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## ARTICLE

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# Chiral Benzo[2.2.1] $\alpha$ -Hydroxyketones from Dirhodium(II)/Bisphosphine-Catalyzed Desymmetrization Addition Reaction

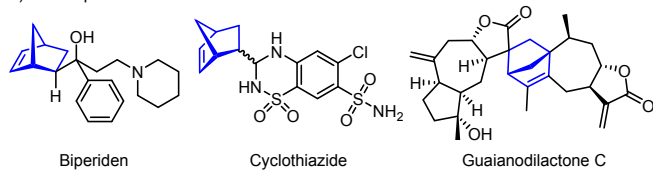
Shuming Zhan,<sup>a</sup> Chengyu Wang,<sup>a</sup> Longhui Duan<sup>a,\*</sup> and Zhenhua Gu<sup>a,b,\*</sup>

The [2.2.1]-bridged bicyclic framework represents a privileged structural motif prevalent in numerous bioactive molecules and functional materials. The development of efficient synthetic methods for constructing these valuable architectures remains highly desirable. In this study, we report a dirhodium(II)/bisphosphine-catalyzed desymmetrization reaction of benzobicyclo[2.2.1]heptane-2,3-diones with various arylboronic acids. This transformation delivers enantioenriched benzo[2.2.1]  $\alpha$ -hydroxy ketones with excellent enantioselectivity (up to 94% ee) across a diverse substrate scope. The synthetic utility of these chiral products is demonstrated through several transformations, including the preparation of chiral phosphine.

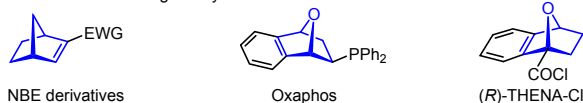
## Introduction

The [2.2.1]-bridged bicyclic scaffold represents a privileged structural motif that appears extensively in natural products,<sup>1</sup> bioactive molecules,<sup>2</sup> and functional materials,<sup>3</sup> exhibiting remarkable versatility in both biological applications and organic synthesis. This structural framework underpins numerous pharmaceutically significant compounds, exemplified by biperiden, which effectively alleviates extrapyramidal disorders secondary to neuroleptic drug administration with an  $IC_{50}$  value of 9  $\mu$ M (Figure 1a).<sup>4</sup> Cyclothiazide, a potent and orally effective therapeutic agent, is widely employed in the management of hypertension and heart failure.<sup>5</sup> Natural products containing this scaffold also demonstrate promising bioactivity, as illustrated by guaianodilactone C, a sesquiterpene lactone dimer isolated from *Carpesium faberi* that exhibits cytotoxicity against human leukemia (CCRF-CEM) cells with an  $IC_{50}$  value of 4.74  $\mu$ M.<sup>6</sup>

a) natural products and bioactive molecules



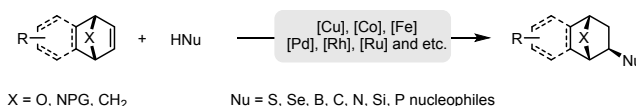
b) useful molecules in organic synthesis



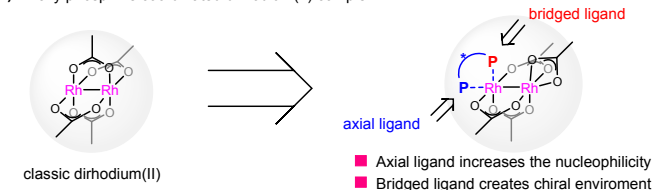
**Figure 1.** [2.2.1]Bicycles in Bioactive Molecules and Functional Materials.

Beyond pharmaceutical applications, the [2.2.1]bridged bicyclic framework serves as a fundamental component in numerous synthetically valuable molecules (Figure 1b). Norbornene(NBE) and its derivatives function as crucial shuttles for "palladium migration"

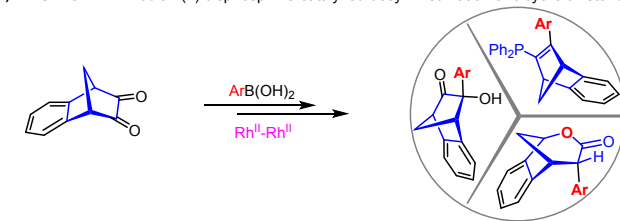
a) The strategy for asymmetric synthesis of [2.2.1]-bridged bicycles



b) Axially phosphine coordinated dirhodium(II) complex



c) THIS WORK: Dirhodium(II)/bisphosphine-catalyzed desymmetrization of bicyclic diketones



**Scheme 1.** Enantioselective Strategies for the Synthesis of [2.2.1]-Bridged Bicycles.

in the Catellani reaction,<sup>7</sup> while oxaphos represents an important chiral phosphine ligand employed in ruthenium-catalyzed arylation of aldehydes.<sup>8</sup> Additionally, (R)-THENA-Cl has established itself as an effective chiral resolving agent for the enantiomeric resolution of 7,7'-disubstituted 1,1'-bi-2-naphthols.<sup>9</sup> These diverse applications underscore the significant synthetic utility and structural importance of the [2.2.1]-bridged bicyclic architecture in contemporary chemical research.

The [2.2.1]-bridged bicyclic framework has attracted significant attention due to its diverse bioactivities and important applications, prompting extensive research into efficient synthetic approaches for constructing these valuable molecular architectures. Current

<sup>a</sup> Department of Chemistry, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026 (P. R. China)

<sup>b</sup> State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China

E-mail: zhgu@ustc.edu.cn

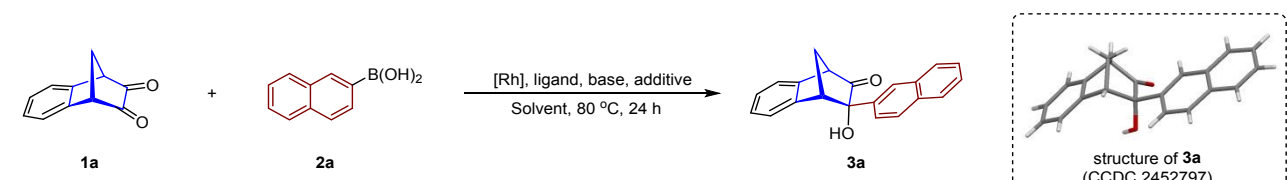
\*Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

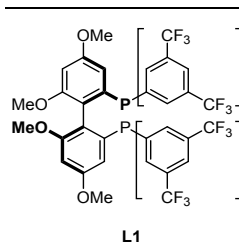


methodologies for accessing enantioenriched [2.2.1]-bridged bicycles primarily include cyclopenta-1,3-diene involved enantioselective cycloaddition reactions<sup>10</sup> and metal-catalyzed addition processes. The latter strategy typically employs metals such as Cu, Co, Fe, Rh, Pd, and Ru with [2.2.1]bicyclic alkenes as substrates, incorporating various nucleophilic reagents including boron, carbon, and nitrogen-based nucleophiles.<sup>11</sup> Dirhodium(II) complexes have been extensively utilized as catalysts for carbene and nitrene-mediated X-H insertion reactions and cyclopropanation etc. These transformations can be rendered asymmetric through the incorporation of chiral carboxylic acids or chiral phosphoric acids. Modification of dirhodium(II) complexes with an additional ligand at the axial site of the paddlewheel Rh(II)-Rh(II) structure induces novel catalytic activities. However, stereochemical control by these complexes is hindered by the significant distance between the reactive site and the chiral ligand, which resides at the opposite axial position, thus limiting applications in asymmetric catalysis. Recently,

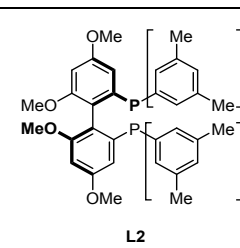
our laboratory developed a novel dirhodium(II)-bisphosphine catalytic system that exhibits unique reactivity patterns and superior stereochemical control. In this system, one of the phosphine moiety sitting at the bridging site of the dirhodium(II) structure establishes a well-defined chiral environment that enables highly enantioselective addition reactions, demonstrating particular efficiency for cyclic 1,2-dicarbonyl compounds.<sup>12</sup> However, the substrate scope was limited to aryl ketone derivatives. An attempt using 1,2-cyclohexanedione as the substrate was unsuccessful, likely due to its facile enolization. By contrast, the carbonyl groups of bridged structure bicyclo[2.2.1]heptane-2,3-diones are known to have low enolization tendency, making them suitable candidates for 1,2-addition reactions. Building upon these findings, herein we report a Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>/GarPhos-catalyzed desymmetrization reaction of benzobicyclo[2.2.1]heptane-2,3-diones, accessing to enantioenriched [2.2.1]-bridged bicyclic structures (Scheme 1c).

**Table 1.** Reaction Condition Optimization<sup>a</sup>

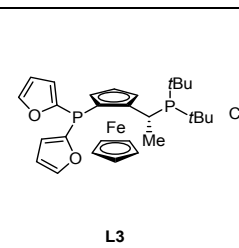




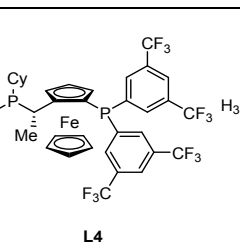
**L1**



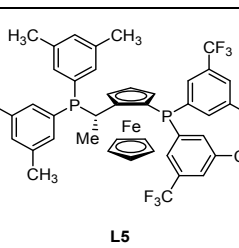
**L2**



**L3**



**L4**



**L5**

Entry <sup>a</sup>	[Rh]	Ligand	Base/equiv.	Solvent	Additive/mol%	Yield/% <sup>b</sup>	ee/% <sup>c</sup>
1	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L1</b>	LiOH·H <sub>2</sub> O (5.0)	toluene	/	62	87
2	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L2</b>	LiOH·H <sub>2</sub> O (5.0)	toluene	/	ND	/
3	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L3</b>	LiOH·H <sub>2</sub> O (5.0)	toluene	/	trace	36
4	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L4</b>	LiOH·H <sub>2</sub> O (5.0)	toluene	/	trace	35
5	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L5</b>	LiOH·H <sub>2</sub> O (5.0)	toluene	/	trace	15
6	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L1</b>	K <sub>2</sub> CO <sub>3</sub> (1.0)	toluene/H <sub>2</sub> O (10:1)	/	trace	90
7	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L1</b>	DABCO (1.0)	toluene/H <sub>2</sub> O (10:1)	/	ND	/
8	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L1</b>	KF (2.0)	toluene/H <sub>2</sub> O (10:1)	/	76	90
9	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L1</b>	CsF (2.0)	toluene/H <sub>2</sub> O (10:1)	/	65	90
10	Rh <sub>2</sub> (OAc) <sub>4</sub>	<b>L1</b>	KF (2.0)	toluene/H <sub>2</sub> O (10:1)	/	73	90
11	Rh <sub>2</sub> (O <sub>2</sub> CC <sub>7</sub> H <sub>15</sub> ) <sub>4</sub>	<b>L1</b>	KF (2.0)	toluene/H <sub>2</sub> O (10:1)	/	70	90
12	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L1</b>	CsF (2.0)	toluene/H <sub>2</sub> O (10:1)	CF <sub>3</sub> CO <sub>2</sub> Na (15)	80	91
13 <sup>d</sup>	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L1</b>	KF (2.0)	toluene/H <sub>2</sub> O (10:1)	CF <sub>3</sub> CO <sub>2</sub> Na (20)	91	91
14 <sup>d</sup>	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L1</b>	KF (2.0)	toluene/H <sub>2</sub> O (10:1)	CF <sub>3</sub> CO <sub>2</sub> Na (30)	98	91
15 <sup>d,e</sup>	Rh <sub>2</sub> (O <sub>2</sub> CCF <sub>3</sub> ) <sub>4</sub>	<b>L1</b>	KF (2.0)	toluene/H <sub>2</sub> O (10:1)	CF <sub>3</sub> CO <sub>2</sub> Na (30)	95	91

<sup>a</sup> Conditions: **1a** (0.10 mmol), **2a** (0.20 mmol, 2.0 equiv.), [Rh<sub>2</sub>X<sub>4</sub>] (2.5 mol %), ligand (5.0 mol %), and base (2.0 equiv) in toluene/H<sub>2</sub>O = 2.0/0.2 mL at 80 °C for 24 h. <sup>b</sup> Isolated yields were given. <sup>c</sup> ee values were determined by HPLC on a chiral column. <sup>d</sup> [Rh<sub>2</sub>(O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>] (3.5 mol %), **L1** (6.0 mol %). <sup>e</sup> The reaction scale of **1a** was 1.0 mmol.

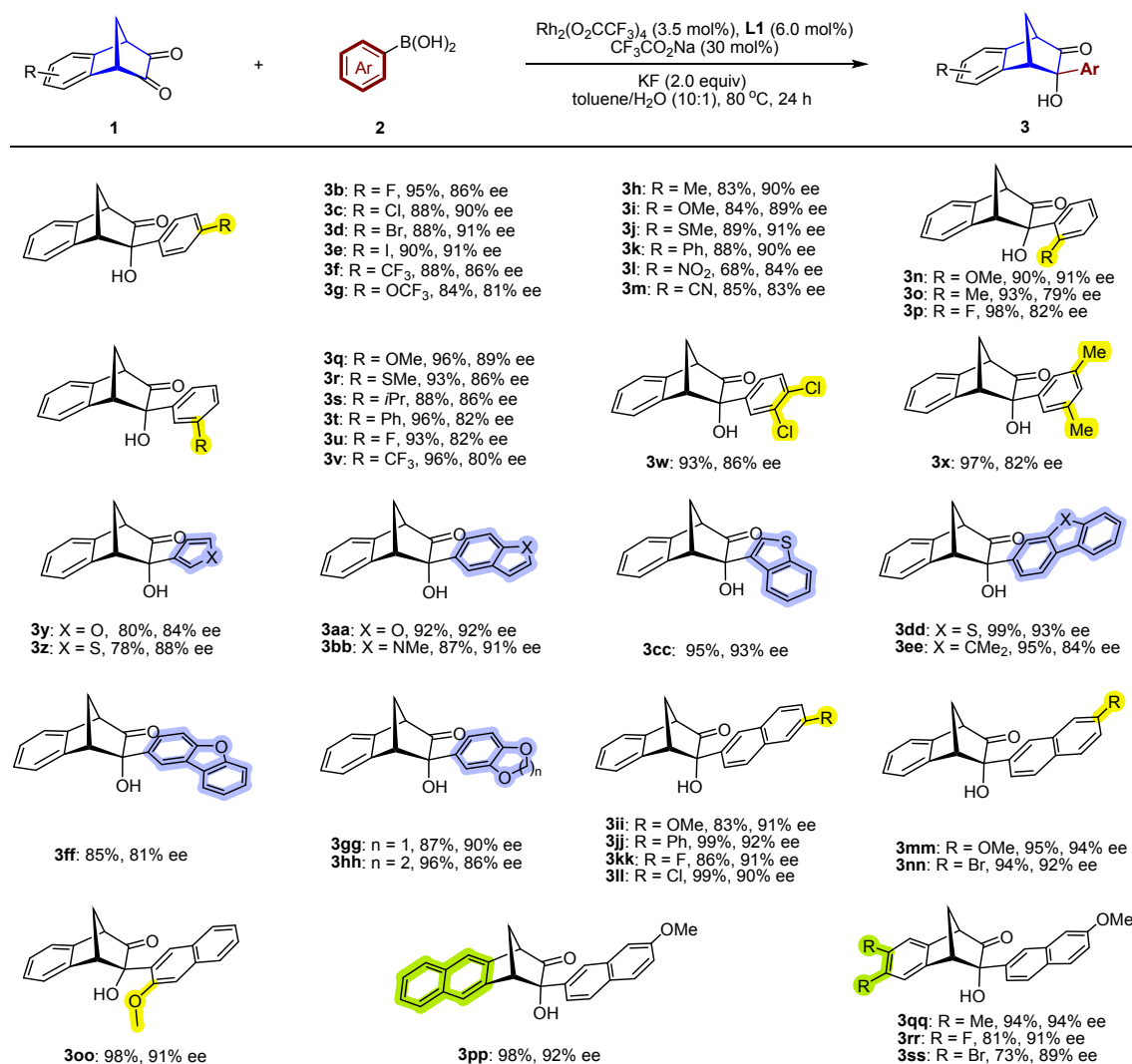


## Results and discussion

## Optimization

To test our hypothesis, we initiated our investigation using 1,4-dihydro-1,4-methanonaphthalene-2,3-dione (**1a**)<sup>13</sup> and naphthalen-2-ylboronic acid as model substrates. Our initial screening revealed that electron-deficient biphenyl ligands were essential for this reaction. Specifically, the catalyst system comprising  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  and (*R*)-BTM-Garphos (**L1**) afforded the desired product **3a** in 62% yield with 87% enantiomeric excess (Table 1, entry 1). In contrast, replacing the trifluoromethyl groups with methyl groups, as in (*R*)-xyl-Garphos (**L2**), completely suppressed product formation (entry 2). The Josiphos ligand family (**L3–L5**) proved similarly ineffective, generating only trace amounts of **3a** with poor enantioselectivity (entries 3–5). We then explored different base additives to improve the reaction's

performance. Potassium fluoride (KF) enhanced both yield and stereoselectivity, which was even more effective than CsF (entries 8 and 9), whereas  $\text{K}_2\text{CO}_3$  and organic bases such as DABCO showed little to no activity (entries 6 and 7). Subsequently, we re-examined the effectiveness of other rhodium catalysts,  $\text{Rh}_2(\text{OAc})_4$  and  $\text{Rh}_2(\text{O}_2\text{CC}_7\text{H}_{15}\text{-}n)_4$ , which resulted in slightly lower yields (entries 10 and 11). The addition of 15 mol%  $\text{CF}_3\text{CO}_2\text{Na}$ , thought to suppress decomposition of  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ , further improved the yield (entry 12). Moreover, with 3.5 mol% of  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ , optimizing the loading of  $\text{CF}_3\text{CO}_2\text{Na}$  led to an optimal yield of 98% (with 30 mol% of  $\text{CF}_3\text{CO}_2\text{Na}$ ) without compromising enantioselectivity (entries 13 and 14). The reaction also proceeded smoothly on a 1.0 mmol scale, demonstrating the robustness of this protocol (entry 15).



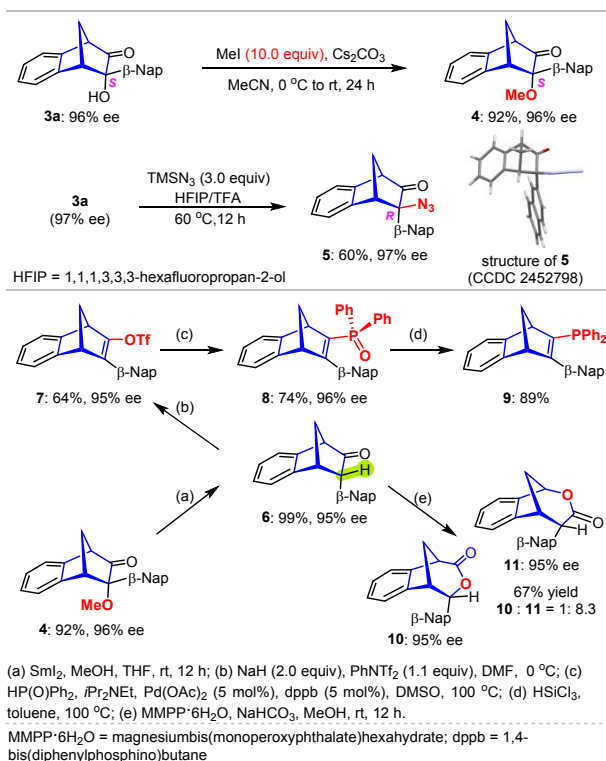
**Scheme 2.** Substrate Scope. Conditions: **1a** (0.20 mmol), **2a** (0.40 mmol, 2.0 equiv.),  $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$  (3.5 mol %), **L1** (6.0 mol %),  $\text{CF}_3\text{CO}_2\text{Na}$  (30 mol%), and KF (2.0 equiv) in toluene/ $\text{H}_2\text{O}$  = 4.0/0.4 mL at 80 °C for 24 h.



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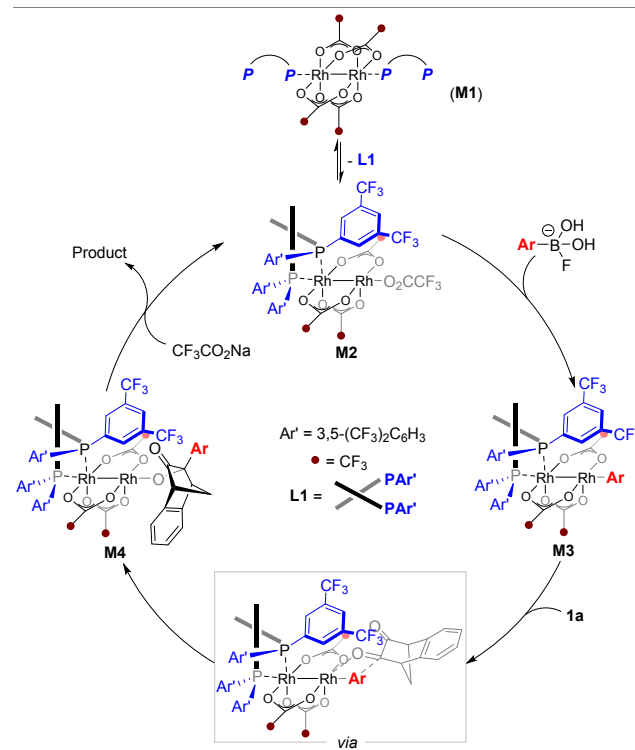
## Substrate scope

With the optimized conditions established, we investigated the substrate scope of this reaction as detailed in Scheme 2. First, we examined a diverse array of arylboronic acids as arylation reagents, including substituted phenylboronic acids, heteroarylboronic acids, and naphthylboronic acids. Phenylboronic acids bearing various *para*-substituents demonstrated good reactivity (**3b–3m**). The weakly electron-withdrawing, electron-donating, and neutral groups maintained high stereoselectivity (**3b–3e**, **3h**, **3i–3k**), while strongly electron-withdrawing substituents would slightly diminish the enantioselectivity (**3f**, **3g**, **3l** and **3m**). Substituents at the *meta* and *ortho* positions of phenylboronic acids exhibited similar electronic effects on stereoselectivity (**3n–3v**), although 3,5-dimethylphenylboronic acid unexpectedly resulted in low enantioselectivity (82% ee) (**3x**). Furthermore, heterocyclic boronic acids, e.g. 3-furyl and 3-thiophenyl boronic acids, proved to be compatible substrates, providing corresponding  $\alpha$ -hydroxy ketones **3y** and **3z** with moderate yields and enantiomeric excesses. Benzo-heterocyclic and 9*H*-fluorenyl-derived boronic acid were also well-tolerated, affording the desired products (**3aa–3hh**) in excellent yields with good enantiopurity. However, 2-pyridinylboronic acid failed to give the desired product. When substituted naphthyl-2-boronic acids containing various functional groups were subjected to the optimal conditions, the corresponding products (**3ii–3oo**) maintained both good stereoselectivity and high yields. We further evaluated the scope of bridged [2.2.1]diketones. All tested naphtho- and substituted benzo- derivatives were smoothly converted to their corresponding alcohols (**3pp–3ss**) with good yields and high enantiomeric excesses. In contrast to **1a**, bicyclo[2.2.1]hept-5-ene-2,3-dione, which lacks the fused benzene ring, afforded only a trace mixture, likely comprising the *exo* and *endo* isomers.



Scheme 3. Synthetic Applications.

To demonstrate the synthetic utility of these compounds, we performed a series of transformations, as shown in Scheme 3. The hydroxyl group in compound **3a** could be methylated with methyl iodide to afford the methyl ether in moderate yield. Notably, treatment of **3a** with  $\text{TMSN}_3$  in HFIP/ $\text{CF}_3\text{CO}_2\text{H}$  produced compound **5** with inversion of the corresponding chiral center from *S* to *R* configuration, suggesting the involvement of a carbocation intermediate. Subsequently, compound **4** was subjected to reduction with  $\text{SmI}_2$  in a THF/MeOH mixed solvent, furnishing the corresponding ketone **6** in 99% yield. Deprotonation of **6** with NaH, followed by the reaction with  $\text{PhNTf}_2$ , yielded trifluoromethanesulfonate **7** in a moderate yield. This intermediate was further utilized in a palladium-catalyzed coupling reaction with diphenylphosphine oxide, followed by reduction, to deliver a chiral phosphine **9**. Additionally, compound **6** smoothly underwent Baeyer–Villiger oxidation: treatment with MMPP· $6\text{H}_2\text{O}$  in methanol provided good chemoselectivity, with compound **11** as the major product (**10**:**11** = 1:8.3), while the reaction involved *m*-CPBA as oxidant delivered a mixture of **10** and **11** with low regioselectivity (see the Supporting Information for details). Notably, Baeyer–Villiger oxidation of **4** either with MMPP· $6\text{H}_2\text{O}$  or *m*CPBA was unsuccessful, resulting a complicated mixture.



Scheme 4. Plausible Catalytic Cycle.

Based on the above results, previous work, and relevant literature,<sup>14,15</sup> we propose a plausible mechanism for this arylation process (Scheme 4). The catalytic cycle begins with the formation of the active catalyst complex **M2**, which is generated from precatalyst **M1** through dissociation of one molecule of the biphosphine ligand **L1**. This is followed by intramolecular coordination of the remaining phosphine at the bridging site of the dirhodium core. Subsequent transmetalation of **M2** with the arylboronic acid, activated by fluoride anion, produces the





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arylrhodium species **M3**. This intermediate then undergoes stereoselective 1,2-addition to the diketone substrate, forming the alkoxide complex **M4**. Finally, hydrolysis of **M4** releases the enantioenriched product while regenerating the active catalyst **M2**, thus completing the catalytic cycle.

## Conclusions

In summary, we have developed a  $\text{Rh}_2(\text{CF}_3\text{CO}_2)_4/(\text{R})\text{-BTfM-GarPhos}$ -catalyzed enantioselective arylation of benzobicyclo[2.2.1]heptane-2,3-diones. The incorporation of  $\text{CF}_3\text{CO}_2\text{Na}$  as an additive significantly enhanced reaction efficiency without compromising stereoselectivity. This protocol provides expedient access to enantioenriched [2.2.1]-bridged bicyclic compounds with good yields and enantioselectivity across a diverse array of arylboronic acids and diketone substrates. The synthetic versatility of these enantioenriched products was demonstrated through various transformations, including the synthesis of a chiral phosphine ligand.

## Author Contributions

S. Zhan: methodology, investigation, data curation, writing – original draft. C. Wang: methodology, investigation. L. Duan: supervision, funding acquisition. Z. Gu: conceptualization, funding acquisition, writing – original draft, writing – review & editing. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the Supplementary Information.

## Acknowledgements

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The data that support the findings of this study are available in the ESI or on request from

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