o-Quinodimethane Atropisomers: Enantioselective Synthesis and Stereospecific Transformation

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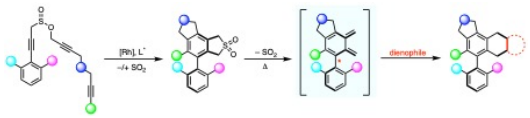
The use of *o*-quinodimethanes as reactive intermediates in Diels-Alder reactions is a versatile approach to synthesize complex polycyclic compounds.[1] There are different precursors to thermally generate *o*-quinodimethanes,[2] but due to the required high temperatures and the high reactivity of *o*-quinodimethanes, stereoselectivity to afford isomerically defined products constitutes a major challenge. Since our group is interested in developing methodologies for the synthesis of axially chiral biaryls by *de novo* ring construction,[3] we aimed to identify atropisomeric *o*-quinodimethanes. In this work we describe an intramolecular catalyst-stereocontrolled [2+2+2] cycloaddition of triyne substrates to generate atropisomeric benzocyclobutenes, benzocyclic sulfones and benzosultines which serve as precursors for the rotationally restricted aryl-o-quinodimethanes. Owing to their remarkable configurational stability, no racemization of the stereogenic axis occurs during the thermal ring opening. This allows for highly stereospecific Diels-Alder reactions of the *in situ* formed *o*-quinodimethanes with various dienophiles to form various polycyclic biaryls.



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