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Cobalt(III)-Catalyzed Enantioselective Intermolecular Carboaminations *via* C–H Functionalizations

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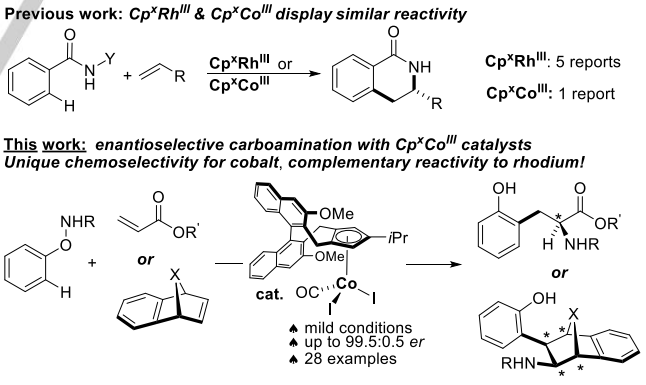
Abstract: High-valent cyclopentadienyl cobalt catalysis is a versatile tool for sustainable C–H bond functionalization. To harness the full potential of this strategy, stereoselectivity control of these processes is necessary. Herein, we report highly enantioselective intermolecular carboaminations of alkenes through C–H activation of *N*-phenoxyamides catalyzed by Co^{III}-complexes equipped with chiral cyclopentadienyl (Cp^x) ligands. The method converts widely available acrylates as well as bicyclic olefins into attractive enantioenriched isotyrosine derivatives as well as elaborated amino-substituted bicyclic scaffolds under very mild conditions. The outlined reactivity is unique to the Cp^xCo^{III} complexes and is complementary to the one corresponding to 4d- and 5d- precious metal catalysts.

The direct and enantioselective functionalization of C–H bonds by cheap and abundant 3d transition-metal complexes holds tremendous potential for the sustainable construction of chiral molecules.[1] The development of such methodologies is highly challenging and often requires a tailored design of new chiral ligands and catalysts.[2] For instance, significant progress in enantioselective functionalizations of C–H bonds by high-valent cobalt complexes[3] has been recently reported by Ackermann,[4] Matsunaga and Yoshino,[5] and Shi.[6] Ackermann and Matsunaga employed achiral Cp^*Co^{III} complex in combination with a chiral acid co-catalyst, enabling stereoselective C–H alkylation of indoles *via* the reversible insertion/enantioselective protonation mechanism.[4,5a] Matsunaga and Yoshino demonstrated that the achiral Cp cobalt species and a chiral carboxylic acid engage in C–H activation of thioamides through an enantioselective CMD process, followed by an amidation.[5b,c] Along the same lines, developments led to functionalization of ferrocenes and additional designs of chiral carboxylic acids.[6,5b] In 2019, we have introduced chiral Cp^xCo complexes for a highly enantioselective synthesis of dihydroisoquinolones through C–H functionalization of *N*-chlorobenzamides with a broad range of alkenes.[7] Notably, the Cp^xCo^{III}-catalysts largely outperformed the corresponding Cp^xRh^{III} methods in terms of regio- and enantioselectivity,[8,9] not only providing a cheaper and more sustainable alternative but also a clear performance incentive.

In general, high-valent cobalt catalysts[3,10] can offer broad opportunities for C–H functionalizations, which often reach beyond and provide complementary catalytic activities to the other group 9 metals.[3c,d] For instance, Glorius reported Cp^*Co^{III} complexes engaging in racemic carboaminations of acrylates through C–H activation of phenoxyacetamides.[11] In stark contrast, related Cp^*Rh^{III} catalysts yielded exclusively Heck-type acrylates *via* a fast β-H elimination.[12] Such divergent behavior between Co^{III}- and Rh^{III}-based systems manifests also in the C–H functionalization of phenoxyacetamides with bicyclic olefins. The Cp^*Co^{III} complexes deliver racemic carboamination products[13] while the Cp^*Rh^{III} analog promoted either intramolecular amide transfer[14] or led to a bridged polycyclic skeleton.[15] Carboamination of alkenes is a sought after technology allowing the access of elaborated amines through an assembly of new C–C and C–N bonds in a single process.[16] However, highly valuable enantioselective carboaminations proceeding through a C–H bond activation are scarce and mostly utilize rhodium-based catalysts.[17] To address this shortcoming, we questioned whether chiral cyclopentadienyl cobalt(III) complexes would be catalytically competent for asymmetric carboaminations of olefins, beyond the scope of Rh-catalysis. Herein, we report Cp^xCo-catalyzed enantioselective intermolecular carboaminations of acrylates and bicyclic olefins giving access to attractive unnatural tyrosine derivatives as well as amino-substituted bicyclic scaffolds in excellent enantioselectivities.

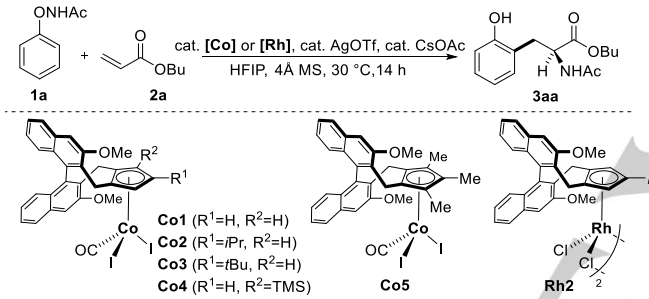


Scheme 1. Exploration of analogous and complementary reactivities of Cp^xRh and Cp^xCo catalysts in enantioselective carboaminations of alkenes *via* C–H activation.

We initially evaluated our hypothesis with a set of chiral Cp^xCo complexes[7] using phenoxyacetamide **1a** as the carboamination donor and butyl acrylate **2a** as acceptor (Table 1). Silver triflate was used as iodide abstractor and cesium acetate as CMD-promoting base.[18] The reactions were conducted in hexafluoroisopropanol (HFIP) in the presence of 4Å molecular sieves at 30 °C (For additional optimization studies, see SI). Using complex **Co1** bearing the standard disubstituted Cp^x ligand,[7,19] carboamination product **3aa** was obtained in a 41% yield,

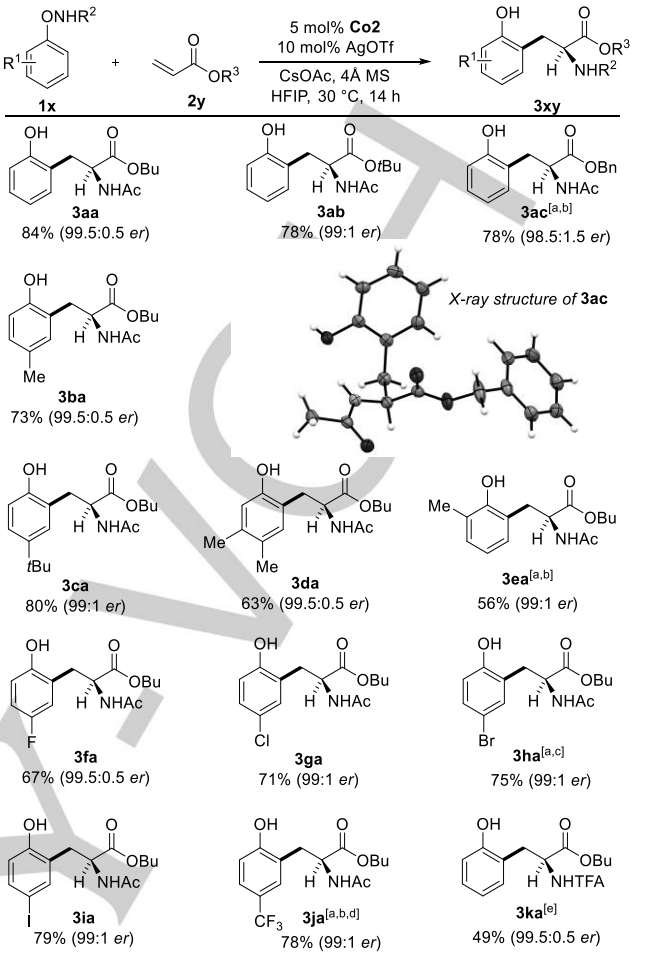
however with a very poor enantiomeric ratio of 55:45 (Entry 1). The substitution pattern on the Cp^x ligand has a very pronounced effect on the efficiency and the stereoselectivity of the transformation. Trisubstituted complexes **Co2** and **Co3**[20] yielded **3aa** in 68% yield and excellent enantiomeric ratio of 99:1 (Entries 2-3). In contrast, **Co4** and **Co5** were not catalytically competent (Entries 4-5). Importantly, the rhodium catalyst **Rh2** failed to deliver the desired product **3aa**. Instead, the corresponding 3-phenylacrylate was formed in 83% yield (Entry 6) *via* oxidative Heck pathway – a result in line with the reactivity under Cp*Rh^{III} catalysis.[12] Increasing the concentration to 0.4 M with **Co2** as the catalyst improved the yield of **3aa** to 88% without affecting the stereoselectivity (Entry 7). The catalyst loading could be lowered to 5 mol% **Co2** without impacting the reaction outcome (Entry 8). Final adjustments of the reaction conditions involved using a small excess of phenoxyacetamide **1a** for a slight improvement in the yield of **3aa** (Entry 9). Increasing the concentration to 0.8 M and execution of the transformation at four-fold scale provided amino acid derivative **3aa** in 86% isolated yield and an enantioselectivity of 99:1 *er* (Entry 11).

Table 1. Optimization studies of the enantioselective Co-catalyzed carboamination.[a]



Entry	Cat. (mol%)	Conc. [M]	% Yield	*er*
1	**Co1** (10)	0.2	41	55:45
2	**Co2** (10)	0.2	68	99:1
3	**Co3** (10)	0.2	68	99:1
4	**Co4** (10)	0.2	<5	-
5	**Co5** (10)	0.2	<5	-
6[b]	**Rh2** (5)	0.2	<5	-
7	**Co2** (10)	0.4	88	99:1
8	**Co2** (5)	0.4	86	99:1
9[c]	**Co2** (5)	0.4	88	99:1
10[d]	**Co2** (5)	0.4	83	99:1
11[d]	**Co2** (5)	0.8	86	99:1

[a] Conditions: 50 µmol **1a**, 50 µmol **2a**, 5.0 µmol [**Co**], 10 µmol AgOTf, 12.5 µmol CsOAc, 20 mg 4Å MS in HFIP at 30 °C for 14 h; yields determined by ^{1}H-NMR with internal standard; [b] 2.5 µmol **Rh2**; [c] with 60 µmol **1a**; [d] 4-fold scale-up, 0.24 mmol **1a**, 0.2 mmol **2a**, isolated yield.

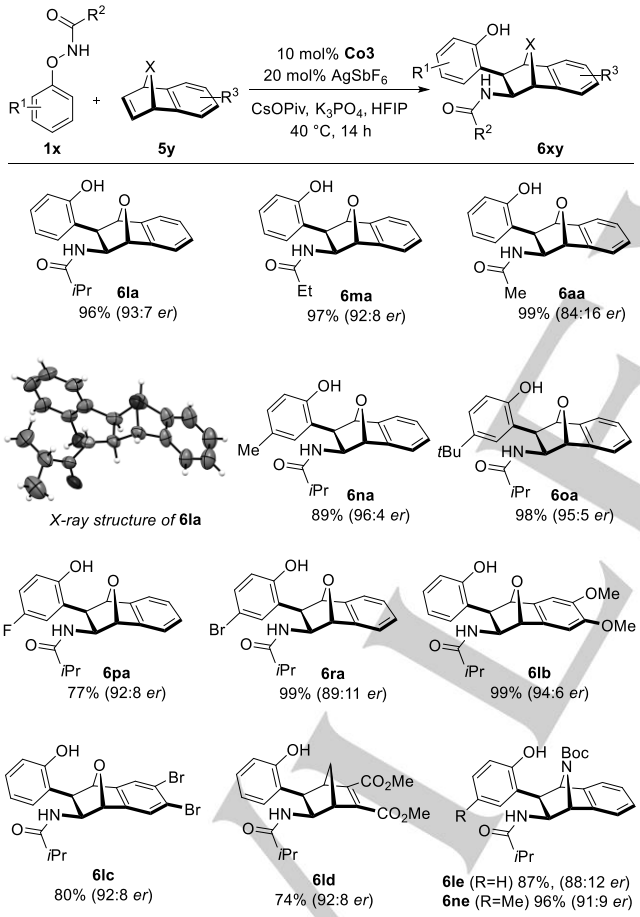


Scheme 2. Scope for the Co-catalyzed carboamination with acrylates. Conditions: 0.24 mmol **1x**, 0.20 mmol **2y**, 10 µmol **Co2**, 20 µmol AgOTf, 50 µmol CsOAc, 80 mg 4Å MS in HFIP (0.8 M) at 30 °C for 14 h; [a] with 20 µmol **Co2**, 40 µmol AgOTf; [b] for 10 h; [c] at 0.4 M; [d] at 50 °C; [e] with 0.12 mmol **1k**, 0.10 mmol **2a** using 10 mol% **Co2** and 20 mol% AgOTf at 0 °C.

The scope of the enantioselective carboamination strategy was evaluated with the aforementioned optimized conditions (Scheme 2). Different acceptors such as *tert*-butyl or benzyl acrylate reacted smoothly with phenoxyacetamide **1a** affording isotyrosine derivatives **3ab** and **3ac** in 78% yield and excellent enantiomeric ratios of 99:1 *er* and 98.5:1.5 *er*, respectively. An X-ray crystal structure analysis of a single crystal of **3ac** allowed assignment of its absolute configuration as L-isotyrosine.[21,22] Further evaluation of the reactivity of the hydroxamates **1** revealed a good tolerance towards structural and electronic variations of its substituents. Hydroxamate substrates with alkyl substituents in the *para*- position gave products **3ba** and **3ca** in equally excellent enantiomeric ratios. Substrates with both *para*- and *meta*- methyl groups resulted in product **3da** as a single regioisomer in 63% yield and 99.5:0.5 *er*. Sterically more encumbered *o*-methyl hydroxamate **1e** required a higher catalyst-loading and in consequence delivered **3ea** in a slightly lower yield but conserved enantioselectivity of 99:1 *er*. Halogenated substrates did not interfere with the reaction and gave isotyrosine derivatives **3fa**-**3ia** while maintaining the general reactivity and selectivity characteristics of the process. The *p*-CF_3 substituent rendered hydroxamate **1j** less reactive. A higher temperature of 50 °C and increased catalyst loading were required to obtain **3ja**

in 78% yield, notably without compromising its enantioselectivity. In contrast, *N*-trifluoroacetyl phenyl hydroxamate **1k** was successfully converted at 0 °C into product **3ka** with an outstanding enantioselectivity. Noteworthily, this substrate could not be converted to **3ka** using achiral Cp*Co(CO)I_2 catalyst.

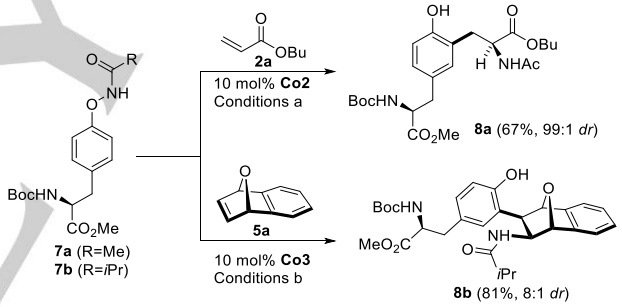
To further expand this enantioselective Co-catalyzed carboamination methodology, additional olefin partners, specifically the bicyclic alkenes were evaluated (Scheme 3). The bulkier **Co3** complex with its *t*Bu group was found to be the best precatalyst, enabling a smooth reaction of *N*-phenoxy-isobutyramide **1l** with 1,4-dihydro-1,4-epoxynaphthalene **5a** leading to targeted carboamination product **6la** in 96% yield (For optimization study, see SI). Compound **6la** bearing four contiguous stereocenters was formed in 93:7 *er* as a single *exo*-diastereomer.[21] Decreasing the bulk of the amide moiety of the substrate from isopropyl (**1l**) to ethyl (**1m**) led only to marginally lower enantioselectivity of product **6ma**. In contrast, conducting the reaction with the previously used *N*-acetyl substrate **1a** resulted in formation of carboamination product **6aa** in 99% yield with a reduced enantiomeric ratio of 84:16 *er.*



Scheme 3. Scope of the Co-catalyzed carboamination with bicyclic alkenes. Conditions: 0.12 mmol **1x**, 0.10 mmol **5y**, 10 µmol **Co3**, 20 µmol $AgSbF_6$, 50 µmol CsOPiv, 50 µmol K_3PO_4 in HFIP (0.8 M) at 40 °C for 14 h.

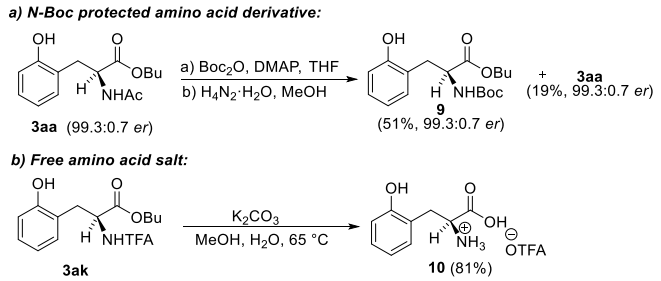
In terms of scope, the addition across oxabicylic alkenes tolerated various substitution patterns of the hydroxamate substrate. For instance, addition products **6na** and **6oa** containing a *p*-Me- and *p*-*t*Bu-phenol moieties were obtained in excellent yields and very good enantiomeric ratios of 96:4 *er* and 95:5 *er*, respectively. A fluorine substituent was also tolerated giving **6pa** in 77% yield and 92:8 *er*, while the corresponding bromine-containing analog **6ra** was formed in a quantitative yield and 89:11 *er*. Variations of the strained alkene acceptor such as 1,4-dihydro-1,4-epoxynaphthalenes bearing methoxy- or bromo-substituents, delivered products **6lb** and **6lc** in high yields and enantioselectivities. Notably, carbon- and nitrogen-bridged bicyclic olefins were identified as competent substrates. In this respect, norbornadiene **5d** reacted under the standard conditions giving densely substituted norbornene **6ld**[21] in 74% yield and 92:8 *er*. Aza-bicyclic alkene **5e** afforded targeted products **6le**[21] and **6nd** in excellent yields, albeit with slightly reduced stereoselectivities.

After demonstration of the catalytic performance of cobalt(III) catalysts **Co2** and **Co3** in the enantioselective carboamination, we targeted diastereoselective functionalizations of tyrosine derivatives **7a** and **7b** with this method (Scheme 4). These elaborated hydroxamates were both smoothly converted to their corresponding carboamination products under standard reaction conditions. Product **8a** bearing two amino ester moieties was obtained in 67% yield and an excellent *dr* of 99:1 completely reflecting the typical enantioselectivity of the acrylate-type substrates. The related transformation of substrate **7b** with oxabicycle **5a** afforded two diastereomers of **8b** with a combined yield of 81%, again in agreement with the selectivities of the bicyclic alkene substrates.[21]



Scheme 4. Diastereoselective carboaminations with tyrosine-derived substrates **7**. a) 0.24 mmol **7a**, 0.2 mmol **2a**, 20 µmol **Co2**, 40 µmol AgOTf, 50 µmol CsOAc, 80 mg 4Å MS in HFIP (0.8 M) at 30 °C for 14 h; b) 0.12 mmol **7b**, 0.1 mmol **5a**, 10 µmol **Co3**, 20 µmol $AgSbF_6$, 50 µmol CsOPiv, 50 µmol K_3PO_4 in HFIP (0.8 M) at 40 °C for 14 h.

The synthetic relevance of the enantioenriched carboamination products **3** was showcased by follow-up transformations (Scheme 5). In this respect, the *N*-acetyl group of **3aa** was converted into the versatile and frequently used Boc-protecting group. Boc-protection and subsequent hydrazinolysis of the acetyl group provided[23] Boc-protected amino acid derivative **9** in 51% yield over two steps along with 19% of recovered **3aa**. The enantiomeric purity was conserved for **9** as well as recovered **3aa**. Trifluoroacetamide bearing product **3ka** could be fully deprotected under mild basic conditions providing corresponding free amino acid **10** as its trifluoroacetate salt in 81% yield.



Scheme 5. Conversion of the carboamination products into amino acid derivatives.

In summary, we have developed a highly enantioselective Cp^xCo^{III}-catalyzed intermolecular carboamination of alkenes. The transformation is enabled by the tailored tri-substituted chiral Cp^x ligands. Two different alkene acceptors – acrylates and bicyclic olefins provide access to attractive synthetic building blocks such as non-natural isotyrosine derivatives and elaborated amino-substituted bicycles. Strikingly, the chemoselectivity – the product range obtained – is specific to cobalt catalysts, underscoring the complementary behavior between cobalt and rhodium-based catalytic systems. These findings will serve as a blueprint for further developments of sustainable methodologies for the enantioselective C–H functionalizations with 3d metal catalysts.

Acknowledgements

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Keywords: Asymmetric Catalysis • Cobalt • C–H functionalization • Carboamination • Chiral Cyclopentadienyl

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[21] Crystallographic data available from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif: 2022936 (**3ac**); 2022937 (**6la**); 2022938 (**6ld**); 2022939 (**6le**); 2022940 (**8b**).

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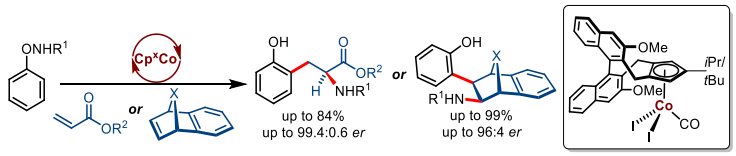
Cobalt(III)-Catalyzed Enantioselective Intermolecular Carboaminations via C–H Functionalizations



A highly enantioselective Chiral Cp^xCo^{III} complexes are efficient catalysts for intermolecular highly enantioselective carboamination of alkenes. The process is enabled by C–H activations of *N*-phenoxyamides converting acrylates and bicyclic olefins to valuable isotyrosine derivatives and elaborated amino-substituted bicycles under mild conditions.