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Iridium-Catalyzed Asymmetric Ring-Opening Reactions of Oxabenzonorbornadienes with Amine Nucleophiles

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Summary: We have explored a new iridium-catalyzed ring-opening reaction of oxabenzonorbornadienes with a variety of primary aromatic amine or N-substituted piperazine nucleophiles, affording the corresponding products in excellent yields (up to 99%) with moderate enantioselectivity (25−81% ee). The trans configuration of product ***2d*** *was confirmed by X-ray crystallography.*

Ring-opening reactions of oxabicyclic alkenes represent a useful method in modern organic synthesis.[1] Research topics related to transition-metal-catalyzed asymmetric ring-opening reactions have attracted increasing attention because those reactions are characterized with excellent yields and high enantioselectivity,[2] as demonstrated by the research works reported by Lautens,[3] Hou,[4] Cheng,[5] et al. Many transition-metal complexes, including copper,[6] palladium,[7] iron,[8] ruthenium,[9] rhodium,[10] and nickel[11] may be used for the asymmetric ring-opening reactions of oxabicyclic alkenes. In recent decades, the transition metal iridium[12] has been widely used as a catalyst for the synthesis of enantiomerically pure compounds. In addition, various nucleophiles have been explored for this type of reaction. For example, Lautens and co-workers reported the rhodium-catalyzed asymmetric ring opening of oxabenzonorbornadiene with a wide range of nucleophiles such as phenols,[3d] organoboronic acids,[3e] dialkylzincs,[3f,g] carboxylates,[3h] sulfur nucleophiles,[3i] amines,[3j] etc.

Recently, we have reported[13] a promising catalytic system for enantioselective asymmetric ring-opening reactions with the transition metal iridium. To further explore this novel catalytic system, in this paper, we report our new findings on ring-opening reactions of oxabicyclic alkenes. The novel catalytic system demonstrates a potential useful method for the synthesis of *trans*-1,2-dihydronaphthalenol derivatives. The products of these reactions are interesting in themselves as potential therapeutic agents and are valuable building blocks for complex polycyclic skeletal motifs.

Results and Discussion. We began our studies by optimizing the iridium catalyst system (Table 1). Aniline was used as nucleophile to react with oxabenzonorbornadiene (**1a**) in the presence of iridium (1.5 mol %) and bisphosphine ligand (3 mol %). We first chose the inexpensive ligand 1,1′-bis-(diphenylphosphino)ferrocene (DPPF), so as to validate the catalytic activity of the iridium complex (Table1 1, entry 1). Then we chose three different chiral ligands which have been widely used in asymmetric ring-opening reactions. We found

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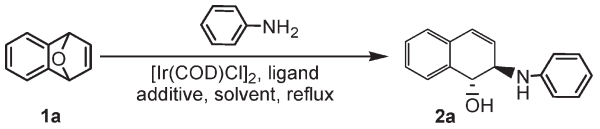
Table 1. Condition Screening for Iridium-Catalyzed Asymmetric Ring Opening of Oxabenzonorbornadiene 1a with Aniline[a]



entry	ligand	solvent	additive[b]	temp[c] (°C)	time (h)	yield[d] (%)	ee[e] (%)
1	DPPF	THF		80	50	23	0
2	(*R*,*S*)-PPF-PtBu$_2$	THF		80	48	36	13
3	(*S*)-BINAP	THF		80	2	91	35
4	(*S*)-*p*-Tol-BINAP	THF		80	2	93	61
5	(*S*)-*p*-Tol-BINAP	DME		90	12	91	53
6	(*S*)-*p*-Tol-BINAP	CH_3CN		90	12	24	31
7	(*S*)-*p*-Tol-BINAP	toluene		110	51	51	17
8	(*S*)-*p*-Tol-BINAP	dioxane		100	12	87	7
9	(*S*)-*p*-Tol-BINAP	THP		100	5	81	46
10	(*S*)-*p*-Tol-BINAP	CH_2Cl_2		50	8	33	63
11	(*S*)-*p*-Tol-BINAP	THF	NH_4F	80	55	n.r.	
12	(*S*)-*p*-Tol-BINAP	THF	NH_4Cl	80	50	25	50
13	(*S*)-*p*-Tol-BINAP	THF	NH_4Br	80	50	52	59
14	(*S*)-*p*-Tol-BINAP	THF	NH_4I	80	24	71	62
15	(*S*)-*p*-Tol-BINAP	THF	Bu_4NI	80	2	94	79

[a] The reaction was carried out with **1a** (0.20 mmol) and 3.0 equiv of aniline (0.9 mmol) in solvent (2.0 mL) in the presence of $[Ir(COD)Cl]_2$ (1.5 mol %) and ligand (3.0 mol %). [b] 1.0 equiv of additive. [c] Oil bath temperature. [d] Isolated yield after silica gel column chromatography. [e] Determined by HPLC with a Chiralcel AD-H column or OD-H column.

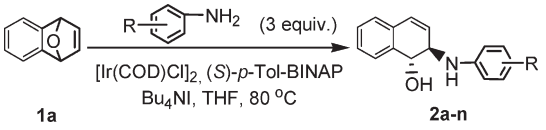
that the ligands (*S*)-*p*-Tol-BINAP and (*S*)-BINAP gave **2a** in reasonable yields (91 and 93%, respectively), but only the ligand (*S*)-*p*-Tol-BINAP offered product **2a** with an enantioselectivity (61%) higher than that of other ligands (Table 1, entries 2−4) in THF. Next, we investigated the impact of solvents on the reaction. It was found that the reactions were slower in DME, THP, dioxane, toluene, CH_2Cl_2, and MeCN than in THF (Table 1, entries 5−10). On the basis of those observations, we chose THF as a solvent. To further optimize the reaction conditions, we had investigated five ammonium halides as additives. Control experiments indicated that, in the presence of Bu_4NI, reactions underwent smoothly and the yield was improved to 94% and the enantioselectivity was up to 79% ee; however, no reaction occurred when NH_4F was used (Table 1, entries 11−15). The use of halide additives may affect the enantioselectivity of the asymmetric ring-opening reaction with amines. Removing the chloride ligand from the coordination sphere of the iridium and replacing it with iodide prior to the addition of reagents and additives further improves the enantioselectivity. Those findings suggested that the additive might play an important role in transition-metal catalysis. Furthermore, we observed the reactivity of halides in the order F < Cl < Br < I. Experimental evidence supports the hypothesis that the halide additives are acting at the iridium metal (Table 1, entries 11−15).

On the basis of these findings, we finalized our optimal conditions as the following: 1.5 mol % of catalyst $[Ir(cod)Cl]_2$, 3 mol % of chiral ligand (*S*)-*p*-Tol-BINAP, 3 equiv of primary amine with 1 equiv of additive in THF at 80 °C and stirring for 2 h.

Having identified conditions which were favorable for the iridium-catalyzed ring opening of **1a** with aniline, we were interested in understanding how the substituted groups in aniline would impact the ring-opening reaction of **1a**. Thus, **1a** reacted with substituted anliline nucleophiles to give the corresponding ring-opening products **2a**−**n** (Table 2).

To evaluate the scope of the reaction, anilines with electron-withdrawing substituent groups were used as nucleophilic reagents; the reaction results are summarized in Table 2.

Table 2. Scope of Ring-Opening Reactions of Oxabenzonorbornadiene 1a with Substituted Aniline[a]

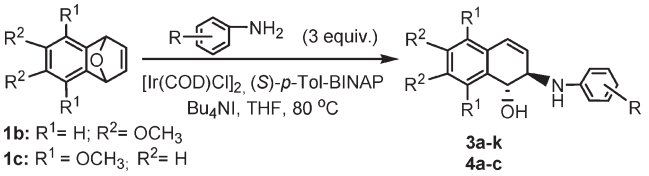


entry	R	product	time (h)	yield[b] (%)	ee[c] (%)
1	H	**2a**	2	94	78
2	4-Br	**2b**	3	95	35
3	2-Br	**2c**	3	80	56
4	3-Br	**2d**	3	96	57
5	2,4-dibromo	**2e**	21	58	45
6	4-Cl	**2f**	2	96	25
7	4-CH_3	**2g**	2	98	47
8	2-CH_3	**2h**	4.5	98	54
9	3-CH_3	**2i**	4.5	97	33
10	4-$CH(CH_3)_2$	**2j**	3	96	50
11	4-$CH_2CH_2CH_3$	**2k**	3.5	96	50
12	4-OCH_3	**2l**	3	94	61
13	2,4-dimethoxy	**2m**	3.5	96	55
14	*N*-naphthyl	**2n**	3	97	54

[a] The reaction was carried out with **1a** (0.30 mmol), 3.0 equiv of substituted aniline (0.9 mmol) and 1.0 equiv of additive in THF (2.0 mL) at 80 °C (oil bath temperature) in the presence of $[Ir(COD)Cl]_2$ (1.5 mol %) and (*S*)-*p*-Tol-BINAP (3.0 mol %). [b] Isolated yield after silica gel column chromatography. [c] Determined by HPLC with a Chiralcel AD-H column or OD-H column.

When R = 2,4-dibromo, the yield was decreased to 58% and a longer reaction time was required; The enantioselectivity was the lowest when 4-chloroaniline was used as a nucleophile reagent (only 25% ee) (Table 2, entry 6). However, treating oxabenzonorbornadiene (**1a**) with 3-bromoaniline, we obtained good yield (96%) and acceptable enantioselectivity (57% ee) (Table 2, entry 4). In the ring-opening reactions of oxabenzonorbornadiene (**1a**) with electron-donating groups, we found that, in almost all cases, we obtained good yields (94−98%) with moderate enantioselectivity (33−61% ee) (Table 2, entries 7−14).

Table 3. Scope of Asymmetric Ring-Opening Reactions of Dimethoxy-Substituted Oxabenzonorbornadienes 1b,c with Substituted Anilines[a]



entry	substrate	R	product	time (h)	yield[b] (%)	ee[c] (%)
1	**1b**	H	**3a**	20	87	64
2	**1b**	4-Br	**3b**	20	93	51
3	**1b**	2-Br	**3c**	5.5	52	70
4	**1b**	3-Br	**3d**	5.5	54	66
5	**1b**	2,4-dibromo	**3e**	9	21	81
6	**1b**	4-CH_3	**3f**	3	97	26
7	**1b**	2-CH_3	**3g**	3	98	64
8	**1b**	3-CH_3	**3h**	5.5	73	68
9	**1b**	4-OCH_3	**3i**	3	97	32
10	**1b**	2,4-dimethoxy	**3j**	6	95	77
11	**1b**	*N*-naphthyl	**3k**	20	38	66
12	**1c**	H	**4a**	3	97	52
13	**1c**	4-Br	**4b**	3	99	52
14	**1c**	4-CH_3	**4c**	3	97	50

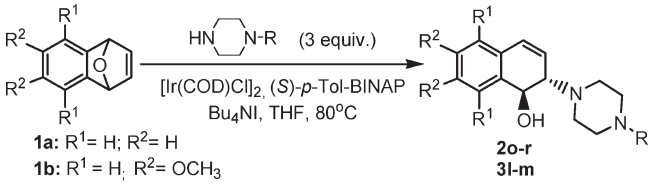
[a] The reaction was carried out with substrate (0.30 mmol), 3.0 equiv of substituted aniline (0.9 mmol), and 1.0 equiv of additive in THF (2.0 mL) at 80 °C (oil bath temperature) in the presence of $[Ir(COD)Cl]_2$ (1.5 mol %) and (*S*)-*p*-Tol-BINAP (3.0 mol %). [b] Isolated yield after silica gel column chromatography. [c] Determined by HPLC with a Chiralcel AD-H column or OD-H column.

To further explore the reaction scope, we used several substituted oxabenzonorbornadienes **1b**,**c** to perform the reactions (Table 3). We found that substrate **1c** underwent addition reactions with various primary aromatic amines proceeded at 80 °C in good yields (97−99%) but with lower enantioselectivities (50−52% ee) (Table 3, entries 12−14) than for the dimethoxyoxabenzonorbornadiene **1b** (Table 3, entries 1−11). However, under the same reaction conditions, the dimethoxy-substituted oxabenzonorbornadiene **1b** with primary aromatic amines afforded the corresponding ring-opening addition products with lower yields and higher enantioselectivities (Table 3, entries 1−11) than for other substrates. As shown in Table 3, when R = 2-Br, 4-CH_3, 4-OCH_3 on aniline, the yields were high and the enantioselectivities were lower (Table 3, entries 2, 6, and 9).

The structures of the ring-opening products were determined and characterized by ^1H and ^{13}C NMR, IR, HRMS, and elemental analysis. We found that these products possess a trans configuration. The absolute configuration of the ring-opening product **2d** was confirmed by single-crystal X-ray analysis. The crystal was obtained by solvent evaporation from its solution in dichloromethane, acetone, ethanol, and petroleum ether. Its configuration was assigned as 1*R*,2*R*, and the hydroxyl group and amine group are in a trans pattern.

Having investigated the ring-opening reactions of oxabenzonorbornadiene with primary aromatic amines, we wish to explore the same ring-opening reaction with secondary amines. Thus, protected piperazine nucleophiles were attempted. The results are shown in Table 4. The results demonstrated that the ring-opening reaction of oxabenzonorbornadiene with protected piperazines offered reasonable yields and moderate entioselectivies in the presence of iridium catalyst (Table 4, entries 1−6). The absolute configuration of **2r** was analyzed by X-ray crystallography, and the 1-hydroxyl group

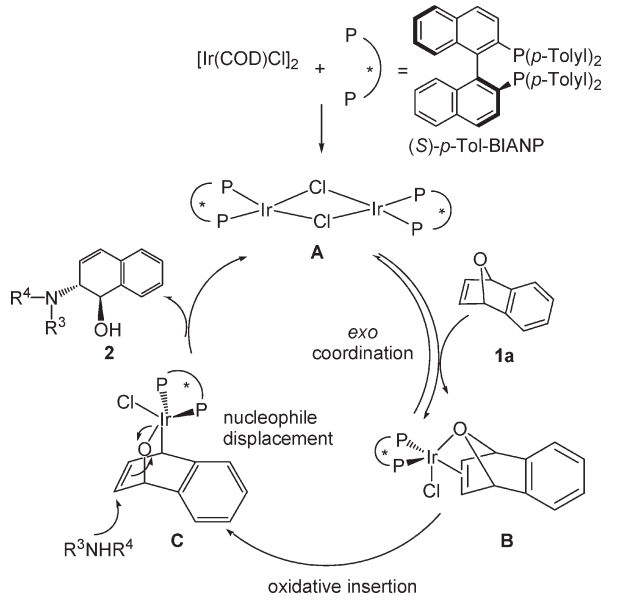
Table 4. Scope of Asymmetric Ring-Opening Reactions of Substituted Oxabenzonorbornadienes 1a,b with N-Substituted Piperazines[a]



entry	substrate	R	product	time (h)	yield[b] (%)	ee[c](%)
1	**1a**	4-methoxyphenyl	**2o**	10	85	54
2	**1a**	2-fluorophenyl	**2p**	10	84	55
3	**1a**	2-chlorophenyl	**2q**	8	89	50
4	**1a**	2,5-difluorophenyl	**2r**	10	97	43
5	**1b**	4-methoxyphenyl	**3l**	24	62	59
6	**1b**	2-fluorophenyl	**3m**	24	79	38

[a] The reaction was carried out with substrate (0.30 mmol), 3.0 equiv of *N*-substituted piperazines (0.9 mmol), and 1.0 equiv of additive in THF (2.0 mL) at 80 °C (oil bath temperature) in the presence of $[Ir(COD)Cl]_2$ (1.5 mol %) and (*S*)-*p*-Tol-BINAP (3.0 mol %). [b] Isolated yield after silica gel column chromatography. [c] Determined by HPLC with a Chiralcel AD-H column.

Scheme 1



and 2-piperzinyl group of **2r** were found to be in trans positions. Its configuration was also assigned as 1*S*,2*S*.

On the basis of our observations and findings, we propose the reaction mechanism detailed in Scheme 1. The chiral dimeric iridium complex A is first formed. The oxygen atom and the double bond of oxabenzonorbornadiene **1a** are then reversibly coordinated to the iridium center of the catalyst to give the intermediate **B**. Oxidative insertion of **B** into the C−O bond forms **C**. Then, attack of the amine nucleophile along with configurational inversion is proposed to occur in an S_N2 displacement of the iridium catalyst. The *trans*-1,2-dihydronaphthalenol product **2** is subsequently released, and **A** is regenerated.

Conclusion. In conclusion, we have explored a new iridium-catalyzed ring-opening reaction of oxabenzonorbornadienes

with a variety of primary aromatic amine or *N*-substituted piperazine nucleophiles to afford the corresponding products with moderate enantioselectivity (25%∼81% *ee*) in excellent yields (up to 99%). New chiral catalysts allowed the isolation of ring-opened products in higher enantiomeric excess using lower catalyst loadings. Studies on further expansion of the scope and synthetic utility of this Ir-catalyzed method are also being pursued in our laboratory.

Experimental Section. Representative Procedure for the Asymmetric Ring-Opening Reactions of Oxabenzonorbornadiene 1a with Primary Amine Nucleophiles. A 5.0 mL round-bottom flask fitted with a reflux condenser was flame-dried under a stream of nitrogen and cooled to room temperature. $[Ir(COD)Cl]_2$ (3.0 mg, 1.5 mol %) and (*S*)-*p*-Tol-BINAP (6.1 mg, 3 mol %) were simultaneously added and followed by addition of anhydrous tetrahydrofuran (2.0 mL). After the mixture was stirred for 10 min, 1.0 equiv. Bu_4NI (110.7 mg) was added. After stirring for another 10 min, oxabenzonorbornadiene **1a** (43.2 mg, 0.3 mmol) was added and the mixture was heated to reflux, followed by adding primary aromatic amine (3 equiv. to **1a**). The temperature was continuously increased to 80 °C until the reaction was completed as judged by thin layer chromatography. The solvent was removed in *vacuo* and the crude mixture was purified by column chromatography (Silica Gel: 200−300 mesh) to give the target product.

(1*R*,2*R*)-2-Phenylamino-1,2-dihydro-naphthalen-1-ol (2a). Following the representative procedure, **2a** was obtained as a white solid (66.8 mg, 94%). R_f = 0.14 on silica gel (1/10 ethyl acetate/petroleum ether, v/v). Mp: 93−95 °C. The ee was determined to be 78% using HPLC analysis on a Chiralcel AD-H column (90/10 hexane/2-propanol, 0.5 mL/min, λ = 254 nm). Retention times were 31.2 min (major) and 40.8 min (minor). $[\alpha]^{20}_D$ = +159.4° (*c* = 1.00, $CHCl_3$). IR (KBr, cm^{-1}): 3233 (s), 3057 (w), 3014 (m), 1601 (s), 1498 (s), 1450 (w), 1425 (w), 1312 (m), 1185 (m), 1046 (m), 783 (s), 695 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 6.4 Hz, 1H), 7.29 (t, *J* = 5.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 6.4 Hz, 1H), 6.78 (t, *J* = 6.8 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 2H), 6.56 (d, *J* = 9.6 Hz, 1H), 6.01 (d, *J* = 7.2 Hz, 1H), 4.84 (d, *J* = 7.6 Hz, 1H), 4.31 (d, *J* = 4.4 Hz, 1H), 3.37 (s, 1H), 2.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 135.6, 131.9, 129.5, 128.5, 128.5, 128.2, 128.0, 127.0, 126.7, 118.4, 114.1, 71.5, 55.6. MS (ESI): calcd *m*/*z* for $C_{16}H_{15}NO$ (M^+) 237.12, found 238.02 $(M + H)^+$. Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.21; H, 6.64; N, 6.12.

The ARO reactions of oxabenzonorbornadiene (**1a**) and the dimethoxy-substituted oxabenzonorbornadienes **1b**,**c** with primary aromatic amines or N-substituted piperazines are the same as the above representative procedure. See the Supporting Information for details of the syntheses of the new compounds **2b**−**r**, **3a**−**m**, and **4a**−**c**.

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Supporting Information Available: Text, figures, and tables giving experimental procedures and full characterization data for all new compounds, including optical rotations, IR, ^1H and ^{13}C NMR, MS, and elemental analyses, and X-ray structure data for compounds **2d**,**r**. This material is available free of charge via the Internet at http://pubs.acs.org.