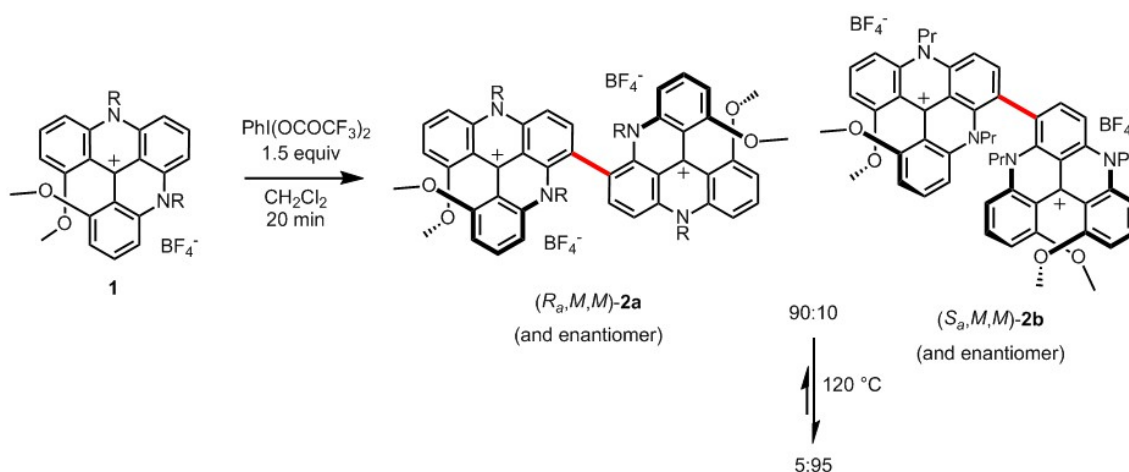


Homochiral recognition and excellent atroposelectivity in the oxidative coupling of cationic [4]helicenes

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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.



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