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Highly Asymmetric Intramolecular Cyclopropanation of Acceptor-Substituted Diazoacetates by Co(II)-Based Metalloradical Catalysis: Iterative Approach for Development of New-Generation Catalysts

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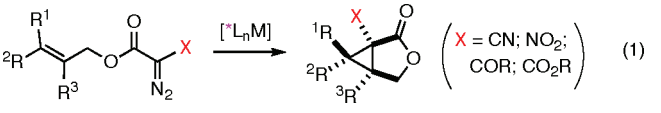
Supporting Information

ABSTRACT: 3,5-Di^{t}Bu-QingPhyrin, a new D_2-symmetric chiral porphyrin derived from a chiral cyclopropanecarboxamide containing two contiguous stereocenters, has been developed using an iterative approach based on Co(II)-catalyzed asymmetric cyclopropanation of alkenes. The Co(II) complex of 3,5-Di^{t}Bu-QingPhyrin, [Co(**P2**)], has proved to be a general and effective catalyst for asymmetric intramolecular cyclopropanation of various allylic diazoacetates (especially including those with α-acceptor substituents) in high yields with excellent stereoselectivities. The [Co(**P2**)]-based intramolecular metalloradical cyclopropanation provides convenient access to densely functionalized 3-oxabicyclo[3.1.0]hexan-2-one derivatives bearing three contiguous quaternary and tertiary chiral centers with high enantiomeric purity.

Metal-catalyzed asymmetric olefin cyclopropanation with diazo reagents stands as one of the most general approaches for the synthesis of optically active cyclopropane derivatives.[1] Its intramolecular variant offers a powerful strategy for stereoselective construction of complex [*n*.1.0]bicyclic ring systems directly from linear unsaturated diazo precursors.[1] The resulting bicyclic molecules have been demonstrated to be versatile intermediates for syntheses of a wide range of important compounds such as pharmaceuticals, peptidomimetics, and natural products.[2] Since the feasibility of intramolecular cyclopropanation was first demonstrated in 1961,[3] significant efforts have been devoted to the development of chiral metal catalysts for controlling the enantioselectivity of the double cyclization reaction, in parallel with the development of intermolecular cyclopropanation.[1,2] Results seem to indicate that a chiral catalyst that is capable of highly asymmetric intermolecular cyclopropanation may not necessarily be effective for enantioselective intramolecular cyclopropanation because of additional constraints in the transition state of the unimolecular process. In fact, asymmetric intramolecular cyclopropanation is a significantly less developed process in comparison with the enormous advancements in asymmetric intermolecular cyclopropanation.[1,2] To date, most achievements in asymmetric intramolecular cyclopropanation have been made for reactions of unsaturated acceptor-substituted diazo reagents, such as diazoacetates and diazoacetamides.[4−7] While there have been several reports on asymmetric reactions of donor/acceptor-substituted diazo reagents with partial success,[8] intramolecular cyclopropanation of acceptor/acceptor-substituted diazo reagents with high enantioselectivity remains a major challenge and is currently limited to the reactions of α-diazo-β-ketone sulfones.[9]

Allyl diazoacetates with α-acceptor substituents such as cyano, nitro, ketone, and ester groups [X = CN, NO_2, C(O)R, and CO_2R, respectively, in eq 1] are a class of common unsaturated acceptor/acceptor-substituted diazo reagents that have not been successfully demonstrated to be effective substrates for asymmetric intramolecular cyclopropanation. Since the resultant 3-oxabicyclo[3.1.0]hexan-2-one derivatives possess three contiguous chiral centers, including one multifunctionalized quaternary stereogenic carbon (eq 1), this family of enantioselective transformations would be highly attractive for synthetic applications. There have been only a few previous reports on catalytic systems for asymmetric cyclopropanation of α-acceptor-substituted allyl diazoacetates. While there has been no report on allyl α-nitrodiazoacetates (X = NO_2),[10] the only report on asymmetric intramolecular cyclopropanation of allyl α-cyanodiazoacetates (X = CN) attained a highest enantioselectivity of 91% ee with a 57% yield using a Rh_2-based catalyst.[11] The enantiocontrol of the catalytic system was shown to be greatly influenced by the substituents around the allyl group, ranging from 29 to 91% ee.[11] Whereas the catalytic process for allyl α-ketodiazoacetates [X = C(O)R] has not been reported,[12] prior efforts were made for asymmetric intramolecular cyclopropanation of allyl α-esterdiazoacetates (X = CO_2R) using both Rh_2- and Cu-based catalysts, which reached a highest enantioselectivity of 83% ee but with a yield of only 24%.[13] Once again, the enantioselectivity was found to be highly substrate-dependent, ranging from 11 to 83% ee.[13] It is evident that asymmetric intramolecular cyclopropanation of α-acceptor-substituted diazoacetates is largely an unsolved problem and faces formidable challenges with respect to both reactivity and selectivity.



(1)

Since they were first introduced in 2004,[14] Co(II) complexes of D_2-symmetric chiral amidoporphyrins [Co(D_2-Por*)] have emerged as a new class of catalysts for asymmetric cyclopropanation.[15] These metalloradical catalysts have been shown to be highly effective for asymmetric intermolecular cyclopropanation of a broad scope of substrates with different classes of carbene sources, particularly including electron-deficient olefins and acceptor/acceptor-substituted

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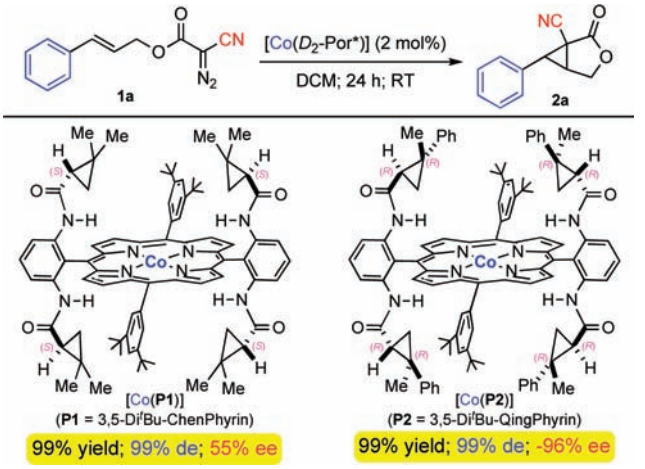
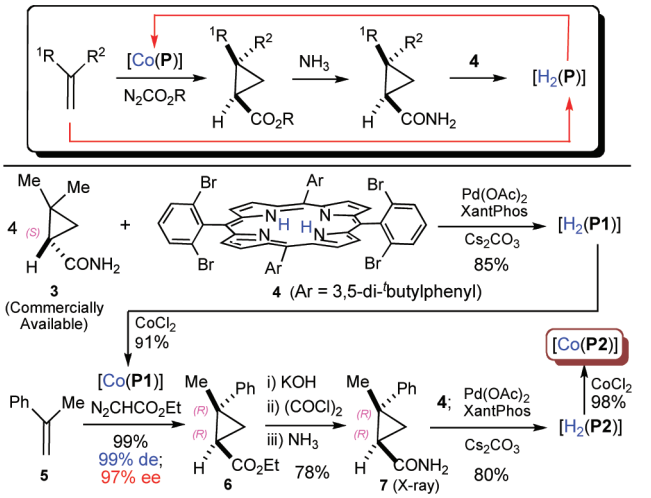
Table 1. Ligand Effect on Asymmetric Intramolecular Cyclopropanation of Cinnamyl α-Cyanodiazoacetate (1a)



Scheme 1. Iterative Approach for the Development of [Co(D_2-Por*)] and Application for Synthesis of [Co(P2)]



diazo reagents, with excellent diastereoselectivity and enantioselectivity.[16,17] Increasing amounts of evidence support an unprecedented reaction mechanism for the Co(II)-catalyzed cyclopropanation that involves an unusual Co(III)−carbene radical intermediate undertaking a stepwise radical addition−substitution pathway.[18] This radical mechanism, which is fundamentally different from the electrophilic metallocarbene mechanism shared by the commonly used Rh_2 and other closed-shell systems, is consistent with the distinct cyclopropanation reactivity profile.[16,17] To date, the Co(II)-based metalloradical cyclopropanation has been demonstrated only for intermolecular reactions. In view of the more demanding steric requirements associated with the double cyclization process, it was unclear whether the confined chiral cavity in [Co(D_2-Por*)] could accommodate intramolecular cyclopropanation reactions. Since the metalloradical catalysis operates in a stepwise radical mechanism, would its diastereoselectivity be comparable to that of the existing concerted catalytic systems? To answer these and related questions and, more importantly, to address the aforesaid challenges in the area, we embarked on a project to study asymmetric intramolecular cyclopropanation. As the outcome of this effort, we report herein a highly effective catalytic system based on a new generation of chiral Co(II) metalloradical catalysts for asymmetric intramolecular cyclopropanation of α-acceptor-substituted diazoacetates (eq 1). In addition to substrates bearing two various acceptor groups, the Co(II)-catalyzed intramolecular cyclopropanation is also suitable for acceptor- and donor/acceptor-substituted diazo compounds, producing the corresponding bicyclic compounds in high yields with excellent diastereo- and enantioselectivity. Furthermore, the metalloradical catalytic process features a practical one-portion protocol that operates at room temperature without slow addition of substrates.

The unsaturated acceptor/acceptor-substituted diazo compound cinnamyl α-cyanodiazoacetate (**1a**) was used as the initial substrate for intramolecular asymmetric cyclopropanation by [Co(D_2-Por*)] (Table 1). Since the metalloradical catalyst [Co(**P1**)] was shown previously to be highly enantioselective for intermolecular cyclopropanation with α-cyanodiazoacetates,[16f] it was first evaluated as a potential catalyst for the reaction of **1a**. Under practical conditions (room temperature without slow addition), it was pleasing to observe that **1a** could be quantitatively transformed to the desired bicyclic product **2a** as a single diastereomer under the catalysis of 2 mol % [Co(**P1**)] (Table 1). However, the enantioselectivity of the [Co(**P1**)]-catalyzed reaction reached only 55% ee, indicating a significant difference between the asymmetric intra- and intermolecular cyclopropanation processes. No major improvements in enantioselectivity were achieved even though extensive attempts employing other existing [Co(D_2-Por*)] catalysts were made.[14,17] Results from these early efforts prompted us to develop new-generation catalysts by exploiting an iterative approach (Scheme 1) based on the combination between the modular design of the D_2-symmetric chiral porphyrins[14] and the high stereoselectivities of [Co(D_2-Por*)]-catalyzed intermolecular cyclopropanation.[16] Starting from optically pure chiral amide **3**, which is available inexpensively from commercial sources, this iterative approach allows for the effective generation of diverse cyclopropanecarboxyamides with high enantiomeric purity that can be further utilized as chiral building blocks for construction of new-generation [H_2(D_2-Por*)] ligands. As one application of this approach, the metalloradical catalyst [Co(**P2**)], which represents the first example of a [Co(D_2-Por*)] complex bearing chiral amides with two contiguous stereocenters, was designed and synthesized from α-methylstyrene [Scheme 1; also see the Supporting Information (SI)]. Gratifyingly, [Co(**P2**)] was found to be a superior chiral catalyst in comparison with [Co(**P1**)] for the asymmetric intramolecular cyclopropanation of **1a**, resulting in the quantitative formation of the desired product **2a** as a single diastereomer with 96% ee (Table 1). It is fascinating to note that the chirality in [Co(**P2**)] originated from [Co(**P1**)].

The new metalloradical catalyst [Co(**P2**)] was shown to be generally effective for asymmetric intramolecular cyclopropanation of allyl diazoacetates with different α-substituted groups (Table 2). In addition to **1a** (entry 1), cinnamyl α-nitrodiazoacetate (**1b**) could also be effectively catalyzed by [Co(**P2**)] under the same practical conditions to give the corresponding cyclopropanation product **2b** in high yield and enantioselectivity (entry 2). This represents the first successful example of asymmetric intramolecular cyclopropanation of allyl α-nitrodiazoacetates.[10] The absolute configurations of the three contiguous stereogenic centers in **2b** were established as (1*S*,5*S*,6*R*) by X-ray crystal structure analysis (Figure S1 in the SI). Under the catalysis of [Co(**P2**)], unsaturated α-ketodiazoacetates could for the first time be asymmetrically cyclopropanated, as exemplified by the

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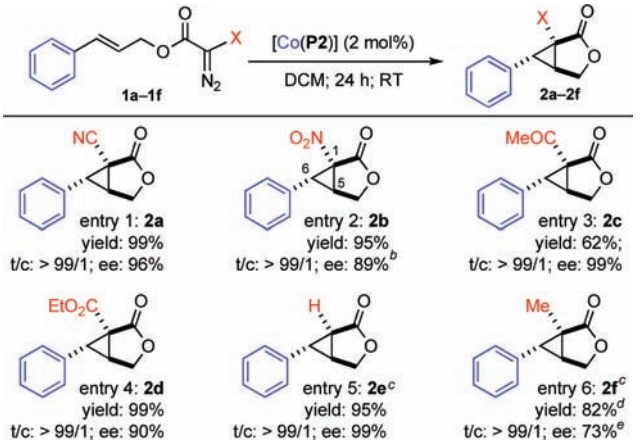
Table 2. Asymmetric Intramolecular Cyclopropanation of Allyl Diazoacetates with Different α-Substituted Groups[a]

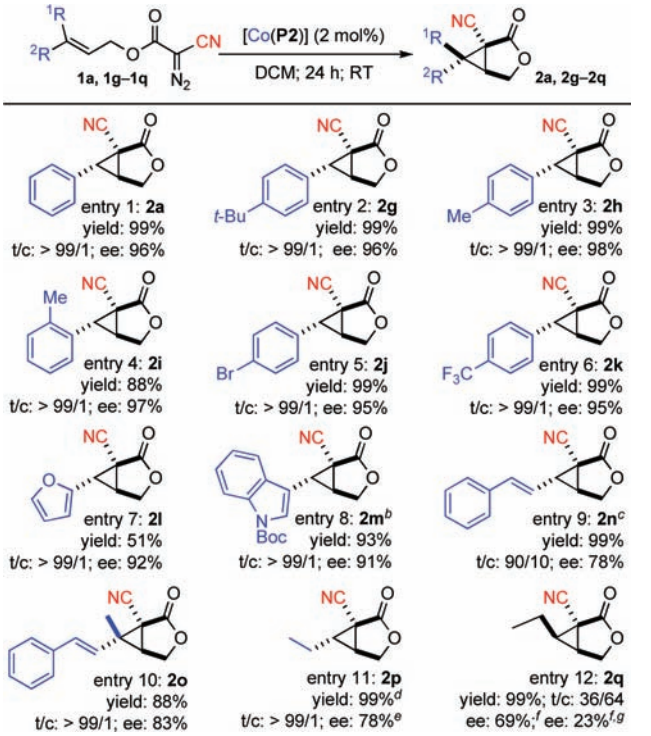


[a] [1] = 0.20 M; Isolated yields; Enantiomeric excess of major trans diastereomer determined by chiral HPLC. [b] [1*S*,5*S*,6*R*] Absolute configuration determined by X-ray crystal structural analysis. [c] In the presence of 0.5 eq DMAP. [d] At 60 °C. [e] Determined by chiral GC.

successful reaction of cinnamyl α-ketodiazoacetate (**1c**).[12] The desired cyclopropanation product **2c** was formed with almost perfect enantioselectivity, albeit in a lower yield (entry 3). The stereocontrol capability of catalyst [Co(**P2**)] was further demonstrated with the highly asymmetric intramolecular cyclopropanation of cinnamyl α-esterdiazoacetate (**1d**). In addition to high enantioselectivity, the corresponding cyclopropanation product **2d** could be obtained in almost quantitative yield (entry 4). Besides acceptor/acceptor-substituted diazo substrates, the [Co(**P2**)]-based system could be also applied to acceptor- and donor/acceptor-substituted diazo compounds, as illustrated by the asymmetric intramolecular cyclopropanations of cinnamyl diazoacetate (**1e**) and α-methyldiazoacetate (**1f**), respectively (entries 5 and 6).

In addition to cinnamyl diazoesters, the [Co(**P2**)]-based metalloradical catalysis could effectively enable asymmetric intramolecular cyclopropanation of other unsaturated diazoesters, as demonstrated using a series of allylic α-cyanodiazoacetates (Table 3). For example, cinnamyl derivatives having alkyl groups substituted at different phenyl positions, such as **1g**−**i**, could be intramolecularly cyclopropanated with similarly high yields and stereoselectivities as for **1a** (entries 1−4). Besides alkyl substituents, the catalytic system worked equally well with derivatives containing electron-withdrawing groups such as Br (**1j**; entry 5) and CF_3 (**1k**; entry 6). The Co(II)-catalyzed cyclopropanation could also be successfully applied to heteroaryl allylic α-cyanodiazoacetates such as **1l** and **1m** (entries 7 and 8). In addition, conjugated allylic α-cyanodiazoacetates, as illustrated with substrates **1n** and **1o**, could be productively catalyzed to form 3-oxabicyclo[3.1.0]hexan-2-one derivates **2n** and **2o**, respectively, although with decreased enantioselectivities (entries 9 and 10). The absolute configurations of the three contiguous stereogenic centers in the major enantiomer of **2n** were established as (1*R*,5*S*,6*S*) by X-ray crystal structure analysis (Figure S2 in SI). It is worthy of note that two of the three contiguous chiral centers in **2o** are all-carbon quaternary stereocenters. Catalyst [Co(**P2**)] was found to be similarly active for alkyl-substituted allylic α-cyanodiazoacetates, as demonstrated by the reactions of **1p** and its cis-isomer **1q**, which formed the corresponding bicyclic products **2p** and **2q** in excellent yields but with moderate enantioselectivities (entries 11 and 12).

Table 3. Catalytic Asymmetric Intramolecular Cyclopropanation of Various Allylic α-Cyanodiazoacetates



[a] See footnotes of Table 2. [b] At 0 °C. [c] [1*R*,5*S*,6*S*] Absolute configuration determined by X-ray crystal structural analysis. [d] GC yield. [e] Determined by chiral GC. [f] Determined via derivatization. [g] cis isomer.

It is noteworthy that all of the above catalytic reactions except for two generated the 3-oxabicyclo[3.1.0]hexan-2-one products as a single diastereomers (Tables 1−3). While diastereoselectivity is not an issue for intramolecular cyclopropanation by concerted catalytic systems, this fact suggests that the last ring-closure step (intramolecular radical substitution) in the stepwise radical addition−substitution pathway of Co(II)-catalyzed intramolecular cyclopropanation is a low-barrier or barrierless process, the same as shown in Co(II)-catalyzed intermolecular cyclopropanation.[18] The two exceptions are the catalytic reactions of conjugated **1n** and cis alkene **1q**, which provided the products **2n** and **2q** as mixtures of two diastereomers (Table 3, entries 9 and 12). These results are consistent with the stepwise radical mechanism.[18]

The demonstrated asymmetric intramolecular cyclopropanation by the [Co(**P2**)]-based catalytic system paves a practicable way to access optically pure 3-oxabicyclo[3.1.0]hexan-2-one derivatives bearing multiple stereocenters with dense functionalities, which should find a myriad of applications in stereoselective synthesis.[2] As an initial exploration of their synthetic applications, we demonstrated that the γ-butyrolactone unit in enantioenriched bicyclo[3.1.0]hexanenitrile **2a** could be selectively opened with nitrogen-based nucleophiles such as aniline in the presence of lithium diisopropylamide (LDA) to produce multifunctionalized cyclopropane derivative **8** as a single diastereomer in high yields without loss of optical purity (eq 2). It is noted that enantioenriched cyclopropane derivatives such as **8** would be difficult or impossible to prepare directly via asymmetric intermolecular cyclopropanation. As another demonstration of a stereoselective transformation, the cyclopropane unit in enantioenriched bicyclo[3.1.0]hexane ester **2d**

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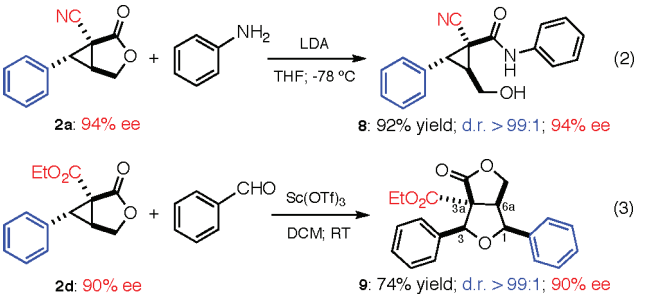
could be enlarged through [3 + 2] dipolar cycloaddition with dipolarophiles such as benzaldehyde to form hexahydrofuro[3,4-*c*]-furan derivative **9** as a single diastereomer in good yield without a change in the optical purity under Lewis acid-catalyzed conditions (eq 3).[19] The absolute configurations of the four contiguous stereogenic centers in **9** were established as (1*S*,3*S*,3a*S*,6a*S*) by X-ray crystal structure analysis (Figure S3 in SI).



In summary, we have successfully applied an iterative approach for the development of the new-generation chiral Co(II) metalloradical catalyst [Co(**P2**)], which proved to be generally effective for highly asymmetric intramolecular cyclopropanation. The [Co(**P2**)]-based catalytic system permits for the first time the efficient transformation of α-acceptor-substituted diazoacetates into enantioenriched 3-oxabicyclo[3.1.0]hexan-2-one derivatives bearing three contiguous stereocenters with multiple functionalities that may serve as valuable intermediates for stereoselective synthesis. The demonstration of Co(II)-based metalloradical catalysis for asymmetric intramolecular cyclopropanation may open the door for the discovery of other enantioselective radical cyclization processes, including polycyclization reactions.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, analytical data for all new compounds, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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