



Planar-Chiral Hydrogen-Bond Donor Catalysts

By Jakob Schneider

 $\label{lem:condition: Neu. Neuware - This thesis focuses on the a condition of the condit$ first synthesis and application of planar-chiral [2.2] paracyclophane-derived hydrogen-bond donor catalysts, thereby inducing a unique chiral motif into the emerging field of thiourea organocatalysis. Reaction acceleration through hydrogen-bond catalysis has made a significant impact on the field, rendering the development of potent catalyst structures extremely valuable. Based on the [2.2] paracyclophane scaffold, mono- and bi-functional thiourea catalysts were prepared. The rigidity of the [2.2] paracyclophane structure leads to a unique setup of the substituents. In pseudo-geminal position to the thiourea moiety, a hydroxy group was selected and introduced as the second functionality. In a 12-step synthesis, the enantiopure hydroxy-substituted [2.2] paracyclophanylene thiourea was obtained. Furthermore, efficient access to enantiopure pseudo-geminally substituted 13-amino-4-bromo[2.2] paracyclophane was developed. The aminobromide was employed in cross-coupling reactions to yield arylated amino[2.2] paracyclophanes, exhibiting a broad range of electronic and steric features useful for organocatalytic applications. The developed catalysts were applied in asymmetric organic transformations and proved most useful in the transfer hydrogenation reaction. The hydroxysubstituted thiourea catalyst particularly exhibited catalytic activity and stereoselectivity. To shed light on the mode of action of this class of hydrogen-bond catalysts, various analytic methods were conducted. Through extensive crystallographic and...



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