Optically Switchable Helical DMAPs in Asymmetric Catalysis of Medicinal Interests

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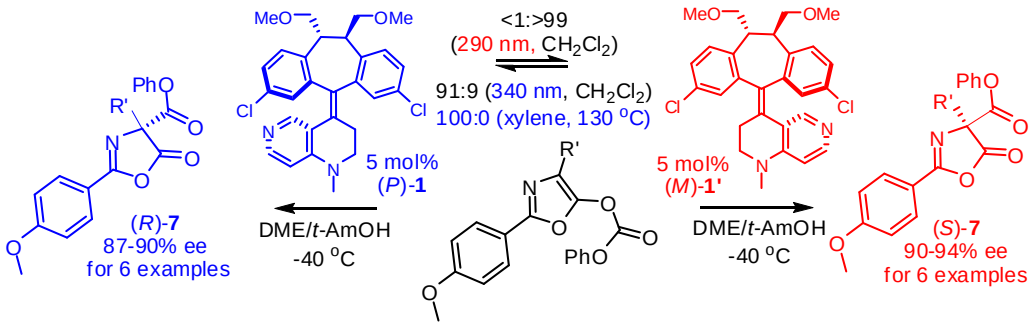
In recent years, we have developed a pseudo-enantiomeric pair of helicenes derived from 3,7-gallamide substituted (10*R*,11*R*)-dimethoxy-methyl-dibenzosuberane and 8-phenyl-α-azo-tetralin in supramolecular assembly.[1] We were then also able to use this system as sergeant dopants to induce asymmetric deracemization of racemic helicenes of up to 99% ee in a complementary fashion.[2] In this presentation, a pseudo-enantiomeric pair of (10*R*,11*R*)-dimethoxymethyl-dibenzosuberane (DBS)-based helicenes which bears a 4-dialkyl- aminopyridine bottom unit was synthesized. The helicenes undergo excellent, complementary photoswitching at 290 nm (*P*/*M*', <1/>99) and 340 nm (*P*/*M*', 91/9). They were utilized to catalyze enantiodivergent Steglich rearrangement of *O*- to *C*-acylated azlactones, resulting in the formation of either enantiomers with up to 90% ee (*R*) and 94% ee (*S*), respectively. They constitute important surrogates of optically active α-maino acids bearing quaternary ecnters. To our knowledge, this system constitutes one of the best complementary enantiocontrol among several light-controlled enantiodivergent reactions.[3]



[1] C.-T. Chen, C.-H. Chen, T.-G. Ong , *J. Am. Chem. Soc.* **2013**, *135*, 5294.

[2] C.-T. Chen, C.-H. Chen, C.-C Tsai, **2016**, submitted.

[3] C.-T. Chen,C.-C. Tsai, P.-K. Tsou, G.-T. Huang, C.-H. Yu ***Chem. Sci.*** **2017, *8*, 524.**

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