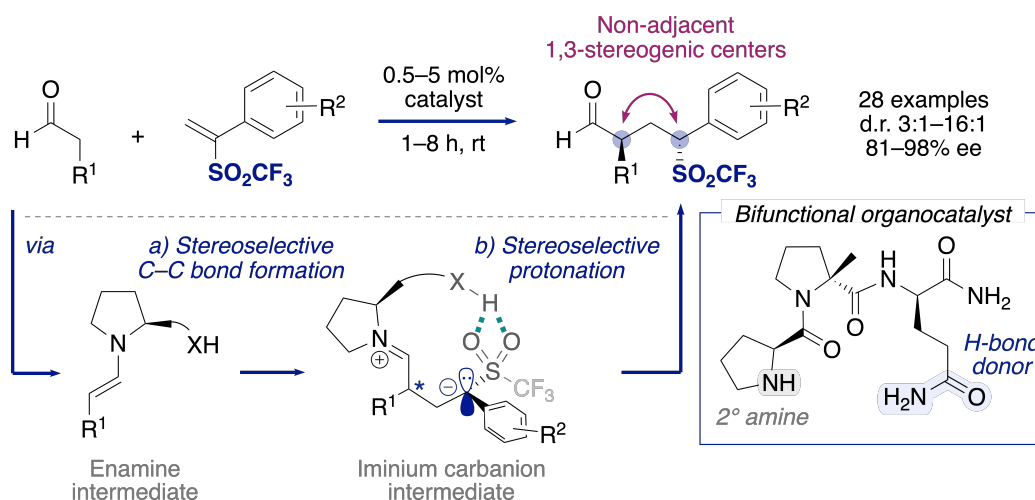


Organocatalytic Synthesis of Triflones Bearing Two Non-Adjacent Stereogenic CentersA. Budinská¹, H. Wennemers^{1*}¹Laboratory of Organic Chemistry, D-CHAB, ETH Zürich

The trifluoromethylsulfonyl (SO₂CF₃, triflyl) group is an intriguing functional group for its properties and unique reactivity since it combines the well-established transformations of alkyl and aryl sulfones with reactivity exclusive to the triflyl group.^[1] Methods to access triflones are therefore enabling tools for organic synthesis. However, strategies to obtain chiral triflones are limited.^[2]

We developed an efficient organocatalytic synthesis of chiral triflones using α -substituted vinyl triflones, building blocks previously unexplored in asymmetric catalysis.^[3] This peptide-catalyzed conjugate addition provides a broad range of γ -triflylaldehydes with two non-adjacent stereogenic centers in high yields and stereoselectivities. The reaction proceeds at a low catalyst loading of 0.5–5 mol% and tolerates a variety of functional groups, including acetal, ester, or ketone moieties. We show that a bifunctional peptide catalyst is crucial for high diastereo- and enantioselectivity through stereocontrol of the conjugate addition and protonation steps. Furthermore, straightforward derivatization of the products into 1,3-disubstituted heterocycles, including δ -sultones, γ -lactones, and pyrrolidines, highlights the versatility of γ -triflylaldehydes. Our results showcase the value of vinyl triflones for organic synthesis and open new possibilities to access chiral compounds with 1,3-stereogenic centers from α -substituted Michael acceptors.



[1] V. Krishnamurti, C. Barrett, G. K. S. Prakash. Synthesis and Applications of Fluorinated Sulfoxides (RSOR_F) and Sulfones (RSO₂R_F). In *Emerging Fluorinated Motifs: Synthesis, Properties and Applications* (Eds.: J. Ma, D. Cahard), Wiley-VCH, Weinheim, **2020**.

[2] X. H. Xu, K. Matsuzaki, N. Shibata, *Chem. Rev.* **2015**, *115*, 731–764.

[3] A. Budinská, H. Wennemers, *Angew. Chem. Int. Ed.* **2023**, e202300537.