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Pd-Catalyzed asymmetric allylic amination with isatin using a P,olefin-type chiral ligand with C–N bond axial chirality

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Full Research Paper

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Abstract

In this study, we implemented the P,olefin-type chiral ligand (a*R*)-(−)-**6**, which contains a cyclohexyl group and a cinnamoyl group on the nitrogen atom, in the Pd-catalyzed asymmetric allylic amination of allylic esters with isatin derivatives **11** as nucleophiles. The reaction proceeds efficiently, yielding the products (*S*)-**13** with good-to-high enantioselectivity. A scale-up reaction was also successfully conducted at a 1 mmol scale. Additionally, when malononitrile was added to the resulting product (*S*)-**13a** in the presence of $FeCl_3$ as the catalyst, the corresponding malononitrile derivative (*S*)-**16** was obtained without any loss in optical purity.

Introduction

Isatin is a well-known natural indole derivative. Due to the broad biological activities of its derivatives, extensive research has been conducted on their synthesis. Furthermore, the isatin framework is a versatile starting material for various transformations, including multicomponent reactions and the synthesis of spirocyclic compounds [1-3]. The nucleophilicity of isatin at the nitrogen atom allows it to participate in reactions such as alkylation [4], arylation [5], and *aza*-Michael addition [6-8]. However, the products obtained from these reactions are primarily achiral or racemic, and only a few studies have reported the use of isatin as a nucleophile in asymmetric reactions [9-11]. On the other hand, it has been revealed that com-

pounds in which the carbon bonded to the nitrogen atom of newly constructed *N*-substituted isatin becomes a chiral center exhibit pharmacological properties in medicinal chemistry. For example, racemic compound **1** (Figure 1) was evaluated for its cytotoxicity against human breast cancer cells (MCF7) in comparison to the standard doxorubicin and exhibited excellent activity against the MCF7 cell line [12]. The optically active compound **2** also showed activity against Huh7.5-FGR-JC1-Rluc2A cells, which carry HCV gt 2a [13].

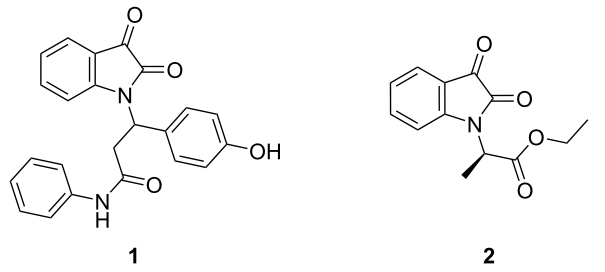


Figure 1: Compound **1** and **2**.

Therefore, developing asymmetric reactions that simultaneously form a carbon–nitrogen bond and construct a chiral center is of great importance. Although a relatively large number of asymmetric allylic amination reactions using palladium catalysts with amines as nucleophiles have been reported [14-25], there have been only a few reports on the *N*-substitution of isatin using asymmetric methods. Recently, Wolf's group reported a transition-metal-catalyzed (Pd-catalyzed) asymmetric allylic amination of allyl esters using isatin as a nucleophile. In this reaction, bisphosphine-type ligands such as BINAP and SEGPHOS derivatives, as well as P,N-type ligands like oxazoline-type ligands, were utilized as chiral ligands [26]. On the other hand, several groups have recently reported new chiral ligands with axial chirality for Pd-catalyzed asymmetric allylic substitution reactions. For example, the Zhou group reported a P,olefin-type chiral ligand **3** with C–C bond axial chirality for this reaction (Figure 2) [27]. Additionally, we have recently reported chiral ligands with C–N bond axial chirality, such as *N*-alkyl-*N*-cinnamyl-type chiral ligands **4** [28,29] and **5** [30], and a P,olefin-type chiral ligand **6** [31] with a cinnamoyl group instead of a cinnamyl group. In particular, the chiral ligand **6** is effective in the Pd-catalyzed asymmetric allylic substitution reaction of allylic esters with indoles. Here, we describe the Pd-catalyzed asymmetric allylic amination of allylic esters with isatin as a nucleophile using chiral ligand **6** and its derivative **7**. Compared to chiral ligand **6**, which has a secondary alkyl group (cyclohexyl) as a substituent on the nitrogen and has already been reported, compound **7** has a primary alkyl group (*n*-propyl). This difference reduces steric hindrance and lowers the rotational barrier around the carbon–nitrogen bond, increasing the likelihood of racemization.

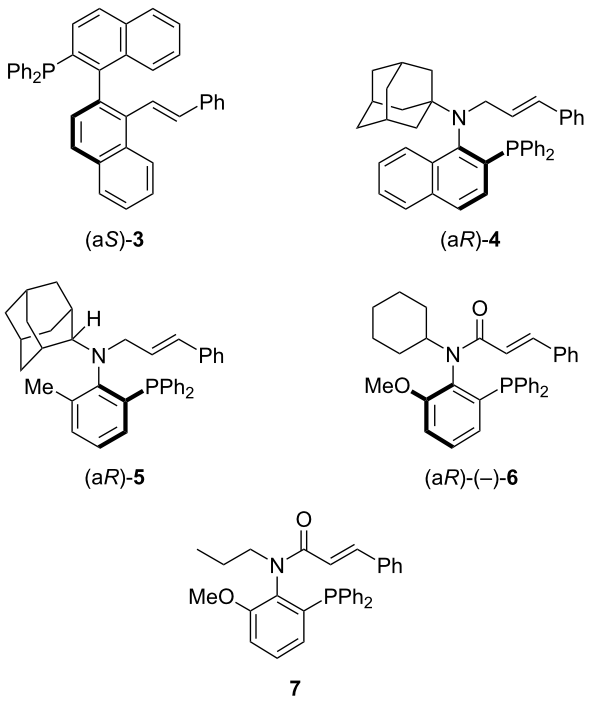
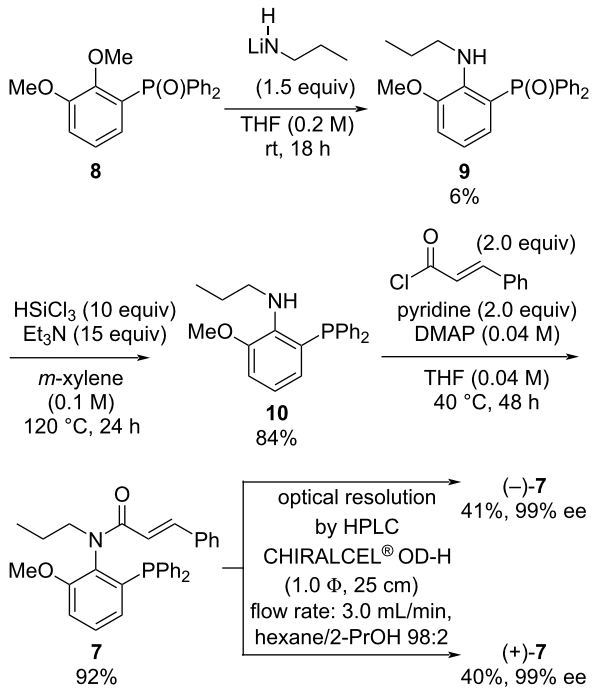


Figure 2: Chiral ligands **3**–**7**.

Results and Discussion

N-Propyl-*N*-cinnamoylamide **7** was prepared from phosphine oxide **8** [32] via an S_NAr reaction with nucleophilic lithium amide from *n*-propylamine, the reduction of phosphine oxide **9** by trichlorosilane/triethylamine, and the *N*-acylation of **10** with cinnamoyl chloride in three steps (Scheme 1). We also analyzed amide compound **7** by HPLC analysis using a chiral stationary phase column with a CD detector and found that the C(aryl)–N(amide) bond axial chirality exists in amide compound **7**. We attempted the optical resolution of racemic compound (±)-**7** and obtained (+)-**7** and (−)-**7** using a semi-preparative chiral HPLC on 50 milligram scales. We also investigated the racemization process associated with the axial chirality of compound **7** (see Supporting Information File 1). The racemization barrier ($\Delta G^{\ddagger}_{rac}$) of (−)-**7** in *n*-dodecane was determined to be 25.0 kcal/mol at 25 °C, as calculated using the Arrhenius and Eyring equations [33-35]. Therefore, the half-life of racemization of ligand (−)-**7** at 25 °C in *n*-dodecane is approximately 1.3 days, which is faster compared to ligand **6**, which has a half-life of about 3.7 days [31].

We next investigated the ability of optically active amides (a*R*)-(−)-**6** and (−)-**7** as chiral ligands for the Pd-catalyzed asym-

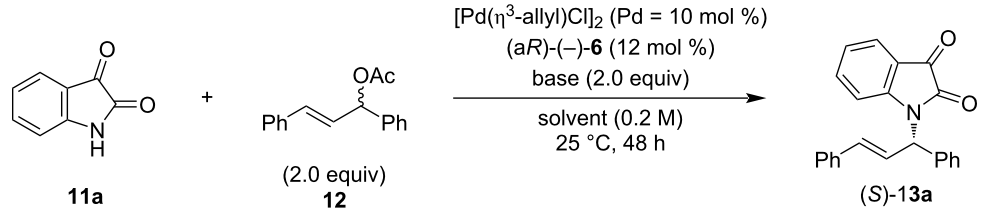


Scheme 1: Preparation and optical resolution of **7**.

metric allylic amination of allylic acetate, such as a 1,3-diphenyl-2-propenyl acetate (**12**) with isatin (**11a**). We began the investigation under conditions using 5 mol % of $[Pd(C_3H_5)Cl]_2$ (Pd = 10 mol %) and 12 mol % of chiral ligands (Table 1).

The reaction with (a*R*)-(−)-**6** as the chiral ligand and K_2CO_3 as the base in $CHCl_3$ gave the desired product (*S*)-**13a** in 72% yield with 87% ee (Table 1, entry 1). In contrast, the reaction with (−)-**7** afforded (*S*)-**13a** in significantly lower yield, albeit with an enantioselectivity similar to that of the reaction with **6** (Table 1, entry 2). This result clarifies that (−)-**7**, with a racemization half-life of only approximately 1.3 days, also has a chiral induction ability. However, improvement is required in terms of the reactivity of the catalytic reaction. Subsequently, we investigated the effect of the base using (a*R*)-(−)-**6** by testing various bases. The reaction in the presence of Na_2CO_3 delivered the product in 99% yield, although the enantioselectivity slightly decreased compared to the reaction using K_2CO_3 (see Table 1, entry 1 vs entry 3). The use of Cs_2CO_3 resulted in a significant drop in the yield (Table 1, entry 4), whereas NaOAc improved the yield but slightly lowered the enantioselectivity (Table 1, entry 5). Other potassium salts such as K_3PO_4 led to a low yield

Table 1: Optimization of conditions for the Pd-catalyzed asymmetric allylic amination of acetate **12** with isatin (**11a**).[a]

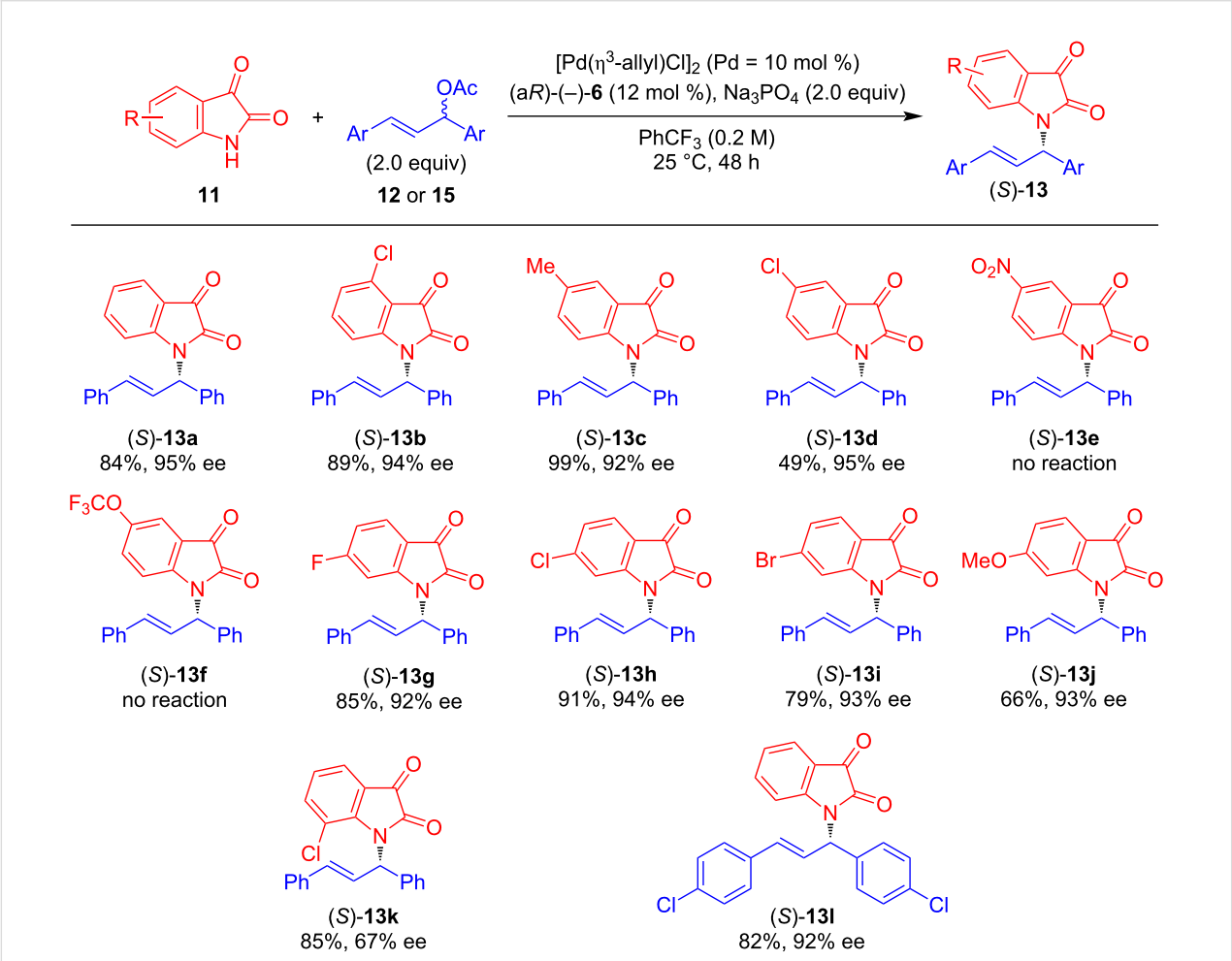


Entry	Base	Solvent	Yield (%)[b]	ee (%)[c]
1	K_2CO_3	$CHCl_3$	72	87
2[d]	K_2CO_3	$CHCl_3$	3	84
3	Na_2CO_3	$CHCl_3$	99	85
4	Cs_2CO_3	$CHCl_3$	19	86
5	NaOAc	$CHCl_3$	89	86
6	K_3PO_4	$CHCl_3$	12	86
7	Na_3PO_4	$CHCl_3$	60	88
8	Na_3PO_4	CH_2Cl_2	88	92
9	Na_3PO_4	CH_3CN	75	93
10	Na_3PO_4	THF	74	93
11	Na_3PO_4	DMF	trace	–
12	Na_3PO_4	$PhCF_3$	84	95
13[e]	Na_3PO_4	$PhCF_3$	50	86
14[f]	Na_3PO_4	$PhCF_3$	80	94

[a]The reaction was carried out at 0.1 mmol scale. [b]Isolated yield. [c]Determined by chiral HPLC analysis using a chiral column. Absolute configuration was assigned by comparison of HPLC analysis with reported data [26]. [d]This reaction was carried out using (–)-**7** instead of (a*R*)-(–)-**6** as a chiral ligand. [e]This reaction was carried out using 1,3-diphenylallyl pivalate (**14**) instead of acetate **12**. [f]This reaction was carried out at a 1.0 mmol scale.

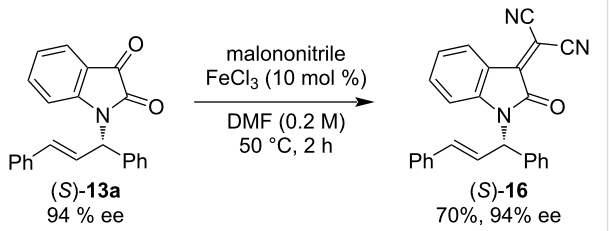
of the product (Table 1, entry 6). Meanwhile, when Na_3PO_4 was tested, the yield decreased, but the enantioselectivity improved to 88% ee (Table 1, entry 7). With Na_3PO_4 as the optimum base, which showed the highest enantioselectivity, we conducted a solvent screening. The reaction in CH_2Cl_2 resulted in better yield and enantioselectivity than in $CHCl_3$ (Table 1, entry 8). The coordinating solvents, CH_3CN and THF, further improved the enantioselectivity to 93% ee (Table 1, entries 9 and 10). In contrast, the reaction barely proceeded when DMF was used (Table 1, entry 11). The reaction in $PhCF_3$ afforded the target product in a good yield with the highest enantioselectivity compared to other solvents (Table 1, entry 12). Furthermore, when (*E*)-1,3-diphenyl-2-propenyl pivalate (**14**) was tested as the allyl ester, the desired product (*S*)-**13a** was obtained with a yield of 50% and an enantioselectivity of 86% ee (Table 1, entry 13). Additionally, the scale-up reaction using 1 mmol of isatin (**11a**) as the nucleophile under the optimal conditions (Table 1, entry 12) afforded the desired product (*S*)-**13a** with nearly the same yield and enantioselectivity as the 0.1 mmol scale reaction (entry 14).

Next, we investigated the substrate scope of the palladium-catalyzed asymmetric allylic amination of 1,3-diphenyl-2-propenyl acetate (**12**) with isatin derivatives **11** as nucleophiles under the optimized conditions using (a*R*)-(−)-**6** as the ligand and Na_3PO_4 as the base in $PhCF_3$ as the solvent (Scheme 2). An isatin derivative bearing a chloro group at the 4-position afforded the desired product (*S*)-**13b** with good yield and enantioselectivity. Similarly, an isatin derivative with a methyl group as an electron-donating group at the 5-position gave (*S*)-**13c** in good yield, although with slightly decreased enantioselectivity. The introduction of the chloro group at the same position led to a moderate yield for (*S*)-**13d**, while the enantioselectivity remained high. In contrast, the reaction with the isatin derivative bearing a nitro group at the 5-position did not proceed, and (*S*)-**13e** was not produced. Likewise, no reaction occurred with



Scheme 2: Pd-catalyzed asymmetric allylic amination of acetate **12** (Ar = Ph) or **15** (Ar = *p*-ClC_6H_4) with isatin derivatives **11** using (a*R*)-(–)-**6** as a chiral ligand: The reaction was carried out at 0.1 mmol scale; yields refer to isolated yields.

a trifluoromethoxy-substituted derivative, resulting in no formation of (*S*)-**13f**. Reactions using isatin derivatives bearing halogen substituents at the 6-position proceeded efficiently, affording (*S*)-**13g–i** in good yields with high enantioselectivities. Conversely, the isatin derivative bearing a methoxy group at the 6-position led to a decreased yield for (*S*)-**13j**, though the enantioselectivity remained high. Additionally, we tested the reaction using an isatin derivative with a chloro group at the 7-position and obtained (*S*)-**13k** in good yield with moderate enantioselectivity. Furthermore, when (*E*)-1,3-di(*p*-chlorophenyl)-2-propenyl acetate (**15**) was utilized as an allylic acetate, the desired product (*S*)-**13l** was obtained in high yield with excellent enantioselectivity. We confirmed that the product **13** from the Pd-catalyzed asymmetric allylic amination of allyl esters with isatin using (a*R*)-(−)-**6** possesses an *S*-configuration. This stereochemical outcome follows the same reaction mechanism as the Pd-catalyzed asymmetric allylic substitution of allyl esters with indoles using (a*R*)-(−)-**6** [31]. To explore further applications of this product, we treated (*S*)-**13a** (94% ee) with malononitrile in the presence of $FeCl_3$ as a catalyst [36] and obtained the corresponding malononitrile derivative (*S*)-**16** without any loss of optical purity (Scheme 3).



Scheme 3: Transformation of the reaction product (*S*)-**13a**: The reaction was carried out at 0.1 mmol scale and the yield refers to the isolated yield.

Conclusion

In this study, *N*-propyl-*N*-cinnamoylamide **7** was synthesized in three steps from phosphine oxide **8**. Chiral HPLC analysis confirmed its axial chirality at the C(aryl)–N(amide) bond. The optical resolution of (±)-**7** yielded (+)-**7** and (−)-**7**. The racemization barrier of (−)-**7** in *n*-dodecane was determined to be 25.0 kcal/mol at 25 °C, with a half-life of approximately 1.3 days. The chiral amides (a*R*)-(−)-**6** and (−)-**7** were evaluated as ligands in Pd-catalyzed asymmetric allylic amination, and while (−)-**7** exhibited promising enantioselectivity, its yield was lower than (a*R*)-(−)-**6**. Further optimization of reaction conditions led to improved yields and enantioselectivities up to 95% ee. Moreover, the reaction was successfully scaled up to 1 mmol. The substrate scope was investigated using various isatin derivatives, yielding high enantioselectivities (up to 95% ee) for most, except for those bearing certain electron-withdrawing groups. Additionally, we demonstrated the further conversion of (*S*)-**13a** into the malononitrile derivative (*S*)-**16** without loss of optical purity.

Supporting Information

Data of thermal racemization of **7**, DFT calculations for investigating racemization mechanism of **7**, general methods and materials, experimental procedures and characterization data, ^1H, ^{13}C and ^{31}P NMR spectra for **9** and **10**, ^1H, ^{13}C and ^{31}P NMR spectra and HPLC charts for (±)-**7**, (+)-**7** and (–)-**7**, ^1H and ^{13}C NMR spectra and HPLC charts for (*S*)-**13a–k** (except (*S*)-**13e**) and (*S*)-**16**.

Supporting Information File 1

Experimental section and compounds characterization.
[https://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-21-83-S1.pdf]

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Author Contributions

Natsume Akimoto: investigation. Kaho Takaya: investigation. Yoshio Kasashima: investigation. Kohei Watanabe: investigation. Yasushi Yoshida: investigation. Takashi Mino: conceptualization; supervision.

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Data Availability Statement

All data that supports the findings of this study is available in the published article and/or the supporting information of this article.

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