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Communication

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A Versatile Cobalt-Catalyzed Enantioselective Entry to Boryl-Functionalized All-Carbon Quaternary Stereogenic Centers

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Supporting Information Placeholder

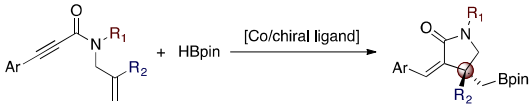
ABSTRACT: We report an asymmetric synthesis of chiral boryl-functionalized γ-lactams containing all-carbon quaternary stereocenters via a Co-catalyzed enantioselective hydroboration/cyclization of amide-tethered 1,6-enynes. These enantio-enriched γ-lactam products can be readily converted to a variety of cyclic and acyclic other chiral γ-lactams, pyrrolidin-2,3-diones, β-amino acid *N*-carboxyanhydrides, and β-amino carboxylic amides.

All-carbon quaternary stereocenters are present in many biologically active natural products and synthetic organic compounds.[1] The synthetic approaches to access these quaternary carbon centers include chiral synthesis from naturally occurring chiral pool,[2] desymmetrization of symmetrical quaternary-carbon-containing molecules,[3] and enantioselective C-C bond-forming reactions.[4] Among these approaches, catalytic enantioselective construction of all-carbon quaternary carbons through C-C bond formation reactions is particularly difficult because of their congested nature. Accordingly, it is still a challenging, but highly desirable task to develop enantioselective protocols for construction of all-carbon quaternary stereocenters, especially functionalized stereocenters that allow versatile derivations to access a series of structurally diverse compounds.[5]

The chiral γ-lactam scaffold is part of the core structures of a variety of bioactive compounds, and γ-lactams also serve as useful building blocks to prepare *N*-heterocyclic compounds because of the versatile chemistry of the amide functionality.[6] Even though numerous enantioselective protocols have been developed to prepare chiral γ-lactams,[7] approaches for enantioselective synthesis of γ-lactams containing all-carbon quaternary stereocenters are very limited.[7e] Considering broad synthetic applications of organoboron compounds in chemical synthesis, we are interested in developing an enantioselective method to prepare boryl-functionalized chiral γ-lactams containing all-carbon quaternary stereocenters.

Enantioselective cycloisomerization and reductive cyclization reactions of 1,6-enynes are widely conducted to prepare chiral five-membered cyclic compounds.[8] The majority of these reactions are used to construct tertiary stereocenters,[9] and only a limited number of reactions afford products containing all-carbon quaternary stereocenters.[10]

To develop asymmetric synthesis of chiral boryl-functionalized γ-lactams containing all-carbon stereocenters, we envisioned that amide-tethered 1,6-enynes containing an internal alkyne and a terminal *gem*-disubstituted alkene unit could undergo Co-catalyzed hydroboration/cyclization to form the desired borylated γ-lactam products (eq 1).[11] Once achieved, γ-lactam products from these reactions should possess versatile chemical reactivity because they have several reactive groups, such as the α,β-unsaturation, amide, and boryl functionalities. These amide-tethered 1,6-enynes have been recently employed for a Pd-catalyzed non-asymmetric hydrohalogenation to prepare racemic halogenated δ-lactams.[12] Herein, we report the first catalytic enantioselective synthesis of chiral boryl-functionalized γ-lactams containing all-carbon quaternary stereocenters. We also show that chiral γ-lactam products can be converted to a series of cyclic and acyclic small molecules bearing all-carbon quaternary stereocenters by standard functional group interconversions.

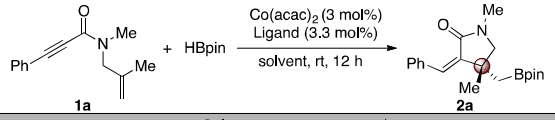


(1)

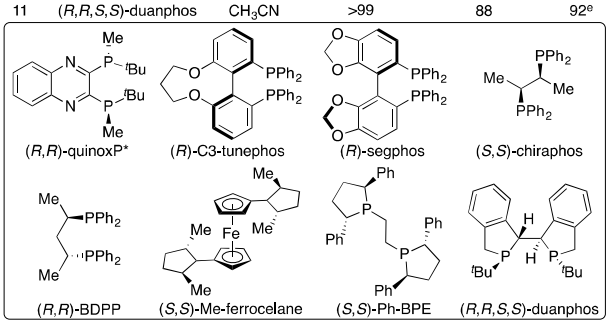
We initiated this study by identifying selective cobalt catalysts and reliable conditions for the reaction of the amide-tethered 1,6-enyne **1a** with HBpin. We evaluated several cobalt catalysts generated in situ from $Co(acac)_2$ and chiral bisphosphine ligands for this asymmetric transformation. In general, these reactions were conducted with 3 mol% cobalt catalysts with **1a** as a limiting reagent in the presence of 1.3 equiv of HBpin, and the results of selected experiments are listed in Table 1. The reaction catalyzed by the combination of $Co(acac)_2$ and (*R*,*R*)-quinoxP* produced the borylated γ-lactam **2a** in a high yield, but with only modest enantioselectivity (65% ee, entry 1 in Table 1). The reactions conducted with catalysts generated from $Co(acac)_2$ and other bisphosphines, such as (*R*)-C_3-tunephos, (*R*)-segphos, (*S*,*S*)-chiraphos, (*R*,*R*)-BDPP, and (*R*,*R*)-Me-ferrocelane, proceeded with low to modest enantioselectivities (entries 2–6 in Table 1). To our delight, the reactions catalyzed by $Co(acac)_2$ and (*R*,*R*,*S*,*S*)-duanphos or (*S*,*S*)-Ph-BPE occurred to full conversions of **1a** and afforded **2a** in high yields with high enantioselectivity (entries 7 and 8 in Table 1). Further studies on the reaction catalyzed by $Co(acac)_2$ and (*R*,*R*,*S*,*S*)-duanphos in various

solvents (entries 8–11 in Table 1) showed that the reaction conducted in CH_3CN afforded **2a** in 88% yield and with 92% ee (entry 11 in Table 1).

Table 1. Evaluation of Conditions for the Reaction of 1a.[a]



Entry	Ligand	Solvent	Conversion [%][b]	Yield **2a** (%)[c]	ee (%)[d]
1	(*R*,*R*)-quinoxP*	THF	>99	88	65
2	(*R*)-C3-tunephos	THF	>99	88	17
3	(*R*)-segphos	THF	>99	90	4
4	(*S*,*S*)-chiraphos	THF	57	50	28
5	(*R*,*R*)-BDPP	THF	28	21	78
6	(*S*,*S*)-Me-ferrocelane	THF	98	87	55
7	(*S*,*S*)-Ph-BPE	THF	>99	88	87
8	(*R*,*R*,*S*,*S*)-duanphos	THF	>99	87	89
9	(*R*,*R*,*S*,*S*)-duanphos	tolene	56	49	88
10	(*R*,*R*,*S*,*S*)-duanphos	hexane	<5	--	--
11	(*R*,*R*,*S*,*S*)-duanphos	CH_3CN	>99	88	92[e]

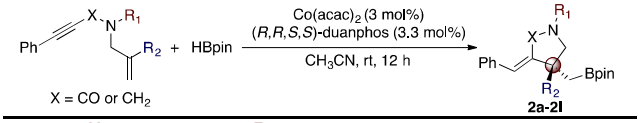


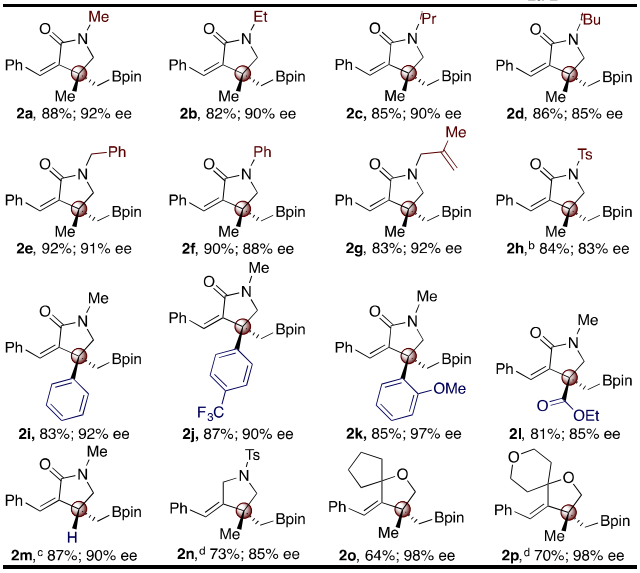
[a]Conditions: **1a** (0.200 mmol), HBpin (0.260 mmol), $Co(acac)_2$ (6.0 μmol), ligand (6.6 μmol), solvent (1 mL), rt, 12 h; [b]The conversion of **1a** was determined by GC analysis with dodecane as an internal standard; [c]isolated yields; [d]ee was determined by chiral HPLC analysis; [e]The configuration of **2a** was determined by single-crystal X-ray analysis on the corresponding alcohol obtained by the oxidation of **2a**.

With an effective catalyst and identified conditions in hand (entry 11 in Table 1), we studied the scope of 1,6-enynes derived from propiolamides that undergo this cobalt-catalyzed asymmetric hydroboration/cyclization and the results are listed in Table 2. In general, a variety of *N*-allyl 3-phenylpropiolamides containing various aliphatic or aromatic substituents on the nitrogen (**1a**–**1h**) or in the allyl groups (**1i**–**1m**) smoothly reacted with HBpin in the presence of 3 mol % $Co(acac)_2$ and (*R*,*R*,*S*,*S*)-duanphos at room termperature, and the corresponding enantiomerically enriched γ-lactams (**2a**–**2m**) are produced in high yields (81–92%) with high enantioselectivity (85–97% ee). 1,6-Enynes containing secondary amides did not undergo this Co-catalyzed reaction. Furthermore, we showed that O- or N-tethered 1,6-enynes also reacted to yield the corresponding cyclic products (**2n**–**2p**) with high enantioselectivity.

The data in Table 2 indicate the steric property of the substituent on the nitrogen of 1,6-enynes has a noticeable influence on the enantioselectivity of this reaction. For example, the substrates with increased steric hindrance around the nitrogen atom reacted with slightly decreased enantioselectivity (**2a**–**2d**). Substrates containing electronically and sterically varied aryl groups on the alkene moiety also reacted with high enantioselectivity (**2i**–**2k**). In addition, the identified catalyst and conditions are also effective to prepare γ-lactam with a tertiary stereogenic center (**2l**). However, secondary *N*-allyl 3-phenylpropiolamides do not undergo this Co-catalyzed cyclization reaction.

Table 2. Scope of 1,6-Enynes.[a]





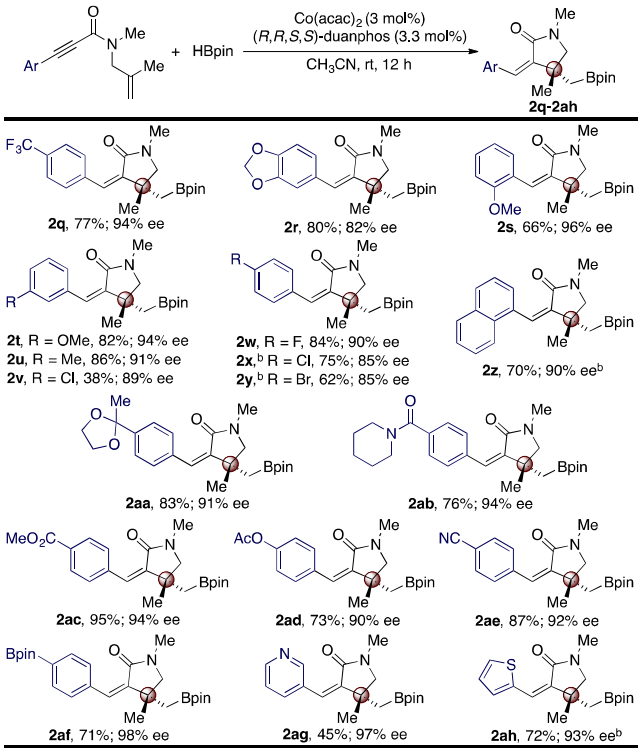
[a]Conditions: see conditions for entry 11 in Table 1; [b]isolated as a *Z*/*E* mixture with *Z*:*E* = 2:1; [c](*R*)-C3-tunephos (6.6 μmol), THF (1 mL); [d]4 mol % catalyst.

Subsequently we studied the substrates containing various aryl groups on the alkyne moiety for this catalytic asymmetric hydroboration/cyclization reaction and the results are listed in Table 3. In general, a range of amide-tethered 1,6-enynes containing *para*-, *meta*-, or *ortho*-substituted aryl groups at acetylic position reacted to afforded the desired chiral γ-lactams (**2q**–**2u**) in high yields with high enantioselectivity. This asymmetric cyclization shows good functional group tolerance, and a variety of reactive groups, such as fluoro (**2w**), chloro (**2v** and **2x**), bromo (**2y**), acetal (**2aa**), amide (**2ab**), carboxylic ester (**2ac** and **2ad**), cyano (**2ae**), and pinacol boronic ester (**2af**), are compatible with the identified reaction conditions. In addition, 1,6-enynes with nitrogen- and sulfur-containing heteroaryl groups also reacted with high enantioselectivity (**2ag** and **2ah**). However, *N*-allyl propiolamides containing alkyl groups bound to the alkynyl unit do not undergo this Co-catalyzed hydroboration/cyclization reaction.

Scheme 1 summarizes the synthetic utility of this Co-catalyzed entry to all-carbon stereogenic centers. The enantioselective synthesis of **2a** on a gram-scale was achieved in 80% yield with 92% ee (Scheme 1A). Chiral alkylboronate **2a** underwent a series of stereospecific transformations without loss of enantiopurity. For example, **2a** could be oxidized by H_2O_2 to form chiral alcohol **3** in 86% yield (Scheme 1B). Homologation of **2a** with $LiCH_2Cl$ produced chiral alkylboronate **4** in 45% yield (Scheme 1C). Alkenylation of **2a** with vinylmagnesium bromide afforded

alkene **5** in 82% yield (Scheme 1D). Alkylboronate **2a** also underwent Pd-catalyzed Suzuki-Miyaura cross-coupling with bromobenzene to give product **6** in 76% yield (Scheme 1E). Furthermore, compound **6** could be converted to chiral pyrolidin-2,3-dione **7** in 80% yield with 92% ee (Scheme 1F). Compound **7** readily underwent Baeyer-Villiger oxidation with *m*-chloroperbenzoic acid to produce *β*-amino acid *N*-carboxyanhydride **8** in almost quantitative yield (Scheme 1G).[13] *β*-Amino acid *N*-carboxyanhydride is a versatile electrophile and reacts with a variety of amine nucleophiles. For example, compound **8** readily reacted with benzylamine and afforded acyclic *β*-amino carboxylic amide **9** in 87% yield with 92% ee (Scheme 1H).

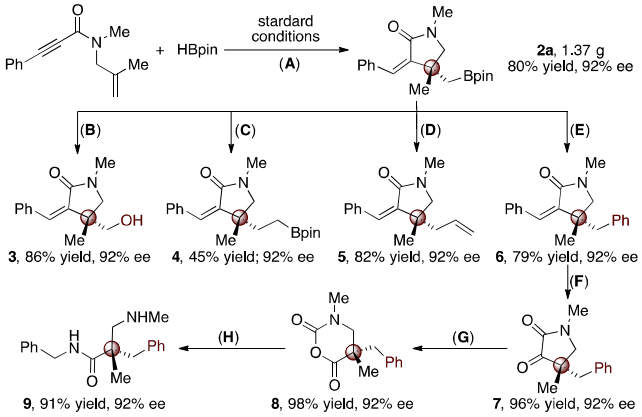
Table 3. Scope of Amide-Tethered 1,6-Enynes.[a]



[a]Conditions: see conditions for entry 11 in Table 1. [b](*S*,*S*)-Ph-BPE (6.6 μmol) instead of (*R*,*R*,*S*,*S*)-duanphos.

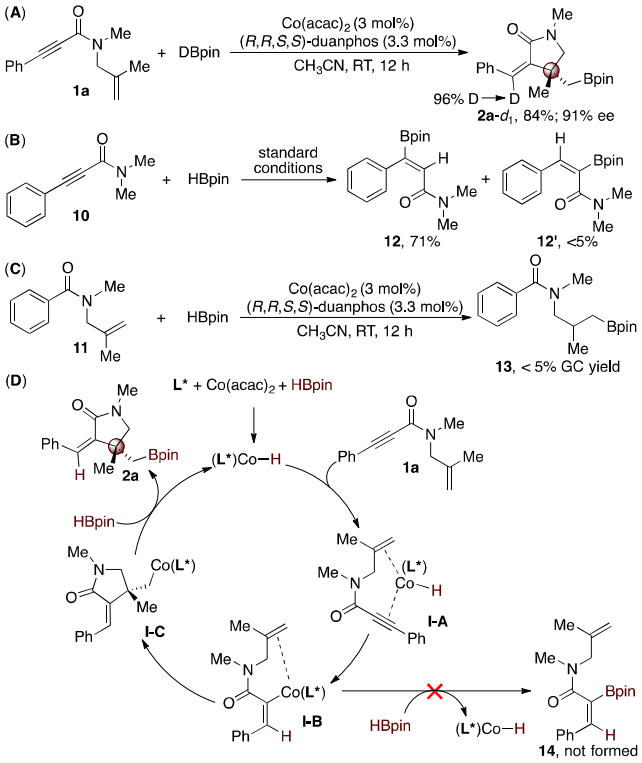
To provide some insights for this Co-catalyzed construction of all-carbon stereocenters, we conducted some deuterium-labeling and control experiments. The reaction of **1a** with DBpin under standard conditions afforded **2a**-d_1 in 84% yield and the deuterium atom in **2a**-d_1 is located on the vinyl-carbon (Scheme 2A). To test the chelating effect of enyne to the cobalt catalyst, we conducted the hydroboration of an amide-containing internal alkyne **10** and *gem*-substituted alkene **11** (Scheme 2B and 2C). The reaction of alkyne **10** under standard conditions provided the vinylboronate **12** in 71% yield, and the other regioisomer **12'** was formed in <5% yield (Scheme 2B). The regioselectivity for hydroboration of the alkyne **10** is opposite to the regioselectivity for hydroboration of the alkyne unit in **2a**. In addition, the hydroboration of the *gem*-substituted alkene **11** was very sluggish and gave product **13** in <5% yield under standard conditions (Scheme 2C). The results of these experiments suggested the chelation of enyne **1a** to the cobalt catalyst.[14]

Scheme 1. Derivatization of Chiral *γ*-Lactam 2a.[a]



[a]Conditions: (**B**) H_2O_2 (30%), NaOH (3 M aq), THF, 0 °C, 3 h; (**C**) CH_2BrCl (2.5 equiv), *n*-BuLi (2.5 equiv), THF, -78 °C, 6 h; (**D**) vinylmagnesium bromide (4 equiv), I_2 (4 equiv), THF, -78 °C, 6 h; (**E**) $Pd(OAc)_2$ (15 mol%), *rac*-BINAP (15 mol %), KOH (5 equiv), PhBr (2 equiv), dioxane/H_2O , 100 °C, 24 h; (**F**) $RuCl_3.xH_2O$ (2 mol %), $NaIO_4$ (3 equiv), CH_2Cl_2/CH_3CN/H_2O, rt, 6 h; (**G**) *m*CPBA (1.2 equiv), CH_2Cl_2, rt, 6 h; (**H**) $BnNH_2$ (1.2 equiv), CH_2Cl_2, rt, 12 h.

Scheme 2. Deuterium-labeling Experiment, Control Experiments and the Proposed Catalytic Pathway



Based on these experimental results, we proposed a pathway for this Co-catalyzed production of chiral boryl-containing *γ*-lactams (Scheme 2D).[15] The activation of $Co(acac)_2$ with HBpin in the presence of chiral ligand **L*** generates a chiral Co(I)-H species (**L***)Co-H.[9g,16] The chelation of enyne **1a** with this (**L***)Co-H forms the intermedi-

ate **I-A**, and the insertion of the alkyne unit of the chelated enyne to Co-H produces a vinylcobalt species **I-B**. The subsequent intramolecular, enantioselective migratory insertion of the alkene unit of **I-B** generates an alkylcobalt intermediate **I-C**, which then reacts with HBpin to release chiral γ-lactam product and regenerate the chrial Co(I)-H species (**L***)Co-H. The vinylboronate **14** from the hydroboration of the alkyne unit in **1a** is not formed, and this indicates that the rate of intramolecular insertion of alkene unit in **I-B** is significantly higher than that of the reaction of **I-B** with HBpin.

In summary, we have developed an effective and enantioselective protocol to prepare chiral boryl-functionalized γ-lactams containing an all-carbon quaternary stereocenter via Co-catalyzed hydroboration/cyclization of amide-tethered 1,6-enynes. These chiral boryl-functionalized γ-lactams can be converted readily to a variety of cyclic and acyclic chiral molecules, such as chiral γ-lactams, pyrrolidin-2,3-diones, β-amino acid *N*-carboxyanhydrides, and β-amino carboxylic amides. Therefore, this Co-catalyzed enantioselective entry provides a general method to prepare a variety of building blocks containing all-carbon quaternary stereogenic carbons for chemical synthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
Experimental/DFT details and characterization data (PDF)
Crystallographic data for **3** (CIF)

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Notes

The authors declare no competing financial interest.

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(15) See the Supporting Information for discussions on an alternative pathway involving a cobaltobicyclo[3,3,0] ring intermediate generated through oxidative cyclometalation of enynes.

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