UPDATES DOI: 10.1002/adsc.202001167 Advanced Synthesis & Catalysis

# Rhodium-Catalyzed Asymmetric Cycloisomerization of 1,3-Diketones with Keto-Vinylidenecyclopropanes: Synthesis of Enantiomerically Enriched Cyclic β-Amino Alcohols

Chen Xu,[+a] Chao Ning,[+a] Song Yang,[a] Yin Wei,[b] and Min Shi[a, b,*]

[a] Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Mei Long Road, Shanghai 200237, People's Republic of China
Fax: (+86)-21-6416-6128;
E-mail: mshi@mail.sioc.ac.cn

[b] State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China

[+] These authors contributed equally to this work

Manuscript received: September 23, 2020; Revised manuscript received: January 14, 2021;
Version of record online: Februar 9, 2021

Supporting information for this article is available on the WWW under https://doi.org/10.1002/adsc.202001167

**Abstract:** We report here an effective and atom-economical method to synthesize enantiomerically enriched cyclic β-amino alcohols via a rhodium-catalyzed asymmetric cycloisomerization of 1,3-diketones with keto-vinylidenecyclopropanes. The reactions proceed through a Rh-catalyzed transformation of keto-vinylidenecyclopropanes via cleavage of the distal C–C bond of the three-membered ring as a three-carbon synthon, allowing the generation of a range of enantiomerically enriched cyclic β-amino alcohols tethered to an alkene and an 1,3-dione moiety in good yields with high ee values under mild conditions. Derivatizations including allylation of the functionalized β-amino alcohols and subsequent RCM reaction as well as the preparation of a pyrazole derivative were carried out as well.

**Keywords:** β-amino alcohols; trimethylenemethane-rhodium (TMM-Rh) complex; vinylidenecyclopropanes (VDCPs); diketone; C–H alkylation;

In bioactive natural products, β-amino alcohols and cyclic β-amino alcohols as well as their derivatives are vital structural components,[1] and have widespread applications in the medicinal chemistry and pharmaceutical industry.[2] Figure 1 presents several bioactive molecules and medical substances containing cyclic β-amino alcohol structures. For example, *Febrifugine* is well-known for its antimalarial effect.[3] *CPC-1* is a pyrrolidinoindoline-type alkaloid.[4] In addition, *Maremycin B*, with high probability to be introduced as a fragment of the cysteine structure used in biosynthesis, was first isolated from a marine streptomyces species.[5] Besides, *hyacinthacine* alkaloids are a relatively recent addition to the group of polyhydroxylated 3-(hydroxymethyl)pyrrolizidine natural products, in which over nineteen *hyacinthacine* alkaloids have been isolated thus far.[6] The class of enantiomerically pure compounds are often prepared by direct reduction of β-amino acids. Thus, the traditional methods for the preparation of β-amino alcohols mostly required enantiopure substrates or reagents as chiral pool or involved with stepwise catalytic asymmetric synthetic processes.[7] However, these synthetic strategies often suffered from either structurally limited substrates/products or relatively low regio- and stereoselectivities.[8] Therefore, nowadays, the development of direct asymmetric synthesis of cyclic β-amino alcohols through novel domino or cascade reaction process in good yields with high stereoselectivities is highly desirable. On the basis of such circumstance, we wish to explore a new synthetic protocol for the rapid construction of enantiomerically enriched cyclic β-amino alcohols from simple starting materials by an atom-economical process.

Asymmetric allylic substitution is a primary strategy for stereoselective construction of carbon-heteroatom and carbon-carbon bond. In this context, allenes could be transformed into electrophilic metal-π-allyl intermediates by iridium, rhodium, ruthenium and other transition metal catalysts to undergo nucleophilic attack.[9] For example, chiral phosphine-coordinated

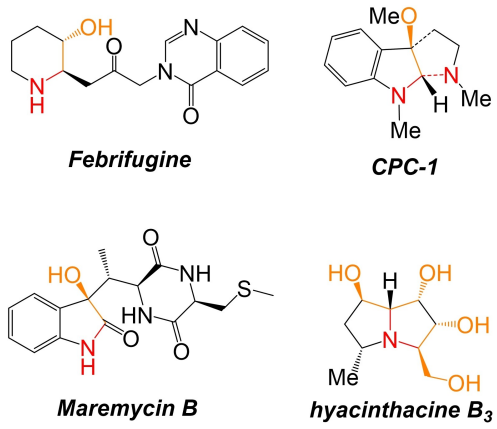
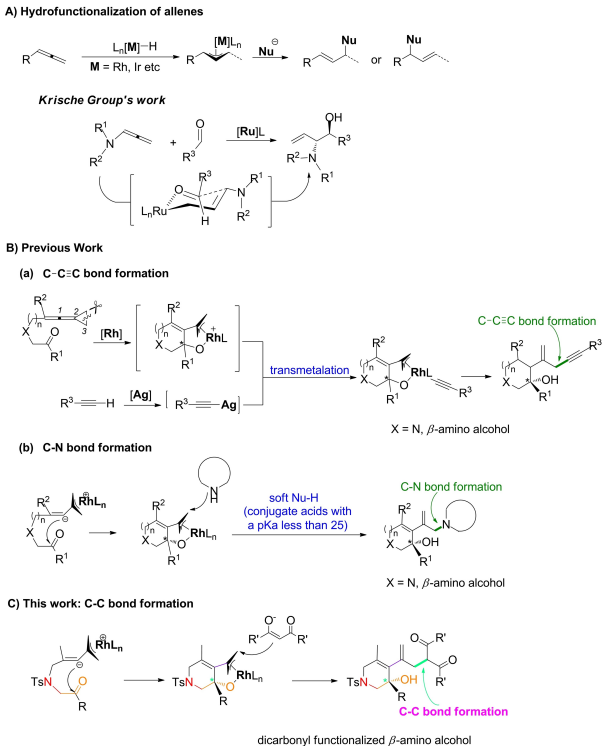



**Figure 1.** Representative bioactive molecules containing cyclic *β*-amino alcohol moiety.

ruthenium(II) complex bearing carbonyl ligands could be used to catalyze the reactions of allyl amides with alcohols or aldehydes, giving *β*-amino alcohols in high ee values (Scheme 1A).[10]

Vinylidenecyclopropanes (VDCPs), bearing an allene group linked to a highly strained cyclopropane ring, act as an essential element in organic synthesis and have continuously fascinated organic chemists for decades.[11] Our processing study on metal-catalyzed conversions of VDCPs, indicates that cationic Rh(I) complexes could insert into the weaker distal bond of the three-membered ring and undergo a structural rearrangement to give a new type of trimethylenemethane-rhodium (TMM-Rh) complex (Scheme 1B-a).[12a] In our previous work, we have demonstrated that terminal alkyne could react with cationic Ag species to provide alkynyl-Ag intermediate, which rapidly underwent trans-metalation to TMM-Rh complex. After reductive elimination, the reaction eventually delivered the functionalized cyclic *β*-amino alcohols in high ee values (when X=N, Scheme 1B-b).[12a] Furthermore, we also succeeded in using a variety of secondary amines as "soft" nucleophiles (those from conjugate acids with a $pK_a$ less than 25) to achieve direct allylic substitution, affording the corresponding functionalized cyclic *β*-amino alcohols in good yields along with high ee values (Scheme 1B-c).[12b] Encouraged by these findings, we envisaged that if using 1,3-diketones as nucleophiles in this transformation,[13] a new type of functionalized cyclic *β*-amino alcohols bearing a diketone moiety could be generated (Scheme 1C, this work).

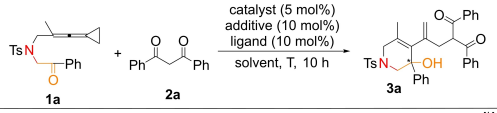



**Scheme 1.** Previous work and this work.

To test the feasibility of our hypothesis, we surveyed the reaction of keto-VDCP **1a** as our initial substrate with dibenzoyl methane **2a** using *in situ* generated cationic Rh(I) complex as catalyst.[12] After preliminary screening, the combination of $[Rh(cod)Cl]_2$ and $NaBAr^F_4$ was found to be an outstanding catalyst system, affording the desired product *rac*-**3a** in 96% yield at 90 °C in toluene (Table 1, entries 1–4). When commercially available $[Rh(cod)_2]BF_4$ (purchased from Adamas) was used as the catalyst, product **3a** was furnished in 74% total yield after stirring the reaction mixture at 90 °C for 24 hours and at 100 °C for another 24 hours (Table 1, entry 5). Changing the solvent from toluene to chlorobenzene, 1,2-dichloroethane, 1,4-dioxane or acetonitrile, we found that the reaction proceeded very well in chlorobenzene to give **3a** in 93% yield; in 1,2-dichloroethane or 1,4-dioxane, **3a** was given in 40% or 50% yield, respectively and in acetonitrile, only trace of **3a** was afforded, indicating a drastic solvent effect in this reaction (Table 1, entries 6–9). Next, we inspected asymmetric variant of this reaction using a bunch of chiral binaphthyl bisdiarylphosphine ligands **L2**–**L5** under the temporally optimized conditions. To our delight, when (*R*)-XylBINAP (**L5**) was employed as a chiral ligand, the desired product **3a** was furnished in 97% yield with 91% ee value (Table 1, entries 10–13). To further improve the enantiomeric excess of **3a**, we decided to reexamine the reaction conditions with catalyst combination of $[Rh(cod)Cl]_2$ and $AgNTf_2$ and the results are shown in entries 14–18 of Table 1 in a variety of solvents such as 1,2-dichloroethane, 1,4-dioxane, acetonitrile or chlorobenzene. We found that performing the reaction in chlorobenzene at 90 °C afforded **3a** in 60% yield; the yield of **3a** could be improved to 91% when the reaction was carried out at 100 °C

**Table 1.** Optimization of Reaction Conditions.




**1a** + **2a** → **3a**

| entry[a] | catalyst | additive | ligand | solvent | T [°C] | yield [%][b] | ee [%][c] |
|---|---|---|---|---|---|---|---|
| 1 | $[Rh(cod)Cl]_2$ | $AgNTf_2$ | (*rac*)-BINAP | Toluene | 90 | 85 | - |
| 2 | $[Rh(cod)Cl]_2$ | AgOTf | (*rac*)-BINAP | Toluene | 90 | 40 | - |
| 3 | $[Rh(cod)Cl]_2$ | $AgSbF_6$ | (*rac*)-BINAP | Toluene | 90 | no product | - |
| 4 | $[Rh(cod)Cl]_2$ | $NaBAr^F{}_4$ | (*rac*)-BINAP | Toluene | 90 | 96 | - |
| 5[d] | $[Rh(cod)_2]BF_4$ | - | (*rac*)-BINAP | Toluene | 90-100 | 74 | - |
| 6 | $[Rh(cod)Cl]_2$ | $NaBAr^F{}_4$ | (*rac*)-BINAP | PhCl | 90 | 93 | - |
| 7 | $[Rh(cod)Cl]_2$ | $NaBAr^F{}_4$ | (*rac*)-BINAP | DCE | 90 | 40 | - |
| 8 | $[Rh(cod)Cl]_2$ | $NaBAr^F{}_4$ | (*rac*)-BINAP | dioxane | 90 | 50 | - |
| 9 | $[Rh(cod)Cl]_2$ | $NaBAr^F{}_4$ | (*rac*)-BINAP | MeCN | 90 | trace | - |
| 10 | $[Rh(cod)Cl]_2$ | $NaBAr^F{}_4$ | (*R*)-TolBINAP | Toluene | 90 | 97 | 87 |
| 11 | $[Rh(cod)Cl]_2$ | $NaBAr^F{}_4$ | (*R*)-BINAP | Toluene | 90 | 93 | 82 |
| 12 | $[Rh(cod)Cl]_2$ | $NaBAr^F{}_4$ | (*R*)-XylBINAP | Toluene | 90 | 97 | 91 |
| 13 | $[Rh(cod)Cl]_2$ | $NaBAr^F{}_4$ | (*R*)-$H_8$-BINAP | Toluene | 90 | 80 | 91 |
| 14 | $[Rh(cod)Cl]_2$ | $AgNTf_2$ | (*rac*)-BINAP | DCE | 90 | 20 | - |
| 15 | $[Rh(cod)Cl]_2$ | $AgNTf_2$ | (*rac*)-BINAP | dioxane | 90 | 30 | - |
| 16 | $[Rh(cod)Cl]_2$ | $AgNTf_2$ | (*rac*)-BINAP | MeCN | 90 | trace | - |
| 17 | $[Rh(cod)Cl]_2$ | $AgNTf_2$ | (*rac*)-BINAP | PhCl | 90 | 60 | - |
| 18 | $[Rh(cod)Cl]_2$ | $AgNTf_2$ | (*rac*)-BINAP | PhCl | 100 | 91 | - |
| **19** | **$[Rh(cod)Cl]_2$** | **$AgNTf_2$** | **(*R*)-TolBINAP** | **PhCl** | **100** | **86** | **96** |
| 20 | $[Rh(cod)Cl]_2$ | $AgNTf_2$ | (*R*)-BINAP | PhCl | 100 | 93 | 93 |
| 21 | $[Rh(cod)Cl]_2$ | $AgNTf_2$ | (*R*)-XylBINAP | PhCl | 100 | 78 | 92 |
| 22 | $[Rh(cod)Cl]_2$ | $AgNTf_2$ | (*R*)-$H_8$-BINAP | PhCl | 100 | 70 | 93 |
| 23 | $[Rh(cod)Cl]_2$ | $NaBAr^F{}_4$ | (*R*)-TolBINAP | PhCl | 100 | 86 | 92 |

[a]Reaction conditions: **1a** (0.05 mmol), **2a** (0.06 mmol), $[Rh(cod)Cl]_2$ (5 mol%), additive (10 mol%), ligand (10 mol%), and solvent (1.0 mL) were used; 10 h. [b]Isolated yield. [c]Determined by HPLC on a chiral stationary phase. [d]The reaction was carried out at 90 °C for 24 h, then at 100 °C for 24 h.

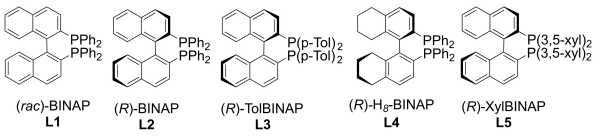
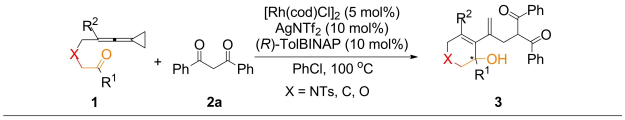
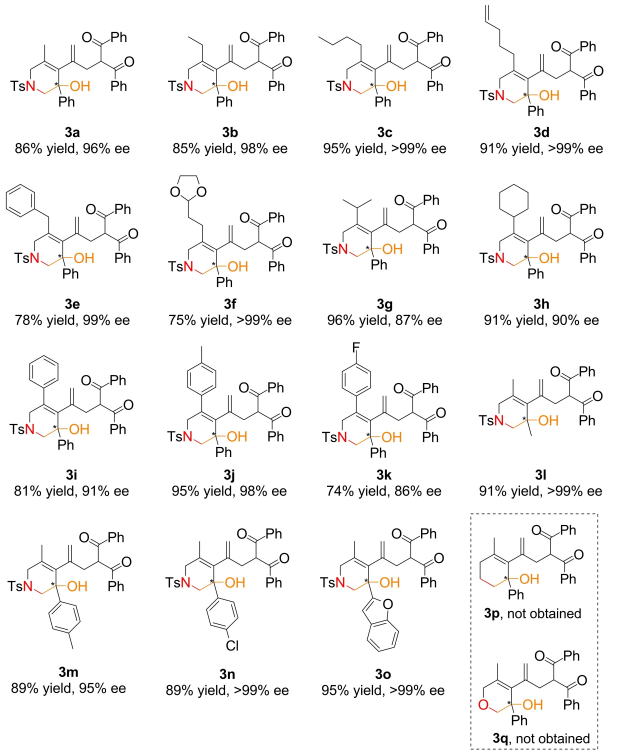



**Table 2.** Substrate Scope of Keto-VDCPs **1**.




**1** + **2a** → **3**




[a]Reaction conditions: keto-VDCPs **1** (0.20 mmol), dibenzoylmethane **2a** (0.24 mmol), $[Rh(cod)Cl]_2$ (5 mol%), $AgNTf_2$ (10.0 mol%), (*R*)-TolBINAP (10.0 mol%), and chlorobenzene (2.0 mL) were used, 10 h. [b]Isolated yield. [c]Determined by HPLC on a chiral stationary phase.

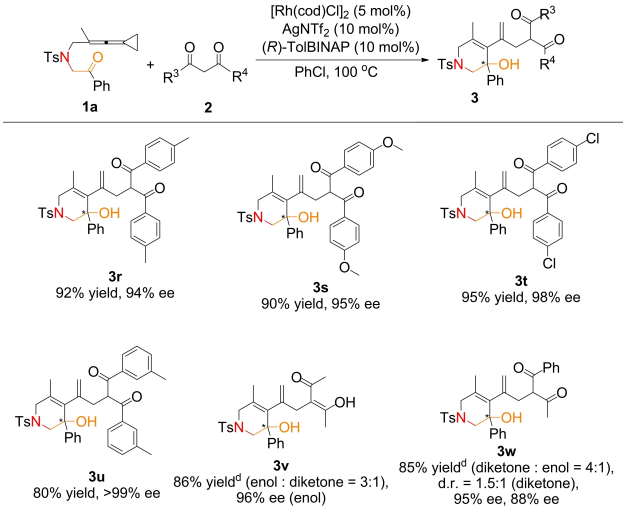
(Table 1, entries 17–18). Gratifyingly, using (*R*)-TolBINAP (**L3**) as a chiral ligand with this catalytic system, **3a** could be obtained in 86% yield along with 96% ee value (Table 1, entry 19). The use of **L2**, **L4** and **L5** as the chiral ligands in this reaction provided **3a** in 70–93% yields but along with 92%–93% ee values (Table 1, entries 20–22). The catalyst combination of $[Rh(cod)Cl]_2$ and NaBArF afforded **3a** in 86% yield along with 92% ee value under this condition (Table 1, entry 23).

With the optimal conditions in hand, the generality of this catalytic asymmetric synthesis of six-membered *β*-amino alcohol was examined. First, various linear alkyl substituents including long-chain alkane or long-chain alkane with a terminal olefin, an aldehyde protected group and benzyl groups were introduced as $R^2$ into keto-VDCP **1**, affording the desired products **3a**–**3f** in good yields ranging from 75% to 95% along with 98% to >99% ee values (Table 2). The branched alkyl substituents such as isopropyl group and cyclohexyl group were tolerated, giving the corresponding products **3g** and **3h** in 96% yield with 87% ee and 91% yield with 90% ee, respectively. $R^2$ group could be also a phenyl group, furnishing the desired product **3i** in 81% yield along with 91% ee value. Moreover, regardless of whether methyl group or a fluorine atom was introduced into the benzene ring of $R^2$ group in keto-VDCP **1**, the reactions delivered the desired products **3j** and **3k** in 95% yield along with 98% ee and 74% along with 86% ee. The further screening of $R^1$ group revealed that methyl group, substituted aromatic group and heteroaromatic group were all compatible, affording the desired products **3l**–**3o** in 89–95% yields along with 95%–>99% ee values. However, changing the linker as an oxygen atom or a carbon atom such as keto-VDCPs **1p** and **1q**, none of corresponding products **3p** and **3q** could be obtained under the standard conditions, perhaps due to steric or electronic effects.

The scope of 1,3-bisaryl-1,3-propanedione was also examined with a variety of *para* or *meta*-substituted aromatic rings, affording the desired products **3r**–**3w** in good yields ranging from 80% to 95% along with 94% to >99% ee values (Table 3). Unexpectedly, when acetylacetone was used as the nucleophile, the desired product **3v** was obtained as enol and diketone isomeric mixture in 86% total yield, in which the enol product was the major one on the basis of NMR

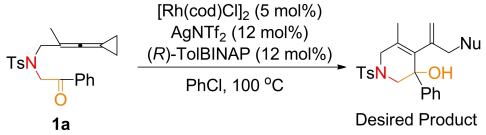
 

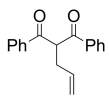
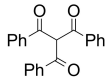
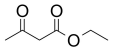
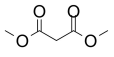
**Table 3.** Substrate Scope of 1,3-Diketones.




[a]Reaction conditions: keto-VDCP **1a** (0.20 mmol), diones **2** (0.24 mmol), $[Rh(cod)Cl]_2$ (5 mol%), $AgNTf_2$ (10.0 mol%), (*R*)-TolBINAP (10.0 mol%), and chlorobenzene (2.0 mL) were used, 10 h. [b]Isolated yield. [c]Determined by HPLC on a chiral stationary phase. [d]Total yield of enol and diketone.

**Table 4.** Non-reactive Nucleophiles **2**.



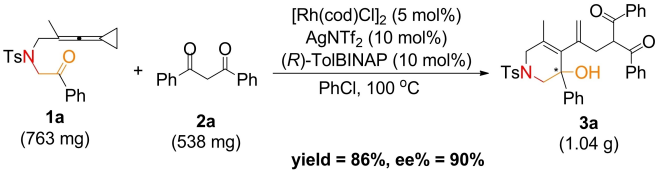

| entry[a] | nucleophile **2** | result | entry[a] | nucleophile **2** | result |
|---|---|---|---|---|---|
| 1 |  | N.R. | 5 |  | N.R. |
| 2 |  | N.R. | 6 |  | N.R. |
| 3 |  | N.R. | 7 |  | N.R. |
| 4 |  | N.R. | 8 |  | N.R. |

[a]Reaction conditions: **1a** (0.05 mmol), **2** (0.06 mmol), $[Rh(cod)Cl]_2$ (5 mol%), $AgNTf_2$ (12 mol%), (*R*)-TolBINAP (12 mol%), and PhCl (dry, 1.0 mL) were used; 10 h. [b]The reaction was carried out at 100 °C for 10 h.

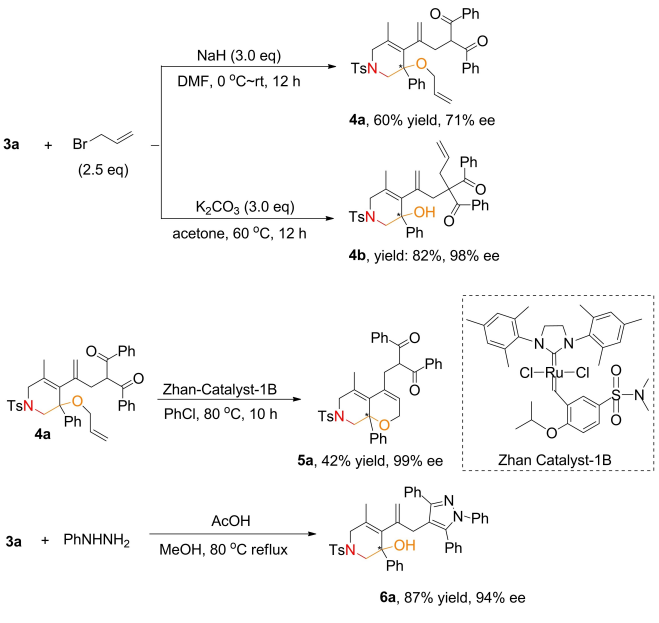
spectroscopic data along with 96% ee value. Next, we further examined the reaction of **1a** with asymmetrical 1-phenylbutane-1,3-dione and found that the corresponding product mixture of **3w** was afforded in 85% total yield along with 4:1 ratio of diketone and enol, in which the diketone was produced as a 1.5:1 diastereomeric mixture along with 95% and 88% ee values, respectively. However, when cyclic diketones or substituted dibenzoyl methanes as well as ethyl 3-oxobutanoate or dimethyl malonate were used as the nucleophiles, none of the desired products could be formed under the standard conditions presumably due to the steric effects (Table 4). For the detailed examinations, see Table S1 in the Supporting Information.

Furthermore, this catalytic asymmetric synthesis of functionalized six-membered *β*-amino alcohol could be conducted at 2.0 mmol scale, affording the desired product **3a** in 86% yield along with 90% ee value (Scheme 2).

Considering that product **3** has two acidic hydrogen atoms, including the remaining α-H of diketone and the O–H of hydroxy group of *β*-amino alcohol, we performed the further allylation reactions under two different conditions (Scheme 3). Using 3.0 equivalents of sodium hydride as a base, single allylated product **4a** was obtained in 60% yield with 71% ee at 0 °C in DMF based on NMR spectroscopic data. On the other hand, when using $K_2CO_3$ (3.0 eq) as a base, the carbonyl α-H of diketone was allylated, giving **4b** in 82% yield with 98% ee. This may be because the hydroxy group in **3a** can be more easily deprotonated by a stronger base such as NaH in DMF at lower temperature and the acidic proton between two




**Scheme 2.** Gram Scale-Up Experiment.

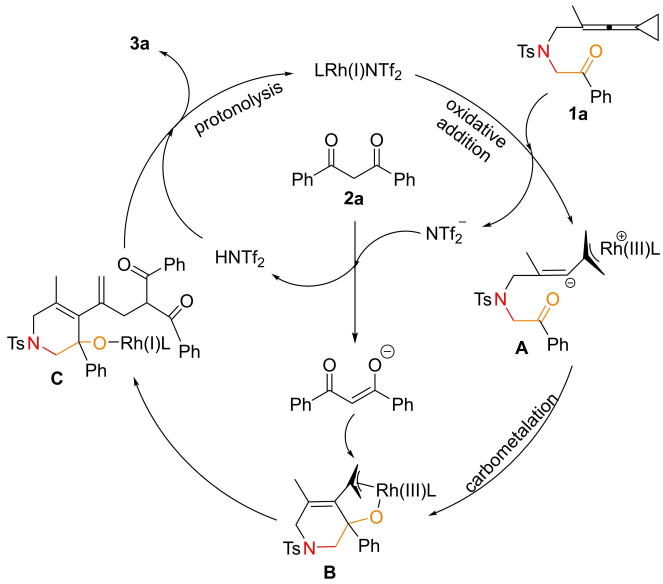



**Scheme 3.** Derivatizations of Product **3a**.

carbonyl groups can be selectively deprotonated by a weaker inorganic base $K_2CO_3$ at higher temperature. The obtained product **4a** could be further used for the RCM reaction using Zhan-1B as the catalyst, affording the corresponding intramolecular RCM product **5a** in 42% yield with 99% ee (Scheme 3). In addition, we also performed the reaction of **3a** with phenylhydrazine upon heating in mixing solvent of methanol and acetic acid, delivering the product **6a** with pyrazole structure in 87% yield with 94% ee value (Scheme 3).[14]

On the basis of above results and the previous reports,[10] a plausible mechanism was proposed for this domino reaction procedure using **1a** and **2a** as model substrates. As shown in Scheme 4, the catalytic cycle started from the insertion of Rh(I) complex into the weaker distal C–C bond of VDCP **1a** via an oxidative addition and the subsequent isomerization to give a TMM-Rh complex **A** (TMM: trimethylenemethane), which underwent an intramolecular ketone carbometallation to generate an electrophilic Rh-π-allyl intermediate **B**. On the other hand, an enolate could be formed from **2a** via the hydrogen abstraction with $NTf_2^-$, which nucleophilically attacked intermediate **B** to give intermediate **C**. The subsequent protonolysis would give the desired product **3a** and regenerated the Rh(I) cationic catalyst.

In summary, we have developed a novel domino reaction process of rhodium-catalyzed asymmetric keto-VDCPs' cycloisomerization with 1,3-ketones as nucleophiles, affording cyclic *β*-amino alcohols in good yields with good to excellent ee values in an atom economic way. The reaction proceeded through a rhodium(I) catalyzed cycloisomerization of cyclopropane in VDCP to give a TMM-Rh complex, an intramolecular ketone carbometallation and the nucleophilic attack of 1,3-diketone, yielding the corresponding functionalized enantiomerically enriched cyclic *β*-amino alcohols. Further investigations to examine the mechanistic details more extensively and exploration of new methodology based on this novel TMM-metal complex generated from functionalized VDCPs are currently underway in our laboratory.




**Scheme 4.** A plausible reaction mechanism.

## Experimental Section

### General Procedure for Synthesis of 3

To a 20 mL flame-dried tube was charged with keto-VDCPs **1** (0.2 mmol, 1.0 equiv.), 1,3-diones **2** (0.24 mmol, 1.2 equiv.), $[Rh(cod)Cl]_2$ (5 mol%, 0.05 equiv.), $AgNTf_2$ (10 mol%, 0.10 equiv.), and (*R*)-TolBINAP (10 mol%, 0.10 equiv.). The reaction tube was evacuated and backfilled with argon (repeated three times). Then, super dry chlorobenzene (2.0 mL) was added into the tube. The reaction mixture was stirred at 100 °C for 10 h. After the reaction was complete, the mixture was filtered through absorbent cotton, and solvent was removed under reduced pressure. The residue was purified by a flash column chromatography ($SiO_2$) to give the corresponding product **3**.

## Supporting Information Available

Detailed descriptions of experimental procedures and their spectroscopic data are presented in the Supporting Information.

## Acknowledgements

*We are grateful for the financial support from the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB20000000) and sioczz201808, the National Natural Science Foundation of China (21372250, 21121062, 21302203, 20732008, 21772037, 21772226, 21861132014 and 91956115).*

## References

[1] a) S. C. Bergmeier, *Tetrahedron* **2000**, *56*, 2561; b) S. R. S. S. Kotti, C. Timmons, G. Li, *Chem. Biol. Drug Des.* **2006**, *67*, 101; c) S. M. Dalby, J. Goodwin-Tindall, I. Paterson, *Angew. Chem. Int. Ed.* **2013**, *52*, 6517; *Angew. Chem.* **2013**, *125*, 6645; d) N. Lin, L. E. Overman, M. H. Rabinowitz, L. A. Robinson, M. L. Sharp, J. Zablocki, *J. Am. Chem. Soc.* **1996**, *118*, 9062; e) F. D. Klingler, *Acc. Chem. Res.* **2007**, *40*, 1367; f) C. Weng, H. Zhang, X. Xiong, X. Lu, Y. Zhou, *Asian J. Chem.* **2014**, *26*, 3761; g) P. Parasuraman, Z. Begum, M. Chennapuram, C. Seki, Y. Okuyama, E. Kwon, K. Uwai, M. Tokiwa, S. Tokiwa, M. Takeshita, H. Nakano, *RSC Adv.* **2020**, *10*, 17486; h) B. Gnanaprakasam, E. Balaraman, Y. Ben-David, D. Milstein, *Angew. Chem. Int. Ed.*

**2011**, *50*, 12240; *Angew. Chem.* **2011**, *123*, 12448; i) R. A. Wohl, *Angew. Chem. Int. Ed.* **1973**, *12*, 920; *Angew. Chem.* **1973**, *85*, 956.

[2] a) T. Kolter, K. Sandhoff, *Angew. Chem. Int. Ed.* **1999**, *38*, 1532; *Angew. Chem.* **1999**, *111*, 1632; b) G. A. Rogers, S. M. Parsons, D. C. Anderson, L. M. Nilsson, B. A. Bahr, W. D. Kornreich, R. Kaufman, R. S. Jacobs, B. Kirtman, *J. Med. Chem.* **1989**, *32*, 1217; c) M. M. Heravi, T. B. Lashaki, B. Fattahi, V. Zadsirjan, *RSC Adv.* **2018**, *8*, 6634; d) R. Morodo, R. Gérardy, G. Petit, J.-C. M. Monbaliu, *Green Chem.* **2019**, *21*, 4422; e) H. Blattmann, R. Mülhaupt, *Green Chem.* **2016**, *18*, 2406; f) M. Wang, L. Liu, Z. Yin, Y. X. Lu, *RSC Adv.* **2018**, *8*, 5816; g) Z. Mardani, R. Kazemshoar-Duzduzani, K. Moeini, A. Hajabbas-Farshchi, C. Carpenter-Warren, A. M. Z. Slawin, J. D. Woollins, *RSC Adv.* **2018**, *8*, 28810.

[3] a) J. B. Koepfli, J. F. Mead, J. A. Brockman, *J. Am. Chem. Soc.* **1947**, *69*, 1837; b) J. B. Koepfli, J. F. Mead, J. A. Brockman, *J. Am. Chem. Soc.* **1949**, *71*, 1048; c) R.-H. Liu, K. Fang, B. Wang, M.-H. Xu, G.-Q. Lin, *J. Org. Chem.* **2008**, *73*, 3307.

[4] M. Kitajima, I. Mori, K. Arai, N. Kogure, H. Takayama, *Tetrahedron Lett.* **2006**, *47*, 3199.

[5] Y.-Q. Tang, I. Sattler, R. Thiericke, S. Grabley, *Eur. J. Org. Chem.* **2001**, *2*, 261.

[6] a) M. D. Lopez, J. Cobo, M. Nogeuras, *Curr. Org. Chem.* **2008**, *12*, 718; b) K. Savaspun, C. W. G. Au, S. G. Pyne, *J. Org. Chem.* **2014**, *79*, 4569.

[7] a) B. M. Trost, C. B. Lee, *J. Am. Chem. Soc.* **1998**, *120*, 6818; b) S. Bansal, Y. Kumar, P. Pippal, D. K. Das, P. Pramanika, P. P. Singh, *New J. Chem.* **2017**, *41*, 2668; c) D. Li, J. Wang, S. B. Yu, S. L. Ye, W. J. Zou, H. B. Zhang, J. B. Chen, *Chem. Commun.* **2020**, *56*, 2256; d) H. Li, J. W. Sheeran, A. M. Clausen, Y.-Q. Fang, M. M. Bio, S. Bader, *Angew. Chem. Int. Ed.* **2017**, *56*, 9425; *Angew. Chem.* **2017**, *129*, 9553; e) M.-Y. Huang, J.-M. Yang, Y.-T. Zhao, S.-F. Zhu, *ACS Catal.* **2019**, 9, 5353; f) B. Xu, S.-F. Zhu, X.-D. Zuo, Z.-C. Zhang, Q.-L. Zhou, *Angew. Chem. Int. Ed.* **2014**, *53*, 3913; *Angew. Chem.* **2014**, *126*, 3994; g) B.-M. Fan, J.-H. Xie, S. Li, L.-X. Wang, Q.-L. Zhou, *Angew. Chem. Int. Ed.* **2007**, *46*, 1275; *Angew. Chem.* **2007**, *119*, 1297; h) B.-M. Fan, S. -Li, J.-H. Xie, L.-X. Wang, Y.-Q. Tu, Q.-L. Zhou, *Science China Chemistry* **2006**, *49*, 81; i) C.-X. Ye, Y. Y. Melcamu, H.-H. Li, J.-T. Cheng, T.-T. Zhang, Y.-P. Ruan, X. Zheng, X. Lu, P.-Q. Huang, *Nat. Commun.* **2018**, *9*, 410.

[8] a) F. Schmidt, F. Keller, E. Vedrenne, V. K. Aggarwal, *Angew. Chem. Int. Ed.* **2009**, *48*, 1149; *Angew. Chem.* **2009**, *121*, 1169; b) K. C. Nicolaou, X. H. Huang, S. A. Snyder, P. B. Rao, M. Bella, M. V. Reddy, *Angew. Chem. Int. Ed.* **2002**, *41*, 834; *Angew. Chem.* **2002**, *114*, 862; c) J. Schwerdtfeger, D. Hoppe, *Angew. Chem. Int. Ed.* **1992**, *31*, 1505; *Angew. Chem.* **1992**, *104*, 1547; d) J.-D. Zhang, X.-X. Yang, Q. Jia, J.-W. Zhao, L.-L. Gao, W.-C. Gao, H.-H. Chang, W.-L. Wei, J.-H. Xu, *Catal. Sci. Technol.* **2019**, *9*, 70; e) R. Tak, M. Kumar, R. I. Kureshy, M. K. Choudhary, N. H. Khan, S. H. R. Abdiab, H. C. Bajaj, *RSC Adv.* **2016**, *6*, 7693; f) L. Jia, M. Makha, C.-X. Du, Z.-J. Quan, X.-C. Wang, Y.-H. Li, *Green Chem.* **2019**, *21*, 3127; g) S. B. Poh, J.-Y. Ong, S. C. Lu, Y. Zhao, *Angew. Chem. Int. Ed.* **2018**, *57*, 1645; *Angew. Chem.* **2018**, *130*, 1661; h) M. Lee, J. R. Lamb, M. J. Sanford, A. M. LaPointe, G. W. Coates, *Chem. Commun.* **2018**, *54*, 12998.

[9] H. Zhou, Y.-N. Wang, L. Zhang, M. Cai, S.-Z. Luo, *J. Am. Chem. Soc.* **2017**, *139*, 3631.

[10] a) E. Skucas, J. R. Zbieg, M. J. Krische, *J. Am. Chem. Soc.* **2009**, *131*, 5054; b) J. R. Zbieg, E. L. McInturff, M. J. Krische, *Org. Lett.* **2010**, *12*, 2514; c) M.-Y. Ngai, E. Skucas, M. J. Krische, *Org. Lett.* **2008**, *10*, 2705.

[11] a) S. Yang, M. Shi, *Acc. Chem. Res.* **2018**, *51*, 1667; b) S. Yang, W. Yuan, Q. Xu, M. Shi, *Chem. Eur. J.* **2015**, *21*, 15964; c) D.-Y. Li, Y. Wei, I. Marek, X.-Y. Tang, M. Shi, *Chem. Sci.* **2015**, *6*, 5519; d) S. Yang, Q. Xu, M. Shi, *Chem. Eur. J.* **2016**, *22*, 10387; e) S. Yang, Q. Xu, M. Shi, *Tetrahedron* **2016**, *72*, 584; f) M. Chen, W. R. Rouge, *Org. Lett.* **2013**, *15*, 1662; g) M. Chen, D. Y. Qian, J. W. Sun, *Org. Lett.* **2019**, *21*, 8127.

[12] a) S. Yang, K.-H. Rui, X.-Y. Tang, Q. Xu, M. Shi, *J. Am. Chem. Soc.* **2017**, *139*, 5957; b) S. Yang, Q.-Z. Li, C. Xu, Q. Xu, M. Shi, *Chem. Sci.* **2018**, *9*, 5074.

[13] a) B. M. Trost, I. Fleming, Eds.; Pergamon Press: New York. **1991**, *3*, 1–63; b) K. Kubota, E. Nakamura, *Angew. Chem. Int. Ed.* **1997**, *36*, 2491; *Angew. Chem.* **1997**, *109*, 2581; c) X. Han, X. Wang, T. Pei, R. A. Widenhoefer, *Chem. Eur. J.* **2004**, *10*, 6333; d) E. Nakamura, K. Kubota, *Tetrahedron Lett.* **1997**, *38*, 7099; e) M. Nakamura, K. Hara, G. Sakata, E. Nakamura, *Org. Lett.* **1999**, *1*, 1505.

[14] R. Mamidala, V. Mukundam, K. Dhanunjayarao, K. Venkatasubbaiah, *Dalton Trans.* **2015**, *44*, 5805.