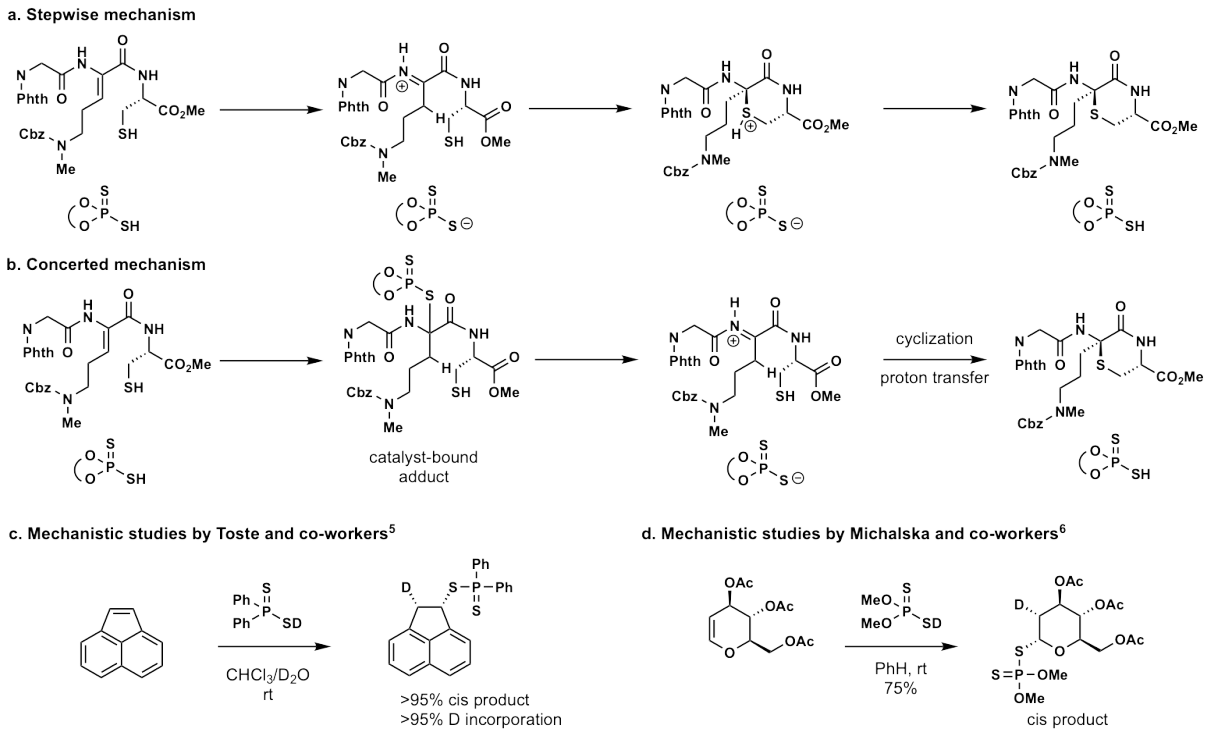

Figure S7. Proposed mechanisms and role of the dithiophosphoric acid catalyst in Markovnikov hydrothiolation. a) Stepwise mechanism by protonation of the dehydroamino acid followed by cyclization with cysteine. b) Concerted mechanism and formation of a catalyst-bound adduct. c) Mechanistic studies by Toste group showing evidence for a concerted mechanism by syn addition of a dithiophosphinic acid.[5] d) Mechanistic studies by Michalska group showing evidence for a concerted mechanism by syn addition of dithiophosphonic acid with glycals.[6]

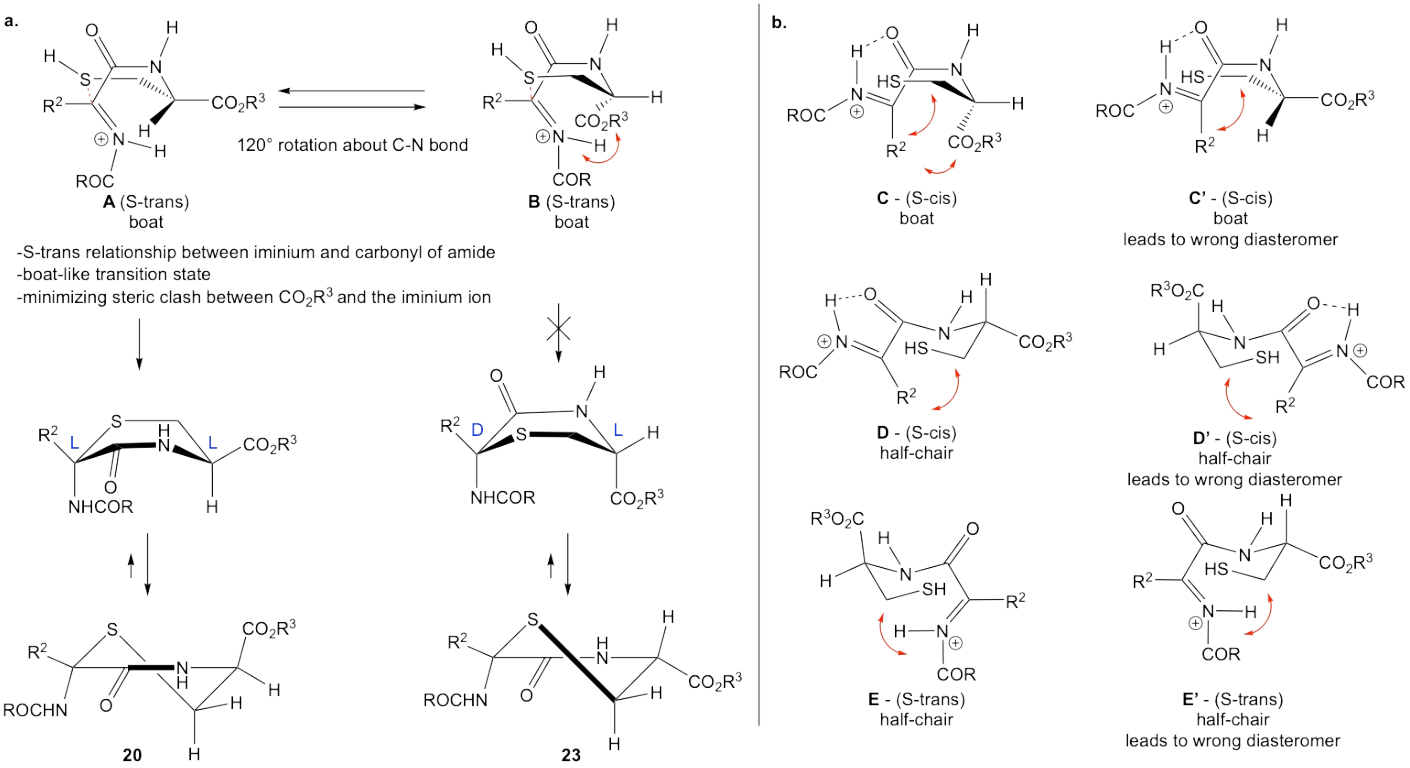

Figure S8. a) Proposed stereochemical model for the diastereoselective Markovnikov hydrothiolation. b.) Alternative models with unfavorable steric interactions. Red double headed arrows show unfavorable steric interactions between substituents.