Asymmetric Synthesis of Axially Chiral Diaryl Ethers by Rh-Catalyzed [2+2+2] Cycloaddition

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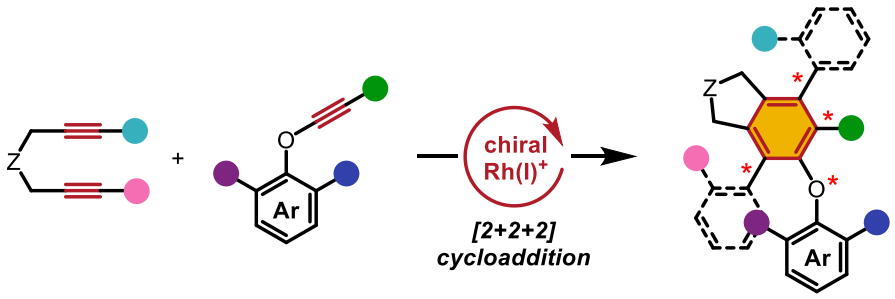
Diaryl ethers with bulky substituents at the ortho positions exhibit stable atropisomerism even at room temperature.[1] Atropisomeric diaryl ethers are expected to be used for novel catalysts and bioactive compounds because of their axial chirality and flexible ether structure, which led to extensive studies on their asymmetric synthesis in recent years. However, due to the instability of axial chirality, the asymmetric syntheses have been limited to desymmetrization reactions,[2] which have restricted the synthetically accessible structures.

In this study, we have developed the enantioselective synthesis of axially chiral diaryl ethers by cationic Rh(I)-catalyzed [2+2+2] cycloadditions of alkynyl ethers with 1,6-diynes. After optimizing the reaction conditions, the reaction proceeded with excellent yield and enantioselectivity. Furthermore, we also investigated the enantio- and diastereoselective synthesis of multiple atropisomeric axes, which have recently garnered significant attention in axially chiral compounds.[3] We also revealed the atropisomerism and their potential applications of synthesized axially chiral diaryl ethers.



✓ Various fanctional groups
✓ High regio-, diastereo and enantiosetectivity
✓ Multiple atropisomeric axes

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