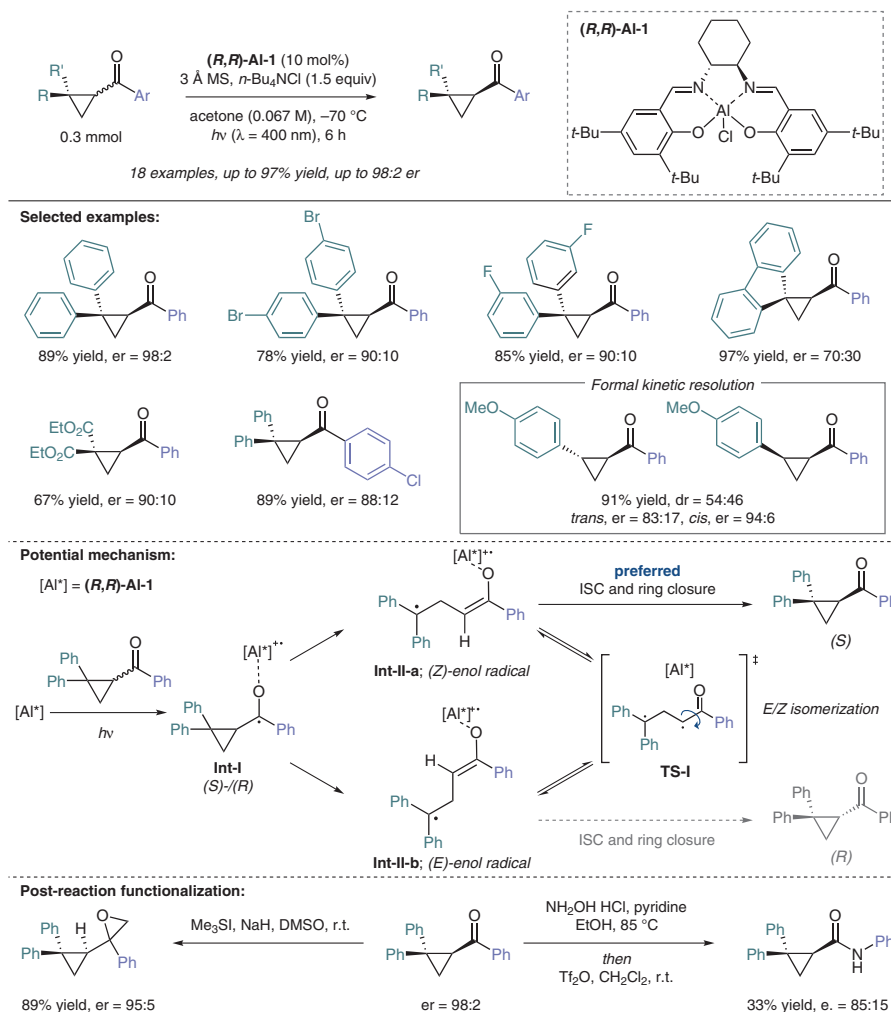


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Light-Enabled Deracemization of Cyclopropanes by Al-Salen Photocatalysis

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Al-Salen Photocatalyzed Deracemization of Cyclopropanes



Significance: Gilmour, Neugebauer and co-workers report the photocatalyzed deracemization of cyclopropyl ketones using a commercially available chiral Al-salen complex, **Al-1**. A series of scaffolds with geminal aryl and ester groups undergo deracemization in a highly efficient manner. Unsymmetrically substituted substrates react to generate equal mixtures of highly enantioenriched diastereomers. In depth mechanistic studies were carried out to elucidate the mechanism, while various derivatizations demonstrate the synthetic utility of the chiral molecules.

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Comment: Computational analysis of the reaction reveals that following the photoexcitation of **Al-1** and formation of the (*S*)-/(*R*)-ketyl radicals, ring opening generates triplet diradicals **Int-II-a** and **Int-II-b**, respectively. Stereoselection appears to occur through the epimerization of the enol radical species via **TS-I** within the chiral environment, leading to the accumulation of (*S*)-cyclopropyl ketone.