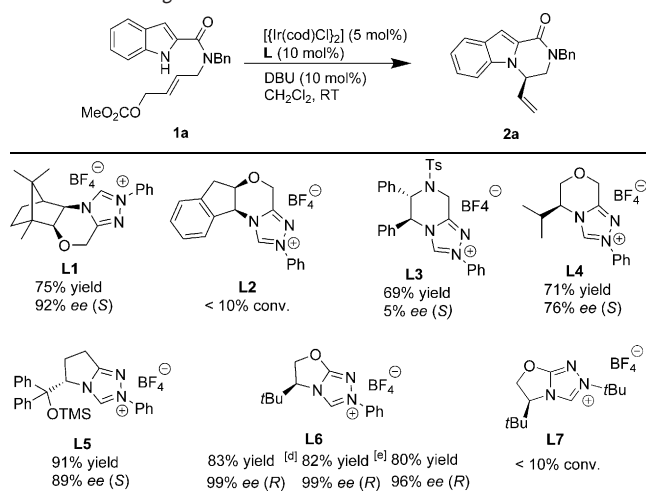
Iridium-catalyzed asymmetric intramolecular allylic amination reactions can provide facile access to versatile biologically important enantioenriched N-containing heterocycles.^[16] Instead of aliphatic amines and anilines generally used as the nucleophiles, we began our study on the Ir/NHC complex catalyzed intramolecular enantioselective allylic amination reaction by utilizing the indole **1a** as a model substrate (Table 1). The results of examining NHCs derived from different triazolium salts are summarized as shown. To our delight, in the presence of 5 mol % of [Ir(cod)Cl]₂, 10 mol % of **L1**,^[17] and 10 mol % of DBU, the reaction of **1a** in CH₂Cl₂ at room temperature afforded the desired allylic amination product **2a** in 75 % yield and 92 % ee without the observation of Friedel–Crafts alkylation reaction at C3 of the indole. Only trace amounts of **2a** were formed with the amino-indanol-derived triazolium salt **L2**.^[18] The reaction proceeded smoothly with the (1*R*,2*R*)-DPEN-derived triazolium salt **L3**,^[19] however, the asymmetric induction was negligible. The ee value was increased to 76 % and 89 % with **L4**^[20] and **L5**,^[21] respectively, as the chiral ligand precursor. When the *L*-*t*-butylalaninol-derived triazolium salt **L6**, introduced by the group of Enders,^[22] was used, the reaction afforded **2a** in 82 % yield and with 99 % ee. No deleterious effect of yield and enantioselectivity was observed with 2.5 mol % of [Ir(cod)Cl]₂. The reaction with 1.25 mol %

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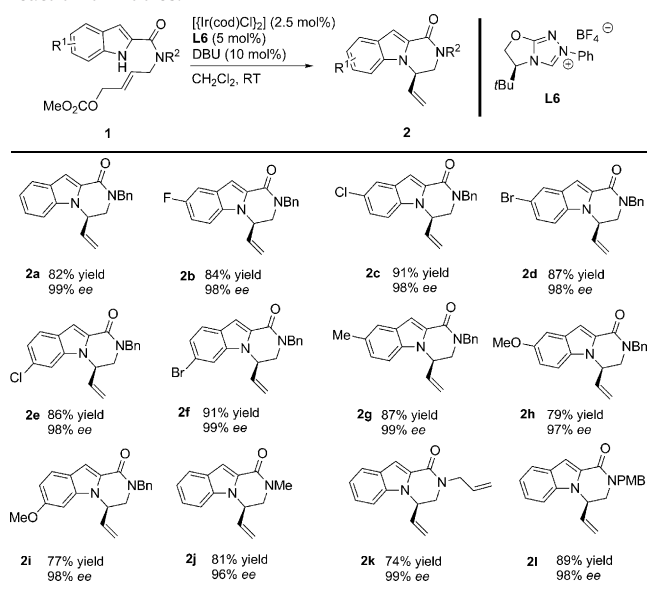
Table 1: Screening of various chiral triazolium salts.^[a,b,c]

[a] Reaction conditions: $[(\text{Ir}(\text{cod})\text{Cl})_2]/\text{L}/\textbf{1a}/\text{DBU} = 0.05:0.1:1.0:0.1$, 0.1 M of **1a** in CH_2Cl_2 . [b] Yield of isolated product. [c] The ee value was determined by HPLC analysis. [d] 2.5 mol % of $[(\text{Ir}(\text{cod})\text{Cl})_2]$ used. [e] 1.25 mol % of $[(\text{Ir}(\text{cod})\text{Cl})_2]$ used. cod = 1,5-cyclooctadiene, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, TMS = trimethylsilyl.

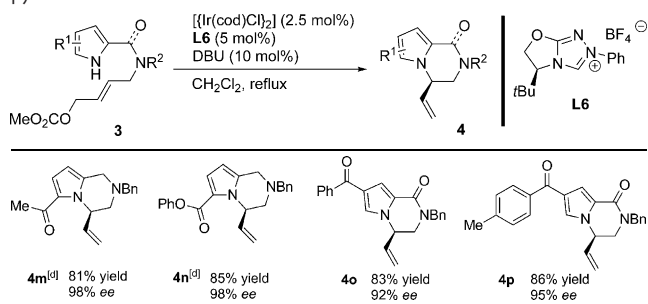
$[(\text{Ir}(\text{cod})\text{Cl})_2]$ also led to **2a** in 96% ee. However, when the triazolium salt **L7** bearing an N-*t*-butyl group was used, no detectable product was observed. Notably, the commonly used phosphoramidite ligands only afforded moderate enantioselectivities in this reaction (see Table S1 in the Supporting Information).

Under the optimal reaction conditions (2.5 mol % of $[(\text{Ir}(\text{cod})\text{Cl})_2]$, 5 mol % of **L6**, 0.2 mmol of **1**, and 10 mol % of DBU in 2 mL CH_2Cl_2 at room temperature), the substrate scope was examined (Table 2). Indole-derived substrates bearing either an electron-withdrawing group (5-F, 5-Cl, 5-Br, 6-Cl, 6-Br; **2b–f**) or an electron-donating group (5-Me, 5-MeO, 6-MeO; **2g–i**) on the phenyl ring of the indoles were well tolerated and led to their corresponding indolopiperazinones in good yields (77–91%) and excellent enantioselectivities (97–99% ee). In addition, substrates with various substituents on the amide N (Bn, Me, allyl, and PMB; **2a, 2j–l**) also reacted smoothly to afford amination products in good yields (74–89%) with excellent enantioselectivities (96–99% ee). In addition, when the substrates **1m** and **1n**, designed, respectively for a seven- and eight-membered ring formation of the intramolecular amination products, were applied, no reaction occurred.

Notably, pyrrole-derived substrates are less reactive compared with indoles but still well tolerated (Table 3). Under the standard reaction conditions, only moderate conversions were observed with pyrrole substrates. By increasing the catalyst loading (5 mol % of $[(\text{Ir}(\text{cod})\text{Cl})_2]$) and the reaction temperature (reflux), the piperazines **4m** and **4n** were obtained in good yields (81–85%) and excellent enantioselectivities (98% ee). Introducing an extra electron-withdrawing group on the pyrrole ring resulted in a lower pK_a value of the NH of pyrrole, thus increasing the reaction rate. Therefore, the cyclization of the substrates **3o** and **3p**

Table 2: Substrate scope of the iridium-catalyzed allylic amination reaction of indoles.^[a,b,c]

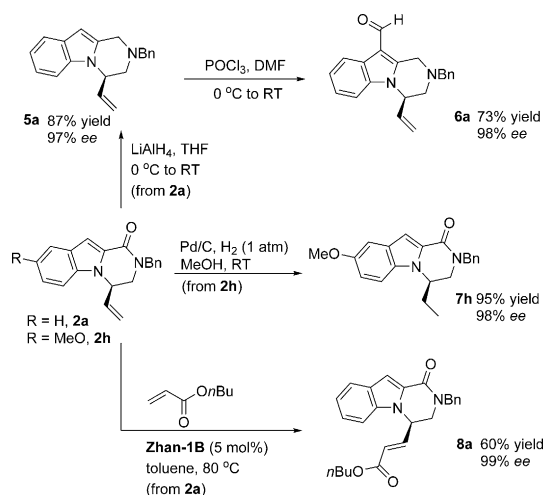
[a] Reaction conditions: $[(\text{Ir}(\text{cod})\text{Cl})_2]/\text{L6}/\textbf{1}/\text{DBU} = 0.025:0.05:1.0:0.1$, 0.1 M of **1** in CH_2Cl_2 at room temperature. [b] Yield is that of isolated product. [c] The ee value was determined by HPLC analysis. PMB = *p*-methoxybenzyl.

Table 3: Substrate scope of iridium-catalyzed allylic amination of pyrroles.^[a,b,c]

[a] Reaction conditions: $[(\text{Ir}(\text{cod})\text{Cl})_2]/\text{L6}/\textbf{3}/\text{DBU} = 0.025:0.05:1.0:0.1$, 0.1 M of **3** in CH_2Cl_2 at refluxed temperature. [b] Yield is that of isolated product. [c] The ee value was determined by HPLC analysis. [d] 5 mol % of $[(\text{Ir}(\text{cod})\text{Cl})_2]$ used.

proceeded smoothly to afford the **4o** and **4p**, respectively, in the presence of 2.5 mol % of $[(\text{Ir}(\text{cod})\text{Cl})_2]$ and 5 mol % of **L6**.

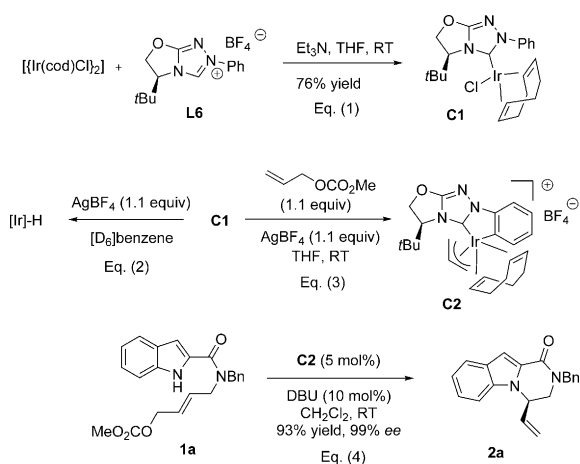
The resulting indolopiperazinones^[23,24] could further undergo versatile transformations (Scheme 1). Treating **2a** with LiAlH_4 led to the corresponding indole-fused piperazine **5a**. The indolyl C3-position could be further functionalized with a formyl group by a Vilsmeier–Haack reaction in 73% yield (**6a**). The double bond of the enantioenriched allylic indolopiperazinones could be easily hydrogenated with Pd/C in methanol at room temperature in 95% yield (**7h**). An olefin cross-metathesis reaction of **2a** and *n*-butyl acrylate afforded the α,β -unsaturated ester **8a** in 60% yield. It is worth mentioning that there is no notable loss of enantiomeric purity for any of the above-mentioned transformations.



Scheme 1. Transformations of the products. DMF = *N,N*-dimethylformamide, THF = tetrahydrofuran.

The iridium(I) NHC complex **C1** can be conveniently synthesized in 76% yield by treating $[\text{Ir}(\text{cod})\text{Cl}]_2$ with **L6** in the presence of Et_3N [Eq. (1)]. **C1** is not sensitive to oxygen and moisture and can be subjected to alumina column chromatography for purification. The structure of **C1** was confirmed by X-ray diffraction analysis (see the Supporting Information).^[25]

A preliminary mechanistic study was carried out to shed light on the active catalytic species. To probe the possible existence of the C–H activation of the catalyst, we treated **C1** with AgBF_4 in $[\text{D}_6]\text{benzene}$. A singlet at $\delta = -35.6$ ppm was observed by ^1H NMR spectroscopy after 10 minutes and it was assigned as a hydride [Eq. (2)]. In addition, when **C1** was treated with AgBF_4 and allyl methyl carbonate in THF at room temperature for 24 h, **C2** with $\text{C}(\text{sp}^2)\text{--H}$ activation of the N-aryl group in the ligand was obtained after simple filtration [Eq. (3)]. The complex **C2** was fully characterized by NMR spectroscopy (see the Supporting Information). This air- and moisture-sensitive species **C2** was able to catalyze the allylic substitution reaction of **1a** [93% yield, 99% ee; Eq. (4)], and is comparable to the results obtained with the in situ formed catalyst.



In summary, this study introduces the chiral triazolium salts as a class of efficient NHC ligands for iridium-catalyzed asymmetric allylic substitution reactions and provides facile access to biologically important enantioenriched indolopiperazinones and piperazinones in good yields and excellent enantioselectivities. Preliminary mechanistic investigation revealed that C–H activation occurs at the *ortho*-position of the N-aryl group of the ligand. An in-depth mechanistic investigation and further applications of Ir/NHC complexes are in progress.

Experimental Section

General procedure for the iridium-catalyzed allylic amination reaction of indoles: A flame-dried Schlenk tube was cooled to room temperature and filled with argon. To this flask were added $[\text{Ir}(\text{cod})\text{Cl}]_2$ (3.4 mg, 0.005 mmol, 2.5 mol %), chiral triazolium salt **L6** (3.3 mg, 0.01 mmol, 5 mol %), **1** (0.20 mmol), DBU (3.1 mg, 0.02 mmol), and CH_2Cl_2 (2 mL). The reaction mixture was stirred at RT. After the reaction was complete (monitored by TLC), the solvents were evaporated in vacuo. The crude reaction mixture was filtrated through celite and washed with EtOAc. The solvents were removed under reduced pressure. Then the residue was purified by silica gel column chromatography to afford the product (eluent: petroleum ether/EtOAc = 4:1).

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Keywords: allylic compounds · asymmetric catalysis · enantioselectivity · iridium · N-heterocyclic carbenes

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- [25] CCDC 1447452 (C1) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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