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Palladium Catalyzed Asymmetric Allylation of 3-OBoc-Oxindoles: An Efficient Synthesis of 3-Allyl-3-hydroxyoxindoles

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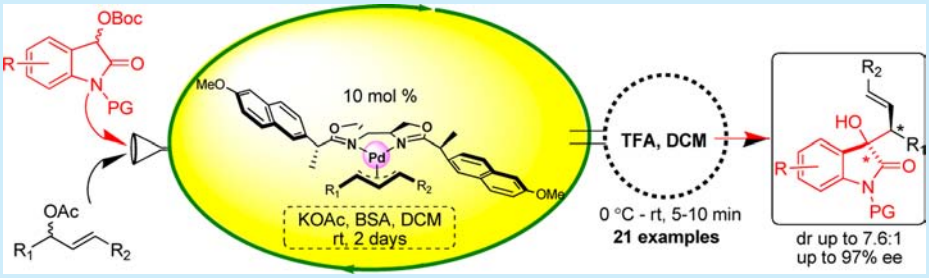
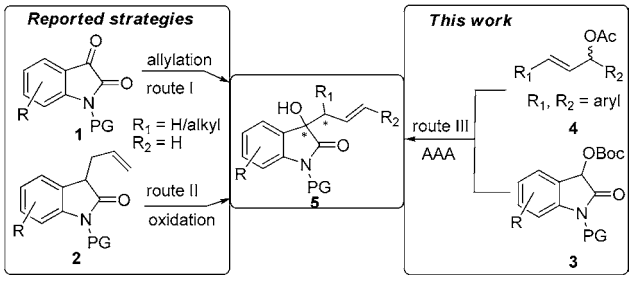
Supporting Information



ABSTRACT: 3-Allyl-3-hydroxyoxindoles were synthesized in very good enantio- (up to 97% ee) and diastereoselectivities (dr up to 7.6:1) with contiguous quaternary and tertiary stereogenic centers by employing tartrate derived bi(oxazoline) in Pd-catalyzed allylation of 3-OBoc-oxindole. Synthetic utility of 3-allyl-3-hydroxyoxindole was demonstrated by synthesizing a highly substituted spiro(oxindole-3,2′-tetrahydrofuran) derivative in good yield and stereoselectivity.

Development of efficient methodologies to access enantioenriched 3-substituted-3-hydroxyoxindoles is of great importance in contemporary organic synthesis, since they can be exploited as important synthons to synthesize various natural products and pharmaceutical lead compounds.[1] Consequently, various protocols on nucleophilic addition to isatins **1** have been developed. Although numerous methods were documented for the synthesis of 3-substituted-3-hydroxyoxindoles, access to 3-allyl-3-hydroxyoxindoles is highly warranted.[2] 3-Allyl-3-hydroxyoxindole **5** is a promising intermediate that can be used to synthesize structurally diverse oxindole derivatives (Scheme 1). In this context, few metal catalyzed strategies enabling the enantioselective synthesis of 3-allyl-3-hydroxyoxindoles have been developed (route I).[3] These methods involve expensive Ir-catalyst or Lewis acids and an excess of allylating reagents such as allylstannanes or allylsilanes which are difficult to synthesize. Organocatalytic allylation of isatins **1** also afforded 3-allyl-3-hydroxyoxindoles with good enantioselectivity (route I).[4] Alternatively, hydroxylation of oxindoles **2** using phase transfer catalysts was also developed (route II).[5] However, these approaches lack substrate diversity as well as the need for preformed sensitive reagents. Hence, identification of suitable nucleophile and electrophile counterparts is very important for accessing 3-allyl-3-hydroxyoxindoles **5**.

Scheme 1. Strategies for the Synthesis of 3-Allyl-3-hydroxyoxindoles



Pd-catalyzed asymmetric allylic alkylation (AAA) is a bedrock method to access structurally diverse scaffolds by the employment of various nucleophiles with allyl acetates/carbonates.[6] In particular, Trost et al. pioneered this method to synthesize numerous natural products and bioactive molecules using different types of nucleophiles including 3-alkyl/aryloxindoles.[7] Although 3-hydroxyoxindoles are demonstrated as effective nucleophiles to synthesize structurally diverse molecules,[8] exploration of 3-hydroxyoxindole in AAA is yet to be documented. This intrigued us to develop an Umpolung strategy by employing a 3-hydroxy protected oxindole (3-OBoc-oxindole) as a nucleophile[9] in a Pd-catalyzed allylic substitution reaction to access 3-allyl-3-hydroxyoxindoles. Earlier successful efforts in AAA in our laboratory motivated us to employ tartrate derived bi(oxazoline) as a ligand.[10] To the best of our knowledge, the AAA strategy is yet to be employed to synthesize substituted 3-allyl-3-hydroxyoxindoles. Herein we wish to report a highly enantio- and diastereoselective synthesis of 3-allyl-3-hydroxyoxindoles **5** via Pd-bi(oxazoline) catalyzed AAA of allyl acetates **4** with 3-OBoc-oxindole **3**.

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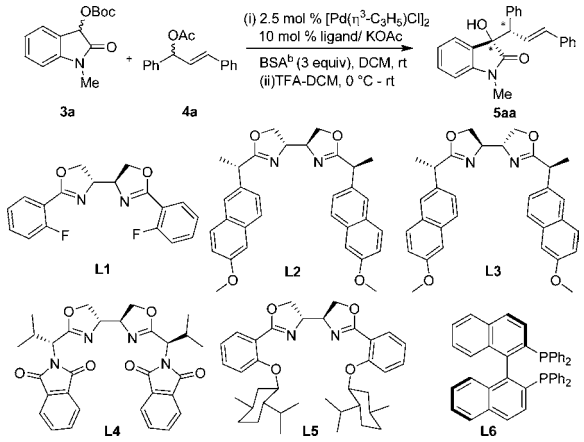
Initial efforts were dedicated to identifying suitable reaction conditions for the model reaction between 3-OBoc-oxindole **3a** and *rac*-1,3-diphenyl-2-propenyl acetate **4a** in dichloromethane using 2.5 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with 10 mol % of a chiral ligand. *O*-Boc protection of the resultant alkylated product was deprotected later by subsequent acidic treatment. Identification of an appropriate ligand was undertaken as a primary task, and chiral ligands **L1**−**6** were examined under identical conditions. The observed results are depicted in Table 1.

Table 1. Examination of Suitable Ligands[a]



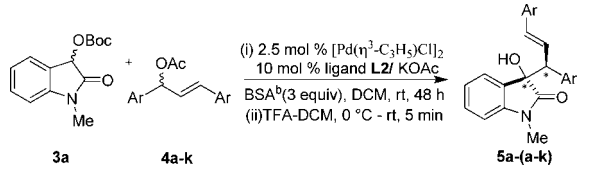
entry	ligand	**5aa** yield (%)[c]	dr[d]	ee (%)[e] of **5aa** major/minor
1	**L1**	69	2:1	44/44
2	**L2**	92	6.6:1	90/90
3	**L3**	67	5:1	−74/−63[f]
4	**L4**	trace	nd	nd[g]
5	**L5**	82	4:1	80/79
6	**L6**	87	4:1	−88/−79

[a]The reactions were conducted with substrates **3a** (0.10 mmol) and **4a** (0.12 mmol) in dichloromethane with 2.5 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 10 mol % of appropriate ligand at 25 °C (2 days). [b]BSA = *N*,*O*-Bis(trimethylsilyl)acetamide. [c]Yield of the isolated product. [d]The diastereomeric ratio was determined by ^{1}H NMR integration of the crude alkylated products. [e]Enantiomeric excess values of major and minor diastereomers were determined by chiral HPLC. [f]The minus sign signifies the opposite enantiomer. [g]Not determined.

The investigation of various bi(oxazoline)s **L1**−**5** clearly indicates the requirement of an additional chiral appendage, since bi(oxazoline) **L1** which is devoid of an extra chiral appendage yielded the product **5aa** with poor stereoselectivity (Table 1, entry 1). Allylic alkylation of 3-OBoc-*N*-methyl-oxindole **3a** occurred with very good diastereo- and enantioselectivities when bi(oxazoline) **L2** was employed (Table 1, entry 2). Only the moderate yield and stereoselectivity of the product **5aa** was noticed (Table 1, entry 3) when ligand **L3** (diastereomeric pair of **L2**) was used. These observations are in resonance with our previous results.[10b,11] Efforts to increase the enantioselectivity further by using structurally diverse bi(oxazoline) ligands **L4** and **L5** were undertaken. Then inability of ligand **L4** to catalyze the formation of the expected product can be attributed to the bulky nature of the chiral appendage which could have prevented the active complex formation (Table 1, entry 4). Use of bi(oxazoline) **L5** afforded the product **5aa** in good yield (Table 1, entry 5), though the stereoselectivity is low when compared to **L2**. Under the identical conditions BINAP **L6** was also investigated. Although a very good yield of product **5aa** was obtained using BINAP **L6**, a slight reduction in stereoselectivity was noticed (Table 1, entry 6). These results clearly imply that ligand **L2** is a more suitable chiral counterpart for Pd-catalyzed asymmetric allylic alkylation of 3-OBoc-*N*-methyl-oxindole **3a**. Hence, further optimization of the reaction conditions was carried out using bi(oxazoline) **L2** as a chiral ligand. Changes in other parameters such as solvents, Pd-salts, and additives improved neither the efficiency nor the stereoselectivity of the reaction.[12] Hence, 2.5 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ with 10 mol % of **L2** as the catalyst, 10 mol % of KOAc as an additive, and 3 equiv of BSA in dichloromethane were identified as the optimal conditions to probe the substrate scope of the reaction.

The effect of different substituents on 1,3-diaryl-2-propenyl acetates **4a**−**k** was investigated with 3-OBoc-oxindole **3a** under the optimized conditions. The observed results are summarized in Table 2. Electron-withdrawing *ortho*-fluoro substituted 1,3-

Table 2. Study of Substrate Scope[a]



entry	Ar (**4a**−**k**)	**5** yield (%)[c]	dr[d]	ee (%)[e] of **5** major/minor
1	C_6H_5 (**a**)	(**5aa**) 92	6.6:1	90/90
2	2-FC_6H_4 (**b**)	(**5ab**) 92	7:1	96/88
3	2-ClC_6H_4 (**c**)	(**5ac**) 00	–	–
4	3-$NO_2C_6H_4$ (**d**)	(**5ad**) 63	1.5:1	36/86
5	3-FC_6H_4 (**e**)	(**5ae**) 88	6.5:1	90/88
6	3-ClC_6H_4 (**f**)	(**5af**) 80	4.4:1	85/84
7	3-BrC_6H_4 (**g**)	(**5ag**) 81	4.8:1	92/85
8	4-FC_6H_4 (**h**)	(**5ah**) 90	5:1	82/78
9	4-ClC_6H_4 (**i**)	(**5ai**) 85	2:1	86/76
10	4-BrC_6H_4 (**j**)	(**5aj**) 77	5:1	93/21
11	2-naphthyl (**k**)	(**5ak**) 69	3:1	80/50

[a]The reactions were conducted with substrates **3a** (0.10 mmol) and **4a**−**k** (0.12 mmol) in dichloromethane with 2.5 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 10 mol % of ligand **L2** at 25 °C (2 days). [b]BSA = *N*,*O*-Bis(trimethylsilyl)acetamide. [c]Yield of the isolated product. [d]The diastereomeric ratio was determined by ^{1}H NMR integration of the crude alkylated products. [e]Enantiomeric excess values of major and minor diastereomers were determined by chiral HPLC.

diaryl-2-propenyl acetate **4b** underwent alkylation smoothly to afford the corresponding product **5ab** with good diastereo- (7:1) and very good enantioselectivity (96/88) (Table 2, entry 2). No formation of expected product **5ac** was observed when *ortho*-chloro substituted 1,3-diaryl-2-propenyl acetate **4c** was subjected to AAA (Table 2, entry 3). This can be attributed to the bulkiness of the chlorine atom which may sterically inhibit the formation of active π-allyl-palladium species. An electron-withdrawing nitro substituent at the *meta*- position hampers the catalytic efficiency which results in the formation of product **5ad** in moderate yield and stereoselectivity (Table 2, entry 4). On the other hand, electron-withdrawing as well as bulky *meta*-halogen substitutions on 1,3-diaryl-2-propenyl acetates **4e**−**g** did not affect the formation of desired products. The respective products **5ae**−**5ag** were isolated in very good yields and stereoselectivities (Table 2, entries 5−7). 4-Fluoro-substituted allyl acetate **4h** furnished the desired alkylated product **5ah** with similar

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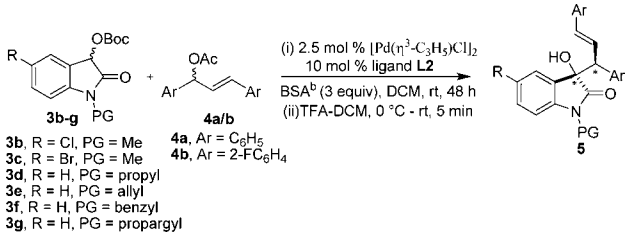
diastereoselectivity as in the case of *meta*-fluoro-substituted **4e**, but with slightly lowered enantioselectivity (Table 2, entry 8). The presence of chloro-substitution at the *para*-position significantly affected the diastereoselectivity of the product **5ai** (Table 2, entry 9) but had an insignificant effect on the enantioselectivity. Very poor enantioselectivity was observed in the case of the minor diastereomer of **5aj** when bromine was present at the *para*-position; however, the enantioselectivity of the major diastereomer remained unaffected (Table 2, entry 10). When more sterically hindered *rac*-1,3-di(napthalen-2-yl)-propenyl acetate **4k** was employed as a substrate, alkylation proceeded with good yield and stereoselectivity (Table 2, entry 11).

Next, the influence of halogen substitutions at the fifth position of the oxindole ring was studied. Under the identical reaction conditions, 3-OBoc-5-chloro-*N*-methyl oxindole **3b** was reacted with *rac*-1,3-diphenyl-2-propenyl acetate **4a**, to furnish the product **5ba** with very good yield as well as diastereo- and enantioselectivity (Table 3, entry 1). The presence of bromine at

Table 3. Effect of Substituents on 3-OBoc-Oxindole[a]



entry	3	4	5 yield (%)[c]	dr[d]	ee (%)[e] of 5 major/minor
1	**3b**	**4a**	(**5ba**) 91	7.6:1	89/85
2	**3c**	**4a**	(**5ca**) 93	5:1	43/53
3	**3d**	**4b**	(**5db**) 73	5:1	96/nd[f]
4	**3e**	**4b**	(**5eb**) 88	3.7:1	96/51
5	**3f**	**4b**	(**5fb**) 85	4.5:1	94/82
6	**3g**	**4b**	(**5gb**) 31	3:1	57/nd

[a]The reactions were conducted with substrates **3b−g** (0.10 mmol) and **4a/b** (0.12 mmol) in dichloromethane with 2.5 mol % of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 10 mol % of ligand **L2** at 25 °C (2 days). [b]BSA = *N*,*O*-Bis(trimethylsilyl)acetamide. [c]Yield of the isolated product. [d]The diastereomeric ratio was determined by ^{1}H NMR integration of the crude alkylated product. [e]Enantiomeric excess values of major and minor diastereomers were determined by chiral HPLC. [f]Not determined.

the fifth position of the oxindole moiety, although unimpactful to the yield and diastereoselectivity, lowered the enantioselectivity for both diastereomers of **5ca** (Table 3, entry 2). Since alkylation of 1,3-bis(2-fluorophenyl)allyl acetate **4b** resulted in very good stereoselectivity, the impact of N_1-substitution on oxindole was similar. Neither the yield nor the stereoselectivity was affected by the presence of propyl **5db** or allyl **5eb** or benzyl **5fb** substituents on the N_1-position (Table 3, entries 3−5). The labile nature of *N*-propargyl protection in the presence of Pd-reagents can be the reason for the low yield and selectivity of product **5gb** (Table 3, entry 6).[13]

Encouraged by these results we expanded the substrate scope to 1,3-unsymmetrically substituted 2-propenyl acetates. Despite the different substitutions on the C1 and C3 centers of 2-propenyl acetates, the reaction proceeded to yield both regioisomers almost equally (up to 1.5:1) with good yields and stereoselectivities (dr up to 6.6:1 and up to 97% ee) (Table S3, entries 1−4).[12]

To determine the absolute stereochemistry of alkylated product **5aa**, the derivative **6aa** was synthesized and the single crystal X-ray analysis of **6aa** revealed that the quaternary and tertiary chiral centers possess *S*,*S* configurations respectively (Figure 1).[14]

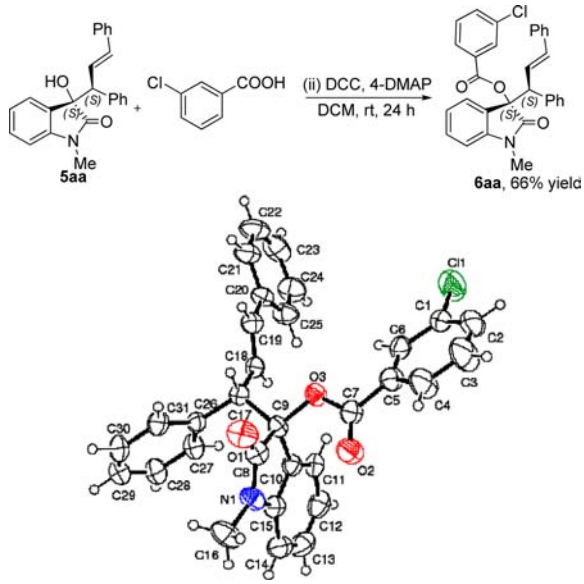
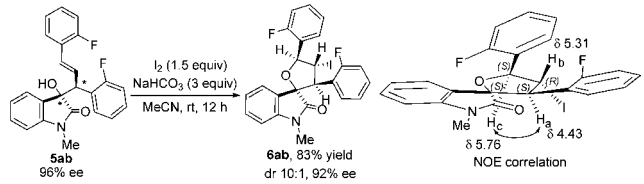


Figure 1. Synthesis and ORTEP diagram of compound **6aa**.

A spirooxindole comprising a 3,2′-tetrahydrofuran moiety is an important candidate possessing anticancer activity. Since, only a few methods describe the synthesis of these scaffolds enantioselectively, an efficient method to access highly substituted spiro(oxindole-3,2′-tetrahydrofuran) is highly desired.[8d,15] This intrigued us to demonstrate the synthetic utility of alkylated product **5ab** in constructing this scaffold enantioselectively. The presence of a homo allyl moiety in product **5ab** paved the way to synthesize spiro(oxindole-3,2′-tetrahydrofuran) derivative **6ab** which contains four contiguous stereogenic centers (Scheme 2). Spirooxindole **6ab** was isolated in 83% yield

Scheme 2. Synthesis of Spiro(oxindole-3,2′-tetrahydrofuran) Derivative and NOE Correlation of 6ab



by treating **5ab** with 1.5 equiv of I_2 and 4 equiv of $NaHCO_3$ in acetonitrile. The relative stereochemistry of the newly generated chiral centers of **6ab** was further confirmed using NOE correlation by irradiation of Ha, Hb, and Hc protons, respectively. It is noteworthy that this is the first method which discloses the synthesis of spirooxindole **6ab** which comprises a tetrahydrofuran ring from 3-allyl-3-hydroxyoxindole with excellent enantioselectivity.

In summary, we have developed a Pd-catalyzed AAA strategy to synthesize 3-allyl-3-hydroxyoxindoles **5** by the treatment of 3-

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OBoc-oxindole **3** with 1,3-disubstituted propenyl acetates **4**. Tartrate derived bi(oxazoline) **L2** provided remarkable asymmetric induction in the Pd-catalyzed allylation of 3-OBoc-oxindole. Under the optimized conditions, high enantio- (up to 97% ee) and diastereoselective (dr up to 7.6:1) synthesis of 3-allyl-3-hydroxyoxindoles was achieved with a wide range of 1,3-symmetrically substituted 2-propenyl acetates. Synthetic utility of 3-allyl-3-hydroxyoxindoles **5ab** was demonstrated by constructing a highly substituted spiro(oxindole-3,2′-tetrahydrofuran) **6ab** derivative with four consecutive chiral centers in excellent enantioselectivity.

■ ASSOCIATED CONTENT

Supporting Information

Complete experimental details and characterization data for the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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