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Cobalt-catalyzed enantioselective desymmetrizing reductive cyclization of alkynyl cyclodiketones†

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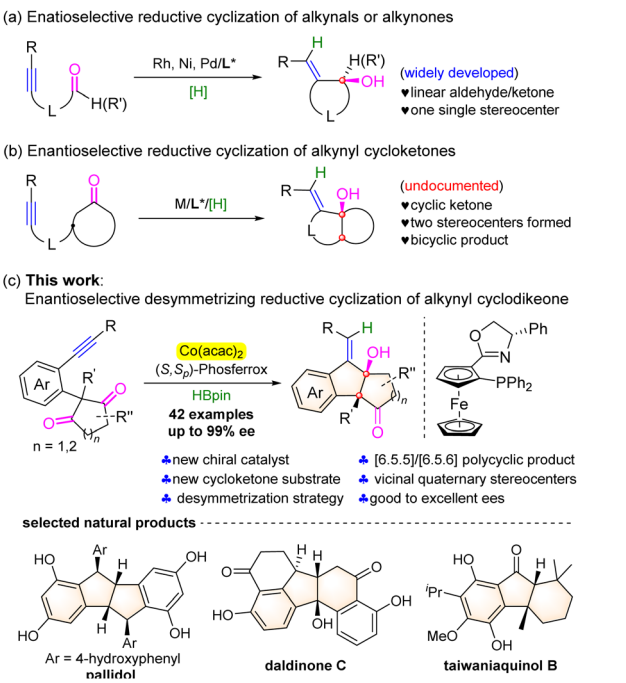
A highly enantioselective cobalt-catalyzed desymmetrizing reductive cyclization of alkynyl cyclodiketones has been developed. Under mild reaction conditions by employing HBpin as a reducing agent and ferrocene-based PHOX as a chiral ligand, a series of polycyclic tertiary allylic alcohols bearing contiguous quaternary stereocenters are achieved in moderate to excellent yields with excellent enantioselectivities (up to 99%). Broad substrate scope and high functional group compatibility are observed in this reaction. A CoH-catalyzed pathway involving alkyne hydrocobaltation followed by nucleophilic addition to the C=O bond is proposed. Synthetic transformations of the product are conducted to demonstrate the practical utilities of this reaction.

Introduction

Cyclic allylic alcohols are important building blocks for organic synthesis and unique structural motifs of natural products and biologically active molecules.[1] The reductive cyclization of alkynyl aldehydes or ketones provides an efficient, straightforward, and atom-economic access to such structural units.[2] A number of transition metal catalysts have been employed in this cyclization reaction by merging with suitable hydride-donating reagents, such as hydrogen, organosilanes, alcohol, and others.[3] As a result, the corresponding enantioselective variants were well established in the presence of Rh-,[3a,b,r] Ni-,[3i–n] and Pd-[3o] based chiral catalysts (Scheme 1a). Despite these important advances, the documented reports are predominantly limited to linear aldehydes or ketones and only one single stereogenic carbon center was formed in these transformations. To the best of our knowledge, the reaction of alkynyl cyclic ketones has remained unexplored probably due to the lower reactivity caused by the increasing steric hindrance and the lack of efficient chiral catalysts,[4] although it would efficiently assemble chiral polycyclic molecules and build two chiral carbocenters in one step (Scheme 1b).

Recently, chiral cobalt complexes have become reliable catalysts for the asymmetric enyne hydrofunctionalization/cyclization reactions.[5] Ge and co-workers disclosed highly enantioselective hydroborylation- or hydrosilylation/cyclization of 1,6- or 1,7-enynes with HBpin or hydrosilanes, leading to a range of important functionalized chiral heterocyclic compounds.[6a–c,f] In addition, the asymmetric hydroarylative or hydroacylative cyclization of enynes involving a C–H functionalization process was also achieved to afford the cyclic products in excellent enantioselectivities with high atom economy.[6d,e,g–i]



Scheme 1 Transition-metal-catalyzed enantioselective reductive couplings of alkynals and alkynones.

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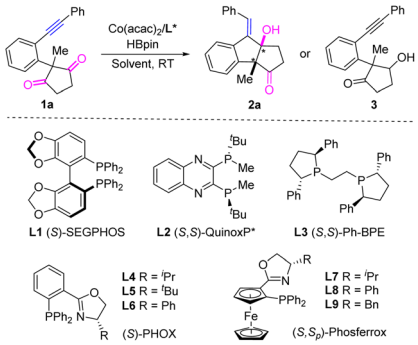
Inspired by these results, we envisioned that the asymmetric reductive coupling of alkynyl cyclic ketones might be possible under the chiral cobalt catalyst. However, this reaction is indeed very challenging since both the triple bond of alkynes[7] and the polar C=O bond of ketones[8] are prone to be reduced. Noteworthy is that Xia and co-workers disclosed recently an intermolecular enantioselective reductive cross-coupling of alkynes and aldehydes by merging cobalt catalysis with photocatalysis.[9] Herein, we communicate an enantioselective desymmetrizing reductive coupling of alkynyl cyclic 1,3-diketones by utilizing the complex of $Co(acac)_2$ and a ferrocene-based chiral phosphine-oxazoline ligand as the catalyst and HBpin as the reducing agent. Through a possible sequential alkyne *syn*-hydrocobaltation followed by desymmetrizing nucleophilic addition to ketones, a number of optically active polycyclic tertiary allylic alcohols bearing vicinal quaternary stereocenters were obtained in moderate to good yields and good to excellent enantioselectivities. The framework of the resulting molecules constitutes the core structure of natural products, such as pallidol, daldinone C, and taiwaniaquinol B (Scheme 1c).[10]

Results and discussion

We commenced the study with alkynyl cyclopentane-1,3-dione **1a** as the model substrate. The initial test showed that the intramolecular reductive cyclization reaction of **1a** proceeded smoothly to afford the desired product **2a** in 29% yield with 23% ee in the presence of $Co(acac)_2$ catalyst and chiral ligand (*S*)-SEGPHOS **L1** by using HBpin as the reducing reagent in toluene at room temperature (Table 1, entry 1). Encouraged by this result, the solvent effect was then examined (entries 2–6). The yield and ee were both increased in THF and 1,4-dioxane (entries 2 and 5), while lower yields were observed in Et_2O, DME, and DCM (entries 3, 4, and 6). No product was detected when using Et_3SiH as the reducing reagent (entry 7). To further improve the yield and ee, other chiral ligands were investigated. Diphosphine ligand (*S*,*S*)-QuinoxP* **L2** led to **2a** in 75% ee and a poor yield of 17%, while (*S*,*S*)-Ph-BPE **L3** resulted in lower yield and lower ee (entries 8 and 9). Moreover, poor yield and ee were observed for a number of BINOL-based chiral phosphoramidite ligands. Next, we turned our attention to the bidentate P,N-ligand PHOX. The use of (*S*)-^{i}Pr-PHOX **L4** afforded **2a** in 61% yield and 43% ee (entry 10), while the corresponding (*S*)-^{t}Bu-PHOX **L5** or (*S*)-Ph-PHOX **L6** led to poor yields and moderate ee values along with the observation of by-product **3** derived from the direct reduction of the C=O bond (entries 11 and 12). Gratifyingly, the ferrocene-based chiral PHOX ligands **L7** and **L8** significantly improved the enantioselectivities to 80% and 99% with 66% and 85% yields, respectively (entries 13 and 14). In comparison, the analogous Bn-ligand **L9** delivered product **2a** in poor yield and poor ee (entry 15). Finally, a fast reaction was observed at 50 °C while the yield was diminished to 63% (entry 16). Control experiments demonstrated that the desymmetrizing reductive cyclization reaction could not occur in the absence of $Co(acac)_2$ or HBpin.

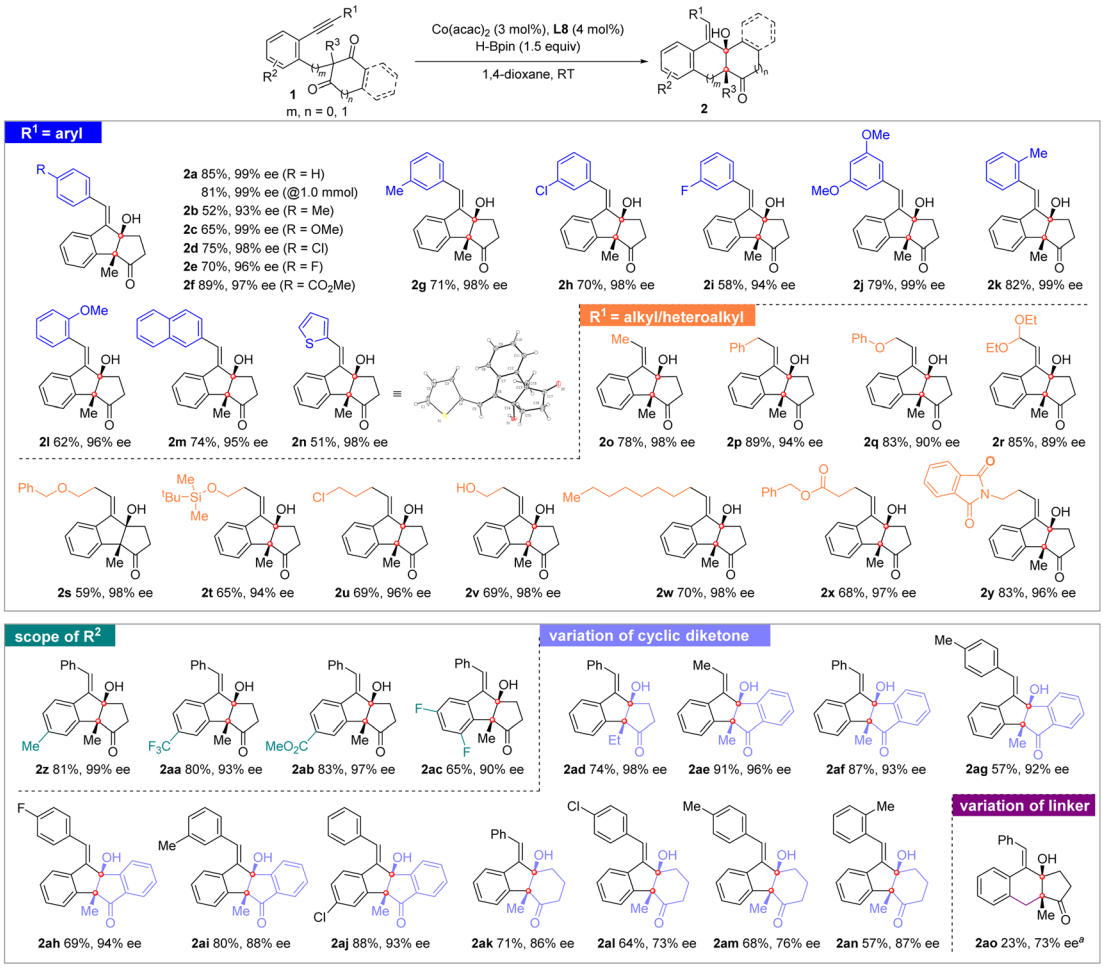
With the optimal conditions in hand, we then investigated the substrate scope of this cobalt-catalyzed reductive cyclization reaction. Excellent enantioselectivities with moderate to good yields were generally observed in the reactions. As shown in Scheme 2, a 1.0 mmol-scale reaction of **1a** led to product **2a** in a slightly lower yield (81%) and 99% ee. The substrates bearing different aryl groups linked to the alkyne moiety were first examined. Various substituents attached to the *para*-, *meta*-, and *ortho*-positions of the benzene ring, either electron-donating groups (methyl: **2b**, **2g**, and **2k**; methoxy: **2c** and **2l**) or electron-withdrawing groups (chloride: **2d** and **2h**; fluoride: **2e** and **2i**; methoxycarbonyl: **2f**) were well tolerated to afford the corresponding products in 52–89% yields and 93–99% ees. No steric effect was observed for these substituents. The reaction of a 3,5-dimethoxy-substrate led to product **2j** in 79% yield and 99% ee. Moreover, a 2-naphthyl substituted substrate reacts smoothly to furnish product **2m** in 74% yield and 95% ee. The thiophenyl group is also compatible in the reaction and the corresponding product **2n** was achieved in 51% yield and 98% ee. The absolute configuration of **2n** was determined to be (3*aR*,8*aR*,*E*) based on X-ray crystallographic analysis.[11]

Table 1 Optimization of the reaction conditions[a]



			2a		3
Entry	L*	Solvent	Yield[b]/%	ee[c]/%	Yield[b]/%
1	**L1**	Toluene	29	23	—
2	**L1**	THF	43	57	—
3	**L1**	Et_2O	26	20	—
4	**L1**	DME	20	41	—
5	**L1**	1,4-Dioxane	53	51	—
6	**L1**	DCM	<10	nd	—
7[d]	**L1**	1,4-Dioxane	nd	—	—
8	**L2**	1,4-Dioxane	17	75	—
9	**L3**	1,4-Dioxane	31	34	—
10	**L4**	1,4-Dioxane	61	43	—
11	**L5**	1,4-Dioxane	11	53	21
12	**L6**	1,4-Dioxane	12	54	18
13	**L7**	1,4-Dioxane	66	80	—
14	**L8**	1,4-Dioxane	85	99	—
15	**L9**	1,4-Dioxane	14	18	28
16[e]	**L8**	1,4-Dioxane	63	99	—

[a] Reaction conditions: **1a** (0.2 mmol), $Co(acac)_2$ (3 mol%), L* (4 mol%), and HBpin (1.5 equiv.) in the solvent (1.0 mL) at room temperature for 48 h. [b] Isolated yields. [c] Determined by chiral HPLC. [d] Et_3SiH instead of HBpin. [e] At 50 °C for 24 h.

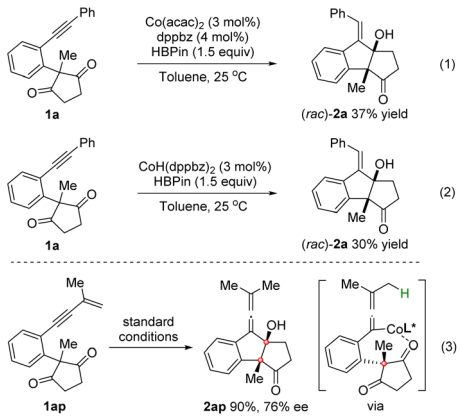


Scheme 2 Substrate scope. Reaction conditions: **1** (0.2 mmol), $Co(acac)_2$ (3 mol%), **L8** (4 mol%), and HBpin (1.5 equiv.) in 1,4-dioxane (1.0 mL) at rt. [a] In THF.

In addition, a series of linear alkyl and heteroalkyl substituents linked to the alkyne moiety were investigated. As shown in Scheme 2, the reactions of methyl, benzyl, and *n*-octyl substrates afforded the corresponding products **2o**, **2p**, and **2w** in moderate to good yields with 94–98% ees. High compatibility of the heteroalkyl groups was observed. A number of functional substituents, including phenoxyl (**2q**), benzyloxyl (**2s**), silyloxyl (**2t**), chloride (**2u**), free hydroxyl (**2v**), ester (**2x**), and imide (**2y**), were all well tolerated to furnish the desired products in 59–83% yields and 90–98% ees. The reaction of a diethoxymethyl-substrate also led to product **2r** in 85% yield and 89% ee. Moreover, the substituent effect of R^2 attached to the linker benzene ring was also evaluated. The methyl (**2z**), trifluoromethyl (**2aa**), methoxycarbonyl (**2ab**), and difluoro (**2ac**) groups were introduced into the substrates and the corresponding products were afforded in moderate to good yields (65–83%) and excellent enantioselectivities (90–99%).

Variation of the cyclic diketone moiety was also conducted. The reaction of the 2-ethyl 1,3-cyclopentanedione substrate led to **2ad** in 74% yield and 98% ee. Excellent ees with moderate to excellent yields were also obtained for the polycyclic [6.5.5.6] products **2ae–2aj** that bear additional fused benzene on the ring of cyclopentanedione. Furthermore, the reactions of the six-membered 1,3-cyclohexanedione-derived substrates also proceeded smoothly to afford the corresponding products **2ak–2an**, although their ee values (73–87%) were relatively lower than those for 1,3-cyclopentanedione substrates. The substrate bearing an additional CH_2 group between benzene and cyclodiketone is also suitable for the desymmetrizing reductive cyclization reaction, affording the desired product **2ao** in 23% yield and 73% ee by using **L8** as the chiral ligand in THF. It is noteworthy that the present chiral cobalt catalyst is inefficient in the intermolecular reductive coupling reaction between alkynes and ketones/aldehydes[9] and the intramolecular reductive cyclization reactions of acyclic alkynyl monoaldehydes or monoketones.[3]

To gain insight into the reaction mechanism, control experiments were conducted (Scheme 3). As shown in eqn (1) and (2), the reactions of **1a** employing either the $Co(acac)_2$/dppbz complex or the preformed $CoH(dppbz)_2$ as the catalyst[6a] could lead to *rac*-**2a** in 37% and 30% yields, which might imply that CoH was the active catalyst for this reductive cyclization reaction.[12]

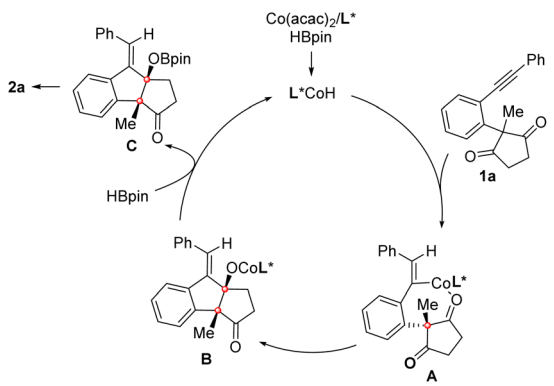


Scheme 3 Control experiments.

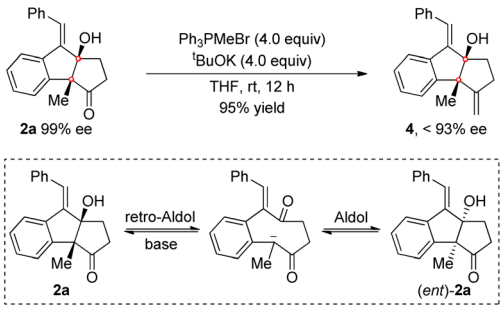
Moreover, the reaction of enynone substrate **1ap** under the standard conditions afforded an allenylic alcohol product **2ap** in 90% yield with 76% ee, in which an allenyl-Co intermediate generated by enyne hydrocobaltation was likely involved (eqn (3)). Based on these results, a CoH-catalyzed reaction pathway was proposed. As depicted in Scheme 4, the active CoH species was initially formed by the reaction of $Co(acac)_2$ with HBpin. Vinyl-Co intermediate **A** was then generated *via* alkyne hydrocobaltation. Subsequent desymmetrizing nucleophilic addition to the C=O bond followed by transmetalation of the resulting cobalt alkoxide **B** with HBpin affords intermediate **C**, which furnishes the product after hydrolysis. The active CoH catalyst is simultaneously regenerated to complete the catalytic cycle.

A number of synthetic transformations of the product were then investigated. The Wittig reaction of **2a** with Ph_3PMeBr was first tested in the presence of ^tBuOK as a base. The target exocyclic olefin **4** was obtained in excellent yield, while the enantiomeric excess was irregularly eroded. We assumed that a retro-Aldol reaction of the β-hydroxyl ketone **2a** followed by aldol reaction might occur under the basic conditions, which would cause racemization of **2a** and consequently lead to a decreased ee value of **4** (Scheme 5). Indeed, the erosion of the ee value was observed when treating **2a** with ^tBuOK.

As shown in Scheme 6, a MOM-protected compound **5** was then prepared to be used as the starting material for the Wittig



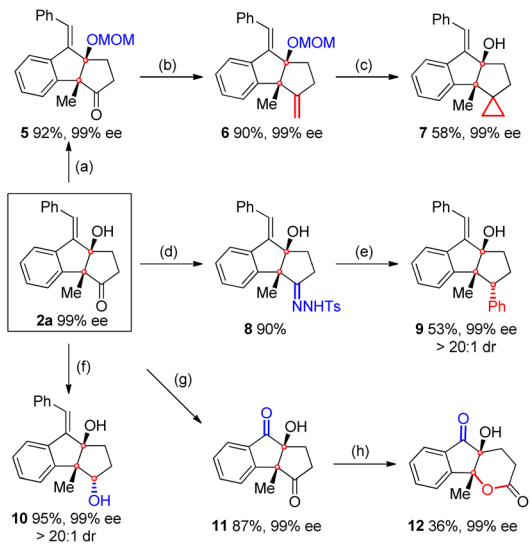
Scheme 4 Proposed reaction mechanism.



Scheme 5 ee erosion in the Wittig reaction of **2a**.

reaction. As expected, the corresponding product **6** was obtained in 90% yield with 99% ee. Compound **6** was further converted to cyclopropane **7** in 58% yield and 99% ee through deprotection followed by a Simmons–Smith reaction. Meanwhile, the condensation of **2a** with $TsNHNH_2$ led to hydrozone **8**, which further coupled with $PhB(OH)_2$ to afford compound **9** (ref. 13) bearing three contiguous stereocenters in 53% yield, 99% ee, and > 20 : 1 dr.

Moreover, the reduction of **2a** with $NaBH_4$ delivered diol **10** in 95% yield, 99% ee, and > 20 : 1 dr. Relative configurations of compounds **9** and **10** were determined by 2D-NOESY analysis. The oxidation of **2a** with O_3 furnished diketone **11** in 87% yield and 99% ee, which was subsequently converted to a polycyclic



Scheme 6 Synthetic transformations. reaction conditions: (a) **2a** (0.2 mmol), CH_3OCH_2Br (2.8 equiv.), and DIPEA (4.4 equiv.) in DCM (4 mL) at 80 °C for 12 h. (b) **5** (0.2 mmol), PPh_3MeBr (4.0 equiv.), and ^tBuOK (4.0 equiv.) in THF (4 mL) at rt for 12 h. (c) (i) **6** (0.2 mmol) and HCl (1 N, 10 mL) in $CHCl_3$/MeOH (1/1, 8 mL) at rt for 12 h; (ii) Et_2Zn (5.0 equiv., 1.0 M in toluene), CH_2I_2 (5.0 equiv.) in DCM for 6 h, −10 °C-rt. (d) **2a** (0.2 mmol) and $TsNHNH_2$ (1.0 equiv.) in MeOH at rt for 24 h. (e) **8** (0.2 mmol), $PhB(OH)_2$ (1.5 equiv.), and K_2CO_3 (1.5 equiv.) in 1,4-dioxane at 110 °C for 12 h. (f) **2a** (0.2 mmol) and $NaBH_4$ (1.2 equiv.) in MeOH at 0 °C for 10 min. (g) **2a** (0.2 mmol) in MeOH/DCM (1/1, 10 mL) was purged with O_3 at −78 °C for 5 min, then PPh_3 (2.0 equiv.) was added. (h) **11** (0.2 mmol) and *m*-CPBA (4.0 equiv.) in DCM at 0 °C for 48 h.

lactone **12** in 36% yield and 99% ee through a Baeyer–Villiger reaction.

Conclusions

In summary, we have developed the first example of cobalt-catalyzed enantioselective desymmetrizing reductive cyclization reaction of alkynyl cyclic 1,3-diketones. An array of polycyclic tertiary alcohols containing an exocyclic trisubstituted olefin and contiguous quaternary stereocenters are afforded in moderate to good yields and good to excellent ees (up to 99%). The protocol features high functional group tolerance and mild reaction conditions. A reaction pathway involving alkyne hydrocobaltation followed by desymmetrizing nucleophilic addition to the C=O bond is proposed. Synthetic transformations are conducted to convert the product to a range of valuable polycyclic molecules.

Data availability

All experimental and characterization data, as well as NMR spectra are available in the ESI.† Crystallographic data for compound **2n** have been deposited in the Cambridge Crystallographic Data Centre (CCDC 2025743).

Author contributions

R.-X. L. and Y.-X. J. conceived the idea and wrote the manuscript. Y.-X. J. supervised the project. R.-X. L. and H.-W. T. performed most of the experiments. J.-L. L., J.-F. X and L.-J. C. prepared some of the substrates, and collected and analysed the spectroscopic data. All authors contributed to discussing the results.

Conflicts of interest

There are no conflicts to declare.

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