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Pd-Catalyzed Desymmetric Intramolecular *O*-Arylation Reaction: Enantioselective Synthesis of (3,4-Dihydro-2*H*-chromen-3-yl)-methanols

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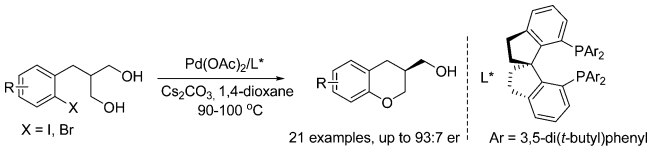
ABSTRACT



An enantioselective intramolecular *O*-arylation was achieved through desymmetrization with Pd-catalyzed coupling reactions. The intramolecular asymmetric aryl C−O coupling reactions of 2-(2-haloaryl)propane-1,3-diols led to the enantioselective formation of chiral (3,4-dihydro-2*H*-chromen-3-yl)methanols in good yields and high enantiomeric selectivity.

Aryl ethers and oxygen heterocycles with an O-arylated moiety have been found to be prevalent structures in many bioactive natural products, pharmaceuticals, cosmetics, and polymers.[1] Classic methods for the formation of aryl C−O bonds include Williamson ether synthesis,[2] direct nucleophilic substitution reactions,[3] and transition metals such as Cu[4,5] and Pd[6] catalyzed coupling reactions of aryl halides with oxygen nucleophiles. Traditionally, Cu-mediated Ullmann-type coupling reactions of aryl halides with phenols and aliphatic alcohols are important methods for

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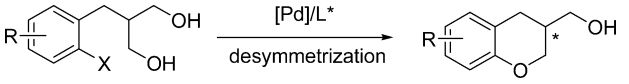
the synthesis of diaryl or aryl alkyl ethers. In recent years, improved protocols have been developed by adding proper copper ligands to promote reactions under relatively much milder conditions. However, limitations such as a limited substrate scope, high temperature, and requirement of a high loading of catalyst still exist.[4,5] The Pd-catalyzed protocol is an alternative for copper-catalyzed methods and has been applied under milder conditions with a broader substrate scope. However, in some cases low yields were obtained for the Pd-catalyzed coupling of aryl halides with primary or secondary alcohols due to the competing β-hydrogen elimination. Thus specially designed ligands are needed for these catalysts to achieve better performance in such reactions.[6d−j]

Although great progress has been made in the Cu and Pd catalyzed coupling of aryl halides with alcohols, little attention has been focused on the asymmetric O-arylation reaction since no chiral carbon center directly was involved in the process of aryl C(sp^2)−O bond formation. The significance in developing novel methods in an enantioselective manner from readily available starting materials has attracted broad interest in the synthetic community. Many transition-metal catalyzed asymmetric aryl C−C or C−N bond formations have been achieved through an "indirect" manner such as desymmetrization[7,8] or kinetic resolution.[9,10] During the course of developing asymmetric aryl C−heteroatom coupling reactions, our group recently developed some copper-catalyzed asymmetric aryl C(sp^2)−N coupling reactions through the asymmetric desymmetrization or kinetic resolution strategies.[11] We believed that such strategies may also be applicable to the asymmetric aryl C(sp^2)−O coupling of aryl halides with a hydroxyl group. To the best of our knowledge, only one example of copper-catalyzed asymmetric aryl C(sp^2)−O coupling was recently reported, which induced an axis chirality in diaryl ether formation with moderate enantioselectivity.[12] No example of a transition metal catalyzed asymmetric O-arylation reaction for the formation of a chiral carbon center has been reported to date. It is perhaps due to the limitations in substrate scope and ligand selection in Cu or Pd catalyzed C−O couplings, which bring more challenges in developing asymmetric reactions as compared with that of C−N or C−C couplings. In this paper, we disclose the research results of the first desymmetrization with a Pd-catalyzed asymmetric O-arylation reaction, which offered a general approach for the enantioselective synthesis of biologically important (3,4-dihydro-2*H*-chromen-3-yl)methanol structures (Scheme 1).[13]

Scheme 1. Design of Pd-Catalyzed Asymmetric Aryl C−O Coupling through Desymmetrization Strategy



Our investigation commenced by examining the desymmetric coupling of 2-(2-iodobenzyl)propane-1,3-diol (**1a**) in the presence of $Pd(OAc)_2$, Cs_2CO_3, and chiral ligands. The challenges in aryl C−O coupling were shown by the results in the ligand selection. A wide range of commercially available chiral ligands, including bidentated diphospine ligands L1−L3, N,P ligand L4, and monodentated ligand L5, failed to induce any desired product or enantioselectivity in the coupling reaction (Table 1, entries 1−5). Finally, we were pleased to find that a commercial spirocyclic biphosphine ligand L6 afforded the desired coupling product **2a** in 66% yield and 63:37 enantiomeric ratios (Table 1, entry 6).[14] Further optimization of the spirocyclic ligands led to the conclusion that a bulky aryl

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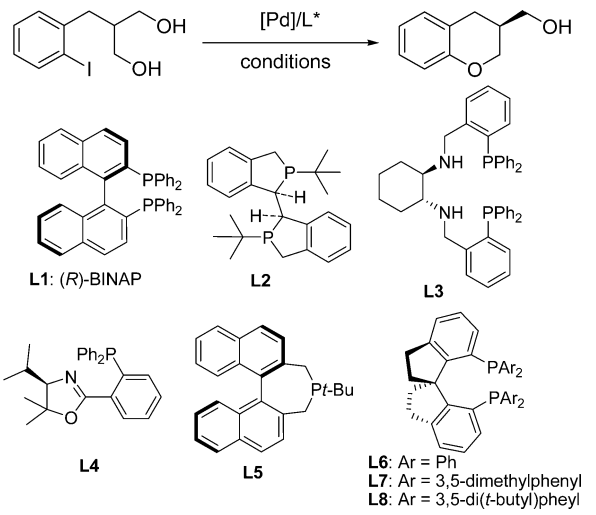
Table 1. Screening Reaction Conditions[a]



entry	L*	Pd	solvent	yield (%)[b]	er[c]
1	L1	$Pd(OAc)_2$	1,4-dioxane	<10	51:49
2	L2	$Pd(OAc)_2$	1,4-dioxane	<10	50:50
3	L3	$Pd(OAc)_2$	1,4-dioxane	n.d.	–
4	L4	$Pd(OAc)_2$	1,4-dioxane	25	49:51
5	L5	$Pd(OAc)_2$	1,4-dioxane	17	51:49
6	L6	$Pd(OAc)_2$	1,4-dioxane	66	63:37
7	L7	$Pd(OAc)_2$	1,4-dioxane	63	70:30
8	**L8**	**$Pd(OAc)_2$**	**1,4-dioxane**	**65**	**90:10**
9	L8	$Pd(OAc)_2$	toluene	17	65:35
10	L8	$Pd(OAc)_2$	MeCN	10	88:12
11	L8	$Pd(OAc)_2$	DMF	n.d.	–
12	L8	$Pd(OAc)_2$	THF	5	91:9
13	L8	$Pd(OAc)_2$	$(MeOCH_2)_2$	35	91:9
14	L8	$PdCl_2$	1,4-dioxane	50	84:16
15	L8	$Pd(PPh_3)_2Cl_2$	1,4-dioxane	15	87:13
16	L8	$Pd_2(dba)_3$	1,4-dioxane	55	90:10

[a] Reagents and reaction conditions: **1a** (0.20 mmol, 1.0 equiv), Pd catalyst (0.006 mmol, 3 mol %), ligand (0.006 mmol, 3 mol %), base, (0.4 mmol, 2.0 equiv), solvent (1.0 mL), 90 °C, 15 h. [b] Isolated yields. [c] Enantiomeric ratios were determined by HPLC analysis (Chirapak AD-H column).

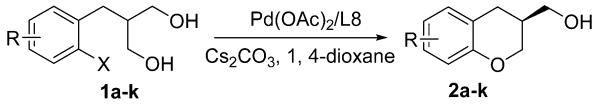
on the phosphorus atom may increase the enantioselectivity. When L7 and L8[15] were tested, the desired product **2a** was obtained in 70:30 er (63% yield) and 90:10 er (65% yield), respectively (Table 1, entries 7 and 8). With L8 as the ligand, other solvents were screened and slightly better enantioselectivity was obtained (91:9 er) in THF and 1,2-dimethoxyethane (Table 1, entries 12 and 13). However, the yields were much lower than that in 1,4-dioxane due to side reactions.[16,17] Different Pd salts were also screened, and

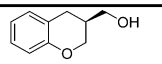
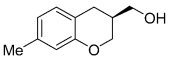
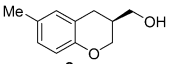
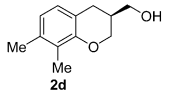
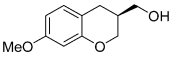
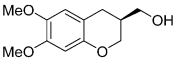
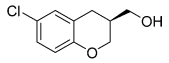
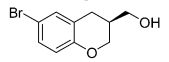
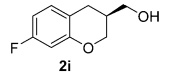
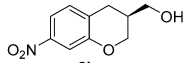
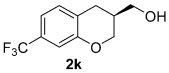
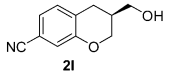
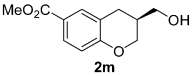
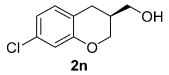
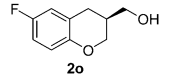
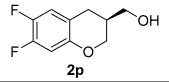
(15) The ligands were synthesized according to literature reported methods; see: Xie, J.-H.; Wang, L.-X.; Fu, Y.; Zhu, S.-F.; Fan, B.-M.; Duan, H.-F.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2003**, *125*, 4404.

(16) Two byproducts were identified in these reactions as dehalogenation and β-H elimination/dehydroxylation byproducts. See Supporting Infromation.

(17) Bases were also screened, and better enantioselectivity (93:7 er) was achieved with CsOH as the base in THF; however, only a 20% yield was obtained.

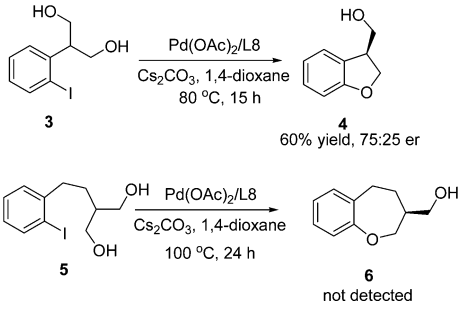
Table 2. Substrate Scope for Pd-Catalyzed Asymmetric Desymmetrization[a]



entry	substrate (X)	product	yield (%)[b]	er[c]
1	**1a** (I)	 **2a**	65	90:10
2	**1a'** (Br)		50	86:14
3	**1b** (I)	 **2b**	61	93:7
4	**1b'** (Br)		48	88.5:11.5
5	**1c** (I)	 **2c**	56	90:10
6	**1c'** (Br)		52	86:14
7	**1d** (I)	 **2d**	72	70:30
8	**1e** (I)	 **2e**	52	91:9
9	**1f** (I)	 **2f**	35	93.5:6.5
10	**1g** (I)	 **2g**	51	90.5:9.5
12	**1h** (I)	 **2h**	53	87:13
13	**1i** (I)	 **2i**	63	89:11
14	**1j** (I)	 **2j**	57	81.5:18.5[d]
15	**1k** (I)	 **2k**	60	87:13
16	**1l** (I)	 **2l**	70	89:11
17	**1m** (I)	 **2m**	45	73.5:26.5
18	**1n** (Br)	 **2n**	44	84:16
19	**1o** (Br)	 **2o**	64	86:14
20	**1p** (Br)	 **2p**	43	88.5:11.5

[a] Reagents and reaction conditions: **1** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.006 mmol, 3 mol %), L8 (0.006 mmol, 3 mol %), Cs_2CO_3 (0.4 mmol, 2.0 equiv), 1,4-dioxane (1.0 mL), 15 h, 90 °C for X = I and 100 °C for X = Br. [b] Isolated yields. [c] Determined by HPLC analysis (Chirapak AD-H or OD-H column). [d] The er value was determined after the one-step transformation.

Scheme 2. Attempt for Construction of a Five- or Seven-Membered Ring through Asymmetric Desymmetrization



$Pd(OAc)_2$ seemed to be the best (Table 1, entries 10 and 14−16). Finally, the absolute configurations of the product **2a** (table 1, entry 8) was assigned to be *S* by comparison with the reported data.[18]

Under the optimal reaction conditions, the substrate scope was explored. First, a variety of 2-(2-iodobenzyl)-propane-1,3-diols **1a**−**m** were subjected to the desymmetrization with the Pd-catalyzed asymmetric O-arylation reaction, and the results were shown in Table 2. In most cases, both the electron-donating and -withdrawing substituents on the aryl ring were well tolerated. The desired products were obtained in high enantiomeric ratios (Table 2, entries 1, 3, 5, and 7−17) and moderate yields, which was caused by the dehalogenation and β-H elimination/dehydroxylation side reactions.[16] Further, 2-(2-bromobenzyl)propane-1,3-diols were also tested in our reaction system in slightly elevated reaction temperatures, and the desired products were obtained in moderate yields (Table 2, entries 2, 4, 6, and 18−20), though the enantioselectivity is slightly inferior to that of products obtained from the corresponding aryl iodide substrates (Table 2, entries 2, 4, 6 and 1, 3, 5).

To further explore the scope of this reaction system, we also tried the desymmetric reactions for the formation of five- or seven-membered rings. The reaction of 2-(2-iodophenyl)-propane-1,3-diol **3** delivered the corresponding dihydrobenzofuran product **4** in 60% yield and 75:25 er. However, the formation of a seven-membered ring was unsuccessful even at 100 °C (Scheme 2).

In summary, a Pd-catalyzed enantioselective O-arylation has been developed through the desymmetrization strategy. Such an intramolecular aryl C(sp^2)−O coupling reaction led to the formation of chiral (3,4-dihydro-2*H*-chromen-3-yl)-methanols in moderate yields and high enantiomeric ratios. Further exploration and applications of this reaction in organic synthesis are underway in our laboratory.

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Supporting Information Available. Full experimental procedures, characterization data for all the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

(18) See Supporting Information.

The authors declare no competing financial interest.