

論文 / 著書情報  
Article / Book Information

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種別(和文)	論文要旨
Type(English)	Summary

## 論文要旨

THESIS SUMMARY

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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

Planar chiral cyclophanes are a macrocyclic molecule consisting of aromatic ring and ansa-chain, which served as a unique chiral platform originated from the facial chemistry derived from the restricted rotation around the aromatic ring core. Since a construction of the cyclophane framework with control of its facial chemistry is one of challenging task in organic synthesis, several synthetic approaches toward chiral planar cyclophanes including natural products have been studied. In this thesis, a generalized synthetic approach toward planar chiral carba-paracyclophanes and their functional applications was described.

In chapter 1, *Synthetic approaches toward the unsymmetric carba-paracyclophanes* is described. The modular synthetic methodology toward the unsymmetric planar chiral paracyclophanes by stepwise coupling of the side chains via successive Suzuki cross coupling reactions was accomplished. First of all, synthetic protocol of the side chain unit was modified by exploiting one-pot iodination/Horner–Wadsworth–Emmons reaction to construct  $\alpha$ -halovinyl sulfoxide side chain system in a more flexible way. By this method, side chain units having different chain length were prepared. Previously, our laboratory has developed the novel synthetic methodology toward the planar chiral paracyclophanes by regulating a local conformation of the side chain of the styrene analogous. Accordingly, two identical side chains were simultaneously introduced to the aromatic core; therefore the method is limited for the synthesis of only  $C_2$ -symmetric paracyclophanes. However, the introduction of different side chains became available in a stepwise way by modifying the aromatic ring unit from diboronic acid to monoboronic acid ester. In this way, the synthesis of [13]paracyclophane, which cannot be attained by the previous procedure, were successfully achieved. Next, this stepwise protocol was applied for the variation of the paracyclophanes. So far, two sulfinyl groups were indispensable to fix the conformation via hydrogen bonding during the ring-closing olefin metathesis, however, it has been clarified that only single hydrogen bond can control the planar chirality during the cyclization. For example, one of the sulfinyl groups in the cyclization precursors was switched to achiral substituent groups, such as methyl or sulfonyl group, and the cyclization of each precursor was executed, which progressed smoothly to give the desired cyclophane products. In

addition, their kinetic behaviors were observed via VT-NMR, and the rotational barrier of sulfonylated side chain was estimated. Finally, cyclization of precursors having no hydrogen bond were studied to figure out the alkyl group of aromatic unit can transform the chiral information of the sulfinyl group to the planar chemistry via the construction of the cyclophane skeleton.

In chapter 2, *Functionalization of the paracyclophanes*, further transformations of the carba-paracyclophanes were described. From our cyclophane systems, functionalization of the paracyclophanes can be possible utilizing the sulfinyl group and phenol. First of all, the sulfinyl group can be applied for the sulfoxide-lithium exchange to generate vinyl anion which can be trapped by either protonating or formylating reagents. From the bis-aldehyde cyclophane derivative, the side chains can be elongated via Wittig reaction, which followed by the ring-closing olefin metathesis to construct the second macrocyclic system. In this way, branched type of double-strand cyclophane derivative can be achieved. After the reduction of the all olefins in the ansa-chain, the generated double-strand cyclophane has  $C_{2h}$ , an achiral molecule. Moreover, quinone derivative was attained by successive deprotection of the phenol group followed by the oxidation reaction. Due to the sterically hindered dual-ansa chain around the aromatic core, this quinone derivative turned out more stable compared to the usual quinone derivatives. In addition, the rotation of the aromatic core around the ansa-chain was restricted. Meanwhile, from the protonated cyclophane derivative, the phenol group was transformed to the nonafluorobutanesulfonyl group to apply the coupling reaction: the phenol group was transformed to the alkyl group via Sonogashira coupling reaction followed by hydrogenation. After several steps, including ring-closing olefin metathesis, the screwed type double-strand cyclophane derivative possessing  $D_2$  symmetry was successfully obtained.

In conclusion, we have established the stepwise coupling of side chains to attain planar chiral paracyclophanes by the stereocontrol based on hydrogen bond. In this way, various unsymmetric paracarbacyclophane derivatives having different functional groups were achieved and their kinetic behavior was described. In addition, from these multifunctional carba-paracyclophane systems, several kinds of paracyclophane derivatives were generated via functionalization such as sulfoxide-metal exchange reaction or cross-coupling reaction by utilizing the sulfinyl group and the phenol group. Throughout these transformations, two types of double-strand paracyclophane derivatives, such as the branched type and the screwed type, was synthesized successfully. Further application of this planar chiral paracyclophane system to develop new molecules and understanding their unusual stereochemical properties is on progress.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

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