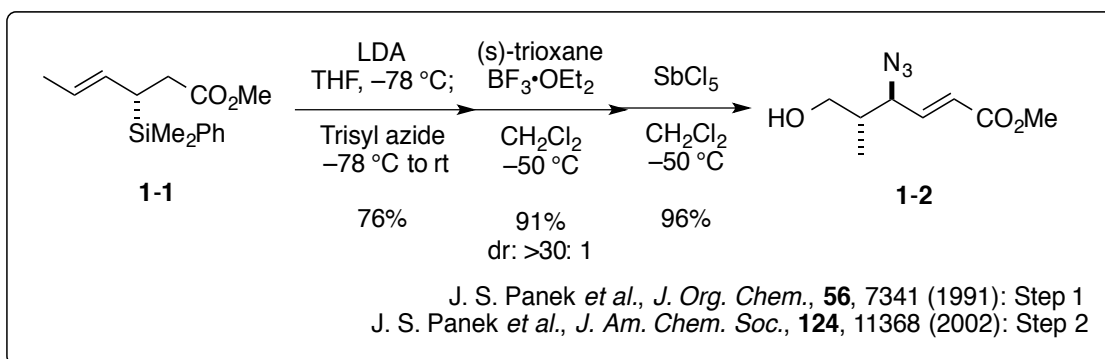


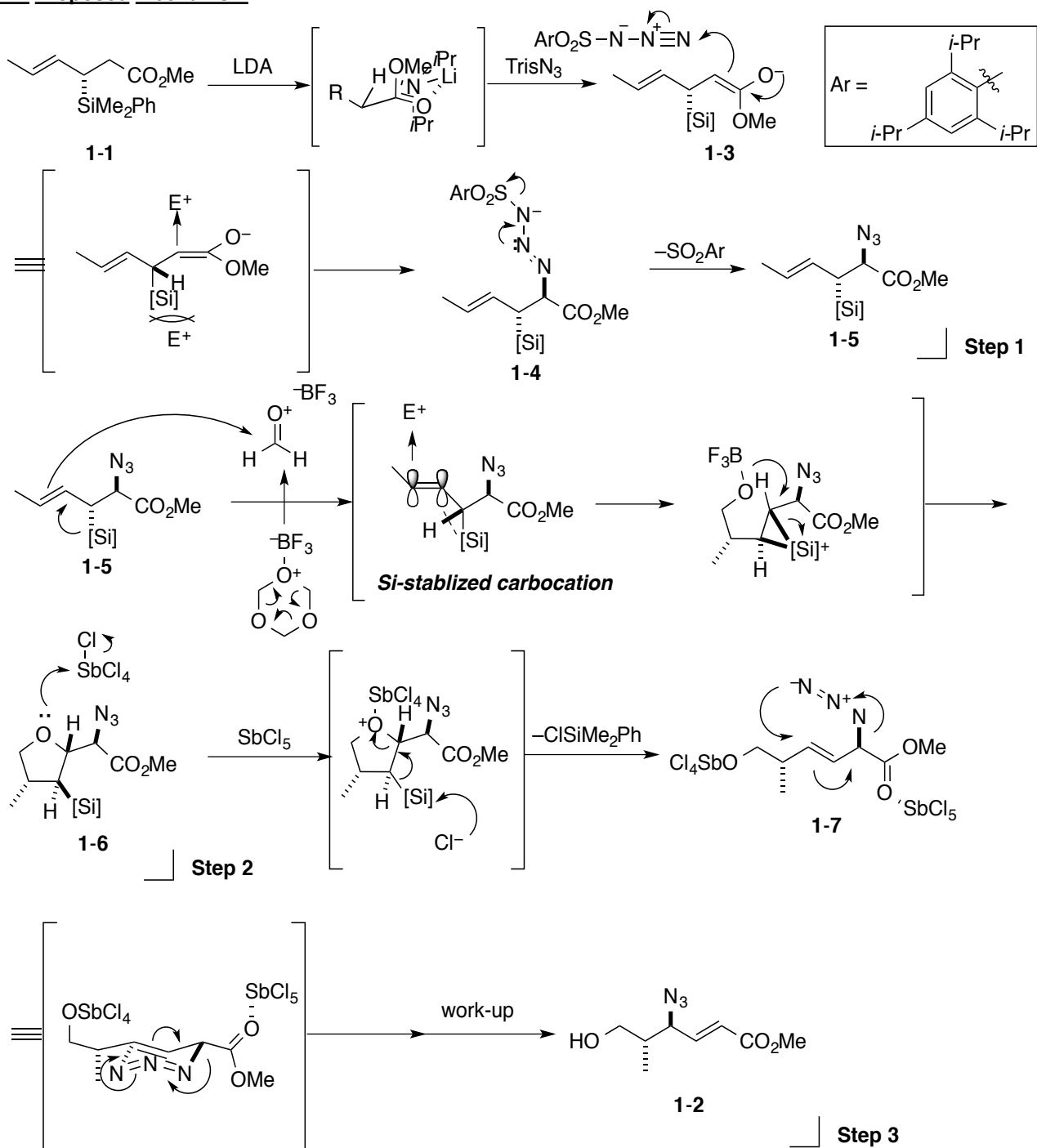
Problem Session (1) Answer

2015/09/12 Hirotatsu Umihara

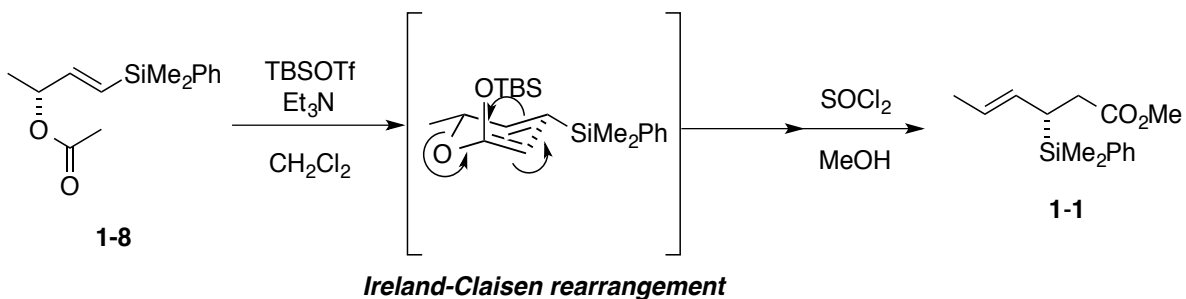
1



1-1 Proposed mechanism

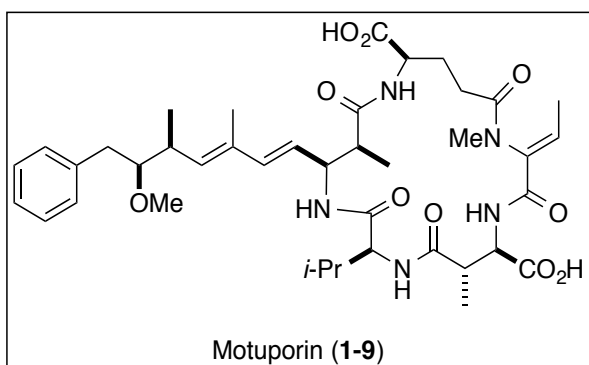


1-2 Preparation of chiral allyl silane



J. S. Panek *et al.*, *J. Org. Chem.*, **56**, 7341 (1991)

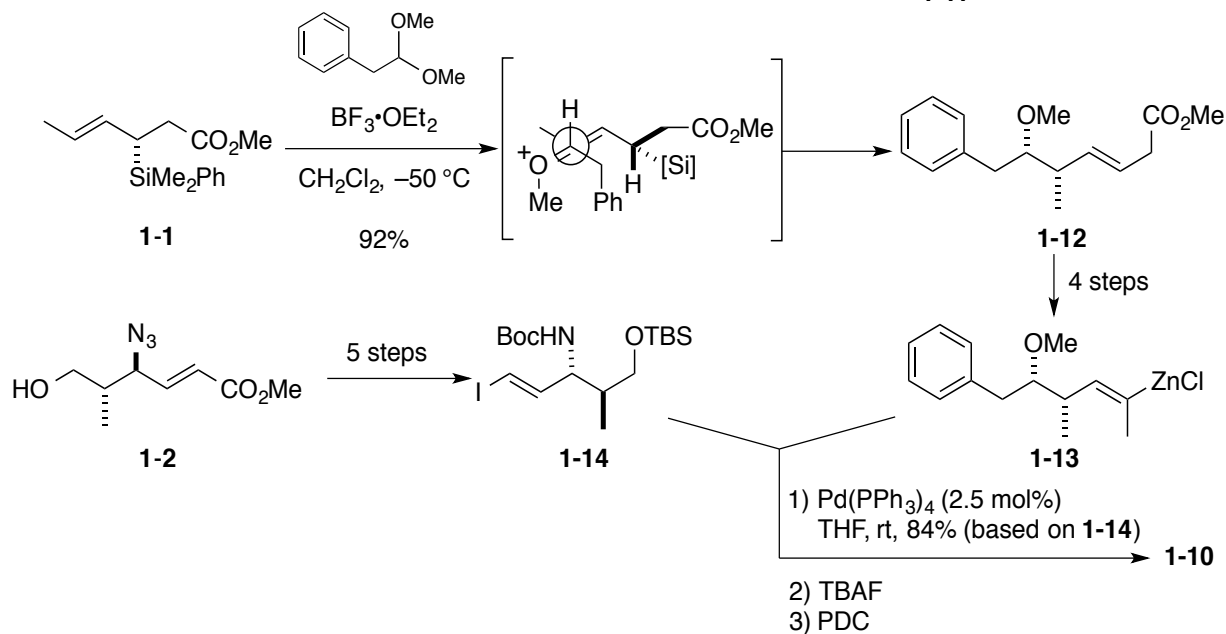
1-3 Total synthesis of (-)-Motuporin



J. S. Panek *et al.*, *J. Am. Chem. Soc.*, **124**, 11368 (2002)

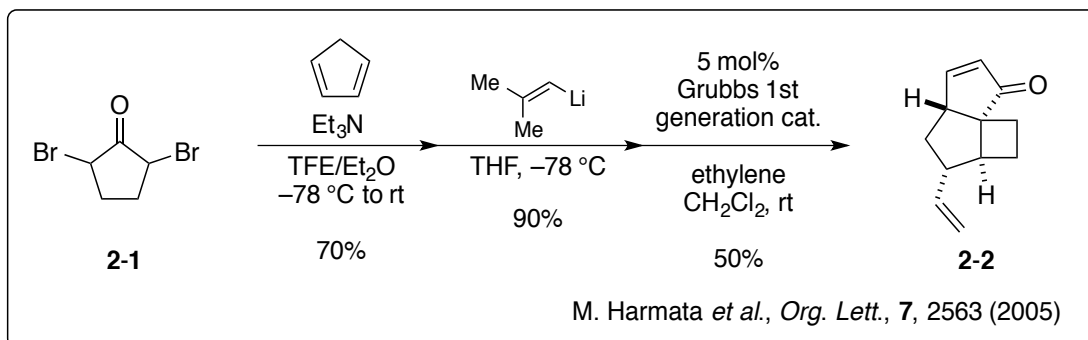
- 6 of 8 stereocenter was constructed using crotylsilan bond construction strategy

synthesis of 1-10

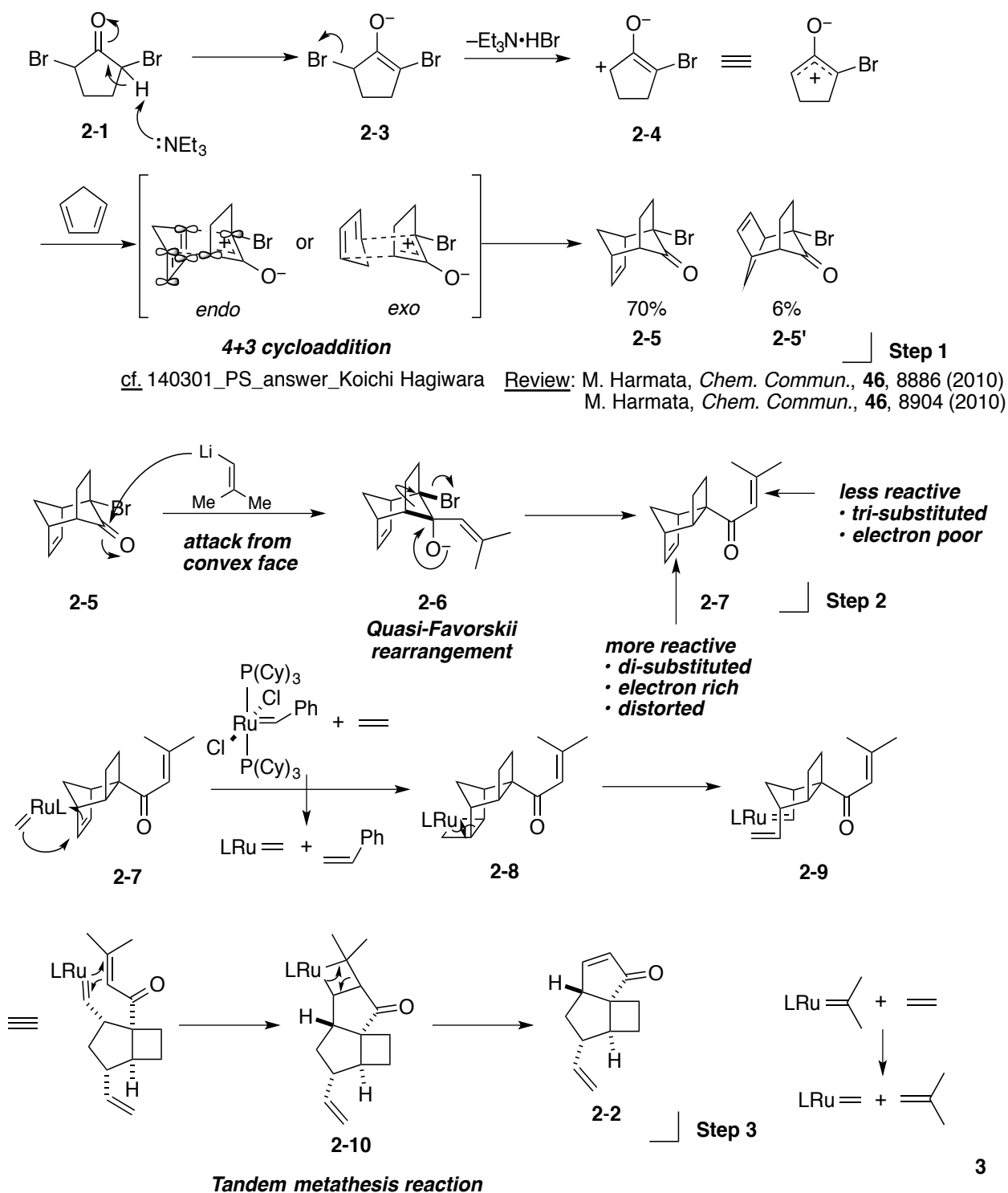


For other reactions related to crotylsilan bond construction, See: *Chem. Rev.*, **95**, 1293 (1995)

2

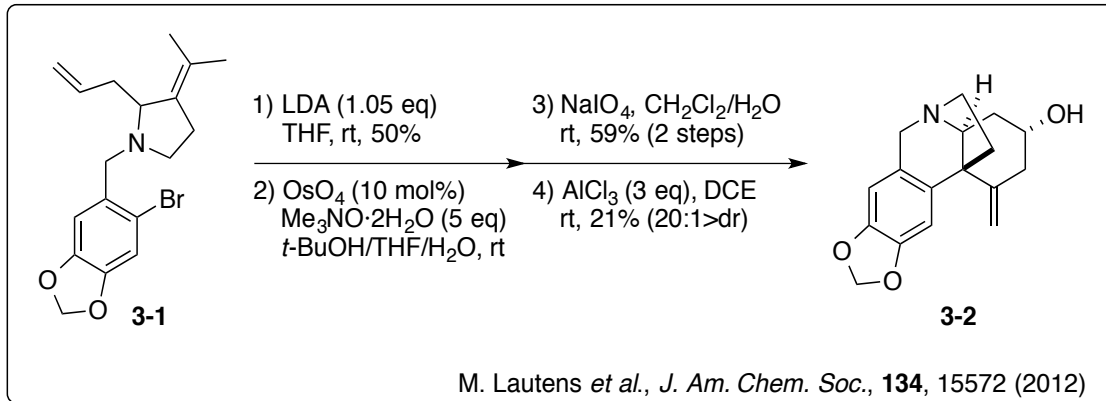


Proposed mechanism

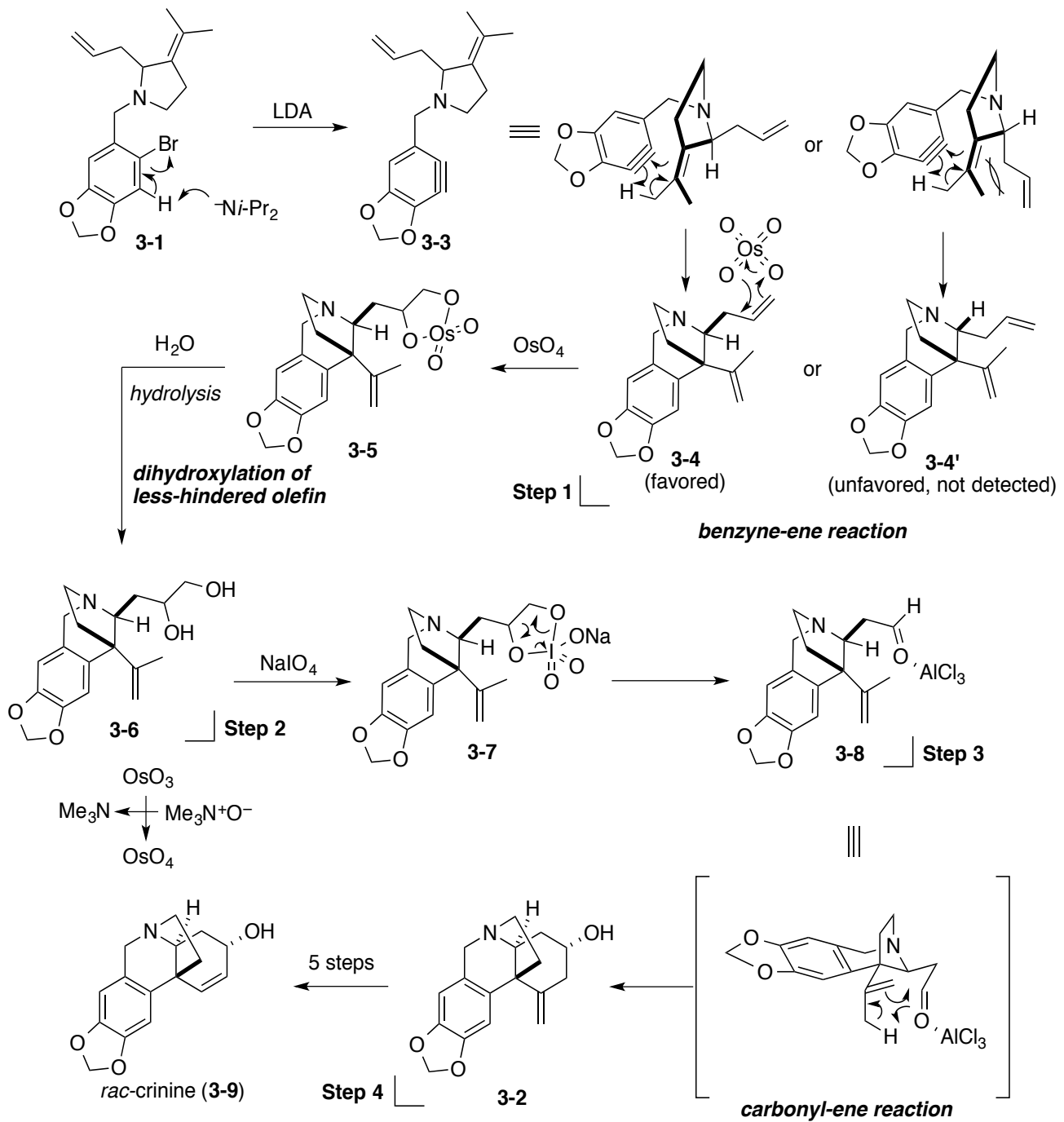


3

3



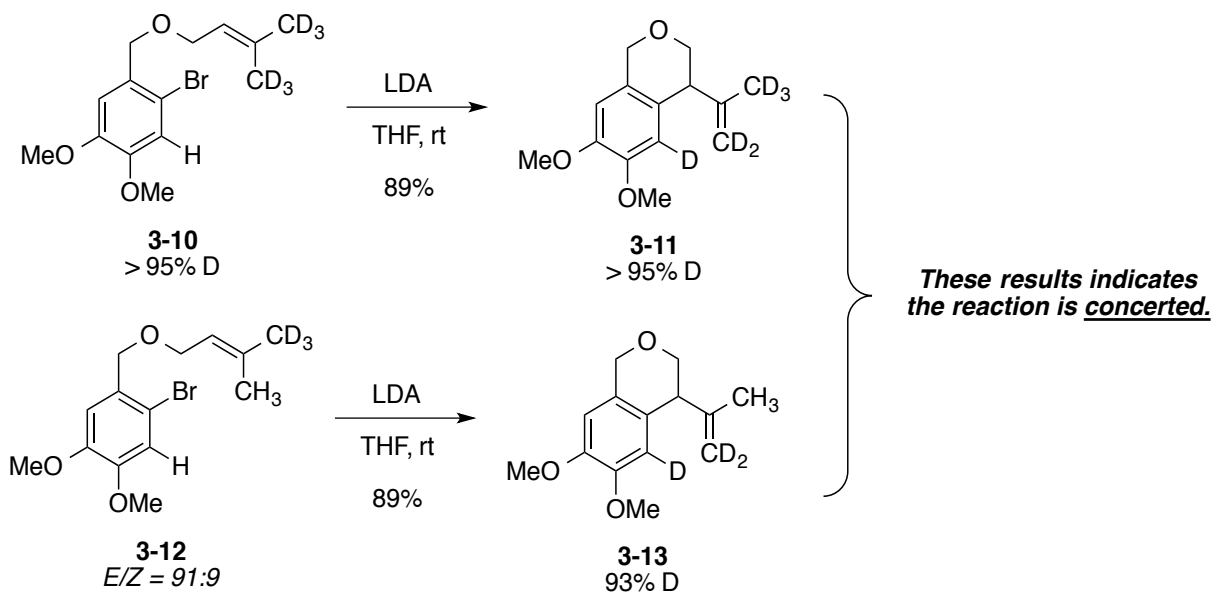
3-1. Proposed mechanism



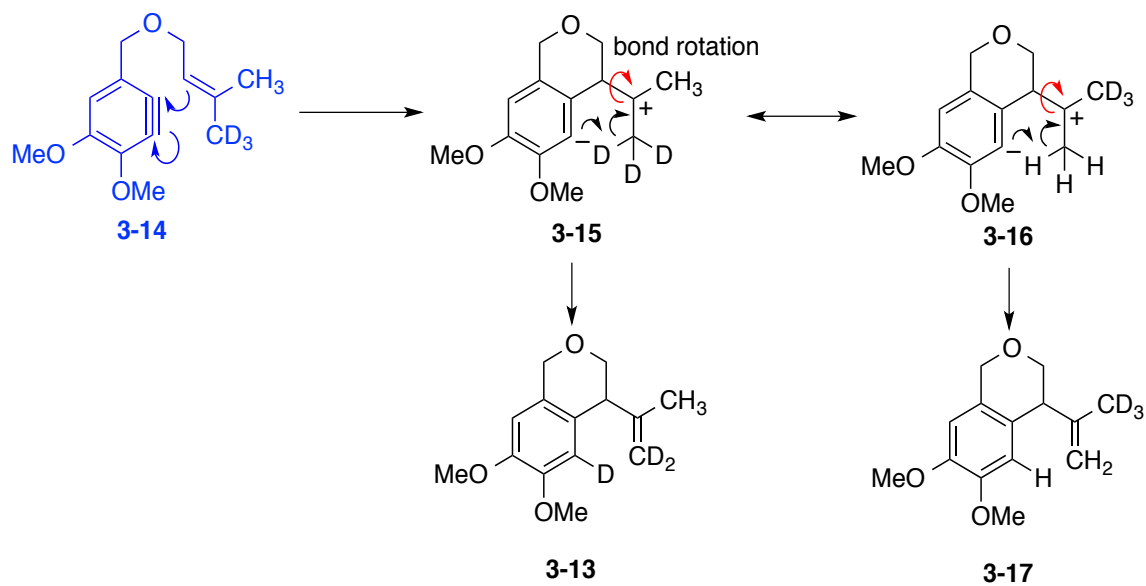
4

3-2. Discussion: benzyne-ene reaction

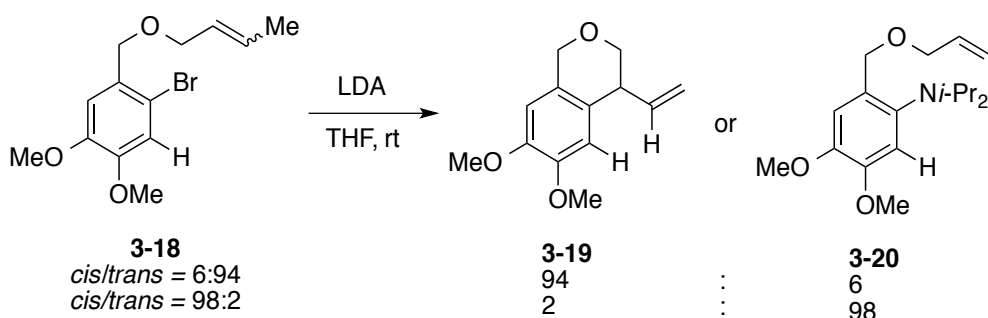
3-2-1. Reaction of deuterium labeled substrates



If polar or radical reaction proceeded...?

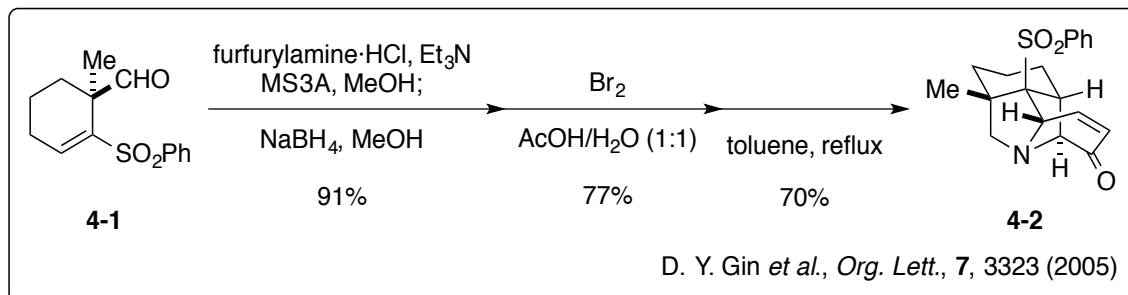


3-2-2. Reaction with *cis*- or *trans* olefin

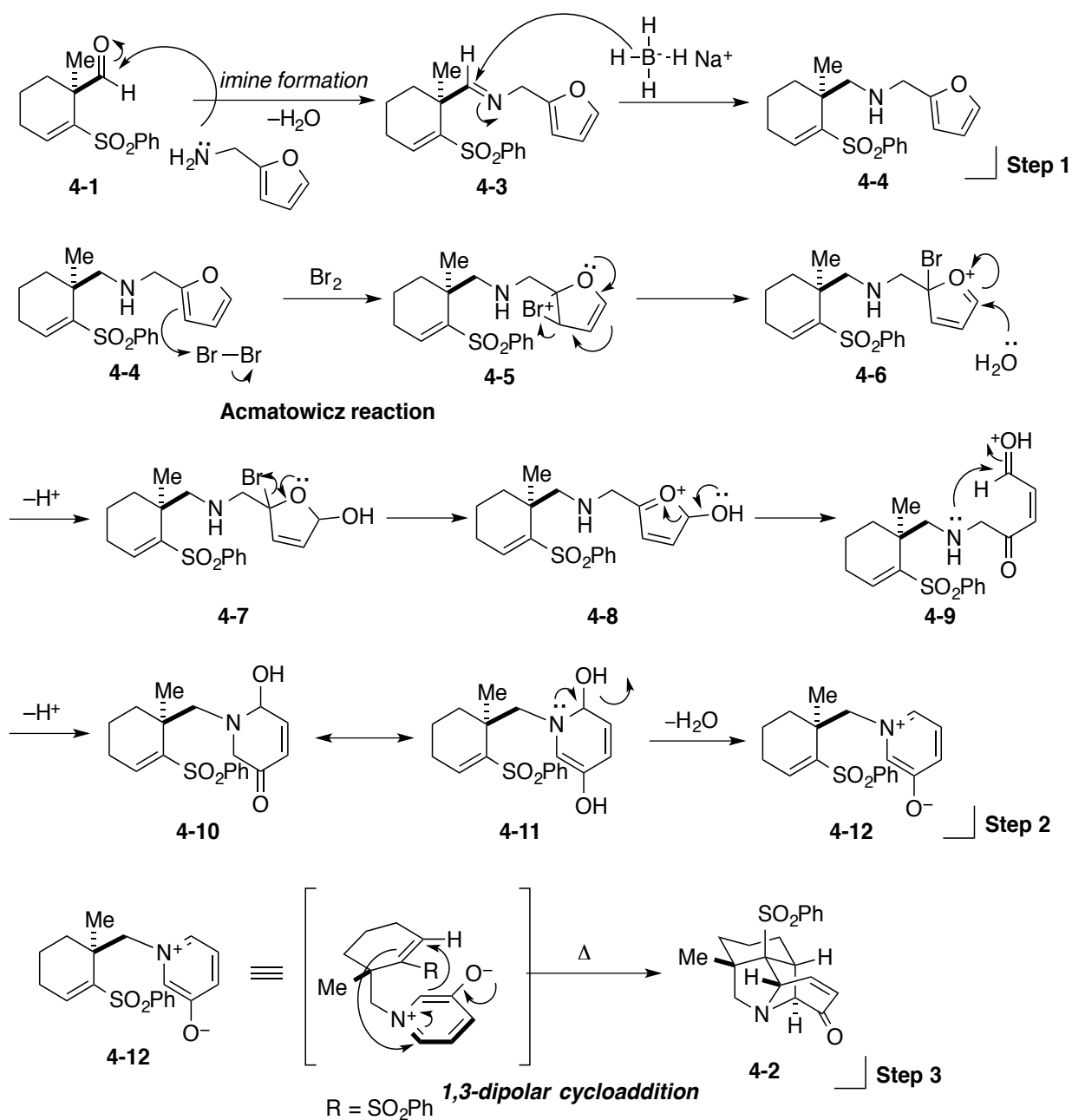


the reaction requires proper alignment

4

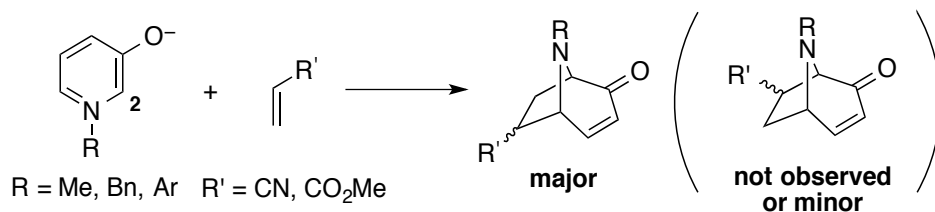


4-1. Proposed mechanism



4-2. Discussion: 1,3-dipolar cycloaddition

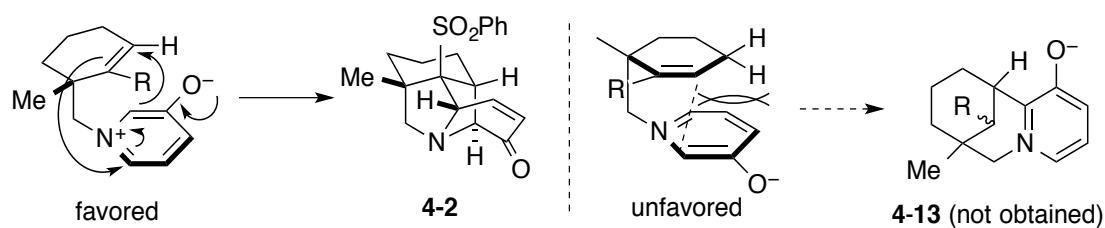
4-2-1. General regioselectivity of intermolecular reaction



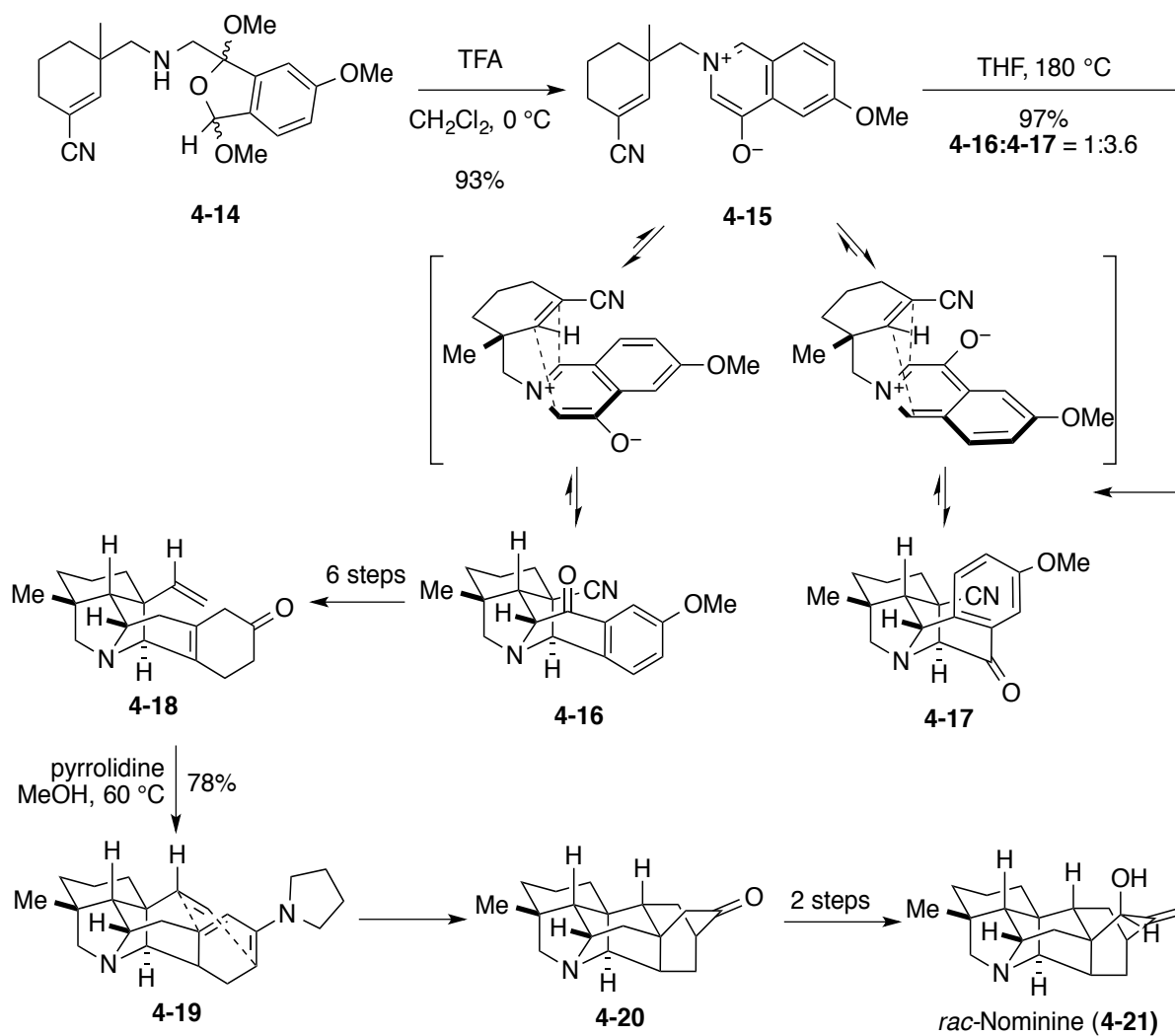
N. Dennis *et al.*, *Angew. Chem. Int. Ed.*, **15**, 1 (1976)

N. Dennis *et al.*, *Chem. Rev.*, **89**, 827 (1989)

4-2-2. Regioselectivity at step 3



4-2-3. Application to the total synthesis



D. Y. Gin *et al.*, *J. Am. Chem. Soc.*, **128**, 8734 (2006)

