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To be cited as: *Chem. Eur. J.* 10.1002/chem.201905519

Link to VoR: http://dx.doi.org/10.1002/chem.201905519

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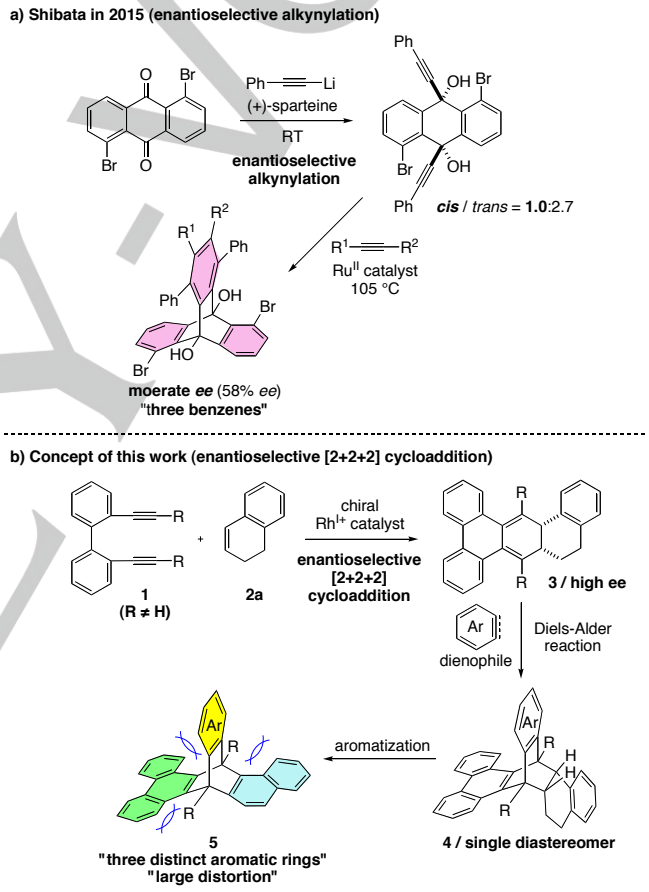
Enantioselective Synthesis of Distorted π-Extended Chiral Triptycenes Consisting of Three Distinct Aromatic Rings by Rhodium-Catalyzed [2+2+2] Cycloaddition

Yukimasa Aida,[a] Yu Shibata,[a] and Ken Tanaka*[a]

Abstract: The enantioselective synthesis of distorted π-extended chiral triptycenes, consisting of three distinct aromatic rings, has been achieved with high *ee* value of 87% by the cationic rhodium(I)/segphos complex-catalyzed enantioselective [2+2+2] cycloaddition of 2,2'-di(prop-1-yn-1-yl)-5,5'-bis(trifluoromethyl)-1,1'-biphenyl with 6-methoxy-1,2-dihydronaphthalene followed by the diastereoselective Diels-Alder reaction and aromatization. Demethoxy derivatives were also synthesized by the C-O bond cleavage. In this synthesis, the use of the electron-deficient diyne and the electron-rich alkene is crucial to suppress the undesired strain-relieving carbocation rearrangement and stabilize the distorted triptycene structure.

Triptycene, a molecule in which three benzene rings are annelated with barrelene, is widely used as a rigid propeller-shaped segment for the development of three-dimensional functional materials.[1] For example, triptycene derivatives have been used in molecular machines,[2] ligands,[3] functional polymers,[4] and domain-boundary-free organic thin films.[5] In 1942, Bartlett achieved the first synthesis of triptycene, while this synthesis was not practical due to long reaction steps.[6a] In 1956, Wittig and Ludwig reported the practical one-step synthesis of triptycene by the Diels-Alder reaction of anthracene with benzyne.[6b] After this report, a number of efficient methods (e.g., the Friedel-Crafts reaction,[6c] the [2+2+2] cycloaddition,[6d,e] and the [2+2] cycloaddition[6f,g] approaches) have been reported for the synthesis of structurally diverse triptycene derivatives.

Besides, since triptycene has two sp^3 carbon atoms, molecular asymmetry is manifested by introducing substituents into the aromatic rings, and chiral triptycene derivatives have been used in chiral ligands[7] and circularly polarized luminescence materials.[8] However, only one example of the enantioselective synthesis of chiral triptycene derivatives has been reported so far,[9] although several examples of optical resolution of racemic chiral triptycene derivatives by using chiral reagents[10] or chiral HPLC columns[11] have been reported. In 2015, Shibata reported the enantioselective synthesis of chiral triptycenes, consisting of three substituted benzene rings, by the sparteine-mediated enantioselective alkynylation of 1,5-dibromoanthracene-9,10-dione followed by the ruthenium(II)-catalyzed [2+2+2] cycloaddition (Scheme 1a).[9] However, the enantioselective alkynylation afforded the desired *cis* isomer as a minor product with moderate *ee* value of 58%.



Scheme 1. Enantioselective synthesis of chiral triptycenes.

Recently, our research group reported the highly enantioselective synthesis of chiral multicyclic cyclohexadienes by the cationic rhodium(I)/difluorphos complex-catalyzed [2+2+2] cycloaddition of biphenyl-linked internal 1,7-diynes with indene.[12,13] From this successful enantioselective catalysis, we came up with the following approach for the enantioselective synthesis of a chiral triptycene. We anticipated that the rhodium(I)-catalyzed enantioselective [2+2+2] cycloaddition[14,15] of biphenyl-linked internal 1,7-diyne **1** with 1,2-dihydronaphthalene (**2a**) instead of indene would also afford chiral multicyclic cyclohexadiene **3** with high yield and *ee* value. The subsequent Diels-Alder reaction with dienophile would proceed selectively on the convex face to give chiral dihydrobarrelene **4** as a single diastereomer. The subsequent

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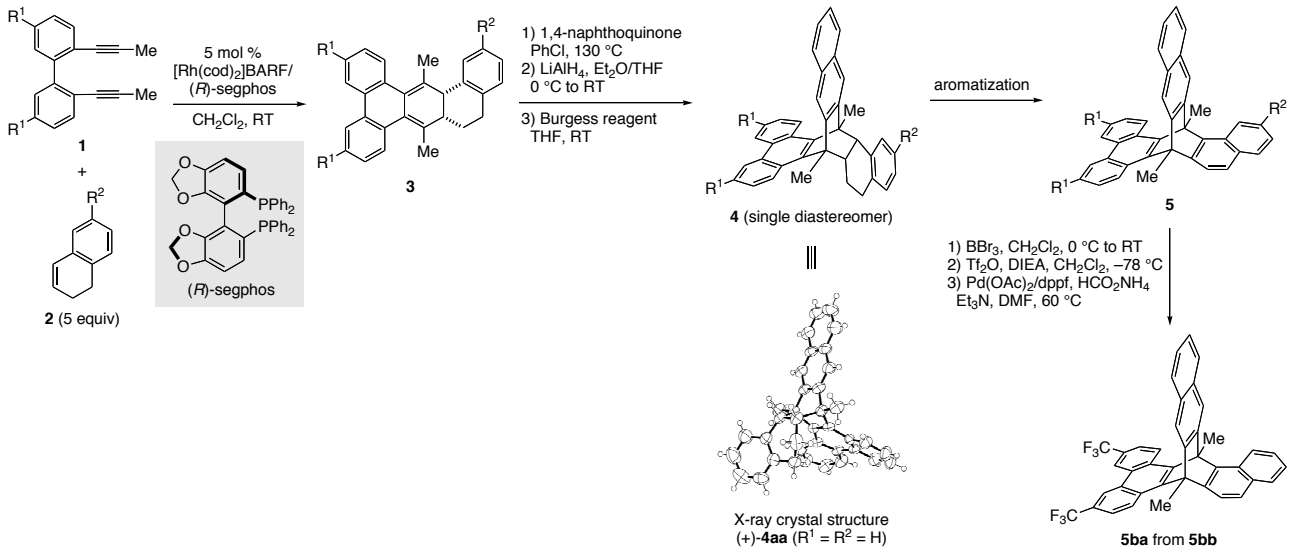
oxidative aromatization would afford π-extended chiral triptycene **5**, consisting of three distinct aromatic rings[16] (Scheme 1b). However, the large distortion would exist in the targeted chiral triptycene **5** due to the presence of three large steric repulsion between the bridgehead substituents (R) and the neighboring aromatic rings.[6g] Because of this large distortion, there are concerns about the stability of **5**. In this Communication, we have established that the appropriate introduction of substituents into the biphenyl-linked 1,7-diyne **1** and 1,2-dihydronaphthalene (**2a**) realizes this concept.

Scheme 2 displays the enantioselective synthesis of chiral triptycene **5**. The enantioselective [2+2+2] cycloaddition of biphenyl-linked internal 1,7-diyne **1a** with 1,2-dihydronaphthalene (**2a**) proceeded at 40 °C in the presence of a cationic rhodium(I)/(*R*)-segphos complex (20 mol %) to give the desired chiral cyclohexadiene (+)-**3aa** in good yield with high *ee* value of 88% (entry 1). Although the Diels-Alder reaction of (+)-**3aa** with benzyne did not proceed, that with 1,4-naphthoquinone followed by reductive aromatization using $LiAlH_4$ and the Burgess reagent[17] proceeded to give the desired triptycene precursor (+)-**4aa** in 30% yield with complete diastereoselectivity. However, unfortunately, the treatment of (+)-**4aa** with DDQ did not afford the desired chiral triptycene (+)-**5aa**, instead, an unidentified complex mixture of products was generated.[18]

Possible reaction pathways for the treatment of **4** with DDQ are shown in Scheme 3. The oxidation of **4** with DDQ would generate tertiary carbocation **A**. However, strain-relieving carbocation rearrangement[19] might proceed to give tertiary carbocation **B**, which leads to a complex mixture of products. We anticipated that the introduction of an electron-donating group at the 6-position (R^2) of 1,2-dihydronaphthalene (**2a**) facilitates the oxidation reaction and induces the generation of regioisomeric secondary carbocation intermediate **C**, in which the carbocation rearrangement dose not proceed. Deprotonation from **C** would afford dihydronaphthalene **D**. Subsequent



Entry	**1** (R^1)	**2** (R^2)	**3** / % yield (% *ee*)	**4** / % yield from **3** (% *ee*)	Aromatization Conditions	**5** / % yield (% *ee*)	**5ba** / % yield from **5bb** (% *ee*)
1[a]	**1a** (H)	**2a** (H)	(–)-**3aa** / 69 (88)	(+)-**4aa** / 30 (87)	DDQ (5 equiv), PhCl 130 °C, 12 h	(+)-**5aa** / 0	–
2[a]	**1a** (H)	**2b** (OMe)	(±)-**3ab** / 63	(±)-**4ab** / 22	DDQ (5 equiv), PhCl 130 °C, 12 h	(±)-**5ab** / 0	–
3[a]	**1b** (CF_3)	**2b** (OMe)	(–)-**3bb** / 72 (78)	–	–	–	–
4	**1b** (CF_3)	**2b** (OMe)	(–)-**3bb** / >99 (88)	–	–	–	–
5[b]	**1b** (CF_3)	**2b** (OMe)	(–)-**3bb** / 95 (88)	(+)-**4bb** / 43 (87)	DDQ (3.2 equiv), PhCl 40 °C, 72 h	(+)-**5bb** / 20 (87)	(+)-**5ba** / 62 (87)
6[b,c]	**1b** (CF_3)	**2b** (OMe)	(+)-**3bb** / 99 (87)	(–)-**4bb** / 41 (87)	DDQ (3.2 equiv), PhCl 40 °C, 72 h	(–)-**5bb** / 19 (87)	(–)-**5ba** / 58 (87)
7[a]	**1b** (CF_3)	**2a** (H)	(±)-**3ba** / 79	(±)-**4ba** / 18	DDQ (5 equiv), PhCl 130 °C, 12 h	(±)-**5ba** / 0	–

Scheme 2. Screening of substituents and reaction conditions for the enantioselective synthesis of chiral triptycenes. **1** (0.20 mmol) was used. BARF = tetrakis[bis(3,5-trifluoromethyl)phenyl]borate. Burgess reagent = (methoxycarbonylsulfamoyl)triethylammonium hydroxide inner salt. DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. Tf_2O = trifluoromethanesulfonic anhydride. DIEA = *N*,*N*-diisopropylethylamine. DDQ = 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. dppf = 1,1'-bis(diphenylphosphino)ferrocene. [a] $[Rh(cod)_2]BF_4$/(*R*)-segphos (20 mol %) was used at 40 °C. cod = 1,5-cyclooctadiene. [b] The preparative-scale reaction using **1b** (1.00 mmol). [c] (*S*)-segphos was used.

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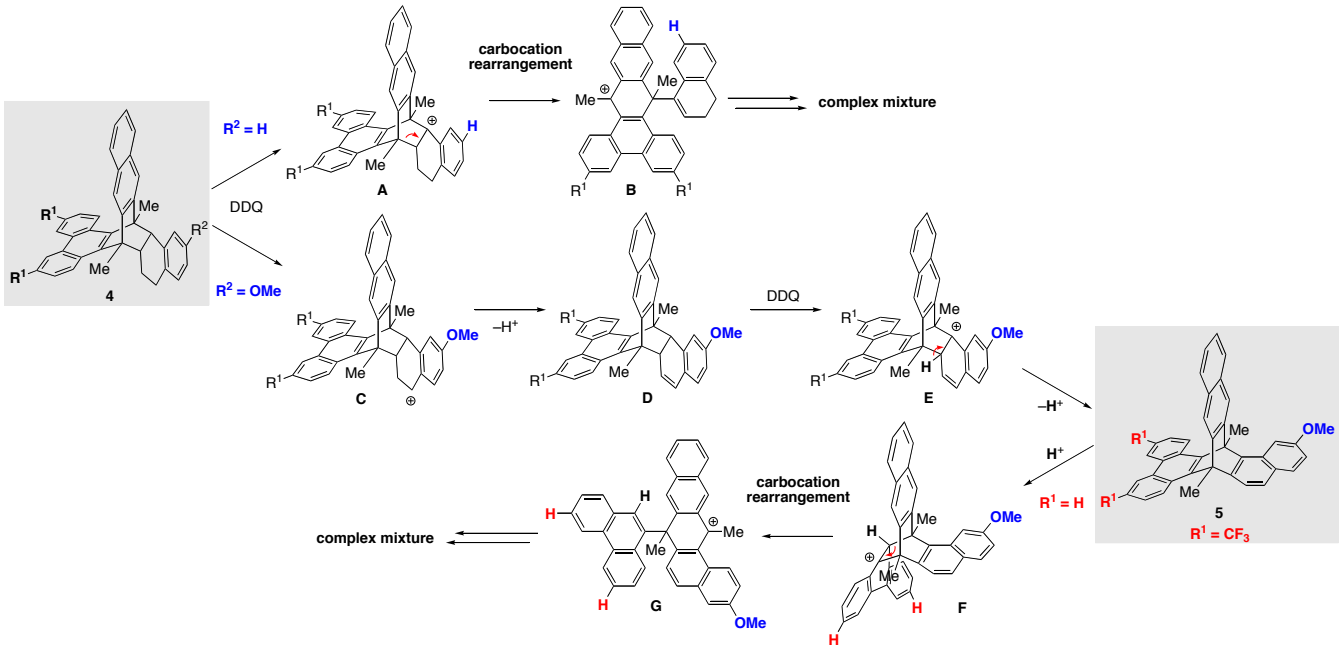

Scheme 3. Possible reaction pathways for treatment of **4** with DDQ.

oxidation with DDQ would afford tertiary carbocation **E**, which is spontaneously aromatized through deprotonation to give the desired triptycene **5**. Thus, the oxidative aromatization of racemic triptycene precursor (±)-**4ab**, prepared from **1a** and **2a**, was conducted with DDQ, but we failed to obtain the corresponding triptycene (±)-**5ab**. We anticipated that protonation of the phenanthrene moiety of **5ab** would occur to generate carbocation **F** due to the large distortion. Subsequent strain-relieving carbocation rearrangement would generate carbocation **G** that leads to the decomposition of **5ab**. We expected that the use of 1,7-diyne **1b**, bearing the electron-withdrawing CF_3 groups at the 5- and 5'-positions (R^1), might inhibit this protonation and stabilize triptycene **5**.

Thus, the enantioselective [2+2+2] cycloaddition of 1,7-diyne **1b** with 6-methoxy-1,2-dihydronaphthalene (**2b**) was conducted under the same conditions for **1a** and **2a**. Although the desired chiral cyclohexadiene (+)-**3bb** was obtained in good yield, the *ee* value was lower than that of (+)-**3aa** (entry 3). Fortunately, optimization of reaction conditions (Table S3) revealed that the use of $[Rh(cod)_2]BARF$ instead of $[Rh(cod)_2]BF_4$ at room temperature improved both the yield and the *ee* value to >99% and 88%, respectively, even using the low catalyst loading of 5 mol % (entry 4). The present enantioselective [2+2+2] cycloaddition was scalable, and the preparative-scale reaction using 1.00 mmol of **1b** afforded (+)-**3bb** in 95% yield with 88% *ee* (entry 5). The Diels-Alder reaction of (+)-**3bb** with 1,4-naphthoquinone followed by reductive aromatization proceeded to give triptycene precursor (+)-**4bb** in higher yield than that of (+)-**4aa**. As expected, the oxidative aromatization of (+)-**4bb** with DDQ proceeded under mild conditions[18] to give the desired chiral triptycene (+)-**5bb** in 20% yield without racemization.[20] The opposite enantiomer (–)-**5bb** was also prepared in a preparative scale by the same sequence used for (+)-**5bb** employing (*S*)-segphos as a ligand (entry 6). Finally, demethoxy derivatives (+)-**5ba** and (–)-**5ba** were synthesized from (+)-**5bb** and (–)-**5bb**, respectively, by demethylation, triflation, and the palladium(0)-catalyzed C-O bond cleavage[21] sequence (Scheme 2). Both electron-deficient diyne **1b** and electron-rich alkene **2b** are necessary to suppress the undesired carbocation rearrangement. Thus, the oxidative aromatization of (±)-**4ba**, derived from **1b** and **1a**, with DDQ was also unsuccessful (entry 7).[22]

A single crystal of (+)-**4aa** was obtained by recrystallization from CH_2Cl_2/MeOH, and its crystal structure was unambiguously determined by a single crystal X-ray diffraction analysis (Scheme 2, Figure S3).[23] Although single crystals of **5bb** and **5ba** were not obtained, the triptycene structures of **5bb** and **5ba** were confirmed by ^1H, ^{13}C, and 2D-NMR spectroscopy, and HRMS (high-resolution mass spectrometry).[18] To confirm the existence of the large distortion, the theoretical optimization of the structure of (9*S*,16*R*)-**5ba** was conducted, as shown in Figure 1. Indeed, the large distortion exists in triptycene **5**, especially in the phenanthrene moiety.

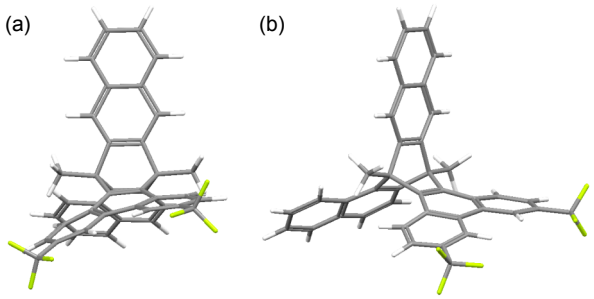

Figure 1. Optimized structures of (9*S*,16*R*)-**5ba** calculated at the wB97XD/6-311G(d) level of theory, (a) side view, (b) diagonal view.

The ECD (electronic circular dichroism) signals were observed from (+)-**5ba** and (–)-**5ba** with opposite signs and similar intensities, namely mirror images (Figure 2). Additionally, the absolute configuration of (+)-**5ba** was determined to be 9*S*,16*R* by comparing the observed ECD spectrum of (+)-**5ba** with the theoretical ECD spectrum of (9*S*,16*R*)-**5ba** (Figure 2). This absolute configuration is consistent with a plausible enantioselection mechanism of the cationic rhodium(I)/(*R*)-segphos complex-catalyzed [2+2+2] cycloaddition of **1b** with **2b** (Figure S2).

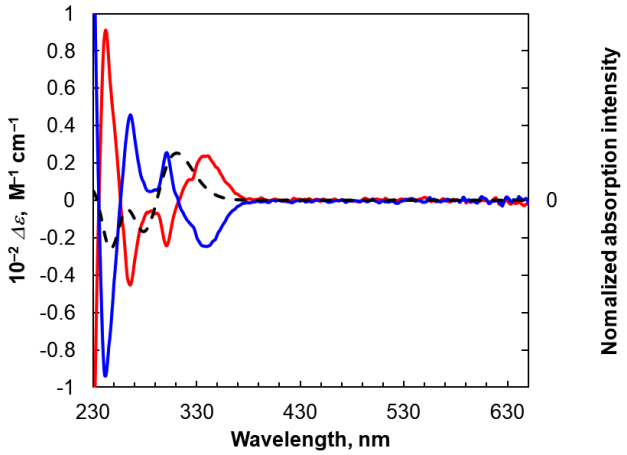

Figure 2. Experimental ECD spectra of (+)-**5ba** (red plain line) and (–)-**5ba** (blue plain line) in EtOH (1.0×10^{-5} M), and theoretical ECD spectrum of (9*S*,16*R*)-**5ba** (black broken line) calculated by the TD-DFT method at the wB97XD/6-311G(d) level with IEFPCM (ethanol).

In summary, we have achieved the highly enantioselective synthesis of distorted π-extended chiral triptycenes, consisting of three distinct aromatic rings, with high enantioselectivity (87% *ee*) by the cationic rhodium(I)/segphos complex-catalyzed enantioselective [2+2+2] cycloaddition of 2,2'-di(prop-1-yn-1-yl)-5,5'-bis(trifluoromethyl)-1,1'-biphenyl with 6-methoxy-1,2-dihydronaphthalene followed by the diastereoselective Diels-Alder reaction, and reductive and oxidative aromatization reactions. Demethoxy derivatives were also synthesized by demethylation, triflation, and the palladium(0)-catalyzed C-O bond cleavage sequence. In this synthesis, the use of the electron-deficient diyne and the electron-rich alkene is crucial to suppress the undesired strain-relieving carbocation rearrangement in the oxidative aromatization step, leading to the desired triptycene. Additionally, the introduction of the electron-withdrawing CF_3 groups to the triptycenes might stabilize the distorted triptycene structure. We believe that the present process would be a useful strategy for the enantioselective synthesis of chiral triptycenes. Future works will include functionalization of the thus obtained chiral triptycenes, leading to chiral ligands.

Acknowledgements

This research was supported partly by Grants-in-Aid for Scientific Research (JP26102004 and JP19H00893) from JSPS (Japan). Y.A. thanks JSPS research fellowship for young scientists (No. 17J08763). We thank Takasago International Corporation for the gift of H_8-binap, segphos, tol-segphos, xyl-segphos, and dtbm-segphos, Umicore for generous support in supplying the palladium and rhodium complexes, and Central Glass Co., Ltd. for the gift of trifluoromethanesulfonic anhydride and 1,1,1,3,3,3-hexafluoro-2-propanol.

Keywords: chiral triptycenes • cyclic alkenes • enantioselective synthesis • rhodium • [2+2+2] cycloaddition

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[20] The oxidative aromatization of dihydrobarrelene **4cb**, bearing the moderately electron-withdrawing chloro groups, with DDQ was also examined. Although the desired triptycene **5cb** was generated in a trace amount, this compound decomposed even under weakly acidic conditions, e.g., isolation on a silica gel chromatography and the NMR measurement in $CDCl_3$.

4cb **5cb** / trace

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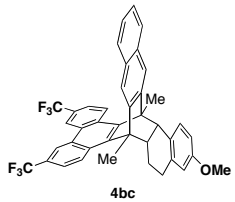
[22] The use of 6-methoxy-1,2-dihydronaphthalene (**2b**) is also crucial, and the oxidative aromatization of **4bc**, derived from 7-methoxy-1,2-dihydronaphthalene (**2c**), with DDQ was unsuccessful.



4bc

[23] CCDC 1957627 [(+)-**4aa**] contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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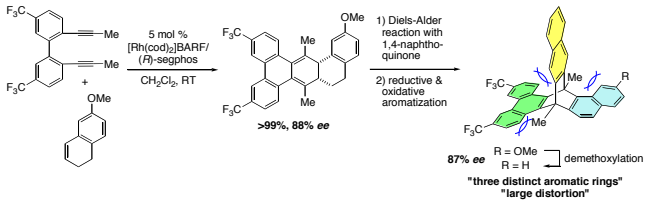

The enantioselective synthesis of distorted π-extended chiral triptycenes, consisting of three distinct aromatic rings, has been achieved with high *ee* value of 87% by the rhodium(I)-catalyzed [2+2+2] cycloaddition followed by the Diels-Alder reaction and aromatization. Demethoxy derivatives were also synthesized by the C-O bond cleavage. In this synthesis, the use of an electron-deficient diyne and an electron-rich alkene is crucial to suppress the undesired strain-relieving carbocation rearrangement and stabilize the distorted triptycene structure.

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Enantioselective Synthesis of Distorted π-Extended Chiral Triptycenes Consisting of Three Distinct Aromatic Rings by Rhodium-Catalyzed [2+2+2] Cycloaddition