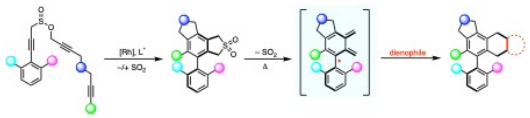
o-Quinodimethane Atropisomers: Enantioselective Synthesis and Stereospecific Transformation

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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.



[1] R. L. Funk, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1980**, *102*, 5253– 5261.

[2] J. L. Segura, N. Martin, *Chem. Rev.* **1999**, *99*, 3199– 3246;

[3] a) A. Link, C. Sparr, *Angew. Chem. Int. Ed.* **2014**, *53*, 5458; b) V. C. Fäseke, C. Sparr, *Angew. Chem. Int. Ed.* **2016**, *55*, 7261; c) R. M. Witzig, V. C. Fäseke, D. Häussinger, C. Sparr *Nat. Catal.* **2019**, *2*, 925.

[4] J. Dong[+], A. Ostertag[+], C. Sparr, *Angew. Chem. Int. Ed.* **2022**, *61*, e202211168.

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