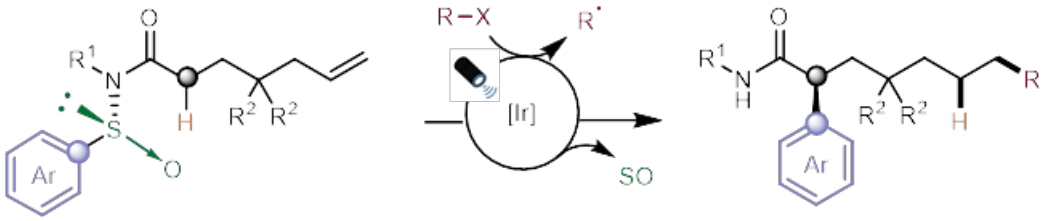
Visible-light-mediated Enantioselective Arylation of Remote C(sp^3)-H Bonds via Hydrogen Atom Transfer and Sulfinyl-Smiles Rearrangement

Y. Hu[1], C. Hervieu[1], E. Merino[2]*, C. Nevado[1]*

[1]University of Zurich, [2]Universidad de Alcalá

Asymmetric remote C(sp^3)-H functionalization, in particular using 1,*n*-Hydrogen Atom Transfer (HAT) events[1], represents a powerful strategy to forge stereogenic carbon centers in otherwise inaccessible positions. Despite significant progress in combining 1,*n*-HAT with enantioselective transition metal catalysis[2], asymmetric arylation of remote C(sp^3)-H bonds remains a largely unsolved problem. Meanwhile, the radical sulfinyl-Smiles rearrangement has emerged in recent years as a versatile tool for asymmetric (hetero)arylation[3].

Herein, we present a visible-light-mediated remote arylation of sulfinyl heptenamide combining a sequential 1,*n*-HAT and a sulfinyl-Smiles rearrangement. With this protocol, a wide variety of chiral amides are obtained with excellent enantioselectivity. Mechanistic investigations, including deuterium labeling experiments and computational studies, have been conducted to support a comprehensive understanding of this transformation.



[1] Weisi Guo, Qian Wang, Jieping Zhu, *Chem. Soc. Rev.* **2021,** *50*, 7359-7377.
[2] Peng Yu, Jin-Shun. Lin, Lei Li, Sheng-Cai Zheng, Ya-Ping Xiong, Li-Jiao Zhao, Bin Tan, Xin-Yuan Liu, *Angew. Chem. Int. Ed.* **2014**, *53*, 11890-11894.
[3] Cedric Hervieu, Mariia S. Kirillova, Tatiana Suárez, Marco Müller, Estíbaliz Merino, Cristina Nevado, *Nat. Chem.* **2021**, *13*, 327-334.