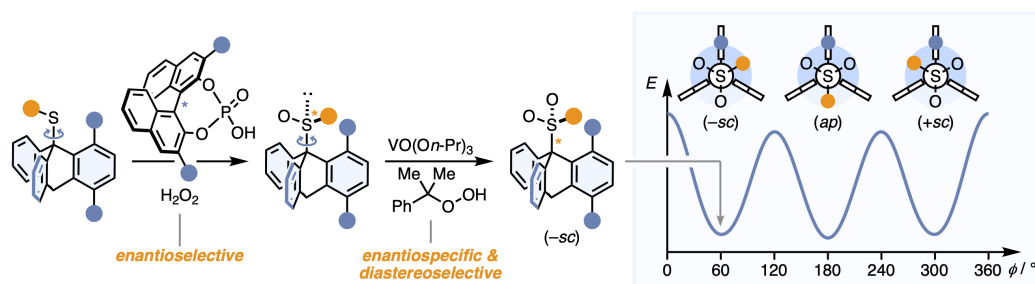


## Catalyst Control over Threefold Stereogenicity: C-S Atropisomeric Sulfones

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Numerous catalytic methods facilitate the stereoselective synthesis of atropisomers with rotationally restricted C-C, C-N, N-N and C-B single bonds between two planar moieties.<sup>[1]</sup> In contrast to these systems with two enantiomeric stereochemical states, catalyst control over atropisomers with more than two stereoisomers arising from one stereogenic axis was not accomplished until recently.<sup>[2]</sup> The Ōki triptycyl sulfones<sup>[3]</sup> exist in the form of three configurationally stable rotamers, namely the enantiomeric ( $\pm sc$ )-isomers and the symmetrical ( $ap$ )-conformer, which result from a rotationally restricted C-S bond connecting two tetrahedral fragments. We were able to stereoselectively access these systems by the catalyst-controlled oxidation of rotationally dynamic thioethers yielding enantioenriched sulfoxides, which subsequently were oxidized to the respective ( $sc$ )-sulfones.<sup>[4]</sup> While a chiral phosphoric acid catalyst defined the configuration of the sulfoxide stereocenter,<sup>[5]</sup> VO(*On*-Pr)<sub>3</sub> in combination with cumene hydroperoxide rendered the second oxidation to the atropisomeric sulfones with threefold stereogenicity a highly enantiospecific and diastereoselective process. Using this strategy, the ( $-sc$ )-sulfones were obtained in high degrees of stereoisomeric enrichment with selectivities of up to 94:6:1 ( $-sc$ ):( $+sc$ ):( $ap$ ), representing the to the best of our knowledge first example of catalyst control over C-S atropisomerism. Moreover, by choosing distinct reaction conditions, the diastereoselectivity of the second oxidation step could be directed towards the ( $ap$ )-sulfone making all three stereoisomeric states selectively accessible under catalyst control.



[1] G.-J. Mei, W. L. Koay, C.-Y. Guan, Y. Lu, *Chem* **2022**, *8*, 1855–1893.

[2] X. Wu, R. M. Witzig, R. Beaud, C. Fischer, D. Häussinger, C. Sparr, *Nat. Catal.* **2021**, *4*, 457–462.

[3] N. Nakamura, M. Ōki, *Chem. Lett.* **1984**, 143–146.

[4] T. A. Schmidt, S. Schumann, A. Ostertag, C. Sparr, *Angew. Chem. Int. Ed.* **2023**, *62*, e202302084.

[5] Z.-M. Liu, H. Zhao, M.-Q. Li, Y.-B. Lan, Q.-B. Yao, J.-C. Tao, X.-W. Wang, *Adv. Synth. Catal.* **2012**, *354*, 1012–1022.