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Facile synthesis of axially chiral styrene-type carboxylic acids *via* palladium-catalyzed asymmetric C–H activation†

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A novel method by a one-step introduction of axial chirality and sterically hindered group has been developed for facile synthesis of axially chiral styrene-type carboxylic acids. With the palladium-catalyzed C–H arylation and olefination of readily available cinnamic acid established, this transformation demonstrated excellent yield, excellent stereocontrol (up to 99% yield and 99% ee), and broad substrate scope under mild conditions. The axially chiral styrene-type carboxylic acids produced have been successfully applied to Cp*Co^{III}-catalyzed asymmetric C–H activation reactions, indicating their potential as chiral ligands or catalysts in asymmetric synthesis.

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Introduction

Enantiopure carboxylic acids, especially natural amino acids, have been widely used as readily available chiral substances for facile syntheses of complex chiral compounds, known as the strategy of 'chiral pool synthesis'.[1] Meanwhile, chiral carboxylic acids serve not only as an important class of organocatalysts for various enantioselective transformations,[2] but also as chiral ligands for transition-metal-catalyzed asymmetric chemical processes ranging from academic to industrial settings.[3,4] With the enormous progress made in the past several decades in enantioselective C–H functionalization,[5] chiral carboxylic acids (CCAs) have recently emerged as powerful ligands for this step- and atom-economic transformation. For instance, chiral amino-acid or cyclopropane-derived dirhodium tetracarboxylates enabled a plethora of asymmetric intra- and inter-molecular C–H functionalizations *via* a stereo-controlled insertion of Rh-carbene into C–H bonds.[3] Although Cp*M^{III} (M = Co, Rh, Ir) has recently been developed as an efficient catalyst for C–H functionalization,[6] the lack of extra coordination sites for extrinsic chiral ligands presented distinct difficulties for catalytic stereo-control of such transformations.[7] To address this issue, CCAs have been used as chiral ligands to enable enantioselective C–H activation without the use of a synthetically difficult chiral Cp*M^{III} catalyst.[4,7] Apart from central[4b–d,f,k–n] and planar CCAs,[4g] highly sterically demanding axial CCAs have been designed and used for efficient recognition of the prochiral C–H bonds. While a sterically hindered aryl group adjacent to the carboxyl group is required to control the enantioselectivity of C–H activation, a multiple-step synthesis to modify the binaphthyl backbone remains still a tedious task and definitely hampers their application in organic synthesis.[4e,h–j]

Although various synthetic methods have been well established for the synthesis of such biaryl atropisomers,[8] their "diphenyl analogs", axially chiral styrenes with the chiral axis between a substituted alkene and an aromatic ring, have long been neglected[9] despite their potential in total synthesis and asymmetric synthesis as chiral catalysts or ligands.[10,11a,b] Besides the "central to axial chirality transfer" strategy which required the use of stoichiometric chiral intermediates,[11] transition-metal or organo-catalyzed asymmetric reactions have recently been developed as efficient approaches for the construction of axially chiral styrenes.[12–15] To mimic the rigidity of biaryls, alkene skeletons with the C=C double bond trapped within six-membered-rings have been used to synthesize chiral arylcyclohexenes.[12] Meanwhile, a structure with the chiral axis between an open-chain alkene and an aromatic ring, which exhibited lower rotation energy, was first constructed by Tan[13] and Yan[14] by incorporation of sterically hindered groups into the alkynes using an organocatalytic addition strategy. Very recently, Pd-catalyzed asymmetric olefination of C–H bonds has been developed by Shi and co-workers to make axially chiral styrenes, although this protocol required the use of strongly coordinating pyridyl or other transient directing groups (TDGs).[15] As part of our continuous efforts in enantioselective C–H functionalizations,[16] we conceived a method in which the readily

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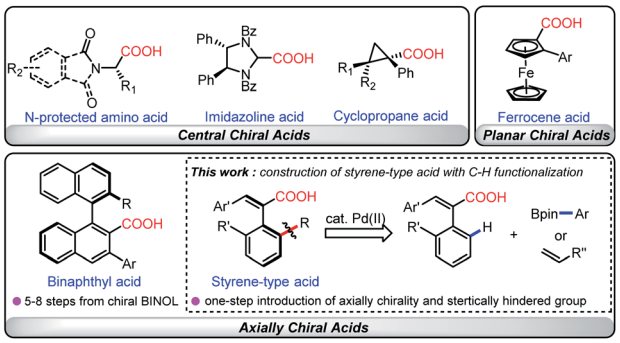


Scheme 1 Chiral carboxylic acids as ligands for asymmetric C–H functionalization.

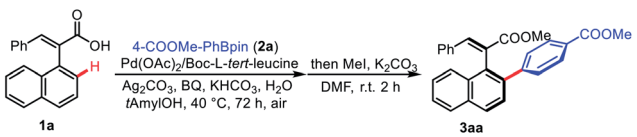
available racemic cinnamic acid derivative could be used as an efficient precursor to make axially chiral styrene-type ligands *via* asymmetric C–H functionalization, which thus provides an efficient and rapid way to furnish novel axially chiral acid ligands by a simple modification of racemic acids (Scheme 1).

Herein, we describe a novel strategy for the facile synthesis of axially chiral styrene-type carboxylic acids by modification of cinnamic acid derivatives *via* palladium(II)-catalyzed C–H arylation or olefination.[17] The carboxyl group, which serves as a key motif in the resulting chiral ligands, plays an important role as a weakly coordinating group in the one-step introduction of axial chirality and sterically hindered group in this catalytic method.[18] This new transformation demonstrated excellent stereocontrol, broad scope under mild conditions, and the produced axially chiral styrene-type carboxylic acids have been successfully applied to Cp*Co^{III}-catalyzed asymmetric C–H activation reactions.

Results and discussion

Our study commenced with the investigation of the Pd(II)-catalyzed C–H arylation of the cinnamic acid derivative *rac*-**1a** with 4-(methoxycarbonyl)benzeneboronic acid pinacol ester **2a** used as the coupling partner. After extensive examination of the reaction conditions, the desired product **3aa** was obtained in 74% yield and 97% ee in the presence of 10 mol% of $Pd(OAc)_2$, 1.5 equiv. of Ag_2CO_3, 0.5 equiv. of BQ, 2.0 equiv. of $KHCO_3$, 0.2 equiv. of Boc-L-*tert*-leucine, and 20.0 equiv. of H_2O in *t*AmylOH at 40 °C for 72 hours in an air atmosphere (Table 1, entry 1). A series of control experiments were then conducted, which indicated that no arylation product was detected in the absence of the palladium catalyst or base (entries 2 and 3). Meanwhile, removing the N-protecting group from Boc-L-*tert*-leucine completely quenched the reaction (entry 4). Furthermore, screening of oxidants showed that the combination of Ag_2CO_3 and BQ was crucial for this transformation, and the replacement of Ag_2CO_3 with Ag_2O or omitting the addition of BQ resulted in a sharp decrease of yields (entries 5 and 6). Interestingly, H_2O played a key role in improving both yield and enantioselectivity in this reaction system (entry 7). A careful examination of bases and solvents clearly showed that $KHCO_3$ and *t*AmylOH were the optimal choices for this asymmetric C–H arylation (see the ESI† for details), while the use of KH_2PO_4 as the base gave **3aa** in only 49% yield (entry 8) and the employment of *i*PrOH as the solvent decreased the yield dramatically to 34%, albeit still with excellent enantioselectivity (entry 9). Meanwhile, the replacement of Boc-L-*tert*-leucine with other N-protected amino acids (MPAAs) as ligands furnished only lower enantioselectivity to some extent. Not surprisingly, raising the reaction temperature to 60 °C led to a better yield but poor enantioselectivity (entry 11).

Table 1 Optimization of reaction conditions[a]



Entry	Change from standard conditions	Yield[b] (%)	Ee[c] (%)
1	None	74	97
2	No $Pd(OAc)_2$	0	—
3	No $KHCO_3$	0	—
4	*tert*-Leucine instead of Boc-L-*tert*-leucine	0	—
5	Ag_2O instead of Ag_2CO_3	51	97
6	No BQ	51	90
7	No H_2O	41	67
8	KH_2PO_4 instead of $KHCO_3$	49	94
9	*i*PrOH as the solvent	34	96
10	Fmoc-L-*tert*-leucine instead of Boc-L-*tert*-leucine	60	92
11	Raising the temperature to 60 °C	86	70

[a] Standard conditions: *rac*-**1a** (0.2 mmol), **2a** (2.0 equiv.), $Pd(OAc)_2$ (0.1 equiv.), Boc-L-*tert*-leucine (0.2 equiv.), BQ (0.5 equiv.), Ag_2CO_3 (1.5 equiv.), $KHCO_3$ (2.0 equiv.), H_2O (20.0 equiv.) in *t*AmylOH 1.0 mL in air at 40 °C for 72 h, the crude mixture was methylated using MeI. [b] Isolated yields. [c] The ee value was determined by HPLC.

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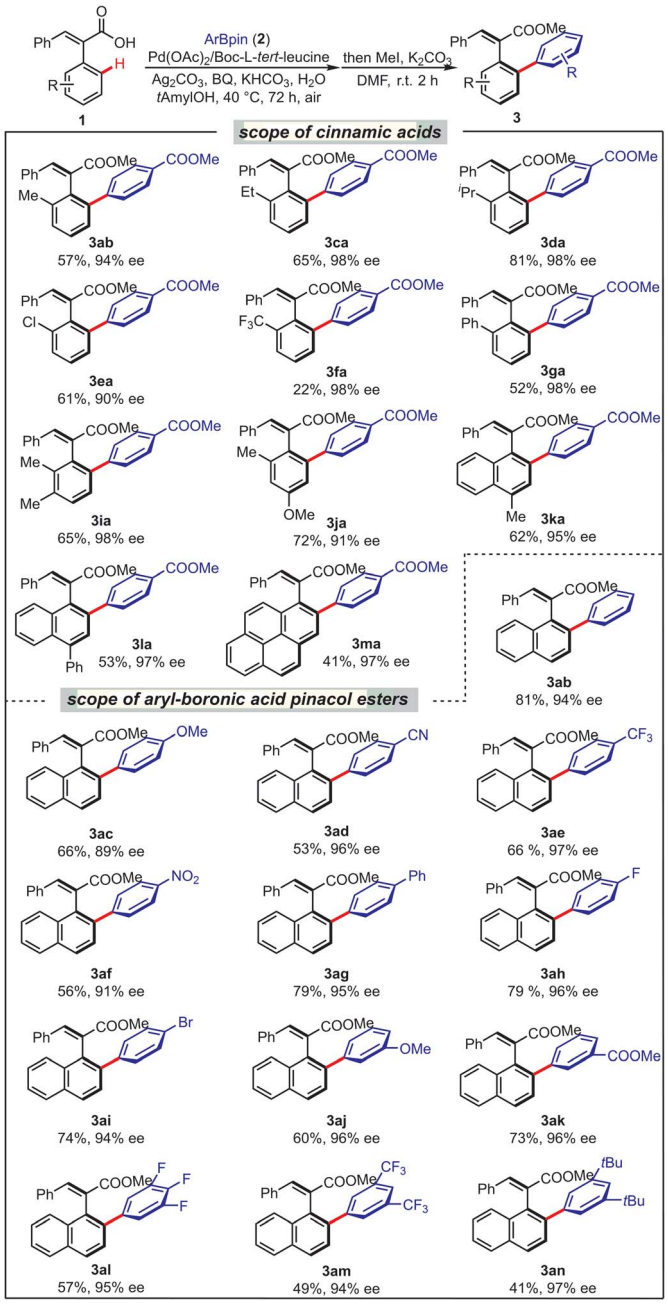
With the optimized conditions in hand, the scope and functional group tolerance of the aryl–aryl coupling were next investigated (Table 2). Firstly, the examination of various *ortho*-substituted phenylacetic acids indicated that sterically bulky substituents were required for high enantioselective control, and larger alkyl groups (**3ba–3da**) gave excellent enantioselectivities (94–98% ee) due to the higher rotational barriers. While the steric hindrance apparently affected the enantioselectivities, they had no influence on the reactivity, and these transformations exhibited moderate to good yield. Unsurprisingly, a strong electron-withdrawing group (–CF_3) on the phenyl ring significantly reduced the reactivity and afforded the desired product in a much lower yield (22%) but still with high enantioselectivity (**1f**, 98% ee). At the same time, Cl- and Ph-substituents were well tolerated to afford **3ea** (61%, 90% ee) and **3ga** (52%, 98% ee) smoothly. Multisubstituted cinnamic acid derivatives **1i** and **1j** were also successfully arylated in good yields and excellent enantioselectivities (**3ia**, 65%, 98% ee; and **3ja** 72%, 91% ee). The substituent effect on naphthalene was also investigated, which showed that methyl and phenyl were quite compatible in this transformation (**3ka**, 62%, 95% ee; **3la**, 53%, 97% ee). Notably, a pyrene group connected to the styrene was also tolerated to provide the desired arylation product (**3ma**) in 41% yield and with 97% ee. The scope of different aryl-boronic acid pinacol esters has also been demonstrated in this C–H arylation system. Electron-withdrawing groups at the *para*-position such as cyano, trifluoromethyl, nitro, and phenyl gave the desired chiral styrenes (**3ad–3ag**) in moderate to good yields and with excellent enantioselectivities. The coupling of **1a** with electron-rich aryl-boronic acid pinacol ester **2c** afforded **3ac** in a yield of 66% with slightly lower enantioselectivity (89% ee). To our delight, halogen substituents were also well tolerated in this reaction, affording **3ah** and **3ai** in 96% and 94% ee, respectively. Such halogenated chiral styrenes could be further transformed into various functional groups through late-stage cross-coupling reactions. *Meta*-substituted aryl-boronic acid pinacol esters **2j** and **2k** were also well compatible with the reaction conditions, furnishing the corresponding products **3aj** and **3ak** both in 96% ee. Multi-substituted substrates afforded the desired products (**3al–3an**) in slightly lower yields with similar enantioselectivities.

To further expand the diversity of such axially chiral styrene-type CCAs, Pd-catalyzed C–H olefination reactions were then explored with **1a** and methyl acrylate **4a** as model substrates (see the ESI† for detailed optimizations). The desired olefination product **5aa** was obtained in 97% yield and 97% ee with 10 mol% $Pd(OAc)_2$ used as the catalyst and 30 mol% Boc-L-*tert*-leucine used as the ligand, and 2.0 equiv. of KOH as the base under 1 atm O_2 in *i*PrOH at 30 °C for 72 h. The absolute configuration of **5aa** was determined to be R by single crystal X-ray diffraction,[19], which is in contrast to that of the product furnished by the TDG strategy in spite of using ligands derived from the same amino acid. To rationalize the origin of the stereoselectivity, according to previous studies, stereo-models of the transition states of two different catalysis systems are proposed in Scheme 2. In **TS-1**, palladium is coordinated with the MPAA ligand and the substrate in a square-planar coordination. The bulky side-chain of the amino acid points upward, which pushes the alkenyl group away from the palladium coordination plane to avoid steric repulsion.[17h,20] However, in **TS-2**, palladium fused with cinnamaldehyde imine presents a square-planar coordination. The upward side-chain extrudes

Table 2 Substrate scope of Pd catalyzed enantioselective C–H arylation[a,b,c]



[a] *Rac*-**1** (0.2 mmol), **2** (2.0 equiv.), $Pd(OAc)_2$ (0.1 equiv.), Boc-L-*tert*-leucine (0.2 equiv.), BQ (0.5 equiv.), Ag_2CO_3 (1.5 equiv.), $KHCO_3$ (2.0 equiv.), H_2O (20.0 equiv.) in *t*AmylOH 1.0 mL in air at 40 °C for 72 h, the crude mixture was methylated using MeI. [b] Isolated yields. [c] The ee value was determined by HPLC.

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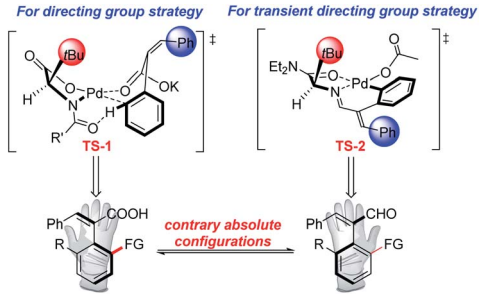


Scheme 2 Transient states of two catalysed models.

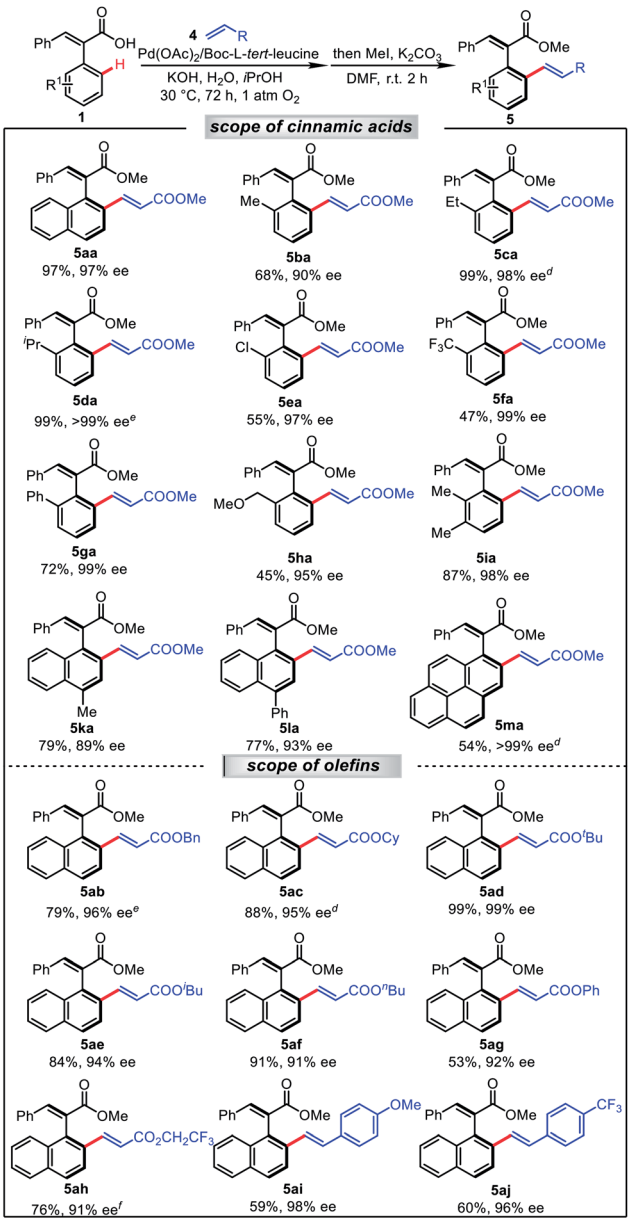
the alkenyl group downward, which leads to contrary absolute configurations.[15b,21]

With the optimized conditions in hand, we sought to test the olefination scope under the standard conditions (Table 3). To our delight, these transformations exhibited high efficiency, and moderate to good yields and excellent enantioselectivities were achieved in most cases. Alkyl groups (**1b–1c**) and chloro- (**1d**) on the cinnamic acid were well-tolerated, giving high enantiocontrol (**5aa–5da**, 90–99% ee). As expected, when a trifluoromethyl substituent was tested, inferior yield was obtained, albeit with a high enantioselectivity (**5fa**, 47%, 99% ee). In addition, phenyl- and $MeOCH_2$- at the *ortho* position were well compatible with this transformation, and furnished the corresponding products **5ga** and **5ha** with high ee in moderate yield. The olefinated product **5ia** was obtained in 87% yield with 98% ee when multisubstituted cinnamic acid derivative **1i** was employed. Notably, substituted naphthalenes (**1k**, **1l**) also served as suitable coupling partners with good stereocontrol as well as high yields (**5ka**, 79%, 89% ee; and **5la**, 77%, 93% ee). To our delight, substrate **1m** bearing a pyrene group gave the desired olefination product smoothly, in a yield of 54% with 99% ee. Various other acrylates were compatible with this reaction, affording corresponding products (**5ab–5ah**) in good yields and excellent enantioselectivities. Most remarkably, 4-methoxystyrene and 4-trifluoromethylstyrene were also suitable partners for this transformation, producing **5ai** and **5aj** in yields of 59% and 60%, respectively, with excellent enantioselectivities of 98% ee and 96% ee.

To gain insights into the utility of the reaction, gram-scale synthesis and transformations were conducted (Scheme 3). First, the reaction of *rac*-**1a** and **2b** on a 5 mmol scale was performed, and the desired **CCA 1** was isolated with retentive enantioselectivity (77%, 94% ee, 1.34 g). The 5 mmol scale reaction of *rac*-**1a** and **4a** gave **5aa** in a yield of 95% and 95% ee. Subsequently, **CCA 1** was reduced to form alcohol **6** under mild conditions with a mild loss in enantioselectivity. The olefination product **5aa** could undergo a van Leusen reaction and afford the hetero-aryl compound **7** in 77% yield and 93% ee.

In order to demonstrate the application prospect of our methodology, both olefinated and arylated axially chiral styrene-type carboxylic acids (**CCA 1–CCA 6**) were treated as chiral ligands in a Co^{III}-catalyzed asymmetric synthesis, as shown in Scheme 4. In 2019, Matsunaga and co-workers demonstrated that the combination of an achiral Co^{III}

Table 3 Substrate scope of Pd catalyzed enantioselective C–H olefination[a,b,c]



[a] *Rac*-**1** (0.2 mmol), **4** (3.0 equiv.), $Pd(OAc)_2$ (0.1 equiv.), Boc-L-*tert*-leucine (0.3 equiv.), KOH (2.0 equiv.), H_2O (10.0 equiv.) in *i*PrOH 2.0 mL in 1 atm O_2 at 30 °C for 72 h, the crude mixture was methylated using MeI. [b] Isolated yields. [c] The ee value was determined by HPLC. [d] 84 h. [e] 108 h. [f] 132 h.

complex and CCA promotes asymmetric C(sp^3)-H amidation reactions of thioamides **8** with dioxazolones **9**.[4f,g] A series of newly developed axially chiral styrene-type CCAs were employed (Scheme 4a), and the desired product **10** was obtained in moderate to good yields. When **CCA 6** was employed, a better enantioselectivity (17 : 83 er) was obtained. Meanwhile, enantioselective 1,4-addition reaction of indole **11** with maleimide **12** which proceeds *via* a C2-selective C–H activation was also conducted.[4i] The product **13** was obtained in 49% yield with

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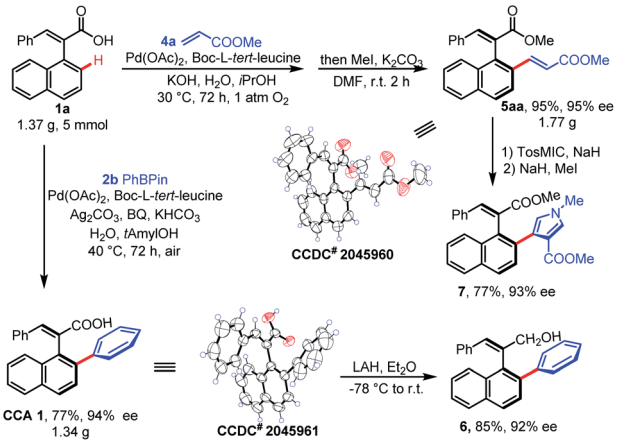
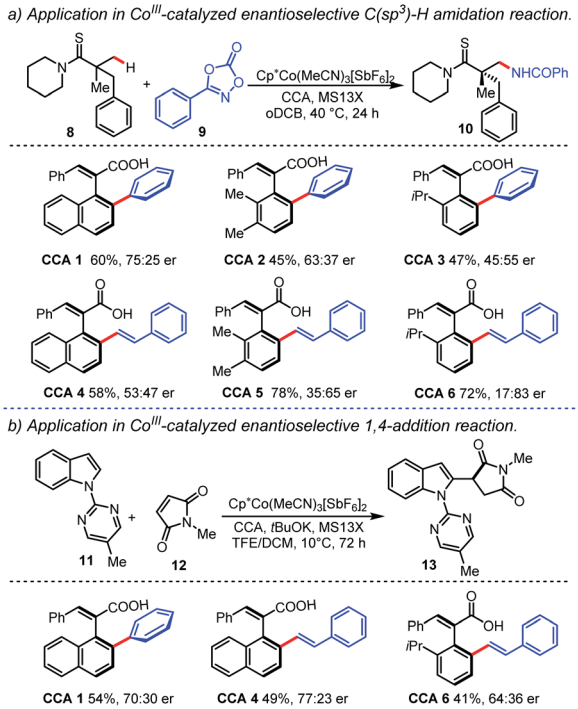


Scheme 3 Gram scale reactions and transformations of CCA 1 and 5aa.



Scheme 4 Application of axially chiral styrene-type carboxylic acids as ligands in Co^{III}-catalyzed enantioselective C–H activation reactions.

77 : 23 er, when **CCA 4** was employed (Scheme 4b). Although the enantioselectivity of the aforementioned transformations needs to be improved, these results demonstrate that the chiral styrene-type CCA skeleton is promising in developing a new class of chiral ligands and may find more applications in catalytic asymmetric transformations.

Conclusions

In conclusion, we have developed palladium-catalyzed C–H arylation or olefination of cinnamic acid derivatives for facile synthesis of axially chiral styrene-type carboxylic acids through a one-step incorporation of axial chirality and sterically hindered group. This method demonstrated broad scope, good yields, excellent enantioselective control, and mild conditions. The axially chiral styrene-type carboxylic acids produced have been successfully applied to Cp^*Co^{III}-catalyzed asymmetric C–H activation reactions as potential chiral ligands. This strategy offered a valuable solution for rapid and efficient construction of novel axially chiral styrenes, which may serve as a class of novel chiral ligands or catalysts in asymmetric synthesis. Further exploration of asymmetric C–H activation to enable axially chiral motifs is underway in our laboratory.

Conflicts of interest

The authors declare no conflict of interest.

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