

Insights: Publications

Generation of Axially Chiral Allenes through a Copper-Catalyzed, Asymmetric β -Fluoride Elimination

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Herein we report the copper-catalyzed silylation of propargylic difluorides to generate axially chiral, tetrasubstituted monofluoroallenes in both good yields (27 examples >80%) and enantioselectivities (82–98% ee). Compared to previously reported synthetic routes to axially chiral allenes (ACAs) from prochiral substrates, a mechanistically distinct reaction has been developed: the enantiodiscrimination between enantiotopic fluorides to set an axial stereocenter. DFT calculations and vibrational circular dichroism (VCD) suggest that β -fluoride elimination from an alkenyl copper intermediate likely proceeds through a *syn*- β -fluoride elimination pathway rather than an *anti*-elimination pathway. The effects of the C1-symmetric Josiphos-derived ligand on reactivity and enantioselectivity were investigated. Not only does this report showcase that alkenyl copper species (like their alkyl counterparts) can undergo β -fluoride elimination, but this elimination can be achieved in an enantioselective fashion.

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