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Asymmetric dearomative cyclopropanation of naphthalenes to construct polycyclic compounds†

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Catalytic asymmetric dearomatization (CADA) reactions is an important synthetic method for constructing enantioenriched complex cyclic systems from simple aromatic feedstocks. However, the CADA reactions of nonactivated arenes, such as naphthalenes and benzenes, have been far less explored than those of electronically activated arenes, such as phenols, naphthols and indoles. Herein, we disclose an asymmetric dearomative cyclopropanation of naphthalenes for the rapid construction of polycyclic compounds. With chiral dirhodium carboxylate as a catalyst, the dearomative cyclopropanation proceeded smoothly under mild conditions and afforded benzonorcaradiene-containing tetracycles in good yield and high enantioselectivity (up to 99% ee). Three stereogenic centers, including two all-carbon quaternary centers, were created in the dearomatization reaction. Moreover, a variety of functional groups are well-tolerated in the reaction. The products could be readily converted into other complex polycycles while maintaining the high ee value.

Introduction

Catalytic asymmetric dearomatization (CADA) reactions have emerged as a unique and powerful method for constructing enantioenriched functionalized cyclic systems.[1] This synthetic strategy enables the direct conversion of simple, planar aromatic feedstocks into complex three-dimensional molecules that often exhibit biological activity and physicochemical properties superior to those of flat molecules.[2] Significant progress has been achieved in this field during recent decade, with a focus on electronically activated aromatic compounds such as phenols, naphthols and indoles.[1] In contrast, more readily available nonactivated arenes, such as naphthalenes and benzenes, have rarely been applied in CADA reactions owing to their inherently low reactivity.[3] The resulting high energy barrier often leads to the need for harsh conditions for this type of transformation, which makes stereocontrol very challenging.

Polycyclic structures are ubiquitous in natural products and pharmaceuticals. The rigidity and well-defined 3D spatial configuration of polycyclic architectures have a significant impact on their biological activities.[4] As strenuous synthetic efforts are often necessary for the synthesis of polycyclic compounds, it is highly desirable to develop simple and efficient synthetic methods for the rapid construction of polycyclic architectures from readily available feedstocks. Dearomatization of naphthalenes has demonstrated to be an effective method for the straightforward construction of polycyclic molecules.[3,5] However, the development of asymmetric versions of this type of transformation remains a formidable challenge because of the lack of efficient chiral catalytic systems or the requirements for harsh reaction conditions. To date, sporadic dearomatization reactions of naphthalenes with high enantioselectivity have been developed.[6–8] Recently, an enantioselective dearomative difunctionalization of naphthalenes was achieved by Sarlah's group, which involved visible-light-mediated [4 + 2] cycloaddition of naphthalenes with an arenophile and subsequent asymmetric ring-opening of the resulting cycloadducts.[6] In 2022, Jia, Zhang and You developed a Pd-catalyzed intramolecular dearomative Mizoroki–Heck reaction of naphthalenes to construct spirooxindole and spiroisoindolin-1-one with high enantioselectivity (Scheme 1b).[7]

The kinetic barrier of chemical reactions can be significantly reduced by using a highly reactive reagent or species, which offers a solution to the dearomatization of nonactivated arenes under mild conditions. Metal-carbenes, which are highly reactive species, are capable of reacting with nonactivated arenes at low temperature to afford the Buchner reaction product cycloheptatriene.[9] In contrast to the well-studied Buchner reaction, arene cyclopropanation with a metal-carbene has been far less

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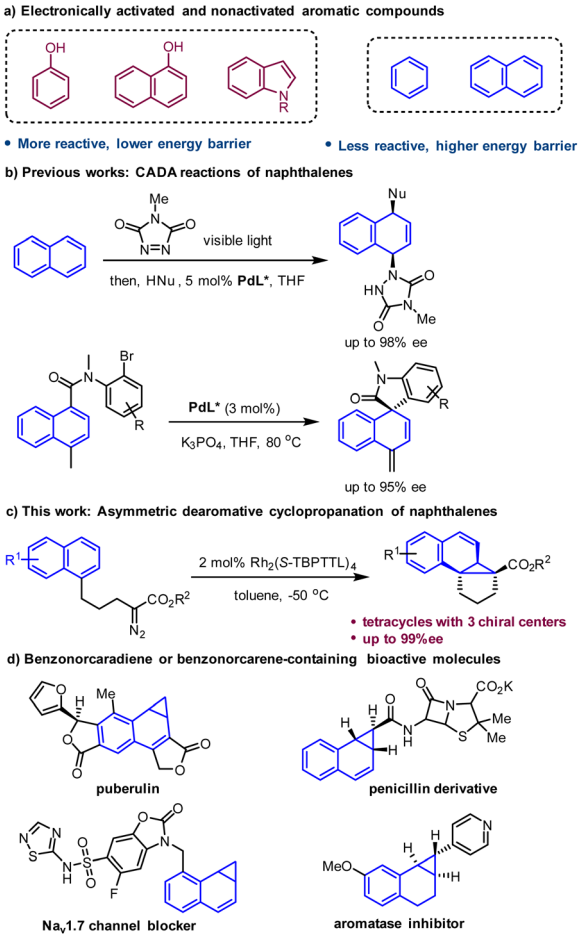


Scheme 1 CADA reactions of naphthalenes.

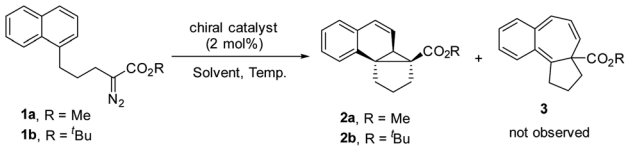
explored due to the facile electrocyclic ring opening of norcaradiene (the arene cyclopropanation product) to form the more stable tautomer cycloheptatriene.[9,10] Herein, we reported a highly enantioselective intramolecular dearomative cyclopropanation of naphthalenes with a metal-carbene intermediate to construct benzonorcaradiene-containing tetracyclic compounds with three stereogenic centers, two of which are all-carbon quaternary centers (Scheme 1c). Benzonorcaradiene and benzonorcarene structures have been found in many biologically active molecules (Scheme 1d).[11]

Results and discussion

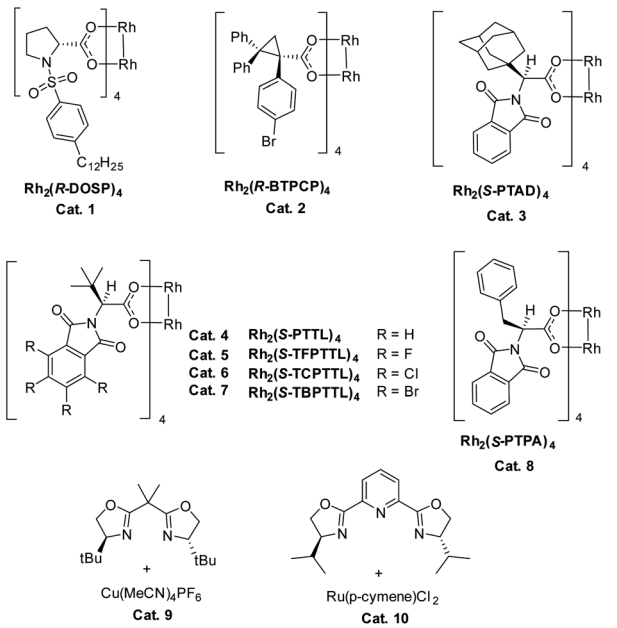
We commenced our study with naphthalene-tethered diazoester **1a** as the model substrate. Initially, we examined a range of chiral catalysts for the asymmetric dearomative cyclopropanation of naphthalenes (Table 1, entries 1–10). When dirhodium carboxylates were used as catalysts, the [2 + 1] cycloaddition proceeded smoothly at low temperature (+78 °C) and afforded polycyclic product **2a** in good yield; no Buchner reaction product **3** was observed. The conversion of benzonorcaradiene **2a** to cycloheptatriene **3** was kinetically and/or thermodynamically disfavored by concomitant dearomatization. Davies's $Rh_2[S\text{-DOSP}]_4$,[12] $Rh_2[R\text{-BTPCP}]_4$[13] and $Rh_2[S\text{-PTAD}]_4$,[14] which exhibited high enantioselectivity for carbene C–H bond insertion and alkene cyclopropanation, afforded **2a** in high yield but with modest enantioselectivity. The *tert*-leucine-derived catalyst $Rh_2[S\text{-PTTL}]_4$[15] that was developed by Hashimoto exhibited good enantiocontrol for the dearomative [2 + 1] cycloaddition, delivering **2a** in 66% ee.

Halogen substituents on the ligand have obvious influence on the performance of this kind of catalyst. As shown in entries

Table 1 Screening of catalysts and reaction conditions[a,b,c]



Entry	R	Catalyst	Solvent	T [°C]	%Yield	ee%
1	Me	Cat. 1	DCM	−78	88	39
2	Me	Cat. 2	DCM	−78	87	42
3	Me	Cat. 3	DCM	−78	89	45
4	Me	Cat. 4	DCM	−78	94	66
5	Me	Cat. 5	DCM	−78	94	45
6	Me	Cat. 6	DCM	−78	90	67
7	Me	Cat. 7	DCM	−78	90	78
8	Me	Cat. 8	DCM	−78	90	21
9	Me	Cat. 9	DCM	0	0	
10	Me	Cat. 10	DCM	0	0	
11	tBu	Cat. 7	DCM	−78	46	90
12	tBu	Cat. 7	DCM	−20	56	95
13	tBu	Cat. 7	DCM	−50	64	97
14	tBu	Cat. 7	Hexane	−50	46	93
15	tBu	Cat. 7	TBME	−50	53	93
16	**tBu**	**Cat. 7**	**Toluene**	**−50**	**80**	**99**



[a] Reactions were conducted with **1a** or **1b** (0.1 mmol) and the catalyst (2 mol%) in 2 ml solvent under Ar. [b] Isolated yields. [c] Determined by HPLC analysis.

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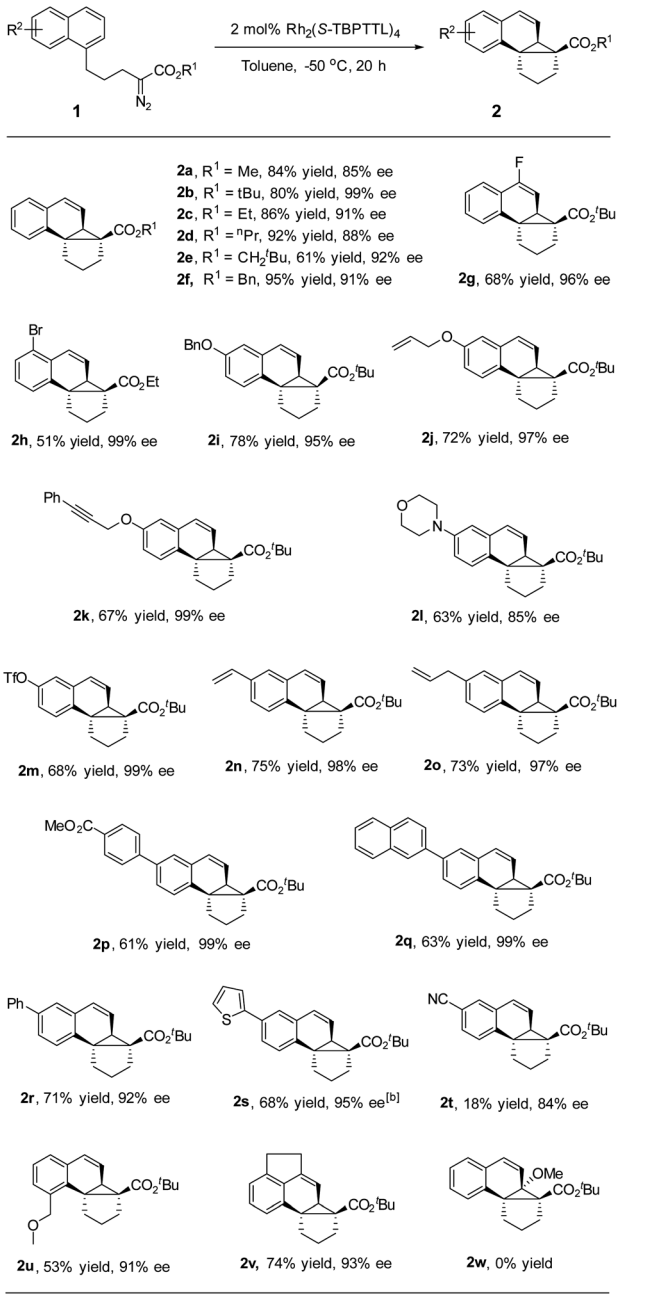
5–7, the fluorinated, chlorinated and brominated analogs of $Rh_2[S\text{-PTTL}]_4$ afforded **2a** in 45% ee, 67% ee and 78% ee, respectively. Compared to $Rh_2[S\text{-PTTL}]_4$, the phenylalanine-derived catalyst $Rh_2[S\text{-PTPA}]_4$ was less effective in achieving enantiocontrol for the reaction, affording **2a** in 21% ee. Other metal catalysts, such as Cu(I)/Box[16] and Ru(II)/Pybox,[17] which have demonstrated to be effective for enantioselective alkene cyclopropanation with diazoesters, failed to catalyze the dearomative cyclopropanation. The major side product was found to be an α,β-unsaturated ester (60–70% yields) generated *via* β-hydrogen migration.[18] With $Rh_2[S\text{-TBPTTL}]_4$ as a catalyst and the use of sterically bulky *tert*-butyl ester, the enantioselectivity was significantly improved to 90% (entry 11), albeit with a lower yield than that achieved with methyl ester. Increasing the temperature from −78 °C to −50 °C improved both the yield and the enantioselectivity of the product. The effect of the solvent was also examined, and toluene proved to be the optimal solvent, affording **2b** in 80% yield and with 99% ee (entry 16). No reaction between **1b** and toluene was observed. The stereochemistry of **2b** was assigned based on single-crystal X-ray diffraction analysis of its analogs **6** and **7**.

After determining the optimized conditions, the substrate scope was examined. As depicted in Table 2, a variety of naphthalene-tethered diazoesters underwent intramolecular dearomative cyclopropanation with excellent enantioselectivity. Compared to sterically bulky *tert*-butyl ester and neopentyl ester, methyl, ethyl, propyl and benzyl esters led to a slightly lower enantioselectivity but higher yields (**2a–2f**). Various substituents at positions **4**, **5**, **6** and **8** of the naphthalene ring were well tolerated in the reaction, regardless of whether they were electron-donating or electron-withdrawing groups, affording the desired products in 84–99% ee. 2-Substituted substrate (**2w**) was not compatible with the reaction and failed to generate the corresponding cycloadduct, presumably due to steric hindrance, and the major product in this reaction was an α,β-unsaturated ester generated *via* β-hydrogen migration. Substrates bearing electron-donating groups (6-alkoxy) exhibited good reactivity and excellent enantioselectivity, affording the desired products in good yield and high enantioselectivity (95–99% ee, **2i–2k**). An electron-withdrawing group (6-CN, **2t**) made the naphthalene ring less reactive for dearomative cyclopropanation, leading to the desired products in lower yield than that achieved by its electron-donating counterparts, which is consistent with the electrophilicity of rhodium-carbene.[9a,b] Notably, alkene and alkyne moieties, which are reactive functional groups in carbene transfer reactions, remained unaffected during rhodium catalysis (97–99% ee, **2j**, **2k**, **2n**, and **2o**). Various aryl substituents, including phenyl, naphthyl and thienyl groups, were well tolerated in the dearomative [2 + 1] cycloaddition, delivering the desired products with high enantioselectivity (92–99% ee, **2p–2s**). Moreover, halide, amino, OTf and ester moieties were compatible with rhodium catalysis and afforded products with high enantioselectivity (85–99% ee, **2g**, **2h**, **2l**, **2m**, and **2p**). These synthetically useful functional groups are expected to enable many further transformations, for instance, various cross-coupling reactions of aryl (pseudo) halides.[19] When an acenaphthene-tethered diazoester was subjected to the rhodium catalysis, a fused pentacycles was obtained in good yield and excellent enantioselectivity (93% ee and **2v**).

The obtained tetracyclic products could be readily converted to other complex polycycles. For instance, the hydrogenation of **2b** with H_2, which was catalyzed by $Pd(OH)_2$ at room temperature, afforded polycycle **4** in 88% yield and 94% ee. Interestingly, when hydrogenation was performed with Pd/C as the

Table 2 Substrate scope[a]



[a] Reactions were conducted with 1 (0.1 mmol) and catalyst (2 mol%) in 2 mL toluene at −50 °C under Ar. [b] −40 °C obtained in good yield and excellent enantioselectivity (93% ee)

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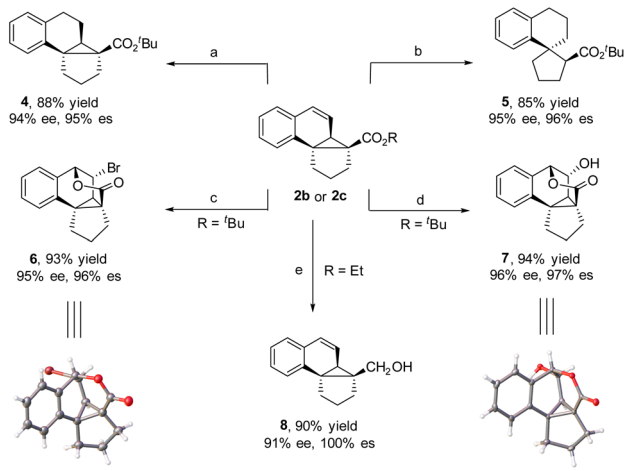

Scheme 2 Synthetic transformation. Reaction conditions: (a) $Pd(OH)_2$, EA, rt, and 4 h. (b) Pd/C (10%), EA, rt, and 6 h. (c) NBS (1.5 equiv.), CH_3OH, 50 °C, and 2 h. (d) CH_3O_3Re (1.5 mol%), pyrazole (12 mol%), H_2O_2, MnO_2 (8 mol%), DCM, and 0 °C–rt. (e) $LiAlH_4$ (1.5 equiv.), THF, rt, and 3 h.

catalyst, **2b** underwent cyclopropane ring opening to generate tricyclic spiro tetrahydronaphthene **5** in 85% yield and 95% ee, where compound **4** is an intermediate in the reaction. When **2b** was treated with NBS at room temperature, bridged pentacycle **6** was obtained as a single stereoisomer in 93% yield and 95% ee. The bridged pentacyclic compound contained five consecutive stereogenic centers, two of which were all-carbon quaternary centers. The cyclization reaction likely proceeded *via* NBS-mediated formation of a bromonium ion with the C=C bond of **2b** and subsequent nucleophilic addition of the ester group to the bromonium ion with concomitant loss of the *tert*-butyl moiety. Similarly, when **2b** was subjected to H_2O_2 and a catalytic amount of CH_3O_3Re and MnO_2 (a protocol for the epoxidation of C=C bonds),[5i] bridged pentacyclic compound **7** was obtained in 94% yield and 96% ee. The structures of **6** and **7** were determined by X-ray crystallographic analysis. Although the α-carbon is a quaternary center with high steric bulk, the ester moiety of polycyclic product **2c** was readily reduced by $LiAlH_4$ at room temperature to a hydroxy group in high yield and high enantioselectivity (**8**) (Scheme 2).

Conclusions

In summary, we developed an enantioselective dearomative cyclopropanation of naphthalenes to construct benzonorcaradiene-containing tetracyclic compounds. Chiral dirhodium catalyst Rh_2[*S*-TBPTTL]$_4$ efficiently promoted the intramolecular dearomatization of naphthalenes in good yield and excellent enantioselectivity. Three stereogenic centers, including two all-carbon quaternary centers, were created in the dearomatization reaction. Moreover, a variety of functional groups were compatible with this rhodium catalysis. The obtained products could be readily converted to other complex polycycles in high yield while retaining the high ee value.

Data availability

We have experimental or computational data associated with this article, and these data have been included in Electronic supplementary information (ESI) which are available free of charge at **https://doi.org/10.1039/d2sc04509e**.

Author contributions

F. G., R. Z. and X. R. conceived and performed the experiments. C.-Y. Z., C. W. and Z. G. conceived and directed the project and wrote the paper. All the authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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