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Water-Promoted Palladium-Catalyzed Asymmetric Ring-Opening of Oxabenzonorbornadienes with Alkoxysilanes

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Abstract: Water-promoted palladium-catalyzed asymmetric ring-opening (ARO) reaction of oxabenzonorbornadienes with a wide variety of alkoxysilanes has been developed in a one-pot fashion, yielding *cis*-1,2-dihydronaphthalen-1-ols in favourable yields (up to 98%) with gratifying enantioselectivities (up to 98% *ee*) under mild conditions. To the best of our knowledge, it represents the first example in the ring-opening reactions of oxabicyclic alkenes with alkoxysilanes. Furthermore, the *cis*-1,2-configuration of product was established by X-ray diffraction analysis, and a possible mechanism for the present catalytic ring-opening reaction was also proposed.

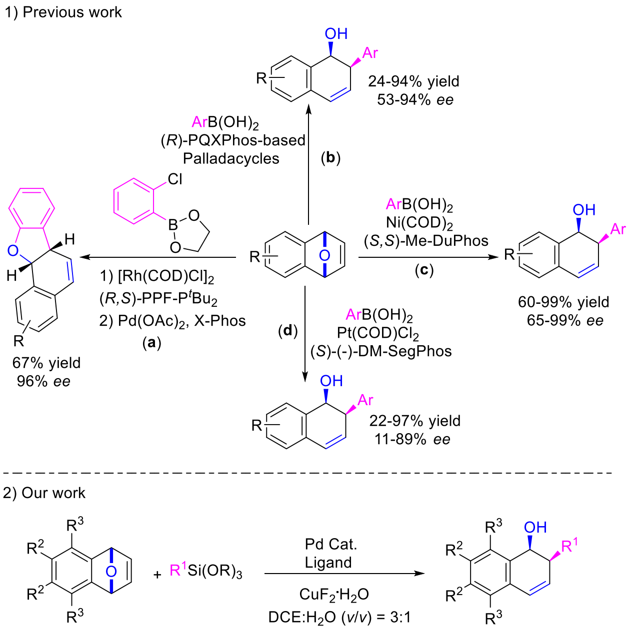
Keywords: Water Promotion; Palladium Catalys; Asymmetric Ring-Opening; Oxabenzonorbornadienes; Alkoxysilanes; One-Pot Reaction

The 1,2-dihydronaphthalene skeleton is found in a wide range of naturally occurring compounds with different biological activities.[1] The transition-metal-catalyzed asymmetric ring-opening (ARO) of oxa- and azabicyclic alkenes is an effective method to construct 1,2-dihydronaphthalenes with new carbon-carbon or carbon-heteroatom bonds.[2] In addition, the transformations are valuable because multiple stereocenters can be established in one step. In this regard, some transition-metal catalysts, including Ir,[3] Ni,[4] Pd,[5] Cu,[6] Rh[7] ect.[8] had been investigated for ARO reaction of heterobicyclic alkenes with various heteroatom and carboanion nucleophilic reagents.

Various reagents, such as organic halides, alkynes, Grignard reagents, zirconium reagents and arylboronic acids[9] have been found as feasible carboanion nucleophiles to construct containing aryl and alkyl ring-opening products. In 2012, Lautens and co-workers reported the Rh/Pd-catalyzed ARO reaction of oxabicyclic alkenes with 2-halogenated arylboronic reagents, which generated dihydrobenzofuran products in good yields (up to 67%) with high enantioselectivities (up to 96% *ee*) (Scheme 1, 1**a**).[10] In 2014, Suginome and co-workers described chiral palladacycle-catalyzed ARO of oxabicyclic alkenes with arylboronic acids to obtain the chiral oxazolidinone products (24–94% yields, 53–94% *ees*) (Scheme 1, 1**b**).[5d]

Inspired by Lautens's studies, we have successfully carried out some researches in the field of ARO reaction of different carboanion nucleophiles to oxa and azabicyclic alkenes. In 2014, we extended the nickel-catalyzed ARO of oxabenzonorbornadienes with arylboronic acids, which generated *cis*-1,2-ring-opening products in high yields (up to 99%) with excellent enantioselectivities (up to 99% *ee*) (Scheme 1, 1**c**).[11] Later, the platinum(II)-catalyzed ARO reaction of arylboronic acids to oxabenzonorbornadienes was developed. The catalyst showed high catalytic activity (up to 97% yield) and asymmetric induced ring-opening (up to 89% *ee*) (Scheme 1, 1**d**).[12] However, there were still some limitations, for example, the reaction operation was complicated and the nucleophilic reagent was one fold. Therefore, it was a challenging task to explore the other carboanion nucleophiles.

Compared to arylboronic acids and other carboanion nucleophile, alkoxysilanes are an ideal class of carboanion nucleophiles, which are low toxicity, nontoxic by-products, structural diversity, air stable and water insensitive. It can be desiliconized and formed a carboanion nucleophilic reagent in the cross-coupling reaction. In addition, in our previous studies, water played an important role in the ring-opening, cycloaddition and addition reaction with oxa(aza)bicyclic alkenes,[13] which in a sense greatly improved the yields of the desired products. Herein, we report a new, versatile and efficient water-promoted palladium-catalyzed ARO reaction of oxabenzonorbornadienes with alkyl, alkenyl and aryl trialkoxysilanes in a one-pot fashion, which afford the corresponding products of *cis*-1,2-dihydronaphthalen-1-ol in good to excellent yields (up to 98%) with high enantioselectivities (up to 98% *ee*).

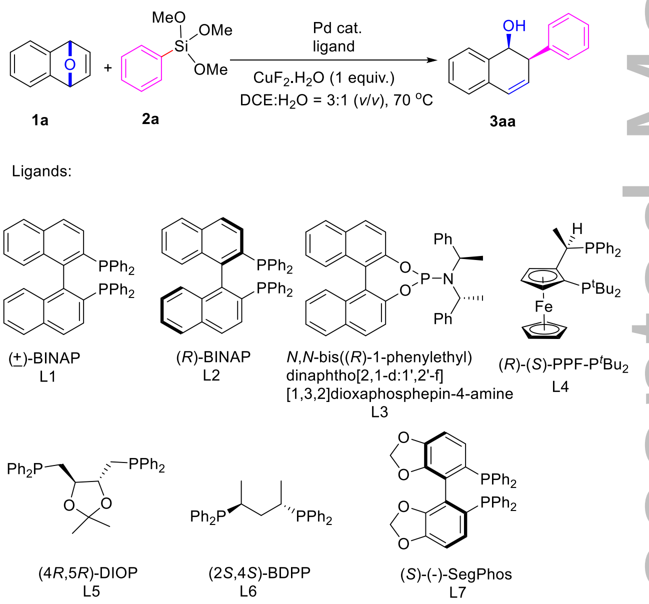


Scheme 1. Previous reports for the ARO of oxabenzonorbornadienes with arylboronic acids and our present work.

We initially chose oxabenzonorbornadiene **1a** and phenyl trimethoxysilane **2a** as model substrates to start our investigation. The reaction was performed in the presence of 2.5% mol of $Pd_2(dba)_3$ as a catalyst, 10 % mol of 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthalene (BINAP) as the ligand and 3 equiv. of $CuF_2{\cdot}H_2O$ as an additive in the mixed solvents consisting of 1,2-dichloroethane (DCE) and H_2O (3:1, *v*/*v*) at 70 °C under an air atmosphere. The desired ring-opening product **3aa** was obtained in 98% yield overnight (Table 1, entry 1). Thereafter, a series of palladium catalysts were an effective in catalyzing the ring-opening reaction (Table 1, entries 7–10). Obviously, the better result, 98% yield with 65% *ee*, was still achieved in the presence of $Pd_2(dba)_3$ (Table 1, entry 7).

To obtain better yields and enantiomeric excess values, the impacts of different parameters including additives, solvents and temperatures were subsequently investigated (Table 2). The results displayed that the $CuF_2{\cdot}H_2O$ was the optimal additive (98% yield, 65% *ee*). If the fluoride salt was not added, the reaction was not occurred (Table 2, entry 1). Different fluoride salts as the additives have a little effect on the enantiomeric excess of the product, but their have a greater impact on the yields (Table 2, entries 2–6). In addition, various types of solvents were also tested (Table 2, entries 6–12). If the ratio of the mixed solvent was consisted of 1:3 (*v*/*v*) of water and polar solvent CH_3CN, the protic solvent *i*-PrOH, the dipolar aprotic solvent dimethyl formamide (DMF) and the aromatic solvent toluene, respectively, the result of enantioselectivities increased slightly and the yield decreased significantly (Table 2, entries 7–10). Therefore, the optimum ratio of the mixed solvent was consisted of DCE and water (3:1, *v*/*v*) (98% yield, 65% *ee*) (Table 2, entry 6). However, enantiomeric excess of the product **3aa** increased slightly (67% *ee*), but the yield declined to 32% when DCE was used as solvent (Table 2, entry 11). And the yield and enantioselectivity are greatly reduced (18% yield, 33% *ee*) while water was used as the solvent (Table 2, entry 12). Furthermore, the influence of reaction temperature was also examined (Table 2, entries 13–15). Room temperature for the ring-opening reaction was the best one, providing product **3aa** in 98% yield with 84% *ee* (Table 2, entry 14). Therefore, the optimized reaction conditions were: 2.5% of $Pd_2(dba)_3$, 10% of (*S*)-(-)-SegPhos, 1 equiv. of $CuF_2{\cdot}H_2O$ and 1.5 equiv. of phenyl trimethoxysilane in the mixed solvents consisting of DCE and H_2O (3:1, *v*/*v*) at room temperature overnight.

Table 1. Effects of palladium catalyst and ligand.[a]

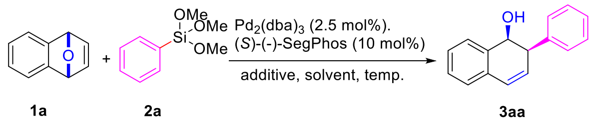


entry	catalyst (mol%)	ligand	yield (%)	*ee* (%)[b]
1	$Pd_2(dba)_3$ (2.5)	L1	98	-
2	$Pd_2(dba)_3$ (2.5)	L2	97	43
3	$Pd_2(dba)_3$ (2.5)	L3	n.r.	-
4	$Pd_2(dba)_3$ (2.5)	L4	96	15
5	$Pd_2(dba)_3$ (2.5)	L5	n.r.	-
6	$Pd_2(dba)_3$ (2.5)	L6	98	7
7	**$Pd_2(dba)_3$ (2.5)**	**L7**	**98**	**65**
8	$Pd(OAc)_2$ (5)	L7	50	61

9	$Pd(PPh_3)_4$ (5)	L7	70	66
10	$Pd(PPh_3)_2Cl_2$ (5)	L7	42	49

[a] Reaction conditions: palladium catalyst, ligand L1−L7 (10 mol%), $CuF_2{\cdot}H_2O$ (1 equiv.), substrate **1a** (0.2 mmol), phenyl trimethoxysilane **2a** (0.3 mmol), DCE : H_2O = 3:1 (*v*/*v*) (3.0 mL), 70 °C, under an air atmosphere overnight. [b] Determined by HPLC with a chiralcel OD-H column.

Table 2. Optimization of additive, solvent and temperature.[a]

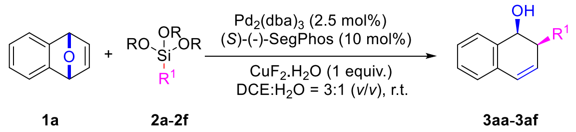


entry	additive	solvent (*v*/*v*)	temp. (°C)	yield (%)	*ee* (%)[d]
1	-	DCE:H_2O (3:1)	70	-	-
2	TBAF[b]	DCE:H_2O (3:1)	70	32	63
3	NH_4F	DCE:H_2O (3:1)	70	20	64
4	CsF	DCE:H_2O (3:1)	70	<5	-
5[c]	$AgSbF_6$	DCE:H_2O (3:1)	70	59	64
6	$CuF_2{\cdot}H_2O$	DCE:H_2O (3:1)	70	98	65
7	$CuF_2{\cdot}H_2O$	MeCN:H_2O (3:1)	70	35	71
8	$CuF_2{\cdot}H_2O$	*i*-PrOH:H_2O (3:1)	70	29	72
9	$CuF_2{\cdot}H_2O$	DMF:H_2O (3:1)	70	30	79
10	$CuF_2{\cdot}H_2O$	PhMe:H_2O (3:1)	70	32	73
11	$CuF_2{\cdot}H_2O$	DCE	70	32	67
12	$CuF_2{\cdot}H_2O$	H_2O	70	18	33
13	$CuF_2{\cdot}H_2O$	DCE:H_2O (3:1)	50	98	72
14	**$CuF_2{\cdot}H_2O$**	**DCE:H_2O (3:1)**	**r.t.**	**98**	**84**
15	$CuF_2{\cdot}H_2O$	DCE:H_2O (3:1)	0	45	64

[a] Reaction conditions: $Pd_2(dba)_3$ (2.5 mol%), (*S*)-(-)-SegPhos (10 mol%), additive (1 equiv.), substrate **1a** (0.2 mmol), phenyl trimethoxysilane **2a** (0.3 mmol), solvent (3.0 mL), under an air atmosphere overnight. [b] Tetrabutylammonium fluoride (TBAF). [c] The additive is 10 mol%. [d] Determined by HPLC with a chiralcel OD-H column.

Under the optimized reaction conditions, a series of aryl, alkenyl and alkyl trialkoxysilanes were performed to evaluate their effects on the reactivity and enantioselectivity (Table 3). Phenyl trimethoxysilane **2a** as nucleophilic reagent gave the corresponding product **3aa** in high yield (98%) with good enantioselectivity (84% *ee*) (Table 3, entry 1). On the contrary, alkenyl and alkyl trialkoxysilanes as the nucleophiles gave the corresponding product **3** in the lower yields with good enantioselectivities due to their weak activity (Table 3, entries 3–4). For example, the reaction of substrate **1a** with benzyl triethoxysilane **2d** gave the corresponding product **3ad** in 28% yield with 98% *ee* (Table 3, entry 4). Unfortunately, owing to the steric hindrance, naphthyl trimethoxysilane **2e** as nucleophilic reagent can only achieve product **3ae** with moderate yield (54%) and very low *ee* (7% *ee*) (Table 3, entry 5). In addition, cyclohexyl triethoxysilane **2f** as nucleophilic reagent did not react with substrate **1a** because of its low activity and the larger steric hindrance (Table 3, entry 6). Moreover, we also screened the effect of temperature on the less active alkoxysilanes. (Table 3, entry 3). The reaction of oxabenzonorbornadiene **1a** with vinyl triethoxysilane **2c** gave the corresponding product **3ac** in lower yield of 7% with 79% *ee* at room temperature. While the temperature was 90 °C, the corresponding product **3ac** was obtained in lower yield of 17% with 79% *ee*. Therefore, when temperature at 70 °C was the best one, providing product **3ac** in 36% yield with 74% *ee*.

Table 3. Palladium-catalyzed ARO of oxabenzonorbornadiene **1a** with various alkoxysilanes **2**.[a]



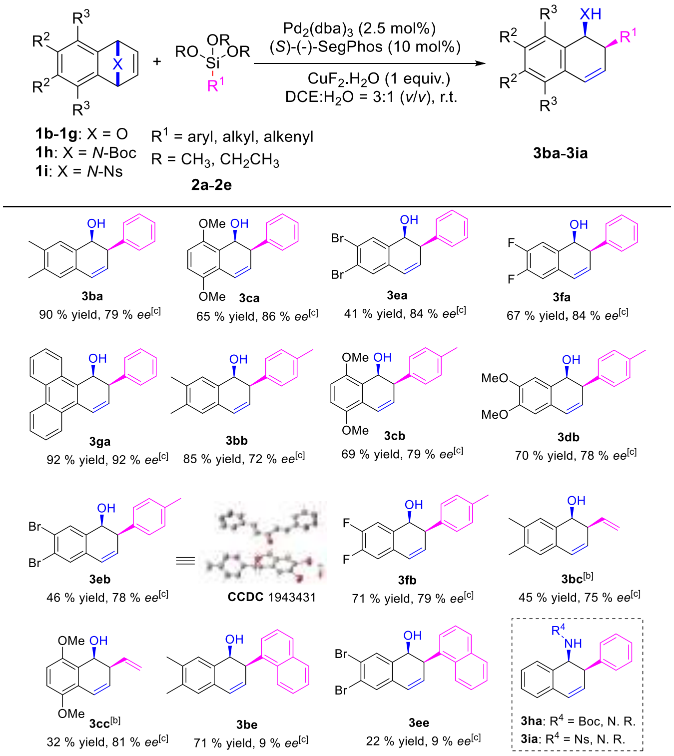
entry	R, R^1	prod.	yield (%)	*ee* (%)[d]
1	**2a**: R = CH_3, R^1 = C_6H_5	**3aa**	98	84
2	**2b**: R = CH_3, R^1 = 4-$CH_3C_6H_4$	**3ab**	89	84
3	**2c**: R = CH_2CH_3, R^1 = vinyl	**3ac**	36[b] (7) [17][c]	74[b] (79) [79][c]
4[b]	**2d**: R = CH_2CH_3, R^1 = $CH_2C_6H_5$	**3ad**	28	98
5	**2e**: R = CH_3, R^1 = 1-naphthyl	**3ae**	54	7
6[b]	**2f**: R = CH_2CH_3, R^1 = cyclohexyl	**3af**	n. r.	-

[a] Reaction conditions: $Pd_2(dba)_3$ (2.5 mol%), (*S*)-(-)-SegPhos (10 mol%), $CuF_2{\cdot}H_2O$ (1 equiv.), substrate **1a** (0.2 mmol), alkoxysilanes **2** (0.3 mmol), DCE:H_2O = 3:1 (*v*/*v*) (3.0 mL), r. t., under an air atmosphere overnight. [b] Reaction temperature is 70 °C. [c] Reaction temperature is

90 °C.[d] Determined by HPLC with a chiralcel OD-H column.

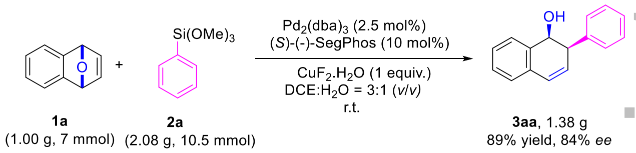
Furthermore, the scope of substrates **1b–1i** were also explored (Table 4). Except for substrate **1a**, all oxabenzonorbornadienes **1b–1g** with different substituents on the phenyl ring reacted smoothly with various alkenyl and aryl trialkoxysilanes **2** to generate the ring-opening product **3** in high yields (up to 92% yield) with good to excellent enantioselectivities (up to 92% *ee*). The results listed in Table 4 that the derivatives of substrate **1** either containing electron-withdrawing or electron-donating groups on the aryl rings has less influence on the enantioselectivity, but the yields were greatly influenced. For example, substrate **1e** reacted with phenyl trimethoxysilane **2a** to provide the corresponding product **3ea** in 41% yield with 84% *ee*, whereas substrate **1c** with phenyl trimethoxysilane **2a** afforded the corresponding product **3ca** in 65% yield with 86% *ee*. Furthermore, the reaction enantioselectivity of naphthyl trimethoxysilane **2e** with various substrates **1** was unsatisfactory. Substrate **1b** reacted with naphthyl trimethoxysilane **2e** to form the corresponding product **3be** in 71% yield with the lower 9% *ee*. However, the desired products **3ha** and **3ia** could not be obtained by using azabenzonorbornadienes **1h–1i** as substrates. The absolute configuration of product **3eb** was assigned as (1*S*, 2*R*) and determined as a *cis*-1,2-configuration by X-ray diffraction analysis (see Supporting Information for details).[14]

Table 4. Scope of palladium-catalyzed ARO of oxabenzonorbornadienes **1** with various alkenyl and aryl alkoxysilanes **2.**[a]



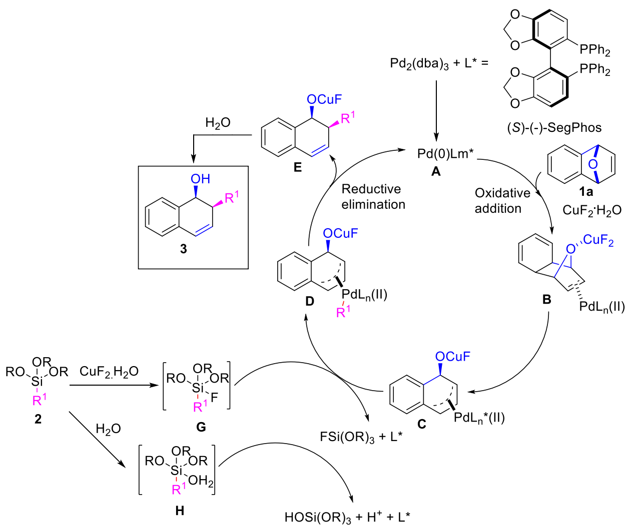
[a] Reaction conditions: $Pd_2(dba)_3$ (2.5 mol%), (*S*)-(-)-SegPhos (10 mol%), $CuF_2·H_2O$ (1 equiv.), substrates **1b–1i** (0.2 mmol), alkenyl or aryl trialkoxysilanes **2** (0.3 mmol), $DCE:H_2O$ = 3:1 (*v*/*v*) (3.0 mL) at room temperature overnight. [b] Reaction temperature is 70 °C. [c] Determined by HPLC with a chiralcel OD-H or chiralpak AD-H column.

The ARO reaction was also carried out on a gram scale to highlight the utility of this reaction system. As shown in Scheme 2, we successfully isolated 1.38 g of the target product **3aa** (89% yield, 84% *ee*), which indicated the efficient nature of the synthetic utility of this transformation.



Scheme 2. Gram-scale experiment.

Based on the experimental observation and the general mechanism of desilication reactions,[15-17] a possible mechanism for the palladium-catalyzed ARO reaction was also proposed, as shown in Scheme 3. Firstly, the active chiral palladium(0) catalyst **A** was formed by replacing the dibenzylideneacetone (dba) ligand of the catalyst precursor $Pd_2(dba)_3$ through (*S*)-(-)-SegPhos. Then, oxidative addition of palladium(0) catalyst **A** and $CuF_2·H_2O$ with substrate **1a** formed intermediate **B**. The intermediate **B** was further rearranged to (*π*-allyl)-palladium(II) intermediate **C.** In addition, the fluorinated intermediate **G** was rationally generated from the alkyl, alkenyl and aryl trialkoxysilanes **2** activated by $CuF_2·H_2O$, which experienced oxidation of intermediate **C** to produce (hydrocarbyl)(*π*-allyl)-palladium(II) intermediate **D**. And the alkyl, alkenyl and aryl trialkoxysilanes **2** also proceeded through desilication by water to give the fluorinated intermediate **H** at the same time, which underwent oxidation by intermediate **C** to form (hydrocarbyl)(*π*-allyl)-palladium(II) intermediate **D**. Then, reductive elimination of intermediate **D** afforded the intermediate **E** and regenerated the Pd(0) species for the next catalytic cycle. Finally, the intermediate **E** protonolysis with water produced the target product **3**.



Scheme 3. Proposed mechanism for the ring-opening oxabicyclic alkene **1a** with alkoxysilane **2.**

In summary, we have developed a new, versatile and highly efficient water-promoted palladium-catalyzed ARO reaction of oxabenzonorbornadienes with alkyl, alkenyl and aryl trialkoxysilanes in a one-pot fashion. This is the first report that alkyl, alkenyl and aryl trialkoxysilanes were used as the carboanion nucleophilic reagents for ARO reactions of oxabicyclic alkenes and it provides a mild reaction condition and a convenient pathway to synthesize *cis*-1,2-dihydronaphthalen-1-ol products containing aryl, alkenyl and alkyl groups in high yields with good enantioselectivities. Compared with the previous Co, Pt and Ni catalysts, this catalyst system was not only air stable and water-insensitive but also lower catalyst loading and higher efficiency and enantioselectivity as well as better functional group tolerance. Further investigations are underway to explore the range of carboanion nucleophiles in the ARO reaction.

Experimental Section

All experiments were carried out under an air atmosphere. $Pd_2(dba)_3$ (2.5 mol%), (*S*)-(-)-SegPhos (10 mol%), $CuF_2{\cdot}H_2O$ (1 equiv.), oxabenzonorbornadienes **1** (0.2 mmol), alkoxysilanes **2** (0.3 mmol), and DCE:H_2O = 3:1 (*v*/*v*) (3.0 mL) as the mixed solvents were simultaneously added to a 10.0 mL round-bottomed flask and stirred at room termperature or 70 °C overnight. After extracted with dichloromethane (3×10 mL) from reaction mixture, the organic layers were combined, dried with anhydrous $MgSO_4$, and then filtered. The filtrate was concentrated under vacuum, and the resulting residue was purified by column chromatography on silica gel (200–300 mesh) using ethyl acetate/petroleum ether as eluent to afford the desired product **3**.

Acknowledgements

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Water-Promoted Palladium-Catalyzed Asymmetric Ring-Opening of Oxabenzonorbornadienes with Alkoxysilanes

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