Helical Structures

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Chiral Palladacycle Catalysts Generated on a Single-Handed Helical Polymer Skeleton for Asymmetric Arylative Ring Opening of 1,4-Epoxy-1,4-dihydronaphthalene**

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Abstract: *Post-polymerization C–H activation of poly(quinoxaline-2,3-diyl)-based helically chiral phosphine ligands (PQXphos) with palladium(II) acetate afforded chiral phosphapalladacycles quantitatively. In situ generated palladacycles exhibited enantioselectivities up to 94% ee in the palladium-catalyzed asymmetric ring-opening arylation of 1,4-epoxy-1,4-dihydronaphthalenes with arylboronic acids.*

There has been increasing interest in metallacyclic catalysts, including pincer-type complexes bearing carbon–transition-metal bonds, as these commonly exhibit unique catalytic activities and are more robust than ordinary transition-metal catalysts bearing heteroatom-based ligands.[1] Palladacycle catalysts are of particular interest because of the richness and wide use of palladium-catalyzed reactions in synthetic organic chemistry.[2] It is noteworthy that a palladacycle catalyst has resulted in excellent turnover numbers in Suzuki–Miyaura cross-coupling reactions.[3] While most palladacycle catalysts are achiral and utilized in non-asymmetric catalytic reactions, such as Heck-type and cross-coupling reactions,[4] some chiral enantiopure palladacycle catalysts have been synthesized and utilized in catalytic asymmetric reactions, including the [3,3] sigmatropic rearrangement of allylic imidates and trichloroacetimidates,[5] Miyaura–Hayashi-type conjugate arylation,[6] hydrophosphination of α,β-unsaturated enones,[7] and Lautens-type arylative ring opening of oxabicyclic alkenes.[8,9] In the latter C–C bond-forming reaction reported by Hou and co-workers, enantioselectivities as high as 83% *ee* have been obtained using a palladacycle catalyst derived from optically pure 2-diphenylphosphino-1,1′-binaphthyl (H-MOP) generated by intramolecular stoichiometric C–H activation.[9c] However, in other attempted asymmetric reactions, relatively low *ee* values have been obtained using chiral palladacycle catalysts.[10]

In recent years, we have developed helical polyquinoxaline-based chiral monophosphine ligands PQXphos for use in various asymmetric reactions where palladium(0)-PQXphos complexes are involved (Figure 1).[11,12] The enantioselectivities are particularly high, often exceeding those obtained with low-molecular-weight chiral ligands. We expected that the scaffold of PQXphos may also provide helical polymer-based chiral palladacycle catalysts showing high enantioselectivity. We report here that a palladacycle structure was generated on a helical polymer scaffold by post-polymerization C–H activation,[13] with the phosphorus pendant of the PQXphos serving as a directing group. The polymer-based palladacycle catalyst showed enantioselectivities up to 94% *ee* in the Lautens-type asymmetric arylative ring opening of 1,4-epoxy-1,4-dihydronaphthalenes.

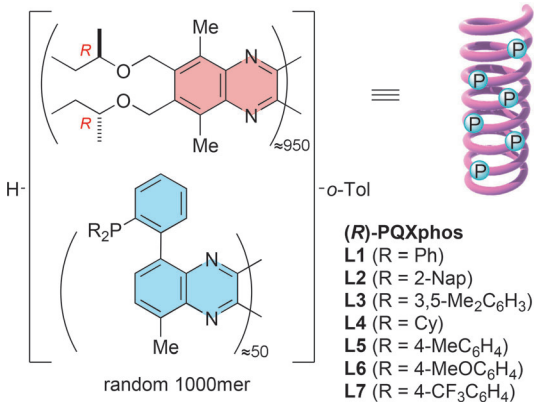

Figure 1. The poly(quinoxaline-2,3-diyl)-based helically chiral phosphine ligand PQXphos.

An initial trial of the asymmetric ring-opening arylation of 1,4-epoxy-1,4-dihydronaphthalene (**1a**) with 4-methylphenylboronic acid (**2a**) was performed using $Pd(OAc)_2$ and (*P*)-(*R*)-PQXphos (**L1**), which bears diphenylphosphino groups (Table 1). After stirring a mixture of **L1**, $Pd(OAc)_2$, and Cs_2CO_3 in chloroform for 5 min, **1a** and **2a** were added. The reaction proceeded at room temperature to form 2-(4-methylphenyl)-1,2-dihydro-1-naphthol (**3aa**) in 92% yield and 86% *ee* (entry 1). Other palladium precursors were also tested. The reaction with $Pd(TFA)_2$ proceeded relatively slowly, with the product formed with 88% *ee* (entry 2), while $[PdCl_2(CH_3CN)_2]$ led to a product with 80% *ee* (entry 3). It is noteworthy that $[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$ did not act as a catalyst, while $[Pd_2(dba)_3]$ provided a high yield of **3aa** but low enantioselectivity (entries 4 and 5). As $Pd(OAc)_2$, $Pd(TFA)_2$, and $[PdCl_2(CH_3CN)_2]$ are widely recognized as palladacycle precursors,[2] we assume that palladacycles generated in situ were acting as efficient chiral catalysts in these reactions.

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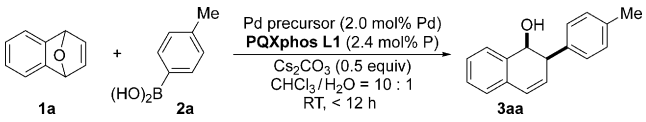
Table 1: Asymmetric ring-opening reaction of 1,4-epoxy-1,4-dihydronaphthalene in the presence of PQXphos.[a]



Entry	Pd precursor	Yield [%][b]	*ee* [%][c]
1	$Pd(OAc)_2$	92	86
2	$Pd(TFA)_2$	91	88
3	$[PdCl_2(CH_3CN)_2]$	94	80
4	$[\{PdCl(\eta^3\text{-}C_3H_5)\}_2]$	< 5	nd
5	$[Pd_2(dba)_3]$	98	19

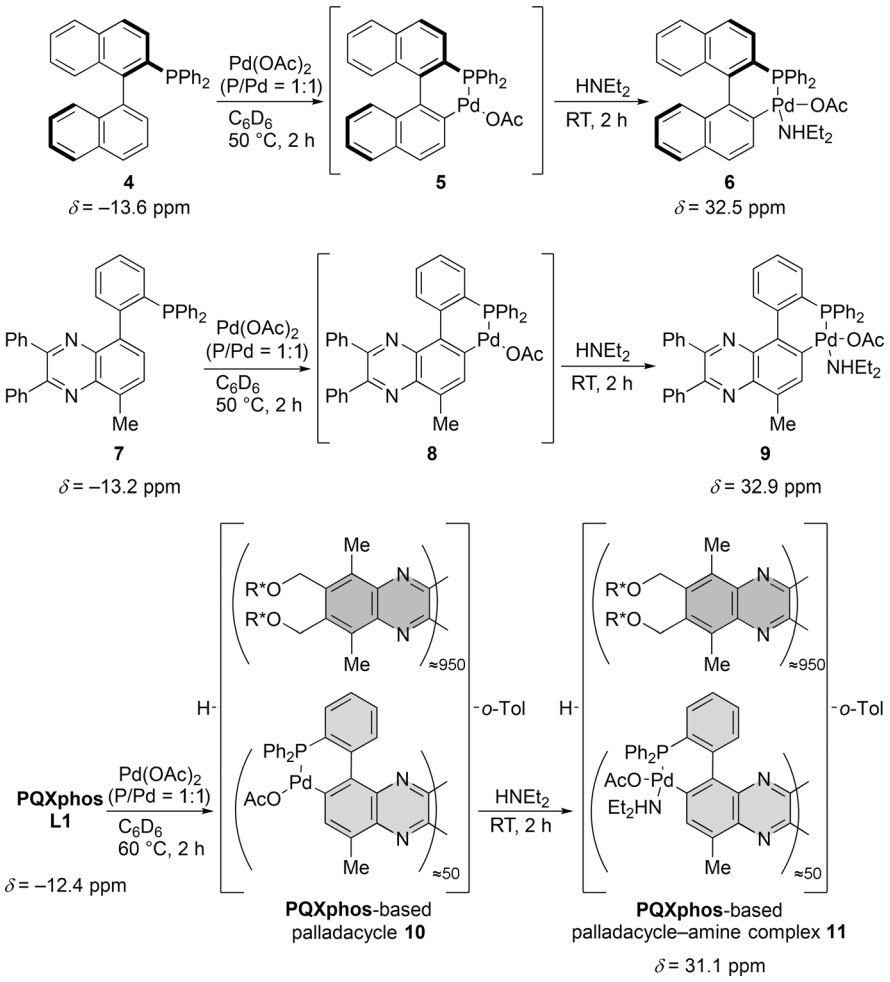
[a] **1a** (0.24 mmol), **2a** (0.20 mmol), Cs_2CO_3 (0.10 mmol), Pd precursor (4.0 μmol Pd), and ligand (4.8 μmol P) were stirred in $CHCl_3$ (800 μL) and H_2O (80 μL) at room temperature. [b] Yield of isolated product. [c] Determined by supercritical fluid chromatography (SFC) analysis on a chiral stationary phase. TFA = trifluoroacetate, dba = dibenzylideneacetone.

The generation of palladacycles on PQXphos was confirmed by comparison with identified low-molecular-weight palladacycles.[14] According to the procedure developed by Hou and co-workers,[8c] the H-MOP-based palladacycle **5** was prepared by stirring a solution of H-MOP and $Pd(OAc)_2$ in benzene at 50 °C for 2 h (Scheme 1). The palladacycle showed a complex NMR spectrum, presumably because of equilibrium between monomeric and dimeric forms. We found that addition of diethylamine led to dissociation to the monomeric form, thus enabling identification by ^{31}P NMR spectroscopy, which showed a signal at $\delta = 32.5$ ppm. This signal is assignable to the monomeric palladacycle coordinated by diethylamine.[15] palladacycle **8** was obtained by using quinoxaline-based triarylphosphine **7** as a model of a phosphine unit of PQXphos. By using the same procedure, palladacycle **8** was confirmed to form an air- and moisture-stable palladacycle-amine complex **9**, which showed a signal at $\delta = 32.9$ ppm in the ^{31}P NMR spectrum. PQXphos-based palladacycle **10** was also obtained as an insoluble material by stirring a solution of **L1** and $Pd(OAc)_2$ in benzene at 60 °C for 2 h. Deaggregation of the palladacycle by the addition of diethylamine made it soluble in benzene, and an amine complex **11** was formed. A shift in the ^{31}P NMR signal from $\delta = -12.4$ to 31.1 ppm indicated quantitative conversion of the phosphine units on PQXphos into palladacycles.

Based on these results, we screened substituents on the phosphorus atom of PQXphos (Table 2). To ensure the generation of palladacycle, **L1** and $Pd(OAc)_2$ were stirred in toluene with Cs_2CO_3 at 60 °C for 2 h prior to the addition of **1a** and **2a**. This procedure for catalyst generation increased the enantioselectivity slightly (entry 1; 88 % *ee*). Although PQXphos bearing a 2-naphthyl group (**L2**) or 3,5-dimethylphenyl group (**L3**) showed moderate enantioselectivities, the cyclohexyl derivative **L4** formed the product with only 10 % *ee* (entries 2–4). We also prepared PQXphos derivatives **L5**–**L7** bearing electron-donating and electron-withdrawing groups, although all showed lower enantioselectivities than **L1** (entries 5–7).

Further optimization of the reaction conditions was performed using **L1** as the ligand of choice. The use of toluene or THF as a solvent resulted in lower enantioselectivities (Table 2, entries 8 and 9). The high catalytic activity of the palladacycle facilitated reduction of the catalyst loading to 1.0 mol % with no decline in the enantioselectivity (entry 10). The use of KF instead of Cs_2CO_3 decreased the reaction rate, and slightly increased the enantioselectivity (entry 11, 90 % *ee*).

Ring-opening arylation also proceeded with phenylboronic acid (**2b**) and its derivatives, including boronic esters and trifluoroborate (Table 3). The reaction with phenylboronic acid (**2b**) afforded **3ab** with 90 % *ee* (entry 1). The use of KF



Scheme 1. Synthesis of palladacycles.

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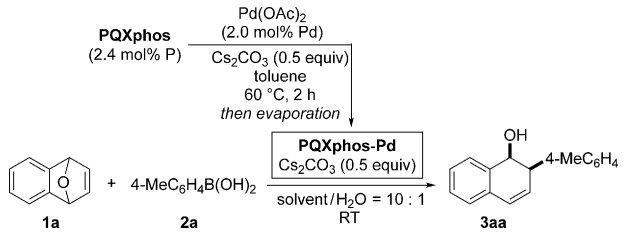
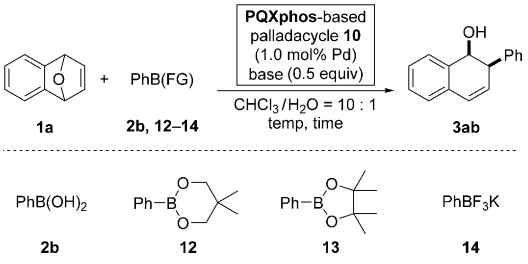
Table 2: Asymmetric ring-opening reaction of 1,4-epoxy-1,4-dihydronaphthalene in the presence of PQXphos derivatives.[a]



Entry	Ligand	Solvent	Yield [%][b]	*ee* [%][c]
1	**L1**	$CHCl_3$	96	88
2	**L2**	$CHCl_3$	87	52
3	**L3**	$CHCl_3$	94	50
4	**L4**	$CHCl_3$	65	10
5	**L5**	$CHCl_3$	88	47
6	**L6**	$CHCl_3$	63	30
7	**L7**	$CHCl_3$	89	63
8	**L1**	toluene	89	76
9	**L1**	THF	90	79
10[d]	**L1**	$CHCl_3$	89	88
11[d,e]	**L1**	$CHCl_3$	97	90

[a] **1a** (0.24 mmol), boronic acid (0.20 mmol), Cs_2CO_3 (0.10 mmol), Pd precursor (4.0 μmol Pd), and ligand (4.8 μmol P) were stirred with solvent (0.40 mL) at room temperature. [b] Yield of isolated product. [c] Determined by SFC analysis on a chiral stationary phase. [d] Pd precursor (2.0 μmol Pd), ligand (2.4 μmol P). [e] KF used instead of Cs_2CO_3.

Table 3: Scope of the boronic acid derivatives.[a]



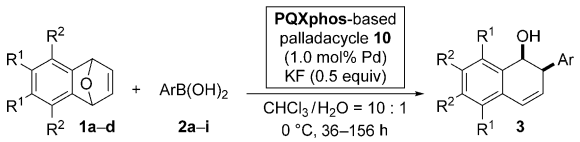
Entry	PhB(FG)	base	*T* [°C]	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**2b**	Cs_2CO_3	RT	12	97	90
2	**2b**	KF	RT	12	87	91
3	**2b**	KF	0	36	97	94
4	**12**	Cs_2CO_3	0	36	90	78
5	**12**	KF	0	96	87	80
6	**13**	Cs_2CO_3	0	120	80	93
7	**13**	KF	0	120	trace	nd[d]
8	**14**	Cs_2CO_3	0	120	82	92
9	**14**	KF	0	120	trace	nd[d]

[a] $Pd(OAc)_2$ (2.0 μmol), PQXphos (2.4 μmol P), and base (0.1 mmol) were heated with toluene at 60 °C for 2 h. After evaporation of the solvent, **1a** (0.24 mmol), PhB(FG) (0.20 mmol), $CHCl_3$ (800 μL), and H_2O (80 μL) were added at 0 °C. [b] Yield of isolated product. [c] Determined by SFC analysis on a chiral stationary phase. [d] Not determined.

instead of Cs_2CO_3 decreased the reaction rate and increased the enantioselectivity (entry 2). The *ee* value of the product was improved (94%) by lowering the reaction temperature to 0 °C (entry 3). This result indicates that the PQXphos-based chiral palladacycle acts as an efficient catalyst in the ring-opening desymmetrization of **1a** with phenylboronic acids and has higher enantioselectivity than the palladacycle catalyst system developed by Hou and co-workers (79% *ee*),[8c] the platinum catalyst system developed by Yang and co-workers (84% *ee*),[8e] and the rhodium catalyst system developed by Lautens et al. (92% *ee*).[8a] Although neopentylglycol ester **12** led to the product with 80% *ee* (entries 4 and 5), readily available pinacol ester **13** and trifluoroborate **14** afforded products with enantioselectiveties as high as that with phenylboronic acid (entries 6 and 8, respectively). Lower reactivities of **13** and **14** relative to that of **2b** were observed when KF was used as a base, with only a trace amount of product being formed after 120 h.

Under the optimized conditions, substrates for the reaction were investigated at 0 °C (Table 4). In some cases the use of Cs_2CO_3 instead of KF increased the enantioselectivity. In the case of 4- or 3-substituted phenylboronic acids, both electron-donating and electron-withdrawing groups led to products with high enantioselectivities (entries 1–6). The use of 2-substituted phenylboronic acids **2h** and **2i** afforded products with slightly decreased enantioselectivities (entries 7 and 8), although the selectivities were much higher than those obtained using a low-molecular-weight palladacycle (**3ah**, 30% *ee*)[8c] and platinum catalysts (**3ah**, 11% ee; **3ai**, 49% *ee*).[8e] Derivatives of 1,4-epoxy-1,4-dihydronaphthalene bearing substituents at the 6,7-positions were applicable for the reaction (entries 9 and 10), although the presence of 5,8-dimethoxy groups lowered the reactivity and led to product with moderate enantioselectivity (entry 11).

Table 4: Asymmetric ring-opening arylation of oxabicyclic alkenes using PQXphos-based palladacycles.[a]



Entry	**1** (R^1, R^2)	**2** (Ar)	Product, **3**	Yield [%][d]	*ee* [%][c]
1	**1a** (H, H)	**2a** (4-MeC_6H_4)	**3aa**	93	94
2	**1a**	**2c** (4-$MeOC_6H_4$)	**3ac**	87	89
3[d]	**1a**	**2d** (4-FC_6H_4)	**3ad**	84	90
4	**1a**	**2e** (4-$CO_2EtC_6H_4$)	**3ae**	81	91
5	**1a**	**2f** (3-$MeOC_6H_4$)	**3af**	68	89
6[d]	**1a**	**2g** (3-ClC_6H_4)	**3ag**	88	90
7	**1a**	**2h** (2-MeC_6H_4)	**3ah**	86	84
8[d]	**1a**	**2i** (2-ClC_6H_4)	**3ai**	75	80
9	**1b** (Me, H)	**2b** (Ph)	**3bb**	88	87
10	**1c** (F, H)	**2b**	**3cb**	79	94
11	**1d** (H, MeO)	**2b**	**3db**	24	53

[a] $Pd(OAc)_2$ (2.0 μmol), PQXphos (2.4 μmol P), and base (0.1 mmol) were heated with toluene at 60 °C for 2 h. After evaporation, **1** (0.24 mmol), boronic acid **2** (0.20 mmol), $CHCl_3$ (800 μL), and H_2O (80 μL) were added at 0 °C. [b] Yield of isolated product. [c] Determined by SFC analysis on a chiral stationary phase. [d] Cs_2CO_3 used instead of KF.

In conclusion, we identified new chiral palladacycle catalysts generated on a helical scaffold which had high enantioselectivities in the asymmetric arylative ring opening

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of 1,4-epoxy-1,4-dihydronaphthalenes with arylboronic acids. The application of these new chiral palladacycle catalysts to other catalytic reactions is now underway.

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