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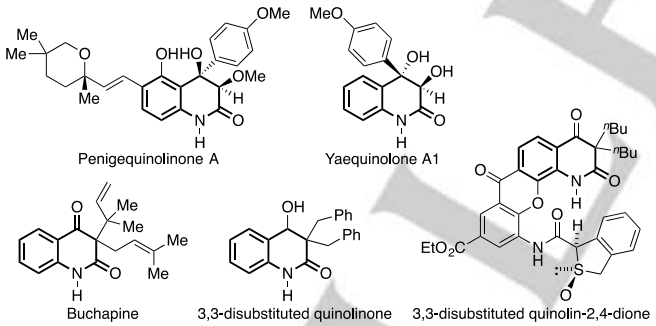
Cobalt-Catalyzed Enantioselective Hydroboration/Cyclization of 1,7-Enynes: Asymmetric Synthesis of Chiral Quinolinones Containing Quaternary Stereogenic Centers

Caizhi Wu, Jiayu Liao and Shaozhong Ge*

Abstract: An asymmetric cobalt-catalyzed hydroboration/cyclization of 1,7-enynes to synthesize chiral six-membered *N*-heterocyclic compounds was developed. A variety of aniline-tethered 1,7-enynes react with pinacolborane to afford the corresponding chiral boryl-functionalized quinoline derivatives in high yields with high enantioselectivity. This cobalt-catalyzed asymmetric cyclization of 1,7-enyens provides a general approach to access a series of chiral quinoline derivatives containing quaternary stereocenters.

Quinolines are privileged heterocycles that are present in a variety of biologically active alkaloids and pharmaceutically relevant molecules.[1] In particular, quinolinones are one of the most useful and versatile families of antibacterial agents (Scheme 1).[2] Due to their great synthetic importance, numerous methods have been developed to prepare chiral quinoline derivatives over the past few decades.[3] For example, asymmetric hydrogenation and transfer hydrogenation of quinolines have been extensively studied for this synthetic purpose.[4] However, the majority of these approaches are limited to quinoline derivatives bearing tertiary stereogenic carbon centers, and enantioselective protocols to access quinoline derivatives containing quaternary carbon centers are extremely rare.[5] Therefore, the asymmetric synthesis of chiral quinoline derivatives with quaternary stereocenters still remains as a synthetic challenge.



Scheme 1. Examples of bioactive natural and synthetic bioactive quinolinones

Transition-metal-catalzyed cyclization of 1,*n*-enynes is considered as one of the most straightforward approaches to access cyclic compounds.[6] The majority of these cyclization reactions convert 1,6-enynes to five-membered carbocyclic or heterocyclic compounds.[7] In contrast, the examples of catalytic cyclization of 1,7-enynes, in particular, the corresponding asymmetric reactions to prepare six-membered chiral heterocyclic compounds,[8] are very rare.[9] This is presumably due to the difficulty in forming a seven-membered 1,7-enyne-metal chelating ring as compared to forming a six-membered 1,6-enyne-metal chelating ring for metal-catalyzed enyne cyclization reactions. Instead, radical cyclization/cascade reactions of 1,7-enynes readily occur due to the formation of more stable six-membered cyclized radical intermediates.[10] However, it is difficult to control the stereochemical outcomes for these radical cyclization reactions.

To develop enantioselective cyclization reactions of 1,7-enynes, we envisioned that the use of chiral catalysts based on small transition metals, such as cobalt catalysts,[11] would help to release the ring strain of 1,7-enyne-metal chelation. In view of the importance of six-membered *N*-heterocycles in organic synthesis and medicinal chemistry,[1,2] we are interested in developing a Co-catalyzed asymmetric hydroboration/cyclization of aniline-tethered 1,7-enynes to access boryl-functionalized chiral quinoline derivatives. Aniline-tethered 1,7-enynes have been widely employed for radical cyclization/cascade reactions in recent years,[12] but enantioselective protocols to make chiral quinoline derivatives from these 1,7-enynes still remain unknown. Herein, we report a highly enantioselective Co-catalyzed hydroboration/cyclization of 1,7-enynes to prepare chiral quinolines and quinolin-2-ones containing a quaternary stereogenic center. Furthermore, we show that chiral quinolin-2-one products can be readily converted to other chiral quinoline derivatives bearing two vicinal stereocenters by standard functional group interconversions.

We initiated our studies on this cobalt-catalyzed enantioselective hydroboration/cyclization of 1,7-enyne by identifying effective chiral cobalt catalysts for the reaction between the 1,7-enyne **1a** and pinacolborane (HBpin). Cobalt catalysts generated in situ from $Co(acac)_2$ and various chiral bisphosphine ligands were tested, and the results were summarized in Table 1. In general, these reactions were carried out with **1a** as the limiting reagent in the presence of 3 mol% $Co(acac)_2$ and 4 mol% chiral ligand in toluene at room temperature for 24 h, and the alkylboronate **2a** was identified as the major product for these reactions.

The reaction catalyzed by the combination of $Co(acac)_2$ and (*R*,*R*)-DIOP (**L1**) proceeded sluggishly to very low conversions of **1a** and product **2a** was obtained in <5% yield. The reactions conducted by $Co(acac)_2$ and chiral ligands **L2**-**L7** occurred smoothly to high conversions of **1a** and afforded the desired product **2a** with modest to high isolated yields (57–87%) and with modest enantioselectivities (54–83% ee). To our delight, the reaction catalyzed by $Co(acac)_2$ and (*S*,*S*)-Ph-BPE (**L8**) afforded **2a** in high isolated yield (86%) and excellent enantioselectivity

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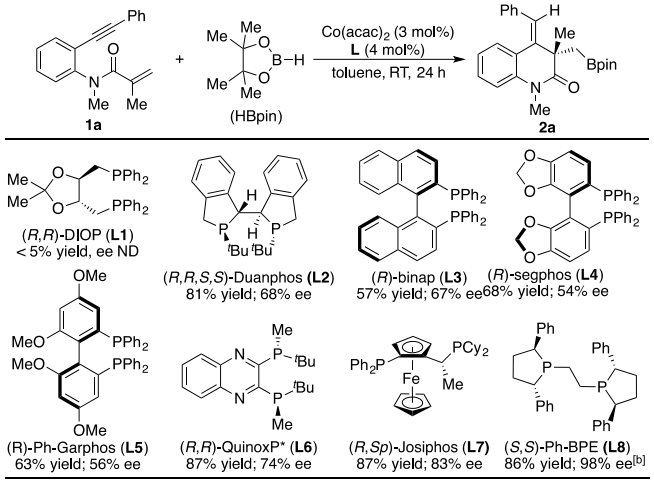
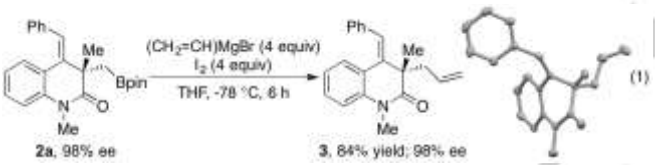
(98% ee). In addition, we also tested other solvents (such as THF, 1,4-dioxane, and cyclohexane) for the reaction catalyzed by $Co(acac)_2$/(*S*,*S*)-Ph-BPE, and similarly high yields and enantioselectivities were obtained for the desired product **2a** (see the SI for the details).

Table 1. Evaluation of conditions for the asymmetric reaction of **1a**.[a]



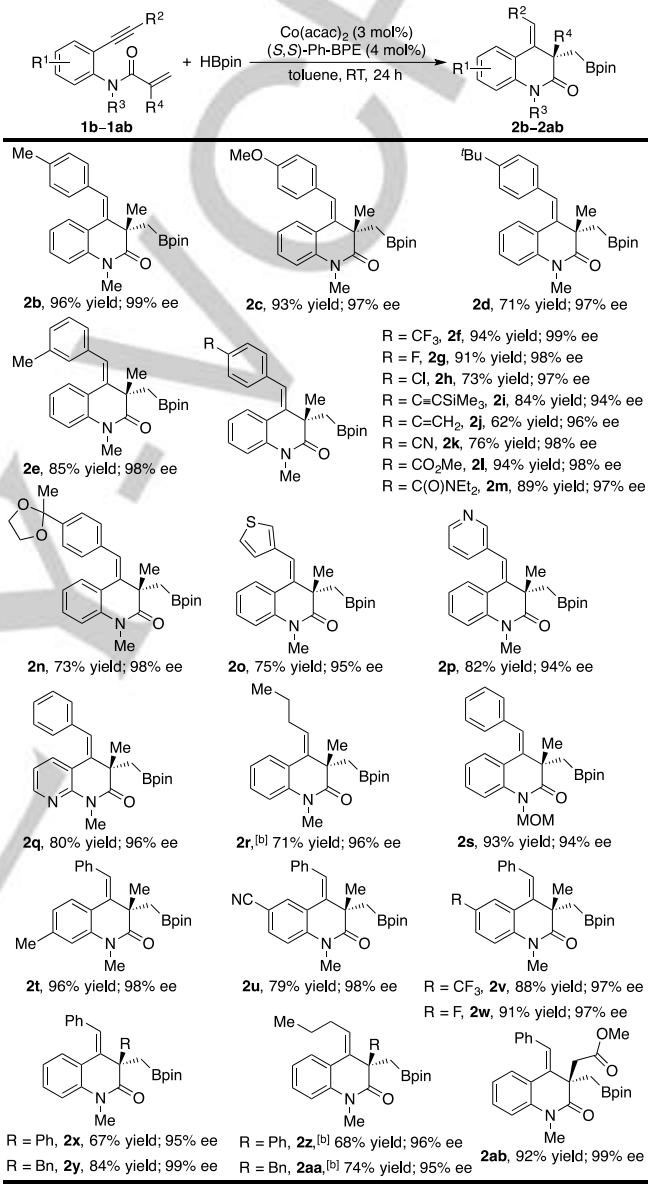
[a] Reaction conditions: **1a** (0.200 mmol), HBpin (0.300 mmol), $Co(acac)_2$ (6.0 μmol), ligand (7.2 μmol), toluene (0.5 mL), room temperature, 24 h, isolated yields; ee was determined by chiral HPLC analysis; [b] The configuration of **2a** was determined by single-crystal X-ray analysis on the vinyl compound **3** obtained by the reaction of **2a** with vinylmagnesium bromide [eq. (1)].



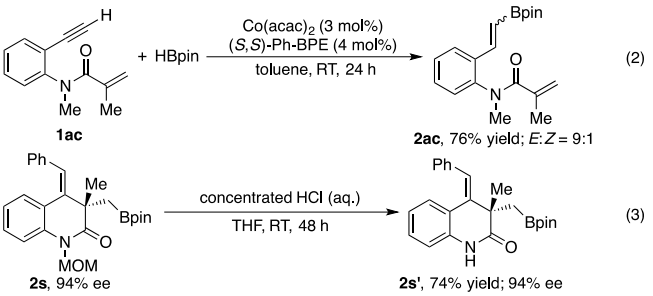
The scope of 1,7-enynes that undergo this cobalt-catalyzed asymmetric reaction is summarized in Table 2. In general, a wide range of anilide-tethered 1,7-enynes containing various aromatic or aliphatic substituents on the alkyne unit (**1b**–**1o**), on the nitrogen atom (**1p**), on the aryl linker (**1q**–**1t**), or on the alkene moiety (**1u**–**1y**) smoothly reacted with HBpin in the presence of 3 mol% $Co(acac)_2$ and 3.6 mol % (*S*,*S*)-Ph-BPE at room temperature, yielding the corresponding enantioenriched quinolin-2-ones (**2b**–**2y**) in high yields (62–96%) with excellent enantioselectivities (94–99% ee). This cobalt-catalyzed reaction shows good functional group tolerance, and a variety of reactive groups, such as fluoro (**2g** and **2t**), chloro (**2h**), alkynyl (**2i**), monosubstituted alkenyl (**2j**), cyano (**2k** and **2u**), carboxylic ester (**2l** and **2ab**), amide (**2m**), and acetal (**2n**) groups, can be tolerated under the identified reaction conditions. In addition, 1,7-enynes containing heteroarenes, such as thienyl (**2o**) and pyridyl (**2p** and **2q**) groups, also reacted to produce the corresponding chiral quinolin-2-ones with high enantioselectivity.

As shown in Table 2, a variety of anilide-tethered 1,7-enynes containing *para*- and *meta*-substituted aryl groups at the acetylic position reacted to afford the desired products (**2b**–**2n**) with high enantioselectivity. However, *ortho*-substituted aryl groups on the alkyne unit cannot be tolerated. Furthermore, anilide-tethered 1,7-enynes containing a terminal alkyne group do not undergo this cobalt-catalyzed hydroboration/cyclization under the standard conditions. For example, the reaction of the 1,7-enyne **1ac** with HBpin afforded (*E*)-vinylboronate **2ac** as the major product [eq. (2)]. In addition, 1,7-enynes containing primary anilide functionality do not undergo this cobalt-catalyzed reaction. However, the 1,7-enyne with a MOM-protected anilide reacted with HBpin to give a MOM-containing quinolin-2-one (**2s** in Table 2) in 93% yield with 94% enantioselectivity. The MOM-protection could be readily removed by the reaction with concentrated hydrochloric acid, yielding the corresponding quinolin-2-one (**2s'**) in 74% yield [eq. (3)], see the SI for the details).

Table 2. The scope of 1,7-enynes for this hydroboration/cyclization. [a]



[a] Reaction conditions: 1,7-enyne (0.200 mmol), HBpin (0.300 mmol), $Co(acac)_2$ (6.0 μmol), (*S*,*S*)-Ph-BPE (7.2 μmol), toluene (0.5 mL), room temperature, 24 h, isolated yields; ee was determined by chiral HPLC analysis; [b] 50 °C.



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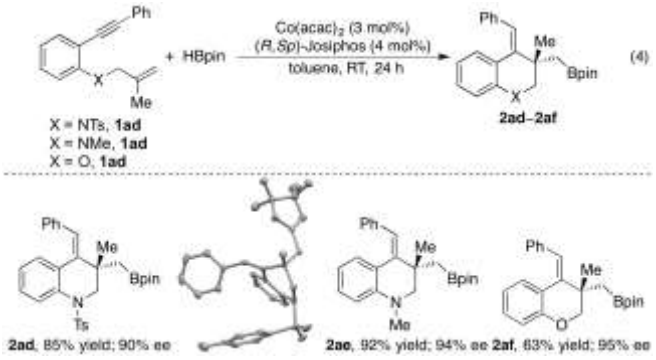
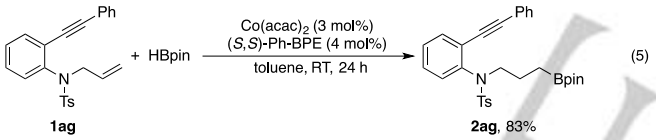
We also tested oxygen- and nitrogen-tethered 1,7-enynes, such as **1ad**–**1af** [eq. (4)], for this cobalt-catalyzed asymmetric reaction. In the presence of $Co(acac)_2$/(*S*,*S*)-Ph-BPE, **1ad** did not react with HBpin, **1ae** reacted with HBpin to afford the desired product **2ae** in 62% yield with only 77% ee, and **1af** reacted with HBpin to form a complex mixture of hydroboration products with only a trace amount of the desired product **2af**. However, when (*R*,*Sp*)-Josiphos (**L7** in Table 1) was used instead of (*S*,*S*)-Ph-BPE, the reactions of these enynes proceeded smoothly and afforded the desired six-membered cyclic compounds **2aa**–**2ac** in good yields with high enantioselectivities [eq. (4)]. The absolute configuration of **2aa** was assigned as (*S*) by single-crystal X-ray diffraction analysis.



(4)

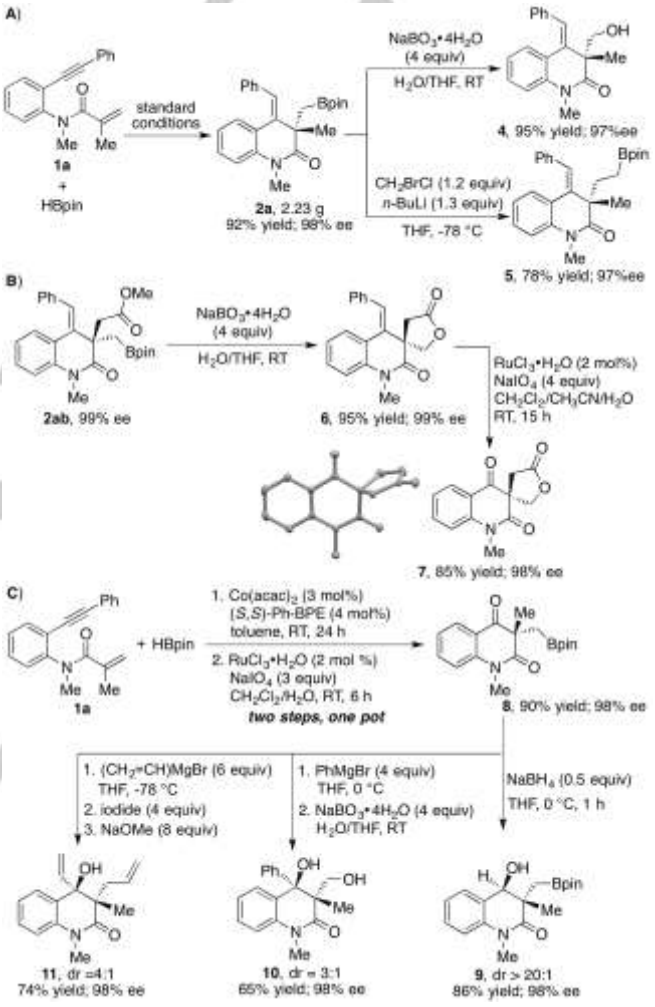
With the attempt to construct tertiary stereogenic centers, we tested the chiral cobalt catalyst generated from $Co(acac)_2$ and (*S*,*S*)-Ph-BPE for the reaction of one 1,7-enyne (**1ag**) containing a mono-substituted alkene. However, this reaction yielded the uncyclized hydroboration product **2ag** in 83% yield [eq. (5)].



(5)

To highlight the synthetic utility of this cobalt-catalyzed asymmetric hydroboration/cyclization, we conducted a gram-scale reaction of the 1,7-enyne **1a** with HBpin under the standard conditions, and this reaction afforded **2a** in 92% isolated yield with 98% enantioselectivity (Scheme 2A). The enantioenriched boryl-functionalized quinolin-2-one products can undergo a series of stereospecific transformations to produce the corresponding chiral quinoline derivatives without the loss of enantiopurity. For example, **2a** could be oxidized by $NaBO_3$ to form the chiral alcohol **4** in 95% yield with 97% ee (Scheme 2A). Homologation of **2a** with $LiCH_2Cl$ produced the chiral alkylboronate **5** in 78% yield with 97% ee (Scheme 2A). The oxidative hydrolysis of quinolin-2-one **2y** followed by the concomitant intramolecular alcoholysis of the carboxylic ester afforded the spirocyclic lactone **6** in 95% isolated yield with 99% ee (Scheme 2B). Further oxidative cleavage of the C=C bond in **6** formed the chiral spirocyclic quinolin-2,4-done **7** in 85% yield with 98% ee (Scheme 2B).

Furthermore, we combined this asymmetric cobalt-catalyzed hydroboration/cyclization and oxidative cleavage of the C=C bond of the resulting quinolin-2-one to develop a one-pot procedure to synthesize chiral quinolin-2,4-diones (Scheme 2C). The enyne **1a** smoothly underwent these one-pot sequential reactions to yield the corresponding quinolin-2,4-dione **8** in 90% isolated yield with 98% ee. Further functionalization of the quinolin-2,4-dione **8** allows the access of several quinolin-2-one derivatives containing two vicinal stereogenic centers. For example, the reduction of **8** with $NaBH_4$ produced 4-hydroxyl-3,4-dihydroquinolin-2(1*H*)-one **9** in 86% isolated yield with 98% ee.[13] The reaction of **8** with phenylmagnesium bromide followed by the oxidation with $NaBO_3$ afforded **10**, a 3,4-dihydroquinolin-2(1*H*)-one containing a chiral 1,3-diol subunit, in 65% yield with 98% ee. In addition, we also showed that the reaction of **8** with vinylmagnesium bromide followed by the reaction with I_2 formed **11**, a 3,4-dihydroquinolin-2(1*H*)-one with chiral allylic alcohol and 1,6-diene structure motifs, in 74% yield with 98% ee. Quinolin-2-one derivatives **9**-**11** were isolated as a single diastereomer by flash chromatography on silica.



Scheme 2. Transformations of chiral quinolin-2-ones and one-pot synthesis of quinolin-2,4-diones.

To verify the chelating effect of 1,7-enynes to the cobalt catalyst, we conducted the control experiments using biarylacetylene **12** and acrylamide **13**, which have similar steric hindrance around the double and triple bonds with the anilide-tethered 1,7-enynes. However, the reactions of **12** or **13** with HBpin did not occur under the standard conditions [eq. (6) and eq. (7)]. The results of these two control experiments and an intramolecular competition reaction between a 1,7-enyne and a more reactive vinylarene [eq. (8)] suggest that the chelation of 1,7-enyne to the cobalt catalyst enables this catalytic hydroboration/cyclization of 1,7-enynes to occur (see the SI for a possible pathway for this catalytic hydroboration/cyclization of

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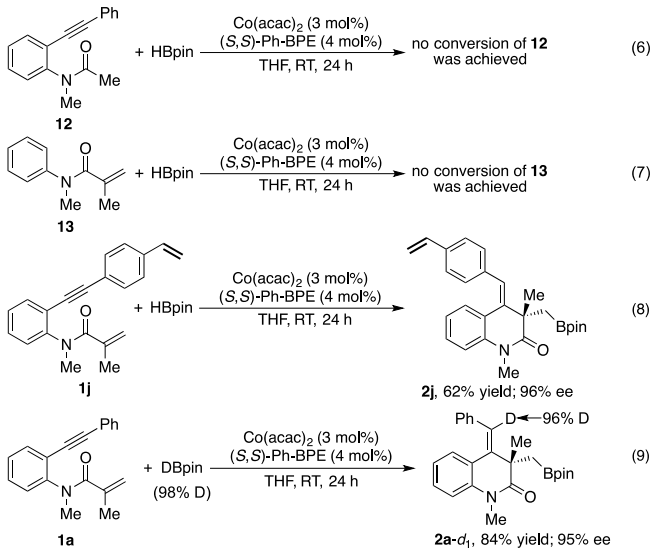
1,7-enynes). In addition, we also performed a deuterium-labelling experiment beween 1,7-enyne **1a** and DBpin [eq. (9)]. This reaction afforded **2a**-d_1 in 84% yield with 95% ee, and the deuterium atom in **2a**-d_1 is located at the vinylic position.



In summary, we have developed a highly enantioselective cobalt-catalyzed hydroboration/cyclization of 1,7-enynes to prepare chiral boryl-containing six-membered cyclic compounds. A wide range of aniline-tethered 1,7-enynes reacted with pinacolborane to produce the corresponding chiral quinolin-2-ones in high isolated yields with excellent enantioselectivity in the presence of a chiral cobalt catalyst generated in situ from $Co(acac)_2$ and (*S*,*S*)-Ph-BPE or (*R*,*Sp*)-Josiphos ligand. The chiral quinolin-2-one products can be readily converted to a variety of chiral six-membered compounds, such as *N*-heterocyclic primary and tertiary alcohols, alkenes, spirocyclic lactones, and quinolin-2,4-diones. Therefore, this Co-catalyzed asymmetric hydroboration/cyclization of 1,7-enynes provides a general foundation to access a series of chiral quinolinine derivatives containing quaternary stereogenic centers.

Acknowledgements

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Keywords: hydroboration/cyclization • 1,7-enynes • cobalt • asymmetric catalysis • *N*-heterocycles

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[13] The absolute configuration of compound **9** was assigned as (3*S*,4*R*) by the single-crystal X-ray analysis on the conressponding diol **9-OH** obtained by the oxidation of **9** with $NaBO_3$, see SI for the details.

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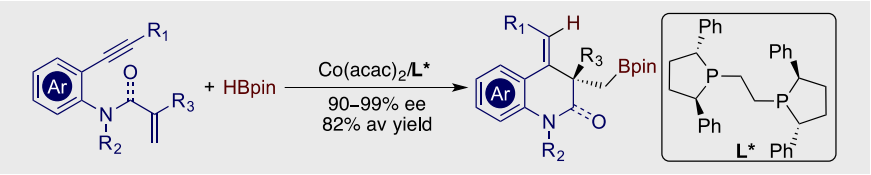

Asymmetric Catalysis: A highly enantioselective cobalt-catalyzed hydroboration/cyclization of 1,7-enynes with pinacolborane (HBpin) using a catalyst generated from $Co(acac)_2$ and (*S*,*S*)-Ph-BPE was developed (see the Picture). This cobalt-catalyzed asymmetric cyclization of 1,7-enyens provides a general approach to access a series of chiral quinoline derivatives containing quaternary stereocenters.

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Cobalt-Catalyzed Enantioselective Hydroboration/Cyclization of 1,7-Enynes: Asymmetric Synthesis of Chiral Quinolinones Containing Quaternary Stereogenic Centers