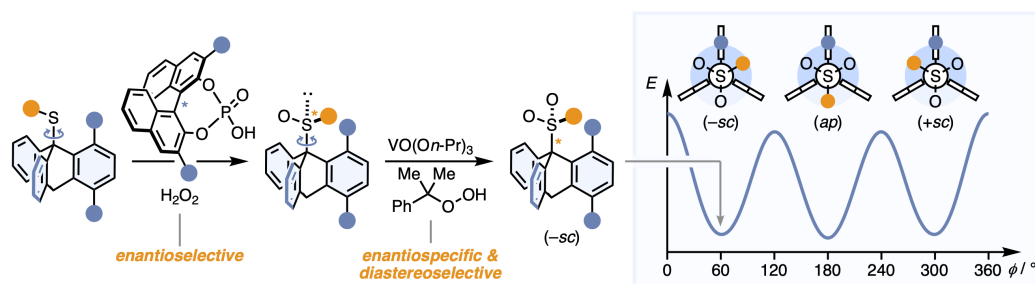


Catalyst Control over Threefold Stereogenicity: C-S Atropisomeric Sulfones

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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.^[1] 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.^[2] The Ōki triptycyl sulfones^[3] 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.^[4] While a chiral phosphoric acid catalyst defined the configuration of the sulfoxide stereocenter,^[5] VO(*On*-Pr)₃ 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.



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