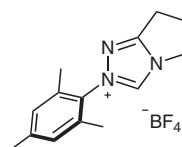
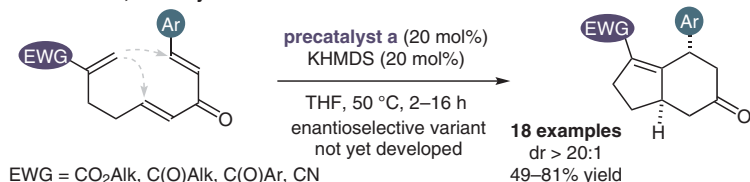
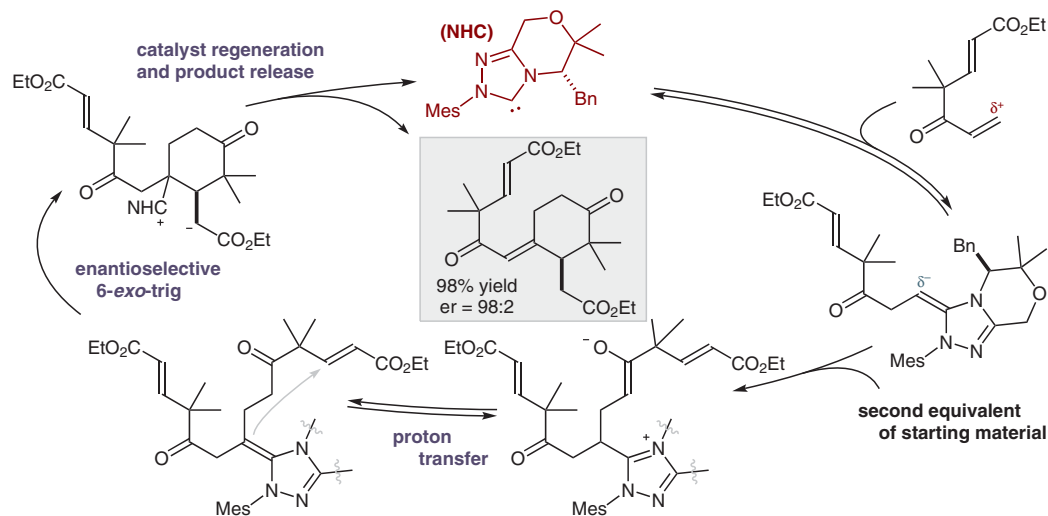
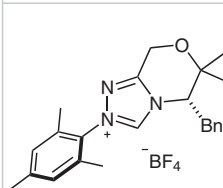
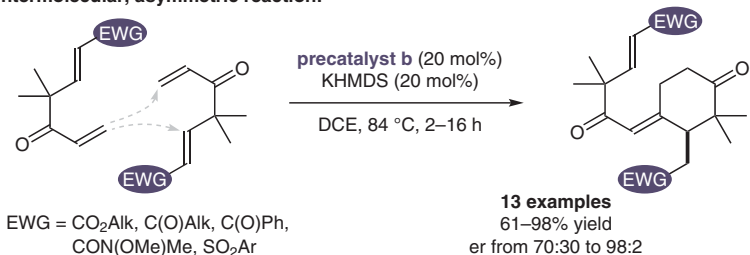


(5+1) Annulations through Double Umpolung of Conjugate Acceptors

Intramolecular, non-asymmetric reaction:



Intermolecular, asymmetric reaction:



Significance: The Lupton group reports a carbene-catalyzed (5+1) annulation that involves sequential polarity inversion of conjugate acceptors, thereby enabling double functionalization of terminal olefins. A nonasymmetric but highly diastereoselective intramolecular cyclization and an asymmetric dimerization are presented. Both reactions proceed with good to excellent yields, with the latter also achieving very good enantioselectivities.

Comment: Preceding literature reports on consecutive umpolung strategies of Michael acceptors exclusively show uncontrolled dimerization or oligomerization reactions. This is the first work that successfully translates the concept into an enantioselective and high-yielding catalytic method. A possible extension of the protocol to more-general substrate classes or an intermolecular cross-conjugate acceptor coupling would be highly desirable.