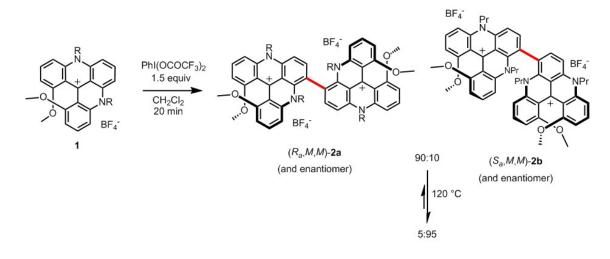
Homochiral recognition and excellent atroposelectivity in the oxidative coupling of cationic [4]helicenes

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Homochiral recognition by non-covalent interactions is a rather common phenomenon in helical structures.^[1] However, this asymmetric trend has been hardly exploited for the formation of covalent bonds between helicenes.^[2] Herein, we report the oxidative coupling of the cationic [4]helicenes **1**, which proceeds with a quasi exclusive homochiral recognition (96% selectivity) to yield chiral (racemic) dimers of type **2**. The lack of *meso* isomers is established by HRMS cross-over experiments. Moreover, this reaction is highly atroposelective forming preferentially (R_a ,M,M)-**2a** over (S_a ,M,M)-**2b** (and enantiomers) (ratio 90:10). The interconversion barrier from **2a** to **2b** is 26.4 kcal/mol at 60 °C in dmso-d₆. Strong chiroptical properties are observed, for both **2a** and **2b**, in the red visible region.



[1] Ryo Amemiya, Masahiko Yamaguchi, *Organic and Biomolecular Chemistry*, **2008**, 6, 26-35. Emmanuel Anger, Hiroki Iida, Tomoko Yamaguchi, Koutarou Hayashi, Daisuke Kumano, Jeanne Crassous, Nicolas Vanthuyne, Christian Roussel, Eiji Yashima, *Polymer Chemistry* **2014**, 5, 4909-4914.

[2] Daisuke Nakano, Rie Hirano, Masahiko Yamaguchi, Chizuko Kabuto, *Tetrahedron Letters*, **2003**, 44, 3683-3686.