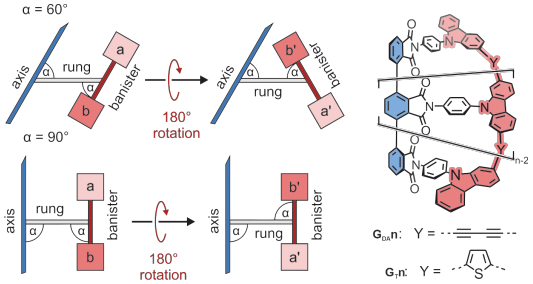
Geländer Molecules with Orthogonal Joints: Design, Synthesis, and Properties

A. D'Addio[1], M. Mayor[1]*

[1]Department Chemie, Universität Basel

Helical chirality can be induced by forcing long tethers around a central axis. Such molecular architectures are reminiscent of a spiral staircase's banister (or “Geländer” in German).[1] By extension of a single stringer (banister) in a ladder polymer, exclusively chiroptical active structures are formed with high racemization barriers.[2-4] In initial endeavors, regioisomers were formed in a late divergent synthetic step, owing to the inherent asymmetry of the designed building blocks. These regioisomers are formed due to the free rotation around the rung between the stringers, resulting in acute or obtuse angles to the nearest neighbor. This severely limits the feasibility of synthesizing oligomers with more than three repeating units.[3,4] This divergent step is circumvented by symmetrizing the molecular design.[5] The helical structures are formed in two subsequent robust homo-coupling steps as racemic mixtures, which are resolved to pure enantiomers by chiral stationary phase HPLC.



The design principle and synthesis of Geländer oligomers with orthogonal joints and their chiroptical study are presented.

[1] B. Kiupel et al., *Angew. Chem. Int. Ed.,* **1998,** 37, 3031.
[2] M. Rickhaus et al., *Chem. Soc. Rev.,* **2016**, 45, 1542.
[3] M. Rickhaus et al., *Angew. Chem. Int. Ed.,* **2014**, 53, 14587.
[4] R. Mannancherry et al., *Chem. Sci.,* **2018**, 53, 5758.
[5] A. D’Addio et al., *Chem. Eur. J.*, **2022**, e202201678.