

Organic & Biomolecular Chemistry

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ARTICLE

Design and Preparation of Novel Imidazolinone Backbone Chiral N, P Ligands and Highly Effective Performances in Enantioselective Allylations

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Based on a patented new concept of general chiral catalysis, a series of new chiral ligands integrated with both a Macmillan imidazolinone organocatalyst and a chiral N, P-ligand scaffolds have been designed and concisely prepared from commercially available chiral α -amino acids and 2-diphenylphosphino-benzaldehyde. Those chiral ligands have shown good to excellent enantioselectivities (up to 97% ee) with satisfactory yields (up to 95%) in enantioselective Pd-catalyzed allylations with 1,3-dicarbonyls and amines.

Introduction

Asymmetric organometallic catalysis has become a powerful tool for chemists and has found wide applications for the effective preparations of chiral molecules and materials.¹ Design and preparations of ideal chiral ligands are the key and ultimate goals for perfect enantioselective catalysis. With the advent of different sorts of chiral ligands, the catalytic efficiency and selectivity of reactions like asymmetric hydrogenations and allylations/aminations have been greatly improved.² Several "privileged" chiral ligands with well-defined geometrical features have been developed and successfully applied in academic and industrial cases in the last few decades^{3a} and have gained wide recognition and applications in several typical enantioselective reactions. Of them, chiral phosphine ligands are outstanding ones for their stout selectivity and generality for most reactions. However, the relatively hard availability, air and moisture sensitivities have become one of the most obstacles for further scale up and commercial applications. Alternatively, relatively stable N, P-ligands as one of the most successful and typical chiral ligands, have played an important role in asymmetric organometallic catalysis. Syntheses and applications of some representing N, P-ligands such as PHOX,^{3b} Trost's,^{4,5} Ikeda's,⁶ Li's,⁷ SIPHOX,⁸ Ding's,⁹ Zheng's,¹⁰ Teng's,¹¹ Jiao's¹² and Dixon's¹³ ligands have been reported and successfully used in sorts of chiral reactions.

Based on our everlasting interests in enantioselective organocatalysis^{14,15} and recent 20 years achievements in metal free small molecular catalysis pioneered by List¹⁶ and Macmillan,¹⁷ and considered the easy availabilities and excellent performances of typical chiral prolines and Macmillan's imidazolinone organocatalysts, we perceived if a phosphino group containing

starting material of easily available 2-diphenylphosphinobenzaldehyde instead of commonly used aldehydes or ketones was applied to construct MacMillan's imidazolinone backbone, both a new kind of MacMillan like organocatalyst and new N,P-ligand may be expected (Figure 1). Obviously, from the structural characteristics, this new imidazolinone scaffold also boasts all the possibilities to be a new kind of N-P chiral ligands. Theoretically, they may be used not only as independent chiral ligands, but also as independent chiral organocatalyst, and cooperatively or synergistically as bifunctional (multifunctional) cocatalyst by tuning the coordinate metal, which we defined and patented as "general chiral/enantioselective catalysis"¹⁷.

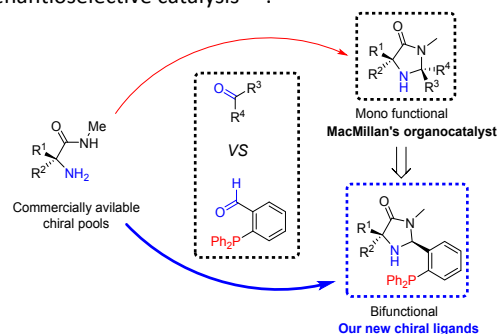


Figure 1. From MacMillan's Organocatalyst to Our New Chiral Ligands.

For N,P- chiral ligands, Pd-catalyzed enantioselective allylations with sorts of chiral ligands and substrate companions have been fully studied and become one of the most powerful tools in asymmetric synthesis.¹⁸ Among which, enantioselective allylation of 1,3-dicarbonyl compounds has become one of the most powerful methods for a new C-X bond formation, those target chiral multifunctional molecules may transformed to diversity of new chiral entities.^{19, 20} As a part and leading work of our new concept, herein, we wish to report the design and synthesis of this kind of new chiral N-P ligands integrated with both an imidazolinone backbone and a phosphine group (Scheme 1) and their proof-of-concept applications

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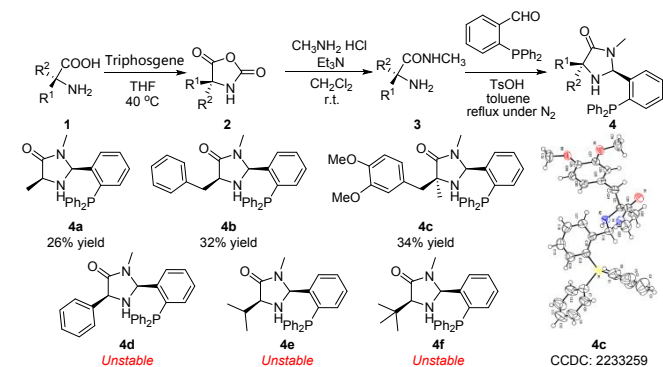
Supplementary Information available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

in Pd-catalyzed allylations²¹⁻²⁵ with 1,3-dicarbonyls for the selective formation of new C-C bond and amines for C-N bond formation for chiral amines.

Results and Discussions

Synthesis of ligands. Ligands 4a-4c were synthesized similarly with MacMillan's organocatalyst²⁶ starting from commercially available α -amino acids (Scheme 1). Amino acid **1** was easily transformed to oxazolidinone **2** with excessive triphosgene in high yields, which successfully reacted with methylamine to give aminoamide **3**. For further ring closure of the aminoamide scaffolds, alcohols such as CH₃OH, C₂H₅OH and *i*-PrOH are generally used as solvents.²⁷⁻²⁹ However, unstable imine intermediates rather than the enclosed imidazolinones were detected even after several days under azeotropic conditions. When toluene used as azeotropic solvent,³⁰ the reaction was performed under fully refluxed temperature, some representing stable target ligands of **4a-4c** were successfully obtained and separated in acceptable yields. Unfortunately, most of the expected imidazolinones (**4d-4f**) were unstable or decomposed within a few hours to a few days, especially under acidic condition, quite differently from MacMillan's organocatalysts (fairly stable as salt for acceptable time). However, those ligands showed remarkable stability in air for at least two months, although most of them decompose due to structural instability, which are potentially significant for the design, screening of new air stable chiral phosphine ligands and their applications in organometallic catalytic reactions, especially oxygen participating or redox process involved ones.

Scheme 1. Synthesis of New Chiral N-P Ligands.



A simple comparison between our ligands and similar MacMillan catalysts may be reasoned: the introduction of a highly steric diarylphosphino group hampered the formation of the imidazolinone backbone via an imine intermediate (Scheme 1),^{27,30} and lead to the instability of the crowded imidazolinone ketals, especially under acidic or moisture conditions.

Evaluations of catalytic activities: enantioselective allylation. To evaluate the catalytic behaviors of the new chiral ligands, a representing Pd-catalyzed enantioselective allylation of 1,3-dicarbonyl was used as a model reaction (entries 1-3, Table 1). Typically, 1,3-diphenylallyl acetate **7a** and ethyl malonate **8a** was performed in the presence of Pd(OAc)₂ and Cs₂CO₃ in methyl tert-butyl ether (MTBE). When **4a** and **4b** as chiral ligands, the corresponding substituted chiral products **9a** were obtained in moderate yields with poor enantioselectivities (26% ee, 66% yield, entry 1; 3% ee, 64% yield, 3% ee entry 2; Table 1). For ligand **4c**, an

obviously improved yield and enantioselectivity (78% ee, 81% yield, entry 3, Table 1) was achieved. Further, different palladium salts were examined in the presence of **4c** under the same condition (entries 4-7, Table 1). Of which, PdCl₂, Pd(PhCN)₂Cl₂ and Pd₂(dba)₃ failed to catalyze the reaction, while [Pd(C₃H₅)Cl]₂ gave a better yield with excellent enantioselectivity (89% ee, 81% yield, entry 7, Table 1). To accelerate the leave of the acetate substitution, typical bases such as K₂CO₃, NaOH, KOH and K₃PO₄ were evaluated and all gave excellent enantioselectivities (87-94% ee, 11-92% yields, entries 8-11, 13-15, Table 1). While Na₂CO₃, DMAP and DBU gave acceptable good enantioselectivities (77-88% ee) with obviously lowered yields (11-20% yields, entries 12, 16-18, Table 1). In CH₂Cl₂, CHCl₃, THF, dioxane or toluene, good yields and enantioselectivities were obtained (93-94% ee, 76-89% yields, entries 19-23, Table 1), while in CH₃CN, obviously lower enantioselectivity was observed (80% ee, entry 24, Table 2). The optimal reaction conditions were established as: **7** (0.15 mmol), **8** (0.225 mmol), [Pd(C₃H₅)Cl]₂ (1.5 mol%), **4c** (6 mol%), K₃PO₄ (0.3 mmol), CH₂Cl₂ (1 mL) at 25 °C.

Table 1. Optimization of Reaction Conditions^{a,b,c,e}.

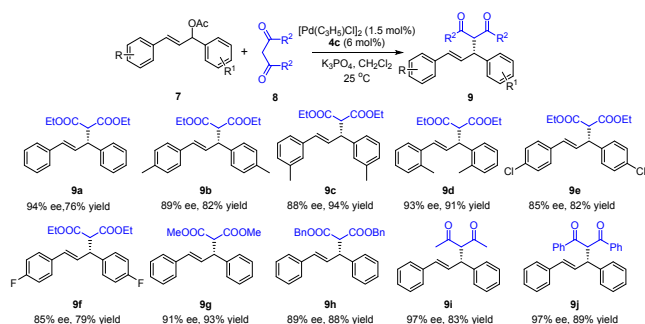
| Entry | L | [Pd] | Base | Solvent | yield (%) | ee (%) |
|----------------|-----------|---|---------------------------------|---------------------------------|-------------------|--------|
| 1 ^d | 4a | Pd(OAc) ₂ | Cs ₂ CO ₃ | MTBE | 66 | 26 |
| 2 ^d | 4b | Pd(OAc) ₂ | Cs ₂ CO ₃ | MTBE | 64 | 3 |
| 3 ^d | 4c | Pd(OAc) ₂ | Cs ₂ CO ₃ | MTBE | 81 | 78 |
| 4 ^d | 4c | PdCl ₂ | Cs ₂ CO ₃ | MTBE | n.d. ^f | - |
| 5 ^d | 4c | Pd(PhCN) ₂ Cl ₂ | Cs ₂ CO ₃ | MTBE | n.d. ^f | - |
| 6 | 4c | Pd ₂ (dba) ₃ | Cs ₂ CO ₃ | MTBE | n.d. ^f | - |
| 7 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | Cs ₂ CO ₃ | MTBE | 81 | 89 |
| 8 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | K ₂ CO ₃ | MTBE | 82 | 91 |
| 9 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | NaOH | MTBE | 88 | 90 |
| 10 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | KOH | MTBE | 92 | 87 |
| 11 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | K ₃ PO ₄ | MTBE | 70 | 94 |
| 12 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | K ₂ HPO ₄ | MTBE | n.d. ^f | - |
| 13 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | Na ₂ CO ₃ | MTBE | 15 | 85 |
| 14 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | DMAP | MTBE | 11 | 77 |
| 15 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | DBU | MTBE | 20 | 88 |
| 16 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | Et ₃ N | MTBE | n.d. ^f | - |
| 17 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | DABCO | MTBE | n.d. ^f | - |
| 18 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | NaOAc | MTBE | n.d. ^f | - |
| 19 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | K ₃ PO ₄ | CH ₂ Cl ₂ | 76 | 94 |
| 20 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | K ₃ PO ₄ | CHCl ₃ | 81 | 93 |
| 21 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | K ₃ PO ₄ | THF | 88 | 93 |
| 22 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | K ₃ PO ₄ | Dioxane | 89 | 93 |
| 23 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | K ₃ PO ₄ | Toluene | 85 | 93 |
| 24 | 4c | [Pd(C ₃ H ₅)Cl] ₂ | K ₃ PO ₄ | CH ₃ CN | 79 | 80 |

^aUnless otherwise noted, the reaction was performed with **7a** (0.15 mmol), **8a** (0.225 mmol), palladium salt (1.5 mol%), Ligand (6 mol%), base (0.3 mmol) in solvent (1 mL) at 25 °C. ^bisolated yield.

^cdetermined by chiral HPLC. ^dpalladium salt (3.0 mol%). ^eabsolute configuration assigned by comparison with known counterparts. ^fnot detected.

The substrate generality was examined under the optimal conditions. As shown in Scheme 2, methyl substitutions at ortho-, meta- or para-positions on aromatic rings of allylic acetate have less effects on enantioselectivities (88-93% ee, 82-94% yields, **9a-9d**, Scheme 2). Allylic acetates bearing electron-withdrawing groups on aromatic rings lead to slight decrease in ee values (85% ee, 82% yield for **9e**; 85% ee, 79% yield for **9f**, Scheme 2). Substitutions on 1,3-dicarbonyls seemed to show slight effects on the results (91% ee, 93% yield for **9g**; 89% ee, 88% yield for **9h**, Scheme 2), while **7a** and 1,3-diones (**8i**, **8j**) gave excellent enantioselectivities (97% ee, 83% yield for **9i**; 97% ee, 89% yield for **9j**, Scheme 2).

Scheme 2. Substrate Generality ^{a,b,c,d}.



^aUnless otherwise noted, the reaction was performed with **7** (0.15 mmol), **8** (0.225 mmol), $[Pd(C_3H_5)Cl]_2$ (1.5 mol%), **4c** (6 mol%), K_3PO_4 (0.3 mmol) in solvent (1 mL) at 25 °C. ^bisolated yield. ^cdetermined by chiral HPLC. ^dabsolute configuration assigned by comparison with known counterparts.

Table 2. Optimization of Reaction Conditions^{a,b,c}.

| Entry | L | [Pd] | Base | Solvent | yield (%) | ee (%) |
|----------------|-----------|--------------------|------------|------------|-------------------|--------|
| 1 | 4a | $[Pd(C_3H_5)Cl]_2$ | Na_2CO_3 | $CHCl_3$ | 50 | 22 |
| 2 | 4b | $[Pd(C_3H_5)Cl]_2$ | Na_2CO_3 | $CHCl_3$ | 91 | 8 |
| 3 | 4c | $[Pd(C_3H_5)Cl]_2$ | Na_2CO_3 | $CHCl_3$ | 91 | 50 |
| 4 ^d | 4c | $Pd(OAc)_2$ | Na_2CO_3 | $CHCl_3$ | 35 | 43 |
| 5 ^d | 4c | $PdCl_2$ | Na_2CO_3 | $CHCl_3$ | n.d. ^f | - |
| 6 ^d | 4c | $Pd(PhCN)_2Cl_2$ | Na_2CO_3 | $CHCl_3$ | n.d. ^f | - |
| 7 | 4c | $Pd_2(dba)_3$ | Na_2CO_3 | $CHCl_3$ | n.d. ^f | - |
| 8 | 4c | $[Pd(C_3H_5)Cl]_2$ | K_2CO_3 | $CHCl_3$ | 95 | 74 |
| 9 | 4c | $[Pd(C_3H_5)Cl]_2$ | K_3PO_4 | $CHCl_3$ | 88 | 29 |
| 10 | 4c | $[Pd(C_3H_5)Cl]_2$ | K_2HPO_4 | $CHCl_3$ | 32 | 3 |
| 11 | 4c | $[Pd(C_3H_5)Cl]_2$ | DABCO | $CHCl_3$ | n.d. ^f | - |
| 12 | 4c | $[Pd(C_3H_5)Cl]_2$ | DBU | $CHCl_3$ | 49 | 0 |
| 13 | 4c | $[Pd(C_3H_5)Cl]_2$ | Et_3N | $CHCl_3$ | n.d. ^f | - |
| 14 | 4c | $[Pd(C_3H_5)Cl]_2$ | Cs_2CO_3 | $CHCl_3$ | 95 | 86 |
| 15 | 4c | $[Pd(C_3H_5)Cl]_2$ | Cs_2CO_3 | Toluene | n.d. ^f | - |
| 16 | 4c | $[Pd(C_3H_5)Cl]_2$ | Cs_2CO_3 | Dioxane | n.d. ^f | - |
| 17 | 4c | $[Pd(C_3H_5)Cl]_2$ | Cs_2CO_3 | CH_2Cl_2 | 87 | 57 |
| 18 | 4c | $[Pd(C_3H_5)Cl]_2$ | Cs_2CO_3 | MTBE | 81 | 9 |
| 19 | 4c | $[Pd(C_3H_5)Cl]_2$ | Cs_2CO_3 | THF | 62 | 25 |
| 20 | 4c | $[Pd(C_3H_5)Cl]_2$ | Cs_2CO_3 | DCE | 79 | 7 |

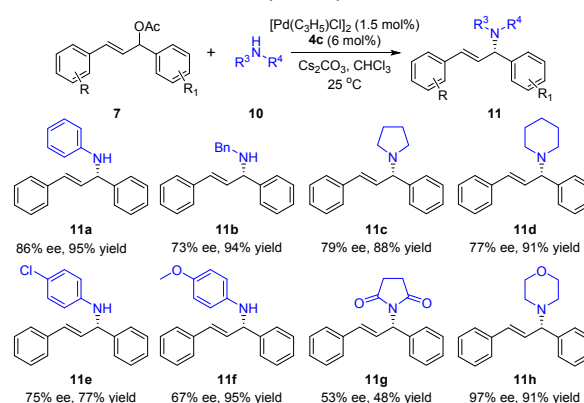
^aUnless otherwise noted, the reaction was performed with **7a** (0.15 mmol), **10a** (0.225 mmol), palladium salt (1.5 mol%), Ligand (6 mol%),

base (0.3 mmol), solvent (1 mL) at 25 °C. ^bisolated yield. ^cdetermined by chiral HPLC. ^dpalladium salt (3.0 mol%). ^eabsolute configuration assigned by comparison with known counterparts. ^fnot detected.

Enantioselective allylic amination. Typically, 1,3-diphenylallyl acetate **7a** and aniline **10a** was performed in the presence of $[Pd(C_3H_5)Cl]_2$ and Na_2CO_3 in chloroform ($CHCl_3$). When **4a** and **4b** as chiral ligands, the corresponding chiral amine **11a** were obtained in moderate yields with poor enantioselectivities (22% ee, 50% yield, entry 1; 8% ee, 91% yield, entry 2; Table 2). For ligand **4c**, an obviously improved yield and enantioselectivity (50% ee, 91% yield, entry 3, Table 2) was achieved. Different palladium salts were examined in the presence of **4c** under the same condition (entries 4-7, Table 2). Of which, $PdCl_2$, $Pd(PhCN)_2Cl_2$ and $Pd_2(dba)_3$ failed to catalyze the reaction, while $Pd(OAc)_2$, gave a 43% ee with 35% yield (entry 4, Table 2). Moderate to good enantioselectivities were obtained when stronger bases like K_2CO_3 and Cs_2CO_3 (74% ee, entry 8; 86% ee, entry 14; Table 2) were used, while K_3PO_4 , K_2HPO_4 and organic bases gave poor results (entries 9-13, Table 2). Solvents greatly affected this substitution, in CH_2Cl_2 , MTBE, THF and DCE, poor enantioselectivities (7%-57% ee, entries 17-20, Table 2) were obtained for all cases. The optimal reaction conditions were established as: **7** (0.15 mmol), **10** (0.225 mmol), $[Pd(C_3H_5)Cl]_2$ (1.5 mol%), **4c** (6 mol%), Cs_2CO_3 (0.3 mmol) in $CHCl_3$ (1 mL) at 25 °C.

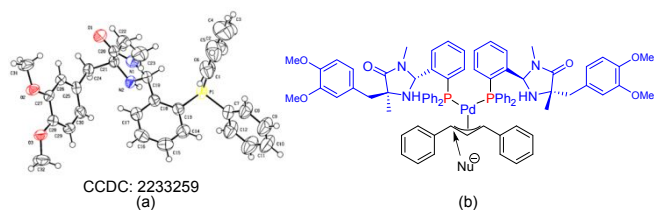
Under optimized reaction conditions, the substrate generality of 1,3-diphenylallyl acetate **7** and amines **10** were studied (Scheme 3). As shown in Scheme 3, amines **10a-e**, gave 73-86% ee with 77-95% yields. Compared with aniline **10a**, **10f** and **10g** gave lowered enantioselectivities (67% ee, 95% yield for **11f**; 53% ee, 48% yield for **11g**, Scheme 3). While for morpholine **10h**, both excellent yield and enantioselectivity were achieved (97% ee, 91% yield for **11h**, Scheme 3).

Scheme 3. Substrate Generality of Allylic Amination ^{a,b,c}.



^aUnless otherwise noted, the reaction was performed with **7** (0.15 mmol), **10** (0.225 mmol), $[Pd(C_3H_5)Cl]_2$ (1.5 mol%), **4c** (6 mol%), Cs_2CO_3 (0.3 mmol) in solvent (1 mL) at 25 °C. ^bisolated yield. ^cdetermined by chiral HPLC. ^dabsolute configuration assigned by comparison with known counterparts.

Based on the absolute configuration of ligand **4c** (Figure 2a) and similar reactions,^{11,12,31} we suggested a plausible mechanism (Figure 2b). Ligand **4c** interacted with Pd in bidentate mode to form the organometallic catalyst. Resonate allylic cations, formed with the help of bases, coordinated with the Pd chiral complex to afford a stabilized transition state. Nucleophilic substitutions from *Re*-face to afford corresponding *R*-alkylation products or *S*-amination products.

Figure 2. Crystal structure of **4c** and Plausible transient state.

(a) Crystal structure of **4c**. (b) Plausible transition state for Pd-catalyzed allylation and allylic amination.

Conclusions

In summary, for the proof of a patented new concept of general chiral catalysis, we have devised and developed a new kind of chiral N-P bidentate ligands based on MacMillan's imidazolinone backbone starting from commercially available chiral amino acids and their catalytic behaviors in palladium catalyzed enantioselective allylation of 1,3-diphenylallyl acetate and 1,3-dicarbonates and 1,3-diphenylallyl acetate amination have been well demonstrated with high activity and excellent enantioselectivities. Excellent yields (up to 95%) and enantioselectivities (up to 97% ee) were obtained. Considering the easily available, inert to moisture and air of our new chiral N, P-bidentate ligands and their excellent performances, further applications and ligand scaffold tunings are underway in our laboratory.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data underlying this study are available in the published article and its online Supporting Information. The Supporting Information is available free of charge on the RSC Publications website.

Acknowledgements

This work was supported by the National Key Research and Development Program of China [2021YFC2102100].

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Data availability

The data underlying this study are available in the published article and its online Supporting Information.
The Supporting Information is available free of charge on the RSC Publications website.