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Design and synthesis of Indol-PHOX: a new class of modular phosphine–oxazoline ligands for palladium-catalyzed enantioselective decarboxylative allylation

Anzhela Karapetyan,[a] Laura Borrel,[b] Virginie Ratovelomanana-Vidal,[a] Phannarath Phansavath,*[a] Tahar Ayad[b] and David Virieux*[b]

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A novel class of chiral and modular P,N-ligands featuring an indolizine core (Indol-PHOX) has been developed, successfully enabling the highly efficient and enantioselective palladium-catalyzed decarboxylative allylation of various α-fluoro-β-ketoesters to access valuable α-allyl-α-fluoro ketones with yields up to 99% and 96% ee. This process exhibits a broad substrate scope, demonstrating good tolerance for both electron-withdrawing and electron-donating groups, as well as substitution patterns of the substrates. The reaction is scalable to the gram level, and subsequent post-functionalization reactions proceed successfully without erosion of enantiopurity.

Introduction

The development of numerous single-enantiomer drugs, along with a broad spectrum of other biologically active substances—including agrochemicals, pheromones, flavors, and fragrances—has been driven by significant advancements in asymmetric catalysis conducted over the past decades.[1] Central to this progress is the design and synthesis of cost-effective ligands that are readily prepared and can be swiftly tailored for a specific chemical transformation. Among the plethora of reported ligands,[2] chiral P,N-ligands, in particular, have gained particular prominence due to their dual functionality, combining the benefits of both phosphorus and nitrogen coordinating atoms.[3] One significant example is the chiral phosphine–oxazoline (PHOX) ligands, which were introduced independently by Pfaltz,[4] Helmchen,[5] and Williams[6] in 1993. These ligands coordinate to transition metals through both electronically hard nitrogen and soft phosphorus atoms. They have demonstrated remarkable efficacy as chiral inducers across a wide range of transition metal-catalyzed reactions. Moreover, their modular design allows for easy fine-tuning of geometric, steric and electronic properties by modifying various components of the ligand scaffold, such as the phosphine group, oxazoline ring, or backbone moiety. With their easy accessibility and the virtually limitless selection of readily available precursors, it is not surprising that, since the initial studies on phosphinooxazolines, a remarkable array of new linkers—only a few major classes of which are shown in Fig. 1—connecting the oxazoline ring to the phosphine backbone has been developed and successfully employed in various asymmetric catalytic transformations.[7]

Nevertheless, despite these significant advancements, it is important to recognize that no universal ligand exists, and that the scaffold plays a determining role in profoundly influencing catalytic performance. As a result, the quest for novel ligands with unique backbones to enhance the selectivity, activity, and

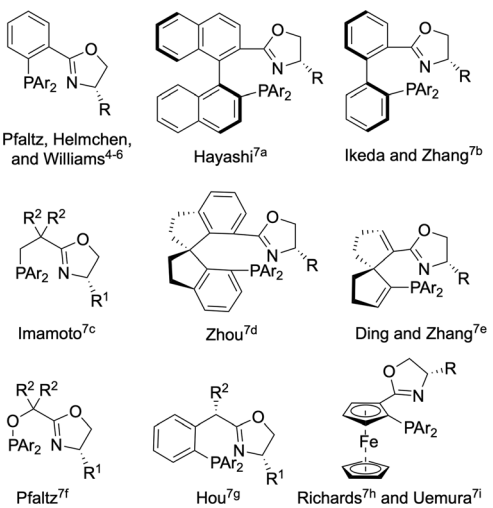
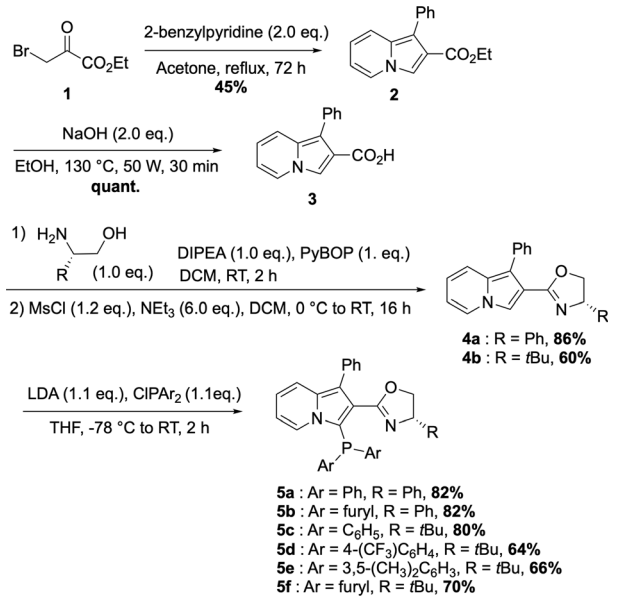


Fig. 1 Representative examples of phosphine–oxazoline (PHOX) ligands (R, R^1, R^2 = alkyl, Ar = aryl).

[a]*PSL University, Chimie ParisTech, CNRS UMR 8060, Institute of Chemistry for Life and Health Sciences, CSB2D Team, 75005 Paris, France. E-mail: phannarath.phansavath@chimieparistech.psl.eu*

[b]*ICGM, Univ. Montpellier, ENSCM, CNRS Montpellier, France. E-mail: david.virieux@enscm.fr*



Scheme 1 Synthesis of Indol-PHOX ligands.

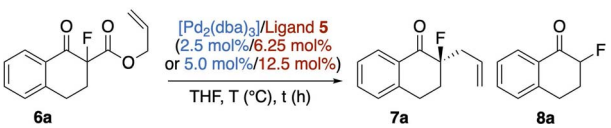
reactivity of transition metal catalysts still remains a formidable challenge. To address this, we have recently initiated a new program dedicated to the design and synthesis of ligands featuring heteroaryl scaffolds, which are underexplored in the realm of chiral ligand design.[8] As part of this effort, we have chosen to focus on the indolizine motif for several compelling reasons, as we believe it holds great promise as a framework for the synthesis of P,N-ligands. Indolizines are electron-rich heteroaromatic compounds that belong to the family of N-fused 5/6-membered heterocycles. They can be easily synthesized on a gram-scale using highly efficient and cost-effective methods, allowing for the introduction of tailored substituents at specific positions. Additionally, indolizines display high and controllable reactivity, enabling straightforward modulation for fine-tuning of steric and electronic properties. In this paper, we present the concise and modular synthesis of a new series of Indol-PHOX ligands, which, to the best of our knowledge, represent the first examples of chiral P,N-chelating indolizine ligands.

Results and discussion

The streamlined synthesis pathway for the preparation of ligands **5** is outlined in Scheme 1. The reaction of commercially available and cost-effective ethyl bromopyruvate **1** with 2-benzylpyridine in refluxing acetone for 72 h, followed by alkaline hydrolysis of the resulting product **2** under microwave irradiation, afforded 3-phenyl-indolizine-2-carboxylic acid **3** on a multi-gram scale.

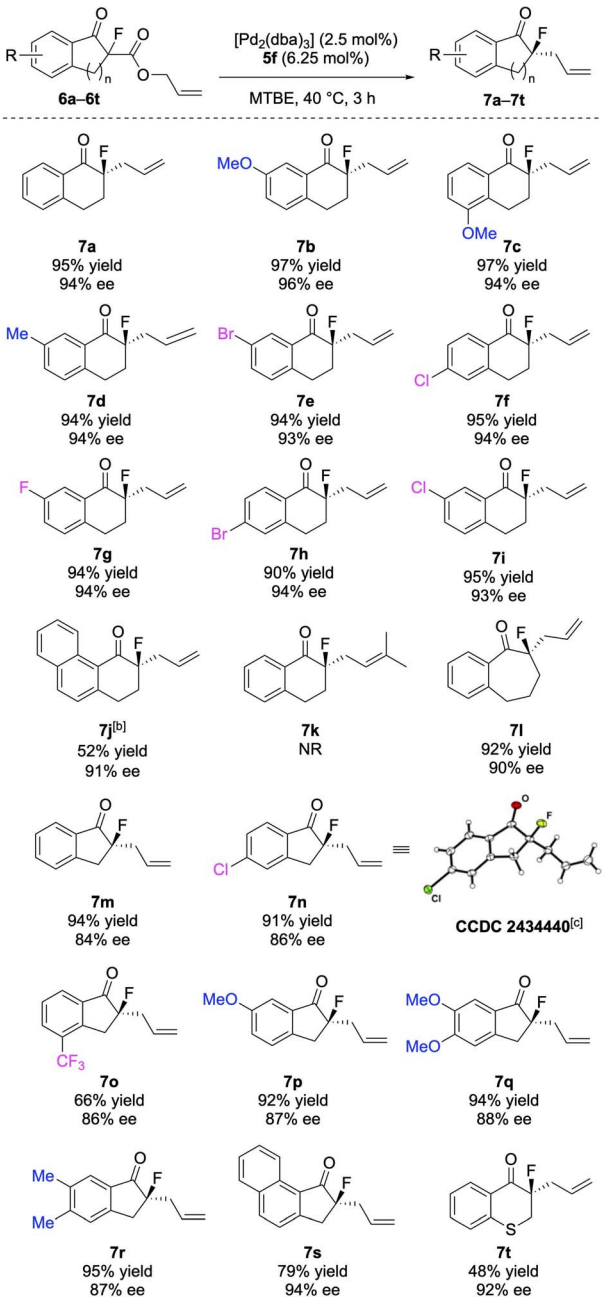
Condensation of **3** with enantiomerically pure (*S*)-*t*-leucinol or (*S*)-2-amino-2-phenylethan-1-ol in the presence of benzotriazol-1-yloxytripyrrolidinophosphonium hexafluorophosphate (PyBOP) and diisopropyethylamine in dichloromethane, yielded the corresponding amide. Without further purification, these amides were converted to the oxazolines **4a** and **4b** *via* treatment with triethyl amine and methanesulfonyl chloride in dichloromethane, in 86% and 60% isolated yields, respectively. Finally, target ligands **5a–5f** were obtained in yields ranging from 64% to 82% through a standard directed *ortho*-lithiation process using lithium diisopropylamide at −78 °C, followed by reaction with readily accessible chlorodiarylphosphines bearing electron-rich and electron-poor substituents or chlorodifurylphosphine.

Table 1 Optimization of the reactions conditions for the enantioselective decarboxylative allylation[a]



Entry	[Pd][b]/L (mol%)	*T* (°C)	*t* (h)	Conv. (%)	**7 : 8** ratio[c]	Yield[d] (%)	ee[e] (%)
1	[Pd]/**5a** (2.5/6.25)	25	48	45	91 : 9	25	14
2	[Pd]/**5b** (2.5/6.25)	25	48	45	91 : 9	25	14
3	[Pd]/**5c** (2.5/6.25)	25	48	33	85 : 15	20	76
4	[Pd]/**5c** (5.0/12.5)	25	15	100	93 : 7	85	80
5	[Pd]/**5d** (5.0/12.5)	30	30	36	78 : 22	25	87
6	[Pd]/**5e** (5.0/12.5)	30	30	59	88 : 12	52	76
7	[Pd]/**5e** (5.0/12.5)	40	24	100	83 : 17	65	80
8[f]	[Pd]/**5e** (5.0/12.5)	40	3	100	100 : 0	95	88
9[f]	[Pd]/**5f** (5.0/12.5)	40	3	100	100 : 0	99	94
10[f]	[Pd]/**5f** (2.5/6.25)	40	3	100	100 : 0	99	94

[a] Conditions: **6a** (0.11 mmol), [$Pd_2(dba)_3$] (2.8 or 5.5 μmol, 2.5 or 5.0 mol%), ligand **5** (7.0 or 14.0 μmol, 6.25 or 12.5 mol%), THF or MTBE (0.05 M), 25–40 °C, 3–48 h. [b] [Pd] refers to [$Pd_2(dba)_3$]. [c] Determined by ^{1}H NMR spectroscopy of the crude product. [d] Isolated yield. [e] Enantiomeric excess for **7a** was determined by HPLC analysis. [f] The reaction was run in MTBE (0.05 M).

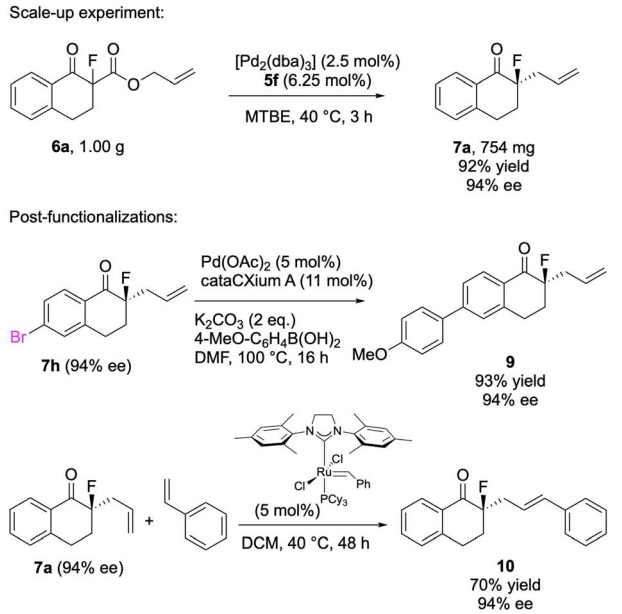


Scheme 2 Substrate scope of the enantioselective decarboxylative allylation.[a] [a]Conditions: **6** (0.13 mmol), $[Pd_2(dba)_3]$ (3.3 μmol, 2.5 mol%, 3.0 mg), ligand **5f** (8.3 μmol, 6.25 mol%, 4.0 mg), MTBE (0.05 M, 2.6 mL), 40 °C, 3 h. Isolated yields. Enantiomeric excesses were determined by HPLC analysis. [b]Reaction time of 20 h. [c]X-ray crystallography of **7n**. Displacement ellipsoids are shown at the 30% probability level.

We chose to evaluate these new series of Indol-PHOX ligands in the palladium-catalyzed enantioselective decarboxylative allylation[9–17] of α-fluoro-β-ketoesters aiming to access valuable α-allyl-α-fluoro ketones. Compound **6a** served as a model substrate for the optimization of the reaction parameters for the enantioselective decarboxylative allylation (Table 1). The reaction was first carried out at 25 °C in THF in the presence of 2.5 mol% of $[Pd_2(dba)_3]$ and 6.25 mol% of ligand **5a** for 48 h (Table 1, entry 1). Under these conditions, a conversion of 45% was achieved and the desired product **7a** was isolated in 25% yield and 14% ee alongside the by-product **8a** resulting from the protonation of the enolate generated during the reaction (with a **7a**/**8a** ratio of 91 : 9). The reaction carried out under the same conditions with ligand **5b** produced identical results in terms of yield and enantioselectivity (Table 1, entry 2). However, a significant increase in enantioinduction was observed with ligand **5c** bearing a *tert*-butyl substituent on the oxazoline ring instead of the phenyl substituent present in ligands **5a** and **5b**. Indeed, although a lower conversion of 33% with a **7a**/**8a** ratio of 85 : 15 was achieved, the enantiomeric excess of **7a** could be improved to 76% (Table 1, entry 3). Increasing the catalyst loading to 5 mol% for $[Pd_2(dba)_3]$ and 12.5 mol% for **5c**, allowed to reach a full conversion within 15 h, with a **7a**/**8a** ratio of 93 : 7 (85% yield and 80% ee for **7a**) (Table 1, entry 4). When the reaction was run with ligands **5d** and **5e**, incomplete conversions of 36% and 59%, respectively, were observed even at a higher temperature of 30 °C (Table 1, entries 5 and 6, 25% and 52% yield respectively for **7a**). However, when the transformation was operated at 40 °C using ligand **5e**, a complete conversion was achieved and **7a** was isolated in 65% yield with 80% ee and a **7a**/**8a** ratio of 83 : 17 (Table 1, entry 7). Interestingly, the formation of by-product **8a** could be prevented by using MTBE as a solvent. In that case the rearrangement product **7a** was obtained in 95% yield and 88% ee using ligand **5e** within a shorter reaction time of 3 h (Table 1, entry 8), whereas ligand **5f** allowed both a higher yield of 99% and a better enantioselectivity of 94% ee (Table 1, entry 9).

Notably, we found that the catalyst loading could be decreased to 2.5 mol% for $[Pd_2(dba)_3]$ and 6.25 mol% for **5f** with no detrimental effect (Table 1, entry 10). However when the catalyst loading was further lowered to 1.0 mol% of $[Pd_2(dba)_3]$ and 2.5 mol% of the ligand, a **7a**/**8a** ratio of 95 : 5 was observed with an isolated yield of 90% for **7a** even though the enantioselectivity of 94% ee remained unaffected. On the other hand, a short solvent screening confirmed MTBE as the more suitable solvent for the reaction since **7a** was obtained in 85% yield with 88% ee (**7a**/**8a** = 100 : 0) in toluene, and in 69% yield and 90% ee in diethyl ether (**7a**/**8a** = 95 : 5). The use of protic solvents significantly lowered the reaction rate, with MeOH affording only 15% conversion (**7a**/**8a** = 40 : 60) and iPrOH giving 18% conversion (**7a**/**8a** = 50 : 50) at 40 °C after 3 h. Thus, the optimized reaction conditions were set as follows: 2.5 mol% of $[Pd_2(dba)_3]$, 6.25 mol% of ligand **5f** in MTBE (0.05 M) at 40 °C for 3 h. It should be noted that when the commercially available (*S*)-i-Pr-PHOX ligand was used instead of ligand **5f**, the reaction led to a **7a**/**8a** ratio of 90 : 10 and the rearrangement product was isolated in 87% yield and 84% ee. When $[Pd(allyl)Cl]_2$ or $Pd(OAc)_2$ were employed as alternative palladium sources, the reaction proceeded with only 13% conversion in the case of $[Pd(allyl)Cl]_2$ and 3% conversion with $Pd(OAc)_2$.

With the optimized reaction conditions in hand, the scope of the enantioselective decarboxylative allylation using the newly developed ligand **5f** was evaluated using the previously synthesized family of substituted β-ketoesters **6a–6t** (Scheme 2). Allyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate



Scheme 3 Scale-up experiment and post-functionalization reactions.

derivatives bearing electron-donating groups such as a methoxy or a methyl substituent on the phenyl ring led to high yields (94–97%) of the rearrangement products **7b–7d** that were formed with excellent enantioinductions of 94–96% ee. In the same manner, the parent substrates having halogen atoms such as bromine, chlorine or fluorine at various positions of the phenyl ring were obtained in 90–95% yield and 93–94% ee (**7e–7i**). The more sterically hindered derivative **7j** having a naphthyl ring instead of the benzene ring was isolated in a lower yield of 52% whereas the enantioselectivity remained similar (91% ee). On the other hand, the enantioselective decarboxylative allylation carried out with the tetralone substrate bearing an isoprenyl substituent failed to give any conversion into **7k** whereas the reaction of a 7-membered carbocycle led to (*R*)-6-allyl-6-fluoro-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one **7l** in 97% yield and 92% ee. Indanone derivatives were also suitable substrates for this transformation giving products **7m–7s** in yields ranging from 66% to 95% and high enantiomeric excesses of 84–94%. As previously observed for the tetralone series, the enantioselectivity of the reaction with indanone derivatives was not dependent on either the electronic nature or the positions of the substituents present on the benzene ring. Indeed, electron-withdrawing substituents such as chlorine or trifluoromethyl (**7n–7o**) led to the same levels of enantioinduction than electron-donating groups such as methoxy or methyl (**7p–7r**). On the other hand, the sterically hindered derivative **7s** bearing a naphthyl ring was formed in 79% yield with an excellent enantiomeric excess of 94%. The reaction was also extended to a heterocyclic substrate, affording the fluorinated thiochromanone **7t** which was obtained in 48% yield and 92% ee. The absolute configuration of compounds **7a**, **7l** and **7m** were assigned by comparison of the optical rotation values with those reported.[18] Additionally, the absolute configuration of compound **7n** was unambiguously assigned as (*R*) by X-ray crystallographic analysis, and by analogy, we conjectured that the remainder of the rearrangement products followed the same trend.

The efficiency of the new ligand **5f** in the enantioselective decarboxylative allylation was further supported by a scale-up experiment performed with substrate **6a** on a gram scale. Under the optimized reaction conditions, the desired product **7a** was obtained in 92% yield and 94% ee (Scheme 3). Furthermore, the rearrangement products **7** can serve as useful intermediates for further post-functionalization reactions. Thus, aryl bromide **7h** was engaged in a Suzuki–Miyaura coupling reaction with 4-methoxyphenylboronic acid using $Pd(OAc)_2$ as a catalyst, cataCXium A as a ligand, and K_2CO_3 as a base, affording the corresponding binaphthyl **9** in 93% yield while maintaining the 94% ee. On the other hand, a cross-metathesis reaction between (*R*)-2-allyl-2-fluoro-3,4-dihydronaphthalen-1(2*H*)-one **7a** and styrene in the presence of 5.0 mol% of the Grubbs catalyst 2nd generation afforded the corresponding alkene (*E*)-**10** in 70% yield and 94% ee.

Conclusions

In summary, we have developed a new, efficient and modular series of chiral P,N ligands, termed Indol-PHOX ligands, representing the first examples of chiral oxazolidinyl indolizine-based ligands. We also demonstrated their successful application in palladium-catalyzed enantioselective decarboxylative allylation. The reactions proceed smoothly under mild reaction conditions and accommodate a wide substrate scope providing valuable α-allyl-α-fluoro ketones that bear an α-quaternary stereocenter. Such compounds were isolated in high yields (up to 99%) and with excellent enantioselectivities (up to 96% ee). The scalability of the process was confirmed through a gram-scale experiment, and the synthetic utility of the resulting chiral α-allyl-α-fluoro ketone products was further demonstrated through successful post-functionalization reactions (Suzuki–Miyaura coupling and cross-metathesis) without erosion of enantiopurity.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

CCDC 2434440 contains the supplementary crystallographic data for this paper.[19]

The data supporting this article have been included as part of the SI. Supplementary information: Experimental procedures, NMR spectra, spectral data and X-ray data. See DOI: https://doi.org/10.1039/d5ra04775g.

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